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# Long-range interactions and dynamics of excited atoms

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# Chapter 1

## Introduction

'All things are made up of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.' - R. P. Feynman, 1963

According to Feynman, this one sentence sums up the most essential causalities in nature. Interatomic interactions and forces between atoms are the fundamentals of the world as we know it. The total interaction between ground state atoms and molecules is often modelled using the simple mathematical model called the Lennard-Jones potential:

$$V(r) \sim \frac{\alpha}{R^{12}} - \frac{\beta}{R^6},$$

where  $R$  is the interatomic distance. It consists of a repulsive part ( $R^{-12}$ ) at short distances between the atoms, due to the Pauli repulsion, and an attractive part ( $R^{-6}$ ) at long distances, caused by the van der Waals force. The ( $R^{-12}$ )-term is empirical, whilst the ( $R^{-6}$ )-term is obtained from second-order perturbation theory.

The study of one of the most, or *the* most fundamental system in atomic physics, i.e. the Coulomb potential in a hydrogen atom, is of special importance when it comes to understanding nature. It is one of the few problems possible to solve both numerically and analytically without approximations.

Atoms with one or more electrons excited into a high principal quantum number,  $n$ , are called Rydberg atoms [1]. They are named after the swedish physicist Johannes Rydberg (1854-1919), who in 1888 presented the Rydberg formula on the relationship between the wavelength of photons and the changes in energy levels of an electron in a hydrogen atom.

The excited electron in a Rydberg atom experiences a Coulomb potential from the ionic core similar to the one experienced by an electron in a hydrogen atom. The radius of a Rydberg atom is of the order  $n^2$ , so Rydberg atoms are extremely large. The largest Rydberg atom to be produced in experiments had  $n = 1600$ , i.e. a radius  $\sim 0.1$  mm! Ref. [2]. The area of the orbit is proportional to  $n^4$ , and since diamagnetic effects of an atom scale with the area of the orbit, Rydberg atoms can be used to detect effects otherwise impossible to see in ground state atoms. The binding energy of an electron is proportional to  $1/r$ , according to the Bohr model, thus for Rydberg atoms it falls off like  $1/n^2$ , making the atoms very easily perturbed by collisions or electric and magnetic fields. Hence they require less advanced experimental treatment than ordinary atoms.

The lifetime of a Rydberg atom is typically microseconds, an eternity in the atomic world. The large size and low binding energy leads to a high magnetic susceptibility and a large electric dipole moment, causing strong interaction between neighbouring Rydberg atoms. One consequence of this is the *Rydberg dipole blockade* [3, 4]. The dipole-dipole interaction between an atom in a Rydberg state A, and a neighbouring atom B, causes a shifting in the energy levels of atom B, thus blocking the excitation to the Rydberg state for atom B. Consider the system of two electrons, both initially in the ground state, denoted  $|gg\rangle$ . Due to the dipole-dipole interaction the excited state  $|ee\rangle$  becomes unpopulated when the atoms are exposed to e.g. a resonant laser field [3]. Instead the final state becomes *entangled*:  $1/\sqrt{2}(|eg\rangle \pm |ge\rangle)$ , which describes the case of only one electron excited (which one remains unknown). This means that the excitation dynamics of one atomic state can be controlled by another, and that is the key in the development of so-called quantum gates used in the realization of quantum computers [5, 6].

Table 1.1 shows the scaling laws for some important quantities in a Rydberg atom [7]:

Rydberg atom scaling laws		
		At $n = 80$
Radius	$\sim n^2$	$r \sim 0.3\mu m$
Lifetime	$\sim n^{3-4.5}$	$\tau_0 \sim 600\mu s$
Dipole moment	$\sim n^2$	$\mu \sim 10^4 ea_0$
Polarizability	$\sim n^7$	$\alpha \sim 10^3 GHz$

**Table 1.1:** Rydberg atom scaling laws

The motivation behind this thesis is to study the dynamics of excited hydrogenic atoms, both isolated and in interaction with each other and external fields. In particular we are interested in the dipole blockade as it appears in numerical calculations. We start by looking at the solutions for the time-independent Schrödinger equation for a hydrogen atom without the presence of electric or magnetic fields. In Chapter 3 we use specific analytical methods to describe the interaction between an ion and an atom, and in Chapter 4 between atom-atom. The Hamiltonian is then diagonalized using numerical methods and the energy levels and the wavefunctions are discussed. In Chapter 5 we apply the results of Chapter 4 for dynamical interactions between atoms and external time-dependent electric fields, in addition to the interaction between two Rydberg atoms. It should be pointed out that the term Rydberg atoms usually is reserved for atoms of much higher  $n$ -value than what we have employed in this thesis. Never the less, we have used the term for the excited states in Chapter 5, since the dynamics we have studied can yield for Rydberg atoms as well.

Throughout this thesis we use the Hartree atomic unit system, in which the electron charge and mass, the reduced Planck's constant and the electrostatic constant are used as measuring units. Table 1.2 lists the units and their value in SI-units, in addition to some useful combinations that also result in unity:



Quantity	Unit	Physical significance	Value in SI-units
Mass	$m_e$	Electron mass	$9.109\ 38 \times 10^{-31}$ kg
Charge	$e$	Absolute value of electron charge	$1.602\ 18 \times 10^{-19}$ C
Angular momentum	mo- $\hbar = h/2\pi$	Planck's constant divided by $2\pi$	$1.054\ 57 \times 10^{-34}$ Js
Electrostatic constant	$4\pi\epsilon_0$	$4\pi$ times the permittivity of free space	$1.112\ 65 \times 10^{-10}$ Fm <sup>-1</sup>
Length	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	Bohr radius of atomic hydrogen	$5.291\ 77 \times 10^{-11}$ m
Energy	$E_h = \hbar^2/m_e a_0^2$	Twice the binding energy of atomic hydrogen	$4.359\ 75 \times 10^{-18}$ J
Time	$\tau_0 = \hbar/E_h$	Time required for electron in first Bohr orbit to travel one Bohr radius	$2.418\ 88 \times 10^{-17}$ s
Velocity	$v_0 = a_0/\tau_0 = 1/\alpha c$	Magnitude of electron velocity in first Bohr orbit	$2.187\ 69 \times 10^6$ ms <sup>-1</sup>
Angular frequency	fre- $\omega_0 = \frac{v_0}{2\pi a_0}$	Angular frequency of electron in first Bohr orbit	$6.579\ 69 \times 10^{15}$ s <sup>-1</sup>
Electric strength	field $F_0 = \frac{e}{(4\pi\epsilon_0)a_0^2}$	Strength of the Coulomb field experienced by an electron in the first Bohr orbit of atomic hydrogen	$5.142\ 21 \times 10^{11}$ Vm <sup>-1</sup>

**Table 1.2:** Fundamental and derived quantities in the atomic unit system [8].



# Chapter 2

## General Theory

We begin this thesis with a short review of the quantum mechanical description of a hydrogen atom. The formalism we have focused most of our attention on, and that we will use throughout this thesis, is the description of a hydrogen atom using spherical coordinates. We have also accounted for the description using other coordinates (parabolic), and the application of this in the presence of an external electric field (Stark effect). The generalized N-dimensional model of a Coulomb problem is mentioned as well. Lastly we present the method of describing a quantum mechanical system using path integral formulation.

### 2.1 Hydrogen atom in spherical coordinates

For an electron in a Coulomb field, the Hamiltonian,  $\hat{H}$ , takes the form

$$\hat{H}(\mathbf{p}, \mathbf{r}) = \frac{\mathbf{p}^2}{2} + V(\mathbf{r}) = -\frac{\nabla^2}{2} - \frac{1}{r}, \quad (2.1)$$

expressed as a function of the momentum,  $\mathbf{p}$ , and the radius,  $\mathbf{r}$ .

The operator  $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is the *Laplacian*.

The *Time Independent Schrödinger Equation* (TISE) becomes

$$\hat{H}\psi(\mathbf{r}) = \left( -\frac{\nabla^2}{2} - \frac{1}{r} \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (2.2)$$

where  $\psi(\mathbf{r})$  is the wave function of the system.

This is an eigenvalue problem and it is convenient to solve using spherical coordinates.

The Cartesian coordinates  $(x, y, z)$  rewrites into spherical coordinates by

$$x = r \sin \theta \cos \phi, \quad (2.3)$$

$$y = r \sin \theta \sin \phi, \quad (2.4)$$

$$z = r \cos \theta, \quad (2.5)$$

$$r = \sqrt{x^2 + y^2 + z^2}, \quad (2.6)$$

with  $\theta \in [0, \pi]$  and  $\phi \in [0, 2\pi)$ .

The Laplacian in spherical coordinates is [9]

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right), \quad (2.7)$$

and the Schrödinger equation for a hydrogen electron becomes

$$-\frac{1}{2} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi(\mathbf{r})}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi(\mathbf{r})}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2 \psi(\mathbf{r})}{\partial \phi^2} \right) \right] - \frac{1}{r} \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (2.8)$$

The solution of (2.8) can be obtained by separation of  $\psi(\mathbf{r})$  into a radial and an angular part

$$\psi(\mathbf{r}) = R(r)Y(\theta, \phi), \quad (2.9)$$

and further

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \quad (2.10)$$

Inserting these in (2.8) we obtain three independent equations, respectively for  $r$ ,  $\theta$  and  $\phi$ .

$$\frac{d^2}{dr^2} R(r) + \frac{2}{r} \frac{d}{dr} R(r) + \left( 2E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right) R(r) = 0 \quad (2.11)$$

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m^2 \Theta \quad (2.12)$$

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi \quad (2.13)$$

The normalized solutions [9] for the angular part,  $Y(\theta, \phi)$ , of the wavefunction, equations (2.12) and (2.13), are called *Spherical Harmonics*

$$Y_l^m(\theta, \phi) = \delta_m \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta) \quad (2.14)$$

$$\delta_m = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m < 0 \end{cases} \quad (2.15)$$

where  $P_l^m(\cos \theta)$  are the *associated Legendre function* defined as

$$\begin{aligned} P_l^m(x) &\equiv (-1)^m (1-x^2)^{m/2} \frac{d^m}{dx^m} (P_l(x)) \\ P_l(x) &\equiv \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2-1)^l \end{aligned} \quad (2.16)$$

For (2.14) to be acceptable solutions we must have

$$\begin{aligned} l &= 0, 1, 2, \dots \\ m &= -l, -l+1, \dots, l-1, 1 \end{aligned} \quad (2.17)$$

$l$  and  $m$  are called the *angular* and the *magnetic* quantum numbers.

The normalized solutions of the radial part, (2.11), can be expressed as [9]

$$R_{nl}(r) = -\sqrt{\left(\frac{2}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{r}{n}} \left(\frac{2r}{n}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{n}\right), \quad (2.18)$$

using the *associated Laguerre polynomials*

$$L_q^p(x) \equiv \left(\frac{d}{dx}\right)^p L_q(x), \quad (2.19)$$

where

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q) \quad (2.20)$$

are the *Laguerre polynomials*.

The new quantum number  $n$  is known as the *principal* quantum number, and takes on the values

$$n = 1, 2, 3, \dots \quad (2.21)$$

Using the exact expression for the radial wavefunction it is possible to derive the expectation values for the radius of a hydrogen atom.

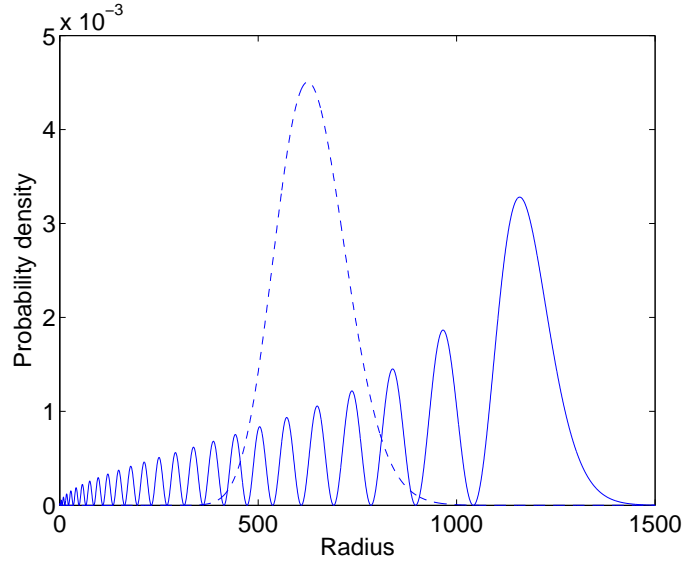
A property of the hydrogen atom is

$$\langle r \rangle = \frac{1}{2}(3n^2 - l^2 - l) \quad (2.22)$$

The radial probability density, defined as

$$P_{nl}(r) = [R_{nl}(r)]^2 r^2, \quad (2.23)$$

is a useful way of describing the wavefunction. Figure 2.1 shows  $P_{nl}(r)$  for  $n = 25$  with different values of  $l$ . We see that for  $l = 24$  the probability of finding the electron is centered around 637.5 a.u., which agrees with the formula for the expectation value (2.22).



**Figure 2.1:** Probability density for the radial wave function of hydrogen for  $R_{nl}(r) = R_{25\ 0}(r)$  (solid line) and  $R_{nl}(r) = R_{25\ 24}(r)$  (dashed line).

The energy levels for bound electronic states in a hydrogen atom are determined by the principal quantum number  $n$ , by the relation:

$$E_n = -\frac{1}{2n^2} \quad n = 1, 2, \dots \quad (2.24)$$

Since for each value of  $n$ , the angular quantum number  $l$  can take the values

$$l = 0, 1, \dots, n - 1 \quad (2.25)$$

and for each  $l$  there are  $(2l+1)$  possible  $m$ -values, the degeneracy of the energy eigenvalues is given by

$$g_n = \sum_{l=0}^{n-1} (2l+1) = n^2 \quad (2.26)$$

## 2.2 Hydrogen atom in other coordinates

The time-independent Schrödinger equation for the Coloumb potential can also be separated using parabolic coordinates. This is useful in the presence of an external electric field. The parabolic coordinates  $(\xi, \eta, \phi)$  relates to the Cartesian coordinates  $(x, y, z)$ , and the spherical coordinates  $(r, \theta, \phi)$  by [9]

$$\begin{aligned} \xi &= r + z, \\ \eta &= r - z, \\ \phi &= \tan^{-1}\left(\frac{y}{x}\right), \\ x &= \sqrt{\xi\eta} \cos \phi, \\ y &= \sqrt{\xi\eta} \sin \phi, \\ z &= \frac{1}{2}(\xi - \eta), \\ r &= \frac{1}{2}(\xi + \eta), \end{aligned} \quad (2.27)$$

with  $\xi \in [0, \infty)$ ,  $\eta \in [0, \infty)$  and  $\phi \in [0, 2\pi)$ .

The time-independent Schrödinger equation for a hydrogen atom (2.2) using parabolic coordinates reads

$$-\frac{1}{2} \left[ \frac{4}{\xi + \eta} \left[ \frac{\partial}{\partial \xi} \left( \xi \frac{\partial}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left( \eta \frac{\partial}{\partial \eta} \right) \right] + \frac{1}{\xi \eta} \frac{\partial^2}{\partial \phi^2} \right] \psi - \frac{2}{\xi + \eta} \psi = E \psi \quad (2.28)$$

Separating the eigenfunctions on the form

$$\psi(\xi, \eta, \phi) = f(\xi)g(\eta)\Phi(\phi) \quad (2.29)$$

and putting these into (2.28), we find solutions of the form [9]

$$\begin{aligned} \psi_{n_1 n_2 m}(\xi, \eta, \phi) &= \frac{1}{n^{|m|+2} + \sqrt{\pi}} \left[ \frac{n_1! n_2!}{[(n_1 + |m|)!(n_2 + |m|)!]^3} \right]^{\frac{1}{2}} e^{-\frac{\xi+\eta}{2n}} (\xi\eta)^{\frac{|m|}{2}} \\ &\times L_{n_1+|m|}^{|m|} \left( \frac{\xi}{n} \right) L_{n_2+|m|}^{|m|} \left( \frac{\eta}{n} \right) e^{im\phi} \end{aligned} \quad (2.30)$$

where  $L_{n+|m|}^{|m|}(x)$  are the *associated Laguerre polynomials* (ref).

The energy eigenvalues corresponding to parabolic eigenstates for bound states in a hydrogen atom, are given by

$$E_n = -\frac{1}{2n^2} \quad (2.31)$$

which agrees with the result for the spherical solutions.

### 2.2.1 Stark effect

The Stark effect is the splitting of the spectral lines of an atom due to the presence of an external electric field. [10] It is named after Johannes Stark, who discovered it in 1913, and hence made an important contribution to the development of quantum mechanics.

If we consider a hydrogen atom in a uniform electric field directed along the  $z$ -axis, the Hamiltonian of the system is

$$\hat{H} = \hat{H}_0 + \hat{H}' = \hat{H}_0 - \mathcal{E}z \quad (2.32)$$

where  $\hat{H}_0$  is the Hamiltonian of the unperturbed hydrogen atom, and  $\mathcal{E}$  is the electric field strength.

