

Dipolar collisions in cooling and trapping of paramagnetic atoms

Zoran Pavlović, Ph.D.

University of Connecticut, 2011

In this dissertation, I present *ab initio* theoretical results on cold and ultra-cold collision of atomic and molecular systems with magnetic and electric dipole moments. The collisions of different isotopes of maximally spin-polarized chromium atoms (^{52}Cr and ^{53}Cr), alkali-metal atom (Rb) - chromium atom, and magnetically trapped hydroxide (OH) with cold supersonic helium beam are considered in this thesis. Spin-changing cross sections and rate constants in Cr-Cr isotopic collision in the presence of a magnetic field are calculated by propagating a set of multichannel equations in the field. The coupling between dipole-dipole allowed and hyperfine channels are included. The short range electrostatic interactions between atoms and atom-molecule are represented with highly-accurate Born-Oppenheimer (BO) potential energy curves. Due to the large spin multiplicity in Cr-Cr and Rb-Cr interactions, more than the usual singlet and triplet channels are obtained. The long-range van der Waals (vdW) interactions between atoms are calculated, for Cr, by including accurate transition frequencies, discrete dipole matrix elements, and photoionization continuum oscillator strengths, and for Rb, using published dynamic polarizabilities. The vdW coefficients for Cr-Cr and Rb-Cr are obtained. In the cold collision regime, I investigate the influence of angular momentum shape resonances on the elastic and inelastic (loss channel) rate coefficients, and when the Zeeman relaxation, resulting in the loss of atoms from the trap, dominates elastic collision. Dipolar collisions are crucial to achieving quantum degeneracy. Magnetically tuned

Fano-Feshbach closed-channel resonances are used to obtain zero-energy scattering lengths in comparison with observation of trap loss. In bosonic chromium collisions, resonances appear due only to dipolar interaction. The interplay between hyperfine and dipolar resonances in mixed-species Cr-Cr and Rb-Cr collisions is studied. In Rb-Cr, it is found that the molecule has broken symmetry and therefore contains a large permanent electric dipole moment in the ground state. A recent collisional experiment at JILA of a supersonic helium beam with a magnetically trapped OH radical found the onset of a quantum threshold in the total OH loss rate. Using *ab initio* BO energy surfaces, I calculated the spin-changing collisions which removed OH from the trap. Only after including the effect of the trapping potential on the collision dynamics, some agreement with observation was found.

Dipolar collisions in cooling and trapping of paramagnetic atoms

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APPROVAL PAGE

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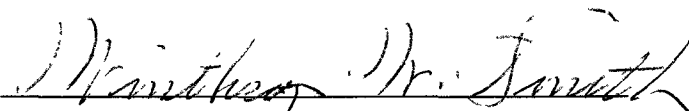
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To the memory of my grandmother Živana

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CHAPTER 1

INTRODUCTION

Since the creation of a first atomic Bose-Einstein condensate (BEC) [2, 3, 4], alkali-metal atoms (Li-Cs) have remained the favorite choice for explorations into the quantum nature of degenerate ultracold gases. Alkali metal atoms have one valence shell electron, with easily accessible cycling transitions for cooling and trapping lasers. The cycling transitions in alkali-metal atoms are readily pumped with high efficiency. In addition, alkali-metal atoms are amenable to accurate theoretical and computational studies, and highly precise interatomic interactions (short- and long-range forces) and collisional data (scattering length, spin exchange, and other trap loss collisional data) are available [5, 6, 7, 8, 9].

While long-range spin-spin dipolar interactions have been recently observed in rubidium [10, 11] and potassium traps, the largest contribution to the interaction between two alkali-metal atoms at ultracold temperatures comes from the zero-range physics (scattering length formalism, see Sec. 2.6), where a single parameter, the scattering length, controls the few- and many-body processes in ultracold samples, and especially quantum ultracold degenerate gases (QDG).

Because atoms do not have permanent electric dipole moments, the dipolar long-range interaction between two atoms is due to magnetic (spin-spin) dipole moment, as opposed to polar molecules, which have permanent electric dipole moments. Electric and magnetic dipole moments can be manipulated by external electric and magnetic

fields, respectively. In atoms, which are polarizable, the induced electric dipole moments lead to much shorter range van der Waals (vdW) interactions [12].

In alkali-metal interactions, the magnetic dipole moment is only one Bohr magneton (μ_B), because there is only valence electron outside of a closed-shell core. To investigate long-range dipolar interactions, atoms with larger magnetic moments, such as Cr ($6\mu_B$), Eu ($7\mu_B$) and Dy ($10\mu_B$) have been cooled to ultra-low temperatures [13, 14, 15, 16, 17, 18, 19, 20]. Recently, the BEC of dysprosium has been achieved (Ben Lev's group at UIUC).

Europium was the first heavy metal atom with a large magnetic moment to be used in a buffer gas cooling scheme [13] in Doyle's group, and the latest theoretical work on its scattering properties can be found in Ref [14]. The same group continued efforts in the direction of a buffer gas loading scheme combined with evaporative cooling [15, 16, 17] for chromium. This scheme failed to cool Cr atoms below 10 mK due to the presence of high inelastic dipolar scattering rates. Fortunately, another route that combined magneto-optical trapping (MOT) [18, 19] with evaporative cooling enabled Pfau and co-workers to circumvent that problem and obtain a chromium BEC [20].

Apart from occasional interest in obtaining a source of single Cr atoms [21] for applications in areas such as atom lithography, quantum computing, fundamental high-precision measurements or quantum information, the main thrust of Cr research in the last decade was for the manifestation of dipolar interactions and new collective phenomena they may lead to. The mechanical effect of the dipolar interaction was observed in the BEC aspect ratio for specific trap magnetic field orientations during the free expansion of the condensate [22, 23]. An alternative way of detecting the dipolar effects in BEC, based on measuring collective excitations was offered in Ref [24]; a suppression of the contact interaction in BEC with respect to the dipolar interaction was achieved by changing the scattering length in the vicinity of a Feshbach resonance

[25], creating a quantum ferrofluid in a Cr BEC, and observing d -wave signature [26] and coherent [27] BEC collapses.

In parallel with the experimental track, a number of theoretical investigations contributed to our understanding of the quantum behavior of chromium and other dipolar systems in general. Dipolar interactions can drive large negative scattering lengths leading to the collapse of the condensate [28], for the formation of vortex states and roton modes in a dipolar BEC [29, 30]; some of which were carried out with ^{52}Cr [31, 32]. The most recent study of the dipolar interactions in Cr gas is done by the Gorceix group [33].

In this thesis, we are primarily concerned with the collisional properties of a cold and ultracold chromium gas, and in particular the elastic and inelastic collision involving long-range dipolar interactions, the role played by Feshbach resonances, the control and manipulation of the interaction by magnetic fields, and the collisions in mixed-species gases. The special role that the scattering length plays in ultracold physics is easily appreciated by consulting any work that uses the Gross-Pitaevskii equation to model BEC behavior [34]. There, the scattering length (a) enters through the contact interaction with a pseudo potential. Based on the sign of the scattering length, the BEC is stable ($a > 0$) or unstable ($a < 0$). Therefore, it is very useful to obtain its value or at least its sign. For chromium in particular, such efforts were carried out in [35, 36].

In ultracold atomic physics, collisions are classified as elastic (*good*) or inelastic (*bad*), based on the conservation of energy and internal states. The ‘good’ and ‘bad’ designations highlight the influence of elastic and inelastic collisions on magnetically trappable Zeeman states. In order for the buffer gas trapping and cooling scheme to work efficiently, it is essential that inelastic collision processes be minimized while elastic processes be sizable for thermalizing the trapped atoms. The same applies to

evaporative cooling, where inelastic processes remove colder atoms out of the sample. In general, the preferred ratio of elastic to inelastic collision rates is > 100 . The main part of this work is dedicated to calculating interaction potentials, vdW coefficients for long-range interactions, and collision rates for all combinations of chromium isotopes (boson-boson, boson-fermion, and fermion-fermion [17, 37, 38]), and comparison with observation. In this work, we explore and systematically map magnetic Feshbach resonances [38] which were measured and assigned (based on a model potential) in [39]. The experimentally obtained positions and widths of Feshbach resonances helps to refine *ab initio* Born-Oppenheimer potentials.

We also attempt to stimulate interest in chromium mixtures with alkali-metals by studying the Cr-Rb gas mixture. This system was first experimentally investigated in a two-species MOT by Pfau's group [40]. The appeal of this system lies in it having at same time a large magnetic moment ($5\mu_B$) while the RbCr molecule has a sizable electric dipole moment (2.9 D) which can provide a control handle with the application of either an electric or a magnetic field, or both.

The outline of this dissertation is as follows. Chapter 2 gives a general description of the scattering formalism using the single-channel and multichannel approaches. Chapter 3 describes the numerical techniques used to solve the scattering problems. Chapter 4 presents the necessary details to assemble the Hamiltonian that describes the interaction between colliding atoms in an external field. Chapters 5, 6, and 7 discuss Cr-Cr, Cr-Rb and He-OH collisions, respectively. Answers to the technical questions that arise in the application of scattering theory are given in the appendices. Atomic units are used throughout this dissertation.

CHAPTER 2

A BRIEF INTRODUCTION TO SCATTERING THEORY

2.1 Basic terms

The scattering of a beam of particles on a fixed target is equivalent to the more general case of two colliding beams of particles. The latter is reduced to the former by separating the relative motion of two particles from the motion of the center of mass. The change from a set of vectors $(\mathbf{r}_1, \mathbf{r}_2)$ representing the positions of two particles to another set of vectors $(\mathbf{r}_{cm}, \mathbf{r})$, where

$$\mathbf{r}_{cm} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \quad (2.1)$$

is the center of mass coordinates of two atoms, and

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \quad (2.2)$$

connects the positions of two atoms, reduces the Schrödinger equation to

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t) . \quad (2.3)$$

The Hamiltonian describing the relative motion of two atoms

$$H = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, t) \quad (2.4)$$

is identical to a Hamiltonian governing the motion of a single particle, with a mass equal to the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad (2.5)$$

in the presence of a potential $V(\mathbf{r}, t)$. The task of solving the time independent Schrödinger equation is reduced to solving

$$(\nabla^2 - U(\mathbf{r}) + k^2)\psi_{\mathbf{k}}(\mathbf{r}) = 0, \quad (2.6)$$

where $E = \hbar^2 k^2 / (2\mu)$ is the relative collision energy, and U stands for $2\mu V / \hbar^2$, the *reduced* potential. At large distances from the scattering center, the wave function

$$\psi_{\mathbf{k}}(\mathbf{r}) \underset{r \rightarrow \infty}{=} e^{i\mathbf{k} \cdot \mathbf{r}} + f_k(\theta, \phi) \frac{e^{ikr}}{r} \quad (2.7)$$

can be decomposed into an incident part and a scattered part, whose amplitude, given as $f_k(\theta, \phi)$, is angle dependent. The polar angles (θ, ϕ) are defined by the scatteredfront from the incoming beam.

The relevant quantity that establishes the connection between experiment and theory is the differential cross section

$$\frac{d\sigma}{d\Omega} = |f_k(\theta, \phi)|^2, \quad (2.8)$$

which connects the scattered flux, I_Ω (the number of scattered particles per second within the solid angle $d\Omega$) to the flux I of the incoming beam (the number of particles

crossing a unit area per second). The scattered flux I_Ω is changed by varying the flux of projectile particles and the solid angle in which the particles are detected (scattered)

$$I_\Omega = \frac{d\sigma}{d\Omega} \cdot I d\Omega. \quad (2.9)$$

At the same time the number of scattered particles crossing an area dS at a distance r from the scattering center is obtained as

$$I_\Omega = \frac{|f_k(\theta, \phi)|^2}{r^2} \left(\frac{\hbar k_f}{\mu} \right) r^2 d\Omega. \quad (2.10)$$

Here, in anticipation of inelastic scattering where the final momentum k_f is not necessarily equal to the initial momentum k_i , we use k_f instead of k_i which is a more appropriate notation for the case of elastic scattering. The incoming flux is calculated as

$$I = \frac{\hbar k_i}{\mu}. \quad (2.11)$$

After substitution of (2.10) and (2.11) into (2.9) we get an expression for the differential cross section that incorporates both elastic and inelastic scattering

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_i} |f_k(\theta, \phi)|^2. \quad (2.12)$$

The total cross section is obtained by integrating (2.8) over the solid angle

$$\sigma(E) = \int \frac{d\sigma}{d\Omega} d\Omega, \quad (2.13)$$

which, after thermal averaging, gives the rate of scattering

$$\mathcal{R} = \left(\frac{8k_B T}{\pi \mu} \right)^{\frac{1}{2}} \frac{1}{(k_B T)^2} \int_0^\infty \sigma(E) E \exp(-E/k_B T) dE. \quad (2.14)$$

Rates are converted from atomic units to $[\text{cm}^3/\text{s}]$ using

$$1 \text{ a.u. for rate} = \frac{a_0^3}{\tau} = a_0^2 c \alpha = 6.126 \cdot 10^{-9} \text{ cm}^3/\text{s}, \quad (2.15)$$

where the atomic unit for time is $a_0/(c\alpha) = 2.419 \cdot 10^{-17}$ sec.

2.2 Partial wave analysis

The use of the partial wave method is straightforward in a case where the potential is spherically symmetric. The wave function $\psi_{\mathbf{k}}$ is decomposed into spherical harmonics

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{m=\ell} R_{\ell m}(r) Y_{\ell m}(\hat{\mathbf{r}}), \quad (2.16)$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$. Making use of the form of ∇^2 in spherical coordinates [41], we obtain for function $R_{\ell}(k, r)$ the following differential equation

$$\left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + k^2 - U(r) - \frac{\ell(\ell+1)}{r^2} \right] R_{\ell}(k, r) = 0. \quad (2.17)$$

Here the index m is dropped if the z axis of the coordinate system is aligned with the incoming $\mathbf{k}$, and the dependence of the solution on the magnitude of $\mathbf{k}$ is made explicit.

When azimuthal symmetry does not hold - such as when an external field is present, the differential equation reads

$$\left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + k^2 - \frac{\ell(\ell+1)}{r^2} - \langle \ell m | U | \ell m \rangle \right] R_{\ell m}(r) = \sum_{\ell' m'} \langle \ell m | U | \ell' m' \rangle R_{\ell' m'}(r), \quad (2.18)$$

with the potential matrix defined as

$$\langle \ell m | U | \ell' m' \rangle = \int Y_{\ell m}^*(\hat{\mathbf{r}}) U(\mathbf{r}) Y_{\ell' m'}(\hat{\mathbf{r}}) d\Omega_{\hat{\mathbf{r}}}. \quad (2.19)$$

This is essentially a set of coupled equations where the potential $U(\mathbf{r})$ is capable of changing the angular momentum of a particle. The functions $R_{\ell m}$ are called channel functions and the full description is obtained by solving the set of *multichannel* equations in (2.18).

The radial equation can be presented in a simpler form by writing

$$R_{\ell}(k, r) = \frac{u_{\ell}(k, r)}{kr}, \quad (2.20)$$

which generates an equation for $u_{\ell}(k, r)$

$$\left[\frac{d^2}{dr^2} + k^2 - U(r) - \frac{\ell(\ell+1)}{r^2} \right] u_{\ell}(r) = 0. \quad (2.21)$$

When the potential $U(r)$ in Eq. (2.21) is zero or we are in the asymptotic region where the potential can be neglected, the two independent solutions are the regular Riccati-Bessel function

$$\hat{j}_{\ell}(kr) = (kr)j_{\ell}(kr), \quad (2.22)$$

and the irregular Riccati-Bessel function

$$\hat{n}_{\ell}(kr) = (kr)n_{\ell}(kr), \quad (2.23)$$

where j_ℓ and n_ℓ are the spherical Bessel functions of the first and second kind respectively, see App. A. Any solution of (2.21) is a linear combination of these two independent solutions,

$$u_\ell(r) = C_1 \hat{j}_\ell(kr) - C_2 \hat{n}_\ell(kr). \quad (2.24)$$

In the case where the potential is zero everywhere (i.e. no interaction or free particle), the boundary condition at the origin which requires $u_\ell(k, r=0) = 0$ eliminates the irregular solution, and we are left with the regular solution only

$$u_\ell(r) = C_1 \hat{j}_\ell(kr). \quad (2.25)$$

The asymptotic behavior ($r \rightarrow \infty$) of the potential free solution is determined by the large argument, $kr \gg l(l+1)/2$, behavior of the Riccati-Bessel functions

$$\hat{j}_\ell(kr) = \sin(kr - l\frac{\pi}{2}), \quad \hat{n}_\ell(kr) = -\cos(kr - l\frac{\pi}{2}). \quad (2.26)$$

This enables us to write (2.24) as

$$u_\ell(r) \underset{r \rightarrow \infty}{=} A_\ell \sin(kr - l\frac{\pi}{2} + \delta_\ell), \quad (2.27)$$

where $\tan(\delta_\ell) = C_2/C_1$. Provided that we have either a numerical or an analytical solution, we can extract the phase shift and construct the scattering amplitude

$$f(k, \theta) = \frac{1}{2ik} \sum_{\ell=0}^{\infty} [e^{2i\delta_\ell(k)} - 1] P_\ell(\cos \theta). \quad (2.28)$$

The derivation of the expression for the partial wave decomposition of the scattering amplitude is done by forcing the solution (2.16) to satisfy the scattering form (2.7).

This is achieved by using the well known expansion of the plane wave in the spherical harmonics basis

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^{\ell} \frac{\hat{j}_{\ell}(kr)}{kr} Y_{\ell m}^*(\hat{\mathbf{k}}) Y_{\ell m}(\hat{\mathbf{r}}). \quad (2.29)$$

To take full advantage of the spherical symmetry, we set the z axis of the coordinate system along the $\mathbf{k}$ vector and use Legendre polynomials instead of the spherical harmonics, since $m = 0$. The simplified version of the plane wave expansion is

$$e^{ikz} = \sum_{\ell=0}^{\infty} i^{\ell} (2\ell + 1) \frac{\hat{j}_{\ell}(kr)}{kr} P_{\ell}(\cos \theta), \quad (2.30)$$

where θ is the angle between $\mathbf{r}$ and the z axis. The disappearance of the angle ϕ and the presence of P_{ℓ} in the above expression is due to a particular choice of a set of axes, where the z axis is set along the direction of the incoming particle momentum.

Also, the expansion of $\psi_{\mathbf{k}}$, (2.16), which parallels that of a plane wave, is

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\ell=0}^{\infty} i^{\ell} (2\ell + 1) \frac{u_{\ell}(r)}{kr} P_{\ell}(\cos \theta). \quad (2.31)$$

Since the whole angular dependence is contained in the Legendre polynomials, it is correct to assume the following form of the scattering amplitude

$$f(\theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} i^{\ell} (2\ell + 1) B_{\ell} P_{\ell}(\cos \theta). \quad (2.32)$$

When matching the solutions (2.31) to the scattering boundary condition (2.7), we can exploit the orthogonality of Legendre polynomials to get an equation for each ℓ

$$u_{\ell}(r) = \hat{j}_{\ell}(kr) + B_{\ell} e^{kr}. \quad (2.33)$$

Then, we can substitute the asymptotic forms for u_ℓ and $\hat{j}_\ell$ so we can get an equation for the unknown coefficients A_ℓ and B_ℓ

$$A_\ell \sin(kr - l\frac{\pi}{2} + \delta_\ell) = \sin(kr - l\frac{\pi}{2}) + B_\ell e^{kr}. \quad (2.34)$$

Considering that the exponential functions $\exp(ikr)$ and $\exp(-ikr)$ are linearly independent, we get two equations for the coefficients A_ℓ and B_ℓ

$$A_\ell e^{+i\delta_\ell} = 1 + 2i^{\ell+1} B_\ell, \quad A_\ell e^{-i\delta_\ell} = 1. \quad (2.35)$$

Apart from expressing the sine function using the identity

$$\sin(x) = \frac{1}{2i}(\exp(ix) - \exp(-ix)), \quad (2.36)$$

it helps to use $\pm i(kr - \ell\pi/2)$ instead of $\pm ikr$ as an argument of the exponential functions. It also helps to modify the term with the B_ℓ coefficient

$$B_\ell e^{kr} = 2i^{\ell+1} B_\ell \cdot \frac{1}{2i} e^{i(kr - l\frac{\pi}{2})}. \quad (2.37)$$

The second equation in (2.35) directly shows the dependence of the coefficient A_ℓ on the phase shift δ_ℓ

$$A_\ell = e^{i\delta_\ell}, \quad (2.38)$$

which after substitution in the first equation reveals the phase shift dependence of the second coefficient

$$B_\ell = \frac{(e^{2i\delta_\ell} - 1)}{2i^{\ell+1}}. \quad (2.39)$$

Having obtained A_ℓ and B_ℓ we can reproduce the partial wave decomposition (2.28) of the scattering amplitude and establish the asymptotic form of the radial scattering wave function

$$u_\ell(r) \underset{r \rightarrow \infty}{=} e^{i\delta_\ell} \sin(kr - l\frac{\pi}{2} + \delta_\ell). \quad (2.40)$$

The form of the expansion in (2.31) is chosen to mimic the expansion of a plane wave. The role of j_ℓ , the radial scattering functions for free particles, is taken over by the radial scattering functions u_ℓ . It can be interpreted that in the asymptotic region the radial function for a free particle

$$\hat{j}_\ell(kr) \underset{r \rightarrow \infty}{=} \sin(kr - l\frac{\pi}{2}) \quad (2.41)$$

acquires a complex phase factor in the presence of the potential, $\exp(i\delta_\ell)$ and becomes shifted by the phase shift δ_ℓ . In low-temperature collisions, only a few partial waves participate significantly in the collision, and the partial wave sum rapidly converges with respect to ℓ .

2.3 Asymptotic forms

Even though the radial wave function is generally complex, up to now we have assumed it to be real. We will insist on using a matrix terminology even though in the particular case of the single-channel study, only a 1D-array of complex numbers is necessary. It is implicitly understood, that asymptotic limits ($r \rightarrow \infty$) of the solutions are used. Here, we will introduce quantities S_ℓ , T_ℓ and K_ℓ which are the single-channel analogs of the corresponding quantities in the multichannel formulation of the scattering theory, namely the S (scattering), T (transition), and K (reaction) matrices.

The S form is used when the solution is expressed in terms of incoming and outgoing traveling spherical waves

$$u_\ell(r)(-2i) = e^{-i(kr - \ell\frac{\pi}{2})} - e^{i(kr - \ell\frac{\pi}{2})} S_\ell, \quad (2.42)$$

where S_ℓ is connected to a phase shift by the following expression

$$S_\ell = e^{i2\delta_\ell}. \quad (2.43)$$

The S_ℓ numbers quantify the change of the outgoing component of the plane wave under the influence of the interaction.

The T form is defined when the solution is decomposed into the sum of an incoming standing wave and an outgoing traveling spherical wave

$$u_\ell(r) = \sin(kr - \ell\frac{\pi}{2}) - e^{i(kr - \ell\frac{\pi}{2})} \frac{T_\ell}{2}, \quad (2.44)$$

where T_ℓ is related to S_ℓ and given with

$$T_\ell = i(S_\ell - 1) = -2e^{i\delta_\ell} \sin(\delta_\ell). \quad (2.45)$$

The K form is used when we want to express the solution as a sum of two standing waves

$$u_\ell(r)(1 - iT_\ell/2) = \sin(kr - \ell\frac{\pi}{2}) + \cos(kr - \ell\frac{\pi}{2}) K_\ell, \quad (2.46)$$

where K_ℓ determines how much of the irregular component is present. The K_ℓ numbers are connected to partial phase shifts through

$$K_\ell = -\frac{T_\ell}{2} \left[1 - i\frac{T_\ell}{2} \right]^{-1} = \tan(\delta_\ell). \quad (2.47)$$

Using (2.45), we can verify that the following relation between S and K numbers is true

$$K_\ell = i(1 - S_\ell)(1 + S_\ell)^{-1}. \quad (2.48)$$

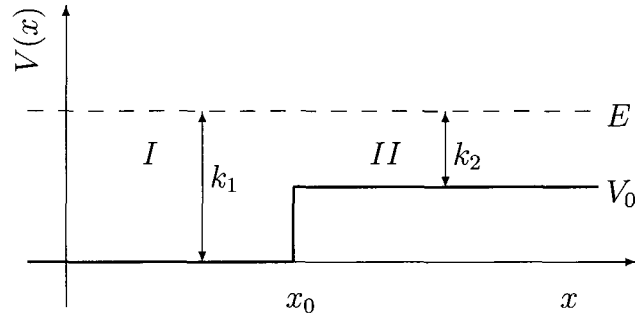
Solving this for S_ℓ yields the expression [42]

$$S_\ell = \frac{1 + iK_\ell}{1 - iK_\ell}, \quad (2.49)$$

which shows how to construct complex S values from real K values.

2.4 Normalization

While a bound state wave function is easily normalizable, i.e. it is box normalized, and hence energy independent, the normalization of an energy or momentum dependent scattering wave function is more involved. Below, we will give a simple prescription on how to normalize a continuum wave function to an energy or momentum delta function. Let us consider the case of 1D-scattering on a step barrier. The step barrier divides the space into two regions, region I where the potential is zero and region II where the potential is non-zero.



If there is a particle of mass m with kinetic energy E , coming from the left, which scatters on the barrier, the solution is

$$\psi_I(x) = \exp(+ik_1x) - A \exp(-ik_1x) \quad (2.50)$$

in region I , and

$$\psi_{II}(x) = -B \exp(+ik_2x) \quad (2.51)$$

in region II . The wave numbers are

$$k_1 = 2mE/\hbar^2, \quad k_2 = 2m(E - V_0)/\hbar^2. \quad (2.52)$$

We can define a reflection coefficient R as the ratio of reflected and incoming flux,

$$R = |A|^2. \quad (2.53)$$

Similarly, a transmission coefficient T is defined as the ratio of transmitted and incoming flux, and in this case it is

$$T = \frac{k_2}{k_1} |B|^2. \quad (2.54)$$

The probability to find the particle in region II within some area bounded by x_1 and x_2 is determined by

$$P_{[x_1, x_2]} = \int_{x_1}^{x_2} |\psi_{II}(x)|^2 dx = |B|^2 |x_2 - x_1|, \quad (2.55)$$

Since there is no particular reason why the normalization coefficient in front of the exponential expressions in the plane wave should be one, we could change it

$$\exp(ik_i x) \rightarrow \frac{1}{\sqrt{k_i}} \exp(ik_i x). \quad (2.56)$$

The immediate consequence of the plane wave renormalization is that after adopting the change in the form of solutions

$$\psi_I(x) = \frac{1}{\sqrt{k_1}} \exp(ik_1 x) - A' \frac{1}{\sqrt{k_1}} \exp(-ik_1 x) \quad (2.57)$$

in region I , and

$$\psi_{II}(x) = -B' \frac{1}{\sqrt{k_2}} \exp(ik_2 x) \quad (2.58)$$

for region II , it follows that the transmission coefficient is

$$t = |B'|^2. \quad (2.59)$$

The coefficient B gives the ratio of transmitted and incoming fluxes, hence the flux normalization terminology. At the risk of becoming redundant, in the first case, B is amplitude (or probability) normalized, while in the second case it is flux normalized.

The transition to the usual scattering terminology is achieved by noting that in the case of barrier scattering, we can define the incoming wave as any plane wave going towards point x_0 where the potential jumps, and outgoing waves as plane waves going out from point x_0 . The elastic channel is represented by the solution in region I and

the inelastic channel is represented by the solution in region II . Then we are ready to identify the first column of the amplitude normalized S matrix

$$S_{11} = A, \quad S_{12} = B, \quad (2.60)$$

while the flux normalization gives

$$S_{11} = A', \quad S_{12} = B'. \quad (2.61)$$

All that was said above should be enough to show the motivation for the presence of $\sqrt{k}$ in the formulation of S matrix

$$u_{\alpha\beta}(r) = \delta_{\alpha\beta} \frac{1}{\sqrt{k_\beta}} e^{-i(k_\beta r - \ell \frac{\pi}{2})} - \frac{1}{\sqrt{k_\beta}} e^{i(k_\beta r - \ell \frac{\pi}{2})} S_{\alpha\beta} \quad (2.62)$$

in the multichannel formalism, where the index α labels the entrance channel and index β labels the exit channels.

Energy normalization. The plane wave basis, (2.29), has the following normalization

$$\langle \mathbf{k} | \mathbf{k}' \rangle = (2\pi)^3 \delta(\mathbf{k} - \mathbf{k}'). \quad (2.63)$$

It is usually taken that plane wave functions are normalized, up to a numerical factor of $(2\pi)^3$, to a delta function in the wave vector space. The question of how to get from a plane wave normalized to a wave vector delta function (*momentum normalization*)

$$\langle \mathbf{k} | \mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}'), \quad (2.64)$$

to a plane wave normalized to the product of an energy delta function and directional delta function (*energy normalization*)

$$\langle E, \hat{\mathbf{k}} | E', \hat{\mathbf{k}}' \rangle = \delta(E - E') \delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}'), \quad (2.65)$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$, is answered with the following renormalization

$$|E, \hat{\mathbf{k}}\rangle = \sqrt{\frac{mk}{\hbar^2}} |\mathbf{k}\rangle. \quad (2.66)$$

The relation above is a specific case of the general form

$$\delta(\mathbf{k} - \mathbf{k}') = \frac{1}{k^2} \frac{dE}{dk} \delta(E - E') \delta(\hat{\mathbf{k}} - \hat{\mathbf{k}}'), \quad (2.67)$$

where the energy dependence is specified by

$$E = \frac{\hbar^2 k^2}{2m}. \quad (2.68)$$

Radial function energy normalization The question that arises is what should the normalization of the radial scattering functions u_ℓ be. It is desirable that the energy normalized radial scattering functions become free-particle energy normalized solutions in the absence of the interaction. The plane wave expansion (2.29) rewritten as

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell Y_{\ell m}^*(\hat{\mathbf{k}}) \left(\frac{\hat{j}_\ell(kr)}{kr} Y_{\ell m}(\hat{\mathbf{r}}) \right) \quad (2.69)$$

shows that we can construct the free-particle solutions with well defined angular momentum and its projection

$$\phi_{klm}(\mathbf{r}) = \frac{\hat{j}_\ell(kr)}{kr} Y_{\ell m}(\hat{\mathbf{r}}), \quad (2.70)$$

where $\hat{j}_\ell$ are Riccati-Bessel functions defined in (2.22). The normalization of the $\phi_{klm}(\mathbf{r})$ functions is

$$\int_0^\infty \phi_{klm}^*(\mathbf{r}) \phi_{k'l'm'}(\mathbf{r}) d\mathbf{r} = \frac{\pi}{2k^2} \delta(k - k') \delta_{\ell\ell'} \delta_{mm'}. \quad (2.71)$$

The transformation coefficients between plane wave functions $\exp(i\mathbf{k} \cdot \mathbf{r})$ and functions $\phi_{k'l'm'}(\mathbf{r})$ are

$$\langle k'l'm' | \mathbf{k} \rangle = \frac{2\pi^2}{k^2} i^\ell Y_{\ell'm'}^*(\hat{\mathbf{k}}) \delta(k - k'). \quad (2.72)$$

The connection between the energy normalized and momentum normalized free-particle functions with a well defined angular momentum is

$$|Elm\rangle = \sqrt{\frac{2mk}{\pi \hbar^2}} |klm\rangle. \quad (2.73)$$

The expansion of the scattering solution that parallels the expansion of the plane wave (2.69) is

$$\psi_{\mathbf{k}}(\mathbf{r}) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell Y_{\ell m}^*(\hat{\mathbf{k}}) \left(\frac{u_{klm}(r)}{kr} Y_{\ell m}(\hat{\mathbf{r}}) \right), \quad (2.74)$$

where, in the asymptotic limit $r \rightarrow \infty$, we have

$$u_{klm}(r) = \sin(kr - l\frac{\pi}{2} + \delta_\ell). \quad (2.75)$$

Now, we want to concentrate on the radial coordinate only. From (2.71) we can see that radial functions $u_{klm}(r)/k$ have the following normalization

$$\int_0^\infty \frac{u_{klm}^*(r)}{k} \frac{u_{klm}(r)}{k} dr = \frac{\pi}{2k^2} \delta(k - k'), \quad (2.76)$$

which lets us define new radial functions $v_{klm}(r) = \sqrt{2/\pi} u_{klm}(r)$ with the asymptotic behavior

$$v_{klm}(r) \underset{r \rightarrow \infty}{=} \sqrt{\frac{2}{\pi}} \sin(kr - l\frac{\pi}{2} + \delta_\ell), \quad (2.77)$$

and *momentum* normalization

$$\int_0^\infty v_{klm}^*(r) v_{klm}(r) dr = \delta(k - k'). \quad (2.78)$$

The next step is to see what other factors we need to obtain an energy normalized radial function. Since we have chosen $\langle r | klm \rangle = u_\ell(r)/kr$ and radial functions v_{klm} have already absorbed a factor $\sqrt{2/\pi}$, then the *energy* normalized radial functions are given with

$$v_{Elm}(r) = \sqrt{\frac{m}{\hbar^2 k}} v_{klm}(r). \quad (2.79)$$

Their asymptotic behavior is

$$v_{Elm}(r) \underset{r \rightarrow \infty}{=} \sqrt{\frac{2m}{\pi \hbar^2 k}} \sin(kr - l\frac{\pi}{2} + \delta_\ell), \quad (2.80)$$

and the normalization satisfies

$$\int_0^\infty v_{Elm}(r) v_{E'\ell m}(r) dr = \delta(E - E'), \quad (2.81)$$

as expected. Once more for reasons of clarity, we give the connection of energy normalized radial functions to $u_{klm}(r)$ functions

$$v_{Elm}(r) = \sqrt{\frac{2}{\pi} \frac{m}{\hbar^2 k}} u_{klm}(r). \quad (2.82)$$

The main points to ponder: the functions $|klm\rangle$ are not normalized, the radial functions $u_{klm}(r)$ do not absorb the $1/k$ factor, and the radial measure in the integration is $r^2 dr$ in one case while in the other it is dr . Most of the time in scattering the only part of the normalization that is important is the square root of the $1/k$ factor.

2.5 Coupled channel formalism

The method of partial wave analysis applied to the case of a spherically symmetric potential yields partial phase shifts, which can then be used to construct the total cross section. The Schrödinger equation for the total wave function is replaced by a set of radial equations; one for each partial wave. Due to the rotational invariance of the interaction, there are no potential terms coupling different radial equations, so they can be treated separately. As hinted in Sec. 2.2, if we do not have spherical symmetry, we need a set of coupled equations. That is the price of reducing multidimensional integration of the Schrödinger equation to one-dimensional integration. The subject is further complicated by the introduction of other degrees of freedom, such as spin. Depending on the choice of the states for the channels, the problem can be simplified if only a limited number of channels are coupled.

In this work the Hamiltonian describing the physics of scattering atoms can be presented in the following general form

$$\hat{H} = \hat{H}^0(x) + \hat{V}(x, s) + \hat{H}_{int}(s). \quad (2.83)$$

The variable x represents some particular degree of freedom we are interested in and the variable s represents all remaining degrees of freedom. We assume that we are able to find the eigenstates of $\hat{H}_{int}$, either analytically or numerically. In the time independent Schrödinger equation

$$H\Psi(x, s) = E\Psi(x, s), \quad (2.84)$$

we use the eigenstate functions $\psi_n(s)$ of the Hamiltonian $\hat{H}_{int}$ to expand the solution,

$$\Psi(x, s) = \sum_n F_n(x) \psi_n(s). \quad (2.85)$$

The underlying assumption is that the set $\{\psi_n\}$ forms a complete basis in the space of functions that depend on the variable s . This set can then be used to account for the s dependence of the total wave function. The dependence on the variable x is transferred to the wave functions $F_n(x)$ which are usually referred to as the channel wave functions. The wave functions ψ_n or quantum numbers that define the eigenstates of H_{int} are referred to as channels as well.

Substituting (2.85) into (2.84) and performing the integration over the variable s gives

$$(H_n^0 + V_n + E_i - E) F_i(x) = - \sum_{i' \neq i} V_{ii'} F_{i'}(x), \quad (2.86)$$

a set of equations where each channel wave function is connected to other channel wave functions through a set of numbers

$$V_{ii'}(x) = \int ds \psi_i^*(s) V(x, s) \psi_{i'}(s) \quad (2.87)$$

representing the coupling matrix $\hat{V}$.

The partitioning of the total Hamiltonian is useful only if there is a small number of channels connected through the coupling $V(x, s)$, otherwise it is just a failed attempt to avoid multidimensional integration. Two typical scenarios exist when couplings

are small compared to the diagonal part of the Hamiltonian $H_u^0 + V_u$ or when, owing to the presence of a symmetry, only a small number of channels are coupled.

The connection of this formalism to our work is established by identifying the magnetic dipolar interaction as the term that couples spatial (x) and spin (s) coordinates. The atomic hyperfine interaction (H_{int}) provides the channel states $\psi_i(s)$. The channel wave expansion (using angular separation) is given as

$$\Psi = \sum_{\ell m} \frac{u_{\ell m}(r)}{r} Y_{\ell m}(r) \psi_i(s), \quad (2.88)$$

where $\psi_i(s)$ are the eigenstates of the atomic hyperfine interaction. Then, (2.86) assumes the following form

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_u(r) + E_i - E \right) u_i(r) = - \sum_{i' \neq i} V_{ii'}(r) u_{i'}(r). \quad (2.89)$$

Energetically open channels are defined with respect to the scattering energy (E) as $E_i > E$, and energetically closed channels as $E_i < E$. This classification is justified only if the coupling potential terms vanish for large r , so it is assumed that the asymptotic limits of diagonal terms are incorporated into the channel energies E_i . The ‘internal’ energies serve as thresholds which determine whether the motion in a particular channel is free or restricted. Namely, if $E > E_i$, then the motion in that channel is free and we call the channel i open, while when $E < E_i$, the motion is bounded and we call the channel closed. There are two extreme limits that are associated with a single-channel situation. The first one is when the total energy E is below the lowest channel energy, which means that the motion in all channels is bounded and this limit represents a truly bound coupled state. The second situation is where the total energy is above the lowest channel energy, which means that the motion in at least one channel is free. Since, in this case, we can always find a solution

for the lowest channel independently of the other channels (unless closed channels do not support the bound state), we conclude that E belongs to the continuous part of the energy spectrum.

2.5.1 Multichannel scattering matrices

The multichannel scattering wave function

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_{\alpha} F_{\alpha}(\mathbf{R}) \psi_{\alpha}(\mathbf{r}) \quad (2.90)$$

has to satisfy the scattering boundary condition

$$\Psi(\mathbf{R}, \mathbf{r}) \underset{R \rightarrow \infty}{=} e^{i\mathbf{k}_{\beta} \cdot \mathbf{R}} \psi_{\beta}(\mathbf{r}) + \sum_{\alpha} f_{\alpha\beta}(\hat{\mathbf{k}}, \hat{\mathbf{R}}) \frac{e^{k_{\alpha} R}}{R} \psi_{\alpha}(\mathbf{r}), \quad (2.91)$$

where $\hat{\mathbf{R}} = \mathbf{R}/R$. The first term describes a plane wave in the entrance channel β , while the second term describes the scattered wave decomposed into outgoing waves in the channels α (including the elastic scattering channel β). The $f_{\alpha\beta}(\hat{\mathbf{k}}, \hat{\mathbf{R}})$ are generalizations of single-channel scattering amplitudes, $f_{\alpha\alpha}$ being the elastic and $f_{\alpha\beta}$ the inelastic scattering amplitudes. The asymptotic wave numbers are

$$k_{\alpha}^2 = k_{\beta}^2 + \frac{2m}{\hbar^2} (E_{\beta} - E_{\alpha}), \quad (2.92)$$

where E_{α} are channel energies.

The differential cross section

$$\frac{d\sigma_{\alpha\beta}(\hat{\mathbf{k}}, \hat{\mathbf{R}})}{d\Omega_{\hat{\mathbf{R}}}} \underset{r \rightarrow \infty}{=} \frac{k_{\alpha}}{k_{\beta}} |f_{\alpha\beta}(\hat{\mathbf{k}}, \hat{\mathbf{R}})|^2 \quad (2.93)$$

is integrated over the direction of the scattered atoms to give partial cross sections

$$\sigma_{\alpha\beta}(\hat{\mathbf{k}}) = \frac{k_\alpha}{k_\beta} \int |f_{\alpha\beta}(\hat{\mathbf{k}}, \hat{\mathbf{R}})|^2 d\Omega_{\hat{\mathbf{R}}} . \quad (2.94)$$

These cross sections are further integrated over the direction of the incident atoms and divided by the full space angle (4π) to obtain the cross sections averaged over the incident direction

$$\sigma_{\alpha\beta} = \frac{1}{4\pi} \int \sigma_{\alpha\beta}(\hat{\mathbf{k}}) d\Omega_{\hat{\mathbf{k}}} . \quad (2.95)$$

To avoid integration over variables R_x, R_y , and R_z , the partial wave decomposition

$$F_\alpha(\mathbf{R}) = \sum_{\ell_\alpha m_\alpha} \frac{F_{\alpha\ell_\alpha m_\alpha}(R)}{R} Y_{\ell_\alpha m_\alpha}(\hat{\mathbf{R}}) \quad (2.96)$$

is used to introduce amplitudes $F_{\alpha\ell_\alpha m_\alpha}(R)$. Though the states $\psi_\alpha(\mathbf{r})Y_{\ell_\alpha m_\alpha}(\hat{\mathbf{R}})$ are not physically accessible, they are still referred to as channel states and the amplitudes $F_{\alpha\ell_\alpha m_\alpha}(R)$ as channel wave functions. The decomposition (2.96) generally enables us to set up a system of coupled equations for the amplitudes $F_{\alpha\ell_\alpha m_\alpha}(R)$. Formally, it is an infinite system of equations with no practical value unless the number of equations can be reduced. In the ultracold regime, only a small number of partial waves are included, with the actual number depending on the collision energy. Given the number of channels (n_α) and the maximum value of angular momentum (ℓ_{max}), we have $N = n_\alpha(\ell_{max} + 1)^2$ coupled equations. Since we are dealing with a system of N coupled equations of the second order, there are $2N$ solutions on which we impose boundary conditions

$$F_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta}(R) \underset{R \rightarrow 0}{=} 0 , \quad (2.97)$$

and

$$F_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta}(R) \underset{R \rightarrow \infty}{=} \delta_{\alpha\beta} \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} \frac{e^{-i(k_\alpha R - l_\alpha \frac{\pi}{2})}}{\sqrt{k_\alpha}} - \frac{e^{i(k_\alpha R - l_\alpha \frac{\pi}{2})}}{\sqrt{k_\alpha}} S_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta} , \quad (2.98)$$

where the index $\beta\ell_\beta m_\beta$ determines the ingoing spherical wave (amplitudes divided by R enter the full solution) in the ‘channel’ $\alpha\ell_\alpha m_\alpha$. The numbers $S_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta}$ form the S -matrix. The purpose of the square root in the denominator is to normalize the S -matrix according to

$$1 = \sum_{\alpha\ell_\alpha m_\alpha} |S_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta}|^2. \quad (2.99)$$

The so-called flux normalization ensures that the ingoing flux in the ‘channel’ $\beta\ell_\beta m_\beta$ is distributed to all ‘channels’ $\alpha\ell_\alpha m_\alpha$. The channel wave functions that satisfy the boundary condition (2.91) are

$$F_{\alpha\beta}(\mathbf{R}) = \frac{2\pi}{R\sqrt{k_\beta}} \sum_{\ell_\alpha m_\alpha} \sum_{\ell_\beta m_\beta} i^{l_\beta+1} F_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta}(R) Y_{\ell_\beta m_\beta}^*(\hat{\mathbf{k}}) Y_{\ell_\alpha m_\alpha}(\hat{\mathbf{R}}) . \quad (2.100)$$

The particulars of this decomposition are evident after the following asymptotic forms,

$$F_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta}(R) \underset{R \rightarrow \infty}{=} -2i \frac{\hat{j}_{\ell_\alpha}(k_\alpha R)}{\sqrt{k_\alpha}} \delta_{\alpha\beta} \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} + i^{-\ell_\alpha} \frac{e^{ik_\alpha R}}{\sqrt{k_\alpha}} T_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta} , \quad (2.101)$$

are substituted into $F_{\alpha\beta}(\mathbf{R})$. The T -matrix elements are connected to S -matrix elements through

$$T_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta} = \delta_{\alpha\beta} \delta_{l_\alpha l_\beta} \delta_{m_\alpha m_\beta} - S_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta} . \quad (2.102)$$

The asymptotic channel wave functions are

$$F_{\alpha\beta}(\mathbf{R}) \underset{R \rightarrow \infty}{=} \delta_{\alpha\beta} e^{i\mathbf{k}_\alpha R} + f_{\alpha\beta}(\hat{\mathbf{k}}, \hat{\mathbf{R}}) \frac{e^{ik_\alpha R}}{R}, \quad (2.103)$$

where the scattering amplitudes for the transition $\beta \rightarrow \alpha$

$$f_{\alpha\beta}(\hat{\mathbf{k}}, \hat{\mathbf{R}}) = \frac{2\pi}{\sqrt{k_\alpha k_\beta}} \sum_{\ell_\alpha m_\alpha} \sum_{\ell_\beta m_\beta} i^{\ell_\beta - \ell_\alpha + 1} T_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta} Y_{\ell_\beta m_\beta}^*(\hat{\mathbf{k}}) Y_{\ell_\alpha m_\alpha}(\hat{\mathbf{R}}) \quad (2.104)$$

are expressed using the T -matrix.

Although $\hat{\mathbf{k}}_\alpha$ and $\hat{\mathbf{k}}_\beta$ appear to depend on channel indices, in practice they do not: $\hat{\mathbf{k}}_\beta$ and $\hat{\mathbf{k}}_\alpha$ are the direction of the incoming and scattered particles, where the latter is fixed by the direction of observation $\mathbf{R}/R$.

We proceed with the integration of the differential cross section using the orthogonality of spherical polynomials to obtain the incident direction-dependent integral cross sections

$$\sigma_{\alpha\beta}(\hat{\mathbf{k}}) = \frac{4\pi^2}{k_\beta^2} \sum_{\ell_\alpha m_\alpha} \sum_{\ell_\beta m_\beta} \sum_{\ell'_\beta m'_\beta} i^{\ell_\beta - \ell'_\beta} Y_{\ell'_\beta m'_\beta}(\hat{\mathbf{k}}) Y_{\ell_\beta m_\beta}^*(\hat{\mathbf{k}}) T_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta} T_{\alpha\ell_\alpha m_\alpha, \beta\ell'_\beta m'_\beta}^*. \quad (2.105)$$

The integral cross section for the scattering of two atoms into channel α from the incident channel β is obtained by averaging over the direction of the incoming atom

$$\sigma_{\alpha\beta} = \frac{1}{4\pi} \int \sigma_{\alpha\beta}(\hat{\mathbf{k}}) d\Omega_{\hat{\mathbf{k}}} = \frac{\pi}{k_\beta^2} \sum_{\ell_\alpha m_\alpha} \sum_{\ell_\beta m_\beta} |T_{\alpha\ell_\alpha m_\alpha, \beta\ell_\beta m_\beta}|^2. \quad (2.106)$$

2.5.2 S matrix computation

A real log-derivative matrix is the basic matrix from which we calculate a real K matrix, see App. A, which is connected to a complex S matrix by

$$S = \frac{1 + iK}{1 - iK} . \quad (2.107)$$

The imaginary and real parts of the S matrix are obtained from

$$(1 + K^2)S_I = 2K, \quad \text{and} \quad S_R = 1 - KS_I . \quad (2.108)$$

S_I is obtained either by using the inverse of the $1 + K^2$ matrix

$$S_I = (1 + K^2)^{-1}(2K), \quad (2.109)$$

or by applying the linear equation system solver to (2.108). For S_R , we use (2.108). When possible, the linear equation system solvers should be used instead of an explicit matrix inversion.

Along the same lines, when evaluating the K matrix which in the log-derivative method has the form

$$K = BA^{-1}, \quad (2.110)$$

we should apply the linear equation system solver to

$$A^T K = B^T. \quad (2.111)$$

If some K matrix elements are large, i.e. the condition number is large, we should use the K^{-1} matrix obtained from

$$B^T K^{-1} = A^T . \quad (2.112)$$

For this case, (2.108) is replaced by

$$S_I = K^{-1}(1 - S_R) \quad \text{and} \quad (1 + (K^{-1})^2)(1 - S_R) = 2 . \quad (2.113)$$

In general, the inversion of a complex matrix

$$C = A + iB = A(1 + iA^{-1}B). \quad (2.114)$$

can be reduced to inversion of real matrices only. By inserting

$$1 = (1 - iA^{-1}B)^{-1}(1 - iA^{-1}B) \quad (2.115)$$

into

$$C^{-1} = (1 + iA^{-1}B)^{-1} \cdot 1 \cdot A^{-1}, \quad (2.116)$$

we obtain the desired form

$$C^{-1} = (1 + (A^{-1}B)^2)^{-1}(1 - iA^{-1}B)A^{-1}. \quad (2.117)$$

2.6 Scattering length

The role of the scattering length in low-energy collisions studies cannot be overemphasized. The basic fact is that at very low energies the elastic cross section can be expressed using the scattering length only,

$$\sigma = 4\pi a^2 \tag{2.118}$$

One could calculate the scattering length directly from the dependence of the s -wave ($\ell = 0$) phase shift on the asymptotic momentum k , as per

$$\lim_{k \rightarrow 0} k \cot \delta(k) = -\frac{1}{a}. \tag{2.119}$$

This approach is good for an initial estimate of the scattering length. Rather than give an extensive list of the ever-increasing number of methods to obtain an accurate value for the scattering length, we prefer to outline a simple method of computing it (Ionel Simbotin, p.c.).

