Bachelor Thesis

Aspects of Van der Waals Interactions

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August 23, 2016
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Abstract:
Van der Waals interactions play an important role throughout large parts of physics. Although their origin is very well-understood in terms of quantum physics, calculating them in a precise way remained an important topic in research. Through Effective Field Theories (EFT) it is now possible to consider the so-called gluonic Van der Waals interactions (strong interaction between colour-neutral objects) as well. A very important quantity to determine the strength of these long-range forces is the polarizability. This thesis is first going to study Van der Waals interactions in terms of non-relativistic quantum mechanics and then to present methods to calculate the polarizability of an object. These methods are applied to obtain an elementary expression for the static polarizability of the hydrogen atom in arbitrary bound states.

Kurzzusammenfassung:
Van der Waals Wechselwirkungen spielen eine wichtige Rolle in weiten Teilen der Physik. Obwohl deren Ursprung im Formalismus der Quantenmechanik sehr gut verstanden ist, bleibt die genaue Berechnung deren Stärke für verschiedene Objekte ein großes Forschungsgebiet. Durch ”Effective Field Theories” ist es nun möglich auch sogenannte gluonische Van der Waals Wechselwirkungen zu betrachten. Dies ist eine Wechselwirkung zwischen farbneutralen Objekten, die durch die starke Wechselwirkung erzeugt wird. Von extremer Wichtigkeit für die Berechnung der Stärke von Van der Waals Wechselwirkungen ist die Polarisierbarkeit der wechselwirkenden Objekte. In dieser Arbeit werden wir Van der Waals Wechselwirkungen hauptsächlich im Formalismus der nichtrelativistischen Quantenmechanik behandeln und Methoden vorstellen, mit denen man die Polarisierbarkeit berechnen kann. Diese werden angewandt um einen geschlossenen Ausdruck für die Polarisierbarkeit von Wasserstoff in beliebigen, gebundenen Zuständen zu bestimmen.
1 Introduction

The topic of this thesis is a fascinating physical phenomenon. If we take two neutral objects, which can be atoms or molecules, for example, we will find, that they attract each other. This attraction might not be very surprising for molecules as they can have a permanent electric dipole moment and can, therefore, attract and repel each other depending on their relative geometrical orientation. However, one discovers that there is also a force between two helium atoms which are both spherically symmetric and thus do not have any permanent multipole moment at all. Having an interaction between particles is one of the main properties that distinguishes a real gas from the ideal one. One of the first to study these gases was J.D. van der Waals [1], after whom these intermolecular forces are named - the Van der Waals forces. The origin of this force is difficult to understand classically and needs a quantum theoretical treatment. London and Eisenschitz were the first who found an explanation of this phenomenon in a quantum mechanical way [2] in 1930. They were able to find an exact form for the interaction potential between two neutral atoms which is \(-\frac{C}{R^6}\) where \(R\) is the distance between the atoms and \(C\) is a positive constant. We will derive this so-called London force in (2.1). This form of the Van der Waals force is very popular and the most useful one in Condensed Matter Physics and Quantum Chemistry. Despite its great success, the applicability of the London form has its limitations. With the development of Quantum Electrodynamics in the 1940s it became apparent that the treatment by London and Eisenschitz was an approximation for the case where the two neutral objects are not extremely far away from each other (i.e. for a situation where the time it takes a photon to travel between the atoms is much smaller than the internal time scales of atoms\(^1\)). This fact was first pointed out in 1948 by Casimir and Polder [3] - the corresponding long-range force is therefore now called the Casimir-Polder force. The corresponding potential is of the form \(-\frac{C'}{R^7}\). We are going to have a closer look at the physical origin of these different regimes in (2). These two regimes have been studied in the past and are now very well understood. However, the interaction between neutral objects continues to be important in today’s research. For example, in 2013 it was the first time that a direct measurement of the Van der Waals force between atoms was successful [4]. The measurement was done on atoms in highly excited states, which have, as we will see later on, a large polarizability. This is important as a large polarizability corresponds to a strong force, which makes the measurement easier and more precise. The distance between the atoms in this measurement was a few micrometres which is in the London regime for these atoms. The results agreed very well with London’s \(R^{-6}\) prediction. A broad research area which Van der Waals forces are crucial for is about a technique called molecular self-assembling. The basic idea is to use molecules that will arrange themselves (thermodynamically, which means without guidance from external sources) and have certain functional properties, which can be electrical properties, for example. Experiments in this direction are also done at the Technical University of Munich [5][6]. The theoretical challenge thereby is to describe the molecules and predict their functional behaviour. The standard approach to describe large molecules is a computational method called Density-Functional Theory. This method originally developed by Hohenberg, Kohn and Sham is based on the observation that all observables of a system in its ground state are completely determined by the electron density of the system. The electron density is, therefore, an equivalent concept to the wavefunction obtained by solving the Schrödinger equation. The formal foundation of this method is the Hohenberg-Kohn theorems [7], whose statement is that there exists a bijective functional dependency between the ground state wavefunction, which is the solution to the Schrödinger equation, and the electron density. Working with the electron density as the fundamental object is computationally very

