University of Crete

Bachelor's Thesis

AMO Physics

Calculations of resonant and nonresonant dipole-dipole interactions between Rydberg atoms

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Chapter 1

Introduction

Highly excited electronic states of atoms are called Rydberg states. Atoms in Rydberg states with large principal quantum number $n \gg 1$ exhibit many remarkable features [1]. These include long lifetime that scale with the principal quantum number as $\tau \propto n^{-3}$, and giant polarizability which stems from the large size $\sim a_0 n^2$ of the Rydberg electron orbit. The resulting strong, long-range, resonant and nonresonant dipole-dipole interactions between the atoms can suppress multiple Rydberg excitations within a certain blockade distance [2, 3, 4, 5]. In combination with laser and microwave field manipulation of atomic states, these interactions form the basis for quantum information processing [4] with individual atoms [2, 7, 6, 8] and atomic ensembles [3, 4]. Furthermore, cold atoms excited to Rydberg states represent a flexible platform to simulate [9] and study few-body [10, 11, 12, 13, 14] and many-body physics [15, 16, 17, 18, 22, 19, 20, 21, 23, 24, 25, 26, 27, 28].

As mentioned above, the large size of the Rydberg electron orbit $\sim a_0 n^2$ and its weak binding to the ionic core makes the Rydberg atoms easily polarizable. This leads to strong, long range interactions between the Rydberg atoms, which is primarily due to the strong dipole moment of the transitions between the atomic Rydberg states. The main purpose of this thesis is to study dipole-dipole interactions between pairs of Rydberg atoms. To that end, we first consider in Chapter 2 the Rydberg electron wavefunction of the Hydrogen-like atoms, i.e. atoms with a singe valence electron. After a brief review of the Bohr model, we outline the exact quantum mechanical solution of the stationary Schöringer equation for a one-electron atom. In Chapter 3 we consider dipole transitions between such Hydrogenic eigenstates of the atoms. Following Ref. [29, 30], we present the semiclassical calculations of the radial transition matrix elements between the Rydberg eigenstates which greatly simplifies the calculation of the dipole moments of the atoms. Then in Chapter 4 we discuss the resonant dipole-dipole exchange interaction between pairs of atoms in Rydberg states. Finally, in Chapter 5 we briefly outline the procedure to derive the effective van der Waals interaction between pairs of atoms, which originate from the non-resonant dipole-dipole interactions in the second-order perturbation theory.

Chapter 2

Wavefunction of the Rydberg electron

In this Chapter, we study the Rydberg states of atoms. We start with the description of the Bohr's Model for the atom, then present the Schrödinder equation for the Hydrogen like atom and derive the energies and wavefunctions of the electron on Rydberg orbits.

2.1 Bohr's atomic model

The Bohr model depicts the atom as a small and heavy, positively charged nucleus surrounded by electrons that travel around it, in circular orbits. It is similar in structure to the Solar System, but instead of gravitation, the attraction of electron to the nucleus is provided by the electrostatic force. It is a relatively primitive model of the hydrogen atom.

2.1.1 Brief history

Rutherford experimentally established that atoms consist of a diffuse cloud of negatively charged electrons surrounding a small, dense, positively charged nucleus. The laws of classical mechanics and Maxwell equations for accelerated charge require that the electron emits electromagnetic radiation while orbiting a nucleus. It would then rapidly spiral inwards collapsing into the nucleus (in time $\tau \sim 16ps$) and the emission would rapidly increase in frequency, as the electron orbit becomes smaller and the velocity and thereby acceleration quickly increases, producing a continuous chirp in frequency of electromagnetic radiation. This model thus predicts that atoms are unstable.

Bohr proposed a model to overcome this difficulty. In this model, electrons can only be in certain "stationary orbits", at a certain discrete set of distances from the nucleus. The stationary orbits are called energy shells or energy levels, because they are associated with definite energies. In these orbits the electron's acceleration does not result in radiation and energy loss as required by classical electromagnetism. This model was based on Planck's quantum theory of radiation. The electrons can only gain and lose energy by jumping from one allowed orbit to another, absorbing or emitting electromagnetic radiation with a frequency ν determined by the energy difference of the levels according to the Planck relation $\Delta E = E_2 - E_1 = h/\nu$, where h is Planck's constant.

Bohr could determine the energy spacing between electron levels and come up with a correct quantum rule: the angular momentum L is restricted to integer multiples of the reduced Plank constant $\hbar = h/2\pi$ as $L = n\hbar$ with $n = 1, 2, 3, \ldots$ Bohr radius is the smallest possible orbital radius of $a_0 = 0.0529$ nm for $n = 1$, and the electron can get no closer to the proton. Starting from the angular momentum quantum rule, Bohr was able to calculate the energies of the allowed orbits of the Hydrogen atom and other hydrogen-like atoms and ions.

Bohr's condition $L = n\hbar$ was later reinterpreted by de Broglie as a standing wave condition: the electron is described by a wave and an integer number of wavelengths must fit along the circumference of the electron's orbit $n\lambda = 2\pi r$. Substituting de Broglie's wavelength $\lambda = h/p$ for an electron with momentum p reproduces Bohr's rule. Bohr justified his rule by appealing to the correspondence principle, without providing any sort of wave interpretation.

After Heisenberg proposed quantum mechanics, Bohr's model was extended into a more accurate model of electron motion. Schrödinger independently discovered Wave mechanics and employed de Broglie's matter waves to advance beyond the Bohr model. He sought wave solutions $|\Psi(r)\rangle$ of a three-dimensional wave equation describing electrons that were constrained to move about the nucleus of a hydrogen-like atom, by being trapped by the potential of the positive nuclear charge. Schrödinger equation incorporates the Uncertainty principle and it tells us about the region where the electrons are likely to be found.

Bohr's theory is not quantum mechanical but Schrödinger's is. The potential energy function and the energy level solutions are the same for both though. The key difference is that in Bohr's theory the electron is a point, while in the Schrödinger model, the electron is governed by a probability distribution permitting it to be at almost all locations in space, some being much more likely than others. The Schrödinger model also calculates the angular momentum correctly and leads to the angular momentum degeneracy of the energy states. A similarity between the results is that the Bohr model orbital radii are equal to the mean radius, $\langle \Psi \mid r \mid \Psi \rangle$, values of some of the angular momentum states.

The only atoms for which the Schrödinger equation has an analytic solution are the one electron atoms i.e. H, He^{+}, Li^{2+}.. That's because with more than one electron the forces between electrons make the equation too hard to solve analytically.

Bohr model gives almost exact results only for a system where two charged points orbit each other at speeds much less than that of light. This not only includes one-electron systems such as the hydrogen atom, singly ionized helium, and doubly ionized lithium, but also positronium and Rydberg states of any atom where one electron is far away from the core consisting of the nucleus and all the other tightly bound electrons orbiting it.

2.1.2 Calculation of the Bohr orbits

The electron is held in a circular orbit by electrostatic attraction to the nucleus, so the centrifugal force is equal to the Coulomb force: $\dfrac{m_e v^2}{r} = \dfrac{Z k_e e^2}{r^2}$ where m_e is the electron's mass, e is the charge of the electron, $k_e = \frac{1}{4\pi\varepsilon_0}$ is Coulomb's constant and Z is the number of protons in the nucleus. We can use the reduced mass of electron and nucleus, $m_{\text{red}} = \dfrac{m_e m_n}{m_e + m_n}$. However, m_{red} and m_e are very nearly the same, due to the much larger mass of the nucleus, $m_n \gg m_e$. The classical electron's velocity at any radius is obtained as

$$v = \sqrt{\frac{Z k_e e^2}{m_e r}} \tag{2.1}$$

and electron's total energy is

$$E = \frac{1}{2} m_e v^2 - \frac{Z k_e e^2}{r} = -\frac{Z k_e e^2}{2r} \tag{2.2}$$

The total energy is negative and inversely proportional to r, meaning that it takes energy to pull the orbiting electron away from the proton. For infinite values of r the energy is zero, corresponding to a motionless electron infinitely far from the proton. The total energy is half the potential energy, which is also true for noncircular orbits by the Virial theorem.

The angular momentum $L = m_e vr$ is an integer multiple of $\hbar$, $m_e vr = n\hbar$, where substituting the expression for the velocity gives an equation for r in terms of n: $m_e\sqrt{\frac{k_e Ze^2}{m_e r}}r = n\hbar$. Thus the allowed orbit radius at any n is

$$r_n = \frac{n^2\hbar^2}{Zk_e e^2 m_e} \tag{2.3}$$

Bohr radius is the smallest possible value of r in the hydrogen atom ($Z = 1$).

Nowadays we replace the idea of the semi-classical "orbit" of Bohr with the fully quantum mechanical notion of orbitals or electron clouds, which give a probability distribution for the position of the electron around the nucleus, but do not imply that the electron is moving in any classical sense. Orbitals for the hydrogen atom are the solutions of the Schrodinger equation with the Coulomb potential energy. The absolute value square of the wave function $|\Psi(x, y, z)|^2$ gives the probability density to find the electron at a specific position (x, y, z) and needs to be integrated over a space interval to give the actual probability of finding the electron in that area of space. Orbitals have different shapes for different angular momenta.

2.1.3 Energy Levels

The energy of the nth state for the hydrogen-like atom is determined by r and n:

$$E = \frac{Zk_e e^2}{2r_n} = -\frac{Z^2(k_e e^2)^2 m_e}{2\hbar^2 n^2} \simeq -\frac{13.6Z^2}{n^2}eV. \tag{2.4}$$

In the lowest energy level, $n = 1$, of the hydrogen atom, $Z = 1$, an electron has about 13.6 eV less energy than a motionless electron infinitely far from the nucleus. The larger values of n give the binding energies of a highly excited atom with one electron in a large circular orbit around the rest of the atom.