The basic problem in computing the scattering length is that most methods used to obtain the scattering length by direct solving of the Schrödinger equation are not optimized for the case of zero energy. The closer to zero energy we are, the further out we have to integrate. This places a burden on computational time and precision so we must stop the integration at some finite distance and try to recover from the truncation error by changing the integration variable, which should compact the region from the cutoff point to infinity. However, for any energy different than zero, we cannot avoid the oscillatory character of the solution by merely changing the integration variable. After the change of variable, the solution in the asymptotic region still contains an infinite number of oscillations that cannot be covered with a finite number of integration steps in a satisfactory manner.

The situation changes qualitatively when we set the scattering energy to zero. The oscillations in the asymptotic region disappear and the wave function approaches a straight line;

$$u(r) \underset{r \rightarrow \infty}{\sim} (r - a) . \quad (2.120)$$

By changing the integration variable $r \rightarrow x = -r_m/r$ in the radial Schrödinger equation, we can map the infinite interval $[r_m, \infty]$ of r onto the finite interval $[-1, 0]$ of x and since this transformation does not introduce oscillatory behavior, the solution can be recovered using a finite number of steps. When the energy is zero ($k = 0$), the Schrödinger equation for $u(r)$,

$$\frac{du(r)}{dr^2} - \frac{2m}{\hbar^2} V(r) u(r) = 0 , \quad (2.121)$$

becomes, after the change of variable,

$$\frac{du(x)}{dx^2} + \frac{2}{x} \frac{du(x)}{dx} - \frac{2m}{\hbar^2} \left[\frac{r_m^2 V(x)}{x^4} \right] u(x) = 0. \quad (2.122)$$

This equation is further reduced to

$$\frac{d\phi(x)}{dx^2} - \frac{2m}{\hbar^2} \left[\frac{r_m^2 V(x)}{x^4} \right] \phi(x) = 0 \quad (2.123)$$

for the function $\phi(x) = xu(x)$. The asymptotic form of the function $\phi(x)$ when $x \rightarrow 0$ ($r \rightarrow \infty$) is

$$\phi(x) \underset{x \rightarrow 0}{\sim} r_m + ax. \quad (2.124)$$

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$$\phi(x) \underset{x \rightarrow 0}{\sim} r_m + ax. \quad (2.124)$$

From this, it follows that the scattering length is

$$a = r_m \left[\frac{\phi'}{\phi} \right]_{x=0}. \quad (2.125)$$

The calculation of the scattering length using the log-derivative method consists of two steps. In the first step, we propagate the solution $u(r)$ (left side of Fig. 2.1) using the potential $V(r)$ to the distance r_m and extract the log-derivative of the

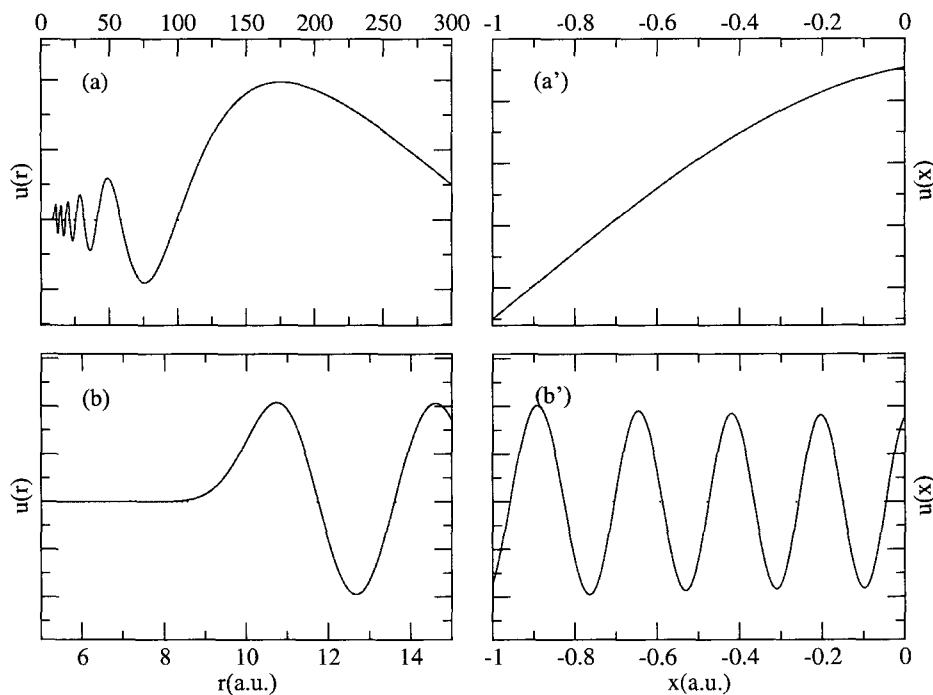


Figure 2.1: Scattering radial functions $u(r)$ and $\phi(x) = xu(x)$, where $x = -r_m/r$. Left panes a and b show radial functions integrated up to $r_m = 300$ and $r_m = 15$ respectively. The rest of the real axis is covered with $\phi(x)$ (solution of (2.123)) in panes a' and b' . Pane a' shows a monotonic function that may be obtained with any constant step propagator using a very small number of integration steps. Pane b' shows that we can perform the change of the variable also inside the oscillatory region.

function $u(r)$ at r_m . Then we construct the value of the log-derivative for $\phi(x)$ at $x = -1$ ($r = r_m$),

$$\left[\frac{\phi'}{\phi} \right]_{x=-1} = r_m \left[\frac{u'}{u} \right]_{r=r_m} - 1, \quad (2.126)$$

which we use to initiate the second step where we propagate the solution $\phi(x)$ (right side of Fig. 2.1) from $x = -1$ to $x = 0$ using $r_m^2 V(x)/x^4$ as the driving potential. The integration yields the log-derivative of $\phi(x)$ at $x = 0$, which is used in (2.125) to extract the scattering length.

The limitations of the method are inferred by analyzing (2.123). If we use the inverse power law potentials $\sim 1/r^n$, the driving potential in (2.123) becomes $\sim x^{n-4}$. For $n > 4$ the Schrödinger equation (2.123) describes a free particle when $x \rightarrow 0$. To extract the scattering length, (2.125) must support two independent solutions with the following $x = 0$ asymptotic behavior

$$f(x) \rightarrow 1 \quad \text{and} \quad g(x) \rightarrow x, \quad (2.127)$$

which is clearly the case for $n > 4$. In the case of $n = 4$, the potential does not go to zero when $x \rightarrow 0$, instead it converges to a constant. The independent solutions $\sinh(\alpha x)/\alpha$ and $\cosh(\alpha x)$ converge to functions x and 1 in the asymptotic region. The constant α depends on the asymptotic limit of the driving potential. Table 2.1 shows the effect of the integration cutoff. We use a Lennard-Jones type (C.28) potential with the following parameters: $V_0 = 20$, $r_0 = 10$, $n = 4$ and $2 \cdot m = 1$. A variable step Runge-Kutta method is used to integrate a radial Schrödinger equation. The left-hand side of the table shows very slow convergence, since even at 100 000 we are not able to obtain the exact value for the scattering length. The right-hand side of the table shows that it is possible to recover 10-12 digits of the exact value by changing the integration variable at $r = r_m$.

Table 2.1: The effect of truncation ($n = 4$ potential.

truncation		no truncation $r \rightarrow x$	
r_m	b	r_m	c
1000	260.058	exact ^a	99.475231045911784
10000	119.251	300 ^b	99.475231045938131
100000	101.473	15 ^c	99.475231046737434

^a a see Sec. C.3

^b see Fig. 2.1, panes: a and a'

^c see Fig. 2.1, panes: b and b'

2.6.1 Scattering length: multichannel case

The workhorse expression for the calculation of the scattering length in the multichannel formalism is the low-energy limit of the S matrix

$$S \underset{k \rightarrow 0}{=} \exp(-i2ka), \quad (2.128)$$

where k is the open channel asymptotic wave number, and a , the scattering length, is by definition complex in order to describe inelastic collision. The linear approximation of the S matrix element

$$\exp(-i2ka) \sim 1 - i2ka, \quad (2.129)$$

valid for $ka \rightarrow 0$, gives for the real and imaginary parts of the scattering length

$$a_R = -\frac{S_I}{2k} \quad \text{and} \quad a_I = \frac{S_R - 1}{2k}. \quad (2.130)$$

Quadratic approximation is obtained using

$$\tanh^{-1}(x) = \frac{1}{2} \ln\left(\frac{1+x}{1-x}\right) \quad \text{and} \quad \tanh(ix) = i \tan(x), \quad (2.131)$$

to get

$$\tan^{-1}(x) = \frac{1}{2i} \ln\left(\frac{1+x}{1-x}\right), \quad (2.132)$$

where we set $x = -ka$, and keep x small enough to apply

$$\frac{1+x}{1-x} = \exp(2x) = S. \quad (2.133)$$

The final expression for the scattering length

$$a = -\frac{1}{k} \tan\left(\frac{1}{2i} \ln(S)\right), \quad (2.134)$$

is more suitable for higher values of k than (2.129), which tends to break down.

CHAPTER 3

NUMERICAL TECHNIQUES

3.1 Propagators

Two widely used numerical techniques for solving the time-independent Schrödinger equation,

$$\frac{d^2\Psi(r)}{dr^2} + \frac{2m}{\hbar^2}(E - V(r))\Psi(r) = 0, \quad (3.1)$$

are Johnson's log-derivative method [43] and the Numerov method [44] with its renormalized variant [45]. Both methods have a per step size (h) error of the order $\sim (h)^6$, and are very simple to implement irrespective of whether a single or multichannel problem is being solved. Since both methods were used in this work, I will describe them here.

Before going any further, it is important to specify the notation used in this chapter. As it is customary, an equidistant radial grid with step h is assumed where any quantity, X , evaluated at grid point r_n is represented by X_n . Following the notation in [45], we also define

$$Q_n = Q(r_n) = \frac{2m}{\hbar^2}(E - V(r_n)). \quad (3.2)$$

3.1.1 Log-derivative method

Since B. R. Johnson published the log-derivative method [43], a number of its variants have appeared, most notably the one described in [46]. This propagator

owes its popularity to two features: the ability to pass through intervals containing a singularity, and simplicity. The log-derivative method's apparent simplicity should not be confused with the ease of its derivation. Unfortunately the original log-derivative method, which involves invariant embedding applied to the integral form of the Schrödinger equation, was never published. The numerical values of alternating weight factors in the method are a signature of Simpson's numerical integration. At the same time, the factor of $1/6$ next to the potential term stems from the correction factor for the discontinuity of the free Green's function at the middle of the integration segment.

Johnson's method. Using a two-point recursive scheme, with the requirement that the range of integration $[r_0, r_N]$ be split into an even number, N , of intervals of length h ,

$$y_n = (1 + hy_{n-1})^{-1}y_{n-1} - (h/3)w_n u_n, \quad (3.3)$$

one is able to obtain the logarithmic derivative of the wave function at the end of the integration range r_N

$$y_N = \Psi'(r_N)/\Psi(r_N). \quad (3.4)$$

The index n runs from 0 to N for the end points of the integration range $[r_0, r_N]$. The quantity u_n is computed as

$$u_n = \begin{cases} Q_n & n = 0, 2, 4, \dots, N, \\ \left(1 + \frac{h^2}{6}Q_n\right)^{-1} Q_n & n = 1, 3, 5, \dots, N-1, \end{cases} \quad (3.5)$$

while the weights w_n are given by

$$w_n = \begin{cases} 1 & n = 0, N, \\ 4 & n = 1, 3, 5, \dots, N-1, \\ 2 & n = 2, 4, 6, \dots, N-2. \end{cases} \quad (3.6)$$

The prescribed rule for the initialization of the propagation in the case of finite $Q(r_0)$ when $\Psi'(r_0) \neq 0$,

$$y_0 = \begin{cases} \infty & \text{if } \Psi_0 = 0, \\ \frac{\Psi'_0}{\Psi_0} - \frac{h}{3}Q_0 & \text{if } \Psi_0 \neq 0 \end{cases} \quad (3.7)$$

suggests that the connection between what is propagated and the true value of the log-derivative is

$$y_n = \frac{\Psi'_n}{\Psi_n} - \frac{h}{3}Q_n, \quad (3.8)$$

for even n , while for odd n , it has the role of a temporary variable whose only purpose is to connect log-derivative values at the end of a two step segment. The weight $\omega_N = 1$ for the final integration step suggests that (3.8) is already incorporated to produce the correct value for the log-derivative of a wave function at the end of the integration.

A variation to Johnson's propagation scheme [47], is used in this section. By introducing a new variable $z_n = hy_n$, and through a repeated use of the identity

$$1 - (1 + X)^{-1} = (1 + X)^{-1}X, \quad (3.9)$$

where X could be a number or a matrix, the log-derivative method can be expressed in terms of $\bar{z}_n = 1 + z_n$

$$\bar{z}_n = \begin{cases} -6 + \left(\frac{1}{8} + \frac{h^2}{48}Q_n\right)^{-1} - \bar{z}_{n-1}^{-1} & \text{for odd } n, \\ 2 - \frac{2}{3}h^2Q_n - \bar{z}_{n-1}^{-1}, & \text{for even } n. \end{cases} \quad (3.10)$$

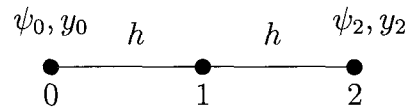
One should not forget to correct the factor $2/3$ in front of h^2Q_n when the last step is done. It should be changed to $1/3$ in order to extract the value of the log-derivative from $\bar{z}_N$ at the last integration point.

The comparative advantage of (3.10) over (3.3) becomes substantial in the coupled channel calculations where numbers become matrices. The original formulation has one unnecessary multiplication, owing to the term

$$(1 + hy_{n-1})^{-1}y_{n-1}, \quad (3.11)$$

which is avoided by the application of (3.9). The same applies to odd numbered u_n in (3.5). Together with the use of the linear algebra algorithms for symmetric matrices, an order of magnitude speedup can be achieved with this method.

A simple derivation of the log-derivative method is presented in [48]. Let us consider any segment made of two intervals,



where index 0 serves as a label for all the quantities on the left side and index 2 denotes all the quantities on the right side, while index 1 specifies the midpoint. The

two main results of [48] are an equation that connects the log-derivatives of a wave function

$$\left(1 - hy_2 - \frac{h^2}{3}Q_2\right)^{-1} + \left(1 + hy_0 - \frac{h^2}{3}Q_0\right)^{-1} = 8 \left(1 + \frac{h^2}{6}Q_1\right)^{-1} - 6, \quad (3.12)$$

and an accompanying equation that connects the wave functions at segment ends.

$$\psi_2 \left(1 - hy_2 - \frac{h^2}{3}Q_2\right) = \psi_0 \left(1 + hy_0 - \frac{h^2}{3}Q_0\right). \quad (3.13)$$

In the equations above, the function values at the midpoint ($n = 1$) and its log-derivatives are absent. Only the value of the potential interaction at the midpoint is present.

To show that (3.10) follows from (3.12), let us first define $\bar{z}$ with

$$\bar{z} = 1 + hy - \frac{h^2}{3}Q, \quad (3.14)$$

and express (3.12) in terms of $\bar{z}$ at segment ends:

$$\left(\left(2 - \frac{2h^2}{3}Q_2\right) - \bar{z}_2\right)^{-1} + \bar{z}_0^{-1} = 8 \left(1 + \frac{h^2}{6}Q_1\right)^{-1} - 6. \quad (3.15)$$

From this equation, we get the value of $\bar{z}$ at the right segment end

$$\bar{z}_2 = \left(2 - \frac{2h^2}{3}Q_2\right) - \left(8 \left(1 + \frac{h^2}{6}Q_1\right)^{-1} - 6 - \bar{z}_0^{-1}\right)^{-1}. \quad (3.16)$$

For the sake of convenience, we use the symbol $\bar{z}_1$ to designate

$$8 \left(1 + \frac{h^2}{6}Q_1\right)^{-1} - 6 - \bar{z}_0^{-1}. \quad (3.17)$$

The values of $\bar{z}$ at the segment end points can be used to extract the log-derivative, while the midpoint values of $\bar{z}$ cannot.

Forward integration. The $\bar{z}_0 \rightarrow \bar{z}_1 \rightarrow \bar{z}_2$ sequence is executed first by calculating the initial value of $\bar{z}$ according to

$$\bar{z}_0 = 1 + hy_0 - \frac{h^2}{3}Q_0, \quad (3.18)$$

where y_0 is the initial value of the wave function log-derivative. Next, we move one step to the right and evaluate $\bar{z}$ at the midpoint

$$\bar{z}_1 = -6 + \left(\frac{1}{8} + \frac{h^2}{48}Q_1 \right)^{-1} - \bar{z}_0^{-1}. \quad (3.19)$$

Last, we use the value of $\bar{z}$ at the midpoint to obtain the value of $\bar{z}$ at the right end of the segment

$$\bar{z}_2 = \left(2 - \frac{2h^2}{3}Q_2 \right) - \bar{z}_1^{-1}. \quad (3.20)$$

At this point, either we extract the value of the log-derivative at the right segment end, y_2 , by solving

$$\bar{z}_2 = 1 + hy_2 - \frac{h^2}{3}Q_2, \quad (3.21)$$

or we continue propagating $\bar{z}$ as many segments as needed before extracting the log-derivative of the wave function.

The function value at the right end of the segment, ψ_2 , is connected to the function value at the left end of the segment, ψ_0 , through

$$\psi_0 = \bar{z}_0^{-1} \bar{z}_1^{-1} \psi_2. \quad (3.22)$$

The above equation stresses the fact that in practice we propagate the log-derivatives from left to right, and the wave function is propagated from right to left after setting an initial value for the wave function at the right end of an integration range.

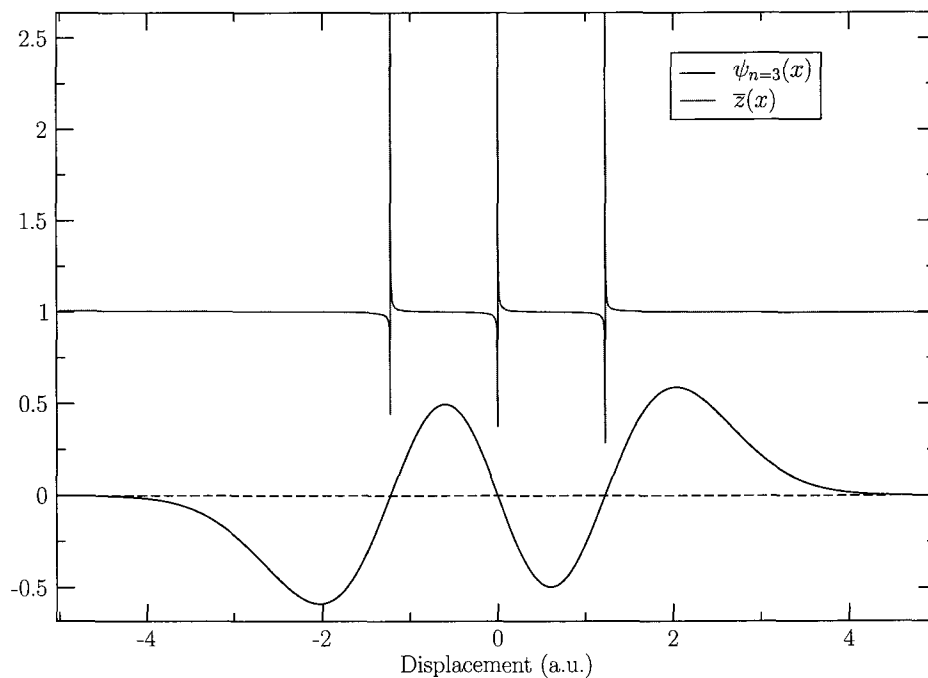


Figure 3.1: Black line: $\psi_{n=3}(x)$ eigenfunction of a Harmonic oscillator; Red line: $\bar{z}(x) = 1 + \hbar\psi'(x)/\psi(x) - \hbar^2 Q(x)/3$.

A typical example of $\bar{z}$ and a wave function, calculated for an arbitrary small step, is presented in Fig. 3.1. The value of $\bar{z}$ generally stays around 1 and changes significantly only around the zeroes of the wave function.

Backward integration. The $\bar{z}_2 \rightarrow \bar{z}_1 \rightarrow \bar{z}_0$ sequence follows from the forward integration scheme, where indices 0 and 2 swap positions and the sign of the integration step changes, $h \rightarrow -h$. The step sign change is reflected in the equation

$$\bar{z} = 1 - hy - \frac{h^2}{3}Q. \quad (3.23)$$

The segment description does not change: $n = 0$ represents the left end of the segment and $n = 2$ represents the right end of the segment.

First, the initial value at the right end of the segment is calculated using

$$\bar{z}_2 = 1 - hy_2 - \frac{h^2}{3}Q_2, \quad (3.24)$$

where y_2 is the initial value of the wave function's log-derivative. Next, we move one step to the left and evaluate $\bar{z}$ at the midpoint

$$\bar{z}_1 = -6 + \left(\frac{1}{8} + \frac{h^2}{48}Q_1 \right)^{-1} - \bar{z}_2^{-1}. \quad (3.25)$$

Last, we use the value of $\bar{z}$ at the midpoint to obtain the value of $\bar{z}$ at the left end of the segment

$$\bar{z}_0 = \left(2 - \frac{2h^2}{3}Q_0 \right) - \bar{z}_1^{-1}. \quad (3.26)$$

At this point we either extract the value of the log-derivative at the left segment end, y_0 , by solving

$$\bar{z}_0 = 1 - hy_0 - \frac{h^2}{3}Q_0, \quad (3.27)$$

or continue propagating $\bar{z}$ as many segments as needed before extracting the log-derivative of the wave function.

The function value at the left end of the segment, ψ_0 , is connected to the function value at the right end of the segment, ψ_2 , through

$$\psi_2 = \bar{z}_2^{-1} \bar{z}_1^{-1} \psi_0 \quad (3.28)$$

The WKB approximate solution can be used to initiate the integration in the classically forbidden region. The radial Schrödinger equation expressed in terms of the log-derivative of the wave function,

$$y'(r) + y(r)^2 + Q(r) = 0, \quad (3.29)$$

then the WKB approximation amounts to neglecting the derivative term and solving the simple algebraic equation

$$y(r)^2 + Q(r) = 0. \quad (3.30)$$

For the case of forward propagation, from left to right, we set the log-derivative initial value using

$$y_0 = +\sqrt{|Q(r_0)|}, \quad (3.31)$$

while for backward propagation, from right to left, we use

$$y_N = -\sqrt{|Q(r_N)|}. \quad (3.32)$$

Fig. 3.2 demonstrates the relevant points. Here, $E < 0$, and we want a bounded solutions. In the classically forbidden region to the left of the inner turning point,

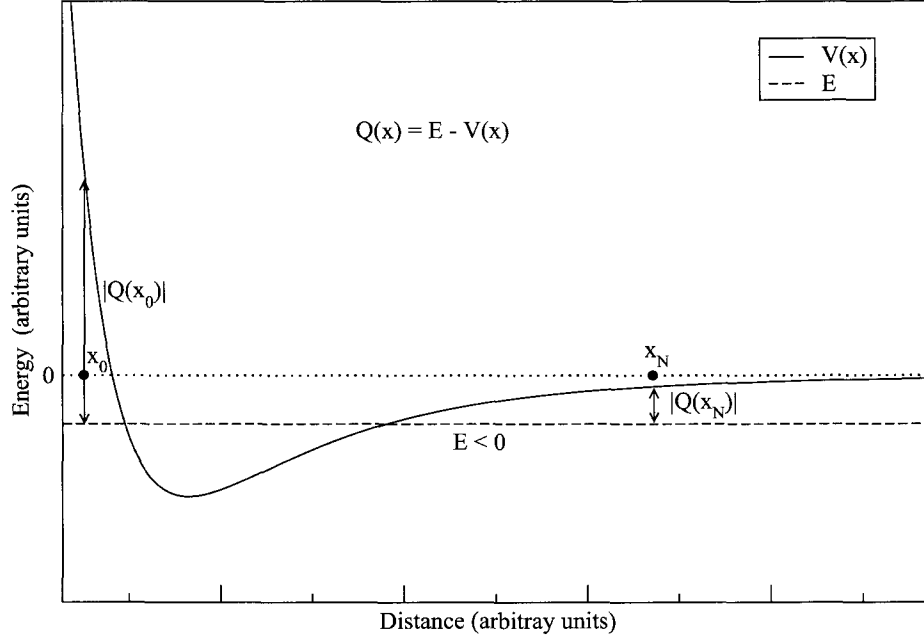


Figure 3.2: WKB boundary conditions.

the solution should decrease, hence $y > 0$. In the classically forbidden region to the right of the outside turning point, the solution should also decrease, hence $y < 0$. If the potential were described by a potential well, then the proper solutions in the forbidden region would behave as $\exp(\pm \kappa r)$, where the plus sign corresponds to a positive log-derivative and the minus sign to a negative log-derivative.

3.1.2 Renormalized Numerov method

The basis for the renormalized Numerov method [45] is the recurrence expression

$$(1 - T_{n+1})\Psi_{n+1} - (2 + 10T_n)\Psi_n + (1 - T_{n-1})\Psi_{n-1} = 0, \quad (3.33)$$

which connects the solutions at three consecutive points on the integration grid, where

$$T_n = -\frac{h^2}{12}Q_n. \quad (3.34)$$

If we first renormalize the wave function

$$F_n = (1 - T_n)\Psi_n \quad (3.35)$$

and define the ratio of the renormalized wave functions at two consecutive integration points, in matrix form for the multichannel case,

$$R_n = F_{n+1}F_n^{-1} \quad (3.36)$$

upon division by F_n , Eq. (3.33) gives the renormalized Numerov method iteration scheme

$$R_n = U_n - R_{n-1}^{-1}, \quad (3.37)$$

where

$$U_n = (1 - T_n)^{-1}(2 + 10T_n). \quad (3.38)$$

By rewriting U_n as

$$U_n = 12(1 - T_n)^{-1} - 10, \quad (3.39)$$

the renormalized Numerov method becomes adapted for the application of linear algebra routines which are optimized for symmetric matrices. The standard boundary condition, $\Psi(0) = 0$, is realized by setting $\Psi(r_0) = 0$ for the first grid point, and $\Psi(r_1) \neq 0$ for the second grid point. This in turn fixes the the initial value for the renormalized method

$$R_0^{-1} = 0. \quad (3.40)$$

3.2 Matching solutions

In the asymptotic region, $r \geq r_N$, where the interaction potentials, except the centrifugal term, should asymptotically vanish, the numerical solution $\Psi(r)$ can be expanded in terms of asymptotic functions

$$\Psi(r) \underset{r \gg r_N}{=} J(r)X - N(r)Y, \quad (3.41)$$

where X and Y are expansion matrices, and $J(r)$ and $N(r)$ are diagonal matrices,

$$J(r) = \begin{pmatrix} J_{oo}(r) & 0 \\ 0 & J_{cc}(r) \end{pmatrix}, \quad N(r) = \begin{pmatrix} N_{oo}(r) & 0 \\ 0 & N_{cc}(r) \end{pmatrix}, \quad (3.42)$$

constructed from the energy normalized, up to a factor $2m/\hbar\pi$, Riccati-Bessel functions. It should be noted that the Riccati-Bessel functions are the potential-free solutions, and similar solutions exist for $-1/r^\alpha$ -type potentials, such as $\alpha = 4$ (polarization) and $\alpha = 6$ (van der Waals) potentials. The general case is assumed, where open and closed channels are included and sorted by energy, from open (o) to closed (c) channels. The grouping of open and closed channels introduces a block structure in any matrix, M , that is represented in this basis,

$$M = \begin{pmatrix} M_{oo} & M_{oc} \\ M_{co} & M_{cc} \end{pmatrix}. \quad (3.43)$$

Multiplying (3.41) from the right by X^{-1} gives the scattering form of the wave function

$$\Psi(r)X^{-1} \underset{r \gg r_N}{=} J(r) - N(r)K, \quad (3.44)$$

where $K = YX^{-1}$ is the augmented scattering matrix. The open-open block K_{oo} in the augmented K matrix contains the normal scattering K matrix. Before going into the details of finding the K matrix with the log-derivative or renormalized Numerov method, it is prudent to define the matching functions for open and closed channels.

Open channels. The matrix elements $J_u(r)$ and $N_u(r)$ are constructed using

$$J(r) = \frac{(kr)j_\ell(kr)}{\sqrt{k}} \text{ and } N(r) = \frac{(kr)n_\ell(kr)}{\sqrt{k}}, \quad (3.45)$$

where k is the asymptotic channel wave number and $j_\ell(kr)$ and $n_\ell(kr)$ are the spherical Bessel functions of the first and second kind. The open channel matrix elements $N_u(r)$ are constructed using

$$J(r) \xrightarrow{kr \gg 1} \frac{1}{\sqrt{k}} \sin(kr - \frac{\ell\pi}{2}), \quad (3.46)$$

$$N(r) \xrightarrow{kr \gg 1} -\frac{1}{\sqrt{k}} \cos(kr - \frac{\ell\pi}{2}). \quad (3.47)$$

Closed channels. The matrix elements $J_u(r)$ and $N_u(r)$ are constructed using

$$J(r) = \sqrt{\kappa r} I_{\ell+1/2}(\kappa r) \text{ and } N(r) = \sqrt{\kappa r} K_{\ell+1/2}(\kappa r), \quad (3.48)$$

where $\kappa = |k|$ is the absolute value of the asymptotic channel wave number and $I_{\ell+1/2}(\kappa r)$ and $K_{\ell+1/2}(\kappa r)$ are the modified Bessel functions of the first and second kind. The corresponding asymptotic forms are

$$J(r) \xrightarrow{\kappa r \gg 1} \frac{1}{2\pi} (\exp(\kappa r) - (-1)^\ell \exp(-\kappa r)),$$

$$N(r) \xrightarrow{\kappa r \gg 1} \frac{\pi}{2} \exp(-\kappa r). \quad (3.49)$$

A quick inspection of the matching functions for closed channels (3.49) shows that for large values of κr we might run into computational problems owing to the

presence of exponential functions. The fact that we need only an open-open block of the augmented K matrix gives a certain freedom in the choice of matching functions. As long as we leave K_{oo} unchanged, we are free to redefine the matching functions. Instead of $J(r)$ and $N(r)$, a new set or redefined Bessel functions

$$\bar{J}(r) = J(r)A, \quad \bar{N}(r) = N(r)B, \quad (3.50)$$

where A and B are constant matrices, can be used. The change of expansion matrices in (3.41)

$$X \rightarrow A^{-1}X, \quad Y \rightarrow B^{-1}Y, \quad (3.51)$$

causes the change in the augmented K matrix; a new augmented $\bar{K}$ matrix is related to the old one through

$$\bar{K} = B^{-1}KA. \quad (3.52)$$

3.2.1 K matrix: log-derivative method

In the log-derivative method, we get the log derivative of the wave function at the end of the grid, so we need to use the first derivative of (3.44),

$$\Psi'(r)X^{-1} = J'(r) - N'(r)K, \quad (3.53)$$

in order to find the log derivative of the solution

$$y = \Psi'(r)\Psi(r)^{-1} \quad (3.54)$$

at the final point r_N ,

$$y_N = (J'(r_N) - N'(r_N)K)(J(r_N) - N(r_N)K)^{-1}. \quad (3.55)$$

This can be in turn solved for the augmented K matrix,

$$K = (y_N N(r_N) - N'(r_N))^{-1}(y_N J(r_N) - J'(r_N)). \quad (3.56)$$

The augmented K matrix contains an open-open block, namely K_{oo} , which is used to construct the S matrix. Since closed-channel Bessel functions contain exponentially growing functions, large values of the product κr might cause an overflow. This problem can be alleviated by using the ratio of the derivative of the Bessel function to the function itself at the matching point r_N .

The short prescription for a change of $J(r)$ functions in the closed-channel space is [43]

$$J_{cc}(r_N) \rightarrow I, \text{ and } J'_{cc}(r_N) \rightarrow J'_{cc}(r_N)J_{cc}(r_N)^{-1}, \quad (3.57)$$

and likewise the $N(r)$ functions in the closed-channel space change according to

$$N_{cc}(r_N) \rightarrow I, \text{ and } N'_{cc}(r_N) \rightarrow N'_{cc}(r_N)N_{cc}(r_N)^{-1}. \quad (3.58)$$

The open channel space functions $J(r)$ and $N(r)$ are left unchanged. A direct way to see why this prescription works is to assume the $\exp(\pm\kappa r)$ behavior in the closed channels and to evaluate the needed terms

$$J'_{cc}(r_N)J_{cc}(r_N)^{-1} = +\kappa, \quad (3.59)$$

$$N'_{cc}(r_N)N_{cc}(r_N)^{-1} = -\kappa. \quad (3.60)$$

This shows that we are evaluating a quantity very close to the absolute value of the asymptotic wave number, depending on how deep we are in the forbidden region at the end of the integration grid. We would still have to check that K_{oo} is independent of the above-mentioned choice of matching functions.

The long prescription would be to find matrices A and B from (3.50) and evaluate the augmented K matrix using $\bar{J}(r)$ and $\bar{N}(r)$, making sure that K_{oo} is left unchanged. A choice of matrices A and B in (3.50) that corresponds to Johnson's matching procedure is:

$$A = \begin{pmatrix} I & 0 \\ 0 & J_{cc}^{-1}(r_N) \end{pmatrix}, \quad B = \begin{pmatrix} I & 0 \\ 0 & N_{cc}^{-1}(r_N) \end{pmatrix}. \quad (3.61)$$

This choice is consistent with (3.60). The redefined Bessel matrices evaluated at the matching point are

$$\bar{J}(r_N) = \begin{pmatrix} J_{oo}(r_N) & 0 \\ 0 & I \end{pmatrix}, \quad \bar{N}(r_N) = \begin{pmatrix} N_{oo}(r_N) & 0 \\ 0 & I \end{pmatrix}. \quad (3.62)$$

The corresponding derivatives are

$$\bar{J}'(r_N) = \begin{pmatrix} J'_{oo}(r_N) & 0 \\ 0 & J'_{cc}(r_N)J_{cc}(r_N)^{-1} \end{pmatrix}, \quad (3.63)$$

and

$$\bar{N}'(r_N) = \begin{pmatrix} N'_{oo}(r_N) & 0 \\ 0 & N'_{cc}(r_N)N_{cc}(r_N)^{-1} \end{pmatrix}. \quad (3.64)$$

The explicit form of the $\overline{K}$ matrix, obtained using (3.52),

$$\overline{K} = \begin{pmatrix} K_{oo} & K_{oc}J_{cc}(r_N)^{-1} \\ N_{cc}(r_N)K_{co} & N_{cc}(r_N)K_{cc}J_{cc}(r_N)^{-1} \end{pmatrix}, \quad (3.65)$$

shows that the physical K matrix (K_{oo}) is invariant. The reader is referred to [49] to verify that K_{oo} , defined for open channels only, could be used to find the physical S matrix.

3.2.2 K matrix: renormalized Numerov method

Since a ratio of the renormalized functions is propagated, we need to renormalize the matching functions by performing the following substitution for $J(r)$,

$$J(r_N) \rightarrow (1 - T_N)J(r_N), \quad (3.66)$$

and for $N(r)$,

$$N(r_N) \rightarrow (1 - T_N)N(r_N). \quad (3.67)$$

Then the ratio of renormalized functions

$$R_N = F_{N+1}F_N^{-1} \quad (3.68)$$

can be used in an equation that can be solved for the unknown augmented K matrix.

The solution is

$$K = (R_N n(r_N) - n(r_{N+1}))^{-1} (R_N j(r_N) - j(r_{N+1})), \quad (3.69)$$

where $j(r)$ and $n(r)$ are the renormalized Riccati-Bessel functions. The notation is only by accident identical to the one adopted for spherical Bessel functions of the first and second kind. The augmented K matrix contains an open-open block, namely K_{oo} that is used to construct the S matrix. Since closed-channel Bessel functions contain exponentially growing functions in the asymptotic region, we use the ratio of closed-channel space Bessel functions at two consecutive points r_{N+1} and r_N at the matching point.

The short prescription for a change of $j(r)$ functions in the closed-channel space is [50]

$$j_{cc}(r_N) \rightarrow I, \text{ and } j_{cc}(r_{N+1}) \rightarrow j_{cc}(r_{N+1})j_{cc}(r_N)^{-1}, \quad (3.70)$$

and likewise the $n(r)$ functions in the closed-channel space change according to

$$n_{cc}(r_N) \rightarrow I, \text{ and } n_{cc}(r_{N+1}) \rightarrow n_{cc}(r_{N+1})n_{cc}(r_N)^{-1}. \quad (3.71)$$

The open channel space functions $j(r)$ and $n(r)$ are left unchanged. A direct way to see why this prescription works is to assume $\exp(\pm\kappa r)$ behavior in the closed channels and evaluate the needed terms

$$j_{cc}(r_{N+1})j_{cc}(r_N)^{-1} \sim \exp(+\kappa h), \quad (3.72)$$

$$n_{cc}(r_{N+1})n_{cc}(r_N)^{-1} \sim \exp(-\kappa h), \quad (3.73)$$

where $j(r)$ and $n(r)$ are Bessel functions up to a normalization factor $1 - T_N$. This shows that we are evaluating exponential functions for $\pm\kappa h$ which is smaller than $\pm\kappa r_N$ in magnitude by a factor of h/r_N . We would still have to check that K_{oo} is independent of the above-mentioned choice of matching functions.

The long prescription would be to find matrices A and B from (3.50) and evaluate the augmented K matrix using $\bar{J}(r)$ and $\bar{N}(r)$, making sure that K_{oo} is left unchanged. A choice of matrices A and B in (3.50) that corresponds to Johnson's matching procedure is:

$$A = \begin{pmatrix} I & 0 \\ 0 & j_{cc}^{-1}(r_N) \end{pmatrix}, \quad B = \begin{pmatrix} I & 0 \\ 0 & j_{cc}^{-1}(r_N) \end{pmatrix}, \quad (3.74)$$

keeping in mind that we use the renormalized matching functions

$$j(r) = (1 - T(r))J(r), \quad n(r) = (1 - T(r))N(r). \quad (3.75)$$

This choice is consistent with (3.73). The redefined Bessel matrices evaluated at point r_N are

$$\bar{j}(r_N) = \begin{pmatrix} j_{oo}(r_N) & 0 \\ 0 & I \end{pmatrix}, \quad \bar{n}(r_N) = \begin{pmatrix} n_{oo}(r_N) & 0 \\ 0 & I \end{pmatrix}. \quad (3.76)$$

The corresponding Bessel matrices at point r_{N+1} are

$$\bar{j}(r_{N+1}) = \begin{pmatrix} j_{oo}(r_{N+1}) & 0 \\ 0 & j_{cc}(r_{N+1})j_{cc}(r_N)^{-1} \end{pmatrix}, \quad (3.77)$$

and

$$\bar{n}(r_{N+1}) = \begin{pmatrix} n_{oo}(r_{N+1}) & 0 \\ 0 & n_{cc}(r_{N+1})n_{cc}(r_N)^{-1} \end{pmatrix}. \quad (3.78)$$

The explicit form of the $\overline{K}$ matrix, obtained using (3.52),

$$\overline{K} = \begin{pmatrix} K_{oo} & K_{oc}j_{cc}(r_N)^{-1} \\ n_{cc}(r_N)K_{co} & n_{cc}(r_N)K_{cc}j_{cc}(r_N)^{-1} \end{pmatrix}, \quad (3.79)$$

shows that the physical K matrix (K_{oo}) is invariant. The reader is referred to [49] to verify that K_{oo} , defined for open channels only, could be used to find the physical S matrix.

CHAPTER 4

INTERACTION HAMILTONIAN

4.1 Choices of Basis Sets

The electron spins, s_1, s_2 and the nuclear spins, i_1, i_2 of two atoms, can be coupled in different ways. In one scheme, we couple the electron and nuclear spins of each atom to obtain the spin

$$\mathbf{f}_i = \mathbf{s}_i + \mathbf{i}_i, \quad (i = 1, 2). \quad (4.1)$$

The basis adapted to this coupling scheme consists of the tensor products of the eigenstates of the total spin operators $\mathbf{f}_1$ and $\mathbf{f}_2$

$$|f_1 m_{f_1}; f_2 m_{f_2}\rangle. \quad (4.2)$$

This basis is called *uncoupled* even though it is coupled with respect to the $|m_{s_1} m_{i_1}; m_{s_2} m_{i_2}\rangle$ basis. It is well suited to the asymptotic form of atom-atom interactions in the absence of external fields where hyperfine interaction is the dominant form of interaction. Hence, this basis is called *the long-range uncoupled hyperfine* basis.

In another coupling scheme, we can separately couple the electron spins

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \quad (4.3)$$

and the nuclear spins

$$\mathbf{I} = \mathbf{i}_1 + \mathbf{i}_2 \quad (4.4)$$

to get the total electron spin S and the total nuclear spin I . The basis adapted to this coupling scheme consists of the products of the eigenstates of $\mathbf{S}$ and $\mathbf{I}$

$$|SM_S; IM_I\rangle. \quad (4.5)$$

This basis is coupled with respect to the $|m_{s_1}m_{i_1}; m_{s_2}m_{i_2}\rangle$ basis in which the short-range Born-Oppenheimer interaction is diagonal. Hence, this basis is called *the short-range uncoupled molecular* basis.

We can continue coupling angular momenta: either we couple $\mathbf{f}_1$ with $\mathbf{f}_2$, or $\mathbf{S}$ with $\mathbf{I}$, in order to get the total spin for the system consisting of two atoms

$$\mathbf{F} = \mathbf{f}_1 + \mathbf{f}_2 = \mathbf{S} + \mathbf{I}. \quad (4.6)$$

The total spin operator $\hat{\mathbf{F}}$ has the standard properties

$$\hat{F}^2|FM\rangle = F(F+1)|FM\rangle \quad (4.7)$$

$$\hat{F}_z|FM\rangle = M|FM\rangle \quad (4.8)$$

when acting on basis $|FM\rangle$ with $M = M_s + M_I$, but the concrete realization of the basis $|FM\rangle$ in the two coupling schemes can be different. The transition from

the $|(SI)FM\rangle$ basis to the $|(f_a f_b)FM\rangle$ basis is established through the use of $9j$ coefficients

$$\langle (s_1 i_1) f_1 (s_2 i_2) f_2; FM_F | (s_1 s_2) S (i_1 i_2) I; FM_F \rangle = \sqrt{(2s_1 + 1)(2s_2 + 1)(2i_1 + 1)(2i_2 + 1)} \begin{Bmatrix} s_1 & s_2 & S \\ i_1 & i_2 & I \\ f_1 & f_2 & F \end{Bmatrix}. \quad (4.9)$$

The main criterion for the choice of the representation basis is simplicity in evaluating the matrix elements of the various interaction terms. The *short range uncoupled molecular* basis extended with rotational quantum numbers, l and m

$$|SM_S; IM_I; lm\rangle, \quad (4.10)$$

is suitable for the evaluation of electronic interactions that depend only on the total electron spin number S . The interaction of atoms with the magnetic field, provided we neglect the nuclear part, is diagonal in the (4.10) basis and depends only on the magnetic projection quantum number M_S . In the same basis, provided we neglect nuclear interaction, the magnetic dipolar interaction matrix can be found by the application of the Wigner-Eckart theorem (B.1) to a tensor of rank two and the subsequent use of (B.4) and (B.5). In practice another path is often chosen where the hyperfine interaction matrix is first calculated in the

$$\textit{long range uncoupled hyperfine } |f_a m_{f_a}; f_b m_{f_b}\rangle \quad (4.11)$$

basis and then using Clebsch-Gordan or $3j$ coefficients transformed into a

$$\textit{long range coupled hyperfine } |(f_a f_b)FM\rangle \quad (4.12)$$

basis which can be connected to the

$$\textit{short range coupled molecular } |(SI)FM\rangle \quad (4.13)$$

basis by employing (4.9). The final step involves the usage of another table of Clebsch-Gordan or $3j$ coefficients in order to switch to the desired

$$\textit{short range uncoupled molecular } |SM_S; IM_I\rangle \text{ basis.} \quad (4.14)$$

A major reason for the choice $|SM_S IM_I lm\rangle$ basis, apart from the simplicity with which electronic, dipolar and Zeeman terms of the Hamiltonian can be described in this basis, is the ease of symmetrization which can be done for identical atoms. It is reduced to keeping only states for which

$$S + I + l \text{ is even,} \quad (4.15)$$

independently of the bosonic or fermionic nature of identical atoms. This can be seen in Sec. 4.1.1 if we recall that the result of exchange operator on the basis state is

$$P_{12}|SM_S IM_I lm\rangle \sim (1 + (-1)^{S+I+l})|SM_S IM_I lm\rangle \quad (4.16)$$

4.1.1 A note on symmetrization

The quantum mechanical description of the scattering of two identical atoms has to account for identical particle symmetry. The total wave function in which only the spatial coordinates of nuclei, $\mathbf{R}$, and electrons, $\mathbf{r}$, are explicitly shown

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_{SM_S IM_I \ell m} \frac{G_{SM_S IM_I}(R)}{R} \psi(\mathbf{r}) |SM_S\rangle |IM_I\rangle Y_{\ell m}(\hat{\mathbf{R}}) \quad (4.17)$$

is to be symmetrized under the exchange of two identical nuclei. We determine the transformation properties of each term: electronic spatial wave function $\psi(\mathbf{r})$, electronic spin wave function $|SM_S\rangle$, nuclear spin wave function $|IM_I\rangle$, and nuclear rotational wave function $Y_{\ell m}(\hat{\mathbf{R}})$. In this work, we only consider the scattering of atoms in the ground state for which the molecular electronic wave functions $\psi(\mathbf{r})$ are $\Sigma^{+/-}$ states, which in the case of identical nuclei (or identical nuclear charges) carry the additional label g (gerade) or u (ungerade). For the purposes of this section we will keep in mind that $\psi(\mathbf{r})$ is a shorthand notation for the $\Sigma_{g,u}^{+/-}$ electronic wave function.

The term describing the orientation of the nuclei behaves under the operation of nuclear exchange, P_N , as

$$P_N |\ell m\rangle = (-1)^\ell |\ell m\rangle, \quad (4.18)$$

while the nuclear spin function $|IM_I\rangle$ changes according to

$$P_N |IM_I\rangle = (-1)^{2i+I} |IM_I\rangle, \quad (4.19)$$

where i denotes the spin of a single nucleus.

The electronic spin function $|SM_S\rangle$ is not affected by the nuclear exchange while the opposite is true for the electronic spatial wave function $\psi(\mathbf{r})$ since it has an implicit dependence on the nuclear orientation. The z axis of the molecule-fixed frame, whose orientation, determined by convention to point from atom A to atom B, and reverses its direction upon the nuclear permutation in Fig. 4.1. The question

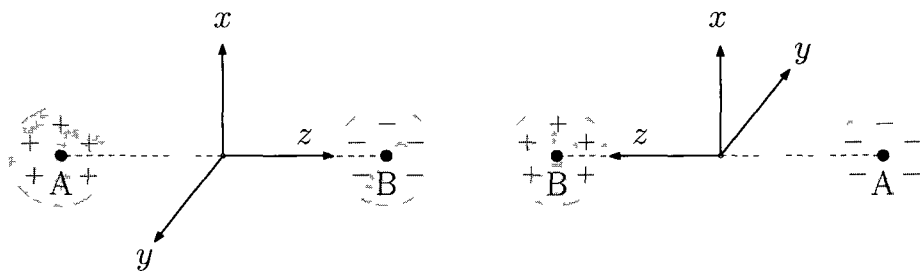


Figure 4.1: Molecular electronic wave function Σ_u^+ constructed using linear combination of atomic s_A and s_B orbitals. Left: molecule-fixed frame before nuclear permutation. Right: molecule-fixed frame after nuclear permutation.

is what happens to our description of electron density when the z -axis changes its direction. In Fig. 4.1 and Fig. 4.2 we graphically represent the Σ_u^+ and Σ_g^+ states constructed as a linear combination of atomic orbitals s_A and s_B . It can be observed that the Σ_u^+ state becomes the $-\Sigma_u^+$ state and the Σ_g^+ state is unchanged after the change of z axis direction. Visual inspection of $\Sigma_{g/u}^-$ states would produce results that have the opposite sign compared to results for the $\Sigma_{g/u}^+$ states.

