# UNIVERSIDAD SANTIAGO DE CHILE FACULTAD DE CIENCIAS Departamento de Física



### van der Waals interaction between Rydberg atoms and polar molecules

Vanessa Carolina Olaya Agudelo

Profesor Guía: Felipe Herrera Urbina

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Dedicada a Juan Manuel Olaya Agudelo

### Resumen

En esta tesis, estudiamos la interacción de largo alcance entre átomos alcalinos de Rydberg con estructura fina  $(n^2 l_i; l \leq 2, 15 \leq n \leq 150)$  y moléculas alcalinas heteronucleares en el estado base electrónico y rovibracional ( $X^{1}\Sigma^{+}$ ; v = 0, J = 0). Utilizando teoría de perturbaciones para la expansión multipolar en coordenadas esféricas para el potencial de largo alcance, calculamos los coeficientes de dispersión  $C_6$  asociados a la interacción entre pares átomo-molécula que involucran átomos de <sup>133</sup>Cs y <sup>85</sup>Rb interactuando con moléculas de KRb, LiCs, LiRb, and RbCs. Los coeficientes de dispersión  $C_6$  dependen de la función de polarizabilidad atómica y molecular de los estados de las partículas interactuantes. La magnitud y naturaleza de la interacción es altamente dependiente del estado de Rydberg y puede ser ajustado con precisión a un polinomio  $\mathcal{O}(n^7)$  para un rango de números cuánticos principales  $40 \leq n \leq 150$ . Para todos los pares átomo-molécula considerados, los estados de Rydberg con l = 0, 1 tiene interacciones atractivas, mientras que para algunos pares interactuantes con l = 2, la interacción resulta ser repulsiva. La energía de interacción a distancias mayores al radio de LeRoy escala como  $n^{-5}$  para n > 40. Para valores intermedios  $n \lesssim 40$ , la energía de interacción tanto atractiva como repulsiva está en el orden de los  $10-1000 \,\mu$ K para casos específicos. La exactitud de los coeficientes  $C_6$  calculados está limitada por la calidad de los defectos cuánticos atómicos, con errores relativos estimados no mayores a 1% en promedio.

### Abstract

In this thesis, we study the long-range interaction between Rydberg alkali-metal atoms with fine structure  $(n^2 l_i; l \le 2, 15 \le n \le 150)$  and heteronuclear alkali-metal dimers in the ground rovibrational state  $(X^1\Sigma^+; v = 0, J = 0)$ . Using perturbation theory for the multipolar expansion in spherical coordinates of the long-range potential, we compute the associated  $C_6$  dispersion coefficients of atom-molecule pairs involving <sup>133</sup>Cs and <sup>85</sup>Rb atoms interacting with KRb, LiCs, LiRb, and RbCs molecules. The C<sub>6</sub> dispersion coefficients depend on the atomic and molecular dynamical polarizability of the interacting particles. The magnitude and nature of the interaction is highly dependent on the Rydberg atomic polarizability and can be accurately fitted to a statedependent polynomial  $\mathcal{O}(n^7)$  over the range of principal quantum numbers  $40 \le n \le 150$ . For all atom-molecule pairs considered, Rydberg states  $n^2S_i$  and  $n^2P_i$  result in attractive  $1/R^6$  potentials. In contrast,  $n^2D_i$  states can give rise to repulsive potentials for specific atom-molecule pairs. The interaction energy at the LeRoy distance approximately scales as  $n^{-5}$  for n > 40. For intermediate values of  $n \lesssim 40$ , both repulsive and attractive interaction energies in the order of  $10 - 1000 \,\mu$ K can be achieved with specific atomic and molecular species. The accuracy of the reported  $C_6$  coefficients is limited by the quality of the atomic quantum defects with relative errors  $\Delta C_6/C_6$  estimated to be no greater than 1% on average.

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# **Chapter 1**

# Introduction

Long-range forces arise from the interaction between well-defined charge distributions at distances between tens to thousands of Bohr radii. These charge distributions can correspond to atoms, molecules, or any other polarizable particle. The interactions energies are small compared with the energy of each interacting particle. Therefore, they must be treated pertubatively and can be relevant in the dynamics of ultracold gases and ultracold collisions processes.

In order to study intermolecular potentials in materials, experimental methods such as spectroscopy, scattering and crystallography have been used. To model the intermolecular potential energy, general expressions have been developed. One example is the well-known Lennard-Jones potential [1]

$$V_{LJ} = 4\epsilon \left[ \left(\frac{R_0}{R}\right)^{12} - \left(\frac{R_0}{R}\right)^6 \right], \tag{1.1}$$

where  $\epsilon$  is the depth of the potential well,  $R_0$  is the distance where  $V_{LJ}(R_0) = 0$  and R is the relative distance between the two centers of mass of the system. Figure 1.1 shows a characteristic Lennard-Jones potential energy curve for a real diatomic molecular system with  $\epsilon = -0.00429$  hartrees and  $R_0 = 7.05 a_0$  [2]. There is also a minimum in Figure 1.1 at  $R = R_m = 7.88 a_0$ , which defines the limit between the repulsive short-range ( $R < R_m$ ) and the attractive long-range ( $R > R_m$ ). The long-range scaling  $R^6$  is characteristic of the *van der Waals* interaction.

The potential curve in Figure 1.1 allows us to set an energy reference for a system composed of a pair of particles approaching each other from infinity. For a relative kinetic energy on the order of the potential well, the collision processes will be insensitive to the long-range tail. If the relative kinetic energy of the incoming particles is negligible in comparison with the potential well, then the collision dynamics is very sensitive to the long-range tail. The latter case is relevant for the study of few- and many-body physics in the ultracold regime [2].

At infinite distances, the intermolecular potential energy tends to zero, but we can set a relative distance  $R = R_{vdW}$  beyond which we can neglect the potential energy compared with the internal energy of the collision partners. On the other hand, for distances  $R < R_{LR}$  short-range processes take place, i.e. the long-range region goes from  $R_{LR}$  up to  $R_{vdW}$ , where  $R_{LR} < R_{vdW}$ .



Figure 1.1: Lennard-Jones potential energy curve according to eq. (1.1) for a realistic neutral diatomic molecule. Using  $\epsilon = -0.00429$  hartrees and  $R_0 = 7.05 a_0$ , where the minimum is found at  $R = R_m = 7.88 a_0$ . Figure taken from Ref. [2]

The characteristic distance  $R_{LR}$  is is known as the LeRoy radius [3], which is the minimum distance at which the particles conserve their identity, i.e. their electronic clouds do not overlap. It is given by

$$R_{LR} = 2\left[\sqrt{\langle r_A^2 \rangle} + \sqrt{\langle r_B^2 \rangle}\right],\tag{1.2}$$

where  $r_A$  and  $r_B$  are the mean radii of interacting particles A and B.

The long-range tail varies as  $C_6/R^6$ , where  $C_6$  is known as the van der Waals coefficient. The energy and the distance of the van der Waals interaction can also be characterized by [4]

$$E_{vdW} = \frac{1}{2} \left( \frac{\hbar^2}{2\mu R_{vdW}^2} \right) \tag{1.3}$$

and

$$R_{vdR} = \frac{1}{2} \left( \frac{2\mu |C_6|}{\hbar^2} \right)^{1/4},$$
(1.4)

where  $\mu$  is the reduced mass of the interacting particles. The van der Waals energy  $E_{vdW}$  is commonly larger than the relative kinetic energy of particles in the ultracold regime. For kinetic energies below  $E_{vdW}$ , the wavefunction of the colliding particles around  $R_{vdW}$  can not be described semi-classically, but purely quantum mechanically [2].

In general, we denote as van der Waals interaction to all those interactions that scale as  $1/R^6$ .

Physically, the origin of the long-range interaction involves permanent or instantaneous inhomogeneities of the interacting charge distributions, and include the London interactions [5], Debye interactions [6] and the Keesom interactions [7].

The van der Waals interaction is not always relevant for gases at room temperature. However, for ultracold gases, the collision dynamics is widely dominated by the long-range tail. Over the last decades, with the development of laser trapping and cooling techniques, the study of long-range interactions for specific systems and their potential application has received special attention in atomic, molecular and optical physics. One of the systems with remarkable applications in a wide variety of areas are Rydberg atoms interacting in the long-range with diatomic molecules. These interacting particles can exchange excitation energies in the microwave regime via Foster processes, which has been proposed as tool for non-destructive detection of molecular states in hybrid molecule-Rydberg systems [8, 9]. Simultaneous trapping of ultracold Rydberg atoms and polar molecules may also be used for direct sympathetic cooling of molecules intro the ultracold regime -a long-standing goal in ultracold physics- through elastic van der Waals atom-molecule collisions [10, 11]. In comparison with dipole-dipole processes, van der Waals collisions do not require molecules to be confined in low-dimensional traps in the presence of static electric fields for shielding detrimental attractive collisions that lead to trap loss [12]. Moreover, van der Waals interactions can be strong even if the relevant transition energies in the collision partners are not resonant, as opposed to Foster processes. Understanding the feasibility of the promising applications of molecule-Rydberg systems thus requires an accurate knowledge of the van der Waals interaction potentials.

In this thesis, we consider atom-molecule systems at low kinetic energies. We focus on alkaliatoms in Rydberg states and polar diatomic molecules in their electronic and rovibrational ground state. Rydberg atoms have exaggerated properties such as orbital sizes of thousands of Bohr radii, long radiative lifetime exceeding microseconds and are extremely sensitive to static electric fields. On the other hand, diatomic molecules have been widely studied and are well characterized and understood in different regimes. At low temperatures, it is possible to prepare atoms and molecules in well-defined quantum states.

The long-range interaction potential of the molecule-Rydberg system is treated perturbatively in comparison with the energy of the Rydberg atom (including the spin-orbit coupling) and the rotational energy of the molecule. Thus, the potential is written as an expansion of the form  $V(R) = \sum_{n} C_n / R^n$ , with  $n \ge 3$ . Since we consider atom-molecule interactions for molecules in their rovibrational ground state, the lowest non-vanishing van der Waals coefficient is found to be  $C_6$  [13, 14, 15].

We compute a large set of van der Waals  $C_6$  coefficients that determine the long-range interaction between selected heteronuclear alkali-metal dimers (LiCs, RbCs, LiRb and KRb) in their electronic and rovibrational ground state ( ${}^{1}\Sigma^{+}, v = 0, J = 0$ ) with  ${}^{85}$ Rb and  ${}^{133}$ Cs atoms in Rydberg states  $n^2l_j$  with  $15 \le n \le 150$ . n is the atomic principal quantum number, l is the atomic orbital angular momentum, j is the total electronic angular momentum,  $\nu$  the vibrational quantum number of the molecule and J is the rotational angular momentum. We focus on molecular [16, 17, 18, 19] and Rydberg atom species [20, 21] that are experimentally relevant. The rest of the thesis is organized as follows: in Chapter 2, we describe the theoretical treatment of the Rydberg wavefunctions and compute numerically the atomic dynamical polarizabilities for Rubidium and Cesium atoms in Rydberg states. An overview of the closed-shell diatomic molecules is given in Chapter 3, where we use the Born-Oppenheimer approximation, the adiabatic approximation and the rigid rotor model to obtain the molecular wavefunctions, energies and the dynamical polarizability of ground state alkali-molecules. Chapter 4 is dedicated to the long-range interaction between Rydberg atoms and molecules. We use the multipolar expansion in spherical coordinates of the long-range interaction, together with pertubation theory, to treat this interaction potential and write it in terms of the atomic and molecular dynamical polarizability functions at imaginary frequencies. We also present the scaling of the  $C_6$  coefficients with the atomic principal quantum number and the effect on the interaction of the molecular dipole moment. Finally, in Chapter 5 we summarize our work and discuss the envisioned applications of our results.

# **Chapter 2**

# **Alkali-Metal Rydberg Atoms**

Atomic Rydberg states [22] are highly excited electronic states with a high principal quantum number n. They were predicted at the end of 19th century for the Balmer's wavelength formula for atomic hydrogen [23]

$$\lambda = \frac{bn^2}{n^2 - 4},\tag{2.1}$$

where b = 3645.6 Å and the wavelegths are given for transitions from n = 2 to atomic states with higher principal quantum number. The inverse of eq. (2.1) gives the energy difference between the states, in frequency units

$$\nu = \frac{1}{4b} \left( \frac{1}{4} - \frac{1}{n^2} \right).$$
(2.2)

Hydrogen was the first atom to be quantitatively understood. Later Liveing and Deway [24] made important contributions to atomic spectroscopy by observing the spectral lines of sodium. After Liveing and Dewar, Rydberg worked with alkali atoms and classified their spectral lines into sharp, principal and diffuse [25] indentifying spectral series with common lower level but upper level in be ns, np and nd states. The frequencies for each series could be expressed as

$$\nu_{i} = \nu_{\infty i} - \frac{R_{y}}{(n - \delta_{i})^{2}},$$
(2.3)

with i = s, p, d where  $\nu_{\infty i}$  are constants and  $\delta_i$  are the so-called quantum defects of the sharp, principal and diffuse series.  $R_y$  is the well-known universal Rydberg constant with a value equal to  $109721.6 \text{ cm}^{-1}$ .

It was not until Bohr's model [23] of the hydrogen atom that the meaning of a high *n* value became clear. For an electron moving in a circular orbit around the atomic core, the assumtion that the angular momentum was quantized in integral units of  $\hbar = h/2\pi$  (*h* is the Plank's constant), along with the observation that the electron does not continuously radiate around a classical orbit, but has well defined energies, allowed Bohr to define and orbital radius given by

$$r_n = \frac{4\pi\varepsilon_0\hbar^2 n^2}{Ze^2m},\tag{2.4}$$

Property	Formula	x
Binding Energy $E_n$	$-rac{R_{Ryd}}{(n^*)^2}$	-2
Energy spacing	$E_n - E_{n-1}$	-3
Orbital radius $\langle r  angle$	$\frac{1}{2}(3(n^*)^2 - l(l+1))$	2
Geo. cross section	$\pi\left\langle r ight angle$	4
Dipole moment	$\langle nd er nf angle$	2
Polarizability	$2\sum_{n'l'm'}\frac{ \langle nlm z n'l'm'\rangle ^2}{E_{nl}-E_{n'l'}}$	7
Radiative lifetime	$2.09 \text{ns}(n^*)^{2.85}$	3
Fine-structure	$4.8 \times 10^{6} \text{ MHz } 5/2(n^{*})^{-3}$	-3

Table 2.1: Properties of the Rydberg atoms, formula and its scaling power x with the effective principal quantum number  $n^{*x}$ . Table taken from Ref. [27].

where  $\varepsilon$  is the vacuum electric permittivity, Z is the atomic number of the atom, e is the electric change of the electron and m the electron mass. Eq. (2.4) showed how the orbital radius increased with the principal quantum number n. The energy W of the state thus decreases with n as

$$W = -\frac{Z^2 e^4 m}{32\pi^2 \varepsilon^2 \hbar^2 n^2}.$$
 (2.5)

The energy difference between two atomic states with principal quantum numbers  $n_1$  and  $n_2$  is given by,

$$\delta W = W_2 - W_1 = -\frac{Z^2 e^4 m}{32\pi^2 \varepsilon^2 \hbar^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$
(2.6)

where  $R_y=\frac{Z^2e^4m}{32\pi^2\varepsilon^2\hbar^2}$  is the Rydberg constant.

The energy dependence with the principal quantum number  $W \sim 1/n^2$  means that for high *n* the valence electron is in a loosely bound orbit. This loosely bound electron character of a Rydberg electron confers Rydberg atoms with exotic properties. One of these well-known properties is their mean radius: for the ground state hydrogen atom the mean radius is about 1  $a_0$  with a binding energy of 1  $R_y$ , while for n = 10 these mean radius is about 100  $a_0$  and has a binding energy of the order 0.01  $R_y$ . Another important property is the geometric cross section, which scales as  $n^4$ . For ground state atoms the geometric cross section is 1  $a_0^2$ , while for n = 10 is  $10^4 a_0^2$ .

The difference between ground state atoms and Rydberg atoms is highlighted when the atoms are exposed to an external electric field. Rydberg atoms are very sensitive to external perturbations. For eletric fields on the order of  $10^6$  V/cm [26], Rydberg atoms can be ionized, while the ground state is barely perturbed by these electric field magnitudes. This sensitivity is due the dipole moment and the polarizability of the Rydberg atoms, which scale as  $n^2$  and  $n^7$ , respectively. Also, the diamagnetic energy shifts are considerably large compared to ground states. These shifts depend on the area of the orbit, increasing as  $n^4$ . These responses to external fields make the Rydberg atoms an useful platform to study light-matter interaction.

Table 2.1 shows some of the properties of Rydberg atoms with a single Rydberg electron and their scaling with the effective principal quantum number  $n^*$ .

The development of atomic theory and high resolution absorption spectroscopy allowed the study

of Rydberg atoms in the 1970's. The first studies to Rydberg atoms aimed to demostrate their exotic properties.

Amaldi and Segre [28] studied the energy shifts of the Rydberg series for K in the presence of a rare atomic gas medium. Since the space between the Rydberg electron and the ionic core is filled with a dielectric medium, red shifts were expected for the atomic transitions. These were observed for K, Ar and He, but for Ne only blue shifts where observed. This observations were latter explained by a theory developed by Fermi [29], in which the energy shifts come from the short range scattering of the Rydberg electron and the atoms in the gas. In 2000, using the Fermi pseudopotential for the short range scattering in the ultracold regime, C. H. Greene, A. S. Dickinson and H. R. Sadeghpour [30] predicted that the oscillatory probability density of the Rydberg electron can create long-range potential wells that are suitable to trap surrouding atoms. Those exotic molecules are known as ultralong-range Rydberg molecules and were observed experimentally in 2009 by V. Bendkowsky et al. [31].

Rydberg atoms have been widely studied at room temperature and the effect of an electrid field in these atoms have been continuously studied and observed due to its potential to create techniques for detection and manupulation of Rydberg atoms. Together with the development of the tunable dye laser [32], it was possible to excite a large number of atoms in a well-defined Rydberg level. This method allowed the measuarement of several properties such as collision cross sections, transition energies and radiative lifetimes for low lying Rydberg levels.

The exaggerated response of Rydberg atoms to the radiation field has motivated the use of these atoms for testing the interaction with the vacuum of a resonant cavity [33]. In the low frecuency regime of high Rydberg state, the wavelengths are sufficiently large to facilitates the design of microwave cavities and the radiative decay rates are also appropriate for the system.

Advances in laser technology, cooling and trapping techniques led to the creation of Rydberg atoms in the ultracold regime. Nowadays it is possible to excite the atoms of an alkali gas into a Rydberg level and trap them with a high density of the order of  $(10^{14} \text{cm}^{-3})$  in the  $\mu$ K regime [34]. Such a high density gas allows the to study of Rydberg-Rydberg interactions [35], which that can be tuned by changing the density of the gas or the principal quantum number of the excited atoms. The Rydberg-Rydberg van der Waals interaction scales as  $n^{11}$  and is strong enough to create molecular Rydberg state with bound lengths of the order of thousand of Bohr radii [36].