First-order perturbation theory gives the following matrix elements for the energy corrections

$$H'_{ij} = -\mathcal{E} \langle n_i l_i m_i | z | n_j l_j m_j \rangle \quad (2.33)$$

Due to symmetry properties, only the matrix elements with  $m_i = m_j$  and  $l_i = l_j + 1$  will be non-zero. For the electron in the excited state  $n = 2$ , the determinant representing the energy corrections for the four eigenstates

$$|2s\rangle, |2p_0\rangle, |2p_-\rangle, |2p_+\rangle, \quad (2.34)$$

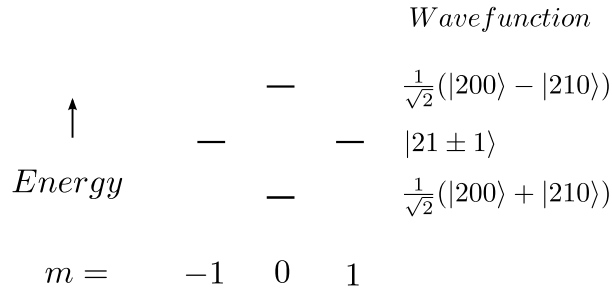
becomes

$$\begin{vmatrix} -\mathcal{E}^{(2)} & 3\mathcal{E} & 0 & 0 \\ 3\mathcal{E} & -\mathcal{E}^{(2)} & 0 & 0 \\ 0 & 0 & -\mathcal{E}^{(2)} & 0 \\ 0 & 0 & 0 & -\mathcal{E}^{(2)} \end{vmatrix} \quad (2.35)$$

This determinant has four roots,  $-e\mathcal{E}$ ,  $e\mathcal{E}$ , 0 and 0, thus the electric field splits the energy level into four levels, one of which is two-fold degenerate. The normalized eigenfunctions corresponding to the mixing states are given by

$$\psi = \frac{1}{\sqrt{2}}(|2s\rangle \pm |2p_0\rangle) \quad (2.36)$$

Figure 2.2 shows how the Stark effect splits the energy line of  $n = 2$  into three sublevels, one line of higher energy and one of lower energy, in addition to the doubly degenerate ( $m = \pm 1$ ) level.



**Figure 2.2:** Splitting of the  $n = 2$  level, due to the linear Stark effect.

The wavefunctions in figure 2.2 are not eigenstates of the angular momentum operator  $\widehat{L}^2$ , so  $l$  is not a good quantum number. The solutions, however, for the time independent Schrödinger equation with the Hamiltonian (2.32), can be separated using parabolic coordinates, giving wavefunctions on the form (2.29). These solutions are called *Stark states*, denoted  $|nkm\rangle$ . Using the unperturbed wavefunctions (2.30), first-order perturbation theory gives that the perturbed energies for a hydrogen in an external electric field are

$$E_{n,n_1,n_2} = -\frac{1}{2n^2} + \frac{3}{2}\mathcal{E}n(n_1 - n_2) \quad (2.37)$$

$n_1$  and  $n_2$  are *parabolic* quantum numbers,  $n$  and  $m$  are the principal and magnetic quantum numbers. We have the relations

$$\begin{aligned} n_1 &= \frac{1}{2}(n - k - |m| - 1) \\ n_2 &= \frac{1}{2}(n + k - |m| - 1) \end{aligned} \quad (2.38)$$

The *Stark quantum numbers*  $k = n_2 - n_1$  and  $m$  fulfills

$$\begin{aligned} -n + 1 &\leq k \leq n - 1 \\ -(n - 1 - |k|) &\leq m \leq n - 1 - |k| \end{aligned} \quad (2.39)$$

$m + k$  is even (odd) when  $n$  is odd(even).

The *Runge-Lenz vector*, defined as

$$\vec{A} = \frac{1}{\sqrt{2|E|}} \left( \mathbf{p} \times \mathbf{L} - \frac{\mathbf{r}}{r} \right) \quad (2.40)$$

is a useful vector in the description of one object orbiting around another. The quantum number  $k$  is the eigenvalue of the z-component of  $\vec{A}$ ,

$$A_z|nkm\rangle = k|nkm\rangle \quad (2.41)$$



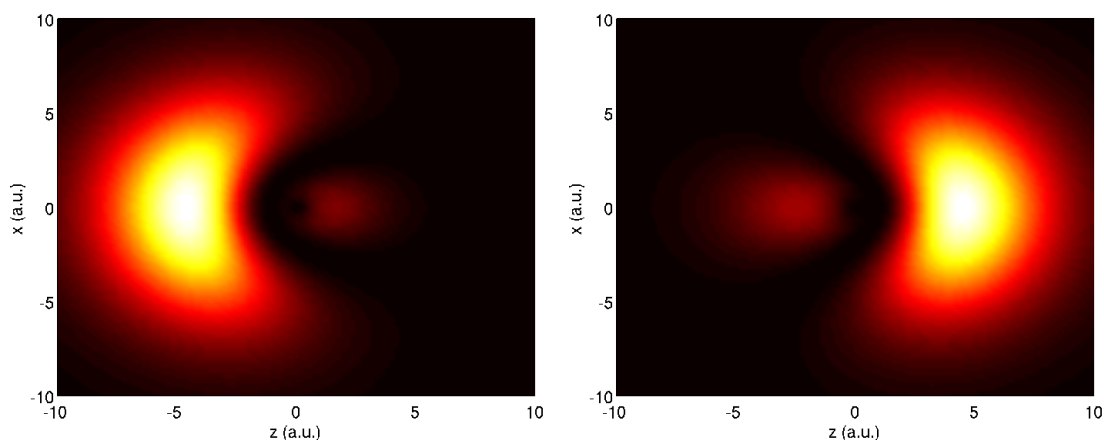
We have the relation  $[\widehat{H}, \widehat{L}_z] = [\widehat{A}_z, \widehat{H}] = [\widehat{A}_z, \widehat{L}_z] = 0$ , thus the Stark states represent a complete basis for the hydrogenic Coulomb problem.

It can be shown [11] that for fixed values of  $n$  and  $m$  any parabolic wavefunction  $\psi_{n_1, n_2, m}(\xi\eta\phi)$  is a linear combination of the wavefunctions in spherical coordinates  $\psi_{nlm}(r, \theta, \phi)$ . The transition from a spherical basis to a Stark basis is given by

$$|nkm\rangle = \sum_l (-1)^l \langle \frac{n-1}{2}, \frac{m-k}{2}, \frac{n-1}{2}, \frac{m+k}{2} | lm \rangle |nlm\rangle, \quad (2.42)$$

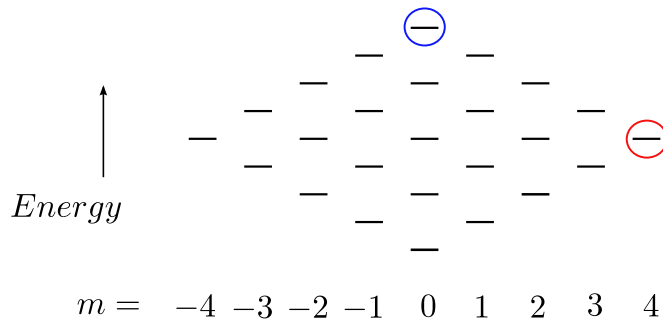
where  $\langle nkm | lm \rangle$  are Clebsch-Gordan coefficients.

In figure 2.3 we have plotted the wavefunction in the x-z plane for the Stark states with  $n = 2$ ,  $k = \pm 1$  and  $m = 0$ . The panel to the left (right) corresponds to the highest (lowest) energy.



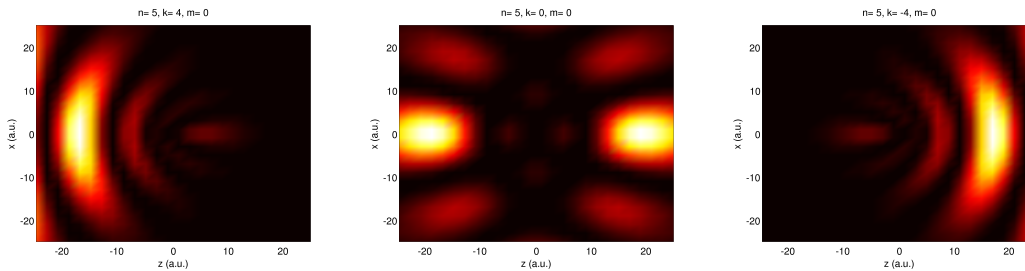
**Figure 2.3:** Wavefunction for the Stark states  $|2, 1, 0\rangle$ (left panel) and  $|2, -1, 0\rangle$ (right panel)

These are so-called maximum polarized Stark states, with the general property  $|n, k = \pm(n-1), m = 0\rangle$ . We will apply similar states later in this thesis. These states are also denoted linear Stark states, as opposed to circular states, which have the property  $|n, k = 0, m = \pm(n-1)\rangle$ . In the spherical basis circular states have quantum numbers with the relation  $|n, l = n-1, m = l\rangle$ . In figure 2.4 the Stark energy levels of  $n = 5$  have been plotted. Red circle points out the circular state (with  $m = +(n-1)$ ), blue circle the most polarized (linear) Stark state (with  $k = +(n-1)$ ):



**Figure 2.4:** Stark energy levels of  $n = 5$ .

Figure 2.5 shows three of the Stark wavefunctions corresponding to  $m = 0$  for the  $n = 5$  level, plotted in the  $xz$ -direction. The outermost panels show the maximum polarized states.



**Figure 2.5:**  $xz$ -plot of the Stark states  $|5, 4, 0\rangle$  (left),  $|5, 0, 0\rangle$  (middle) and  $|5, -4, 0\rangle$  (right).

## 2.2.2 N-dimensional Coulomb problem vs. D-dimensional harmonic oscillator

In this thesis we restrict the treatment of the Coulomb problem to three dimensions. It can be useful, however, to present a short version of a general treatment, i.e. the Coulomb potential in  $N$  dimensions.

From the master-thesis of Sælen/Nepstad (2006), we find that the *hyperspherical* coordinates are given by the transformation

$$\begin{aligned}
 x_1 &= r \sin(\phi_{N-1}) \sin(\phi_{N-2}) \dots \sin(\phi_1) \\
 x_2 &= r \sin(\phi_{N-1}) \sin(\phi_{N-2}) \dots \cos(\phi_1) \\
 &\vdots \\
 x_{N-1} &= r \sin(\phi_{N-1}) \cos(\phi_{N-2}) \\
 x_N &= r \cos(\phi_{N-1})
 \end{aligned} \tag{2.43}$$

Here the  $x_i$ 's are Cartesian coordinates, the  $\phi_i$ 's hyperspherical angles and  $r$  the hyper-radius. The angles are defined as

$$\begin{aligned}
 \phi_1 &= \tan^{-1} \left( \frac{x_1}{x_2} \right) \\
 \phi_2 &= \tan^{-1} \left( \frac{\sqrt{x_1^2 + x_2^2}}{x_3} \right) \\
 &\vdots \\
 \phi_{N-1} &= \tan^{-1} \left( \frac{\sqrt{x_1^2 + \dots + x_{N-1}^2}}{x_N} \right)
 \end{aligned} \tag{2.44}$$

with  $\phi_1 \in [0, 2\pi]$  and  $\phi_{2 \dots N-1} \in [0, \pi]$ .

As for the Coulomb problem in three dimensions, we can separate the solution of the wavefunction for the  $N$ -dimensional system into an angular and a radial part. Without

showing the procedure, we just repeat the solutions given by Sælen/Nepstad in Ref. [8]. The *Hyperspherical Harmonics* are given by

$$\mathcal{Y}_{\mathcal{L}}(\Omega_{N-1}) = \mathcal{N}_{\mathcal{L}} \Theta_{l_{N-1}, l_{N-2}}^{(N)}(\phi_{N-1}) \Theta_{l_{N-2}, l_{N-3}}^{(N-1)}(\phi_{N-2}) \cdots \Theta_{l_2, l_1}^{(3)}(\phi_2) \Theta_{l_1}^{(2)}(\phi_1) \quad (2.45)$$

where

$$\Theta_{l_1}^{(2)}(\phi_1) = e^{il_1\phi_1} \quad (2.46)$$

The functions  $\Theta_{lm}^{(N)}(x)$  are called the associated Gegenbauer polynomials, expressed as a function of the Gegenbauer polynomials  $\mathcal{C}_n^{(\alpha)}(x)$  :

$$\Theta_{lm}^{(N)}(x) = (1-x^2)^{m/2} \frac{d^m}{dx^m} \mathcal{C}_l^{(\frac{N-2}{2})}(x) \quad (2.47)$$

$\mathcal{L}$  denotes the set of angular quantum numbers  $l_{N-1}, l_{N-2}, \dots, l_1$ .

The radial equation in hyperspherical coordinates reads

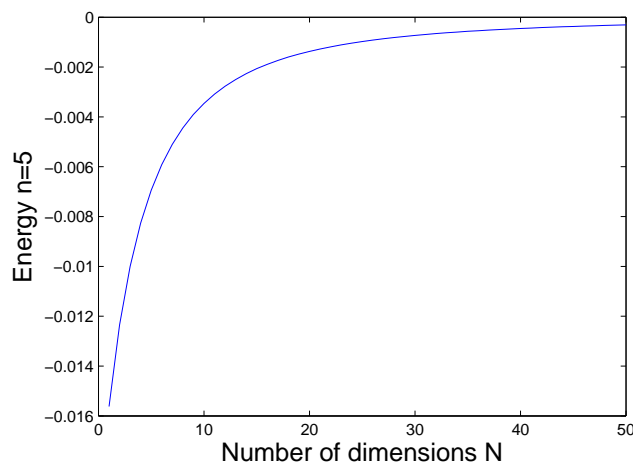
$$R_{nl}(\rho) = \mathcal{N}_{nl} e^{-\rho/2} \rho^l L_{n-L-1}^{2l+N-2}(\rho) \quad (2.48)$$

with  $L_{\lambda}^{(\nu)}(\rho)$  being the associated Laguerre polynomials, known from the 3-D case.  $\mathcal{N}_{nl}$  is just a normalization constant.

The energy for the Coulomb problem in N-dimensions can be expressed by

$$E_n = -\frac{1}{2(n + \frac{N-3}{2})^2}, \quad n = 1, 2, 3, \dots \quad (2.49)$$

For the 3-D case, it is easy to see that (2.49) becomes (2.24). In the limit  $n \rightarrow \infty$  and  $N \rightarrow \infty$ , the energy approaches zero. This is shown in figure 2.6, where we have plotted the energy as a function of N, for the case of  $n = 5$ .



**Figure 2.6:** Energy vs. number of dimensions for the Coulomb problem with  $n=5$ .

The solutions of the N-dimensional Coulomb problem can also be related to the solutions for a harmonic oscillator in arbitrary dimensions. There exists [12] a relation between the radial solutions (2.48), and the solutions

$$\Phi_{n',L}(D; r) = C_{n',L} e^{\frac{r^2}{2}} r^L L_{n'/2-L/2}^{L+D/2-1}(r^2) \quad (2.50)$$

where  $L'_\lambda(r^2)$  is the associated Laguerre polynomials,  $D$  is the dimension,  $L$  and  $n'$  are quantum numbers and  $r$  the hyperradius, for the harmonic oscillator given by

$$R_{nl}(N; \rho) = \Lambda \Phi_{n',L}(D; r) \quad (2.51)$$

$\Lambda$  is just a constant connected to the normalization of the eigenfunctions with value

$$\Lambda = \left( \frac{1}{2[n + \frac{1}{2}(N - 3)]^{N+1}} \right)^{\frac{1}{2}} \quad (2.52)$$

The quantum numbers of the two different systems are related by

$$D = 2N - 2, \quad n' = 2(n - 1), \quad \text{and} \quad L = 2l \quad (2.53)$$

### 2.2.3 Feynman's path-integral formulation

The description of a quantum mechanical system using path integral formulation was an approach first presented by Paul Dirac in a paper from 1933, and later developed into a complete method by Richard Feynman in 1948 [13]. The method involves replacing the classical notion of a single, unique trajectory for a system with a sum of (or integral over) an infinite number of possible trajectories to compute a probability amplitude. We will in present the solution of the hydrogen atom using path integral formulation, as it was presented by Duru and Kleinert in 1979.

Green's function, i.e. the probability amplitude for a particle to move from position  $x_a$  at time  $t_a$  to position  $x_b$  at time  $t_b$ , in a Coulomb potential, is by Feynman's method [14, 15]

$$K(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a) = \int_{x_a, t_a}^{x_b, t_b} \mathcal{D}^3x \frac{\mathcal{D}^3p}{(2\pi)^3} \exp \left( i \int_{t_a}^{t_b} dt \left( \mathbf{p} \cdot \frac{\mathbf{x}}{dt} - \frac{\mathbf{p}^2}{2} + \frac{1}{r} \right) \right) \quad (2.54)$$

It can be shown [14] that for  $E < 0$  this can be written as a sum over oscillator wavefunctions

$$K(\mathbf{x}_b, \mathbf{x}_a; E) = -\frac{1}{p_0^2} \sum_{n=0}^{\infty} \frac{i}{1 - \nu/n} \int_0^{2\pi} d\alpha_b (\sqrt{p_0/8n} \psi_{n_1, n_2, n_3, n_4}(u_b) \sqrt{p_0/8n} \psi_{n_1, n_2, n_3, n_4}(u_a)^*) \quad (2.55)$$

where  $n$  is the principal quantum number,  $p_0 = (-2E)^{1/2}$ ,  $\nu = (-1/2E)^{1/2}$ ,  $u = r^{1/2}$  and  $\psi_{n_1, n_2, n_3, n_4}(u_a)$  denotes the product of four oscillator wavefunctions, with

$$\sum_{i=1}^4 n_i = 2(n - 1) \quad (2.56)$$

From 2.55 we get the energy for the bound states in a hydrogen atom

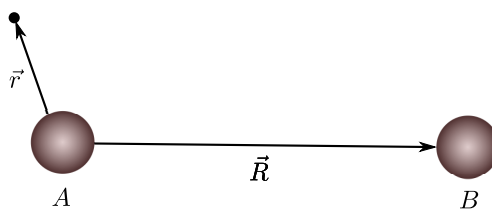
$$E_n = -\frac{1}{2n^2}, \quad n = 1, 2, 3, \dots \quad (2.57)$$

which agrees with 2.24.

# Chapter 3

## Perturbed Hydrogen Atom

In this chapter the perturbation of an excited atom by a positive charged particle placed (at rest) a large distance from the hydrogen atom compared to the spatial extension of the hydrogenic charge cloud is considered. The multipole expansion is introduced and applied to obtain the long range behavior of the matrix elements pertaining to a fixed  $n$ -level of the hydrogen atom. The matrices are then diagonalized and the properties of the states are discussed.



