# Numerical Simulations of Cooling and Topological Excitations of Quantum Gases

# Dissertation

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# Numerische Simulationen des Kühlens und topologischer Anregungen von Quantengasen

## Zusammenfassung

Die vorliegende Arbeit beschreibt die numerische Untersuchung der Erzeugung ultrakalter Teilchen-Ensembles und die Manipulation von Wolken aus Bose-Einstein-kondensierten Teilchen (BEK). Ultrakalte Teilchen-Ensembles werden gewöhnlich in mehreren Kühlungsschritten erzeugt, von denen der letzte und effektivste die Verdampfung von Teilchen aus der Falle ist. Unter besonderer Berücksichtigung der Eigenheiten und Probleme, die sich bei den magnetischen Auffang- und Kühlungsprozessen molekularen Sauerstoffs ergeben, wurde ein Simulationsprogramm für den Verdampfungskühlungsprozeß entwickelt.

Zusätzlich wurde mit den Mitteln der Quantenchemie eine Potenzialenergiefläche (PES) für den molekularen  $O_2$ - $O_2$  Kollisionsprozeß berechnet, um verbesserte Daten für die Bestimmung elastischer und inelastischer Kollisionsparameter zu gewinnen. In den quantenchemischen Berechnungen werden die einzelnen Moleküle als starre Rotatoren behandelt und es wird ein *ab initio* Ansatz gemacht, um die PES numerisch als Funktion des totalen molekularen Spins, des intermolekularen Abstands und der relativen Molekülorientierung zu bestimmen.

Für die Implementierung des Programms zur Simulation der Verdampfungskühlung mussten etliche Algorithmen angepaßt und verbessert werden, um das zu untersuchende physikalische Problem korrekt zu simulieren. Insbesondere müssen ein großer anteiliger Teilchenverlust aus der Magnetfalle, sehr starke Dichteinhomogenitäten und ein weites Teilchenenergiespektrum konsistent beschrieben werden. Das Programm wird benutzt, um den Verdampfungskühlungsprozeß in harmonischen und in linearen Quadrupolmagnetfallen zu untersuchen.

Zwecks der Simulation topologischer Anregungen wie Wirbel (Vortices) und Solitonen in Bose-Einstein Kondensatwolken nahe der absoluten Temperatur wurde von uns ein Simulationsprogramm entwickelt, das die dreidimensionale numerische zeitliche Entwicklung der quantenmechanischen makroskopischen Materiewellenfunktion auf modernen Arbeitsplatzrechnern erlaubt. Die physikalische Beschreibung des Bose-Einstein Kondensats ist dabei gegeben durch die nichtlineare Gross-Pitaevskii Gleichung. In Zusammenarbeit mit zwei Experimentalphysikgruppen in Oxford/UK und Konstanz wurde eine Anzahl verschiedener Fragestellungen modelliert und bearbeitet.

Eine Anwendung ist die Simulation der Reaktion eines Zentralvortexzustands eines Bose-Einstein Kondensats auf äußerliche Störungen. Die Abhängigkeit der kollektiven Anregungsenergien der Kondensatwolke von der Präsenz von Wirbeln wird untersucht, und die resonante Anregung von Kelvin Moden eines zentralen Vortexkerns wird gezeigt. Zusätzlich wird die Abhängigkeit der Expansion einer BEK Wolke in einer räumlichen Richtung besonderer Fallenstärke von der Abbaugeschwindigkeit eines residualen optischen oder magnetischen Fallenfeldes aufgezeigt. Dies ist insofern von praktischer Bedeutung, als die Expansion von BEK Wolken besonders häufig als Standardmethode experimenteller destruktiver Beobachtungstechniken eingesetzt wird.

Eine weitere Anwendung unseres BEK Simulationsprogramms ist die Modellierung und Untersuchung der Solitonenbildung in BEK Wolken in periodischen optischen Gitterpotenzialen. In solchen durch stehende Laser-Lichtwellen erzeugten Potenzialen können helle Bandkantensolitonen experimentell präpariert werden. Der Solitonenbildungsprozeß ist grundsätzlich eindimensional, er kann allerdings im dreidimensionalen Raum näherungsweise nachgebildet werden wenn die überzähligen Dimensionen durch ein besonders starkes Fallenpotenzial eingezwängt werden. Die kleinskaligen Details der Solitonenprozesse erfordern eine Abänderung des BEK Simulationsprogramms zur Ausnutzung der radialen Wolkensymmetrie zwecks einer Reduktion der numerischen Komplexität. Diese Entwicklungen erlauben eine quantitative Untersuchung und Modellierung der Experimente, in denen solche Solitonen realisiert werden.

# Abstract

This thesis describes the numerical investigation of the production of ultra-cold particle ensembles and the manipulation of Bose-Einstein condensate (BEC) clouds. Ultra-cold particle ensembles are commonly obtained by several cooling steps, the last and most effective of which is the evaporation of particles from a trap. A simulation program has been developed for the simulation of the evaporative cooling process, paying particular attention to the intricacies and problems encountered in the trapping and cooling processes of molecular oxygen.

Additionally, for the purpose of calculating improved elastic and inelastic collision data, needed in the evaporative cooling simulation program, a potential energy surface (PES) for the molecular  $O_2$ - $O_2$  collision problem has been computed using methods of quantum chemistry. In these computations, individual molecules are treated as rigid rotators and a full ab-initio approach is used to numerically derive the PES as a function of total molecular spin, intermolecular distance and the orientation of the molecules.

For the evaporative cooling simulation program several algorithms had to be adapted and improved in order to correctly simulate the physical system under investigation. In particular, large fractional particle loss from the magnetic trap, very strong density inhomogeneities and a large particle energy range must be consistently controlled. The program is used to investigate cooling in harmonic traps and in quadrupole linear magnetic traps.

For the investigation of topological excitations, such as vortices and solitons in BEC clouds near the absolute temperature, we developed a simulation program, which allows a three-dimensional numerical time propagation of the quantum mechanical macroscopic matter-wavefunctions on modern workstation computers. The physical description of the BEC is given by the nonlinear Gross-Pitaevskii equation. In cooperation with two experimental workgroups in Oxford/UK and Konstanz, a number of different problems are modelled.

One application is the simulation of a central vortex state in a BEC cloud, reacting to external perturbations. The dependence of collective cloud excitation energies on the presence of vortices is investigated and the resonant excitation of Kelvin wave excitation modes of a central vortex core is demonstrated. Additionally, the dependence of BEC cloud expansion in strongly confined spatial dimensions on the decay of residual optical and magnetic trap confinement fields is demonstrated. This is of practical interest, because BEC cloud expansion is heavily used as a common procedure in experimental destructive imaging techniques. A second application of our BEC simulation program is the modelling and investigation of soliton formation in BEC clouds, confined in periodic optical lattices. Bright gap solitons can be prepared experimentally in such potentials, which are realised by standing laser light fields. The soliton formation process is essentially one-dimensional, it can, however, be approximated in threedimensional space by means of strong radial trap confinement. The fine scale detail of the soliton processes requires an adaptation of the BEC simulation program to exploit the radial symmetry of the problem in order to reduce the numerical complexity. These developments allow a quantitative investigation and modelling of experimental soliton realisations.

# Contents

1	Inti	roduction 1
	1.1	Cold Atoms and Molecules
	1.2	Evaporative Cooling
	1.3	Bose-Einstein Condensation
	1.4	Computer simulations 5
	1.5	Motivation for this work
	1.6	This Work
		1.6.1 Overview
		1.6.2 Program codes
		1.6.3 Collaborations
		1.6.4 Publications $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 9$
0	ъ	1 1 1
2	Bac	ckground 11
	2.1	
		2.1.1 Classical scattering theory - Hard sphere model 12
		2.1.2 Inelastic collisions in the hard sphere model
		2.1.3 Limitations of classical scattering theory
		2.1.4 Basic concepts of quantum scattering theory 14
		2.1.5 Theory of inelastic Collisions
		2.1.0 Inelastic comsions in trapped gases
		2.1.7 Other quantum scattering energy as the second
	<u> </u>	2.1.6 Semi-classical approach to quantum scattering theory 50 Trapping of poutral atoms
	2.2	2.2.1 Quadrupolo magnetia trap
		2.2.1 Quadrupole magnetic trap $\dots \dots \dots$
		2.2.2 101 map
		2.2.9 Gravity encets
		2.2.4 External magnetic field cheets
	23	Trap loss processes 36
	2.0	2.3.1 Background gas collisions 37
		2.3.2 Majorana spin flips 37
	2.4	Evaporative Cooling 38
	2.1	2.4.1 Basic principles of evaporative cooling
		2.4.2 Thermalisation
		2.4.3 Adiabatic compression and expansion
		2.4.4 The hydrodynamic collision regime

## CONTENTS

		245	Evaporative cooling efficiency	12
		2.4.0 246	Effective Volumes	42
		2.4.0		10
3	Pot	ential	Energy Surfaces	<b>45</b>
	3.1	Physic	cs of the $O_2$ molecule $\ldots \ldots \ldots$	45
		3.1.1	Electronic configuration and ro-vibrational excitations	46
		3.1.2	Rotational levels in homonuclear diatomic molecules $\ldots$	47
		3.1.3	Prospects for evaporative cooling	47
	3.2	Metho	ods of Quantum Chemistry	50
		3.2.1	Hartree-Fock Theory	50
		3.2.2	Restricted open shell Hartree-Fock (ROHF)	53
		3.2.3	2nd order Møller-Plesset perturbation theory (MP2) $\ldots$	55
	3.3	Ab Ind	<i>itio</i> Computation of an $O_2 - O_2$ PES	56
		3.3.1	Computational Setup	58
		3.3.2	Exploiting symmetries to reduce complexity	60
		3.3.3	Spin orbital basis set and methods	61
		3.3.4	Data processing, dealing with gaps	61
		3.3.5	Numerical fit to angular functions	62
		3.3.6	Radial fit of angular coefficients	62
		3.3.7	Computation of virial coefficients	63
	3.4	Result	s and critical review of <i>ab initio</i> methods	67
4	<b>C</b> :	lat:a.	a of Europenative Cooling	71
4	3111 1 1	Numo	ricel methods	71
	4.1	1 1 1	Boltzmann Equation approaches	71 79
		4.1.1	Molecular Dynamics simulations	14 73
		4.1.2	The Direct Simulation Monte Carlo (DSMC) Method	73
		4.1.0	Bandom numbers	76
	12	Coolir	tranuon numbers	77
	4.2	4.2.1	Initial thermal distribution in a tran	77
		4.2.1	Peak densities	70
		422	Collision rates	80
		4.2.5	Bandom sampling	81
		425	Maximum particle energy in a trap	81
		4.2.6	Rejection method	83
		4.2.0	Transformation method	83
		4.2.1	Statistical fluctuations	85
	43	The $h$	ird simulation program	86
	1.0	431	Adaptation of DSMC to evaporative cooling	86
		432	Program structure	88
		433	Collision cross sections	88
	44	Thern		91
	1.1	4 4 1	Initial state quality	02
		449	Cross dimensional thermalisation in a harmonic tran	92
		1.1.2 1 1 3	Ergodicity in linear traps	92
		т.т.э ДДД	Cross dimensional thermalisation in a linear tran	95 95
	45	T.T.T Eveno	rative cooling	05
	ч.0	Буаро		50

vi

		4.5.1	Natural evaporation and forced cooling		. 95
		4.5.2	Forced evaporative cooling strategy		. 98
		4.5.3	Majorana loss model		. 99
		4.5.4	Evaporative cooling of oxygen		. 100
		4.5.5	Dimple trap and optical plug		. 102
	4.6	Result	S		. 103
<b>5</b>	Sim	ulatior	ns of Bose-Einstein Condensates		105
	5.1	Bose-F	Einstein Condensation		. 106
		5.1.1	Mean field theory and the GP Equation $\ldots \ldots$		. 106
		5.1.2	Irrotational flow and vortices		. 108
	5.2	The $G$	PEsim program		. 109
	5.3	Numer	rical Techniques		. 110
		5.3.1	Computational units		. 110
		5.3.2	Fast Fourier transform method		. 111
		5.3.3	Unitary split step algorithm		. 112
		5.3.4	Runge-Kutta algorithm		. 112
		5.3.5	Discretisation, Accuracy and Speed		. 113
		5.3.6	Cylindrical symmetry and pseudo-3D	• •	. 115
		5.3.7	Initial state generation	• •	. 117
		5.3.8	Applicability of 2D simulations to 3D experiments .	• •	. 120
		5.3.9	BEC cloud angles	• •	. 122
		5.3.10	Vortex detection		. 122
	5.4	Collect	tive cloud excitations in a BEC	• •	. 123
		5.4.1	Scissors mode	• •	. 124
	5.5	Impler	nentation of full tilted-TOP trap dynamics in 3D	• •	. 126
	5.6	The su	perfluid gyroscope	• •	. 127
	5.7	Vortex	core excitations	• •	. 130
	5.8	BEC e	expansion dynamics	• •	. 134
	5.9	Solitor	ns in BEC	• •	. 136
		5.9.1	Dark solitons	• •	. 137
		5.9.2	Bright solitons	• •	. 137
		5.9.3	Bloch theory and band structure	• •	. 138
		5.9.4	Group velocity and effective mass	• •	. 139
		5.9.5		• •	. 140
		5.9.0	Excitation of side bands	• •	. 141
	F 10	5.9.7 C:1-	Simulation data processing	• •	. 141
	5.10	5imula	Soliton simulations in 1D	• •	. 142
		5.10.1	Soliton simulations in 1D	• •	. 143
		5.10.2	Soliton simulations in 3D	• •	. 147
6	Con	clusio	ns and Outlook		151
$\mathbf{A}$	Data	a analy	ysis and visualisation		155
	A.1	Jpeg in	mages and film sequences		. 155
	A.2	3D me	thods		. 156

в	Ang. momentum coupling, Mathematica	157
С	Natural Atomic Units	159
D	Scaling laws for evaporative cooling	161
$\mathbf{E}$	Memory efficient RK4	163
$\mathbf{F}$	Finite difference derivative operator	165

# List of Figures

1.1	Particles in a 3D trap 2
1.2	Population of states in classical and in quantum statistics $\ldots 5$
0.1	
2.1	Hard sphere scattering
2.2	Quadrupole magnet
2.3	Truncated Maxwell-Boltzmann velocity distribution 40
3.1	$O_2$ lowest energy Zeeman levels $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 49$
3.2	CAS-SCF Levelscheme
3.3	$O_2$ - $O_2$ dimer
3.4	$O_2$ - $O_2$ configurations
3.5	Flowchart of queuing program
3.6	$O_2$ - $O_2$ PES section
3.7	PES relevant configuration cuts
3.8	Second virial coefficient B(T)
4.1	Spatial particle distribution harmonic trap
4.2	Spatial particle distribution linear trap
4.3	Velocity histogram of 2000 particles
4.4	Recursive cell subpartitioning
4.5	Linked List Object Structures
4.6	Collision cross sections of ${}^{52}Cr$
4.7	Collision cross sections of $O_2$
4.8	$^{133}$ Cs cross dimensional thermalisation
4.9	Collisionless ergodic mixing in linear traps
4.10	Natural evaporation from a linear traps
4.11	Energy distribution natural evaporation
4.12	Effect of Majorana spin flips on $O_2$ cooling $\ldots \ldots \ldots$
4.13	Effect of reduced dimensionality $O_2$ evaporation
4.14	Quadrupole dimple trap potential in 2D
51	Evolution of BEC aloud sizes during initial state generation 118
5.2	Evolution of DEC cloud sizes during initial state generation $\dots$ 110 BEC cloud <i>x</i> cuts during initial state generation 110
5.2 5.3	BEC operation initial state generation
5.0 5.4	Energy spectrum of BEC collective excitations
0.4 5 5	Cloud angle agaillations superfluid superfluid supersone
0.0 5.6	Cloud angle oscillation superirul gyroscope
0.0	Cloud angle oscillation spectrum

### LIST OF FIGURES

5.7	Vortex core oscillations superfluid gyroscope
5.8	Excited vortex core
5.9	Combined density and phase slices of vortex excitation 131
5.10	Vortex excitation
5.11	Vortex oscillations
5.12	Vortex oscillation spectrum
5.13	BEC cloud expansion simulation
5.14	Bright gap soliton in a periodic potential
5.15	Scaling properties of a 1D gap soliton
5.16	Preparation of a bright gap soliton
5.17	Analysis of 1D soliton simulation
5.18	Wavefunction density/phase of 3D soliton simulation 148
5.19	Analysis of 3D soliton simulation
5.20	Scaling properties of an atomic gap soliton
A.1	Data processing flow

# Chapter 1

# Introduction

# 1.1 Cold Atoms and Molecules

From cryogenic kelvin temperatures to room temperature and above, particles in dilute gases can macroscopically be regarded as a collection of "billiard balls" of specific small sizes, which bounce around at random in an entirely classical fashion, undergoing occasional elastic collisions with neighbouring particles. On a microscopic scale, however, the particle collision problem becomes more complicated. Multi-particle effects of the atomic or molecular electronic structure need to be taken into account in order to describe the scattering effects accurately. Fine quantum mechanical details determine the simple macroscopic picture of the billiard balls in terms of their collision properties, which we may naively macroscopically associate with different ball sizes.

As the temperature decreases from kelvins to millikelvins, the macroscopic properties of the atomic and molecular billiard balls change, just as if their sizes were in some way dependent on the velocity of their motion. At such low temperatures and respective collision energies, quantum mechanical effects influence the scattering properties of atoms and molecules in ways, which are completely counterintuitive from a classical point of view (Quantum scattering will be discussed in more detail in section 2.1). The parameters determining such scattering effects are the potential energy surfaces (PES), which describe the inter-particle potentials for all possible spatial configurations of the colliding particles. While PES for atomic collisions are fairly simple and isotropic, molecular PES are generally much more intricate and anisotropic. Such collision data is difficult to measure experimentally, especially for particle species, which have so far not been cooled to low millikely in temperatures. To investigate the feasibility of the trapping and cooling of "new" species, such as molecular oxygen, collision data may be derived from PES, which are obtained theoretically by means of quantum chemical *ab initio* calculations. In *ab initio* calculations, the inter-particle potential is calculated "from the beginning", using the basic known system features, such as electronic orbitals, particle distances and the quantum mechanical properties of atomic or molecular electronic structure. In the process of the present work we have conducted such calculations for the PES of oxygen molecules (described in chapter 3).

Cold dilute gas samples of atoms and molecules, trapped magnetically [1] or optically [2] in particle traps, which can be experimentally prepared in vacuum apparatuses, are of great scientific interest. Reductions in temperature significantly decrease all thermal noise and thus allow vast improvements in the precision measurement of fundamental constants and time [3].



Figure 1.1: Illustration of 500 particles in a three-dimensional isotropic harmonic trap (with projection of particle positions into three planes). Particles are randomly sampled from a normal distribution in all spatial directions. Cooling can be achieved by removing the fastest particles, which also have the largest trap oscillation amplitudes and can thus be selected using a spatial cutoff.

A further temperature T decrease to microkelvins ( $\mu$ K) can be achieved by laser cooling or evaporative cooling. The de Broglie wavelength of the trapped particles, which is  $\lambda = h/\sqrt{2\pi m k_B T}$  (where m is the particle mass,  $k_B$  is the Boltzmann constant and h is the Planck constant) increases, and particles become more and more wave-like, acting as individual wave packets with momentum-position uncertainty. Wave packet overlap at further decreased temperatures and increased densities marks the beginning of quantum statistical effects, eventually leading to Bose-Einstein condensation (BEC) at temperatures on the nanokelvin scale. At this point the individual wave packets form one giant single coherent matterwave. To achieve the enormous temperature decrease of nine orders of magnitude, counting from cryogenic kelvin temperatures, several cooling methods need to be applied to the trapped samples.

## **1.2** Evaporative Cooling

While cooling to cryogenic temperatures in the order of kelvins has been possible for many decades using standard cryogenic methods of simple liquid-gaseous phase transitions with liquid Helium as a coolant, or the <sup>3</sup>He-<sup>4</sup>He dilution refrigerator, temperatures in the order of  $\mu$ K have only been reached after the advent of evaporative cooling and optical laser cooling methods [4]. Laser cooling, however, is only available for certain atomic species, which have the appropriate

#### 1.3. BOSE-EINSTEIN CONDENSATION

spectral level schemes. But it has the big advantage that the cooling process does not deplete the trapped population. On the contrary, optical laser cooling methods can be used to load large particle numbers into magnetic traps. Cryogenic setups are usually not required for optically trappable particle species, since they can be optically decelerated and trapped from a background gas at room temperature. Thus the trap loading process is much more efficient than in purely magnetic setups with simple background buffer gas cooling and without optical cooling.

Evaporative cooling is a more universally applicable cooling method. It was proposed by Hess in 1986 for the cooling of spin polarised hydrogen, magnetically trapped at cryogenic temperatures [5]. The evaporative cooling method's fundamental principle is well known from daily life, as all steaming hot cups lose heat in a similar way, evaporating the "hottest" part (or "tail") of the thermal Maxwell-Boltzmann particle distribution. In atomic and molecular traps, this method can be applied to remove the fastest-moving particle fraction, retaining a colder but smaller sample. The remaining sample will consequently rethermalise by means of elastic collisions, reproducing a predictable fraction of fast-moving ("hot") particles. This allows the process to proceed to very low temperatures as the fastest particles are continuously removed by spatially selective radio-frequency state transfer.

While both laser cooling and evaporative cooling allow the reaching of  $\mu$ K temperatures (starting from cryogenically precooled particles in the evaporative cooling case), only the combination of both techniques led to the production of particle samples, which are colder than anything else in the universe, undergoing Bose-Einstein condensation at temperatures of merely nanokelvins. Evaporative cooling is typically used as a last cooling step to reach temperatures significantly below the photon recoil energy, starting with high particle numbers from an optically precooled sample at  $\mu$ K temperature.

In this work we have developed a simulation program for trapped particle ensembles undergoing evaporative cooling in different types of magnetic and optical traps, which allows particles at cryogenic temperatures to be cooled down to temperatures close to the BEC transition threshold. Several modifications to the standard Direct Simulation Monte Carlo (DSMC) procedure, which is known from molecular gas dynamics, have been necessary to allow a description of trapped particle ensembles. We describe our work in this area in chapter 4.

## **1.3** Bose-Einstein Condensation

Bose-Einstein condensates (BEC) are often called a "fifth state of matter", in addition to the better known other four states represented by solids, liquids, gases and plasmas. Bose-Einstein condensation describes the process of a phase transition, which only results from the quantum statistics of identical bosonic particles. Below a critical very low temperature  $T_c$  in the order of nanokelvins, bosons (which are particles of integer spin) accumulate in the lowest quantum state, an effect predicted by Einstein and Bose in 1925.

This effect occurs at a high phase space density, i.e. at high particle number

density and extremely low temperature, when the de Broglie wavelengths of the individual particles approach the size of the inter-particle separation, leading to a spatial overlap. Many physical systems owe their properties to quantum degeneracy and the phenomenon of Bose-Einstein condensation, but it took 15 years from the prediction of BEC before this connection was made. Better known effects are the superfluidity of liquid helium and the superconductivity of many materials at cryogenic temperatures. Effects in other physical systems, such as excitons in semiconductors, and properties of nuclear and subnuclear matter are also due to bosonic quantum statistics [6].

Liquid helium at low kelvin temperatures was found to owe its superfluid properties to Bose-Einstein condensation effects. However, interparticle interactions in the <sup>3</sup>He and <sup>4</sup>He quantum liquids are fairly strong, and thus the condensate fraction is very small, with a quantum depletion of 90%. The properties of the weakly interacting dilute degenerate quantum gases of atomic vapours are quite different and have very high condensate fractions with less than 1% quantum depletion in alkalis, according to the Bogoliubov theory of condensate excitations. The conditions, under which BEC in such dilute and weakly interacting gases can occur, are extreme by all standards and for many decades it could not be experimentally achieved.

The first initially unsuccessful efforts to achieve BEC in dilute gases were made with cryogenically cooled spin-polarised hydrogen. Significant progress in the field was made only after the advent of magnetic trapping [1] and laser optical cooling [4], which made cooling to  $\mu$ K temperatures possible. In 1997 S. Chu, C. Cohen-Tannoudji and W. Phillips were awarded the Nobel Prize for their theoretical and experimental development of optical cooling techniques. BEC was finally reached in 1995 [7], after combining the magneto-optical cooling techniques with evaporative cooling to reach the critical densities in phase space and the nanokelvin BEC transition temperature. Bose-Einstein condensates of a growing number of different atomic species have been experimentally realised since 1995 [7,8,9,10,11,12], making BEC more than just a phenomenon of statistical physics.– It can be regarded as an entirely new window into the quantum world, which is particularly valuable, because it allows direct experiments with macroscopic matter-waves.

In a way, the relationship between ordinary matter and a coherent BEC matterwave is the same as the relationship between the incoherent light of a lightbulb and the coherent light of a laser. In both cases of the laser and the BEC, the bosonic quantum statistics lead to a pure macroscopic population of just a single quantum state. The mean population of a single particle state in Bose-Einstein quantum statistics can be described as

$$\langle n \rangle = \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} - 1},\tag{1.1}$$

where  $\epsilon$  is the energy of the state and  $\mu$  is the chemical potential in the grand canonical ensemble. The critical temperature  $T_c$ , for which  $e^{(\epsilon-\mu)/(k_BT_c)} = 1$ and all ensemble bosons undergo Bose-Einstein condensation into the lowest energetic state, is [13]

$$T_c = \frac{2\pi\hbar^2}{mk_B} \left(\frac{2.612}{\rho}\right)^{\frac{2}{3}},$$
 (1.2)

where  $\rho = N/V$  is the mean particle density of the system and *m* is the particle mass. The numerical value arises from the value  $\zeta(3/2) \approx 2.612$  of the Riemann zeta function in the theoretical derivation [14, 15].



Figure 1.2: Temperature and energy dependence of mean state occupation numbers in bosonic Bose-Einstein (dashed, green) and fermionic Fermi-Dirac (dot-dashed, blue) quantum statistics, compared with classical Maxwell-Boltzmann statistics (solid, red).

Figure 1.2 shows the single state population for classical Maxwell-Boltzmann and for Fermi-Dirac and Bose-Einstein quantum statistics. Note the divergence at  $(\epsilon - \mu)/(k_B T) = 1$  in BE quantum statistics, leading to the phenomenon of BEC.

The quantum degenerate regime of BEC of dilute gases near the absolute temperature is the subject of the second part of this work. Using a computer simulation program, which we have developed, we numerically investigated several aspects of the resulting macroscopic matter-wavefunctions. More details about the properties of BEC and methods to find numerical solutions of BEC problems will be presented in chapter 5.

### **1.4** Computer simulations

Computational physics is often regarded as a new segment in science, linked heavily into the theoretical side but exhibiting a profound experimental approach. Using the mathematical foundations of theoretical physics, computational physics creates virtual laboratories, where models can be investigated using experimental techniques. A computer simulation represents an imitation of a real physical system, incorporating all of the best known theoretical knowledge about the system, or making well justified simplifications. Thus a numerical simulation implements certain or all known features of the behaviour of a real physical system or of an abstract mathematical model by means of the deterministic behaviour of a universally programmable computer.

Such simulational imitations of real systems are important in situations, where detailed direct observations on the real physical system would be destructive or prohibitively expensive. Furthermore, simulations of mathematical abstract models can lead to new discoveries, and simulations can be used to refine models and the theoretical understanding of complicated systems.

With numerical processing power of computers still continuously improving at an amazing pace for the forseeable future [16], computational physics in general is rapidly gaining importance in all areas of science and technology.

The functional basis of these new physics methods are the computer program codes developed to represent the physical systems under investigation. Since the resulting code represents an experimental lab setup, in principle it deserves the same amount of scientific scrutiny as any real experiment used for the production of published data. Unfortunately, however, in computational physics openness concerning program codes has been lacking, leading to irreproducible data and a lot of duplicated work by groups trying to reproduce third party numerical results. The author acknowledges this important point, also expressed in [17], and has made an effort to keep his computer program codes clean, readable and modular, for future re-use by others.

## 1.5 Motivation for this work

In the past few years BEC of many different atomic species has been achieved, and the process is slowly becoming a standard procedure in many laboratories around the world. The consistent and reliable production of condensates with very large particle numbers and the condensation of molecular gases, however, still poses great challenges in experimental and theoretical physics. Ultra-cold molecular samples and, ultimately, molecular BEC are of fundamental interest, as they will doubtlessly lead to better and more precise insights into molecular structure and quantum mechanical properties. Eventually it may even become possible to achieve ultra-low temperatures in ensembles of "macroscopic" particles such as  $C_{60}$  buckyball molecules, DNA or even viruses.

Very little is known about most molecular species at low and ultra-cold temperatures. Paramagnetic oxygen, particularly its isotope  ${}^{17}O_2$ , for example, was identified as a potential candidate for magnetic trapping, evaporative cooling and ultimately BEC. Little data, however, exists about molecular collisional interaction in this species due to the lack of experiments in the temperature range and the technical difficulty of theoretically solving complex quantum mechanical many-body problems.

The collaboration with Prof. Achim Peter's work group, which built a cryogenically cooled superconducting magnetic quadrupole trap for oxygen trapping experiments, motivated the first half of the present work. Due to technical advances in computer power it became practical to attempt the *ab initio* computation of oxygen potential energy surfaces as a base for the calculation of more precise collision data. This data, in turn, was then to be used in the computer simulation of trapped molecular oxygen.

In addition to making quantum chemistry computations practical for our purposes on common x86-Linux workstation computers, recent technical advances also allow the computer simulation of the quantum degenerate BEC superfluid on such affordable computers. The experimental observation of manipulations of BEC clouds is a long and tedious process and optical probing and imaging usually cause the destruction of the sample. The quantum system under investigation, however, can be described within a zero-temperature mean field approximation in a rather simple and comprehensive way by the Gross-Pitaevskii equation (GPE). Thus for the planning of experiments, the profiling of parameter ranges and for detailed visual and quantitative predictions of experimental outcome, a simulation program represents a valuable resource.

This motivated the development of our BEC simulation program, which has since been successfully applied to a wide range of different experimental problems, including the investigation of topological excitations, such as vortices and solitons.

## 1.6 This Work

#### 1.6.1 Overview

In chapter 2 we give an outline of the theoretical background, upon which this work is based. After presenting the basic classical and quantum mechanical collision theory, we summarise, how scattering cross sections and rate constants can be determined from potential energy surface data. We proceed with the theory behind magnetic trapping and evaporative cooling of atoms and molecules, describing the traps most commonly used in cold atom experiments. The simple quadrupole trap, which can be turned into a Time Orbiting Potential (TOP) trap by using additional fields, is subject of much of our numerical work on evaporative cooling. The importance of this type of trap is due to the fact that static quadrupole traps are simple enough by design to handle the high superconducting coil currents and magnetic fields required in molecular oxygen trapping experiments. We identify and explain processes leading to loss of trapped particles and we describe the basic theory of evaporative cooling.

In chapter 3 we describe the work done in order to numerically calculate a molecular potential energy surface for oxygen  $O_2$ . We start with an outline of the methods of quantum chemistry. These methods are used to find approximate solutions to the complicated many-body problems of electronic structure by means of powerful computer program packages like "Gaussian" and "Gamess", the latter of which we have used for our purposes. The most important approximation for electronic structure calculations is the Hartree-Fock approximation of averaged mean electronic fields. This approximation constitutes the origin of the concept of distinguishing individual electronic orbitals, which are consequently given universal labels like "1s", "2p" and so on. Starting from the Hartree-Fock solution, a large number of different methods exists, which can be used to improve the numerical solutions. We take a brief look at the theory of such methods and describe the methods and procedures we have employed in the course of the project. Before we present and discuss the results we have finally obtained, a detailed description of our quantum chemistry problem and its solution using the Gamess program is presented.

Chapter 4 describes the numerical work on evaporative cooling. We start with an outline of the numerical methods we have used. We present several improvements to existing algorithms and novel techniques applying Monte Carlo methods to the problem of evaporatively cooling particles in a trap, with particular attention to linear potentials of quadrupole traps. We present results of oxygen trapping and evaporative cooling simulations, investigating the feasibility of experimental realisations in the light of Majorana spin flip losses at low temperatures and adverse magnetic field effects on the inelastic collision rate.

In chapter 5 we present numerical work done on simulations of Bose-Einstein condensed matter waves at zero temperature. A universal simulation program for the Gross-Pitaevskii equation has been developed and we present the numerical algorithms before we describe the specific problems, which we have solved using our simulation program.

#### 1.6.2 Program codes

In the context of the present work I have developed several computer programs for the simulation of the physical systems, which are subject of this dissertation. Development of these programs constitutes a significant amount of work, and care was taken to keep them as modular and extensible as possible to make a future re-use of them or parts of them possible.

The *bird\_simulation* program (named after G. A. Bird, the author of the DSMC algorithm, which is presented in section 4.1.3) simulates a general microscopic particle system in a trap. It can model many sorts of evaporative cooling procedures and it can handle strong inhomogeneities and trap losses. Program details and results are presented in chapter 4.

The *GPEsim* BEC simulation program, which I have also developed for this work, is very universal and can be applied to all kinds of zero temperature BEC problems in many different trap configurations in 1D, 2D or 3D. It can also be applied to general numerical problems involving linear or nonlinear Schrödinger equations and it is fast enough to handle extensive simulations on discrete 3D grids on present workstation hardware. An additional visualisation program written in OpenGL (see appendix A.2) makes the user independent of expensive graphics software packages such as *Matlab*.

Several other little programs have been developed, notably a C++ class for the direct output of simulation data in form of JPG images and a queuing program to exploit a number of different Linux workstations for a large scale computation (see chapter 3).

Since it is not possible to publish all of this code within this thesis, a CD-ROM will be submitted to the library and archive files will appear for download on the author's university webpage. Distribution and use shall be governed by the GNU General Public Licence (GPL) [18].

#### 1.6.3 Collaborations

Work on this dissertation was done in the context of collaborations with several experimental groups, who inspired many aspects of this work and who benefited from many of the results.

The work group of Prof. Achim Peters at the University of Konstanz built a strong quadrupole magnetic trap using superconducting field coils suitable for the trapping of molecular oxygen. Dennis Weise [19] was involved in the trap design and work on oxygen spectroscopy. Oliver Vogelsang [20] worked on trap design and the cryogenics. Computer simulations modelling this system will be presented in chapter 4.

Work on the quantum chemical computation of oxygen potential energy surfaces benefited from close consultations with Dr. Frank Neese (Max Planck Institute for Radiation Chemistry, Mülheim, Germany). His expertise was invaluable in setting up the base function sets and other parameters for the quantum chemistry computations.

Very early during my research time in Konstanz, Prof. Christopher J. Foot and his work group from Clarendon Labs at Oxford university showed interest in my emerging simulation program for Bose-Einstein condensates. Furthermore, the Oxford group also had some experience with evaporative cooling in experiment and simulation. I was more than happy to follow an invitation to work at the Clarendon Labs for two months during September and October of 2003.

During my work I also got involved in another collaboration with the group of Prof. Markus Oberthaler, formerly based at the University of Konstanz, on the subject of bright gap solitons in Bose-Einstein condensates. This inspired the GPE simulations in cylindrical symmetry (Section 5.3.6). My Bose-Einstein condensate simulation code and knowledge also contributed to work done by Hilligsøe et. al. in [21, 22].

In late 2003 my supervisor Prof. Karl-Peter Marzlin moved to Calgary, Canada, joining the quantum information theory work group of Barry Sanders. Prof. Sanders was very kind to fund an extended stay with his work group in Calgary in January and February 2004.

#### 1.6.4 Publications

My research over the past years has yielded results in several areas. In the following I will summarise the topics, on which a publication of research papers is being considered or prepared.

Extensive research and programming work has gone into the simulation methods for evaporative cooling. The algorithmic advancements now allow consistent and robust simulation runs through many orders of magnitude of trapped particle loss and temperature. At the same time, the program is capable of handling highly inhomogeneous situations such as the case of particles trapped in a quadrupole trap with its high peak central density. In combination with more detailed data on evaporative cooling of molecular oxygen, we are planning to prepare a research paper on this subject in the future. In the area of BEC simulations two publications are forthcoming. One publication in collaboration with the Oxford experimental physics group of Prof. Foot is presently being prepared on the subject of BEC expansion dynamics of strongly confined clouds in highly anisotropic traps. A second one, on observations and simulation of the central vortex tilting mode (section 5.7), has already been submitted for publication [23].

On the subject of bright gap solitons in BEC, confined in periodic potentials, my one-dimensional simulations have resulted in good qualitative results, agreeing with experimental observations in reference [24]. Subsequent further programming work has resulted in an extension of the simulation program capabilities to cylindrically symmetric geometries (section 5.10), which lead to a more accurate quantitative numerical description of the experimental observations. We are planning to publish the results of the three-dimensional soliton simulations.

# Chapter 2

# Background

## 2.1 Cold Collisions

In this section, we want to give a brief review of the physics involved in cold atomic and molecular collisions. A profound understanding of the processes involved in cold collisions is necessary in order to simulate evaporative cooling and to optimise experimental realisations.

A cold collision is simply another expression for a "slow" collision, where the particles involved have a low relative velocity [25]. This is the case at low temperatures, reached by laser cooling and evaporative cooling. When talking about "cold collisions", one usually refers to a collisional energy range between about 1 eV and  $10^{-2}$  eV. In this range, the velocity of the atomic nuclei is very slow compared with the velocities of the electrons in the valence shell (which typically move at  $\approx 10^6$  m/s), yet the de Broglie wavelength  $\lambda = \sqrt{2\pi\hbar^2/(mk_BT)}$  of the particles is still small compared with the size of the interatomic interaction region. These conditions allow us to make a few simplifying approximations as we will see further below, especially the semi-classical approach ( $10^{-2}$  eV to  $10^2$  eV) to scattering effects for higher temperatures. A "cold" collision process with a collision energy of  $10^{-2}$  eV, corresponds to a temperature (scaling the energy with the Boltzmann constant  $k_B$ ) of about 116 K.

The most important approximation is the binary collision approximation (BCA). It is based on the fact that atomic densities achieved in magneto-optical traps (MOT) are in the range of  $10^{12} - 10^{15}$  m<sup>-3</sup>. While the collisions are relatively long-ranged (using for example the 12-6-Lennard-Jones potential [26]), they can still be regarded as binary events at these densities and the low temperatures achieved by laser cooling. Since the spontaneous decay time of possible electronic excitations is much smaller than the mean collision time, all memory of previous collisions, except for changes in kinetic energy, is effectively erased, so that the BCA is justified.

The BCA is also justified by the way we look at scattering effects. The large number of individual collisions taking place change a system of the kind we are concerned with on a large scale. While the scatterer is represented by a potential of finite range, the interesting effects of the scatterer will only be evaluated at a point far away from the scattering potential. Firstly, because it is impossible to place detectors near the event itself, and secondly because we are mainly interested in effects, which the scattering has on the ensemble as a whole.

#### 2.1.1 Classical scattering theory - Hard sphere model

The hard sphere classical scattering model is very simple. Particles are regarded as spheres of diameters  $d_1$  and  $d_2$ , and masses  $m_1$  and  $m_2$ . On contact at distance  $d_{12} = (d_1 + d_2)/2$ , they will undergo a scattering event by a deltapeak force, conserving energy and momentum. At this point we shall not allow inelastic collisions, although they can be incorporated into the hard sphere scattering model.

The relative velocities between the two colliding particles are  $\mathbf{c}_r = \mathbf{c}_1 - \mathbf{c}_2$ before the collision and  $\mathbf{c'}_r = \mathbf{c'}_1 - \mathbf{c'}_2$  after the collision, and the centre of mass velocity is

$$\mathbf{c}_m = \frac{m_1 \mathbf{c}_1 + m_2 \mathbf{c}_2}{m_1 + m_2} = \frac{m_1 \mathbf{c'}_1 + m_2 \mathbf{c'}_2}{m_1 + m_2}.$$
 (2.1)

From these requirements the following relations for the velocities before and after the collision arise. The velocities of the particles before the collision event are

$$\mathbf{c}_1 = \mathbf{c}_m + \frac{m_2}{m_1 + m_2} \mathbf{c}_r, \quad \mathbf{c}_2 = \mathbf{c}_m - \frac{m_1}{m_1 + m_2} \mathbf{c}_r.$$
 (2.2)

After the collision these velocities have become

$$\mathbf{c}'_1 = \mathbf{c}_m + \frac{m_2}{m_1 + m_2} \mathbf{c}'_r, \quad \mathbf{c}'_2 = \mathbf{c}_m - \frac{m_1}{m_1 + m_2} \mathbf{c}'_r.$$
 (2.3)

The magnitude of the relative velocity remains unchanged.  $c'_r = c_r$ .



Figure 2.1: Collision geometry for the hard sphere scattering model. Collision interaction by delta-force contact potential. Impact parameter b, incoming (relative) velocity  $\mathbf{c}_r$  and post-collision relative velocity  $\mathbf{c}'_r$ , scattering angle  $\chi$ .

#### 2.1. COLD COLLISIONS

Figure 2.1 shows a 2D representation of the collision parameters. The differential collision cross section is  $\sigma \ d\Omega = b \ db \ d\epsilon$ , with  $d\Omega = \sin \chi \ d\chi \ d\epsilon$ . Here,  $d\epsilon$ is simply an angular differential perpendicular to the 2D collision plane shown in the diagram (since we are considering the 3D case), and  $d\Omega$  is a solid angle differential. For  $\sigma$  we get

$$\sigma = \frac{b}{\sin \chi} \left| \frac{db}{d\chi} \right|. \tag{2.4}$$

Due to the simple geometry in hard sphere scattering  $b = d_{12} \sin \theta_A = d_{12} \cos(\chi/2)$ , and thus

$$\left|\frac{db}{d\chi}\right| = \frac{1}{2}d_{12}\sin(\chi/2). \tag{2.5}$$

Putting this in (2.4), the differential collision cross section is  $\sigma = d_{12}^2/4$  and the total collision cross section becomes

$$\sigma_T = \int \sigma d\Omega = \pi d_{12}^2 \tag{2.6}$$

As one would expect,  $\sigma$  exhibits no dependence on the scattering angle  $\chi$ , and scattering is fully isotropic.

#### 2.1.2 Inelastic collisions in the hard sphere model

A classical description of inelastic collisions needs to incorporate the effects of internal degrees of freedom of the particles. Within the simple hard sphere model discussed in the previous section, inelastic collisions can release or bind energy in a collision process. The total collision energy  $E_c = E_t + E_i$ , where  $E_t$  is the kinetic energy of the collision and  $E_i$  is the internal energy of the particles. While  $E_c = E'_c$  before and after the collision event, the kinetic energy after the collision depends on  $E'_i$ :

$$E'_{t} = E_{c} - E'_{i} = E_{t} + E_{i} - E'_{i}$$
(2.7)

As explained earlier, the postcollisional kinetic energy is now distributed among the collision partners depending on their masses. For the relative speed  $c'_r$ in the centre of mass frame, a random new direction can be chosen within the approximations of the hard sphere model, because just as in the elastic collision case, inelastic scattering is isotropic in this model. The magnitude of the postcollision relative velocity is

$$c_r' = \sqrt{\frac{2E_t'}{m_r}},\tag{2.8}$$

where the reduced mass  $m_r = m_1 m_2 / (m_1 + m_2)$ .

#### 2.1.3 Limitations of classical scattering theory

Due to its simplicity the classical hard sphere scattering model is obviously incapable of describing the fine details of atomic and molecular scattering phenomena. Therefore, by itself it does not allow meaningful simulations of real physical systems. In trapped dilute gases at relatively high (kelvin to millikelvin) temperatures however, a classical description in not entirely unfounded. This is because the approximations, which can be reasonably applied to such a system are the ones characterising a hard sphere scattering model:

Between relatively rare binary scattering events, the particle wave packets travel on trajectories, which are almost completely classical, since there is no significant overlap between particle wavefunctions. Long range effects of interparticle potentials are largely negligible and, except for individual binary collision events, particles travel through space freely. The whole evaporative cooling process, taking place on the macroscopic level of the particle trap, appears to be well described by an almost entirely classical picture. Quantum effects on the level of the binary interactions influence the macroscopic evaporative cooling process only in terms of the collision rates, which are determined by them.

There is no doubt, however, that quantum effects need to be taken into account on the microscopic scale of the discrete scattering events, determining the collisional cross sections and state transition probabilities. This is data, which can be used in a numerical simulation by means of lookup tables and interpolation, once it is available. The spatial trap symmetry of the particle ensembles under observation also provides a point in support of a treatment in terms of a hard sphere model. It allows anisotropic quantum scattering effects averaged over all possible trap single particle trajectories to be approximated by a more simple isotropic model on a macroscopic scale. Such a modified hard sphere model needs to incorporate the said averaged macroscopic effect of quantum scattering in terms of collision cross sections and transition rates for possible elastic and inelastic scattering channels.

Well aware of the classical limitations on the microscopic scattering scale, we find that a dilute gas ensemble in a trap at kelvin to millikelvin temperatures undergoing evaporative cooling appears to be well described by a classical model incorporating the fundamental quantum nature of scattering effects by means of collision cross sections and transition probabilities. The classical approximation reaches its validity limits once the cooling process reaches ultra-cold temperatures on the nanokelvin scale, where the individual particle wave packets are no longer well localised and distinguishable and Bose-Einstein statistics starts to deviate significantly from the classical Boltzmann statistics approximation. Also at these temperatures the binary collision approximation (BCA) breaks down. Wave packet overlap causes the onset of quantum statistics effects and the beginning of the Bose-Einstein condensation process for bosons.

In the following sections, we will outline the theory of quantum scattering and the way it is used to calculate and understand scattering cross sections, scattering channels and inelastic transition probabilities, ultimately for the more complex cases of molecular scattering.