Quantum information processing is another area in which Rydberg atoms can also be exploited. By using the strong dipole-dipole interactions between Rydberg atoms, fast phase gates have been implemented [37], where the ground state levels are used to store information, while the Rydberg states that strongly interact create the entangled states. For a short period, the atoms will be decoupled from the environment decreasing the decoherence. For mesoscopic systems, Lukin [38] proposed to forget about the tricky single atom control by using the *dipole blockade* in which the interaction between excited atoms inhibits several Rydberg exitation in the neighboring atoms.

These application along with the description given in Chapter 1 are some of the applications that show the richness of Rydberg physics. This chapter explains the theoretical treatment used to

study Rydberg atoms and elaborates on some of their physical properties that are required to understand the role of Rydberg atoms when they interact with ground state molecules in the long-range.

### 2.1 Rydberg atom wavefunctions

This section discusses the theoretical treatment of the Rydberg alkali-atom wavefunction. We use a hydrogen-like Schrödinger equation to model the electron-core system. We use an effective radial interaction potential  $V_l(r)$  (r is the distance between the electron and the ionic core) that accounts for the effect of the inner electrons of the core over the valence electron and behaves as a Coulomb potential at large distances ( $r \rightarrow \infty$ ). The Rydberg energies are described using the quantum defects  $\delta_{nlj}$  and the spin-orbit coupling of the atom is mapped through the quantum defects by adding a dependence of the total angular momentum j. Hyperfine structure is neglected.

The radial Schrödinger equation obtained at the end of the next section is solved numerically using the Numerov algorithm. These numerical wavefunctions allow us to study several properties of Rydberg alkali-atoms.

Atomic units are used throughout this Thesis unless otherwise stated.

### 2.1.1 Schrödinger equation

We start with the Schrödinger equation of the electron-core system written in terms of the relative distance r and the relative angular orientation  $(\theta, \varphi)$ ,

$$\left[-\frac{\nabla^2}{2\mu} + V_l(r)\right]\Psi(r,\theta,\varphi) = E_{n,l}\Psi(r,\theta,\varphi),$$
(2.7)

where  $\mu = m_e m_c / (m_e + m_c)$  is the reduced mass,  $m_c$  is the mass of the nucleus plus the inner electrons and  $m_e$  is the electron mass.  $E_{n,l}$  is the energy of the valence electron, which depends on the principal quantum number n and the orbital angular momentum l. The effective interaction potential depends on the orbital angular momentum as well.  $\Psi(r, \theta, \phi)$  is the wavefunction of the system.

The  $\nabla^2$  operator in spherical coordinates is given by

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}.$$
(2.8)

The square of angular momentum operator l<sup>2</sup> can be written in spherical coordinates as,

$$\mathbf{l}^{2} = \frac{1}{\sin\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^{2}\theta} \frac{\partial^{2}}{\partial\varphi^{2}}.$$
 (2.9)

Therefore, eq. (2.8) can be written as

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\mathbf{l}^2.$$
(2.10)

Inserting eq. (2.10) into the Schrödinger eq. (2.7) gives

$$\left[-\frac{1}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\mathbf{l}^2}{2\mu r^2} + V_l(r)\right]\Psi(r,\theta,\varphi) = E_{n,l}\Psi(r,\theta,\varphi).$$
(2.11)

The system wavefunction can be separated into a radial and angular part as  $\Psi(r, \theta, \phi) = R(r) \times Y_l^m(\theta, \phi)$ , where  $Y_l^m(\theta, \phi)$  is the spherical harmonic of order l with component m, explicitly given by

$$Y_{l}^{m}(\theta,\phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{l}^{m}(\cos\theta)e^{im\varphi},$$
(2.12)

where  $P_l^m$  are the associated Legendre polynomials [39]. The angular equation (in units  $\hbar = 1$ ) can be written as  $l^2 Y_l^m = l(l+1)Y_l^m$ . The radial equation is thus given by

$$\left(-\frac{1}{2\mu}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right] + \left[\frac{l(l+1)}{2\mu r^2} + V_l(r) - E_{n,l}\right]\right)R(r) = 0.$$
(2.13)

### 2.1.2 Atomic State notation

For alkali-atoms, we must consider the electronic spin angular momentum s, which is coupled to the orbital angular moment operator I to form the total angular momentum operator j = 1+s, which is a vector addition of I and s and follows the so-called triangular condition, namely

$$m = m_l + m_s \tag{2.14}$$

and

$$|l-s| \le j \le |l+s| \tag{2.15}$$

where  $m, m_l, m_s$  are the projection of **j**, 1, **s** in the reference frame, respectively, and *j*, *l*, *s* are the magnitude of the corresponding vectors. For the Rydberg alkali-atoms considered in this Thesis (<sup>133</sup>Cs and <sup>85</sup>Rb), the electronic spin is s = 1/2.

We will refer to an atomic Rydberg state by their quantum numbers n, l, s, j, m using indistinctly the state notations  $|n(ls)jm\rangle$ , or  $|nljm\rangle$ , or  $|n^{2s+1}l_j, m\rangle = |n^2l_j, m\rangle$ .

#### 2.1.3 Core potential

Marinescu et al. [40] developed a model that accounts for the penetration and polarization of the atomic core due to the valence electron. For a valence electron with low-lying angular momentum  $(l \leq 3)$  its orbit is elliptic and can create an unscreened nuclear charge that affects the Coulombic



Figure 2.1: Core potential  $V_l(r)$  for Rubidium with l = 0, 1, 2, 3 using the parameters  $a_i$  (i = 1, 2, 3, 4) tabulated in Table 2.2.  $V_l$  is compared with the Coulomb potential -Z/r.

behavior of the potential at short distances. Explicitly,  $V_l(r)$  has the form [40]

$$V_l(r) = -\frac{Z_{n,l}(r)}{r} - \frac{\alpha_c}{2r^4} \left(1 - e^{-(r/r_c)^6}\right),$$
(2.16)

where  $\alpha_c$  is the static dipole polarizability of the core, and  $r_c \sim \alpha_c^{1/3}$  is the critical penetration radius between the valence electron and the core at which the short range contribution to the effective potential (2.16) is not well defined. The first term is related to the core penetration, similar to the Coulomb potential with an effective charge  $Z_{n,l}$  of the core, that is given by

$$Z_{n,l} = 1 + (Z - 1)e^{-a_1r} - r(a_3 + a_4r)e^{-a_2r},$$
(2.17)

where Z is the regular nuclear charge of the atom,  $a_i$  (i = 1, ..., 4) are parameters that depend on the atomic species and on the angular momentum of the valence electron. The parameters  $a_i$  are tabulated in Table 2.2 for different alkali-atoms.

The second term in eq. (2.16) accounts for the core polarization due to the electron and describes the long range potential mostly determined by the core polarizability  $\alpha_c$ , which depends of number of electrons in the core. This potential was parametrically fitted to one-electron energy level with an accuracy of  $10^{-5}$  and successfully predicted several resonant phenomena observed in alkaliatoms. Fig. 2.1 shows the core potential function  $V_l(r)$  for Rubidium using the potential parameters of Table 2.2 for l = 0, 1, 2, 3.  $V_l$  tends to zero faster that the Coulomb potential for the same atom.

### 2.1.4 Quantum defects

The electrons in the core for alkali-atoms also influence the energy of the valence electron and this is the main difference between hydrogen and alkali-atoms. For the latter, the energy of the

l	$r_c$	$a_1$	$a_2$	$a_3$	$a_4$						
	$^{133}$ Cs, $\alpha_c = 15.6440$										
0	1.92046930	3.49546309	1.47533800	-9.72143084	0.02629242						
1	2.13383095	4.69366096	1.71398344	-24.65624280	-0.09543125						
2	0.93007296	4.32466196	1.61365288	-6.70128850	-0.74095193						
$\geq 3$	1.99969677	3.01048361	1.4000001	-3.20036138	0.00034538						
		<sup>85</sup> R	b, $\alpha_c = 9.0760$	0							
0	1.66242117	3.69628474	1.64915255	-9.86069196	0.19579987						
1	1.50195124	4.44088978	1.92828831	-16.79597770	-0.81633314						
2	4.86851938	3.78717363	1.57027864	-11.65588970	0.52942835						
$\geq 3$	4.79831327	2.39848933	1.76810544	-12.07106780	0.77256589						

Table 2.2: Core potential parameters  $a_i$ , critical penetration radius  $r_c$  and core polarizability  $\alpha_c$  for Cesium and Rubidium. Parameters taken from Ref. [40].

valence electron is given by

$$E_{n,l} = -\frac{hcR_{\infty}}{(n-\delta_{n,l})^2},\tag{2.18}$$

where  $hcR_{\infty} = 1/2$  is the Rydberg constant in atomic units. As the valence electron is further away from the core, it feels a positive net charge. However, as the electron gets closer, this is not true anymore and the core can be polarized for states with low angular momentum. This phenomenon can be encoded into an effective principal quantum number  $n^* = n - \delta_{n,l}$ , where  $\delta_{n,l}$  is called the quantum defect and has a greater value for lower orbital angular momentum. For  $l \ge 3$  the quantum defects are effectively zero, corresponding to a pure Coulombic potential.

The effect of the single-electron spin-orbit potential  $V_{so}(r) = (\alpha/r^2)\mathbf{l} \cdot \mathbf{s}$  is negligible on the calculations of the radial wavefunctions ( $\alpha \approx 1/137$ ). Therefore, it is possible to effectively include the spin-orbit interaction by replacing  $\delta_{n,l}$  with  $\delta_{n,l,j}$  using the extended Rydberg-Ritz formula,

$$\delta_{n,l,j} = a + \frac{b}{(n-a)^2} + \frac{c}{(n-a)^4} + \frac{d}{(n-a)^6} + \frac{e}{(n-a)^8} + \dots$$
(2.19)

The Rydberg-Ritz coefficients *a-e* are taken from experimental data. Table 2.3 shows the Rydberg-Ritz coefficients for <sup>133</sup>Cs and <sup>85</sup>Rb.

Figure 2.2 shows the transition energy gaps between atomic states with different angular momentum quantum numbers as a function of n. The smallest energy gap for Rubidium and Cesium is found for the transition  $n^2D_{3/2} \rightarrow n^2D_{5/2}$  which range between 1000 to 1 MHz for n = 20 to n = 200, respectively. For the transition  $n^2P_{1/2} \rightarrow (n+1)^2S_{1/2}$  the energy gap is of the order of 10 GHz for  $n \sim 71$  in Rb atoms and  $n \sim 73$  for Cs.

Tables 2.4 and 2.5 show the transition energies between different Rydberg states computed using the quantum defects from Table 2.3 for <sup>133</sup>Cs and <sup>85</sup>Rb, respectively. Our computed energies have an error smaller than 0.1% compared with available experimental data [41, 42].

$l_j$	a	b	c	d	$n_{min}$				
<sup>133</sup> Cs									
$S_{1/2}$	4.049352(38)	0.238(7)	0.24044	0.12177	6				
$P_{1/2}$	3.5916(5)	0.36(1)	0.34284	1.23986	6				
$P_{3/2}$	3.5590(7)	0.38(1)	0.28013	1.57631	6				
$D_{3/2}$	2.475454(20)	0.010(4)	-0.43324	-0.96555	5				
$D_{5/2}$	2.466308(30)	0.015(6)	-0.43674	-0.74442	5				
$F_{5/2}$	0.033587	-0.213732	0.70025	-3.66216	4				
		$^{85}$ Rb							
$S_{1/2}$	3.1311804(10)	0.1784(6)	-1.8	_	14				
$P_{1/2}$	2.6548849(10)	0.2900(6)	-7.9040	116.4373	11				
$P_{3/2}$	2.6416737(10)	0.2950(7)	-0.97495	14.6001	13				
$D_{3/2}$	1.34809171(40)	-0.60286(26)	-1.50517	-2.4206	4				
$D_{5/2}$	1.34646572(30)	-0.59600(18)	-1.50517	-2.4206	4				
$F_{j}$	0.016312	-0.064007	-0.36005	3.2390	4				

Table 2.3: Rydberg-Ritz coefficients for <sup>85</sup>Rb and <sup>133</sup>Cs. The last column  $n_{min}$  is the minimum value of n for which the expansion is estimated to be valid. Data taken from Ref. [27].

$n^2 l_j \to n'^2 l'_{j'}$	Ref. [41]	This work
$45^2 P_{3/2} \to 49^2 S_{1/2}$	287476.992	287464.770
$59^2 P_{3/2} \to 68^2 S_{1/2}$	265898.688	265894.066
$67^2P_{3/2} \rightarrow 81^2S_{1/2}$	261818.142	261815.154
$72^2 P_{3/2} \to 90^2 S_{1/2}$	257008.756	257006.406
$59^2 P_{3/2} \to 66^2 D_{5/2}$	255306.920	255067.697

Table 2.4: Transition energy in MHz between selected Rydberg states of  $^{133}$ Cs compared with experimental data taken from Ref. [41].

	$n^2S_{1/2}$ -	$\rightarrow n^2 P_{1/2}$	$n^2S_{1/2} \rightarrow n^2P_{3/2}$		
n	Ref. [42] This work Ref. [42]		This work		
27	223664.264	223671.632	-	_	
28	197990.586	197996.151	203322.762	203321.703	
29	176100.586	176104.837	180848.640	180847.820	
30	157322.108	157325.423	161568.406	161567.725	
31	141121.445	141124.021	144934.120	144933.648	
32	127070.956	127072.994	130507.152	130506.799	
33	114825.466	114827.083	117933.187	117932.887	
34	104104.194	104105.474	_	_	

Table 2.5: Transition energy in MHz between selected Rydberg states of  $^{85}$ Rb compared with experimental data taken from Ref. [42].



Figure 2.2: Transition energy  $\Delta E_{nlj}$  between atomic states  $n^2 D_{3/2} \rightarrow n^2 D_{5/2}$ ,  $n^2 S_{1/2} \rightarrow (n + 1)^2 P_{3/2}$  and  $n^2 P_{1/2} \rightarrow (n + 1)^2 S_{1/2}$  as a function of the principal quantum number *n*, for (a)<sup>133</sup>Cs and (b)<sup>85</sup>Rb. Logarithmic scale (base 10) is used for  $\Delta E_{nlj}$ .

#### 2.1.5 Radial wavefunction

In order to compute the radial wavefunction of a Rydberg atom, we come back to eq. (2.13) and define the scaled radial function U(r) = r R(r) to remove the first derivative, obtaining

$$\frac{d^2 U(r)}{dr^2} + \left(2\mu \left[E_{n,l,j} - V_l(r)\right] - \frac{l(l+1)}{r^2}\right) U(r) = 0.$$
(2.20)

The radial wavefunction U(r) has stronger oscilations as the radial coordinate r decreases. These oscillations lead to accumulation of errors at small radii. To smoothen these oscillations, the radial Schrödinger eq. (2.20) can be rescaled by defining the function  $\chi(r) = r^{-1/4}U(r)$  and the radial coordinate as  $u = \sqrt{r}$  [43]. Thus eq. (2.20) becomes

$$\frac{d^2\chi}{du^2} + \left(8\mu u^2 \left[E_{n,l,j} - V_l(u)\right] - \frac{4l(l+1) + 3/4}{u^2}\right)\chi = 0.$$
(2.21)

n	Ref. [45]	This work
6	15.7	15.7
10	82.0	82.3
20	458	459
22	589	570
25	758	759
30	1133	1135
35	1584	1585
40	2110	2111
45	2710	2711.5
50	3386	3387
55	4136	4138
60	4961	4963

Table 2.6: Mean radius  $\langle r \rangle$  in atomic units  $(a_0)$  for Cesium Rydberg atom in a nD state. The values computed numerically in this work (third column) are compared with the results obtained in Ref. [45] using the scaling formula  $\langle r \rangle = [3(n - \delta_{nl})^2 - l(l+1)]/2$ .

n	Ref. [46]	This work
15	274(75)	254
20	520(150)	474
25	800(300)	762
30	1200(400)	1118
35	1800(650)	1542
37	1800(800)	1730
40	2100(850)	2033
45	2700(1900)	2593
50	3500(1900)	3220
55	3800(2300)	3914

Table 2.7: Radial integral  $\langle n^2 l_j | r | n'^2 l'_{j'} \rangle$  of the atomic transition  $n^2 D \rightarrow (n+1)^2 P$  for Rubidium taken from Ref. [46] compared with the values computed in this work using j = 3/2. The parenthesis shown in the second column correspond to the experimental error band.



Figure 2.3: Radial probability density function (first column) and radial function (second column) for (a), (b) Cesium and (c), (d) Rubidium atoms in a Rydberg state using the Numerov algorithm [44].

Inserting the core potential in terms of the variable u, eq. (2.21) then reads

$$\frac{d^2\chi(u)}{du^2} + \left[8\mu Z_{n,l}(u^2) + \frac{4\mu\alpha_c}{u^6} \left(1 - e^{-(u^2/u_c^2)^6}\right) - \frac{4\mu u^2}{(n-\delta_{n,l})^2} - \frac{4l(l+1) + 3/4}{u^2}\right]\chi(u) = 0.$$
(2.22)

Eq. (2.22) is an ordinary differential equation of second-order, which has the form  $\chi''(y) + g(y)\chi(y) = 0$  and can be solved using the Numerov algorithm [44] (see Appendix A). In this algorithm, the continuous solution y(x) is transformed into a discrete solution  $y_i$  (evaluated at the *i*-th step) for integration purposes, and the numerical implementation requires to know *a priori* the values of the function  $y_0$  and  $y_1$  or the values  $y_N$  and  $y_{N-1}$ , if N is the number of integration steps.

Due to the core potential for alkali-atoms (2.16), the rescaled wavefunction  $\chi(u)$  instead of exponentially decay to zero for small values of u, it diverges in this classically forbidden range [27]. Therefore, the range of integration must be truncated, for Rydberg alkali-atoms, the inner radius is set to be  $r_a = \alpha_c^{1/3}$ , while the outer integration radius is set as  $r_b = 2n(n + 15)$ , which is larger than classical turning point of the wavefunction. In order to minimize the errors at small values u, the integration is performed inwards and we assume that the wavefunction tends to zero at  $r_b$ . The error introduced by the range truncation for Rydberg state is only 0.01% [27], setting the radial step of integration as h, then  $N = \frac{r_b - r_a}{h}$  and the integration error using the Numerov method scales as  $\mathcal{O}(h^6)$ .

Up to this point, the Numerov algorithm gives us a radial wavefunction that must be normalized

using a normalization constant  $N_{n,l}$ , which is found by evaluating the integral

$$N_{n,l} = \int_{r_a}^{r_b} |R'(r)|^2 r^2 dr,$$
(2.23)

using cubic interpolation [47]. The normalized wavefunction  $R_{n,l}(r) = R'(r)/\sqrt{N_{nl}}$  allows us to compute matrix elements of the electric multipole operator (see Section 2.1.6) and thus, it is possible to calculate numerically some important properties of Rydberg atoms (see Section 2.2). In order to illustrate the results of the numerical integration, in Tables 2.6 and 2.7, we present the mean radius  $\langle r \rangle$  for <sup>133</sup>Cs Rydberg atom in a nD state and the radial integrals  $\langle n^2 l_j | r | n'^2 l'_{j'} \rangle$  for selected atomic transitions of <sup>85</sup>Rb, respectively. Our numerical results compare very well with available experimental data [45, 46], within the experimental error band.