**Figure 3.1:**  $H_2^+$ -molecule

We will describe the system containing an electron bound to an infinitely heavy positive charge,  $A$ , and perturbed by another infinitely heavy positive charge,  $B$ , a large distance  $R$  from the origin, cf. figure 3.1. The Hamiltonian of the system then becomes

$$\hat{H} = \hat{H}_0 + \frac{1}{R} - \frac{1}{|\mathbf{R} - \mathbf{r}|} = \hat{H}_0 + H' \quad (3.1)$$

with  $H_0$  being the hydrogen Hamiltonian of the previous chapter. The departure from a real system made in the expression above is movement and coordinate mixing (center of mass coordinates) due to finite proton masses. Both terms are of the order electron mass over proton mass,  $m_e/m_p$ , and can be neglected from a qualitative point of view. We are thus left with a one-electron static problem which can be studied by perturbation theory or more accurate numerical methods. We will consider perturbations from the eigenstates of  $\hat{H}_0$ , whose spectrum is described by spherical states,  $\psi_i(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$ , i.e. the spherical states of Chapter 2.

Intermediate and small values of  $R$  will in general require a two-center treatment. For  $R \gg r$ , we can apply the Taylor expansion  $(1 + \epsilon)^{\frac{1}{2}} = 1 - \frac{1}{2}\epsilon + \frac{3}{8}\epsilon^2 + \mathcal{O}(\epsilon^3)$  on the terms

in the Hamiltonian 3.1, giving:

$$\begin{aligned}\frac{1}{|\mathbf{R} + \mathbf{r}|} &= \frac{1}{R} \left( 1 + \frac{2\mathbf{r} \cdot \mathbf{e}_R}{R} + \frac{r^2}{R^2} \right)^{\frac{1}{2}} + () \\ &= \frac{1}{R} - \frac{\mathbf{r} \cdot \mathbf{e}_R}{R^2} + \frac{-r^2 + 3(\mathbf{r} \cdot \mathbf{e}_R)^2}{2R^3} + \mathcal{O}(R^{-4})\end{aligned}\quad (3.2)$$

The two lowest terms of  $\widehat{H}'$  thus cancel and give the following asymptotic form of the interaction,

$$H' \approx -\frac{\mathbf{r} \cdot \mathbf{e}_R}{R^2} - \frac{-r^2 + 3(\mathbf{r} \cdot \mathbf{e}_R)^2}{2R^3}\quad (3.3)$$

The vector  $\mathbf{e}_R$  is a unit vector along the  $\hat{z}$ -axis. Thus, the final form of the interaction becomes

$$H' \approx -\frac{z}{R^2} - \frac{(2z^2 - x^2 - y^2)}{2R^3}\quad (3.4)$$

Using this expression and first order perturbation theory we can conclude that the perturbation of the ground state will be weaker than  $\mathcal{O}(R^{-2})$  since all matrix elements

$$\langle ns|z|ns\rangle\quad (3.5)$$

vanish due to symmetry. We see that ground state electrons leave only a  $R^{-3}$ -term for the total interatomic interaction. For  $p, d, \dots$  states the situation is less obvious and we need to move to a more systematic treatment.

To find the matrix elements

$$\langle j|H'|i\rangle = \langle j|\frac{1}{R} - \frac{1}{|\mathbf{R} - \mathbf{r}|}|i\rangle = \langle j|\frac{1}{R}|i\rangle - \langle j|\frac{1}{|\mathbf{R} - \mathbf{r}|}|i\rangle\quad (3.6)$$

we use the *Multipole Expansion* [Jackson]

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{LM} \frac{4\pi}{2L+1} \frac{r_{<}^L}{r_{>}^{L+1}} Y_{LM}^*(\hat{r}_2) Y_{LM}(\hat{r}_1),\quad (3.7)$$

where  $r_{<} (r_{>})$  is the smaller (larger) of  $|\mathbf{r}_1|$  and  $|\mathbf{r}_2|$ , and  $\hat{r}$  denotes the angular components of  $\mathbf{r}$ .  $l$  and  $m$  denote the total angular and magnetic quantum number of the system. The angular and magnetic quantum numbers for the states can take the values

$$l_{ij} = 0, 1, 2, \dots\quad (3.8)$$

$$m_{ij} = l, l-1, \dots, -l\quad (3.9)$$

When the angular integrals are to be performed the general vector relation between the total angular momenta applies,

$$|j_1 - j_2| \leq j \leq j_1 + j_2,\quad (3.10)$$

where  $j_1, j_2$  refer to the angular integrals of each spherical harmonics of the two electronic states. To avoid non-zero integral in addition, the selection rule states that the sum  $j + j_1 + j_2$  must be even.

We will now consider the matrix element between the electron-nuclei interaction and a pair of hydrogenic  $2p_0$ -states in detail. The relevant integral to calculate is

$$M_{2p_0-2p_0} = \langle 2p_0 | \frac{1}{|\mathbf{R} - \mathbf{r}|} | 2p_0 \rangle \quad (3.11)$$

The hydrogenic wavefunctions are given by [Hemmer]

$$|2p_0\rangle = \psi_{2p_0}(r, \hat{r}) = \frac{1}{\sqrt{3 \cdot 2^3}} r e^{-\frac{r}{2}} Y_{10}(\hat{r}) \quad (3.12)$$

where

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta \quad (3.13)$$

Using  $z \parallel R$ , and using the expansion (3.7), the matrix element can be rewritten into

$$\begin{aligned} \langle 2p_0 | \frac{1}{|\mathbf{R} - \mathbf{r}|} | 2p_0 \rangle &= \int d^3r \psi_{2p_0}^* \frac{1}{|\mathbf{R} - \mathbf{r}|} \psi_{2p_0} \quad (3.14) \\ &= \int r^2 dr d\hat{r} \frac{1}{\sqrt{4!}} r e^{-\frac{r}{2}} Y_{10}^*(\hat{r}) \sum_{LM} \frac{4\pi}{2L+1} \frac{r_{<}^L}{r_{>}^{L+1}} Y_{LM}^*(\hat{r}) Y_{LM}(\hat{R}) \frac{1}{\sqrt{4!}} r e^{-\frac{r}{2}} Y_{10}(\hat{r}) \\ &= \frac{1}{4!} \sum_{LM} \frac{4\pi}{2L+1} \int_0^\infty dr r^4 e^{-r} \frac{r_{<}^L}{r_{>}^{L+1}} \iint d\hat{r} Y_{10}^*(\hat{r}) Y_{10}(\hat{r}) Y_{LM}(\hat{r}) Y_{LM}(0,0) \end{aligned}$$

Summation rules combined with the selection rule give the total  $M$  and  $L$

$$M = m_1 + m_2 = 0 \quad (3.15)$$

$$l_1 = l_2 = 1 \quad \implies \quad L = 0, 2, \quad (3.16)$$

and since we assume  $\hat{R} = (0, 0)$ , (3.14) becomes

$$\begin{aligned} \langle 2p_0 | \frac{1}{|\mathbf{R} - \mathbf{r}|} | 2p_0 \rangle &= \frac{1}{4!} 4\pi \int_0^\infty dr r^4 e^{-r} \frac{r_{<}^0}{r_{>}^1} \iint d\hat{r} Y_{10}^*(\hat{r}) Y_{10}(\hat{r}) Y_{00}(\hat{r}) Y_{00}(0,0) \\ &\quad + \frac{1}{4!} \frac{4\pi}{5} \int_0^\infty dr r^4 e^{-r} \frac{r_{<}^2}{r_{>}^3} \iint d\hat{r} Y_{10}^*(\hat{r}) Y_{10}(\hat{r}) Y_{20}(\hat{r}) Y_{20}(0,0) \end{aligned} \quad (3.17)$$

The radial integrals

$$\int_0^\infty dr r^4 e^{-r} \frac{r_{<}^0}{r_{>}^1} = \int_0^R r^4 e^{-r} \frac{1}{R} dr + \int_R^\infty r^4 e^{-r} \frac{1}{r} dr \quad (3.18)$$

have solutions of the form

$$\int x^n e^{cx} dx = \frac{1}{c} x^n e^{cx} - \frac{n}{c} \int x^{n-1} e^{cx} dx \quad (3.19)$$

$$\int x^2 e^{cx} dx = e^{cx} \left( \frac{x^2}{c} - \frac{2x}{c^2} + \frac{2}{c^3} \right) \quad (3.20)$$

All the exponential terms disappear when  $R \rightarrow \infty$ , thus the only contribution to (3.11) comes from the first integral on the right side of (3.18).

In the case of  $L = 0$  we get for large values of  $R$ :

$$\langle 2p_0 | \frac{1}{|\mathbf{R} - \mathbf{r}|} | 2p_0 \rangle = \frac{1}{R} \quad (3.21)$$

and equivalently for  $L = 2$ :

$$\langle 2p_0 | \frac{1}{|\mathbf{R} - \mathbf{r}|} | 2p_0 \rangle = \frac{12}{R^3} \quad (3.22)$$

The final expression for the matrix element is hence

$$\langle 2p_0 | \frac{1}{|\mathbf{R} - \mathbf{r}|} | 2p_0 \rangle = \frac{1}{R} + \frac{12}{R^3} \quad (3.23)$$

The present method can be applied to calculate any matrix element of the form  $\langle nlm | \frac{1}{|\mathbf{R} - \mathbf{r}|} | n'l'm' \rangle$ . For the  $n = 2$  level the method results in a monopole  $1/R$ -contribution when the quantum numbers are identical. Furthermore only  $m = 0$  contributes since  $z \parallel R$ . The matrix element between  $2s$  and  $2p_0$  results in,

$$\langle 2s | \frac{1}{|\mathbf{R} - \mathbf{r}|} | 2p_0 \rangle = -\frac{3}{R^2} \quad (3.24)$$

### 3.1 Asymptotic states of $n=2$

Based on the calculations above the  $n=2$  manifold can now be diagonalized for any (asymptotic) internuclear distance since the perturbation Hamiltonian expressed in the basis of the four  $n = 2$  basis functions, respectively

$$2s, 2p_0, 2p_{-1}, 2p_1, \quad (3.25)$$

is

$$H' = \begin{pmatrix} 0 & 3/R^2 & 0 & 0 \\ 3/R^2 & -12/R^3 & 0 & 0 \\ 0 & 0 & -6/R^3 & 0 \\ 0 & 0 & 0 & -6/R^3 \end{pmatrix} \quad (3.26)$$

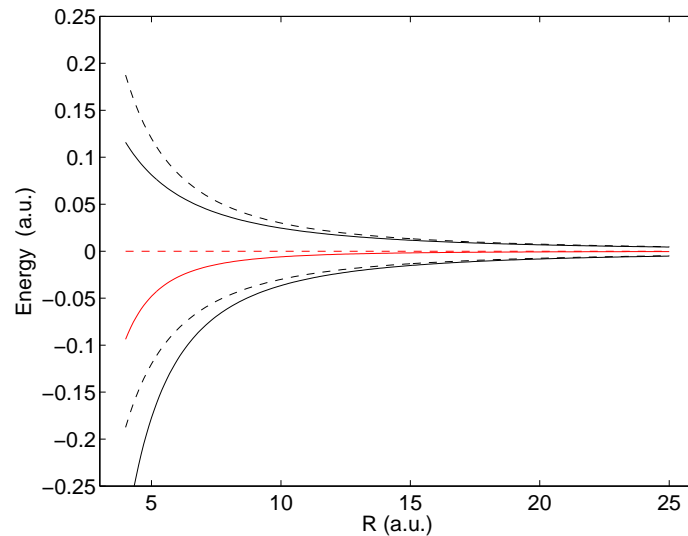
We observe that in the limit where  $R^{-3}$  terms can be neglected the perturbation matrix is identical to the matrix resulting from a constant electric field in the  $\hat{z}$ -direction. In that limit the eigenstates are Stark states as described in the previous chapter.

Without making this approximation the energy levels of the two mixing states become

$$E_{\pm} = \begin{cases} -\frac{6}{R^3} + \frac{1}{2} \sqrt{\frac{36}{R^4} + \frac{144}{R^6}} \\ -\frac{6}{R^3} - \frac{1}{2} \sqrt{\frac{36}{R^4} + \frac{144}{R^6}} \end{cases} \quad (3.27)$$



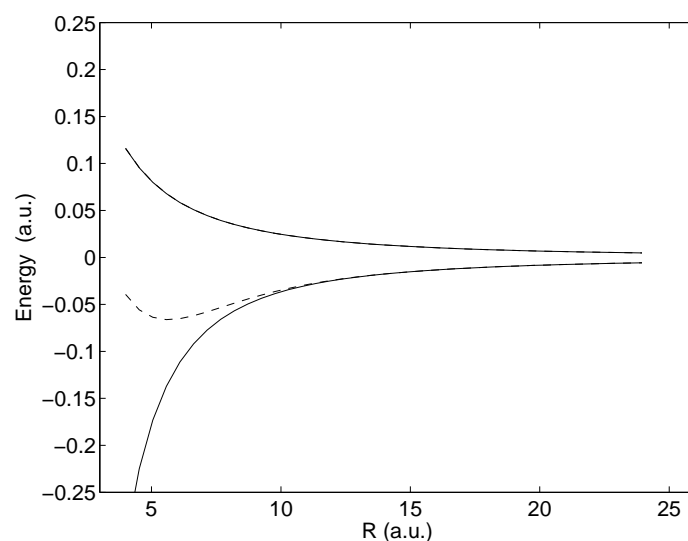
In the figure below we have plotted the energy levels for  $n=2$ , both for the asymptotic states and for the Stark states.



**Figure 3.2:** Energy eigenvalues of hydrogenic Stark states (dashed lines) and asymptotic states (solid lines) for the mixing states of  $n = 2$ . The red solid line is the term  $-6/R^3$ .

We see that the energy levels for the Stark states are symmetric about the x-axis. The wavefunctions corresponding to these eigenstates, i.e.  $|2, 1, 0\rangle$  and  $|2, -1, 0\rangle$ , are the ones plotted in Chapter 2, figure 2.3.

In figure 3.3 we compare the eigenvalues of the asymptotic Hamiltonian with the ones obtained when diagonalizing the  $n = 2$  level exactly, which amounts to keeping all nonzero terms in the multipole expansion above. We see that for  $R > 10$  the asymptotic energy levels and the Stark energy levels are concurrent.



**Figure 3.3:** Energy eigenvalues of the exact states (dashed line) and asymptotic states (solid lines) for  $n = 2$ .

### 3.1.1 Asymptotic states of $n=3$

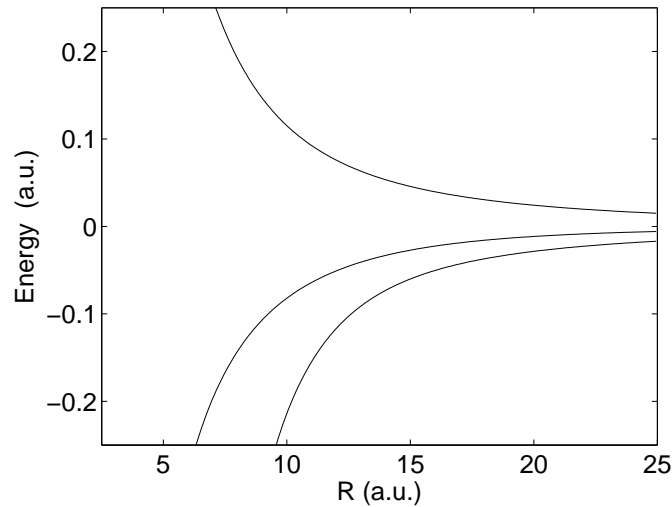
For the case of  $n = 3$ , the (asymptotic) Hamiltonian matrix for the three basis states corresponding to  $m = 0$ , that is

$$3s, 3p_0, 3d_0 \quad (3.28)$$

becomes

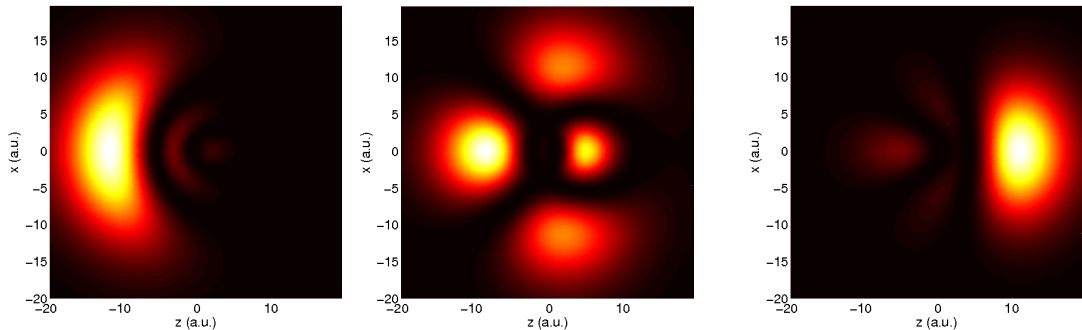
$$H' = \begin{pmatrix} 0 & 7.35/R^2 & 63.64/R^3 \\ 7.35/R^2 & -72/R^3 & 5.20/R^2 + 701.48/R^4 \\ 63.64/R^3 & 5.20/R^2 + 701.48/R^4 & -36/R^3 - 7290/R^5 \end{pmatrix} \quad (3.29)$$

In the figure below we have plotted the energy lines of these three asymptotic states



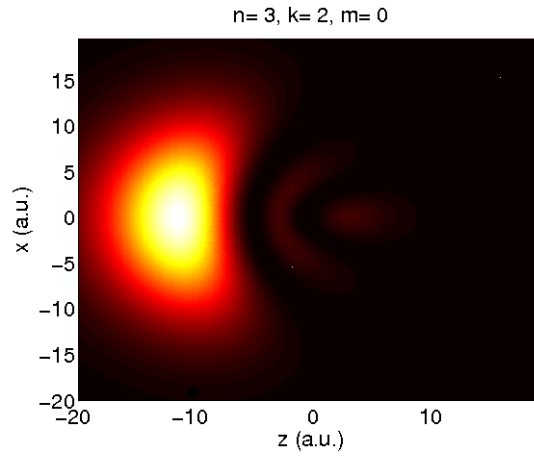
**Figure 3.4:** Energy eigenvalues for the ( $n = 3, m = 0$ )-states in a hydrogen atom perturbed by an ion (proton).