#### 2.1.4 Basic concepts of quantum scattering theory

We can assume in a simple example, that the interaction potential V(r) depends only on the distance between two particles. Thus the wavefunction describing the problem of scattering by a central force depends on r only. After the scattering process, and at large r, we get

$$\Psi(k,\mathbf{r}) \to \Psi'(k,\mathbf{r}) + \frac{f(k,\theta)}{r} e^{i\mathbf{k}\mathbf{r}}$$
 (2.9)

 $\mathbf{k} = \mathbf{p}/\hbar$  is the collision wavevector, depending on the collision kinetic energy

$$E_{kin} = \frac{\hbar^2 k^2}{2m}.\tag{2.10}$$

The incoming wavefunction  $\Psi(k, \mathbf{r})$  becomes a scattered wavefunction consisting of two components. An unaffected component  $\Psi'(k, \mathbf{r})$  representing the wavefunction of the system in absence of the scattering potential, and a radially outgoing scattered component with energy dependent angular scattering amplitude distribution  $f(k, \theta)$ , where  $\theta$  stands for the angle of observation with respect to the incoming wave. For finite range local potentials V(r), which only depend on position, an expression for the scattering amplitude can be found:

$$f(k,\theta) = -\frac{2m}{\hbar^2} \int V(\mathbf{r}) \Psi(k,\mathbf{r}) \frac{e^{-ikr}}{4\pi} dr d\theta d\phi.$$
(2.11)

The net effect of the scattering collision can be described by a collision cross section by integrating the scattered amplitude over all scattered directions [27].

$$\sigma(k) = \int_{\phi} d\phi \int_{\theta} |f(k,\theta)|^2 \sin(\theta) d\theta \qquad (2.12)$$

A rigorous quantum mechanical derivation of eq. (2.12) in terms of the Lippmann-Schwinger equation can be found in [28]. In inelastic collisions,  $f(\theta, \phi)$  generally also depends on the internal states of the colliding particles and the collision energy. We will look at inelastic collisions later.

The main goal of scattering theory, as we are applying it to our problem of low energy particle collisions, is to provide a means of obtaining the scattering amplitude and the scattering cross section for any scattering event, given the interatomic or intermolecular potential and the internal states of the participating particles. It should be noted, however, that scattering theory, in its original application to high energy nuclear collisions, has traditionally been developed and used for the inverse problem– the calculation of inter-particle potentials after the experimental measurement of scattering data.

In the following we will look at how the scattering amplitudes  $f(k, \theta)$ , representing the differential collision cross sections

$$\frac{d\sigma(k,\theta)}{d\Omega} = |f(k,\theta)|^2 \tag{2.13}$$

can be obtained.

Coming back to expression (2.9), one must start with a partial wave expansion and analysis in order to calculate scattering amplitude and cross section.

For simplicity we define a potential

$$U(r) = \frac{2mV(r)}{\hbar^2}.$$
 (2.14)

With this potential, the Schrödinger equation can now be written in a reduced form as follows:

$$\left[\nabla^2 + k^2 - U(r)\right] \ \Psi(\mathbf{r}) = 0 \tag{2.15}$$

In a central scattering potential, which is a good approximation for elastic collisions, angular momentum is conserved and  $\Psi(\mathbf{r})$  can be expanded in terms of spherical harmonics  $Y_{l,m}(\theta, \phi)$ , the angular momentum eigenstates. Since scattering will also be independent of  $\phi$  and m = 0, the spherical harmonics become the Legendre polynomials  $P_l(\cos \theta)$ . The wavefunction  $\Psi(\mathbf{r})$  can thus now be expanded as follows:

$$\Psi(k,\mathbf{r}) = \frac{1}{r} \sum_{l=0}^{\infty} A_l \psi_l(r) P_l(\cos\theta).$$
(2.16)

Coefficients  $A_l$  follow from the condition that  $\Psi(\mathbf{r})$  must asymptotically satisfy expression (2.9) as  $r \to \infty$ . For simplicity, we define radial functions  $u_l(r) = A_l(r)\psi_l(r)$ . Using an effective *l*-dependent radial potential

$$U_l(r) = U(r) + \frac{l(l+1)}{r^2}$$

and the purely radial functions  $u_l(r)$ , one gets a set of one dimensional radial equations from the Schrödinger equation (2.15):

$$\left[\frac{d^2}{dr^2} + k^2 - U_l(r)\right] \ u_l(r) = 0.$$
(2.17)

For effective potentials  $U_l(r)$ , which vanish rapidly as  $r \to \infty$  (i.e.  $rU_l(r) \to 0$ , for  $r \to \infty$ ), in the asymptotic limit  $(r \to \infty)$  the partial waves  $u_l(r)$ , which make up the scattered wavefunction as described above, have an incoming part proportional to  $e^{ikr}$  and an outgoing part proportional to  $e^{-ikr}$ . Since the particle number is conserved in elastic scattering, the incoming and the outgoing particle flux must be equal. Due to conservation of angular momentum, this condition applies to all partial waves  $u_l(r)$  in the expansion individually.

In the asymptotic limit  $(r \to \infty)$ , this can thus be written as<sup>1</sup>

$$u_l(r) \sim \frac{1}{2i} \left[ \exp(ikr + i\delta_l) - \exp(-ikr - i\delta_l) \right] = \sin(kr + \delta_l).$$
(2.18)

The phase term  $\delta_l$  is real-valued (due to equal amplitudes of incoming and outgoing partial waves under conservation of angular momentum) and depends on the effective potential function  $U_l(r)$  containing the scattering potential. The scattering process can now be understood as follows: Elastic scattering affects the relative phase of the partial waves and thus the scattering amplitude  $f(k, \theta)$  represents the interference pattern of all contributing partial waves.

<sup>&</sup>lt;sup>1</sup>This condition is true for typical interatomic or intermolecular potentials such as the Lennard-Jones potential, but it is not fulfilled, and needs to be modified as in [27], for the case of scattering by, for example, a Coulomb potential  $U(r) = \beta/r$ .

#### 2.1. COLD COLLISIONS

In total, the asymptotic solution of the full scattering problem differs from the potential free solution with V(r)=0 (no scatterer) by a phase shift of  $2\eta_l(k)$ (factor of 2 by convention) of the outgoing partial waves only.

$$\Psi(k,\mathbf{r}) \sim \frac{1}{2ikr} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\theta) \left[ (-1)^{l+1} e^{-ikr} + e^{2i\eta_l(k)} e^{ikr} \right]$$
(2.19)

In the V(r)=0 no scattering case, the plane wave  $\Psi(k, \mathbf{r})$  is simply analysed as incoming and outgoing spherical waves with a phase shift of 0 or  $\pi$  depending on l parity by the above expression.

The phase shifts  $\delta_l$  from equation (2.18), due to the full potential  $U_l(r)$ , can be separated into a part  $\eta_l$  due to the scattering potential U(r), and a contribution  $\tilde{\delta}_l$  by the centrifugal correction term  $l(l+1)/r^2$ . Using spherical Bessel functions to solve (2.17) substituting the correction term, it can be shown that the resulting solutions  $\tilde{\Psi}_l(r)$  have the asymptotic form

$$\tilde{\Psi}_l(r) \sim \sin\left(kr - l\frac{\pi}{2}\right).$$
(2.20)

This means that  $\tilde{\delta}_l = -l\pi/2$ , and the phase factor  $\eta_l$ , which is commonly used in the literature and represents the phase shift due to the scattering potential V(r) alone, becomes

$$\eta_l = \delta_l - \tilde{\delta}_l = \delta_l + l\frac{\pi}{2}.$$
(2.21)

A plane wave incident on a scattering potential V(r) is a typical problem of scattering calculations. The angular distribution of the scattered wave and the scattering cross section need to be determined. Using the orthogonality of the Legendre-functions

$$\int_{-1}^{1} P_l(x) P_{l'}(x) dx = \left[2/(2l+1)\right] \delta_{ll'},\tag{2.22}$$

(where  $\delta_{ll'}$  is the Kronecker symbol and not a phase shift) and the large r boundary conditions as described above, in a partial wave expansion (eq. 2.16) of a plane wave  $\Psi(k, \mathbf{r}) = e^{ikx}$ , we get a scattering amplitude of

$$f(k,\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)(e^{2i\eta_l(k)} - 1)P_l(\cos\theta)$$
(2.23)

and scattering cross section

$$\sigma(k) = 2\pi \int_0^\pi |f(k,\theta)|^2 \sin\theta d\theta = \frac{4\pi}{k^2} \sum_{l=0}^\infty (2l+1) \sin^2\eta_l(k).$$
(2.24)

The resulting elastic collision cross section is dependent on the collision energy and the scattering phase shifts, which depend on the interaction potential V(r)and need to be determined by solving the radial equations (2.17) applying equation (2.19).

#### **Identical Particles**

For identical particles undergoing a collision, it is impossible to distinguish between a scattering by angle  $\theta$  and an angle  $\pi - \theta$ . In order to take this into account, the initial scattering wavefunction (2.9) needs to be symmetrised and the differential scattering cross section under consideration in (2.12) becomes

$$\frac{d\sigma(k,\theta)}{d\theta d\phi} = |f(\theta) + f(\pi - \theta)|^2.$$
(2.25)

Partial waves of uneven parity will no longer contribute to the scattering, while partial waves of even parity count twice. This leads to a bosonic scattering cross section of

$$\sigma(k) = \frac{8\pi}{k^2} \sum_{l \ even} (2l+1) \sin^2 \eta_l(k).$$
(2.26)

For purely s-wave (l = 0) scattering, this yields the characteristic factor of 2 for bosonic scattering cross sections.

#### **Scattering Matrices**

In literature on scattering, the scattering matrix  $S_{ij}$  is frequently used, describing the scattering amplitudes from channel *i* into channel *j*. We can define an *S*-matrix element

$$S_{ij}(k) = e^{2i\eta_{ij}(k)},$$
 (2.27)

the modulus squared of which describes the transition probabilities between eigenstates before and (long) after the collision process. For elastic collisions, where the state does not change within the collision process, all but the diagonal  $S_{ii}$  elements vanish and the *S*-matrix equals the unity operation. Scattering phases  $\eta_{ii}(k)$  thus describe elastic collisions and are real-valued.

It is evident that inelastic collisions are much more complicated than elastic collisions. Evaluation of elastic and inelastic collision rates requires knowledge about all possible scattering channels (state transitions with finite probabilities) and the respective transition rates. The scattering matrix  $S_{ij}$  has as many rows and columns as the number of incoming (pre-collision) and outgoing (post-collision) channels in the scattering problem.

#### Low l scattering at low collision energies

Slow (or "cold") collisions are unique in so far as only collisions with the very lowest angular momentum l values in the centre of mass system contribute to the collisional cross sections. This is because only low l collisions allow the participating particles to approach each other close enough to experience the interatomic (or intermolecular) interaction potential. High l collisions have a classical turning point at large values of R because of the centrifugal potential  $V_l(R) \sim l(l+1)/r^2$ , which increases with l and leads to a centrifugal barrier at the energy

$$E_B = V(r_B) + \frac{\hbar^2 l(l+1)}{2m_r r_B^2},$$
(2.28)

where  $r_B$  is the radial distance of the barrier peak. This potential barrier  $E_B$  effectively shields the short-range scattering potential V(r) for collision energies smaller than  $E_B$ . This effect leads to the observation, that for very low temperatures and collision energies the *elastic* collision cross section approaches a constant value, which is the pure *s*-wave (l=0) component. This is, for example, evident in the chromium data (figure 4.6) and in the oxygen collision cross section data (figure 4.7).

For small collision energies k, the contribution of the l partial wave to the scattering cross section  $\sigma_l(k)$  vanishes proportional to  $k^{4l}$ , as shown in [28]. Thus for ultra-low temperatures, when the collision energy approaches  $E \to 0$ , we get

$$\lim_{k \to 0} f(k) = -a.$$
 (2.29)

a is the the so-called scattering length. The scattering cross section for identical particles becomes  $\sigma_s = 8\pi a^2$  in the zero energy s-wave scattering limit. The scattering length is of great importance in Bose-Einstein condensation (BEC) of dilute gases, determining the interparticle interaction at BEC temperatures. The scattering length a can also be negative for some atomic species such as <sup>7</sup>Li [9]. This leads to an attractive interaction, and BECs are only stable in this regime as long as a certain maximum number of trapped particles is not exceeded, as this would lead to a collapse of the dilute gas cloud into the solid phase. <sup>7</sup>Li has hyperfine states with positive and negative scattering lengths at ultra-cold temperatures.

In general, a large (preferably positive) scattering length a is desirable for the realisation of BECs. Large |a| will allow rapid thermalisation and efficient evaporative cooling with an elastic collision rate of  $\gamma_{el} = n\sigma_s \bar{v}$ , as we will see later (n is the particle density and  $\bar{v}$  the mean relative particle velocity). A positive a will also ensure a repulsive cloud interaction, keeping the dilute gas assumption  $na^3 \ll 1$  valid. For typical experimental BEC (<sup>87</sup>Rb)  $na^3$  has a value of approximately 1e-4.

It is interesting to note that symmetry forbids *s*-wave scattering in fermionic ultra-cold clouds. The consequence of this is that there is no scattering and the cloud cannot be cooled using the common techniques of evaporation, as this requires thermalising collisions.

#### Scattering resonances

The temperature dependent collision cross section  $\sigma(T)$  of some atomic and molecular species exhibits peaks, where the value increases significantly. This effect arises from scattering resonances.

If the centrifugal barrier is very high, then it is theoretically possible to trap particles inside between the barrier and the short range repulsive potential V(r). For finite barrier heights, the trapping would only be meta-stable because particles in trapped states would have a finite probability to escape tunneling through the barrier. Such quasi-bound states cause scattering resonances when their energy is slightly above zero, matching the kinetic energy of the incoming wave. Whether such quasi-bound states exist for l > 0 partial waves depends on the short range potential V(r).

In a case where such a resonance occurs, the scattering phase shift  $\eta_e(k)$  becomes  $\pi/2 \pmod{\pi}$  for resonant k, and the partial wave contribution to the total scattering cross section in equation (2.24) reaches its maximum of  $4\pi(2l+1)/k^2$ . Such a scattering resonance for the *d*-wave (*l*=2) in <sup>87</sup>Rb occurs at scattering energies between 2e-4 K and 3e-4 K, increasing the elastic scattering cross section by a factor of four.

#### 2.1.5 Theory of inelastic Collisions

Inelastic collisions encompass all collision processes, which do not conserve translational kinetic energy. In a trapped gas there are usually exothermic exit channels (see section 2.1.6 below) so that most inelastic collisions will lead to the loss of trapped particles due to state transitions in the coupling of spin angular momentum to translational angular momentum in the collision process. In addition to the states and channels associated with trap spin polarisation effects and translational angular momentum, inelastic collisions also involve channels with changes in the internal particle structure, such as rotational-vibrational modes in molecules. We will look at a typical scattering example involving a molecular internal rotational degree of freedom in the following section.

#### Quantum scattering by an anisotropic potential

In elastic collisions, total angular momentum as well as the components of translational (orbital) angular momentum l and any internal angular momentum jof the particles are strictly conserved. There is no exchange between these two components by definition, and the scattering potentials can be considered central isotropic potentials V(r). Inelastic collisions couple these components and allow angular momentum exchange between them. Inelastic scattering effects cannot occur in central potentials, where l and j are individually constants of the motion. Thus in the most general inelastic scattering case the scattering potentials are not assumed to be isotropic or central. At ultra-low temperatures, with vibrational modes frozen out, molecular scattering resembles scattering between rigid rotators. The theory of these processes involves the treatment of angular momentum coupling problems [29,27].

As an example, we will outline how scattering amplitudes between channels can be determined for a simple case. We will take a look at a quantum scattering event between an atom and a rigid molecular rotator, following along the lines of the presentation of the problem in [27].

In the scattering event, the total angular momentum J and its projection M are conserved. The quantisation axis chosen for this example is about the incident direction and it is spatially fixed. The rotator is assumed to be rigid, as would be the case for such a molecule at low temperatures in the absence of vibrational excitations. Thus the rotator has a fixed moment of inertia I. The molecular rotation has angular momentum j and eigenfunctions of the molecular rotation are the spherical harmonics  $Y_{jm_j}(\theta, \phi)$ , where  $m_j$  is the projection of the the rotational angular momentum to the chosen fixed quantisation axis.

#### 2.1. COLD COLLISIONS

The equation describing molecular rotation is

$$H_{rot}Y_{jm_j}(\theta,\phi) = \frac{\hbar^2}{2I}j(j+1)Y_{jm_j}(\theta,\phi).$$
 (2.30)

The vector  $\mathbf{r}$  connects the centre of the rigid rotator with the position of the incident atom.  $\hat{\mathbf{r}} = (\theta, \phi)$  describes its angular orientation. The nuclear separation within the scattering rigid rotator molecule is described by the vector  $\mathbf{s}$ , the angular orientation of which is described by  $\hat{\mathbf{s}}$ . The angle between  $\mathbf{r}$  and  $\mathbf{s}$  is  $\chi$ , so that the Hamiltonian for the combined system becomes

$$H = \frac{\hbar^2}{2I}j(j+1) - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(r,\chi), \qquad (2.31)$$

where  $\mu = m_1 m_2 / (m_1 + m_2)$  is the reduced mass of molecule  $(m_1)$  and atom  $(m_2)$ , and  $V(r, \chi)$  is the anisotropic scattering potential.

The scattering potential and the total system wavefunction  $\Phi_J^M(\mathbf{r}, \hat{\mathbf{s}})$  need to be expanded in terms of eigenstates of the total system angular momentum J and its projection M, which is a result of the coupling of rotational angular momentum j (projection  $m_j$ ) and orbital angular momentum l. Orbital angular momentum arises through the relative motion between molecule and atom and has the projection  $m_l$ . These eigenstates of the coupled angular momenta are

$$\mathcal{Y}_{Jj'l'}^{M}(\hat{\mathbf{r}}, \hat{\mathbf{s}}) = \sum_{m_{l}m_{j}} (j'l'm_{j'}m_{l'}|j'l'JM) \ Y_{j'm_{j'}}(\hat{\mathbf{s}}) \ Y_{l'm_{l'}}(\hat{\mathbf{r}}),$$
(2.32)

where the  $(j'l'm_{j'}m_{l'}|j'l'JM)$  are the angular momentum vector-coupling coefficients, also known as the Clebsch-Gordon (CG) coefficients. The total system wavefunction can be written as

$$\Phi_J^M(\mathbf{r}, \hat{\mathbf{s}}) = \frac{1}{r} \sum_{j'l'} \psi_{j'l'}^J(r) \mathcal{Y}_{Jj'l'}^M(\hat{\mathbf{r}}, \hat{\mathbf{s}}).$$
(2.33)

Here, the  $\psi_{j'l'}^J(r)$  are radial functions, which must satisfy a set of coupled equations equivalent to (2.17) in the elastic scattering case:

$$\left[\frac{d^2}{dr^2} + k_{j'}^2 - \frac{l'(l'+1)}{r^2}\right]\psi_{j'l'}^J(r) = \sum_{j''l''} \langle j'l'; J|U|j''l''; J\rangle\psi_{j''l''}^J(r)$$
(2.34)

With partial wave wavenumber  $k_j$ ,

$$k_{j'}^2 = \frac{2m}{\hbar^2} \left( E - \frac{\hbar^2 j'(j'+1)}{2I} \right).$$
(2.35)

U is the potential matrix, which is diagonal in J and independent of the projection M. The radial wave equations  $\psi_{jl}^J(r)$  share this property and lack a superscript M.

U is found by an expansion of the potential  $V(r, \chi)$  in terms of Legendre polynomials

$$V(r,\chi) = \sum_{n} V_n(r) P_n(\cos\chi), \qquad (2.36)$$

so that

$$\langle jl; J|U|j'l'; J \rangle = \frac{2m}{\hbar^2} \iint d^2 \hat{\mathbf{r}} \ d^2 \hat{\mathbf{s}} \ [\mathcal{Y}_{Jjl}^M]^* \ V(r, \chi) \ \mathcal{Y}_{Jjl}^M$$

$$= \frac{2m}{\hbar^2} \sum_n V_n(r) \langle jl; J|P_n(\cos\theta)|j'l'; J \rangle$$

$$(2.37)$$

The relevant matrix elements can be calculated in terms of Wigner 3j-symbols  $\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}$  and Racah coefficients W(abcd; ef) [30] as follows

$$\langle jl; J|P_n(\cos\theta)|j'l'; J\rangle$$

$$= (-1)^{J+n} \sqrt{(2j+1)(2j'+1)(2l+1)(2l'+1)} \begin{pmatrix} j \ j' \ n \\ 0 \ 0 \ 0 \end{pmatrix} \begin{pmatrix} l \ l' \ n \\ 0 \ 0 \ 0 \end{pmatrix} W(jj'll'; nJ)$$
(2.38)

Usually one is interested in the outcome of a scattering event with a specific known entrance channel. We need to define a scattering matrix  $S^J$  picking components (jl|S|j'l') as solutions of equations (2.34) in such a way that for a total angular momentum J only one incoming term is non-vanishing. Such a solution of (2.34) will be symbolised as  $\psi_{j'l'}^{Jjl}(r)$ , with an additional superscript jl indicating the single (j, l) entrance channel.

$$\psi_{j'l'}^{Jjl}(r) \underset{r \to \infty}{\sim} \delta_{jj'} \delta_{ll'} \ e^{-ik_j r} - \sqrt{\frac{k_j}{k_{j'}}} \ i^{-l-l'}(jl|S^J|j'l') \ e^{ik_{j'} r}$$
(2.39)

The partial waves corresponding to this radial solution need to be combined into a full system wavefunction  $\Phi_J^M(\mathbf{r}, \hat{\mathbf{s}})$  (equation 2.33) with an incoming term only containing  $Y_{l0}(\hat{\mathbf{r}})Y_{jm_j}(\hat{\mathbf{s}})$  since there can be no orbital angular momentum about the incident direction of  $\hat{\mathbf{r}}$ .

Such a scattering event leads to the final result

$$\Psi_{jm_j}(\mathbf{r}, \hat{\mathbf{s}}) \underset{r \to \infty}{\sim} e^{-ik_j z} Y_{jm_j}(\hat{\mathbf{r}}) + \sum_{j'm''} f(jm_j, j'm_{j'}|\theta, \phi) \frac{e^{ik_{j'}r}}{r} Y_{j'm_{j'}}(\hat{\mathbf{r}}), \quad (2.40)$$

where the scattering amplitude is calculated as

$$f(jm_{j}, j'm_{j'}|\theta, \phi) = \sum_{J} \sum_{ll'} \sum_{m_{l'}} \sqrt{\frac{\pi(2l+1)}{k_{j}k_{j'}}} i^{l-l'}$$

$$\times (jlm_{j}0|jlJm_{j})(jl|T^{J}|j'l')(j'l'Jm_{j}|j'l'm_{j'}m_{l'})Y_{l'm_{l'}}(\theta, \phi).$$
(2.41)

In the above expression we have used a matrix  $T^J$ , which is defined by the scattering matrix  $S^J$  as

$$T^{J}(jl;j'l') = \delta_{jj'}\delta_{ll'} - S^{J}(jl;j'l').$$
(2.42)

 $f(jm_j, j'm_{j'}|\theta, \phi)$  is the (anisotropic and thus  $\theta, \phi$  dependent) scattering probability amplitude from incoming channel  $(j, m_j)$  to outbound channel  $(j', m'_{j'})$ . The total scattering cross sections for these channels can be obtained by integration, analog to the elastic collision case presented in an earlier section.

#### 2.1.6 Inelastic collisions in trapped gases

Inelastic collisions cause one or both participating collision partners to change its state. In a magnetically trapped gas these inelastic collisions usually lead to the loss of one or both participating particles, since the post-collision states are usually at a lower energy level and untrapped (for a diagram of the Zeeman energy levels in molecular oxygen see figure 3.1).

#### Hamiltonian

Inelastic collisions are due to several coupling effects. There are at least three major distinct physical processes involved, opening inelastic scattering "channels". Two of these processes apply to collisions of ultracold atoms as well as to collisions of ultracold molecules, one is unique to molecules [31].

- Spin exchange collisions
- Spin-spin magnetic dipolar interactions
- Spin-molecular rotation interactions (unique to molecules)

Furthermore, there are the following processes, whose influence on molecular scattering must be considered:

- Molecular rotation-nuclear spin coupling
- Spin-molecular vibration coupling
- long-range anisotropies (relevant for polar molecules, [32, 33])

Spin exchange collisions are due to the angular momentum coupling effects of collision partners at close proximity due to anisotropic interaction potentials. The internal molecular angular momentum coupling situation between nuclear spins, electronic spins and molecular rotation of the two collision partners interacts when the particles approach each other.

One can think about it in a simplified picture as follows: The angular momentum projection of each participating particle at a specific imagined location will split into a superposition of different multiplets with slightly different scattering cross sections when they start interacting with the angular momentum components of the second particle. After the reflection of the partial waves at the scattering potential at a closer distance, the different multiplet partial waves return and "recombine" with slightly different scattering phases (without a change in system orbital angular momentum). Thus after the collision, when the particles fly apart again, the individual angular momentum projections of the molecules are slightly dephased and the molecules have a non-vanishing probability to find themselves in a channel leading to trap loss. Spin exchange collisions can be minimised by preparing the magnetically trapped particles in their "stretched" spin states, with spin, nuclear spin and rotation aligned and at a maximum with the laboratory fixed projection axis. Angular momentum conservation then suppresses spin exchange collisions in this situation. However, spin exchange collisions also occur in the pure s-wave scattering regime at

ultra-low temperatures and they are the leading cause for exothermic inelastic collisions and trap loss in trapped atomic gases.

The separate dipolar magnetic spin-spin interaction  $V_{dd}$  has been studied in [34] and can be written as

$$V_{dd}(\mathbf{r}, \mathbf{S}_a, \mathbf{S}_b) = -\sqrt{6} g_e^2 \mu_B^2 r^{-3} \sum_m (-1)^m C^{(2)}(\hat{\mathbf{r}}) [\mathbf{S}_a \otimes \mathbf{S}_b]_{-m}^{(2)}, \qquad (2.43)$$

where  $C^{(2)}(\hat{\mathbf{r}})$  is a Racah spherical harmonic,  $\mu_B$  is the Bohr magneton,  $g_e = 2.0023$ , and the tensor product of the spin vectors is generally defined with the appropriate Clebsch-Gordan coefficients as (T symbolising a general tensor)

$$[\mathbf{T}^{(l_a)} \otimes \mathbf{T}^{(l_b)}]_m^{(l)} = \sum_{m_a, m_b} T_{m_a}^{(l_a)} T_{m_b}^{(l_b)}(l_a, m_a; l_b, m_b | l, m).$$
(2.44)

Spin-spin interaction can typically be neglected in atomic and molecular trapped gases since their effects are small [31].

The most important effect, unique to molecules, is due to molecular fine structure interaction, the coupling between molecular spins S and molecular rotation N. Spin-rotation interactions [35] arise from the coupling of the molecular rotational motion about its centre of mass to the angular momentum of the molecular spins. During the collision process, the molecular rotation is influenced by torques exerted by short- and long-range components  $V_s$  and  $V_{lr}$  of the specific potential energy surface (PES) between the molecules, which can be highly anisotropic. This coupling in combination with orbital angular momentum opens up the largest number of scattering (loss) channels for molecular collisions.

The theory of hyperfine interactions in cold atomic and molecular collisions is fairly complex due to the large number of individual angular momenta involved. The most important hyperfine interaction is the coupling between molecular rotation and nuclear spin because it can invert spins. However, this can be neglected in most cases since the effect on particles prepared in their stretched spin states is small [31]. In oxygen microwave spectra it has been observed that not only are such interactions an order of magnitude smaller than the finestructure interactions, but that they also require a considerable energy in the order of many mK to cause hyperfine transitions [36]. At low and ultra-low temperatures, such interactions can thus safely be considered to be forbidden.

Similar considerations exclude spin-vibration coupling, since vibrations are neglected at low temperatures within the molecular rigid rotator approximation.

Long range anisotropies in the molecular interaction potentials, arising from dispersion and electronic quadrupole-quadrupole interactions, are only a primary concern for the electrostatic trapping of polar molecules.

Thus in the Hamiltonian for a molecular collision event between molecules a and b

$$H = E_{kin,a} + E_{kin,b} + V_s + V_{lr} + V_{dd} + H_{hfs}, \qquad (2.45)$$

only the kinetic energies  $E_{kin}$  as well as the short-  $(V_s)$  and long-range  $(V_{lr})$  contributions to the potential are of greater importance for our purposes.  $V_s$
and  $V_{lr}$  are the components, which make up the anisotropic (angular dependent) molecular potential energy surfaces. The expansion of the PES in terms of radial and angular functions will be described in detail in chapter 3.

In the following we will describe how the complicated angular momentum coupling problems encountered in molecular collisions create a large number of possible inelastic collision channels.

## Scattering channels

As we have discussed above, all of the coupling effects influence the scattering Hamiltonian of the collision system, leading to a number of scattering channels. This number depends on the system under investigation and can be quite large, complicating calculations of scattering rates. We will look at an example.

Consider magnetically trapped oxygen  ${}^{16}O_2$  undergoing collisions with a helium background gas (for simplicity). We will count the number of channels, which such a trapped molecule can inelastically scatter into. Initially, the molecule is trapped in the "stretched" projection of J = N + S (combination of molecular rotation and electronic spin). S=1 and the molecule can assume odd integer rotational values  $N = (1, 3, 5, \cdots)$ . Trapping appears to be possible for this molecule with N=1 and J=2 (projections  $m_J=2$  or  $m_J=1$ ) (see figure 3.1). This system is treated as a rigid rotator, because vibrational excitations in  $O_2$  have excitation energies in the order of  $10^3$  K, which are entirely frozen out for the cold and ultra-cold temperatures we are interested in. The  $O_2$ -He system differs from the simplified rigid rotator model in section (2.1.5) in the aspect that an additional molecular spin is coupled to molecular rotation and orbital angular momentum. For S=0 we reproduce the model.

In the collision, total angular momentum  $\mathcal{J}$  and the projection  $M_{\mathcal{J}}$  are conserved. Note that the total angular momentum  $\mathcal{J}$  is a good quantum number in the absence of an external magnetic field. For a scattering event we have to account for angular momentum coupling between the oxygen spin S=1 and the oxygen molecular rotation. Combination of rotational excitations N=1,3,5(truncating at 5) and S=1 yields 7 possible values of  $J = N + S = (0, 1, \dots, 6)$ , with two independent realisations of J=2 and 4. Combining these with 5 possible orbital angular momenta L = 0, 2, 4, 6, 8 (truncating after the 8th partial wave; partial waves are even valued due to the homonuclear molecular end over end symmetry) to total angular momentum  $\mathcal{J}$ , we get 45 different combinations, of which 21 are different realisations for a conserved post-collision angular momentum  $\mathcal{J} = 2$ . These realisations are different in S, N and/or L number. This means that a molecule trapped with a specific total angular momentum  $\mathcal J$  has a large number of untrapped states a collision can scatter it into. For an arbitrary total  $\mathcal{J}$  (since the orbital angular momentum L may vary widely for different collisions), there are a total number of 555 relevant channels, only few of which leave the molecule in a trapped state. This number was determined in [37] for rotational states up to N=5 and partial waves up to L=10, which are generous limits for ultracold oxygen. Note, however, that these cutoffs are arbitrary. Theoretically an unlimited amount of channels exists.

For two rigid rotator molecules the situation is an even more complicated

angular momentum coupling problem [38, 30]. We now have two individual molecules (index 1, 2), in which spin S combines with molecular rotation N to J.  $J_1$  and  $J_2$  combine to J', which combines with L to  $\mathcal{J}$ .  $\mathcal{J}$  has a conserved projection  $\mathcal{M}_{\mathcal{J}}$ . In [31] Avdeenkov and Bohn calculate the reduced matrix elements analog to the simplified model in equation (2.38), applied to the rather complex angular momentum coupling problem in O<sub>2</sub> molecules. The molecular interaction potential for these calculations was expressed in angular functions as used by ourselves in chapter 3 and the molecular calculations for  ${}^{17}\text{O}_2$ , which is a promising candidate for evaporative cooling, encompass 836 scattering channels for N=0,2 and L ranging from 0 to 10.

To appreciate these large numbers of channels for molecules, we can compare them with the situation for pure *s*-wave scattering (no orbital angular momentum) in the ultra-cold alkali <sup>87</sup>Rb. Here, only 8 loss channels for inelastic collisions, which are due to dipolar relaxation in the trap magnetic field, exist [39].

## From PES to scattering cross sections

For a given molecular potential energy surface (PES), such as the one resulting from our quantum chemical *ab initio* calculations for  $O_2$ - $O_2$  in chapter 3, it is possible to derive collision cross sections. This has been done for a PES other than the one computed in the present work in [31] by Avdeenkov and Bohn.

The first step in the derivation consists of expressing the Hamiltonian in an appropriate angular momentum basis for the  $O_2$  molecule, so that the wave-function can be written in this basis as

$$\Phi_{\mathcal{J},\mathcal{M}}(r,\hat{\mathbf{r}},\hat{\mathbf{s}}_{1},\hat{\mathbf{s}}_{2},\sigma_{1},\sigma_{2}) = \frac{1}{r} \sum_{L,\mathcal{J},J_{1},J_{2},N_{1},N_{2},S_{1},S_{2}} \psi_{L,\mathcal{J},J_{1},J_{2},N_{1},N_{2},S_{1},S_{2}}(r)$$
$$I_{L,\mathcal{J},J_{1},J_{2},N_{1},N_{2},S_{1},S_{2}}(\hat{\mathbf{r}},\hat{\mathbf{s}}_{1},\hat{\mathbf{s}}_{2},\sigma_{1},\sigma_{2}).$$
(2.46)

(See Appendix B.) The notation is analog to the basis expansion for scattering by a rigid rotator (section 2.1.5) in equation (2.33).  $\sigma_{1,2}$  as spin coordinates arise due to the fact that different expansions apply to singlet triplet and quintet  $O_2$ - $O_2$  spin configurations. The coupled angular momentum functions I of the two molecules are defined by tensor products of the single molecule angular functions and angular functions of the orbital angular momentum L.

Solving the coupled channel equations analog to the ones in equation (2.34) yields the scattering matrix  $S(\mathcal{J})$ . The number of rows and columns of the scattering matrix is equal to the (large) number of channels considered, limited only by an arbitrary cut-off in rotational numbers N and partial waves L.

Since we are considering magnetically trapped molecular oxygen, the stateto-state cross sections need to be evaluated in the basis  $|N_1N_2J_1J_2, M_{J_1}M_{J_2}\rangle$ . Note that in the zero magnetic field case the cross sections depend on total angular momentum  $\mathcal{J}$  and are independent of the projection  $\mathcal{M}$ .

In this angular momentum basis and with the help of an appropriately expanded potential energy surface, the scattering amplitudes can be derived along the general lines of the rigid rotator example presented in section 2.1.5. The

## 2.1. COLD COLLISIONS

details of this  $O_2$ - $O_2$  case are much more intricate due to the more voluminous angular momentum coupling calculations.

From the scattering amplitudes the scattering cross sections  $\sigma$  are obtained by integration over all angular coordinates of the scattered wave. For channels with indistinguishable final spin states, symmetry requires integration over half of the angular space only to avoid double counting. One gets

$$\sigma_{(N_1N_2)J_1M_{J_1}J_2M_{J_2}LM_L \to (N_1'N_2')J_1'M_{J_1}J_2'M_{J_2}L'M_L'} = \frac{(1 + \delta_{J_1J_2}\delta_{N_1N_2}\delta_{M_{J_1}M_{J_2}})}{k_{N_1N_1J_1J_2}^2}$$
$$\cdot \sum_{LM_LL'M_L'} \left| \langle (N_1N_2)J_1M_{J_1}J_2M_{J_2}LM_L | \mathcal{T} | (N_1'N_2')J_1'M_{J_1}J_2'M_{J_2}L'M_L' \rangle \right|^2, \quad (2.47)$$

where  $k_{N_1N_1J_1J_2}$  is the channel wavenumber and  $\mathcal{T}$  is derived from the scattering matrix  $\mathcal{S}$  as in equation (2.42)  $\mathcal{T} = \mathcal{I} - \mathcal{S}$ . Energy dependence of the collision cross sections and transition rates comes about through the channel wavenumber, which depends on the collision energy E as in equation (2.35)

$$k_{N_1N_1J_1J_2} = \sqrt{\frac{2m}{\hbar^2}(E - E_{N_1J_1} - E_{N_2J_2})},$$
(2.48)

where  $E_{N_1J_1}$  and  $E_{N_2J_2}$  are the fine structure energy levels of the two molecules involved.

Note that general collision cross sections for diatomic nonvibrating molecules have also been derived in [40] and [41] using a classical kinetic theory approach, starting from a linearised form of the classical Boltzmann equation collision integral.

## **Transition** rates

In many situations it is preferable to use collision- and transition rates instead of collisions cross sections. A rate defines how many collisions or transitions occur in a specific volume during a specific amount of time. The energy dependent transition rate for a collision process between two particles a and b in initial states  $|a\rangle$  and  $|b\rangle$  and final states  $|a'\rangle$  and  $|b'\rangle$  is defined as the expectation value of  $\sigma(E)v$ .

$$K_{|a,b\rangle \to |a',b'\rangle}(E) = \langle \sigma_{|a,b\rangle \to |a',b'\rangle}(E)v\rangle, \qquad (2.49)$$

where E is the collision energy depending on the relative particle velocity v. Averaging over many such processes, the (relative) particle velocity depends on the ensemble temperature T.

Therefore, for our simulation purposes we will average the energy dependent rate coefficient by integrating it over the temperature dependent velocity distribution of the trapped particles. Details about this will be presented in section 4.3.3.

## 2.1.7 Other quantum scattering effects

Beside the typical two-body elastic and inelastic collision processes described in the previous sections, several other quantum scattering effects occur in cold and ultra-cold gas clouds. Some of these effects, such as the three-body collisions and radiative heating are inelastic in character and thus largely undesirable, leading to increased trap loss rates. Others, such as scattering resonances have great experimental potential and can be exploited to an advantage.

In the following, we will look at a few processes, which are subject of present research. However, most of these processes are not of immediate importance to the subjects of the present work.

#### Inelastic three-body collisions

Trapped cold or ultra-cold atomic and molecular gases exist in a regime of extremely low density. This can be expressed as  $na^3 \ll 1$ , where *n* is the particle number density and *a* is the scattering length. In this regime, binary interaction is dominant and hardly any three-body collisions will occur. So few, in fact, that three-body collisions can safely be neglected. However, it is now possible to fine-tune particle interaction using Feshbach resonances (see further below), allowing realisations of arbitrarily large scattering lengths, so that three-body effects can be studied in more detail.

Particle loss from a trapped cloud due to inelastic two-body and inelastic three-body collisions can be expressed in terms of the two-body loss rate  $K_2$  and three-body loss rate  $K_3$  as

$$\frac{\partial n}{\partial t} = -K_2 n^2 - K_3 n^3, \qquad (2.50)$$

With increasing density n the three-body loss rate will become significant and rapidly bypass the two-body loss rate. Note that three-body collisions are mostly inelastic leading to trap loss, as these collisions are the only way the undercooled gas can reach the solid phase mandated thermodynamically by the low ensemble temperature. In the recombination process, two particles aggregate in the presence of a third particle, transferring a large amount of (kinetic) energy to the third. Thus most often all three participating particles are lost from the trap– the aggregated two since they end up in an untrapped state and the third due to its large kinetic energy, which is orders of magnitude larger than that of the remaining ensemble particles.

In <sup>133</sup>Cs, where three-body effects cannot be neglected, Weber et. al. [42] found a  $K_3 \sim a^4$  dependence of the three-body loss rate coefficient on the elastic scattering length a, which can be controlled precisely by magnetic tuning of a Feshbach resonance.

#### Feshbach resonances

Exploiting the energetic coupling of different elastic and inelastic scattering channels, the collisional cross section of atoms in specific spin states with specific collision energies can in some cases be tuned on a wide parameter range using an offset magnetic field in an effect known as Feshbach resonance [43].

As we have already shown in section (2.1.4), quasi-bound states can have a tremendous effect on the scattering properties. One must distinguish between

different types of resonances. Simple scattering resonances, as discussed earlier, are called shape resonances. They can arise due to a potential barrier and the bound wavefunction belongs to the same system internal state as the continuum wavefunction. No internal state transitions are required.

Feshbach resonances arise when an incoming channel is resonantly coupled to a different channel in such a way that the wavefunction for the incoming continuum state and the wavefunction for the quasi-bound state belong to a different internal state of the particle. For a Feshbach resonance, the bound state is semi-stable and cannot decay into any channel other than the incoming channel.

In magnetically trapped alkali gases and BEC, the continuum and bound internal states relevant for the Feshbach resonance effects are states of the trap magnetic field. In some cases their Zeeman energy changes at a different rate for a change in magnetic field magnitude *B*. Thus, using a simple homogeneous offset magnetic field, the Feshbach scattering resonance can be tuned, allowing a precise adjustment of the particle *s*-wave scattering length in the BEC over an extremely wide range.

Scattering in molecular gases is more strongly influenced by such scattering resonances than is the case in atomic samples, due to the large number of coupled channels and internal rotational molecular states. Feshbach resonances involving changes in one or both molecules' rotational quantum numbers can be very long-lived and lead to resonance lines, which are broad in temperature and thus relevant over a wide range of collision energies.

## **Optical Shielding of cold collisions**

It is possible to effectively shield collisions of particles in specific states by means of a laser field. The laser is tuned to resonance with a transition of the entrance channel to a state with a repulsive interaction [44, 45]. Particles approaching each other, attracted by the long range part of the inter-particle potential, are coupled into an upper state by a laser beam resonant with the transition at a specific particle separation  $R_c$ . This separation  $R_c$  marks the Condon-point for the transition, where the potential difference matches  $h\nu$ , where  $\nu$  is the laser frequency. Further approach is quickly halted and reversed by the particle repulsion in the upper state. Outbound, the particles couple back into the initial state when they reach the resonance distance  $R_c$  again. Upper state life times are important for this effect. Rapid decay times make it less efficient.

Partial upper state survival causes the optical shielding process to have a slightly inelastic character. Outbound particles remaining in the upper state will transform the optical excitation energy into kinetic energy heating the trapped particle ensemble. This can be considered to be a radiative heating process.

## **Radiative Heating**

All cold atom and molecule experiments require the use of optical traps at least during some of their stages. In low temperature collisions, the collision time scales, that is the time the collision partners spend at ranges of separation, where they experience the interaction potential, is roughly comparable with the time scales of electronic excitation and relaxation. Thus a certain amount of "interferences" between the two processes can be expected, even in non-resonant conditions. This has been shown experimentally and studied computationally in [46, 47].

The optical trapping laser field drives transitions of a fraction of the colliding particles into an excited quasi-molecular state during the collision process. A fraction of these atoms, just as in the optical shielding resonant coupling case, will not be coupled back and will spontaneously decay back into the ground state at a later time, likely after "rolling down" the excited state potential [46]. Thus these particle transfer optical excitation energy into kinetic energy, dispersing it in subsequent collisions and thus heating the trapped ensemble. This effect is called "radiative heating" and puts a lower limit on the temperatures that can be reached in optical cooling processes. Radiative heating effects are most significant at temperatures below the Doppler laser cooling limit  $T_D$ .

## Photoassociation

Optical transitions can also be used to transfer atoms into molecules while they are undergoing a collision process. In such a case, at a specific interparticle separation  $R_c$  both participating atoms absorb a laser photon and couple to an excited molecular state. This effect has been used experimentally in [48] to measure detuning dependent transition rate modulations in the sodium ground state, so-called Condon modulations, which allow precise derivation of *s*-wave scattering lengths [49].

## 2.1.8 Semi-classical approach to quantum scattering theory

As we have outlined in the previous section, the microscopic description of quantum scattering effects is very complicated. Particularly for molecules with a rich internal angular momentum coupling structure, a number of different processes in scattering events open up an even larger number of scattering channels. Each of them has its own specific transition probability for a given initial state. An analytical treatment needs to make approximations, truncating, for example, the number of partial waves contributing to a given scattering event. The complexity encountered in this type of problem mandates the use of computer algebra systems to obtain transition rates and collision cross sections from PES data [31].

Despite the microscopic complexity of such molecular systems, a trapped cloud of oxygen molecules or, in a simpler case, alkali atoms, appears to be remarkably simple. Scattering is isotropic in all situations, and all macroscopic effects like temperature, density, cooling rate, trap lifetime and others are determined by only two essential parameters: Elastic collision rate and inelastic collision rate (which is almost synonymous with the trap loss rate).

It appears prudent to base a numerical simulation of evaporative cooling on this important observation. All quantum effects will be contained in the said two scattering parameters, while the rest of the physics involved can be treated classically. This general approach, together with many other algorithmic solutions, makes numerical simulations of the molecular trapping problem feasible.

## 2.2 Trapping of neutral atoms

Magnetic traps exploit the effect that paramagnetic particles experience spinpolarisation in an external magnetic field. Particles whose spin is oriented parallel or anti-parallel with an external magnetic field, experience a force towards or away from a magnetic field minimum. For static magnetic fields Maxwell's equations do not allow field extremes in free space. Allowed, however, are zero crossings and thus free space minima of the magnetic field magnitude. Because of this, only weak field seeking particle states, i.e. particle states attracted to low field magnitudes, are trappable magnetically. The spin alignment with the trap magnetic field will follow the field orientation adiabatically when the particles move around within the trap. The interaction energy between particle spin and trap magnetic field,  $V = -\mu_B \mathbf{S} \cdot \mathbf{B}$ , is proportional to the field magnitude  $|\mathbf{B}|$ .

The particle magnetic moment  $\vec{\mu}$  remains parallel or antiparallel with **B** while the adiabaticity condition is observed. The adiabaticity approximation requires that the rate of change of the magnetic field direction for each individual particle within the trap needs to be much smaller than the Larmor frequency  $\omega_l$ .

$$\omega_l = g_l m_F \mu_B \frac{|\mathbf{B}|}{\hbar} \tag{2.51}$$

## 2.2.1 Quadrupole magnetic trap

The most simple trap design is the magnetic quadrupole trap. In a quadrupole trap two magnetic field coils are used, the axes of which are aligned (axial Helmholtz configuration). Both coils conduct electric current in opposite directions so that in the centre of the trap between the two coils the magnetic field has a zero crossing and thus a vanishing local magnitude. From this point at the centre of the trap, the magnetic field magnitude increases linearly in all spatial directions.

$$\mathbf{B} = B_x \mathbf{\hat{x}} + B_y \mathbf{\hat{y}} + B_z \mathbf{\hat{z}} = (B'_a x) \mathbf{\hat{x}} + (B'_a y) \mathbf{\hat{y}} + (2B'_a z) \mathbf{\hat{z}}$$
(2.52)

where  $B'_q$ , the gradient of the magnetic field in radial or (x,y) directions, is constant, and x, y and z are displacements from the origin at the trap centre.