Fig. 2.3 shows the radial probability density function  $|R_{n,l}|^2 r^2$  and the normalized radial function  $R_{n,l}(r)$  for selected Rydberg states of Rubidium and Cesium atoms, in which the Numerov algorithm has been used. The radial density is shifted towards larger radius as the principal quantum number increases, illustrating the large orbital radii of the Rydberg states. The radial function plots still have oscillations near to the core that are flattened as r increases.

#### 2.1.6 Electric multipoles in the fine structure basis

In order to compute the exotic properties of Rydberg atoms, we need to evaluate the matrix elements of the electric multipole using a fine structure basis. The angular part of the matrix elements can be easily calculated using angular momentum algebra, and the radial part can be calculated using the radial wavefunctions obtained following the procedure in Section 2.1.5.

Let us consider the coupled basis  $\{|n(ls)jm\rangle\}$  for an atomic state. The matrix elements  $I_{ato}(k,q)$  of a spherical tensor operator  $\hat{Q}_k^q$  [48], giving the dipole moment operator for k = 1 and the quadrupole moment operator for k = 2, are given by the expression,

$$I_{ato}(k,q) = \langle n'(l's')j'm' | \hat{Q}_{k}^{q} | n(ls)jm \rangle.$$
(2.24)

Eq. (2.24) is an atomic integral that can be rewritten using angular momentum algebra and the pure radial wavefunctions showed in the previous section. The spherical tensor operator acts on the electronic coordinates, therefore it does on the orbital angular momentum states which need to be decoupled. From the Wigner-Eckart theorem [48] we have

$$I_{ato}(k,q) = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle n'(l's')j'| |\hat{Q}_k| |n(ls)j\rangle.$$
(2.25)

where the circular brakets are the 3j-symbols and  $\langle n'(l's')j' | |\hat{Q}_k| | n(ls)j \rangle$  is the reduced matrix element [48]. Using angular momentum algebra the reduced matrix element can be decoupled as

[48]

$$\langle n'(l's')j'||\hat{Q}_k||n(ls)j\rangle = \delta_{s's}(-1)^{j+l'+s'+k}[j']^{1/2}[j]^{1/2} \left\{ \begin{array}{cc} l' & j' & s\\ j & l & k \end{array} \right\} \langle n'l'||\hat{Q}_k||nl\rangle \,, \quad \text{(2.26)}$$

where  $[j] \equiv 2j+1$ . The curly brakets is a 6j-symbol [48] and the integral  $\langle n'l' | | \hat{Q}_k | | nl \rangle$  is the orbital reduced matrix element. These matrix elements can be evaluated using the angular momentum wavefunctions  $Y_l^m$  and the Wigner-Eckart theorem, which are given by

$$\langle n'l' | |\hat{Q}_k| | nl \rangle = (-1)^{l'} [l']^{1/2} [l]^{1/2} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix} \langle n'l' | \hat{Q}_k | nl \rangle.$$
(2.27)

The radial atomic integrals  $\langle n'l' | \hat{Q}_k | nl \rangle$  can be computed by solving the electronic structure according to the previous section and represent the overlap of the wavefunctions and the tensor operator,

$$\langle n'l' | \hat{Q}_k | nl \rangle = \int_{r_i}^{r_f} R_{n'l'}(r) \hat{Q}_k(r) R_{nl}(r) r^2 dr.$$
 (2.28)

Finally, using eqs. (2.27), (2.26) and (2.25), we obtain the final expression

$$I_{ato}(k,q) = \delta_{s's}(-1)^{j'+j-m+s+k} [l']^{1/2} [l]^{1/2} [j']^{1/2} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \begin{cases} l' & j' & s \\ j & l & k \end{cases} \langle n'l' | \hat{Q}_k | nl \rangle.$$
(2.29)

### 2.2 Atomic polarizability function

In this section, we discuss the dynamical polarizability function of Rydberg atoms using the results from previus sections. This function is relevant to study the long-range interaction between Rydberg atoms and molecules in the next chapters.

We start by considering the general expression of the qq-component of the dynamical polarizability function shown in Appendix B (eq. (B.23), for an atomic state  $k = |n(ls)jm\rangle$ ,

$$\alpha_{qq'}^{nljm}(\omega) = 2(-1)^{q} \sum_{n'} \sum_{l's'} \sum_{j'm'} \frac{(E_{n'l'j'} - E_{nlj})}{(E_{n'l'j'} - E_{nlj})^{2} - \omega^{2}} \\ \langle n(ls)jm|\hat{Q}_{1}^{q}|n'(l's')j'm'\rangle \langle n'(l's')j'm'|\hat{Q}_{1}^{-q'}|n(ls)jm\rangle,$$
(2.30)

where  $\hat{Q}_1^q$  is the dipole moment operator. Expression (2.30) can be further developed for angular momentum states. Since the dipole operator ( $\hat{Q}_1^q$ ) acts over the electronic angular momentum state  $|lm_l\rangle$ , the matrix elements  $\langle nljm|\hat{Q}_1^{-q}|n'(l')j'm'\rangle$  can be rewritten using eq. (2.29). From the symmetry properties of 3j-symbols [48], the only non-zero components of the polarizability are



Figure 2.4: Atomic dynamical polarizability function components calculated for Rydberg states  $40^2 P_{3/2}$ , m = 1/2 of (a)<sup>133</sup>Cs and (b)<sup>85</sup>Rb at imaginary frequency  $\alpha_{qq}(i\omega)$ .



Figure 2.5: Atomic static polarizability components  $\alpha_{qq}(\omega = 0)$  calculated for  $n^2 D_{3/2}$ , m = 1/2Rydberg states of <sup>133</sup>Cs and <sup>85</sup>Rb atoms.

those for which q = q', thus  $\alpha_{qq}^{nljm}$  is given by

$$\begin{aligned} \alpha_{qq}^{nljm}(\omega) &= \delta_{ss'} \sum_{n'l'j'm'} (-1)^{2j'+2j-m'-m+q+1} \left[ \frac{2(E_{n'l'j'}-E_{nlj})}{(E_{n'l'j'}-E_{nlj})^2 - \omega^2} [j][l][j'][l'] \\ &\times \left( \begin{pmatrix} l' & 1 & l \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{array}{cc} l & j & s \\ j' & l' & 1 \end{array} \right\}^2 \left( \begin{array}{cc} j' & 1 & j \\ -m' & -q & m \end{array} \right)^2 |\langle n'l'| er | nl \rangle |^2 \right]. \end{aligned}$$
(2.31)

We use eq. (2.31) to compute the non-zero components of the polarizability for Rydberg atomic states ( $n \ge 15$ ) and include all intermediate states in the summation (2.31) to ensure its convergence, that is  $n' = n \pm 10$ , giving a relative change  $\delta \alpha / \alpha$  smaller than a fixed tolerance  $\varepsilon = 0.01$ .

Figure 2.4 shows the atomic dynamical polarizability components  $\alpha_{qq}^{nljm}$  evaluated at imaginary frequency for <sup>133</sup>Cs and <sup>85</sup>Rb in a  $40^2P_{3/2}$ , m = 1/2 Rydberg state. The polarizability function tends quickly to zero. Figure 2.5 shows how the static values of the polarizability increases in magnitude as a functions of the principal quantum number n for <sup>133</sup>Cs and <sup>85</sup>Rb in a  $n^2D_{3/2}$ , m = 1/2.

n	$\alpha_{sca}$ (theo)	$\alpha_{sca}(\exp)$	%error	error	$\alpha_{ten}$ (theo)	$\alpha_{ten}(\exp)$	%error	error	$\alpha_{00}^{nljm}$ (theo)
15	8.42[7]	8.60[7]	2.34	0.20[7]	3.72[7]	3.54[7]	5.23	0.19[7]	4.70[7]
20	6.25[8]	6.43[8]	2.50	0.16[8]	3.62[8]	3.58[8]	1.35	0.05[8]	2.63[8]
25	2.76[9]	2.97[9]	7.00	0.19[9]	2.08[9]	2.01[9]	3.40	0.07[9]	0.68[9]
30	1.05[10]	1.05[10]	0.40	0.042[9]	7,80[9]	7.84[9]	0.51	0.04[9]	2.70[9]
35	2.69[10]	2.97[10]	5.40	0.15[10]	2.57[10]	2.49[10]	3.39	0.087[10]	0.12[10]
40	7.45[10]	7.43[10]	0.27	0.02[10]	6.61[10]	6.43[10]	3.13	0.20[10]	0.84[10]
45	1.60[11]	1.69[11]	4.80	0.077[11]	1.59[11]	1.57[11]	1.03	0.01[11]	0.01[11]
50	3.43[11]	3.42[11]	0.50	0.017[11]	3.35[11]	3.30[11]	1.83	0.06[11]	0.08[11]
55	5.95[11]	6.59[11]	9.80	0.58[11]	6.99[11]	6.55[11]	6.75	0.47[11]	-1.04[11]

Table 2.8: Scalar and tensor static polarizabilities for <sup>85</sup>Rb in  $n^2D_{3/2}$  state calculated theoretically in this work (theo) and compared with the experimental data available [46] (exp). The %error and the corresponding absolut value of error for each polarizability component are also shown. The last column shows the 00-component of the polarizability  $\alpha_{00}^{nljm} = \alpha_{sca} - \alpha_{teo}$  for j = 3/2, m = 1/2. The square parenthesis A[x] in the fifth column means  $A \times 10^x$ .

#### **Error estimation**

Figure 2.6 and 2.7 show the 00-component of the static polarizability as a function of the principal quantum number n in different angular momentum states  $|n^2l_j\rangle$  compared with the available experimental data for <sup>133</sup>Cs and <sup>85</sup>Rb. Most of the results obtained are in good agreement with the data, except for Rubidium in  $D_{3/2}$ , m = 1/2 state. Due to the non-monotonic behavior of this polarizability in the range of n between 30 and 60 (see Fig. 2.7(c)), we consider it as a separate case.

The 00-component of the atomic polarizability (2.31) can also be written in tensorial form, which allows to define a scalar and tensor polarizability as follows [50]

$$\alpha_{00}^{nljm} = \alpha_{sca}(j) + \alpha_{ten}(j) \frac{3m^2 - j(j+1)}{j(2j-1)}.$$
(2.32)

For the state  $n^2 D_{3/2}$ , m = 1/2, we compute and compare the scalar ( $\alpha_{sca}$ ) and tensor ( $\alpha_{ten}$ ) static polarizabilities using the sum-over-states expressions given in eq. (2.32). The results are shown in Table 2.8. The 00-component of the polarizability in terms of  $\alpha_{sca}$  and  $\alpha_{ten}$  is given by  $\alpha_{00}^{nljm} = \alpha_{sca} - \alpha_{ten}$  for j = 3/2 and m = 1/2. For n = 35, 45, we found that the static polarizability  $\alpha_{00}^{nljm}$  (see last column of Table 2.8) is smaller than the error values of its corresponding scalar and tensor components. For states with n = 25, 40, 50 the total polarizability is of the order of the error. We conclude that in the region 30 < n < 60, the error band does not allow us to estimate a reliable polarizability for Rubidium  ${}^2D_{3/2}$ , m = 1/2 states.

For the rest of the atomic states of Rubidium and for all the atomic states of Cesium the estimated errors for the qq-components of the polarizabilities are less than 1% compared with the available experimental data.



Figure 2.6: 00-component of the atomic static polarizability  $\alpha_{00}(\omega = 0)$  computed for several Rydberg states of <sup>133</sup>Cs and compared with the avalaible data. This work<sup>\*</sup>, [49]<sup>†</sup>.



Figure 2.7: 00-component of the atomic static polarizability  $\alpha_{00}(\omega = 0)$  computed for several Rydberg states of <sup>85</sup>Rb and compared with the avalaible data. This work\*, [46]<sup>§</sup>, [51]<sup>‡</sup>. For  ${}^{2}D_{3/2} m = 1/2$  state, there are visible dicrepancies between all references, this is explained using eq. (2.32) and Table 2.8.

# **Chapter 3**

# **Heteronuclear Diatomic Molecules**

The complete mechanical description of the simplest diatomic molecule is difficult to achieve, even classically. In 1927, Born and Oppenheimer [52] established a good approximation to describe an isolated molecule, in which the molecule is characterized by its several types of motion, namely, translational, rotational, vibrational and electronic. This approximation relies on by the difference between the masses of the electrons and the nuclei that form the molecule. The electron mass m is about four orders of magnitude smaller than the mass of the nucleus M. Therefore, electrons can move much faster than nuclei. Born and Oppenheimer proposed the separation of the electronic and nuclear motion in the molecule by setting the parameter

$$\kappa = \left(\frac{m}{M}\right)^{1/4} \sim \frac{1}{10},\tag{3.1}$$

and showed that

$$\frac{\Delta E_{nuc}}{\Delta E_{ele}} \approx \kappa^2, \qquad \frac{\Delta E_{rot}}{\Delta E_{vib}} \approx \kappa^2, \tag{3.2}$$

where  $\Delta E_{nuc}$ ,  $\Delta E_{ele}$ ,  $\Delta E_{rot}$  and  $\Delta E_{vib}$  are the separation between nuclear, electronic, rotational and vibrational energy levels, respectively. This energy classification is well-known as the *Born–Oppenheimer separation* and is very appropriate for molecules in closed shell ground states.

This Chapter discusses the fundamentals of closed shell diatomic molecules using the Born–Oppenheimer approximation. In order to find the molecular wavefuntion, the Born adiabatic approximation and the rigid rotor model are also used. The molecular eigenstates and eigenvalues are used to compute the molecular dynamical polarizability, which will be needed to study the long-range interaction between Rydberg atoms and ground state molecules.

### 3.1 Molecular Hamiltonian and wavefunctions

The internal kinetic energy of a diatomic molecule can be written in terms of kinetic energy operator of the eletrons and nuclei in the laboratory frame as [53] (atomic units),

$$T = -\sum_{\beta=1}^{2} \frac{\nabla_{\beta}^{2}}{2M_{\beta}} - \sum_{i=1}^{N_{e}} \frac{\nabla_{i}^{2}}{2},$$
(3.3)

where  $\beta$  and *i* are sums over the nuclei of masses  $M_{\beta}$  and the  $N_e$  electrons, respectively. We can transform the kinetic energy expression (3.3) in the space-fixed frame to the center of mass of the nuclei, located at

$$\mathbf{R}_N = \frac{\sum_{\beta} M_{\beta} \mathbf{R}_{\beta}}{M_1 + M_2}.$$
(3.4)

Using the internuclear vector  $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$ , the kinetic energy defined in a system frame where the origin is at center of the nuclei is given by [53],

$$T = -\frac{\nabla_N^2}{2M_N} - \frac{\nabla_R^2}{2\mu_{mol}} - \sum_i \frac{\nabla_i'^2}{2} - \sum_{ij} \frac{\nabla_i' \nabla_j'}{2M_N},$$
(3.5)

where  $M_N = M_1 + M_2$  is the total mass of the nuclei and their reduced mass is defined as  $\mu_{mol} = M_1 M_2 / M_N$ . The operator  $\nabla'_i$  acts over the relative coordinate  $\mathbf{R}_i - \mathbf{R}_N$ . The first term on the righthand side of eq. (3.5) represents the kinetic energy due to the translational motion of the molecule, which can be ignored in the absence of spacially inhomogeneous external fields. The second term is the kinetic energy of the nuclei, which describes the vibrational and rotational motion. The term  $-\sum_i \frac{\nabla_i'^2}{2}$  is the kinetic energy of the electrons. The last term  $-\sum_{ij} \frac{\nabla_i' \nabla_j'}{2M_N}$  is commonly known as the mass polarisation term and accounts for the small fluctuations of the position of the center of mass of the nuclei due to the movement of the electrons within the molecule.

The non-relativistic molecular Hamiltonian  $\mathcal{H}_{mol}$  of a diatomic molecule in free space can thus be separated into electronic and nuclear contributions

$$\mathcal{H}_{ele} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \frac{1}{2M_{N}} \sum_{i,j} \nabla_{i} \cdot \nabla_{j} + \sum_{i \neq j} \frac{1}{R_{ij}} - \sum_{i,\beta} \frac{Z_{\beta}}{R_{i\beta}},$$
(3.6)

$$\mathcal{H}_{nuc} = -\frac{1}{2\mu_{mol}} \nabla_R^2 + \frac{Z_1 Z_2}{R}.$$
(3.7)

These Hamiltonians contain the kinetic energy terms from eq. (3.5) and the potential energy corresponding to the interaction between the particles.  $Z_{\beta}$  is the atomic charge of the nucleus and  $R_{a,b}$  is the relative distance between the particle a = i, j (electrons) and b = j (electron),  $\beta$  (nucleus).

The Schrödinger equation of a diatomic molecule in a field-free space can be written in the molecule-fixed frame as,

$$(\mathcal{H}_{ele} + \mathcal{H}_{nuc})\Psi_{rve} = E_{rve}\Psi_{rve},\tag{3.8}$$

where  $\Psi_{rve} = \Psi_{rve}(\mathbf{r}_i, R, \theta, \varphi)$  is the total molecular wavefunction which depends on the electronic coordinates  $\mathbf{r}_i$  and the nuclear spherical coordinates  $(R, \theta, \varphi)$ . Since the electron mass is approxi-

mately 1800 times smaller than the nuclear mass, the ratio  $m_e/\mu_{mol}$  is very small, and the nuclear Hamiltonian  $-\frac{1}{2\mu_{mol}}\nabla_R^2$  is a perturbing operator compared with the electronic Hamiltonian [54]. Therefore, The zero-th order wavefunctions are written as the product of electronic and nuclear states as  $\Psi_{rve}^{(0)} = \Psi_e^{(0)}\Psi_{rv}^{(0)}$ . This is known as the Born–Oppenheimer approximation.

The molecular wavefunction  $\Psi_{rve}$  can be expanded as complete set of orthonormal electronic  $\Psi_e^n$ and nuclear  $\Psi_{rv}^n$  functions as

$$\Psi_{rve} = \sum_{n} a_n \Psi_e^n(\mathbf{r}_i, R) \Psi_{rv}^n(R, \theta, \varphi).$$
(3.9)

The eigensystem for the electronic Hamiltonian is written as

$$\mathcal{H}_{ele}\Psi_e^n(\mathbf{r}_i, R) = E_e^n \Psi_e^n(\mathbf{r}_i, R)$$
(3.10)

where  $\int d\mathbf{r}_i^3 [\Psi *_e^{n'} \Psi_e^n] = \delta_{nn'}$ . Each fixed distance *R* determines different configurations of the electronic coordinates  $\mathbf{r}_i$  to solve eq. (3.10), making the electronic equation to depend parametrically depend on the internuclear distance.