Figure 3.5 shows the wavefunctions, plotted in the  $xz$ -plane, corresponding to the energy eigenvalues in figure 3.4 for  $R = 10$ .



**Figure 3.5:** Wavefunctions corresponding to the energy levels of the states  $n = 3, m = 0$  for  $R=10$ . Left panel is the highest energy, and the right panel shows the lowest energy.

Below we have plotted the maximum polarized Stark wavefunction for the  $n = 3$  level.



**Figure 3.6:** Stark state  $|3, 2, 0\rangle$ .

When comparing this with the plot in the right panel in figure 3.6, we see that the wavefunctions for the two situations behave in somehow similar manners, but they are not identical. This is in contrast to the  $n = 2$  level, where the spherical wavefunction and the Stark wavefunction for  $R = 10$  have almost equal distribution.



# Chapter 4

## Long Range Atom-Atom Interaction

The formalism of the previous chapter is in this chapter extended to the situation addressed in the introduction of the thesis: The asymptotic form of the attractive interaction between atoms. The chapter starts by reviewing the classical electromagnetic interaction between two dipoles, since this interaction turns out to be particularly important in the quantum treatment. Then we review the procedures in use for calculating the asymptotic doubly excited states of neutral atoms. Finally one method is applied to calculations of energy levels and structure of the wavefunction.

### 4.1 Classical electromagnetic interaction

The potential outside a sphere, due to a charge density  $\rho(\mathbf{x}')$  on the inside, can be written as [16]

$$\Phi(\mathbf{x}) = \int \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x' \quad (4.1)$$

Using the expansion,

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi), \quad (4.2)$$

we obtain the *multipole expansion* for the potential

$$\Phi(x) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} q_{lm} \frac{Y_{lm}(\theta, \phi)}{r^{l+1}}, \quad (4.3)$$

with  $q_{lm}$  being the *multipole moments* given by

$$q_{lm} = \int Y_{lm}^*(\theta', \phi') r'^l \rho(\mathbf{x}') d^3x' \quad (4.4)$$

4.3 can be written as an Taylor expansion using rectangular coordinates

$$\Phi(\mathbf{x}) = \frac{q}{r} + \frac{\mathbf{p} \cdot \mathbf{x}}{r^3} + \frac{1}{2} \sum_{i,j} Q_{ij} \frac{x_i x_j}{r^5} + \dots \quad (4.5)$$

where  $q$  is the total charge,  $Q_{ij}$  is the quadrupole moment tensor and  $\mathbf{p}$  is the electric dipole moment defined as

$$\mathbf{p} = \int \mathbf{x}' \rho(\mathbf{x}') d^3x \quad (4.6)$$

The electric field  $\mathbf{E}$ , relates to the potential  $\Phi(\mathbf{x})$  by the equation

$$\mathbf{E} = -\nabla\Phi \quad (4.7)$$

Using this expression, and the multipole expansion (4.3) of the potential, we can find the spherical components of the electric field for a given multipole. The field at position  $\mathbf{x}$ , due to a dipole at  $\mathbf{x}'$  aligned along the  $\hat{z}$ -axis, is found by taking the negative gradient of the dipole term of equation (4.5), resulting in:

$$\mathbf{E}(\mathbf{x}) = \frac{3\mathbf{n}(\mathbf{p} \cdot \mathbf{n}) - \mathbf{p}}{|\mathbf{x} - \mathbf{x}'|^3} \quad (4.8)$$

where  $\mathbf{n}$  is the unit vector from  $\mathbf{x}'$  to  $\mathbf{x}$ .

Considering a charge distribution  $\rho(\mathbf{x})$  placed in an *external* potential, the electrostatic energy of the system is described by:

$$W = \int \rho(\mathbf{x})\Phi(\mathbf{x})d^3x \quad (4.9)$$

If the potential is slowly varying, we can Taylor-expand it around a chosen origin, like

$$\Phi(\mathbf{x}) = \Phi(0) - \mathbf{x} \cdot \mathbf{E}(0) - \frac{1}{2} \sum_i \sum_j x_i x_j \frac{\partial E_j}{\partial x_i}(0) + \dots \quad (4.10)$$

Here we have employed the relation between the electric field and the potential (4.7). This expression inserted into (4.9), combined with some definition replacements, gives the following expression for the energy

$$W = q\Phi(0) - \mathbf{p} \cdot \mathbf{E}(0) - \frac{1}{6} \sum_i \sum_j Q_{ij} \frac{\partial E_j}{\partial x_i}(0) + \dots \quad (4.11)$$

This shows that the monopole interact with the potential, the dipole with the electric field, the quadrupole with the field gradient, and so on...

To find the interaction between two dipoles  $\mathbf{p}_1$  and  $\mathbf{p}_2$ , we can insert the expression for the dipole field (4.8) into (4.11) and obtain:

$$W_{12} = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\mathbf{p}_1 \cdot \mathbf{n})(\mathbf{p}_2 \cdot \mathbf{n})}{|\mathbf{x}_1 - \mathbf{x}_2|^3} \quad (4.12)$$

Here  $\mathbf{n}$  is a unit vector pointing in the direction from  $\mathbf{x}_2$  to  $\mathbf{x}_1$ .

For two parallel dipoles the interaction is attractive if the dipoles are oriented parallel to a line joining their centers, and repulsive if they are perpendicular to the line. For antiparallel dipoles, the opposite is the case. Averaged over the relative positions of the dipole, the value of the interaction for two dipoles with fixed orientation and separation is zero.

## 4.2 Quantum treatment - general

We will now consider the interactions between two atoms. We use the diatomic molecule composed of two hydrogen atoms, e.i. two nuclei A and B separated by a distance  $\mathbf{R}$ , each with one electron, respectively with the position vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ .

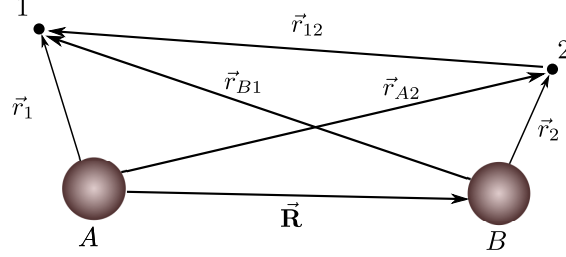


Figure 4.1:  $H_2$ -molecule

As in figure 3.1 we let the internuclear vector  $\mathbf{R}$  define a z-axis from nucleus A to nucleus B.

The operator for the total interatomic potential energy can be written as

$$\widehat{V}(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{R} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} = \frac{1}{R} - \frac{1}{|\mathbf{R} - \mathbf{r}_1|} - \frac{1}{|\mathbf{R} + \mathbf{r}_2|} + \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} \quad (4.13)$$

This expression consists of one term for the repulsion between the two nuclei, two terms for the attraction between one nucleus and the opposite electron and one term for the repulsion between the electrons.

For large values of  $R$ , the Hamiltonian can be expanded using the Taylor expansion from Chapter 3. Putting these expansions into equation (4.13) the  $R^{-1}$  and  $R^{-2}$  terms cancel, and we are left with

$$\widehat{V} = \frac{1}{R^3}(\mathbf{r}_1\mathbf{r}_2 - 3(\mathbf{r}_1 \cdot \mathbf{e}_R)(\mathbf{r}_2 \cdot \mathbf{e}_R)) \quad (4.14)$$

which is the interaction between two dipoles given in equation (4.12).

Given that  $\mathbf{R}$  points along the  $\hat{z}$ -axis, first order perturbation theory

$$\lambda E_n^{(1)} = \langle n | \lambda H' | n \rangle \quad (4.15)$$

gives zero contribution to the energy, since  $\langle x_1 x_2 \rangle = \langle x_1 \rangle \langle x_2 \rangle = 0$ . Thus we must use second order perturbation theory to find the corrections to the unperturbed energy:

$$E_n^{(2)} = \sum_{m(\neq n)} \frac{\langle m | H' | n \rangle \langle n | H' | m \rangle}{E_n^0 - E_m^0} \quad (4.16)$$

One way of calculating the long-range interaction between two  $H(n=2)$ -atoms was presented in a paper from 2005 by Flannery et al. Ref. [17]. The basic idea is that the interaction operator  $\widehat{V}$  for large values of  $R$ , can be written by the multipole expansion [17]

$$V(\mathbf{R}, \mathbf{r}_{1A}, \mathbf{r}_{2B}) = \sum_{L_1, L_2=1}^{\infty} \sum_{M=-L_<}^{L_<} \frac{(-1)^{L_2} f_{L_1 L_2 M}}{R^{L_1+L_2+1}} \hat{Q}_{L_1 M}(\mathbf{r}_{1A}) \hat{Q}_{L_2-M}(\mathbf{r}_{2B}), \quad (4.17)$$

where

$$f_{L_1 L_2 M} = \frac{(L_1 + L_2)!}{[(L_1 + M)!(L_1 - M)!(L_2 + M)!(L_2 - M)!]^{1/2}}, \quad (4.18)$$

and  $\hat{Q}_i$  is the multipole operator for each atom given by

$$\hat{Q}_{LM}(\mathbf{r}) = \left( \frac{4\pi}{2L+1} \right)^{1/2} r^L Y_{LM}(\hat{r}) \quad (4.19)$$

We now consider the states that give the maximum interaction, i.e. the most elongated (parallel or anti-parallel) Stark states  $\psi_{n_1 n_2 m}$ , as described in chapter 2:

$$\begin{aligned} \psi_{(n-1)00}(\mathbf{r}_{1A}) &\equiv |+\rangle \\ \psi_{0(n-1)0}(\mathbf{r}_{2B}) &\equiv |-\rangle \end{aligned} \quad (4.20)$$

This is equivalent with two atomic dipoles aligned along the  $R$ -axis.

The average of the first-order interaction (4.17) over the Stark states  $|\alpha\rangle_A$  of atom  $A(n)$  and  $|\beta\rangle_B$  of atom  $B(n')$ :

$$V(R) = \langle \beta |_B \langle \alpha |_A V(\mathbf{R}, \mathbf{r}_{1A}, \mathbf{r}_{2B}) | \alpha \rangle_A | \beta \rangle_B \quad (4.21)$$

can be expanded in terms of the averaged multipoles  $Q_i$  for each atom of the form

$$V(R) = \sum_{i=1}^N \sum_{j=1}^{N'} V_{ij} = \sum_{i=1}^N \sum_{j=1}^{N'} (-1)^j \frac{(i+j)!}{i!j!} \frac{Q_i^A Q_j^B}{R^{i+j+1}}, \quad (4.22)$$

where  $N = 2(n-1)$  and  $N' = 2(n'-1)$ , and  $n$  ( $n'$ ) is the principal quantum number of atom A (B). The full long-range interaction is found by calculating the interaction of the dipole, quadrupole, etc. of atom A with each of the multipoles of atom B, and finally summing over all terms. From [17] we find that

$$V(R) = -\frac{2}{R^3} Q_1^A Q_2^B - \frac{3}{R^4} (Q_1^A Q_2^B - Q_2^A Q_1^B) - \frac{2}{R^5} [2(Q_1^A Q_3^B + Q_3^A Q_1^B) - 3Q_2^A Q_2^B] - \dots \quad (4.23)$$

We see from the expression (4.23) that the leading term for the asymptotic interaction between  $H(n) - H(n')$  is of order  $R^{-3}$ .

According to Flannery et al. the interaction between two parallel dipoles does not contain the  $R^{-4}$ -term, since  $Q_j^A = Q_j^B$ . Hence for two hydrogen atoms with  $n = 2$ , the first order perturbation theory gives energy on the form

$$E \sim \frac{c_1}{R^3} + \frac{c_1}{R^5} \quad (4.24)$$

This method can be directly applied to calculate matrix elements between pairs of quantum states connected to each atom. One observes that it basically only requires ability to calculate one electron momenta of various powers of  $r$ ,  $\int \psi_i(\mathbf{r}) r^n \psi_j(\mathbf{r}) d^3r$ . The limitation of this method is, however, that one only has access to asymptotic terms.



### 4.3 Quantum treatment - new approach

We start by observing that the matrix element between two pairs of states connected for the two ionic potentials can be calculated with the same method as in Chapter 3, and that it is non-zero only for identical matrix element of the "other variable",

$$\langle lk | \frac{1}{|\mathbf{R} - \mathbf{r}|} |ij\rangle = \delta_{l,i} \langle k | \frac{1}{|\mathbf{R} - \mathbf{r}|} |j\rangle \quad (4.25)$$

The electron-electron repulsion, on the other hand, needs some extra consideration and we will here modify a method derived by Hovland et al. in Ref. [18] for the matrix element between the electron-electron interaction and two pairs of atomic states connected with each nucleus separated a distance  $R$ .

Referring to the coordinate system of figure 4.1 the matrix integral is [18]

$$\begin{aligned} M_{fi}(R) &= \langle lk | \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} |ij\rangle \\ &= \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi_l^*(\mathbf{r}_1) \psi_k^*(\mathbf{r}_2) \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \end{aligned} \quad (4.26)$$

We use the Bethe integral for the electron-electron interaction

$$\frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} = \frac{1}{2\pi^2} \int \frac{d^3p}{p^2} e^{ip(\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1)} \quad (4.27)$$

and define a momentum space function  $\tilde{F}(\mathbf{p})$ , which is a Fourier transform of a product of two atomic states

$$\tilde{F}(\mathbf{p}) = \int d^3r e^{i\mathbf{p}\mathbf{r}} \psi_a^*(\mathbf{r}) \psi_b(\mathbf{r}) \quad (4.28)$$

Replacing the exponential with the plane-wave expansion

$$e^{-i\mathbf{p}\mathbf{r}} = 4\pi \sum_{LM} (-i)^L j_L(pr) Y_{LM}^*(\hat{r}) Y_{LM}(\hat{p}), \quad (4.29)$$

where  $j_L(pr)$  are the *Bessel-functions*, per definition

$$j_n(x) = (-x)^n \left( \frac{1}{x} \frac{d}{dx} \right)^n \frac{\sin x}{x} \quad (4.30)$$

in spherical coordinates.

The integration over the  $r$ -space is done by the use of [19]

$$\int_0^\infty x^n e^{-\alpha x} \sin(xy) dx = n! \left( \frac{\alpha}{\alpha^2 + y^2} \right)^{n+1} \times \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} (-1)^m \binom{n+1}{2m+1} \left( \frac{y}{\alpha} \right)^{2m+1} \quad (4.31)$$

and

$$\int_0^\infty x^n e^{-\alpha x} \cos(xy) dx = n! \left( \frac{\alpha}{\alpha^2 + y^2} \right)^{n+1} \times \sum_{0 \leq 2m \leq n+1} (-1)^m \binom{n+1}{2m} \left( \frac{y}{\alpha} \right)^{2m} \quad (4.32)$$

We see that the functions  $\tilde{F}(\mathbf{p})$  thus are linear combinations of well known functions of "momentum space form" for the hydrogen atom. They connect a few angular momentum quantum numbers determined by the two pairs of quantum numbers of the two  $r$ -space wavefunctions involved.

$$\tilde{F}(\mathbf{p}) = \sum_i a_i \frac{p_i^b}{(p^2 + \alpha_i^2)^c} Y_{l_i, m_i}(\hat{p}) \quad (4.33)$$

Putting these into (4.26) we get

$$M_{fi}(R) = \frac{1}{2\pi^2} \int \frac{d^3p}{p^2} e^{ip\mathbf{R}} \tilde{F}_1(-\mathbf{p}) \tilde{F}_2(\mathbf{p}) \quad (4.34)$$

and by employing the plane-wave expansion for the exponential once more, we arrive at the following expression for the matrix element

$$M_{fi}(R) = \frac{2}{\pi} \int \frac{d^3p}{p^2} \tilde{F}_1(-\mathbf{p}) \tilde{F}_2(\mathbf{p}) \sum_{LM} (i)^L j_L(pR) Y_{LM}(\hat{R}) Y_{LM}^*(\hat{p}) \quad (4.35)$$

From formula (4.33) and (4.30) it is now clear that the matrix integral can be written as a finite number of terms of the form:

$$G_{k',m}(R) = \int_0^\infty dp \frac{p^{k'}}{(p^2 + \alpha^2)^{m+1}} \times \begin{cases} \cos(pR) & k' = 2k, k \in \{0, 1, 2, \dots\} \\ \sin(pR) & k' = 2k + 1, k \in \{-1, 0, 1, \dots\} \end{cases} \quad (4.36)$$

here simplified for the case of identical 'target' and 'projectile' atoms.

$$\alpha = Z_p \left( \frac{1}{n_l} + \frac{1}{n_i} \right) = Z_t \left( \frac{1}{n_k} + \frac{1}{n_j} \right) \quad (4.37)$$

where  $Z_p$  ( $Z_t$ ) are the projectile (target) nuclear charge. For the calculated example of  $H$  ( $n = n' = 2$ ) in the next section, we have  $\alpha = 1$ .

To perform the  $p$ -integration we need the following Fourier-sine and -cosine transforms [19],

$$\int_0^\infty \frac{x^{2m}}{(x^2 + z)^{n+1}} \cos(xR) dx = (-1)^{m+n} \frac{\pi}{2} \frac{1}{n!} \frac{d^n}{dz^n} (z^{m-1/2} e^{-Rz^{1/2}}), \quad (4.38)$$

$|\arg z| < \pi, \quad 0 \leq m \leq n + 1$

$$\int_0^\infty \frac{x^{2m+1}}{(x^2 + z)^{n+1}} \sin(xR) dx = (-1)^{m+n} \frac{\pi}{2} \frac{1}{n!} \frac{d^n}{dz^n} (z^m e^{-Rz^{1/2}}), \quad (4.39)$$

$$|\arg z| < \pi, \quad 0 \leq 2m \leq 2n \quad (4.40)$$

and

$$\int_0^\infty \frac{\sin(xR)}{x(x^2 + \alpha^2)^n} dx = \frac{\pi}{2} \alpha^{-2n} \left[ 1 - 2^{1-n} e^{-\alpha R} \frac{F_{n-1}(\alpha R)}{(n-1)!} \right] \quad (4.41)$$

with

$$\begin{aligned} F_n(z) &= (z + 2n)F_{n-1}(z) - z \frac{dF_{n-1}(z)}{dz}, \\ F_0(z) &= 1 \end{aligned} \quad (4.42)$$

We see that only the integrals where  $k' = -1$  give a non-exponential term, hence we are left to consider

$$\int_0^\infty \frac{\sin pR}{p(p^2 + \alpha^2)^8} dp \quad (4.43)$$

From (4.41) it is clear that this integral goes to  $\frac{\pi}{2}$  when  $R \rightarrow \infty$  for  $\alpha = 1$ .