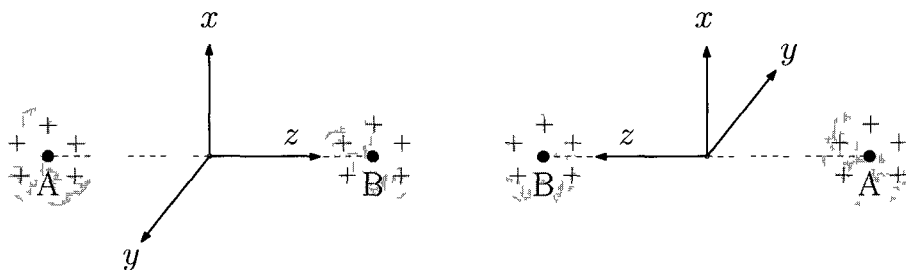


Figure 4.2: Molecular electronic wave function Σ_g^+ constructed using linear combination of atomic s_A and s_B orbitals. Left: molecule-fixed frame before nuclear permutation. Right: molecule-fixed frame after nuclear permutation.

In what follows, we formally describe the transformation of molecular electronic wave function: an inversion of electrons and nuclei in the laboratory-fixed frame followed by an inversion of electrons only in the molecule-fixed frame. The result

of the latter transformation is determined by a rotation by 180 degrees, followed by a reflection in the plane (perpendicular to the axis of rotation), giving the (+/-) symmetry notations into play. While changing the z axis we chose to leave the x axis unaffected as opposed to y direction which has to be change in order to preserve the right handedness of the molecule-fixed frame. Hence, the electronic coordinates transform according to

$$\begin{aligned}x &\rightarrow x \\y &\rightarrow -y \\z &\rightarrow -z .\end{aligned}\tag{4.20}$$

The same result can be achieved by a successive application of lab-fixed inversion of all coordinates (nuclear and electronic) and molecule-fixed inversion of electronic coordinates. The latter transformation is used to classify electronic states of homonuclear molecules according to

$$\psi(-x, -y, -z) = \begin{cases} +\psi(x, y, z) & \text{for gerade symmetry,} \\ -\psi(x, y, z) & \text{for ungerade symmetry .} \end{cases}\tag{4.21}$$

The lab-fixed inversion is equivalent to a rotation of the molecule for 180 degrees around the x axis followed by a reflection in the yz plane. The rotation of the molecule does not change the electronic wave function since it is defined in the molecule-fixed frame. On the other hand, the reflection is used to classify electronic states into states with + and - parity according to

$$\psi(-x, y, z) = \begin{cases} +\psi(x, y, z) & \text{for + parity,} \\ -\psi(x, y, z) & \text{for - parity .} \end{cases}\tag{4.22}$$

It is common practice to affix a superscript $+$ or $-$ to such an electronic wave function.

The effect of the nuclear permutation on the electronic wave function can be obtained once the labels g/u and $+/-$ are known. Table 4.1 shows the sign change of an electronic wave function that has either gerade or ungerade and $+$ or $-$ symmetry

Table 4.1: Nuclear exchange effect on ψ .

	+	-
g	+1	-1
u	-1	+1

wave. For example, according to this table an electronic function that has g and $-$ symmetries, ψ_g^- , would change sign after nuclear permutation. If we assign a discrete variable σ with values $\{0, 1\}$ to the reflection symmetry, then its action on the electronic wave function is

$$\sigma_{yz}\psi^\sigma = (-1)^\sigma \psi^\sigma . \quad (4.23)$$

Along the same lines, the molecule-fixed inversion can be assigned a discrete variable p with values $\{0, 1\}$ so the action of inversion i is represented by

$$i\psi_p = (-1)^p \psi_p . \quad (4.24)$$

Then, the combined action of these two symmetry operators represents the action of nuclear permutation on the electronic wave function

$$i\sigma_{yz}\psi_p^\sigma = (-1)^{\sigma+p} \psi_p^\sigma . \quad (4.25)$$

With this we conclude that the basis in (4.17) transforms under the nuclear exchange according to

$$\psi_p^\sigma(\mathbf{r})|SM_S\rangle|IM_I\rangle Y_{\ell m}(\hat{\mathbf{R}}) \rightarrow (-1)^{\sigma+p+2i+I+\ell} \psi_p^\sigma(\mathbf{r})|SM_S\rangle|IM_I\rangle Y_{\ell m}(\hat{\mathbf{R}}) \quad (4.26)$$

Then the properly symmetrized basis is obtained through the use of symmetrizer (antisymmetrizer)

$$(I + (-1)^{2i} P_N) \psi_p^\sigma(\mathbf{r})|SM_S\rangle|IM_I\rangle Y_{\ell m}(\hat{\mathbf{R}}) = (1 + (-1)^{\sigma+p+I+\ell}) \psi_p^\sigma(\mathbf{r})|SM_S\rangle|IM_I\rangle Y_{\ell m}(\hat{\mathbf{R}}). \quad (4.27)$$

From the above equation, it follows that only a basis state that satisfies

$$\sigma + p + I + \ell = \text{even} \quad (4.28)$$

should be used in the expansion (4.17).

In this work we are mainly concerned with two identical chromium atoms, bosonic and fermionic isotopes. The molecular ground state manifold belongs to + reflection symmetry ($\sigma = 0$) and the lowest energy state is a gerade state with total electronic spin equal to zero. While the energy of the state in this manifold increases, the inversion property alternates between gerade and ungerade, and the total electronic spin increases. The alternation of inversion number is such that $(-1)^p = (-1)^S$ is satisfied. At this point, we can state that the result of the nuclear permutation operator on the channel basis is

$$\psi_S(\mathbf{r})|SM_S\rangle|IM_I\rangle Y_{\ell m}(\hat{\mathbf{R}}) \rightarrow (-1)^{S+2i+I+\ell} \psi_S(\mathbf{r})|SM_S\rangle|IM_I\rangle Y_{\ell m}(\hat{\mathbf{R}}). \quad (4.29)$$

Here, we use the total electronic spin S instead of the index p .

4.1.2 An example

A typical example is a molecular state built from the atomic state of two atoms whose nuclei are labeled A and B. Alkali atoms with their well defined states with quantum numbers nlm provide a good example that can be extended to more complex systems if the angular momentum number l is understood to label the total electronic orbital angular momentum, and the quantum number n represents all other quantum numbers necessary for the completeness of the quantum description. In the uncoupled (with respect to orbital angular momentum) picture, we can have a wave function with quantum numbers $n_1\ell_1m_1$ centered on nucleus A with an electron whose label is 1, and another wave function with quantum numbers $n_2\ell_2m_2$ centered on nucleus B with an electron whose label is 2. The symmetrization of this product with respect to electron exchange is schematically represented with

$$\psi_{n_1\ell_1m_1}^A(1)\psi_{n_2\ell_2m_2}^B(2) \rightarrow \psi_{n_1\ell_1m_1}^A(1)\psi_{n_2\ell_2m_2}^B(2) + (-1)^S\psi_{n_1\ell_1m_1}^A(2)\psi_{n_2\ell_2m_2}^B(1) , \quad (4.30)$$

where S is the total spin of two electrons. The expression on the right-hand side of the arrow can be combined with the spin only function to form $|SM_S\rangle$ the total wave function that is properly symmetrized. For future reference, this expression is designated as A.

Similarly, we could have started from the situation where the role of atomic states was exchanged, atomic state $n_2\ell_2m_2$ was centered on the nucleus A and atomic state $n_1\ell_1m_1$ centered on the nucleus B. In the same manner as for the term A we get the term B after symmetrization of the aforementioned product and multiplying it with the spin function $|SM_S\rangle$

$$\psi_{n_2\ell_2m_2}^A(1)\psi_{n_1\ell_1m_1}^B(2) \rightarrow \psi_{n_2\ell_2m_2}^A(1)\psi_{n_1\ell_1m_1}^B(2) + (-1)^S\psi_{n_2\ell_2m_2}^A(2)\psi_{n_1\ell_1m_1}^B(1) . \quad (4.31)$$

Being equipped with terms A and B we can proceed to the construction of a molecular state that has the molecule-fixed inversion symmetry (gerade/ungerade). The ansatz for the electronic wave function is

$$\Psi = A + \alpha B , \quad (4.32)$$

where the unknown parameter α has to allow for gerade/ungerade property. Before examining how terms A and B change under inversion of the electronic coordinates, i , we will illustrate the behavior of the orbital part using atomic p orbitals. Take the $m = 1$ orbital for example (see Fig. 4.3): the real orbitals p_x and p_y transform as

$$p_x^A \rightarrow -p_x^B , \quad p_y^A \rightarrow -p_y^B , \quad (4.33)$$

and vice versa for orbitals centered on the nucleus B. Since

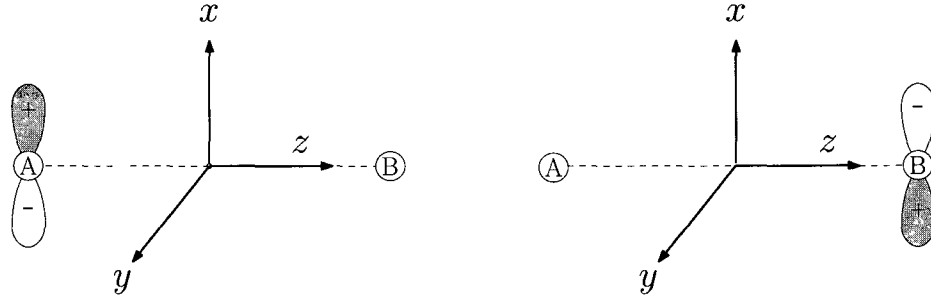


Figure 4.3: Left: p_x orbital before the molecule-fixed inversion. Right: p_x orbital after the molecule-fixed inversion.

$$p_{+1} \sim p_x + ip_y \quad (4.34)$$

we can derive similar properties for complex p orbitals

$$p_{+1}^A \rightarrow -p_{+1}^B , \quad (4.35)$$

and vice versa for orbitals centered on the nucleus B. In general, an atomic $|\ell m(A)\rangle$ orbital centered on the nucleus A becomes an $(-1)^\ell |\ell m(B)\rangle$ orbital centered on the nucleus B. As a consequence, terms A and B transform under the molecule-fixed inversion according to

$$iA = (-1)^{\ell_1+\ell_2+S} B , \quad \text{and} \quad iB = (-1)^{\ell_1+\ell_2+S} A . \quad (4.36)$$

It is straightforward to check that the constant α which determines the g/u symmetries is given by

$$\alpha = (-1)^{p+\ell_1+\ell_2+S} , \quad (4.37)$$

where $p = 0$ for the gerade symmetry and $p = 1$ for the ungerade symmetry . Finally, the fully expanded expression for the electronic wave function with gerade/ungerade symmetry is

$$\begin{aligned} \Psi = & [\psi_{n_1\ell_1m_1}^A(1)\psi_{n_2\ell_2m_2}^B(2) + (-1)^S \psi_{n_1\ell_1m_1}^A(2)\psi_{n_2\ell_2m_2}^B(1)] + \\ & (-1)^{p+\ell_1+\ell_2+S} [\psi_{n_2\ell_2m_2}^A(1)\psi_{n_1\ell_1m_1}^B(2) + (-1)^S \psi_{n_2\ell_2m_2}^A(2)\psi_{n_1\ell_1m_1}^B(1)] . \end{aligned} \quad (4.38)$$

4.2 The Hamiltonian terms

We consider collisions of atoms in ground S state, in particular $\text{Cr}(^7S_3)$ and $\text{Rb}(^2S_{1/2})$ atoms. The model Hamiltonian is

$$\hat{H} = -\frac{1}{2\mu R^2} \frac{\partial}{\partial R^2} R + \frac{\hat{\ell}^2}{2\mu R^2} + \hat{V}_{es} + \hat{V}_{dd} + \hat{H}_1^{int} + \hat{H}_2^{int} , \quad (4.39)$$

where R is the distance between two atoms, $\hat{\ell}$ is the rotational (orbital) angular momentum operator, $\hat{V}_{es}$ is the Coulomb interaction, $\hat{V}_{dd}$ is the spin-spin magnetic dipolar interaction and $\hat{H}_i^{int}$ are the atomic internal Hamiltonians. The internal Hamiltonians are comprised of atomic hyperfine interaction and interaction with magnetic field (Zeeman interaction). In what follows, we specify each term of the Hamiltonian.

4.2.1 Electrostatic interaction

In the Born-Oppenheimer (BO) approximation, the electrostatic interactions of all charged particles in a molecule are given through a spectral decomposition

$$\hat{V}_{es} = \sum_S V_S(R) \hat{P}_S, \quad (4.40)$$

where the operator

$$\hat{P}_S = \sum_{M_S} |SM_S\rangle \langle SM_S| \quad (4.41)$$

projects onto the subspace spanned by the basis in which the total electron spin S of a molecule is fixed. Consequently, in any basis with a definite total electron spin, the operator $\hat{V}_{es}$ is diagonal, with the BO electronic potentials $V_S(r)$ as diagonal values. Examples of such basis sets are the short-range uncoupled $|SM_SIM_I\rangle$ and the coupled $|(SI)FM\rangle$ basis sets.

4.2.2 Interaction with the magnetic field (Zeeman term)

The interaction energy of an atom in a magnetic field $\mathbf{B}$ is

$$V = -\mathbf{B} \cdot \mathbf{m}, \quad (4.42)$$

where $\mathbf{m}$ is the magnetic moment of the atom.

The transition from the classical to the quantum physics description of an atom with angular momentum $\hat{\mathbf{j}}$ is achieved by

$$\hat{\mathbf{m}} = \gamma \hat{\mathbf{j}}, \quad (4.43)$$

where γ is the gyro-magnetic ratio. Since we consider only atoms in the ground state with total orbital angular momentum equal to zero, and we neglect the contribution from the nucleus, we take $\hat{\mathbf{j}}$ to be the total electron spin operator, $\hat{\mathbf{s}}$. In that case, (4.42) becomes

$$\hat{V}_Z = -\gamma \mathbf{B} \cdot \hat{\mathbf{s}} \quad (4.44)$$

Depending on whether we take $\hat{\mathbf{s}}$ to have dimensions or not, the γ factor changes. To be more specific, let us use an electron as an example, namely

$$\gamma_e = -g_e \frac{e}{2m_e}, \quad (4.45)$$

where g_e is a g-factor for the electron, and e is the absolute value of the electron charge, hence the negative sign. If we were to use $\hat{\mathbf{s}}$ in units of $\hbar$, then the Zeeman term becomes

$$\hat{V}_Z = g_e \mu_B \mathbf{B} \cdot \hat{\mathbf{s}}, \quad (4.46)$$

where $\mu_B = e\hbar/(2m_e) = 5.788 \cdot 10^{-5}$ eV/T is called the Bohr magneton, and the spin is dimensionless.

The relation that connects μ_B and γ_e is

$$\gamma_e = -g_e \frac{\mu_B}{\hbar} = -1.760859 \cdot 10^{11} \text{T}^{-1} \text{s}^{-1} \quad (4.47)$$

given $g_e = 2.002319$. The Zeeman interaction of two atoms is described by

$$\hat{V}_Z = -\mathbf{B} \cdot (\gamma_1 \hat{\mathbf{s}}_1 + \gamma_2 \hat{\mathbf{s}}_2). \quad (4.48)$$

In the case of identical atoms or atoms with the same electron spin (neglecting the nuclear spins) we can set $\gamma_1 = \gamma_2 = \gamma$ and use the total electron spin operator, $\hat{\mathbf{S}} = \hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2$, to simplify the expression for the Zeeman interaction:

$$\hat{V}_Z = -\gamma \mathbf{B} \cdot \hat{\mathbf{S}}. \quad (4.49)$$

The Zeeman interaction evaluated in the $|SM_S IM_I l m\rangle$ basis becomes diagonal with elements

$$\left\langle SM_S IM_I l m \left| \hat{V}_Z \right| S' M'_S I' M'_I l' m' \right\rangle = -\gamma \delta_{S,S'} \delta_{M_S,M'_S} \delta_{I,I'} \delta_{M_I,M'_I} \delta_{l,l'} \delta_{m,m'} M_S B, \quad (4.50)$$

where $\mathbf{B}$ field is assumed to be along the direction of the the z axis. Atomic units are implied.

There are situations where we would like to compute the z component of any spin operator, either electron or nuclear, in the $|f_1 m_{f_1}; f_2 m_{f_2}\rangle$ basis. To show how it is done, we will use the electron spin operator of the first atom $(s_1)_z$ as an example. After the identification of this operator as the zero component of the spherical tensor

representation of the spin operator $s_q^{(1)}$, we can apply the Wigner-Eckart theorem (B.1)

$$\left\langle f_1 m_{f_1}; f_2 m_{f_2} \left| s_0^{(1)} \right| f'_1 m_{f'_1}; f'_2 m_{f'_2} \right\rangle = \left\langle f_1 m_{f_1} \left| s_0^{(1)} \right| f'_1 m_{f'_1} \right\rangle \delta_{f_1, f'_1} \delta_{m_{f_2}, m_{f'_2}}. \quad (4.51)$$

to the matrix element on the right-hand side of this equation

$$\left\langle f_1 m_{f_1} \left| s_0^{(1)} \right| f'_1 m_{f'_1} \right\rangle = (-1)^{f_1 - m_{f_1}} \begin{pmatrix} f_1 & 1 & f'_1 \\ m_{f_1} & 0 & m_{f'_1} \end{pmatrix} \langle f_1 || s^{(1)} || f'_1 \rangle \quad (4.52)$$

Finding the reduced matrix element entails the use of (B.4), because we couple $\mathbf{i}_1$ to $\mathbf{s}_1$ to get the total spin $\mathbf{f}_1 = \mathbf{s}_1 + \mathbf{i}_1$ of the first atom,

$$\langle f_1 || s^{(1)} || f'_1 \rangle = (-1)^{(s_1 + s_2 + f_1 + 1)} \begin{Bmatrix} s_1 & s_2 & f_1 \\ f'_1 & 1 & s'_1 \end{Bmatrix} \langle s_1 || s^{(1)} || s'_1 \rangle, \quad (4.53)$$

where according to (B.6),

$$\langle s_1 || s^{(1)} || s'_1 \rangle = \sqrt{s_1(s_1 + 1)(2s_1 + 1)} \delta_{s_1, s'_1}. \quad (4.54)$$

4.2.3 The hyperfine interaction

For two atoms in their ground states with hyperfine interaction constants A_1 and A_2 , the internal interaction energy is the sum of atomic hyperfine Hamiltonians

$$\hat{V}_{hf} = A_1 \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{i}}_1 + A_2 \hat{\mathbf{s}}_2 \cdot \hat{\mathbf{i}}_2. \quad (4.55)$$

The matrix elements of $\hat{V}_{hf}$ in the $|f_1 m_{f_1}; f_2 m_{f_2}\rangle$ or $|f_1 f_2 F M_F\rangle$ basis, become diagonal, with energies

$$E_{hf} = \frac{A_1 \hbar^2}{2} (f_1(f_1 + 1) - i_1(i_1 + 1) - s_1(s_1 + 1)) + \frac{A_2 \hbar^2}{2} (f_2(f_2 + 1) - i_2(i_2 + 1) - s_2(s_2 + 1)) \quad (4.56)$$

As it will be shown later in the Sec. 4.3, we will need to find the eigenstates of the asymptotic $r \rightarrow \infty$ Hamiltonian that includes both hyperfine and Zeeman term

$$\left[A_1 \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{i}}_1 + A_2 \hat{\mathbf{s}}_2 \cdot \hat{\mathbf{i}}_2 - (\gamma_1 \hat{\mathbf{s}}_1 + \gamma_2 \hat{\mathbf{s}}_2) \cdot \mathbf{B} \right] \Psi = E_{hfz} \Psi. \quad (4.57)$$

It might be appealing to compute the hyperfine interaction matrix in the basis $|SM_S IM_I\rangle$ since it has certain advantages, such as

- the electronic potential matrix is diagonal,
- the Zeeman interaction is diagonal,
- the atom-atom magnetic dipolar interaction has a clear physical interpretation,
- the wave functions can be more easily symmetrized, $S + I + \ell$ is even.

There are two options for calculating the matrix elements of the hyperfine operators in (4.57). The first path is to go through a sequence of basis changes,

$$|f_1 f_2 F M_F\rangle \rightarrow |S I F M_F\rangle \rightarrow |S M_S I M_I\rangle, \quad (4.58)$$

where, in the first step, we can apply (4.9), while for the second step the basic use of Clebsch-Gordan or $3j$ coefficients is sufficient. If we were to start from the

$|f_1 m_{f_1}; f_2 m_{f_2}\rangle$ basis then an additional set of $3j$ coefficients that connect to the $|f_1 f_2 F M_F\rangle$ basis would be required.

The second path is to apply the spherical tensor formalism. As an illustration, we concentrate on one atomic hyperfine term only, namely $\mathbf{s}_1 \cdot \mathbf{i}_1$, and drop the atomic label. First, we express the scalar product using spherical tensors

$$\mathbf{s} \cdot \mathbf{i} = \sum_{q=-1}^1 (-1)^q s_{-q}^{(1)} i_q^{(1)} \quad (4.59)$$

in order to find the matrix element

$$\begin{aligned} \langle SM_S IM_I | \mathbf{s} \cdot \mathbf{i} | S' M_{S'}' IM_I' \rangle = \\ \sum_{q=-1}^1 (-1)^q \langle SM_S | s_{-q}^{(1)} | S' M_{S'}' \rangle \langle IM_I | i_q^{(1)} | I' M_{I'}' \rangle. \end{aligned} \quad (4.60)$$

Then, we apply the Wigner-Eckart theorem (B.1) to $s_{-q}^{(1)}$ to obtain

$$\langle SM_S | s_{-q}^{(1)} | S' M_{S'}' \rangle = (-1)^{S-M_S} \begin{pmatrix} S & 1 & S' \\ -M_S & -q & M_{S'}' \end{pmatrix} \langle S || s^{(1)} || S' \rangle. \quad (4.61)$$

Next, we apply (B.4) to calculate the reduced element of operator $\hat{\mathbf{s}}_1$ in the $|SM_S\rangle$ basis

$$\begin{aligned} \langle S || s^{(1)} || S' \rangle = \\ (-1)^{s_1+s_2+S'+1} \sqrt{(2S+1)(2S'+1)} \begin{Bmatrix} s_1 & s_2 & S \\ S' & 1 & s_1' \end{Bmatrix} \langle s_1 || s^{(1)} || s_1' \rangle. \end{aligned} \quad (4.62)$$

From (B.6), it follows that the last reduced element is

$$\langle s_1 || s^{(1)} || s'_1 \rangle = \sqrt{s(s+1)(2s+1)} \delta_{s,s'}. \quad (4.63)$$

By substituting $s \rightarrow i$, $S \rightarrow I$ and $-q \rightarrow q$, we can reproduce all necessary expressions to assemble the matrix element $\langle IM_I || i_q^{(1)} || I'M_{I'} \rangle$.

4.2.4 Magnetic dipolar interaction

Classically, the interaction between two magnetic dipoles is given as

$$V_{dd} = \frac{\mu_0}{4\pi r^3} [\mathbf{m}_1 \cdot \mathbf{m}_2 - 3(\mathbf{m}_1 \cdot \hat{\mathbf{n}})(\mathbf{m}_2 \cdot \hat{\mathbf{n}})], \quad (4.64)$$

where $\mathbf{m}_1$ and $\mathbf{m}_2$ are two magnetic dipole moments, r is the separation between them, $\hat{\mathbf{n}}$ is a unit vector on the line connecting the two atoms and μ_0 is the magnetic permeability.

Following (4.43), the classical expression attains its quantum mechanical form

$$\hat{V}_{dd} = \gamma_1 \gamma_2 \frac{\mu_0}{4\pi r^3} [\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2 - 3(\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{n}})(\hat{\mathbf{s}}_2 \cdot \hat{\mathbf{n}})] \quad (4.65)$$

The presence of electron spin operators $\hat{\mathbf{s}}_i$ instead of total spin operators $\hat{\mathbf{j}}_i$ reflects our decision to neglect the contribution from the nuclei to magnetic dipolar interaction, as $(\gamma_e/\gamma_n) \sim 10^3$.

The dipolar interaction operator (4.65) expressed in terms of spherical tensor operators is

$$\hat{V}_{dd} = -\gamma_1 \gamma_2 \frac{\mu_0}{4\pi r^3} \sqrt{\frac{24\pi}{5}} \sum_{q=-2}^2 (-1)^q Y_q^{(2)} \hat{S}_{-q}^{(2)}, \quad (4.66)$$

where

$$\hat{S}_q^{(2)} = \sum_{q_1} (1, 1, q_1, q - q_1 | 1, 1, 2, q) s_{q_1}^{(1)} s_{q - q_1}^{(1)}, \quad (4.67)$$

is a spherical tensor operator of rank 2. Here, the bracket is the Clebsch-Gordan coefficient involved in the coupling of two angular momenta $\mathbf{j}_1$, and $\mathbf{j}_2$

$$(j_1 = 1, j_2 = 1, m_1 = q_1, m_2 = q - q_1 | j_1 = 1, j_2 = 1, j = 2, m = q). \quad (4.68)$$

Because the dipolar interaction couples spinor states, its matrix elements are more naturally suited to the $|SM_S IM_I; lm\rangle$ basis which is adapted to the product of spherical tensors. The evaluation of

$$\langle SM_S IM_I; lm | \hat{V}_{dd} | S' M_{S'} I' M_{I'}; l' m' \rangle \quad (4.69)$$

reduces to finding the matrix elements of the $Y_q^{(2)}$ operator in the $|lm\rangle$ and of the $\hat{S}_q^{(2)}$ operator in the $|SM_S\rangle$ basis. The nuclear spin part of the matrix element is accounted for through Kronecker-delta function products, $\delta_{II'} \delta_{M_I M_{I'}}$. The orbital part of the matrix elements is obtained by applying (B.1) to $Y_q^{(2)}$

$$\langle lm | Y_q^{(2)} | l' m' \rangle = (-1)^{l-m} \begin{pmatrix} l & 2 & l' \\ -m & q & m' \end{pmatrix} \langle l || Y^{(2)} || l' \rangle, \quad (4.70)$$

where

$$\langle l || Y^{(2)} || l' \rangle = (-1)^l \sqrt{\frac{5(2l+1)(2l'+1)}{4\pi}} \begin{pmatrix} l & 2 & l' \\ 0 & 0 & 0 \end{pmatrix}. \quad (4.71)$$

Similarly,

$$\left\langle SM_S \left| \hat{S}_{-q}^{(2)} \right| S' M_{S'} \right\rangle = (-1)^{S-M_S} \begin{pmatrix} S & 2 & S' \\ -M_S & -q & M_{S'} \end{pmatrix} \left\langle s_1 s_2 S \left\| \hat{S}^{(2)} \right\| s'_1 s'_2 S' \right\rangle. \quad (4.72)$$

Upon some manipulation involving Wigner symbols, using (B.4), (B.5) the general expression for the reduced matrix element is obtained

$$\left\langle s_1 s_2 S \left\| \hat{S}^{(2)} \right\| s'_1 s'_2 S' \right\rangle = \sqrt{5(2S+1)(2S'+1)} \begin{Bmatrix} s_1 & s'_1 & 1 \\ s_2 & s'_2 & 1 \\ S & S' & 2 \end{Bmatrix} \left\langle s_1 \left\| s^{(1)} \right\| s'_1 \right\rangle \left\langle s_2 \left\| s^{(1)} \right\| s'_2 \right\rangle. \quad (4.73)$$

Considering the specific nature of the reduced elements of the individual spin operators s_1 and s_2 , that is they are zero unless $s'_1 = s_1$ and $s'_2 = s_2$, the general expression for the reduced element further simplifies to

$$\left\langle s_1 s_2 S \left\| \hat{S}^{(2)} \right\| s_1 s_2 S' \right\rangle = \sqrt{5(2S+1)(2S'+1)} \begin{Bmatrix} s_1 & s_1 & 1 \\ s_2 & s_2 & 1 \\ S & S' & 2 \end{Bmatrix} \left\langle s_1 \left\| s^{(1)} \right\| s_1 \right\rangle \left\langle s_2 \left\| s^{(1)} \right\| s_2 \right\rangle. \quad (4.74)$$

Because the dipole-dipole interaction in (4.66) only couples electronic spins, we get the trivial selection rules for the nuclear spin

$$\Delta I = 0, \quad \text{and} \quad \Delta m_I = 0. \quad (4.75)$$

The rotational (orbital) selection rules come from the $3j$ coefficient in (4.70) and from the $3j$ coefficient in (4.71). From (4.70) we get

$$|\Delta l| \leq 2, \quad (4.76)$$

while the $3j$ coefficients in (4.71) establishes that only $|\Delta l| = 0, 2$ transitions are allowed, with $l = 0 \rightarrow l' = 0$ not allowed.

The electron spin selection rules can be obtained from (4.72), $|\Delta S| \leq 2$ while transitions

$$\begin{aligned} S = 0 &\rightarrow S' = 0, \\ S = 0 &\rightarrow S' = 1, \\ S = 1 &\rightarrow S' = 0, \end{aligned} \quad (4.77)$$

are not allowed. For the case of identical atoms or atoms with the same value of electronic spin, we have an additional restriction, from (4.74)

$$S + S' = \text{even}. \quad (4.78)$$

Combining this condition with the general one for the change of the total electron spin S , we get a selection rule similar to the one determining the allowed orbital angular momentum numbers

$$\Delta S = 0, \pm 2 \quad \text{while the transition } S = 0 \rightarrow S' = 0 \text{ is forbidden.} \quad (4.79)$$

An interesting consequence of the selection rules for magnetic dipolar interaction, for the alkali atoms, is that only the triplet ($S=1$) wave function is affected by the

magnetic dipolar interaction. There is no dipolar coupling between the triplet and singlet wave functions, since ΔS can only be 0 because the total spin is either 0 or 1. Remembering that the selection rules exclude the $S = 0 \rightarrow S' = 0$ transition, that leaves only $S = 1 \rightarrow S' = 1$ transitions.

The selection rules for the magnetic projection numbers are

$$\Delta m = -\Delta M_S, \quad |\Delta m| = 0, \pm 1, \pm 2. \quad (4.80)$$

4.3 Asymptotic basis

In the asymptotic region, $r \rightarrow \infty$, the total Hamiltonian reduces to the sum of atomic hyperfine and Zeeman interactions. The spin states that diagonalize this interaction represent channel states. Since the asymptotic Hamiltonian is expressed as a sum of two atomic Hamiltonians, the diagonalization can be done for each atom separately and the final channel states can be constructed as products of eigenstates of atomic asymptotic Hamiltonians.

For a given magnetic field B , an atomic hyperfine interaction is described by

$$\hat{H} = \frac{\alpha}{\hbar^2} \hat{\mathbf{s}} \cdot \hat{\mathbf{i}} + (\gamma_e \hat{s}_z - \gamma_n \hat{i}_z) B, \quad (4.81)$$

where the z axis is oriented along the magnetic field. The hyperfine constant α has units of energy, while $\gamma\hbar$ is given in units of energy over magnetic field strength. Also, we use the absolute value for the electron gyro-magnetic factor, γ_e .

Before discussing the general method for finding the eigenstates of the Hamiltonian (4.81), two limiting cases should be mentioned. In the first limit, when the magnetic field $B \rightarrow 0$, the states $|(si)fm_f\rangle$ diagonalize the Hamiltonian because the spin term can be represented as

$$\hat{\mathbf{s}} \cdot \hat{\mathbf{i}} = \frac{1}{2}(\hat{\mathbf{f}}^2 - \hat{\mathbf{s}}^2 - \hat{\mathbf{i}}^2). \quad (4.82)$$

In the $B \rightarrow \infty$, high magnetic field limit, the states $|m_s m_i\rangle$ diagonalize the Hamiltonian, provided we neglect the nuclear contribution since the ratio γ_e/γ_n is of the order $\sim 10^3$.

For all other B fields, the solutions are a linear combination of the $|(si)fm_f\rangle$ or the $|m_s m_i\rangle$ state vectors. What is common for both the hyperfine and the Zeeman magnetic interactions is that they preserve m_f . The spin-spin operator is a linear combination of the squares of the angular momentum operator, and each of them leaves the total magnetic projection number unchanged. In the magnetic part, the z -axis electron and the nuclear spin operators acting on $|m_s m_i\rangle$ leave the respective magnetic numbers unchanged, that is a space spanned by the basis vectors with same total magnetic projection number is invariant with respect to spin-spin and spin projection operators.

The existence of invariant subspaces is reflected in the block structure of the Hamiltonian matrix. The problem of diagonalizing the whole Hamiltonian matrix is then reduced to the diagonalization of smaller blocks. Throughout this chapter, alkali atoms will be used as an example which shows how the case of a total electron spin different from $1/2$ can be treated.

Fig. 4.4 shows the schematic diagram of the total spin $\mathbf{f} = \mathbf{s} + \mathbf{i}$ space partition into subspaces labeled with the magnetic projection number m_f . The value of spin f goes from $f_{min} = |s - i|$ to $f_{max} = s + i$ and the number of different m_f subspaces is equal to $2f_{max} + 1$. Each m_f subspace is represented by a row in Fig. 4.4 where the bottom row has $m_f = -f_{max}$ and for the top one $m_f = f_{max}$. The dimension of each m_f subspace for which $|m_f| \leq f_{min}$ is equal to $f_{max} - f_{min} + 1$. For the values of m_f where $|m_f| = f_{min} + 1$ the dimensions of the two spaces decrease by one. This pattern

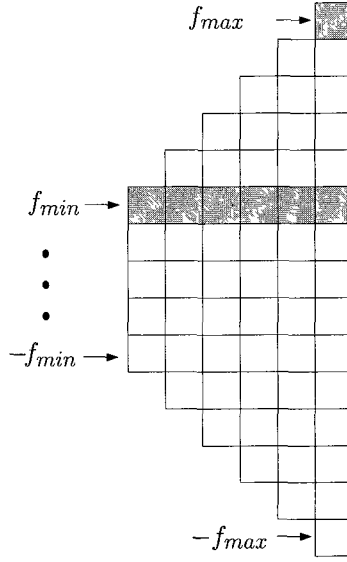


Figure 4.4: Partition of total spin space into m_f subspaces (rows): squares represent $|f m_f\rangle$ vectors; m_f increases by one for each row from bottom ($m_f = -s - i$) to top ($m_f = s + i$); f increases by one for each column from left ($f = |s - i|$) to right ($f = s + i$).

repeats until $|m_f|$ attains its maximal value, f_{max} , and the dimension reduces to one. The one dimensional spaces are spanned by either of $|f_{max}, \pm f_{max}\rangle$ states, which are expressed as $|s, i\rangle$ and $|-s, -i\rangle$ in the uncoupled representation $|m_s, m_i\rangle$.

When evaluating matrix elements of the hyperfine Hamiltonian, we have to decide which representation basis to use. We can work with the uncoupled $|m_s m_i\rangle$, coupled $|f m_f\rangle$ or both basis sets. The spin-spin term evaluation is straightforward in the coupled basis, while magnetic term evaluation is best done in the uncoupled basis.

4.3.1 Uncoupled basis

When using an uncoupled basis, $|m_s m_i\rangle$, we choose not to use the formalism of irreducible tensors and instead use the basic properties of angular momentum operators such as

$$\hat{\mathbf{j}}^2|jm\rangle = j(j+1)|jm\rangle \quad (4.83)$$

for the square of angular momentum or

$$j_z|jm\rangle = m|jm\rangle, \quad (4.84)$$

for the component of angular momentum along z axis, and

$$j_{\pm}|jm\rangle = \sqrt{j(j+1) - m(m\pm 1)}|j, m\pm 1\rangle \quad (4.85)$$

for the raising and lowering operators.

The magnetic field interaction matrix elements are determined by

$$\langle m_s m_i | s_z | m'_s m'_i \rangle = m_s \delta_{m_s, m'_s} \delta_{m_i, m'_i}, \quad \langle m_s m_i | i_z | m'_s m'_i \rangle = m_i \delta_{m_s, m'_s} \delta_{m_i, m'_i}. \quad (4.86)$$

The hyperfine interaction can be written as

$$\hat{\mathbf{s}} \cdot \hat{\mathbf{i}} = s_z i_z + \frac{1}{2}(s_+ i_- + s_- i_+). \quad (4.87)$$

The matrix elements are term by term

$$\begin{aligned} \langle m_s m_i | s_z i_z | m'_s m'_i \rangle &= m_s m_i \delta_{m_s, m'_s} \delta_{m_i, m'_i}, \\ \langle m_s m_i | s_+ i_- | m'_s m'_i \rangle &= \\ &\sqrt{s(s+1) - m_s m'_s} \sqrt{i(i+1) - m_i m'_i} \delta_{m_s, m'_s+1} \delta_{m_i, m'_i-1}, \end{aligned} \quad (4.88)$$

and

$$\langle m_s m_i | s_- i_+ | m'_s m'_i \rangle = \sqrt{s(s+1) - m_s m'_s} \sqrt{i(i+1) - m_i m'_i} \delta_{m_s, m'_s-1} \delta_{m_i, m'_i+1}. \quad (4.89)$$

4.3.2 Coupled basis

The calculation of matrix elements in the coupled basis $|(si)f m_f\rangle$ involves the use of expression (4.82) for the hyperfine interaction term, and (4.83) for any of the angular momentum squares.

$$\langle (si)f m_f | \hat{\mathbf{s}} \cdot \hat{\mathbf{i}} | (si)f' m_{f'} \rangle = \frac{1}{2} [f(f+1) - s(s+1) - i(i+1)] \delta_{f, f'} \delta_{m_f, m_{f'}}. \quad (4.90)$$

For the magnetic interaction term, the calculation of the s_z matrix elements involves the application of (B.4) to the operator s_z , and the use of (B.5) for the operator i_z . The selection rules are

$$\Delta f = 0, \pm 1. \quad (4.91)$$

For the $f \rightarrow f$ transition, we can use the analytical form of the $3j$ and $6j$ coefficients from (B.7) and (B.8), respectively, to obtain the s_z matrix elements

$$\langle f m_f | s_z | f m_f \rangle = \frac{m_f}{2} \frac{[f(f+1) + s(s+1) - i(i+1)]}{f(f+1)}, \quad (4.92)$$

and the i_z matrix elements

$$\langle f m_f | i_z | f m_f \rangle = \frac{m_f}{2} \frac{[f(f+1) + i(i+1) - s(s+1)]}{f(f+1)}. \quad (4.93)$$

For $\Delta f = \pm 1$ transitions, we can use the analytical form of the $3j$ and $6j$ coefficients from (B.1) and (B.10), respectively. Here, we first list the matrix elements for the s_z

operator

$$\boxed{f-1 \rightarrow f}$$

$$\langle f-1m_f | s_z | fm_f \rangle = \frac{1}{2f} \sqrt{\frac{f^2 - m_f^2}{4f^2 - 1} [(s+i+1)^2 - f^2][f^2 - (s-i)^2]} \quad (4.94)$$

$$\boxed{f+1 \rightarrow f}$$

$$\begin{aligned} \langle f+1m_f | s_z | fm_f \rangle = \\ \frac{1}{2(f+1)} \sqrt{\frac{(f+1)^2 - m_f^2}{4f^2 - 1} [(s+i+1)^2 - (f+1)^2][(f+1)^2 - (s-i)^2]} \end{aligned} \quad (4.95)$$

The matrix elements for the i_z operator differ from the ones given for s_z in sign only

$$\langle f\pm 1, m_f | i_z | fm_f \rangle = - \langle f\pm 1, m_f | s_z | fm_f \rangle. \quad (4.96)$$

4.3.3 An example: alkali atoms

In the case of alkali atoms, an analytical form exists for the eigenvalues and eigenvectors for the Hamiltonian comprised of hyperfine and Zeeman terms [51]. Because the alkali metal atoms are effectively one electron atoms, they have only two values for f : $f_{min} = i - 1/2$ and $f_{max} = i + 1/2$. Thinking in terms of the f, m_f quantum numbers, we can conclude that all m_f values that are allowed for f_{min} are also allowed to appear in the f_{max} manifold. This means that all m_f subspaces are two-dimensional except for the $|m_f| = f_{max}$ subspaces which are one-dimensional. These two spaces are generated by states that represent both spins maximally polarized. Working in the $|m_s m_i\rangle$ representation, we can reproduce all the conclusions stated in the $|fm_f\rangle$ representation.

Uncoupled basis $|m_s m_i\rangle$. In the one-dimensional subspace, spanned by $|+, i\rangle$, both spins are oriented along the magnetic field, while in the second subspace, spanned by $|-, -i\rangle$, both spins are oriented against the magnetic field. The remaining subspaces are generated by vectors having the same total spin magnetic projection $m_f = m_s + m_i$

$$|+, m_i\rangle, \quad |-, m_i + 1\rangle. \quad (4.97)$$

Fig. 4.5 shows all relevant points. Here we list the matrices necessary to assemble the

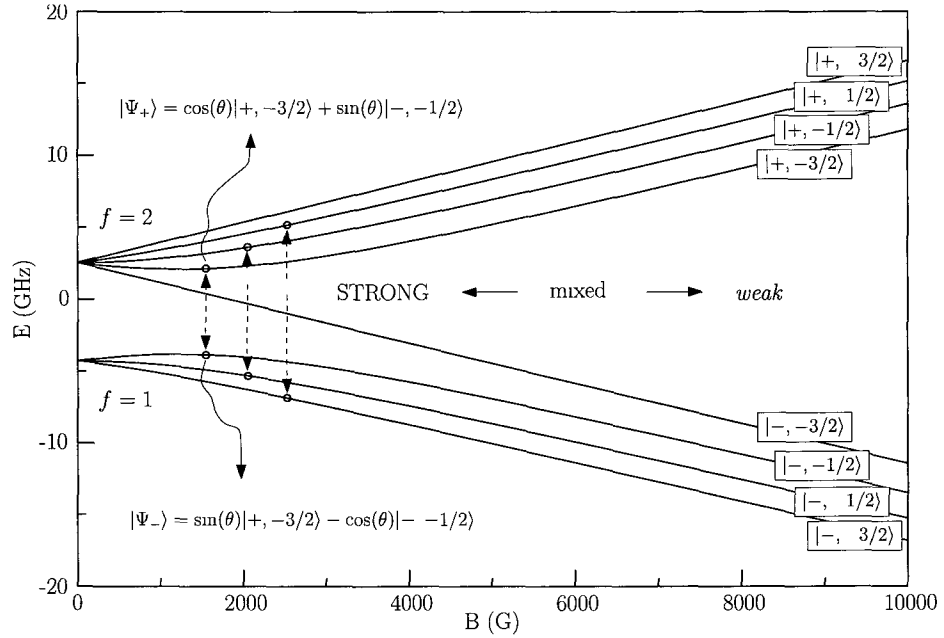


Figure 4.5: Zeeman energy levels of ^{87}Rb ($i=3/2$) with hyperfine interaction ($\alpha = 3417.34$ MHz) in the $|m_s, m_i\rangle$ basis. For low magnetic field, the dominant hyperfine interaction couples spins while for high magnetic field the dominant interaction of atom with magnetic field decouples spins.

Hamiltonian matrix: the hyperfine matrix

$$\hat{\mathbf{s}} \cdot \hat{\mathbf{i}} = \frac{\hbar^2}{2} \begin{pmatrix} m_f - \frac{1}{2} & \sqrt{(i + \frac{1}{2})^2 - m_f^2} \\ \sqrt{(i + \frac{1}{2})^2 - m_f^2} & -(m_f + \frac{1}{2}) \end{pmatrix}, \quad (4.98)$$

and the spin projection matrices

$$s_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad i_z = \frac{\hbar}{2} \begin{pmatrix} 2m_f - 1 & 0 \\ 0 & 2m_f + 1 \end{pmatrix}, \quad (4.99)$$

in the $|m_s, m_i\rangle$ basis. A (2×2) Hermitian matrix

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \quad (4.100)$$

has for eigenvalues [52]

$$E_{\pm} = \frac{1}{2}(H_{11} + H_{22}) \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + |H_{12}|^2} \quad (4.101)$$

and eigenvectors

$$\Psi_+ = \begin{pmatrix} \cos \theta \\ \sin \theta \end{pmatrix}, \quad \Psi_- = \begin{pmatrix} \sin \theta \\ -\cos \theta \end{pmatrix}, \quad (4.102)$$

where the mixing angle θ

$$\tan(2\theta) = \frac{2|H_{21}|}{H_{11} - H_{22}}, \quad 0 \leq \theta < \frac{\pi}{2}. \quad (4.103)$$

The eigenvalues for the Hamiltonian in (4.81) are

$$E_{\pm} = -\frac{\alpha}{4} - m_f \gamma_n \hbar B \pm \frac{1}{2} \sqrt{\alpha^2 (i + \frac{1}{2})^2 + 2\alpha m_f (\gamma_e + \gamma_n) \hbar B + (\gamma_e + \gamma_n)^2 \hbar^2 B^2}, \quad (4.104)$$

where the two energy branches are labeled with the $\pm$ symbol.

It is practical to change units for the magnetic field by defining a reduced magnetic field $\tilde{B}$,

$$B = \tilde{B} \left(\frac{|\alpha|}{\hbar\gamma_e} \right) \quad (4.105)$$

so that only the hyperfine constant has the units of energy. The energy curves expressed in the new unit for the magnetic field are

$$E_{\pm} = |\alpha| \left(-\frac{\text{sgn}(\alpha)}{4} - m_f \frac{\gamma_n}{\gamma_e} \tilde{B} \pm \frac{1}{2} \sqrt{\left(i + \frac{1}{2}\right)^2 + 2 \text{sgn}(\alpha) m_f \left(1 + \frac{\gamma_n}{\gamma_e}\right) \tilde{B} + \left(1 + \frac{\gamma_n}{\gamma_e}\right)^2 \tilde{B}^2} \right). \quad (4.106)$$

To be able to assemble eigenvectors, we have to solve the equation that defines the parameter θ in the $|m_s, m_i\rangle$ basis

$$\tan(2\theta) = \frac{|\alpha| \sqrt{\left(i + \frac{1}{2}\right)^2 - m_f^2}}{\alpha m_f + (\gamma_e + \gamma_n) \hbar B} = \frac{\sqrt{\left(i + \frac{1}{2}\right)^2 - m_f^2}}{\text{sgn}(\alpha) m_f + \left(1 + \frac{\gamma_n}{\gamma_e}\right) \tilde{B}}. \quad (4.107)$$

When evaluating the mixing angle θ , we must ensure that it is in the first quadrant of the trigonometric circle. We first label the numerator and denominator of the above equation as C_m and Z_m respectively, giving us

$$\tan(2\theta) = \frac{C_m}{Z_m}. \quad (4.108)$$

With the help of

$$R_m = \sqrt{Z_m^2 + C_m^2}, \quad (4.109)$$

we obtain the expressions for the sine and cosine of the mixing angle θ

$$\sin(\theta) = + \frac{1}{\sqrt{1 + \frac{(Z_m + R_m)^2}{C_m^2}}}, \quad \cos(\theta) = + \sqrt{1 - \sin^2(\theta)}. \quad (4.110)$$

Coupled basis $|f m_f\rangle$. In the one-dimensional subspace, spanned by $|f = i + 1/2, m_f = i + 1/2\rangle$, the maximal spin projection is along the magnetic field direction, while in the second subspace, spanned by $|f = i + 1/2, m_f = -i - 1/2\rangle$, the maximal spin projection is opposite to the magnetic field direction. The remaining subspaces are of dimension two and they are generated by vectors having different total spin f but the same total spin magnetic projection m_f

$$|f = i + \frac{1}{2}, m_f\rangle, \quad |f = i - \frac{1}{2}, m_f\rangle. \quad (4.111)$$

Fig. 4.6 shows the relevant points. Here we list the matrices necessary to assemble the Hamiltonian matrix: the hyperfine matrix

$$\hat{\mathbf{s}} \cdot \hat{\mathbf{i}} \rightarrow \hbar^2 \begin{pmatrix} i & 0 \\ 0 & -(i+1) \end{pmatrix}, \quad (4.112)$$

and the electron spin projection matrix,

$$s_z \rightarrow \frac{\hbar}{2i+1} \begin{pmatrix} m_f & \sqrt{(i + \frac{1}{2})^2 - m_f^2} \\ \sqrt{(i + \frac{1}{2})^2 - m_f^2} & -m_f \end{pmatrix}, \quad (4.113)$$

and the nuclear spin projection matrix

$$i_z \rightarrow \frac{\hbar}{2i+1} \begin{pmatrix} 2m_f i & -\sqrt{(i + \frac{1}{2})^2 - m_f^2} \\ -\sqrt{(i + \frac{1}{2})^2 - m_f^2} & m_f 2(i+1) \end{pmatrix}, \quad (4.114)$$

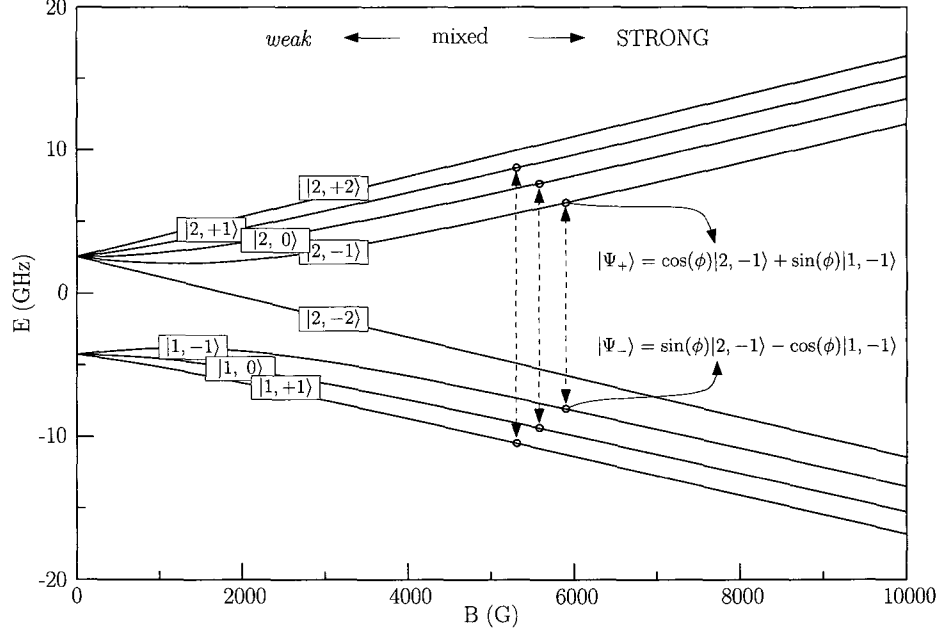


Figure 4.6: Zeeman energy levels of ^{87}Rb ($i=3/2$) with hyperfine interaction ($\alpha = 3417.34$ MHz) in the $|fm_f\rangle$ basis. For low values of magnetic field, the dominant hyperfine interaction decouples spins while for high values of magnetic field the dominant interaction of atom with magnetic field couples spins.

in the $|fm_f\rangle$ basis. Using (4.101), we can confirm that the eigenvalues of the Hamiltonian are the same in both basis sets. It is the mixing parameters which are different.