\(^1\)For a detailed discussion of the conditions where retardation effects become important, see section 2. In general, this depends on the atoms involved. The following numbers are helpful to get an intuition. The size of an atom is typically several Angström \((10^{-10}m)\), the London regime is accurate for distances up to about \(5nm\) whereas the Casimir-Polder force is dominant at distances larger than \(20nm\).
advantageous because it has only three independent variables instead of the least \(3N\) variables where \(N\) is the number of particles, one needs for the wavefunction. Unfortunately, an exact form for this bijective function called Kohn-Sham functional, is not known. Typical approximations, which work very well in describing covalent bonds, are called Local-Density Approximation and Generalized Gradient Approximation. Possible functionals are given in [8][9][10]. As Van der Waals interactions are long-range forces, and these functionals are local approximations, they do not account for them. This is very problematic if one, for example, wants to describe the interaction of self-assembling molecules with the surface they assemble on because the long-range forces are extremely important there [11]. For a long time, there were no really good approaches to tackle this problem and to account for long-range forces, but a lot of progress has been made since the beginning of the 21st century [12]. For a commonly used functional see [13]. The possibility to include long-range interactions has given rise to a lot of calculations in Quantum Chemistry, [14] for example. Before going on with current research interests in nuclear physics involving Van der Waals interactions, we will introduce a substantial quantity, called the polarizability. The need to find methods to calculate this quantity accurately is the primary motivation for this thesis.

1.1 The polarizability

If one puts an atom into an external field, the atom will respond to that perturbation. If the external field is, for example, an electric one, then the atom develops a so-called induced dipole moment. In general, if we have an object that responds to a weak external electric field we can expand the dipole moment \(\vec{\mu}(\vec{E})\), which depends on the strength and the direction of the field, into a power series.

\[
\vec{\mu}(\vec{E}) = \vec{\mu}(0) + \alpha \vec{E} + O(\vec{E}^2)
\]  

(1.1)

In the following discussion, we assume the electric field to be weak\(^2\), so that the non-linear terms are negligible and we, therefore, have a linear response. We will call the Matrix \(\alpha\) the electric polarizability. For spherically symmetric objects, like atoms, this matrix reduces to a constant. A quantum mechanical expression and thus a proper definition for the dynamic polarizability (i.e. the response of an atom to an oscillating field), will be derived in this section and is given in (1.14). The interpretation of (1.1) is that the total dipole moment of the object \(\langle \vec{\mu}(\vec{E}) \rangle\) is the sum of the intrinsic \(\langle \vec{\mu}(0) \rangle\) and the induced one \(\langle \alpha \vec{E} \rangle\).

Indeed, one can define the polarizability as a linear response constant for any interaction. For the electromagnetic interaction, there is also the magnetic polarizability, which is defined as the linear response of an object to an external magnetic field. As the precise expression for this quantity is not necessary for our mathematical treatment of the Van der Waals interactions in the electromagnetic theory (atoms, molecules), we will not elaborate on that any further. In the theory of strong interactions the corresponding quantities, which are called chromoelectric and chromomagnetic polarizability, play a significant role in the description of Van der Waals interactions between colour-neutral objects. We will come back to that later on.

We are now going to develop a quantum mechanical expression for the (dynamic) electric polarizability of atoms. We consider an atom which has the Hamiltonian \(\hat{H}_{\text{Atom}}\) and turn on an electric field \(\vec{E}(t)\), at \(t = 0\). We assume \(\vec{E}(t)\) to be of the form \(\vec{E}(t) = (1 - e^{-\frac{t}{T}})\vec{E}_0 \cos \omega t\), where \(T\) is a parameter interpreted as the switch-on-time. In order to get a clean analysis it is necessary to switch on the field slowly, as the electron-cloud will start to oscillate internally otherwise, which