Replacing eq. (3.9) into (3.8), multiplying from the left by  $\Psi_e^{*n'}$  and integrating over the electronic coordinates, we obtain

$$a_n \left( E_e^n + V_{nuc} - E_{rve} \right) \Psi_{rv}^n + \sum_n a_n C_{n'n} \Psi_{rv}^n = 0,$$
(3.11)

where  $V_{nuc} = \frac{Z_1 Z_2}{R}$  and  $C_{n'n} \Psi_{rv}^n = \int \Psi_e^{*n'} \left( -\frac{1}{2\mu_{mol}} \nabla_R^2 \right) \Psi_e^n d\mathbf{r}_i \Psi_{rv}^n$  are the non-adiabatic coupling functions. The nuclei are assumed to be fixed in space, and electrons follow the nuclear motion adiabatically, i.e. the electronic state is changing very slowly according to the nuclear displacements, i.e.  $C_{nn'} \Psi_{rv}^n \approx \left( -\frac{1}{2\mu_{mol}} \nabla_R^2 \right) \delta_{nn'} \Psi_{rv}^n$ , and the nuclear Schrödinger equation (3.11) becomes

$$\left[-\frac{1}{2\mu_{mol}}\nabla_R^2 + V_{nuc} + E_e^n\right]\Psi_{rv}^n(R,\theta,\varphi) = \mathcal{E}_{rve}[\Psi_{rv}^n(R,\theta,\varphi)].$$
(3.12)

Following the procedure in Chapter 2, Section 2.1.1 we can write the operator  $\nabla_R^2$  as,

$$\nabla_R^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{\csc \theta}{R^2} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\csc^2 \theta}{R^2} \left( \frac{\partial^2}{\partial \varphi^2} \right)$$
(3.13)

The first term is related to the vibrational motion of the nuclei and the rest is of the expression related to the rotational motion. By introducing the angular momentum operator  $\mathbf{J}$  of the molecular system as

$$\mathbf{J}^{2} = \csc\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta}\right) + \csc^{2}\theta \frac{\partial^{2}}{\partial\varphi^{2}},\tag{3.14}$$

we can simplify expression for the operator (3.13) to read

$$\nabla_R^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{\mathbf{J}^2}{R^2}.$$
(3.15)

The nuclear wavefunction can be solved by separating the radial and the angular dependence



Figure 3.1: Lowest ten electronic potentials of the <sup>23</sup>Na<sup>6</sup>Li molecule. The energy U(r) is in atomic units (a.u.) and R in units of Bohr radius  $a_0$ . Potentials are taken from Ref. [55].

(vibrations and rotations) as

$$\phi_{rv}^{n}(R,\theta,\varphi) = \frac{S(R)}{R} Y_{J}^{M}(\theta,\varphi), \qquad (3.16)$$

where  $Y_J^M(\theta, \varphi)$  are spherical harmonics with M being the component of total angular momentum J along the space-fixed *z*-axis. The spherical harmonic functions obey the relation

$$\mathbf{J}^{2}Y_{I}^{M} = J(J+1)Y_{I}^{M},\tag{3.17}$$

and they correspond to angular momentum states of the system, i.e.

$$|JM\rangle = Y_J^M(\theta,\varphi). \tag{3.18}$$

Applying the angular momentum state relation (3.17) into eq. (3.12), we obtain a radial nuclear equation of the form

$$\left[-\frac{1}{2\mu_{mol}}\left(\frac{d^2}{dR^2}\right) + \frac{J(J+1)}{2\mu_{mol}R^2} + V(R)\right]S(R) = \mathcal{E}_{rve}S(R).$$
(3.19)

The second term is the rotational energy that acts as a centrifugal barrier to the vibrational motion. The effective nuclear potential is  $V(R) = V_{nuc}(R) + E_e^n(R)$ .

The radial wavefunction describes the vibration of the nuclei about a given position (R) and the angular wavefunction describes the rotation of the molecule about its center of mass. In general, even when this separation of varibles has been done, these two types of motions are coupled [53].

To solve eq. (3.19), it is necessary to know V(R), which is found by solving the electronic Schrödinger equation (3.10) for several internuclear distances, giving potential curves for V(R) like those shown in Figure 3.1 for <sup>23</sup>Na<sup>6</sup>Li molecules.


Figure 3.2: Molecular electronic potential displaying several vibrational levels and comparison with the harmonic approximation around the equilibrium position  $R_e$ .

Figure 3.2 shows a typical electronic potential curve. For  $R \to 0$  the potential represents a strong repulsive barrier between the nuclei. As R increases, the potential energy reaches its minimum value at equilibrium position  $R_e$ . From this point the potential increases with R, tending to an asymptotic value at  $R \to \infty$ , where molecules eventually dissociate.

Back to the radial equation (3.19), V(R) can be expressed as a Taylor series around the equilibrium position ( $R_e$ ) obtaining

$$V(R) = \frac{k_e}{2} (R - R_e)^2, \qquad k_e = \frac{d^2 V(R_e)}{dR^2}.$$
(3.20)

This is an harmonic potential model and it works for low rotational levels (near the equilibrium position  $R_e$ ). Replacing (3.20) into (3.19) and taking  $R = R_e$  for the rotational energy, the radial eq. (3.19) becomes

$$\left[-\frac{1}{2\mu_{mol}}\left(\frac{d^2}{dR^2}\right) + \frac{J(J+1)}{2\mu_{mol}R_e^2} + \frac{k_e}{2}(R-R_e)^2\right]S(R) = \mathcal{E}_{rve}S(R).$$
(3.21)

Setting  $R = R_e$  to obtain eq. (3.21) is known as the *rigid rotor* approximation, which states that while the molecule rotates the internuclear distance does not change. The mathematical justification is supported by a Taylor series of a rotational term about  $R_e$ .

Finally, with  $q = R - R_e$  and the rotational term  $\frac{J(J+1)}{2\mu_{mol}R_e^2} = E_{rot}$ , eq. (3.21) is rewritten as

$$\left[-\frac{1}{2\mu_{mol}}\left(\frac{d^2}{dq^2}\right) + \frac{k_e}{2}q^2\right]S(q) = \left(\mathcal{E}_{rve} - E_{rot}\right)S(R).$$
(3.22)

The energy levels for this harmonic oscillator are given by<sup>1</sup>,

$$E_{vib} = \left(v + \frac{1}{2}\right)h\nu_e, \quad \nu_e = \frac{1}{2\pi} \left(\frac{k_e}{\mu_{mol}}\right)^{\frac{1}{2}}, \quad v = 0, 1, 2, 3, \dots$$
(3.23)

The rovibrational energies of diatomic molecules in the rigid rotor approximation are thus given by

$$E_{vJ} = \left(v + \frac{1}{2}\right)hv_e + J(J+1)B_e.$$
 (3.24)

Where  $B_e = \frac{1}{2\mu_{mol}R_e}$  (in atomic units) is the *rotational constant*, which ranges between 1-20 GHz for alkali-heteronuclear diatomic molecules [57].

The rigid rotor and harmonic oscillator models are approximations valid for low excited energy levels (vibrational and rotational). For higher excited levels, it is required to take more terms in the Taylor series for the potential V(q), in a general form [53]

$$V(q) = a_0 q^2 (1 + a_1 q + a_2 q^2 + a_3 q^3 + ...),$$
(3.25)

where  $a_0 = hw_e^2/4B_e$  and  $a_i$  with i = 1, 2, 3... are constants. Equation (3.25) represents the anharmonic deviations of the harmonic model (3.20). The rotational term can also be expanded as a power series in q as (Planck constant h = 1)

$$H_{rot} = \frac{1}{2\mu_{mol}R_e}J(J+1)[1+c_1q+c_2q^2+c_3q^3+...],$$
(3.26)

where  $c_i$  with i = 1, 2, 3... are constants. Eqs. (3.25) and (3.26) can be treated using ordinary non-degenerate perturbation theory [53], giving a total rovibrational energy of the form

$$E_{(v,J)} = \sum_{kl} Y_{kl} (v+1/2)^k J^l (J+1)^l.$$
(3.27)

The coefficients  $Y_{kl}$  are explicitly given by Dunham [58]. Eq. (3.27) is well-known as the Dunham expansion.

In general, the vibrational energy is about three orders of magnitude greater than the rotational energy  $v_e > B_e$ . This is due to the dependence with the reduced mass;  $v_e \propto \mu_{mol}^{-\frac{1}{2}}$ , while  $B_e \propto \mu_{mol}^{-1}$ . Therefore, a mainfold of rotational energy levels are associated to one particular vibrational state [59]. There is another relevant energy scale, corresponding to the changes in the electronic levels. This energy scale is at least two orders of magnitude greater than the vibrational energy [59].

So far we have not considered the interaction Hamiltonian of the electronic angular momentum and the electronic spin  $\mathcal{H}(\mathbf{L}, \mathbf{S})$ , which is related to smaller energy scales in the molecular structure. Considering this interaction Hamiltonian, the general form of the angular momentum states

<sup>&</sup>lt;sup>1</sup>Using the harmonic oscillator model it is found that  $S_v(q) = \left(\frac{\alpha}{\Pi}\right)^{1/4} \frac{\mathbf{H}_v(\alpha^{1/2}q) \exp{-\alpha q^2/2}}{(2^v v!)^{1/2}}$  [56].  $\mathbf{H}_v$  are the Hermite polynomials,  $\alpha = \frac{\mu_{mol}\omega_e}{\hbar}$  and  $\omega_e = 2\pi v_e$ .

becomes [53]

$$|J\Omega M\rangle = \left[\frac{2J+1}{4\pi}\right]^{1/2} \mathcal{D}_{M\Omega}^{(J)}(\theta,\varphi,\chi), \tag{3.28}$$

and the rotational energy is given by,

$$E_{rot} = \frac{1}{2\mu_{mol}R^2} \left[ J(J+1) - \Omega^2 \right]$$
(3.29)

where  $\Omega = \Lambda + \Sigma$ , which are the eigenvalues of the operators  $\mathbf{L}_z$  and  $\mathbf{S}_z$ , respectively, and  $\mathcal{D}_{M\Omega}^{(J)}$  is an element of the Wigner rotation matrix [48] specified by the Euler angles  $(\theta, \varphi, \chi)$  [48].

Since we work with closed-shell molecules in the  $X^1\Sigma^+$  state, all the electronic angular momenta are zero ( $\mathbf{L} = \mathbf{S} = \mathbf{0}$ ), therefore  $\Omega = 0$  and eq. (3.28) becomes

$$|J0M\rangle = \left[\frac{2J+1}{4\pi}\right]^{1/2} \mathcal{D}_{M0}^{(J)}(\theta,\varphi) = Y_J^M,$$
(3.30)

as given in eq. (3.16).

Finally, the state for an isolated diatomic molecule under the Born–Oppenheimer approximation and the rigid rotor model can be written as

$$\Psi_{rve} \equiv |\gamma\rangle |vJ\rangle |J\Omega M\rangle, \qquad (3.31)$$

where  $|\gamma\rangle$  denotes de electronic state,  $|vJ\rangle$  is the rovibrational state and  $|J\Omega M\rangle$  is angular momentum state. For molecules in the electronic and rovibrational ground state, in which we are interested, the system state is given by  $|X^1\Sigma^+\rangle |v=0, J=0\rangle |J=0, \Omega=0, M=0\rangle$ .

#### 3.2 Molecular polarizability function

In this section, we study the frequency-dependent polarizability of ground state molecules ( $X^{1}\Sigma^{+}, v = 0, J = 0$ ) and compute this function for KRb, LiCs, LiRb and RbCs molecules. We focus on the low-frequency regime, in which these molecules interact at long-range distances with Rydberg alkali-atoms.

In the space-fixed frame, the dynamical dipole polarizability components (see Appendix B) for a molecular state  $|\gamma v J\Omega M\rangle$  with energy  $E_{\gamma v J}$  can be written as

$$\alpha_{qq'}^{\gamma v J\Omega M}(\omega) = \sum_{\gamma' v'} \sum_{J'\Omega'M'} \left[ \frac{2(-1)^q (E_{\gamma' v'J'} - E_{\gamma vJ})}{(E_{\gamma' v'J'} - E_{\gamma vJ})^2 - \omega^2} \times \langle \gamma v J\Omega M | \hat{Q}_1^q | \gamma' v'J'\Omega'M' \rangle \langle \gamma' v'J'\Omega'M' | \hat{Q}_1^{-q'} | \gamma v J\Omega M \rangle \right].$$
(3.32)

Where  $\hat{Q}_1^q$  is a multipole moment, a spherical tensor operator of rank 1 and component q. To evaluate the molecular dipole integrals  $\langle \gamma v J \Omega M | \hat{Q}_1^q | \gamma' v' J' \Omega' M' \rangle$  in the space-fixed frame, the q-

component of the dipole operator must be written in terms of the molecule-fixed *p*-components through the unitary transformation  $\hat{Q}_1^q = \sum_p \mathcal{D}_{qp}^{*(1)} \hat{Q}_1^p$ . Transforming to the molecule-fixed frame is convenient since the electronic and nuclear eigenfunctions are usually computed in the molecule-fixed frame. The matrix elements of the spherical tensor operator are given by,

$$\langle \gamma v J \Omega M | \hat{Q}_1^q | \gamma' v' J' \Omega' M' \rangle = \sum_p \langle J \Omega M | \mathcal{D}_{qp}^{*(1)} | J' \Omega' M' \rangle \langle \gamma v | \hat{Q}_1^p | \gamma' v' \rangle .$$
(3.33)

The matrix elements  $\langle J\Omega M | \mathcal{D}_{qp}^{*(1)} | J'\Omega' M' \rangle$  can be evaluated using the expression for the angular integral of the Wigner rotation matrix [48]

$$\int \mathcal{D}_{M'_{3}M_{3}}^{J_{3}}(K) \mathcal{D}_{M'_{2}M_{2}}^{J_{2}}(K) \mathcal{D}_{M'_{1}M_{1}}^{J_{1}}(K) dK = 8\pi^{2} \begin{pmatrix} J_{1} & J_{2} & J_{3} \\ M'_{1} & M'_{2} & M'_{3} \end{pmatrix} \begin{pmatrix} J_{1} & J_{2} & J_{3} \\ M_{1} & M_{2} & M_{3} \end{pmatrix},$$
(3.34)

where  $dK = d\varphi \sin\theta d\theta d\chi$  is the solid angle element and the circular brakets are the 3j-symbols [48]. Therefore, the matrix element  $\langle J\Omega M | \mathcal{D}_{qp}^{*(1)} | J'\Omega' M' \rangle$  can be written as

$$\langle J\Omega M | \mathcal{D}_{qp}^{*(1)} | J'\Omega' M' \rangle = (-1)^{M-\Omega} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J' & 1 & J \\ -M' & -q & M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -\Omega' & -p & \Omega \end{pmatrix},$$
(3.35)

and eq. (3.32) becomes

$$\alpha_{qq'}^{\gamma v J\Omega M}(\omega) = \sum_{\gamma',v'} \sum_{J'\Omega'M'} 2(-1)^{M+M'-\Omega-\Omega'} \frac{E_{\gamma'v'J'} - E_{\gamma vJ}}{(E_{\gamma'v'J'} - E_{\gamma vJ})^2 - (\omega)^2} \times [J][J'] \begin{pmatrix} J' & 1 & J \\ -M' & -q & M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -M' & q' & M \end{pmatrix} \times \sum_{pp'} \begin{pmatrix} J' & 1 & J \\ -\Omega' & -p & \Omega \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & -p' & \Omega' \end{pmatrix} \langle \gamma v | \hat{Q}_1^p | \gamma'v' \rangle \langle \gamma'v' | \hat{Q}_1^{p'} | \gamma v \rangle , \qquad (3.36)$$

where  $[J] \equiv 2J+1$ . According to the symmetry properties of the 3*j*-symbols [48], the non-vanishing terms in eq. (3.36) are those with q' = q and -p = p'. Expression (3.36) can then be rewritten as

$$\alpha_{qq}^{\gamma v J\Omega M}(\omega) = \sum_{\gamma', v'} \sum_{J'\Omega'M'} 2(-1)^{M+M'-\Omega-\Omega'} [J] [J'] \frac{E_{\gamma'v'J'} - E_{\gamma vJ}}{(E_{\gamma'v'J'} - E_{\gamma vJ})^2 - (\omega)^2} \\ \sum_{p} \left( \begin{array}{cc} J' & 1 & J \\ -M' & -q & M \end{array} \right)^2 \left( \begin{array}{cc} J' & 1 & J \\ -\Omega' & -p & \Omega \end{array} \right)^2 |\langle \gamma v | \hat{Q}_1^p | \gamma'v' \rangle|^2.$$
(3.37)

Eq. (3.37) can be separated into diagonal and non-diagonal terms with respect to  $\gamma$  as follows

$$\alpha_{qq}^{\gamma v J\Omega M}(\omega) = \alpha_{qq}^{rv}(\omega) + \alpha_{qq}^{ele}(\omega), \qquad (3.38)$$

where

$$\alpha_{qq}^{rv}(\omega) = \sum_{v'} \sum_{J'\Omega'M'} 2(-1)^{M+M'-2\Omega} [J] [J'] \frac{E_{\gamma v'J'} - E_{\gamma vJ}}{(E_{\gamma v'J'} - E_{\gamma vJ})^2 - (\omega)^2} \\ \sum_{p} \begin{pmatrix} J' & 1 & J \\ -M' & -q & M \end{pmatrix}^2 \begin{pmatrix} J' & 1 & J \\ -\Omega & -p & \Omega \end{pmatrix}^2 |\langle \gamma v | \hat{Q}_1^p | \gamma v' \rangle|^2,$$
(3.39)

and

$$\alpha_{qq}^{ele}(\omega) = \sum_{\gamma'(\neq\gamma)} \sum_{v'} \sum_{J'\Omega'M'} 2(-1)^{M+M'-\Omega-\Omega'} [J] [J'] \frac{E_{\gamma'v'J'} - E_{\gamma vJ}}{(E_{\gamma'v'J'} - E_{\gamma vJ})^2 - (\omega)^2} \\ \sum_{p} \left( \begin{array}{cc} J' & 1 & J \\ -M' & -q & M \end{array} \right)^2 \left( \begin{array}{cc} J' & 1 & J \\ -\Omega' & -p & \Omega \end{array} \right)^2 |\langle \gamma v| \hat{Q}_1^p | \gamma'v' \rangle|^2.$$
(3.40)

Eq. (3.39) is known as the rovibrational polarizability and corresponds to sum over the molecular states inside the same electronic curve, i.e.  $\gamma' = \gamma$ . Due to the symmetry properties of the 3j-symbols, p = 0 thus  $\Delta \Omega = 0$ .  $\alpha_{qq}^{rv}(\omega)$  becomes

$$\alpha_{qq}^{rv}(\omega) = \sum_{v'J'M'} (2J+1)(2J'+1) \frac{2(E_{v'J'} - E_{vJ})}{(E_{v'J'} - E_{vJ})^2 - \omega^2} \begin{pmatrix} J' & 1 & J \\ -\Omega & 0 & \Omega \end{pmatrix}^2 \begin{pmatrix} J' & 1 & J \\ -M' & -q & M \end{pmatrix}^2 |\langle vJ|\hat{Q}_1^0|v'J'\rangle|^2,$$
(3.41)

where the electronic index  $\gamma$  has been omitted for simplicity.