Thus the force  $F = -\nabla V = \mu \mathbf{B}$ , which the trapped particles experience towards the trap centre, is also constant for all radial directions.

One serious problem with the simple quadrupole magnetic trap is the violation of the adiabaticity condition at its centre. The effects of this adiabaticity violation will be discussed in section 2.3.2 below.



Figure 2.2: Magnetic field magnitude  $|\mathbf{B}|$  in a superconducting magnetic quadrupole trap. Colour scale in units of Tesla [T]. The field magnitude vanishes in the centre and increases linearly in all directions within the trap centre region. The axial gradient is twice the radial gradient. Design and construction by Dennis Weise and Olaf Vogelsang [19,20]. Figure used with permission.

## 2.2.2 TOP trap

A dynamic modification of the quadrupole trap is, for example, the time orbiting potential (TOP) trap [50]. The design of this trap avoids particle trajectories within the trap crossing through the zero field magnitude point. Because spin aligned particles cannot follow the field direction adiabatically close to this point, an additional particle loss caused by so-called Majorana spin flips into untrapped states cannot be avoided in a simple quadrupole trap. A TOP trap is built using two pairs of additional Helmholtz coils, positioned radially around the axial quadrupole coils, perpendicular to each other. The bias field generated by these radial coils allows shifting the quadrupole magnetic zero field magnitude point out of the trap centre. Appropriate control of the two pairs of coils allows moving this problematic point around, circling the trap centre in the z = 0 plane, by superposing the following additional magnetic field with the static quadrupole field (2.52).

$$\mathbf{B}_{top} = B_{bias} \left[ \cos(\omega_{top} t) \mathbf{\hat{x}} + \sin(\omega_{top} t) \mathbf{\hat{y}} \right]$$
(2.53)

### 2.2. TRAPPING OF NEUTRAL ATOMS

In the trap centre region this will create a time-averaged harmonic magnetic trapping potential  $\bar{V}$ , in the centre of which the magnetic field magnitude does not vanish.

$$\bar{V} = \mu B_{average} \approx \mu B_{bias} + \mu \frac{B_q'^2}{B_{bias}} \frac{1}{4} (\bar{r}^2 + 8\bar{z}^2).$$
 (2.54)

The TOP bias field rotation angular velocity  $\omega_{top}$  is chosen to be less than the Larmor frequency  $\omega_l$  and faster than the trap oscillation frequency  $\omega_{trap}$  of the resulting harmonic trap.

$$\omega_l \gg \omega_{top} \gg \omega_{trap} \tag{2.55}$$

This allows stable tapping of particle populations over longer periods of time than those possible using a simple quadrupole trap.

TOP traps are useful for evaporatively cooling after loading with a laser cooled gas cloud. In what can be called 2-dimensional evaporation because the zero field point is moving in a plane, this zero magnetic field point can be used to "carve" a circle of radius  $r_0 = B_{bias}/B'_q$  into the trapped particle cloud. The adiabaticity violation at this point causes spin flips into the untrapped state, primarily of hot atoms in the outer cloud regions. The remaining particles subsequently rethermalise at a lower temperature by means of elastic collisions. TOP traps are necessarily quite shallow because radial offset coil current control does not allow for very strong currents and fields. This rules out TOP traps for magnetic trapping of oxygen, which requires very strong magnetic field gradients due to its small magnetic moment of  $2\mu_B$ .

## 2.2.3 Gravity effects

Gravity along the z (axial) axis changes the potential gradients in a linear trap. The force above the magnetic field minimum point increases. Below the zero field point the potential gradient is smaller, decreasing the force on a trapped particle towards the trap centre. Defining a parameter  $\gamma = mg/(2\mu B'_q)$ , where g is the gravitational acceleration and  $2\mu B'_q$  is the axial force on a particle due to the magnetic field gradient, it is clear that particles can only be trapped while  $\gamma < 1$ . The effect of gravity on a harmonic trap is more intuitive, as it only shifts the equilibrium position.

In practice, gravity modifies the TOP trap frequencies as follows [51].

$$\omega_{\perp} = \omega_{\perp,0} (1 - \gamma^2)^{1/4} (1 + \gamma^2)^{1/2}, \qquad \omega_z = \omega_{z,0} (1 - \gamma^2)^{3/4}$$
(2.56)

Thus the trap frequency ratio  $\lambda$  changes as

$$\lambda = \frac{\omega_z}{\omega_\perp} = \sqrt{8} \sqrt{\frac{1 - \gamma^2}{1 + \gamma^2}},\tag{2.57}$$

so that in addition to the typical oblate clouds ("pancake shape") in a TOP trap, even trap conditions for spherical and prolate clouds ("cigar shape") can be realised. Prolate shape, however, can only be realised for very weak trapping fields as  $\gamma \to 1$ .

For evaporative cooling using radio-frequency (RF) Zeeman transition evaporation, the instantaneous magnetic field is important. Thus a shifted population will be at resonance with an RF field at different spatial positions. The anisotropy caused by an axial gravity field will cause the evaporation surface to change from a spherical region to a plane intersecting with the cloud [52]. Thus RF evaporation is reduced in efficiency as it effectively becomes onedimensional.

## 2.2.4 External magnetic field effects

Inelastic atomic [53] and molecular scattering effects are changed significantly in external magnetic fields due to shifts in energy levels of the scattering exit channels relative to the entrance channel. Volpi and Bohn [54] investigated this effect for  ${}^{17}\text{O}_2$ , which is the most promising candidate for magnetic trapping of molecular oxygen. Apart from intermolecular inelastic collisions, they also investigate  ${}^{17}\text{O}_2$ -<sup>3</sup>He inelastic collisions, which are relevant for buffer gas cooling at low temperatures using common dilution refrigerators for the purpose.

In addition to the components of the collision Hamiltonian in equation (2.45), an external magnetic field contributes a spin coupling term

$$H_B = g\mu_B \ \mathbf{S} \cdot \mathbf{B},\tag{2.58}$$

where **B** is the external trap magnetic field, g is the electronic Lande factor and  $\mu_B$  is the Bohr magneton. In a Hund's case b coupling [55] basis set, molecular rotation is not strictly a good quantum number, due to the fact that the hyperfine and the external field interactions couple different rotational states. Total  $M_J$ , however, is conserved and due to the weak coupling effect, we can still use the  $|N J M_J\rangle = |0 \ 1 \ 1\rangle$  notation for the trapped  ${}^{17}\text{O}_2$  state. Volpi and Bohn derive a simple universal fitting formula, based on the complex underlying coupling phenomena, which can also be adapted to inelastic collisions of other molecular species. The fitting formula approximates the inelastic transition rates  $K_{NJM_J \rightarrow N'J'M'_J}$ , or simply the overall inelastic (loss) rate  $K_{loss}$ .

$$K_{NJM_J \to N'J'M'_J} = K_0 \left(\frac{E + \Delta M_J g \mu_B B}{E_0}\right)$$
(2.59)

 $K_0$  is the scaling constant, which can be derived from the |B|=0 magnetic field case. E is the collision energy, which increases by  $\Delta E_B = \Delta M_J g \mu_B B$  due to the linear Zeeman effect. Note that this simple approximation neglects the quadratic Zeeman shift.  $E_0$  is the height of the centrifugal *d*-wave barrier in the exit channel and  $\Delta M_J = M_J - M'_J$  is the difference in the angular momentum projection in the channels involved.  $\Delta M_J$  assumes values of 1 or 2 for the  ${}^{17}\text{O}_2$ case, where the final states in the exit channels are  $|0 \ 1 \ 0\rangle$  and  $|0 \ 1 \ -1\rangle$ .

It is important to note that the  $\Delta E_B$  term significantly changes the scattering rate at low collision energies, as it may exceed E by far.

The above approximation is valid for small collision energies and relatively small magnetic fields. The Zeeman energy splitting between initial and final states needs to be smaller than the height of the *d*-wave centrifugal barrier. For the <sup>17</sup>O<sub>2</sub>-<sup>3</sup>He case, the barrier height is  $E_0=0.59$  K and 13 mK for <sup>17</sup>O<sub>2</sub>-<sup>17</sup>O<sub>2</sub>. This makes the approximation valid for fields up to 2430 G ( $\Delta M_J=1$ ) and 4860 G ( $\Delta M_J=2$ ) in the <sup>17</sup>O-<sup>3</sup>He case. For intermolecular inelastic O<sub>2</sub> collisions, the validity limit is reached at merely 53 G. Making matters worse, Volpi and Bohn note that for fields exceeding these thresholds, the inelastic transition rates very rapidly reach and exceed the elastic collision rate.

The strong magnetic field dependence of the inelastic transition rates are a big disadvantage in attempts to trap oxygen molecules in magnetic traps. Volpi and Bohn's calculations cast a shadow on buffer gas and evaporative cooling experiments. However, buffer gas cooling may still provide a large enough number of trapped cold molecules to allow evaporative cooling runs with a rapid decrease of the trap depth (and thus |B|) to quickly leave the parameter region of high inelastic scattering rates.

## 2.2.5 Buffer gas cooling

One very important part in the magnetic trapping of any particle species is the initial "filling" of the trap. Since magnetic traps are relatively shallow, with depths in the order of Kelvins at the maximum, the particles-to-be-trapped (the sample) must be precooled to temperatures significantly below the trap depth in order to collect a substantial sample population in the conservative trapping field. For atomic gases, such as for the alkalis, the precooling can be done using photon scattering in Zeeman slowers and with laser cooling in magneto-optical traps (MOTs). This procedure, however, is largely limited to a small number of atomic species, which have the simple optical transition schemes required for these processes [2]. In general other particle species, and particularly molecules with their complex internal ro-vibronic energy levels, cannot be cooled using such simple optical schemes.

While optical methods simplify the trap loading procedures significantly, for many atomic species traditional cryogenic methods are necessary to reach the low temperatures required for trap loading. For this purpose the buffer gas cooling (BGC) method [56] has proven to be very successful. It relies on the thermalisation of an evaporated atomic or molecular sample with an (untrapped) helium buffer gas by means of elastic collisions. The buffer gas is cryogenically cooled to mK temperatures and can thus dissipate the translational energy of the sample. The buffer gas can eventually be removed from the trap region relatively quickly using vacuum pumps and a further reduction of the cryostat temperature.

At sub-Kelvin temperatures all atomic and molecular species have a negligibly small vapour pressure, with the exception of helium. This makes helium an ideal buffer gas. Additionally, the  ${}^{3}\text{He}/{}^{4}\text{He}$  isotope system allows dilution refrigeration [57] to reach temperatures on the mK scale. The species-to-becooled, however, needs to be brought into the gaseous phase, which is often done by laser ablation of a solid or liquid sample. The initially hot evaporated sample thermalises with the buffer gas by elastic collisions and forms a supercooled gas cloud in the magnetic trap, which is only meta-stable in its gaseous form because of the very low particle densities. Extreme dilution effectively rules out three-body recombination into the liquid or solid phases.

Collisions of the sample gas particles with the walls of the cooled vacuum system will cause them to stick there, removing them from the system. Thus the buffer gas pressure needs to be high enough for the sample to thermalise to close within the buffer gas temperature *before* impinging on the trap walls. This puts a lower limit on the buffer gas temperature, as a certain minimum buffer gas pressure is required for this.

In [56], a simple model is introduced, which allows calculation of the number of collisions required for a sample particle species with mass M at a (high) temperature T' to thermalise with the buffer gas of mass m at (low) temperature T. The temperature change of the sample in one collision is  $\Delta T = (T' - T)/\kappa$ , where  $\kappa = (M + m)^2/(2Mm)$ . For l collisions, we get the differential equation

$$\frac{\partial T_l}{\partial l} = -\frac{T_l - T}{\kappa},\tag{2.60}$$

where  $T_l$  is the sample temperature after undergoing l collisions with the buffer gas. The solution of this differential equation is

$$l = \kappa \left[ \ln(T' - T) - \ln(T_l - T) \right].$$
(2.61)

Assuming an ablated sample temperature of  $\approx 1000$  K and a sample to buffer gas mass ratio of  $M/m \approx 50$ , approximately 100 elastic collisions are required to cool the sample to within 30% of the buffer gas temperature. With an assumed elastic collision cross section between sample and buffer gas of  $10^{-14}$  cm<sup>2</sup>, the <sup>3</sup>He buffer gas needs a density of at least  $10^{-16}$  cm<sup>-3</sup> and thus the temperature cannot be chosen much lower than 240 mK, according to its *T* dependent vapour pressure curve. Sample species, which can be fed into the trap at significantly lower temperatures can thermalise at temperatures below this, but the helium vapour pressure curve rules out loading temperatures significantly below a figure of 100-200 mK.

## 2.3 Trap loss processes

In the previous sections (2.1.6ff and 2.1.7ff), we have discussed inelastic collision effects. In a trapped gas, inelastic collisions will invariably lead to loss of one or both particles from the trap, since they will end up in untrapped or antitrapped states. Inelastic collisions are most frequent at high particle densities close to the trap centre. Thus particles with below-average energies are removed, leaving behind a heated remaining ensemble. Furthermore, inelastic collisions usually have exothermic exit channels and some of the Zeeman energy of the particle in the magnetic trap will be turned into particle motion. In the antitrapped case, the particles are further accelerated out of the trap. While leaving the trap, such particles may undergo further elastic or inelastic collisions, dispersing some of their energy into the remaining cloud of trapped particles. Thus it can be said that all inelastic collision processes are associated with trap heating and adverse to evaporative cooling efforts. In equation (2.50) we have expressed two-body and three-body loss with differential equations in terms of the particle density. For two-body loss we get  $\dot{n} = -K_2 n^2$  and for three-body loss  $\dot{n} = -K_3 n^3$ . In the following we will look at two other important loss mechanisms.

## 2.3.1 Background gas collisions

In experimental realisations of magnetic traps, the quality of the vacuum and the temperature of the trap walls will put an ultimate limit on the lifetimes of trapped particles. Macroscopic trap walls can be cooled to cryogenic temperatures of around 20mK at best using expensive <sup>3</sup>He dilution refrigeration [57]. Unavoidable background particles will have substantially higher energies than the trapped particles, especially in experiments without cryogenic cooling of the trap, such as in most BEC experiments. Background gas collisions therefore will always lead to substantial energy transfer and particle loss. This results in an exponential trap decay (aside from all other trap loss processes), described by a characteristic trap lifetime  $\tau$ :

$$\dot{n} = -n/\tau \tag{2.62}$$

## 2.3.2 Majorana spin flips

As noted above, the quadrupole trap in particular violates the adiabaticity condition for stable magnetic trapping in a region around the trap origin, where the magnetic field magnitude vanishes [50, 58, 59]. In this region, the rate of change of the magnetic field direction experienced by a particle crossing through can be larger than the particle's Larmor frequency  $\omega_l = \mu |B|/\hbar$ , where  $\mu$  is the particle's magnetic moment  $\mu = g_F m_F \mu_B$ , depending on the Bohr magneton  $\mu_B$  and the particle's spin projection.

The maximum rate of change of the magnetic field *direction* can be characterised by the particle's closest approach b to the trap centre on its orbit through the trap and its velocity v. The maximum angular velocity around the trap centre, and thus the maximum rate of change of the trap magnetic field direction, is the expressed by the ratio v/b. With this it is possible to calculate that the predominant loss area due to this effect is an ellipsoid (due to different radial and axial trap magnetic field gradients in a quadrupole trap) with the radius

$$b_0 = \sqrt{\frac{v\hbar}{\mu B'_q}} \tag{2.63}$$

The trap loss due to this effect is proportional to the particle flux through the surface area ( $\sim b_0^2$ ), the mean particle density and the particle velocity. The loss increases as the trap ensemble is evaporatively cooled, gets denser and spends more time close to the trap centre. In some cases it eventually becomes so large that evaporative cooling is no longer sustainable.

In a simple quadrupole trap, gravity (see section 2.2.3) does not alleviate this problem.– Particles will experience an offset in their time averaged position, but they will still cross through the zero field region. Gravity is counteracted by a certain minimum magnetic field gradient. Particles will simply fall out of the trap if this minimum is not exceeded by the trapping field. Thus, as long as particles are trapped in a quadrupole trap under the influence of gravity, they will still have to cross through the zero magnetic field region suffering Majorana loss. We can imagine the effect of gravity as simply "tilting the cone" of a linear potential. In a time averaged harmonic potential (TOP trap), gravity offsets (downshifts) the equilibrium position of trapped particles. Majorana loss is effectively prevented in the TOP trap case by keeping the cloud away from the zero field point at all times. Conversely, the Majorana spin flip effect can be exploited in TOP traps to selectively evaporate particles from the cloud border by "cutting" into the cloud with the zero magnetic field orbit (see section 2.2.2). Here the effect is much enhanced in comparison to the static quadrupole case by the rapid motion of the magnetic field zero point.

## 2.4 Evaporative Cooling

The scattering length a as introduced in the previous sections is crucial for evaporative cooling of bosonic gases, as it determines the rate of elastic collisions within the cold gas. Since evaporative cooling requires high elastic collision rates  $\gamma_{el} = n\sigma_s \bar{v}$ , large values of the elastic scattering cross section are of advantage.

The situation is entirely different for fermions. Because of symmetry considerations, fermions cannot undergo *s*-wave scattering. Thus, in ultracold ensembles of fermions, there will be no elastic collisions, ruling out a traditional evaporative cooling process to reach quantum degeneracy of a Fermi gas.

In the following sections we will outline the theoretical aspects of evaporative cooling of bosonic gases. While our simulations will start at mK temperatures and take samples down to temperatures close to quantum degeneracy, we will not consider the effects of evaporative cooling in relation to condensate growth. Readers interested in this topic are referred to [60].

## 2.4.1 Basic principles of evaporative cooling

In order to explain the method of evaporative cooling, people often compare it with the cooling process of a hot cup of coffee. While the hot steam, which consists of particles of above-average energy, is removed from the system, a collection of colder particles remains in the cup. The remaining particles rethermalise and reproduce the hot tail of the Boltzmann distribution, which has been removed in the evaporation process. This leads to a Boltzmann distribution of a lower temperature. This highlights the importance of elastic collisions, which provide a constant re-supply of particles of above-average velocity, as required for efficient cooling.

The evaporative cooling of an atomic or a molecular cloud of trapped particles can be done much more efficiently and faster than in the example of a hot cup of coffee, because it is possible to evaporate particles, and thus remove them from the remaining ensemble, at almost arbitrary cut-off energies. In contrast, in a hot cup of coffee the evaporation threshold is sharply defined by the surface energy of the liquid. Only particles with larger kinetic energy will undergo the

## 2.4. EVAPORATIVE COOLING

phase transition and be removed, unless there is not enough convection in the gas phase. (Removing the steam/vapor improves the cooling efficiency of this process by increasing the temperature and vapor gradients.)

In order to minimise particle loss over the complete evaporation process, the ensemble has to be kept as close to a thermal equilibrium Maxwell-Boltzmann distribution as possible. The cloud needs to be allowed to rethermalise and thereby regenerate the hot tail of the distribution, as this is where energy can be removed most efficiently. The cut energy  $E_{cut}$  must thus be decreased slowly compared with the elastic collision time scale. This is the adiabaticity condition. When it is observed, the cloud undergoing forced evaporation will stay in a quasi-equilibrium state (close to thermal equilibrium) described by a truncated Maxwell-Boltzmann distribution [61]

$$f(E) = n_0 \lambda_{th}^3 e^{-\beta E} \Theta(E_t - E).$$

$$(2.64)$$

 $\Theta(x)$  is the Heaviside step function which is  $\Theta(x) = 1$  for  $x \ge 0$  and  $\Theta(x) = 1$  for x < 0, and  $\lambda_{th}$  is the thermal de Broglie wavelength.

Figure 2.3 shows an example of a blunt (non-adiabatic) cooling step. The initial 3D Maxwell-Boltzmann velocity distribution representing oxygen molecules at T = 5K temperature is cut at a particle velocity of  $v_{cut} = 130$  m/s. This is equivalent to an energy cut as in equation (2.64). Experimentally, velocity cuts are commonly achieved by flipping particles into an untrapped state at a specific trap radius using radio-frequency Zeeman transitions. In the presented example, the velocity cut evaporates the fastest 7.5% of the particles, which carry 22.7% of the kinetic energy. Thereafter the remaining particles will rethermalise by elastic collisions and reestablish a Maxwell-Boltzmann distribution at temperature T = 4.2 K after several milliseconds.

## 2.4.2 Thermalisation

Thermalisation describes the process, by which a disturbed system reestablishes its thermodynamic equilibrium. In the evaporative cooling context, where the equilibrium is disturbed by removing the hot tail of the Maxwell-Boltzmann velocity distribution, the cloud thermalises by means of elastic collisions. The faster this equilibration process is, the more efficiently only the particles with the highest energies<sup>2</sup> can be removed and the more efficiently the evaporation procedure becomes.

The number of collisions required for thermalisation has been determined to be around 2.7. This figure was derived analytically in Boltzmann equation calculations and has been supported by numerical simulation [62, 63]. When the ergodicity of the system is sufficient, this figure seems to be valid even for gases reaching quantum degeneracy at low temperatures [64].

The observation of a nearly constant number of collisions for thermalisation leads to the conclusion that for efficient and quick cooling runs, high densities

 $<sup>^{2}</sup>$ The fastest particles are sometimes called the "hottest" particles, which is obviously not a correct physical description, but it nicely illustrates the relation between temperature and [mean] particle velocity [of the ensemble].



Figure 2.3: Truncated Maxwell-Boltzmann three dimensional velocity distribution of molecular oxygen. The hot tail of the T = 5 K initial distribution (red line) is cut at  $v_{cut} = 130$  m/s (dashed line). After several elastic collision times (several ms), the remaining particles rethermalise at temperature T = 4.2 K (blue line). Total initial population is normalised.

are favourable. While this also increases inelastic collisions and two- and threebody loss processes, rapid cooling decreases the effects of Majorana flips and background gas losses, which scale linearly with time.

## Thermalisation and ergodicity

In an ergodic system, the distribution of particles in phase space depends only on their energy. This is not always the case, because particularly in harmonic traps the energies along different directions can be separated and consequently described by separate temperatures. However, unlike the DSMC method, several numerical simulation algorithms rely on the ergodicity assumption, which is only valid when the thermalisation time between spatial directions is smaller or equal to the collision time.

The ergodic mixing time between the three spatial dimensions is usually longer than the inelastic collision time, aggravating the adverse effects of cooling mechanisms reduced in dimensionality, for example by gravity (see section 2.2.3). In such cooling situations, ergodicity is not given, ruling out simulation methods based on this assumption. Wu and Foot [65] have investigated crossdimensional mixing in simulations of forced evaporative cooling in one and two dimensions. They found that cross-dimensional thermalisation can be described well by an exponential function with a time constant of several collision times, with full cross-dimensional thermalisation taking tens of collision times. We will return to this problem in section 4.4.2.

## 2.4.3 Adiabatic compression and expansion

Collision rates can be increased by a compression of the trap. This is done by adiabatically increasing the potential by a factor n. While the phase space density does not change during this process, ensemble temperature and particle density increase by a factor of

 $n^{2\delta/(2\delta+3)}$  and  $n^{3\delta/(2\delta+3)}$ 

respectively, where  $\delta$  is the so-called potential parameter.  $\delta$  characterises the component of potential energy, which depends on the trap type,  $\delta = 3$  for a linear potential trap, and  $\delta = 3/2$  for a harmonic potential. Increasing temperature and density is done in order to speed up thermalisation of the ensemble. By increasing the trapping potential by a factor of n, the evaporative cooling process is speed up by a factor of  $n^{4\delta/(2\delta+3)}$  and thus suffers less particle loss by dipolar relaxion and background gas collisions [62, 39].

Adiabaticity of the compression or expansion procedure prevents additional heating effects. The adiabaticity condition requires that the rate of change in the trapping potential is very small, compared with the potential, at all times. Furthermore, adiabaticity requires the rate of change to be small compared with the elastic particle collision time to ensure thermal equilibration.

The adiabatic compression techniques have proven to be essential in reaching BEC temperatures in experiments. The large increase in the elastic collision rate is a huge advantage and experimental groups tune their evaporative cooling setups to the tightest confinements before the disadvantages of increasing threebody effects and collisional thickness in the high density "hydrodynamic" regime start outweighing the benefits.

## 2.4.4 The hydrodynamic collision regime

Trapped gases at high densities can reach a regime, where the cloud cannot be considered to be a "dilute gas" anymore. Particularly species with a very large elastic and inelastic collision cross sections like <sup>133</sup>Cs, which thus require high trap compressions for effective cooling, can reach this regime, where the mean free path  $\lambda$  between particle collisions decreases to values significantly below the characteristic cloud size. This is expressed in terms of the Knudsen number

$$(Kn) = \lambda/L, \tag{2.65}$$

where L is the characteristic length scale of the system under consideration. When the Knudsen number decreases to values smaller than one, the cloud becomes collisionally "thick" and evaporative cooling efficiency sharply decreases to a point, where the adverse heating effects of density dependent inelastic collisions and particle loss due to three-body recombination cannot be overcome by evaporation.

This is due to the fact that in this regime, rethermalisation through the cloud slows down significantly and is limited to the transition time of a thermal perturbation through the cloud [66]. This transition time of thermal perturbations is largely independent of the particle density, with which the detrimental

inelastic collisions scale up. Furthermore, particles evaporated at the cloud borders have only average energies, effectively precluding evaporative cooling.

The effects of this so-called "hydrodynamic" regime on the evaporative cooling process are catastrophic and cannot be overcome easily. They have been a major obstacle in the effort to reach BEC in caesium for a long time. However, ways to work around the limitations of this collision regime have eventually been devised. A reduction of the elastic collision rate and thereby the "thickness" is possible using magnetic control of Feshbach resonances in otherwise all-optical traps. Weber et. al. [67] have recently succeeded in producing a <sup>133</sup>Cs BEC by achieving a final critical phase space density increase by passively filling a small optical "trap dimple" potential depression with a sufficiently precooled population. This method is described in more detail in section 4.5.5.

## 2.4.5 Evaporative cooling efficiency

Evaporative cooling (with the ultimate goal of reaching the Bose-Einstein condensate quantum degeneracy) can be monitored by utilising the phase space density D, which is defined in terms of the spatial particle density n and the de Broglie wavelength  $\lambda_{dB}$ .

$$D = n\lambda_{dB}^3; \qquad \lambda_{dB} = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$
(2.66)

As long as  $D \ll 1$ , D is equivalent to the quantum occupation number of the lowest energy state of the system under consideration. For bosonic particles, Bose-Einstein condensation will set in when D exceeds a value of 2.612 [62].

It is desirable to cool an ensemble of particles in such a way that the amount of particles lost during the process is at an absolute minimum. This is because the amount of particles available to the cooling process is limited by the processes used to load the magnetic and/or optical traps, and so far they cannot be continuously refilled during the cooling process. Typically, traps are initially filled with some  $10^7$  to  $10^{10}$  particles.

All parameters important to evaporative cooling, such as temperature, atom number and phase space density, change by certain factors within specific time intervals. The natural time interval for this is the mean collision time

$$\tau(T) = \frac{1}{n\sigma(T)\bar{v}} = \frac{1}{n\sigma(T)}\sqrt{\frac{\pi m}{8k_B T}},$$
(2.67)

where n is the density,  $\sigma(T)$  is the total collision cross section and m is the particle mass. We can define a parameter  $\alpha$  describing this exponential process, which characterises the temperature decrease of the ensemble undergoing evaporative cooling per particle lost in terms of logarithmic derivatives.

$$\alpha = \frac{d(\ln T)}{d(\ln N)} \tag{2.68}$$

For temporal discretisation this becomes

$$\alpha = \frac{\ln(T'/T)}{\ln(N'/N)} \quad \text{with } T' = T + \Delta T \text{ and } N' = N + \Delta N \tag{2.69}$$

#### 2.4. EVAPORATIVE COOLING

and the temperature decrease can be seen to follow a simple exponential curve as long as  $\alpha$  is constant during the cooling sequence:

$$\frac{T(t)}{T(0)} = \left(\frac{N(t)}{N(0)}\right)^{\alpha} \tag{2.70}$$

However,  $\alpha$  only describes the temperature, which, as we have seen in the previous sections, can be increased or reduced by trap compression and relaxation without gaining a phase space increase. Optimisation of the evaporative cooling process should thus concentrate on the phase space density D. Analog to equation (2.69), which describes the temperature decrease, we characterise the phase space density increase by a parameter  $\gamma$  [62]

$$\gamma = \frac{d(\ln D)}{d(\ln N)} = \frac{\alpha(\delta + \frac{3}{2})}{1 + \frac{\lambda}{R}} - 1, \qquad (2.71)$$

where  $\delta$  is the potential factor ( $\delta = 3$  for a 3D linear potential, and  $\delta = 3$  for a 3D harmonic potential),  $R = \tau_{loss}/\tau_{el}$  is the ratio between inelastic and elastic collision times and  $\lambda = \tau_{ev}/\tau_{el} \approx (\sqrt{2}/\eta)e^{\eta}$  is the ratio between evaporation time  $\tau_{ev}$  and elastic collision time  $\tau_{el}$ . The evaporation time depends on the trap depth  $\eta = V_{cutoff}/(k_BT)$  (also see discussion in section 4.5.1).

Optimisation of the evaporative cooling process requires finding the optimal truncation trap depth  $\eta$  for the systems present R ratio. When the system is in the "runaway evaporation" regime with large enough R, cooling will be rapid and efficient, leading to an increase in phase space density of many orders of magnitude. In some cases cooling will be throttled by other effects reducing R, such as Majorana loss or three-body recombinations. The runaway evaporation regime is characterised by evaporation at constant or continuously increasing elastic collision rate

$$\frac{\partial (n\sigma\bar{v})/\partial t}{n\sigma\bar{v}} = \frac{1}{\tau_{el}} \left( \frac{\alpha(\delta - \frac{1}{2}) - 1}{\lambda} - \frac{1}{R} \right).$$
(2.72)

(Obtained using the table of scaling laws for evaporative cooling [62], reproduced in Appendix D.) Thus R needs to be larger than

$$R_{min} \le \frac{\lambda}{\alpha(\delta - \frac{1}{2}) - 1}.$$
(2.73)

For R = 5000, 1000, 200, linear traps have the highest cooling efficiencies at trap truncation depths of approximately  $\eta = 9$ , 7, 6. The best total cooling efficiency is achieved, when 2.71 is optimal at every point in time.

$$\gamma_{tot} = \frac{\ln(D_{final}/D_{initial})}{\ln(N_{final}/N_{initial})}$$
(2.74)

## 2.4.6 Effective Volumes

When dealing with problems of trapped gases, in many situations it is useful to know the "proper size" of the cloud, which in practice is only bounded by the size of the trapping region, spreading out through most of it at a very low density [68, 56]. We can introduce a replacement "effective volume"  $V_{eff}$ , defined to yield the number of trapped particles when multiplied with  $n_0$ , the peak trap density.

$$N = n_0 V_{eff} \tag{2.75}$$

The effective volume thus depends strongly on the trap geometry and the temperature of the trapped atoms or molecules.

Defining a relative density  $\tilde{n}(\mathbf{r}) = n(\mathbf{r})/n_0$ , we can calculate  $V_{eff}$  as

$$V_{eff} = V_0 \int_{V_0} \tilde{n}(\mathbf{r}) d\mathbf{r}, \qquad (2.76)$$

where  $V_0$  is the volume of the trap region.

Similarly, a two-body collision effective volume can be defined as

$$\Lambda_{eff} = V_0 \int_{V_0} \tilde{n}^2(\mathbf{r}) d\mathbf{r}, \qquad (2.77)$$

which is useful to determine the mean collision rate  $\overline{\Gamma}$ , which is the total collision rate  $\Gamma$  divided by the number of particles.

$$\bar{\Gamma} = \frac{\Gamma}{N} = \frac{\Lambda_{eff}}{V_{eff}} n_0 \sigma \bar{v}_r \tag{2.78}$$

where  $\bar{v}_r$  is the mean relative particle velocity, and  $\sigma$  the scattering cross section.

The effective volumes approach yields a few useful analytical expressions for simple cases, such as for a spherically symmetric linear trap, where  $V_{eff} \simeq 6V_0/\eta^3$ . Here,  $\eta = U_w/(k_BT)$  is the trap depth with the maximum potential  $U_w$  of a trapped particle. In the same trap one gets  $\Lambda_{eff} = 3V_0/(4\eta^3)$ , so that the mean collision rate becomes  $\bar{\Gamma} = n_0 \sigma \bar{v}_r/8$ .

In our numerical simulation, the effective volumes approach provides convenient algorithms to compute expected collision rates for consistency checks.

# Chapter 3 Potential Energy Surfaces

For accurate simulations of evaporative cooling and other cold collision processes the knowledge of precise potential energy surfaces (PES) for the colliding and interacting particle species is required. PES is the term for the full set of potential energy curves for all angular configurations, showing the potential energy between two particles depending on the interparticle separation. For oxygen O<sub>2</sub>-O<sub>2</sub> this multi-dimensional hypersurface depends on the molecular separation and three angles. Additionally, for oxygen with molecular spin S = 1, three individual PES for the singlet, triplet and quintet spin manifolds need to be determined.

We found that available data on  $O_2$  PES [69, 70] is comparatively old and unreliable. In order to operate our simulation of evaporative cooling on a more modern solid foundation, we decided to attempt the computation of an improved PES using the electronic structure methods of quantum chemistry. The theory at the base of quantum chemical computations necessary for the treatment of oxygen molecules, the procedures we went through and the results we finally obtained will be the subject of the following sections in this chapter.

## 3.1 Physics of the $O_2$ molecule

Oxygen exists in three natural isotopes of different abundances and nuclear spins [71].

Isotope	$^{16}\mathrm{O}$	$^{17}O$	$^{18}\mathrm{O}$
Natural abundance	99.757(16)%	0.038(1)%	0.205(14)%
Nuclear spin	0	5/2	0

Thus six isotopically different  $O_2$  molecules exist, three of which have nonzero nuclear spin *I*. Molecular oxygen is one of the most simple paramagnetic diatomic molecules. And since some of the molecular oxygen isotopomers have weak field seeking ground states they can be confined in magnetic traps. This makes molecular oxygen a target of great interest as a possible future candidate for Bose-Einstein condensation.

## 3.1.1 Electronic configuration and ro-vibrational excitations

Atomic Oxygen has an electronic  $1s^22s^22p^4$  configuration. The O<sub>2</sub> molecule has a ground state electronic configuration of

$$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^2.$$

This state is also called  ${}^{3}\Sigma_{g}^{-}$ . Molecular states are labelled according to their total orbital angular momentum  $L_{z} = \hbar\Lambda$  along the molecular axis. In analogy to the naming conventions for single electron states with  $\sigma, \pi, \delta, \ldots$ , the molecular orbital angular momentum states are named  $\Sigma$ ,  $\Pi, \Delta, \ldots$ , for  $\Lambda = 0, 1, 2, \ldots$ . The first upper left index (2S+1) in the oxygen ground state  ${}^{3}\Sigma_{g}^{-}$  indicates the S=1 total molecular spin. This homonuclear state has even parity, as it does not experience a sign change undergoing an inversion through its molecular centre. This is indicated by the lower right index g, which is part of the standard notation for molecular states, where g is derived from German gerade, which means even. At the same time the state is antisymmetric when mirrored at a plane perpendicular through the line connecting the two nuclei, symbolised by the negative upper right index. Note that in spectroscopic literature the ground state is often referred to as X, with electronic excited states labelled  $A, B, \ldots$ according to their energy levels from the bottom up [72].

The  $O_2$  molecule has five kinetic degrees of freedom.– Three translational, one vibrational and one rotational degree. In a simple first order approximation, the kinetic energy can be written as a sum over the three translational components, molecular vibration and rotation:

$$E(\mathbf{p},\nu,N) = \frac{\mathbf{p}^2}{2m} + h\nu_0 \left(\nu + \frac{1}{2}\right) + \frac{\hbar^2 N(N+1)}{2\mu r_e^2}$$
(3.1)

 $\nu$  is the vibration quantum number and N is the rotational quantum number.  $\mu = m_1 m_2/(m_1 + m_2)$  is the reduced mass , which equates to m/2 for homonuclear molecules, and  $r_e$  is the nuclear separation. Molecular rotation occurs only around the major molecular inertial axis at moderate and low temperatures, because, due to the minute moment of inertia around the remaining axis, the respective excitation quanta are very large.

Due to Maxwell's principle of equipartition of energy, an average of  $\frac{1}{2}k_BT$  is assigned to each independent degree of freedom, and thus the average energy of the oxygen molecule is  $3(\frac{1}{2}k_BT)$  at very low temperatures, equal to that of an ideal gas. The molar heat capacity is  $\frac{3}{2}R$ , where R is the universal gas constant. At higher temperatures, molecular rotations become excited. Eventually vibrational excitation sets in, once the average molecular kinetic energy exceeds the vibrational excitation quantisation. This increases the heat capacity to  $\frac{5}{2}R$ .

As far as our work is concerned, we are mostly interested in the electronic and vibrational ground state and the lowest rotational states. For oxygen, the rotational excitation energy is  $0.18 \cdot 10^{-3}$  eV or 2.1 K (by dividing the energy by the Boltzmann constant  $k_B$ ). This is smaller by a factor of  $10^3$  compared with the vibrational excitation energy of 0.19 eV, or 2200 K. Thus, at ultralow temperatures rotational excitations will still be present, while vibrational excitations are frozen out.

## 3.1. PHYSICS OF THE $O_2$ MOLECULE

Considering cold and ultracold molecular collisions we need to keep in mind the orders of magnitude of the energy levels in typical molecular spectra. While electronic transitions have large energies in the order of 1 eV (10<sup>15</sup> Hz), molecular vibrational level spacing is of the order of 0.1 eV (10<sup>12</sup> Hz), specifically 0.19 eV for O<sub>2</sub>. The smallest energy differences are found between rotational levels, in the order of  $10^{-4}$  eV ( $10^{10}$  Hz) [73], which corresponds to  $\approx 1$  K. In the oxygen molecule, rotational excitations have an energy of  $1.8 \cdot 10^{-4}$  eV, which is equal to approximately 2K (energy divided by the Boltzmann constant  $k_B$ ). Thus at temperatures of this magnitude, we effectively only need to consider few rotational levels while the electronic and vibrational spectra are completely "frozen out" [55, 74, 75].

## 3.1.2 Rotational levels in homonuclear diatomic molecules

Homonuclear molecules have a significant difference compared with corresponding heteronuclear molecules or molecules consisting of two nuclei of different isotopes of one element such as in the <sup>16</sup>O<sup>18</sup>O molecule. These differences are brought forward by the nuclear exchange symmetry, which requires the total molecular wavefunction to satisfy the Pauli principle. The total molecular wavefunction must be symmetric if  $I_a$  (=  $I_b$ ) is integer, and antisymmetric if the nuclear spins are half-integer.

The contribution of the nuclear spins to the full molecular wavefunction is either symmetric or antisymmetric. The electronic component of the full molecular state is symmetric in the  ${}^{3}\Sigma_{g}^{-}$  ground state, which we are considering. The ground state of vibrational excitations is also symmetric. Molecular rotational excitations can be described by spherical harmonics, which have  $(-1)^{N}$  parity, and thus the rotational component of the total molecular state  $\psi$  is symmetric for even rotational quantum numbers N and antisymmetric for odd N.

Applying the Pauli principle to the symmetry relations of the full molecular wavefunction, one finds that for even (and zero) integer total nuclear spin (bosonic nuclei) only odd rotational quantum numbers N will occur, while for odd integer total nuclear spin (fermionic nuclei) only even rotational quantum numbers N will be found, such as in the <sup>17</sup>O<sub>2</sub> case [36].

## 3.1.3 Prospects for evaporative cooling

A close investigation [71, 31] of the coupling of molecular and nuclear spins in the oxygen molecule shows that several states, which can be trapped magnetically, are among the molecular states of the three different oxygen isotopes.– The interaction energy of these states increases with increasing magnetic field magnitude.

In the Zeeman level scheme shown in figure 3.1, it becomes clear that the  $|N, JM_J\rangle = |0, 11\rangle$  state of the <sup>17</sup>O<sub>2</sub> molecule in particular is well suited for magnetic trapping: In contrast to molecules of the other oxygen isotopes, spin statistics in this molecule do not allow an energetically lower lying untrappable J = 0 state. (In the above context N is the rotational quantum number, J is the spin quantum number, and  $M_J$  stands for the quantum number of the spin

projection in the external trap magnetic field.)

A lower lying untrapped state within the N = 1 manifold provides an exothermal decay channel from J = 2 to J = 0 for the most abundant  ${}^{16}O_2$ and  ${}^{16}O^{18}O$  molecular oxygen isotopomers. In the N = 0 manifold, which we find the  ${}^{17}O_2$  molecule in, no such decay channel exists and the only significant trap loss channel is a change in spin-projection from  $M_F = 1$  to  $M_F = 0$  or -1. Except for the Zeeman splitting in the trap magnetic field these states are energetically degenerate and the transition rates are small [31]. Therefore the  $M_F = 1$  state is an excellent candidate for magnetic trapping.

A more recent study has shown that the external trap magnetic field has a larger than expected influence on the scattering properties of magnetically trapped particles. In [54] Volpi and Bohn show for  ${}^{17}O_2$  that the evaporative cooling condition for magnetic fields larger than approximately 50 G (10000 Gauss = 1 Tesla) no longer holds true. For efficient evaporative cooling the elastic scattering rate  $K_{el}$  needs to be about a hundred times larger than the inelastic scattering rate  $K_{loss}$ . Using an oxygen-helium PES [76], they also find that the inelastic collision rate with a He buffer gas increases considerably in a magnetic field, which is of less concern. At the lowest buffer gas cooling temperature, it should be possible to obtain a magnetically trapped sample, large enough to start the evaporative cooling process.

However, magnetic trapping of molecular oxygen requires fairly strong magnetic fields, much larger than 50 G, in the Tesla range (see section 2.2.1), because laser cooling is not feasible and trap loading needs to be done at the comparatively high temperatures of buffer gas cooling (section 2.2.5). Thus evaporative cooling of molecular oxygen proves to be trickier than expected.



Figure 3.1: The lowest Zeeman energy levels of  $O_2$ . a) Shows the molecular manifold for odd N rotational quantum numbers and b) for even N. Which manifold a homonuclear  $O_2$  isotopomer belongs into depends on its combined nuclear spin I. For even I, it belongs into the odd N manifold and vice versa. Zeeman energies for states, which can potentially be trapped magnetically are drawn in red. Figure from [31] used with permission.

## **3.2** Methods of Quantum Chemistry

The accurate solution of the quantum mechanical many-body Schrödinger equation is the main concern of large areas of physics and chemistry. While analytical solutions are only possible for two-body problems such as the hydrogen atom or contrived examples of particles in square wells, the really interesting problems are many-body problems. In quantum chemistry, which is concerned with solutions to the Schrödinger equation of electronic wavefunctions, anything more than a  $H_2^+$  ion is a difficult multi-electron problem, which generally does not have analytical solutions. Exceptions are large and highly symmetrical molecules, such as  $C_{60}$  molecules and a number of polymers. This general lack of analytical solutions for most multi-particle systems is the reason, why approximate theories and methods in this field are of tremendous importance.

The quantum chemistry program package we have used for our computations uses the approximative Hartree-Fock (HF) theory and its techniques. A brief overview of Hartree-Fock theory and its application by quantum chemistry programs will be given in the following sections. Partially this will follow along the lines and use the conventions of the presentation found in [77, 78].

A different and also very successful approach to problems of electronic structure uses Quantum Monte Carlo (QMC) techniques, which we have not used in this work. For an overview and an introduction to QMC we refer the reader to [79,80].

## 3.2.1 Hartree-Fock Theory

Hartree-Fock and most other theories of electronic structure are based on the Born-Oppenheimer approximation and the neglect of relativistic effects such as potential retardations. Within these approximations, nuclei and electrons have a negligible momentum exchange because of their huge differences in mass. Carrying similar amounts of momentum, electrons move very fast within their orbitals, compared with the motion of the nuclei. For electronic structure considerations it can thus be assumed that the nuclei are virtually at rest while electronic orbitals have ample time to relax into their ground states or follow any nucleic motion adiabatically.

This allows simplifications to the Hamiltonian for the electronic problem since the nuclear motion and the electrostatic nuclear repulsion can be separated. The separated nuclear electrostatic repulsion provides a constant offset to the Hamiltonian for the electronic problem and its eigenvalues. The Hamiltonian for nuclear motion (including electron shells) then contains only the nuclear kinetic energy part, nuclear-nuclear electrostatic repulsion and an electronic potential, depending on nuclear separation, which is in fact the PES as resulting from the solution of the electronic problem. The nuclei, or the molecules in our  $(O_2)_2$  problem, thus move within the PES, explaining its importance for all scattering effects.

The separated Hamiltonian for the electronic problem is the following (in

#### 3.2. METHODS OF QUANTUM CHEMISTRY

atomic units as described in appendix C):

$$H = \sum_{i} -\frac{1}{2} \nabla_{i}^{2} - \sum_{i} \sum_{a} \frac{Z_{a}}{r_{ia}} + \frac{1}{2} \sum_{i} \sum_{j \neq i} \frac{1}{r_{ij}}$$
(3.2)

This Hamiltonian describes the electron kinetic energy (first term) and the Coulomb interaction of N electrons of unit negative charge and ions of charge  $Z_a$ . Distances are relative distances of the type  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . The second term describes the Coulomb attraction between electrons and ions,  $V_{eN}$ , and the third term,  $V_{ee}$ , describes the repulsion between the electrons.