Thus we have showed that the electron-electron interaction can be calculated completely analytically without approximations. We have modified the previous Hovland code to perform the calculation. It performs the symbolic operations in Fortran and evaluates the integral for any number of  $R$ -values in the end. The number of symbolic terms grows rapidly, but in our case we collect only the asymptotic forms, i.e. we neglect all terms which have an exponential form and keep only the  $R^{-k_i}$  forms. This results in a final form of the asymptotic matrix element as

$$M_{fi}(R) = \sum_{i=1}^{N_t} c_i R^{k_i} Y_{L_i M_i}(\hat{R}) \quad (4.44)$$

We have found a final asymptotic formula in terms of increasing negative powers of  $R$ . Again, keeping the internuclear separation parallel with the  $\hat{z}$ -axis only  $M = 0$  terms are nonzero.

### 4.3.1 Matrix element example for $n=n'=2$

As examples, and tests of the Fortran code, we explicitly calculate a few matrix elements pertaining to the double  $n = 2$  levels of two hydrogen atoms.

We start by two electrons in the  $2p_0$  level. Using the method described above, we calculate the expression for the electron-electron repulsion term,  $M_{fi}(R) = \langle 2p_0 2p_0 | \frac{1}{|r_2 - r_1|} | 2p_0 2p_0 \rangle$ :

$$\begin{aligned} \tilde{F}(\mathbf{p}) &= \int d^3 \mathbf{r} e^{i\mathbf{p}\mathbf{r}} \psi_a(\mathbf{r}) \psi_b(\mathbf{r}) \\ &= 4\pi a^2 \left[ (10|00|10) Y_{00}(\hat{p}) \int r^4 e^{-r} \frac{\sin(pr)}{pr} dr \right. \\ &\quad \left. - (10|20|10) Y_{20}(\hat{p}) \int r^4 e^{-r} \left( \left( \frac{3}{(pr)^3} - \frac{1}{pr} \right) \sin(pr) - 3 \frac{\cos(pr)}{(pr)^2} \right) dr \right] \quad (4.45) \end{aligned}$$

In this case we have  $\tilde{F}_1(-\mathbf{p}) = \tilde{F}_2(\mathbf{p}) = \tilde{F}(\mathbf{p})$ , so

$$\begin{aligned} \tilde{F}_1(-\mathbf{p}) \tilde{F}_2(\mathbf{p}) = \tilde{F}(\mathbf{p})^2 &= (4\pi a^2)^2 \left[ \frac{1}{4\pi} \frac{24^2}{(p^2 + \alpha^2)^8} (p^2 - 1)^2 Y_{00}^2(\hat{p}) \right. \\ &\quad + \frac{1}{\sqrt{4\pi}} \frac{1}{\sqrt{5\pi}} (4 \cdot 24^2 \frac{p^2}{(p^2 + \alpha^2)^8} (p^2 - 1) Y_{00}(\hat{p}) Y_{20}(\hat{p}) \\ &\quad \left. + \frac{1}{5\pi} 4 \cdot 24^2 \frac{p^4}{(p^2 + \alpha^2)^8} Y_{20}^2(\hat{p}) \right] \quad (4.46) \end{aligned}$$

Hence the expression for the matrix element becomes:

$$M_{fi}(R) = \frac{2}{\pi} (4\pi a^2)^2 \iiint dp d\hat{p} \left[ \frac{24^2}{4\pi} f_0(p) Y_{00}^2(\hat{p}) + \frac{1}{\sqrt{4\pi}} \frac{1}{\sqrt{5\pi}} 4 \cdot 24^2 f_2(p) Y_{00}(\hat{p}) Y_{20}(\hat{p}) + \frac{1}{5\pi} 4 \cdot 24^2 f_4(p) Y_{20}^2(\hat{p}) \right] \times \sum_{LM} (-i)^L j_L(pR) Y_{LM}(\hat{R}) Y_{LM}^*(\hat{p}) \quad (4.47)$$

where

$$f_0(p) = \frac{(p^2-1)^2}{(p^2+\alpha^2)^8}$$

$$f_2(p) = \frac{p^2}{(p^2+\alpha^2)^8} (p^2 - 1)$$

$$f_4(p) = \frac{p^4}{(p^2+\alpha^2)^8}$$

Since  $\hat{R} = (0, 0)$ , we get the following values for the angular integrals:

$$\int_0^{2\pi} \int_0^\pi d\hat{p} Y_{00}^3(\hat{p}) Y_{00}(\hat{R}) = \frac{1}{4\pi} \quad (4.48)$$

$$\int_0^{2\pi} \int_0^\pi d\hat{p} Y_{00}(\hat{p}) Y_{20}^2(\hat{p}) Y_{20}(\hat{R}) = \frac{1}{4} \frac{\sqrt{5}}{\pi} \quad (4.49)$$

$$\int_0^{2\pi} \int_0^\pi d\hat{p} Y_{00}(\hat{p}) Y_{20}^2(\hat{p}) Y_{00}(\hat{R}) = \frac{1}{4\pi} \quad (4.50)$$

$$\int_0^{2\pi} \int_0^\pi d\hat{p} Y_{20}^3(\hat{p}) Y_{20}(\hat{R}) = \frac{5}{14\pi} \quad (4.51)$$

$$\int_0^{2\pi} \int_0^\pi d\hat{p} Y_{20}^2(\hat{p}) Y_{40}(\hat{p}) Y_{40}(\hat{R}) = \frac{9}{14\pi} \quad (4.52)$$

We thus obtain the matrix element for the long-range interaction between the electron-electron repulsion and two  $2p_0$ -states:

$$M_{fi}(R) = \langle 2p_0 2p_0 | \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} | 2p_0 2p_0 \rangle = \frac{1}{R} + \frac{24}{R^3} + \frac{864}{R^5} \quad (4.53)$$

The total interaction  $\hat{V}(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2)$  results in:

$$\begin{aligned} \langle 2p_0 2p_0 | \hat{V} | 2p_0 2p_0 \rangle &= \frac{1}{R} - \langle 2p_0 | \frac{1}{|\mathbf{R} - \mathbf{r}_1|} | 2p_0 \rangle - \langle 2p_0 | \frac{1}{|\mathbf{R}| + \mathbf{r}_2} | 2p_0 \rangle \\ &\quad + \langle 2p_0 2p_0 | \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} | 2p_0 2p_0 \rangle \\ &= \frac{1}{R} - \frac{1}{R} - \frac{12}{R^3} - \frac{1}{R} - \frac{12}{R^3} + \frac{1}{R} + \frac{24}{R^3} + \frac{864}{R^5} = \frac{864}{R^5} \end{aligned} \quad (4.54)$$

### 4.3.2 Diagonalization of the asymptotic $H(n=2) - H(n'=2)$ levels

With direct product expansion of two  $H(n=2)$  atoms, the basis for calculating the Hamiltonian matrix consists of 16 states. But since only  $M=0$  gives non-zero matrix

elements, the basis reduces to the following 6 product states:

$$2s2s, 2p_02p_0, 2s2p_0; 2p_-2p_+, 2p_+2p_- \quad (4.55)$$

The Hamiltonian matrix takes the following form,

$$H_{n=n'=2} = \begin{pmatrix} 0 & -18/R^3 & 0 & 0 & -9/R^3 & -9/R^3 \\ -18/R^3 & 864/R^5 & -108/R^4 & 108/R^4 & 432/R^5 & 432/R^5 \\ 0 & -108/R^4 & 0 & -18/R^3 & -54/R^4 & -54/R^4 \\ 0 & 108/R^4 & -18/R^3 & 0 & 54/R^4 & 54/R^4 \\ -9/R^3 & 432/R^5 & -54/R^4 & 54/R^4 & 216/R^5 & 216/R^5 \\ -9/R^3 & 432/R^5 & -54/R^4 & 54/R^4 & 216/R^5 & 216/R^5 \end{pmatrix} \quad (4.56)$$

The asymptotic form of the  $H(n=2) - H(n'=2)$  system was recently studied by Vane/Jonsell et al. in two papers. Ref. [20, 21]. The second paper [21] corrects a mistake concerning matrix element evaluation that occurred in the first one [20]. The product basis above does not correctly describe the system since the states do not behave correctly with respect to symmetry and particle interchange.

Since electrons (and protons) are indistinguishable particles, the problem of finding the long-range interaction between two H-atoms, can be reduced due to symmetry properties of the system. Consider a system containing two protons,  $A$  and  $B$ , (at rest) with coordinates  $\mathbf{r}_A$  and  $\mathbf{r}_B$ , and two electrons,  $e_1$  and  $e_2$ , with coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . The internuclear distance  $\mathbf{R} = \mathbf{r}_B - \mathbf{r}_A$  is assumed to be so large that electron-electron exchange can be neglected and we can treat the problem using perturbation theory.

We consider the symmetry properties of the electronic Hamiltonian,  $\hat{H}$ , the unperturbed Hamiltonian,  $\hat{H}_0$ , and the perturbation operator  $\hat{V}$ .

Introducing atom-centered coordinates

$$\begin{aligned} \boldsymbol{\rho}_1 &\equiv \mathbf{r}_1 - \mathbf{r}_A \\ \boldsymbol{\rho}_2 &\equiv \mathbf{r}_2 - \mathbf{r}_B \end{aligned} \quad (4.57)$$

into the operators, we see that the electronic Hamiltonian  $\hat{H}$  is invariant under inversion  $\mathcal{I}$  of all electronic coordinates with respect to the center of mass  $\mathbf{R}_{cm} = (\mathbf{r}_A + \mathbf{r}_B)/2$ , to electron exchange  $\mathcal{P}_{12}$ , and to reflection  $\mathcal{R}$  by a plane containing the protons.  $\hat{H}_0$  and  $\hat{V}$  is invariant under  $\mathcal{R}$ , but not under  $\mathcal{P}_{12}$  or  $\mathcal{I}$ . Introducing the transformation

$$\mathcal{B} = \mathcal{P}_{12}\mathcal{I} = \mathcal{I}\mathcal{P}_{12} \quad (4.58)$$

we find that  $\mathcal{B}$  used on the coordinates gives

$$\begin{aligned} \mathbf{r}_1 &\rightarrow 2\mathbf{R}_{cm} - \mathbf{r}_2 \Leftrightarrow \boldsymbol{\rho}_1 \rightarrow -\boldsymbol{\rho}_2 \\ \mathbf{r}_2 &\rightarrow 2\mathbf{R}_{cm} - \mathbf{r}_1 \Leftrightarrow \boldsymbol{\rho}_2 \rightarrow -\boldsymbol{\rho}_1 \end{aligned} \quad (4.59)$$

and we have invariance for both  $\hat{H}_0$  and  $\hat{V}$  with respect to  $\mathcal{B}$ .

This transformation results in a reduced set of quantum numbers used to describe the eigenvectors  $\hat{H}_0$  and  $\hat{H}$ :  $\tau \equiv \{M, p_\beta, [p_r]\}$ . Here  $p_\beta = p_i p_s$ , and  $p_i$ ,  $p_s$  and  $[p_r]$  are respectively the parities associated with  $\mathcal{I}$ ,  $\mathcal{P}_{12}$  and  $\mathcal{R}$ .

$M = 0, \pm 1, \pm 2, \dots$  is the projection quantum number of the total electronic orbital angular momentum. Each  $M$ -value is associated with one of the following symbols

$$\begin{array}{cccc} 0 & \pm 1 & \pm 2 & \dots \\ \uparrow & \uparrow & \uparrow & \\ \Sigma & \Pi & \Delta & \dots \end{array}$$

The orthonormal set  $\{|i\rangle\tau\rangle\}$  of symmetry-adapted eigenfunctions of the unperturbed Hamiltonian  $\widehat{H}_0$ , with the eigenvalue  $E_0 = -0.25$  a.u. is given by [21]

$$|\{1\}\Sigma_+^+\rangle = |2s2s\rangle \quad (4.60)$$

$$|\{2\}\Sigma_+^+\rangle = |2p_02p_0\rangle \quad (4.61)$$

$$|\{3\}\Sigma_+^+\rangle = \frac{1}{\sqrt{2}}(|2s2p_0\rangle - |2p_02s\rangle) \quad (4.62)$$

$$|\{4\}\Sigma_+^+\rangle = \frac{1}{\sqrt{2}}(|2p_-2p_+\rangle + |2p_+2p_-\rangle) \quad (4.63)$$

$$|\{1\}\Sigma_-^+\rangle = \frac{1}{\sqrt{2}}(|2s2p_0\rangle + |2p_02s\rangle) \quad (4.64)$$

$$|\{1\}\Sigma_-^-\rangle = \frac{1}{\sqrt{2}}(|2p_-2p_+\rangle - |2p_+2p_-\rangle) \quad (4.65)$$

$$|\{1\}\Pi_+\rangle = \frac{1}{\sqrt{2}}(|2s2p_+\rangle - |2p_+2s\rangle) \quad (4.66)$$

$$|\{2\}\Pi_+\rangle = \frac{1}{\sqrt{2}}(|2p_02p_+\rangle + |2p_+2p_0\rangle) \quad (4.67)$$

$$|\{1\}\Pi_-\rangle = \frac{1}{\sqrt{2}}(|2p_02p_+\rangle - |2p_+2p_0\rangle) \quad (4.68)$$

$$|\{2\}\Pi_-\rangle = \frac{1}{\sqrt{2}}(|2s2p_+\rangle + |2p_+2s\rangle) \quad (4.69)$$

$$|\{1\}\Delta_+\rangle = |2p_+2p_+\rangle \quad (4.70)$$

Here  $i = 1, \dots, g_\tau$  enumerates the states with symmetry  $\tau$ , and dimension of degeneracy  $g_\tau$ . The lower right  $\pm$ -sign of the states denotes the parity  $p_\beta = \pm 1$  under the transformation  $\mathcal{B}$ . The matrix representing the perturbation  $\widehat{V}$  becomes block diagonal, with the block matrices:

$$V(\Sigma_+^+) = \begin{pmatrix} 0 & -18/R^3 & 0 & -9\sqrt{2}/R^3 \\ -18/R^3 & 864/R^5 & -108\sqrt{2}/R^4 & 432\sqrt{2}/R^5 \\ 0 & -108\sqrt{2}/R^4 & 18/R^3 & -108/R^4 \\ -9\sqrt{2}/R^3 & 432\sqrt{2}/R^5 & -108/R^4 & 432/R^5 \end{pmatrix}$$

$$V(\Sigma_-^+) = (-18/R^3); \quad V(\Sigma_-^-) = (0), \quad V(\Delta_+) = (216/R^5)$$

$$V(\Pi_+) = \begin{pmatrix} -9/R^3 & 108/R^4 \\ 108/R^4 & -864/R^5 \end{pmatrix}; \quad V(\Pi_-) = \begin{pmatrix} 0 & 0 \\ 0 & 9/R^3 \end{pmatrix} \quad (4.71)$$

Thus the  $M = 0$  ( $6 \times 6$ )-manifold above can be characterised as four  $\Sigma_+^+$  states, and two  $\Sigma_+^-$ ,  $\Sigma_-^-$  states which do not couple between themselves or with the  $\Sigma_+^+$  states. Calculating the matrix element for the symmetrized basis of  $M = 0$  states

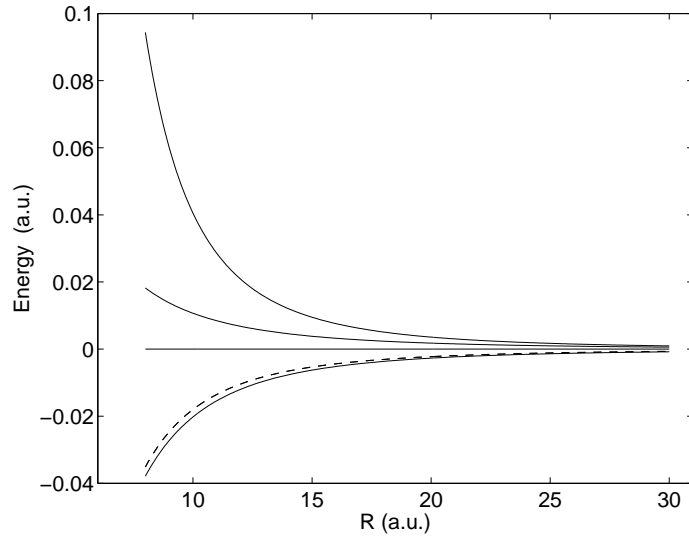
$$\begin{aligned} & 2s2s, 2p_02p_0, \frac{1}{\sqrt{2}}(|2s2p_0\rangle - |2p_02s\rangle), \frac{1}{\sqrt{2}}(|2p_-2p_+\rangle + |2p_+2p_-\rangle), \\ & \frac{1}{\sqrt{2}}(|2s2p_0\rangle + |2p_02s\rangle), \frac{1}{\sqrt{2}}(|2p_-2p_+\rangle - |2p_+2p_-\rangle) \end{aligned} \quad (4.72)$$

based on the matrix of the unsymmetrized basis (4.56) we obtain,

$$H_{n=n'=2}^{SYM} = \begin{pmatrix} 0 & -18/R^3 & 0 & -9\sqrt{2}/R^3 & 0 & 0 \\ -18/R^3 & 864/R^5 & -108\sqrt{2}/R^4 & 432\sqrt{2}/R^5 & 0 & 0 \\ 0 & -108\sqrt{2}/R^4 & 18/R^3 & -108/R^4 & 0 & 0 \\ -9\sqrt{2}/R^3 & 432\sqrt{2}/R^5 & -108/R^4 & 432/R^5 & 0 & 0 \\ 0 & 0 & 0 & 0 & -18/R^3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

which is identical to the result of Vanne et al.