Eq. (3.40) accounts for the sum over different electronic states, i.e.  $\gamma' \neq \gamma$ , and it is denoted as the electronic polarizability. This contribution  $\alpha_{qq}^{ele}(\omega)$  can be separated into two terms, p = 0 and  $p = \pm 1$ . For a molecule in the electronic ground state  $X^1\Sigma^+$ , these can written as follow

$$\alpha_{00}(\omega) = \alpha_{\parallel}(\omega) = \sum_{\Sigma'v'} \frac{2(E_{\Sigma'v'J'} - E_{\Sigma vJ})}{(E_{\Sigma'v'J'} - E_{\Sigma vJ})^2 - (\omega)^2} |\langle \Sigma v | \hat{Q}_1^0 | \Sigma'v' \rangle|^2,$$
(3.42)

and

$$\alpha_{\pm 1\pm 1}(\omega) = \alpha_{\perp}(\omega) = \sum_{\Pi'v'} \frac{2(E_{\Pi'v'J'} - E_{\Sigma vJ})}{(E_{\Pi'v'J'} - E_{\Sigma vJ})^2 - (\omega)^2} |\langle \Sigma v | \hat{Q}_1^{\pm 1} | \Pi'v' \rangle |^2.$$
(3.43)

The term  $\alpha_{\parallel}(\omega)$  is the parallel electronic polarizability and involves transitions with excited electronic states with  $\Omega = 0$  and  $\alpha_{\perp}(\omega)$  is the perpendicular electronic polarizability, related with transition to states with  $\Omega = \pm 1$  known as  $\Pi$  states. Using eqs. (3.42) and (3.43), the electronic

Molecule	$lpha_{\parallel}(0)$	$\alpha_{\perp}(0)$
KRb	748.7	382.9
LiCs	597.0	262.5
LiRb	524.3	246.5
RbCs	904.0	492.3

Table 3.1: Parallel and perpendicular electronic static polarizabilities used to compute the total dynamical polarizability in eq. (3.45). Data taken from Ref. [57].

polarizability  $\alpha_{qq}^{ele}$  for the molecular state  $|X^1\Sigma^+, v=0, J=0, M=0\rangle$  can be written as

$$\alpha_{qq}^{\text{el}}(\omega) = \sum_{J'M'} (2J+1)(2J'+1) \begin{pmatrix} J' & 1 & J \\ -M' & -q & M \end{pmatrix}^{2} \\
\begin{bmatrix} \begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix}^{2} \alpha_{\parallel}(\omega) + 2 \begin{pmatrix} J' & 1 & J \\ 1 & -1 & 0 \end{pmatrix}^{2} \alpha_{\perp}(\omega) \end{bmatrix}.$$
(3.44)

The energy frequency of the transitions considered in eq. (3.44) are of the order of  $E_{\gamma'v'J'} - E_{\Sigma vJ}/\hbar \sim 10^2$  THz for alkali-diatomic molecules. Then in low frequency regime ( $\omega < 5000$  GHz),  $\alpha_{\parallel}(\omega)$  and  $\alpha_{\perp}(\omega)$  will remain constant, thus they can be replaced by their static values  $\alpha_{\parallel}(0), \alpha_{\perp}(0)$ . Combining eqs. (3.41) and (3.44) (using  $\alpha_{\parallel}(0), \alpha_{\perp}(0)$ ) into eq. (3.38), the explicit expression for the total dynamical polarizability function of the molecular state  $|X^1\Sigma^+, v = 0, J = 0, M = 0\rangle$  in the low frequency regime is given by

$$\alpha_{qq}^{JM}(\omega) = \sum_{J'M'} (2J+1)(2J'+1) \begin{pmatrix} J' & 1 & J \\ -M' & -q & M \end{pmatrix}^{2} \times \\
\left[ \sum_{v'} |\langle vJ| \hat{Q}_{1}^{0} | v'J' \rangle |^{2} \frac{2(E_{v'J'} - E_{vJ})}{(E_{v'J'} - E_{vJ})^{2} - \omega^{2}} \begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix}^{2} \\
+ \begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix}^{2} \alpha_{\parallel}(0) + 2 \begin{pmatrix} J' & 1 & J \\ 1 & -1 & 0 \end{pmatrix}^{2} \alpha_{\perp}(0) \right],$$
(3.45)

where we have dropped the  $\Sigma$  and v labels of the state notation for simplicity. The radial dipole integrals  $\langle vJ | \hat{Q}_1^q | v'J' \rangle$  can be explicitly evaluated using the rovibrational wavefunctions  $|vJ\rangle$  and energies  $E_{vJ}$ . We obtain  $|vJ\rangle$  and  $E_{vJ}$  by solving the corresponding nuclear Schrödinger equation (i.e., vibrations plus rotations) using the Discrete Variable Representation (DVR) [60]. This method requires the potential energy and the electric dipole function for the ground state ( $X^1\Sigma^+, v = 0, J =$ 0) as a function of the internuclear distance, which are taken from Ref. [61] for the molecules used in this work: KRb, LiCs, LiRb and RbCs. Addicionally, the reported experimental values used for  $\alpha_{\parallel}(0)$  and  $\alpha_{\perp}(0)$  are tabulated in Table 3.1 as taken from Ref. [57].

Fig. 3.3 shows the dynamical polarizability for selected ground state molecules evaluated at imaginary  $i\omega$  and real  $\omega$  frequencies up to  $\omega \sim 5$  THz (KRb, RbCs, LiRb and LiCs) using eq. (3.45). At



Figure 3.3: Molecular dynamical polarizability computed at (a) imaginary frequencies ( $i\omega$ ) and (b) real frequencies ( $\omega$ ) using eq. (3.45) for different diatomic molecules in the electronic and rovibrational ground state  $|X^1\Sigma^+, v = 0, J = 0, M = 0\rangle$ . The molecular transition  $v = 0 \rightarrow v = 1$  is highlighted at  $\omega \approx 1.5$  THz for RbCs.

imaginary frequencies, the figure shows the decreasing monotonic character of all molecular polarizability functions studied. Whereas at real frequencies, the molecules show their characteristic resonances of the rovibrational transitions expected for  $\omega < 5$  THz.

Table 3.2 compares the static values of the total polarizability (eq. (3.45)) and the electronic polarizability (eq. (3.44)) with other theoretical results. Our numerical calculation does not exceed 1% error.

Molecule	α(0) <b>[61]</b>	$\alpha(0)$ [This work]	$\alpha^{ele}(0)$ [61]	$\alpha^{ele}$ [This work]
KRb	1.141[5]	1.138[5]	513.1	504.8
LiCs	1.890[6]	1.890[6]	377	374
LiRb	9.198[5]	9.065[5]	346.1	339.1
RbCs	1.076[6]	1.065[6]	621.5	629.5

Table 3.2: Total and electronic molecular static polarizabilities ( $\omega = 0$ ) computed using eq. (3.45) and (3.44), respectively, for molecules in a  $X^1\Sigma^+$  state with v = 0 and J = 0. Our data is compared with numerical data taken from Ref. [61]. The square parenthesis A[x] means  $A \times 10^x$ 

As the frequency  $\omega$  increases and reaches the THz regime ( $\omega > 5$  THz), all molecular functions  $\alpha_{qq}^{JM}(\omega)$  tend asymptotically to their isotropic static polarizabilities  $\alpha_{iso}^{el}$ , and remain constant over

a large frequency range up to several hundred THz [61]. It was shown in Ref. [61], that for frequencies up to  $\sim 10^3$  THz, the isotropic electronic molecular polarizability can be accurately approximated by

$$\alpha_{\rm iso}^{\rm el}(\omega) = \frac{2\omega_{\Sigma} d_{\Sigma}^2}{\omega_{\Sigma}^2 - \omega^2} + \frac{2\omega_{\Pi} d_{\Pi}^2}{\omega_{\Pi}^2 - \omega^2},\tag{3.46}$$

where the parameters  $\omega_{\Sigma}$  and  $d_{\Sigma}$  are the effective transition energy and dipole moment associated with the lowest  $\Sigma \to \Sigma$  transition. The parameters  $\omega_{\Pi}$  and  $d_{\Pi}$  are associated with the lowest  $\Sigma \to \Pi$ transition. For the alkali-metal dimers used in this work, we use the effective parameters listed in Ref. [61] to estimate the electronic contribution to the molecular polarizability over the frequencies of interest.

### Chapter 4

# Long-range interaction between Rydberg alkali-atoms and diatomic molecules

In this Chapter, we describe the theoretical framework used to study the long-range interaction betweeen an atom and a diatomic molecule. We derive the multipolar expansion of the electrostatic interaction between two charge distributions in the spherical basis. We treat this interaction pertubartively. For ground state molecules, the first-order correction energy is zero regardless of the atomic state. The second-order correction corresponds to the van der Waals interaction energy, expressed in terms of the state-dependent dynamical polarizabities of the colliding particles.

#### 4.1 Multipolar expansion of the electrostatic interaction

We consider two charge distributions A and B interacting through electrostatic forces that give rise to a potential energy. We assume classical point-like charges for each distribution that do not overlap with each other as shown in Fig. 4.1. The positions  $\mathbf{r}_i$  ( $\mathbf{r}_j$ ) of the charges  $q_i$  ( $q_j$ ) in A (B) are given with respect to the center of mass  $A_C$  ( $B_C$ ) of the distribution A (B). The vector joining  $A_C$  and  $B_C$  is denoted by  $\mathbf{R}$ . Without loss of generality, the center of mass  $A_C$  is fixed in the laboratory and is the origin of the coordinate frame xyz. The electrostatic potential energy  $V_{AB}$ between the two clouds in atomic units is given by

$$V_{AB} = \sum_{i \in A} \sum_{j \in B} \frac{q_i q_j}{|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|}.$$
(4.1)

Since the charge clouds do not overlap, we consider them to be far away such that

$$|\mathbf{R}| \gg |\mathbf{r}_i|, |\mathbf{r}_j| \quad \forall i \in A, \ \forall j \in B.$$
(4.2)



Figure 4.1: Charge distribution A and B in the xyz coordinate system.

The distance between two charges from different clouds can thus be written as

$$|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i| = \sqrt{(\mathbf{R} - (\mathbf{r}_i - \mathbf{r}_j))^2} = \sqrt{R^2 - 2\mathbf{R} \cdot \mathbf{r}_{ij} + r_{ij}^2},$$
(4.3)

where  $R = |\mathbf{R}|$  and the vector  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$  with norm  $r_{ij} = |\mathbf{r}_{ij}|$ . Let us denote the unit vector in **R**-direction as  $\hat{u}$ , where  $\mathbf{R} = R\hat{u}$  and the angle between the vectors  $\hat{u}$  and  $\mathbf{r}_{ij}$  as  $\theta_{ij}$ . Eq. (4.3) takes the form

$$|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i| = R\sqrt{1 - \frac{2\hat{u} \cdot \mathbf{r}_{ij}}{R} + \frac{r_{ij}^2}{R^2}} = R\sqrt{1 - \frac{2\mathbf{r}_{ij}\cos\theta_{ij}}{R} + \frac{r_{ij}^2}{R^2}}.$$
 (4.4)

The reciprocal of eq. (4.4) can be we expanded using the generating series of Legendre polynomials  $P_L(x)$  as [48],

$$\frac{1}{R\sqrt{1-\frac{2\mathbf{r}_{ij}\cos\theta_{ij}}{R}+\frac{r_{ij}^2}{R^2}}} = \sum_{L=0}^{\infty} \frac{r_{ij}^L}{R^{L+1}} P_L(\cos\theta_{ij}).$$
(4.5)

We denote the body-fixed coordinate system as uvw, with the  $\hat{u}$ -axis joining the centers of mass of the distributions. If we assume that the vector  $\hat{u}$  lies along the  $\hat{z}$ -axis, the Legendre polynomial in eq. (4.5) is proportional to the spherical harmonics  $Y_L^0(\theta_{ij}, \varphi_{ij})$  [48] where  $\varphi_{ij}$  is the azimuthal angle giving the orientation of  $\mathbf{r}_{ij}$  in the body frame,

$$P_L(\cos\theta_{ij}) = \sqrt{\frac{4\pi}{2L+1}} Y_L^0(\theta_{ij},\varphi_{ij}).$$
(4.6)

Using eqs. (4.6) and (4.5), eq. (4.1) in the body-fixed frame (BF) becomes

$$V_{AB}^{BF} = \sum_{i \in A} \sum_{j \in B} \sum_{L=0}^{\infty} q_i q_j \frac{r_{ij}^L}{R^{L+1}} \sqrt{\frac{4\pi}{2L+1}} Y_L^0(\theta_{ij}, \varphi_{ij}).$$
(4.7)

We can introduce the spherical coordinates  $(r_i, \theta_i, \varphi_i)$  of the vector  $\mathbf{r}_i$  and  $(r_j, \theta_j, \varphi_j)$  of  $\mathbf{r}_j$  in the

body frame by using the following relation for the factor  $r_{ij}^L Y_L^M(\theta_{ij}, \varphi_{ij})$  [62],

$$r_{ij}^{L}Y_{L}^{M}(\theta_{ij},\varphi_{ij}) = \sqrt{4\pi(2L+1)} \sum_{L_{A},L_{B}=0}^{\infty} \delta_{L_{A}+L_{B},L} \frac{(-1)^{L_{B}}r_{i}^{L_{A}}r_{j}^{L_{B}}}{\sqrt{(2L_{A}+1)(2L_{B}+1)}} \\ \times \sum_{M_{A}=-L_{A}}^{L_{A}} \sum_{M_{B}=-L_{B}}^{L_{B}} C_{L_{A}M_{A},L_{B}M_{B}}^{LM}Y_{L_{A}}^{MA}(\theta_{i},\varphi_{i})Y_{L_{B}}^{MB}(\theta_{j},\varphi_{j}),$$
(4.8)

where  $C_{L_AM_A,L_BM_B}^{LM} = \langle L_AM_A, L_BM_B | LM \rangle$  is a Clebsch-Gordan coefficient, which can be written explicitly as [48]

$$\langle L_A M_A, L_B M_B | LM \rangle = \delta_{M_A + M_B, M} \left[ (2L+1) \frac{(s-2L)!(s-2L_B)!(s-2L_A)!}{(s+1)!} \times (L_A + M_A)!(L_A - M_A)!(L_B + M_B)!(L_B - M_B)!(L+M)!(L-M)! \right]^{1/2} \times \sum_{\nu} (-1)^{\nu} / \left[ \nu!(L_A + L_B - L - \nu)!(L_A - M_A - \nu)!(L_B + M_B - \nu)! \times (L - L_B + M_A + \nu)!(L - L_A - M_B + \nu)! \right]$$
(4.9)

where  $s = L_A + L_B + L$  and the index  $\nu$  ranges over all integral values for which the factorial arguments are nonnegative. According to eqs. (4.7) and (4.8)  $L = L_A + L_B$ , therefore, the sum over  $\nu$  in eq. (4.9) is restricted to  $\nu = 0$  and the Clebsch-Gordan coefficient for  $L = L_A + L_B$  becomes

$$C_{L_A M_A, L_B M_B}^{LM} = \sqrt{\frac{(2L_A)!(2L_B)!(L+M)!(L+M)!}{(2L)!(L_A + M_A)!(L_A - M_A)!(L_B + M_B)!(L_B - M_B)!}}.$$
(4.10)

Combining the relations (4.10) and (4.8) into (4.7), we find that  $M = 0 \rightarrow M_A = -M_B$ . Setting the variable  $q = M_A = -M_B$ , the final expression for  $V_{AB}^{BF}$  reads

$$V_{AB}^{BF}(R) = \sum_{L_A=0}^{\infty} \sum_{L_B=0}^{\infty} \sum_{q=-L_{<}}^{L_{<}} \frac{f_{L_A L_B q}}{R^{1+L_A+L_B}} Q_{L_A}^q(r_A) Q_{L_B}^{-q}(r_B),$$
(4.11)

where  $L_{<}$  is the smallest of the integers  $L_{A}$  and  $L_{B}$ . The multipole moments  $Q_{L_{X}}^{q}(\mathbf{r}_{X})$  associated with a particle X = (A, B) are written as,

$$Q_{L_X}^q(r_X) = \left(\frac{4\pi}{2L_X + 1}\right)^{1/2} \sum_i q_i r_i^{L_X} Y_{L_X}^q(\theta_i, \varphi_i).$$
(4.12)

Expectation values of the multipole moments depend on the electronic structure of the particle. The factor  $f_{L_A L_B q}$  in eq. (4.11) becomes

$$f_{L_A L_B q} = \frac{(-1)^{L_B} (L_A + L_B)!}{\sqrt{(L_A + q)! (L_A - q)! (L_B + q)! (L_B - q)!}}.$$
(4.13)

The BF is chosen the reference frame, thus the superscript "BF" is dropped henceforth for simplic-

#### ity.

#### 4.2 Perturbation theory for the long-range interaction

In this Section, we consider the charge distribution A to correspond to a ground state heteronuclear diatomic molecule and the distribution B to an alkali-metal atom in a Rydberg state. In the asymptotic limit  $R \to \infty$ , the interaction potential  $V_{AB}$  can be treated using quantum perturbation theory [56], since the interaction energy is smaller than the transition energy between Rydberg states ( $\Delta E_{nlj}$ ) and the rotational transition ( $\Delta E_{rot} = 2B_e$ ) of the molecule.

The asymptotic two-particle eigenstates can be written as

$$|\Phi_{AB}\rangle = |\Psi_A\rangle |\Psi_B\rangle, \qquad (4.14)$$

where the state for the molecule is  $|\Psi_A\rangle \equiv |\gamma v J\Omega M\rangle$ , an the atomic state is  $|\Psi_B\rangle = |n(ls)jm\rangle$ . The asymptotic energy of the atom-molecule system state is given by

$$E_{AB}^{(0)} = E_A^{(0)} + E_B^{(0)}, (4.15)$$

where  $E_A^{(0)} \equiv E_{\gamma vJ}$  and  $E_B^{(0)} \equiv E_{nlj}$ .