The Rydberg constant is the combination of natural constants in the energy formula

$$R_E = \frac{(k_e e^2)^2 m_e}{2\hbar^2} = \frac{1}{2}(m_e c^2)\alpha^2 \tag{2.5}$$

with $m_e c^2$ the electron's rest mass and $\alpha = \frac{k_e e^2}{\hbar c} \simeq \frac{1}{137}$ the fine structure constant. The energy levels of hydrogen are then $E_n = -\frac{R_E}{n^2}$.

The actual energy levels for multielectron atoms cannot be obtained analytically because the electrons are not only affected by the nucleus but also interact with each other via the Coulomb force.

When the electron in an atom gets excited from its original energy level to a higher one, it then jumps back to the original level, resulting in a photon emission with energy $E = hc/\lambda$. The energy of a photon emitted by a hydrogen atom is given by the difference of two hydrogen energy levels: $E = E_i - E_f = R_E\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$, where n_f is the final energy level, and n_i is the initial energy level. This is known as the Rydberg formula. Bohr's derivation of the Rydberg constant was one reason that his model was immediately accepted.

The Rydberg equation is an approximation because it does not take into account the electronic fine structure which originated from the spin-orbit interaction of the electron. Rydberg's formula only works if the electron is transferred between two different shells, and returns a value of 0 if used for different orbitals in the same shell. However it's a pretty good approximation. It works because for a one electron atom the energy of the orbitals ignoring fine structure is proportional to $\frac{1}{n^2}$. The Rydberg formula only works where the potential energy of the electron varies as r^{-1}.

2.1.4 Bohr's Model for heavier atoms

Bohr extended the model of hydrogen to give an approximate model for heavier atoms, where each discrete orbit could only hold a certain number of electrons, giving the atom a shell structure in which each shell corresponds to a Bohr orbit. This model is even more approximate than the model of hydrogen, because it treats the electrons in each shell as non-interacting. The repulsions of electrons are taken into account somewhat by the phenomenon of screening, where the electrons in outer orbits do not only orbit the nucleus, but they also move around the inner electrons, so the effective charge Z that they feel is reduced by the number of the electrons in the inner orbit. The screened Coulomb potential is expressed as $V(r) = Ze\frac{e^{-qr}}{r}$, where r is the distance to the nucleus of the embedded ion, q is the screening parameter that determines the range of the potential, and effective charge Z is usually noninteger.

Bohr model just includes the angular momentum of supposedly orbiting electrons discretized. The model says nothing of the angular momentum of radiation. As far as Bohr was concerned, there was no such thing as angular momentum selection rules for radiative transitions. The Bohr model was extended by Sommerfeld who was able to predict all the Hydrogen atom quantum numbers. This theory is referred by the name "Old quantum theory". The basic idea of this theory is that closed classical trajectories lead to discrete quantum numbers. The quantization is obtained through modified condition, now known by the name "Bohr-Sommerfeld condition". The application of this theory becomes difficult for many electron atoms where exact classical solutions are not available. This theory was abandoned after the discovery of the Schrödinger equation which gave precise predictions for many electron atoms spectra. The old quantum theory is only an approximation to the correct quantum theory which is valid in general for large quantum numbers.

Finally, we conclude that the Bohr atom physically corresponds most closely to the Rydberg atoms, where the high n states are called Rydberg states and in these states the binding energy of the valence electron decreases as $\sim n^{-2}$. In other words, in Rydberg atoms the valence electron is in a large loosely bound orbit and spends most of its time near its classical outer turning point, defining the classically allowed region as the one between the inner and outer turning points.

2.2 Rydberg atom Wavefunction

The wavefunction of the valence electron of the Rydberg atom is described by the Schrödinger equation for the Hydrogen atom. We thus start by describing the Hydrogen atom.

The Hamiltonian for an electron subjected to a central potential $V(r) \sim \frac{1}{r}$ is

$$\hat{H} = -\frac{\hbar^2 \nabla^2}{2m_e} + V(r). \tag{2.6}$$

The central potential depends only on the length of the distance, $r = |\boldsymbol{r}|$, so it is spherically symmetric, meaning that it has no angular dependence.

If we express ∇^2 in spherical coordinates, the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r) \tag{2.7}$$

The angular momentum operator is defined as $\boldsymbol{L} = -i\hbar\boldsymbol{r}\times\boldsymbol{\nabla}$, with the components

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\varphi}$$

$$\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

It is easy to see that $[\hat{\boldsymbol{L}}^2, \hat{L}_z] = 0$ but $[\hat{L}_i, \hat{L}_j] \neq 0$.

Using the expression for $\hat{\boldsymbol{L}}^2$ in equation (2.7) we obtain

$$\hat{H} = \frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\boldsymbol{L^2}}{\hbar^2 r^2}\right] + V(r) \tag{2.8}$$

Due to the spherical symmetry, the angular momentum operator commutes with the Hamiltonian, $[\hat{\boldsymbol{L}}^2, \hat{L}_z] = [\hat{H}, \hat{\boldsymbol{L}}^2] = [\hat{H}, \hat{L}_z] = 0$, so the operators $\hat{H}, \hat{\boldsymbol{L}}^2, \hat{L}_z$ share the same eigenvalues. The eigenstates of the operators $\{\hat{\boldsymbol{L}}^2,\hat{L}_z\}$ are the spherical harmonics Y_l^m and we will describe their properties later.

The stationary Schrödinger equation for an electron (setting $\hbar = 1$) is

$$\left[\frac{-\nabla^2}{2m_e} + V(r)\right]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi) \tag{2.9}$$

Because the central potential $V(r)$ has no angular dependence, the wavefunction $\Psi(r,\theta,\phi)$ is separable into the radial and angular parts, so the solution can be written as a separation of variables.

$$\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{2.10}$$

with $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ having no radial dependence. Substituting $\Psi(r,\theta,\phi)$ into the Schrödinger equation (2.9), we obtain three separate differential equations for the electron

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{l(l+1)}{r^2}R^2 - \frac{2m_e}{\hbar^2}V(r)R + \frac{2m_eE}{\hbar^2}R = 0 \tag{2.11}$$

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

$$\frac{d^2\Phi}{d\varphi} = -m^2\Phi \tag{2.13}$$

where m^2 and $l(l+1)$ are separation constants with physical significance discussed below. Irrespective of the particular form of $V(r)$, as long as it is central, the resulting solutions for $\Phi(\phi)$ and $\Theta(\theta)$ are always the same.

$$\Phi_m = \frac{e^{im\phi}}{\sqrt{2\pi}} \tag{2.14}$$

$$\Theta_l^m = -1^m\left[\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right]^{/2} P_l^m(\cos\theta) \tag{2.15}$$

where $P_l^m(x)$ are the associated Legendre polynomials (polynomials of degree l) with $|m| \leq l$, and m, l integers. The functions $Y_l^m(\theta, \phi) = \Phi_m \Theta_l^m$ are known as spherical harmonics.

The solutions of the equation for the radial part depends on the form of $V(r)$ and on the angular momentum l. The radial equation can be simplified introducing a radial function $u_{E,l}(r) = rR_{E,l}(r)$, then the new radial equation is expressed as

$$\left[-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2m_e r^2} + V(r)\right] u_{E,l}(r) = E u_{E,l}(r) \tag{2.16}$$

This equation is equivalent to the 1-D Schrödinger equation, assuming the effective potential that includes the repulsive term of the angular momentum

$$V_{\text{eff}}(r) = V(r) + \frac{l(l+1)\hbar^2}{2m_e r^2} \tag{2.17}$$

Thus the radial equation takes the final form

$$\frac{d^2u(r)}{dr^2} + \frac{2m_e}{\hbar^2}[E - V_{\text{eff}}(r)]u(r) = 0 \tag{2.18}$$

We notice that for large values of r, V_{eff} approaches zero, resulting in the differential equation

$$\frac{d^2u(r)}{dr^2} + \frac{2m_e E u(r)}{\hbar^2} = 0 \tag{2.19}$$

which indicates that every positive energy eigenvalue is an acceptable solution, leading to a continuous spectrum of eigenvalues.

For negative energy eigenvalues we have a discrete spectrum. For convenience we introduce the variables

$$\rho = \sqrt{-\frac{8m_e E}{\hbar^2}}r \tag{2.20}$$

and

$$\lambda = \frac{Ze^2}{4\pi\varepsilon_0\hbar}\sqrt{-\frac{m_e}{2E}} \tag{2.21}$$

so the Schrödinger radial equation becomes

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right] u_{E,l} = 0. \tag{2.22}$$

First, we search for the solutions of the asymptotic behavior of $u_{E,l}(\rho)$, i.e, for $\rho \to \infty$. The $1/\rho^2$ and $1/\rho$ terms tend to zero, so the above equation becomes

$$\left[\frac{d^2}{d\rho^2} - \frac{1}{4}\right] u_{E,l}(\rho) = 0 \tag{2.23}$$

whose solutions are $e^{\pm\rho/2}$, accepting only the $u_{E,l}(\rho) \sim e^{-\rho/2}$ as they have to be square integrable.

Thus we can search for a general solution of the total wavefunction of the form

$$u_{E,l}(\rho) = e^{-\frac{\rho}{2}} f(\rho) \tag{2.24}$$

so the equation (2.22) becomes

$$\left[\frac{d^2}{d\rho^2} - \frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}\right] f(\rho) = 0 \tag{2.25}$$

We expanded $f(\rho)$ in power-series as $f(\rho) = \rho^{(l+1)} g(\rho)$ with

$$g(\rho) = \sum_{k=0}^{\infty} c_k \rho^k, c_k \neq 0$$

using the fact that $u_{E,l}(\rho) \sim \rho l + 1$ as $\rho \to 0$ and consequently $f(\rho)$ behaves as ρ^{l+1} for small values of ρ in potentials that approach zero faster than r^{-2}. Substituting $f(\rho)$ in the above equation, $g(\rho)$ satisfies the differential equation

$$\left[\rho \frac{d^2}{d\rho^2} + (2l + 2 - \rho)\frac{d}{d\rho} + (\lambda - l - 1)\right] g(\rho) = 0 \tag{2.26}$$

where substituting $g(\rho)$ and setting the proper restriction for the coefficients c_k requiring that the power series terminates at some $k = n_r$ leads to the condition that λ be an integer

$$\lambda = n = n_r + l + 1$$

The energy eigenvalues are then given by

$$E = -\frac{Z^2 e^4 m_e}{2\hbar^2 n^2 (4\pi\varepsilon_0)^2} \tag{2.27}$$

which means that, for a pure Coulomb potential, the eigenvalues depend only on the indices n, not l and m, and coincide with those of Bohr model. This coincidence occurs due to the fact that we have not included relativistic phenomena and phenomena that occur at the atomic core. By convention, the energies are negative, indicating that the electron is bound to the center (nucleus).