The full electronic wavefunction  $\Psi$  of an atom can be approximatively described by a combination of individual single electron orbitals. This approach is known as "Linear Combination of Atomic Orbitals" (LCAO). Molecular orbitals (MO) are also formed by LCAO. Because of the fermionic nature of electrons, two electrons of equal spin cannot occupy a single orbital. Electronic spatial orbitals  $\psi(\mathbf{r})$  thus must have a spin component, which is usually symbolised by the two orthonormal spin  $(\uparrow/\downarrow)$  functions  $\alpha(\omega)$  and  $\beta(\omega)$ , and are then referred to as spin-orbitals  $\chi(\mathbf{x}) = \psi(\mathbf{r})\alpha(\omega)$  or  $\chi(\mathbf{x}) = \psi(\mathbf{r})\beta(\omega)$ , where  $\mathbf{x}$  has three spatial and one spin coordinate. In order to satisfy the fermionic Pauli exclusion principle, LCAO requires the product of individual single electron spin-orbitals to be antisymmetrised, so that an exchange of any two electrons causes a sign change in the product and so that two electrons with parallel spin are explicitly correlated.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots) = -\Psi(\mathbf{x}_2, \mathbf{x}_1, \cdots)$$
(3.3)

For two spin-orbitals  $\chi_1(\mathbf{x}_1)$  and  $\chi_2(\mathbf{x}_2)$ , the product state thus becomes

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)]$$
(3.4)

For products of two or more single electronic spin-orbitals the antisymmetric product can conveniently be written as a Slater determinant, which has all the properties required by the antisymmetrisation. In particular, the determinant vanishes when any two spin-orbitals are the same. It can also be written using the ket notation as a short-hand.

$$\Psi(\mathbf{x}_{1}, \mathbf{x}_{2}, \cdots, \mathbf{x}_{N}) = (N!)^{-\frac{1}{2}} \begin{vmatrix} \chi_{1}(\mathbf{x}_{i}) & \chi_{1}(\mathbf{x}_{j}) & \cdots & \chi_{1}(\mathbf{x}_{k}) \\ \chi_{2}(\mathbf{x}_{i}) & \chi_{2}(\mathbf{x}_{j}) & \cdots & \chi_{2}(\mathbf{x}_{k}) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{N}(\mathbf{x}_{i}) & \chi_{N}(\mathbf{x}_{j}) & \cdots & \chi_{N}(\mathbf{x}_{k}) \end{vmatrix}$$
$$= |\chi_{1}(\mathbf{x}_{i}), \chi_{2}(\mathbf{x}_{j}), \cdots, \chi_{N}(\mathbf{x}_{k}) \rangle$$
(3.5)

The combination of spin-orbitals that best describes the ground state  $\Psi_0$  will have the lowest energy eigenvalue  $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$  in the Schrödinger equation  $H\Psi = E\Psi$  with the simplified Hartree-Fock Hamiltonian as discussed above.

By choosing an orthonormal set of spin-orbitals  $\langle \chi_i | \chi_j \rangle = \delta_{ij}$ , we can now minimise the energy with respect to the spin-orbitals  $\chi_i$ , where the  $\epsilon_i$  are the

orbital energies of the spin-orbitals  $\chi_i$ , acting as Lagrange multipliers introduced due to the minimisation side condition of normalised orbitals in the rigorous derivation (see [77]) of the Hartree-Fock equation.

$$\frac{\partial}{\partial \chi} \left[ \langle H \rangle - \sum_{i} \epsilon_{i} \int |\chi_{i}|^{2} d\mathbf{x} \right] = 0$$
(3.6)

The resulting equations for the best spin-orbitals (minimising the energy) are the Hartree-Fock integro-differential equations

$$\epsilon_{i}\chi_{i}(\mathbf{x}_{i}) = \left(-\frac{1}{2}\nabla_{i}^{2} - \sum_{A} \frac{Z_{a}}{r_{iA}}\right)\chi_{i}(\mathbf{x}_{i}) + \sum_{j}\int d\mathbf{x}_{j}\frac{|\chi_{j}(\mathbf{x}_{j})|^{2}}{r_{ij}}\chi_{i}(\mathbf{x}_{i})$$
$$-\sum_{j}\delta_{\sigma_{i}\sigma_{j}}\int d\mathbf{x}_{j}\frac{\chi_{j}^{*}(\mathbf{x}_{j})\chi_{i}(\mathbf{x}_{i})}{r_{ij}}\chi_{j}(\mathbf{x}_{j}), \qquad (3.7)$$

where  $r_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$ . The first term is the kinetic energy of the electrons. The sum over A in the second term calculates the Coulomb potential by A ions, static within the Born-Oppenheimer approximation. The third term is the Hartree term describing the electrostatic effect of the other electrons averaged over their individual probability distributions. The unphysical self-interaction for i = j in the Hartree term is cancelled in the fourth term, the exchange term, mandated by the Pauli principle. This term will vanish unless the two electrons have the same spin  $\sigma$ .

In the literature, a Fock operator

$$f = h + \sum_{j} [\mathcal{J}_j - \mathcal{K}_j] \tag{3.8}$$

is often defined so that equation (3.7) can be written as  $f|\chi_i\rangle = \epsilon_i |\chi_i\rangle$ , where h is the single particle Hamiltonian for an electron moving in the field of the A ions (**x**-dependence omitted).  $\mathcal{J}$  represents a Coulomb operator, averaging the interaction  $r_{12}^{-1}$  of a second electron density distribution over all space and spin coordinates. The antisymmetric exchange operator  $\mathcal{K}$  is a nonlocal operator because it does not define a simple spatial potential; it takes care of the spin exclusion requirement.

For numerical computations, the spatial part of the spin-orbitals is expanded in a finite set of N functions  $\phi$  with coefficients  $C_{ki}$ 

$$\psi_i(\mathbf{r}) = \sum_{k=1}^N C_{ki} \phi_k(\mathbf{r}). \tag{3.9}$$

The choice of this finite set will ultimately restrict the accuracy of the Hartree-Fock molecular orbitals to the space spanned by this basis. While it seems prudent to choose the basis functions close to actual orbital functions, such as Slater orbitals proportional to  $e^{-\xi |\mathbf{r}|}$ , consideration of computational tractability dictate basis sets which are easy to integrate analytically, such as Gaussian orbital functions proportional to  $e^{-\zeta |\mathbf{r}|^2}$ . This is because the above expansion reduces the problem of calculating the electronic orbitals to the problem of finding the appropriate coefficients  $C_{ki}$  for the chosen basis, which requires a large number of integrations of the basis set as we will outline below.

In a closed-shell approach, the spin-orbitals are restricted to doubly occupied (opposite spin) spatial orbitals, and the spin component can be eliminated from the Hartree-Fock equation. Using the above basis expansion in this Hartree-Fock equation and defining basis function overlap integral matrix  $S_{kl} = \int d\mathbf{r}_1 \phi_k^*(\mathbf{r}_1) \phi_l(\mathbf{r}_1)$  (due to a non-orthogonal set of basis functions) and a Fock matrix  $F_{kl} = \int d\mathbf{r}_1 \phi_k^*(\mathbf{r}_1) f(\mathbf{r}_1) \phi_l(\mathbf{r}_1)$ , we get the Roothaan equations

$$\sum_{l} F_{kl} C_{li} = \epsilon_i \sum_{l} S_{kl} C_{li}, \qquad (3.10)$$

where i is the index of the basis set expansion chosen for the problem.

The set of matrix equations for the coefficients  $C_{li}$  can be solved numerically using techniques such as iterative diagonalisation, in what is called a self-consistent field (SCF) method. Starting from an initial guess at the correct spin-orbitals, iterations are carried out, consecutively replacing and improving the initial guess with the result of the previous step. This proceeds until the resulting orbitals, as defined by the set of coefficients, do not change (much) any more and the solution has thus become self-consistent in the iteration process.

It must be noted that the concept of universally labelling molecular and atomic orbitals by their angular momenta is an artifact which can be attributed to the Hartree-Fock single electron orbital approach, where the distribution of many electrons is given simply by the sum of the single electron densities. Furthermore the single-determinant Hartree-Fock method neglects electron correlations, using the simple non-local average potential of the other electrons.

These limits of Hartree-Fock theory can be improved by a number of other elaborate methods, such as for example perturbative methods, as described in 3.2.3, or using the Configuration Interaction (CI) and Coupled Cluster (CC) methods. Of the large number of methods used in quantum chemistry we will outline only the ones relevant for our work.

## 3.2.2 Restricted open shell Hartree-Fock (ROHF)

The closed shell Hartree-Fock method described in the previous section assumes that spin-orbitals are occupied by two electrons with opposite spin. In an open shell approach, orbitals occupied by single electrons of arbitrary spin are respected in addition to doubly occupied orbitals, resulting in a larger basis function set. This can easily be done using a (larger) Slater determinant of single electron spin orbitals. Thus within the Slater determinant representing the system LCAO in the unrestricted open shell HF approach, individual singly occupied orbitals may appear twice with opposite spin components.

In all other respects the open shell approach is very similar to the closed shell approach [26]. It is important, however, to choose an appropriate number of higher orbitals in the open shell approach, depending on the situation at hand. The drawback of the open shell method is that the Slater determinant in this setting is not necessarily an eigenfunction of the total spin anymore. (It is in the closed shell approach, where all electronic spins are paired with an electron of opposite spin in all contributing spatial orbitals.) Since the total spin S commutes with the Hamiltonian in equation 3.2, it is important for systems with non-zero total spin to choose Slater determinants which are eigenfunctions of the total spin for calculations using the open shell methods.

An open shell ansatz for the wavefunction is required, which ensures that the corresponding Slater determinants are already eigenfunctions of the total spin. This ansatz for the wavefunction is called the Restricted Open shell Hartree-Fock (ROHF) method. This is the method used in our  $O_2$ - $O_2$  supermolecule PES calculations, which require an open shell approach due to their non-zero total spin.

The ROHF ansatz starts out from a spin S=0 closed shell wavefunction (all electrons paired with one of opposite spin). Then it is assumed that one single electron of a high orbital is excited from state m to state n, undergoing a spin flip at the same time, yielding a triplet state with a z component of -1.

$${}^3_{-1}\Psi^n_m = |\Psi_1\bar{\Psi}_1\cdots\Psi_g\bar{\Psi}_g\bar{\Psi}_m\bar{\Psi}_m| \tag{3.11}$$

Here, the  $\overline{\Psi}$  spinorbitals have spin down. The *n* and *m* indices in  ${}^{3}_{-1}\Psi_{n}^{m}$  symbolise the excitation from orbital *m* to *n*. Eigenstates of the total spin S=1 can now be obtained by application of the spin operator  $S_{+}$ , which raises the spin *z* component by 1.

$$S_{+} = \sum_{j} [\sigma_x(j) + i\sigma_y(j)], \qquad (3.12)$$

where  $\sigma_x$  and  $\sigma_y$  are the common spin matrices and j enumerates the electron they operate on. Applying the  $S_+$  operator once and twice, we get the remaining two states of the S=1 triplett as [26]

$${}^{3}_{0}\Psi^{n}_{m} = |\Psi_{1}\bar{\Psi}_{1}\cdots\Psi_{g}\bar{\Psi}_{g}\Psi_{m}\bar{\Psi}_{n}| - |\Psi_{1}\bar{\Psi}_{1}\cdots\Psi_{g}\bar{\Psi}_{g}\Psi_{n}\bar{\Psi}_{m}|$$

$${}^{3}_{1}\Psi^{n}_{m} = |\Psi_{1}\bar{\Psi}_{1}\cdots\Psi_{g}\bar{\Psi}_{g}\Psi_{m}\bar{\Psi}_{n}|$$

$$(3.13)$$

With a set of such restricted spin orbital functions, which are now insured to be eigenfunctions of the total spin S, Hartree-Fock equations can be derived by variation of the energy with respect to the set of spin orbital wavefunctions, analog to the method described for the closed shell case in section 3.2.1.

## Complete active space self-consistent field (CAS-SCF)

The CAS-SCF algorithm uses a set of Slater determinants in the molecular "active space", spin orbitals representing molecular states with non-zero total spin (compare level scheme in figure 3.2). Active space orbitals are created by spin ladder operator  $S_+ = \sum_j [\sigma_x(j) + i\sigma_y(j)]$  acting on the Slater determinant of the singly occupied spin orbitals. (The sum runs over the electrons and the  $\sigma_{x,y}$  symbolise the common spin matrices.) These active orbitals can be thought of as filled with an unpaired electron raised from a paired lower orbital and undergoing a spin flip. This results in a non-zero spin. These orbitals are important for electronic interaction within the supermolecule and have not been accounted for in previously published work. In our numerical work we

have used an active space of four electrons and four orbitals. This spans a space of possible configurations (Slater determinants) for singlet, triplet and quintet (total spin S = 0, 1, 2) states of O<sub>2</sub>, with a single realisation of S = 2, 12 possible realisations of S = 1 and 35 realisations of S = 0.

The SCF method to iteratively solve this problem for each of the three total spin configurations (singlet, triplet, quintet) uses a linear combination of Slater determinants  $\Psi_I$  of the active space configurations.

$$\Psi^{S_{total}} = \sum_{I} c_{I}^{S_{total}} \Psi_{I}, \qquad (3.14)$$

where  $c_I$  represents the Slater determinant coupling coefficients, which are predetermined by spin and spatial symmetry. The introduction of several Slater determinants makes the CAS-ROHF method computationally more difficult than the closed shell Hartree-Fock method.



Figure 3.2: Spin orbital level scheme used for CAS-SCF numerical solution of the  $O_2$ - $O_2$  supermolecule electronic problem using the Gamess quantum chemistry program. The spin orbitals are classified into three subspaces. Spin orbitals bracketed in D are doubly occupied with electrons of anti-parallel spins. Bracket A marks the "active space", which is only partially occupied, allowing multi-configuration non-zero total spin eigenfunctions within a ROHF approach. The V bracket, which is unbounded towards higher orbitals, marks virtually occupied orbitals used in perturbative calculations.

## 3.2.3 2nd order Møller-Plesset perturbation theory (MP2)

As we have outlined, the Hartree-Fock methods presented in the previous sections impose several limitations on the resulting orbitals. The Hartree-Fock result  $E_{HF}$  can be considered to be a 0th-order approximation of the exact electronic energy  $E_{exact}$ . The difference is due to the LCAO approximation ansatz of Hartree-Fock theory. The true combined wavefunction of two or more electrons is not exactly equal to the LCAO anti-symmetrised product of the single particle wavefunctions used therein. Hartree-Fock theory only accounts for electronic interaction using the average field by integrating over the electronic probability distributions. Thus electrons in the SCF spin orbitals are effectively too close together and the Hartree-Fock methods yield an overestimate of the true electron-electron interaction.

Improvements to the approximations can be made using perturbation theory approaches, for example. This allows the errors, due to neglected electronic correlations within the Hartree-Fock method, to be reduced by determination of the correlation energy  $E_c$  to a higher order.

$$E_c = E_{exact} - E_{HF} \tag{3.15}$$

Møller-Plesset perturbation theory (MPPT) is an application of Rayleigh-Schrödinger many-body perturbation theory (RSPT) using the Hartree-Fock Hamiltonian as a 0th-order Hamiltonian  $H_0 = H_{HF}$ . The Hamiltonian used in the perturbation calculations is  $H = H_0 + H_{pert}$ , with

$$H_{pert} = \frac{1}{2} \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_j \left[ \mathcal{J}_j - \mathcal{K}_j \right], \qquad (3.16)$$

where  $\mathcal{J}$  is the Coulomb integral operator and  $\mathcal{K}$  is the exchange integral operator as defined by equations (3.7) and (3.8). This perturbation Hamiltonian "undoes" the simplifications of Hartree-Fock theory and replaces the electronic interaction with the exact  $r_{ij}^{-1}$  operator. With this Hamiltonian, numerical MP2 implementations are able to recover up to 98% of the correlation energy  $E_c$  in most situations [81]. MP2 employs Taylor series expansions of  $H_0$  eigenstates and energies, taking into consideration unoccupied virtual spin orbitals marked in bracket V in the level scheme shown in figure 3.2. Figuratively, correlated electrons avoid each other by populating unoccupied V orbitals, which are part of the approximative expansion of the exact electronic orbitals, with a non-zero probability.

The Hartree-Fock result  $E_{HF}$  consists of the 0th and first order energies as obtained from the perturbation Hamiltonian (3.16).  $E_{HF} = E^{(0)} + E^{(1)}$ , due to the two similar terms in the respective Hamiltonian  $H_{HF}$ . The first perturbation result improving the Hartree-Fock result is thus the second order energy  $E^{(2)}$ . Higher order corrections can also be calculated at increasing numerical expense. For a detailed derivation of MP2 method and algorithm, see [77].

## 3.3 Ab Initio Computation of an $O_2-O_2$ Potential Energy Surface

An important input for the simulation of evaporative cooling are the elastic (spin-preserving) and inelastic (spin-changing) scattering rates. A comparison of elastic collision and loss rates, integrating scattering rates over all elastic and inelastic channels, allows judgement about whether evaporative cooling of a molecule will be feasible or not. While these rates are now well-known for alkali atoms, where the potential energy surfaces (PES) are simple and isotropic, the rates are not easily accessible for molecules.

Recently, Avdeenkov and Bohn have calculated oxygen-oxygen scattering rates in [31], based on potential energy surfaces obtained by Bussery and Wormer [69, 70, 82]. The PES were calculated employing a perturbation theoretical Hartree-Fock approach (LCAO-MO) for separate  $O_2$  molecules. Subsequently second-order perturbation theory was used to include the interaction between two  $O_2$  molecules.

The problem with the scattering data is that the scattering rates depend strongly on the scattering potential (described in full by the PES). Thus, very accurate theoretical estimates or (preferably) experimental values are needed. In order to improve the PES data available for such computations of molecular scattering data, we have theoretically derived a PES by a full Hartree-Fock *ab initio* approach. Unlike Bussery and Wormer, we have used a O<sub>4</sub> supermolecule approach in the rigid rotor approximation. This means that for each O<sub>2</sub> molecule subset of the O<sub>4</sub> super molecule, the binding length is kept constant at all times. We have calculated the electronic wavefunctions and the total energy with all nuclear coordinates fixed. To obtain the full PES, this method requires calculation of a large number of nuclear position configurations, which are parametrised by the three orientational angles  $\theta_1$ ,  $\theta_2$  and  $\phi$ , and the distance R between the two O<sub>2</sub> subsets of the supermolecule. Some important configurations are shown in figure 3.4.



Figure 3.3: O<sub>2</sub>-O<sub>2</sub> Dimer example configuration illustrating the four degrees of freedom  $(\mathbf{R}, \theta_a, \theta_b, \phi)$  in configurational space.

We ran the "gamess" quantum chemistry program [83] on a cluster of eight dual-processor Linux workstations which needed several weeks of computation time to complete the data set. The numerical techniques employed by the Gamess program to obtain approximate solutions for the electronic supermolecular  $O_2$ - $O_2$  problem have been outlined above in section 3.2. In the following sections we will describe this work in more detail and present the results.



Figure 3.4: Illustration of the O<sub>2</sub>-O<sub>2</sub> supermolecule in H, X, T and L configurations.

## 3.3.1 Computational Setup

The computational work that needed to be done for the discrete calculation of the PES with a resolution sufficient to provide a solid base for improvement of the best known collisional properties of oxygen was huge. A single workstation computer would have been busy with this task for months or even years.

However, the problem presents a natural parallelism in the fact that it consists of discrete and independent points that need to be calculated. What this means is that the task can be computed by a large number of independent computers working on it at the same time. In a parallel setup like this the time required to complete the task scales inversely proportional to the number of computers used, once it has all been configured. We needed an automatic control program that would run in the background of a master node, which was able to distribute the workload over all available workstation computers. At the same time care was needed not to overload the systems so that the normal daily work routine of colleagues would not be affected by this large scale computation. Eventually, after trying out a few publicly available programs [84], it was found that none was suitable, so we decided to develop our own.

An automatic work queuing and job distribution program was written using the Perl [85] script programming language. This language has proven to be invaluable in all sorts of numerical and computer administrative data handling problems that the author has encountered during his studies. It is ideally suited to process text and data files, and it is easy to "throw in" as a quick solution interfacing different data formats and programs. At the same time it is fast because Perl compiles its scripts before execution and it also allows more complex and modular programs to be built by using a vast library of code, which is freely available online. Perl has been adapted as a flexible tool for data acquisition and processing in other projects related to this work. Some of the procedures have been outlined in appendix A.

A version of the Perl::SSH module [86] was used by our automatic load balancing program to periodically log into each of our workstations and check the load and the status of individual computation jobs. The Perl::SSH module unfortunately does not seem to be actively maintained by its creator and we needed to adapt it for use with the latest versions of OpenSSH, which has become the standard to remotely log in and use computers in a secure way.

A job input list was kept on the master node which allowed the entering of new computation jobs into the queue while the program was running. Additionally, the number of computational processes per working subordinate workstation node and the maximum loads could also be configured on the master node without interrupting the program. Once this had been set up, the system proved to be very tolerant against crashing nodes and required a minimum of administration. Failed jobs were identified during post-computational processing of the resulting data files and could be reentered into the work queue after making necessary changes to their configurations.



Figure 3.5: Simple flowchart of the queuing program allowing distributed parallel processing of the individual quantum chemical calculations using the "gamess" quantum chemistry program package.

#### 3.3.2Exploiting symmetries to reduce complexity

The  $(R, \theta_1, \theta_2, \phi)$  parameter space needed to be discretised in order to run the quantum chemistry program for every chosen discrete point in this space. Various symmetries of the  $O_2$ - $O_2$  supermolecule can be exploited to cut down on the amount of points needed to compute a full PES. Only 1/8 of the total parameter space in  $\theta_a$ ,  $\theta_b$  and  $\phi$  needs to be sampled. The particular symmetries allowing this are the following.

$$V(\theta_a + \pi, \theta_b, \phi) = V(\theta_a, \theta_b, \phi)$$
(3.17)

$$V(\theta_a, \theta_b + \pi, \phi) = V(\theta_a, \theta_b, \phi)$$

$$V(\theta_a, \theta_b - \phi) = V(\theta_a, \theta_b, \phi)$$

$$(3.18)$$

$$(3.19)$$

$$V(\theta_a, \theta_b, -\phi) = V(\theta_a, \theta_b, \phi)$$

$$(3.19)$$

$$V(\theta_a, \theta_b, -\phi) = V(\theta_a, \theta_b, \phi)$$

$$(3.19)$$

$$V(\theta_a, \theta_b, -\phi) = V(\theta_a, \theta_b, \phi)$$

$$V(-\theta_a, -\theta_b, \phi) = V(\theta_a, \theta_b, \phi)$$

$$V(\theta_a, -\theta_b, \phi - \pi) = V(\theta_a, \theta_b, \phi)$$

$$V(\theta_b, \theta_b, \phi) = V(\theta_b, \theta_b, \phi)$$

$$(3.20)$$

$$(3.21)$$

$$(3.21)$$

$$(3.22)$$

$$V(\theta_a, -\theta_b, \phi - \pi) = V(\theta_a, \theta_b, \phi)$$
(3.21)

$$V(\theta_b, \theta_a, \phi) = V(\theta_a, \theta_b, \phi)$$
(3.22)

The first two rules exploit the atom exchange symmetry in the homonuclear oxygen molecules. Rules number three and four show that negative angles do not change the system as long as  $\theta_a$  and  $\theta_b$  are treated the same. Also, all three angles can be negated at once without changing the system. – All symmetry rules can be combined. The last two rules characterise the effect of a single  $\theta$  angle negation and the effect of  $\theta$  angle exchange respectively. These symmetries reduce the parameter space that needs to be sampled to the intervals.

$$\begin{aligned}
\theta_a &\in [0, \pi/2] \\
\theta_b &\in [0, \pi/2] \\
\phi &\in [0, \pi]
\end{aligned}$$
(3.23)

In order to allow a maximum resolution of up to  $l_{a,b} = 8$  partial waves in the compiled PES after the computation has been done, the angular discretisation needed to be high. To avoid aliasing beyond the Nyquist frequency, we need more than 4 samples on a  $\pi/2$  angle interval. A resolution exceeding this was chosen in order to be able to handle a small number of data gaps in the final PES compilation. We took 7 samples at the  $\theta$  angles (in degrees: 0, 22.5, 35, 45, 67.5, 80, 90), 9 samples of  $\phi$  (0, 22.5, 45, 67.5, 80, 90, 112.5, 135, 157.5) and 24 radial samples of R on the angle intervals described above and on a radial interval of  $R = [2.5\text{\AA}, 10\text{\AA}]$  (2.5, 2.625, 2.75, 2.876, 3.0, 3.125, 3.25, 3.375, 3.5, 3.625, 3.75, 3.875, 4.0, 4.125, 4.25, 4.375, 4.5, 4.75, 5.0, 5.5, 6.0, 7.0,8.0, 10.0 Å). The radial resolution of the sample points is arbitrary, as it is possible to calculate individual independent PES "shells" at specific radii. In order to get a meaningful model of the radial dependence and to investigate the PES minima, our 24 points proved to be a reasonable choice. Some degenerate configuration overlap (for example  $\phi=0, 180$ ) was tolerated deliberately in order to do some consistency checks on the resulting data. We also ignored the  $\theta$ exchange symmetry, which leads to two different sets of configuration data for the same physical problem. Sometimes one of the equivalent calculations would fail while the corresponding other one yielded results.
Since the whole 10x10x9x24/2 parameter space (subtract 9x9x24 for  $\phi$  degeneracy in the  $\theta = 0$  case) had to be calculated for the three  $O_2$ - $O_2$  spin manifolds (singlet, triplet and quintet), we had to compute 26568 individual points. Added redundancy and repeated computation of failed runs multiplied this figure by more than 2. Every individual gamess job ran for approximately half of an hour on our workstation computers (typically a Pentium3 with 1 GHz). Since they all have two CPUs, they could handle two jobs at the same time. Running 24 hours a day on 8 dual CPU workstations, the raw computational task was completed after approximately 2 months.

#### 3.3.3 Spin orbital basis set and methods

The spin-orbitals  $\chi_i(\mathbf{x})$  used in the quantum chemistry program *Gamess* for our O<sub>2</sub>-O<sub>2</sub> computations are expanded in a fairly large "correlation-consistent polarised Valence Triple Zeta" (cc-pVTZ) basis set [87].

Correlation-consistent basis sets are optimised for computation of correlation energies as part of the numerical procedure. This optimisation is independent of the method which is eventually used to compute correlation energies after the initial Hartree-Fock calculations. While we have used Møller-Plesset (MP2), the basis set can also be used within the Configuration Interaction (CI) or the Coupled Cluster (CC) methods [77].

The valence orbitals of the basis set are split into three separate parts (valence triple zeta, VTZ), which are then combined by variational methods used in the numerical algorithms to obtain best possible results from the Hartree-Fock method. The polarisation part consists of orbitals which are not occupied in a free atom. In the oxygen case these are the 2d and the 1f orbitals.

In a first step of the numerical calculation, the expansion coefficients and the determinant prefactors  $c_I$  (from equation 3.14) are varied to minimise the energy using a CAS-SCF algorithm as outlined in sections 3.2.1 and 3.2.2.

As a second step, second-order Møller-Plesset perturbation theory (MP2) (section 3.2.3) was used to improve the dynamic electronic correlation energy, an important effect not observed by simple Hartree-Fock theory. The optimised basis set improves the performance and accuracy of the MP2 part of the calculations.

### 3.3.4 Data processing, dealing with gaps

On such a large configuration data set it is almost impossible to investigate the reason for the failure of individual configuration gamess runs. As mentioned above, we resorted to a certain redundancy in the input configuration data set by ignoring the  $\theta$  exchange symmetry and having a  $\phi = 0$  and  $\phi = \pi$  configuration overlap. These measures also served as consistency checks, which are necessary on such a largely automated process. It also allowed us to close many gaps in the PES data recovered from the "first" non-redundant part of the run.

While the PES data set we computed in this way was almost complete, some of the  $O_2$ - $O_2$  configurations consistently failed in the gamess program. Even after several tries with slight modifications and different approaches an interaction energy could not be found in some configurations. Thus the PES raw data we obtained after the *ab initio* gamess calculation had several small "holes", which we subsequently closed by radially fitting each  $(\theta_a, \theta_b, \phi)$  configuration set to the following model potential function using the nonlinear fitting functions of the *Mathematica* computer algebra system [88].

$$V_{fit}(R) = c1 + c2\left(e^{-c3/(R-R_0)} - 1\right)^2 + \frac{c4}{R^6} + \frac{c5}{R^{12}}$$
(3.24)

Fitting the raw data to this function, care was taken to find and appropriately weight the potential minima  $R_0$  and the asymptotic behavior for large radii. The fitted function was then used to determine the missing data points in our raw PES.

#### 3.3.5 Numerical fit to angular functions

The patched PES can be expanded in spherical harmonics in order to separate the angular and radial dependencies of the intermolecular potential [70, 69, 89, 90, 91]:

$$V(R, \theta_a, \theta_b, \phi) = \sum_{l_a, l_b, l} V^{l_a l_b l}(R) A^{l \ 0}_{l_a l_b}(\theta_a, \theta_b, \phi)$$
(3.25)

The angular functions as used above are defined as follows:

$$A_{l_{a}l_{b}l}^{l\ 0}(\theta_{a},\theta_{b},\phi) = \sqrt{\frac{2l+1}{4\pi}} \sum_{m_{a}=-l_{a}}^{l_{a}} \begin{pmatrix} l_{a} & l_{b} & l\\ m_{a} & m_{b} & 0 \end{pmatrix} \cdot \cdot Y_{l_{a},m_{a}}(\theta_{a},\phi)Y_{l_{b},-m_{a}}(\theta_{b},0)$$
(3.26)

where the sum actually runs from  $-\min(l_a, l_b) \leq m \leq \min(l_a, l_b)$  because of the homonuclear exchange symmetry. Here, the  $Y_{lm}$  are spherical functions defined as

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l+m)!}{(l-m)!}} P_{lm}(\theta) e^{im\phi}.$$
 (3.27)

Using only even numbers (for the  ${}^{17}\text{O}_2$  even N manifold) and limiting  $l_a$  and  $l_b$  to a maximum value of 8 and l to 14 in our numerical expansion, we obtain a set of 54 angular functions  $A_{l_a l_b}^{l 0}$ . Since only the most simple of these functions are short enough to be written and used by humans, the work was done using the *Mathematica* program.

#### 3.3.6 Radial fit of angular coefficients

The result of the fitting of our PES to the angular functions is a set of  $V^{l_a l_b l}(R)$  coefficients. For each angular function this set contains 24 points, one for each discrete radial step.

The result from the angular fit is a radially dependent list of coefficients for the individual spherical functions. We found that this coefficient list can be radially fitted to the following model function with 8 free variables c1 to c7 and  $R_0$ , where  $x = (R - R_0)/R_0$ , and  $R_0$  usually is the minimum of the function to be fitted.

$$c1 + (c2 + c3 x + c4 x^{2}) e^{-c5 x - c6 x \tanh(c7 x)}$$
(3.28)

In combination the angular and the radial fits cut down the data needed to describe our PESs for each spin multiplet to only 8 coefficients for each of the 54 angular functions (for an expansion up to  $(l_a, l_b, l) = (8, 8, 14)$  angular functions). A 3D section of a fitted full S = 3 multiplet PES in comparison with the raw computed data is shown in Fig. 3.6. Radial cuts of the fitted PES for specific configurations are shown in Fig. 3.7.

#### **3.3.7** Computation of virial coefficients

Finally, in order to check the quality of the angular fit of the full PES, we have calculated the second virial coefficients B(T) at temperature T for oxygen (Shown in Fig. 3.8). The second virial coefficient for a given temperature is computed as a four dimensional numerical integration of the potential  $V(R, \theta_a, \theta_b, \phi)$  for each of the three spin manifolds.

$$B(T) = \frac{N_A}{2} \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta_a d\theta_a \int_0^{\pi} \sin \theta_b d\theta_b$$
$$\cdot \int_0^{\infty} R^2 dR \left[ 1 - e^{-\frac{V(R, \theta_a, \theta_b, \phi)}{kT}} \right]$$
(3.29)

We used a Gauss-Legendre integration method as outlined in [92] in a C++ program for this purpose. The three PESs could were imported into the program using the radial and angular analytical expansion discussed above.

The second virial coefficient characterises the difference of a physical gas compared with the ideal gas in the high temperature approximation and is thus directly related to the a and b values in the van der Waals (VDW) equation

$$RT = \left(p + \frac{a}{V^2}\right)(v - b), \qquad (3.30)$$

where R is the universal gas constant and v = V/n is the molar volume.

The relation between the van der Waals equation and the second virial coefficient is shown in detail in references [93] and [94]. Therefore, we are only going to summarise it here.

The second virial coefficient can be split into a long range, where the intermolecular potential V(R) is attractive (for  $R > 2r_0$ ) and a short range component, where V(R) is repulsive for  $0 < R < 2r_0$ . Here,  $r_0$  is an approximative "molecular radius".

$$B(T) = N_A 2\pi \int_{0}^{2r_0} [1 - e^{-\beta V(R)}] R^2 dR + N_A 2\pi \int_{2r_0}^{\infty} [1 - e^{-\beta V(R)}] R^2 dR \qquad (3.31)$$

With  $\beta = 1/(k_B T)$ . Thus the exponential in the first integral is approximately unity and the integral becomes

$$2\pi \int_{0}^{2r_0} R^2 dR = \frac{16}{3}\pi r_0^3 = 4v_0 = b, \qquad (3.32)$$

where b is the b-coefficient in the VDW equation and  $v_0$  is an approximated "molecular volume"  $v_0 = (4/3)\pi r_0^3$ .

The second integral in equation (3.31) can be developed for  $|\beta V| \ll 1$  and we eventually get as an approximative result for this part

$$-\frac{a}{k_B T} = 2\pi \int_{2r_0}^{\infty} V(R) R^2 dR,$$
 (3.33)

where a is the *a*-coefficient in the VDW equation. Thus the second virial coefficient can be written as

$$B(T) = b - \frac{a}{k_B T}.$$
(3.34)

It is evident that the second virial coefficients provide an excellent way to compare our computed PES with experimental data at high temperatures.



Figure 3.6: Section of the O<sub>2</sub>-O<sub>2</sub> PES for the spin quintet configuration.  $\theta_a = 45^{\circ}$ ,  $\theta_b = 67.5^{\circ}$ ,  $\phi$  into the paper plane  $\phi = [0,\pi]$ , radius R (drawn horizontal) in Å units, interaction energy  $V(R, \theta_1, \theta_2, \phi)$  vertical in  $\mu$ Hartree ( $\mu$ H) units. The original raw potential energy surface is drawn in blue, while the radially fitted PES is drawn in red. The high quality of the numerical fit makes them hard to distinguish in this *Mathematica* plot. The PES approaches V = 0 for large R.



Figure 3.7: Potential energy surface cuts for relevant  $(\theta_a, \theta_b, \phi)$  configurations of the O<sub>2</sub> dimer. Plotted are the potentials for the three spin manifolds (S = 0singlet, S = 1 triplet, S = 2 quintet). The singlet potential is the deepest (red line), the triplet potential is represented by the middle lines (dashed blue), and the quintet potential is the most shallow (solid line). The four configurations are **H** (90,90,0), **X** (90, 90, 90), **T** (0, 90, 0) and **L** (0, 0, 0).

## 3.4 Results and critical review of *ab initio* methods

In this part of the present work we have completed a full quantum chemical ab initio computation of the oxygen-oxygen collision problem for the three oxygen spin multiplets. Great care was taken in the choice of spin orbital base functions, the fine tuning of the computational setup of the *Gamess* quantum chemistry program and the initial parameters of the individual O<sub>2</sub>-O<sub>2</sub> configuration data points. The symmetries inherent in the oxygen-oxygen collision problem have been identified and exploited to reduce the complexity and the volume of the calculations and make the project tractable. Additionally, a robust and eventually largely automated queuing system was developed and put into place for the distributed processing of the large number of time-consuming individual computation runs.

After the completion of the raw computations, we have developed methods and programs to collect and process the individual numerical computation results, while gracefully handling small gaps in the raw data. Such missing data resulted from a small number of configuration points, for which the quantum chemistry computations did not converge and manual intervention and parameter tuning did not yield results. By processing the large volumes of raw data, we have eventually achieved a complete and consistent gaplessly compiled numerical fit of the whole PES for the three spin multiplets, which can in the future be used, for example, to calculate collision cross section data for  $O_2$ - $O_2$ collisions or for a fitting and scaling of the PES with experimentally obtained collision data to improve the best presently known values. We have presented parts of the PES in figures 3.6 and 3.7.

Since the final results of our PES have eventually turned out to be unsatisfactory in comparisons with experimentally measured data, as we will explain further below, we will critically review the *ab initio* methods, which we have employed, in the following paragraphs.

Ab initio calculations in general have become reliable tools for calculation of complex molecular potentials. The precision of such calculated potentials that can be achieved with modern quantum chemistry programs is generally high at "higher" temperatures below and above the room temperature range (in contrast to "low" temperatures in the cryogenic high millikelvin and kelvin ranges). Problems arising from a finite numerical precision and the limits of various approximations in the applied quantum chemistry programs are very intricate, however, and tend to manifest themselves particularly at very low temperatures and collisional energies. This is an important point and we need to consider that ultra-cold collisions and bound states, which are able to influence the collision processes, have energy scales in the order of only  $10^{-7}$  eV. This is the same energy scale as the one, on which the particle de Broglie wavelengths become larger than the immediate short-range Coulomb potentials. A precise evaluation thus necessitates taking into account the effects of relativistically retarded potentials, which have scales in the order of 100 nm for typical wavelengths of virtual exchange photons [95]. Thus on these scales, the inter-particle potentials change due to retardations.- The long-range part, for example, changes from  $\sim r^{-6}$  to  $\sim r^{-7}$ . In addition to relativistic potential

retardations, QED effects become significant on this energy scale. Such effects are all able to cause additional small modifications to the potentials, possibly even larger in magnitude than the relativistic retardations alone.

Additionally and more importantly, one needs to realise that *ab initio* calculations are complex multi-body problems, which can be iteratively approximated at best, but cannot be solved with analytical precision. Thus quantum chemistry programs invariably need to neglect higher order effects in order to make computations on present day computers feasible. The approximations which are generally made tend to be a reasonable for room-temperature chemistry. For ultra-cold collisions, however, minute changes in the PES alter integrable variables like the collision cross sections considerably. Thus, at present, the best approach to PES calculations for low temperature effects may be to fine tune the numerically computed PES, and the collision data derived from them, by means of experimental observations in the low temperature regime in the same way as scattering theory has originally been used in nuclear physics.

We proceeded with the *ab initio* calculation project aware of the problems associated with this approach at very low temperatures, because the present knowledge about oxygen PES is limited and poor in accuracy, promising great improvements through the application of modern computational methods. We need to point out that the virial coefficients computed for our final PES results (shown in figure 3.8 for the three multiplets) do not match existing experimental data, which was obtained at higher temperatures [90]. A comparison indicates that our computed potentials lie significantly too low. Our virial coefficients show an offset of -80 at T = 300 K compared with experimental data. The offset is worse for lower and better for higher temperatures. This result may in part be due to problems with our choice of spin-orbital base functions, which were a result of a collaboration [87]. We hope, however, that our work will contribute to an improved picture in the future through an integration of our results with other theoretical and experimental data in this field.



Figure 3.8: Virial coefficient B(T) computed from our final *ab initio* PES. Shown are the results for the individual three spin manifolds (S = 0 singlet, S = 1 triplet, S = 2 quintet).

## Chapter 4

# Simulation of Evaporative Cooling

In this chapter we describe the implementation and application of a computer program we have developed for the simulation of a trapped particle ensemble on a microscopic level. While such programs have been developed for specific applications before [65, 63, 66], we have developed and adapted the basic algorithms to allow them to handle a broad range of similar problems such as multi-component ensembles, large temperature range in cooling simulations and large fractional particle loss.

Simulations of evaporative cooling using DSMC algorithms, just as the experimental realisation, are conducted in a regime of large Knudsen number  $(Kn) = \lambda/L$ , where  $\lambda$  is the particle mean free path and L is the characteristic system size (cloud size or trap size). This regime is bounded on the dilute gas side by the free-particle limit (large Knudsen number), where a lack of particle interactions precludes realisation of evaporative cooling, and on the high density side by the hydrodynamic limit (Knudsen number much smaller than 0.1), where strong interactions localise the thermalisation effects due to the elastic collisions and thus decrease cooling efficiency. For Knudsen numbers smaller than 0.1, systems in a discrete particle model are more accurately described by methods of molecular dynamics and molecular hydrodynamics. For very small Knudsen numbers, accurate description favours a continuum model using the Navier-Stokes equations [96].

In the following sections we will first take a general look at numerical simulations of cold particle systems and describe the DSMC method, which we have used. We then shed light on the trapped particle problem and trap initial states in section 4.2, before we proceed to the program implementation. In section 4.4, we explore the properties of simulated particle systems in traps before we proceed to simulations of evaporative cooling.

## 4.1 Numerical methods

Several approaches to the problem of a numerical description of a physical many-particle system are possible. A mathematical approach will start out from the Boltzmann equation using methods of computational fluid dynamics (CFD). Microscopic physical approaches such as Molecular Dynamics (MD) and Direct Simulation Monte Carlo (DSMC) have proven to be very successful and overcome many of the problems associated with the more mathematical ones.

The following sections will discuss different numerical approaches to simulating particle systems by means of computer programs.

#### 4.1.1 Boltzmann Equation approaches

If the temperature is high enough and/or if the density is low enough so that the particles in an ensemble can be treated as localised wavepackets whose de Broglie wavelength is small compared with the mean free path, the system can be modelled using classical kinetic theory [94]. This condition can be expressed as

$$\frac{\hbar}{\sqrt{2mk_BT}} \left(\frac{N}{V}\right)^{\frac{1}{3}} \ll 1,\tag{4.1}$$

where m is the particle mass, T the temperature, N the number of particles and V the volume of the gas.

A complete analytical description of the dynamics of a dilute gas in phase space using single particle distribution functions  $f(\mathbf{r}, \mathbf{v}, t)$  (where  $\mathbf{r}$  symbolises the spatial,  $\mathbf{v}$  the velocity coordinates of phase space  $\{\mathbf{r}, \mathbf{v}\}$  and t stands for the time) is given by the Boltzmann equation:

$$\frac{\partial}{\partial t}(nf) + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}(nf) + \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{v}}(nf)$$
$$= \int_{-\infty}^{\infty} d\mathbf{v}_1 \int_{0}^{4\pi} d\Omega \, n^2 \left(f^* f_1^* - f f_1\right) \, v_r \sigma \tag{4.2}$$

Here n is the phase space number density  $n = N/d\mathbf{r}$ , **F** is an external force per unit mass and values marked with a \* symbolise post-collision values.

The Boltzmann equation describes the phase space density changes of component f due to collisions with component  $f_1$ . This entails a collision integral over the complete angular cross section  $\sigma$  (with relative velocity  $v_r$  and solid angle element  $d\Omega$ ), and an integration over the full velocity space of  $\mathbf{v}_1$ .

This equation is justified if the following assumptions (which are not necessarily independent of each other) are met [97]: Microscopic Hamiltonian dynamics, a large number of particles in the ensemble (affecting the numerical tractability), a low gas density allowing the assumption of short range pairwise interactions, the absence of bound particle states, uncorrelated interparticle collisions, which bring about irreversibility in the temporal evolution process, negligible spatial gradients of the distribution function on an atomic scale and a negligible effect of external forces during the collision. Irreversibility comes in through the molecular chaos assumption of uncorrelated particle phase space coordinates. This allows the use of a simple product of single particle states. Note that particles are only uncorrelated on the incoming side of the particle trajectories. The Boltzmann equation (4.2) as derived from kinetic theory provides a mathematically precise analytical description of gases. A lot of work has gone into investigations applying the kinetic theory and the Boltzmann equation to molecular gases and collisions [98, 99, 100]. However, the major drawback of the Boltzmann equation approach is that is impossible to solve the equations analytically for geometrically complex or inhomogeneous cases of gas clouds or flows. Additionally, various practical problems prevent it from being widely used in numerical simulations [101]. Most importantly, numerical solutions suffer from the equation's high dimensionality. Simulations in 6 dimensional phase space let the number of grid points required grow out of all computationally reasonable bounds, even for small particle numbers. This applies to molecular gases particularly, where the dimensions of phase space are increased by the internal molecular degrees of freedom.

A second fundamental problem associated with the numerical solution of the Boltzmann equation is the difficulty in finding and setting the upper bounds for a discrete grid in velocity space. The upper limit is particularly interesting and important for evaporative cooling processes, so that this shortcoming disqualifies the method for these purposes. Additionally, evaluation of the collision integral requires a very large number of operations. Schemes to reduce the numerical impact of the collision integral include Monte Carlo sampling techniques and a focus on the non-equilibrium parts of the collision integral [102, 103].

While many of these efforts were successful for specific applications, these methods do not improve the computational load greatly for the general type of 3D simulation that is the subject of this work.

#### 4.1.2 Molecular Dynamics simulations

Molecular Dynamics (MD) was the first simulation method that approached the problem from a physical perspective. The mathematical analytical approach was dropped in favour of a microscopic description using a large number of individual simulated particles that are traced through time [104]. The method is fundamentally deterministic, although particles may initially be placed using probabilistic methods.– Collisions occur when the particle cross-sections overlap, and there is no fixed temporal step-size. Computational complexity scales with the square of the number of simulated particles. This is the method's greatest disadvantage and it limits the scope of its applicability, since the number of particles is determined by the geometry of a system and the gas density.– Even for small and extremely dilute systems the number of particles is prohibitively large. This makes the method impractical for our purposes.

MD has been successful in many other areas and it can be parallelised on super-computers by splitting into smaller sections when a certain overhead for boundary operations is taken into account.