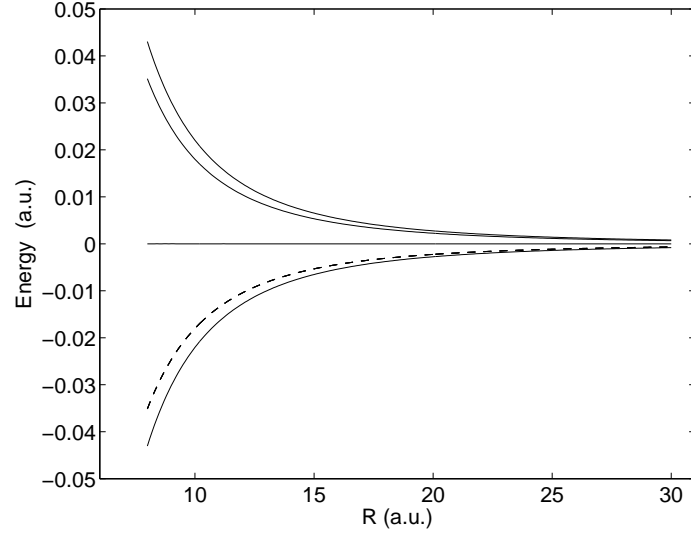
We end this chapter by considering the asymptotic energy curves and diagonal states of the  $\Sigma$  states. In fig 4.2 we have plotted the energy eigenvalues of the symmetrized matrix  $H_{n=n'=2}^{SYM}$ .



**Figure 4.2:** Energy eigenvalues for the four  $\Sigma_+^+$  states (solid lines). Dashed line corresponds to the  $\Sigma_+^-$  state.

We see that the atom-atom interaction results in two energy levels of higher energy compared to the unperturbed  $n = 2$  level, two of lower energy and a level of  $E' = 0$ , which is doubly degenerate.

Figure 4.3 shows the energy eigenvalues only for the dipole-dipole terms of the symmetrized matrix  $H_{n=n'=2}^{SYM}$ . As in the figure above, the interaction leads to two energy levels with a weaker bond, and two with a stonger bond in addition to the doubly degenerate level of  $E' = 0$ .

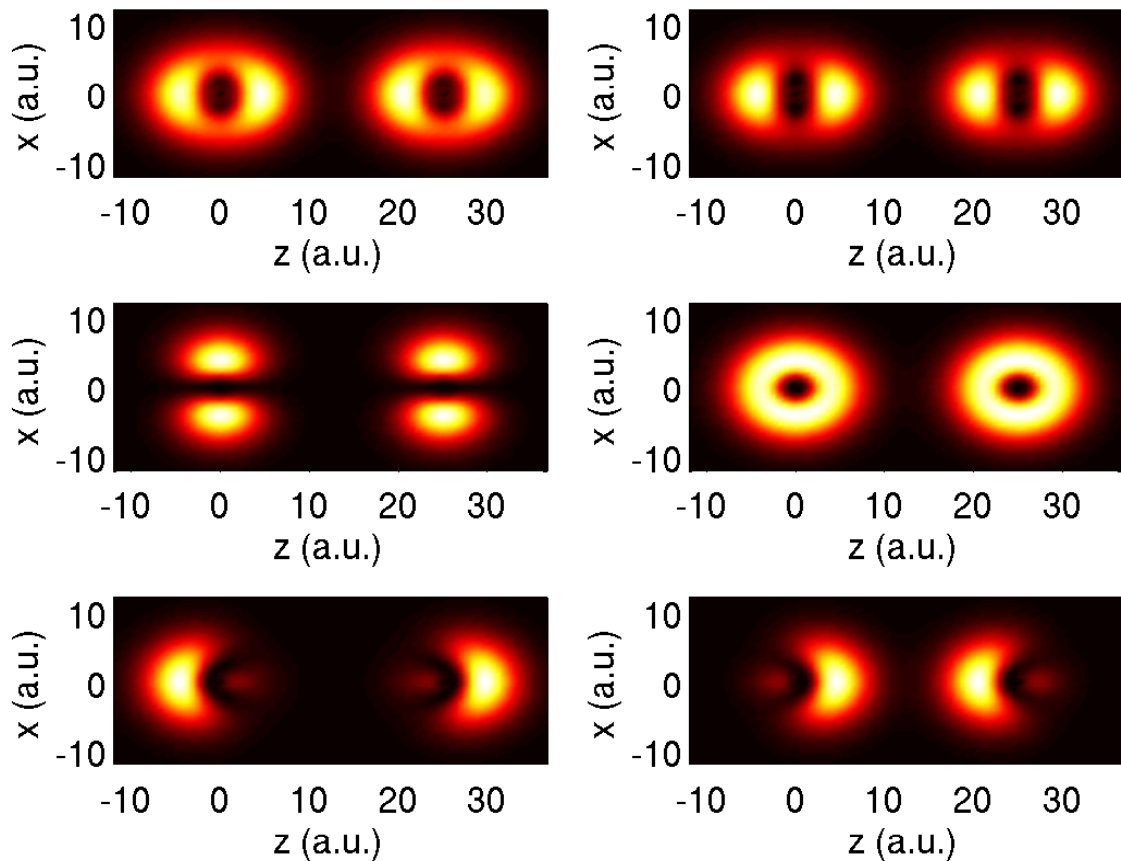


**Figure 4.3:** Energy levels for the dipole-dipole interaction of  $H_{n=n'=2}^{SYM}$ . As in the previous figure, the dashed line is the  $\Sigma_+^-$  state.

For the case of  $R \rightarrow \infty$  figures 4.3 and 4.2 approaches the same limit,  $E' \rightarrow 0$ .

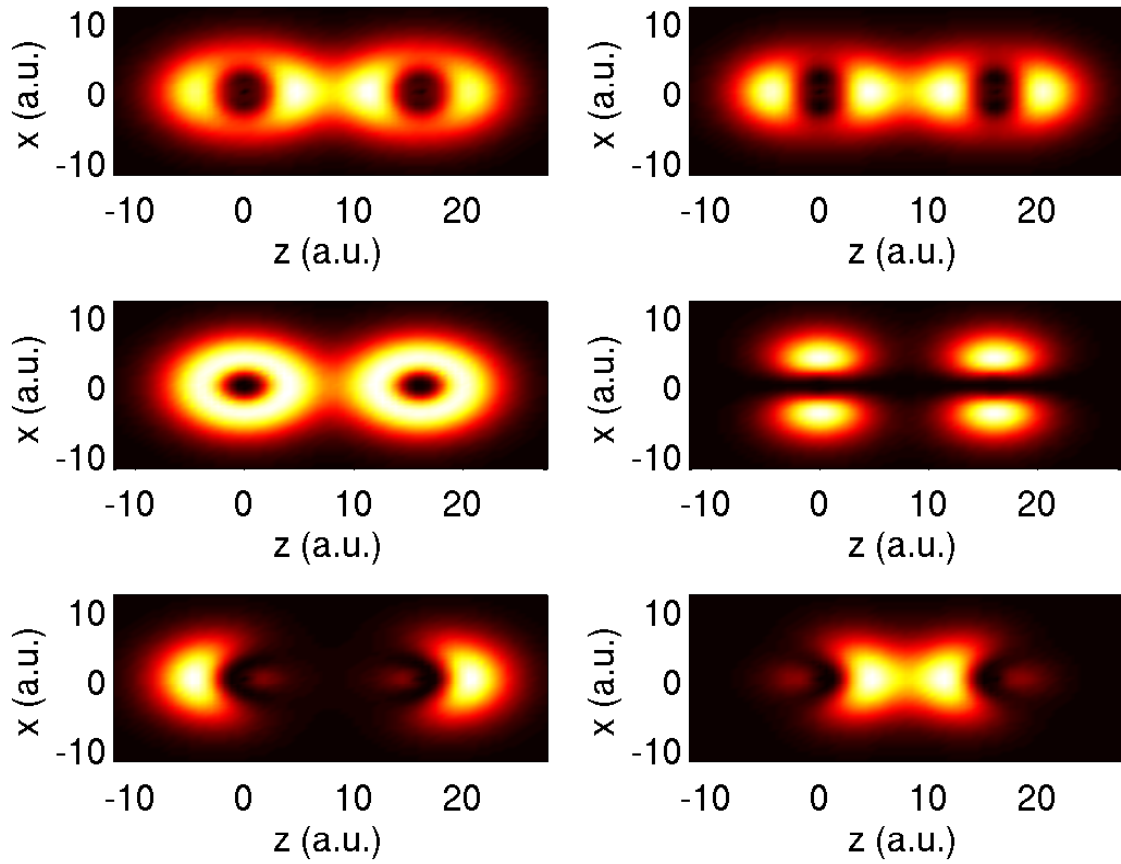


To see how the wavefunction is perturbed by the atom-atom interaction, we have plotted the wavefunctions of  $H(n = n' = 2)$ , corresponding to three different values for  $R$ , respectively  $R = 25$ ,  $R = 16$  and  $R = 30$ . In addition we have plotted the wavefunctions for the dipole-dipole interaction for  $R = 25$ .



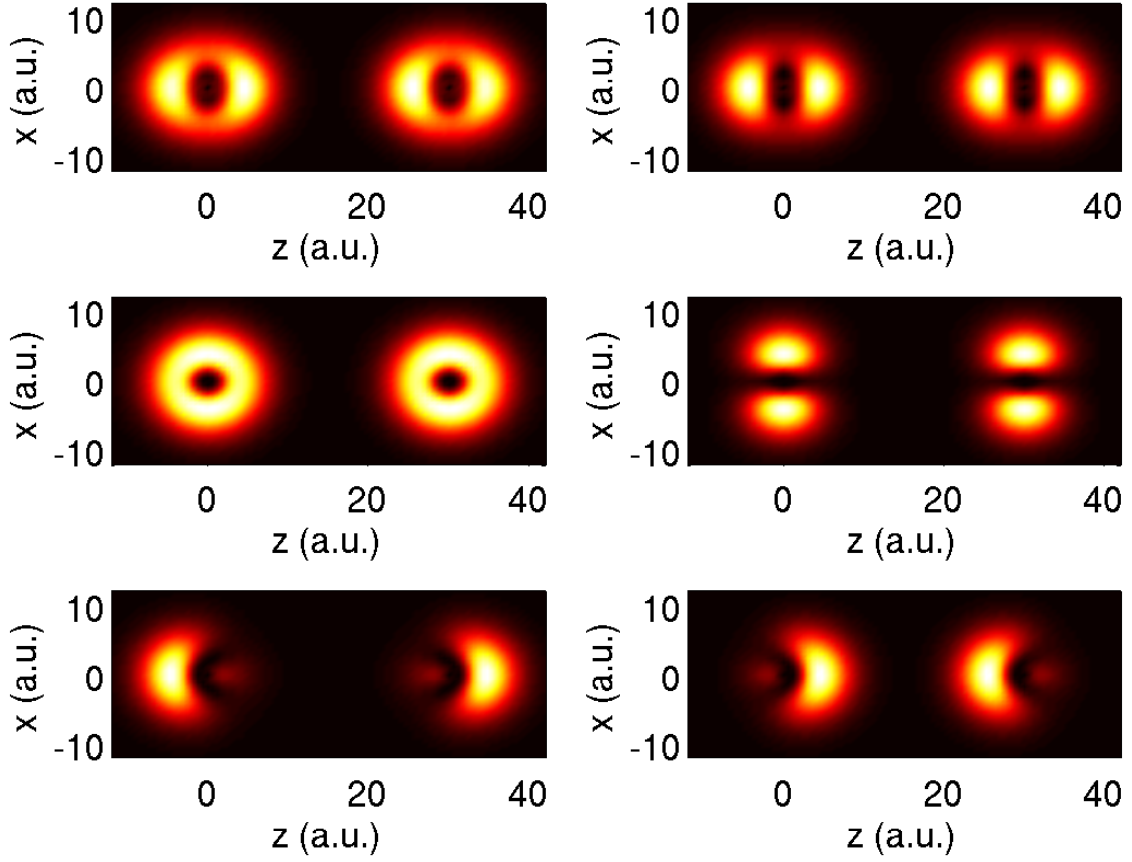
**Figure 4.4:** Wavefunctions of  $H(n = n' = 2)$  for the lowest energy state (upper left panel), to the highest energy state (lower right panel) for  $R=25$ .

The upper left panel of 4.4 shows the case of lowest energy, and we see that the electron clouds are almost symmetric around each atom, but with slightly more in the middle. The two panels in the middle shows the circular states with  $E' = 0$ . It is interesting to observe that the two wavefunctions polarized towards and away from each other, plotted in the two lowest panels, both correspond to the highest energies.



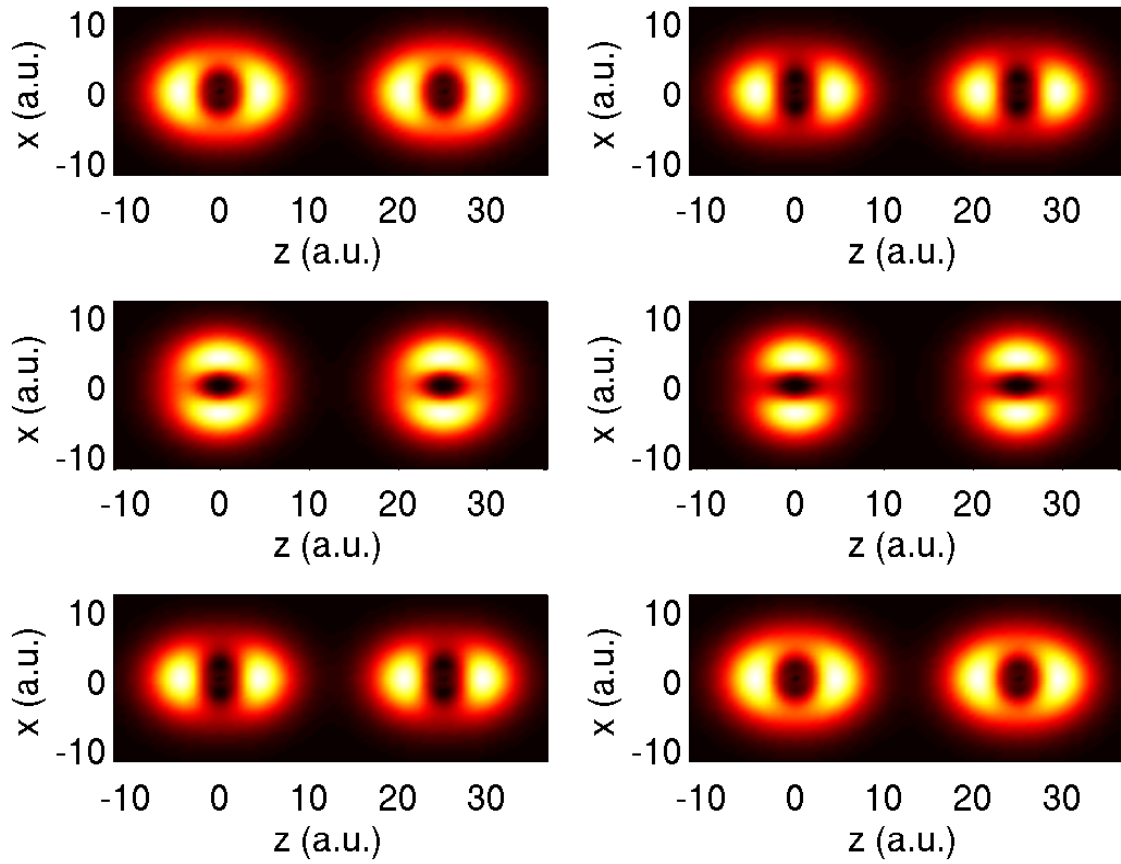
**Figure 4.5:** Wavefunctions of  $H(n = n' = 2)$  from the lowest energy state (upper left panel), to the highest energy state (lower right panel) for  $R=16$ .

For the case of  $R = 16$ , the wavefunctions behave in almost the same manner, but now the distributions overlap, and for  $R = 30$ , they look just like for  $R = 25$ , only farther apart.



**Figure 4.6:** Wavefunctions of  $H(n = n' = 2)$  from the lowest energy state (upper left panel), to the highest energy state (lower right panel) for  $R=30$ .

In figure 4.7 the dipole-dipole interaction wavefunctions are plotted for  $R = 25$ . The upper panels are identical to the ones in 4.4, but we see that the higher order terms in  $H_{n=n'=2}^{SYM}$  become significant for the wavefunctions for the higher energies.



**Figure 4.7:** Wavefunctions corresponding to only the dipole terms of  $H(n = n' = 2)$ . The lowest energy state (upper left panel), to the highest energy state (lower right panel) for  $R=25$ .

# Chapter 5

## Dynamics

In the previous chapters we have been concerned with isolated atoms and atoms in static electric fields. In this final chapter we will see how to deal with systems in time-dependent fields, and how Rydberg atoms interact with each other. We begin with the matrix representation of the time-dependent Schrödinger equation, and proceed to the case of one Rydberg atom in a electric and magnetic field. An example of analytical solutions from a thesis by M.Førre [22] has been added. Finally, a brief summary of the interaction between two Rydbergs atoms, with focus on the *Rydberg blockade* as it appears in numerical calculations.