The naturally acceptable solution of equation (2.26) for $\lambda = n$ are expressed through the so-called associated Laguerre polynomials $L_n^k(\rho)$. Namely, the total normalized radial wavefunctions of hydrogen-like atom are given by

$$R_{n,l}(r) = \left[\left(\frac{Ze^2 m_{re}}{2n\hbar^2 \pi\varepsilon_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{\frac{1}{2}} e^{-\frac{\rho}{2}} \rho^l L_{n+l}^{2l+1}(\rho) \tag{2.28}$$

where

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n_r} (-1)^{k+1} \frac{\rho^k [(n+l)!]^2}{k!(n_r - k)!(2l+1+k)!} \tag{2.29}$$

For $l \neq 0$ the fact that $R_{n,l} \sim r^l$ for small values of r, results in small values for the wavefunction close to the core. With increasing l the wavefunction at the origin further decreases. This happens because of the repulsive centrifugal potential that doesn't allow the electron to get close to the core. The solutions obey the orthonormality condition

$$\int_0^{\infty} R_{nl}^* R_{n'l'} dr = \delta_{nn'} \delta_{ll'} \tag{2.30}$$

2.2.1 Eigenfunctions of the Hydrogen-like atom

The complete set of eigenfunctions for the Hydrogen-like atom, labeled by the three indices, is

$$\Psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi) \tag{2.31}$$

with the orthonormality condition

$$\int_0^\infty dr \int_0^{2\pi} d\phi \int_0^\pi \sin(\theta) d\theta \Psi^*_{nlm} \Psi_{n'l'm'} = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

The three indices nlm are referred to as quantum numbers of the states of the system. This suggests the more compact ket notation $|nlm\rangle$ for the eigenstates, with the orthonormality condition now reading as

$$\langle nlm|n'l'm'\rangle = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

Since $n > l$ the quantum numbers l and m can have more than one value, as for each value of l there are $(2l-1)$ values for m, we have the case of a set of eigenfunctions separated in subsets with the same eigenvalue (accidental degeneracy). In other words, there are more than one eigenstate with the same energy, so the spectrum is then said to be degenerate. This is due to the spherical symmetry of the system as well as the special form of the Coulomb potential. For a potential which is central but not Coulomb, the degeneracy in m remains, which is a direct consequence of spherical symmetry, but the degeneracy in l is lifted. The degeneracy in m is lifted if the atom is placed in a magnetic field, known as the Zeeman effect, because of which m is also referred to as the magnetic quantum number.

By convention, states with $l = 0, 1, 2, 3, 4, 5, 6, 7, ...$ are denoted by $s, p, d, f, g, h, i, k, ...$ and often the electronic states of the atom are abbreviated as ns, np, etc.

Parity of the wavefunction

The parity operator is defined as $\hat{P}f(\boldsymbol{r}) = f(-\boldsymbol{r})$ where $f(\boldsymbol{r})$ is an arbitrary function.

The eigenvalue equation for the parity operator is $\hat{P}\Psi_\alpha(\boldsymbol{r}) = \alpha\Psi_\alpha(-\boldsymbol{r})$ where its eigenvalues are $\alpha = \pm 1$. For $\alpha = +1$ the corresponding eigenfunction $\Psi_+(\boldsymbol{r})$ is an even function of $\boldsymbol{r}$, while for $\alpha = -1$ the eigenfunction $\Psi_-(\boldsymbol{r})$ is odd.

Regarding the central potentials, the action of the parity operator onto the wavefunction in spherical coordinates (r, θ, ϕ) ($\boldsymbol{r} \to -\boldsymbol{r}$) changes them to $(r, \pi - \theta, \phi + \phi)$, so the Hamiltonian of the central potential doesn't change under this change of constants, resulting to the commutation $[\hat{P}, \hat{H}] = 0$. Hence the parity operator and the Hamiltonian have the same eigenstates. We thus have

$$\hat{P}[R_{n,l}(r)Y_{l,m}(\theta, \phi)] = R_{n,l}(r)Y_{l,m}(\pi - \theta, \phi + \pi) \tag{2.32}$$

where for the spherical harmonics we have

$$Y_{l,m}(\pi - \theta, \phi + \pi) = (-1)^l Y_{l,m}(\theta, \phi) \tag{2.33}$$

leading to

$$\hat{P}\Psi(r, \theta, \phi) = (-1)^l \Psi(r, \theta, \phi) \tag{2.34}$$

from where it is now obvious that the wavefunction Ψ is characterized by the parity of l.

2.2.2 The spin-orbit coupling

The electron has an internal magnetic moment $\boldsymbol{\mu}_e$ connected with its intrinsic spin $\boldsymbol{s}$ through the relation $bm\mu_e = 2\mu_B \boldsymbol{s}$, where $\mu_B = e\hbar/2m_e c$ is a physical constant known as the Bohr magneton. Since the electron carries electric charge, its orbital motion around the nucleus is equivalent to an electric current. An electric current generates a magnetic moment which in this case is called orbital magnetic moment $\boldsymbol{\mu} = \mu_B \boldsymbol{l}$. This magnetic moment interacts with the spin magnetic moment and affects the energies of the atomic levels obtained without consideration of the spin. The energy of interaction, as obtained from the relativistic generalization of the theory, through the Dirac equation, is

$$V = \frac{\hbar^2 Ze^2}{2m_e^2c^2}\frac{\boldsymbol{l}\cdot\boldsymbol{s}}{4\pi\varepsilon_0 r^3} \tag{2.35}$$

with

$$\boldsymbol{l}\cdot\boldsymbol{s} = \frac{j(j+1)-l(l+1)-s(s+1)}{2}$$

We now have two angular momenta, the orbital $\boldsymbol{l}$ and the spin $\boldsymbol{s}$, which are coupled through a mutual interaction. Each of them has its own vector space but a complete description of the atom incorporating both requires the combination (tensor product) of the two spaces. This means that we need to consider states of the form $|nlm_l\rangle\,|sm_s\rangle$ specifying the orbital as well as the spin state, in terms of uncoupled product states.

We consider the vector operator $\boldsymbol{j}=\boldsymbol{l}+\boldsymbol{s}$ resulting from the addition of two vector operators. $\boldsymbol{j}$ is an angular momentum operator which possesses eigenstates of the form $|jm\rangle$. If we combine the entire basis $|lm_l\rangle$ with the basis $|sm_s\rangle$, we obtain a basis for the tensor product space, whose vectors describe both the orbital and the spin state of the system, thus any state of the system could be written as a linear combination of tensor products of the eigenstates of the form $|lm_l\rangle|sm_s\rangle$. Such a basis must be equivalent to the basis of the eigenstates $|j,m\rangle$ containing all eigenstates in this representation, which includes all js resulting from the combination of all ls with s. The two bases are related by a transformation matrix. The quantity j is called total angular momentum and it can take values $\mid l-s\mid \leq j \leq l+s$ in integer steps. Its eigenstates can in general be expressed as

$$|j,m\rangle = \sum_{m_l,m_s} = C^j_{m_l,m_s}|lm_l\rangle|sm_s\rangle \tag{2.36}$$

where the coefficients $C^j_{m_l,m_s} \equiv \langle lm_l;sm_s|j,m\rangle$ are the Clebsch-Gordan coefficients. They are non-zero only for values of m_l and m_s such that $m_l+m_s=m$. Obviously the inverse transformation can also be obtained.

Each atomic state in a one-electron atom is characterized by the total angular momentum j. Each state $|nlm_l\rangle$ of the electron without spin when coupled with the spin states leads to two new states with total angular momenta $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$, with m-values according to the standard rules for angular momentum projection. Thus a state that was labeled as $|nlm_l\rangle$ before, when combined with the electron spin, gives rise to the states labeled as $|nlm_l;l+\dfrac{1}{2},m\rangle$ and $|nlm_l;l-\dfrac{1}{2},m\rangle$.

The principal quantum number n is unaffected by angular momentum.

Since the value of the spin s is always $\frac{1}{2}$, it is often omitted in the notation. For example, a state with $l=0$ (s-state) gives rise to one new state with $j=1/2$, often denoted in the abbreviated notation as $s_{1/2}$. In this notation, the ground state of the Na atom, which has principal quantum number $n=3$, is denoted by $3s_{1/2}$. The first excited state, which has $n=3$ and $l=1$ (p-state), generates two states with $j=1/2$ and $3/2$, denoted by $3p_{1/2}$ and $3p_{3/2}$, respectively.

The energies of the new $|nl_j\rangle$ states are shifted from the position of the energy of the nl state, typically the one with $j=l+1/2$ upwards and $j=l-\dfrac{1}{2}$ downwards. This change of energies, known as the fine structure splitting of the energy levels characterized by the same principal n and orbital l quantum numbers, is due to the interaction between the orbital and spin magnetic moments given by equation (2.35).

The hyperfine interaction couples the total angular momentum of the electron J to that of the nucleus I, further lifting the degeneracy of the states which are split according to the total angular momentum $F = J + I$. For the Rydberg states the hyperfine splitting is typically small, since the electron is far from the core. The hyperfine splitting can thus be neglected, treating Rydberg atoms in the fine-structure basis.