#### 4.1.3 The Direct Simulation Monte Carlo (DSMC) Method

For the numerical description and simulation of our trapped particle problems we use a Direct Simulation Monte Carlo (DSMC) technique, which is also often called the "Bird" method after its inventor [105, 106]. DSMC does is fact stand for a class of probabilistic simulation methods depending on the dilute gas assumption and the assumption of molecular chaos. This distinguishes DSMC from molecular dynamics (MD) simulations, which are carried out at high densities and with many restrictions concerning the number of simulated particles, as explained above.

The assumption of molecular chaos, that is the assumption that collision impact parameters within the gas are completely isotropic, justifies a simple hard sphere collision model with isotropic scattering. This does not mean that anisotropic quantum effects are not taken into account in determining the actual collision rates. It is only assumed that over the overwhelming number of such events taking place within a gas cloud, the anisotropic scattering effects average out, so that the macroscopic experience can be described in terms of a simple isotropic model [107].

The dilute gas assumption makes the approximation that the physical space occupied by molecules and atoms, that is the sum of their total physical spherical volumes, is negligible compared with the volume of the trap they are flying around in. This constitutes part of the ideal gas approximation and it is reasonable in rarefied gas dynamics. Furthermore in dilute gases it is assumed that potentials are local and collisions binary. This allows the essential DSMC approximation, which is the uncoupling of particle motion and inter-particle collisions over a small time step. While the above approximations hold, and while the uncoupled time step is small compared with the mean collision time, its actual size does not matter.

One major advantage DSMC methods have over MD methods is the following. Because of the uncoupling of collisions and propagation on a microscopic level and a statistical description, a large number of particles may collectively be described by a single numerical particle "unit". While this optimisation allows treatment of macroscopic systems over macroscopic time scales (which is not numerically feasible using MD on workstation computers), it comes at the expense of larger fluctuations. This, however, is a small price to pay and the effect of this is very small when using simulated particles numbers in the order of N = 1e4 to 1e5.

The particle propagation constitutes the first part of the DSMC procedure. Trajectories of simulated particles in an external potential (for example within a quadrupole trap) are computed using a simple Runge-Kutta method, neglecting particle interactions. Purely harmonic external potentials allow precise analytical trajectory calculation and in the case of vanishes external potentials, a simple Euler type algorithm is sufficient for the purpose.

To make good use of the basic DSMC uncoupling principle, the simulation space is partitioned into cells, each of which contains only a fraction of the total number of simulated particles. These cells need to be small compared with the local particle mean free path, since the exact location of atoms within these cells will be meaningless for the purposes of the collision calculation. A probabilistic number of collision pairs (see below) will be chosen from a cell at random. This approximation is bound to yield poor results if there are strong gradients of macroscopic gas parameters across the cell, since cell spacing marks the smallest resolution of macroscopic parameters within the simulation. A good choice for the cell size, sidelength L, is roughly a third of the mean free path  $\lambda$ .  $L \approx \lambda/3$ . In cases with strong macroscopic gradients, the chosen cell size needs to be smaller. This makes the DSMC method an ideal fit for simulations of dilute gases at Knudsen numbers larger than (Kn)=0.1. The averaging effect of choosing collision pairs at random from within a cell, disregarding exact locations, can be alleviated to a certain extent by cell subsampling for the collision calculations. In 3D space a cell may be subsampled into 8 subcells. When using subsampling, collision pairs will be chosen from within a subcell or, if there is none available, from a neighbouring subcell. This will reduce the average distance between two randomly chosen collision partners and thus allow stronger gradients. However, we will later propose a scheme able to handle gradients in a different way, adjusting cell sizes to suit the problem (See section 4.3.1).

After the propagation part the simulated particles are assigned to the cellgrid according to the positions they end up at and the collision procedure is invoked. Thermodynamics requires that for each cell with particle number  $n_i$ and  $F_N$  numerical particle multiplicity (the number of physical particles, which one simulated particle represents)

$$N_{coll} = \frac{F_N n_i (n_i - 1)}{2}$$
(4.3)

collision could occur and need to be considered with a probability of

$$p_j = \frac{c_{r,j}\sigma\Delta t}{V_c} \tag{4.4}$$

each. Here,  $c_r$  is the relative velocity between two potential collision partners,  $\sigma$  is the collision cross section,  $\Delta t$  is the DSMC uncoupling timestep and  $V_c$ is the cell volume. Carrying out all these possible collisions with a relatively low probability is very inefficient and it scales badly with particle number. It is better to consider only a fraction of the collision, which occur with a high probability. We consider

$$N_{coll} = \frac{F_N n_i (n_i - 1) \sigma c_{r,max} \Delta t}{2V_c} \tag{4.5}$$

collisions, which occur with a high, "rescaled" probability of

$$p_j = \frac{c_r, j}{c_{r,max}}.$$
(4.6)

It is important here for efficiency to determine the highest possible relative velocity in each cell and to adjust it regularly to the encountered maximum values. The  $n_i$  and the  $c_{r,max}$  need to be subindexed for multi-species simulations. For example, for a two-component simulation of particles with different mass and different inter-component collision cross section, we need to choose  $N_{p,q} = n_p(n_q - 1)(\sigma c_{r,max})_{p,q}/(2V_c)$  per cell with the appropriate probability  $c_{r,j}/(c_{r,max})_{p,q}$ . Problems arising from small species populations simulated within larger ones are discussed in great detail in [106], but do not concern our application of this method.

#### 4.1.4 Random numbers

When numerical algorithms are used, a very important point concerning all probabilistic methods is often neglected because it does not seem to be very important.— The source of the randomness used for the simulation. To put the importance of this into perspective, one must consider that several random uniform deviates are used for each individual collision operation in the many particle DSMC simulation. Multiple uniform deviates are needed to obtain non-uniform probabilistic distributions [108]. This adds up to many millions, or even billions of random numbers needed for a complete simulation run.

Computers are completely deterministic machines, which makes them programmable and useful. Randomness and software random number generators (RNGs) on computers have thus always been problematic and a target of mathematical research. On a philosophical side it might even seem to be a paradox to use computers to generate random numbers. However, today many software pseudo random number generators (PRNGs) are available. These are iterative programs, ideally "seeded" by a piece of true randomness, which are used to churn out "random" numbers of flat probability distribution and with extremely long repetition cycles. After passing rigorous statistical tests for randomness and periodicity, many such algorithms are deemed good enough for all but the most security sensitive areas, such as cryptography. It is interesting to note that cryptographic stream ciphers, like for example the widely used "RC4", are nothing but sophisticated purpose-built PRNG algorithms. The RC4 cryptographic algorithm in its deceptive simplicity can be stated in very few lines of code [109]. However, a lot of good research has suffered (and it still does) from the effects of bad random numbers. The authors of "Numerical Recipes" [92] even claim that library shelves would be "considerably lighter" if such flawed research was to be removed from them.

Several different approaches have led to better random number generation. Computers have been used to collect truly random event data such as keystroke and mouse motion timings and network packet arrival times (these sources are used for example by the Linux operating system built-in kernel device /dev/random). In general the rate at which this true randomness can be collected in this way is very small, in the order of several bytes per minute. Static noise on open microphone and sound port connectors has also been used to generate random numbers after carefully removing all correlations and periodicity. This allows an increased collection rate. More advanced applications with large demand for true randomness have purpose-built computer chips collecting randomness from quantum noise on integrated circuit devices.

All these methods may be used to generate truly random cryptographic keys, or in the context of computer simulations to "seed" a PRNG. That is, to put the PRNG into an initial random starting state within its deterministic (long) cycle. A continuously re-seeded PRNG (the re-seeding rate depends on the rate the system can gather randomness) is available on a system level through the Linux operating system device /dev/urandom, which will provide arbitrary amounts of random numbers at great speed.

In our evaporative cooling simulation the requirements for random numbers

are not as high as in other areas such as the security sector.– For our purposes it is not important that it is impossible to reproduce a random number stream. On the contrary, it simplifies software debugging efforts over multiple numerical simulation re-runs if they are based on a reproducible stream of random numbers. This can be achieved by seeding the PRNG function chosen for the program at the time with the same initial seed. To check the validity of our numerical results, however, we have also used different RNGs from time to time. Random numbers in the context of our simulations are deemed "good enough", when different PRNGs (over several runs using different seeds for the same PRNG) reproduce the same results for otherwise identical simulation runs. A particularly fast and simple RNG proved to be the ran2() generator, described in [92]. We also found that the "rand()" function from the linux standard library works well for us, although standard library rand() functions have acquired a bad reputation due to broken implementations of the algorithm on some compilers and architectures.

## 4.2 Cooling atoms and molecules

In the previous section we outlined the general methods that can be used to approach a many particle problem. Methods like DSMC constitute what can be called the "engine" of the program, doing the hard work. While this is the most important part of a simulation, there are other important aspects that need to be resolved. For the simulation of atoms and molecules in a magnetic trap it is important to find a correct starting point.

Since we are interested in manipulations of trapped ensembles, we start out from a trap filled with a specific number of particles in thermal equilibrium, as one experimentally obtains by optical cooling or by thermalisation with a cold buffer gas. The way such a randomly sampled initial population can be generated will be described in the following section.

#### 4.2.1 Initial thermal distribution in a trap

A numerical simulation of atoms and molecules in a specific magnetic trap geometry needs to start out from a physically correct initial thermal distribution. This is described by the Maxwell-Boltzmann equation.

$$f(\mathbf{r}, \mathbf{p}) \, d\mathbf{r} \, d\mathbf{p} = e^{-\frac{E(\mathbf{r}, \mathbf{p})}{k_B T}} \, d\mathbf{r} \, d\mathbf{p}, \tag{4.7}$$

where for a harmonic trap geometry  $E(\mathbf{r}, \mathbf{p})$  has the form

$$E(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^{3} \left( \frac{p_i^2}{2m} + \frac{1}{2} m \omega_i^2 x_i^2 \right).$$
(4.8)

For static magnetic quadrupole trap geometries (linear traps),  $E(\mathbf{r}, \mathbf{p})$  is

$$E(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^{3} \frac{p_i^2}{2m} + g_F M_F \mu_B \sqrt{\sum_{i=1}^{3} |\nabla B_i|^2 x_i^2}, \qquad (4.9)$$

where the  $|\nabla B_i|$  are the constant linear field gradients in the three spatial dimensions *i*.  $g_F$  and Bohr's magneton  $\mu_B$  characterise the strength of the magnetic field interaction of the trapped atomic or molecular spin projection with quantum number  $M_F$ .

Assuming a distribution independent of the spatial direction in a spherically symmetrical trap, using the transformation into spherical coordinates  $d\mathbf{r} \rightarrow r^2 \sin\theta \, d\theta \, d\phi \, dr$ , the distribution functions  $f(\mathbf{r}, \mathbf{p})$  become

$$\int f(\mathbf{r}, \mathbf{p}) \, d\mathbf{r} \, d\mathbf{p} = \int 16\pi^2 r^2 p^2 f(r, p) \, dr \, dp \tag{4.10}$$

Using the normalisation condition

$$\int f(\mathbf{r}, \mathbf{p}) \, d\mathbf{r} \, d\mathbf{p} = 1, \tag{4.11}$$

the distribution function for particles in a spherical harmonic trap with trap frequency  $\omega$  becomes:

$$f(r,p) = \frac{\omega^3 p^2 r^2}{\pi (k_B T)^3} e^{\frac{p^2/m + m r^2 \omega^2}{k_B T}}.$$
(4.12)

In a spherically symmetric magnetic quadrupole trap, the normalised distribution function is

$$f(r,p) = \frac{c^3 p^2 r^2}{2m^{3/2} \sqrt{2\pi} (k_B T)^{9/2}} e^{-\frac{p^2 + 2mcr}{2mk_B T}},$$
(4.13)

where we have substituted  $c = g_F M_F \mu_B |\nabla B|$  for the strength of the linear trapping potential, the trapping force (units [N]).



Figure 4.1: Radial spatial particle distribution in a spherically symmetrical harmonic trap. Note that r is not scaled to any specific trap strength or temperature.

For the harmonic trapping potential, both the momentum and spatial distributions have Gaussian shape. (Shown in Fig. 4.1 for the spatial particle distribution function p(r) in a harmonic trapping potential.) This can be derived from the above distribution functions by integrating over the whole range of one of the variables, r or p, and dividing the result by the appropriate scaling factor for the phase space volume element.

#### 4.2.2 Peak densities

This leads to a temperature dependent peak density at the trap centre of

$$n_0(T) = N\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \omega^3.$$
 (4.14)

Assuming an arbitrary trap with trapping frequencies  $\omega_x$ ,  $\omega_y$ ,  $\omega_z$ , evaluation of the integrals shows that the individual trap frequencies become simple factors in the above expression for the general *T*-dependent peak density at the trap centre:

$$n_0(T) = N \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \omega_x \omega_y \omega_z.$$
(4.15)

An analytical expression for the peak trap density is useful since the peak trap density also characterises the peak phase space density  $n_0(T)\lambda_{dB}^3$ , which is of great interest for evaporative cooling efficiency and eventual transition to BEC.  $\lambda_{dB}$  is the temperature dependent de Broglie wavelength of the trapped particles. The phase space density can be understood as a measure of the number of particles in the volume defined by the de Broglie wavelength. Phase space density values above 1 indicate a significant wavefunction overlap. The critical phase space density, at which the BEC formation process leads to a macroscopic ground state population is 2.612.

For the linear quadrupole trapping potential, the spatial particle distribution function p(r) has an exponential shape and thus it is strongly peaked in the central region. We integrate equation (4.13) over the whole momentum range and scale by the r volume element:

$$p(r) = \frac{1}{4\pi r^2} \int_{\infty}^{\infty} f(r, p) \, dp = \frac{c^3}{8\pi (k_B T)^3} e^{-\frac{c r}{k_B T}}$$
(4.16)



Figure 4.2: Radial spatial particle distribution in an isotropic linear trap. Note that r is not scaled to any specific trap strength or temperature.

The strongly peaked nature of this spatial distribution function for the linear trap case (shown in Fig. 4.2) caused a lot of problems in our initial attempts to

simulate such an ensemble using an unmodified Bird DSMC algorithm (compare section 4.1.3).

The peak density in a symmetrical linear trap is

$$n_0(T) = N \frac{1}{8\pi} \left(\frac{c}{k_B T}\right)^3,$$
 (4.17)

where c is the gradient of the confinement as known from the above equations. This result proved difficult to abstract to a general trap with three independent gradients, because the normalisation factor cannot easily be calculated analytically. However, it can be shown that doubling the linear confinement  $c_i$  in one spatial dimension will double the central peak density. Doubling all three parameters (corresponding to doubling c in eq. (4.17)) increases the central peak density by a factor of 8. Note that the strongly peaked spatial particle distribution will in practice be smoothed out to a small extent due to the effects of collisions, discretisation and finite sampling.

We can now easily work out for isotropic traps, how strong the trap confinements in terms of c and  $\omega$  need to be for equal peak phase space densities at equal total population and temperatures in the two types of traps. Equating (4.14) and (4.17) at equal N and T, we get

$$\omega = \sqrt{\frac{\pi^{1/3}}{2mk_BT}} c. \tag{4.18}$$

This shows that as the forced cooling proceeds, the peak density development in a quadrupole trap can only be matched by a progressive compression (increasing of  $\omega$ ) in a corresponding harmonic trap. Without looking at the zero magnetic field problem and the corresponding Majorana spin flip particle loss at the centre of the quadrupole trap, this would give the quadrupole trap a natural advantage. This also allows decreasing the magnetic field gradient with decreasing temperatures in situations, where the compressing effect of the quadrupole trap during cooling runs is not needed. It may also reduce to a certain extent the problem of increased inelastic collision rates at large magnetic field magnitudes, which we have outlined in section 2.2.4. The main problem for evaporative cooling, however, is still the necessity to reach low trap initial temperatures in a way not depending on magnetic traps and evaporation due to the large inelastic collision rates at high T and |B|.

#### 4.2.3 Collision rates

It is clear from figures 4.1 and 4.2 that the mean densities for distributions with the same peak density differ. In a quadrupole trap the mean density is smaller compared with the harmonic trap, where the mean density is  $n_0/(2^{3/2})$ , resulting in a smaller thermalisation rate. The mean collision rate  $\bar{\nu}$  is defined as

$$\bar{\nu}(T) = \bar{n}(\mathbf{r}, T)\sigma(T)\bar{v}_r(T), \qquad (4.19)$$

where n is the density,  $\sigma$  the collision cross section and  $\bar{v}_r$  the mean relative velocity between two trapped particles. Kinetic theory yields  $\bar{v}_r = \sqrt{2} \bar{v}_a$ ,

where  $\bar{v}_a$  is the mean particle velocity, which depends on the temperature of an equilibrium Maxwell-Boltzmann distribution with particle mass m as follows.

$$\bar{v}_a = \sqrt{\frac{8k_BT}{\pi m}} \tag{4.20}$$

The mean density in a simulated ensemble can be easily calculated using the discrete summation equivalent of its definition

$$\bar{n}(\mathbf{r}) = \frac{\int n^2(\mathbf{r}) d\mathbf{r}}{\int n(\mathbf{r}) d\mathbf{r}} = \frac{\int n^2(\mathbf{r}) d\mathbf{r}}{N}$$
(4.21)

#### 4.2.4 Random sampling

For numerical simulations using Monte Carlo methods, many random samples of particles with characteristic distribution functions as described above are needed, while additionally the directions of the  $\mathbf{r}$  and  $\mathbf{v}$  vectors need to be randomly sampled over  $4\pi$  solid angle. In order to do this, there are at least two different methods that can be utilised.

- Rejection method
- Transformation method

Both methods have their specific advantages and shortcomings. We will describe them in more detail below and look at them individually after finding the appropriate high energy boundaries.

#### 4.2.5 Maximum particle energy in a trap

In an experimental trap, the maximum particle energy is limited by the trap cutoff size. This can either be the physical container wall or a virtual line, for example, where a state transition of the trapped particles becomes resonant with a radio frequency field flipping the trapped particles into an untrapped state.

In the creation of an initial distribution, the maximum particle energy needs to be known in order to make the sampling procedures as efficient as possible. In the rejection procedure, the maximum radial spatial position of a trapped particle and the maximum trap energy mark the limits of the random sampling range. In the transformation procedure these values are the limits of the transformation tables.

As in equation (4.9), the total energy of a particle of mass m in an anisotropic linear trap can be written as

$$E = \frac{1}{2}m\sum_{i=1}^{3}v_i^2 + \sqrt{\sum_{i=1}^{3}c_i^2x_i^2},$$
(4.22)

where the  $c_i$  characterise the linear gradients of potential energy in the three trap dimensions. For a magnetic dipole trap, these  $c_i$  factors depend on the magnetic dipole interaction of the para-magnetic atomic or molecular particle with the magnetic field.

$$c_i = g_f M_f \mu_B |\nabla B_i|, \tag{4.23}$$

where  $g_F$  is the Lande factor,  $m_f$  the magnetic quantum number and  $\mu_B$  Bohr's magneton. The magnetic quantum number, the projection of the particle's magnetic moment into the direction of the trap magnetic field, also determines the trap state of the concerned particle. A flip of the particle spin and its magnetic moment can mark the transition into an anti-trapped state, which will eventually lead to the loss of the particle from the trap.

In a spherically symmetric trap the particle energy (4.22) becomes

$$E = \frac{1}{2}mv_r^2 + \frac{L^2}{2mr^2} + c_r r, \qquad (4.24)$$

where  $c_r = c_i$  is the isotropic linear radial gradient of the trap potential energy,  $r = \sqrt{\sum x_i^2}$  and  $v_r$  is the radial particle velocity. A trapped particle with the highest permitted energy will orbit the trap centre with constant maximum angular momentum  $L = m \mathbf{r} \times \mathbf{v}$  at the maximum radius  $r = r_{max}$  with a radial velocity  $v_r = 0$ . Calculation of dE/dr = 0 yields

$$c_r r = \frac{L^2}{mr^2} \tag{4.25}$$

for circular orbits. Substitution into (4.24) leads to the following expression for the energy of a circular trap orbit

$$E = \frac{3L^2}{2mr^2}.$$
 (4.26)

A comparison of (4.25) with  $c_r r = c_r r_{max} = E_{pot,max}$  and (4.26) shows that the maximum trapped particle energy is given by

$$E_{max} = \frac{3}{2}c_r r_{max} = \frac{3}{2}E_{pot,max}.$$
 (4.27)

The same procedure for a harmonic trapping potential  $V = \frac{1}{2}m\omega^2 r^2$  yields the relationship  $E_{max} = 2E_{pot,max}$ .

The maximum velocity for a trapped particle can also be derived as follows. Regardless of its location within the trapping region, any particle will fall out of the trap within the next collision-free trap oscillation time if its velocity exceeds

$$v_{max} = \sqrt{\frac{2E_{pot,max}}{m}}.$$
(4.28)

This is intuitively clear, since only a particle at the trap centre travelling outwards at  $v_{max}$  will reach the border of the trapping region at v = 0 (and then fall back inwards). In a harmonic trap, where  $E_{max} = 2E_{pot,max}$ , a particle with  $v_{max}$  will orbit the trap at radius  $r_{max}$  with maximum allowed angular momentum. In a linear trap, the kinetic energy of an orbiting particle at radius  $r_{max}$  is only  $E_{pot,max}/2$ . Thus such orbits have smaller maximum velocities by a factor of  $1/\sqrt{2}$ .

#### 4.2.6 Rejection method

As we have seen, software makes it fast and simple to generate large numbers of uniform random deviates over any interval. In many situations, however, we want to obtain random deviates not from a uniform, but from within a specific probability distribution. This can be achieved by using more than one uniform deviate to generate a single non-uniform deviate in what is called the *rejection method*.

The method in its simplest form uses an algorithm as follows: Pick a sample at a randomly chosen position x on the appropriate interval, if a second random number, chosen from an interval between zero and the distribution function peak, is smaller than the sampled distribution function p(x) at x. Reject the sample and try again, if the second random number is larger than p(x).

It is obvious, that this method is extremely inefficient for strongly peaked distribution functions on large intervals, because in this case the two-dimensional "reject" area described by the two orthogonal random numbers greatly exceeds the "accept" area. The rejection area can be reduced by introducing an analytically integrable function f(x), which is larger than the distribution function p(x) for all x. The sample position x is then not chosen directly, but from the range of the integral  $\int f(x)dx$  on the appropriate x range, and x is obtained by inversion of the integral function. The second random number is then taken from the interval between zero and f(x), rejecting the whole sample if it lies in the gap between f(x) and p(x) [92].

This method is particularly well suited for deviates of distribution functions, which can be approximated by an analytically integrable function. Integrable distribution functions are more easily sampled using the transformation method, which we will describe below.

#### 4.2.7 Transformation method

A more efficient method to generate a random deviate for a known probability distribution is the transformation method. We assume a uniform probability distribution p(x), of which we can easily get any number of deviates. If we now take any function y(x) of the uniform deviates generated to obtain a ydistribution of p(y), the probability distribution becomes

$$p(y) = p(x) \left| \frac{dx}{dy} \right| = p(x)f(y).$$
(4.29)

x is uniformly distributed, thus it fulfills

$$p(x) = \begin{cases} 1 : 0 < x < 1 \\ 0 : \text{ otherwise} \end{cases}$$
(4.30)

and we can write

$$p(y) = f(y) = \frac{dx}{dy},$$
(4.31)

which has the solution x = F(y), obtained by simple integration. A simple variable inversion takes us to the function which turns our easily obtained uniform

deviate into the desired non-uniform deviate:

$$y(x) = F^{-1}(x). (4.32)$$

In many situations it is easy to obtain the inverted function of  $y = F^{-1}(x)$ analytically. In situations like ours, where the inversion is not possible analytically, it is still possible to use the inversion method by means of a numerical inversion. (Arbitrarily long) evenly spaced lists ranging from the minimum to the maximum of x = F(y) and of the corresponding values of y are initialised. x is then chosen from a uniform distribution over its complete used range, the corresponding value of x is found in the x-list and the appropriate y value can subsequently be obtained from the parallel y-list at the same position.

The transformation method can also be extended to non-uniform distributions with multiple variables with little difficulty. This, however, was not necessary when the method was applied to the trapped particle problem.

#### Application to the trapped ensemble problem

The transformation method is ideally suited for initial state generation in the trapped ensemble problem because the distribution function equation (4.7) allows separation into a product of single variable distributions, each dependent on either space or momentum coordinate for the harmonic (equation 4.12) and the linear (equation 4.13) trapping fields, which we are interested in. For example, the factor  $f(v)dv = v^2dv \exp(-mv^2/(2k_BT))$  in the product of single variable distribution functions for trapped particles can formally be integrated yielding

$$x = F(v) = \int f(v)dv = \sqrt{\frac{\pi}{2}} \operatorname{Erf}\left(\sqrt{\frac{mv^2}{2k_BT}}\right) \left(\frac{k_BT}{m}\right)^{-3/2} - v\frac{k_BT}{m}e^{-\frac{mv^2}{2k_BT}}.$$
(4.33)

This function cannot be inverted easily and we have resorted to numerical tables and interpolation, which can be done very quickly. Thus sampling from f(v) is done by taking a uniform random deviate on the interval from zero to  $x_{max} = F(v_{max})$  and subsequent numerical inversion to find the v sample. Similarly, samples for r are found using the appropriate function  $x = F(r) = \int f(r)dr$ (for anisotropic traps the directional components of the r samples can simply be scaled appropriately as a last step). Random directions  $(\theta, \phi)$  for the vector  $\mathbf{r}$  and  $\mathbf{v}$  can be found by inverting a uniform random deviate of  $F(\theta) = -\cos(\theta)$ for  $\theta$  and by taking a simple uniform random deviate on the interval  $[0, 2\pi]$  for  $\phi$ .

The quality of the initial trap distributions resulting from this method is investigated in section 4.4.1 by propagating such a trap initial state for a long time using our DSMC simulation algorithm. Without natural evaporation (suppressed by using a very deep trap) and without inelastic collisions, initial states of good quality will have constant temperature and energy over arbitrarily long times.

#### 4.2.8 Statistical fluctuations

Finite sample sizes, as we have used in all of our numerical simulations, give rise to statistical fluctuations in the system parameters and variables we measure. Figure 4.3 shows an example of a velocity histogram, randomly sampled for  $N = 2000^{-133}$ Cs atoms using the transformation method for the linear trap case at a low temperature of  $T = 1 \ \mu$ K. With 2000 sampled particles, the outcome is very close to the target temperature. – A numerical evaluation of the sample shown in the figure yields  $T = \pi m \bar{v}^2/(8k_B) = 1.01 \ \mu$ K for the sample. In general, the central limit theorem causes the sample mean value to converge to the absolute central value with increasing sample size.



Figure 4.3: Velocity histogram of N = 2000 trapped particles at  $T = 1 \ \mu \text{K}$ . Statistical fluctuations, which are proportional to  $N^{-1/2}$ , of the particle number in the 200 histogram sample boxes are evident. The solid line shows the theoretically expected Maxwell-Boltzmann velocity distribution for the sampled case.

$$\bar{v}_{sample} = \bar{v} \pm \frac{\sigma}{\sqrt{N}},\tag{4.34}$$

where  $\bar{v}$  is the central limit and  $\sigma$  the standard deviation of the velocity samples in the distribution function.

Fluctuations in particle number in individual histogram boxes is described in terms of a binomial distribution function [110]

$$W_p^N(m) = \binom{N}{m} p^m q^{N-m} \quad (m = 0, 1, 2, \dots, N),$$
(4.35)

describing the probability of getting m particles into a specific histogram box, when N samples are taken. p is the probability of a single sample being in the specific box and q = 1 - p. For large N this binomial distribution can be approximated by a normal distribution with a standard deviation  $\sigma_{hist} = \sqrt{pq/N}$ .

Thus for meaningful numerical results, an appropriately large number of samples is necessary. We have usually used simulated (multi)particle numbers in the order of 10000 particles.

## 4.3 The *bird\_simulation* program

In the following sections we describe our adaptions and improvements to the numerical DSMC simulation method and outline its implementation details and we will discuss the program structure.

#### 4.3.1 Adaptation of DSMC to evaporative cooling

The evaporative cooling process is very efficient in reducing the ensemble temperature. However, this goes in parallel with an enormous loss of particles, which by itself would cause the Bird DSMC method to fail before the particle number decreases by only one order of magnitude.

#### Particle "Cloning"

In order to scale the simulation through many orders of magnitude, the amount of simulated particles has to be kept within a comparatively narrow tolerable range. This can be done by an occasional doubling of the simulated particles, as soon as their total number has decreased to 50% of the initial value. At the same time the simulated particle multiplicity number is halved in order to keep the simulation in a consistent state.

This process of "cloning" simulated particles has been applied by Dalibard [111]. The "cloned" particle is placed into the simulated trap at a position *mirroring* the original particle. This method causes grave problems in anisotropic traps and asymmetrical settings, and it does not conserve angular momentum. In the present work we propose a novel more straight forward solution, simply putting the clone at the same place as the original particle. This method originates from the idea of a simulated particle representing a large number of corresponding real particles. It does not cause an unphysical increase of the collision rate because the collision probability between particles at identical positions and velocities vanishes. Collisions between two such "cloned twins" will only happen subsequently, once they have drifted apart due to at least one of the two particles undergoing a collision with a third particle. Only then will the two twins have a non-zero relative velocity. This is an ideal and consistent extension of the simulation concept of numerical particles with large multiplicity numbers.

#### **Recursive subpartitioning**

The cell based DSMC algorithm allows flexible handling of the cellsizes and shapes. Customised cell designs have been used for many different problems, where the cell geometries had to be fitted to suit system boundaries like for example the surface shape of a shuttle orbiter in simulations of atmospheric re-entry aerodynamics [106].

In simulations of particle traps however, one faces a completely different problem: The real issue is not the smooth approximation of a surface, since the trapped particles are freely floating in space, held by the magnetic and optical trapping fields. The problem in this application is the large density

#### 4.3. THE BIRD\_SIMULATION PROGRAM

inhomogeneity from the relatively dense trap centre population peak to the extremely dilute outer regions, the vacuum, where hardly any particles can be found. The problem is worsened by the evaporative cooling process, which decreases the temperature and densities by orders of magnitude. If the cells are not adapted to the changing environment, eventually all particles will reside in the corners of the central eight cells and the simulation will produce questionable or invalid results.

While one author [63] has dealt with the problem by continuously shrinking the cell grid with decreasing cloud size, this approach was unsatisfactory for our simulations of particles trapped in a quadrupole trap, where the probability distribution is sharply peaked (section 4.2.1). In the present work we have developed a novel recursive algorithm, which can handle the cellsize problem much more flexibly. Starting from a relatively coarse static grid of 1000 cells, fitted to the initial particle distribution, the program will subpartition the cells as needed as the simulation progresses. This method is significantly faster than a complete "regridding" and it makes simulations of quadrupole traps possible. When the program detects cells exceeding a specified population number, the cell is split into eight subcells, which are linked into the linked cell list. The particles contained in the top-level cell are distributed into the appropriate subcells and all global and all cell-specific parameters are adjusted or distributed appropriately. The algorithm developed for this purpose almost entirely automates the gridding problem.

It has later been found that similar subpartitioning algorithms using 3D cell octants are employed in accelerated graphics for computer games [112].



Figure 4.4: Recursive DSMC simulation cell subpartitioning adapted to cope with strongly peaked spatial particle distributions in linear trapping potentials, as shown in a) 2D and b) 3D. The trap center is to the bottom right of the two figures. The figures only show one quadrant, i.e. one eighth, of the available space.

#### 4.3.2 Program structure

The *bird\_simulation* program has been designed to be as modular and fast as possible, and it uses C++ object oriented programming. Relevant functions are encapsulated in classes, which are structurally and logically independent units with strict interfaces. Among several other classes, there is a particle class called "Atom", a "Cell" and a "Trap" class. These classes encapsulate and hide their data and allow access by class member functions and strictly defined "public" interfaces only.

Simulated particles are organised as a list of linked instances of the "Atom" object class. In order to allow fast assignments of particles to cells according to their spatial positions, and in order to make random access to particles within individual cells very fast, we use more linked lists of these object instances. Most simulation operations then become simple list operations, adjusting pointers appropriately. Random access amounts to a traversal of a linked list by a random number of elements.

Figure 4.5 shows a simplified example of an initial linked atom list (top rows). A subset of the atom object instances is positioned within a specific spatial cell (linked list shown in the bottom row), represented by a Cell object. Atom objects within this particular Cell are linked into a list by means of a "nextAtomInCell" pointer in the Atom particle class. In the presented example the initial particle object is being pointed to by the Cell pointer "firstAtomInCell".

With this structural design, removal of random elements, the cloning procedure and the DSMC-type random collision events between atoms within individual cells have a minimal administrative overhead. Thus the program scales up well and allows tracking of a large number of such numerical particle "Atom" objects, as well as a flexible recursive "Cell" partitioning concept, which we have outlined in the previous section.

#### 4.3.3 Collision cross sections

The most important data for any simulation of evaporative cooling are the collision cross sections of the considered particles. The collision cross sections determine the collision rates at the ensemble temperature and thus the response of the ensemble to perturbations, like the removal of fast moving ("hot") particles. In a trap, the relation between elastic and inelastic collision rates determines whether an ensemble may efficiently be cooled using particle evaporation or not. If the rethermalisation time characterised by the elastic collision rate (among other ensemble properties) is too small, no trapped particles will be left in the trap by the time the ensemble would have undergone sufficient cooling.

While a great deal of information about collision cross sections for the more simple monatomic gases like for example the alkali metals and helium is known [113, 37], collision data for molecules at low temperatures is still scarce. This is the reason why an effort was made to improve the data available for the computation of oxygen-oxygen collision cross sections (Chapter 3). At low temperatures, the collision cross sections of atomic and molecular gases in particu-



Figure 4.5: Simplified example of linked object lists within the *bird\_simulation* DSMC simulation program. The example shows the assignment of a (random) subset of "Atom" objects to one of the linked "Cell" objects. Assignment to this particular cell is achieved by linking the "Atom" objects by means of a *nextInCell* pointer. This "high-level" list (highlighted by bold lines) is adjusted according to present particle positions after every time step. The list is terminated by a NULL pointer.

lar, are subject to significant quantum effects [31, 49, 43], the full computation of which is difficult for even the most simple particles.

Thus several approximative classical models have been used within DSMC simulations to describe the dependence of the elastic and inelastic collision cross sections  $\sigma$  on ensemble temperature [106].

- Hard sphere model
- Variable hard sphere model
- Variable soft sphere model
- Maxwell model
- Generalised hard sphere model

The basic classical scattering theory, which these models are based upon, has been outlined in section 2.1.1. Most of the models are well suited for room temperature or higher T, at which DSMC simulations have been applied to problems of gas flow and super sonic shock waves [106].

It has been found that variations in collision cross section magnitudes exhibit more pronounced effects on the outcome of numerical simulations than the omission of a precise physical representation of anisotropic directional scattering effects. Particularly this holds true for largely isotropic ensembles, like gases in spherically or cylindrically symmetrical traps, which are generally used for evaporative cooling. The simple explanation to this observation is the fact that molecular chaos sufficiently randomises directional events, resulting in an isotropic macroscopic picture. Thus a phenomenological approach to simulations of gas ensembles is practical, separating the quantum mechanical effects, which determine the collision properties, from the classical simulation of the large macroscopic ensemble.

In our simulations we use tabulated collision data, employing the simple hard sphere collision model with isotropic scattering. At all encountered collision energies and ensemble temperatures, table lookups will individually provide the best known compiled data for an otherwise classical numerical simulation.

#### Chromium

During the development of our DSMC simulation program we have done simulations for chromium, which has a large magnetic moment of  $\mu = 6\mu_B$  due to its large spin of S = 3. It can thus easily be trapped in magnetic traps [114]. However, chromium exhibits a large inelastic collision cross section, which increases with decreasing temperature as shown in figure 4.6 and limits the low temperatures that can be achieved with evaporative cooling. We have thus



Figure 4.6: <sup>52</sup>Cr collision data obtained by J. Doyle et. al. [115]. Interpolation between the approximations (dashed line) was used in numerical simulations.

concentrated on simulations of caesium and oxygen ensembles for the purposes of this work and we show the chromium collision data as an example, where efficient evaporative cooling to temperatures below approximately 10 mK is unlikely to be achieved.

#### Caesium

<sup>133</sup>Cs has an *s*-wave scattering length of  $a = 1.1906 \cdot 10^{-7}$  m [116,66] and can be magnetically trapped in its  $|F = 3, m_F = -3\rangle$  state, which has a *g* factor of g = -1/4. The temperature dependence of the collision cross section at very low temperatures can be approximated [66] as

$$\sigma(T) = \frac{8\pi a^2}{1 + k^2 a^2},\tag{4.36}$$

where k is the de Broglie wavenumber  $k = mv/\hbar$ , and  $v = \sqrt{8k_BT/(\pi m)}$  is the temperature dependent mean particle velocity. The inelastic collision loss coefficient  $K_2$  (equation 2.50) can be approximated by  $K_2 = K_2^0/(1.017 + \alpha T)$ , with  $K_2^0 = 23.608 \cdot 10^{-19} \text{ m}^3 \text{s}^{-1}$  and  $\alpha = 5.3 \cdot 10^6 \text{ K}^{-1}$ .

As expressed in the model above, the elastic collision cross section for Caesium exhibits strong gradients with temperature. While it generally increases with decreasing temperature, which is beneficial for runaway evaporative cooling, the thermal gradient of the collision cross section slows down thermalisation within the trapped ensemble from an average of approximately 2.7 collision times to 10.7 collision times. This has proved to be crippling to the efficiency of the evaporative cooling process in the presence of high inelastic loss rates [117].

#### Oxygen

Oxygen molecules have a magnetic moment of  $\mu = 2\mu_B$ , with a g factor of 2 and magnetic trapping can possibly be achieved in the  $m_J=1$  state (compare with figure 3.1 on page 49). Figure 4.7 shows the O<sub>2</sub>-O<sub>2</sub> collision data computed by Bohn and Avdeenkov in [31] for vanishing magnetic field strengths. Thermally averaged curves are obtained by integrating over the appropriate energy distribution function for each temperature (averaged data is shown in dashed lines):

$$\bar{K}(T) = \sqrt{\frac{8k_BT}{\pi m}} \frac{1}{(k_BT)^2} \int_0^\infty E\sigma(E) e^{-E/k_bT} dE$$
(4.37)

Such thermally averaged data is useful in numerical simulations of particle ensembles, assuming that the ensemble is close to thermal equilibrium at all times. This allows the use of collision data, which has a simple dependence on the average ensemble temperature.

## 4.4 Thermalisation

In this section we will present the results of simulation runs involving thermalisation. These simulations serve as important test cases and as comparisons with previous work in the literature. In some of the simulations, we use the parameters for magnetically trapped Caesium <sup>133</sup>Cs, as this is an isotope of interest for Bose-Einstein condensation.



Figure 4.7:  $O_2$ - $O_2$  collision data calculated by Bohn/Avdeenkov [31]. The dashed lines are thermal averages calculated according to equation (4.37).

#### 4.4.1 Initial state quality

In order to verify the quality of the initial trap distributions generated using the transformation algorithm, states ware propagated in their appropriate trap geometries, setting the inelastic collision cross section to zero. Cloud sizes, peak and mean densities and the elastic collision rate then needed to remain constant for long propagation times. This was done as a consistency check for all problems we have done simulation runs for. Such runs also allowed us to verify energy conservation in the trap, which is easily maintained at the microscopic collision level, but which can be violated due to small numerical errors within the particle propagation code, accumulating over a large number of time steps.

For particle propagation in the harmonic trapping potential, we use the analytical harmonic solution in the three linearly independent spatial directions. Consequently, energy conservation is fully observed in this case. In the quadrupole trapping potential, we use a fourth order numerical Runge-Kutta solver, which is very accurate. Over the course of a long simulation run we will lose not more than about half of a percent of the particle energy due to accumulating numerical inaccuracies.

#### 4.4.2 Cross dimensional thermalisation in a harmonic trap

Wu et. al. [63] have investigated thermalisation and evaporative cooling of  $^{133}$ Cs before, using a different simulation program, which was not available to us for comparison. Thus we compare our simulation results to data published

in [63, 65]. Caesium <sup>133</sup>Cs at  $T = 30 \ \mu\text{K}$  is trapped in a harmonic trap with trap oscillation frequencies  $(\omega_x, \omega_y, \omega_z) = 2\pi \ (16.2, 17.6, 9.8)$  Hz. The mean number density is  $5 \cdot 10^{15} \text{ m}^3$  and the collision cross section is kept constant at  $1.5 \cdot 10^{-16} \text{ m}^2$ . We achieve this trap number density with  $10^4$  simulated particles representing a trapped ensemble of  $5 \cdot 10^7$  caesium atoms. The trapped region was chosen large enough so that the potential depth was around  $\eta T = 30 \text{ mK}$ . This was large enough to achieve complete confinement without any particle loss due to natural evaporation.

The resulting development of the temperatures in the three linearly independent directions, after doubling the x temperature by multiplying particle x positions and velocities by  $\sqrt{2}$ , shows small fluctuations with the respective spatial oscillation frequencies and a thermalisation mediated by elastic collisions. The thermalisation is described by a decaying exponential function with time constant  $\tau = 2.4 t_c$ , where  $t_c$  is the initial mean particle collision time. This is in good agreement with [63], where a time constant of  $\tau = 2.5 t_c$  was measured.



Figure 4.8: Cross dimensional thermalisation of <sup>133</sup>Cs at  $T = 30 \ \mu\text{K}$  in a harmonic trap. Time is scaled in units of the initial mean collision time ( $t_c = 16$  s). Temperature in x was doubled at t = 0. Thermalisation fitted to exponential function with  $\tau = 2.4 \ t_c$ . (Upper dashed curve).

#### 4.4.3 Ergodicity in linear traps

While harmonic traps are non-ergodic by nature, with cross-dimensional mixing only occurring due to elastic collisions, linear (quadrupole type) traps exhibit a certain inherent ergodicity due to the potential coupling the spatial directions. In this type of trap, orbits have different periods and thus quickly dephase against each other after an external perturbation. Thus directional heating can be achieved experimentally by a rapid small shift of the trap centre. In our simulations, we simply double the particle kinetic energy in one spatial direction by multiplying the appropriate velocity component by  $\sqrt{2}$ . In order to demonstrate the ergodic effects in quadrupole traps, we did three different simulations, in all of which we disabled collisions by setting the collision cross sections to zero.



Figure 4.9: Collisionsless ergodic mixing in a linear trap. (5000 simulated particles at T = 100 mK, representing an ensemble of N = 5e7 oxygen molecules; x blue, y green, z red lines.) A) spherical linear trap. After initial dephasing of the instantaneous  $\sqrt{2}$  directional velocity increase in x, a moderate amount of cross dimensional mixing occurs. After 0.2 seconds, the system evolution is nonergodic. B) Ergodic mixing occurs between the two radial directions in a quadrupole trap. C) Mixing is not observed in a quadrupole trap after heating in the axial direction.

Increasing one velocity component  $v_i$  by  $\sqrt{2}$  in a spherical linear trap shows that after an initial period of rapid dephasing, which is expected since the particle positions in the nonadiabatic heating step are kept constant, the trap appears to evolve largely nonergodic, maintaining different temperatures along its three axes after a moderate amount of initial cross dimensional mixing. (Figure 4.9 A).) A similar result has been found in [118].

One dimensional heating along one of the weakly confined directions in a realistic quadrupole trap shows that complete mixing occurs between the two radial directions, while the axial direction is unaffected. (Figure 4.9 B).)

Heating in the strongly confined z direction of a realistic quadrupole trap shows a nonergodic evolution. No measurable cross dimensional mixing occurs. (Figure 4.9 C).) It can be concluded that linear traps are nonergodic to the same extent as harmonic traps. Complete mixing can only be achieved by means of elastic collisions. The ergodic mixing in the radial directions of a quadrupole trap will be of little advantage in evaporative cooling, since gravity sag will maintain the axial symmetry of the system with little or no mixing occurring between (x,y) and axial z directions.

#### 4.4.4 Cross dimensional thermalisation in a linear trap

A cross dimensional thermalisation simulation run in the nonergodic case of a realistic quadrupole trap with heating in the axial (z) direction gave results qualitatively equivalent to the ones shown in figure 4.8. With a collision time of 4 s, the temperature fit of a 20 s run yielded a time constant of  $\tau = 2.72 t_c$ for the thermalisation. This shows that within a small margin of error, which may be due to the differences in central peak densities and the cell mapping algorithm used in the DSMC simulation, we can reproduce the literature results obtained for harmonic traps in quadrupole traps.

## 4.5 Evaporative cooling

Rapid thermalisation is crucial for evaporative cooling strategies. However, in simulations of trap thermalisation, the phase space density remains constant and nothing tangible is gained in terms of the ultimate goal of reaching very low temperatures. The same applies to adiabatic compression and relaxation of the trap. While these processes change the temperatures and densities, the phase space density will remain constant or decrease due to a lack of complete adiabaticity and consequent heating effects. In the following sections we will look at evaporation processes, which will increase the phase space density, removing energy from the trapped ensemble.

#### 4.5.1 Natural evaporation and forced cooling

Natural evaporation occurs, when the trap depth is finite. In this situation particularly fast particles, which appear with low probabilities in the "tail" of a Maxwell-Boltzmann thermal distribution, can escape from the trap by crossing a spatial cut-off limit. Consequently, the ensemble loses energy and the system rethermalises towards a new equilibrium equilibrium state. This means that in practice all ensembles in finite traps undergo a natural evaporation and are always found out-of-equilibrium, regenerating the truncated "hot tails" of their thermal distribution functions. In deep traps with  $\eta > 10$ , however, natural evaporation is highly suppressed. The trap depth  $\eta = V_{cutoff}/(k_BT)$  is defined as the ratio between cut-off potential energy and the ensemble thermal energy characterised by  $k_BT$ . Occasionally, the trap depth is also referred to as a temperature  $V_{cutoff}/k_B$  and can similarly be compared with the ensemble temperature.

The fraction of particles truncated at a specific kinetic energy  $E = \eta k_B T$ 

can be calculated as

$$c = \frac{\int_{\eta k_B T}^{\infty} \sqrt{E} e^{-E/(k_B T)} dE}{\int_{0}^{\infty} \sqrt{E} e^{-E/(k_B T)} dE},$$
(4.38)

which approaches  $c = 2\sqrt{\eta/\pi} e^{-\eta}$  for truncation parameters larger than  $\eta \ge 5$  [68].