Transformation matrix $\langle m_s m_i | fm_f \rangle$. Although all matrix evaluations can be done within one basis set as shown, sometimes it is advantageous to calculate the hyperfine interaction term in the $|fm_f\rangle$ basis, while other interaction terms are represented in the $|m_s m_i\rangle$ basis. Then in order to obtain all interaction terms in the same basis we have to use a transformation matrix that connects the two basis sets.

For the case of alkali atoms, where $s = 1/2$, the expansion of the $|f, m_f\rangle$ basis into the $|m_s, m_i\rangle$ basis is well known:

$$|f = i + \frac{1}{2}, m_f = m\rangle = \frac{1}{2i+1} \left(\sqrt{(i + \frac{1}{2})^2 + m} |+, m - \frac{1}{2}\rangle + \sqrt{(i + \frac{1}{2})^2 - m} |-, m + \frac{1}{2}\rangle \right), \quad (4.115)$$

and

$$|f = i + \frac{1}{2}, m_f = m\rangle = \frac{1}{2i+1} \left(\sqrt{(i + \frac{1}{2})^2 - m} |+, m - \frac{1}{2}\rangle - \sqrt{(i + \frac{1}{2})^2 + m} |-, m + \frac{1}{2}\rangle \right). \quad (4.116)$$

The unitary transformation U , connecting the two representations of any operator, s_s for example, is

$$s'_z = U^\dagger s_z U, \quad (4.117)$$

where s'_z and s_z are matrix representations of the $\hat{s}_z$ operator in the $|fm_f\rangle$ and $|m_s m_i\rangle$ bases respectively. The transformation matrix

$$U = \frac{1}{2i+1} \begin{pmatrix} \sqrt{(i + \frac{1}{2})^2 + m} & \sqrt{(i + \frac{1}{2})^2 - m} \\ \sqrt{(i + \frac{1}{2})^2 - m} & -\sqrt{(i + \frac{1}{2})^2 + m} \end{pmatrix} \quad (4.118)$$

is a real and symmetric matrix.

CHAPTER 5

CR-CR COLLISIONS

Chromium appears in nature in four isotopes ^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr . The relative abundance of ^{52}Cr (80%), followed by ^{53}Cr (10%), makes these two isotopes primary candidates for research and applications. The latter isotope is the only one with non-zero nuclear spin, $3/2$, and with its hyperfine structure and fermionic nature, stands apart from other bosonic isotopes. The ^{52}Cr chromium atom in its ground state 7S_3 exhibits significant magnetic moment $6\mu_B$, which allows its trapping in the low-field seeking Zeeman state at relatively high temperatures, up to 1 Kelvin. Owing to its large magnetic moment, a range of effects caused by the presence of magnetic dipolar interactions was demonstrated [25]. The detection of chromium is done via optical transition from the ground state to the 7P_3 excited state. The interest in the fermionic isotope stems from the possibility of creating a Bose-Fermi degenerate gas mixture. Our initial interest in studying chromium collisions was to address the buffer-gas cooling experiment of John Doyle's group where the colliding atoms were in the highest energy low-field seeking Zeeman state. It was later expanded to the investigation of the Feshbach magnetic resonances present in the collision of atoms in the lowest-energy high-field seeking Zeeman state.

In the ultracold regime, the s-wave scattering dominates, which allows us to model short range interactions using the so-called *contact interaction*

$$V_{\text{contact}} = \frac{4\pi a \hbar^2}{M} \delta(R), \quad (5.1)$$

where M is the mass of Cr atoms. This interaction is short range ($\sim \delta(R)$), isotropic (depends on R only) and is parametrized by the s-wave scattering length a . For two Cr atoms with parallel magnetic dipole moments, the dipolar interaction is given by

$$V_{dd} = \frac{\mu_0 m^2}{4\pi} \frac{[1 - \cos^2(\theta)]}{R^3}, \quad (5.2)$$

where m is the magnetic dipole moment. This interaction is long range ($\sim 1/R^3$) and has anisotropic character (depends on θ). Since it scales as the square of the magnetic moment, we expect it to be 36 times stronger in Cr than in alkali metal samples.

The strength of the dipolar interactions, for systems with an electric or magnetic dipole moment, can be parametrized using dipolar length and relative dipolar strength

$$a_{dd} = \frac{\mu_0 m^2 M}{12\pi \hbar^2}, \quad \epsilon_{dd} = \frac{\mu_0 m^2 M}{12\pi a \hbar^2}. \quad (5.3)$$

Lahaye *et al.* [53] tabulates the values of these parameters for various systems (see Table 5.1).

Table 5.1: Dipolar constants for various systems.

Species	Dipole moment	a_{dd}	ϵ_{dd}
^{87}Rb	$1.0 \mu_B$	$0.7 a_0$	0.007
^{52}Cr	$6.0 \mu_B$	$16 a_0$	0.16
KRb	0.6 D	$2.0 \times 10^3 a_0$	20
ND ₃	1.5 D	$3.6 \times 10^3 a_0$	36
HCN	3.0 D	$2.4 \times 10^3 a_0$	240

Compared to systems with electrical dipole moment, Cr dipolar interaction is several orders of magnitude smaller, but, on the other hand, compared to a typical alkali system (^{87}Rb), the trend is reversed.

The interplay of dipolar interaction and long range interaction in Cr is shown in Fig. 5.1. It can be seen that for distances up to $R = 70$ a.u. the long range interaction is at least an order of magnitude stronger and it becomes dominated by dipolar interaction for $R > 150$ a.u.

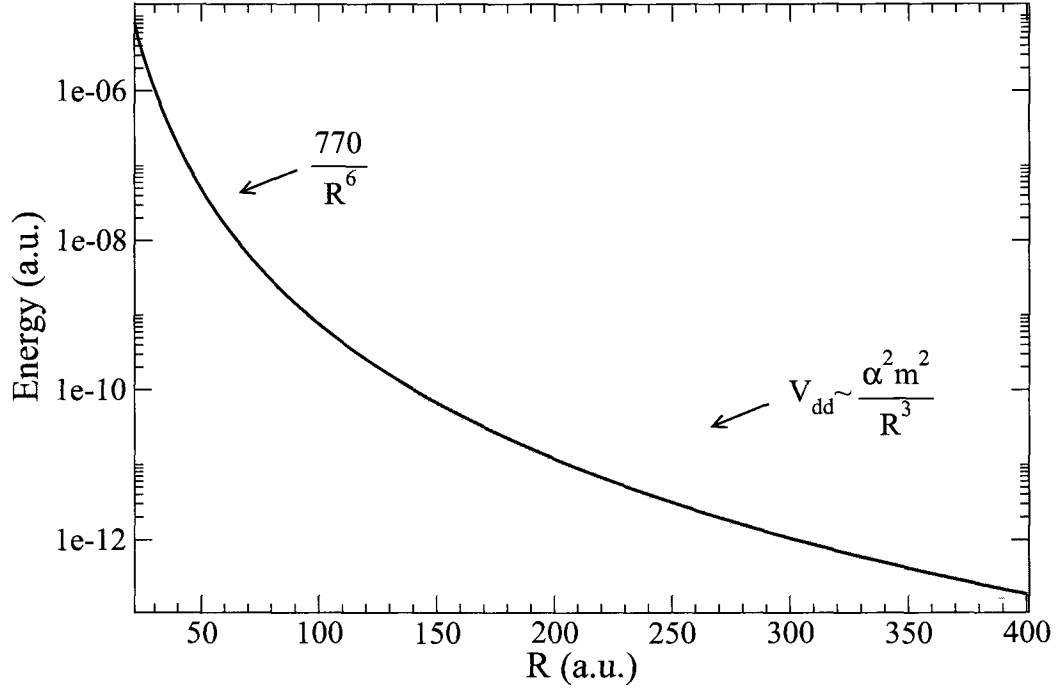


Figure 5.1: Full line: the magnitude of van der Waals interaction; Shaded area: the magnitude of dipolar interaction diagonal matrix elements in $|SM_S; \ell m_\ell\rangle$ basis (see Sec. 5.4.3).

5.1 Born-Oppenheimer (BO) potential energy curves

5.1.1 Short range interactions

The chromium dimer occupies a peculiar place among the transition metal homonuclear diatomic molecules. Its singlet ground state $^1\Sigma_g^+$ is formed by two Cr atoms with electronic configuration $3d^54s(^7S_3)$. Chromium is the first atom in the periodic table with a half-filled d shell. Twelve unpaired electrons (five $3d$ and one $4s$ electron from each atom) have to be paired into a singlet molecular state. Judging by the size of $4s$ (1.945 Å) and $3d$ (0.72 Å) orbitals, a plastic description of how the pairing of the twelve electrons can be envisaged [54].

Due to the marked difference in the size of $4s$ and $3d$ orbitals, the pairing of electrons starts between $4s$ electrons at larger interatomic separation (~ 3 Å), while the $3d$ electrons remain localized but with opposite spins. At shorter interatomic separation an anti-ferromagnetic coupling between $3d$ electrons is responsible for significant delocalization of electrons that results in a singlet ground state.

From the theoretical point of view, the calculation of the electronic spectrum of the Cr_2 dimer is a difficult task. According to an estimate of Langhoff and Bauschlicher [55] it would require more than ten billion interaction configurations to obtain a satisfactory numerical description. To date, the best attempt to calculate the chromium interaction potential curves is a multiconfiguration second-order perturbation theory with complete active space self-consistent field (CASSCF/CASPT2) [56, 57, 58, 59]. While spectroscopic constants for the ground electronic state ($^1\Sigma_g^+$ symmetry) exist [60, 61], there is no spectroscopic data available for the interaction of two Cr atoms in the other electronic spin state.

In this work, we explored the collisional properties of Cr atoms at cold and ultracold temperatures by revisiting the electronic structure of the dimer. Accurate Born-Oppenheimer potential energy curves dissociating to two ground Cr atoms, shown in

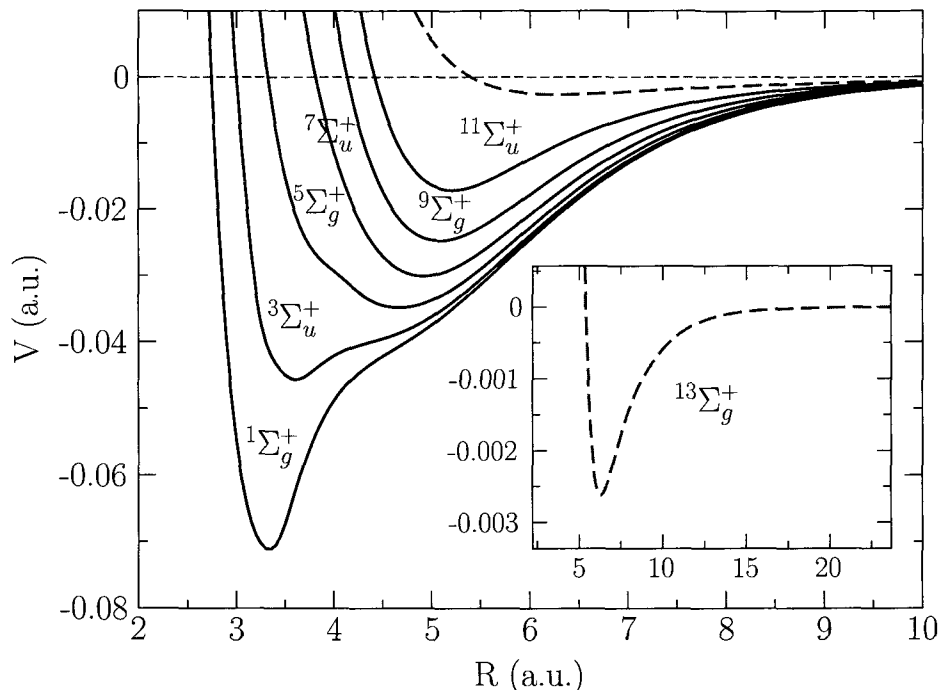


Figure 5.2: Potential curves for the ground state manifold of Cr_2 computed with the CASSCF/CASPT2 method. The maximally spin-stretched electronic state, $^{13}\Sigma_g^+$, is shown as a dashed line and in detail in the inset.

Fig. 5.2, were constructed from three regions joined smoothly together. First, *ab initio* potential curves were computed using the CASSCF/CASPT2 method [56, 57, 58, 59]. The CASSCF wave function is formed by distributing 12 electrons in the $3d$ and $4s$ active orbitals while keeping the inactive $1s$, $2s$, $2p$, $3s$, and $3p$ orbitals occupied. The remaining dynamic electron correlation energy is obtained through second order perturbation theory (CASPT2). The basis set used in the calculations is of the atomic natural orbital (ANO-RCC) type contracted to $9s8p7d5f3g$. This basis set is relativistic and includes functions for correlating the $3s$ and $3p$ electrons [62]. The Douglas-Kroll Hamiltonian was used with Fock-type correction $0.5 * \mathbf{g}_1$, see [63].

The full counterpoise method was used to correct energies for the basis set superposition error (BSSE). Convergence to 10^{-10} , in hartrees, was achieved, and numerical accuracy in computed binding energies is about 10^{-8} . For separations $R \leq R_1^\lambda$, where

R_1^λ is the smallest separation of the *ab initio* data for the potential energy $V_\lambda(R)$, each curve was joined smoothly to the exponential form

$$V_\lambda(R) = c_\lambda \exp(-b_\lambda R), \quad (5.4)$$

with the coefficients c_λ and b_λ determined by matching both the potential curve and its first derivative continuously at R_1^λ . At large values of R , the *ab initio* data were matched to the asymptotic form

$$V_\lambda(R) = -C_6/R^6 + A_\lambda R^\nu e^{-\beta R}, \quad (5.5)$$

where the parameters of the exchange energy are determined according to Smirnov and Chibisov [64, 65]: $\nu = \frac{7}{\beta} - 1$ and $\beta = 2\sqrt{2I}$, where I is the ionization energy of the atom ($I = 0.248664314$ a.u. for Cr). The parameters A_λ were found by fitting the *ab initio* curves at separations where the exchange energy was still considerable (e.g. R between 10 and 14 a.u. for $^{13}\Sigma_g^+$).

5.1.2 Long range interactions

There is no exact definition of the long-range region. It is assumed that it begins at the internuclear distance where the overlap of electronic clouds from two atoms can be neglected. On the interaction level, it means that the exchange interaction can be neglected in comparison to the Coulomb interaction between electrons. Occasionally, some estimates of where the long range starts are helpful, such as the well known Le-Roy radius

$$R_{Le-Roy} = 2(\langle r^2 \rangle_A^{1/2} + \langle r^2 \rangle_B^{1/2}), \quad (5.6)$$

where $\langle \dots \rangle_{A(B)}^{1/2}$ is the r.m.s distance of the outermost electron on atom $A(B)$. The dispersion interaction of atoms in a spherically symmetric ground state can be expanded into the inverse powers of the interatomic distance R

$$V(R) = - \sum_{n=3} \frac{C_{2n}}{R^{2n}}. \quad (5.7)$$

For very large distances, retardation effects must be taken into account [66]. A number of methods capable of extracting the dispersion coefficients exists, and two methods will be briefly outlined here for illustration purposes only.

The first method relies on the fact that van der Waals coefficients, C_{2n} , have an integral representation that involves dipole, quadrupole, octupole and higher order dynamic polarizabilities. As an example we list expressions for the first three coefficients

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_1(i\omega) \alpha_1(i\omega) d\omega, \quad (5.8)$$

$$C_8 = \frac{15}{\pi} \int_0^\infty \alpha_1(i\omega) \alpha_2(i\omega) d\omega, \quad (5.9)$$

$$C_{10} = \frac{28}{\pi} \int_0^\infty \alpha_1(i\omega) \alpha_3(i\omega) d\omega + \frac{35}{\pi} \int_0^\infty \alpha_2(i\omega) \alpha_2(i\omega) d\omega, \quad (5.10)$$

where functions α_1 , α_2 , and α_3 are dipole, quadrupole and octupole dynamic polarizabilities evaluated at the imaginary frequency $i\omega$. Higher order dispersion coefficients require higher order 2^l -pole polarizabilities. Once the dynamic polarizabilities are known, the dispersion coefficients are readily evaluated [67, 68].

The second method involves a two-center expansion of the long-range electrostatic interaction

$$\hat{V} = \sum_{q=1} \frac{V_q}{R^q}, \quad (5.11)$$

where the coefficients V_q include charge-charge, charge-dipole, dipole-dipole and higher order multipole interactions. For the case of neutral atoms, the expansion coefficients V_1 and V_2 are null, and the complete expression for V_q with all necessary details can be found in [69]

$$V_q = \sum_{i,j} \sum_{l=1}^{m=q-2} \sum_{m=-l}^{l} G(l, m) Y_{l,m}(\hat{\mathbf{r}}_i) Y_{q-l-1,-m}(\hat{\mathbf{r}}_j) , \quad (5.12)$$

where index $i(j)$ runs over all electrons of one of the atoms, $\hat{\mathbf{r}}_i(\hat{\mathbf{r}}_j)$ are the direction vectors from the corresponding nucleus, and $l_<$ is the smaller of l and $q - l - 1$. If we choose Hund case (a), the appropriate long-range limits $|LAS\Sigma\rangle$ of molecular wave functions $|\Lambda S\Sigma\rangle$, as our representation basis for $\hat{V}$, then solving the secular determinant

$$\det |V - EI| = 0 , \quad (5.13)$$

yields first order values or expressions for the long-range potentials. From these, the leading dispersion coefficient can be easily determined [70, 71]. The long range potential expansion (5.7) is reduced to the C_6/R^6 term as we focus on the first dispersion coefficient C_6 , and for its calculation we follow the approach described by Margenau [12]. It is based on London's expression

$$C_6 = -\frac{3}{2} \left(\frac{e^2 \hbar^2}{m} \right)^2 \sum_{i,j} \frac{f_{0i} f_{0j}}{(E_0 - E_i)(E_0 - E_j)(2E_0 - E_i - E_j)} , \quad (5.14)$$

for which we need to know the oscillator strengths f_{0i} for transitions from the ground state with energy E_0 to excited states with energy E_i (E_j). It is understood that summation includes integration over continuum, in which case discrete variables E_i and

f_{0i} are replaced with continuous variables E and df/dE . Introducing dimensionless quantities v_i and ϵ defined as

$$v_i = 1 - \frac{E_i}{E_0}, \quad \epsilon = \frac{E}{-E_0} \quad (5.15)$$

allows us to rewrite (5.14) as

$$C_6 = A \left(\sum_{i,j} \frac{f_{0i} f_{0j}}{v_i v_j (v_i + v_j)} + 2 \sum_i \int_0^\infty \frac{f_{0i} (df/d\epsilon) d\epsilon}{v_i (1 + \epsilon) (1 + v_i + \epsilon)} + \int_0^\infty \int_0^\infty \frac{(df/d\epsilon_1)(df/d\epsilon_2) d\epsilon_1 d\epsilon_2}{(1 + \epsilon_1)(1 + \epsilon_2)(2 + \epsilon_1 + \epsilon_2)} \right), \quad (5.16)$$

where we have isolated contributions from the discrete-discrete, discrete-continuum, and continuum-continuum types of electronic transitions. Since terms inside the brackets are dimensionless, the constant A given as

$$A = -\frac{3}{2} \left(\frac{e^2 \hbar^2}{m} \right)^2 \frac{1}{|E_0|^3} \quad (5.17)$$

dictates the dimensions of C_6 . A couple of notes are in order: first, London's expression (5.14) is given in the c.g.s system of units. Therefore, in the atomic system of units we have

$$\frac{e^2 \hbar^2}{m_e} = E_H^2 a_0^3. \quad (5.18)$$

Second, in the atomic system of units the constant A is

$$A = -\frac{3}{2|E_0|^3}. \quad (5.19)$$

However, if we want to input energy in rydbergs and obtain C_6 in units of $E_h a_0^6$, we should use

$$A = -\frac{12}{|E_0|^3} . \quad (5.20)$$

The expression for C_6 can be rearranged in a more compact form

$$C_6 = A \left(\sum_{i,j} \frac{f_{0i} f_{0j}}{v_i v_j (v_i + v_j)} + 2 \sum_i \frac{f_{0i} G(1 + v_i)}{v_i} + \int_0^\infty \frac{(df/d\epsilon) G(2 + \epsilon) d\epsilon}{(1 + \epsilon)} \right) , \quad (5.21)$$

which is better suited for numerical evaluation of integrals over continuous spectra. The integration over two variables is reduced to the integration over one variable by introducing an auxiliary function

$$G(\alpha) = \int_0^\infty \frac{(df/d\epsilon) d\epsilon}{(1 + \epsilon)(\alpha + \epsilon)} . \quad (5.22)$$

In order to get an estimate of the accuracy with which C_6 is computed, we can check how well other sum rules involving oscillator strengths are satisfied. For example, the number of electrons N_e is connected to oscillator strengths

$$\sum_i f_{0i} = N_e . \quad (5.23)$$

In the case of Cr there are 24 electrons. The atomic static polarizability can be represented with a sum involving oscillator strengths

$$\alpha = \frac{e^2 \hbar^2}{m} \sum_i \frac{f_{0i}}{(E_0 - E_i)^2} . \quad (5.24)$$

The recommended [72] value of static polarizability α for Cr is 82 ± 20 a.u. Using previously introduced v_i , ϵ and $G(\alpha)$ we can transform the equation for polarizability into

$$\alpha = B \left\{ \sum_i \frac{f_{0i}}{v_i^2} + G(1) \right\} , \quad (5.25)$$

where the constant B given as

$$B = \left(\frac{e^2 \hbar^2}{m} \right) \frac{1}{|E_0|^2} , \quad (5.26)$$

dictates units for polarizability. In atomic units, α is measured in a_0^3 and the constant B is given by

$$B = \frac{1}{|E_0|^2} . \quad (5.27)$$

For the sake of completeness, we mention that if one uses rydbergs as the energy unit, the coefficient B has to be multiplied by a factor of four. The values of discrete oscillator strengths and energy levels are taken from the NIST Atomic Spectra Database [73] and [74] and continuous oscillator strengths, $df/d\epsilon$, were constructed using Verner's [75] analytic fits for partial photoionization cross sections. The relation between continuous oscillator strength df/dE and the cross section σ , given in SI units, is

$$\frac{df}{dE} = 4\pi\epsilon_0 \frac{mc}{\pi e^2 h} \sigma . \quad (5.28)$$

If we measure the energy in rydbergs and cross section in m^2 , then

$$\frac{df}{dE} = \frac{1}{4\pi^2 \alpha a_0^2} \sigma , \quad (5.29)$$

where $\alpha \approx 1/137$ is the fine-structure constant and a_0 is the Bohr radius. When σ is reported in megabarns (1 Mbarn = 10^{-22}m^2) then we have

$$\frac{df}{dE} \sim 0.124\sigma . \quad (5.30)$$

One additional step is needed, a change to dimensionless $df/d\epsilon$, which is inferred from the integral part of the expression for the number of electrons

$$\int_0^\infty \frac{df}{dE} dE = \text{constant} , \quad (5.31)$$

which should not depend on the choice of energy units. If we decide to measure energy in portions of $|E_0|$ that is $E \rightarrow \epsilon = E/|E_0|$, then we have

$$\frac{df}{d\epsilon} = |E_0| \frac{df}{dE} . \quad (5.32)$$

Table 5.2 shows the contribution of different parts in the expression (5.14) to the dispersion coefficient, where disc. (cont.) refer to the nature of oscillator strengths. Similarly, Table 5.3 shows the breakdown of the number of electrons N_e , and static

Table 5.2: van der Waals coefficient.

	disc. - disc.	disc. - cont.	cont. - cont.	Total
C_6	568	155.4	21.8	745

polarizability α , into discrete and continuous parts.

5.2 Elastic cross sections: quasi-classical approximation

For the range of energies above 1 cm^{-1} , we can apply the quasi-classical approximation [76]. In this approximation the elastic cross section for two atoms with re-

Table 5.3: Control values.

	disc.	cont.	Total	Expected
N_e	1.92	20.38	22.3	24
α	78.7	6.3	85.0	82 ± 20

duced mass μ , collision energy E , interacting through a potential whose long distance behavior scales as C_n/R^n where $n > 2$, is given by

$$\sigma_{el} = 2\pi^{n/(n-1)} \sin\left(\frac{\pi(n-3)}{2(n-1)}\right) \Gamma\left(\frac{n-3}{n-1}\right) \left[\frac{\Gamma(\frac{n-1}{2})}{\Gamma(\frac{n}{2})}\right]^{2/(n-1)} \left(\frac{C_n}{\hbar v}\right)^{2/(n-1)}, \quad (5.33)$$

where $E = \mu v^2/2$ holds. In the case of $n = 6$, the above expression further reduces to

$$\sigma_{el} = \frac{\pi}{2} 6^{2/5} \sin\left(\frac{3\pi}{10}\right) \Gamma(3/5) \left[\sqrt{2\mu} C_6 \frac{1}{\sqrt{E}}\right]^{2/5}, \quad (5.34)$$

where $\Gamma(3/5) = 1.4891922488128$. From Fig. 5.3, we conclude that the contribution of dipolar interaction to the elastic cross section in the energy range above 1 cm^{-1} can be neglected compared to the effect of the dispersion force. The quantum mechanical calculations were performed for two magnetic field values to show that the contribution of Zeeman interaction can be neglected too. Simply put, at the higher energies, the collision is determined by the dominant short-range interaction.

With the choice of $n = 3$, we get the expression for dipolar elastic cross section

$$\sigma_{el} = 2\pi^2 \frac{C_3}{\hbar v}. \quad (5.35)$$

Due to the small value of the constant C_3 ($\sim \alpha^2$) for dipolar force, the contribution of the dipolar force to the elastic cross section can be neglected.

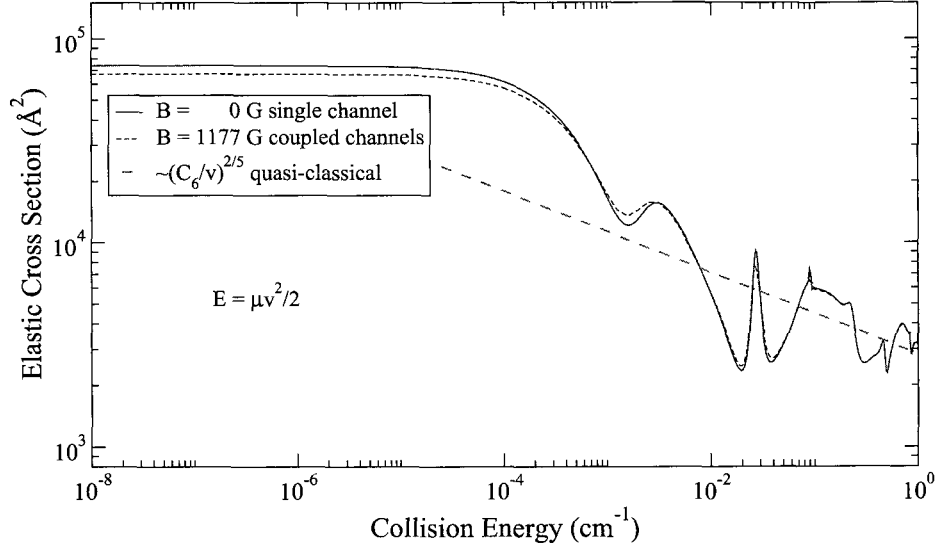


Figure 5.3: Energy dependence of the elastic cross section. Quantum mechanical calculation (full or dashed line) vs. quasi-classical approximation (dotted line).

5.3 Cross sections: Born approximation

In the Born approximation, the scattering amplitude for the transition from a state $|a\rangle$ to a state $|a'\rangle$ is given as

$$f_{aa'} = -\frac{2\mu}{4\pi\hbar^2} \int d^3r e^{i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}} \langle a | \hat{V} | a' \rangle, \quad (5.36)$$

where $\hat{V}$ is interaction, and $\mathbf{k}_i$ and $\mathbf{k}_f$ are initial and final momentum vectors. After substituting the interaction potential with the magnetic dipolar interaction, (see (4.2.4)), we are faced with the evaluation of the integral expression

$$I = \int r^2 dr d\hat{\mathbf{r}} e^{i\mathbf{u} \cdot \mathbf{r}} Y_{2q}(\hat{\mathbf{r}}) \frac{1}{r^3}, \quad (5.37)$$

where vector $\mathbf{u}$ is the difference of the initial and final momentum vectors

$$\mathbf{u} = \mathbf{k}_i - \mathbf{k}_f. \quad (5.38)$$

Given the plane wave expansion

$$e^{i\mathbf{u}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^l j_l(kr) Y_{lm}^*(\hat{\mathbf{u}}) Y_{lm}(\hat{\mathbf{r}}), \quad (5.39)$$

an orthonormality relation for spherical harmonics

$$\int d\hat{\mathbf{r}} Y_{lm}(\hat{\mathbf{r}}) Y_{2q}(\hat{\mathbf{r}}) = (-1)^q \delta_{l,2} \delta_{m,-q}, \quad (5.40)$$

and an integral identity for the $n = 2$ spherical Bessel functions

$$\int_0^\infty dr j_2(r)/r = \frac{1}{3}, \quad (5.41)$$

we can perform all the necessary steps to obtain the following expression for the scattering amplitude

$$f_{aa'}(\mathbf{k}_i, \mathbf{k}_f) = \frac{2\mu\alpha^2}{\hbar^2} \sqrt{\frac{24\pi}{45}} \sum_q Y_{2q}^*(\hat{\mathbf{u}}) \langle a | S_q^2 | a' \rangle, \quad (5.42)$$

where vector $\hat{\mathbf{u}}$ is the normalized difference of initial and final momentum vectors

$$\hat{\mathbf{u}} = \frac{\mathbf{k}_i - \mathbf{k}_f}{|\mathbf{k}_i - \mathbf{k}_f|}. \quad (5.43)$$

Finally, with the help of an integral identity

$$\frac{1}{4\pi} \int d\hat{\mathbf{k}}_i \int d\hat{\mathbf{k}}_f Y_{2q}^*(\hat{\mathbf{u}}) Y_{2q}(\hat{\mathbf{u}}) = 1 \quad (5.44)$$

we find the expression for the cross section to be

$$\sigma_{aa'} = \frac{k_f}{k_i} \frac{1}{4\pi} \int d\hat{\mathbf{k}}_i \int d\hat{\mathbf{k}}_f |f_{aa'}|^2 = \frac{k_f}{k_i} \frac{2\mu\alpha^2}{\hbar^2} \frac{8\pi}{15} |\langle a | S_q^2 | a' \rangle|^2. \quad (5.45)$$

In the above derivation, we dropped the summation over the index q since we work in the coupled basis $|SM_S IM_I\rangle$ for which we have selection

$$q = \Delta M_S = M_S - M_{S'}. \quad (5.46)$$

In this section we use a notation in which the $|SM_S\rangle$ state is a function of both electronic spin and electronic spatial coordinates. In the case of identical nuclei, the scattering amplitude must be symmetrized with respect to the exchange of nuclei. It is enough to symmetrize the final state

$$e^{\mathbf{k}_f \cdot \mathbf{r}} |S' M_{S'} I' M_{I'}\rangle \rightarrow (1 + (-1)^{2I} P_N) e^{\mathbf{k}_f \cdot \mathbf{r}} |S' M_{S'} I' M_{I'}\rangle = \left(e^{\mathbf{k}_f \cdot \mathbf{r}} + (-1)^{S'+I'} e^{-\mathbf{k}_f \cdot \mathbf{r}} \right) |S' M_{S'} I' M_{I'}\rangle, \quad (5.47)$$

which further reflects on the expression for the cross section

$$\sigma_{aa'} = \frac{k_f}{k_i} \frac{1}{8\pi} \int d\hat{\mathbf{k}}_i \int d\hat{\mathbf{k}}_f |f_{aa'}(\mathbf{k}_i, \mathbf{k}_f) + (-1)^{S'+I'} f_{aa'}(\mathbf{k}_i, -\mathbf{k}_f)|^2. \quad (5.48)$$

When compared to the case of non-identical nuclei, an extra factor of $1/2$ is present in order to avoid the double counting of final states. To calculate the cross section, the direct product terms $f_{aa'}^*(\mathbf{k}_i, \mathbf{k}_f) f_{aa'}(\mathbf{k}_i, \mathbf{k}_f)$ and $f_{aa'}^*(\mathbf{k}_i, -\mathbf{k}_f) f_{aa'}(\mathbf{k}_i, -\mathbf{k}_f)$ need to be integrated using (5.43), (5.44) and vector $\hat{\mathbf{v}}$, a normalized sum of initial and final momentum vectors,

$$\hat{\mathbf{v}} = \frac{\mathbf{k}_i + \mathbf{k}_f}{|\mathbf{k}_i + \mathbf{k}_f|} \quad (5.49)$$

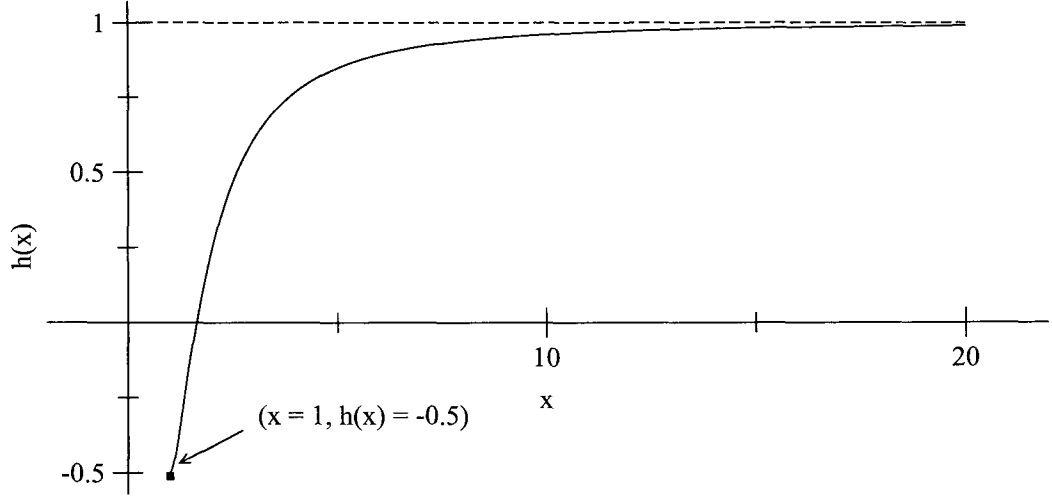


Figure 5.4: Auxiliary function $h(x)$: determines cross sections in the Born approximation, where parameter x is either 1 or the ratio k_f/k_i of final and initial wave numbers .

on an equal footing with vector $\hat{\mathbf{u}}$. The evaluation of the cross product term

$f_{aa'}^*(\mathbf{k}_i, \mathbf{k}_f) f_{aa'}(\mathbf{k}_i, -\mathbf{k}_f)$ requires the application of

$$\frac{1}{4\pi} \int d\hat{\mathbf{k}}_i \int d\hat{\mathbf{k}}_f Y_{2q}^*(\hat{\mathbf{u}}) Y_{2q}(\hat{\mathbf{v}}) = h(\xi), \quad (5.50)$$

where the auxiliary function $h(\xi)$ defined as

$$h(\xi) = -\frac{1}{2} - \frac{3}{8} \frac{(1 - \xi^2)^2}{\xi(1 + \xi^2)} \log \left(\frac{(1 - \xi^2)^2}{(1 + \xi^2)^2} \right) \quad (5.51)$$

depends on the ratio of magnitudes of final and initial momenta, $\xi = k_f/k_i$. The monotonic function $h(\xi)$, shown in Fig. 5.4, has two limits: $h(1) = -1/2$ and $h(\infty) = 1$. After rearranging terms we get the expression for the cross section in the case of scattering of atoms with identical nuclei

$$\sigma_{aa'} = \left(\frac{2\mu\alpha^2}{\hbar^2} \right)^2 \frac{8\pi}{15} \left(1 + (-1)^{S'+I'} h(\xi) \right) \xi \left| \langle a | S_q^2 | a' \rangle \right|^2. \quad (5.52)$$

This expression is correct for identical atoms as well, since the states $|SM_S\rangle$ already have proper symmetrization with respect to electronic coordinates.

The rest of this section illustrates the application of (5.52) to the case of scattering of two identical ^{52}Cr atoms initially in the highest (top line in Fig. 5.5) Zeeman state: $|s_1 = 3, m_{s_1} = 3\rangle |s_2 = 3, m_{s_2} = 3\rangle$. In the coupled representation, the two atoms

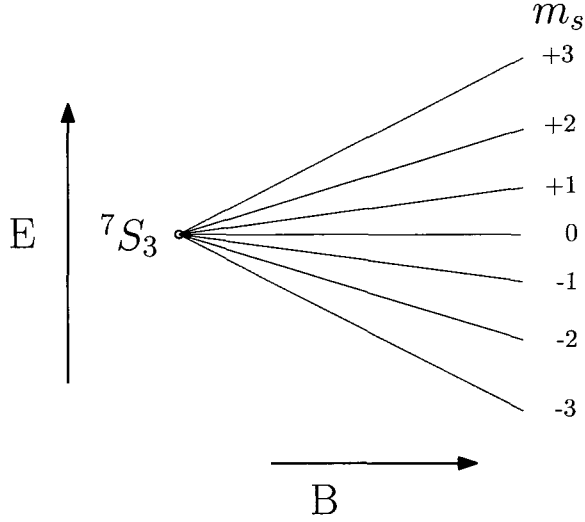


Figure 5.5: Zeeman diagram for ^{52}Cr atom in the ground state with electronic spin $s = 3$ ($m_s = -3 \cdots 3$) and zero orbital angular momentum (S state).

initially in the channel state $|S = 6, M_S = 6\rangle$ can be found after the collision in the following channel states

$$|S = 6, M_S = 6\rangle \quad (\Delta M_S = 0) \quad (5.53)$$

$$|S = 6, M_S = 5\rangle \quad (\Delta M_S = 1) \quad (5.54)$$

$$|S = 6, M_S = 4\rangle, \quad |S = 4, M_S = 4\rangle \quad (\Delta M_S = 2) . \quad (5.55)$$

The last line shows that for the $\Delta M_S = 2$ process, we must add cross sections for $|S = 6, M_S = 6\rangle \rightarrow |S = 6, M_S = 4\rangle$ and $|S = 6, M_S = 6\rangle \rightarrow |S = 4, M_S = 4\rangle$ to

obtain the total inelastic cross section. The required squares of the absolute values of the S_q^2 amplitudes are

$$\langle 66 | S_0^2 | 66 \rangle = 54, \langle 66 | S_1^2 | 65 \rangle = 27, \langle 66 | S_2^2 | 64 \rangle = \frac{54}{11}, \langle 66 | S_2^2 | 44 \rangle = \frac{45}{11}. \quad (5.56)$$

For each value of $\Delta M_S = 0, 1, 2$, in the Born approximation the cross sections for no spin-flip, one spin-flip, and two spin-flip transition are respectively

$$\sigma_{\Delta M_S=0} = (2\mu\alpha^2)^2 \frac{8\pi}{15} (1 + h(1)) 2 \cdot 3^3, \quad (5.57)$$

$$\sigma_{\Delta M_S=1} = (2\mu\alpha^2)^2 \frac{8\pi}{15} (1 + h(\xi)) \xi \cdot 3^3, \quad (5.58)$$

$$\sigma_{\Delta M_S=2} = (2\mu\alpha^2)^2 \frac{8\pi}{15} (1 + h(\xi)) \xi \cdot 3^2. \quad (5.59)$$

For large enough values of the magnetic field B , that is when the ratio $k_f/k_i \gg 1$, the function $h(\xi)$ becomes constant. Since the magnetic field enters the expression for spin-flip cross sections through the ratio

$$\frac{k_f}{k_i} = \sqrt{1 + \Delta M_S \frac{4\mu\varepsilon}{\hbar^2 k^2}}, \quad (5.60)$$

which depends on the energy gap $\varepsilon = 2\mu_B B$, it becomes clear that for *high* magnetic fields the spin-flip cross sections have a $\sqrt{B}$ dependence. From Fig. 5.6, it can be seen that for low values of the magnetic field the Born approximation approaches the low-energy end of cross sections. For higher energies, the cross section in the Born approximation assumes a constant value. Without consulting Fig. 5.7 it is tempting to conclude that the Born approximation gives a satisfactory treatment of the dipolar cross sections. In Fig. 5.7, we plot the full multichannel and Born approximation calculations for a range of magnetic field values. It is clear that the two calculations show opposite trends with respect to the magnetic field.

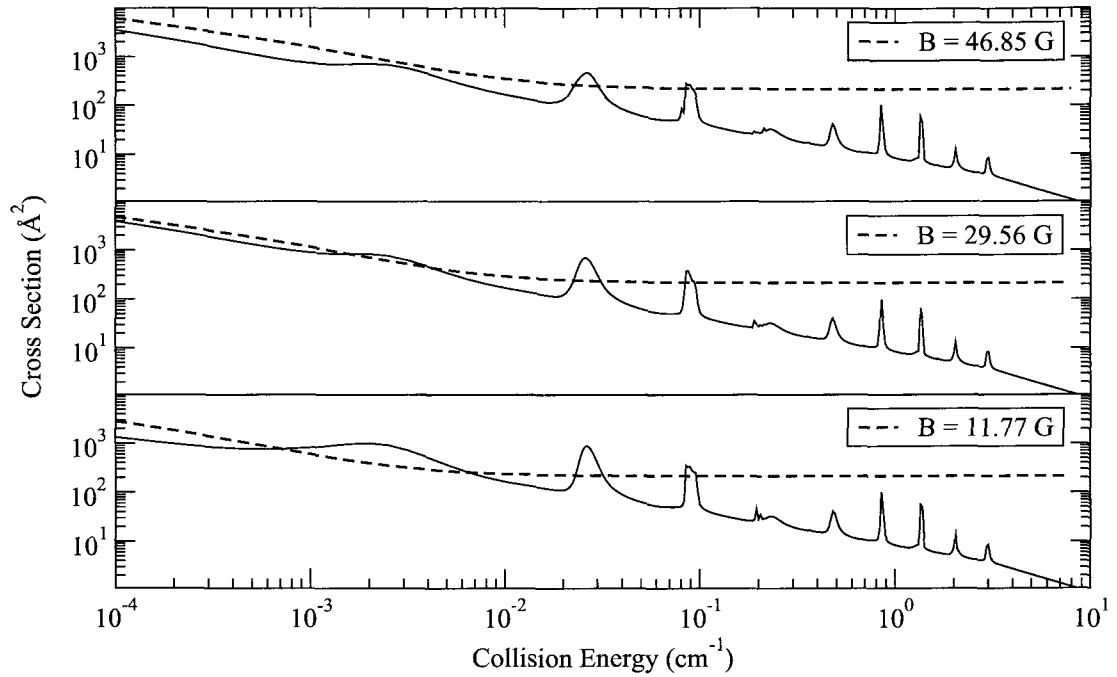


Figure 5.6: Multichannel calculations vs. Born approximation of the inelastic cross sections for ^{52}Cr atom collision in the highest energy Zeeman state. Full line: full multichannel calculations. Dashed line: Born approximation.

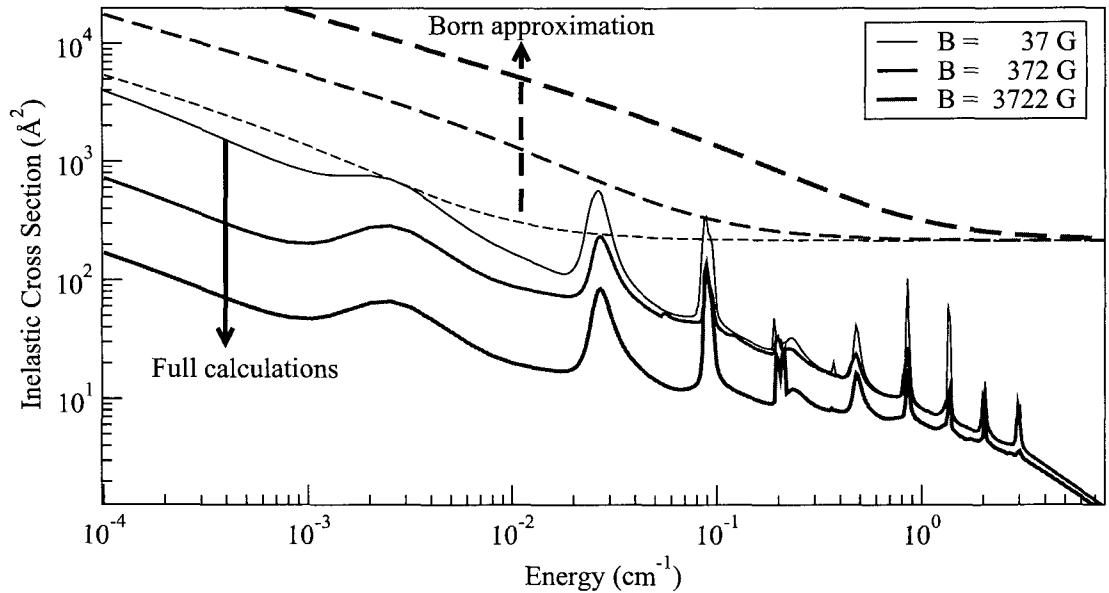


Figure 5.7: Opposite trends in the full multichannel and Born approximation calculations of the inelastic cross sections for the collision of ^{52}Cr atoms in the highest energy Zeeman state. Full line: full multichannel calculations. Dashed line: Born approximation.

5.4 Boson-boson scattering ($^{52}\text{Cr} - ^{52}\text{Cr}$)

5.4.1 Cross sections

The initial channel spin state in the uncoupled representation $|s_1 = 3, m_{s_1} = 3\rangle|s_2 = 3, m_{s_2} = 3\rangle$ is represented by the $|S = 6, M_S = 6\rangle$ spin state in the coupled representation. Referring back to Sec. 4.2.4, we deduce that only even spins are relevant, since dipolar interaction for identical atoms separates even spin states from odd and our initial channel is an even spin state. Other interactions included in this work, such as the electrostatic and Zeeman interactions, do not change the total electronic spin S or rotational numbers ℓ and m_ℓ . On the other hand, the dipolar interaction can change the rotational numbers and it separates even from odd ℓ 's. In order to select the proper parity of ℓ , the symmetrization rule stating

$$S + \ell = \text{even}, \quad (5.61)$$

must be invoked. Since we already have chosen even total spin numbers, then the even rotational numbers (ℓ) must be selected.