2.2.3 Quantum Defect

The alkali (Rydberg) atoms have one valence electron moving around a center of force determined by the charge of the nucleus, while all of the other electrons form spherically symmetric shells around the nucleus. The closed electron shells screen the nuclear charge and result in an effectively finite size core. The net charge that the outer electron feels is still practically $Z = 1$, but the force, although central, is not a pure Coulomb force. As a result, the radial parts of the wavefunction are now more complicated and the energy eigenvalues depend on n as well as on l.

For the low orbital angular momentum states with $l \leq 3$, the electron orbit is extremely elliptic and can penetrate the closed electron shells. This exposes the valence electron to the unscreened nuclear charge. The inner electrons can also be polarized by the valence electron. These two interactions with the core combine to increase the binding energy of the low-l Rydberg states relative to the equivalent Hydrogenic states. This difference in binding energy is parameterized using the quantum defects δ_l which accounts for the corrections to the Coulomb potential by the closed electron shells surrounding the nucleus.

For $l > 3$ the wavefunction of the valence electron has vanishing amplitude at the origin and the electron sees purely Coulombic core potential. As the result, the quantum defects are zero, and the corresponding states are referred to as the hydrogenic states, which are degenerate for a given n.

The quantum defect δ_l is an empirically observed quantity that depends on the atom as well as on the orbital angular momentum l. The s states have the largest defects as they have a significant core penetration, followed by the p states and the d states. The allowed energy eigenvalues for a non-hydrogenic Rydberg atoms are given by.

$$E = -\frac{R_E}{(n - \delta_l)^2} \tag{2.37}$$

Chapter 3

Electric dipole transitions

In the previous Chapter we discussed the eigenfunctions of the Rydberg electron. Here we will consider electric dipole transitions between the Rydberg states.

3.1 Dipole matrix elements

The non-relativistic Hamiltonian for a one-electron atom in an electromagnetic field bound in a central potential $V(r)$, is given by

$$H = \frac{1}{2m_e}(\boldsymbol{P} - e\boldsymbol{A})^2 + V(\boldsymbol{r}) \tag{3.1}$$

with $\boldsymbol{P} = -i\hbar\boldsymbol{\nabla}$ the momentum operator and $\boldsymbol{A}$ the vector potential of the field at the electrons position $\boldsymbol{r}$. We work in the Coulomb gauge $\boldsymbol{\nabla} \cdot \boldsymbol{A}$ (transversality condition). Then for any function $f(\boldsymbol{r})$ we have

$$[\boldsymbol{P} \cdot \boldsymbol{A} - \boldsymbol{A} \cdot \boldsymbol{P}]f(\boldsymbol{r}) = \frac{\hbar}{i}[f\boldsymbol{\nabla} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{\nabla} f - \boldsymbol{A} \cdot \boldsymbol{\nabla} f] = \frac{\hbar}{i} f\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0$$

leading to $\boldsymbol{P} \cdot \boldsymbol{A} = \boldsymbol{A} \cdot \boldsymbol{P}$. This allows us to write $[\boldsymbol{P} - e\boldsymbol{A}]^2 = \boldsymbol{P}^2 - 2e\boldsymbol{P} \cdot \boldsymbol{A} + e^2\boldsymbol{A}^2$. The Hamiltonian then becomes

$$H = \frac{\boldsymbol{P}^2}{2m} + V(\boldsymbol{r}) - \frac{e}{m_e}\boldsymbol{P} \cdot \boldsymbol{A} + \frac{e^2}{2m_e}\boldsymbol{A}^2 \tag{3.2}$$

The first two terms represent the Hamiltonian of the atom alone H_A, whose eigenstates were discussed in the previous Chapter. The last two terms represent the interaction (coupling) of the atomic electron with the radiation field, V_{AF}. This interaction can be considered as a weak perturbation. In fact it is much smaller than the eigenvalue differences between typical atomic bound states. Moreover, the first term $\sim \boldsymbol{A}$ is much larger than the second term $\sim \boldsymbol{A}^2$. This allows us to neglect the second term in further calculations.

Now we have a perturbation $V_{AF} = -\dfrac{e}{m_e}\boldsymbol{P} \cdot \boldsymbol{A}$ that may drive transitions between the atomic states and we need to calculate the matrix elements of V_{AF} between eigenstates of the unperturbed atomic Hamiltonian H_A. Here the so-called unperturbed system is governed by the Hamiltonian H_A with the stationary states of the Hydrogen-like atom.

From the Maxwell equations for (free) electromagnetic field, we have that $\boldsymbol{A}(\boldsymbol{r}, t)$ can be written as a product of a spatial and a temporal parts (typical separation of variables approach), with the solutions of the spatial part having the form $\exp(\pm i\boldsymbol{k} \cdot \boldsymbol{r})$ and the corresponding solutions of the temporal part have the form $\exp(\mp i\omega t)$ with $\omega = kc$. To account for the vector character of $\boldsymbol{A}$, we consider the solutions $\hat{e}_{\boldsymbol{k}\lambda}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$, where $\hat{e}_{\boldsymbol{k}\lambda}$ are unit vectors, which must be chosen such that the transversal condition $\nabla \cdot \boldsymbol{A} = 0$ is satisfied. This means that for every $\boldsymbol{k}$, we should choose two unit vectors, perpendicular to each other and of course to $\boldsymbol{k}$, labeled as $\hat{e}_{\boldsymbol{k}\lambda}$ with λ assuming the values 1 and 2,

$$\hat{e}_{\boldsymbol{k}\gamma} \cdot \hat{e}_{\boldsymbol{k}\gamma'} = \delta_{\gamma\gamma'}, \quad \boldsymbol{k} \cdot \hat{e}_{\boldsymbol{k}\gamma} = 0 \tag{3.3}$$

These two unit vectors, known as polarization vectors because they represent the polarization properties of the radiation, together with $\boldsymbol{k}$ are usually chosen so as to form a right handed system of orthogonal vectors. The three spatial components $\hat{e}^x_{\boldsymbol{k}\gamma}$, $\hat{e}^y_{\boldsymbol{k}\gamma}$ and $\hat{e}^z_{\boldsymbol{k}\gamma}$ of the polarization vectors satisfy the relation

$$\sum_{\gamma=1,2} \hat{e}^i_{\boldsymbol{k}\gamma} \hat{e}^j_{\boldsymbol{k}\gamma} = \delta_{ij} - \frac{k_i k_j}{\boldsymbol{k}^2}, \quad i, j = x, y, z. \tag{3.4}$$

The vector potential $\boldsymbol{A}(\boldsymbol{r})$ in general depends on r through the expansion in terms of the spatial eigenfunctions $\boldsymbol{u}_{\boldsymbol{k}\gamma}(\boldsymbol{r}) = \hat{e}_{\boldsymbol{k}\gamma} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ as

$$\boldsymbol{A}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\gamma} [A_{\boldsymbol{k},\gamma} \hat{e}_{\boldsymbol{k}\gamma} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + A^*_{\boldsymbol{k}\gamma} \hat{e}_{\boldsymbol{k}\gamma} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}] \tag{3.5}$$

where $A_{\boldsymbol{k},\gamma}(t) = A_{\boldsymbol{k},\gamma} e^{-i\omega_k t}$ with $\omega_k = ck$ being the frequency of the field with corresponding wave vector $\boldsymbol{k}$.

3.1.1 Electric Dipole Approximation

We now expand the term $e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = 1 - i\boldsymbol{k}\cdot\boldsymbol{r} + ...$ in a Taylor series, with $\boldsymbol{k}$ denoting the wavevector of the oscillating electric field, while $\boldsymbol{r}$ represents the distance between the electron and the nucleus of the atom. As long as one is interested in phenomena involving radiation of long wavelength, meaning large compared to the size of the atom $a_0 n^2$, the spatial dependence of the field, when considering its effect on the classical motion of an electron bound to an atom, can be neglected. We thus assume that $r \ll \lambda$ and therefore $\boldsymbol{k}\cdot\boldsymbol{r} \ll 1$, and keep only the first term of the expansion, $e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \simeq 1$ which amounts to the dipole approximation $\boldsymbol{A}(\boldsymbol{r}) \simeq \boldsymbol{A}(0)$.

We proceed now to calculation of the matrix elements of V_{AF} between pairs of atomic eigenstates $|nlm_l\rangle$ and $|n'l'm'_l\rangle$

$$\langle nlm_l|V_{AF}|n'l'm'_l\rangle = -\boldsymbol{A}\frac{e}{m_e}\langle nlm_l|\boldsymbol{P}|n'l'm'_l\rangle \tag{3.6}$$

Since $[V(\boldsymbol{r}), \boldsymbol{r}] = 0$ we have the commutator $[\boldsymbol{r}, H_A] = \frac{i\hbar}{m_e}\boldsymbol{P}$ and we can write for the above matrix element

$$\frac{e}{m_e}\langle nlm_l|\boldsymbol{P}|n'l'm'_l\rangle = -\frac{ie}{\hbar}\langle nlm_l|\boldsymbol{r}H_A - H_A\boldsymbol{r}|n'l'm'_l\rangle = i\omega_{nn'}e\langle nlm_l|\boldsymbol{r}|n'l'm'_l\rangle \tag{3.7}$$

where $\omega_{nn'} = \dfrac{E_n - E_{n'}}{\hbar}$ is the frequency of the atomic transition $|n'l'm'_l\rangle \longrightarrow |nlm_l\rangle$. For a monochromatic field of frequency $\omega \simeq \omega_{nn'}$, the electric field can be expressed through the vector potential as $\boldsymbol{E} = i\omega\boldsymbol{A}$. The atom-field interaction then can be cast as $V_{AF} \equiv -e\boldsymbol{r}\cdot\boldsymbol{E}$ which looks exactly like the classical expression for the dipole in an electric field. Therefore the atomic operator $\boldsymbol{p} = e\boldsymbol{r}$ is often referred to as the dipole moment operator and transitions involving this operator as dipole transitions. The matrix elements of the dipole operator are $\langle nlm|\boldsymbol{p}|n'l'm'\rangle = e\langle nlm \mid \boldsymbol{r} \mid n'l'm'\rangle$.