Figure 4.10: Natural evaporation from a quadrupole trap. N = 5e10 particles in thermal equilibrium at T = 50 mK are transferred from a deep trap into a shallower trap of 250 mK depth at t = 0. The first subplot shows the energies of the trapped and lost fractions, and the total energy. The second subplot shows the temporal evolution of the temperature of the remaining trapped particles. In the third subplot the phase space density is plotted versus the number of trapped particles in the trap. Over time the system moves in the direction indicated by the arrow.

The three plots in figure 4.10 show a simulation of natural evaporation (with no inelastic collisions) at an initial temperature of T = 50 mK from a quadrupole trap after a three-dimensional spatial truncation of the confining trap to a new finite depth of  $\eta = 5$ . Figure A) shows the energies of the trapped and the evaporated particle fraction, and the constant total energy (constant to better than 1% after 20 s. Small deviation due to accumulated numerical inaccuracies). Figure B) shows the ensemble temperature based on the mean particle velocity. Since temperature is only strictly defined for equilibrium conditions, physically


Figure 4.11: Evolution of the energy distribution function f(E) over the natural evaporation process detailed in figure 4.10. The particle energy histogram (in arbitrary units) is plotted every second over the 20 s simulation duration.

valid readings are expected only several collision times after the initial nonadiabatic decrease of the trap depth. However, the trend and the cooling effect are clearly visible. As the density increases, the collision time  $t_c$  decreases from an initial value of 0.15 s to 0.025 s after 20 s of simulation time in the run shown in the figures.

Figure C) shows the development of the mean phase space density D versus the number of remaining trapped particles N. The motion of the system state over time is indicated by the arrow. It can be seen how the cooling efficiency, defined as the gradient  $\gamma$  in figure C)

$$\gamma = -\frac{d(\ln D)}{d(\ln N)} \tag{4.39}$$

increases continuously as the elastic thermalisation reproduces "hot" particles. Fast particles carry away more energy with smaller particle loss, increasing the cooling efficiency. The initial reduction in trap depth leads to the instantaneous evaporation of the fastest 20% of the trapped particles. As time progresses, the particle loss rate decreases exponentially as the system thermalises asymptotically, reaching T = 18 mK after 20 s. The increased density and decreased temperature during this cooling step represent an increase in phase space density of more than one order of magnitude.

Note that without the heating effects of inelastic collisions, the temperature would keep decreasing indefinitely due to natural evaporation, at a continuously slowing rate.

#### 4.5.2 Forced evaporative cooling strategy

Any experimental realisation of evaporative cooling will try to reach the "runaway" evaporation regime. Decreasing ensemble temperature due to cooling go along with decreased particle number and decreased average particle velocity. Thus elastic collision rates also decrease, increasing the ensemble thermalisation time. Unlike in square well potentials, the density in inhomogeneous traps (harmonic or linear) increases with decreasing temperatures, offsetting the particle loss and velocity reductions.

"Runaway evaporation" can be reached when the elastic thermalisation rate increases as the ensemble cools down and over-compensates for particle loss and velocity decreases. In such a situation, the cooling proceeds faster and faster leading to large increases in phase space density and making it possible in some cases to reach the BEC transition temperature.

The minimum ratio  $R = \tau_{loss}/\tau_{el}$  between inelastic and elastic collision time for runaway evaporation to be achieved is approximately 400 for harmonic, and 100 for quadrupole traps [62, 117], giving the linear trap a clear advantage, which is due to the compression effects discussed in section 4.2.2.

Theoretically, evaporative cooling can be optimised, when all the parameters in equations (2.71) for the cooling efficiency  $\gamma$  are known (see section 2.4.5). Thus an ideal trap truncation depth  $\eta$  exists for all possible values of R. Ketterle and van Druten [62] show diagrams of evaporation efficiency  $\gamma$  versus truncation parameter  $\eta$  for a wide range of R values in different traps, which we have used to design simplified near optimal evaporation ramps in our simulations. Essentially, the truncation parameter needs to be small for small values of R; cooling efficiency is small for small values of  $\eta$ , since evaporation less selective. For truncation parameters chosen too high for small values of R (corresponding to large inelastic loss rates), too few particles will be evaporated while the cloud rapidly loses population due to inelastic collisions. However, efficient evaporation can generally be achieved with truncation parameters of around  $\eta = 6$ , when R is in a typical range between 200 and 1000.

Evaporative cooling is experimentally realised by means of radio-frequency induced spin flips into an untrapped Zeeman-state at a specific cloud radius, which is determined by the Zeeman energy shift of the trapped particles and the RF field frequency [117]. Since the optimum truncation parameter typically increases as the sample cools down and R increases, the evaporation "ramp" chosen in experimental realisations is usually of exponential shape, with the RF frequency decreasing as  $\nu = \nu_0 e^{-t/\tau}$ .

Several important points need to be taken into account in the experimental tuning of such evaporation ramps. Firstly, the ramp needs to be slow enough to allow thermalisation of the remaining particles and fast enough so that inelastic loss does not deplete the cloud before low temperatures or quantum degeneracy is reached. Secondly, the starting and finishing points of the "cut" need to

#### 4.5. EVAPORATIVE COOLING

be positioned precisely to achieve the desired optimal truncation parameters. Additionally, the RF field intensity must not be too large, so that spectral power broadening does not spread out the cutting area too much, preventing precise evaporation at lower temperatures.

Yamashita et. al. have investigated optimal cooling ramps in [119]. They report that the last cooling phase can be accelerated by a linear ramp following an initial exponential ramp.

In our simulation program, the optimal truncation parameters can be derived from the precise knowledge of the elastic and inelastic collision rates, using a simple model adapted from [62]. Figure 4.12 (in the next section) shows simulation runs optimised accordingly, demonstrating the adverse effects of Majorana spin flip loss at lower temperatures.

#### 4.5.3 Majorana loss model

We have implemented a model for particle loss due to Majorana spin flips at the central quadrupole trap zero magnetic field region as outlined in section 2.3.2. After every particle propagation procedure in the simulation, particles which have moved into a region closer to the trap centre than  $b_0 = \sqrt{v\hbar/(\mu B'_q)}$ (equation 2.63) will be transferred into their corresponding untrapped states, accelerating out of the trap. This causes additional heating as accelerating anti-trapped particles dissipate energy into the remaining ensemble by elastic collisions with trapped particles. The largest heating effect of Majorana spin flips, and inelastic collisions in general, is due to the fact that these happen at large densities in the trap centre, where particles have below average energies.

We have found that trap loss due to this process becomes significant only at temperatures below 500  $\mu$ K and, in our case, at phase space densities above  $10^{-4}$ . At cryogenic temperatures on the mK scale this effect is small, but it can eventually stop the evaporative cooling process at  $\mu K$  temperatures. Figure 4.12 shows the effect of different Majorana spin flip models on the evaporative cooling of oxygen, where we have not taken into account the adverse effects of large magnetic fields (as outlined in section 2.2.4). While runaway evaporative cooling proceeds all the way into the quantum degenerate regime, reaching phase space densities in the order of D = 1, presence of Majorana spin flips preclude the cooling process at phase space densities orders of magnitude smaller, using identical truncation and simulation parameters parameters. In figure 4.12, we show the effect of a Majorana loss region defined by a radius of  $b_0$  (optimistic model) and  $2b_0$  (pessimistic model), where  $b_0 = \sqrt{\bar{v}\hbar/(\mu B'_q)}$  is defined as in equation (2.63) in section 2.3.2. In our simulation, we have used the mean particle velocity  $\bar{v}$  and assumed a loss probability of 1 for particles entering the critical region, as suggested in [50]. Particles entering the Majorana loss region may have a finite probability to remain trapped, however, so that our optimistic model could be closer to the truth than the pessimistic one. Note that quantum degeneracy may still be reached in the presence of Majorana losses, when the truncation parameter, which corresponds to the experimental evaporation "ramp", is adapted to deal with increasing inelastic loss at lower temperatures.



Figure 4.12: Evaporative cooling of  $O_2$  in a linear trap (without taking into account magnetic field effects on the inelastic collision rate). Quantum degeneracy could be reached in the absence of Majorana spin flips. A pessimistic and an optimistic Majorana loss model preclude evaporative cooling at 100  $\mu$ K and 30  $\mu$ K respectively, while the effect is negligible at temperatures above 1 mK.

An optimisation in this respect will decrease the cooling efficiency, but similar phase space densities would still be reached with smaller particle numbers.

#### 4.5.4 Evaporative cooling of oxygen

In the previous section we have described a model and demonstrated the effects of Majorana spin flip losses on the evaporative cooling process of oxygen in simulations using the elastic and inelastic collision data shown in figure 4.7. The most notable characteristic feature of the oxygen collision data is the fact that the inelastic collision rate drops off to values significantly below the elastic collision rate only at temperatures colder than 50 mK. This temperature is already somewhat too low to be reached by buffer gas cooling, as we have explained in section 2.2.5. However, to reach the runaway cooling regime with this molecular particle species, we need to assume a fictitious optimistic model and start out with a temperature of T = 50 mK and a very large particle number of  $N = 5 \cdot 10^{10}$ . This value for the particle number is very high and difficult to achieve even in modern MOTs using easily trappable alkali gases [39]. Our oxygen cooling simulations should be seen in this light. Unless a trap loading mechanism other than buffer gas cooling can be found for oxygen, which rivals the MOTs used for trapping of alkali atoms, our simulations for oxygen are unlikely to be realised experimentally.



Figure 4.13: Evaporative cooling with reduced dimensionality, starting at T = 50 mK. 3D evaporation yields the best results. 2D evaporation in the radial quadrupole trap dimensions is significantly less efficient, but leads to a significant phase space density increase. 1D evaporation is infeasible under the given conditions and leads to a decrease in phase space density. The total simulation time of the shown runs, and the final temperatures are: 1D 1.39 s, 23.9 mK; 2D 0.88 s, 2.2 mK; 3D 0.23 s, 675  $\mu$ K.

In addition to the Majorana trap losses at low temperatures, the effect of the trap magnetic field on the inelastic collision rate of oxygen cannot be neglected, as we have pointed out in section 2.2.4. The model proposed by Volpi and Bohn in [54] would only allow trap depths of 7.1 mK (maximum magnetic field 0.0053 T) before the inelastic collision rate exceeds the elastic collision rate and precludes magnetic trapping. Even at lower magnetic field strengths, which would be possible at lower temperatures with shallower traps, the inelastic collision rate is increased considerably due to this effect, limiting trap lifetimes or ruling out evaporative cooling altogether.

Neglecting the two adverse effects on the inelastic rates mentioned above, oxygen can be evaporatively cooled, reaching the quantum degeneracy limit with particle numbers as high as  $10^5$  or  $10^6$ , following a steep path through orders of magnitude in phase space density, using a near optimal truncation parameter  $\eta$ . It can be seen in figure 4.12, how the small initial truncation parameter, due to large initial inelastic collision rate, causes inefficient initial cooling. This is necessary to reach the runaway regime with a minimal particle loss.

The mean collision time at the fictitious initial values of T and N chosen for

the simulation is in the order of 1 ms, so that the optimal evaporation process can proceed rapidly and reaches high phase space densities after only seconds. Conversely, the initial trap lifetime due to the inelastic collisions is small, casting further doubt on whether such conditions may be achieved experimentally using any trap loading technique.

To assess the effect of evaporation in lower dimensionality, as is the case in quadrupole traps under the influence of gravity, we show three different evaporation runs in figure 4.13, comparing 2D radial and 1D axial evaporation with the 3D evaporation case. While two-dimensional (radial) evaporation still leads to cooling and phase space density increase, cross-dimensional thermalisation cannot supply enough fast moving molecules for efficient cooling in the 1D case (axial cooling). Thus, evaporation from a quadrupole trap under the influence of gravity may lead to additional problems.

#### 4.5.5 Dimple trap and optical plug

Technical difficulties with the trapping and evaporative cooling processes of particles in quadrupole traps can be alleviated through the use of optical methods. A far-detuned repulsive laser beam (blue-detuned) can for example be used as an optical "plug" to repel trapped atoms from the critical trap centre region, where the Majorana losses occur at low temperatures. However, this interferes with the thermalisation process because it restricts particle motion.

A more interesting application of optical methods is the use of an attractive red-detuned laser beam in what can be called a "dimple" trap. Such an additional Gaussian "dimple" trap potential with a time-dependent magnitude can be expressed as

$$W(\mathbf{r},t) = W_d(t) \ e^{-\left(\frac{|\mathbf{r}-\mathbf{r}_d|}{w_d/2}\right)^2},$$
 (4.40)

where  $W_d(t)$  is the peak magnitude at the dimple centre position  $\mathbf{r}_d = x_d \hat{\mathbf{x}} + y_d \hat{\mathbf{y}}$ . The laser beam shines into the trap along the axial z axis and provides an additional trap confinement mostly along its radial directions. The Gaussian profile has a width of  $w_d$ . The previously mentioned "plug" potential has the same shape, but exhibits a repulsive force on the trapped atoms. In numerical simulations it is possible to approximate the Gaussian dimple by a simple harmonic trap region.

BEC of <sup>133</sup>Cs was achieved applying the dimple technique [67]. The last stages of evaporative cooling in caesium are low in efficiency, because of the increasing amount of particle loss due to inelastic collisions and long thermalisation times. The process of adiabatically ramping up the optical dimple creates a deepening trap well, which slowly fills up with the coldest atoms of the ensemble. Inelastic collision rates of particles within this region of the trapping potential are of little importance, since atoms in all magnetic states are trapped in the attractive optical dimple potential. At the end of a standard evaporative cooling process in a quadrupole trap, such a dimple potential can thus provide the critical increase in phase space density, which is required to reach BEC quantum degeneracy. In simulations of trapped particles in linear and harmonic traps, we could also observe increases in the peak phase space density of several orders of magnitude, when an attractive dimple potential was ramped up adiabatically. It is notable that without detrimental effects, the position of the dimple potential could be chosen slightly off-centre in the quadrupole potential. This was done in order to yield a larger reduction in the Majorana loss rate at the zero magnetic field centre region. This technique may thus become a practical method to achieve BEC phase space densities with particle species, which have sub-optimal collision properties. A Gaussian trap dimple is shown at a far off-centre position in figure 4.14.



Figure 4.14: Linear quadrupole trap potential in two spatial dimensions with a "dimple potential" depression (harmonic approximation) at an offset (x,y) position from the central potential minimum.

## 4.6 Results

Oxygen  ${}^{17}\text{O}_2$  was identified as a molecular species, which can potentially be trapped in magnetic traps due to its favourable Zeeman energy levels (shown in figure 3.1 b on page 49). We find, however, that the feasibility of evaporative cooling of oxygen strongly depends on the lowest temperatures and initial population sizes, which can be achieved by trap loading procedures, such as buffer gas cooling, as a starting point for the evaporative cooling process. The lower the initial temperature is, the larger the ratio between elastic and inelastic collisions will be. Additionally, for oxygen trapping, magnetic traps need to

be very shallow due to the adverse influence of strong magnetic fields on the inelastic collision rate, as explained in section 2.2.4 (page 34).

This practically rules out magnetic traps for trapping at high temperatures in the millikelvin range, since oxygen with its relatively small magnetic moment of  $\mu = 2\mu_B$  requires fairly strong magnetic field gradients for trapping at such high temperatures. For a practical maximum magnetic field magnitude of 53 G, as pointed out in [54], the magnetic trap needs to be very shallow with a depth of merely 7 mK, and it would naturally need to be loaded at temperatures significantly below this figure. Presently no trap loading mechanism of this performance exists for molecular oxygen. Purely optical trapping and evaporation from optical traps may prove to be more feasible.

In our computer simulations of evaporative cooling of oxygen we have made optimistic assumptions about the starting parameters for evaporative cooling, and we have shown the feasibility of the evaporative cooling process in the presence of the adverse effects of Majorana spin flip particle loss. Furthermore we have shown how reduced dimensionality of the cooling process decreases the cooling efficiency and may make it infeasible, particularly if sufficiently low starting temperatures for the evaporative cooling runs cannot be achieved in the trap loading procedures.

We have investigated traps combining magnetic and optical potentials, and we have shown that an optical "dimple" potential can lead to significant increases in peak phase space density. The combination of magnetic and optical trapping methods has proven to work for problematic particle species, such as caesium, which could not be cooled to quantum degeneracy in purely magnetic traps. Thus we are confident that BEC phase space densities may in the future also be reached in oxygen experiments using such combined methods. One major obstacle for  $O_2$  cooling, however, is the large inelastic collision rate at temperatures above 10 mK.

In the future, further computational work is planned on cooling using combined magnetic and optical methods. Sympathetic cooling using multiple particle species may turn out to be a viable route to BEC of molecular oxygen. Our simulation program has been designed for use with ensembles of multiple particle species and can also be applied to a wide range of other dynamical particle ensemble problems in addition to magnetic trapping and cooling.

## Chapter 5

# Simulations of Bose-Einstein Condensates

Bose-Einstein Condensates (BEC) in dilute atomic quantum gases are coherent macroscopic matter-wavefunctions. Experimentally realised BEC clouds typically consist of  $10^5$ - $10^7$  atoms and have sizes in the  $\mu$ m range. Despite the extremely small physical size of the BEC, accurate simulation of such clouds is a big challenge for computational physics. Computers have significantly evolved over the last decade and are now capable of making accurate fully three-dimensional numerical simulations of condensate clouds possible on normal workstation computers using the Gross-Pitaevskii Equation (GPE).

While 1D and even 2D simulations are possible using limited hardware, even using slow high-level programming languages like Matlab [120] or Octave [121], 3D simulations are a class of its own. They require a lot of memory and CPU time. High level languages are inefficient and cannot be used fir this purpose because of the overhead associated with them. Most importantly, such long running simulations also mandate a consistent operating environment, which is able to run for many days or even months without overheating or crashing. These requirements strongly favour well-chosen computer hardware, the Linux operating system, compiled programming languages and carefully debugged software. The author would like to explicitly mention the C++ memory debugging utility *valgrind* [122], which is an invaluable tool for hunting down memory leakages and sloppy programming. Large and complex programs would not be possible without this or similar tools.

As an example for memory demands, consider a  $128^3$  spherically symmetric discrete numerical grid of complex double precision floating point numbers to hold the complex wavefunction. At 16 Bytes for a complex double, we need 32 Megabytes for a single wavefunction. In order to do numerical work, we need at least three copies of this wavefunction in memory (see section 5.3.4 and appendix E), increasing the memory required to close to 100MB. Note that 128 gridpoints in one dimension cannot be considered to be a very good resolution and that a factor of two improvement in grid resolution increases memory demand by a factor of  $2^3$ . Computer memory is very cheap today and thus the bottleneck for most numerical simulations is the computational power of the computer CPU and the limited speed at which data can be read and written from and to main memory, rather than its actual size. One conceptual ansatz to improving the situation is parallelisation. Parallelisation involves identifying program components which can be split into several smaller chunks that can be processed by different computers or CPUs simultaneously. After separate computation, the constituent parts are then put back together again to form the solution or an intermediate solution. This approach works well for problems like weather forecasts on large scale parallel so-called "super computers". In our GPE simulations we also use parallelisation across the system's CPUs for Fourier transforms.

In the following sections we will outline the theory behind the numerical simulations and describe the implementation of our simulation program before we discuss the problems we have investigated and applied the simulation program to. Much of the work described in this chapter has been done in collaboration with experimental BEC groups in Oxford and Konstanz.

## 5.1 Bose-Einstein Condensation

In this section we outline some of the basic theoretical concepts required to understand the simulation work presented in the subsequent sections, since a more detailed introduction is beyond the scope of this thesis. The interested reader will find a large body of literature on the subject. A good starting point can be found in [123].

#### 5.1.1 Mean field theory and the GP Equation

A theoretical description of interacting ultra-cold bosonic gases starts with the many-body Hamiltonian for N bosons trapped in an external potential  $V_{ext}(\mathbf{r}, t)$ 

$$\hat{H} = \int d\mathbf{r} \hat{\Psi}^{\dagger} \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{ext} \right] \hat{\Psi} + \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \hat{\Psi}^{\dagger} \hat{\Psi}^{\dagger} V(\mathbf{r} - \mathbf{r}') \hat{\Psi} \hat{\Psi}, \qquad (5.1)$$

where  $\hat{\Psi}(\mathbf{r}, t)$  is the Bose field operator and  $V(\mathbf{r}-\mathbf{r'})$  is the particle interaction potential.

Particle interactions have a tremendous influence on the physics of a BEC. In liquid helium, where first observations of superfluidity were made and the occurrence of BEC was suggested in 1938 [124], particle interactions are strong due to its liquid nature. Today, we know that BEC in liquid He is highly depleted, which means that there is a significant amount of excitations into states other than the lowest bosonic energy state, and that only a fraction of approximately 10% of the particles are condensed into the BEC.

In contrast to the situation for liquid helium, for dilute gases such as alkali BEC in magnetic traps the interactions are very weak and the interaction potential is determined by simple s-wave scattering only (see section 2.1.4). For this case we may replace the interaction potential with the simple binary collision effective interaction potential

$$V(\mathbf{r} - \mathbf{r}') = U_0 \delta(\mathbf{r} - \mathbf{r}'), \qquad (5.2)$$

#### 5.1. BOSE-EINSTEIN CONDENSATION

where  $U_0 = 4\pi\hbar^2 a/m$ , containing the *s*-wave scattering length *a*. A simple description of the BEC based on the assumption of a mean field  $\Psi(\mathbf{r}, t)$ , which makes up the full Bose field  $\hat{\Psi}(\mathbf{r}, t)$  in combination with a small and negligible amount of excitations  $\hat{\delta}(\mathbf{r}, t)$  [125]

$$\hat{\Psi}(\mathbf{r},t) = \Psi(\mathbf{r},t) + \hat{\delta}(\mathbf{r},t).$$
(5.3)

 $\Psi(\mathbf{r},t) = \langle \hat{\Psi}(\mathbf{r},t) \rangle$  is the mean field of the Bose field operator and represents a complex wavefunction, the dynamics of which are described by the Schrödinger equation.

With the Heisenberg equation of motion for the Bose field operator

$$i\hbar\frac{\partial}{\partial t}\hat{\Psi} = [\hat{\Psi}, \hat{H}], \qquad (5.4)$$

and replacing the Bose quantum field operator by a classical mean field wavefunction  $\hat{\Psi} \to \Psi$ , we get the time-dependent so-called Gross-Pitaevskii (GP) equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[-\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m} + V_{trap}(\mathbf{r},t) + U_0|\Psi(\mathbf{r},t)|^2\right]\Psi(\mathbf{r},t)$$
(5.5)

Note that we use the normalisation convention  $\int |\Psi|^2 d\mathbf{r} = 1$ , while some other authors may use the BEC particle number  $N_0$  in the normalisation  $\int |\Psi|^2 d\mathbf{r} = N_0$ . In such cases the Bose quantum field operator  $\hat{\Psi}$  would be replaced by a classical field  $\Psi$  as in  $\hat{\Psi} \to \sqrt{N_0}\Psi$ . The GP equation thus describes the atomic field in a classical approximation neglecting quantum field fluctuations. Due to particle interactions, a non-vanishing quantum depletion of the bosonic ground state is not avoidable. Beyond the mean field treatment in terms of the GP equation, BECs with small excitations can be described by the BogoliubovdeGennes equations, which are obtained substituting equation (5.3) into the equation of motion (5.4) for the full Bose quantum field operator [126].

A more thorough derivation of the GP equation can be found, for example, in [15]. Therein, Castin points out the interesting view that a pure BEC at T=0 is a classical state of the atomic quantum field in the same way as a laser is a classical state of the electromagnetic quantum field.

Eigenstates of the trapping potential exhibit no dynamic spatial evolution. In such cases the wavefunction  $\Psi(\mathbf{r}, t)$  can be separated into a part of spatial and a second part of temporal dependence.

$$\Psi(\mathbf{r},t) = \Psi(\mathbf{r})e^{-i\mu t/\hbar} \tag{5.6}$$

Substituting this into the time-dependent GP equation leads to the time-independent GP equation.  $\mu$  is the chemical potential of the wavefunction.

$$\mu\Psi(\mathbf{r}) = \left[ \left( -\frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m} + V_{trap}(\mathbf{r}) \right) + U_0 |\Psi(\mathbf{r})|^2 \right] \Psi(\mathbf{r})$$
(5.7)

An excellent theoretical review of the dynamics of Bose-Einstein condensation can be found in [127].

#### The Thomas-Fermi approximation

In cases of strong nonlinearity as in large condensate clouds, the kinetic energy term in the time-independent GP equation can be neglected in comparison with the remaining energetic contributions. This leads to an approximation of the ground state cloud shape, which has the form of an inverted parabola for a harmonic external trap potential  $V_{trap}$ 

$$|\Psi|^2 = \frac{1}{U_0} (\mu - V_{trap}) \tag{5.8}$$

In practice, only the immediate cloud borders deviate from this approximation, as can be seen in the gradual improvement of a Gaussian initial state guess in figure 5.2.

#### 5.1.2 Irrotational flow and vortices

The GP equation describes a superfluid, which cannot exhibit the common rotational flow known from and observed in normal fluids due to its nature as a complex wavefunction  $\psi = |\psi|e^{iS}$ , where  $S = \arg \psi$  is the wavefunction phase. The phase is multi-valued in the sense that the phase S as the complex argument is specified only on the range  $\arg \psi \in (-\pi, \pi]$ , where it is determined plus or minus an integer number multiple of  $2\pi$ .

With a condensate density of  $n(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2$ , a BEC at zero temperature T=0 fulfills the hydrodynamic continuity and force equations of superfluids. The continuity equation applying to the condensate is

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{v}) = 0. \tag{5.9}$$

The force equation, with g characterising the interaction strength of the particles with mass m in an external potential  $V_{ext}$ , is

$$m\frac{\partial \mathbf{v}}{\partial t} + \nabla \left( V_{ext} + gn + \frac{mv^2}{2} \right) = 0, \qquad (5.10)$$

where we have neglected the kinetic pressure term  $\frac{\hbar^2}{2m\sqrt{n}}\nabla^2\sqrt{n}$  from inside the brackets. This is a reasonable approximation to make for large particle numbers and strong interactions. Under such conditions the condensate density is very smooth and homogeneous in a cloud centre region making this term negligible. Deviations due to a breakdown of this approximation must be expected at the cloud borders.

The velocity field  $\mathbf{v}(\mathbf{r},t)$  is related to the wavefunction phase S by [128]

$$\mathbf{v}(\mathbf{r},t) = \frac{\hbar}{m} \nabla S(\mathbf{r},t). \tag{5.11}$$

For our choice of computational units, the velocity field  $\mathbf{v}(\mathbf{r}, t)$  of a BEC is given by  $\mathbf{v} = 2\nabla S$ . With equations (5.9) and (5.10) this leads to the result that the flow is irrotational.– The curl, or the vorticity, of the velocity field vanishes:

$$\nabla \times \mathbf{v} = 0 \tag{5.12}$$

Exceptions are points where the phase is undefined. This can only occur for zero probability density. Thus BEC flow can only "go around" points of zero density and undefined phase. Such "holes" are called vortices. Around such points the phase circulation

$$\int_{\sigma} (\arg \psi) d\mathbf{s} = m2\pi \tag{5.13}$$

assumes values  $m \neq 0$ , where *m* denotes the integer valued multiplicity of the vortex.  $\sigma$  symbolises the closed path the phase is integrated along using line element ds.

Vortices in superfluids are quantised. In a 3D BEC cloud with a central vortex line, the angular momentum in computational units will be  $\hbar$ , which is our numerical unit of angular momentum. The angular momentum operator is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{P},\tag{5.14}$$

where  $\mathbf{P}$  is the momentum operator. In our dimensionless numerical formalism we have  $\mathbf{P} = -i\nabla$ . Due to the cylindrical cloud symmetry in most traps, we are mainly interested in the z component  $L_z = xP_y - yP_x$  (which is also the only L component in cartesian 2D simulations). Unlike in superfluid Helium, the angular momentum  $L_z$  of a gas cloud depends on the vortex position due to its inhomogeneous density profile. Application of a continuous torque (for example using an optical stirrer in [129]) will cause a vortex to move in from the outer "Oort cloud" to the BEC centre as the angular momentum reaches unity.

## 5.2 The *GPEsim* program

An extensible Gross-Pitaevskii equation (GPE) solver has been implemented from scratch using the C++ programming language exclusively. Avoiding the perils of interpreted languages like Matlab [120] or GNU Octave [121] scripts, a portable compiled C++ implementation of a GPE simulation package allows full three dimensional (3D) simulations which run at reasonable speeds on present workstation computers, where the GNU C++ compiler [130] is available.

The author's implementation makes heavy use of the fast "FFTW" Fourier transform package [131], which is able to use multiple processors in multi-threaded environments, like dual processor workstation computers. It has been optimised for low memory footprint in order to allow the largest possible computational grids under given computer hardware constraints, making use of some of the optimised algorithms described in [132].

The simulation program has grown quite large over time as more and more modules were added to handle specific types of problems. The modular structure in the C++ programming language has helped to keep the complexity manageable. Furthermore, the re-use of existing code modules in adaptions of the program to different types of potentials and even to different geometries (such as cylindrical symmetry in section 5.3.6) has lead to a proven and welldebugged simulation program core. In the following section we will discuss the numerical techniques used in the development of the program before we proceed to the problems we have applied it to.

## 5.3 Numerical Techniques

In this section we will present and explain some of the key techniques used in our GPE simulation programs. The interested reader should also refer to the program source code, which is too large to attach to this work and will be available on the author's web pages (and also on CD-ROM in the Konstanz university library). In self-interest an effort was made to sufficiently comment the source code. This helps with debugging work at later times and additionally it allows code re-use by others. In general, program source code should gain significance in public perception, particularly in science, since it deserves at least as much scrutiny as the scientific publications based on such numerical techniques.

#### 5.3.1 Computational units

Dimensionless units are used for the numerical representation of the GP equation within the computer simulation. The GP equation in its dimensionless form is this:

$$\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = i\left[\nabla_{\mathbf{r}}^2 - V(\mathbf{r},t) - C|\Psi(\mathbf{r},t)|^2\right]\Psi(\mathbf{r},t)$$
(5.15)

All variables in the above equation are dimensionless and need to be converted into SI units by scaling factors.

$$t_{SI} = t_0 t, \quad t_0 = -\frac{1}{\omega_x}$$
 (5.16)

$$x_{SI} = x_0 x, \quad x_0 = \sqrt{\frac{\hbar}{2m\omega_x}} \tag{5.17}$$

$$E_{SI} = E_0 E, \quad E_0 = \hbar \omega_x \tag{5.18}$$

For more than one-dimensional simulations, the remaining axis (y,z) of the spatial vector **r** are also scaled into dimensionless units using the scaling factor  $x_0$ . Note that the scaling of energy in harmonic oscillator units also applies to the potential  $V_{SI} = E_0 V$ . These scaling factors are easily obtained from manipulations of eq. (5.5). For 3D simulations the nonlinearity factor in the dimensionless GP equation becomes

$$C = N \frac{4\pi\hbar a}{m\omega_x x_0^3} = 8\pi a N \sqrt{\frac{2m\omega_x}{\hbar}},$$
(5.19)

where N is the number of particles in the simulated BEC, and a is the elastic inter-particle scattering length. In simulations for less then three dimensions the nonlinearity factor changes. This will be looked at in more detail in section 5.3.8.

#### 5.3. NUMERICAL TECHNIQUES

For the numerical computation process the right hand side of the dimensionless GP equation is usually separated into two parts using a  $\hat{D}$  and a  $\hat{N}$  operator.

$$\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{D}\Psi(\mathbf{r},t) + \hat{N}\Psi(\mathbf{r},t)$$
(5.20)

The  $\hat{D}$  operator contains only the spatial derivatives and is often referred to as the "diffusion part" because it links grid points (note that with vanishing  $\hat{N}$  it reproduces a diffusion equation), while the  $\hat{N}$  operator contains all the potentials and interactions which only act locally.

$$\hat{D} = i\nabla_{\mathbf{r}}^2, \qquad \hat{N} = -iV(\mathbf{r}, t) - iC|\Psi(\mathbf{r}, t)|^2$$
(5.21)

V is the trapping potential and C is the nonlinearity as defined above. In some situations it is important to include gravity effects of the type +iGy into the  $\hat{N}$  operator, where G represents the dimensionless gravitational potential along the y axis in this example.

#### 5.3.2 Fast Fourier transform method

In cartesian coordinates a very simple and efficient way to calculate the derivatives in the diffusion part of the GPE uses Fourier transforms (FT). While other methods can be used to compute this part on discrete grids, the FT method achieves accuracies comparable to 11-point finite differencing methods [133]. Additionally this method is easily extended to multiple dimensions and allows the use of existing highly proven and optimised FT libraries, such as "FFTW" [131].

In an interaction picture with respect to the  $\hat{D}$  operator, the wavefunction  $\Psi(\mathbf{r}, t)$  becomes

$$\Psi^{I}(\mathbf{r},t) = e^{-D(t-\tau)}\Psi(\mathbf{r},t), \qquad (5.22)$$

where  $\tau$  represents the time at which the interaction pictures separates from the Schrödinger picture. Now the time-dependent GP equation (5.20) becomes

$$\frac{\partial}{\partial t}\Psi^{I}(\mathbf{r},t) = \hat{N}^{I}\Psi^{I}(\mathbf{r},t) = (e^{-\hat{D}(t-\tau)}\hat{N}e^{\hat{D}(t-\tau)})e^{-\hat{D}(t-\tau)}\Psi(\mathbf{r},t)$$

$$= e^{-\hat{D}(t-\tau)}\hat{N}\Psi(\mathbf{r},t)$$
(5.23)

In this interaction picture representation, the diffusion operator becomes diagonal and its eigenfunctions are the Fourier base function  $\exp(ikx)$  (in 1D). In the interaction picture, the Laplacian operator eigenvalues are the squares of the Fourier space coordinates  $k_i$ , so that an evaluation of the  $\hat{D}$  operator in Fourier space consists of a simple multiplication with these. Thus, application of the  $\hat{D}$  operator to a discrete numerical wavefunction can be done by moving the wavefunction into the interaction picture using a Fourier transform, multiplying the result with the squares of the Fourier coordinates and eventually moving the result back into the normal picture by applying an inverse FT [52, 134]. This is a very efficient method. Additionally, it inherits its high precision from the FFT algorithm.

#### 5.3.3 Unitary split step algorithm

A very simple method to propagate the GP equation in time uses the unitary time evolution operator. A wavefunction  $\Psi(\mathbf{r}, t = 0)$ , which is a solution of the GP equation (5.15) at time t = 0, will become (with  $H=\hat{D}+\hat{N}$ )

$$\Psi(\mathbf{r},\Delta t) = e^{-i[D+N]\Delta t}\Psi(\mathbf{r},0)$$
(5.24)

after a short time interval  $\Delta t$ . To second order accuracy due to the Baker-Campbell Hausdorff formula [28], the unitary time evolution operator can be approximated as follows

$$e^{-i[\hat{D}+\hat{N}]\Delta t} \approx e^{-\frac{i\hat{D}\Delta t}{2}} e^{-i\hat{N}\Delta t} e^{-\frac{i\hat{D}\Delta t}{2}} + O(t^3)$$
(5.25)

In this approximation, the timestep has been split in half, a measure increasing the accuracy to third order for  $\hat{N}$  operator local potentials varying slowly over time. Additionally a split timestep makes the algorithm numerically more stable. The  $\hat{D}$  operator can be evaluated with the Fourier method as described in the previous section. In total, propagation over one timestep will thus require 4 Fourier transforms in the split step case and only 2 transforms in the full step case. This algorithm is easy to implement and requires very little memory, not much more than the space required to store a single copy of the wavefunction. The limited accuracy, however, makes Runge-Kutta based algorithms the better choice as we will show in the next section.

Note than in this algorithm, due to the unitarity of the operators, the wavefunction norm will stay constant at all times during the propagation and cannot be used as an indicator for the numerical accuracy of the numerical solutions.

#### 5.3.4 Runge-Kutta algorithm

As we have shown above, the Fourier transform method allows us to evaluate the spatial differentials with great precision. A method to achieve comparably high accuracy in a temporal propagation is now required. The unitary split step method is not well suited for long-running simulations, because it requires a large number of timesteps to achieve reasonable accuracy.

With the definition of a function  $f(\Psi^{I}, t)$  as equation (5.23)

$$f(\Psi^{I},t) := \frac{\partial}{\partial t} \Psi^{I}(t) = \hat{N}^{I} \Psi^{I}(\mathbf{r},t)$$
(5.26)

the fourth order Runge-Kutta interaction picture algorithm (RK4IP) to propagate a nonlinear Schrödinger equation such as the GPE from timestep n to timestep n+1 can be written as follows:

$$\Psi^{I}(t_{n+1}) = \Psi^{I}(t_{n} + \Delta t) = \Psi^{I}(t_{n}) + \left[\frac{k_{1}}{6} + \frac{k_{2}}{3} + \frac{k_{3}}{3} + \frac{k_{4}}{6}\right] \Delta t$$
(5.27)

The shorthands  $k_1$  to  $k_4$  represent the four evaluations of the differential term, the weighted sum of which determines the wavefunction value at the next timestep. As in [92] they are

$$k_{1} = f(\Psi^{I}, t_{n})$$

$$k_{2} = f(\Psi^{I} + k_{1}\frac{\Delta t}{2}, t_{n} + \frac{\Delta t}{2})$$

$$k_{3} = f(\Psi^{I} + k_{2}\frac{\Delta t}{2}, t_{n} + \frac{\Delta t}{2})$$

$$k_{4} = f(\Psi^{I} + k_{3}\Delta t, t_{n} + \Delta t)$$
(5.28)

The interaction picture separation time in the  $\hat{D}$  operator can be chosen to the centre point between two timesteps ( $\tau = \Delta t/2$ ) saving two Fourier transforms. In total this algorithm requires eight Fourier transforms per timestep and a considerably larger amount of computer memory because several modified copies of  $\Psi$  need to be computed and kept before they are combined. We have chosen a memory efficient implementation of the RK4IP algorithm described by Caradoc-Davies in [132]. It is summarised in appendix E and requires memory storage space equivalent to three copies of the discretised wavefunction (plus some program overhead).

We have tried to trade in memory consumption for gains in computational speed by expanding the phase factors used in the interaction picture evaluation of the spatial derivatives into large memory tables the size of another wavefunction copy. This however gave mixed results on different workstation machines. Usually gains (or losses) in speed were small. The reason for this is that presently the memory bus is the bottleneck for computer speed. The GPE solver program is very heavy on memory I/O due to the large wavefunction grids, particularly in 3D. Thus the computer CPU seems to be waiting for data to be read from or written to memory most of the time and these operations can in fact be slower than the calculation of the tabulated values from a much smaller data set, which may happen to fit into the CPU caches. Raw CPU speed seems to be secondary for computations of this kind, and an optimal system will not feature the latest processor but the latest and fastest type of memory and internal bus system.

The RK4IP method has become the method of our choice for all types of simulations because its fourth order accuracy makes it faster than the unitary split step algorithm by a factor between 8 and 16 when operating at the same level of accuracy.

#### 5.3.5 Discretisation, Accuracy and Speed

In our numerical simulations we represent the continuous quantum mechanical wavefunction by a grid of discrete points of complex numbers. Additionally, time is also discretised into steps through which the computer program evolves dynamic effects of the simulated system. This does not pose a problem as long as we are aware of the potential pitfalls arising from this treatment.

A discretisation will invariably have a limited resolution and the spatial and temporal "grid" can be set too coarse for a valid physical description of the effects under investigation. On the other hand, a resolution chosen too high will waste time and resources without gaining additional information. Thus it is important to choose a discretisation "just right" for a specific problem.

We have to make sure that the phase difference between two grid points will never exceed  $\pi$ , as this is the aliasing limit.– Values larger than  $\pi$  will appear to be  $x-2\pi$ . This affects the maximum cloud velocities which can be represented on a given grid resolution, since condensate velocity **v** is given by the spatial gradient of the wavefunction phase S (in computational units):

$$\mathbf{v} = 2\nabla S \tag{5.29}$$

Velocities that are too high will change sign at the aliasing limit.

Temporal step size determines the accuracy of the numerical solution. Doubling the number of timesteps for the same time span will increase the accuracy by a factor of four for the second order unitary split step algorithm (section 5.3.3) and by a factor of 16 for the fourth order RK4IP algorithm (section 5.3.4). Such error calculations can be easily done by using the numerical algorithms to propagate wavefunctions for cases which have analytical solutions ( $\psi^{true}$ ) and comparing those with the numerical results ( $\psi^{comp}$ ) [134]. For smaller time steps one finds the same improvements for the average error per grid point  $\sum_{i}^{N} |\psi_{i}^{comp} - \psi_{i}^{true}|/N$  and for the maximum absolute error max( $|\psi_{i}^{comp} - \psi_{i}^{true}|$ ).

The maximum allowable time step size (tolerating the accuracy loss due to the numerical solver) largely depends on the chemical potential  $\mu$  of the wavefunction as defined by the time-independent GP equation (5.7). Increasing the time step to a value larger than  $\Delta t = \pi/\mu$  will cross the aliasing limit. Local difference in the chemical potential (which is only homogeneous for trap eigenstates) will result in ambiguous phase gradients and thus in the destruction of the cloud during the diffusion calculation. Thus in practice the time step needs to be chosen much smaller than this.

Changes in grid and temporal resolution are not completely independent of each other. Working on a much finer grid will also require a finer timestep as we will see in the following considerations. For simplicity we will look at the situation for a 1D grid on the x coordinate.

The grid resolution  $\Delta x$  determines the spectral resolution in Fourier space and thus the maximum momentum  $k = p/\hbar$  of the wavefunction.– Dynamic problems require high grid resolutions. As we have shown in previous sections the numerical solution is computed applying operators similar to  $e^{-iH\Delta t/\hbar}$  to the wavefunction  $\Psi(\mathbf{r}, t)$ . Since we are only interested in the relationship between spatial and temporal resolution, we may for simplicity assume a situation where the Hamiltonian H consists merely of the kinetic term  $\mathbf{p}^2/(2m)$  in the absence of an external potential and nonlinear interaction. In this case, the requirement for temporal resolution is that the exponent be much smaller than the chemical potential  $\mu$ , or for simplicity, much smaller than 1:

$$\frac{\hbar k^2}{2m} \Delta t \ll 1 \tag{5.30}$$

Combining this with the relation between spatial resolution and maximum mo-

mentum  $k_{max} \sim 1/\Delta x$ , we get

$$\frac{\hbar}{2m} \frac{\Delta t}{(\Delta x)^2} \ll 1. \tag{5.31}$$

This relation explains why the use of finer spatial grids is overproportionally expensive to compute. Doubling of the grid points (dividing  $\Delta x$  by 2) requires four times as many time steps to fulfill the numerical requirements for  $\Delta t$ .

While the  $\Delta t$  adjustment in such cases may not have to be quite as dramatic, since we will in practice never operate at the numerical aliasing limit and since there is some room for adjustment as suggested by the inequality, the above relationship does explain why true 3D simulations of bright gap solitons (section 5.10) are impractical with present workstation computers. The fine scale dynamics and spatial periodicity in these simulations requires very high grid resolutions. Additionally, the simulations have to be run for very long time intervals to allow comparisons with experimental results. The small size of timesteps mandated by the high spatial grid resolution then causes impractically long program running times in the order of weeks or months for individual configurations. Symmetry considerations however make soliton simulations practical in 2D as we will show in the next section.

#### 5.3.6 Cylindrical symmetry and pseudo-3D

In situations where two axes of the problem are degenerate, the symmetry can be exploited to cut down on the computational complexity of the simulations that need to be carried out. If, for example, the problem has a spherical symmetry and no effects with  $(\theta, \phi)$  angular dependence may occur, the numerical simulation can be conducted in 1D, where the only free spatial parameter xstands for the radius r. This is called *spherically symmetric pseudo-3D*. When the symmetry is cylindrical, i.e. axes x and y are degenerate, the problem can be described fully using two free parameters, r and z, in what is called a cylindrically symmetric pseudo-3D simulation.

The computational complexity grows exponentially with increasing dimensionality. A resolution of  $10^3$  spatial points in 1D requires a grid of  $10^6$  points in 2D and a mesh of  $10^9$  points in 3D. Thus, exploiting such dimensionality-decreasing symmetries is crucial. However, this requires some non-trivial changes to existing computer programs designed for simulations in cartesian coordinates. Except for the cartesian 2D and 3D cases, the cylindrically symmetric case is the most important for our work. Therefore, we will discuss it here as an example.

The time-dependent GP equation (5.5) simplifies for a cylindrically symmetric potential as follows:

$$i\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(r,z,\phi,t) + \left[V_{trap}(r,z,t) + U_0|\Psi(r,z,\phi,t)|^2\right]\Psi(r,z,\phi,t)$$
(5.32)

For cylindrically symmetric wavefunctions  $\Phi(r, z, t)$  such that  $\partial \Phi / \partial \phi = 0$ , this

simplifies to

$$i\frac{\partial\Phi(\mathbf{r},t)}{\partial t} = -\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}\right)\Phi(r,z,t) + \left[V_{trap}(r,z,t) + U_0|\Psi(r,z,t)|^2\right]\Phi(r,z,t)$$
(5.33)

For  $\phi$ -dependent wavefunctions  $\Phi(r, z, t)e^{-im_z\phi}$  with  $m_z \neq 0$ , angular momentum is conserved by the cylindrical symmetry of the potential, and a centrifugal barrier term  $m_z^2/r^2$  needs to be retained in addition to  $V_{trap}$  in (5.33).