In order to be able to map out cross sections for a range of magnetic field and energy values, it is important to reduce the size of the $|SM_S; \ell m_\ell\rangle$ basis. The full multichannel calculations of the dipolar relaxation of two atoms in the highest energy state can be safely replaced with the one having only a limited number of channels. Namely, it is not necessary to include all sums of the magnetic projection number, $-6 \leq M \leq 6$. It is enough to restrict the maximum change of M to 2 units. This is confirmed in Fig. 5.8, where it can be seen that for a range of magnetic field values, the contribution of the channel $S = 4, M_S = 4$ (bottom line) is of the order of a percent. To summarize, the channels used in this work

$$SM_S = \{66, 65, 64, 44\}, \quad (5.62)$$

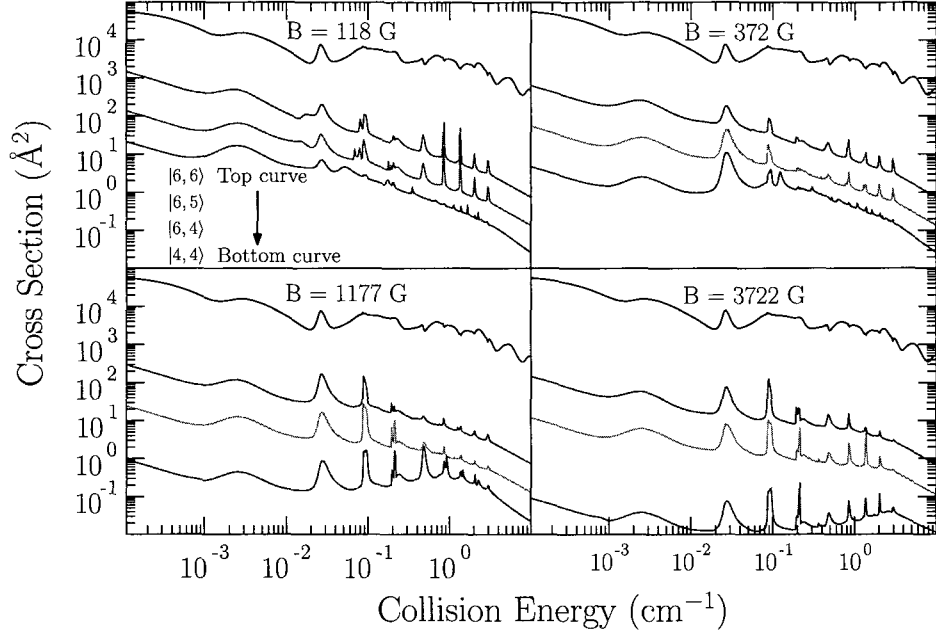


Figure 5.8: Channel distribution of the inelastic cross section for the collision of ^{52}Cr ground state atoms in the highest energy Zeeman state for different magnetic field values: full multichannel calculations.

were further furnished with even rotational numbers ℓ and m_ℓ chosen in such a way to preserve the total magnetic projection $M_S + m_\ell = 6$. Figure 5.7 shows the energy dependence of the cross sections for the relaxation of ^{52}Cr atoms in the maximally stretched state $M_S = +6$ at several magnetic field strengths. Its basic features are: the decrease of the cross section with increase of magnetic field strength, contrary to what the Born-approximation predicts, the increase of cross sections towards the lower end of magnetic field strength, and the appearance of a number of shape resonances whose positions are unaffected by the magnetic field.

The cross section behavior for low magnetic field strengths at ultracold collision energy ($\sim 10^{-14}$ a.u.) is somewhat surprising (see Fig. 5.9). The cross section for the Zeeman transition vanishes in the absence of a magnetic field [77]. In a magnetic field, different than zero, the cross section tends to go to infinity when the collision

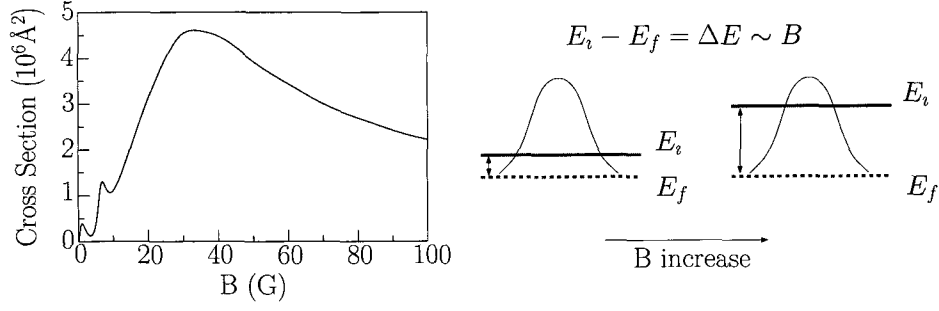


Figure 5.9: The effect of a barrier in the exit channel.

energy decreases (see Fig. 5.7), which in turn leads to the increase of the cross section with magnetic field increase when the collision energy is kept in the ultracold regime [78]. At ultracold energies, the $\ell = 0$ partial wave dominance in the entrance channel is not preserved in the outgoing channel, because the dipolar interaction is capable of imparting angular momentum. This in turn creates the centrifugal barrier in the final channel which suppresses the transition probability when the magnetic field is low enough so the energy difference between the final and initial channel is negligible compared to the height of the centrifugal barrier. Increasing the magnetic field reduces the suppressing role of the barrier which reflects in the increase of the cross section. At high magnetic fields, the relaxation cross section should decrease according to the energy-gap law [79]. For the region of magnetic field strengths between the two extremes, the cross section shows a maximum. For the typical atomic and molecular systems, the location of the maximum is around the magnetic field strength of 1 – 2 T. It seems that the low value of the magnetic field (40 G) at which the role of the centrifugal barrier is mitigated can be attributed to the relatively large ^{52}Cr mass. Apparently, the large mass reduces the height of the centrifugal barrier so as little as 40 G is enough to suppress the role of the barrier in the final channel.

5.4.2 Collision rates

The initial motivation for this work was to study a system for which a buffer gas cooling experiment was performed by John Doyle's group [15]. The potential curves for Cr show significant separation at finite interatomic distance (see Fig. 5.2), which suggests the existence of substantial spin anisotropy in atom-atom collision [80]. The relaxation of ^{52}Cr atoms in the maximally polarized states, $M_S = +6$, is therefore rapid and it is governed by the magnetic dipolar interaction. The temperature range covered in the experiment was $0.01 - 1$ K and due to technical difficulties the lower temperature limit could not be pushed down. The results, experimental and theoretical, are best summarized in Fig. 5.10 taken from [17]. The common feature, apart from discrepancies, of the theoretical rate coefficients and the experimental two-body loss rates, is that when the sample temperature approaches 10 mK the ratio of elastic and inelastic collision rates falls below 100, a generally accepted ratio necessary to perform evaporative cooling.

5.4.3 Magnetic Fano-Feshbach resonances

Here we discuss at length the identification and mapping of magnetic Fano-Feshbach resonances observed by Pfau and co-workers [39] in the sample of trapped ^{52}Cr atoms. Using the $^7S_3 \rightarrow ^7P_3$ transition the atoms were optically transferred from the $m_s = +3$ to $m_s = -3$ state (top $\rightarrow$ bottom line in Fig. 5.5). The sole purpose of this manipulation was to avoid the loss of atoms due to magnetic dipolar scattering. The fundamental differences compared to alkali atoms are the absence of the hyperfine interaction and much stronger magnetic dipolar interaction, approximately 36 times higher due to larger magnetic moment ($6\mu_B$). It is this interaction that is responsible for the coupling of the $M_S = -6$ state to higher energy Zeeman states. The Feshbach formalism tells us that two atoms prepared in the lowest energy Zeeman

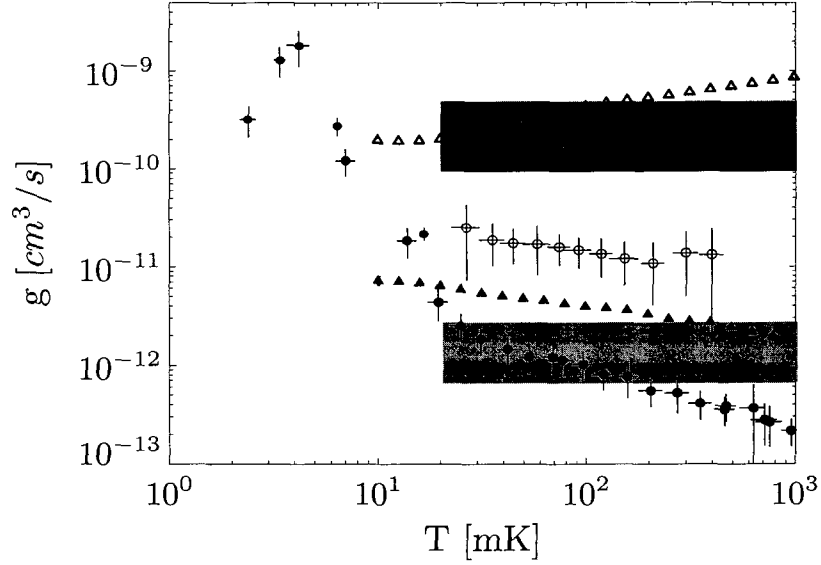


Figure 5.10: ^{52}Cr elastic and inelastic collision rate coefficients : solid shapes - elastic, open shapes - inelastic. Triangles - theoretical results. The circles with error bars are measured two-body loss rates. Horizontal bars represent inferred collision rates from the evaporation data.

states, $m_s = -3$, form an open channel state, which in the short range and for the magnetic fields in the vicinity of Feshbach resonance is coupled to a closed-channel state. Since neither of these states is an eigenstate state of the total interaction, a number of oscillations happen, which prolong the time it takes atoms to scatter back into the open channel.

Table 5.4: Resonances $\ell = 2, 4$.

$\ell = 2$		$\ell = 4$			M_S
$S = 6$	$S = 4$	$S = 6$	$S = 4$	$S = 2$	
589.1	$\times$	205.6	$\times$	$\times$	-5
290.3	499.9	98.5	286.6	$\times$	-4
E_{-1}	E_{-1}	65.1	188.3	$\times$	-3
		50.1	143.9	379.2	-2
		E_{-1}	E_{-1}	E_{-1}	

Here there is only one open channel state, $|S = 6, M_S = -6\rangle$, which serves as the initial and final scattering channel.

The identification of 11 out of the 14 observed resonances is summarized in Table 5.4, where the table header is composed of the total electronic spin S , the total magnetic projection number M_S and the rotational angular momentum number ℓ used to label Feshbach resonances while their positions are tabulated using gauss as a unit for magnetic field strength. At the bottom of the table there is an indication to which bound level generates the resonance. The index -1 refers to the top bound level, index -2 refers to the next lower level and so on.

Closed-channel $\ell = 2$ resonances: To simplify matters we will start our analysis with $\ell = 2$ (d -wave) resonances and later include $\ell = 4$ (g -wave) resonances. The basis state $|S = 6, M_S = -6; \ell = 0, m_\ell = 0\rangle$ has to be expanded with $\ell = 2$ states which have to satisfy the requirement $M_S + m_\ell = -6$. As before, only even spins and rotational numbers ought to be included. The complete list of basis states is in Table 5.5.

Table 5.5: $s + d$ -wave basis.

S	M_S	ℓ	m_ℓ	
6	-6	0	0	} open
6	-6	2	0	
6	-5	2	-1	} closed
6	-4	2	-2	
4	-4	2	-2	

A typical plot of the scattering length versus magnetic field is contained in the top pane of Fig. 5.11. It shows nearly constant background scattering length ($a_{bg} \sim 100 a_0$) except around the Fano-Feshbach resonances where it changes according to

$$a(B) = a_{bg} \left(1 - \frac{\Delta B}{B - B_c} \right). \quad (5.63)$$

The width of the resonance, ΔB , is extracted by measuring the distance between a point B_c where the scattering length diverges and a point where the scattering length becomes zero. The bottom pane of Fig. 5.11 contains bound level positions for a range of magnetic field strengths.

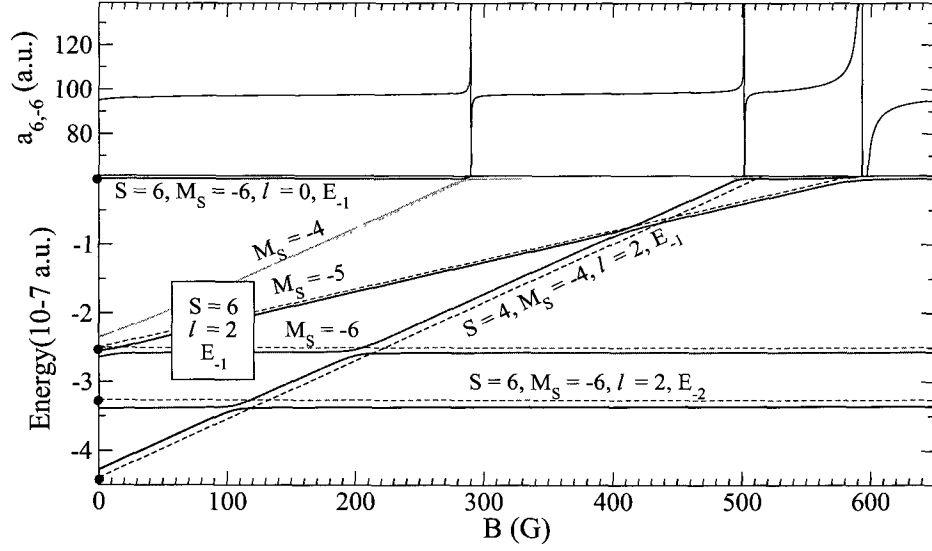


Figure 5.11: Bound levels and resonances, $l_{max} = 2$.

The energy is measured with respect to the lowest energy Zeeman level $M_S = -6$, the zero energy limit in the scattering. The positions of Feshbach resonances coincide with the bound levels crossing the continuum. For comparison purposes we plot the relevant vibrational levels obtained from the molecular potentials in the presence of magnetic field (dashed lines) and bound levels obtained when dipolar couplings are included (full lines). In other words we are comparing single-channel versus multichannel bound level computations. We can see that the top bound level $E_{-1} = -2.495 \cdot 10^{-7}$ a.u. formed in $S = 6$, and $\ell = 2$ potential can move along three Zeeman lines with $M_S = -6, -5, -4$ in the presence of magnetic field. The

bound level that moves with the magnetic field along the $M_S = -6$ Zeeman line never crosses the continuum since it is parallel with the entrance channel limit. The mid-position resonance can be attributed to the bound level $E_{-1} = -4.393 \cdot 10^{-7}$ a.u. formed in $S = 4$, and $\ell = 2$ potential which moves along the $M_S = -4$ Zeeman line. The multichannel calculations (full lines) show typical avoided crossings due to dipolar interaction. Following one of the bound levels we can see how the bound state changes through the crossing area, attaining its single-channel level limits in the areas far enough from the crossings. Apart from the zero magnetic field splittings of the bound level, based on M_S , and constant shift, the dipolar interaction does not deviate much from the single-channel picture. However, if the entrance channel has a low-lying level, a horizontal line close to the continuum threshold, then the formation of avoided crossings with other bound levels due to dipolar interaction will affect the results for resonance positions which were based on single-channel predictions.

Closed-channel $\ell = 4$ resonances. When in the scattering channels, the number of angular momentum states is increased to $l_{max} = 4$, the mid portion of Table 5.4 shows g -wave resonances. Their identification is performed following the way it was done for the d -wave resonances. First, the basis was expanded by the $\ell = 4$ basis states, Table 5.6. Second, for each single-channel potential

$$V_S(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad (5.64)$$

a set of bound levels was determined, Table 5.7. It was found that top bound levels, for example $E_{-1} = -8.302 \cdot 10^{-8}$, when added the appropriate Zeeman shift, in this particular case $M_S = -5, 4, -3, -2$, produce Zeeman lines which cross the continuum line approximately at the positions contained in Table 5.4; the $\ell = 4, S = 6$ column in particular. We do not show the plot of multichannel versus single-channel bound levels since no insight is gained, but we do present the multichannel results for 11

Table 5.6: g -waves.

S	M_S	ℓ	m_ℓ
6	-6	4	0
6	-5	4	-1
6	-4	4	-2
6	-3	4	-3
6	-2	4	-4
4	-4	4	-2
4	-3	4	-3
4	-2	4	-4
2	-2	4	-4

resonances where we included $\ell = 0, 2, 4$ (s, d, g -waves) basis states (see Fig. 5.12). The $\ell = 4$ resonances are narrower than the $\ell = 2$ resonances since direct coupling of closed channel states is zero according to the selection rule $\Delta\ell = 0, 2$. Instead, the coupling arises through second order interaction.

Table 5.7: Single-channel energy levels (10^{-6} a.u.).

	$\ell = 2$			$\ell = 4$		
	S=6	$S = 4$	$S = 2$	$S = 6$	$S = 4$	$S = 2$
E_{-1}	-2.495e-1	-4.393e-1	-6.012e-2	-8.302e-2	-2.413e-1	-6.595e-1
E_{-2}	-1.635	-2.218	-9.129e-1	-1.320	-1.880	-3.041
E_{-3}	-4.963	-6.193	-3.434	-4.505	-5.720	-7.985

The existence of experimental results on Feshbach resonances enables us to fine tune molecular potentials. Since the positions of resonances are determined by the positions of top bound levels which in turn are intrinsically connected to the scattering length values, we can change the latter (and former) by varying the long-range interaction parameters (C_6). Additionally, we can slightly modify the short-range po-

tentials by changing the position of the zero energy classical inner turning point, thus changing the scattering length. The affected part of the potential is the inner wall

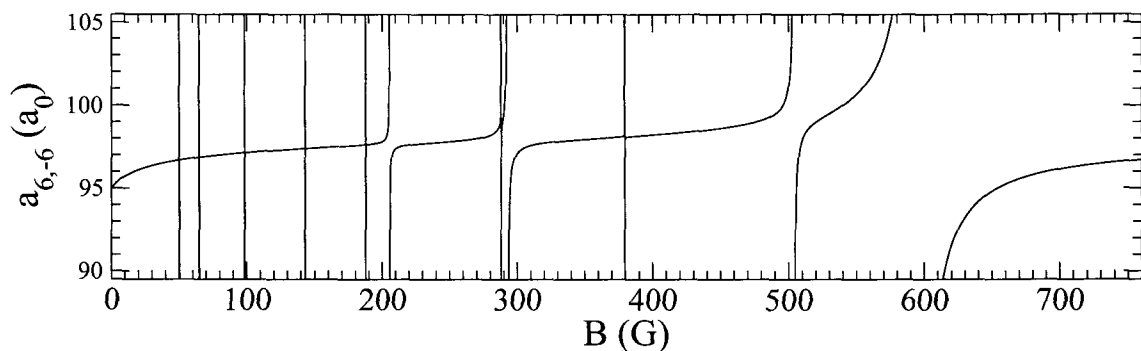


Figure 5.12: Scattering length dependence on the magnetic field for the collision of ^{52}Cr atoms in the lowest energy Zeeman state ($\ell_{\text{max}} = 4$).

which is situated to the left of the equilibrium point, that is all points with separation distance R less than equilibrium distance R_e . The modification is done by shifting the separation distance R according to

$$R \rightarrow R_{\text{shifted}} = R + s \frac{R - R_e}{R_c - R_e}, \quad (5.65)$$

where s is the shift parameter and R_c is the zero energy classical inner turning point. The potential value for shifted points R_{shifted} was obtained using the potential value, $V(R)$, at the original point according to

$$V(R_{\text{shifted}}) = V(R). \quad (5.66)$$

In this work, the short-range and long-range parameters were manually varied in an effort to reproduce the experimental values from Table 5.8 while trying to keep the scattering lengths within the experimental error (see Table 5.9).

Table 5.8: Feshbach resonances for ^{52}Cr atoms in $|s = 3, m_s = -3\rangle$ entrance channel.

$ S, M_S, l, m_l\rangle$	B_c^{calc} [G]	B_c^{exp} [G]	ΔB^{calc} [mG]	ΔB^{exp} [mG]
$ 6, -2, 4, -4\rangle$	50.1	50.1	0.000236	< 0.001
$ 6, -3, 4, -3\rangle$	64.9	65.1	0.0024	0.006
$ 6, -4, 4, -2\rangle$	98.5	98.9	0.159	0.3
$ 4, -2, 4, -4\rangle$	143.0	143.9	0.0254	0.12
$ 4, -3, 4, -3\rangle$	187.6	188.3	0.106	0.22
$ 6, -5, 4, -1\rangle$	205.6	205.8	12.1	12.0
$ 4, -4, 4, -2\rangle$	288.0	286.6	1.53	12.0
$ 6, -4, 2, -2\rangle$	293.0	290.3	53.4	51.0
$ 2, -2, 4, -4\rangle$	379.2	379.2	0.29	0.42
$ 4, -4, 2, -2\rangle$	503.8	499.9	81.0	81.0
$ 6, -5, 2, -1\rangle$	595.0	589.1	1530.0	1700.0

Results pertaining to other entrance channels and different values of C_6 were published in [38]. The more precise and automated procedure using the non-linear least squares fitting method can be found in [39].

Table 5.9: ^{52}Cr scattering length (a.u.)

state	$^{13}\Sigma_g^+$	$^9\Sigma_g^+$	$^5\Sigma_g^+$
Pfau	112(14)	58(6)	-7(20)
this work	102	54	-22

5.5 Boson - fermion scattering ($^{52}\text{Cr} - ^{53}\text{Cr}$)

Owing to the presence of hyperfine interaction in one of the colliding partners, the channel structure becomes more complex than in the case where both atoms are bosons. In particular, the fermionic isotope ^{53}Cr , with its non-zero nuclear spin ($i = 3/2$), offers 28 hyperfine states (right pane Fig. 5.13) while there are only 7 Zeeman states provided by the bosonic isotope ^{52}Cr (left pane Fig. 5.13). Thus, in

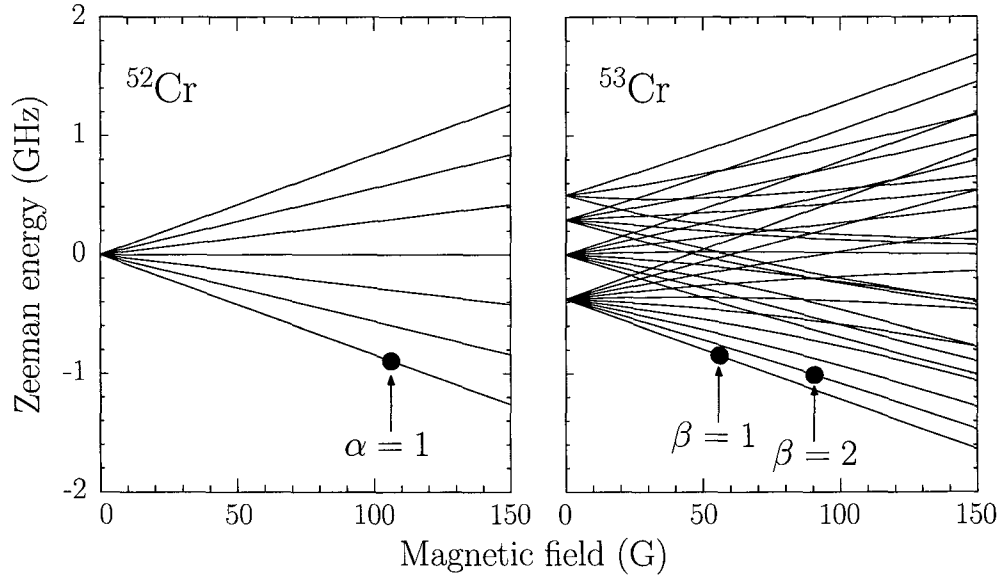


Figure 5.13: Entrance channels for bosonic and fermionic chromium: labeling from bottom to top.

our calculations we include only the first two allowed rotational numbers $\ell = \{0, 2\}$. The g -wave resonances were left out of consideration. Since none of the interactions considered here mixes odd and even rotational numbers and in the entrance channel we have the $l = 0$ rotational number, the odd rotational numbers were left out. We use the label α for bosonic atoms and the label β for fermionic atoms when showing the entrance channel composition.

Entrance channel $\alpha = 1$, $\beta = 1$. A list of basis states used to find Feshbach resonances when two atoms are scattered in their respective lowest internal states can

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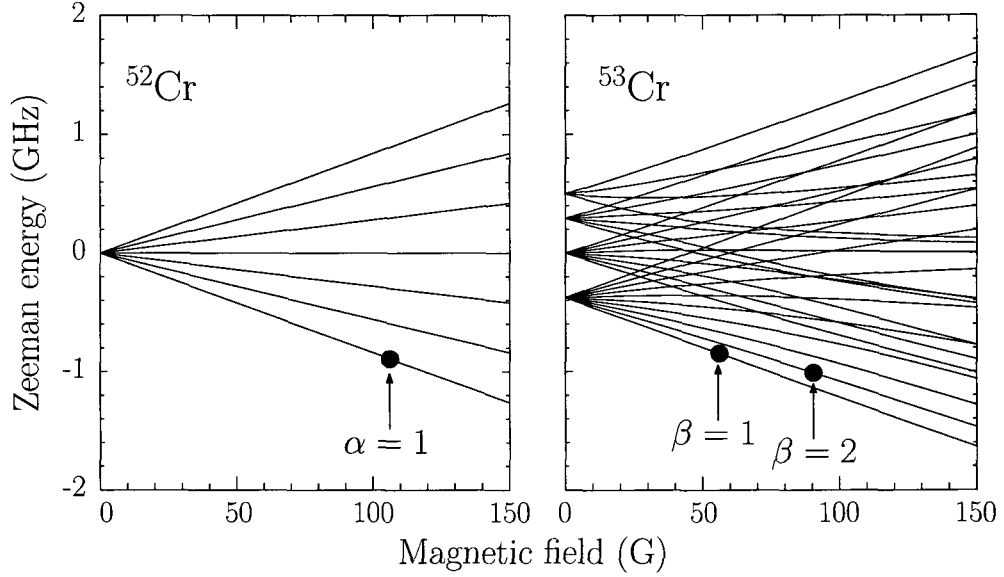


Figure 5.13: Entrance channels for bosonic and fermionic chromium: labeling from bottom to top.

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Entrance channel $\alpha = 1$, $\beta = 1$. A list of basis states used to find Feshbach resonances when two atoms are scattered in their respective lowest internal states can

Table 5.10: ^{52}Cr - ^{53}Cr entrance channel $\alpha = 1$, $\beta = 1$ basis states.

No.	S	M_S	I	M_I	ℓ	m_ℓ
0	6	-6	1.5	-1.5	0	0
1	6	-6	1.5	-1.5	2	0
2	5	-5	1.5	-1.5	2	-1
3	6	-6	1.5	-0.5	2	-1
4	6	-5	1.5	-1.5	2	-1
5	4	-4	1.5	-1.5	2	-2
6	5	-5	1.5	-0.5	2	-2
7	5	-4	1.5	-1.5	2	-2
8	6	-6	1.5	0.5	2	-2
9	6	-5	1.5	-0.5	2	-2
10	6	-4	1.5	-1.5	2	-2

be found in Table 5.10. Owing to the negative hyperfine constant, $A_{hf} = -80.023$ MHz, the hyperfine multiplet is inverted so the lowest energy state $\beta = 1$ is maximally stretched spin state which does not have any partners with the same magnetic projection number. This leads to the absence of pure hyperfine interaction resonances in this channel for $\ell = 0$. We can only see dipolar resonances where $\ell = 0$ channel is connected to other $\ell = 2$ states. The Feshbach resonances are presented in Fig. 5.14, top pane. There we selected three resonances wide enough for any feasible experimental treatment. The labels and percentages next to the resonances are for identification purposes. The percentage is a relative portion of a particular basis state in the norm of the whole bound state responsible for the resonance appearance, lower pane of Fig. 5.14. The zero energy for bound states is set at the value of the entrance channel energy. All resonances for magnetic field in the range of 0 – 1000 gauss , with their respective positions and widths are presented in Table 5.11.

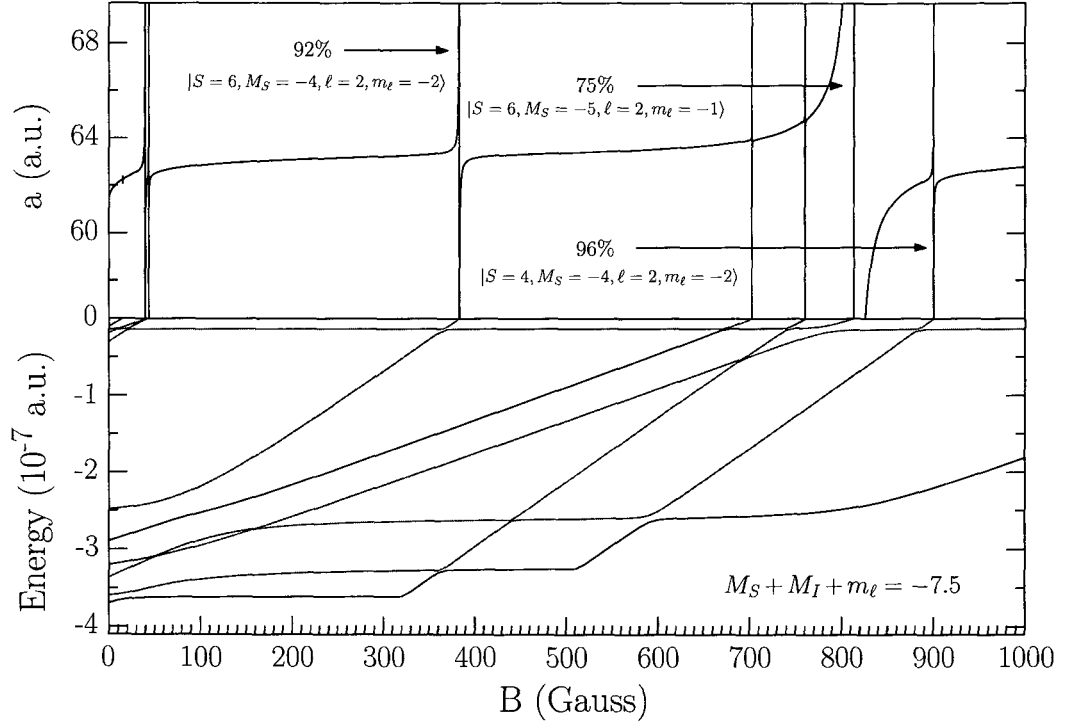


Figure 5.14: Top pane: ^{52}Cr - ^{53}Cr entrance channel $\alpha = 1$, $\beta = 1$ Feshbach resonances. Percentage reveals the dominant component in the multichannel bound state wave function at threshold. Bottom pane: multichannel bound levels. The zero energy reference is the entrance channel Zeeman energy. No hyperfine resonances.

Table 5.11: ^{52}Cr - ^{53}Cr entrance channel $\alpha = 1$, $\beta = 1$: Resonance positions and widths.

B_c [G]	Δ [mG]
15.246	< 1
39.615	16
43.642	3
382.894	35
702.330	1
760.233	< 1
813.330	1310 ⁽¹⁾
900.235	11

⁽¹⁾ corresponds to ^{52}Cr - ^{52}Cr resonance at 600 G

Entrance channel $\alpha = 1$, $\beta = 2$. For this entrance channel, where the fermionic partner is in the second lowest energy state, we list basis states in Table 5.12.

Table 5.12: ^{52}Cr - ^{53}Cr , entrance channel $\alpha = 1$, $\beta = 2$ basis states.

No.	S	M_S	I	M_I	ℓ	m_ℓ
0	5	-5	1.5	-1.5	0	0
1	6	-6	1.5	-0.5	0	0
2	6	-5	1.5	-1.5	0	0
3	6	-6	1.5	-1.5	2	1
4	5	-5	1.5	-1.5	2	0
5	6	-6	1.5	-0.5	2	0
6	6	-5	1.5	-1.5	2	0
7	4	-4	1.5	-1.5	2	-1
8	5	-5	1.5	-0.5	2	-1
9	5	-4	1.5	-1.5	2	-1
10	6	-6	1.5	0.5	2	-1
11	6	-5	1.5	-0.5	2	-1
12	6	-4	1.5	-1.5	2	-1
13	3	-3	1.5	-1.5	2	-2
14	4	-4	1.5	-0.5	2	-2
15	4	-3	1.5	-1.5	2	-2
16	5	-5	1.5	0.5	2	-2
17	5	-4	1.5	-0.5	2	-2
18	5	-3	1.5	-1.5	2	-2
19	6	-5	1.5	0.5	2	-2
20	6	-4	1.5	-0.5	2	-2
21	6	-6	1.5	0.5	2	-2
22	6	-3	1.5	-1.5	2	-2

Compared to the previous case, where the fermionic Cr atom was in the lowest energy state which was maximally stretched and therefore without hyperfine resonance for $\ell = 0$, here we have a strong hyperfine resonance positioned around 176 gauss and 8 gauss wide. The influence of the dipolar interaction is seen in the upper pane of Fig. 5.15, where other resonances are a consequence of an expanding basis with $\ell = 2$

states and of the inclusion of dipolar interaction that connects an open channel to the closed channels. A major difference compared to the types of resonances considered

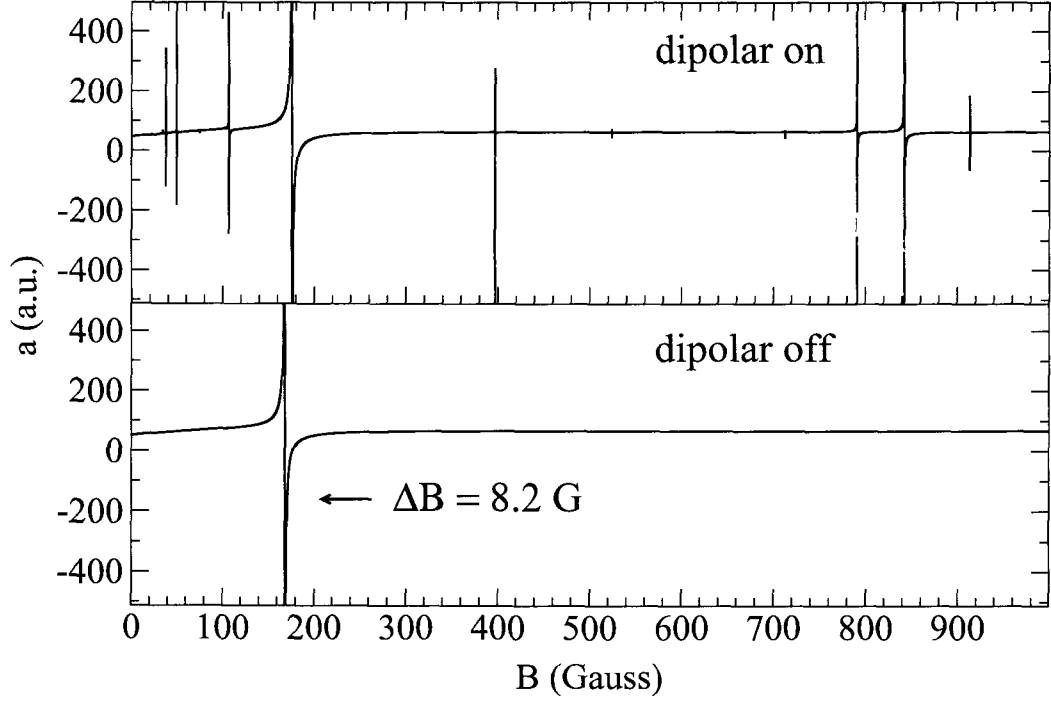


Figure 5.15: ^{52}Cr - ^{53}Cr entrance channel $\alpha = 1$, $\beta = 2$ Feshbach resonances. Bottom pane: $\ell = 0$ entrance channel, hyperfine interaction only. Top pane: dipolar interaction couples $\ell = 0$ entrance channel to $\ell = 2$ channels.

up to now is that here we have more than one open channel and (5.63) does not predict correct behavior of the scattering length. Instead, we have to account for the inelastic nature of Feshbach resonances by using

$$a = a_{bg} \left(1 - \frac{\Delta B}{B - B_c - i\gamma_B/2} \right) \quad (5.67)$$

to describe the real and imaginary parts of the scattering length, [81]. All resonances for magnetic field in the range of 0 – 1000 gauss , with their respective positions and widths are presented in Table 5.13.

Table 5.13: ^{52}Cr - ^{53}Cr entrance channel $\alpha = 1$, $\beta = 2$: Resonance positions and widths.

B_c [G]	Δ [mG]
15.19	< 1
34.10	*
37.763	22
49.532	31
74.950	*
106.768	174
175.890	8700
272.311	< 1
396.921	34
427.369	< 1
523.880	< 1
618.885	< 1
654.922	< 1
712.698	< 1
780.498	< 1
790.935	320
842.120	980
904.021	1
913.595	10
971.981	< 1

(*) unable to fit data

5.6 Fermion - fermion scattering ($^{53}\text{Cr} - ^{53}\text{Cr}$)

Scattering calculations of ^{53}Cr atoms have to accommodate for the fact that we are dealing with identical atoms (fermions), so the identical particle symmetrization of the wave function is necessary. The entrance channel configuration is shown in Fig. 5.16.

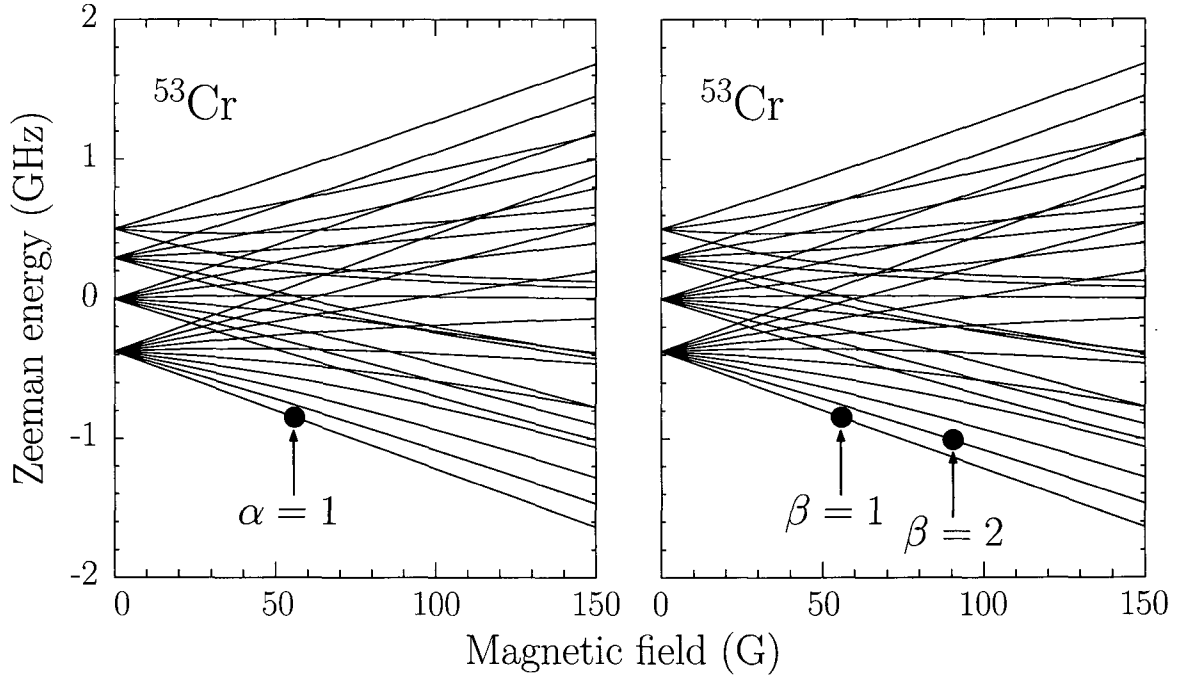


Figure 5.16: Entrance channels for fermionic-fermionic chromium scattering: labeling from bottom to top.

Entrance channel $\alpha = 1$, $\beta = 1$. Both atoms are in the lowest energy Zeeman state. Since both atoms in the entrance channel are in the same spin state, the s -wave scattering is suppressed: only odd rotational wave numbers are allowed. The results are presented in Fig. 5.17 where the effect of the dipolar interaction coupling of the $\ell = 1$ entrance channel to $\ell = 3$ channels is shown.

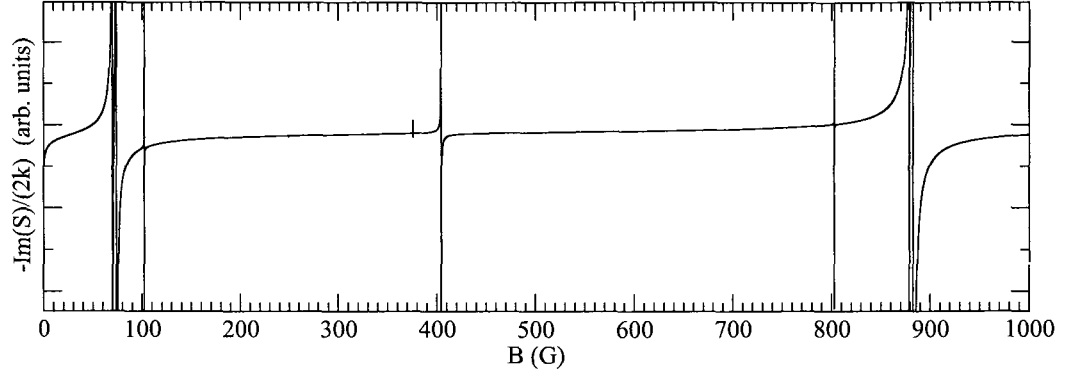


Figure 5.17: ^{53}Cr - ^{53}Cr entrance channel $\alpha = 1$, $\beta = 1$ Feshbach resonances. Imaginary part of S matrix dependence on magnetic field.

Entrance channel $\alpha = 1$, $\beta = 2$. Here we consider one of the atoms in the second lowest energy Zeeman state. For a range of magnetic field values (up to 1000 gauss), we can see only one Feshbach resonance when the dipolar interaction is turned off, bottom pane of Fig. 5.18. The effect of dipolar interaction can be seen in the top pane of Fig. 5.18. The resonance positions and widths are collected in Table 5.14.

Table 5.14: ^{53}Cr - ^{53}Cr , entrance channel $\alpha = 1, \beta = 2$: Resonance positions and widths.

B_c [G]	Δ [mG]
31.889	≤ 1
66.001	26
115.740	5
122.875	< 1
206.386	8
208.098	< 1
375.300	8500
519.650	450
794.990	7
994.653	6

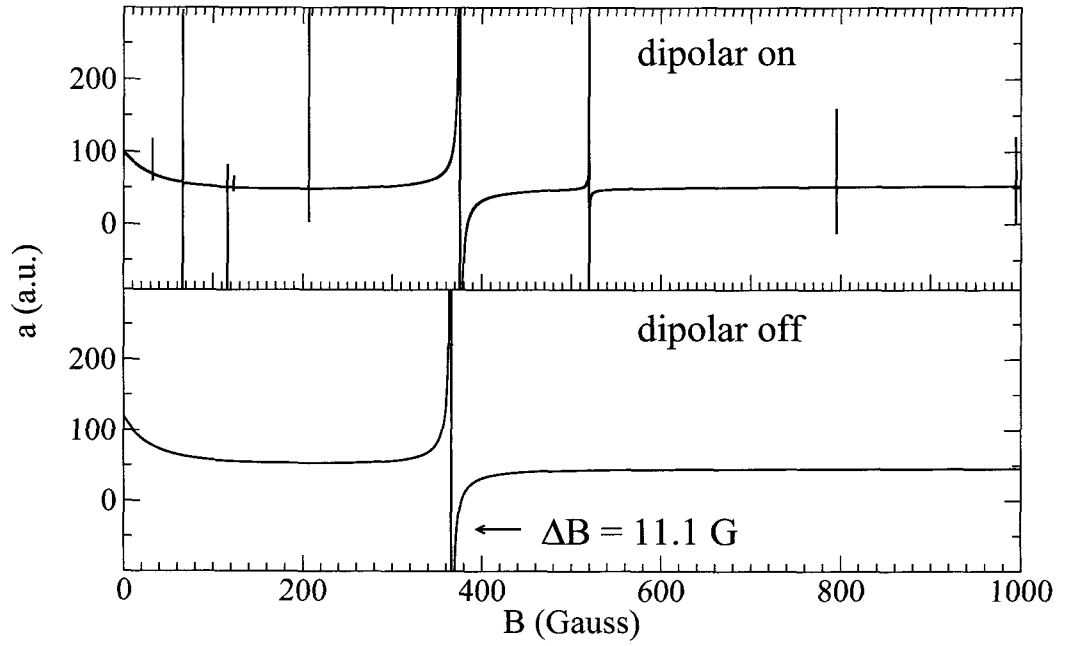


Figure 5.18: ^{53}Cr - ^{53}Cr entrance channel $\alpha = 1$, $\beta = 2$ Feshbach resonances. Bottom pane: hyperfine interaction only. Top pane: including dipolar interaction.

CHAPTER 6

CR-RB COLLISIONS

In this chapter, we analyze the electrostatic interaction of Rb and Cr atoms in their ground state and the long-range dispersion C_6 coefficient. We use Björn Roos's Born-Oppenheimer (BO) potential energy curves to calculate the elastic and relaxation cross sections, hyperfine and dipolar Fano-Feshbach resonances which can be used to tune the interactions, and present the long-range dispersion coefficient for the interaction between ground state Cr and Rb atoms. We also investigate the hyperfine and dipolar collisions between trapped Cr and Rb atoms, finding elastic to inelastic cross section ratio of 10^2-10^3 .

CrRb is a heteronuclear molecule, and may therefore possess a sizable permanent electric dipole moment. In its ground electronic state, it has a magnetic moment of five Bohr magnetons ($5\mu_B$), so it can be magnetically tuned. In its most abundant form (84%), ^{52}Cr has no nuclear spin, $i = 0$, but its fermionic isotope ^{53}Cr (9.5% abundance) has nuclear spin, $i = 3/2$, that couples to electronic spin, $s = 3$, to produce a number of hyperfine levels. Therefore, bosonic-fermionic mixtures of CrRb can be formed with large electric and magnetic dipole moments, with potentially interesting applications for degenerate dipolar Fermi gases and spinor physics.

There is no spectroscopic information available for the CrRb molecule. A two-species magneto-optical trap (MOT) for Cr and Rb was realized in 2004 [40], in which some 4×10^6 ^{52}Cr atoms and 3×10^6 ^{87}Rb atoms were loaded. Cr is known to have large inelastic two-body spin-flip losses, so it cannot be maintained in a MOT

[82, 19, 38]. Owing to its large magnetic moment, magnetic trapping (MT) of Cr is possible [82, 19], which allows the atoms to be trapped in its lowest high-field seeking state with total electronic spin $s = 3$ and its projection $m_s = -3$. In the Rb-MOT + Cr-MT configuration, Hensler *et al.*[40] measured the two-body loss rate constant to be $\beta_{\text{RbCr}} \sim 1.4 \times 10^{-11} \text{ cm}^{-3}/\text{s}$ and $\beta_{\text{CrRb}} \sim 10^{-10} \text{ cm}^{-3}/\text{s}$, where the former refers to the loss due to the introduction of Cr into the Rb-loaded MOT, and the latter refers to loading of the Cr-MT first. The latter loss coefficient is about an order of magnitude larger than the former loss coefficient, because in the more shallow Cr-MT, interspecies dipolar interactions lead more quickly to spin depolarizing collisions, hence depletion of the trap.

6.1 BO potential energy curves

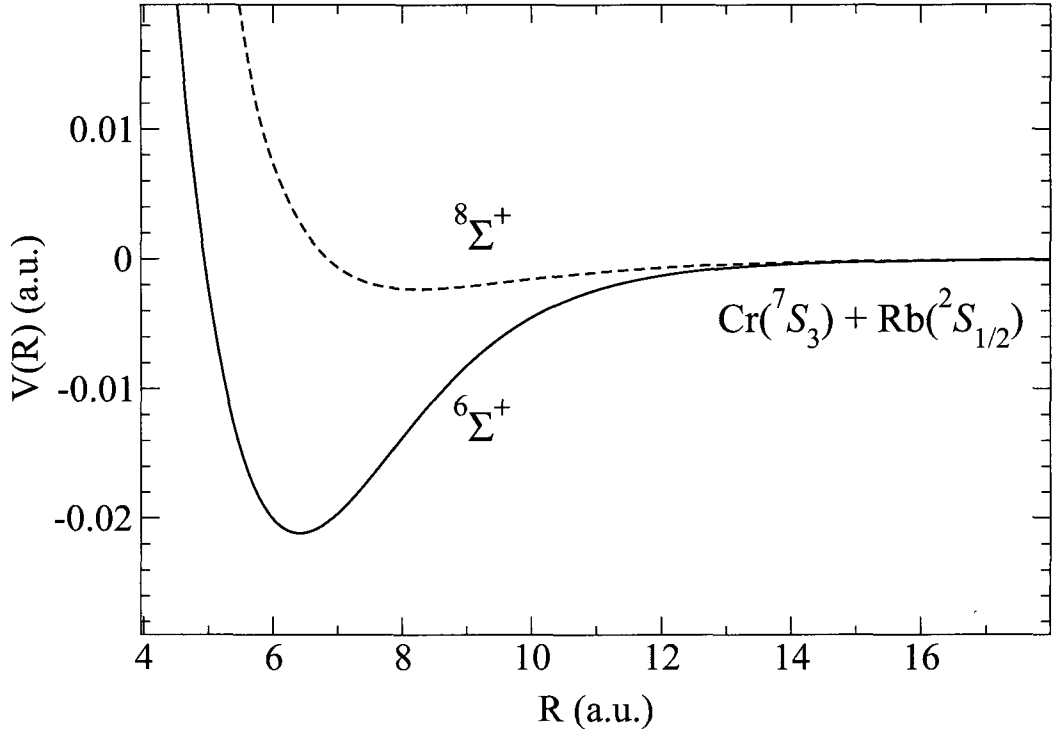


Figure 6.1: The $6\Sigma^+$ and $8\Sigma^+$ potential energy curves for CrRb, correlating to $\text{Cr}(^7S_3)$ and $\text{Rb}(^2S_{1/2})$ ground states.