\(^2\)The study of the effects of strong external fields, which can be generated by lasers, is a different branch of physics called non-linear optics.
is an effect we do not want to investigate on. Later we will see why we introduced the factor 
\((1 - e^{-\frac{t}{T}})\) for this purpose.
Mathematically the system has the following Hamiltonian:
\[
\hat{H}(t) = \hat{H}_{\text{atom}} - \bar{\mu} \hat{E}(t) := V(t)
\]
with \(\bar{\mu}\) being the dipole moment operator of the atom. The atom has atomic number \(Z\) and we denote by \(\{\vec{r}_i\}\) the coordinates of the electrons relative to the nucleus of the atom. The dipole moment operator then reads:
\[
\vec{\mu} := Z \sum_{i=1}^{Z} -e\vec{r}_i
\]
with \(e\) is the elementary charge, which is a positive quantity. Without loss of generality we define \(\vec{E}\) to point in \(z\)-direction (\(\vec{E} = E\vec{e}_z\)). For the expectation value of the dipole moment, which we will refer to as the (total) dipole moment - corresponding to \(\bar{\mu}(\vec{E})\) in (1.1), we get:
\[
\mu_z(t) = \langle n(t) | \hat{\mu}_z | n(t) \rangle
\]
with \(|n(t)\rangle\) being the state of the atom, which has been an eigenstate of \(\hat{H}_{\text{atom}}\) at \(t = 0\) (i.e. before switching on the external field), with eigenvalue \(E_n\). The time-evolution of this state is governed by the Schrödinger equation with the Hamiltonian \(\hat{H}(t)\). To get an expression for the time dependence of \(|n(t)\rangle\) we will use time dependent perturbation theory. This is most practical in the interaction-picture.
Recall, that in the interaction-picture the states and operators are defined as follows:
\[
|\Psi(t)\rangle_I := e^{i \hat{H}_{\text{Atom}} t} |\Psi(t)\rangle_S
\]
\[
\hat{A}_I(t) := e^{i \hat{H}_{\text{Atom}} t} \hat{A}_S e^{-i \hat{H}_{\text{Atom}} t}
\]
and evolve in time as:
\[
i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle_I = V_I(t) |\Psi(t)\rangle_I
\]
\[
dt \hat{A}_I(t) = \frac{i}{\hbar} [\hat{H}_{\text{Atom}} I, \hat{A}_I] + \left( \frac{\partial \hat{A}_S}{\partial t} \right)_I
\]
where subscript \(S\) and \(I\) denote the Schrödinger- and the Interaction- picture. If there is no ambiguity we will usually suppress writing the subscript \(S\) for the Schrödinger picture.

In time dependent perturbation theory the evolution of the state \(|n(t)\rangle_I\) is governed by the Dyson-Series, which directly arises by repeated integration and substitution from (1.7) and is an expansion in powers of \(|\vec{E}|\). It reads:
\[
|n(t)\rangle_I = |n(0)\rangle + \frac{1}{i\hbar} \int_0^t V_I(\tau) |n(0)\rangle d\tau + \frac{1}{(i\hbar)^2} \int_0^t \int_0^\tau V_I(\tau)V_I(\tau') |n(\tau')\rangle_I d\tau' d\tau
\]
\[
= |n(t)\rangle_I + O(\vec{E}^2)
\]
If we plug this in (1.4) and neglect terms quadratic in $E$, we get:

$$
\mu_z(t) = \langle n(t)\mid \hat{\mu}_z \mid n(t)\rangle_S = \langle n(t)\mid \hat{\mu}_z \mid n(t)\rangle_I
$$

where we used $e^{i\frac{\hat{H}_{Atom}}{\hbar} t} |n\rangle = e^{i\frac{E_n}{\hbar} t} |n\rangle$ twice. The first term $\langle n\mid \hat{\mu}_z \mid n\rangle$ is the expectation value of the dipole moment without an external field. It should, therefore, be interpreted as the intrinsic dipole moment of the atom ($\langle \hat{\mu}(0) \rangle$). It will be zero in spherically symmetric states. The remaining term is proportional to the strength of the electric field and will, therefore, yield an expression for the polarizability. In order to get that expression we will now expand $\hat{\mu}_z$ into eigenstates of $\hat{H}_{Atom}$, which we denoted by $|k\rangle$.

$$
\mu_z(t) = \langle n\mid \hat{\mu}_z \mid n\rangle - 2\Re \left\{ \frac{E}{i\hbar} \sum_k \langle n\mid e^{i\frac{\hat{H}_{Atom}}{\hbar} t} \hat{\mu}_z \mid k\rangle e^{-i\frac{E_k}{\hbar} t} \langle k\mid \hat{\mu}_z \mid n\rangle \int_0^t e^{i\frac{\hat{H}_{Atom}}{\hbar} \tau} (1 - e^{-\frac{T}{\hbar}}) \cos(\omega \tau) d\tau \right\}
$$

We define $\Delta \omega_{kn} := \frac{E_k - E_n}{\hbar}$ and evaluate the integral:

$$
\int_0^t e^{i\Delta \omega_{kn} \tau} (1 - e^{-\frac{T}{\hbar}}) \cos(\omega \tau) d\tau = \frac{1}{2} \sum_{\pm} \left\{ e^{i(\Delta \omega_{kn} \pm \omega) T} \frac{1}{i(\Delta \omega_{kn} \pm \omega)} - \frac{T}{i(\Delta \omega_{kn} \pm \omega)} e^{-\frac{T}{\hbar}} \right\}
$$

We are interested in the behaviour of the system a long time after switching on the electric field ($t \gg T$). Term (a) is, therefore, negligibly small. For atoms a typical value of $\Delta \omega_{kn}$ is about $10^{15}\text{s}^{-1}$. We will, therefore, assume that $|T(\Delta \omega_{kn} \pm \omega)|$ is much larger than 1 and get a cancellation of (b) and (c). This cancellation is the true reason for introducing the $(1 - e^{-\frac{T}{\hbar}})$ term in the electric field. If we set $T = 0$ the last terms would not cancel and account for an internal oscillation of the electron-cloud. Plugging this result into (1.11) yields:

$$
\mu_z(t) = \langle n\mid \hat{\mu}_z \mid n\rangle + \frac{2E \cos(\omega t)}{\hbar} \sum_{|k\rangle: E_k \neq E_n} \frac{\Delta \omega_{kn} |\langle k\mid \hat{\mu}_z \mid n\rangle|^2}{\Delta \omega_{kn}^2 - \omega^2}
$$