### 5.1 Solving the time-dependent Schrödinger equation

For a system with a weak, time-dependent perturbation, the Hamiltonian can be expressed as

$$\hat{H}(\mathbf{r}, t) = \hat{H}_0(\mathbf{r}) + \hat{V}(\mathbf{r}, t) \quad (5.1)$$

where  $\hat{H}_0$  is the Hamiltonian of the unperturbed system, with the stationary eigenstates

$$\Psi_n^0(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_n t} \quad (5.2)$$

The solutions to the *Time-Dependent Schrödinger Equation* (TDSE)

$$i\frac{\partial\Psi}{\partial t} = H\Psi = (\hat{H}_0 + \hat{V})\Psi \quad (5.3)$$

can be expanded using these known eigenstates

$$\Psi(\mathbf{r}, t) = \sum_{k=0}^{\infty} a_k(t)\psi_k(\mathbf{r})e^{-iE_k t} \quad (5.4)$$

where  $a_k(t)$  are the time-dependent expansion coefficients, satisfying the equation

$$\sum_k |a_k(t)|^2 = 1 \quad (5.5)$$

Putting the solutions (5.4) into the TDSE gives

$$\sum_k i \left( \frac{da_k(t)}{dt} - iE_k a_k(t) \right) \psi_k(\mathbf{r})e^{-iE_k t} = (\hat{H}_0(\mathbf{r}) + \hat{V}(\mathbf{r}, t)) \sum_k a_k(t)\psi_k(\mathbf{r})e^{-iE_k t} \quad (5.6)$$

Since  $\widehat{H}_0\psi_k = E_k\psi_k$ , this reduces to

$$\sum_k i \frac{da_k(t)}{dt} \psi_k(\mathbf{r}) e^{-iE_k t} = \sum_k a_k(t) \widehat{V}(\mathbf{r}, t) \psi_k(\mathbf{r}) e^{-iE_k t} \quad (5.7)$$

Multiplying both sides with  $\psi_n^*(\mathbf{r})$ , and integrating over the whole space, we are left with

$$i \frac{da_n(t)}{dt} e^{-iE_n t} = \sum_k a_k(t) V_{nk}(t) e^{-iE_k t} \quad (5.8)$$

where

$$V_{nk}(t) \equiv \langle n | \widehat{V} | k \rangle \quad (5.9)$$

This can be represented using matrix mechanics as

$$i \frac{d}{dt} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & V_{13}e^{i\omega_{13}t} & \cdots \\ V_{21}e^{i\omega_{21}t} & V_{22} & V_{23}e^{i\omega_{23}t} & \cdots \\ V_{31}e^{i\omega_{31}t} & V_{32}e^{i\omega_{32}t} & V_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \quad (5.10)$$

Here  $\omega_{nk} \equiv E_n - E_k$ .

Alternatively we can include the exponential  $e^{-iE_k t}$  in the expansion coefficient  $a'_k(t)$ . The expansion of the wavefunction thus looks like

$$\Psi(\mathbf{r}, t) = \sum_{k=0}^{\infty} a'_k(t) \psi_k(\mathbf{r}) \quad (5.11)$$

and the matrix system representing the TDSE becomes

$$i \frac{d}{dt} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1 + V_{11} & V_{12} & \cdots \\ V_{21} & E_2 + V_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} \quad (5.12)$$

Both systems (5.10) and (5.12) are totally equivalent to the full TDSE. The solutions, however, are not trivial, and we must do some approximations to be able to solve them. By limiting the number of states in the expansion of the wavefunction (5.4) to a finite number  $N$

$$\Psi(\mathbf{r}, t) \simeq \sum_{k=0}^N a_k(t) \psi_k(\mathbf{r}) e^{-iE_k t} \quad (5.13)$$

the matrix system reduces to a set of  $N$  linearly independent equations. In the case of  $N = 2$  it becomes

$$i \frac{d}{dt} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} E_1 + V_{11} & V_{12} \\ V_{21} & E_2 + V_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (5.14)$$

which can be solved analytically for constant matrix elements and special cases, and numerically for all systems.

## 5.2 Rydberg atoms

The Hamiltonian for a hydrogenic Rydberg atom interacting with a weak time-dependent electric and magnetic field can be written as:

$$\hat{H} = \hat{H}_0 + \mathbf{E}(t) \cdot \hat{\mathbf{r}} + \frac{1}{2} \mathbf{B}(t) \cdot \hat{\mathbf{L}} \quad (5.15)$$

where  $\hat{H}_0$  is the unperturbed Hamiltonian,  $\mathbf{E}(t)$  and  $\mathbf{B}(t)$  are the electric and magnetic fields, and  $\hat{\mathbf{L}}$  is the angular momentum operator. To keep the principal  $n$ -shells preserved for the bound states in question, the electric field strength must be smaller than the *Inglis-Teller* limit,  $1/(3n^5)$ , and the magnetic field strength smaller than  $1/(n^4)$  [22].

If we expand the wavefunction as above, equation (5.4), and insert it into the TDSE, it leads to a first-order coupled matrix system for the expansion coefficients,  $a_k(t)$ ,

$$i \frac{d}{dt} \mathbf{a} = \mathbf{H}(t) \mathbf{a} \quad (5.16)$$

with the coupling matrix  $\mathbf{H}$ .

By defining two general spins by  $\hat{J}_{\pm} = \frac{1}{2}(\hat{\mathbf{L}} \pm \hat{\mathbf{A}})$ , where  $\hat{\mathbf{A}}$  is the Runge-Lenz vector, it can be shown that [22, 11] by some operator replacements, the Hamiltonian (5.15) becomes

$$\hat{H} = \boldsymbol{\omega}_+ \cdot \hat{J}_+ + \boldsymbol{\omega}_- \cdot \hat{J}_- \quad (5.17)$$

The problem is thus transformed into two uncoupled spin systems,  $\hat{J}_{\pm}$ , rotating in two fictitious fields  $\boldsymbol{\omega}_{\pm} = \frac{1}{2} \mathbf{B}(t) \pm \frac{3}{2} n \mathbf{E}(t)$ . The wavefunction of the total system is separable into two components,  $|\Psi\rangle = |\Psi_{-}\rangle \cdot |\Psi_{+}\rangle$ , where

$$|\Psi_{\pm}\rangle = \sum_{M=-J}^J b_{J,M}^{\pm}(t) |JM\rangle, \quad (5.18)$$

with  $J = (n - 1)/2$ .

From the Majorana theorem we know that an arbitrary spin system  $J$  in a field  $\boldsymbol{\omega}(t)$  is equivalent to  $2J$  spin- $\frac{1}{2}$  particles rotating in the same field. Thus, we may expand the spin systems,  $\hat{J}_{\pm}$ , where  $\hat{J}_{\pm} = \sum_{i=1}^{2J} \hat{j}_i$ , in each spin- $\frac{1}{2}$  component:

$$|jm\rangle = c_{-\frac{1}{2}}(t) |\frac{1}{2} - \frac{1}{2}\rangle + c_{+\frac{1}{2}}(t) |\frac{1}{2} \frac{1}{2}\rangle \quad (5.19)$$

This gives the matrix system, like equation (5.16), for any hydrogenic  $n$ -level:

$$i \frac{d}{dt} \begin{pmatrix} c_{-\frac{1}{2}} \\ c_{+\frac{1}{2}} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -\omega_z^{\pm} & \omega_x^{\pm} + i\omega_y^{\pm} \\ \omega_x^{\pm} - i\omega_y^{\pm} & \omega_z^{\pm} \end{pmatrix} \begin{pmatrix} c_{-\frac{1}{2}} \\ c_{+\frac{1}{2}} \end{pmatrix} \quad (5.20)$$

This system can be solved numerically. It is also possible to solve it analytically in many cases. As an example, we will show a method that employ explicit transformation formulas derived by Førre et al. in Ref. [22].

We start by looking at an initially excited Stark state, placed in a rotating microwave field in the  $xy$ -direction combined with a constant electric field in the  $z$ -direction, described by:

$$\mathbf{E}(t) = [e_0 \cos(\omega t), -e_0 \sin(\omega t), -E_z] \quad (5.21)$$

The microwave field drives only transitions with  $\Delta m = \pm 1$  and  $\Delta k = \pm 1$ . To keep the microwave field in resonance with the Stark splitting we require that  $\omega = \omega_z = -\frac{3}{2}nE_z$ . The matrix system takes the form:

$$i\frac{\partial}{\partial t}\mathbf{c}_{\pm} = \pm\frac{1}{2}\begin{pmatrix} -\omega & \omega_S e^{-i\omega t} \\ \omega_S e^{i\omega t} & \omega \end{pmatrix}\mathbf{c}_{\pm} \quad (5.22)$$

with  $\omega_S = \frac{3}{2}ne_0$ .

By the tranformation

$$\mathbf{c}_{\pm} = \begin{pmatrix} e^{-i\frac{1}{2}\omega t} & 0 \\ 0 & e^{i\frac{1}{2}\omega t} \end{pmatrix}\mathbf{d}_{\pm} \quad (5.23)$$

we obtain two spin- $\frac{1}{2}$  systems, respectively,

$$i\frac{\partial}{\partial t}\mathbf{d}_+ = \begin{pmatrix} -\omega & \frac{\omega_S}{2} \\ \frac{\omega_S}{2} & \omega \end{pmatrix}\mathbf{d}_+ = \widehat{M}_+\mathbf{d}_+ \quad (5.24)$$

$$i\frac{\partial}{\partial t}\mathbf{d}_- = \begin{pmatrix} 0 & -\frac{\omega_S}{2} \\ -\frac{\omega_S}{2} & 0 \end{pmatrix}\mathbf{d}_- = \widehat{M}_-\mathbf{d}_- \quad (5.25)$$

$\widehat{M}_+$  and  $\widehat{M}_-$  are the coupling matrices of each system. The analytical solutions are given on the form

$$\begin{aligned} \mathbf{d}_+ &= [\widehat{I} \cos\left(\sqrt{\omega^2 + \frac{\omega_S^2}{4}}t\right) - i\frac{1}{\sqrt{\omega^2 + \frac{\omega_S^2}{4}}}\widehat{M}_+ \sin\left(\sqrt{\omega^2 + \frac{\omega_S^2}{4}}t\right)]\mathbf{d}_+(t=0) \\ \mathbf{d}_- &= [\widehat{I} \cos\left(\frac{\omega_S}{2}t\right) - i\frac{2}{\omega_S}\widehat{M}_- \sin\left(\frac{\omega_S}{2}t\right)]\mathbf{d}_-(t=0) \end{aligned} \quad (5.26)$$

with  $\widehat{I}$  being the indentity matrix.

In the limit  $|\omega_S| \ll |\omega|$ , i.e. the situation of  $e_0 \ll E_z$ , the state vectors  $\mathbf{d}_+$  and  $\mathbf{d}_-$  become

$$\begin{aligned} \mathbf{d}_+ &= [\widehat{I} \cos(\omega t) - i\frac{1}{\omega}\widehat{M}_+ \sin(\omega t)]\mathbf{d}_+(t=0) \\ \mathbf{d}_- &= [\widehat{I} \cos\left(\frac{\omega_S}{2}t\right) - i\frac{2}{\omega_S}\widehat{M}_- \sin\left(\frac{\omega_S}{2}t\right)]\mathbf{d}_-(t=0) \end{aligned} \quad (5.27)$$

hence after a time  $t = \pi/\omega_S$  a spin particle described by  $\mathbf{d}_+$  remains in it's initial state, while a particle described by  $\mathbf{d}_-$  goes through a full inversion. If the initial state is a linear Stark state  $|k_{min}, 0\rangle$ , the final state will thus be the circular state  $|0, m_{max}\rangle$ .

In the following the analytical expression above is tested numerically. We then integrate the Schrödinger equation (5.16) with a standard ODE solver based on a precalculation of the matrix elements. We have employed the approximation

$$\frac{da(t)}{dt} \approx \frac{a(t + \Delta t) - a(t)}{\Delta t}, \quad (5.28)$$

resulting in

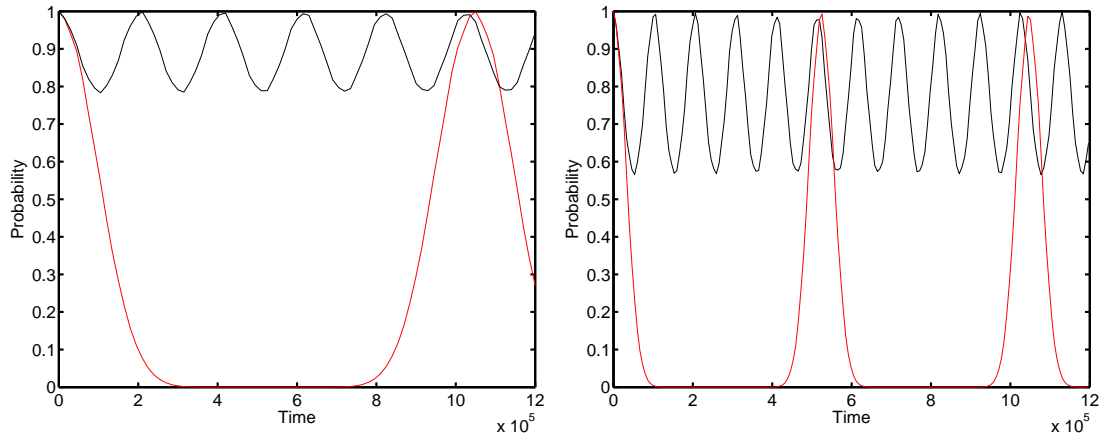
$$a(t + \Delta t) = -i\mathbf{H}a(t)\Delta t + a(t) \quad (5.29)$$

for the matrix system (5.16). The initial state is chosen to be the circular state  $m = l$  in all cases. Thus the initial condition becomes  $\vec{a}_{l,m}(t=0) = \delta_{l,m}$  for any  $n$ . After



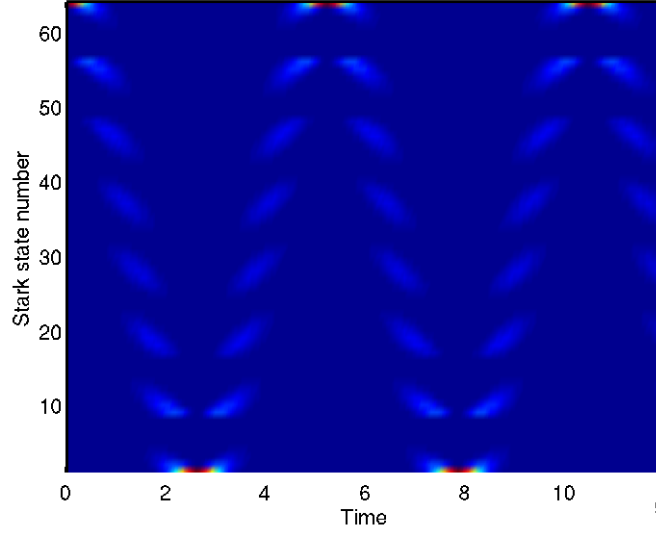
integration probabilities for population of the Stark states are obtained by transforming the amplitudes according to equation (2.42) in Chapter 2. The numerical codes for the essential calculations are printed in Appendix A.

In figure 5.1 we have plotted the probability distribution for a circular Stark state in the  $n = 4$  and  $n = 8$ -levels as a function of time. The red line shows the situation in which the parameters for the field fulfill the conditions for resonance given above. We see that this leads to a full depletion of the circular state, before it returns to its initial distribution after  $t = 2\pi/\omega_S$ . If the electric field strength is increased, so that the resonance condition no longer holds, the initially circular state never gets completely drained, which is demonstrated by the black line.



**Figure 5.1:** Probability distribution for a circular Stark state with  $n = 4$  (left panel) and  $n = 8$  (right panel). Left panel: The red line corresponds to  $e_0 = 10^{-6}$ ,  $E_z = 10^{-5}$  and  $\omega = 6 \cdot 10^{-5}$ . These parameters fulfill the conditions for resonance. The black line corresponds to  $e_0 = 10^{-6}$ ,  $E_z = 1.5 \cdot 10^{-5}$  and  $\omega = 6 \cdot 10^{-5}$ . Right panel:  $e_0 = 10^{-6}$ ,  $E_z = 10^{-5}$  and  $\omega = 1.2 \cdot 10^{-5}$  (red line), and  $e_0 = 10^{-6}$ ,  $E_z = 1.5 \cdot 10^{-5}$  and  $\omega = 6 \cdot 10^{-5}$  (black line).

Figure 5.2 shows the time-development of the Stark states of  $n = 8$ . As aforementioned the initial state is a circular state. We see that after the time  $t = 2\pi/\omega_S \approx 2.6e^5$ , the maximum polarized state is reached, after which the system returns to the original state in a periodic pattern.