The calculations of the BO potential energy curves and the permanent electric dipole moments were performed with the multiconfiguration complete active space self-consistent field (CASSCF/CASPT2) method [56, 83]. The basis set was of VQZP quality with the primitives obtained from the relativistic ANO-RCC basis set ($7s6p4d3f2g1h$ for Cr and $8s7p4d2f1g$ for Rb)[84, 85]. Scalar relativistic effects are included in the calculations using the Douglas-Kroll-Hess Hamiltonian, as is standard in the MOLCAS software. Two active spaces were used. The first comprised the Cr $3d$ and $4s$ orbitals and the Rb $5s$, thus seven orbitals with seven active electrons. In the second set of calculations, a second set of $3d$ orbitals was added to describe the $3d$ double shell effect: 12 orbitals with seven electrons. All calculations were performed with the MOLCAS-7 quantum chemistry software [86]. In Fig. 6.1, we plot the BO potential energy curves for CrRb in the ground electronic states. The equilibrium separation for the molecule in the ground state ${}^6\Sigma^+$ is $R_e = 3.34 \text{ \AA}$ (6.31 a.u.). The value of the permanent dipole moment at the equilibrium distance for the ${}^6\Sigma^+$ ground state molecule is $d_e = 2.90 \text{ D}$ (1.14 a.u.), which is reasonably large.

Long-range: There are two electronic states which correlate to Rb ($6s \text{ } {}^2S$) and Cr($3d^5 4s \text{ } {}^7S$) ground states, ${}^6\Sigma^+$ and ${}^8\Sigma^+$. At large separation, R , these curves are well described by $-C_6/R^6$, where C_6 is the van der Waals (vdW) coefficient. We calculate C_6 using the Casimir-Polder [87] integral

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_{\text{Cr}}(i\omega) \alpha_{\text{Rb}}(i\omega) d\omega, \quad (6.1)$$

where the dynamic polarizability of each atom, $\alpha(i\omega)$, is given by

$$\alpha(i\omega) = \sum_{\lambda} \frac{f_{0\lambda}}{\epsilon_{\lambda}^2 + \omega^2}. \quad (6.2)$$

The calculation of the dynamic polarizability requires knowledge of the oscillator strengths $f_{0\lambda}$ between the atomic ground state of energy ϵ_0 and the atomic excited states of energy ϵ_λ . The summation is understood to also include integration over continuum. Our calculated value of C_6 for the Cr + Rb system, 1770 a.u., is obtained from the highly-accurate values of the Rb dynamic polarizability at imaginary frequencies [68] and the recently accurate values for the Cr dipole polarizability [36, 39]. This should be compared to the values of $C_6(\text{Rb}_2) = 4691$ a.u. [68, 87], and $C_6(\text{Cr}_2) = 770$ a.u., [38]. Both $^6\Sigma^+$ and $^8\Sigma^+$ curves share the same C_6 coefficient.

The calculated static dipole polarizability for the molecule is $\alpha_{\text{CrRb}}(0) = 701$ a.u. We should mention that $\alpha_{\text{Rb}}(0) = 319$ a.u. [88] and $\alpha_{\text{Cr}}(0) = 86$ a.u. [36]. The molecular value is 40% larger than the sum of atomic polarizabilities. Having van der Waals coefficients and static polarizabilities for Cr and Rb, the value of $C_6 = 1753$ for CrRb is obtained using, [89],

$$C_6^{\text{CrRb}} = \frac{2\alpha_{\text{Cr}}\alpha_{\text{Rb}}C_6^{\text{Cr}}C_6^{\text{Rb}}}{C_6^{\text{Cr}}\alpha_{\text{Rb}}^2 + C_6^{\text{Rb}}\alpha_{\text{Cr}}^2}. \quad (6.3)$$

The relative difference of this estimate and the previously computed value is of the order of 1%.

The dearth of spectroscopic and collisional information about the CrRb molecule limits what can be extracted from our calculations at ultracold temperatures. Nevertheless, we can inform the discussion by modifying the interaction potentials and evidence the changes to the phase shifts and/or cross sections at very low energies. Our vdW coefficient is sufficiently accurate to describe the potentials at large separations.

6.2 Cross sections

In the short range repulsive wall region, we shift the potential energy curves, according to the prescription in our earlier work [36], and the results for the elastic cross sections are shown in Fig. 6.2. Several points can be made: while the cross

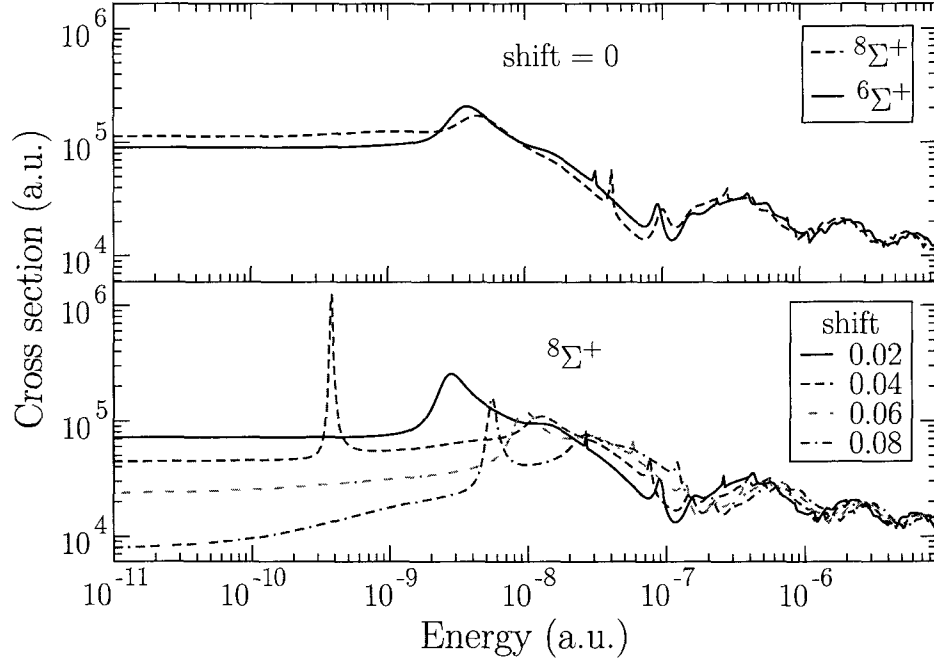


Figure 6.2: Top panel: Elastic cross section for the ${}^6\Sigma^+$ and ${}^8\Sigma^+$ curves without shift in the inner wall ($s = 0$). Bottom panel: Effect of the positive shifts on the elastic cross section along ${}^8\Sigma^+$ curve. Potential energy points for which $R < R_e$ are shifted according to $R_s = R + s(R - R_e)/(R_t - R_e)$, where s is the shift of the zero-energy classical inner turning point, R_t , and R_e is the equilibrium distance. Several different values for s were used.

sections are insensitive to the shifts for energies above $E \geq 10^{-8}$ a.u., they tend to decrease (increase) with increasing positive (negative) shifts at very low energies. However, when the shifts are large enough that an additional bound state (see for instance Fig. 6.3) is pulled in from the continuum, the above trend does not hold.

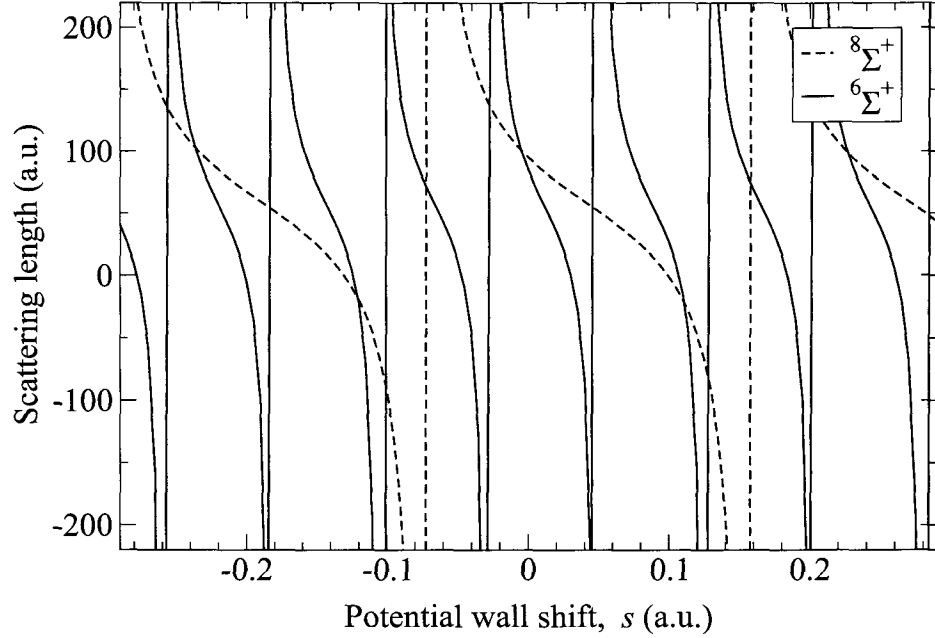


Figure 6.3: The dependence of the energy of the last bound state in the ${}^6\Sigma^+$ and ${}^8\Sigma^+$ potentials on the shift parameter (s), see Fig. 6.2 for the shift definition. The “resonances” occur when an additional bound state is pulled in from the continuum as s decreases.

6.3 Zeeman cascade

The scattering between Cr and Rb atoms in the presence of a homogeneous magnetic field, $\mathbf{B}$, is governed by the following Hamiltonian

$$\hat{H} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{l}^2}{2\mu R^2} + \hat{V}_{\text{es}} + \hat{V}_{\text{dip}} + 2\mu_B (\mathbf{s}_A + \mathbf{s}_B) \cdot \mathbf{B} + A_{\text{hf}} \mathbf{s}_B \cdot \mathbf{i}_B, \quad (6.4)$$

where the constants μ , μ_B and A_{hf} represent the reduced mass of the CrRb molecule, the Bohr magneton, and the Rb isotropic hyperfine interaction constant of the ground state, respectively. The first two terms in the Hamiltonian represent the nuclear kinetic energy of the molecule, where $\mathbf{l}$ is the rotational angular momentum of the nuclei. The explicit form of $\hat{V}_{\text{es}}$, the operator of the electrostatic interaction, and $\hat{V}_{\text{dip}}$, the operator of the magnetic dipolar interaction, will be given below. The spin

operators $\mathbf{s}_A(\mathbf{i}_A)$ and $\mathbf{s}_B(\mathbf{i}_B)$ represent the electronic (nuclear) spins of atom A (Cr) and atom B (Rb), respectively. For the $^{52}\text{Cr} + ^{87}\text{Rb}$ system, the electronic and nuclear spins are $s_A = 3$, $i_A = 0$, $s_B = 1/2$ and $i_B = 3/2$. The linear atomic Zeeman terms and the isotropic hyperfine interaction for Rb are also given. The R -independent terms in the Hamiltonian (6.4) determine the scattering channels, which can be related through a unitary transformation $|\beta\rangle = \sum_{\alpha} U_{\beta\alpha}|\alpha\rangle$, to the product states of the total electronic spin, $\mathbf{S} = \mathbf{s}_A + \mathbf{s}_B$, and the nuclear spin, $\mathbf{I} = \mathbf{i}_A + \mathbf{i}_B$, $|\alpha\rangle = |SM_SIM_I\rangle$. In this work, we neglect the interaction of the Rb nuclear magnetic moment with $\mathbf{B}$.

The matrix of the dipolar interaction (4.66) can be evaluated analytically as demonstrated in (4.69), or elsewhere [90, 91]. It is the only term in the Hamiltonian that can couple channel wave functions with different rotational numbers, l , according to

$$\Delta l = 0, \pm 2; \quad \text{while} \quad 0 \rightarrow 0 \quad \text{is forbidden.} \quad (6.5)$$

A similar rule holds for the change of the total electronic spin of two atoms

$$\Delta S = 0, \pm 1, \pm 2. \quad (6.6)$$

The dipolar interaction preserves the angular projections, M_I and $M_S + m_l$, independently.

The Zeeman interaction term is $2\mu_0 B M_S$, where M_S is the projection of $\mathbf{S}$ on $\mathbf{B}$. The hyperfine interaction term can be directly evaluated in the coupled basis $|f_A f_B F M_F\rangle$, where $\mathbf{f}_A = \mathbf{i}_A + \mathbf{s}_A$, $\mathbf{f}_B = \mathbf{i}_B + \mathbf{s}_B$, and $\mathbf{F} = \mathbf{f}_A + \mathbf{f}_B$, and then through the chain of transformations

$$|f_A f_B F M_F\rangle \rightarrow |S I F M_F\rangle \rightarrow |S M_S I M_I\rangle, \quad (6.7)$$

expressed in the $|SM_S IM_I m_l\rangle$ basis. On how to calculate the hyperfine interaction matrix elements directly in the $|SM_S IM_I m_l\rangle$ basis see (4.60) or elsewhere [92, 93].

The highest low-field seeking state is chosen as the initial channel for the Zeeman relaxation of maximally stretched Cr and Rb atoms. In this state, the spin numbers for ^{52}Cr are $f = 3$ and $m_f = 3$, while for ^{87}Rb the relevant spin numbers are $f = 2$ and $m_f = 2$ (see Fig. 6.4). The results do not change much when we exclude states

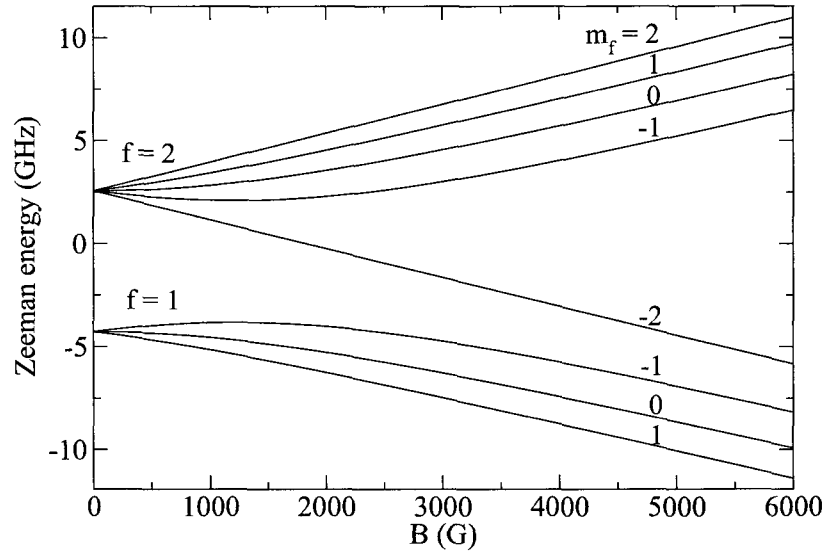


Figure 6.4: Zeeman diagram for ^{87}Rb atoms in the ground state. Upper manifold corresponds to $f = 2$ spin, lower manifold corresponds to $f = 1$ spin.

which represent the decrease of the total spin projection, M_F , by more than 2 units. Figure 6.5(a) contains the cross sections as a function of energy at three values of B . The cross sections display characteristic dipolar shape resonances, and roughly correspond to cross sections for Cr-Cr scattering scaled down 10 times. The inelastic cross section contribution from the dipolar interaction scales as [37]

$$\frac{\sigma_{inel}^{\text{CrRb}}}{\sigma_{inel}^{\text{CrCr}}} \sim \left(\frac{s_{\text{Rb}}}{s_{\text{Cr}}} \right)^{3/2} \left(\frac{\mu_{\text{CrRb}}}{\mu_{\text{CrCr}}} \right)^2. \quad (6.8)$$

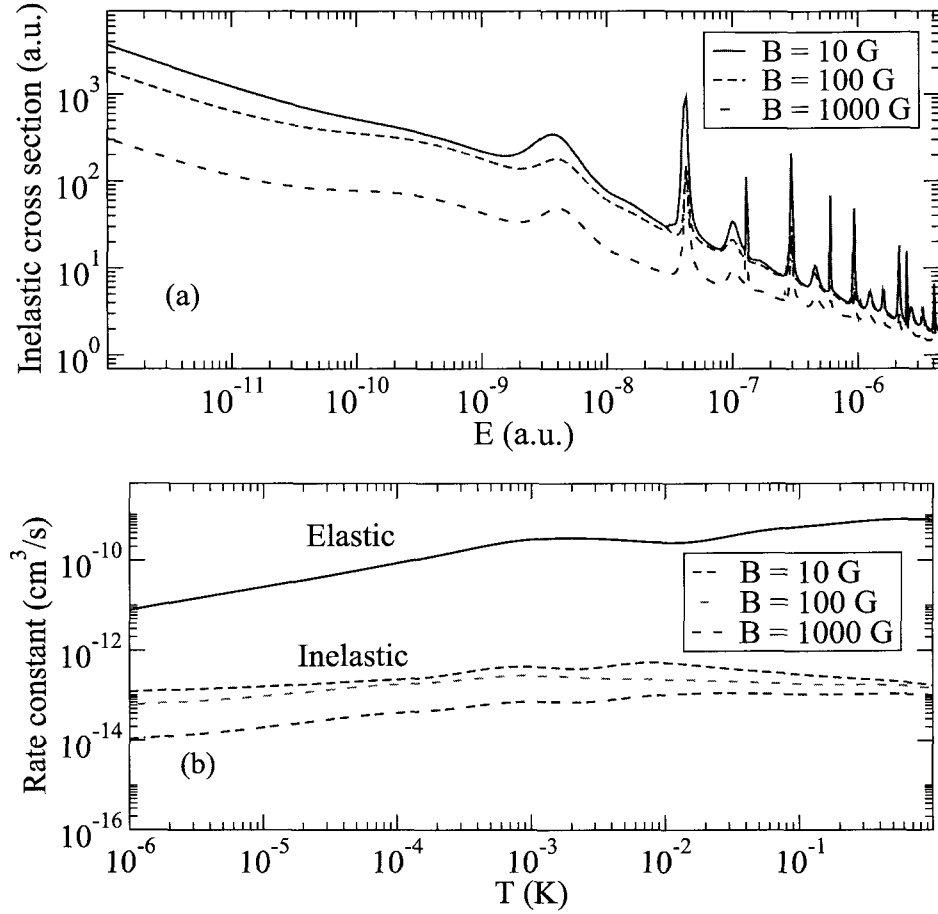


Figure 6.5: (a) Energy dependence of inelastic cross sections for the relaxation of maximally stretched ^{52}Cr , $|f=3, m_f=3\rangle$, and ^{87}Rb , $|f=2, m_f=2\rangle$, atoms in the presence of a magnetic field. (b) Rate constants for elastic and inelastic scattering processes presented in (a).

The Zeeman relaxation rates, Fig. 6.5(b), provide a valuable tool in assessing the efficiency of CrRb evaporative cooling in a magnetic or optical trap. Ratios of elastic to inelastic collisions in the μK regime of about 100–1000 times are possible.

6.4 Resonances

In CrRb, we have an interesting system where strong hyperfine and dipole-dipole interactions compete to produce rich spectra. When only the hyperfine interac-

tion in ^{87}Rb is considered, the scattering length dependence on the magnetic field, Fig. 6.6 (bottom panel), shows a number of hyperfine-coupled Fano-Feshbach resonances, where the initial state $|^{52}\text{Cr} : f=3, m_f=-3; ^{87}\text{Rb} : f=1, m_f=1; l=0, m_l=0\rangle$ is the lowest high-field seeking state. When the Cr magnetic dipole interaction with the spin of the Rb atom is turned on, a much richer spectrum (top panel in Fig. 6.6) is obtained, where the additional resonances, due to the dipolar interaction, have (s, d) wave character.

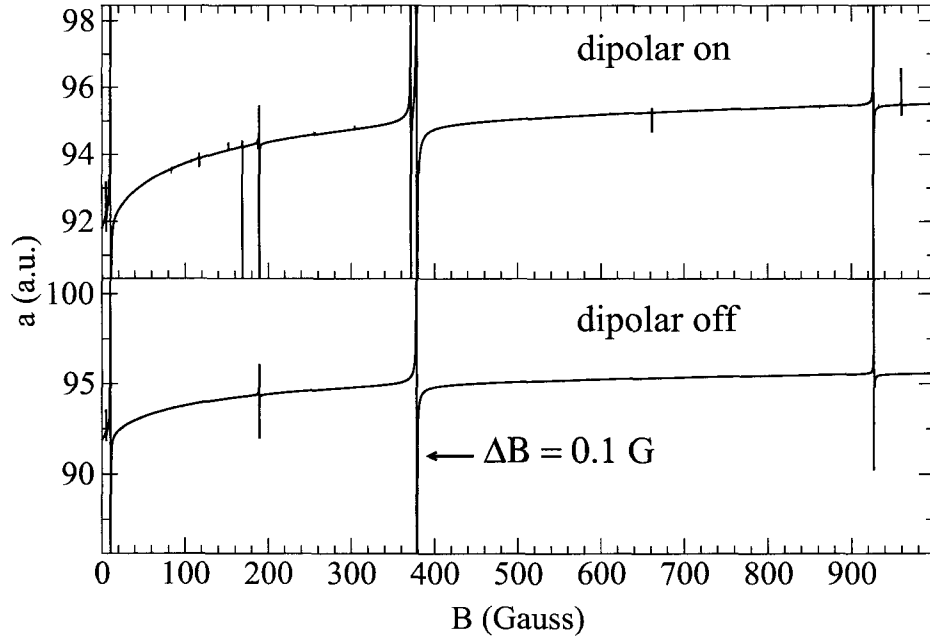


Figure 6.6: Competing hyperfine and dipolar interactions in the $l = 0$ entrance channel state: $|f=3, m_f=-3\rangle$ for ^{52}Cr , and $|f=1, m_f=1\rangle$ for ^{87}Rb . Bottom panel: Resonances caused by Rb hyperfine interaction, Top panel: Effect of dipolar interaction coupling the entrance s -wave channel to the closed d -wave channels.

CHAPTER 7

HE-OH($^2\Pi$) COLLISIONS

In this chapter we present rigorous quantum calculations for low-temperature collisions of OH($^2\Pi$) molecules with He atoms in the presence of external electric and magnetic fields. Understanding the mechanism of inelastic collisions and chemical reactions of open-shell molecules is necessary for quantitative modeling of processes in atmospheric chemistry [94], combustion [95], and astrochemistry [96]. The main theoretical challenge in describing these processes comes from the complicated energy level structure of molecules in degenerate electronic states, which can be perturbed by fine, hyperfine, spin-rotation, spin-spin, and Coriolis interactions [97]. Therefore, in addition to purely rotational energy transfer, collisions of molecular radicals may lead to spin depolarization and non-adiabatic mixing of different electronic states [98, 99, 100, 101, 102, 103]. Studies of such transitions often provide a wealth of valuable information about the non-adiabatic effects in chemical dynamics [104] and photodissociation [105].

The OH radical is of fundamental importance to astrophysics [96], atmospheric chemistry [94], and precision spectroscopy [106]. The ground electronic state of OH is of $^2\Pi$ symmetry, so the molecule can be efficiently manipulated with time-varying electric fields. In a series of groundbreaking experiments, Meijer and co-workers combined Stark deceleration [107] with electrostatic trapping [108] to carry out high-resolution spectroscopic measurements of the radiative lifetime of OH($v = 1$) [109], and to study cold collisions of OH molecules with Xe atoms in crossed molecular

beams [110]. Also, collisions of OH molecules with He and Ar atoms were studied in crossed molecular beam experiments [98] and strong steric effects were observed in the presence of an external electric field [99]. Similar measurements were also reported for metastable CO($^3\Pi$), NH($^3\Pi$), and ground-state ammonia molecules [107]. Generally, molecules are confined in electrostatic traps in their highest-energy Stark level of the ground rotational state, but collisions with background atoms lead to depopulation of the Stark level and trap loss. Therefore, understanding the mechanisms of collision-induced Stark relaxation is essential for minimizing trap losses and optimizing evaporative cooling of molecules in electrostatic traps [111, 112].

The formal quantum-mechanical theory for collisions of Π -state molecules with atoms was developed by Klar [113], Shapiro and Kaplan [114], and Alexander [115]. Alexander and co-workers were able to calculate the cross sections for transitions between fine-structure and Λ -doublet levels of OH, NO, CN, and CH molecules in collisions with structureless particles [116, 117, 118]. Avdeenkov and Bohn analyzed the effects of electric fields on the collision dynamics of OH molecules and discovered new field-linked molecular states [119, 120, 121]. The propensity rules for state-to-state inelastic transitions in ultracold He-OH collisions were analyzed by González-Sánchez *et al.* [122]. In the recent past, Lara *et al.* have improved the theoretical approach taking into account the non-adiabatic and hyperfine interactions and applied it to calculate the rate constants for inelastic relaxation in collisions of OH molecules with Rb atoms [111, 112]. In the following sections, we briefly outline the theory of collisions between OH molecules in $^2\Pi$ electronic states with $^3,^4\text{He}$ atoms and then discuss the results of their collisions in the presence of external electric and magnetic fields.

7.1 Theory

The collision between an atom and a diatomic molecule can be described by the Hamiltonian

$$\hat{H} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{\ell}^2}{2\mu R^2} + \hat{V}(R, r, \theta) + \hat{H}_{\text{mol}}, \quad (7.1)$$

where $r = |\mathbf{r}|$ is the internuclear distance in the diatomic molecule, $R = |\mathbf{R}|$ is the length of the atom-molecule separation vector, θ is the angle between the vectors $\mathbf{R}$ and $\mathbf{r}$ (see Fig. 7.1), μ is the atom-molecule reduced mass, and $\hat{\ell}$ is the orbital angular momentum for the relative motion of the collision partners (here He and OH).

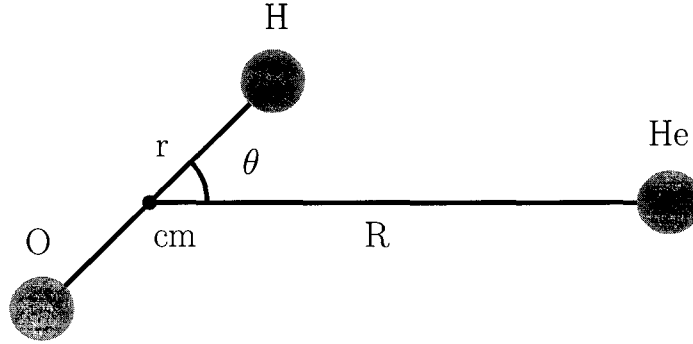


Figure 7.1: He-OH system

Because the fundamental frequency of OH ($\omega = 3569.64 \text{ cm}^{-1}$) by far exceeds the energy scale of cold collisions (1 mK - 200 K), we can assume that the vibrational motion of OH is frozen out, that is $r = r_e$, where $r_e = 1.226 \text{ \AA}$ is the equilibrium distance of OH in the ground electronic state. The Hamiltonian $\hat{H}_{\text{mol}}$ determines the energy level structure of the molecule in the presence of external fields. The effective Hamiltonian for the ground vibrational state can be written as [123, 124, 125]

$$\hat{H}_{\text{mol}} = B_e[\hat{J}^2 - 2J_z^2 - \hat{J}_+\hat{S}_- - \hat{J}_-\hat{S}_+] + (A + 2B_e)\hat{L}_z\hat{S}_z + \hat{H}_B + \hat{H}_E + \hat{H}_\Lambda, \quad (7.2)$$

where B_e is the rotational constant of the molecule, $\hat{J} = \hat{N} + \hat{L} + \hat{S}$ is the total angular momentum, $\hat{N}$ is the rotational angular momentum of the nuclei, $\hat{L}$ is the electronic orbital angular momentum, and $\hat{S}$ is the electron spin. The first two terms in Eq. (7.2) represent the rotational and spin-orbit (SO) Hamiltonians expressed through the ladder operators $\hat{J}_{\pm}\hat{S}_{\mp}$ and the molecule-fixed projection of the total angular momentum $\hat{J}_z$. We neglect the weak hyperfine interaction due to the H nuclear spin [123]. The term $A\hat{L}_z\hat{S}_z$ accounts for the diagonal part of the SO interaction parametrized by the SO constant A . The off-diagonal part of the SO interaction mixes the ground ($^2\Pi$) and excited ($^2\Sigma$) electronic states, leading to Λ -doubling effects described by the Hamiltonian $\hat{H}_{\Lambda}$ [123]. Also included in Eq. (7.2) is the interaction

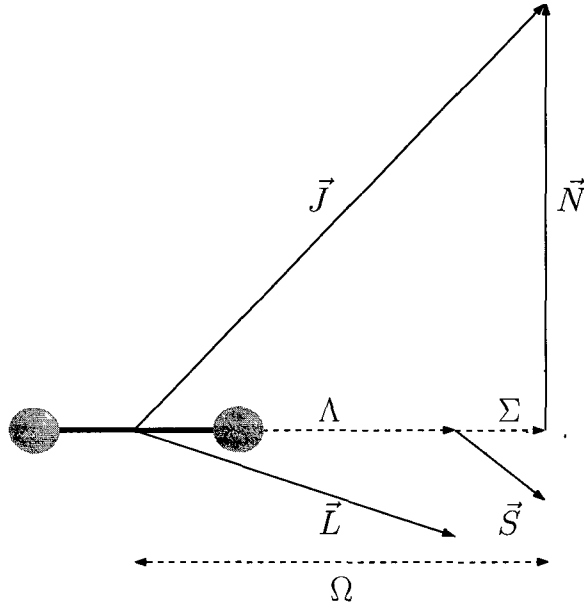


Figure 7.2: Hund's case (a) angular momentum coupling scheme.

of the permanent electric dipole moment of the molecule d with a dc electric field E

$$\hat{H}_E = -Ed \cos \theta_r, \quad (7.3)$$

which depends on the orientation angle θ_r of molecular axis in the space-fixed frame. The interaction with magnetic fields is given by

$$\hat{H}_B = \mu_0 B (\hat{L} + 2\hat{S}) \cdot \hat{B}, \quad (7.4)$$

where B is the field strength and μ_0 is the Bohr magneton. We assume that the electric and magnetic fields are co-aligned along the space-fixed z -axis [126]. Changing the orientation of the quantization axes does not alter the collision dynamics except near infrequently occurring avoided crossings [127].

The eigenfunctions of the Hamiltonian (7.2) can be expanded in parity-adapted Hund's case (a) basis functions (see Fig. 7.2)

$$|JM\bar{\Omega}\epsilon\rangle = \frac{1}{2} [|JM\bar{\Omega}\rangle |\Lambda = 1, \Sigma = \bar{\Omega} - 1\rangle + \epsilon(-)^{J-1/2} |JM-\bar{\Omega}\rangle |\Lambda = -1, \Sigma = -\bar{\Omega} + 1\rangle] . \quad (7.5)$$

where the primitive case (a) functions are

$$|JM\Omega\rangle |\Lambda\Sigma\rangle = \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{M\Omega}^{J\star}(\chi_r, \theta_r, 0) |\Lambda\Sigma\rangle. \quad (7.6)$$

Here, M and Ω are the projections of the total angular momentum J on the space-fixed and molecule-fixed quantization axes, respectively, $D_{M\Omega}^{J\star}$ is the Wigner D -function, $|\Lambda\Sigma\rangle$ is the electronic wave function, and $\bar{\Omega} = |\Omega|$. The z -axis of the molecule-fixed coordinate frame coincides with that of the diatomic molecule, whose orientation in the space-fixed frame is specified by two Euler angles χ_r and θ_r . For $^2\Pi$ electronic states, the molecule-fixed projections of $\hat{L}$ and $\hat{S}$ are $\Lambda = \pm 1$ and $\Sigma = \pm 1/2$, so the parity-adapted basis functions are characterized by the absolute value of $\bar{\Omega} = 1/2$,

3/2. The parity quantum number $\epsilon = \pm 1$ in Eq. (7.5) characterizes the symmetry of the basis functions with respect to inversion. For an isolated $^2\Pi$ molecule in the absence of external fields, ϵ is conserved, but intermolecular interactions and electric fields break the inversion symmetry and couple the states with different ϵ .

The eigenstates of the OH molecule can be written as linear combinations of Hund's case (a) basis functions

$$|\gamma\rangle = \sum_{J,M,\bar{\Omega},\epsilon} C_{JM\bar{\Omega}\epsilon,\gamma} |JM\bar{\Omega}\epsilon\rangle, \quad (7.7)$$

where the field-dependent coefficients $C_{JM\bar{\Omega}\epsilon,\gamma}$ can either be obtained by numerical diagonalization of the Hamiltonian matrix or estimated using perturbation theory. In order to solve the scattering problem, we expand the total wave function of the atom-molecule system as [123]

$$\Psi = \frac{1}{R} \sum_{\beta} F_{\beta}(R) \psi_{\beta}(\hat{R}, \hat{r}), \quad (7.8)$$

where

$$\psi_{\beta}(\hat{R}, \hat{r}) = |JM\bar{\Omega}\epsilon\rangle |\ell m_{\ell}\rangle, \quad (7.9)$$

are the uncoupled angular basis functions composed of direct products of Hund's case (a) functions (7.5) and the spherical harmonics $|\ell m_{\ell}\rangle$ describing the relative motion of the collision partners in the space-fixed coordinate frame. In Eq. (7.8), β is used as a collective index for $\{J, M, \bar{\Omega}, \epsilon, \ell, m_{\ell}\}$. When substituted into the Schrödinger equation, the expansion (7.8) yields a set of close-coupled (CC) differential equations

$$\left[\frac{d^2}{dR^2} + 2\mu E \right] F_{\beta}(R) = 2\mu \sum_{\beta'} \langle \psi_{\beta}(\hat{R}, \hat{r}) | \hat{V}(R, \theta) + \frac{\hat{\ell}^2}{2\mu R^2} + \hat{H}_{\text{mol}} | \psi_{\beta'}(\hat{R}, \hat{r}) \rangle F_{\beta'}(R), \quad (7.10)$$

which can be solved by using a log-derivative algorithm [128, 129].

The interaction of a $\text{OH}(^2\Pi)$ molecule with a structureless He atom is characterized by two potential energy surfaces (PESs) of A' and A'' symmetries [115]. In this work, we use the most recent *ab initio* interaction potentials calculated by Lee *et al.*, [130], using the partially spin-restricted coupled cluster method with single and double excitations and non-iterated triples [RCCSD(T)] with an aug-cc-pVTZ one-electron basis set extended with bond functions. The matrix elements of the interaction potentials in Eq. (7.10) can be readily evaluated from their expansions in associated Legendre polynomials [123, 131].

After transforming the asymptotic wave function to the field-dressed scattering basis, the scattering S -matrix elements can be determined by analyzing the asymptotic form of the solutions $F_{\gamma\ell m_\ell}(R)$ [126]. The cross sections for elastic energy transfer and inelastic scattering for a given collision energy E_{coll} and electric field strength are calculated as the sum of the S -matrix elements as described in detail in Sec. 2.5.1

$$\sigma_{\gamma \rightarrow \gamma'} = \frac{\pi}{k_\gamma^2} \sum_{M_{\text{tot}}} \sum_{\ell, m_\ell} \sum_{\ell', m'_\ell} |\delta_{\gamma\gamma'} \delta_{\ell\ell'} \delta_{m_\ell, m'_\ell} - S_{\gamma\ell m_\ell; \gamma'\ell' m'_\ell}^{M_{\text{tot}}}|^2, \quad (7.11)$$

and the thermal rate constants are obtained by averaging the cross sections over a Maxwell-Boltzmann distribution of collision energies for transitions between the individual Stark states.

7.2 Results

Before getting into the details of the collision cross sections and rate coefficient, I discuss briefly the effect of external electric and magnetic fields on the $^2\Pi$ electronic state of the OH molecule.

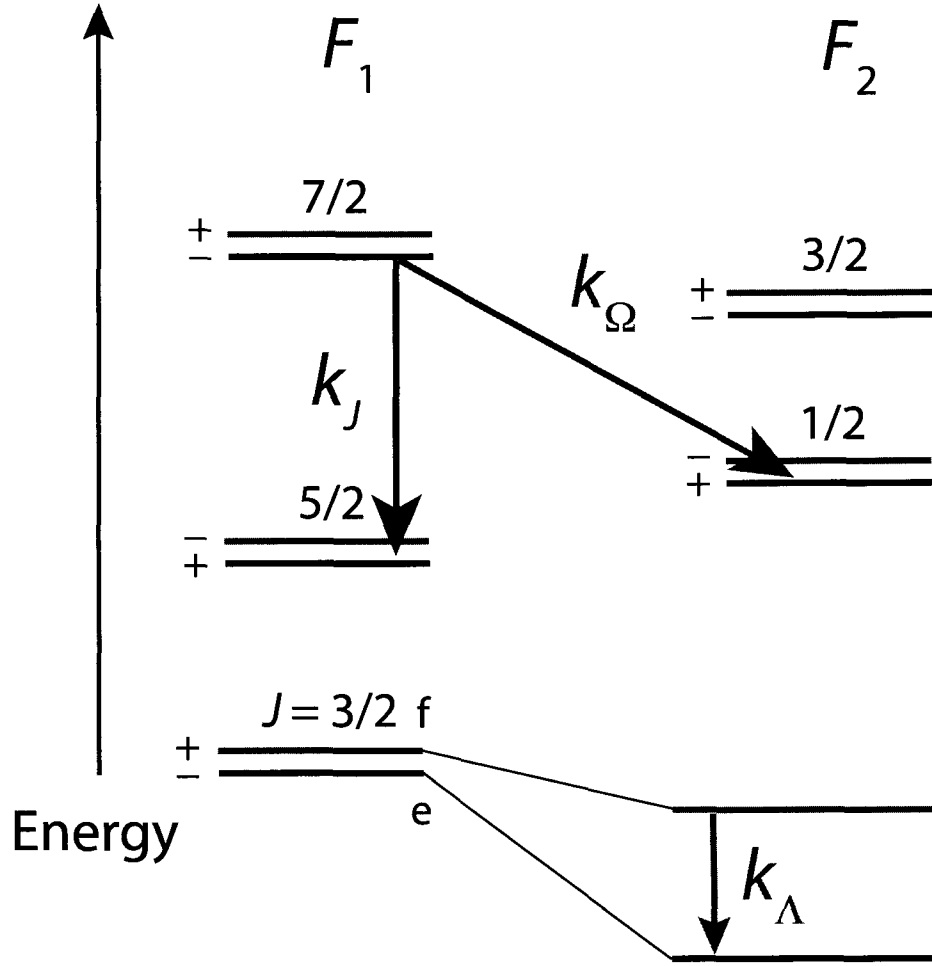


Fig. 7.3: A schematic representation of the energy levels of OH in the absence of external fields. The individual Λ -doublet sublevels are labeled according to their inversion parity $\epsilon = \pm$. The e/f notation is illustrated for the $F_1, J = 3/2$ energy level. Different pathways for collision-induced inelastic relaxation: fine-structure (k_Ω), rotational (k_J), and Λ -doublet changing (k_Λ).

7.2.1 Energy levels of OH

The energy levels of OH molecules in the absence of external fields are shown in Fig 7.3. Collisions with the He atoms can follow three different pathways for inelastic relaxation through fine-structure (k_Ω), rotational (k_J), and Λ -doublet (k_Λ) coupling. Since the rotational constant of OH molecule is not negligible compared to the SO constant ($|A/B_e| = 7.5$), different values of $\bar{\Omega}$ are coupled by the cross terms $\hat{J}_\pm \hat{S}_\mp$ in

Eq. (7.2). The rotational states in the F_1 manifold can be expanded in Hund's case (a) basis functions as

$$|F_1, J = \frac{3}{2}, M, \epsilon\rangle = a_J |J = \frac{3}{2}, \bar{\Omega} = \frac{3}{2}, M, \epsilon\rangle + b_J |J = \frac{3}{2}, \bar{\Omega} = \frac{1}{2}, M, \epsilon\rangle, \quad (7.12)$$

where the expansion coefficients a_J and b_J characterize the degree of mixing of different $\bar{\Omega}$ -states (in a pure Hund's case (a) molecule, the $\bar{\Omega}$ -states are uncoupled). The coefficients (a_J, b_J) are (0.985, 0.174) for $J = 3/2$, (0.964, 0.264) for $J = 5/2$, and (0.943, 0.337) for $J = 7/2$. The F_2 states can be expanded in the same way as in Eq. (7.12), with the coefficients given by (0, 1) for $J = 1/2$, (-0.174, 0.985) for $J = 3/2$, and (-0.266, 0.964) for $J = 5/2$. The Coriolis interaction between different $\bar{\Omega}$ -states also becomes stronger with increasing J and the molecule starts to approach Hund's case (b) limit. The only exception is the lowest rotational level in the F_2 manifold, which can be represented by a single basis function.

In Fig. 7.4 we show the electric field dependence of the energy levels displayed in Fig. 7.3. At small electric fields ($E < E^* = d/\Delta_\Lambda$, where $\Delta_\Lambda = 0.057 \text{ cm}^{-1}$ is the Λ -doublet splitting in OH) the energy levels depend quadratically on the electric field strength. As the electric field approaches the critical value of $E^* \sim 5 \text{ kV/cm}$, the first-order Stark effect starts to set in. At $E > E^*$, all energy levels exhibit linear Stark shifts. Because the matrix elements of the Λ -doubling Hamiltonian increase linearly with J and so does the splitting Δ_Λ [97], rotationally excited levels of OH exhibit progressively smaller Stark shifts as J increases. The same conclusion applies to Σ -state molecules [132] because the energy separation between the rotational levels J and $J - 1$ increases linearly with J .

The presence of quasi-degenerate, opposite-parity levels in $^2\Pi$ molecules pushes the onset of the first-order Stark effect to low E -fields ($\sim 10 \text{ kV/cm}$ for a typical Λ -doublet splitting of $\sim 0.1 \text{ cm}^{-1}$). In contrast, the Stark effect in Σ -state molecules is

determined by couplings between different *rotational* states. Typical rotational level splittings in most molecules are >10 times larger than the Λ -doublet splittings, so large electric fields are required to induce appreciable Stark shifts in Σ -state molecules. For example, the first-order Stark effect in CaH ($B_e = 6.1 \text{ cm}^{-1}$) occurs at electric fields above 200 kV/cm, and for the heavy YbF molecule ($B_e = 0.24 \text{ cm}^{-1}$), this value

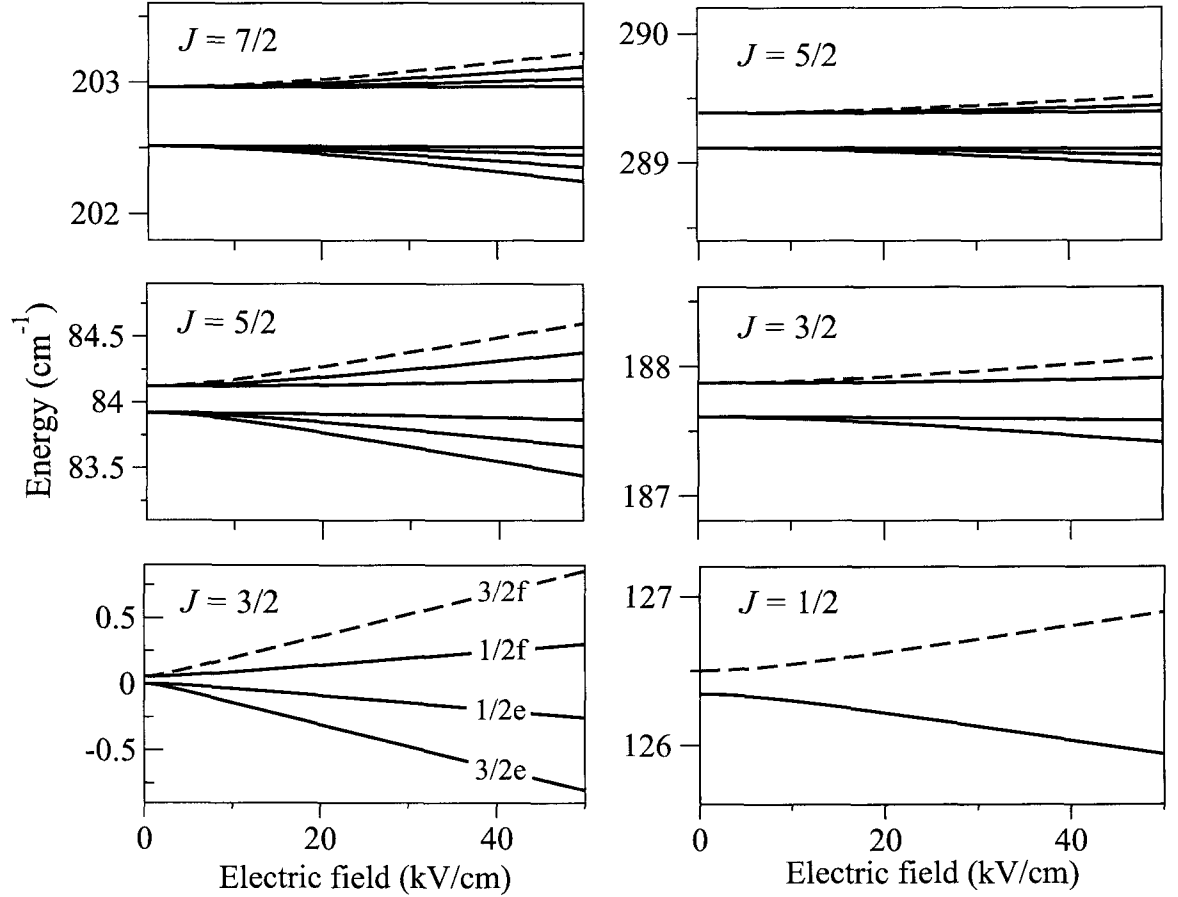


Fig. 7.4: (Left panel): Stark levels in the F_1 manifold ($^2\Pi_{3/2}$) vs the applied electric field. (Right panel): Stark levels in the F_2 manifold ($^2\Pi_{1/2}$) vs the applied electric field. The initial states for scattering calculations are shown by dashed lines. The Stark levels in different J -manifolds are drawn to scale and labeled for $J = 3/2$ by the absolute value of M . The label e (f) denotes the lower (upper) Λ -doublet in the absence of an electric field. The zero of energy corresponds to the ground state of $\text{OH}(^2\Pi)$ at zero electric and magnetic fields.

is about 50 kV/cm. We therefore expect that collisions of Π -state molecules will be more sensitive to electric fields than collisions of Σ -state molecules.

7.2.2 Cross sections - the effect of electric field

The CC equations (7.10) were integrated out to $R_{\max} = 60 a_0$ using the improved log-derivative algorithm [128, 129] with a constant step size of $0.1 a_0$. The spectroscopic constants of OH used in scattering calculations are (in cm^{-1}): $B_e = 18.55$, $A = -139.273$, $p = 0.235608$, and $q = -0.03877$ (where p and q are the Λ -doubling parameters[124, 125, 123]). We use $d = 1.68$ D for the permanent electric dipole moment of OH in the $v = 0$ vibrational state [133, 121]. The basis set expansion included the rotational states up to $J_{\max} = 11/2$ and partial waves up to $\ell_{\max} = 5$. In order to make calculations at higher collision energies feasible, we reduced the basis set to $J_{\max} = 7/2$ and augmented it with partial waves up to $\ell_{\max} = 30$. The resulting cross sections were converged to better than 5%. Fig. 7.5 shows the cross sections for inelastic relaxation in collisions of OH molecules in different initial rotational states with ^3He atoms as functions of collision energy. The initial states are the fully stretched low-electric-field-seeking states $|F_1, J, M = J, f\rangle$ shown by dashed lines in Fig. 7.4. The total inelastic cross section is the sum of the cross sections for transitions between different fine-structure, rotational, and Stark levels (see Fig. 7.3). At low collision energies, the OH molecules prepared in the ground state $|F_1, J = 3/2, M = 3/2, f\rangle$ can only undergo downward transitions to the Stark states $|F_1, J = 3/2, M', \epsilon'\rangle$ as long as the collision energy does not exceed the splitting between the ground and the first excited rotational levels ($\sim 84 \text{ cm}^{-1}$). The Stark relaxation is mainly determined by the couplings between the different M components of the $J = 3/2$ state induced by the anisotropy of the interaction potential [123]. As an important consequence, the rates for collision-induced Stark relaxation of $^2\Pi$ molecules are large and insensitive

to the magnitude of the rotational constant. This is in contrast with the relaxation dynamics of Σ -state molecules, where different M -sublevels of the ground rotational state are uncoupled [127, 132]. The large inelastic rates of $^2\Pi$ molecules prevent their sympathetic cooling using ^3He buffer gas but can be mitigated by electric fields at temperatures below 0.01 K [123]. As shown in the upper panel of Fig. 7.5, the cross sections for inelastic transitions in collisions of ground-state OH molecules are highly sensitive to the electric field strength. An electric field of only 7 kV/cm leads to the enhancement of the inelastic cross sections by two orders of magnitude at a collision energy of 100 mK. The rate constants for inelastic transitions in ^3He -OH collisions at a temperature of 0.5 K are presented in Table 7.1. The rate constants in general, increase with increasing field strength. Also, the rate constants increase (decrease) with increasing the initial J for the F_1 (F_2) manifolds.