This has now exactly the form of (1.1) and yields the definition of the dynamic polarizability of an atom, which is the main result of this section.

$$
\alpha(\omega) := \frac{2}{\hbar} \sum_{|k\rangle: E_k \neq E_n} \frac{\Delta \omega_{nk} |\langle k\mid \hat{\mu}_z \mid n\rangle|^2}{\Delta \omega_{nk}^2 - \omega^2}
$$

Note that $|n\rangle := |n(0)\rangle_S = |n(0)\rangle_I$. Also, expectation values are the same in all pictures.

For $\omega = 0$ the summation over states $|k\rangle$ with $E_k = E_n$ needs a slightly different treatment of the integration. One can easily see from (1.11) that this part of the sum is purely imaginary then and does not contribute, because we take the real part.
A special case of the dynamic polarizability is the static polarizability, which we obtain by taking the limit $\omega \to 0$. This corresponds to applying a static electric field. It reads:

$$\alpha(0) := -\frac{2}{\hbar} \sum_{|k\rangle: E_k \neq E_n} \frac{|\langle k| \hat{\mu}_z | n \rangle|^2}{E_k - E_n}$$  \hspace{1cm} (1.15)$$

We can also interpret the polarizability as a measure of the variance (square of the standard deviation) of the electric dipole moment of the atom. We can see that by noting that the denominator $(E_k - E_n)$ does not vary very much throughout the summation (at least for bound states, which we assume to be the dominant contribution), which is the reason why we can treat it approximately as an effective constant $\frac{1}{\Delta \tilde{E}_{kn}}$ in front of the sum$^5$.

$$\alpha(0) := -\frac{2}{\hbar} \sum_{|k\rangle: E_k \neq E_n} \frac{|\langle k| \hat{\mu}_z | n \rangle|^2}{E_k - E_n} \approx -\frac{2}{\hbar \Delta \tilde{E}_{kn}} \sum_{|k\rangle: E_k \neq E_n} |\langle k| \hat{\mu}_z | n \rangle|^2$$  \hspace{1cm} (1.16)$$

This is a summation over all states except $|n\rangle$. $^6$ We will use the completeness relation (by adding and subtracting $|\langle n| \hat{\mu}_z | n \rangle|^2$) to get:

$$\alpha(0) \approx -\frac{2}{\hbar \Delta \tilde{E}_{kn}} \left[ \langle n| \hat{\mu}_z^2 | n \rangle - |\langle n| \hat{\mu}_z | n \rangle|^2 \right] = \Delta \mu^2$$  \hspace{1cm} (1.17)$$

The term labeled $\Delta \mu^2$ is the variance of the probability distribution of the dipole moment. It is thus that the polarizability is also a measure for the uncertainty of the dipole moment of a certain energy state. The fluctuations associated with this uncertainty of the dipole moment are the physical reason for the Van der Waals interaction, as we will see in section 2, and are therefore of extreme importance.

As the polarizability has many applications, there have been many attempts to measure it. A lot of methods have been developed but extremely high accuracy is hard to achieve experimentally. An overview of different methods can be found for example in Chapter 5 of [15]. The most accurate measurements rely on a modern method, called atom interferometry, which has been introduced first in [16].

Van der Waals interactions are not only of interest in the electromagnetic theory (QED) but also in the theory of the strong interaction (QCD). In QCD the analogue for the charge is called colour, whereas the force is carried by gluons instead of photons. One of the main differences between these theories is that gluons carry colour, while photons are neutral particles. Gluons, therefore, can also interact with each other. As there exist colour neutral objects$^7$ (mesons and baryons) which are bound systems of quarks, it is physically clear that these objects are polarizable in an analogous way as atoms in the theory of electromagnetism. It is thus clear that the quantities analogous to the electric and magnetic polarizability, called chromoelectric and chromomagnetic polarizability, will play a significant role if one wants to study Van der Waals interactions in QCD. Despite these similarities, the theoretical study of Van der Waals interactions is much more challenging in QCD than it is in QED. The reason for that is that not all aspects of these long-range forces can be treated perturbatively in QCD, as they can be in QED. However, this difficulty is also the main concern in a theoretical study of these forces, because the long-range properties of QCD are still not very well understood from first principles. Recent theoretical progress in the study

$^5$This is known as the closure approximation and is the same idea as the Unsöld approximation of section 2.1.1

$^6$This might not be rigorously true if $|n\rangle$ is degenerate. We would then have to subtract some off-diagonal terms to use the completeness of states. This does not change the interpretation.