The 2D cylindrically symmetric case expressed in eq. (5.33) can be discretised and solved with comparatively low numerical effort by a explicit Dufort-Frankel type scheme [135] as follows. (Upper indices- time step, lower indicesr, z spatial steps.)

$$i\frac{\psi_{jk}^{n+1} - \psi_{jk}^{n-1}}{2\Delta t} = -\frac{\psi_{j+1,k}^{n} - (\psi_{jk}^{n+1} + \psi_{jk}^{n-1}) + \psi_{j-1,k}^{n}}{\Delta r^{2}} - \frac{1}{r_{j}}\frac{\psi_{j+1,k}^{n} - \psi_{j-1,k}^{n}}{2\Delta r} - \frac{\psi_{j,k+1}^{n} - (\psi_{jk}^{n+1} + \psi_{jk}^{n-1}) + \psi_{j,k+1}^{n}}{\Delta z^{2}} + V_{trap}(r, z, t)\frac{\psi_{jk}^{n+1} - \psi_{jk}^{n-1}}{2} + U_{0}|\psi_{jk}^{n}|^{2}\frac{\psi_{jk}^{n+1} - \psi_{jk}^{n-1}}{2}$$

$$(5.34)$$

The grid is chosen such that  $r_j = (j-1/2)\Delta r$ , with  $\Delta r = R/(n+1)$ , avoiding the coordinate origin. This scheme promises the most efficient numerical solution, but it suffers the problems of explicit algorithms. While semi-explicit algorithms have also been applied to this problem [136], we decided to continue using our proven GPE-solver and RK4IP algorithm (section 5.3.4), making the necessary changes to allow 2D cylindrically symmetric simulations.

While it would be possible to optimise the existing code to operate on an interval r = [0, R] instead of the typical x = [-L, L], this would mean heavy changes in the low proven level code in the simulation. Instead of doing this, we sacrifice some efficiency and operate on an interval r = [-R, R], interpreting the negative r-part as an azimuthal rotation of the positive r-part by an angle of  $\pi$ . The symmetry requires that  $\Phi(-r, z) = \Phi(r, z)$ . This is the reason why efficiency could be improved on the DFT level by using symmetric discrete cosine transforms (DCT) instead of DFTs. In practice, however, the negative part can simply be ignored as ballast here.

Analog to the explanation of the RK4IP algorithm in section 5.3.4, we can write equation (5.33) as

$$\frac{\partial \Phi}{\partial t} = i [D_{cyl} + N_{cyl}] \Phi, \qquad (5.35)$$

where  $D_{cyl}$  is

$$D_{cyl} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}$$
(5.36)

The problematic part in integrating this equation into the RK4IP algorithm is the fact that the  $D_r = (1/r)(\partial/\partial r)$  part is not diagonal in the Fourier basis and must be handled separately.

#### 5.3. NUMERICAL TECHNIQUES

The evaluation of  $D_r$  can be achieved, with precision comparable to the precision achieved in evaluating the derivatives in D, using the Fourier method (section 5.3.2), by employing multi-point central differencing schemes (see appendix F). An 11-point scheme yields precision equivalent to a Fourier type differential evaluation [133]. In order to allow a conventional Fourier evaluation of the remaining part  $\tilde{D}$  of  $D_{cyl} = \tilde{D} + D_r$ , we put the evaluation of  $D_r$  into the N operator, so that we get

$$N_{cyl} = D_r + N = D_r - V(\mathbf{r}, t) - C|\Psi|^2 = \frac{1}{r}\frac{\partial}{\partial r} - V(\mathbf{r}, t) - C|\Psi|^2.$$
(5.37)

In the interaction picture representation this becomes

$$[D_r + N]_I = [N_{cyl}]_I = e^{i(t-t')\hat{D}} [D_r + N_{cyl}] e^{-i(t-t')\hat{D}}.$$
 (5.38)

With the additional evaluation of the  $D_r$  term using a finite differencing method, it is thus possible to use the proven and efficient code developed for cartesian 2D and 3D problems to solve cylindrically symmetric problems in "pseudo-3D".

#### 5.3.7 Initial state generation

The natural choice for a simulation initial state is a trap eigenstate, in particular the trap ground state. An important feature of the trap ground states is that it has a long simulation lifetime and rests in the trap. Thus it is an ideal state for code debugging and an excellent test case. Furthermore it can serve as a starting point for simulations of manipulation and excitation of condensate clouds.

Analytical methods to determine trap eigenstates using conjugate gradient techniques have been described in [133]. These methods are also suitable to calculate higher order excitation states. However, these methods are relatively difficult to implement numerically and may require further interpolation to project onto numerical grids [132]. For the sake of simplicity and at the expense of CPU computing time, we have used a method for generating eigenstates, which allows the use of the existing and proven GPE simulation code. This method will be outlined below.

Trap ground states  $\Psi_0(\mathbf{r}, t)$  evolve over time according to the equation

$$\Psi_0(\mathbf{r},t) = \Psi_0(\mathbf{r}) e^{-i\mu t}, \qquad (5.39)$$

where  $\mu$  is the chemical potential, which can be written as

$$\mu = \sum_{i=1}^{3} E_{kin,i} + \sum_{i=1}^{3} E_{pot,i} + 2E_{int}$$
(5.40)

for a wavefunction normalised to unity  $(\int \Psi^* \Psi = 1)$ . The energies are calculated as integrals over all space V as follows.

$$E_{kin} = -\int_{V} \Psi^* \nabla^2 \Psi \, dV \tag{5.41}$$

$$E_{pot} = \int_{V} \Psi^* V_{trap} \Psi \, dV \tag{5.42}$$

$$E_{int} = \frac{1}{2}C \int_{V} |\Psi|^{4} dV$$
 (5.43)



Figure 5.1: Evolution of cloud shape during the initial state calculation process using the negative imaginary time GPE propagation technique. The solid line shows the radial (x,y) FWHM, the dashed line shows the z-FWHM, multiplied by a factor of 15 for clarity. 4e5 (real) timesteps are equivalent to one full trap cycle.

 $E_{int}$  is the interaction energy, often called the self-energy, due to the nonlinear interaction C as defined in section 5.3.1.  $E_{kin}$  is the kinetic energy, which is small and may be neglected in the Thomas-Fermi approximation to obtain approximate ground states.  $E_{pot}$  is the potential energy due to the external trap magnetic field. As we can see in eq. (5.39), the only parameter that changes during the trap eigenstate's temporal evolution is its phase. We can use this fact to find ground states iteratively starting from an approximate solution.

Note that if we were to propagate this state in so called "negative imaginary time", the  $e^{-i\mu t}$  factor would turn into a homogeneous damping factor. This can be used in a very simple and elegant technique to find the eigenstate iteratively. An initial guess, which can, for example, be the linear (gaussian) solution, is propagated over a small negative imaginary timestep and renormalised afterwards. Repeated application of this procedure will iterate towards a state with a homogeneous flat  $\mu$  across the whole cloud. Regions with larger values of  $\mu$  will experience stronger damping and regions with smaller values of  $\mu$  will experience weaker damping. Thereby the cloud will slowly change its shape towards the eigenstate solution. Technically this is an algorithm using the method of steepest descends [137], and in its simplicity it can be implemented with minimal changes to the RK4IP algorithm solver.

Figure 5.1 shows the evolution of the radial and axial width of a cloud during iterative damping into an eigenstate. Figure 5.2 shows cloud density profiles along y = z = 0. It is evident that the final values are reached asymptotically with a very small rate of change after long run times. The Thomas-Fermi shape is not perfectly reached after 15000 iterations. The convergence process



Figure 5.2: Cloud density cuts along x-axis at iteration levels 1500, 3000 and 15000 (blue, green, red). From an initial Gaussian (not drawn), the cloud spreads out into typical inverted parabola Thomas-Fermi shape.

could theoretically be speeded up by enlarging the magnitude of the imaginary negative timestep size with increasing number of iterations. In doing this, however, care must be taken not to amplify errors due to finite machine floating point precision.

Since eigenstates generated using this method are only close to perfect, it is important to control their quality in order to judge whether or not it will be good enough for a specific simulation. Quality is usually only an issue for high precision measurements where remaining residual excitations such as quadrupole modes will have disturbing effects and for extremely long running simulations. Rapid profiling of parameter spaces with cloud eigenstates on coarse discrete grids will not be quite as demanding on eigenstate quality. Therefore, in practice, small deviations are not a problem. Before "production use" eigenstates can be continuously improved running the damping program in the background on spare CPU time.

One useful measure of trap eigenstate quality can be found by mean of the virial theorem. Through the use of scaling transforms in expressions for the trap eigenstate and the fact that the eigenstate energy remains constant for small variations [126], we get the following relations (for individual dimensions i and for total values):

$$E_{kin,i} - E_{pot,i} + \frac{1}{2}E_{int} = 0 (5.44)$$

$$2E_{kin} - 2E_{pot} + 3E_{int} = 0 (5.45)$$

Figure 5.3 shows how these relations approach zero during the iterative damping process (same situation as in figure 5.1). Eigenstate quality will still



Figure 5.3: Evolution of cloud energies during the initial state calculation process using the negative imaginary time GPE propagation technique.  $2E_{kin} - 2E_{pot} + 3E_{int}$  exponentially approaches zero, while the component energies approach a steady solution. 4e5 (real) timesteps are equivalent to one full trap cycle.

improve in terms of this sensitive measure long after noticeable changes in the cloud shape have stopped.

### 5.3.8 Applicability of 2D simulations to 3D experiments

In many situations, one is limited to simulating BEC problems in only two dimensions because full 3D simulations are computationally too expensive and thus too time-consuming. This is exactly the situation in our simulations of the formation of bright atomic band gap solitons. Here, we are required to consider a large spatial range in one of the spatial dimensions (x) because we need to simulate many nodes of the modulated periodic potential created by the standing laser light field. At the same time, each of the nodes has a fine scale density structure and strong phase gradients. Because of this, we need fine temporal resolution, which adds up to large numerical grids and a large number of timesteps.

Because of the strong radial confinement of the essentially cylindrical symmetric problem in the remaining two dimensions (y,z), a transition to a twodimensional description is prudent. However, due to the nonlinearity of the GPE, the three dimensions are not completely independent and a simulation with a reduced dimensionality will necessarily imply introducing another approximation level. If the dimension we want to omit in the numerical simulation is strongly confined by the trapping potential, we can make the reasonable assumption that the wavefunction is separable:

$$\Psi(x, y, z) \approx \Psi(x, y)\Phi_0(z) \tag{5.46}$$

Here,  $\Phi_0(x)$  is the ground state in the strongly confined (z) direction, which can be written as a Gaussian

$$\Phi_0(z) = \frac{1}{\sqrt{\sqrt{\pi}w}} e^{-\frac{z^2}{2w^2}},$$
(5.47)

chosen such that  $\int \Phi_0^*(z)\Phi_0(z)dz = 1$  with  $w = \sqrt{\hbar/m\omega_z}$ . Now the time dependent GPE can be written as

$$i\Psi(x,y)\Phi_0(z) = \Phi_0(z)H_{x,y}\Phi(x,y) + E_{0,z}\Phi_0(z)\Phi(x,y) + C_{3D}|\Phi_0(z)|^2\Phi_0(z)|\Phi(x,y)|^2\Phi(x,y),$$
(5.48)

where  $E_{0,z}$  is the ground state energy of  $\Phi_0(z)$ .

One can now multiply the above equation by the complex conjugate of  $\Phi_0(z)$ and integrate over (z). Since  $\Phi_0(z)$  is normalised, the only term in the GPE affected by this is the nonlinear term. We get

$$i\Psi(x,y) = (H_{x,y} + E_{0,z})\Psi(x,y) + C_{3D} \int |\Phi_0(z)|^4 dz |\Phi(x,y)|^2 \Phi(x,y). \quad (5.49)$$

We can now introduce a new  $C_{2D}$ , which is

$$C_{2D} = \frac{C_{3D}}{\sqrt{2\pi}w}.$$
 (5.50)

This shows the relationship between the nonlinearity factors of a 3D and a 2D simulation describing the same physical situation. Since w has the dimensionality of a distance, the factor between the two nonlinearities is often referred to as the nonlinear reduction length.

In numerical units, where spatial dimensions are scaled by the harmonic oscillator length  $x_0 = \sqrt{\hbar/2m\omega_x}$ , the transition between 2D and 3D nonlinearities is described by a simple factor. Assuming we want to reduce dimensionality by integrating strongly confined dimension (z), the nonlinear reduction length w in scaled dimensionless units becomes

$$\frac{w}{x_0} = \sqrt{2\frac{\omega_x}{\omega_z}}$$

and thus

$$C_{2D} = \frac{C_{3D}}{\sqrt{4\pi\omega_x/\omega_z}}.$$

Reducing the dimensionality from 3D to 1D, we get an additional factor of  $(\sqrt{2\pi} w)^{-1}$ . Thus:  $C_{1D} = C_{3D}/(2\pi w^2)$ . The situation is different for simulations in "pseudo-3D" as described in sections 5.3.6 and 5.10.2. In these simulations the cylindrical symmetry is exploited to reduce the numerical complexity from 3D to 2D. However, no dimension is "frozen out" in the way described above, so that the pseudo-3D simulations must be regarded as true three-dimensional simulations with regard to the nonlinearity.

#### 5.3.9 BEC cloud angles

In many simulations, such as those of the scissors mode (section 5.4.1), it necessary to monitor oscillations of the condensate cloud. While this is a difficult problem in an experimental BEC observation, requiring a large number of destructive "shots" at different simulation times, numerically this can be done at every timestep by calculating a few sums over our wavefunction grid. For a normalised discrete wavefunction  $\sum_i \psi_i = 1$  it is easy to calculate the centre of gravity coordinate  $\mathbf{r}_{com}$  as

$$\mathbf{r}_{com} = \sum_{i} \mathbf{r}_{i} |\psi_{i}|^{2}.$$
(5.51)

With this the inertial tensor of the cloud can be calculated numerically as

$$I_{ij} = \sum_{i} |\psi_i|^2 \begin{pmatrix} y_i'^2 + z_i'^2 & x_i'y_i' & x_i'z_i' \\ y_i'x_i' & x_i'^2 + z_i'^2 & y_i'z_i' \\ z_i'x_i' & z_i'y_i' & x_i'^2 + y_i'^2 \end{pmatrix},$$
(5.52)

where we use coordinates  $\mathbf{r}' = (x', y', z')$  relative to the cloud's centre of mass  $\mathbf{r}' = \mathbf{r} - \mathbf{r}_{com}$ . The BEC clouds in our simulations usually have an oblate shape ("pancake") with cylindrical symmetry and relative sizes  $(l_x, l_y, l_z) = (1, 1, \sqrt{8})$ . This is due to the trapping potentials commonly used in BEC experiments (see section 5.5).

In order to find the cloud angle relative to an initial direction, we need to track the three inertial axes over time, which are eigenvectors of the inertial tensor. Numerically this problem can easily be solved using library functions from the GNU scientific library [138].

#### 5.3.10 Vortex detection

Spatial detection of vortices in BEC clouds is an important method for data acquisition in simulations of the superfluid gyroscope and excitations of Kelvin modes (section 5.7). Again, numerically this problem is more easily and accurately solved than in laboratory BEC experiments.

Vortices appear as points in 2D simulations in the shape of straight or curved lines in 3D simulations. The detection algorithm will always consider individual 2D planes. Vortices are identified by their phase signature, which is a positive or negative multiple of  $2\pi$ , depending on their multiplicity and handedness, when tracing out a closed path around them. Evaluting the phase differences around any non-vortex grid point will show phase individual differences from  $-\pi$  to  $\pi$ between any two points on the eight intervals. An enclosed vortex, however, causes a jump larger than  $\pi$  or smaller than  $-\pi$  somewhere along the path because of the equivalence of phases  $S = 0, 2\pi, 4\pi, \ldots$  Counting these jumps along paths around all grid points thus allows the detection of vortex position and handedness. For eight-interval paths, the detection limit is reached for vortices of multiplicity  $m=\pm 3$ . This is because we want to the detect the vortex orientation, but cannot distinguish between phase differences larger than  $\pi$  and a smaller negative value. Thus the true limit for eight intervals is  $8\pi = 4 \cdot 2\pi$ , vortices with  $m=\pm 4$ , but this cannot be reached in practice.

We have also used a version of this algorithm with only four intervals tracing out a closed path around a grid gap. This version will detect only singly charged vortices, which is sufficient for many applications and faster.

The vortex detection algorithm needs to take into account the fact that the low density areas of our discretised wavefunction, areas where the wavefunction vanishes for all practical purposes, appear to be full of vortices. The low density regions abound with extremely weak high frequency excitations with wild phase fluctuations- extremely small floating point complex numbers with almost random phases. This can be called an "Oort cloud" in reference to a cloud of rocky or comet-like small objects in the outer regions of our solar system. Unlike these, the Oort vortices do not have any physical importance and we can avoid counting and detecting them by specifying a minimum density  $|\psi_i|^2$  for the detection algorithm.

## 5.4 Collective cloud excitations in a BEC

As we have outlined in section 5.3.7, the most important feature of the BEC trap ground state is that it rests motionless in its trap for arbitrary lengths of simulation time. Meaningful experiments and simulations, however, will investigate dynamics of the trapped BEC cloud, which can be excited in many different ways. For the time being we will look into low frequency and low energy collective excitations of the whole cloud. Low excitation energy in this context means that the energies are much smaller than the mean-field interaction between the atoms (the chemical potential). Excitations of this scale are of collective nature. Angular excitations in form of vortices have been glanced in section 5.1.2 and high frequency excitations up to finite temperature effects cannot be treated reliably within the mean field approximation of the GP equation.

The most simple excitations of a trapped BEC cloud are the dipole oscillations performed by the cloud, when the initial state is not centered within the harmonic potential. In a TOP trap (with harmonic potential), the x and y oscillations are energetically degenerate and have the oscillation frequency  $\omega_{x,y}$ . The z dipole oscillation has a frequency of  $\omega_z = \sqrt{8} \omega_{x,y}$  due to the TOP-averaged double axial magnetic field gradient as described in section 2.2.2.

In addition to the dipole excitations, quadrupole excitations exist in several different modes. These modes do not necessarily correspond to the harmonic oscillator frequencies directly because of the atomic interactions. In a an axially symmetric trap like the TOP trap, angular momentum about the symmetry axis is conserved and m is a good quantum number, which can be used to denote the excitation states. The lowest lying quadrupole mode is the m=2 mode, which involves deformation of the cloud in the xy-plane with no motion along the z axis. This mode is doubly degenerate ( $m = \pm 2$ ) and involves two "tidal waves" oscillating around the cloud in the xy-plane in clockwise or anti-clockwise orientation with a frequency of  $\sqrt{2} \omega_{x,y}$ . A superposition of both



Figure 5.4: Energy spectrum of collective excitations of a BEC cloud in a TOP trap. Presence of a central vortex breaks the degeneracy of the |m|=2 and |m|=1 modes.

equally excited modes will not exhibit a "rotation" when looking down onto the cloud along the z-axis.

In the low lying m=0 quadrupole mode, the radial and axial cloud sizes oscillate in anti-phase. In the high lying m=0 mode, the axial and radial directions oscillate in phase. This is often called the "breathing" mode of the BEC cloud. The frequencies for the m=0 quadrupole modes have been derived by Stringari in [128] using the GP equation and hydrodynamic theory. With the trap frequency ratio  $\lambda = \omega_z / \omega_{x,y}$  these are

$$\frac{\omega^2(m=0)}{\omega_{x,y}^2} = 2 + \frac{2}{3}\lambda^2 \pm \frac{1}{2}\sqrt{9\lambda^4 - 16\lambda^2 + 16},$$
(5.53)

where the + sign stands for the "breathing" mode and the - sign stands for the low-lying mode. Further quadrupole modes are the so-called "scissors" modes, which we will look at more closely in the following section. The spectrum of the low frequency excitations of a BEC cloud in a TOP trap is shown in figure 5.4.

#### 5.4.1 Scissors mode

The scissors mode is an odd-parity collective excitation of a BEC cloud in an anisotropic trap. It is known as an excitation in atomic nuclei, predicted theoretically by geometric models and found experimentally in 1984 [139]. In a BEC the scissors mode allows the direct observation of the superfluid nature of the condensate. The scissors mode can be excited by a small angle trap tilt about the y or x axis. This causes an oscillatory response of the cloud about the respective axis, which distinctly depends on the nature of the cloud. Maragò et. al. have used the response for experimental investigations of a (partially) condensed cloud at finite condensate temperatures [140, 51, 141].

A theoretical investigation of the scissors mode and a calculation of its excitation frequency has been published by Guére-Odelin in [142]. The derivation starts from the condensate irrotational flow field

$$\mathbf{v}(\mathbf{r},t) = (\hbar/m)\nabla S(\mathbf{r},t),$$

where S is the wavefunction phase, and the superfluid hydrodynamic equations (5.9) and (5.10), as discussed above in section 5.1.2. Considering the Thomas-Fermi density distribution and a small angle scissors tilt, one additionally finds that the scissors motion is independent of compressional modes. Thus the flow is steady:

$$\nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0. \tag{5.54}$$

The above constraints lead to the following expression for the condensate phase

$$S(\mathbf{r},t) = (m/\hbar)\beta(t)xz. \tag{5.55}$$

Consequently the hydrodynamic equations yield for the trap angle  $\theta$  and the phase parameter [51]

$$\dot{\theta}(t) = -\beta(t)/\epsilon, \quad \dot{\beta}(t) = 2\bar{\omega}^2 \epsilon \theta(t),$$
(5.56)

where the trap deformation parameter  $\epsilon$  and the frequency  $\bar{\omega}$  are defined as

$$\epsilon = \frac{\omega_z^2 - \omega_x^2}{\omega_z^2 + \omega_x^2}, \quad \bar{\omega} = \sqrt{\frac{\omega_x^2 + \omega_z^2}{2}}.$$
(5.57)

The correct initial conditions in equation (5.56) then leads to the solution

$$\theta(t) = \theta_0 \cos(\omega_{sc} t), \quad \beta(t) = \epsilon \theta_0 \omega_{sc} \sin(\omega_{sc} t), \quad (5.58)$$

where the scissors frequency for the TOP trap case with  $\omega_z = \sqrt{8} \omega_x$  becomes  $\omega_{sc} = 3\omega_x$ . In general, for axial trap anisotropies  $\lambda = \omega_z/\omega_{\perp}$ , the scissors mode frequency is

$$\omega_{sc} = \sqrt{1 + \lambda^2} \,\,\omega_\perp. \tag{5.59}$$

Thus at zero temperature, the two energetically degenerate scissors modes, which are individually characterised by functions of the form f(r)xz and f(r)yz [143], represent an undamped single frequency oscillation, provided that the trap rotation angle used to excite the scissors mode is small.

The superfluid scissors mode oscillation is the result of a strongly quenched moment of inertia of the condensed cloud. For finite temperatures, the moment of inertia approaches the (larger) rigid body value of  $\Theta = mN\langle x^2 + y^2 \rangle$  (average over N ensemble particles) as the condensate fraction decreases. The different oscillation frequencies and amplitude damping at finite temperature can be used as a detector for BEC.

## 5.5 Implementation of full tilted-TOP trap dynamics in 3D

#### Full dynamical TOP trap

Experimental preparation of BEC clouds is often done in TOP traps, which have been introduced in section 2.2.2. TOP traps are relatively simple to set up and they offer a great deal of control over the experimental parameters. While this can be safely neglected, the trap magnetic field, however, is only approximately harmonic in its temporal average and the microscopic dynamics are more intricate than often thought. This is evident in multi-state coupling effects and cloud micromotion over the TOP field orbit period [52].

In the numerical simulation the external trap potential  $V_{ext}$  was given the explicit time dependence due to the TOP bias field given in equation (2.53), a linear quadrupole field orbiting the trap centre with  $\omega_{TOP}$  in the range of 20 to 60  $\omega_{x,y}$ . The rapid dynamics of this required decreasing the simulation time steps by a factor of 10 to 100, slowing simulations down accordingly.

#### Tilted dynamical TOP trap

In experiments with scissors mode excitations in BEC at zero and at finite temperatures, the Oxford group gathered data which pointed to coupling effects between the m=2 quadrupole mode with a frequency of  $\sqrt{2} \omega_{x,y}$  and the xz-scissors mode. In order to rule out a coupling due to effects of the TOP trap setup, several long-running numerical simulation of a condensate with full 3D TOP trap dynamics were carried out. In many simulations with quadrupole excited initial states and scissors mode excitations in tilted TOP traps, we found that TOP trap geometry and dynamical effects do not change the outcome of GPE simulations in any significant way, as far as collective cloud excitations and effects averaged over several TOP orbit periods  $\tau_{TOP} = 2\pi/\omega_{TOP}$  are concerned. This proved that for single state simulations at zero temperature the numerically much less expensive time-averaged description is sufficient.

The numerical implementation of a tilted TOP trap is not as straight forward as it initially seems, because the introduction of an oscillating magnetic bias field in the z-direction in addition to the static quadrupole field and the usual oscillating TOP bias field modifies the time-averaged trap frequencies as detailed in [51]. This also requires adjustments to the shape of initial states used for simulations in such a trap. Furthermore the need to flexibly adapt the initial cloud angle to put a cloud into various angular scissors excitations or resting positions for tilted TOP traps required the simulation program to handle two different tilt angles.– The trap tilt due to the z-bias field (note that the shifted quadrupole field retains perfect axial symmetry at all times) and secondly the initial cloud tilt angle of the initial state. For consistency, the states were always generated without any tilt-angle. The resting position of a BEC cloud in the tilted TOP trap, however, corresponds to a tilt (by a different angle) of the initial state.

## 5.6 The superfluid gyroscope

The superfluid nature of a BEC as a single macroscopic wavefunction constrains the flow patterns, which are allowed within a BE condensed particle cloud. Flow is always irrotational and application of external torques will cause a unique response, causing vortex formation (see sections 5.1.2 and 5.3.10).

A very peculiar state of a BEC cloud is one with a single central vortex, when all participating atoms have an angular momentum of  $\hbar$ . Macroscopically the cloud has an angular momentum of  $\langle L_z \rangle = N\hbar$  in the central vortex state. A thorough theoretical investigation into the stability of central vortex states in various trap geometries at zero and at finite temperatures has been published by Isoshima et. al. in [144].

In TOP style traps with oblate BEC clouds and axial cylindrical symmetry (trap frequencies  $\omega_z = \sqrt{8} \omega_{\perp}$ ), central vortex states can be created using several techniques, such as using slightly eccentric ( $\omega_x/\omega_y = 1.04$ ) TOP fields [145] to exert a torque on the cloud, or by immediate stirring of the condensate using a detuned attractive or repulsive laser beam [146].



Figure 5.5: This plot shows the oscillations of the cloud's main inertial axis around the x (dashed) and y axis (solid), after an initial trap tilt of 7° around the y axis to excite the scissors mode in a superfluid gyroscope. The low frequency gyroscopic cloud precession at approximately 0.14  $\omega_{\perp}$  is evident in the beat pattern between the xz and yz scissors modes.

The presence of the central vortex lifts the degeneracies of the |m|=2 quadrupole and the |m|=1 scissors modes. Thus a typical |m|=2 quadrupole mode excitation (as a superposition of both modes with equal amplitudes) will start



Figure 5.6: The beat pattern in figure 5.5 is due to the lifted degeneracy of the two |m|=1 scissors modes. This spectrum of the scissors mode oscillations of the cloud main inertial axis in x (dashed line) and y (solid line) at  $3\omega_{\perp}$  reveals a splitting by  $\Omega = 0.14\omega_{\perp}$ , which causes two overlapping and hardly distinguishable peaks at a frequency resolution (in this long run) of  $\Delta\omega = 0.08$ .



Figure 5.7: Spectrum of the oscillations (in x and y) of the vortex core after an initial trap tilt of 7° around the y axis to excite the scissors mode in a superfluid gyroscope. It is evident that in addition to a scissors mode oscillation at  $3\omega_{\perp}$ , a Kelvin mode is excited at approximately 0.7  $\omega_{\perp}$ .

precessing around the cloud [147, 148] with a small angular velocity of

$$\Omega = \frac{\omega_+ - \omega_-}{2} = \frac{\langle L_z \rangle}{2Nm\langle x^2 + y^2 \rangle}.$$
(5.60)

Similar effects result from the excitation of the xz scissors mode by a sudden trap tilt around the y axis. The xz scissors mode, consisting of a superposition of both  $(x \pm iy)z$  modes (|m|=1), which are energetically degenerate in the absence of a central vortex, will precess around the cloud centre with angular velocity  $\Omega$ , periodically changing from a xz to a yz scissors oscillation, because the two  $(x \pm iy)z$  modes have an energy splitting in the presence of the central vortex.

This precession affects the cloud's main inertial axis, which defines the "scissors" tilt angle around x and y relative to the trap. The scissors motion precessing around the cloud is vaguely comparable to the precession of a tilted

#### 5.6. THE SUPERFLUID GYROSCOPE

gyroscope toy. Thus we are looking at a "superfluid gyroscope".

The angle oscillations of the main inertial axis around x and y in a simulation of the superfluid gyroscope is shown in figure 5.5. The scissors modes are excited by an initial sudden tilt of the harmonic trap potential by an angle of 7° around the y axis. The cloud oscillates (mainly) at the scissors frequency  $\omega_{sc} = 3 \omega_{\perp}$ , while the orientation slowly precesses around the cloud. This is visible in the beat patterns. The precession frequency is approximately  $\Omega = 0.14 \omega_{\perp}$ , which agrees with theoretical calculations [148] for our simulation with N = 70000<sup>87</sup>Rb atoms. The beat patterns reveal their two frequency components in the spectrum shown in figure 5.6. The spectral resolution is  $\Delta \omega = 0.08 \omega_{\perp}$ , causing significant overlap of the two peaks.

The initial trap tilt not only excites the scissors modes in the central vortex state, as can be seen in a spectrum of the *vortex core oscillation* in figure 5.7. The time series for this spectrum was collected by the determination of the xy spatial position of the vortex core within a layer at approximately z = 2.5. It is evident that the vortex core has a helical excitation, oscillating around the cloud in opposite direction to the vortex flow, in addition to oscillations at the scissors frequency, which are due to the cloud's scissors oscillation.

## 5.7 Vortex core excitations

As we have shown in the previous section, vortex lines in a BEC are rather dynamical objects. Similar to a classical string, transversal helical vibrations can be excited. This has been calculated for classical vortex lines by Lord Kelvin as early as 1880 [149]. The classical results can be adapted to a vortex line in a homogeneous superfluid BEC [150]. The excitation energy of a so-called kelvon is [144]

$$\hbar\omega_K \simeq \frac{\hbar^2 k^2}{2m} \ln\left(\frac{1}{k\xi}\right),\tag{5.61}$$

where  $\xi = 1/\sqrt{8\pi na}$  is the healing length, *n* is the particle density of the fluid, *a* is the scattering length and *m* is the particle mass. *k* is the kelvon wave vector and for the excitation to be stable  $k\xi \ll 1$  is required. In general, the healing length is the length scale associated with the energy of the mean-field inter-particle interactions,  $U_{int} = 4\pi\hbar^2 na/m$ . The spatial size of topological structures such as vortices and solitons is in the order of the healing length.



Figure 5.8: Vortex core with a Kelvin wave excitation. This picture is a snapshot from the simulation of the superfluid gyroscope with an initial 7° trap tilt around y, primarily exciting the scissors cloud oscillation mode. The snapshot was taken at t=0.7 (in numerical units  $[\omega_{\perp}^{-1}]$ ) and shows only an iso-density surface ( $|\Psi|^2=9e-4$ ) of the central section of the cloud without phase colouring.

Aside from Kelvin excitations of many parallel axial vortex lines as ob-



Figure 5.9: This plot shows the combination of wavefunction density  $|\Psi|^2$  (left) and phase (right) for a simulation snapshot equivalent to figure 5.8. Shown are (from top to bottom) slices of the three perpendicular planes xy, xz and yz. The density is shown on a logarithmic colour scale. The phase graphs are cropped at a cutoff density of 1e-10.

served experimentally in [23], "vortex lattices" in rapidly rotating BEC clouds [151, 152] can exhibit Tkachenko excitations. Tkachenko modes are elastic excitations of the parallel ordering of vortex lines in the xy-plane, which have been observed experimentally in [153] and studied numerically by Simula et. al. in [154]. We have not considered this type of excitation and have restricted ourselves to BEC clouds with a single vortex.

Bretin et. al. [155] observed the decay of a m = -2 quadrupole mode into a pair of kelvons with wave vectors k and -k. Kelvin modes always rotate in the opposite sense as the vortex associated with them and thus the angular momentum of a kelvon of a n = 1 vortex line is  $-\hbar$ .

To demonstrate the resonant coupling between the scissors mode excitation and the first odd normal Kelvin mode [156], we carried out a simulation, in which we excited the central vortex state with two sinusoidal scissors style trap tilting cycles with a 4 degree tilt amplitude around the x axis (y=z=0). The trap tilt is driven with  $\theta(t) = 4$  degrees  $*\sin(46.5 \text{ Hz } t)$ . In numerical units, one trap tilt period is equivalent to  $\tau = 1.33$  ( $\tau = 1$  is the  $\omega_{\perp}$  radial trap period). After the two driven cycles, the trap is stationary after t = 2.66.

Figure 5.10 shows the precession of the excited vortex line. The figure plots show four iso-density surfaces at  $|\Psi|^2$ =9e-4 density (the wavefunction density is scaled so that the full spatial density integral is unity), coloured with the wavefunction phase. The phase goes through the full jet-colourmap as it "wraps around" the vortex line. Shown are four snapshots over a full Kelvin precession

cycle, sliced open at the front to exhibit the central vortex line.

The absence of a significant scissors mode excitation after the driving cycles is characteristic for the resonant driving conditions exciting the Kelvin mode. The x, y vortex oscillation time series in figure 5.11 and the spectral analysis of the vortex oscillations in figure 5.12 testify the resonant excitation of the Kelvin mode. Small residual scissors mode excitations are probably due to non-adiabatic effects and possibly a small driving frequency mismatch. It can also be seen in the bottom row of figure 5.11, how the breaking of scissors mode degeneracy due to the central vortex causes a slow beat pattern between the xz and yz residual scissors mode amplitudes.

These simulation results and experimental observations of the same "tilting mode" in a lattice of vortices in a  ${}^{87}$ Rb BEC are to be published in [23].



Figure 5.10: Surfaces of constant density  $|\Psi|^2=9e-4$  of a condensate cloud (wave function normalised to 1), sliced open to show a central vortex state excited by resonant driving for two vortex precession periods in the yz plane with a driving amplitude of 4°. The iso-surface is colour-coded with the wavefunction phase, and the cloud represents a <sup>87</sup>Rb BEC with approx. N=70000 atoms.  $\omega_r=62$ Hz,  $\omega_z=175$ Hz. Figures from left top to right bottom show the following times, t=7.80, 8.13, 8.46, 8.79 in units of  $\omega_r^{-1}$ . One full vortex precession cycle  $\tau=1.33 \omega_r^{-1}$ . The numerical spatial units in this figure are almost exactly equal to 1  $\mu$ m in SI units.


Figure 5.11: BEC cloud and vortex oscillations as a response to resonant driving using a trap scissors tilt for two periods of  $\tau=1.33$ . Lower two curves: Main inertial axis tilt angle in degrees in xz plane (solid line) and yz (dashed line). Upper two curves: Response of the top of the vortex line in xz plane (solid) and yz (dashed) in arbitrary units (centered at y=10 for clarity).



Figure 5.12: Power spectrum of vortex core oscillations in x (solid line) and y (dashed line). The resonant driving excites the vortex precession at 0.7  $\omega_r = 43.4$  Hz almost exclusively.

## 5.8 BEC expansion dynamics

Because of the small physical size of BEC clouds and because of their sensitivity, experimental observation is usually destructive [123]. Recording of time-series images requires the reproducible production of multiple condensate clouds. One of the most common imaging methods drops the BEC from the trap and images the expanding cloud after a certain specific flight/expansion time.

Full 3D simulations modelling the experimental setup of the Oxford <sup>87</sup>Rb BEC experiment were carried out in order to investigate how the cloud size and shape depend on the process of trap release and to verify assumptions made about the decay times of the optical and magnetic trap potentials. Additionally, the simulation and experimental results were compared with simple trap expansion models used in BEC experiment data processing.

#### The Castin-Dum BEC expansion model

In BEC clouds, where the particle interaction is dominant, the chemical potential  $\mu$  is much larger than the harmonic oscillator energy  $\hbar \bar{\omega}$ , where  $\bar{\omega}$  is defined for anisotropic traps as  $\bar{\omega} = \sqrt[3]{\omega_x \omega_y \omega_z}$ . In this regime, the Thomas-Fermi approximation may be used to solve the GP equation. Castin and Dum [157] found a way to approximate the BEC expansion process within the Thomas-Fermi approximation with simple differential equations.

$$\frac{d^2}{d\tau^2}\lambda_{\perp} = \frac{1}{\lambda_{\perp}^3\lambda_z}, \quad \frac{d^2}{d\tau^2}\lambda_z = \frac{\epsilon^2}{\lambda_{\perp}^2\lambda_z^2}$$
(5.62)

 $\epsilon$  in the above is determined by the trap frequency ratio before the trap release,  $\epsilon = \omega_z(0)/\omega_{\perp}(0)$ , and  $\lambda$  stands for the characteristic cloud size in the appropriate spatial direction.

#### **3D BEC expansion simulation results**

For the GPE expansion simulations 3D grid sizes of  $128 \times 128 \times 256$  (x,y,z) points were used. While the initial states have a cylindrical oblate shape, with strong confinement axis along z, the grid has been designed to accommodate for rapid expansion along the z-axis. The simulations also modelled the situation of quasi-2D regimes in strong axial confinement, which is experimentally achieved by axially "squeezing" a condensate cloud in a TOP trap between two repulsive laser light sheets.

We found that the temporal decay of the trap confining fields plays a crucial role in the outcome of BEC expansions, particularly along strongly confined axes. While simulations for a typical  $2\pi \cdot 62$  Hz ( $\omega_x$ ) by  $2\pi \cdot 175$  Hz ( $\omega_z$ ) TOP trap state expansion exhibit no noticeable difference between an instantaneous loss and a typical  $\tau = 1$  ms decay of confinement, the difference is significant and needs to be taken into account for trap geometries such as for example ( $\omega_{\perp}, \omega_z$ ) ( $2\pi \cdot 40$  Hz,  $2\pi \cdot 1000$  Hz) and ( $2\pi \cdot 30$  Hz,  $2\pi \cdot 1000$  Hz). We have modelled a linear downramp of the (optical) dipole potential part of the strong axial confinement within t = 1 ms and an exponential decay of the magnetic field confinement

#### 5.8. BEC EXPANSION DYNAMICS

part with time constants between  $\tau = 1$  ms and 3 ms. Figure 5.13 shows the expansion of a  $(2\pi \cdot 62 \text{ Hz}, 2\pi \cdot 1000 \text{ Hz})$  cloud of N = 75000 atoms (<sup>87</sup>Rb). The significant differences to cloud expansions with weaker axial confinement and/or quasi-instantaneous trap release are evident. Expansion is not smooth with a constant velocity after an initial acceleration phase. Properties of trap field decay heavily influence the cloud size for given expansion times. It can be seen how the axial expansion slows down after an initial rapid acceleration when the cloud runs into the residual, more slowly decaying magnetic trap field. The initially shrinking radial cloud size can be attributed to a rapid density loss due to axial expansion. The radial cloud profile changes from TF shape to Gaussian shape as the nonlinear interaction decreases.



Figure 5.13: The left graph shows the radial (dashed) and axial FWHM size of a BEC cloud undergoing expansion after trap release. The decay of the initial trap potential with 1000 Hz (axial) and 62 Hz (transversal) is modelled as shown in the right figure. The optical component of the axial part decays linearly within 1 ms, while the magnetic components decay exponentially with a time constant of  $\tau = 3$  ms.

Due to the highly dynamic nature of the BEC expansions, particularly at strong z confinements, the numerical grid spacing and the temporal resolution of the simulation steps had to be very small. Temporal resolution ranged from 128 steps/ms, for the comparatively slow expansion rate from a TOP trap ground state, to 480 steps/ms for a rapidly expanding  $(2\pi \cdot 30 \text{ Hz}, 2\pi \cdot 1000 \text{ Hz})$ strongly confined initial state. The simulation program was used to propagate the initial BEC cloud until an asymptotic expansion with constant expansion rate was reached after approximately 5-10 ms. The simulation program currently does not allow much longer expansion times because of grid boundary constraints imposed by computer memory size and CPU performance.

In BEC experiments effects of finite trap potential decay are often overlooked (in most cases justifiably) and may contribute (small) systematic errors to the measurement of macroscopic values such as the number of condensed atoms in cases of strong confinements. Furthermore, the widely accepted simple BEC expansion model for instantaneous trap release is invalid for strongly confined BEC clouds, when the cloud profile along one axis is not of Thomas-Fermi type anymore and becomes Gaussian in response to strong spatial confinement. In this case, the assumption at the base of many approximate theoretical models, that  $Na/a_{ho} \gg 1$ , is no longer valid. (This must also be given for the Thomas-Fermi approximation to be valid.)  $a_{ho} = \sqrt{\hbar/(m\omega_{ho})}$  is the harmonic oscillator length.

We are presently working on a publication of our results regarding failure and improvements to the BEC expansion models [158].

## 5.9 Solitons in BEC

Solitons in general are steady solutions of the wave equation in nonlinear media. Usually they occur in form of non-spreading localised wave packets called "bright solitons". As such, solitons occur as ocean Tsunamis, as "freak waves" in narrow channels, as pulses in nerve stimulus propagation and as light pulses in fiber optics. Less often "dark solitons" occur as non-spreading localised intensity dips of solitonic shape in a non-vanishing background.

In a vacuum with a linear dispersion relation  $\omega = c_0 k$ , where  $c_0$  is the vacuum speed of light, all frequency components of an optical pulse travel at the same speed and solitons will not occur. Pulses of any shape will not experience dispersion and retain their spatial and temporal shape. In the vacuum, phase velocity equals group velocity equals vacuum speed of light. In a medium with refractive index n, the phase velocity usually becomes a function of the frequency,  $c(\omega) = c_0/n(\omega)$ . Thus different frequency components of a wave packet travel at different velocities and the packet disperses. Sound dispersion can be experienced by listening to the distorted noise transmitted over distances in the ice sheet on a frozen lake.– High frequency components arrive before low frequency components [159], turning pulses into chirps.

Looking at an optical pulse with an envelope A(x,t) and a central wave vector  $k_0$ 

$$E(x,t) = \Re(A(x,t)e^{ik_0x - \omega_0 t}),$$
(5.63)

in a dispersive medium, the component wave numbers  $k(\omega) = \omega/c(\omega) = \omega n(\omega)/c_0$ can be expanded about  $k_0$  and  $\omega_0$  as

$$k(\omega) = k_0 + \frac{dk}{d\omega}(\omega - \omega_0) + \frac{1}{2}\frac{d^2k}{d\omega^2}(\omega - \omega_0)^2 + \mathcal{O}(\omega^3)$$
(5.64)

The group velocity  $v_g$ , which is defined as the inverse of  $k' = dk/d\omega = 1/v_g$ , is the velocity, that the envelope function A(x,t) is travelling at, while it disperses due to non-vanishing group velocity dispersion  $k'' = d^2k/d\omega^2$ .

Nonlinear media exhibit an intensity dependence of the refractive index, also known as the "positive Kerr-effect".

$$n(\omega, I) = n_0(\omega) + n_1 |E|^2.$$
(5.65)

This leads to a so-called self-phase modulation of a wavepacket, which, by itself, also causes a broadening of the pulse spectrum, leading to signal chirp.

#### 5.9. SOLITONS IN BEC

The combination of group velocity dispersion and self-phase modulation leads to the following wavepacket envelope propagation equation.

$$i\frac{\partial A(x,t)}{\partial x} = \frac{1}{2}k''\frac{\partial^2 A(x,t)}{\partial t^2} - \gamma |A(x,t)|^2 A(x,t)$$
(5.66)

This equation has solutions for "bright" solitons with  $\operatorname{sign}(k''\gamma) = -1$ , and for "dark" solitons with  $\operatorname{sign}(k''\gamma) = 1$ . These solutions may be achieved by various combinations of positive/negative dispersion and positive/negative Kerr-effect.

A BEC as described by the GP equation, which is a nonlinear Schrödinger equation, provides a physical realisation of a system in which solitons can appear [160].– Matter waves have a group velocity dispersion in the vacuum and the attractive or repulsive particle interaction provides an amplitude dependent self-phase modulation. While several types of solitons are possible under different conditions, they all share the important property that the dispersive term in the equation is balanced by the nonlinear term. Thus the soliton structure is stable and exhibits no dispersion.

## 5.9.1 Dark solitons

Dark solitons arise as solutions of the GP equation, for N particles of mass m, of the type

$$A(x,t) = \sqrt{\frac{N}{2x_0}} \tanh\left(\frac{x-vt}{x_0}\right) e^{-\frac{i\pi t}{4\tau_s}},\tag{5.67}$$

where v is the velocity of the soliton envelope. The characteristic soliton size  $x_0$  and the soliton period  $\tau_S$  are defined as

$$x_0 = \frac{2\hbar^2}{Nm\gamma}, \qquad \tau_s = \frac{\pi m x_0^2}{2\hbar} \tag{5.68}$$

Such dark solitons are possible as stable solutions in "normal" condensates with positive scattering length a (repulsive particle interaction) and positive particle mass. As we will see shortly, it is possible for particles to have a negative effective mass in periodic potentials under specific conditions. Such solitons are called "black" when the intensity reduction goes to zero at its minimum, "grey" if not. Dark solitons in BEC are a characteristic density "notch" with a  $\pi$  phase step across it and as such they can be created by imprinting a  $\pi$  phase shift into one half of a BEC cloud. This is easy to do numerically and was used by us as a testcase in the development of our BEC simulation program. In the experiment, localised phase imprinting is technically difficult, but dark solitons in BEC have been observed by Denschlag et. al. in 2000 [161].