The scalar product $\boldsymbol{E}\cdot\boldsymbol{r}$ of the vectors $\boldsymbol{E} = E\hat{\varepsilon}$ and $\boldsymbol{r} = r\hat{r}$ can be expanded as

$$\boldsymbol{E}\cdot\boldsymbol{r} = E\sum_{q=-1}^{1}(-1)^q \varepsilon_q r_{-q} \tag{3.8}$$

where the spherical components of the vectors are related to their Cartesian components via

$$\begin{aligned} \varepsilon_1 &= -\frac{1}{\sqrt{2}}(\varepsilon_x + i\varepsilon_y) \\ \varepsilon_0 &= \varepsilon_z \\ \varepsilon_{-1} &= \frac{1}{\sqrt{2}}(\varepsilon_x - i\varepsilon_y) \end{aligned}$$

and

$$r_1 = -\frac{1}{\sqrt{2}}(x+iy) = -r\frac{1}{\sqrt{2}}\sin\theta e^{i\phi} = r\sqrt{\frac{4\pi}{3}}Y_{1,1}(\theta,\phi) \tag{3.9}$$

$$r_0 = z = r\cos\theta = r\sqrt{\frac{4\pi}{3}}Y_{1,0}(\theta,\phi) \tag{3.10}$$

$$r_{-1} = \frac{1}{\sqrt{2}}(x-iy) = -r\frac{1}{\sqrt{2}}\sin\theta e^{-i\phi} = r\sqrt{\frac{4\pi}{3}}Y_{1,-1}(\theta,\phi) \tag{3.11}$$

with the z axis taken along the linear polarization direction of the field. We thus have

$$\hat{\varepsilon}\cdot\hat{r} = \varepsilon_x \sin\theta\cos\phi + \varepsilon_y \sin\theta\sin\phi + \varepsilon_z\cos\theta = \sqrt{\frac{4\pi}{3}}\left(\varepsilon_z Y_{10} + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{11} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{1-1}\right)$$

The transition matrix elements are

$$-e\langle lm_l|\boldsymbol{E}\cdot\boldsymbol{r}|l'm_l'\rangle = -Ee\langle lm_l|\hat{\varepsilon}\cdot\boldsymbol{r}|l'm_{l'}\rangle \tag{3.12}$$

where

$$\langle nlm_l|\hat{\varepsilon}\cdot\boldsymbol{r}|n'l'm_l'\rangle = \int_0^\infty r^3 dr R_{nl}^* R_{n'l'}\int d\Omega Y_{lm}^*\hat{\varepsilon}\cdot\hat{r}Y_{l'm'} =$$

$$\int_0^\infty r^3 dr R_{nl}^* R_{n'l'}\int d\Omega Y_{lm}^* Y_{l'm'}\sqrt{\frac{4\pi}{3}}\left(\varepsilon_z Y_{10} + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{11} + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y_{1-1}\right) \tag{3.13}$$

We see that calculation of the dipole transition matrix elements reduces to the calculation of the radial dipole matrix element and the angular dependent matrix elements. For the latter, we can use Wigner-Eckart theorem as we will explain below.

3.1.2 Dipole transitions

There are three types of transitions commonly observed in atomic systems: the electric dipole (E1), the magnetic dipole (M1) and the electric quadrupole (E2) transitions. Of these, the electric dipole transition is by far the most common and strongest, therefore we neglect the other transitions in this thesis.

The transition dipole moment is a vector that quantifies the direction and magnitude of the electron cloud displacement. The interaction strength of an atom with a photon is proportional to the scalar product of the transition dipole moment and the photon polarization.

The transition amplitude for a dipole transition is proportional to the matrix element $\langle nlm|V_{AF}|n'l'm'\rangle$. It is not necessary to calculate this matrix element for all the possible states because most of them will be zero. That is why instead we usually determine which ones are non-zero, and then calculate the non-zero matrix elements with the aid of the Wigner-Eckart theorem.

Selection rules

We have three parts of the matrix elements to consider: the wavefunctions of the initial and final states and r, which is a function with odd parity. The integral represented by the matrix element represents a volume integration over 4π. Thus, if the integrand is odd with respect to inversion, the matrix element will be identically zero. In this way we can construct the selection rules for the allowed dipole transitions. Thus, the first requirement for a non-zero dipole transition matrix element is that $\langle nlm|$ and $|n'l'm'\rangle$ have opposite parity, which is defined by the quantum number l. Consequently in order to have non-zero matrix elements we must have $\Delta l = \pm 1$.

The matrix elements do not involve the principal quantum number n, thus there are no restrictions on n.

We will develop the procedure that gives us the selection rule later in this chapter.

3.2 Calculation of the radial matrix elements for bound-bound transitions between Rydberg states

We begin with the calculation of the radial transition matrix elements of the dipole transitions. Exact calculation of the dipole matrix elements for the atomic transitions are usually time consuming and in some cases involve certain difficulties, especially between highly-excited states. Therefore methods have been developed for simplified but accurate calculations of the dipole matrix elements. We follow here the method of Ref. [29].

3.2.1 Coulomb and semiclassical approximation

In non-hydrogenic atoms, the Coulomb approximation is often used for the calculation of the radial matrix elements, i.e. the radial integrals of bound-bound dipole interactions. The Coulomb approximation assumes that the main contribution to the radial integral comes from region $r > r_0$ where the interaction between the valence electron and the core can be approximately considered as a Coulomb one, with $r_0 \sim a_0$ the core radius. This approximation works very well for Rydberg states with high principal quantum number $n \gg 1$ as the Rydberg electron orbit has a large size $r \sim n^2 a_0 \gg r_0$ and thus the Rydberg electron sees a nearly point charge of the core.

Further simplification comes from the semiclassical approximation treating the Rydberg electron as a classical particle on a Bohr orbit in a Coulomb potential of the core. The results of semi-classical calculations can be improved by choosing a special mean value of the effective quantum numbers $\nu \gg 1$ involved. Under these approximations, the radial wavefunction for the electron in Rydberg state $|nl\rangle$ takes a relatively simple form

$$R_{nl}(r) = \frac{A \cos \Phi_{\nu l}}{r\sqrt{p_{\nu l}(r)}} \tag{3.14}$$

where A is a normalization factor,

$$\Phi_{nl}(r) = \int_{\alpha}^{r} p_{\nu l}(r')dr' - \frac{\pi}{4} + \mu \tag{3.15}$$

and

$$p_{\nu l}(r) = \sqrt{-\frac{Z^2}{\nu^2} + \frac{2Z}{r} - \frac{\lambda^2}{r^2}} \tag{3.16}$$

Here α is the left-hand classical turning point in the Coulomb potential ($p_{\nu l}(\alpha) = 0$). A classical turning point is the point where the system's total energy E equals the potential energy V and the region past this point is classically forbidden. μ is the non-Coulomb part of the phase shift, that after the Bohr-Sommerfeld quantization rule becomes $\delta = \pi\mu$, with $\mu = n - \nu$ being is the quantum defect. In light atoms the quantum defects are considerable only for $l \leq 3$ and are zero for $l > 3$ because the classically accessible region and the non-Coulomb region do not overlap ($r_0 < \alpha$) due the strong centrifugal potential, so the core potential is purely Coulombic. The normalization factor for $\nu \gg l$ reduces to $A = \sqrt{\dfrac{2Z^2}{\pi\nu^3}}$ with Z the core charge.

Thus we restrict ourselves to the case $\nu, \nu' \gg l$, where the integral for radial matrix elements in equation (3.13)

$$R_{\nu l}^{\nu' l'} = \int_0^\infty r^3 dr R_{nl}^* R_{n'l'} = \frac{AA'}{2} \int [\cos(\Phi^{\nu l} - \Phi_{\nu' l'}) + \cos(\Phi^{\nu l} + \Phi_{\nu' l'})] \frac{r dr}{\sqrt{p_{\nu l}(r) p_{\nu' l'}(r)}} \tag{3.17}$$

where to ensure that the radial integral is not small, we have to assume that νl and $\nu' l'$ states are closely spaced, ending up with the restrictions $|\Phi_{\nu l} - \Phi_{\nu' l'}| \ll \Phi_{\nu l}$ and $|p_{\nu l}^2 - p_{\nu' l'}^2| \ll p_{\nu l}^2$. We then obtain

$$R_{\nu l}^{\nu' l'} = \frac{AA'}{2} \int_{\alpha_c}^{b_c} \cos\left[\int_{\alpha_c}^{r} \left(\omega - \frac{\lambda'^2 - \lambda^2}{2r'^2} \right) \frac{dr'}{p_{\nu_c l_c}(r)} - \pi\Delta\nu \right] \frac{r dr}{p_{\nu_c l_c}(r)} \tag{3.18}$$

where $\omega = \dfrac{Z^2}{2} \dfrac{\nu'^2 - \nu^2}{(\nu\nu')^2}$ and b is the right-hand turning point.

We introduce the mean values $\nu_c = \left(\dfrac{2\nu^2\nu'^2}{\nu + \nu'} \right)^{\frac{1}{3}}$ and $l_c = \dfrac{1}{2}(l + l')$, which leads to the orbital moment $\lambda_c = \dfrac{1}{2} + l_c = \dfrac{1}{2}(\lambda + \lambda')$, where $\Delta\lambda = \lambda' - \lambda = \pm 1$ because $\Delta l = \pm 1$.