Table 7.1: The total rate constants for inelastic transitions (in 10^{-12} cm³/s) from different initial rotational states in the F_1 and F_2 manifolds for several electric field strengths (in kV/cm) at $T = 10$ mK.

Electric field	0	5	50	100
J	F_1			
3/2	0.02	0.09	0.60	0.89
5/2	0.34	0.98	2.76	3.49
7/2	3.13	3.76	4.43	5.52
J	F_2			
1/2	10.3	10.3	10.8	10.9
3/2	7.67	7.62	8.16	9.15
5/2	6.18	6.22	7.41	8.20
7/2	5.44	5.50	7.44	7.93

Similarly to Fig. 7.5, the cross sections for inelastic relaxation of rotational states in the F_2 manifold are shown in Fig. 7.6.

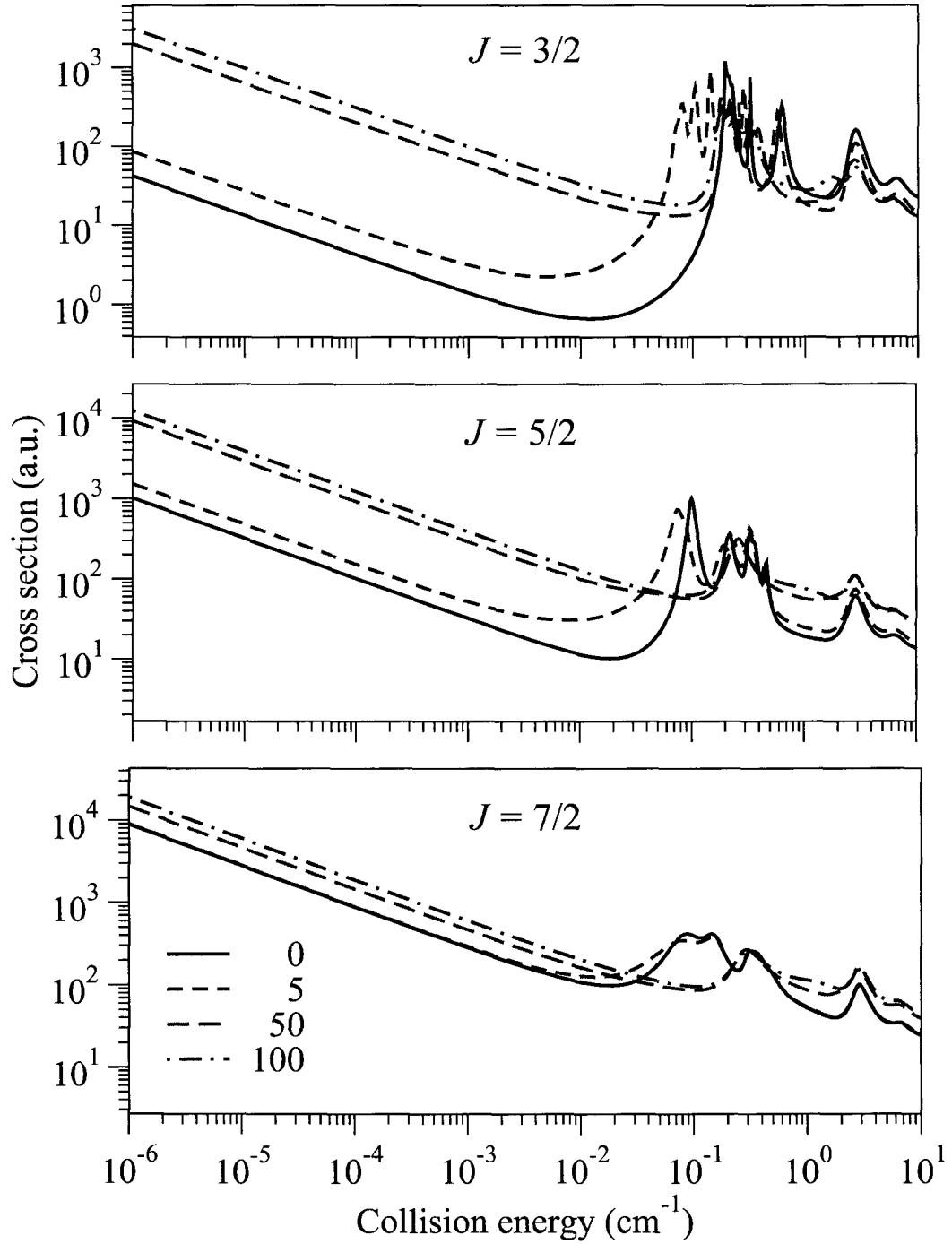


Fig. 7.5: Collision energy dependence of the inelastic cross sections for He-OH($^2\Pi$) collisions. The OH molecules are in the maximally stretched $|F_1, J, M = J, f\rangle$ initial states with $J = 3/2$ (upper panel), $J = 5/2$ (middle panel), and $J = 7/2$ (lower panel). Different curves in each panel refer to different electric fields: zero (full line), 5 kV/cm (short dashed line), 50 kV/cm (long dashed line), and 100 kV/cm (dash-dotted line). The magnetic field is 1 G.

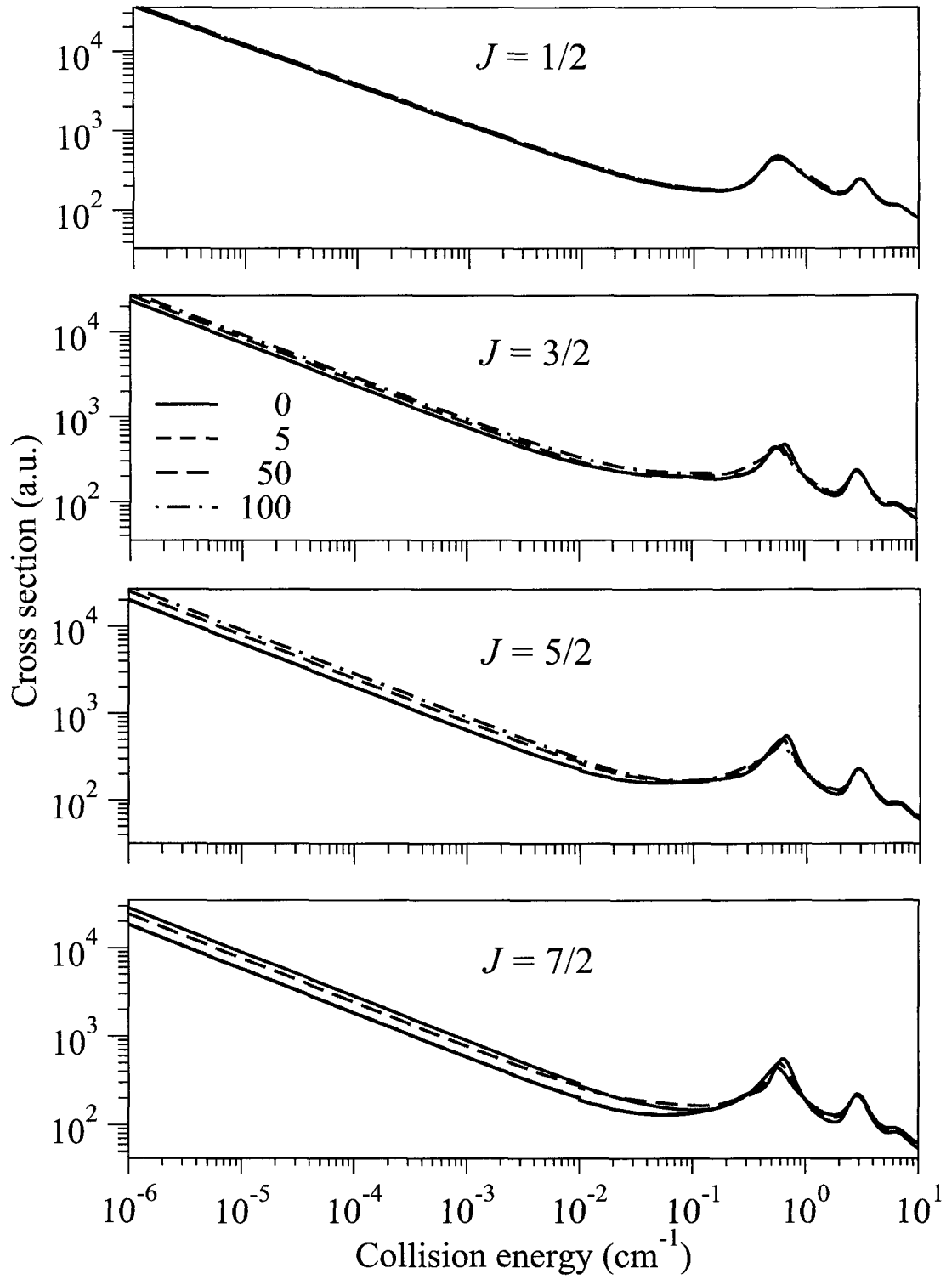


Fig. 7.6: Same as in Fig. 7.5 but for the SO excited initial states $|F_2, J, M = J, f\rangle$.

The corresponding rate constants are presented in Table 7.1. The variation of the cross sections with electric field and initial rotational state is insignificant, because of the presence of efficient fine-structure relaxation channels $|F_2, J\rangle \rightarrow |F_1, J'\rangle$. Indeed, the partial rate constants $k_{\bar{\Omega}}$ presented in Table 7.2 are ten times larger than those for J -changing and Λ -doublet changing transitions. Figure 7.7 shows the inelastic cross sections for $^3\text{He-OH}$ as functions of electric field at a collision energy of 10^{-3} cm^{-1} , which corresponds to the s -wave regime in Fig. 7.5. The cross sections display a complicated resonance structure at electric fields between 7 and 30 kV/cm, and grow monotonously as the field strength increases past 30 kV/cm. The resonance structure occurs only for collisions of molecules in the ground rotational state $|F_1, J = 3/2\rangle$. For higher rotational states, the availability of many decay channels leads to more efficient inelastic relaxation (cf. Fig. 7.5), leading to suppression of scattering resonances [81]. This tendency is even more pronounced for the initial states in the F_2 manifold. The

Table 7.2: The rate constants for $\bar{\Omega}$ -changing, J -changing, and Λ -changing transitions (see Fig. 7.3) for different electric field strengths (in kV/cm). The rate constants are given in units of $10^{-12} \text{ cm}^3/\text{s}$ for the initial states $|F_1, J = 5/2, M = 5/2, f\rangle$ and $|F_2, J = 3/2, M = 3/2, f\rangle$ at $T = 10 \text{ mK}$.

Electric field	0	5	100
F_1			
k_{Λ}	0.023	0.115	1.55
k_J	0.312	0.865	1.91
F_2			
k_{Λ}	0.033	0.037	0.365
k_J	0.697	0.683	0.593
$k_{\bar{\Omega}}$	6.87	6.90	7.92

lower panel of Fig. 7.7 shows that the cross sections for inelastic relaxation out of the $|F_2, J\rangle$ states are almost independent of the electric field. Rotational excitation

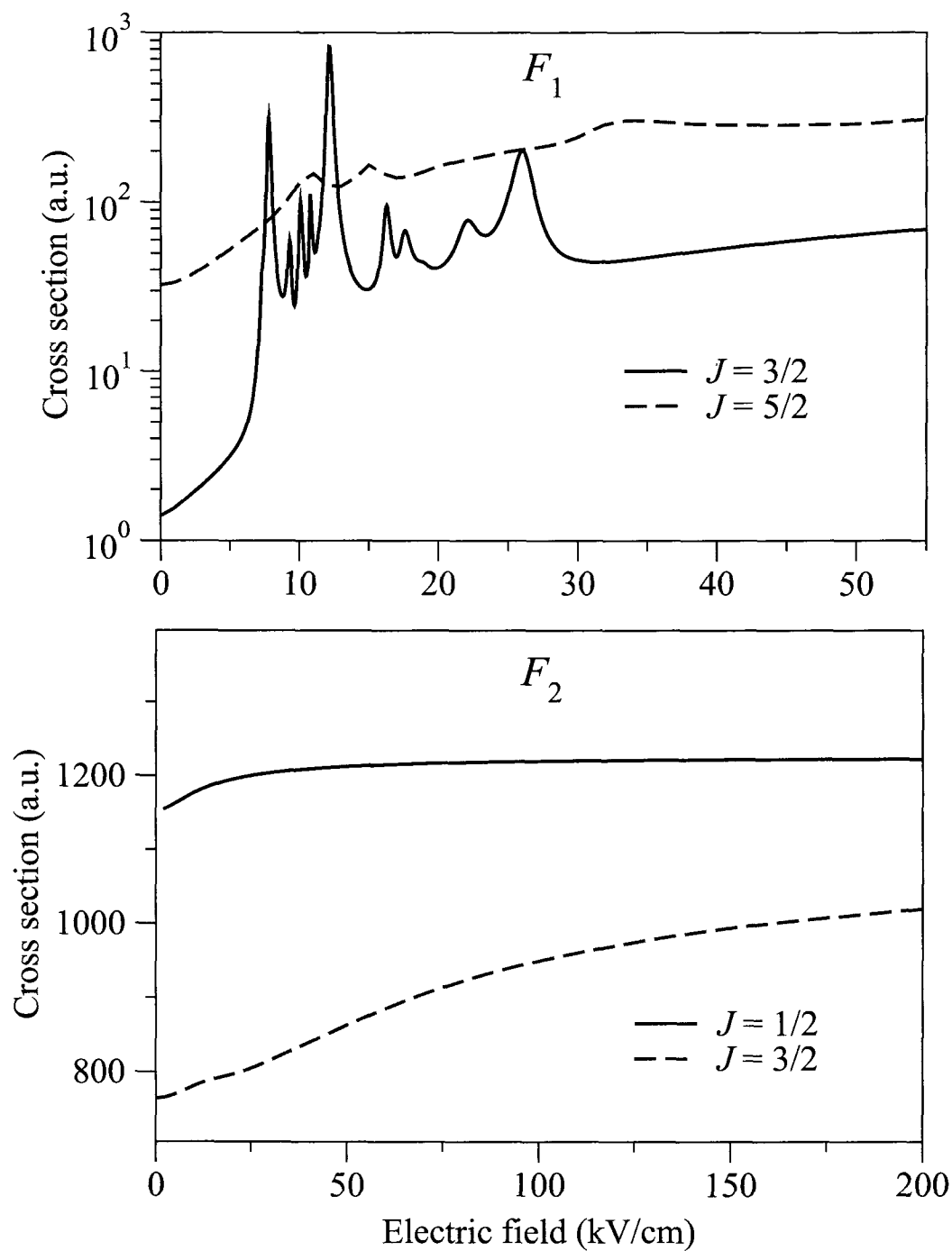


Fig. 7.7: (Upper panel) Electric field dependence of the cross sections for inelastic scattering of $\text{OH}(F_1, J, M = J, f)$ with He for different initial rotational states J . (Lower panel) Same as in the upper panel but for the $\text{OH}(F_2, J, M = J, f)$ initial state. The collision energy is 10^{-3} cm^{-1} .

of molecules opens up new pathways for relaxation. As shown in Fig. 7.3, the OH molecules in the $J = 7/2$ state can undergo Λ -doublet changing, J -changing, and fine-structure transitions. The relative efficiency of these relaxation pathways can be quantified in terms of the partial rate constants k_Λ , k_J , and $k_{\bar{Q}}$. The rate constants for these processes are presented in Table 7.2 for a temperature of 10 mK. The rate constants for Λ -doublet changing transitions increase by two orders of magnitude with increasing electric field from zero to 100 kV/cm. The electric field dependence of the Λ -doublet changing rates for rotationally excited OH molecules is not as dramatic. Similarly, the rate constants for rotational relaxation become less sensitive to the electric field strength with increasing J . The collision dynamics of SO-excited OH molecules is determined by the very efficient fine-structure relaxation process $|F_2, J\rangle \rightarrow |F_1, J'\rangle$, which is insensitive to electric field. In order to elucidate the rich resonance structure shown in Fig. 7.5, it is useful to analyze the cross sections for individual Stark transitions [Eq. (7.11)]. A plot of the state-resolved cross sections versus collision energy for different final states is shown in the upper panel of Fig. 7.8. A few distinct propensity rules are immediately apparent from Fig. 7.8. The dominant transition $|F_1, J = 3/2, M = 3/2, f\rangle \rightarrow |F_1, J' = 3/2, M' = 1/2, f\rangle$ conserves the inversion parity and corresponds to a minimal change of M . However, this propensity rule breaks down near the shape resonance at $E_{\text{coll}} \sim 0.2 \text{ cm}^{-1}$, where the parity-changing transition $|F_1, J = 3/2, M = 3/2, f\rangle \rightarrow |F_1, J' = 3/2, M' = 3/2, e\rangle$ dominates. A closer inspection of Fig. 7.8 shows that, in general, the probability for the transition $|F_1, JM\epsilon\rangle \rightarrow |F_1, J'M'\epsilon'\rangle$ decreases with increasing $\Delta M = M' - M$ and $\Delta\epsilon$. This is on a par with the observations made by González-Sánchez *et al.* in their computational study of ^4He -OH collisions [122].

At zero electric field, the state-to-state cross sections exhibit a series of resonance peaks. Because the total angular momentum projection, $M_{\text{tot}} = M + M_\ell$, is conserved,

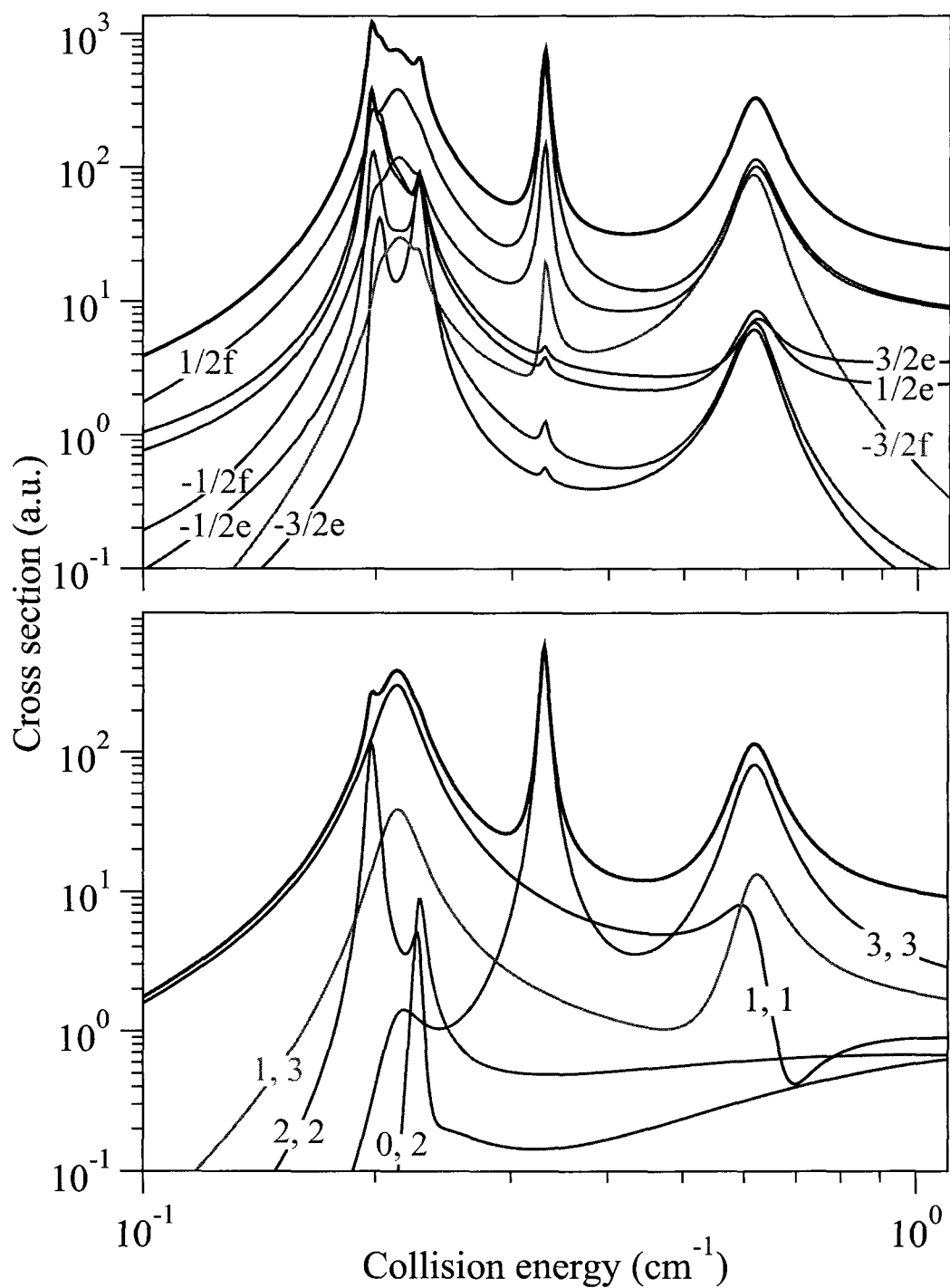


Fig. 7.8: (Upper panel): State-to-state cross sections for inelastic scattering of $\text{OH}(F_1, J = 3/2, M = 3/2, f)$ with ^3He at zero electric field. The magnetic field is 1 G. (Lower panel) Partial wave contributions to the cross section marked as “3/2e” in the upper panel. The magnetic field is 1 G. See text for details.

the inelastic transition $M \rightarrow M'$ must necessarily be accompanied by the transition $m_\ell \rightarrow m_\ell + \Delta M$ [123]. Thus, even for s -wave collisions ($\ell = 0$), there is always a centrifugal barrier in the outgoing collision channel, which may lead to temporary trapping of the collision partners to form a quasi-bound state (or shape resonance). Outside the s -wave regime, the quasibound states can also occur in the incoming collision channel. The lower panel of Fig. 7.8 shows the decomposition of the cross section for the inelastic transition $|F_1, J = 3/2, M = 3/2, f\rangle \rightarrow |F_1, J' = 3/2, M' = 1/2, f\rangle$ into different partial-wave contributions [cf. Eq. (7.11)]

$$\sigma_{\gamma\ell \rightarrow \gamma'\ell'} = \frac{\pi}{k_\gamma^2} \sum_{M_{\text{tot}}} \sum_{m_\ell} \sum_{m'_\ell} |\delta_{\gamma\gamma'} \delta_{\ell\ell'} \delta_{m_\ell, m'_\ell} - S_{\gamma\ell m_\ell; \gamma'\ell' m'_\ell}^{M_{\text{tot}}}|^2. \quad (7.13)$$

By analyzing the ℓ -resolved cross sections as functions of collision energy, each resonance can be assigned the quantum numbers ℓ and ℓ' . The analysis shows that the broad peak at $E_{\text{coll}} \sim 0.65 \text{ cm}^{-1}$ can be identified as an $\ell = 3$ shape resonance, and the lowest-energy peak is due to an $\ell = 1$ shape resonance (in these cases, $\ell' = \ell$, i.e., the resonances occur in both the incoming and outgoing collision channels). There are also resonances corresponding to the centrifugal barriers in the outgoing collision channel. An example of such a resonance due to the $\ell = 0 \rightarrow \ell' = 2$ transition is shown in the lower panel of Fig. 7.8. We note that many of the resonances shown in the lower panel of Fig. 7.8 do not show up in the total cross section because of the averaging, which occurs when different partial wave contributions are added together. Electric fields couple the opposite parity states ($\Delta\epsilon = \pm 2$), which alters the selection rules for individual Stark transitions. The upper panel of Fig. 7.9 shows the state-to-state inelastic cross sections as functions of collision energy in the presence of an electric field of 5 kV/cm. A comparison with Fig. 7.8 shows that electric fields alter field-free propensity rules in such a way that the incoming collision flux gets

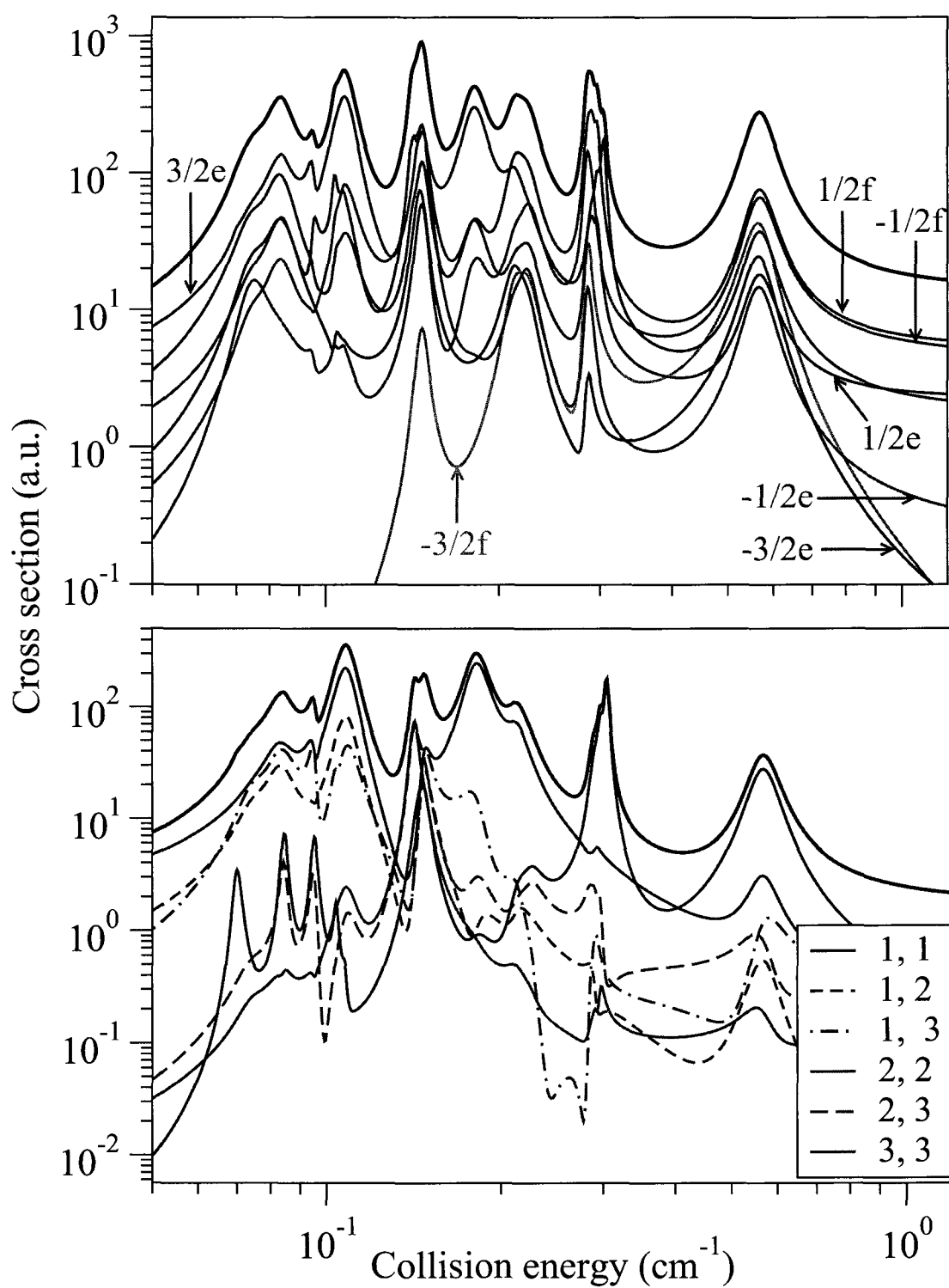


Fig. 7.9: Same as in Fig. 7.8 but for the electric field of 5 kV/cm.

redistributed more evenly between different outgoing channels. The absolute values of the cross sections and the number of shape resonances increase considerably compared to the field-free case.

The electric-field-induced couplings of the opposite parity states lead to indirect couplings between different partial waves [134]. This, in turn, leads to the suppression of diagonal contributions to the scattering amplitude ($\ell \rightarrow \ell$) and enhancement of non-diagonal transitions ($\ell \rightarrow \ell \pm 1$) [134]. As a result of these indirect couplings, many more partial waves become involved in the collision process and shape resonances get suppressed. As illustrated in the lower panel of Fig. 7.9, the $\ell \rightarrow \ell \pm 1$ transitions result in many additional resonant contributions, which shift and split the individual resonance lines, leading to electric-field-induced resonance “broadening”.

In order to explore the generality of our results, we analyze the sensitivity of the cross sections to various parameters of the Hamiltonian (7.2). In Fig. 7.10, we plot the total cross section for Stark relaxation in $^3\text{He-OH}$ collisions from the $|F_1, J = 3/2, M = 3/2, f\rangle$ initial state calculated with the rotational constant of the OH molecule multiplied by factors of 0.5 and 2. Although the scaled cross sections exhibit a different resonant structure, the background value of the cross sections at $E_{\text{coll}} > 0.1 \text{ cm}^{-1}$ is not sensitive to the rotational constant. This confirms our previous conclusion [123] that M -changing transitions in $^2\Pi$ molecules occur via direct couplings of different Stark levels induced by the anisotropy of the interaction potential. As these couplings are typically strong, the collision dynamics of $^2\Pi$ molecules tends to be insensitive to their rotational structure.

7.2.3 Comparison with experiment

The cross sections for electronic and rotational energy transfer in collisions of $^2\Pi$ molecules with rare gas atoms were measured in a number of experiments

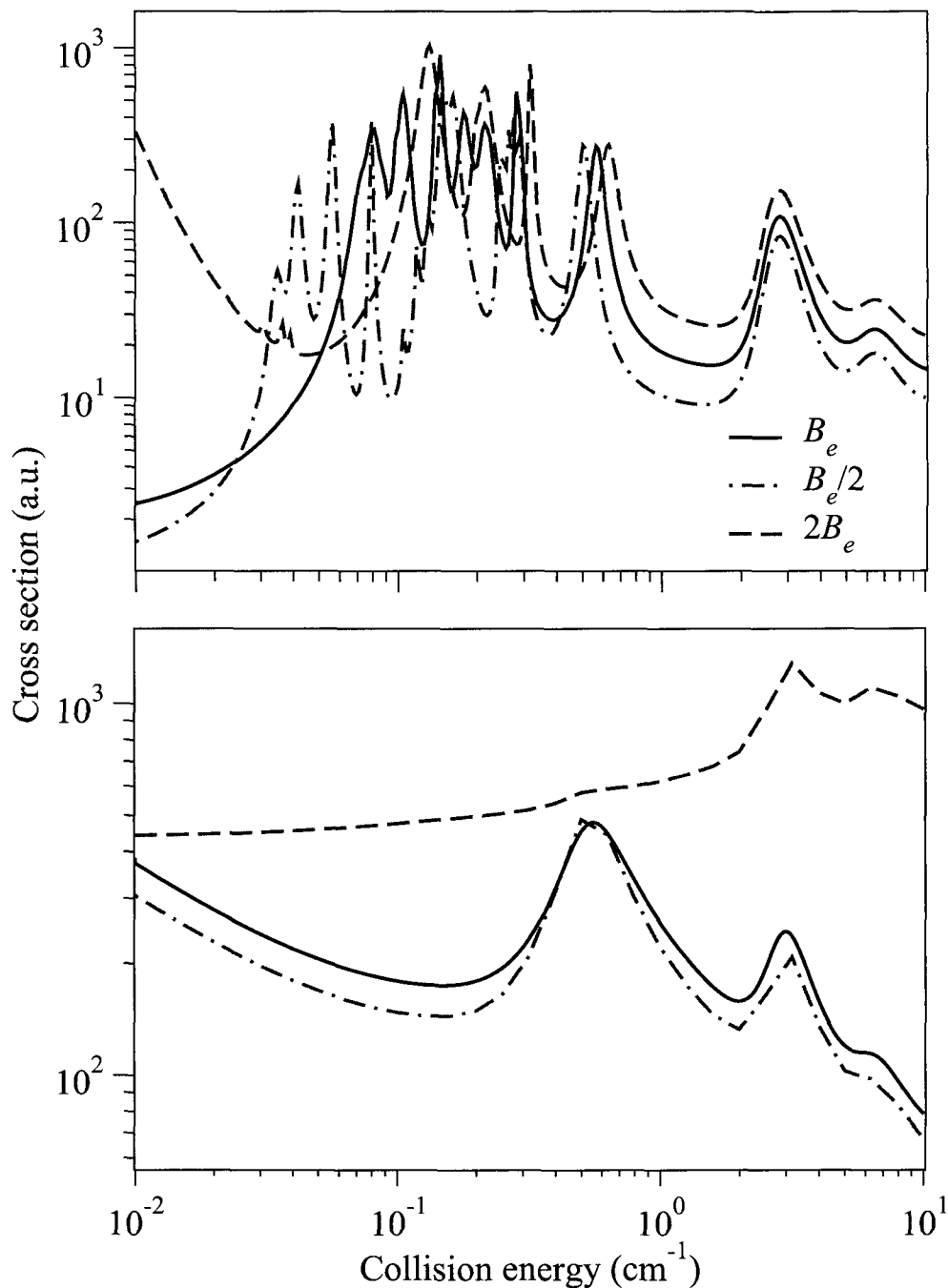


Fig. 7.10: (Upper panel): Collision energy dependence of the inelastic cross sections for $\text{OH}(F_1, J = 3/2, M = 3/2, f)$ with ^3He at an electric field of 5 kV/cm calculated with the rotational constant of OH multiplied by factors of 0.5 (dashed line) and 2 (dotted line). The original ^3He -OH cross section (full line) is also shown for comparison. (Lower panel): same as in the upper panel but for the OH molecules initially in the $|F_2, J = 1/2, M = 1/2, f\rangle$ state. The magnetic field is 1 G (upper panel) and 10^4 G (lower panel)

[98, 99, 100, 101, 102, 110, 135]. In a recent experimental study, Sawyer *et al.* observed collisions of magnetically trapped OH molecules in the $|F_1, J = 3/2, M = 3/2, f\rangle$ initial state with a supersonic beam of ^4He atoms [135]. By analyzing the time dependence of trap loss, they were able to measure the absolute scattering cross sections at seven collision energies between 60 cm^{-1} and 200 cm^{-1} . The measured cross sections displayed an interesting variation over a narrow interval of collision energies from 70 to 130 cm^{-1} , which was attributed to a threshold effect. As shown in Fig. 7.4, the Λ -doublet components of the first rotationally excited state ($J = 5/2$) lie 83.9 and 84.1 cm^{-1} above the field-free ground state ($J = 3/2$). An electric field of 5 kV/cm further splits the components into six thresholds lying within 0.1 cm^{-1} of each other. According to the Wigner threshold law for s -wave scattering, the cross section for rotational excitation $J = 3/2 \rightarrow J' = 5/2$ should vary as $\sqrt{E - E_{\text{thr}}}$, where E_{thr} is the threshold energy and E is the total energy [136].

In order to interpret the experimental findings of Ref. [135], we extended our quantum calculations to higher collision energies to obtain converged cross sections for elastic scattering and rotationally inelastic transitions in ^4He -OH collisions (throughout this section, we consider collisions with the ^4He isotope). The calculations were performed at the seven collision energies probed in the experiment [135]. To elucidate the role of inelastic transitions in He-OH collisions, we complemented the multichannel CC calculations with a simple model, which ignores the anisotropy of the atom-molecule interaction potential. This approximation decouples the CC equations (7.10) to yield a set of one-dimensional (1D) Schrödinger equations, which we solve for a given partial wave ℓ and collision energy E_{coll} . By summing the resulting partial cross sections over ℓ , we obtain the total elastic cross section. To parametrize the 1D model, it is most natural to use the isotropic part of the atom-molecule interaction potential given by

$$V_0(R) = \int_0^\pi \frac{1}{2}[V_{A'}(R, \theta) + V_{A''}(R, \theta)] \sin \theta d\theta, \quad (7.14)$$

where $V_{A'}(R, \theta)$ and $V_{A''}(R, \theta)$ are the He-OH interaction potentials of A' and A'' symmetry [130]. The 1D model is advantageous since the calculations are less computationally intensive compared to the full multichannel CC calculations. As shown below, the isotropic model (1D) does a good job at describing elastic energy transfer in He-OH collisions. We expect the 1D model to yield a comparable level of accuracy for many other atom-molecule systems, where elastic collisions dominate over inelastic relaxation. We therefore recommend the 1D model as a fast and simple way to estimate the elastic cross sections for atom-molecule system collisions. The upper panel of Fig. 7.11 shows the calculated and measured total cross sections for collisions of OH molecules initially in the $|F_1, J = 3/2, M = 3/2, f\rangle$ state with He atoms at an electric field of 5 kV/cm. The calculated cross sections decrease monotonically with increasing collision energy while the observed cross sections follow the opposite trend. At variance with experimental data, the calculated total cross sections display no threshold structure near $E_{\text{coll}} \sim 84 \text{ cm}^{-1}$. However, the inelastic cross sections shown in the lower panel of Fig. 7.11 do increase significantly as the collision energy is tuned across the $J = 5/2$ threshold. The absence of the threshold structure in the total cross section becomes clear when we compare the absolute magnitudes of the elastic and inelastic contributions: on average, the inelastic cross section accounts for less than 5% of the total cross section. The good agreement between the results of the 1D model and full multichannel CC calculations shown in Fig. 7.11 also suggests that the total cross section is dominated by the elastic contribution.

Figure 7.12 shows the cross sections for elastic and inelastic scattering in He-OH collisions calculated on a fine grid of collision energies in the vicinity of the $J = 5/2$ threshold.

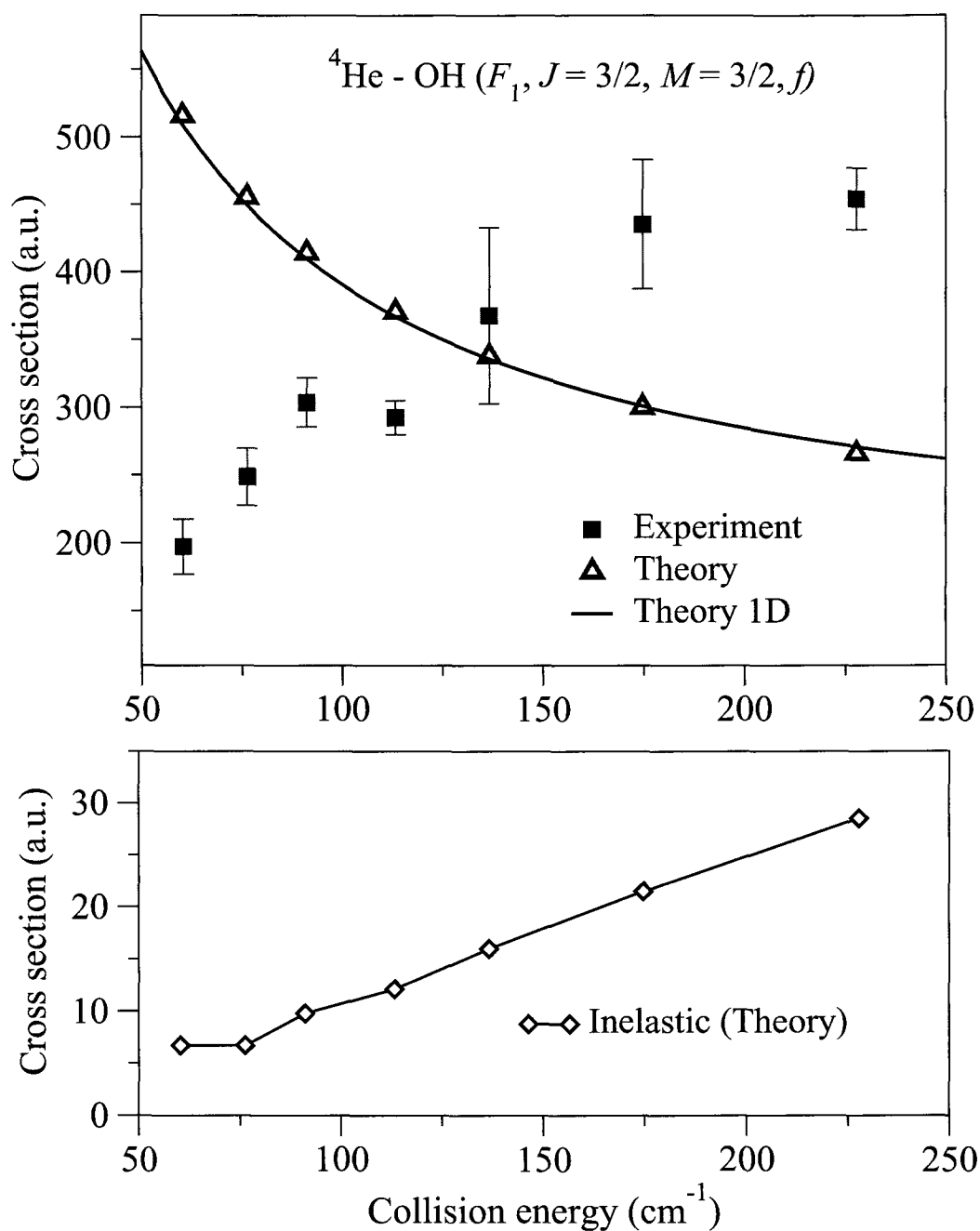


Fig. 7.11: (Upper panel): Total cross sections for ${}^4\text{He-OH}(F_1, J = 3/2, M = 3/2, f)$ as functions of collision energy: multichannel CC calculations (triangles), isotropic model (full line), experiment (squares with error bars). (Lower panel) Collision energy dependence of the inelastic cross section for the same system from multichannel CC calculations. The electric field is 5 kV/cm, the magnetic field is 1 G.

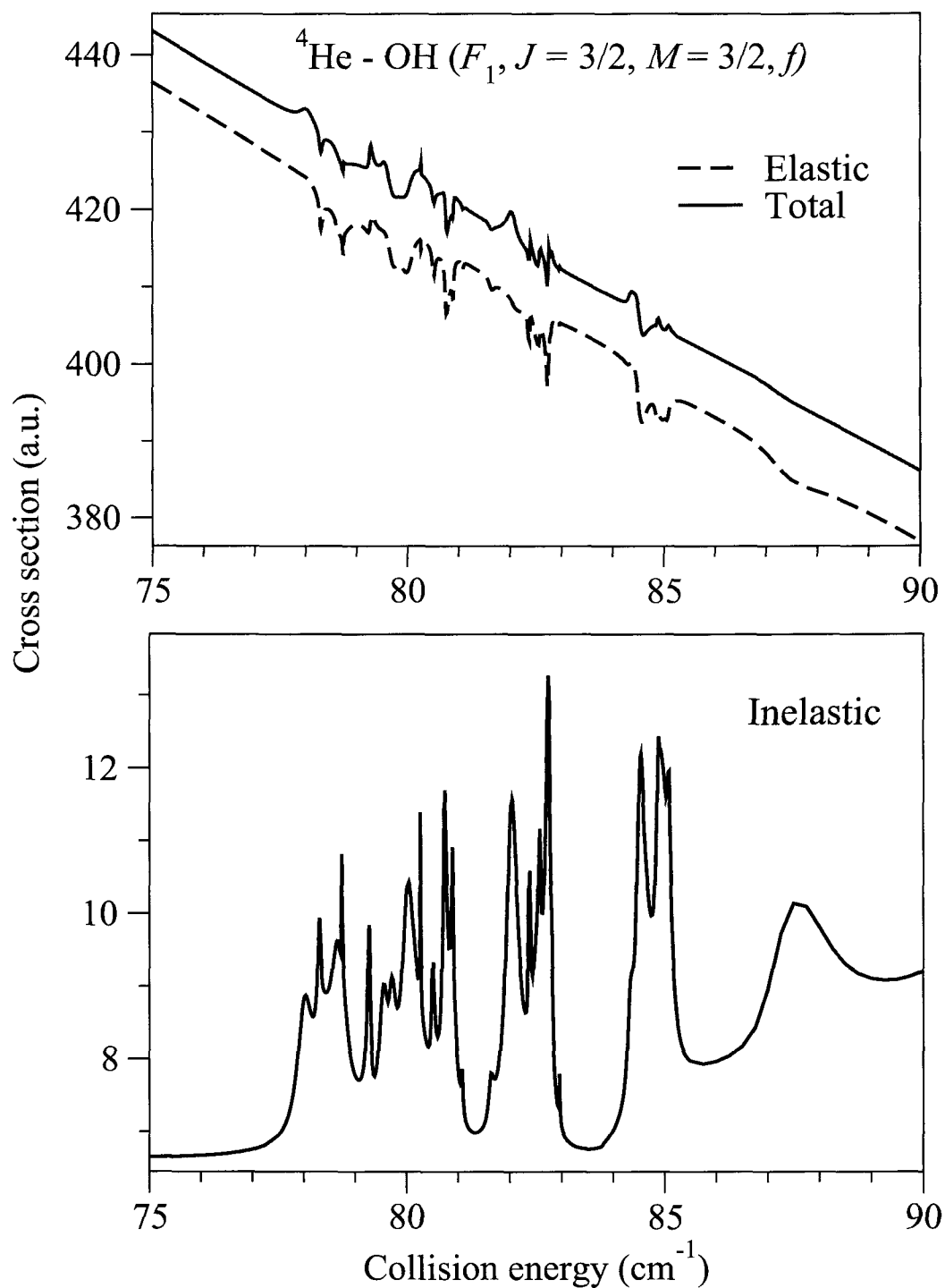


Fig. 7.12: (Upper panel) Calculated total (full line) and elastic (dashed line) cross sections as functions of collision energy near threshold. (Lower panel) The inelastic cross section as a function of collision energy near threshold. Note the different Y-axis scaling for total and inelastic cross sections. The electric field is 5 kV/cm, the magnetic field is 1 G [1].

The complicated resonance structure in the lower panel of Fig. 7.12 is due to the overlapping threshold dependencies of the cross sections for inelastic transitions from the rotationally ground state to the first rotationally excited state. As shown in Figs. 7.11 and 7.12, the *total* cross section is dominated by elastic scattering, and hence shows little sensitivity to collision energy near threshold. These observations agree well with the previous experimental and theoretical studies of Xe-OH collisions near threshold based on multichannel CC calculations and accurate *ab initio* interaction potentials [110] calculated using the same *ab initio* method as the He-OH potentials used in this work. The calculations of Gilijamse *et al.* shown in Fig. 7.5 of their paper [110] demonstrate that the inelastic cross section accounts for only a small fraction ($<10\%$) of the total Xe-OH scattering cross section for collision energies from 50 to 300 cm^{-1} . In our calculations, this fraction is even smaller due to the weaker anisotropy of the He-OH interaction. A possible source of the disagreement between theory and experiment may be traced to the He-OH interaction potentials used in scattering calculations. In order to explore the sensitivity of our results to variations of the interaction potential, we calculated the elastic cross sections with the isotropic term (7.14) multiplied by a constant scaling factor f_s . To avoid expensive multichannel calculations, we employed the 1D model to calculate the elastic cross sections as functions of collision energy for several values of f_s . The results presented in Fig. 7.13 demonstrate that scaling the isotropic part of the interaction potential by factors 0.5 and 1.5 modifies the magnitude of the cross sections but not their dependence on collision energy. The scaling factors chosen are large given the accuracy level typical of present-day *ab initio* interaction potentials ($\sim 10\text{-}20\%$). An independent calculation of the bound states of the He-OH van der Waals complex yielded good agreement with high-resolution spectroscopic measurements [137], further supporting the reliability of the *ab initio* interaction potentials calculated by Lee *et al.* [130]. We therefore

believe that the uncertainties in our calculated cross sections are significantly smaller than shown in Fig. 7.13 for $f_s = 0.5$ and 1.5.