#### 4.2.1 First-order energy correction

The first-order correction to the two-particle energy is obtained by diagonalizing the interaction matrix  $\hat{V}_{AB}$  in a given degenerate subspace  $S = |\gamma v J \Omega M\rangle |n(ls)jm\rangle$ , which is (2J+1)(2j+1)-fold degenerate. The matrix elements  $\langle \Psi'_A | \langle \Psi'_B | \hat{V}_{AB} | \Psi_A \rangle | \Psi_B \rangle$  are given by

$$\langle \Psi_A' | \langle \Psi_B' | \hat{V}_{AB} | \Psi_A \rangle | \Psi_B \rangle = \langle \gamma' v' J' \Omega' M' | \langle n'(l's') j' m' | \hat{V}_{AB} | n(ls) jm \rangle | \gamma v J \Omega M \rangle.$$
(4.16)

Inserting eq. (4.11) we explicitly have

$$\langle \Psi_{A}' | \langle \Psi_{B}' | \hat{V}_{AB} | \Psi_{A} \rangle | \Psi_{B} \rangle = \sum_{L_{A}=0}^{\infty} \sum_{L_{B}=0}^{\infty} \sum_{q=-L_{<}}^{L_{<}} \frac{f_{L_{A}L_{B}q}}{R^{1+L_{A}+L_{B}}} I_{A} \times I_{B},$$
(4.17)

where

$$I_A = \langle \gamma' v' J' \Omega' M' | \hat{Q}^q_{L_A}(\hat{r}_A) | \gamma v J \Omega M \rangle , \qquad (4.18)$$

and

$$I_B = \langle n'(l's')j'm' | \hat{Q}_{L_B}^{-q}(\hat{r}_B) | n(ls)jm \rangle.$$
(4.19)

$L_A, L_B$	$\Delta l$	$\Delta j$	$\Delta J$
$L_A = L_B = 1$	$\pm 1$	$0,\pm 1$	$\pm 1$
$L_A = 1, \ L_B = 2$	$0,\pm 2$	$0, \pm 1, \pm 2$	$\pm 1$
$L_A = 2, \ L_B = 1$	$\pm 1$	$0, \pm 1$	$0,\pm 2$
$L_A = L_B = 2$	$0,\pm 2$	$0,\pm 1,\pm 2$	$0,\pm 2$

Table 4.1: Selection rules for the angular momentum states interacting via perturbing potential  $\hat{V}_{AB}$ . These conditions are derived from the 3j-symbols of eqs. (4.20) and (4.21), where we took  $\Omega = \Omega' = 0$  corresponding to electronic ground state molecules.

We use angular momentum algebra to rewrite  $I_A$  and  $I_B$  in a more explicit form. As discussed in Chapter 3, Section 3.2, the molecular integral can  $I_A$  can be written in a general form as

$$I_{A} = (-1)^{M' - \Omega'} [J']^{1/2} [J]^{1/2} \begin{pmatrix} J' & L_{A} & J \\ -M' & q & M \end{pmatrix}$$
$$\times \sum_{p} \begin{pmatrix} J' & L_{A} & J \\ -\Omega' & p & \Omega \end{pmatrix} \langle \gamma' v'(J') | \hat{Q}_{L_{A}}^{p} | \gamma v(J) \rangle , \qquad (4.20)$$

where [J] = 2J + 1.

The atomic integral  $I_B$  can be computed as in Chapter 2, Section 2.1.6 to give,

$$I_{B} = (-1)^{j'+j-m'+s+l} [l']^{1/2} [l]^{1/2} [j']^{1/2} [j]^{1/2}$$

$$\times \begin{pmatrix} l' & L_{B} & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & L_{B} & j \\ -m' & -q & m \end{pmatrix}$$

$$\times \begin{cases} l & j & s \\ j' & l' & L_{B} \end{cases} \langle n'(l')| er^{L_{B}} |n(l)\rangle.$$
(4.21)

#### Selection rules for the interaction

Let briefly recall the triangle condition that 3j-symbol must satisfy in order to be different than zero. For a 3j-symbol given by

$$\left(\begin{array}{ccc} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{array}\right), \tag{4.22}$$

 $|j_1 + j_2| \ge j_3 \ge |j_1 - j_2|$  and  $m_1 + m_2 + m_3 = 0$ . Table 4.1 show the selection rules for different values of  $L_A$  and  $L_B$  in eqs. (4.20) and (4.21), where we have assumed that the molecule has a zero electronic angular momentum state ( $\Omega = \Omega' = 0$ ). The 3*j*-symbols from eqs. (4.20) and (4.21) define the selection rules for two given values of  $L_A$  and  $L_B$ , which determine the inverse power of atom-molecule distance in the multipole expansion (4.11).

According to Table 4.1, the diagonal elements of the interaction  $\hat{V}_{AB}$  do not vanish for  $L_A$  =

 $L_B = 2$ , giving rise to a first-order correction energy that scales as  $R^{-5}$ . We are interested in the rotational ground state ( $J_A = J'_A = 0$ ), for which there is no first-order atom-molecule interaction because the molecules are neutral, i.e.,  $\langle Q^0_{(L_A=0)} \rangle = 0$ . A similar argument is valid for atoms in *S* states. Atom-molecule interaction for molecules in the rotational ground state (or *S* state atoms) would thus be expected to result in second-order corrections in the interaction potential.

The contribution of higher powers of R ( $L_A, L_B > 2$ ) to first order in perturbation theory would not be considered because the second-order contributions associated with the polarizabilities are expected to be dominant for Rydberg atomic states.

#### Symmetries of the long-range potentials

From the 3*j*-symbols in eqs. (4.20) and (4.21), we find that the following relations must be satisfied

$$-M' + q + M = 0, \qquad -m' - q + m = 0.$$
(4.23)

Therefore, we identify the following conserved quantity

$$\Omega = M + m = M' + m', \tag{4.24}$$

which characterizes the system state during the interaction.  $\Omega$  is the projection of the total angular momentum  $\mathbf{J}_Z = \mathbf{J}_{ZA} + \mathbf{J}_{ZB}$  of the system *AB* along the atom-molecule axis (not to be confused with the angular momentum projection  $\Omega$  in Chapter 3).

#### 4.2.2 Second-order energy correction

Since the first-order correction to the energy of the asymptotic state  $|\Phi_{AB}\rangle = |X^1\Sigma, v = 0, J = 0, M = 0\rangle |n(ls)jm\rangle$  vanishes, we proceed to compute the energy correction up to a second-order. This is given by the general expression

$$E_{AB}^{(2)} = \sum_{A'B'(\neq AB)} \frac{\langle \Phi_{AB} | \hat{V}_{AB} | \Phi_{A'B'} \rangle \langle \Phi_{A'B'} | \hat{V}_{AB} | \Phi_{AB} \rangle}{(E_A^{(0)} - E_{A'}^{(0)}) + (E_B^{(0)} - E_{B'}^{(0)})}.$$
(4.25)

The first non-zero contribution to the second-order interaction energy is given by the dipole-dipole  $(L_A = L_B = 1)$  term in the multipole expansion, that is

$$\hat{V}_{AB}(R) = -\frac{2}{R^3} \sum_{q=-1}^{1} \frac{\hat{Q}_1^q(\hat{r}_A)\hat{Q}_1^{-q}(\hat{r}_B)}{\sqrt{(1+q)!(1-q)!(1+q')!(1-q')!}},$$
(4.26)

which can be inserted in eq. (4.25) to give,

$$E_{AB}^{(2)} = -\frac{4}{R^{6}} \sum_{A'B(\neq AB)} \frac{1}{(E_{A'}^{(0)} - E_{A}^{(0)}) + (E_{B'}^{(0)} - E_{B}^{(0)})} \times \sum_{qq'} \left[ \frac{\langle \Psi_{A}^{(0)} | \hat{Q}_{1}^{q} | \Psi_{A'}^{(0)} \rangle \langle \Psi_{B}^{(0)} | \hat{Q}_{1}^{-q} | \Psi_{B'}^{(0)} \rangle \langle \Psi_{A'}^{(0)} | \hat{Q}_{1}^{-q'} | \Psi_{A}^{(0)} \rangle \langle \Psi_{B'}^{(0)} | \hat{Q}_{1}^{q'} | \Psi_{B}^{(0)} \rangle}{(1+q)!(1-q)!(1+q')!(1-q')!} \right]. \quad (4.27)$$

Equation (4.27) can be expressed as

$$E_{AB}^{(2)}(R) = \frac{C_6}{R^6},$$
(4.28)

where  $C_6$  is the dispersion coefficient, also known as van der Waals coefficient. From eq. (4.25) it can also be infered that there are more terms to consider in eq. (4.27), i.e.  $V_{AB}(R) = \sum_n \frac{C_n}{R^n}$  associated with other possibles values of  $L_A$  and  $L_B$ . However, we neglect those terms since they are expected to be small compared with the contribution of  $C_6$ .

We use the molecular state  $|\Psi_A\rangle \equiv |X^1\Sigma, v=0, J=0, M=0\rangle$  and the atomic state  $|\Psi_B\rangle = |n(ls)jm\rangle$  in eq. (4.27) to define the products of transition dipole moments

$$\mathcal{T}_{A}(\gamma'v'J'M') = \langle \Sigma v J M | \hat{Q}_{1}^{q}(\hat{r}_{B}) | \gamma'v'J'M' \rangle \langle \gamma'v'J'M' | \hat{Q}_{1}^{-q'}(\hat{r}_{A}) | \Sigma v J M \rangle,$$
(4.29)

and

$$\mathcal{T}_{B}(n'j'l'm') = \langle n(ls)jm | \hat{Q}_{1}^{-q}(\hat{r}_{A}) | n'(l's)j'm' \rangle \langle n'(l's)j'm' | \hat{Q}_{1}^{q'}(\hat{r}_{A}) | n(ls)jm \rangle.$$
(4.30)

Using eqs. (4.29) and (4.30) the atom-molecule  $C_6$  coefficient is thus given by

$$C_{6} = -\sum_{qq'} \sum_{n'} \sum_{j'l'm'} \sum_{\gamma'v'} \sum_{J'M'} K(q,q') \frac{\mathcal{T}_{A}(\gamma'v'J'M')\mathcal{T}_{B}(n'j'l'm')}{(E_{n'j'l'} - E_{njl}) + (E_{\gamma'v'J'} - E_{\Sigma vJ})},$$
(4.31)

where  $K(q,q') \equiv 4/[(1+q)!(1-q)!(1+q')!(1-q')!]$ . Since the atomic and molecular transitions that contribute to the atom-molecule interaction are in the microwave frequency domain, we can restrict the summation over molecular states to the rovibrational levels of the ground electronic states and the molecular energy will correspond to the rovibrational energies  $E_{vJ}$ , thus eq. (4.31) becomes

$$C_{6} = -\sum_{qq'} \sum_{n'} \sum_{j'l'm'} \sum_{v'} \sum_{J'M'} K(q,q') \frac{\mathcal{T}_{A}(\gamma v'J'M')\mathcal{T}_{B}(n'j'l'm')}{(E_{n'j'l'} - E_{njl}) + (E_{v'J'} - E_{vJ})}.$$
(4.32)

The  $C_6$  dispersion coefficient can be written in a more practical form by using and alternative approach for the evaluation of summations in eq. (4.32). This approach relies on the identities

$$\frac{1}{a+b} = \frac{2}{\pi} \int_0^\infty d\omega \frac{ab}{(a^2 + \omega^2)(b^2 + \omega^2)},$$
(4.33)

and

$$\frac{1}{a-b} = \frac{2}{\pi} \int_0^\infty d\omega \frac{ab}{(a^2 + \omega^2)(b^2 + \omega^2)} + \frac{2a}{a^2 - b^2},$$
(4.34)

which are valid for a and b positive. We identify the parameters in the identities with the transition

energies from the denominators in eq. (4.32) as

$$a = E_{v'J'} - E_{vJ} \tag{4.35}$$

for molecular states. This parameter is always positive in our case since we consider the molecule to be in the rovibrational ground state. The parameter b > 0 is defined as

$$b = E_{n'l'j'} - E_{nlj} \tag{4.36}$$

for upward transitions  $(E_{n'l'j'} > E_{nlj})$ , and

$$b = E_{nlj} - E_{n'l'j'}$$
(4.37)

for downward transitions ( $E_{n'l'j'} < E_{nlj}$ ). Using these definitions it is possible to rewrite the sumover-states in eq. (4.32) as a sum of two contributions of the form

$$C_{6} = -\sum_{q,q'} K(q,q') \left[ \int_{0}^{\omega_{\text{cut}}} \frac{d\omega}{2\pi} \alpha_{-q-q'}^{nljm}(i\omega) \alpha_{qq'}^{JM}(i\omega) + \sum_{n'l'j'm'} \Theta(-\Delta E_{n'l'j'}) \alpha_{qq'}^{JM}(\Delta E_{n'l'j'}) \mathcal{T}_{nljm}(n'l'j'm') \right],$$

$$(4.38)$$

where  $\omega_{\rm cut}$  is a cut-off frequency chosen such that the integral term converges.

The arguments of integral in eq. (4.38) are the dynamic atomic polarizability component  $\alpha_{-q-q'}^{nljm}(z)$  (see eq.(2.31)) and the dynamic molecular polarizability component  $\alpha_{qq'}^{JM}(z)$  (see eq. (3.45)), each evaluated at the imaginary frequency  $z = i\omega$ . The second term in the square bracket represents contributions from the molecular polarizability evaluated at the real downward atomic transitions, with  $\Delta E_{n'l'j'} = E_{n'l'j'} - E_{nlj}$ . The Heaviside function  $\Theta(x)$  enforces the downward character of the transitions that contribute to this term. These terms are weighted by the product of the atomic transition dipole integrals.

### 4.3 Dispersion coefficients of Rydberg alkali-atoms interacting with ground state molecules

In this Section, we use the previous approach for the analysis on the long-range interaction between two sets of collision partners: (*i*) <sup>133</sup>Cs Rydberg atoms interacting with LiCs and RbCs molecules; (*ii*) <sup>85</sup>Rb Rydberg atoms interacting with KRb, LiRb and RbCs molecules. We use eq. (4.38) to compute the  $C_6$  coefficient of each atom-molecule pair considered, as a function of the principal quantum number n of the atomic Rydberg state  $|n^2l_j\rangle$ . We restrict our calculations to atomic states with  $15 \le n \le 150$  and  $l \le 2$ .

As it was mentioned in Section 4.2.1, the total angular momentum projection along the quantization axis  $\Omega = m + M$  is a conserved quantity for an atom-molecule collision. For molecules in the

$n^2 l_j$	$R_{LR}(a_0)$	$R_{LR}(nm)$
$15^2 P_{1/2}$	410.89	21.74
$20^2 S_{1/2}$	806.23	42.66
$40^2 D_{5/2}$	4452.82	235.63
$60^2 P_{3/2}$	10076.97	533.25
$80^2 D_{3/2}$	19006.65	1005.79

Table 4.2: LeRoy radius for several Rydberg states of a cesium atom.

rovibrational ground state (J = 0), we have  $\Omega = m$ .

Following the usual convention, we have that  $C_6 < 0$  defines an attractive potential, and  $C_6 > 0$  defines a repulsive potential.

The interaction length of the system is taken to be greater that the LeRoy radius [3]

$$R_{LR} = 2\left[\sqrt{\langle r_{JM}^2 \rangle} + \sqrt{\langle r_{nl}^2 \rangle}\right],\tag{4.39}$$

where  $\langle r_{JM}^2 \rangle$  and  $\langle r_{nl}^2 \rangle$  are the mean square length of the molecular and atomic electronic cloud, respectively. For ground state diatomic molecules,  $\langle r_{JM} \rangle$  is of the order of  $1 - 10 a_0$ , while  $\langle r_{nl} \rangle$  is of the order  $10^2 - 10^3 a_0$  for the Rydberg states considered in this work. We can thus approximate eq. (4.39) as

$$R_{LR} \approx 2\sqrt{\langle r_{nl}^2 \rangle}.$$
(4.40)

Since  $\sqrt{\langle r_{nl}^2 \rangle}$  scales as  $n^2$ , also  $R_{LR}$  does. Table 4.2 shows the values of the LeRoy radius  $R_{LR}$  using eq. (4.40) for a molecule-atom system that involves a Cs atom in a Rydberg state.

#### 4.3.1 Cesium + Molecule

In Fig. 4.2 we plot the  $C_6$  coefficients for <sup>133</sup>Cs Rydberg states  $n^2 l_j$  interacting with LiCs and RbCs molecules in the ground state  $|X^1\Sigma, v = 0, J = 0\rangle$ , as a function of the atomic principal quantum number n, for all allowed values of  $|\Omega|$ .

For cesium Rydberg atoms in  ${}^{2}S_{1/2}$ ,  ${}^{2}P_{1/2}$  and  ${}^{2}P_{3/2}$  states (see panels (a), (b), (d), and (e) Fig. 4.2), the interaction with LiCs and RbCs ground state molecules is attractive over the entire range of *n* considered.

The main contribution to the  $C_6$  coefficients comes from the integral (4.41), in which the molecular dynamical polarizability is completely positive for the ground state, therefore the attractive interaction is due to the mostly positive character of the atomic polarizability functions for the  ${}^2S_{1/2}$ ,  ${}^2P_{1/2}$  and  ${}^2P_{3/2}$  states at imaginary frequencies  $\alpha(i\omega)$ .

On the other hand, Cs atoms in  ${}^{2}D_{3/2}$  and  ${}^{2}D_{5/2}$  Rydberg states give rise to repulsive  $1/R^{6}$  potentials. This repulsive character of the atom-molecule interaction is due to the predominantly negative atomic polarizability function  $\alpha(i\omega)$ , while the molecular polarizability function remains positive.



Figure 4.2: Long-range interaction coefficients  $C_6$  as a function of the atomic principal quantum number n, using <sup>133</sup>Cs in a Rydberg state  $|n^2l_j\rangle$  with (a),(b), and (c) for LiCs and (d), (e) and (f) for RbCs molecules in the electronic and rovibrational ground state  $|X^1\Sigma^+\rangle |v = 0, J = 0\rangle$  for all cases. The figures are sorted by the total angular momentum projection of the system  $\Omega = m + M$  along the atom-molecule axis, which is a conserved quantity through out the collision. Also, the quantum angular momentum numbers  ${}^2l_j$  of the interacting atom are shown in all panels. We assume the interaction to happen at long distances ( $R > R_{LR}$ ), where the system state can be express as tensor product of each particle state  $|n^2l_j, m\rangle \otimes |X^1\Sigma^+vJM\rangle$ .

#### 4.3.2 Rubidium + Molecule

In Fig. 4.3 we plot the  $C_6$  coefficients for <sup>85</sup>Rb Rydberg states  $|n^2l_j\rangle$  interacting with KRb, LiCs and RbCs molecules in the rovibrational ground state, as a function of the atomic principal quantum number n, for  $l \leq 2$ . The  $C_6$  coefficients for  ${}^2S_{1/2}$ ,  ${}^2P_{1/2}$  and  ${}^2P_{3/2}$  atomic Rydberg states behave the same as interacting Cs atoms with ground state molecules, giving rise to attractive potentials. In this case,  ${}^2D_j$  states do not give rise to repulsive potentials. Both, the atomic and the molecular dynamical polarizability are predominantly positive.