We replace r in the above radial expression with $r = \dfrac{\nu_c^2}{Z}(1 - \varepsilon \cos\xi)$ where $\varepsilon = \sqrt{1 - (\lambda_c^2)/\nu_c^2}$ is the eccentricity of the classical elliptic orbit of the electron with energy $E = -Z^2/2\nu_c^2$. Finally after integration by parts we obtain

$$R_{\nu l}^{\nu' l'} = \frac{Z\nu_c^2}{\omega(\nu\nu')^{3/2}} [U_\gamma(\varepsilon\gamma) \cos \pi\Delta\nu + V_\gamma(\varepsilon\gamma) \sin \pi\Delta\nu + W_\gamma] \tag{3.19}$$

where $\gamma = \nu^3\omega/Z^2$

$$U_\gamma(\psi) = J'_\gamma(\psi) + \Delta\lambda \frac{(1-\varepsilon^2)^{1/2}}{\varepsilon} J_\gamma(\psi)$$

$$V_\gamma(\psi) = E'_\gamma(\psi) + \Delta\lambda \frac{(1-\varepsilon^2)^{1/2}}{\varepsilon} \left(E_\gamma(\psi) - \frac{1}{\pi\gamma} \right) + \frac{1-\varepsilon}{\pi}$$

$$W_\gamma = \frac{\sin[\pi(\Delta\nu - \gamma)]}{\pi\gamma} \left(\gamma(1+\varepsilon) + \Delta\lambda \frac{\sqrt{1-\varepsilon^2}}{\varepsilon} \right)$$

with $J_\gamma(\psi)$ the Anger function and $E_\gamma(\psi)$ the Weber function and their derivatives.
For the case of $\Delta\nu \equiv \nu' - \nu \ll \nu$, we have $\omega = Z^2\Delta\nu/\nu_c^3$ for any definiton of ν_c and thus $\Delta\nu = \gamma$ and $W = 0$.

Thus we have

$$R_{\nu l}^{\nu' l'} = \frac{Z\nu_c^2}{\omega(\nu\nu')^{3/2}} [U_{\Delta\nu}(\varepsilon\Delta\nu) \cos \pi\Delta\nu + V_{\Delta\nu}(\varepsilon\Delta\nu) \sin \pi\Delta\nu] \tag{3.20}$$

This equation is valid when the states are close, $\omega \leq \dfrac{Z^2}{\lambda_c^3} \iff \nu \geq \lambda_c^{3/2}$. This implies that the main contribution to the integral comes from the region $r \sim p = (Z/\omega^2)^{1/3}$ which provides the condition of validity of Coulomb approximation ($p > r_0$) with

$$\omega < (Z/r_0^3)^{1/2} \iff \omega \leq \frac{Z^2}{\lambda_0^3} \tag{3.21}$$

with λ_0 corresponding to $\mu = 0$. For large λ the classical electron cannot penetrate into the non-Coulomb region due to the strong centrifugal potential ($r_0 < \alpha \simeq \lambda^2/2Z$) and so μ reduces to zero. That is why the expression for $R^{\nu\ell}_{\nu\ell}$ is applicable provided the Coulomb approximation is valid.

To conclude, using the semi-classical radial wavefunction and considering the case $\Delta\nu \ll \nu$, we end up with the expression (3.20) which in fact is also valid for $\Delta\nu > \nu$ and $\Delta\nu \sim \nu$, as described thoroughly in Ref. [29]. In Figure 3.1 we show the n dependence of radial dipole matrix elements calculated for the Rb atom $ns \to n'p$ and $np \to n'd$ transitions.

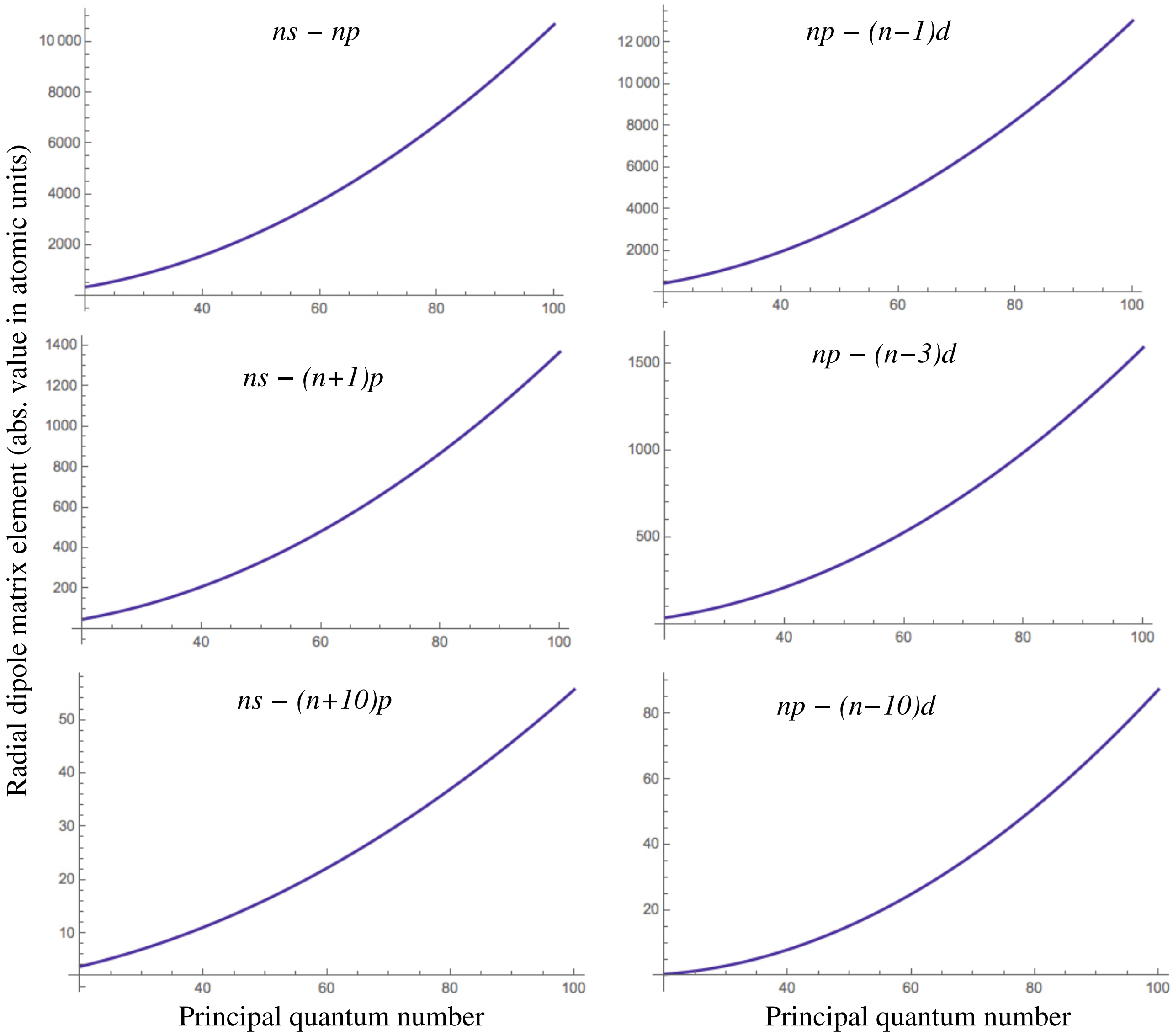

Figure 3.1: Radial dipole matrix elements (in units of a_0) for the transitions $nl \to n'l'$ for Rb atom, calculated from Eq. (3.20). The quantum defects of the s, p and d states are $\mu_s = 3.13$, $\mu_p = 2.64$ and $\mu_d = 1.35$.

The radial matrix elements for dipole allowed transitions between states with $n \gg 1$ are strongest for transitions between the states with the closest eigenenergies and hence similar radial wavefunctions. For the Rydberg atoms, the largest matrix elements are generally of order $0.5 - 1.5 a_0 n^2$. For example the matrix elements from $nl = 90d$ to $\{91p, 92p, 89f, 88f\}$ in Rb are $\{1.3, 0.76, 1.3, 0.80\} n^2 a_0$ respectively, while to all other states are less than $0.17 n^2 a_0$.

3.3 Calculation of the Angular Parts

We need to calculate the matrix element of the dipole transition

$$e\langle nlsjm|\, r_q \,|n'l's'j'm'\rangle = e\langle r\rangle\langle lsjm|\, \sqrt{4\pi/3}Y_{1q} \,|l's'j'm'\rangle \tag{3.22}$$

where $\langle r\rangle = \int R_{nl}(r)R_{n'l'}(r)r^3dr$ is the purely radial matrix element between the two states $|nl\rangle$ and $|n'l'\rangle$.

To that end, we can employ the Wigner-Eckart Theorem to calculate the expectation values of tensor operators T_{kq}

$$\langle lsjm|\, T_{kq} \,|l's'j'm'\rangle = (-1)^{j+m'-k}(lsj \parallel T_k \parallel l's'j')\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \tag{3.23}$$

where the expression in the parenthesis is the Wigner 3j symbol and $(lsj \parallel T_k \parallel l's'j')$ is the reduced matrix element.

The symmetry relations for the 3j symbols are

$$\begin{pmatrix} j & 1 & j' \\ -m & -q & m' \end{pmatrix} = (-1)^{j+j'+q}\begin{pmatrix} j' & 1 & j \\ m' & -q & -m \end{pmatrix} = \begin{pmatrix} j' & 1 & j \\ -m' & q & m \end{pmatrix} \tag{3.24}$$

For the 3j symbol to be non-zero we need $-m-q+m' = 0$ and $-m'+q+m = 0$, so, $q = m'-m$. The 3j symbol is related to the usual Clebsch-Gordon coefficient for combining two angular momenta l_1 and l_2 into a total momentum j by

$$(l_1l_2m_1m_2 \mid l_1l_2jm) = (-1)^{-l_1+l_2-m}\sqrt{2j+1}\begin{pmatrix} l_1 & l_2 & j \\ m_1 & m_2 & -m \end{pmatrix} \tag{3.25}$$

The reduced matrix element in Eq. (3.23) is given by

$$\langle lsj\|T_k\|l's'j'\rangle = (-)^{j'+l+s+k}\langle l\|T_k\|l'\rangle\sqrt{(2j+1)(2j'+1)}\begin{Bmatrix} l & j & s \\ j' & l' & k \end{Bmatrix} \tag{3.26}$$

where the expression in the curly braces is 6j symbol.