**Figure 5.2:** Stark state population of the  $n = 8$ -level.

### 5.3 Two Rydberg atoms

The Hamiltonian of a system of two Rydberg atoms, separated a distance  $R$ , in an electric field, is given by

$$\hat{H} = \sum_{i=1,2} \hat{H}_i + \hat{V}(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2) \quad (5.30)$$

where  $\hat{H}_i$  is the Hamiltonian of each atom isolated,

$$\hat{H} = \hat{H}_0 + \mathbf{E}(t) \cdot \hat{r} \quad (5.31)$$

The  $\hat{V}$ -operator is the interaction operator between the atoms, presented in Chapter 4. We can expand the total wavefunction of the system using the eigenstates of each atom, here denoted  $|i\rangle$  and  $|j\rangle$ :

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{i,j} a_{ij}(t) |i\rangle |j\rangle \quad (5.32)$$

In the case of  $R \rightarrow \infty$ , the interaction between the atoms ceases, i.e.  $\hat{V} \rightarrow 0$ , and

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \quad (5.33)$$

Hence we can write the wavefunction as a product of the wavefunctions of each isolated system

$$\Psi = \Psi_1 \cdot \Psi_2 \quad (5.34)$$

By expanding each of these wavefunctions like (5.4)

$$\Psi_1 = \sum_i a'_i(t) |i\rangle \quad , \quad \Psi_2 = \sum_j a'_j(t) |j\rangle \quad (5.35)$$

we see that the probability amplitude of two-electron transitions is just the product of one-electron probability amplitudes

$$a_{ij} = a'_i \cdot a'_j \quad (5.36)$$

For finite  $R$ , on the other hand, the atoms interact with each other, and the TDSE must be solved with the Hamiltonian of equation (5.30). The matrix elements of equation (5.16) becomes

$$\langle i', j' | \widehat{H}_1 + \widehat{H}_2 + \widehat{V}(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2) | i, j \rangle \quad (5.37)$$

The matrix elements

$$\langle i' | \widehat{H}_1 | i \rangle \delta_{j'j} \quad \text{and} \quad \langle j' | \widehat{H}_2 | j \rangle \delta_{i'i} \quad (5.38)$$

can be separated for each of the components of the electric field, giving matrix elements of the form

$$\langle n', l', m' | x | n, l, m \rangle, \quad \langle n', l', m' | y | n, l, m \rangle, \quad \langle n', l', m' | z | n, l, m \rangle \quad (5.39)$$

The  $x, y, z$ -operators obey certain selection rules [23], reducing the number of matrix elements needed to be solved. As an example we see from Ref. [11] that the selection rule for the  $x$ -operator gives the following solutions

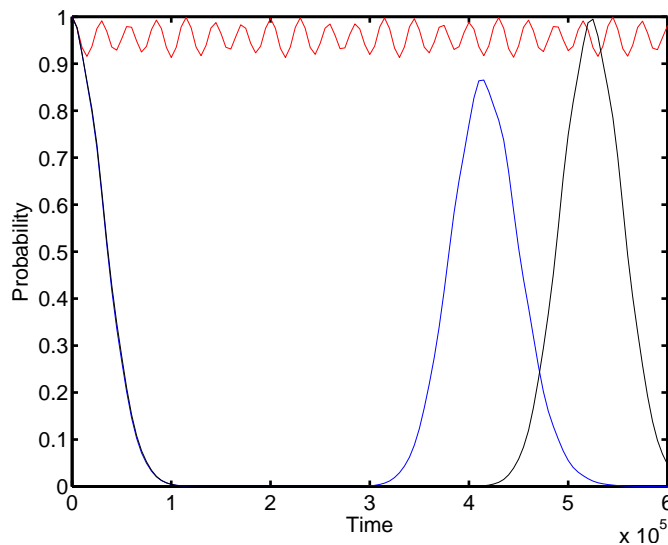
$$\begin{aligned} \langle n, l, m | x | n, l-1, m \pm 1 \rangle &= \pm \frac{3}{2} n \sqrt{\frac{(l \mp m - 1)(l \mp m)(n^2 - l^2)}{4(2l-1)(2l+1)}} \\ \langle n, l, m | x | n, l+1, m \pm 1 \rangle &= \mp \frac{3}{2} n \sqrt{\frac{(l \pm m + 1)(l \pm m + 2)(n^2 - (l+1)^2)}{4(2l+1)(2l+3)}} \end{aligned} \quad (5.40)$$

The matrix elements

$$\langle i' j' | \widehat{V}(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2) | i, j \rangle \quad (5.41)$$

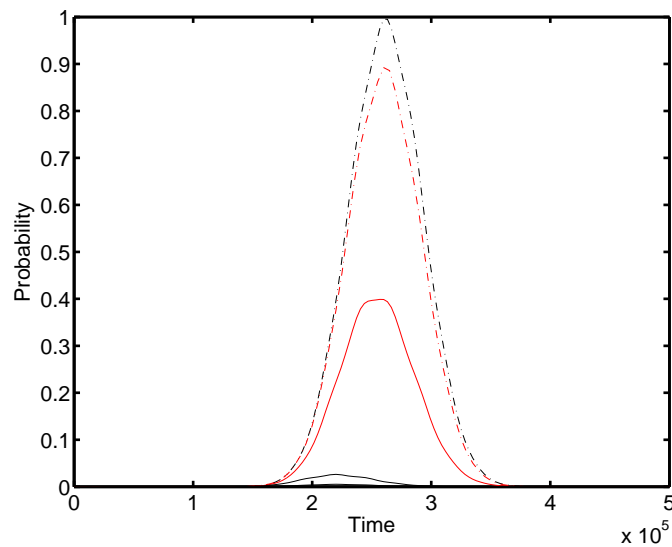
have solutions given in Chapter 4.

Finally we display the probability evolution of the initial state for two-electron transitions. In figure 5.3 we have plotted the probability distribution for the circular state as a function of time, for different values of the interatomic distance  $R$ .



**Figure 5.3:** Probability distribution for the two-electron transitions. Initial state is the circular Stark state of  $n = 8$ . Black line:  $R = 10000$ . Blue line:  $R = 500$ . Red line:  $R = 150$ .

The black line shows the situation that can be compared to  $R \rightarrow \infty$ . The two-electron system behaves as two independent one-electron systems, giving the same dynamics as in figure 5.1. For the blue line the separation between the atoms is reduced, so that the interaction between the atoms can no longer be ignored, and we see that the probability for both electrons to again reach the circular state after some time, is less than 1. In addition the time is shifted towards left, showing that the circular state is repopulated 'sooner' than for the case of independent one-electron transitions. One possible reason for this is that, as figure 5.4 shows, the population of the maximum polarized state becomes less and less for decreasing  $R$ . The dashed line that reaches 1, shows  $\sim R \rightarrow \infty$ . It is clear that when the atoms approach each other, the probability for both electrons to reach the linear Stark states simultaneously, goes to zero. For the case of very small separations, we observe from the red line of figure 5.3 that the two-electron system of initially circular states, stays almost unchanged, i.e. the system is locked in the initial state.



**Figure 5.4:** Population distribution of the maximum polarized Stark states for two-electron transitions for respectively  $R = 10000$  (highest),  $R = 1000$ ,  $R = 700$  and  $R = 500$  (lowest).

We have, in this chapter, demonstrated that intrashell dynamics of two excited atoms show some interesting features. For the smallest interatomic distances the dynamics become locked. For intermediate distances the dynamics are conditional, in the sense that the state evolution of one atom depends on the other. Thus entanglement and strong interatom interaction prohibit both atoms from reaching the "top level" (maximum polarized Stark state), completely in accordance with the Rydberg blockade mechanism involving excitation from the ground state. Unfortunately, the limited time of the present project, has not allowed a full investigation of these initial findings.

# Chapter 6

## Conclusion and outlook

The present thesis has been a theoretical and numerical effort towards the exploration of a so far not discussed subject related to blockade and quantum information based on excited atoms. In Chapter 2 we started with the treatment of a single hydrogen atom using various approaches, and the applications of these in different problems. The transformation between spherical and Stark representation was also presented, since we have used this later in the thesis.

We then applied the theory in calculations of the asymptotic matrix elements for interacting atom and ion, in Chapter 3. The matrix elements of the long-range interaction were calculated for the  $n = 2$  and  $n = 3$  levels, before the Hamiltonian of the system was diagonalized and the eigenstates and eigenvalues were discussed. We saw that the perturbations experienced by the atom from the ion had similarities to those an atom experiences in an external electric field, causing the electronic energy levels to shift upwards and downwards. For increasing energy, the electron cloud was centered 'behind' the atom, for the opposite case the electron was most likely to be found between the atoms.

The long-range atom-atom interaction, studied in Chapter 4, needed some more attention, due to the electron-electron repulsion term. The matrix element of this interaction was calculated using a method derived by Hovland et al. in Ref. [18], before the Hamiltonian again was diagonalized numerically. Energy levels and wavefunctions were discussed as in the previous case.

In the final Chapter systems in time-dependent fields were investigated. We started with the matrix representation of the TDSE, and continued with an example of an analytical solution derived by Forre et al. [22]. Next we described the numerical treatment of the problem, and finally, we displayed the first numerical results showing the population evolution for initially circular Stark states of one- and two-electron problems.

In closing, it is clear that the encouraging results of "Stark-blockade" found in the Chapter 5 should be investigated further. Questions which immediately come to mind are: (i) How does the blockade depend on field parameters and  $n$  level? (ii) To what degree is the total wavefunction entangled and how can it be characterized? (iii) To which degree can the dynamics be explained classically? Furthermore, the study of the orientation of the field-free wavefunctions should be explored.

From the result in Chapter 4, it is clear that the speculations of Flannery et al. [17] concerning a possible formation of a stable Rydberg gas based on a chain of maximum polarized Stark states do not hold, at least for not for  $n = 2$ . The possible generalization of our results should also be pursued.

In the light of this, it seems appropriate to end with another quote by Feynman:  
'We are at the very beginning of time for the human race. It is not unreasonable that we grapple with problems. But there are tens of thousands of years in the future. Our responsibility is to do what we can, learn what we can, improve the solutions, and pass them on.'

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# Appendix A

## Code listing

Program for diagonalizing the Hamiltonian. The program calls other programs that apply the methods for calculations described in this thesis.

```
program diaghh
```

```
Diagonalize the two-electron SCROEDINGER EQUATION in a basis  
of product one-electron states which are hydrogenic one-electron effective charge  
The  $\vec{R}$  is taken to point along the z-axis
```

```
c
```

```
    implicit none  
    integer nstat  
    parameter (nstat=10000)
```

```
c Basis:
```

```
    INTEGER  n1(nstat),l1(nstat),m1(nstat)  
    integer  n2(nstat),l2(nstat),m2(nstat)  
    double precision zeff1(nstat), zeff2(nstat)
```

```
c V(r-R) - expansion:
```

```
    integer cski(100000),ncs  
    double precision csfi(100000),csai(100000)
```

```
c POTENTIAL:
```

```
    double precision Vai(100),Vfi(100)  
    integer Vki(100)
```

```
c LM couplings + facs + lagures:
```

```
    double precision lint(100)  
    integer mval1, lval1(100), asym, maxpow  
    double precision multfact  
    double precision fac,HM(nstat,nstat)
```

```
    integer nr1,nr2
```

```
    double precision tkf1(0:100), tkf2(0:100),alf1,alf2  
    integer tekp1(0:100),tekp2(0:100)
```

```
c R-values:
```

```
    integer nr,kk
```

```

double precision r(100)

c locals:
double precision fourpi, ss, RRR, icount
integer i,j, ij, nV,k,k3,ns,nol, nk, ik

COMMON /CLEBSC/ RRR(180)

integer nmax
parameter(nmax=500000)
double complex HAI(nmax), FHAI(nmax)
double precision HALFI(nmax), FHALFI(nmax)
integer HKF(nmax), FHKF(nmax),HLI(nmax),HMI(nmax),NH
c
fourpi = 4*acos(-1.0d0)
CALL FSTART
call crebs
c
c Read Basis:
read(*,*)ns, asym, maxpow
write(*,*)'Number of basis states: =',ns
write(*,*)'Asymptotics or not: =',asym
write(*,*)'MAxpower: =',maxpow
c write(*,*)'Basis:'
do 90 i = 1,ns
read(*,*)n1(i),l1(i),m1(i),zeff1(i),n2(i),l2(i),m2(i),zeff2(i)
c write(*,*)n1(i),l1(i),m1(i),zeff1(i),n2(i),l2(i),m2(i),zeff2(i)
90 continue
c
c Read Potential (This version assumes nV=1 - Hydrogen):

read(*,*)nV
read(*,*)(Vai(j), j = 1,nV)
read(*,*)(Vfi(j), j = 1,nV)
read(*,*)(Vki(j), j = 1,nV)

c Read number of R's and the R_i:
read(*,*) nr
read(*,*) (R(i), i = 1,nr)
c-----
c Done input. Set up coupling structure for all nonzeroes;
c-----
write(*,*)' ns=',ns
open(10,file='struct.dat')
do i = 1,ns
write(*,*)' doing i = ',i
do j = i,ns
c-----

```

```

c <i1|H1|j1> if i2=j2:
c-----

      if ((n2(i).eq.n2(j)).and.(l2(i).eq.l2(j)).and.
$      (m2(i).eq.m2(j)) .and. (m1(i).eq.m1(j)) ) then

      call mlrang(lval1,mval1,l1(i),m1(i),l1(j),m1(j),nol,lint)
c      if (mval1.eq.0) lint(1)= 1.0/fourpi**0.5d0

      call lgure(zeff1(i),n1(i),l1(i),TKF1,TEKP1,ALF1,NR1)
call lgure(zeff1(j),n1(j),l1(j),TKF2,TEKP2,ALF2,NR2)

      ncs=0
      do k = 1,nol
c FOR each L,M value calculate the two r1 dependent structures
          nk=ncs
          call r1stru(lval1(k),nk,TKF1,TEKP1,ALF1,NR1,
$          TKF2,TEKP2,ALF2,NR2,csai,csfi,cski,ncs)

          multfact=lint(k)/dsqrt((2*lval1(k)+1)/(fourpi))*Vai(1)
c          write(*,*)'i,j,multfact - i2=j2: ',i,j,multfact
          do ik = nk+1,ncs
              csai(ik)=csai(ik)*multfact
          enddo

      enddo

      call comprs(csai,cski,csfi,ncs,asym,maxpow)
      call cprint(csai,cski,csfi,ncs)
c Store result :
      if (ncs. gt. 0) then
c          open(10,file='struct.dat',append)
              write(10,*)i,j,ncs
              write(10,'(100E20.10)')(real(csai(k)),k=1,ncs)
              write(10,'(100I8)')(cski(k),k=1,ncs)
              write(10,'(100E20.10)')(csfi(k),k=1,ncs)
c          close(10)
              endif
          endif
c-----

c <i2|H2|j2> if i1=j1:
c-----

      if ((n1(i).eq.n1(j)).and.(l1(i).eq.l1(j)).and.
$      (m1(i).eq.m1(j)) .and. (m2(i).eq.m2(j))) then

      call mlrang(lval1,mval1,l2(i),m2(i),l2(j),m2(j),nol,lint)
      call lgure(zeff2(i),n2(i),l2(i),TKF1,TEKP1,ALF1,NR1)

```

```

call lgure(zeff2(j),n2(j),l2(j),TKF2,TEKP2,ALF2,NR2)

ncs=0
do k = 1,nol
c FOR each L,M value calculate the two r1 dependent structures

        nk=ncs
        call r1stru(lval1(k),nk,TKF1,TEKP1,ALF1,NR1,
$           TKF2,TEKP2,ALF2,NR2,csai,csfi,cski,ncs)
        multifact=lint(k)/dsqrt((2*lval1(k)+1)/(fourpi))* Vai(1)
c
c R-> -R
        multifact=multifact*(-1)**lval1(k)
c           write(*,*)'i,j, multifact - i1=j1: ',i,j,multifact
        do ik = nk+1,ncs
            csai(ik)=csai(ik)*multifact
        enddo
    enddo

    call comprs(csai,cski,csfi,ncs,asym,maxpow)

        call cprint(csai,cski,csfi,ncs)
c Store result :
        if (ncs .gt. 0) then

            write(10,*)i,j,ncs
            write(10,'(100E20.10)')(real(csai(k)),k=1,ncs)
            write(10,'(100I8)')(cski(k),k=1,ncs)
            write(10,'(100E20.10)')(csfi(k),k=1,ncs)

        endif
    endif
c-----
c <i1,i2|V12|j1j2>:
c-----
        nh=0
        call heidi(zeff1(i),n1(i),l1(i),m1(i),
$           zeff2(i),n2(i),l2(i),m2(i),
$           zeff1(j),n1(j),l1(j),m1(j),
$           zeff2(j),n2(j),l2(j),m2(j),
$           HAI,HKF,HALFI,HLI,HMI,NH,asym,maxpow)

        call hprint(HAI,HKF,HALFI,HLI,HMI,NH)
c
c Multiply last Ylm(R para with z) AND drop R(-1), R(-2) terms):
c
kk=0
do k=1,NH

```

```

if (HMI(k).eq.0) then
  if ( (abs(HALFI(k)).lt.1e-9).and. (HKF(k).lt.-2) ) then
    kk=kk+1
    FHAI(kk) = HAI(k)*dsqrt((2*HLI(k)+1)/(fourpi))
    FHALFI(kk) = -HALFI(k)
    FHKF(kk) = HKF(k)
  endif
endif
enddo

NH=kk
do k = 1,NH
  HAI(k)=FHAI(k)
  HALFI(k)=FHALFI(k)
  HKF(k)= FHKF(k)
enddo

      call hcompr(HAI,HKF,HALFI,NH)

c Store result :
  if (NH .gt. 0) then
c      open(10,file='struct.dat',append)
        write(10,*)i,j,NH
        write(10,'(10E20.10)')(real(HAI(k)),k=1,NH)
        write(10,'(100I8)')(HKF(k),k=1,NH)
        write(10,'(10E20.10)')(HALFI(k),k=1,NH)
c      close(10)
  endif

      enddo
enddo

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
program for plotting of the wavefunctions
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

R=0.25:0.1:25;
nR=size(R); nR=nR(2); Estark=zeros(3,nR);
for i=1:nR
Hamstark=[0 7.35/R(i).^2 63.64/R(i).^3;
          7.35/R(i).^2 -72/R(i).^3 5.20/R(i).^2+701.48/R(i).^4;
          63.64/R(i).^3 5.20/R(i).^2+701.48/R(i).^4 -36/R(i).^3-7290/R(i).^5];

      Estark(:,i)=eig(Hamstark);
end;

```

```

figure(1); plot(R,Estark,'k'); hold on;
set(gca,'fontsize',18);
xlabel('R (a.u.)','fontsize',18)
ylabel('Energy (a.u.)','fontsize',18)
axis([2.5 25 -0.25 0.25])

print -depsc fig4-2.eps

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Plott av egentilstander - asymptotisk:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
i=1;
j=1;

sbf=[];
zz=-12:.6:12;
xx=-12:.6:12;
y=0.00001;

for z=zz
    i=1;
    for x=xx
        r=sqrt(x^2+y^2+z^2);
        tetha=acos(z/r);
        if x>=0
            fi=0;
        else
            fi=pi;
        end

        n=2; l=0; m=0;
        funk=psi(n,l,m,r,tetha,fi);
        sbf(i,j)=r^2.*abs(funk)^2;
        i=i+1;
    end
    j=j+1;
end
figure(2)
pcolor(zz,xx,sbf); colormap hot; shading interp;
set(gca,'fontsize',16);
xlabel('z (a.u.)','fontsize',16)
ylabel('x (a.u.)','fontsize',16)
title('2s2s','fontsize',16)
axis square;

```