Figure 4.3: Long-range interaction coefficients  $C_6$  as a function of the atomic principal quantum number n, using <sup>85</sup>Rb in a Rydberg state  $|n^2l_j\rangle$  with (a),(b), and (c) for KRb and (d), (e), and (f) for LiRb and (g), (h), and (i) for RbCs molecules in the electronic and rovibrational ground state  $|X^1\Sigma^+\rangle|v=0, J=0\rangle$  for all cases. The figures are sorted by the total angular momentum projection of the system  $\Omega = m + M$  along the atom-molecule axis, which is a conserved quantity through out the collision. Also, the quantum angular momentum numbers  ${}^2l_j$  of the interacting atom are shown in all panels. We assume the interaction to happen at long distances ( $R > R_{LR}$ ) between the particles, where the system state can be express as tensor product of each particle state  $|n^2l_j, m\rangle \otimes |X^1\Sigma^+vJM\rangle$ .



Figure 4.4:  $I_6$  and  $D_6$  contributions as a function of the atomic principal quantum number for (a), (b) RbCs-Cs, with the molecule in the electronic and rovibrational ground state  $X^1\Sigma^+$ , v = 0, J = 0 and the atom in  $D_{5/2}$  state and for (c), (d) RbCs-Rb in the same molecular and atomic states. The results are presented for different total angular momentum projection  $\Omega$ .

#### 4.3.3 Frequency integral contribution

According to eq. (4.38) there are two terms that contribute to the  $C_6$  coefficients, the integral term and the downward transitions term, given respectively by

$$I_{6} = \left| \sum_{q,q'} K(q,q') \left[ \int_{0}^{\omega_{\text{cut}}} \frac{d\omega}{2\pi} \alpha_{-q-q'}^{nljm}(i\omega) \alpha_{qq'}^{JM}(i\omega) \right] \right|$$
(4.41)

and

$$D_{6} = \left| \sum_{q,q'} \sum_{n'l'j'm'} K(q,q') \Theta(-\Delta E_{n'l'j'}) \alpha_{qq'}^{JM}(\Delta E_{n'l'j'}) \mathcal{T}_{nljm}(n'l'j'm') \right|.$$
(4.42)

We studied the contributions to  $C_6$  coming from (4.41) and (4.42), separately. Figure 4.4 shows the values of the  $I_6$  and  $D_6$  for RbCs molecules in the ground state interacting with Cs in a  ${}^2D_{5/2}$ state as a function of the atomic principal quantum number (panel (a) for  $I_6$  and panel (b) for  $D_6$ ). Panels (c) and (d) show  $I_6$  and  $D_6$  respectively for RbCs-Rb, with Rubidium in the atomic state  ${}^2D_{5/2}$ . Results are shown for different values of  $|\Omega|$ . Panel (d) of Fig. 4.4 shows a nonmonotonic behavior of  $D_6$  as a function of n. This is due to the approximate elimination of resonant frequencies. Since  $D_6$  involves the evaluation of the atomic transitions energy  $\Delta E_{n'l'j'}$  into the



Figure 4.5: Relative change  $\Delta C_6/C_6$  at different cutoff frequencies  $\omega_{cut}$  for a ground state KRb molecule interacting with Rubidium in a Rydberg state  $n^2 l_j$ . The results are presented for different total angular momentum projection  $|\Omega|$ .

molecular polarizability function  $\alpha_{qq'}^{JM}$ , those terms which are equal to the rotational transitions in the molecule, i.e.  $\Delta E_{n'l'j'} = 2B_e$ , are removed from the summation of eq. (4.42). Resonant terms would contribute to the  $C_3$  coefficients, which describe resonant energy transfer via dipole-dipole interaction between the molecule and the atom.

As *n* increases, the  $I_6$  contribution becomes larger compared with the contribution of  $D_6$  (see Fig. 4.4). The ratio of  $I_6/D_6$  is of the order of  $10^2$  for n = 15 and reaches values of  $10^{12}$  for n = 150. Therefore, the main contribution to the  $C_6$  coefficients comes from the integral term (4.41). We find a strong dependence of  $C_6$  on the atomic and molecular dynamical polarizability.

One way to qualitatively understand this result is to compare the  $n^7$  scaling of the static atomic polarizability  $\alpha(0)$  (related to  $I_6$ ) with the  $n^2$  scaling of the radial dipole integrals  $\langle r_{nl} \rangle$  for Rydberg states (related to  $D_6$ ). The ratio between  $I_6$  (polarizability) and  $D_6$  (dipole), in terms of n, can thus scale at least as  $n^3$ .

On the other hand, both  $I_6$  and  $D_6$  depend on the molecular polarizability. For  $I_6$  involving  $\alpha_{qq'}^{JM}(i\omega)$ , this function in the low frequency regime  $\omega \leq 5$  THz is completely positive and decreases rapidly from  $10^6$  a.u. to  $10^2$  a.u. for all considered dimers (see Fig. 3.3 (a)). For  $D_6$  involving  $\alpha_{qq'}^{JM}(\omega = \Delta E_{n'l'j'})$ , this function is evaluated at real frequencies with an approximate constant polarizability value of the order of  $10^2$  a.u. (see Fig. 3.3 (b)).

Based on the results above, we conclude that the behavior of  $C_6$  coefficients presented here for alkali diatomic molecules in the electronic and rovibrational ground state and alkali Rydberg atoms, exhibit a strong dependence on the atomic dynamical polarizability. Therefore, mostly negative atomic polarizability functions are expected to give rise to repulsive long-range potentials, while mostly positive atomic polarizability functions would give rise to attractive potentials.

The integral  $I_6$  involves a cut-off frequency  $\omega_{\rm cut}$ . In order to estimate  $\omega_{\rm cut}$ , we tested the numerical convergence of the integration by increasing the value of the cutoff until the relative change  $\Delta C_6/C_6$  was smaller than a predefined tolerance  $\varepsilon$ . Fig. 4.5 shows the results of this study. For molecule-atom pairs involving <sup>133</sup>Cs and <sup>85</sup>Rb atoms, the polarizability integral converges faster with increasing cutoff for intermediate and high values of  $n \gtrsim 30$ , in comparison with low-*n* states. The latter result in a slower convergence. We converged all our  $n \approx 15$  integrals at  $\omega_{\rm cut} = 3$  THz with a tolerance  $\varepsilon = 0.01$ , which ensures convergence over an entire range of *n*.

#### 4.3.4 Scaling of $C_6$ with n

For both attractive and repulsive interactions, the magnitude of  $C_6$  scales as  $\sim n^7$  over a wide range of n. We fit the computed  $C_6$  coefficients as a function of the atomic principal quantum number n to the polynomial

$$C_6 = \gamma_0 + \gamma_4 n^4 + \gamma_6 n^6 + \gamma_7 n^7.$$
(4.43)

This scaling is valid in the range  $n \approx 40 - 150$ , with a fit quality that improves with increasing n. We list the fitting coefficients for Cs-LiCs and Cs-RbCs pairs in Table 4.4 for all atomic angular momentum states considered. The corresponding fitting coefficients for the collision pairs Rb-KRb, Rb-LiRb, and Rb-RbCs, are given in Table 4.5.

The  $n^7$  scaling found for  $C_6$  is the same scaling of the static polarizability of Rydberg atoms [22]. This suggests that the long-range interaction potential is dominated by the giant Rydberg polarizability, as expected.

Also, Table 4.3 compares the  $C_6$  coefficients computed with eq. (4.38) and (4.43) for a ground state KRb molecule interacting with Rb atom in a  ${}^2P_{3/2}$ , with  $|\Omega| = 3/2$ . Eq. (4.43) predicts the  $C_6$  coefficients with an error smaller that 10% for n > 50.

Given the  $n^2$  scaling of the LeRoy radius  $R_{LR}$  (4.40) and the  $n^7$  scaling of the atom-molecule  $C_6$  coefficients, thus, the van der Waals energy should approximately scale as  $U_{\rm vdW} \equiv C_6/R_{LR}^6 \sim n^{-5}$ . We find this scaling to be most accurate for  $n \gtrsim 50$ .

n	C <sub>6</sub> (eq. 4.38)	C <sub>6</sub> fit (eq. 4.43)	Error
40	-1.4476[10]	-1.4552[10]	0.007[10]
50	-6.8177[10]	-8.5246[10]	1.707[10]
60	-2.2892[11]	-2.6258[11]	0.337[11]
70	-6.2135[11]	-6.4374[11]	0.224[11]
80	-1.4146[12]	-1.3749[12]	0.040[12]
120	-1.2839[13]	-1.2843[13]	0.0004[13]
150	-4.1326[13]	-4.1326[13]	0.00005[13]

Table 4.3: Comparison of the  $C_6$  coefficients computed using eq. (4.38) and (4.43) with the parameter shown in Table 4.5 for KRb-Rb for an atomic state  ${}^2P_{3/2}$ ,  $|\Omega = 3/2|$ . The notation A[x] means  $A \times 10^x$ .

Molecule	l	j	$ \Omega $	$\gamma_0$	$\gamma_4$	$\gamma_6$	$\gamma_7$
	S	1/2	1/2	1.518[11]	-1.035[5]	-30.94	0.1630
	P	1/2	1/2	2.104[12]	-1.984[6]	162.1	-1.606
		3/2	1/2	2.307[12]	-2.366[6]	238.2	-2.375
			3/2	2.149[12]	-2.186[6]	225.5	-2.236
LiCs		3/2	1/2	-1.428[12]	1.708[6]	-226.6	1.879
		3/2	3/2	-5.864[11]	7.756[5]	-134.4	1.090
	D		1/2	-1.431[12]	1.909[6]	-289.5	2.469
		5/2	3/2	-1.081[12]	1.462[6]	-234.1	1.973
			5/2	-3.809[11]	5.716[5]	-123.2	0.9800
	S	1/2	1/2	-2.907[10]	2.757[4]	-13.25	0.05058
	Р	1/2	1/2	-3.542[11]	-1.737[5]	-3.808	-0.4723
		3/2	1/2	4.866[11]	-2.753[5]	18.15	-0.7826
			3/2	4.425[11]	-2.588[5]	19.43	-0.7408
RbCs	D	3/2	1/2	-3.906[11]	2.610[5]	-31.40	0.5847
			3/2	-2.156[11]	1.565[5]	-26.86	0.3579
		5/2	1/2	-4.818[11]	3.501[5]	-53.47	0.8316
			3/2	-3.846[11]	2.821[5]	-45.57	0.6657
			5/2	-1.901[11]	1.458[5]	-29.63	-0.3334

Table 4.4: Parameters for the fitting  $C_6 = \gamma_0 + \gamma_4 n^4 + \gamma_6 n^6 + \gamma_7 n^7$ , for selected atom-molecule pairs involving <sup>133</sup>Cs atoms in Rydberg states  $|n^2 l_j\rangle$ , interacting with LiCs and RbCs molecules in the ground electronic and rovibrational state.  $\Omega = m$  is the total angular momentum projection of the collision pair.  $C_6$  is in atomic units  $(a_0^3)$ . The fitting is accurate in the range n = 40 - 150. The notation A[x] means  $A \times 10^x$ .

Molecule	l	j	$ \Omega $	$\gamma_0$	$\gamma_4$	$\gamma_6$	$\gamma_7$
	S	1/2	1/2	4.340[9]	-1905	-0.5274	4.695[-4]
		1/2	1/2	1.155[10]	27.48	-6.706	0.02190
	P	3/2	1/2	1.429[10]	-840.9	-7.419	0.02381
			3/2	1.227[10]	9.555	-7.089	0.02286
KRb		3/2	1/2	4.907[9]	-3284	0.1596	-1.883[-3]
		3/2	3/2	6.531[9]	-2307	-2.039	6.199[-3]
	D		1/2	3.298[9]	-2486	0.4228	-2.302[-3]
		5/2	3/2	4.481[9]	-2337	-0.5691	1.173[-3]
			5/2	6.782[9]	-2026	-2.521	8.018[-3]
	S	1/2	1/2	1.381[11]	-1.085[5]	6.408	-0.04418
		1/2	1/2	5.353[11]	-4.224[5]	-13.06	0.01194
	P	3/2	1/2	6.063[11]	-4.839[5]	-12.77	1.718[-3]
			3/2	5.598[11]	-4.420[5]	-14.57	0.01386
LiRb	D	3/2	1/2	1.091[11]	-1.040[5]	11.58	-0.06377
			3/2	2.100[11]	-2.024[5]	3.214	-0.03349
		5/2	1/2	8.086[10]	-7.309[4]	10.89	-0.05510
			3/2	1.317[11]	-1.237[5]	7.670	-0.04539
			5/2	2.309[11]	-2.225[5]	1.254	-0.02591
	S	1/2	1/2	1.316[10]	-3897	-2.743	-7.242[-3]
		1/2	1/2	-1.576[10]	5.049[4]	-39.63	0.07148
RbCs	P	3/2	1/2	-1.225[10]	5.381[4]	-44.40	0.07713
			3/2	-1.640[10]	5.347[4]	-41.94	0.07316
	D	3/2	1/2	2.285[10]	-1.490[4]	1.265	-0.01663
			3/2	9.039[9]	7469	-12.55	0.01839
		5/2	3/2	5.808[10]	-1.796[4]	-1.099	-0.01126
			5/2	5.978[10]	-2261	-13.17	0.01667

Table 4.5: Parameters for the fitting  $C_6 = \gamma_0 + \gamma_4 n^4 + \gamma_6 n^6 + \gamma_7 n^7$ , for selected atom-molecule pairs involving <sup>85</sup>Rb atoms in Rydberg states  $|n^2 l_j\rangle$ , interacting with RbCs, LiRb and KRb molecules in the ground electronic and rovibrational state.  $\Omega = m$  is the total angular momentum projection of the collision pair.  $C_6$  is in atomic units  $(a_0^3)$ . The fitting is accurate in the range n = 40 - 150. The notation A[x] means  $A \times 10^x$ .

#### **4.3.5** Error bounds on *C*<sub>6</sub> values

There are two terms that must be consider in order to estimate the accuracy of the frequency integral in eq. (4.38) which has the major contribution to the van der Waals coefficients as we explaneid in Section 4.3.3. The first one is the the molecular dynamical polarizability and the second one is the atomic dynamical polarizability of a Rydberg state.

The rovibrational structure and electrostatic response of most alkali-metal dimers in the ground  $X^{1}\Sigma$  state is well-known from precision spectroscopy experiments and accurate *ab-initio* studies [57, 19, 63]. Therefore, the molecular polarizability function  $\alpha_{qq}^{JM}$  in eq. (3.45) is assumed to be known with very high precision, our computed static molecular polarizabilities differ from the results in Ref. [61] by less than 1%, as we showed in Chapter 3. These polarizability functions evaluated at imaginary frequencies  $\alpha_{qq}^{JM}(i\omega)$  is always positive and have their maximum value at  $\omega = 0$ , as the frequency increses the polarizabilities tend asymptotically to their isotropic static values  $\alpha_{iso}^{el}$  for each considered molecule. Therefore the molecular polarizabilities are bounded from above by their static value.

For the atomic Rydberg states considered, the polarizability functions obtained from eq. (2.31) are predominantly monotonic as a function of frequency, although we found specific states  $|n^2 l_j, m\rangle$  with non-monotonic frequency dependence (see Chapter 3). Again, the maximum absolut value of the atomic polarizability at imaginary frequencies occur when  $\omega = 0$ . For higher frecuencies the polarizability increases or decreases, depending on the atomic states, and tend to an asymptotic value up to a cutoff frequency  $\omega_{cut}$  of a few THz. In general, for all the atomic states considered, we find that  $|\alpha_{aq}^{nljm}(i\omega)|$  is always bounded from above by its value at  $\omega = 0$ .

The accuracy of our computed atomic polarizability functions  $\alpha_{qq}^{nljm}(i\omega)$  is limited by the precision of the quantum defects used, which we take from spectroscopic measurements [27].

The error of the computed  $C_6$  coefficients can thus be estimated for  $n \ge 15$  as follows. Ignoring the downward transition terms ( $D_6$ ), and the error in the molecular polarizability function, eq. (4.38) can be written as  $\tilde{C}_6 = C_6 \pm \delta C_6$ , where  $\tilde{C}_6$  is the dispersion coefficient obtained in our calculations, and the error is approximately given by

$$\delta C_6 \approx -\sum_{q,q'} \frac{K(q,q')}{2\pi} \int_0^{\omega_{\rm cut}} \frac{d\omega}{2\pi} \,\delta\alpha_{qq'}^{nljm}(i\omega) \,\alpha_{-q-q'}^{JM}(i\omega), \tag{4.44}$$

where  $\delta \alpha_{qq'}^{nljm}(i\omega)$  is the error in the atomic polarizability function evaluated at imaginary frequencies. The order of magnitude of the product integral  $\int \alpha_{qq'}^{nljm}(i\omega) \alpha_{-q-q'}^{JM}(i\omega)$  is the same for all qq'-components, thus we can assume that the relative error  $\delta \alpha_{qq}^{nljm}(i\omega)/\alpha_{qq}^{nljm}(i\omega)$  is the same for all qq'-components and remains constant over all frequencies up to the cutoff  $\omega_{cut}$ . We use the fact that  $|\alpha(i\omega)|$  is bounded from above by its static value in the atomic and molecular cases, we can estimate an approximate error bound for  $C_6$  in terms of the relative error of the 00-component as

$$\left|\frac{\delta C_6}{C_6}\right| \lesssim \left|\frac{\delta \alpha_{00}^{nljm}(0)}{\alpha_{00}^{nljm}(0)}\right|.$$
(4.45)

In other words, the accuracy of our  $C_6$  calculations cannot expected to be better than the accuracy

of the static atomic polarizability. The static polarizabilities of several Rydberg states of <sup>85</sup>Rb and <sup>133</sup>Cs are known from laser spectroscopy measurements in static electric fields [64, 46, 65], and also from precision calculations using state-of-the-art *ab-initio* pseudo-potentials [49]. Therefore, we estimated  $\delta \alpha_{00}^{nljm}(0)$  for several atomic Rydberg states  $|n^2l_j, m\rangle$ , by comparing with available data (see Table 2.8). The average relative errors for Rb is -0.02% for  ${}^2S_{1/2}$  states over the range  $15 \le n \le 50$  for  ${}^2S_{1/2}$  states, +0.27% for  ${}^2D_{5/2}$  states with m = 5/2, and +0.13% for  ${}^2D_{3/2}$  states with m = 3/2. Similar accuracies are obtained for Cs.

Another possible source of error in our  $C_6$  calculations is the choice of the high frequency cutoff  $\omega_{\text{cut}}$  in the numerical integration of eq. (4.38).

#### 4.3.6 Effect of the molecular dipole moment

In Fig. 4.6 we show the increase in the magnitude of  $C_6$  as the permanent dipole moment of alkalimetal dimers increases, for selected states  $n^2 P_{1/2}$  of <sup>85</sup>Rb. The  $C_6$  coefficient for the Rb-LiRb pair is larger than the corresponding values for RbCs and KRb, which have a smaller dipole moment. The same trend also holds for other  $|n^2 l_j\rangle$  states of <sup>85</sup>Rb, and for atom-molecule pairs involving <sup>133</sup>Cs atoms.