Using the general expression

$$(l \parallel Y_k \parallel l') = (-1)^l\sqrt{\frac{(2l+1)(2l'+1)(2k+1)}{4\pi}}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \tag{3.27}$$

we get

$$(l \parallel \sqrt{4\pi/3}Y_1 \parallel l') = (-1)^{l_{\max}-l}\sqrt{l_{\max}}\delta_{l',l\pm 1} \tag{3.28}$$

where $l_{\max} = \max(l, l')$.

We thus have

$$\langle nlsjm|\, \boldsymbol{E}\cdot\boldsymbol{r} \,|n'l's'j'm_{l'}\rangle = E\langle r\rangle\sum_q(-1)^q\varepsilon_q\langle lsjm|\, r_q \,|l's'j'm'\rangle \tag{3.29}$$

Each terms q in this expression describes the coupling of the linearly ($q=0$) or circularly ($q=\pm 1$) polarized radiation to the corresponding atomic transition with $\Delta m = 0$ or $\Delta m = \mp 1$, respectively. The $\Delta m = 0$ is commonly called π-transition, and $\Delta m = \pm 1$ are called $\sigma_\pm$ transitions, with the corresponding notation for the field polarization.

Chapter 4

Dipole-dipole interactions between Rydberg atoms

The character of the forces exerted between pairs of neutral atoms changes with the magnitude of the distance R separating the atoms. In general, a localized charge distribution at a far distance looks like a point charge. At smaller distances, a neutral total charge distribution would produce dipole, quadrupole, etc. potentials.

As an example, consider an electric dipole consisting of two equal and opposite charges q separated by distance d. If we denote by $\boldsymbol{R}_\pm$ the distance from $\pm q$, the potential is $V = \dfrac{q}{4\pi\varepsilon_0}\left(\dfrac{1}{\boldsymbol{R}_+} - \dfrac{1}{\boldsymbol{R}_-}\right)$. Using $R_\pm^2 = R^2\left(1 \pm \dfrac{d\cos\theta}{R} + \dfrac{d^2}{4R^2}\right)$, at a point far from the dipole $R \gg d$ the third term is negligible and we have $\dfrac{1}{R_\pm} \simeq \dfrac{1}{R}\left(1 \mp \dfrac{d\cos\theta}{R}\right)^{-1/2} \simeq \dfrac{1}{R}\left(1 \pm \dfrac{d\cos\theta}{2R}\right)$, which yields $\dfrac{1}{R_+} - \dfrac{1}{R_-} \simeq \dfrac{d\cos\theta}{R^2}$.

Hence the potential of a static dipole is $V(\boldsymbol{R}) = \dfrac{1}{4\pi\varepsilon_0}\dfrac{qd\cos\theta}{R^2}$ and falls off as $1/R^2$ at large R. If we put together a pair of equal and opposite dipoles to make a quadrupole, the potential goes like $1/r^3$, while for back-to-back quadrupoles (octopole) it goes like $1/r^4$ and so on.

In this Chapter, we are concerned with the interaction between Rydberg atoms. We consider two one-electron atoms with the positions of the electrons being $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ with respect of the corresponding nucleus. The nuclei are separated by $\boldsymbol{R}$ and we assume that their positions are fixed.

If the interatomic distance R is of the order of atomic dimensions, the electronic wave functions overlap, so the two atoms attract each other and tend to form a molecule. At greater distances the electrons can no longer move from one atom to the other. Here we are only interested in the interatomic distances for which the Rydberg atoms are well separated, where the dominant effect is the interaction between the Rydberg electrons.

Le Roy radius

At small distances the interaction potential between two Rydberg atoms has a dipolar character. This is valid down to the Le Roy radius where the exchange interaction of the electrons can no longer be neglected.

Let us assume that the atoms are initially in the states $|a\rangle = |n_1, l_1, j_1, m_{j_1}\rangle$ and $|b\rangle = |n_2, l_2, j_2, m_{j_2}\rangle$. In order for the electron wavefunctions not to overlap, we require that the interatomic distance be larger than

$$R_{LR} = 2(\langle n_1, l_1|r_1^2|n_1, l_1|\rangle^{1/2} + \langle n_2, l_2|r_2^2|n_2, l_2|\rangle^{1/2})$$

The extent of the electronic wavefunction of a Hydrogen-like atom scales with the principal quantum number as $a_0 n^2$. Then the Le Roy radius for a pair of alkali atoms in the same state increases approximately with the square of principal quantum number and with the angular momentum as

$$R_{LR} = a_0\sqrt{8n^2(5n^2 + 1 - 3l(l+1))}$$

In all subsequent calculations, we will thus assume $R > R_{LR}$.

4.1 Multipole expansion of the interaction Potential between the Rydberg atoms

Neglecting the retardation effects, the electrostatic interaction energy between two Hydrogen-like (single-electron) atoms is

$$H_{int}(\boldsymbol{R}) = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\boldsymbol{R} + \boldsymbol{r}_2 - \boldsymbol{r}_1|} + \frac{1}{|\boldsymbol{R}|} - \frac{1}{|\boldsymbol{R} - \boldsymbol{r_1}|} - \frac{1}{|\boldsymbol{R} + \boldsymbol{r_2}|}\right) \tag{4.1}$$

Here $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the positions of the electrons of the first and second atom with respect to the position of the corresponding nucleus, as shown in Fig. 4.1.

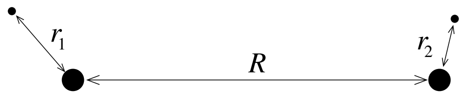

Figure 4.1: Scheme of the two-atom system: Each atomic electron is at the distance r_i from the corresponding nucleus, with internuclear separation R.

With a quick look, we can suppose that the large value of interatomic separation $R = |\boldsymbol{R}|$ in the above denominators would lead to close to zero interaction energy, because both distances in the denominators are almost equal to each other. So the goal of the multipole expansion of the interaction Hamiltonian is not to lose the accuracy. The Coulomb interaction between the particles of the first and second atoms can be expanded using the multipole expansion, which is a series expansion of the interaction potential in powers of $\rho = k_1 + k_2 + 1$ of the inverse interatomic distance $1/R$

$$H_{int}(\boldsymbol{R}) = \sum_{k_1,k_2=1}^{\infty} \frac{V_{k_1k_2}}{4\pi\varepsilon_0|\boldsymbol{R}|^{k_1+k_2+1}} \tag{4.2}$$

The series expansion starts at $\rho = 3$ with the values of k being $k_1 = k_2 = 1$ corresponding to the dipole term with distance dependence R^{-3}. For higher values of $k = 2, 3$ we obtain the quadrupole, octapole term e.t.c..

The exact form of the $V_{k_1k_2}$ depends on the choice of the coordinate system used to label the position of the electrons $\boldsymbol{r_1}$ and $\boldsymbol{r_2}$. Choosing a coordinate system such that the z-axis is along $\boldsymbol{R}$, we have

$$V_{k_1,k_2} = (-1)^{k_2} \sum_{q=-k_<}^{k_<} \sqrt{\begin{pmatrix} k_1 & + & k_2 \\ k_1 & + & q \end{pmatrix}\begin{pmatrix} k_1 & + & k_2 \\ k_2 & + & q \end{pmatrix}}\, p_{k_1q}^{(1)} p_{k_2-q}^{(2)} \tag{4.3}$$

with $k_< = \min(k_1k_2)$ and $p_{kq}^{(1)}$, $p_{kq}^{(2)}$ being the spherical multipole moments that become the spherical multipole operators $\hat{p}_{kq}^{(1)}$, $\hat{p}_{kq}^{(2)}$ that operate on the first and second Rydberg atom respectively, when the above result is converted to quantum mechanics by canonical quantization. The parenthesis in the square root are the binomial coefficients of the multipole expansion in a shortened notation.

The multipole expansion of the potential from a charge distribution in space can be expressed in series of spherical harmonics. The spherical multipole operators for ith atom are of the form

$$\hat{p}_{kq}^{(i)} = e\hat{r}_q^k = er^k\sqrt{\frac{4\pi}{2k+1}}Y_{kq}(\hat{\theta},\hat{\phi})$$

where e is the electron charge and we have used the spherical basis, so $\hat{r}_q^k$ corresponds to the spherical components with $q = -k, -k+1, \ldots, k-1, k$.

4.1.1 Dipolar interaction terms

The advantage of the multipole expansion is that it produces the formulas for the multipole-multipole interactions. We are concerned here with the lowest order term of the expansion ($k_1 = k_2 = 1$) corresponding to the dipole-dipole interaction. The dipole operators are then $\hat{p}_q = e\hat{r}_q$ with $k = 1$ and $q = 0, \pm 1$ as used in chapter 3:

$$\hat{p}_1^{(i)} = -\frac{e}{\sqrt{2}}(\hat{x}+i\hat{y}) = -\frac{e}{\sqrt{2}}r\sin\theta e^{i\phi} = er\sqrt{\frac{4\pi}{3}}Y_{1,1}(\theta,\phi)$$

$$p_0^{(i)} = e\hat{z} = er\cos\theta = er\sqrt{\frac{4\pi}{3}}Y_{1,0}(\theta,\phi)$$

$$\hat{p}_{-1}^{(i)} = \frac{e}{\sqrt{2}}(\hat{x}-i\hat{y}) = -\frac{e}{\sqrt{2}}r\sin\theta e^{-i\phi} = er\sqrt{\frac{4\pi}{3}}Y_{1,-1}(\theta,\phi)$$