$^7$Due to confinement free particles are always colour-neutral.
of these long-range properties has been achieved through effective field theories (EFT) [17]. An EFT is an approximation to the complete equations, of QED or QCD for example, at the scale of interest. It is based on the observation that the dynamics at that scale, for example, the low energy dynamics of bound systems, does not depend on details of the large number of degrees of freedom of the high energy dynamics. An EFT can, therefore, be seen as a kind of averaging process over these degrees of freedom. EFTs that are suitable to study the properties of bound states in QCD are called non-relativistic QCD (NRQCD) [18] and potential-NRQCD (pNRQCD) [19]. In this framework, a description of the polarizabilities (chromoelectric and chromomagnetic), as well as new expressions for the long-range properties of bottomonium, have been achieved recently [17]. Experimentally one currently tries to analyse Van der Waals interactions via scattering the $J/\Psi$ meson (charmonium) at nuclei. This experimental setup is advantageous to study the Van der Waals interactions because it has been shown theoretically by Brodsky and Miller [21] that Van der Waals interactions due to multi-gluon exchange dominate over all other QCD effects in $J/\Psi$ scattering. This experiment should, therefore, give a direct view of this process. Even though there have been many attempts to study these very interesting interactions, theoretically as well as experimentally, a lot more work remains to be done to a full understanding of all these issues.

The motivation of this thesis is to look into calculation techniques for polarizabilities, which we will study in the framework of non-relativistic quantum mechanics. This thesis is structured as follows: In chapter 2 we study the interaction between two neutral atoms. We will start doing this with a physical discussion of the short- and long-range regimes. A detailed mathematical discussion of the short-range regime will be followed by the discussion of the precise connection between the polarizability and the constant $C$ of the London potential. We will finish this chapter with an accurate numerical evaluation of the constant $C$ of the system of two hydrogen atoms. In chapter 3 we will present methods to calculate the polarizability of the hydrogen atom. The first method is based on finding particular solutions to a related differential equation whereas for the second method we use a representation of the Coulomb Greens function.

Let us make a short note on units. In the introduction we used (implicitly) SI-units because these were most useful to get a general feeling on typical scales in terms of familiar units. In the perturbative calculations of section 2 it is most useful to use natural units which we define by setting $\hbar = c = 4\pi\epsilon_0 = 1$. These units will be used in section 2.1.1. For concrete calculations involving an explicit form of the wavefunctions of hydrogen it is most useful to use atomic units, which are defined by setting $\hbar = c = m_e = e = 1$ with the elementary charge $e$ and the mass of the electron $m_e$.

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8This discussion benefits a lot from the discussion in [20].

9A consequence of these units is that the elementary charge is connected to the fine-structure constant by $e = \sqrt{\alpha}$

10Implications of these units are that the Bohr radius is equal to 1, the ground state energy of hydrogen is $-\frac{1}{2}$ and the speed of light is $\frac{1}{\alpha} \approx 137$, which the fine-structure constant $\alpha$. 


2 Van der Waals interactions between atoms

In this chapter, we want to describe the interaction of two atoms A and B, which are separated by a distance $R$. The distance $R$ should be large enough such that the overlap of the wavefunctions of the individual atoms is small. This is true if $R$ is much larger than the Bohr radius. In a classical model of an atom as a sphere with some radius, this statement means that these spheres should not touch each other. The interaction is electromagnetic in nature. The fundamental theory to describe it, therefore, is Quantum Electrodynamics (QED). In QED the force is carried by photons, which travel at the speed of light. To get a first insight let us assume that the distance between the atoms is small enough, so that in a good approximation one can consider the interaction as being instantaneous (i.e. electrostatic). In a classical treatment, we would model the situation as the interaction of two multipoles. If we further assume the atoms to be spherically symmetric, then all multipole-moments would be zero, and thus no interaction would occur. As we will see, this corresponds to a vanishing expectation value of the dipole moment and therefore for a vanishing first order term in quantum mechanical perturbation theory. In quantum mechanics though the Hamiltonian operator does not commute with the electric dipole operator, which implies, that the energy eigenstate of the atom is not an eigenstate of the dipole operator. This physically means that we will measure a non-zero dipole moment each time. As there is no preferred direction, the average value will still be zero. Thus the dipole moment of an atom can have so-called fluctuations, which means that the atom develops a dipole moment at some instant. The situation, therefore, is not static but involves two randomly fluctuating dipoles - the atoms A and B. Now we have a dipole in an electric field, which causes a shift in the total energy. We are now getting a bit more quantitative. The electric field $E_B$ at the location of atom B, which is generated by the instantaneous dipole $\Delta\mu_A$ of atom A, is proportional to the dipole moment $\Delta\mu_A$ and falls off as $R^{-3}$. $E_B \sim \frac{\Delta\mu_A}{R^3}$. This field induces a dipole moment $\mu_B$ in the atom B, which is proportional to the polarizability $\alpha_B$ of B and the electric field $E_B$. $\mu_B = \alpha_B E_B$. (See also (1.1)). The energy $\Delta E$ of the induced dipole $\mu_B$ in the electric field $E_B$ is given by $\Delta E = -\mu_B E_B$. Combining these considerations gives:

$$\Delta E = -\mu_B E_B = -\alpha_B E_B^2 \sim -\frac{(\Delta\mu_A)^2 \alpha_B}{R^6}$$  \hspace{1cm} (2.18)