Figure 4.6: Bar plots  $\log_{10}|C_6|$  for n = 15, 50, 80 for atom-molecule pairs involving <sup>85</sup>Rb atoms in the  $n^2P_{1/2}$  state with KRb, RbCs and LiRb molecules in the rovibrational ground state. The permanent dipole moment of each molecule is shown in parenthesis on the horizontal axis [57].

### **Chapter 5**

## **Conclusions and Outlook**

In this Thesis, we theoretically study the long-range interaction between Rydberg alkali-atoms and diatomic molecules. The interaction potential in the molecule-Rydberg system at large distances is small compared with the energy of each particle, therefore it is treated using quantum pertubation theory and given in terms of the atomic and molecular dynamical polarizability functions. We study <sup>133</sup>Cs and <sup>85</sup>Rb atoms in a Rydberg state  $|n^2l_j, m\rangle$  with  $l \leq 2$  and 15 < n < 150 interacting with KRb, LiCs, LiRb and RbCs molecules in the electronic and rovibrational ground state  $|X^1\Sigma^+, v = 0, J = 0, M = 0\rangle$ . For this molecular state the interaction is determined by the  $C_6$  van der Waals coefficient and the interaction scales in terms of the particles relative distance as  $C_6/R^6$ . We found that the atomic polarizability function evaluated at imaginary frequencies  $i\omega$  has a crucial role in the interaction: determines the magnitude and the nature of the interaction, i.e. whether it is attractive ( $C_6 < 0$ ) or repulsive ( $C_6 > 0$ ).

We also found that the interaction is not only determined by atomic properties and quantum numbers, the interacting molecule may enhance the interaction according to its permanent dipole moment, i.e. polar molecules with higher permanent dipole moment experience a stronger interaction compare with molecules with smaller permanent dipole moment, assuming that both are interacting with the same atomic species and in the same atomic quantum state. Therefore, it is possible to find an atomic Rydberg state and a molecule that gives an attractive or repulsive potential with a desired interaction strength.

Repulsive van der Waals interactions may be used for sympathetic cooling of alkali-metal dimers via elastic collisions with ultracold Rydberg atoms. For example, for the LiCs-Cs system with <sup>133</sup>Cs in the  $n^2D_{5/2}$  state and  $|\Omega = 5/2|$ , the van der Waals potential is repulsive (Fig. 4.2(c)) and can be estimated in absolute units with a collisional barrier reaching  $U_{vdW} \approx 38$  MHz for n = 20. This should be sufficient to avoid short-range collisions for atom-molecule pairs with relative kinetic energy up to 1.82 mK. By increasing the atomic quantum number to n = 40, the potential barrier drops to  $U_{vdW} \approx 0.43$  MHz for the same collision pair. Since inelastic and reactive ultracold collisions [66, 67] can lead to spontaneously emitted photons carrying energy away from a trapped system [10], it should be possible to measure the elastic-to-inelastic scattering rates and follow the thermalization process of a co-trapped atom-molecule mixture.

Attractive van der Waals potentials can be exploited to form long-range alkali-metal trimers via photoassociation [68]. Using eq. (1.1) from Chapter 1, we can extend the long-range potential to the short-range by setting  $R_0 = C_6$  and compute the system wavefunction in the whole range, by finding the Franck-Condon overlap [69, 70] between two system states, we can estimate the photoassociation rates.

We can extend the formalism in this work to also obtain van der Waals coefficients for excited rovibrational states of alkali-metal dimers. In this case,  $C_5$  coefficients do not vanish in general [15]. The interplay between  $C_5$  and  $C_6$  with opposite signs at long distances can possibly lead to long-range potential wells that can support Rydberg-like metastable bound states accessible in photoassociation spectroscopy [13, 14, 15, 71].

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## **Appendix A**

## **Numerov algorithm**

In this Appendix we derive the Numerov algorithm, which is designed to numerically solve ordinary differential equations of the form

$$\frac{d^2y(x)}{dx^2} + k^2(x)y(x) = 0.$$
 (A.1)

We start by applying the operator  $1 + \frac{h^2}{12} \frac{d^2}{dx^2}$ , where *h* is very small number, into eq. (A.1) to obtain

$$\frac{h^4}{12}y^{(4)} + y^{(2)} + \frac{h^2}{12}\frac{d^2}{dx^2}\left[k^2(x)y(x)\right] + k^2y(x) = 0,$$
(A.2)

where  $y^{(n)} \equiv \frac{d^n y(x)}{dx^n}$ . Expanding y(x+h) and y(x-h) in Taylor series around h and -h, respectively,

$$y(x+h) = y(x) + hy^{(1)}(x) + \frac{h^2}{2!}y^{(2)}(x) + \frac{h^3}{3!}y^{(3)}(x) + \frac{h^4}{4!}y^{(4)}(x) + \dots,$$
 (A.3)

and

$$y(x-h) = y(x) - hy^{(1)}(x) + \frac{h^2}{2!}y^{(2)}(x) - \frac{h^3}{3!}y^{(3)}(x) + \frac{h^4}{4!}y^{(4)}(x) + \dots$$
 (A.4)

Adding y(x+h) and y(x-h),

$$y(x+h) + y(x-h) = 2y(x) + h^2 y^{(2)}(x) + \frac{h^4}{12} y^{(4)}(x),$$
 (A.5)

and solving for  $y^{(2)}$ , we obtain

$$y^{(2)}(x) = \frac{y(x+h) + y(x-h) - 2y(x)}{h^2} - \frac{h^4}{12}y^{(4)}(x).$$
(A.6)

We replace eq. (A.6) into (A.2) to obtain

$$\frac{y(x+h) + y(x-h) - 2y(x)}{h^2} + \frac{h^2}{12} \frac{d^2}{dx^2} \left[k^2(x)y(x)\right] + k^2 y(x) = 0.$$
(A.7)

The expression  $\frac{d^2}{dx^2} \left[k^2(x)y(x)\right]$  can be approximate using the derivative definition given by

$$\frac{d}{dx} \left[ k^2(x)y(x) \right] \approx \frac{k^2(x+h)y(x+h) - k^2(x)y(x)}{h},$$
(A.8)

explicitly,

$$\frac{d^2}{dx^2} \left[ k^2(x)y(x) \right] \approx \frac{\frac{k^2(x+h)y(x+h)-k^2(x)y(x)}{h} - \frac{k^2(x)y(x)-k^2(x-h)y(x-h)}{h}}{h},\tag{A.9}$$

$$\frac{d^2}{dx^2} \left[ k^2(x)y(x) \right] \approx \frac{k^2(x+h)y(x+h) - 2k^2(x)y(x) + k^2(x-h)y(x-h)}{h^2}.$$
 (A.10)

Replacing eq. (A.10) into (A.7) and solving for y(x + h), we obtain

$$y(x+h) = \frac{y(x)\left[2 - \frac{5h^2}{6}k^2(x)\right] - y(x-h)\left[1 + \frac{h^2}{12}k^2(x-h)\right]}{1 + \frac{h^2}{12}k^2(x+h)}.$$
 (A.11)

If we label de continuos variable x as a discrete one as j, then eq. (A.11) becomes

$$y_{j+h} = \frac{2y_j \left[1 - \frac{5h^2}{12}k_j^2\right] - y_{j-h} \left[1 + \frac{h^2}{12}k_{j-h}^2\right]}{1 + \frac{h^2}{12}k_{j+h}^2}.$$
(A.12)

According to eq. (A.12), this algorithm requires to know the values of  $y_0$  and  $y_1$  to move forward through the lattice, or know the values at last lattice sites  $y_{N-1}$  and  $y_N$  to move backwards through the lattice.

### **Appendix B**

## **Dynamical polarizability function**

In this Appendix a detailed derivation of the dynamical polarizability function is provided for general polarizable system. The polarizability is found by considering the lowest order correction to the electric-dipole moment of the system [50].

Let  $\psi_k^{(0)}$  for k = 1, 2, 3... be the eigenfunctions of the unperturbed Hamiltonian  $\hat{H}_0$  that satisfies the time-independent Schrodinger equation

$$\hat{H}_0 \psi_k^{(0)} = E_k^{(0)} \psi_k^{(0)},\tag{B.1}$$

where  $E_k^{(0)}$  is the unperturbed energy corresponding to the *k*-th state.

Supose that we apply a time-dependent perturbing Hamiltonian  $\hat{H}_{I}(t)$  given by

$$\hat{H}_I(t) = \hat{V}e^{i\omega t} + h.c., \tag{B.2}$$

where h.c. is the Hermitian conjugate and the operator  $\hat{V}$  is given by

$$\hat{V} = -\frac{1}{2}\hat{\mathbf{p}} \cdot \mathbf{E}_0,\tag{B.3}$$

where  $\hat{\mathbf{p}}$  is the quantum dipole moment operator, given by

$$\hat{\mathbf{p}} = \sum_{i} q_i \hat{\mathbf{r}}_i,\tag{B.4}$$

where  $q_i$  is the charge of the *i*-th particle in the system at the  $\hat{\mathbf{r}}_i$  position. Assuming a timedependent electric field oscillating with frequency  $\omega$  and form

$$\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t} + \mathbf{E}_0^{\dagger} e^{i\omega t}.$$
(B.5)

where  $\mathbf{E}_0$  is the vector amplitude that contains the polarization of the field.

Let us consider the system to be initially in the quantum state k and the perturbing Hamiltonian
couples the inicial state with the state l, we can write the system wavefuncion in a general way as

$$\phi(t) = a_k(t)\psi_k^{(0)}e^{-iE_k^{(0)}t/\hbar} + a_l(t)\psi_l^{(0)}e^{-iE_l^{(0)}t/\hbar}$$
(B.6)

where  $a_k, a_l$  are chosen in such a way that they satisfy the Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\phi(t) = \left[\hat{H}_0 + \hat{H}_I\right]\phi(t).$$
(B.7)

Replacing eq. (B.6) into (B.7) we obtain

$$i\hbar \dot{a}_k \psi_k^{(0)} e^{-iE_k^{(0)}t/\hbar} + i\hbar \dot{a}_l \psi_l^{(0)} e^{-iE_l^{(0)}t/\hbar} = a_k \hat{H}_I \psi_k e^{-iE_k^{(0)}t/\hbar} + a_l \hat{H}_I \psi_l e^{-iE_l^{(0)}t/\hbar},$$
(B.8)

where  $\dot{a}_k \equiv \frac{d}{dt}a_k$  and we have omitted the time-dependency of the coefficients  $a_k, a_l$ . Multipling the eq. (B.8) by  $\psi_l^{*(0)} e^{iE_l^{(0)}t/\hbar}$  from the left and integrating over the spacial coordinates, eq. (B.8) becomes

$$i\hbar\dot{a}_{l}(t) = a_{k}(t) \left[ V_{lk}e^{i(\omega_{lk}-\omega)t} + V_{lk}^{\dagger}e^{i(\omega_{lk}+\omega)t} \right]$$
(B.9)

where  $w_{lk} = \left(E_l^{(0)} - E_k^{(0)}\right)/\hbar$  and  $V_{lk}$  is a matrix element of the perturbing potential, explicitly

$$V_{lk} = \int \psi_l^{*(0)} \hat{V} \psi_k^{(0)} d^3 \mathbf{r},$$
(B.10)

where  $d^3\mathbf{r}$  is the volume element. We had assumed in eq. (B.9) that the diagonal elements of the interaction Hamiltonian are cero, i.e.  $V_{ii} = 0$ . Eq. (B.9) can be integrated assuming that the amplitude  $a_k(t)$  varies much slowly than the oscillating frequency  $\omega_{lk} \pm \omega$  at the interval  $[t_0, t]$ , where  $|a_l(t_0)| = 0$  and  $|a_k(t_0)| = 1$ . Therefore, the solution for the amplitude  $a_l$  becomes

$$a_{l}(t) = -a_{k}(t_{0}) \left[ \frac{V_{lk}(e^{i(\omega_{lk}-\omega)t} - e^{i(\omega_{lk}-\omega)t_{0}})}{\hbar(\omega_{lk}-\omega)} + \frac{V_{lk}^{\dagger}(e^{i(\omega_{lk}+\omega)t} - e^{i(\omega_{lk}+\omega)t_{0}})}{\hbar(\omega_{lk}+\omega)} \right].$$
 (B.11)

Let's consider a general operator  $\hat{G}$  that is time-independent, using the general system state  $\phi(t)$ , we will compute the matrix element of  $\hat{G}$  as

$$\int \left[\phi^* \hat{G} \phi\right] d^3 \mathbf{r} = |a_k|^2 G_{kk} + a_k^* a_l G_{kl} e^{-i\omega_{lk}t} + a_k a_l^* G_{lk} e^{i\omega_{lk}t} + |a_l|^2 G_{ll}, \tag{B.12}$$

where

$$G_{kl} = \int \psi_k^{*(0)} \hat{G} \psi_l^{(0)} d^3 \mathbf{r}.$$
 (B.13)

is time-independent. The first term on the right hand side of eq. (B.12) is the zeroth-order correction of the operator and it is independent of the perturbing potential (B.2). The last term is second-order in the perturbing Hamiltonian (involving  $|a_l|^2$ ). The two intermediate terms are the first-order correction and we will focus in this correction. We can replace eq. (B.11) into (B.12) keeping only the first-order correction, making  $|a_k(t)| = |a_k(t_0)| = 1$  and retaining only the harmonic terms  $\omega t$ , eq. (B.12) to the first-order becomes

$$\left[\int \phi^* \hat{G} \phi d^3 \mathbf{r}\right]^{(1)} = -\left[e^{-i\omega t} \left(\frac{V_{lk} G_{kl}}{\hbar(\omega_{lk} - \omega)} + \frac{V_{kl} G_{lk}}{\hbar(\omega_{lk} + \omega)}\right) + e^{i\omega t} \left(\frac{V_{kl}^* G_{kl}}{\hbar(\omega_{lk} + \omega)} + \frac{V_{lk}^* G_{lk}}{\hbar(\omega_{lk} - \omega)}\right)\right].$$
(B.14)

We will briefly recall the time-independent perturbation theory [56] in order to obtain the static polarizability expression.

The energy correction of the k state under a perturbing potential  $\hat{V}$  is given by

$$E_k = E_k^{(0)} + V_{kk} + \sum_{l(\neq k)} \frac{|V_{kl}|^2}{E_k^{(0)} - E_l^{(0)}} + \dots,$$
(B.15)

Let's focus on the second-order correction term of the energy in eq. (B.15) that using eq. (B.3) can be written as

$$E_k^{(2)} = \sum_{l(\neq k)} \frac{\hat{\mathbf{p}}_{kl}^* \hat{\mathbf{p}}_{lk}}{E_k^{(0)} - E_l^{(0)}} \mathbf{E}_0^2.$$
(B.16)

Or using the well-known expression

$$E_k^{(2)} = -\frac{1}{2}\alpha \mathbf{E}_0^2$$
(B.17)

where  $\alpha$  is the static polarizability given by

$$\alpha = 2 \sum_{l(\neq k)} \frac{\hat{\mathbf{p}}_{kl}^* \hat{\mathbf{p}}_{lk}}{E_k^{(0)} - E_l^{(0)}}.$$
(B.18)

We must consider an external electric field  $\mathbf{E}$  of the form (B.5) in order to obtain the explicit expression of the frequency-dependent polarizability, which is defined by only considering the first-order correction to the diagonal matrix element of the dipole operator [50]. Therefore, for an harmonic external electric field the induced dipole moment can be written as

$$\hat{\mathbf{p}}_{kk}^{(1)}(t) = \frac{1}{2} \left[ \hat{\mathbf{p}}_{kk} e^{-i\omega t} + c.c. \right],$$
(B.19)

where *c.c.* is the complex conjugate of previous expression. We can relate the diagonal matrix element of the *i*-th component of the electric dipole moment operator with the polarizability tensor by [50]

$$(\hat{\mathbf{p}}_i)_{kk} = (\hat{\alpha}_{ij})_{kk} (\mathbf{E}_0)_j, \tag{B.20}$$

where  $(\hat{\alpha}_{ij})_{kk}$  is the *ij*-th component of the polarizability tensor at frequency  $\omega$  for a system in the *k*-th state. If we take the electric dipole moment operator  $\hat{\mathbf{p}}_i$  instead of  $\hat{G}$  and replace  $\hat{V} = (1/2)\hat{\mathbf{p}} \cdot \mathbf{E}_0$ , eq. (B.14) takes the form

$$(\hat{p}_{i})_{kk}^{(1)} = \frac{1}{2} \sum_{l(\neq k)} \left[ e^{-i\omega t} \left( \frac{(\hat{p}_{i})_{kl}(\hat{p}_{j})_{lk}(E_{0})_{j}}{\hbar(\omega_{lk} - \omega)} + \frac{(\hat{p}_{i})_{lk}(\hat{p}_{j})_{kl}(E_{0})_{j}}{\hbar(\omega_{lk} + \omega)} \right) + e^{i\omega t} \left( \frac{(\hat{p}_{i})_{kl}(\hat{p}_{j})_{kl}^{*}(E_{0})_{j}^{*}}{\hbar(\omega_{lk} + \omega)} + \frac{(\hat{p}_{i})_{lk}(\hat{p}_{j})_{lk}^{*}(E_{0})_{j}^{*}}{\hbar(\omega_{lk} - \omega)} \right) \right].$$

$$(B.21)$$

The sum over *l* consider in eq. (B.21) is the general expression of (B.14) considering that the

purturbing Hamiltonian couples the state k with several quantum states [50]. Comparing eq. (B.21) with eqs. (B.20) and (B.19) we find the *ij*-th component of the polarizability tensor at frequency  $\omega$  for a system in the *k*-th state, given by

$$(\hat{\alpha}_{ij})_{kk}(\omega) = \sum_{l(\neq k)} \left[ \frac{(\hat{p}_i)_{kl}(\hat{p}_j)_{lk}}{\hbar(\omega_{lk} - \omega)} + \frac{(\hat{p}_i)_{lk}(\hat{p}_j)_{kl}}{\hbar(\omega_{lk} + \omega)} \right].$$
(B.22)

Since the matrix elements of the electric dipole operator are real, i.e.  $(\hat{p}_j)_{kl}^* = (\hat{p}_j)_{kl}$  and for convenience of the angular momentum states consider in this work  $\psi_k \equiv |k\rangle$ , we can write the dipole moment operator using the spherical tensor operators as  $\hat{p}_q \equiv \hat{Q}_1^q$ , where  $(\hat{Q}_1^q)^{\dagger} = (-1)^{-q} \hat{Q}_1^{-q}$ . The final expression for the dynamical polarizability can be written as,

$$(\hat{\alpha}_{qq'})_{kk}(\omega) = 2(-1)^q \sum_{l(\neq k)} \frac{E_l^{(0)} - E_k^{(0)}}{\left(E_l^{(0)} - E_k^{(0)}\right)^2 - \omega^2} \langle k|\hat{Q}_1^q|l\rangle \langle l|\hat{Q}_1^{-q'}|k\rangle,$$
(B.23)

where we had used qq' instead of ij.