The interaction Hamiltonian is then

$$\begin{aligned}
\hat{H}_{int}(\boldsymbol{R}) &= \frac{1}{4\pi\varepsilon_0}\left(\frac{\hat{\boldsymbol{p}}^{(1)}\cdot\hat{\boldsymbol{p}}^{(2)}}{R^3} - \frac{3(\hat{\boldsymbol{p}}^{(1)}\cdot\boldsymbol{R})(\hat{\boldsymbol{p}}^{(2)}\cdot\boldsymbol{R})}{R^5}\right) \qquad (4.4)\\
&= \frac{1}{4\pi\varepsilon_0 R^3}\cdot[p_1^{(1)}p_{-1}^{(2)} + p_{-1}^{(1)}p_1^{(2)} + p_0^{(1)}p_0^{(2)}(1-3\cos^2\theta)\\
&\quad -\frac{3}{2}\sin^2\theta(p_1^{(1)}p_1^{(2)} + p_1^{(1)}p_{-1}^{(2)} + p_{-1}^{(1)}p_1^{(2)} + p_{-1}^{(1)}p_{-1}^{(2)})\\
&\quad -\frac{3}{\sqrt{2}}\sin\theta\cos\theta(p_1^{(1)}p_0^{(2)} + p_{-1}^{(1)}p_0^{(2)} + p_0^{(1)}p_1^{(2)} + p_0^{(1)}p_{-1}^{(2)})],
\end{aligned}$$

The dipole moment for atoms with spherically symmetric electron cloud distribution in a given energy eigenstate $|a\rangle = |nljm\rangle$ vanishes, since the expectation value of the electron position is $\langle \boldsymbol{r}\rangle = 0$. The action of an external field may separate the centers of positive and negative charges and produce an induced electric dipole (mixing l states by an external field leads to Stark eigenstates with permanent dipole moments). Alternatively, the dipole operator for the allowed transition between two atomic states $|a\rangle = |nljm\rangle$ and $|b\rangle = |n'l'j'm'\rangle$ is non-zero, $\boldsymbol{p} = \langle a|\, e\boldsymbol{r}\, |b\rangle$. Hence, two atoms can interact via the resonant dipole-dipole interaction which causes the two atom transition $|a\rangle_1 |b\rangle_2 \rightarrow |b\rangle_1 |a\rangle_2$ with rate $D = \langle a_1, b_2|\, H_{int}\, |b_1, a_2\rangle$. This rate obviously depends on the dipole transition strengths of each atom, and also on the angle θ between the interatomic separation vector $\boldsymbol{R}$ and the quantization direction.

In Fig. 4.2 we show the dependence of the exchange coefficient D on the angle θ for the various transitions Δm (q) of the two atoms. For the atoms initially in states $|a\rangle = |100s_{1/2}, m\rangle$ and $|b\rangle = |100p_{1/2}, m'\rangle$, we obtain the radial matrix elements $R_{nl}^{n'l'} = 10693ea_0$. The products of the angular parts for the various transitons are: $\frac{1}{3}\times\frac{1}{3}$ for $\pi-\pi$; $\frac{\sqrt{2}}{3}\times\frac{1}{3}$ for $\sigma-\pi$; and $\frac{\sqrt{2}}{3}\times\frac{\sqrt{2}}{3}$ for $\sigma_\pm - \sigma_\mp$.

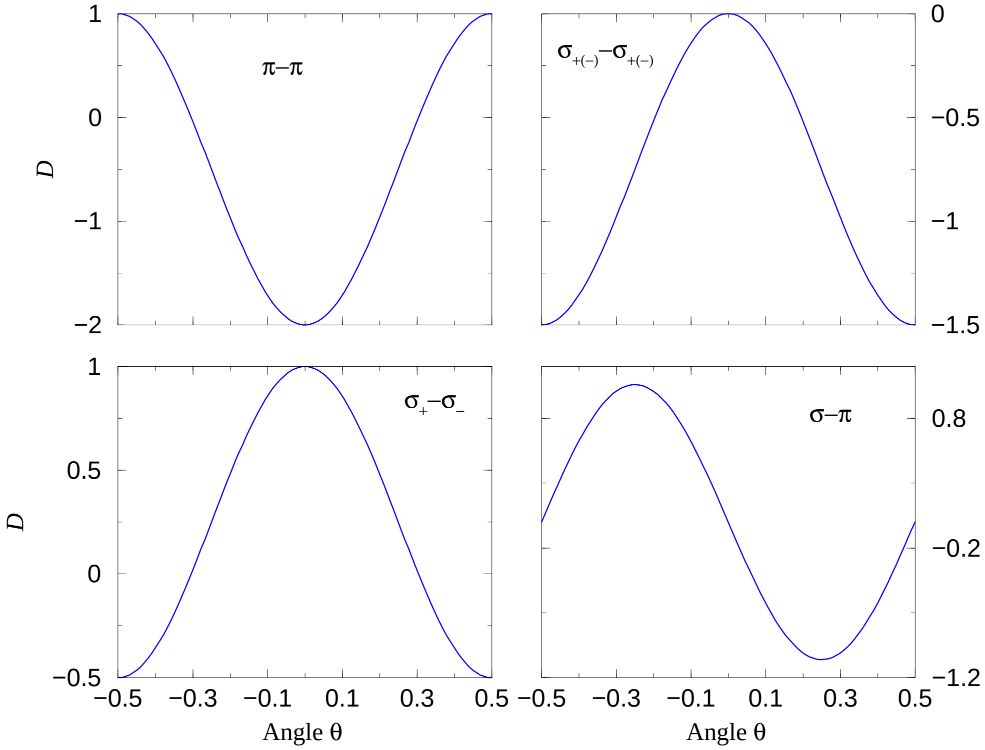

Figure 4.2: Angular dependence of the exchange coefficient $D \propto p_q p'_{q'}$ for the $\pi - \pi$ $(q = q' = 0)$, $\sigma_\pm - \pi$ $(q = \pm 1, q' = 0)$, and $\sigma_\pm - \sigma_\mp$ $(q = \pm 1, q' = \mp 1)$ transitions of the two atoms.

Chapter 5

Non-resonant dipole-dipole interactions

In the previous Chapter, we considered the resonant dipole-dipole interactions between the Rydberg atoms. Let us assume that we have a pair of atoms in the Rydberg states $|r\rangle$ and $|r'\rangle$. There are Rydberg levels below and above these initial states that we denote by $|a\rangle$ and $|b\rangle$. The frequency ω_{ar} of transition $|r\rangle \to |a\rangle$ can be equal to the frequency $\omega_{r'b}$ of transition $|r'\rangle \to |b\rangle$, a situation corresponding to, e.g., $|r\rangle = |b\rangle$ and $|r'\rangle = |a\rangle$. Then the resonant dipole-dipole interaction between the two atoms will result in the coherent swap process $|r\rangle|r'\rangle \leftrightarrow |a\rangle|b\rangle$ with the rate $D_{rr'}^{ab} \simeq p_{ra}p_{r'b}/R^3$ as given in the previous Chapter and is shown schematically in Figure 5.1. If the states $|r\rangle$ ($|b\rangle$) and $|a\rangle$ ($|r'\rangle$) correspond to, e.g. states $|ns\rangle$ and $|np\rangle$, then the matrix elements $p_{ra} \propto n^2$, and the exchange interaction strength scales as $D_{rr'}^{ab} \propto n^4$.

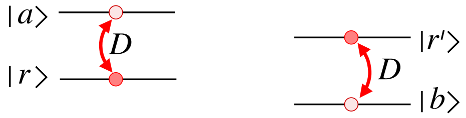

Figure 5.1: A pair of atoms in the Rydberg states $|r\rangle$ and $|r'\rangle$ undergo dipole-dipole exchange interaction $|r\rangle|r'\rangle \leftrightarrow |a\rangle|b\rangle$ with the rate D.

In a more typical situation, states $|r\rangle$ and $|r'\rangle$ are the same ($|r\rangle = |r'\rangle = |ns\rangle$) as they are excited from the ground state by the same resonant laser. The transitions $|r\rangle \to |a\rangle$ and $|r\rangle \to |b\rangle$ then have different frequencies, $\hbar\omega_{ar} = E_a - E_r$ and $\hbar\omega_{rb} = E_r - E_b$, where the energies $E_i \simeq -R_E/n_i^2$ are given by the Rydberg formula. For states $|a\rangle = |np\rangle$ and $|b\rangle = |(n-1)p\rangle$, the frequency difference $\delta\omega_F = \omega_{ar} - \omega_{rb}$, known as the Förster defect, scales as $\delta\omega_F \sim 2R_E/n^3$. At large enough distances, when $D \ll \delta\omega$, the transition $|r\rangle|r\rangle \leftrightarrow |a\rangle|b\rangle(|b\rangle|a\rangle)$ is nonresonant. Using the second order perturbation theory, we then obtain that the two-atom state $|r\rangle|r\rangle$ experiences an energy shift $W = \frac{2D^2}{\delta\omega_F}$ which scales with the principal quantum number n as $W \propto n^{11}$ and with the interatomic distance R as $W \propto 1/R^6$.

More precisely, this van der Waals interaction energy is obtained by summing contributions of the non-resonant transitions to all the pair of levels $|a\rangle$ and $|b\rangle$ as

$$W_{rr} = \sum_{a,b} \frac{p_{ra}p_{rb}}{\omega_{rb} - \omega_{ar}} \tag{5.1}$$

Typically, only several levels $|a\rangle$ and $|b\rangle$ that are closest to $|r\rangle$ contribute the most in this sum, since their transition matrix elements are larger and the frequency mismatch smaller. Depending on the sign of the frequency difference in the denominator, the van der Walls interaction can then be repulsive $W > 0$ or attractive $W < 0$.

Owing to the large dipole moments of the Rydberg states of atoms, they thus exhibit very strong interactions, on the MHz scale for $n \simeq 60-100$, at mesoscopic distance of μm interatomic separations. A remarkable effect that stems from these interactions is the Rydberg blockade: an atom resonantly excited by a laser to the Rydberg state $|r\rangle$ blocks subsequent resonant excitation of the second, third, etc atoms within the so-called blockade volume. The reason for this blockade is that strong interactions between the Rydberg levels of atoms shift the resonance frequency of all the atoms in the vicinity of an already excited atom, which thus suppresses multiple excitations.

To conclude, the Rydberg state interactions and Rydberg blockade can be used to implement high-fidelity quantum logic gates and to simulate and study few- and many-body physics of strongly-interacting systems. This field is currently one of the hot topics of quantum optics and quantum computation, as attested by many theoretical and ground-breaking experimental results.

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