It is very reasonable to identify the size of the instantaneous dipole $\Delta\mu_A$ with the standard deviation of the quantum mechanical probability distribution of the dipole moment. For this quantity, we found an expression in terms of the polarizability of A in (1.17). $\Delta\mu_A \propto \sqrt{\alpha_A}$. The final result is, therefore:

$$\Delta E \sim -\frac{\alpha_{AB}}{R^6}$$  \hspace{1cm} (2.19)

The most important aspect we can extract from these considerations is the attractive $\frac{1}{R^6}$ dependence of the interaction potential. The force is attractive because the induced dipole is always parallel to the instantaneous one. We will derive the same form of the potential in a mathematical treatment using quantum mechanics. In the beginning, we said that the force is not instantaneous but is carried by photons, which travel at the speed of light, which is fast but finite. Having the Bohr model in mind, we think of the electrons moving around the nucleus in some orbit. The time it takes for orbiting the nucleus once is in the order of $T \sim \frac{1}{E_n - E_0}$ with $E_n$ being the energies.

\[ ^{11}\text{It is hereby defined that we use natural units in this chapter (} \hbar = c = 4\pi \epsilon_0 = 1\text{).} \]

\[ ^{12}\text{The precise expression for the electric field of a dipole } \mu \text{ at position } \vec{R} \text{ is: } \vec{E}(\vec{R}) = \frac{3(\vec{\mu} \cdot \vec{R})\vec{R} - \vec{\mu}}{|\vec{R}|^3} \text{ with } \vec{R} \text{ being the unit vector in direction of } \vec{R}. \]
of the orbitals. We, therefore, expect the fluctuating dipole moments to change at a rate of \( \frac{1}{T} \). In QED the interaction process described above happens to be a two-photon process. (i.e. one photon travelling from A to B and one in the opposite direction).

As the photons travel at the speed of light, it takes them the time \( t_\gamma = \frac{R}{c} \) to travel between the atoms. It is therefore clear, that if \( t_\gamma \) is of the order of magnitude of \( T \) the explanation from above needs some corrections. For the case where \( t_\gamma \gg T \) the potential was calculated by Casimir and Polder [3]. It reads:

\[
\Delta E = -\frac{23\alpha_A \alpha_B}{R^7}
\]

(2.20)

The intermediate region is much more difficult but is studied in [22][23].

To summarize: the system of two atoms has two independent scales, the times \( T \) and \( t_\gamma \). As written above \( T \) is related to the binding energy of the atom via \( T \sim \frac{1}{m_e \alpha^2} E \). The typical binding energy of atoms is in the order of the Rydberg energy, which is \( E_{Ry} = m_e \alpha^2 \), \( m_e \) is the mass of the electron and \( \alpha \) is the fine-structure constant\(^{13}\). We therefore have \( \frac{1}{T} \sim m_e \alpha^2 \). \( t_\gamma \) is directly related to the distance between the atoms via \( \frac{1}{t_\gamma} = \frac{1}{R} \). The short range regime (London) is characterized by \( T \gg t_\gamma \), which is, due to the relations above, equivalent to \( \frac{1}{R} \gg m_e \alpha^2 \). As \( R \) also needs to be larger than the Bohr radius \( (a_0 = \frac{1}{m_e \alpha}) \) we finally have the relation

\[
m_e \alpha^2 \ll \frac{1}{R} \ll m_e \alpha
\]

(2.21)

for the London regime. Following the same reasoning, the long-range regime (Casimir-Polder) is characterized by:

\[
m_e \alpha^2 \gg \frac{1}{R}
\]

(2.22)

A systematic approach to mathematically deal with the different regimes is through EFTs [23]. Typically the electrons of the atoms can be treated non-relativistically. The appropriate theories to study them thus are non-relativistic QED (NRQED) [24] and potential NRQED (pNRQED) [25].

NRQED emerges from QED by integrating out the relativistic energy scales, which are at the size of the electron mass \( m_e \), or larger. pNRQED then emerges from NRQED by also integrating out the typical momentum scale of an atom, which is of order \( m_e \alpha \) (inverse of the Bohr radius). pNRQED is perfect to study Van der Waals interactions as it contains all the relevant scales \( (m_e \alpha^2, \frac{1}{R}) \) - see (2.21) and is as simple as possible. An important result of this theory is that terms accounting for the magnetic interactions between the atoms are suppressed by a factor \( \frac{1}{m_e} \), when compared to the electric interaction. This means that the magnetic terms can be neglected.