## 5.9.2 Bright solitons

Bright solitons in BEC require a negative particle scattering length, representing attractive interactions. While BEC species with attractive interaction exist, they are technically challenging, unstable and limited to very small clouds. The right conditions for bright solitons can also be created for repulsively interacting particles in periodic potentials, where the particles experience anomalous dispersion, which can be explained in terms of an effectively "negative mass" [162]. Such bright solitons are solutions of the GP equation of the type

$$A(x,t) = \sqrt{\frac{N}{2x_0}} \operatorname{sech}\left(\frac{x-vt}{x_0}\right) e^{-\frac{i\pi t}{4\tau_s}}$$
(5.69)

Here the mass may be effectively negative in the definition of the soliton size  $x_0$  and period  $\tau_s$  in equation (5.68). A(x,t) represents the envelope function, whereas the spatial density profile in the periodic potential exhibits several peaks. We show an example of a soliton in a periodic potential in figure 5.14.



Figure 5.14: Spatial composite figure showing wavefunction density distribution  $|\psi|^2$  (bold solid line) of a bright gap soliton and the periodic potential (thin solid line). It can be seen how the soliton stretches over several individual wells of the periodic potential. The dashed line shows the soliton envelope, a fit to the characteristic sech() envelope function A(x,t). Data taken from a 1D soliton simulation.

## 5.9.3 Bloch theory and band structure

The periodic potential is experimentally realised by means of a standing laser light field, detuned far from resonance, repelling atoms from high intensity interference nodes.

$$V(x) = \frac{V_0}{2}\cos(2k_L x)$$
(5.70)

 $V_0$  is the modulation depth, which is chosen close to the photon recoil energy  $E_{rec} = \hbar^2 k_{rec}^2/(2m)$ , where  $k_L$  is the laser wave vector. Thus a periodic potential with lattice constant  $R = 2\pi/k_L$  arises. Potentials in the order of magnitude of  $E_{rec}$  (note that  $k_L = k_{rec}$  when  $V_0 = E_{rec}$ ) do not provide a very strong binding force and confinement of the particles to individual wells. Thus the trapped

particles can still propagate through the optical lattice without the need for comparatively slow tunneling processes.

According to the Bloch theorem [163], eigenstates  $\Phi(x)$  for any periodic potential can be found as a product of a plane wave and a function u(x) with periodicity matching the system lattice periodicity.

$$\Phi_{n,k}(x) = e^{ikx} u_{n,k}(x), \quad \text{where} \quad u_{n,k}(x+R) = u_{n,k}(x). \tag{5.71}$$

The Bloch functions for the periodic potential V(x) used in our situation can be found as eigenfunctions of the Hamiltonian  $\tilde{H} = \tilde{p}^2/2m + (V_0/2)\cos(2k_L\tilde{x})$ . Because of the periodic potential with  $2\pi/k_L$  periodicity,  $\tilde{H}$  commutes with operator  $e^{i\tilde{p}\pi/k}$ , as this characterises the standing wave solutions. Thus the functions we are looking for are also eigenfunctions of this operator.

In the periodic potential we can now define a "quasi-momentum" q, which describes the momentum of the wavepacket within one Brillouin zone  $q \in$  $[-\pi/d, \pi/d]$ , so that  $p = q + n2\hbar k_{rec}$ . That is, p can only have integer multiples of  $2k_{rec}$ , which is defined by the optical potential, in addition to the quasimomentum q. The Bloch functions  $\Phi_{n,q}(x)$  can now be expressed in terms of a plane wave expansion:

$$\Phi_{n,q}(x) = e^{iqx} \sum_{l} c_l(n,q) e^{il2k_{rec}x}$$
(5.72)

The  $\Phi_{n,q}(x)$  can be calculated by solving the eigensystem

$$\tilde{H}\Phi_{n,q} = E_{n,q}\Phi_{n,q},\tag{5.73}$$

which only requires diagonalisation of a tri-diagonal matrix, because of the simple cosine shape of the potential. (The  $c_l(n,q)$  are only coupled to the  $c_{l\pm 1}(n,q)$  elements.)

The dispersion relation  $E = E_n(k)$  in terms of the Bloch functions  $\Phi_{n,k}(x)$  exhibits a band structure with characteristic periodicity in terms of the Brillouin zone introduced above. n is the band index of the Bloch functions. Figure 5.16 shows the soliton preparation procedure within the Brillouin zone. The band structure with the energy band gap between the two lowest bands is clearly visible.

### 5.9.4 Group velocity and effective mass

A BEC wavefunction in a periodic potential as outlined above is described by its expansion in terms of Bloch functions  $\Phi_{n,k}(x)$  as

$$\Psi(x,t) = \sum_{n} \int_{-k_{L}}^{k_{L}} c_{n}(k) \Phi_{n,k}(x) e^{-iE_{n}(k)t/\hbar} dk, \qquad (5.74)$$

where the  $c_n(k)$  are the band coefficients. For a narrow quasi-momentum distribution (i.e. much narrower than the Brillouin zone, with  $\Delta k \ll 2k_L$ ) the uncertainty principle requires a large spatial envelope function stretching over many individual wells of the periodic potential. Without external interactions, the BEC should initially be prepared in the lowest n = 1 energy band.

If the above assumptions hold true, the dispersion in the lowest energy band can be expanded around the centre momentum  $k_0$  analog to equation (5.66):

$$E(k) = E(k_0) + \frac{\partial E(k)}{\partial k}(k - k_0) + \frac{1}{2}\frac{\partial^2 E(k)}{\partial k^2}(k - k_0)^2 + \mathcal{O}(k^3)$$
(5.75)

We can now identify group velocity  $v_g$  and effective mass  $m_{eff}$  as [164]

$$v_g(k) = \frac{1}{\hbar} \frac{\partial E(k)}{\partial k}, \qquad \frac{1}{m_{eff}(k)} = \hbar^2 \frac{\partial^2 E(k)}{\partial k^2}.$$
 (5.76)

Thus the effective mass describes the curvature of the dispersion relation E(q). It varies from positive to large positive values as the wave packet approaches the edge of the Brillouin zone. Here, dispersion is strongly suppressed. Further towards the edges,  $m_{eff}$  goes through positive and negative infinity and approaches small negative values at the edge. Therefore, dispersion can be controlled by preparing the wavepacket at a specific location in the Brillouin zone.

While it is necessary to resolve the fine details of the wavefunction in the periodic potential in numerical simulations, these cannot be resolved experimentally and only the slowly varying soliton envelope function A(x,t) is of experimental interest, which can be obtained from equation (5.74) as follows [165]. We assume simplified Bloch functions  $\Phi_k(x) = u_k(x)e^{ikx}$ , where  $u_k(x)$  varies much more slowly in k than  $c_n(k)$  in (5.74), which holds true whenever a periodic description of the situation is merited. We may then go as far as to replace  $u_k(x)$  by  $u_{k_0}(x)$ . To second order in  $(k - k_0)$  we get for the lowest (n=1) band

$$\Psi(x,t) = \Phi_{k_0}(x)e^{-iE(k_0)t/\hbar} \int_{-k_L}^{k_L} c(k)e^{i(k-k_0)(x-v_g(k_0)t)}e^{-i\frac{\hbar(k-k_0)^2t}{2m_{eff}(k_0)}}dk$$
$$= \Phi_{k_0}(x)e^{-iE(k_0)t/\hbar} A(x,t), \qquad (5.77)$$

where we have identified the integral as the envelope function A(x,t). Figure 5.16 shows, in an inset on the right hand side, the energy dispersion band structure (1st diagram), the effective mass as the curvature of the dispersion (2nd diagram) and the group velocity of a wavepacket prepared at a specific location (3rd diagram from the top).

#### 5.9.5 Soliton stability

The solitons discussed above arise in one-dimensional periodic optical lattices. A dynamical stability analysis by Hilligsøe et. al. [21,22] investigated the temporal development of small perturbations using the Bogoliubov-de Gennes equations. A finite temperature analysis of soliton stability can be found in [166]. The Bogoliubov-de Gennes equations arise when a perturbation  $\delta \psi(\mathbf{x}, t)$  is added to the wavefunction

$$\psi(\mathbf{x},t) = e^{-i\mu t/\hbar} [\psi_0(\mathbf{x},t) + \delta\psi(\mathbf{x},t)].$$
(5.78)

in the context of the GP equation. Such perturbations lead to a spectrum of Bogoliubov modes within the Bloch energy bands. It was found that perturbations  $\delta \psi(\mathbf{x}, t)$  do not grow over time. Solitons in 1D are thus dynamically stable.

The situation in two and three dimensions is different. In the best of all cases, a real physical system can be considered to be quasi-one-dimensional when all dimensions but one are strongly confined. This results in large transversal excitation energies, which are "frozen out" due to too low system energies at low temperatures. Such situations allow the wavefunction to be separated into quasi-independent axial and transversal parts as

$$\psi(\mathbf{x},t) = \psi(z,t)\phi_0(x,y),\tag{5.79}$$

where  $\phi_0(x, y)$  represents the transversal ground state. Solitons may arise in the axial (z) direction due to a one-dimensional optical lattice along z.  $\psi(\mathbf{x}, t)$  in equation (5.79) may then be identified as a quasi-one-dimensional wavefunction  $\psi_{quasi}(z, t)$ .

In practice, however, excitations of several low energy transversal modes cannot be avoided. The stability analysis in [22] found that excited transversal modes have dispersion curves parallel to the lowest energy mode. Solitons, which are necessarily prepared at the upper band edge, are thus unstable against decay into energetically resonant transverse excitations. It was found however, that a quasi-gap soliton behaves like a truly one-dimensional (stable) gap soliton for times smaller than the smallest decay time of the unstable Bogoliubov modes. Thus, with a reasonable transversal confinement, such quasi-gap solitons will be stable for times smaller than  $t = 1/(0.133\omega_{\perp})$ , where  $\omega_{\perp}$  is the (smallest) transverse trap frequency.

#### 5.9.6 Excitation of side bands

Higher energy bands will not become significantly excited as a result of the preparation process of the wave packet in quasi-momentum space q, as long as the prepartion is done slowly enough. The adiabaticity criterion can be expressed in terms of the rate of change and the energy levels as

$$\left|\langle n,k|\frac{\partial}{\partial t}|1,k\rangle\right|^2 \ll \frac{|E_n(k) - E_1(k)|^2}{\hbar^2} \tag{5.80}$$

The experimental realisation, and the simulation accordingly, uses a simple twostep acceleration procedure, which causes a small amount of excitations. (See section 5.10.) However, this non-adiabatic effect seems to be small enough to be negligible.

## 5.9.7 Simulation data processing

In order to detect the presence of a soliton and to determine its size, processing of the wavefunction data files produced by the simulation program was necessary. Firstly, for two- and three-dimensional simulations, the radial part of the wavefunction is expressed in terms of harmonic oscillator eigenfunctions to allow separation of the axial quasi-soliton. Here we call "radial" the axis perpendicular to the axial standing light field creating the optical lattice periodic potential. Due to strong radial confinement in the magnetic trap, radial excitations are largely absent and "frozen out". Excitations do however occur due to the non-linearity, which couples together otherwise independent spatial modes. Thus not only the ground state lowest energy harmonic oscillator eigenfunction is excited. This can also be understood by looking at the BEC cloud size, which is much wider than the harmonic oscillator length  $l_{ho} = \sqrt{2m\omega_r/\hbar}$ . Thus at least roughly the lowest three harmonic oscillator states are significantly excited in the nonlinear cloud ground state. Excitations of radial modes are also due to a not fully adiabatic preparation of the wavefunction at the band edge. In the cartesian 2D case the transversal base is

$$\phi_n(x) = (l_{ho})^{1/4} \sqrt{\frac{1}{2^n n! \sqrt{\pi}}} e^{-\frac{x^2}{2(l_{ho})^2}} H_n(x/l_{ho}), \qquad (5.81)$$

where the  $H_n(x)$  are the Hermite polynomials [110].

In radial 2D (axes r,z), the expansion functions are somewhat more complicated, since the transverse ("radial") axis stands for two dimensions in cylindrical symmetry. The radial states thus need to be expanded in terms of eigenfunctions of the radial 2D Hamiltonian  $H_{\perp} = \hbar \omega (a_x^{\dagger} a_x + a_y^{\dagger} a_y)$ , taking into account that only states without angular momentum are permitted. Operators  $c_{\pm}^{\dagger} = (a_x^{\dagger} \pm i a_y^{\dagger})/\sqrt{2}$  [167] create states with angular momentum  $l=\pm 1$ , so that we need to look for transversal eigenstates  $|n\rangle = (1/n!)(c_{+}^{\dagger}c_{-}^{\dagger})^n|0\rangle$ . The calculation results in transversal cylindrical eigenstates  $\phi_n(r_{\perp})$ , expressed in terms of the harmonic oscillator eigenstates in eq. (5.81) as follows:

$$\phi_n(r_{\perp}) = \frac{1}{2^n} \sum_{m=1}^n \sqrt{\binom{2m}{m} \binom{2(n-m)}{n-m}} \phi_{2m}(x) \phi_{2(n-m)}(y)$$
(5.82)

Here x and y are linked by the zero angular momentum condition and x and y may be eliminated from the resulting functions by simply using  $x^2 = r^2 - y^2$ .

To analyse the effect of the periodic potential and the energy band structure arising from it, all transverse modes of the wavefunction are subsequently expanded in terms of Bloch eigenfunctions in the axial direction. The theory behind this has been outlined in section 5.9.3 above.

## 5.10 Simulation of bright gap solitons

The simulation procedure for the creation and investigation of solitons follows closely the experimental procedure developed by Eiermann et. al. in [24, 168].

A small BEC cloud of only  $3000^{87}Rb$  atoms is produced by evaporative cooling in a TOP trap (phase space density ~0.03), transfer into a far-off-resonance optical dipole trap (FORT) and further forced evaporation. The cloud size is then reduced further to approximately 900 atoms by application of a Bragg

pulse. Preparation of the soliton is then achieved as follows. Shortly after the population coupled out by the Bragg pulse has left the remaining condensate, an optical lattice in the form of a standing lightwave (far off-resonant at  $\lambda_l = 783$  nm) is ramped up to its final intensity over 4 ms. Once its full intensity is reached, the dipole trap beam confining the cloud axially is switched off. Now the optical lattice is accelerated to the recoil velocity  $v_r = h/(m\lambda_l)$  in two phases. The first fast acceleration to 80%  $v_r$  over 0.67 ms and the remaining 20% within the following 0.67 ms. This is done to make the acceleration process almost adiabatic. The soliton preparation procedure is shown schematically in figure 5.16 on page 145.

In the numerical simulation of the experiment, we found that replacing the Bragg pulse by a simple instantaneous reduction of the condensate interaction simplified the problem by avoiding the need to deal with a large amount of fast-moving outcoupled population. We thus generate an initial cloud of 3000 atoms on a grid of 2048 or 4096 axial points. In cartesian 2D and in 2D with radial symmetry (pseudo-3D) we found that a radial resolution of 32 grid points was sufficient. We replace the Bragg pulse by a reduction of the cloud interaction to a value representing the post-Bragg population of 900 atoms. This method also leads to a collapse and compression of the initial condensate cloud while the optical lattice potential is ramping up. All other parameters and procedures were set and followed exactly as in the experiment.

It was necessary to deal with population leaving the condensate cloud in axial directions after the preparation of the cloud at the band edge. Since only a fraction of the BEC forms the dynamically stable soliton in the reference frame of the (now moving) optical lattice, the remaining population will leave the cloud and eventually hit the borders of our finite numerical discrete grid. Velocity matched absorbers as developed and described in [52] remove this population from the grid border regions with a minimal amount of reflections.

## 5.10.1 Soliton simulations in 1D

The primary concern of the GPE simulations with parameters identical to the experimental setup was validation of the experimental results. Our numerical simulations resulted in clear evidence for the formation of a soliton at the band gap. By means of the Bloch function expansion we could determine the soliton envelope function and determine the characteristic soliton size  $x_0$  by numerically fitting it to the sech() soliton function. The particle population forming the soliton was subsequently determined by numerical spatial integration of the wavefunction density over the soliton region.

The soliton cloud, which was experimentally realised by Eiermann et. al., was stable for longer time intervals than we could practically simulate (due to interferences of outcoupled population reflecting off the grid borders after more than approximately t = 70 ms). For several different depths of the periodic optical lattice potential, ranging from 0.4  $E_{rec}$  to 1.4  $E_{rec}$ , we have determined the size and population of the soliton in a time interval from immediately after the complete formation until the appearance of interference effects due to numerical grid border reflections. The depth of the optical lattice determines



Figure 5.15: The results of 1D soliton simulations, qualitatively showing the linear scaling properties of a bright atomic gap soliton in 1D as predicted by equation (5.84). The dashed line represents a linear fit of the data.

the curvature of the lowest energy band at the band edge and thus the effective (negative) mass of atoms prepared at this point. Figure 5.17 shows a snapshot from the data processing procedure for a soliton at 0.7  $E_{rec}$ .

For a soliton to fulfill the definition, the energy component of the soliton wavefunction due to energy dispersion,  $E_d$ , and the nonlinear interaction energy  $E_{nl}$ , the nonlinear term in the GP equation, need to cancel out.

$$E_d = \frac{\hbar^2}{2m_{eff}x_0^2}, \qquad E_{nl} = C_{1d}|A(x,t)|^2.$$
(5.83)

Equating these terms, one finds a linear relation between  $x_0N$  and  $-m/m_{eff}$ , which a genuine soliton needs to fulfill.

$$Nx_0 = \frac{2\hbar^2}{C_{1d}m} \ \frac{m}{m_{eff}}$$
(5.84)

The linear relation, which we have found in 1D simulations of solitons in the range of optical lattice potential depths from 0.4  $E_{rec}$  to 1.4  $E_{rec}$  with the corresponding effective masses, is shown in figure 5.15. Note that the measured values of  $x_0$  and N have a large margin of error, as they needed to be determined from a system, which had not (yet) reached a truly steady equilibrium state after the soliton preparation procedure. Furthermore, a comparison with the experimental results is merely qualitative, as these simulations have been conducted in simple 1D. The experimental results in [24] consequently show larger atom numbers in the prepared solitons and a larger gradient for varying depths of the lattice potential. However, these simple 1D simulations strongly support the viability of the soliton preparation procedure and merited further investigations. For this purpose we have developed simulation code for BEC in cylindrical symmetry, which can be computed in two dimensions (r and z),

as described in section 5.3.6, since truly cartesian three-dimensional soliton simulations proved to be computationally infeasible.



Figure 5.16: Preparation of a bright atomic band gap soliton at the band edge in an optical lattice. Figure by Eiermann et. al. [24]. Figure part a) shows the energy dispersion for atoms in a weak periodic potential, steps c)-e) show the preparation procedure schematically. The insets on the right hand side show (from top to bottom) the energy dispersion, effective mass, and group velocity at the band edge (compare with section 5.9.3). After reaching BEC in b), the optical lattice is ramped up in c). In d) the BEC cloud is released into the quasi-1D waveguide, while the periodic potential is accelerated to the recoil velocity  $v_r = h/(m\lambda_l)$ . The BEC cloud reaches the band edge of the lowest band forming a soliton, and it moves along with the optical lattice in e).



Figure 5.17: Processing the data of a 1D soliton simulation. Snapshot at t = 45.5 ms. Top left diagram shows the spatial wavefunction density  $|\psi|^2$  in the optical lattice. The sharp peak on the left represents the soliton. The second peak consists of outcoupled atoms leaving the soliton region. The right top figure shows the expansion of the wavefunction in Bloch functions. The two curves shown are the populations in the lowest and in the first excited energy bands in quasi-momentum space q. The left bottom figure shows the envelope functions A(x,t) for the Bloch functions, obtained from an inverse FT of the Bloch expansion and an averaging integration as expressed in eq. (5.77). The obtained envelope function is used for the numerical fits yielding soliton size and population. The right bottom shows the phase (complex argument) of the envelope functions.

## 5.10.2 Soliton simulations in 3D

After the simple 1D soliton simulations showed promising qualitative results, we ran cartesian 2D and 3D simulations of the soliton formation process. As in 1D, the 2D simulations are not a satisfactory physical description and consequently provided only qualitative results, comparable to the 1D simulations. 3D simulations of the process proved to require unacceptably large program running times, owing to the large numerical grids required and to the fine scale dynamics of the soliton formation process.

We have found a solution to these problems, exploiting the cylindrical symmetry inherent in the experimental setup. The simulation program has been adapted accordingly and we have described the details of the implementation in section 5.3.6. The full 3D problem can thus be treated using only the two cylindrical coordinates r and z, where the axial z-axis is the direction of the periodic optical potential, which gives rise to the solitons.

In figure 5.18 we show the spatial representation of a soliton wavefunction in a 2D computational grid representing r and z in cylindrical symmetry. For technical reasons explained in section 5.3.6, we use a grid including a negative radial range. The upper half shows the wavefunction density  $|\Psi|^2$ , and the lower half a picture of the spatial distribution of the wavefunction phase. Both plots use the same colour codes for wavefunction density and phase as introduced in figure 5.9 on page 131. Because of the inhomogeneous spatial grid resolutions, the radial axis is shown vertically with a resolution of 32 grid points. The soliton is prepared in the axial periodic optical lattice, which is shown horizontally with a grid resolution of 4096 points. A time series of such figures (not printed) shows the radial excitations due to the preparation process and excess trap population escaping axially from the soliton region at the centre of the figure.

In figure 5.19 we present the analysis of the spatial wavefunction shown in figure 5.18. The analysis in cylindrical 3D is largely equivalent to the analysis shown in figure 5.17 for the 1D case, with the appropriate modifications discussed in section 5.3.6. The stationary soliton with its flat phase signature (right bottom figure) can clearly be seen, while the radially excited population (green) moves out to the sides. Note the very small amplitude of excited states in the upper band (right top figure), owing to a largely adiabatic soliton preparation procedure.

The time series of such analysis frames allowed us to determine the end of the soliton formation process and to numerically compute the soliton sizes and populations during the subsequent steady interval. Since the soliton formation is a rather dynamical process and due to numerical constraints, such as grid border interference effects, the simulation time is limited. This leads to a certain margin of error in the computations of soliton sizes and populations. Our results for the soliton sizes are however in excellent agreement with the theoretical prediction in equation (5.84), and with the experimental observations in [24]. Figure 5.20 shows our results; the errorbars represent the worst-case error and the solid black line is the theoretical prediction. A publication of our results is in preparation [169].



Figure 5.18: Wavefunction density (top half) and phase (bottom half) in a quasi-3D soliton simulation with cylindrical symmetry (for clarity, r ranges from [-R, R] in this figure). Snapshot at t = 22.6 ms showing a bright gap soliton near the axial grid centre (z axis shown horizontally, r axis vertically) and radially excited excess population moving away to the sides. The initial population is N = 900 atoms, the periodic potential depth is 1.3  $E_{rec}$ , the full radial range is 15  $\mu$ m, the full axial range 100  $\mu$ m, numerical grid resolution is 32x4096 discrete points.



Figure 5.19: Processing the data of a quasi-3D soliton simulation in cylindrical symmetry (spatial data shown in figure 5.18). Snapshot at t=22.6 ms. Top left diagram shows the spatial wavefunction density  $|\psi|^2$  in the optical lattice resolved into three populated transversal harmonic oscillator states. The left bottom shows the envelope functions with sech() fit (dotted). The right top graph shows transversal excitations and (on top at the "second level") the same for population in the excited Bloch band. The bottom right shows the phases of the envelope functions.



Figure 5.20: Scaling properties of an atomic gap soliton. The data shown in this figure was obtained from numerical simulations in cylindrical symmetry. The scaling theoretically predicted in equation (5.84) is represented by the solid (black) line. Our simulation results and the experimental observations in [24] are in agreement with the theoretical prediction.

## 150 CHAPTER 5. SIMULATIONS OF BOSE-EINSTEIN CONDENSATES

## Chapter 6

# **Conclusions and Outlook**

In the first part of this thesis we developed a numerical simulation program for the evaporative cooling of atoms and molecules in harmonic and linear traps. Particular attention was paid to the requirements for the trapping of molecular species in quadrupole traps, such as oxygen.

In this context, we have additionally done a full *ab initio* computation of an oxygen-oxygen collision potential energy surface, in order to improve the presently best known data. This was done to create a more solid base for the scattering theory of this molecular species, and to provide improved temperature dependent collision cross section data for the evaporative cooling simulations.

The numerical simulation program, which we have developed for the modelling of evaporative cooling (chapter 4), significantly improves on existing DSMC techniques. It is now possible to simulate the evaporation process through many orders of magnitude of particle loss and temperature change. Our algorithm is able to recursively adapt to strong density inhomogeneities and thus allows simulations of strongly peaked density distributions, as for example those occurring in magnetic quadrupole traps.

We have done simulations investigating the viability of magnetic trapping and evaporative cooling of molecular oxygen. We found that due to its large inelastic scattering cross section at temperatures, which may realistically be reached using cryogenic buffer gas cooling and trap loading techniques, it is unlikely that sufficient population numbers for runaway evaporation can be reached. Under ideal, fictitious assumptions, runaway evaporation with decreasing inelastic rates can be achieved, however, and we show that the problem of Majorana trap loss at the centre of linear quadrupole magnetic traps can be overcome by optimized evaporative cooling ramps. This effect only becomes significant for temperatures below approximately 0.5 mK.

The lack of optical cooling methods, and thus a lack of high trap densities at the start of the evaporative cooling runs, is likely, however, to preclude cooling long before quantum degeneracy can be reached. Another important point, which casts doubt on the prospect of oxygen trapping and cooling, is the strong sensitivity of this species' inelastic collision cross section to external magnetic fields. A model proposed by Volpi [54] shows that trap depths for efficient cooling must be unrealistically shallow. The inelastic rate approaches the elastic rate for magnetic field magnitudes larger than only 53 G, which translates to a trap depth of merely 7 mK.

We further modelled combined optical and magnetic trapping methods, which have yielded experimental results with problematic particle species. We could show in our simulations, how the use of an optical "dimple" trap potential can be used to achieve a peak phase space density increase of several orders of magnitude in harmonic and in linear traps. At the same time, this technique can be used to alleviate the Majorana loss effects at the quadrupole trap centre by using a dimple potential, which is slightly off centre.

In its current form, owing to its heritage describing gas flows, the adapted DSMC algorithm also allows the simulation of systems other than simple particle traps. Presently, cold particle research strives towards the production of cold samples of heavier and heavier molecules and particles for purposes of higher precision measurements. One possible application of our simulation program, as suggested by Prof. Foot, could be the modelling of a system, in which ultra-heavy molecules, or even biological particles, with narrow velocity spreads in supersonic jets, are translationally cooled by a counterpropagating flow of lightweight ultra-cold atoms.

In the second half of the present work we have developed a highly universal simulation program for BEC clouds at zero temperature. The program achieves good performance on present day standard computer hardware, even for simulations on large three-dimensional grids. We have applied this simulation program to many different problems. The code is modular and extensible, and the author hopes that in the future it will be used, adapted and extended even further by others.

We have simulated the collective excitation modes of a central vortex state in BEC clouds in close collaboration with the Oxford University experimental workgroup of Prof. Foot at the Clarendon Labs, and we have demonstrated the experimentally observed resonant excitation of vortex tilting modes in our numerical model. A joint publication on this topic has already been submitted for publication [23].

Further work went into simulations of BEC expansion after the release of the BEC cloud from the trap for the purpose of destructive imaging. This is a problem of great interest for experimental work groups and poses challenges for the numerical simulation algorithms, due to the rapid dynamics of the cloud expansion. Further projects simulating eccentric TOP trap effects, and methods using multi-state effects and Berry's phase for the direct production of vortices in TOP traps, have been started. We can conclude that the rich dynamics of the TOP magnetic trap still has potential for interesting new observations and the development of new methods, all of which can be modelled using the BEC simulation program developed in the present work.

We have conducted numerical simulations of BEC clouds trapped in optical lattices. Specific preparation techniques allow the creation of bright solitons at the band gap under these conditions. We have numerically verified recent experimental results [24] in 1D simulations. Additionally, we have developed 3D simulations for the vortex preparation experiments, which required several large changes in the simulation program to tackle the computational complexity posed by the highly dynamical effects and the very high grid resolutions required for such simulations. We completed 3D simulations, exploiting the inherent cylindrical symmetry of the soliton preparation experiments, and we have been able to quantitatively reproduce the experimental results.

Future work using the DSMC particle simulation program, which was developed in the first part of this thesis, may extend its capabilities into the ultra-low temperature regime, where effects of quantum degeneracy at finite temperatures lead to the BEC phase transition. Our BEC simulation program may be used to investigate clouds in potentials other than the typical harmonic or TOP traps in the future. Presently, we are planning to use the simulation program for further work in the area of soliton formation and behaviour.

## Appendix A

# Data analysis and visualisation techniques

Data acquisition from the individual computer simulation runs for all parts of this thesis was mainly text based. Console output of data is very simple to implement and can be quickly adapted to the problems immediately at hand. By defining several debug levels the programs are as verbose as needed during the several stages of program development, debugging and production use. Saved program console output was subsequently processed by PERL scripts to extract and convert data into a format appropriate for higher level visualisation tools, such as Octave.

## A.1 Jpeg images and film sequences

In many situations immediate visual output and interpretation of the data is more useful than the console textfile approach. Visual representation also allows efficient storage of what would else become a too large amount of raw data.

For these purposes a C++ program class to create Jpeg image files was developed. Using this class, one dimensional data, such as  $|\Psi|^2$  densities or wavefunction phases from rapid 1D simulations, can be plotted as simple curves. 2D data can be potted as colour-coded image maps using different colour schemes for wavefunction densities and phases. Data from 3D simulations, which when saved in detail for later analysis will quickly fill up even the largest of todays hard disk drives, can be represented by three separate perpendicular slices through the volume using the 2D colourmaps as for genuine 2D data.

Jpeg images can subsequently turned into file sequences by an encoder program. Under Linux we have used the now somewhat antiquated mpeg\_encode [84] program to compile mpg films. A more flexible option is the modern "MPlayer" free software package, which comprises an encoder for various popular formats, including the highly compressed DivX.

## A.2 3D methods

At times it could not be avoided to use large amounts of storage for detailed analysis of the data representing 3D BEC time evolution series. For a truly three dimensional representation we use the iso-density approach: A large data-set representing a wavefunction at a specific simulation time is read into memory. Then a surface of constant  $|\Psi|^2$  density is calculated and then plotted and shaded within a wire-mesh cube. For added effect the surface colour can be chosen according to the wavefunction phase at each individual surface point.

One program able to do this satisfactorily is Matlab. However, Matlab is very slow at this and not available on many computers due to restrictive and expensive licensing.

A more generic software called the "waveexplorer" was developed by us for this purpose. It uses the OpenGL hardware accelerated graphics rendering infrastructure, which is available in all present "3D" graphics cards and is also available on the Linux architecture favoured by us. The program allows skipping through the wavefunction time series saved in the large simulation data output files, while dynamically shifting the iso-surface density and "flying" through the scene in a flight-simulator fashion using keyboard and mouse. The program reuses parts of the free GPLIGC [170] program and makes use of the universal GTS grid library [84]. The waveexplorer program also allows the output of Jpeg file image sequences and thus the making of films.



Figure A.1: Schematic flow diagram of the computer simulation and data analysis process. Image and console data output are most useful for development and parameter range scanning purposes. Detailed data is needed mostly for production use.

## Appendix B

# Angular momentum coupling calculations using Mathematica

We have developed a program to calculate the Clebsch-Gordan coupling coefficients and channels for several angular momenta in the Mathematica computer algebra system. This was helpful studying and understanding the literature on scattering theory, such as [37, 31]. While angular momentum coupling of  $j_1$  and  $j_2$  with projection  $m_1$  and  $m_2$  (with  $m_1 + m_2 = m$ ) leads to coupled representation j and m in a unitary transform

$$\psi_{jm} = \sum_{m_1m_2} C(j_1 j_2 j; m_1 m_2 m) \psi_{j_1m_1} \psi_{j_2m_2}, \tag{B.1}$$

the inverse expansion [30]

$$\psi_{j_1m_1}\psi_{j_2m-m_1} = \sum_j C(j_1j_2j;m_1,m-m_1)\psi_{jm}$$
(B.2)

is more instructive in identifying exit channels in inelastic collisions with specific incoming channels.

With substitution rules, Mathematica allows the calculation of almost arbitrarily complicated stacked multi-component coupling problems, such as the one encountered in the  $(O_2)_2$  scattering problem. The substitution rules are applied recursively and repetitively by the Mathematica system, until no further simplification is possible.

The following is a verbatim copy of the Mathematica replacement rules, defining a  $|j, m, \text{"comment"}\rangle$  "Ket" structure (the comment helps identifying the resulting components in the coupled representation in more complex problems).

prod	=	<pre>{Ket[j1_, m1_, comment1_] ** Ket[j2_, m2_, comment2_] -&gt;</pre>
		Sum[CG[{j1, m1}, {j2, m2}, {j, m1 + m2}]*
		<pre>Ket[j, m1 + m2, "(" &lt;&gt; comment1 &lt;&gt; "," &lt;&gt; comment2 &lt;&gt; ")"],</pre>
		{j, Abs[j1 - j2], j1 + j2, 1}]};
addprod	=	{p_ ** (q_ + r_) -> p ** q + p ** r,
		(p_ + q_) ** r> p ** r + q ** r};
calccg		{CG[{j1_, m1_}, {j2_, m2_}, {j_, m_}]
		-> ClebschGordan[{j1, m1}, {j2, m2}, {j, m}]};
null	=	{0 ** p> 0, p_ ** 0 -> 0};
one	=	{1 ** p> p, p_ ** 1 -> p, -1 ** p> -p, p_ ** (-1) -> -p};
scalprod	=	<pre>{Ket[j_, m_, comment_]c&gt; c ** Ket[j, m, comment],</pre>
		(m_ ** Ket[j_, m_, comment_]) c> c m ** Ket[j, m, comment],
		<pre>c_ ** m_ ** Ket[p_, q_, comment_] -&gt; c m ** Ket[p, q, comment],</pre>
		1 ** Ket[p_, q_, comment1_]/c_ ** Ket[1_, m_, comment2_]
		-> 1/c ** Ket[p, q, comment1] ** Ket[l, m, comment2]};
factor	=	<pre>{Ket[p_, q_, comment_]c&gt; c ** Ket[p, q, comment],</pre>
		<pre>(x_ ** Ket[p_, q_, comment_])z&gt; x z Ket[p, q, comment],</pre>
		(Ket[p_, q_, comment_] ** x_)z> x z Ket[p, q, comment]};
sumup	=	<pre>{c_ ** Ket[p_, q_, comment1_] + d_ ** Ket[p_, q_, comment1_]</pre>
		-> (c + d) ** Ket[p, q, comment1]};
productify	=	<pre>{c_ ** Ket[p_, q_, comment_] -&gt; c Ket[p, q, comment]};</pre>
reduce	=	<pre>Flatten[{prod, addprod, calccg, null, one, scalprod, factor}];</pre>

The following two functions do the work, applying the defined rules. While "vadd[]" results in analytical expressions, "givenumbers[]" will give the coupling coefficients numerically.

```
vadd[x_] := Module[{tmp}, tmp = x //. reduce;
  tmp = tmp //. sumup;
  tmp = Simplify[tmp]]
givenumbers[x_] := Module[{tmp}, tmp = x //. sumup;
  tmp = tmp //. productify;
  N[tmp]]
```

The following is a very simple example coupling two angular momenta  $|j_1, m_1\rangle = |1, 1\rangle$  and  $|j_2, m_2\rangle = |1, -1\rangle$ , resulting in probabilities (square of the coefficients) for  $|j, m\rangle$  of 50%  $|1, 0\rangle$ , 33.3%  $|0, 0\rangle$  and 16.6%  $|2, 0\rangle$ .

## Appendix C

# Natural Atomic Units

In literature on quantum chemistry, natural atomic units are widely used. How these arise can be seen if we consider the Schrödinger equation of the hydrogen atom:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right]\phi = E\phi \tag{C.1}$$

We can obtain a dimensionless equation by casting the problem into dimensionless, often called "computational", units  $E' = E/E_a$  and  $r' = r/\lambda$ . In dimensionless units, the Schrödinger equation of the hydrogen atom will take the following simple form:

$$\left[-\frac{1}{2}\nabla^{\prime 2} - \frac{1}{r^{\prime}}\right]\phi = E^{\prime}\phi.$$
 (C.2)

We can obtain this shape from the original equation by replacing  $x, y, z \rightarrow \lambda x', \lambda y', \lambda z'$ .

$$\left[-\frac{\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\epsilon_0\lambda r'}\right]\phi' = E\phi'.$$
 (C.3)

If we now choose  $\lambda$  in such a way that

$$\frac{\hbar^2}{m\lambda^2} = \frac{e^2}{4\pi\epsilon_0} = E_a,\tag{C.4}$$

we can factor out the constants in front of the expressions for kinetic and potential energy. This results in  $E_a$  being a natural atomic unit of energy called the *Hartree*. For  $\lambda$  we get

$$\lambda = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0. \tag{C.5}$$

The scaling factor  $\lambda$  for our dimensionless units is the natural length scale of the problem, called the *Bohr radius*  $a_0$ .

Physical quantity	Conv. factor to SI units	Value in SI units
Length	$a_0$	$5.2918 \cdot 10^{-11} \text{ m}$
Mass	$m_e$	$9.1095 \cdot 10^{-31} \text{ kg}$
Charge	e	$1.6022 \cdot 10^{-19} \text{ C}$
Energy	$E_a$	$4.3598 \cdot 10^{-18} \text{ J}$
Angular momentum	$\hbar$	$1.0546 \cdot 10^{-34} \text{ Js}$
Electric dipole moment	$ea_0$	$8.4784 \cdot 10^{-30} \text{ Cm}$

## Appendix D

# Scaling laws for evaporative cooling

In the theory of evaporative cooling, several system parameters exhibit specific scaling laws with the particle number N, depending on the type of the trapping potential

$$U(r) \propto r^{d/\delta},$$
 (D.1)

where d is the dimensionality, usually d = 3 in real space, and  $\delta$  determines the trap type.  $\delta = 3$  for linear traps and  $\delta = 3/2$  for harmonic traps.

 $\alpha$  characterises the dependence of the ensemble temperature T on the particle number.

$$\alpha = \frac{\dot{T}/T}{\dot{N}/N} = \frac{d(\ln T)}{d(\ln N)} \tag{D.2}$$

The following table has been adapted from Ketterle and van Druten [62].

Quantity	Symbol	Exponent $x$
Number of particles	N	1
Temperature	T	$\alpha$
Volume	V	$\delta lpha$
Particle density	n	$1 - \delta \alpha$
Phase space density	D	$1 - \alpha(\delta + 3/2)$
Elastic collision rate	$n\sigmaar{v}$	$1 - \alpha(\delta - 1/2)$

## 162 APPENDIX D. SCALING LAWS FOR EVAPORATIVE COOLING

## Appendix E

## Memory efficient RK4

The fast and memory efficient Runge-Kutta-4 interaction picture (RK4IP) algorithm, which was developed for 3D simulations of the GP equation in [132], comprises the following 19 steps. The following shorthands for the numerical procedures involved will be used:

- C and the ← symbol stand for copy operations in the direction indicated by the arrow.
- D, diffusion operation. Executes the diffusion operator.
- N, non-diffusion operation. Executes the N operator, containing trap and other potentials, gravity and nonlinear particle interaction.
- S, weighted sum operations involving the argument wavefunctions.

Step	Assignm	ent operation	Operator
1.	$\Psi_k \leftarrow$	$\Psi$	С
2.	$\Psi  \leftarrow$	$\mathrm{D}(\Psi)$	D
3.	$\Psi_i  \leftarrow$	$\Psi$	С
4.	$\Psi_k \leftarrow$	$N(\Psi_k, t)$	Ν
5.	$\Psi_k \leftarrow$	$\mathrm{D}(\Psi_k)$	D
6.	$\Psi \leftarrow$	$\Psi + \Psi_k/6$	S
7.	$\Psi_k \leftarrow$	$\Psi_k/2 + \Psi_i$	S
8.	$t  \leftarrow$	$t + \Delta t/2$	
9.	$\Psi_k \leftarrow$	$N(\Psi_k, t)$	Ν
10.	$\Psi  \leftarrow$	$\Psi + \Psi_k/3$	S
11.	$\Psi_k \leftarrow$	$\Psi_k/2 + \Psi_i$	S
12.	$\Psi_k \leftarrow$	$N(\Psi_k, t)$	Ν
13.	$\Psi  \leftarrow$	$\Psi + \Psi_k/3$	S
14.	$\Psi_k \leftarrow$	$\Psi_k + \Psi_i$	S
15.	$\Psi_k \leftarrow$	$\mathrm{D}(\Psi_k)$	D
16.	$\Psi  \leftarrow$	$\mathrm{D}(\Psi)$	D
17.	$t \leftarrow$	$t + \Delta t/2$	
18.	$\Psi_k \leftarrow$	$N(\Psi_k, t)$	Ν
19.	$\rightarrow \Psi$	$\Psi + \Psi_k/6$	S

## Appendix F

# Finite difference derivative operator

For the computation of the radial derivative part of the diffusion operator in cylindrical symmetry (section 5.3.6) a finite differencing method was used instead of the Fourier transform method because the operator part is not diagonal in the Fourier picture and can thus not be computed in the usual and precise way.

Because of the specific shape of our problem, with the cylindrically symmetric wavefunction  $\Psi(r, z, t)$  rapidly approaching zero at the grid borders in r, we can use a multi-point central differencing method, which uses the same number of forward points r and backward points l on the grid relative to the grid position  $x_i$  the operator is evaluated at. In general the derivative at  $x_i$  can be written as

$$\psi'(x_i) = \frac{1}{\Delta x} \sum_{k=-l}^{r} c_k \psi(x_i + k\Delta x), \qquad (F.1)$$

where k for a central differencing method with l=r runs over the appropriate number of points, which are weighted with coefficients  $c_k$  according to a predetermined stencil.

As outlined in [171], these stencils can be determined for any number of evaluation points  $n_d = l + r + 1$  using a set of functions, for which the finite differencing equation (F.1) needs to yield exact results. Usually the first  $n_d$  polynomial functions  $\{p_0(x), p_1(x), \dots, p_{n_d-1}(x)\}$ , with  $p_k(x) = x^k$ , are used. Expansion of the *n*th derivative of  $p_k(x)$  (in our case we are only interested in the first derivative), written as  $p_k^{(n)}(x)$ , gives rise to the following system of linear equations, from which the stencil **c** can be calculated:

$$\mathbf{p}(n) = P(l, r)\mathbf{c} \tag{F.2}$$

With

$$\mathbf{c}^{T} = [c_{l}, c_{l+1}, \cdots, c_{0}, \cdots, c_{r}] \text{ and } \mathbf{c}^{T} = [p_{0}^{(n)}(0), p_{1}^{(n)}(0), \cdots, p_{n_{d}-1}^{(n)}(0)]$$

and

$$P(l,r) = \begin{bmatrix} p_0(l) & p_0(l+1) & \cdots & p_0(r) \\ p_1(l) & p_0(l+1) & \cdots & p_1(r) \\ \vdots & \vdots & & \vdots \\ p_{n_d-1}(l) & p_{n_d-1}(l+1) & \cdots & p_{n_d-1}(r) \end{bmatrix}$$
(F.3)

For simplicity the equations may be evaluated using  $x_i=0$  and a unit spacing of  $\Delta t=1$ .

While the accuracy of the numerical derivative increases with higher number of evaluation points  $n_d$ , we found that seven points yielded excellent results in all cases. Also see [133] for a discussion of the accuracies of the individual stencils.

Including the normalisation factor as in equation (F.1), the resulting central differencing stencils  $\mathbf{c}^{T}$  are as follows:

$$\begin{array}{ll} n_d = 3: & \frac{1}{2\Delta x} & [-1,0,1] \\ n_d = 5: & \frac{1}{2\Delta x} & [1,-8,0,8,-1] \\ n_d = 7: & \frac{1}{60\Delta x} & [-1,9,-45,0,45,-9,1] & (F.4) \\ n_d = 9: & \frac{1}{840\Delta x} & [3,-32,168,-672,0,672,-168,32,-3] \\ n_d = 11: & \frac{1}{2520\Delta x} & [-2,25,-150,600,-2100,0,2100,-600,150,-25,2] \end{array}$$

Solution of the system of linear equations proved to be slow in *Mathematica* and impossible for more than  $n_d = 7$  points for unknown reasons. A port of the script to the *Maple* algebra system [172, 173] solved the problem and yielded the results for  $n_d = 9$ , 11.

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## List of frequently used abbreviations

BCA	Binary Collision Approximation
$\mathbf{BE}$	Bose-Einstein
BEC	Bose-Einstein Condensate
BGC	Buffergas Cooling
BO	Born-Oppenheimer
CAS	Complete Active Space
CC	Coupled Cluster
$\mathbf{CG}$	Clebsch-Gordan
CI	Configuration Interaction
CPU	Central Processing Unit
DSMC	Direct Simulation Monte Carlo
$\mathbf{FD}$	Fermi-Dirac
FFT	Fast Fourier Transform
FORT	Far-off-resonance optical trap
$\mathbf{FT}$	Fourier Transform
FWHM	Full Width Half Mean
GNU	GNU is not Unix
GP	Gross-Pitaevskii
GPE	Gross-Pitaevskii Equation
GPL	General Public License
HF	Hartree-Fock
I/O	Input/Output
IP	Interaction Picture
LCAO	Linear Combination of Atomic Orbitals
MB	Maxwell-Boltzmann
MD	Molecular Dynamics
MO	Molecular Orbital
MOT	Magneto-Optical Trap
$\mathbf{MP2}$	2nd order Møller-Plesset
MPPT	Møller-Plesset Perturbation Theory
NLSE	Nonlinear Schrödinger Equation
PES	Potential Energy Surface
PRNG	Pseudo-Random Number Generator
$\mathbf{QC}$	Quantum Chemistry
$\mathbf{QED}$	Quantum Electrodynamics
$\mathbf{QMC}$	Quantum Monte Carlo
$\mathbf{RAM}$	Random Access Memory
$\mathbf{RF}$	Radio Frequency
RK4	Runge-Kutta 4th order
RNG	Random Number Generator
ROHF	Restricted open shell Hartree-Fock
SCF	Self-consistent field
$\mathbf{TF}$	Thomas-Fermi
TOP	Time Orbiting Potential
VDW	van der Waals

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