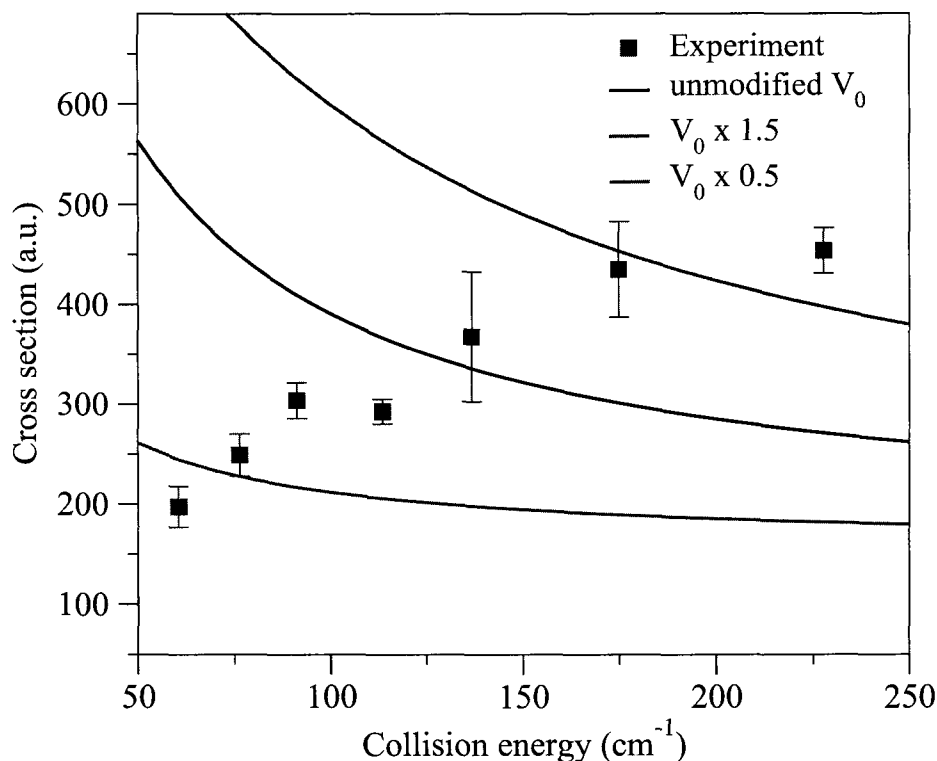


Fig. 7.13: Same as in the upper panel of Fig. 11, but for the isotropic interaction potential multiplied by 0.5 (lower trace) and 1.5 (upper trace).

The cross sections for elastic scattering are also sensitive to the location of the repulsive wall of the interaction potential [138]. We performed calculations with the interaction potential shifted to smaller or larger R by $1 a_0$. Figure 7.14 shows that these modifications do not affect the dependence of the cross sections on collision energy and the overall effect is very similar to that produced by scaling the interaction potential by a constant factor (see Fig. 7.13). As with the scaling procedure mentioned above, shifting the interaction potential by $1 a_0$ is a substantial modification that increases the rotational constant of the He-OH weakly bound complex by as much as

30% (the inaccuracy of the calculated rotational constants is normally on the order of a few percent [130]).

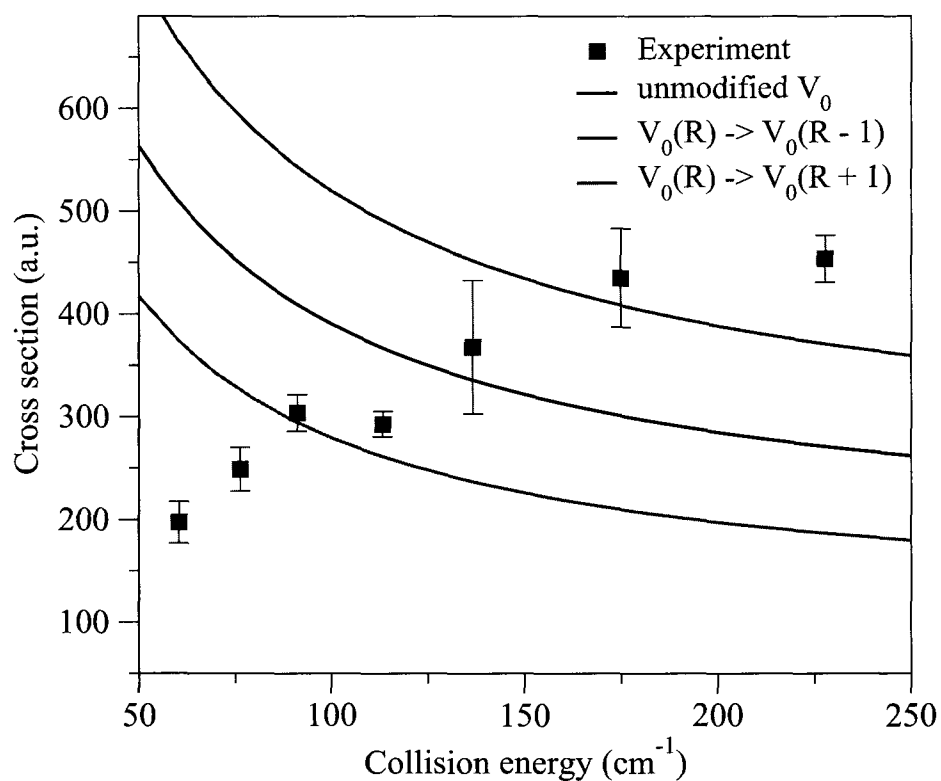


Fig. 7.14: Same as in the upper panel of Fig. 11, but for the isotropic interaction potential shifted by $1 a_0$ to the left (upper trace) and right (lower trace).

CHAPTER 8

CONCLUSION

In this work, the prominence of magnetic dipole-dipole interaction on cold and ultracold collision dynamics between paramagnetic atoms (Cr and Rb) was investigated. Chromium atoms have been used to illustrate the mechanical effect of the magnetic dipolar force on a superfluid gas of Cr atoms and the collapse of a pure dipolar BEC has been demonstrated. Zeeman relaxation of Cr spin states in cold and ultracold collision of Cr isotopes was calculated by quantum multichannel methods and the scattering lengths for the spin multiplets were obtained by tuning the short-range parameters with magnetic fields through Fano-Feshbach resonances. New resonances have been predicted. The short-range molecular interactions were calculated with *ab initio* techniques and accurate Born-Oppenheimer potential energy curves were matched to numerically calculated long-range dispersion potential energies. In the bosonic collisions, all resonances are due to dipolar collision and for the mixed-isotopic cases, the interplay between the dipolar and hyperfine resonances is studied. Detailed comparisons with observations are made. Calculations presented in this thesis have been helpful for buffer-gas cooling experiments. In Cr-Rb collision, a molecular state with a large permanent electric dipole moment is identified. This molecule has both large electric and magnetic dipole moments.

Paramagnetic molecules, such as hydroxide (OH), are also buffer gas cooled and magnetically trapped. In this work, *ab initio* quantum collisional techniques were used to calculate the cross sections for collision of trapped OH molecules with a cold

supersonic atomic helium beam. It was shown that by considering the effect of the trapping potential on the collision, it may be possible to obtain reasonable agreement with observations.

Larger Bohr magneton paramagnetic atoms (such as dysprosium) are now Bose condensed with an eye toward simulation of many-body systems with strong dipolar interactions. The techniques developed in this thesis will be useful for determining the efficiency of production for strongly-interacting systems. Inelastic collisions, which can be harmful to trapping of atoms and molecules, are extremely important for isolating the infinity of the Hilbert system.

APPENDIX A

BESSEL FUNCTIONS

The reaction matrix K is determined by the asymptotic form of the wave function

$$\Psi(r) \underset{r \rightarrow \infty}{=} J(r) - N(r)K, \quad (\text{A.1})$$

where $J(r)$ and $N(r)$ are diagonal matrices constructed using spherical and modified spherical Bessel functions, respectively. In this work we use

$$[J(r)]_{ii} = \frac{1}{\sqrt{k_i}}(k_i r) j_{l_i}(k_i r) \quad (\text{A.2})$$

$$[N(r)]_{ii} = \frac{1}{\sqrt{k_i}}(k_i r) n_{l_i}(k_i r) \quad (\text{A.3})$$

for open channels, and

$$[J(r)]_{ii} = \sqrt{\frac{2}{\pi}}(\kappa_i r) i_{l_i}(\kappa_i r) \quad (\text{A.4})$$

$$[N(r)]_{ii} = \sqrt{\frac{\pi}{2}}(\kappa_i r) k_{l_i}(\kappa_i r) \quad (\text{A.5})$$

for closed channels. Here, l_i is the orbital angular momentum quantum number and k_i is the absolute value of the channel momentum. For the Bessel functions, we follow the conventions set in [41]:

Spherical Bessel functions of the first and second kind

$$\begin{aligned}
j_0(x) &= \frac{1}{x} \sin(x) \\
j_1(x) &= \frac{1}{x^2} \sin(x) - \frac{1}{x} \cos(x) \\
j_2(x) &= \left(\frac{3}{x^3} - \frac{1}{x} \right) \sin(x) - \frac{3}{x^2} \cos(x) \\
n_0(x) &= -\frac{1}{x} \cos(x) \\
n_1(x) &= -\frac{1}{x^2} \cos(x) - \frac{1}{x} \sin(x) \\
n_2(x) &= -\left(\frac{3}{x^3} - \frac{1}{x} \right) \cos(x) - \frac{3}{x^2} \sin(x)
\end{aligned}$$

Modified spherical Bessel functions of the first and second kind

$$\begin{aligned}
i_0(x) &= \frac{1}{x} \sinh(x) \\
i_1(x) &= \frac{1}{x} \cosh(x) - \frac{1}{x^2} \sinh(x) \\
i_2(x) &= \left(\frac{3}{x^3} + \frac{1}{x} \right) \sinh(x) - \frac{3}{x^2} \cosh(x) \\
k_0(x) &= \frac{1}{x} \exp(-x) \\
k_1(x) &= \left(\frac{1}{x^2} + \frac{1}{x} \right) \exp(-x) \\
k_2(x) &= \left(\frac{3}{x^3} + \frac{3}{x^2} + \frac{1}{x} \right) \exp(-x)
\end{aligned}$$

The asymptotic forms of $[J(x)]_{ii}$ and $[N(x)]_{ii}$ are

$$[J(r)]_{ii} = \frac{1}{\sqrt{k_i}} \sin \left(k_i r - l_i \frac{\pi}{2} \right) \quad (\text{A.6})$$

$$[N(r)]_{ii} = -\frac{1}{\sqrt{k_i}} \cos \left(k_i r - l_i \frac{\pi}{2} \right) \quad (\text{A.7})$$

for open channels, and

$$[J(r)]_{ii} = \frac{1}{\sqrt{2\pi}} [\exp(\kappa_i r) - (-1)^{l_i} \exp(-\kappa_i r)] \quad (\text{A.8})$$

$$[N(r)]_{ii} = \sqrt{\frac{\pi}{2}} \exp(-\kappa_i r) \quad (\text{A.9})$$

for closed channels.

The exponential character of the closed-channel functions defined by (A.4), the exponential decrease in particular, is a potential source of numerical difficulties, namely overflow and underflow. The rest of this appendix shows how to avoid this problem by calculating the matching function ratios instead. In this work we limit ourselves to two propagation methods: log-derivative and renormalized Numerov.

Bessel function ratios

As we have seen, there is a need for either the log-derivative of closed-channel functions or the ratio of closed-channel functions at two consecutive grid points. The simple approximation yields $+k_i$, $-k_i$ for the log-derivative method and $\exp(+k_i h)$, $\exp(-k_i h)$ for the renormalized Numerov method. If we want more precision, then there are two cases to consider.

A.1 Log-derivative method

Here, the prescribed way (see [43]) of handling boundary conditions requires evaluation of the log-derivative of the modified spherical Bessel functions

$$i'_N(\kappa r)/i_N(\kappa r), \quad \text{and} \quad k'_N(\kappa r)/k_N(\kappa r). \quad (\text{A.10})$$

The evaluation of $i'_N(z)/i_N(z)$, where $z = \kappa r$, involves a recursive scheme [41]

$$i_{n-1}(z) - i_{n+1}(z) = \frac{2n+1}{z} i_n(z) \quad (\text{A.11})$$

$$ni_{n-1}(z) + (n+1)i_{n+1}(z) = (2n+1)i'_n(z). \quad (\text{A.12})$$

After dividing both equations with $i_n(z)$ and rearranging the terms we get

$$I_n(z) = -\frac{2n+1}{z} + I_{n-1}^{-1}(z) \quad (\text{A.13})$$

$$\frac{i'_n(z)}{i_n(z)} = -\frac{(n+1)I_n(z) + nI_{n-1}^{-1}(z)}{2n+1}, \quad (\text{A.14})$$

where we use the ratio

$$I_n(z) = \frac{i_{n+1}(z)}{i_n(z)}. \quad (\text{A.15})$$

To find the ratio $i'_N(z)/i_N(z)$ using (A.14) we need $I_N(z)$ and $I_{N-1}^{-1}(z)$, which are obtained from (A.13). The solution of (A.13) is initiated with

$$\frac{i_1(z)}{i_0(z)} = \coth(z) - \frac{1}{z}, \quad (\text{A.16})$$

and iterated from $n = 1$ to $n = N$. The evaluation of $k'_N(z)/k_N(z)$ also involves a recursive scheme [41]

$$k_{n-1}(z) - k_{n+1}(z) = -\frac{2n+1}{z} k_n(z) \quad (\text{A.17})$$

$$nk_{n-1}(z) + (n+1)k_{n+1}(z) = -(2n+1)k'_n(z). \quad (\text{A.18})$$

After dividing both equations with $k_n(z)$ and rearranging the terms we get

$$K_n(z) = \frac{2n+1}{z} + K_{n-1}^{-1}(z) \quad (\text{A.19})$$

$$\frac{k'_n(z)}{k_n(z)} = -\frac{(n+1)K_n(z) + nK_{n-1}^{-1}(z)}{2n+1}, \quad (\text{A.20})$$

where we use the ratio

$$K_n(z) = \frac{k_{n+1}(z)}{k_n(z)}. \quad (\text{A.21})$$

The ratio $k'_N(z)/k_N(z)$ from (A.20) depends on $K_N(z)$ and $K_{N-1}^{-1}(z)$, which are obtained from (A.19). The solution of (A.19) is initiated with

$$\frac{k_1(z)}{k_0(z)} = 1 + \frac{1}{z}. \quad (\text{A.22})$$

A.2 Renormalized Numerov method

Here, the prescribed way (see [45]) of handling boundary conditions requires evaluation of the ratios of modified spherical Bessel functions at two consecutive points

$$\frac{z_2 i_N(z_2)}{z_1 i_N(z_1)}, \quad \text{and} \quad \frac{z_2 k_N(z_2)}{z_1 k_N(z_1)}, \quad (\text{A.23})$$

where $z_1 = \kappa r$, $z_2 = \kappa(r+h)$, r is the matching distance and h is the integration step.

The evaluation of $[z_2 i_N(z_2)]/[z_1 i_N(z_1)]$ involves a recursive scheme [41]

$$i_n(z) = q_n(z) \sinh(z) + q_{-(n+1)}(z) \cosh(z), \quad (\text{A.24})$$

where functions $q_n(z)$ are themselves defined through a recursive equation

$$q_{n-2}(z) = q_n(z) + \frac{(2n-1)}{z} q_{n-1}(z), \quad (\text{A.25})$$

which is initialized with $q_0(z) = 1/z$ and $q_1(z) = -1/z^2$. After multiplying (A.24) with z and introducing $\bar{q}_n(z) = zq_n(z)$, we get

$$zi_n(z) = \bar{q}_n(z) \sinh(z) + \bar{q}_{-(n+1)}(z) \cosh(z). \quad (\text{A.26})$$

To find $\bar{q}_n(z)$ and $\bar{q}_{-(n+1)}(z)$, for $n \geq 3$, we use

$$\bar{q}_n(z) = \bar{q}_{n-2}(z) - \frac{(2n-1)}{z} \bar{q}_{n-1}(z) \quad (\text{A.27})$$

$$\bar{q}_{-(n+1)}(z) = \bar{q}_{-(n-1)}(z) - \frac{(2n-1)}{z} \bar{q}_{-n}(z). \quad (\text{A.28})$$

The initial values are determined by $i_0(z)$,

$$zi_0(z) = \sin(z) \longrightarrow \bar{q}_0(z) = 1, \quad \bar{q}_{-1}(z) = 0, \quad (\text{A.29})$$

and $i_1(z)$,

$$zi_1(z) = -\frac{1}{z} \sinh(z) + \cosh(z) \longrightarrow \bar{q}_1(z) = -\frac{1}{z}, \quad \bar{q}_{-2}(z) = 1. \quad (\text{A.30})$$

Equation (A.27) is initialized with $\bar{q}_0(z) = 1$ and $\bar{q}_1(z) = -1/z$, while (A.28) is initialized with $\bar{q}_{-1}(z) = 0$ and $\bar{q}_{-2}(z) = 1$. With the help of the basic properties of hyperbolic functions

$$\sinh(z_1 + \kappa h) = \sinh(z_1) \cosh(\kappa h) + \cosh(z_1) \sinh(\kappa h) \quad (\text{A.31})$$

$$\cosh(z_1 + \kappa h) = \cosh(z_1) \cosh(\kappa h) + \sinh(z_1) \sinh(\kappa h), \quad (\text{A.32})$$

we get the final expression for the required ratio

$$\frac{z_2 i_N(z_2)}{z_1 i_N(z_1)} = \frac{\bar{q}_N(z_2) [\sinh(\kappa h) + \cosh(\kappa h) \tanh(z_1)] + \bar{q}_{-(N+1)}(z_2) [\cosh(\kappa h) + \sinh(\kappa h) \tanh(z_1)]}{\bar{q}_N(z_1) + \bar{q}_{-(N+1)}(z_1) \tanh(z_1)}, \quad (\text{A.33})$$

where $\cosh(\kappa h)$ and $\sinh(\kappa h)$ are less prone to numerical difficulties, due to of $\kappa h \ll z_1, z_2$. The evaluation of $[z_2 k_N(z_2)]/[z_1 k_N(z_1)]$ is based on a recursive equation for the modified spherical Bessel functions of the second kind

$$k_n(z) = \exp(z) f_n(z), \quad (\text{A.34})$$

since $f_n(z)$ is itself defined through recursion

$$f_n(z) = f_{n-2}(z) + \frac{2n-1}{x} f_{n-1}(z), \quad (\text{A.35})$$

in which the initial values are $f_0(z) = 1/z$ and $f_1 = (z+1)/z^2$. After multiplying (A.34) with z and introducing $\bar{f}_n(z) = z f_n(z)$, we get

$$z k_n(z) = \exp(-z) \bar{f}_n(z) \quad (\text{A.36})$$

where $\bar{f}_n(z)$ are found using the recursive equation

$$\bar{f}_n(z) = \bar{f}_{n-2}(z) + \frac{2n-1}{x} \bar{f}_{n-1}(z), \quad (\text{A.37})$$

which is initialized with $\bar{f}_0(z) = 1$ and $\bar{f}_1 = (z+1)/z$. The final expression for the required ratio is

$$\frac{z_2 k_N(z_2)}{z_1 k_N(z_1)} = \exp(-\kappa h) \frac{\bar{f}_N(z_2)}{\bar{f}_N(z_1)}. \quad (\text{A.38})$$

APPENDIX B

WIGNER-ECKART THEOREM

The Wigner-Eckart theorem enables us to find the matrix elements of an irreducible tensor operator $T_q^{(k)}$ in a basis that includes angular momentum numbers:

$$\langle \gamma j m | T_q^{(k)} | \gamma' j' m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \langle \gamma j || T^{(k)} || \gamma' j' \rangle, \quad (\text{B.1})$$

where the variable γ represents all other quantum numbers. The conventional interpretation is that the geometric part gets factored out through $3j$ Wigner coefficients, and the rest, which depends on the specific interaction, is contained in the reduced element $\langle \gamma j || T^{(k)} || \gamma' j' \rangle$.

Special attention should be paid to different phase definitions and to the scaling of the reduced elements. Some authors choose to keep the phase coefficient $(-1)^{2k}$ explicit even though k has to be an integer, hence the phase factor is identical to one. The half integer rank tensors would represent non-physical operators that mix fermions and bosons. In this work we follow the conventions set in [92].

Very often, while working in the coupled basis, we need to evaluate operators that act in only one of the uncoupled spaces and are extended by tensor product onto the coupled space according to

$$T_1 \rightarrow T_1 \otimes I_2, \quad \text{and} \quad T_2 \rightarrow I_1 \otimes T_2. \quad (\text{B.2})$$

The coupling scheme of two angular momenta serves as an example

$$\hat{\mathbf{j}} = \hat{\mathbf{j}}_1 + \hat{\mathbf{j}}_2. \quad (\text{B.3})$$

The relation between the reduced matrix elements of T_1 in the coupled ($|j, m\rangle$) and uncoupled ($|j_1, m_1\rangle$) representations is

$$\begin{aligned} \left\langle (j_1 j_2) j \left\| T_1^{(k)} \right\| (j'_1 j'_2) j' \right\rangle = \\ \delta_{j_2, j'_2} (-1)^{j_1 + j_2 + j' + k} \sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} j_1 & j_2 & j \\ j' & k & j'_1 \end{Bmatrix} \left\langle j_1 \left\| T_1^{(k)} \right\| j'_1 \right\rangle, \end{aligned} \quad (\text{B.4})$$

and likewise for T_2

$$\begin{aligned} \left\langle (j_1 j_2) j \left\| T_2^{(k)} \right\| (j'_1 j'_2) j' \right\rangle = \\ \delta_{j_1, j'_1} (-1)^{j_1 + j'_2 + j + k} \sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} j_1 & j_2 & j \\ k & j' & j'_2 \end{Bmatrix} \left\langle j_2 \left\| T_2^{(k)} \right\| j'_2 \right\rangle. \end{aligned} \quad (\text{B.5})$$

To fix the convention, we give the reduced matrix element for the angular momentum operator

$$\left\langle j \left\| \hat{\mathbf{j}} \right\| j' \right\rangle = \sqrt{j(j+1)(2j+1)} \delta_{j, j'}. \quad (\text{B.6})$$

B.1 An example

The direct application of the above expressions is useful when we need the matrix elements of the electron spin operator s_z in the coupled basis defined by the angular momentum operator $\mathbf{f} = \mathbf{s} + \mathbf{i}$. Since we want to evaluate the matrix elements of

angular momentum operators, which are irreducible tensors of rank 1 ($k = 1$), the zero component ($q = 0$) in particular, we list only the coefficients for which $\Delta j = 0$ or 1 and $\Delta m = 0$.

For the $j \rightarrow j$ transition matrix element evaluation, we need the following $3j$ coefficient in (B.1)

$$\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix} = (-1)^{j-m} \frac{m}{[j(j+1)(2j+1)]}, \quad (\text{B.7})$$

and a $6j$ coefficient from (B.4) or (B.5)

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ 1 & j_3 & j_2 \end{Bmatrix} = (-1)^{s+1} \frac{2[j_3(j_3+1) + j_2(j_2+1) - j_1(j_1+1)]}{\sqrt{2j_2(2j_2+1)(2j_2+2)2j_3(2j_3+1)(2j_3+2)}}, \quad (\text{B.8})$$

where $s = j_1 + j_2 + j_3$.

For the $j-1 \rightarrow j$ transition matrix element evaluation, we need the following $3j$ coefficient in (B.1)

$$\begin{pmatrix} j+1 & j & 1 \\ m & -m & 0 \end{pmatrix} = (-1)^{j-m-1} \left[\frac{(j+1)^2 - m^2}{(2j)(2j+1)(2j+2)} \right], \quad (\text{B.9})$$

and a $6j$ coefficient from (B.4) or (B.5)

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ 1 & j_3-1 & j_2 \end{Bmatrix} = (-1)^s \sqrt{\frac{2(s+1)(s-2j_1)(s-2j_2)(s-2j_3+1)}{2j_2(2j_2+1)(2j_2+2)(2j_3-1)2j_3(2j_3+1)}}, \quad (\text{B.10})$$

where $s = j_1 + j_2 + j_3$.

B.2 Symmetry properties of $3j$, $6j$ and $9j$ symbols

A quick glance at any table of Wigner coefficients shows that not all arrangements of a given set of constituent angular momentum numbers are included: in short, tables are compacted by exploiting symmetry properties of Wigner symbols. We may encounter a situation where we have the listed values of Wigner symbols, be they numerical or analytical expressions, but the constituent numbers are in the “wrong” order. Only the absolute values of the symbols are known, but to extract the correct signs we must manipulate the symbols using their symmetry properties [92], listed below:

3j) - Column permutation introduces sign change ϵ :

$$\begin{pmatrix} j_{P(1)} & j_{P(2)} & j_{P(3)} \\ m_{P(1)} & m_{P(2)} & m_{P(3)} \end{pmatrix} = \epsilon \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \quad (\text{B.11})$$

where ϵ depends on the parity of the permutation P

$$\epsilon = \begin{cases} 1 & \text{even permutation,} \\ (-1)^S & \text{odd permutation,} \end{cases} \quad (\text{B.12})$$

and $S = \sum_{i=1}^3 j_i$.

- Sign change of all magnetic projection numbers introduces sign change

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \quad (\text{B.13})$$

6j) - Column permutation leaves the 6j symbol unchanged

$$\begin{Bmatrix} j_{P(1)} & j_{P(2)} & j_{P(3)} \\ l_{P(1)} & l_{P(2)} & l_{P(3)} \end{Bmatrix} = \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix}. \quad (\text{B.14})$$

- Simultaneous interchange of any two numbers in the top row with the corresponding numbers in the bottom row leaves the 6j symbol unchanged

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} = \begin{Bmatrix} l_1 & l_2 & j_3 \\ j_1 & j_2 & l_3 \end{Bmatrix} = \begin{Bmatrix} j_1 & l_2 & l_3 \\ l_1 & j_2 & j_3 \end{Bmatrix} = \begin{Bmatrix} l_1 & j_2 & l_3 \\ j_1 & l_2 & j_3 \end{Bmatrix}. \quad (\text{B.15})$$

9j) - Reflection about any of two diagonals leaves the 9j symbol unchanged

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{Bmatrix} = \begin{Bmatrix} j_1 & j_4 & j_7 \\ j_2 & j_5 & j_8 \\ j_3 & j_6 & j_9 \end{Bmatrix} = \begin{Bmatrix} j_9 & j_6 & j_3 \\ j_8 & j_5 & j_2 \\ j_7 & j_4 & j_1 \end{Bmatrix}. \quad (\text{B.16})$$

- The 9j symbol changes its sign under permutation of columns

$$\begin{Bmatrix} j_{P(1)} & j_{P(2)} & j_{P(3)} \\ l_{P(1)} & l_{P(2)} & l_{P(3)} \\ k_{P(1)} & k_{P(2)} & k_{P(3)} \end{Bmatrix} = \epsilon \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \\ k_1 & k_2 & k_3 \end{Bmatrix} \quad (\text{B.17})$$

or rows

$$\begin{Bmatrix} j_{P(1)} & l_{P(1)} & k_{P(1)} \\ j_{P(2)} & l_{P(2)} & k_{P(2)} \\ j_{P(3)} & l_{P(3)} & k_{P(3)} \end{Bmatrix} = \epsilon \begin{Bmatrix} j_1 & l_1 & k_1 \\ j_2 & l_2 & k_2 \\ j_3 & l_3 & k_3 \end{Bmatrix}, \quad (\text{B.18})$$

where the sign ϵ depends on the parity of permutation P

$$\epsilon = \begin{cases} 1 & \text{even permutation,} \\ (-1)^S & \text{odd permutation,} \end{cases} \quad (\text{B.19})$$

and $S = \sum_{i=1}^3 (j_i + l_i + k_i)$.

APPENDIX C

TESTING EXAMPLES

Here, we give a list of a number of known solutions for the Schrödinger equation

$$\psi''(x) + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0 \quad (\text{C.1})$$

that are simple enough to implement and yet sufficient to verify the correctness of a single-channel or a multichannel solver execution.

C.1 Harmonic oscillator

This is a well known example for which the analytical solutions of (C.1) for the harmonic potential

$$V(x) = \frac{1}{2}m\omega^2x^2, \quad (\text{C.2})$$

where x is a displacement variable, are expressed using the Hermite polynomials. The bound type solutions, normalized to unity, are

$$\psi_n(x) = \frac{1}{\sqrt{\pi^{1/2}2^n n!}} \exp(-x^2/2) H_n(x) \quad (\text{C.3})$$

and the corresponding bound state energies are

$$E_n = (n + \frac{1}{2}), \quad (\text{C.4})$$

where we set $\hbar = m = \omega = 1$. To calculate wave functions we need Hermite polynomials, the first five of which are given below:

$$\begin{aligned}
H_0(x) &= 1 \\
H_1(x) &= 2x \\
H_2(x) &= 4x^2 - 2 \\
H_3(x) &= 8x^3 - 12x \\
H_4(x) &= 16x^4 - 48x^2 + 12
\end{aligned} \tag{C.5}$$

The polynomial series grows very quickly so its evaluation becomes difficult and another approach is needed. The following recurrence relation can be used instead

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x), \tag{C.6}$$

initialized with

$$H_0(x) = 1, \quad H_1(x) = 2x. \tag{C.7}$$

The first derivative of the Hermite polynomial is obtained using

$$H'_n(x) = 2nH_{n-1}(x), \tag{C.8}$$

while the first derivative of the wave function is

$$\psi'_n(x) = \sqrt{\frac{n}{2}}\psi_{n-1}(x) - \sqrt{\frac{n+1}{2}}\psi_{n+1}(x). \tag{C.9}$$

If only the log-derivative of the wave function is needed, Hermite polynomials are sufficient, since

$$\frac{\psi'_n(x)}{\psi_n(x)} = \frac{H'_n(x)}{H_n(x)} - x . \quad (\text{C.10})$$

C.2 Morse potential

The Morse potential [139]

$$V(x) = D \exp(-ax) (\exp(-ax) - 2) , \quad (\text{C.11})$$

where x is a displacement variable and the parameter D determines the depth of the potential, has the known expression for bound levels

$$E_n = -\frac{\hbar a^2}{2m} (n - s)^2 , \quad (\text{C.12})$$

where the parameter s is given by

$$2s + 1 = \frac{2\sqrt{2mD}}{a\hbar} . \quad (\text{C.13})$$

The corresponding wave functions are

$$\psi_n^s(y) = N_n y^{s-n} \exp(-y/2) L_n^{2(s-n)}(y) , \quad (\text{C.14})$$

where $L_n^{2(s-n)}(y)$ are associated Laguerre functions of the variable y defined by

$$y = (2s + 1) \exp(-ax) . \quad (\text{C.15})$$

The values of the gamma function $\Gamma(x)$ are required for the computation of the normalization constant

$$N_n = \sqrt{\frac{a(2s-2n)\Gamma(n+1)}{\Gamma(2s-n+1)}} . \quad (\text{C.16})$$

The associated Laguerre polynomials (the first four) are given below:

$$\begin{aligned} L_0^\alpha &= 1 \\ L_1^\alpha &= -x + \alpha + 1 \\ L_2^\alpha &= \frac{1}{2}x^2 - (\alpha+2)x + \frac{1}{2}(\alpha+2)(\alpha+1) \\ L_3^\alpha &= -\frac{1}{6}x^3 + \frac{1}{2}(\alpha+3)x^2 + \frac{1}{2}(\alpha+3)(\alpha+1)x + \frac{1}{6}(\alpha+3)(\alpha+2)(\alpha+1) \end{aligned} \quad (\text{C.17})$$

The polynomial evaluation for higher orders becomes cumbersome and is replaced with a recursive scheme

$$(n+1)L_{n+1}^\alpha(x) = (2n+1+\alpha-x)L_n^\alpha(x) - (n+\alpha)L_{n-1}^\alpha(x) , \quad (\text{C.18})$$

with the following initialization

$$L_0^\alpha = 1, \quad L_1^\alpha = -x + \alpha + 1 . \quad (\text{C.19})$$

The first derivative of associated Laguerre functions is obtained using

$$L_n^{\alpha'}(x) = -L_{n-1}^{\alpha+1}(x) . \quad (\text{C.20})$$

C.3 Scattering length and phase shifts

Attractive exponential potential

For the exponential potential,

$$V(r) = -A \exp(-\mu r), \quad (\text{C.21})$$

where the constant $A > 0$ determines the strength and $\mu > 0$ determines the range of the interaction, the analytical expression for the scattering phase shift is, [42],

$$\delta = \arg [J_{i2k/\mu}(\alpha)] + \arg \left[\Gamma(1 + i\frac{2k}{\mu}) \right] - \frac{2k}{\mu} \ln(\frac{\alpha}{2}), \quad (\text{C.22})$$

where $J_{i2k/\mu}(\alpha)$ are cylindrical Bessel functions of the first kind, and $\Gamma(1 + i2k/\mu)$ are Gamma functions of the complex argument. The Bessel functions of complex order are evaluated at

$$\alpha = \frac{2\sqrt{2mA}}{\mu\hbar}. \quad (\text{C.23})$$

The wave number $k = 2mE/\hbar^2$, with $E > 0$. Both Bessel and Gamma functions yield complex values.

For the case of $E = 0$, the expression for the scattering length is

$$a = \frac{1}{\mu} \left(2 \left(\gamma + \ln(\frac{\alpha}{2}) \right) - \pi \frac{Y_0(\alpha)}{J_0(\alpha)} \right), \quad (\text{C.24})$$

where $\gamma = 0.577 \dots$ is the Euler-Mascheroni constant, and J_0, Y_0 are zero order Bessel functions of the first and second kind, respectively.

Repulsive exponential potential

By changing the sign of the attractive exponential potential, we get the repulsive exponential potential

$$V(r) = A \exp(-\mu r), \quad (\text{C.25})$$

keeping constant A positive, for which the analytical expression for the phase shift is, [42],

$$\delta = \arg [I_{i2k/\mu}(\alpha)] + \arg \left[\Gamma(1 + \frac{2k}{\mu}) \right] - \frac{2k}{\mu} \ln(\frac{\alpha}{2}). \quad (\text{C.26})$$

The transition in the phase shift expression from the attractive interaction to repulsive interaction is effected by replacing the Bessel functions of the first kind J with the modified Bessel functions of the first kind I .

For the case of $E = 0$, the expression for the scattering length is

$$a = \frac{2}{\mu} \left(\gamma + \ln(\frac{\alpha}{2}) + \frac{K_0(\alpha)}{I_0(\alpha)} \right), \quad (\text{C.27})$$

where I_0 , K_0 are zero order modified Bessel functions of the first and second kind, respectively. All other definitions are unchanged with respect to the case of attractive exponential potential.

Lennard-Jones potential

For this potential,

$$V(r) = V_0 \left[\left(\frac{r_0}{r} \right)^{2n-2} - \left(\frac{r_0}{r} \right)^n \right], \quad (\text{C.28})$$

where V_0 denotes the potential depth and r_0 the minimum position, the analytical expression for the scattering length is, [140],

$$a = r_0 \left(\frac{2x}{n-2} \right)^{\frac{1}{n-2}} \frac{\Gamma\left(\frac{-x+n-1}{2n-4}\right) \Gamma\left(\frac{n-3}{n-2}\right)}{\Gamma\left(\frac{-x+n-3}{2n-4}\right) \Gamma\left(\frac{n-1}{n-2}\right)}, \quad (\text{C.29})$$

where x , a dimensionless parameter, is

$$x = r_0 \sqrt{\frac{2mV_0}{\hbar^2}}. \quad (\text{C.30})$$

C.4 A three-channel bound state example

A step further in complexity in the bound single-channel calculations is to use a potential matrix instead of a single potential. A simple choice is to use a diagonal potential matrix to form a multichannel Schrödinger equation

$$\phi''(r) + \frac{2m}{\hbar^2} (E - DV(r)) \phi(r) = 0. \quad (\text{C.31})$$

The potential structure is given by a diagonal matrix

$$D = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, \quad (\text{C.32})$$

where real numbers a , b , and c can be used to create different scenarios in which we can have either all or some of the energy levels degenerate. The wave function, solution of (C.31), is a column made of three functions (one for each channel)

$$\phi(r) = \begin{pmatrix} \phi^{(a)}(r) \\ \phi^{(b)}(r) \\ \phi^{(c)}(r) \end{pmatrix}. \quad (\text{C.33})$$

Since $V(r)D$ is a diagonal matrix, meaning there are no couplings, solving (C.31) is reduced to solving a system of three uncoupled differential equations:

$$\begin{aligned} \phi^{(a)''}(r) + \frac{2m}{\hbar^2}(E - aV(r))\phi^{(a)}(r) &= 0, \\ \phi^{(b)''}(r) + \frac{2m}{\hbar^2}(E - bV(r))\phi^{(b)}(r) &= 0, \\ \phi^{(c)''}(r) + \frac{2m}{\hbar^2}(E - cV(r))\phi^{(c)}(r) &= 0. \end{aligned} \quad (\text{C.34})$$

Assuming that we can find the bound energy spectrum for each channel, that is we have $E_i^{(a)}$ and $\phi_i^{(a)}(r)$, for channel a , $E_j^{(b)}$ and $\phi_j^{(b)}(r)$ for channel b , $E_k^{(c)}$ and $\phi_k^{(c)}(r)$ for channel c , the multichannel solution is then expressed as

$$\phi(r) = C^{(a)}\phi_i^{(a)}(r) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + C^{(b)}\phi_j^{(b)}(r) \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + C^{(c)}\phi_k^{(c)}(r) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (\text{C.35})$$

This decomposition suggests that there could be a triple degenerate level if it happens that each of the equations in (C.34) supports a normalizable solution for the same value of energy, E . In that case, any bound state solution is a linear combination of three basic solutions:

$$\begin{pmatrix} \phi_i^{(a)}(r) \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ \phi_j^{(b)}(r) \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 0 \\ \phi_k^{(c)}(r) \end{pmatrix}. \quad (\text{C.36})$$

In the case of the non-degenerate level, the sum collapses to one term only.

The next step is to complicate the uncoupled picture (C.34) using an orthogonal matrix Q ($Q^{-1} = Q^T$) to obtain a potential that couples components of the solution ϕ , (C.35). To do that, we form a non-diagonal matrix

$$A = QDQ^{-1}. \quad (\text{C.37})$$

After multiplying, from the left, equation (C.31) with the matrix Q and introducing a new solution $\psi(r) = Q\phi(r)$, we get the coupled Schrödinger equation

$$\psi''(r) + \frac{2m}{\hbar^2}(E - AV(r))\psi(r) = 0. \quad (\text{C.38})$$

The term $V(r)QD\phi(r)$ was processed by inserting the identity matrix $Q^{-1}Q$ between the matrix D and the vector $\phi(r)$, and then applying (C.37). If we think of the orthogonal matrix Q as consisting of three orthogonal basis column vectors

$$A = [v_1; v_2; v_3], \quad (\text{C.39})$$

then its action on another basis set

$$e_i = \begin{pmatrix} \delta_{1,i} \\ \delta_{2,i} \\ \delta_{3,i} \end{pmatrix} \quad (\text{C.40})$$

is given by $Ae_i = v_i$. Now, a simple substitution, $e_i \rightarrow v_i$, yields the result of the action of Q on $\phi(r)$:

$$\psi(r) = Q\phi(r) = C^{(a)}\phi^{(a)}(r)v_1 + C^{(b)}\phi^{(b)}(r)v_2 + C^{(c)}\phi^{(c)}(r)v_3, \quad (\text{C.41})$$

which shows that we can have up to three vectors

$$\phi^{(a)}(r)v_1, \quad \phi^{(b)}(r)v_2, \quad \text{and} \quad \phi^{(c)}(r)v_3, \quad (\text{C.42})$$

as linearly independent solutions of the coupled Schrödinger equation (C.38) for the same energy E .

For illustration purposes we will use the Morse potential

$$V(r) = \exp(2(r - r_0)) - 2 \exp(r - r_0), \quad (\text{C.43})$$

where r_0 is an arbitrary minimum position, and we set $2m = 1$ and $\hbar = 1$. The orthogonal matrix Q ($Q^{-1} = Q^T$) is constructed using the three orthogonal column vectors

$$\frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix}, \quad \frac{1}{\sqrt{6}} \begin{pmatrix} -1 \\ -1 \\ 2 \end{pmatrix}, \quad \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}. \quad (\text{C.44})$$

The general solution of (C.38) is

$$\psi = C^{(a)} \phi_i^{(a)}(r) \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix} + C^{(b)} \phi_j^{(b)}(r) \frac{1}{\sqrt{6}} \begin{pmatrix} -1 \\ -1 \\ 2 \end{pmatrix} + C^{(c)} \phi_k^{(c)}(r) \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}. \quad (\text{C.45})$$

The first term describes a solution where one component is zero and the two other components are of the same magnitude and have the opposite sign. The second term

describes a solution where two components are the same and the third one is twice larger in magnitude than the first one and has the opposite sign. The third term describes a solution where all components are equal.

Non-degenerate levels

Setting $a = 3$, $b = 5$ and $c = 7$ in the diagonal matrix

$$D = \begin{pmatrix} 3 & 0 & 0 \\ 0 & 5 & 0 \\ 0 & 0 & 7 \end{pmatrix} \quad (\text{C.46})$$

will cause all levels to be non-degenerate

$$E = \begin{cases} -(\sqrt{3} - i - 0.5)^2; & i = 0, 1 & \text{(from channel } a), \\ -(\sqrt{5} - j - 0.5)^2; & j = 0, 1 & \text{(from channel } b), \\ -(\sqrt{7} - k - 0.5)^2; & k = 0, 1, 2 & \text{(from channel } c). \end{cases} \quad (\text{C.47})$$

The rotated matrix , QDQ^{-1} , with non-zero coupling elements is:

$$A = \frac{1}{3} \begin{pmatrix} 14 & 5 & 2 \\ 5 & 14 & 2 \\ 2 & 2 & 17 \end{pmatrix} \quad (\text{C.48})$$

Partially degenerate levels

Considering that

$$A^2 = QD^2Q^{-1}, \quad (\text{C.49})$$

we can use the diagonal potential matrix

$$D^2 = \begin{pmatrix} 9 & 0 & 0 \\ 0 & 25 & 0 \\ 0 & 0 & 49 \end{pmatrix} \quad (\text{C.50})$$

to obtain the coupled potential structure matrix

$$A^2 = \begin{pmatrix} 25 & 16 & 8 \\ 16 & 25 & 8 \\ 8 & 8 & 33 \end{pmatrix}. \quad (\text{C.51})$$

According to the uncoupled potential structure matrix D^2 , the bound spectrum is

$$E = \begin{cases} -(3 - i - 0.5)^2; & i = 0, 1, 2 \quad (\text{from channel } a), \\ -(5 - j - 0.5)^2; & j = 0, 1, \dots, 4 \quad (\text{from channel } b), \\ -(7 - k - 0.5)^2; & k = 0, 1, \dots, 6 \quad (\text{from channel } c). \end{cases} \quad (\text{C.52})$$

Out of the seven bound levels, the lowest two are non-degenerate, the next two are double degenerate, and the last three are triple degenerate.

C.5 A two-channel free state example

A simple two-channel example that connects the scattering K matrix elements in the coupled picture to the phase shifts δ in the uncoupled picture is presented here. Using potentials from Sec. C.3 and the potential structure matrix D with $\lambda > 0$,

$$D = \begin{pmatrix} \lambda & 0 \\ 0 & -\lambda \end{pmatrix}, \quad (\text{C.53})$$

the two-channel Schrödinger equation

$$\phi''(r) + \frac{2m}{\hbar^2} (E - DV(r)) \phi(r) = 0 , \quad (\text{C.54})$$

for $E > 0$, has the solutions with the asymptotic ($r \rightarrow \infty$) form

$$\phi_1(r) = \sin(kr) + \cos(kr) \tan(\delta_1) \quad (\text{C.55})$$

$$\phi_2(r) = \sin(kr) + \cos(kr) \tan(\delta_2) ,$$

where $k = 2mE/\hbar^2$. Next we change the representation picture using an orthogonal matrix

$$Q = \begin{pmatrix} \cos(\theta/2) & -\sin(\theta/2) \\ \sin(\theta/2) & \cos(\theta/2) \end{pmatrix} , \quad (\text{C.56})$$

where θ is a real number. It is done by rotating the potential structure matrix D

$$A = QDQ^T, \quad (\text{C.57})$$

and transforming the solution ϕ according to $\psi(r) = Q\phi(r)$. Thus, we obtain the coupled two-channel Schrödinger equation

$$\psi''(r) + \frac{2m}{\hbar^2} (E - AV(r)) \psi(r) = 0 , \quad (\text{C.58})$$

where the potential structure matrix A has non-zero couplings

$$A = \lambda \begin{pmatrix} \cos(\theta) & \sin(\theta) \\ \sin(\theta) & -\cos(\theta) \end{pmatrix}. \quad (\text{C.59})$$

The scattering boundary conditions in the coupled picture

$$\psi_1(r) = \sin(kr) + \cos(kr)K_{11} \quad (\text{C.60})$$

$$\psi_2(r) = \cos(kr)K_{21}$$

are further transformed, using $\phi(r) = Q_T\psi(r)$, into the scattering boundary conditions in the uncoupled picture

$$\phi_1(r) = \cos(\theta/2)(\sin(kr) + \cos(kr)[K_{11} + \tan(\theta/2)K_{21}]) \quad (\text{C.61})$$

$$\phi_2(r) = -\sin(\theta/2)(\sin(kr) + \cos(kr)[K_{11} - \cot(\theta/2)K_{21}]),$$

where we can identify the phase shifts, δ , for each channel:

$$\tan(\delta_1) = K_{11} + \tan(\theta/2)K_{21} \quad (\text{C.62})$$

$$\tan(\delta_2) = K_{11} - \cot(\theta/2)K_{21}.$$

By adding and subtracting two equations, we get the expressions for the K matrix element in the first channel

$$K_{11} = \frac{\cot(\theta/2) \tan(\delta_1) + \tan(\theta/2) \tan(\delta_2)}{\cot(\theta/2) + \tan(\theta/2)}, \quad (\text{C.63})$$

and for the K matrix element in the second channel

$$K_{21} = \frac{\tan(\delta_1) + \tan(\delta_2)}{\cot(\theta/2) + \tan(\theta/2)}. \quad (\text{C.64})$$

APPENDIX D

BASIC CHROMIUM PROPERTIES

The ground state 7S_3 configuration of chromium atoms: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$.

Table D.1: Basic properties

Isotope	Nuclear Spin	Nuclear Symmetry	Atom Symmetry	A_{hf} [MHz]
${}^{52}\text{Cr}$	0	Boson	Boson	0
${}^{53}\text{Cr}$	$3/2$	Fermion	Fermion	-83.5985 ± 0.0015

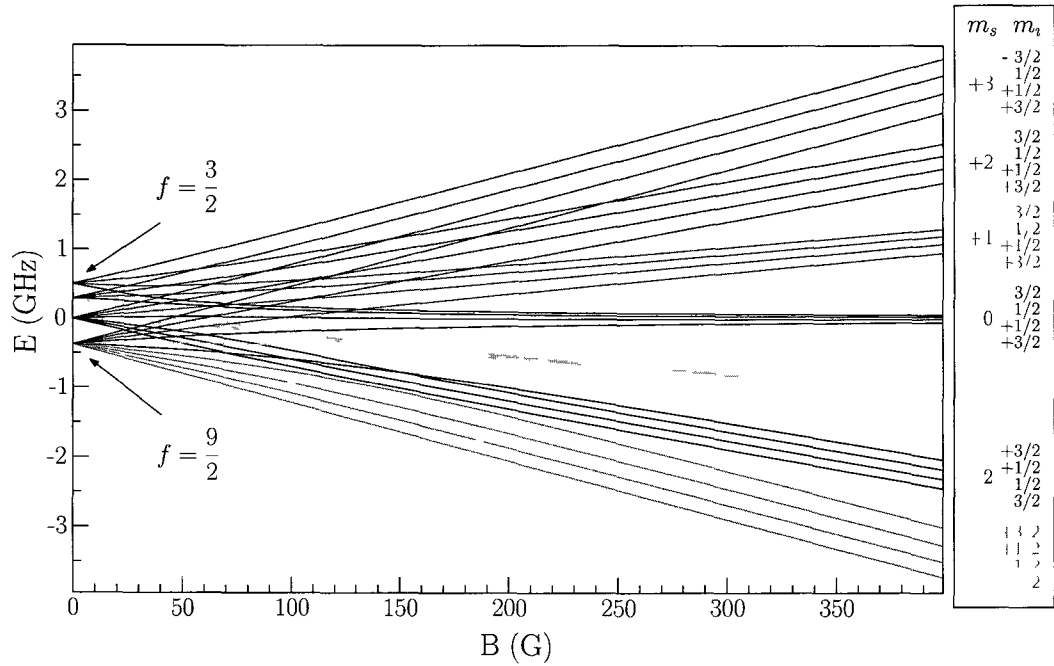


Figure D.1: ${}^{53}\text{Cr}$ hyperfine energy plot. Zero magnetic field: hyperfine spin numbers are $3/2, 5/2, 7/2, 9/2$ (top to bottom ordering).

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