2.1 The London force

2.1.1 General treatment

We will now discuss in detail the case of the London force\(^{14}\). Following the discussion of the previous section we are now going to study mathematically two atoms A and B, with atomic numbers \( Z_A \) and \( Z_B \), separated by a large distance \( R \). In this context large means that the overlap of the wavefunctions of the individual atoms can be neglected. As we are studying the short-range

\(^{13}\alpha = e^2 \approx \frac{1}{137}, \ e \) is the elementary charge

\(^{14}\)We still use natural units in this section
case, it is sufficient to describe the interaction between the particles electrostatically. We will also neglect energetic effects of spin, as these effects are suppressed by $m_e^{-1}$ as discussed above. For our mathematical treatment, we are also going to assume that the nuclei are at a fixed position in space. (A bit more precisely we assume, that their relative motion is much slower than the time it takes the electrons to get into their configuration. This is known as the Born-Oppenheimer approximation). The Hamiltonian we are now going to study looks as follows (See also Figure 1 for illustration):

$$
\hat{H} = - \sum_{i=1}^{Z_A+Z_B} \frac{1}{2m_e} \Delta \vec{r}_i + \frac{\alpha Z_A Z_B}{|\vec{R}|} - \sum_{i=1}^{Z_A+Z_B} \frac{\alpha Z_A}{|\vec{r}_i + \vec{R}/2|} - \sum_{i=1}^{Z_A+Z_B} \frac{\alpha Z_B}{|\vec{r}_i - \vec{R}/2|}
$$

with the fine structure constant $\alpha$ defined (in natural units) $\alpha := e^2$. This equation cannot be solved in terms of elementary functions. To extract the physics, we will rewrite the Hamiltonian and identify three terms; two terms describe the atoms $A$ and $B$ without an interaction and the third term accounts for the interaction between these two atoms. As the atoms are far apart from each other, the interaction energy will be small in comparison to the energy of the non-interacting system. We are therefore going to apply time-independent perturbation theory to get a correction to the ground-state energy level. This correction should be interpreted as the potential of a force between the atoms.

As we are studying the interaction of two neutral atoms, we choose the first $Z_A$ electrons to belong to atom $A$ and the last $Z_B$ electrons to atom $B$. This can be made manifest by introducing new relative coordinates for the electrons as follows: $\vec{r}_{A,i} := \vec{r}_i + \vec{R}/2$ for $1 \leq i \leq Z_A$ and $\vec{r}_{B,i} := \vec{r}_i - \vec{R}/2$.

---

15The Born-Oppenheimer approximation assumes that the wavefunction of the nuclei can be separated from the wavefunction of the electrons. This is valid if there are well-separated energy levels for any configuration of the atoms - for any $\vec{R}$. 

---

Figure 1: Two neutral atoms
\[ \vec{r}_{i+Z_A-1} - \frac{\vec{R}}{2} \text{ for } 1 \leq i \leq Z_B. \]

The meaning of these new coordinates is also illustrated in Fig.1. Also note, that choosing the first electrons to belong to A and the latter to belong to B is arbitrary (i.e. it could be any permutation of them). In fact, while considering the non-interacting system, the electrons of atom \( A \) will be distinguishable from the ones of atom \( B \), which clearly violates the Pauli-principle. However, the (anti)symmetrization postulate tells us, that we have to symmetrize the wavefunctions obtained from the Schrödinger equation manually after solving it. This can be done in every single step of perturbation theory. The resulting change of the energy is comparable to the fall-off of the atomic wavefunction, which is very rapid (\( \propto e^{-R} \) for the hydrogen atom) and can, therefore, be neglected.

After all, the preference of choosing the affiliation of electrons to the atoms will not change the result and is therefore valid. If we finally plug the newly introduced variables \( \{\vec{r}_{A,i}\}^{16} \) and \( \{\vec{r}_{B,i}\} \) into (2.23), we get:

\[
\hat{H} = \sum_{i=1}^{Z_A} \left[ \frac{1}{2m_e} \Delta \vec{r}_{A,i} - \frac{\alpha Z_A}{|\vec{r}_{A,i}|} + \sum_{j=i+1}^{Z_A} \frac{\alpha}{|\vec{r}_{A,i} - \vec{r}_{A,j}|} \right]
\]

\[ := \hat{H}_A \]

\[
+ \sum_{i=1}^{Z_B} \left[ \frac{1}{2m_e} \Delta \vec{r}_{B,i} - \frac{\alpha Z_B}{|\vec{r}_{B,i}|} + \sum_{j=i+1}^{Z_B} \frac{\alpha}{|\vec{r}_{B,i} - \vec{r}_{B,j}|} \right]
\]

\[ := \hat{H}_B \]

\[
+ \frac{\alpha Z_A Z_B}{|\vec{R}|} - \sum_{i=1}^{Z_A} \frac{\alpha Z_A}{|\vec{r}_{A,i} + \vec{R}|} \sum_{i=1}^{Z_B} \frac{\alpha Z_B}{|\vec{r}_{B,i} - \vec{R}|} + \sum_{i=1}^{Z_A} \sum_{j=1}^{Z_B} \frac{\alpha}{|\vec{r}_{B,j} - \vec{r}_{A,i} - \vec{R}|}
\]

\[ := W(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\}) \]

This is the claimed separation into three terms. \( \hat{H}_A \) and \( \hat{H}_B \) are the Hamiltonians of the non-interacting atoms and the interaction between them is isolated in the function \( W(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\}) \). In this interaction function the parameter \( |\vec{R}| \) appears only in the denominator. We consider \( |\vec{R}| \) to be a large quantity in comparison to \( |\vec{r}_{A,i}| \) or \( |\vec{r}_{B,i}| \) which is exactly the same as the statement that the wavefunctions of the atoms \( A \) and \( B \) do not have a significant overlap. \( W(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\}) \) is therefore a small quantity and can be treated as a perturbation on the non-interacting system, which is described by the Hamiltonian \( \hat{H}_0 := \hat{H}_A + \hat{H}_B \).

If we assume that the Hamiltonians of the individual atoms are solved, then the combined, but non-interacting system, can be solved by the product ansatz:

\[
psi^{\alpha,\beta}_{AB}(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\}) = psi^\alpha_A(\{\vec{r}_{A,i}\}) \cdot psi^\beta_B(\{\vec{r}_{B,i}\})
\]

with \( psi^\alpha_A(\{\vec{r}_{A,i}\}) \) and \( psi^\beta_B(\{\vec{r}_{B,i}\}) \) being the eigenfunctions of the operators \( \hat{H}_A \) and \( \hat{H}_B \) with eigenvalues \( E^A_\alpha \) and \( E^B_\beta \) respectively (i.e. the energy eigenfunctions and eigenvalues of the single unperturbed atoms \( A \) and \( B \)). \( \alpha \) and \( \beta \) are (possibly continuous) indices for the eigenfunctions of these single atoms.

\[ ^{16} \text{We will use the short notation } \{\vec{r}_{A,i}\} \text{ and } \{\vec{r}_{B,i}\} \text{ for } \{\vec{r}_{A,i}: 1 \leq i \leq Z_A\} \text{ and } \{\vec{r}_{B,i}: 1 \leq i \leq Z_B\} \]
This yields:

\[
\hat{H}_0\psi_{AB}^{\alpha\beta} = (\hat{H}_A + \hat{H}_B) \cdot \psi_{A}^\alpha(\{\vec{r}_{A,i}\}) \cdot \psi_{B}^\beta(\{\vec{r}_{B,i}\})
\]

\[
= \psi_{B}^\beta(\{\vec{r}_{B,i}\})[\hat{H}_A\psi_{A}^\alpha(\{\vec{r}_{A,i}\})] + \psi_{A}^\alpha(\{\vec{r}_{A,i}\})[\hat{H}_B\psi_{B}^\beta(\{\vec{r}_{B,i}\})]
\]

\[
= (E_A^\alpha + E_B^\beta) \cdot \psi_{AB}^{\alpha\beta} := E_{\alpha,\beta} \psi_{AB}^{\alpha\beta}
\]

(2.26)

which proves that if we knew the wavefunctions of the individual atoms, we also would know the wave function of the non-interacting system which is described by the Hamiltonian \(\hat{H}_0\). We further define \(E_{\alpha,\beta} := E_A^\alpha + E_B^\beta\).

Let us now have a closer look at the interaction function \(W(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\})\), which can be rewritten as follows:

\[
W(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\}) = \frac{\alpha Z_A Z_B}{|\vec{R}|} - \sum_{i=1}^{n} \frac{\alpha Z_A}{|\vec{r}_{B,i} - \vec{R}|} - \sum_{i=1}^{n} \frac{\alpha Z_B}{|\vec{r}_{A,i} - \vec{R}|} + \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{\alpha}{|\vec{r}_{A,i} - \vec{r}_{B,j} - \vec{r}_{A,i} + \vec{R}|}
\]

(2.27)

As mentioned above we physically consider \(|\vec{r}_{A,i}| \ll |\vec{R}|\) and \(|\vec{r}_{B,i}| \ll |\vec{R}|\), as \(\vec{r}_{A,i}\) and \(\vec{r}_{B,i}\) are interpreted as coordinates of the electrons relative to their associated atoms. \(|\vec{r}_{A,i}|\) and \(|\vec{r}_{B,i}|\) are thus at the order of magnitude of the Bohr radius \((m_e \alpha)^{-1}\). It is therefore natural (as \(|\vec{r}_{A,i}|\) and \(|\vec{r}_{B,i}|\) are always divided by \(|\vec{R}|\)) to Taylor-expand \(W(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\})\) in these small quantities. Despite the good physical arguments for this, one might be a bit worried about the mathematics created by this expansion, as \(\vec{r}_{A,i}\) and \(\vec{r}_{B,i}\) are parameters and can therefore in principle have an arbitrary value, even though a very large absolute value is very unlikely from the physical point of view. The reason why one might have doubts is that the expansion, which is carried out below (2.28) has only a finite radius of convergence. This implies that if one takes into account all terms of the expansion, all matrix elements of the expanded function will be infinite. This is because the probability is low but non-zero for large values of \(\vec{r}_{A,i}\) or \(\vec{r}_{B,i}\), where the series does not converge. To save the expansion and to justify that we can get the correct result by only taking a finite (small) number of terms into account, we notice that we can expand \(W(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\})\) for all parameters inside the radius of convergence and leave it as it is outside of this radius. The probability for large absolute values of \(\vec{r}_{A,i}\) and \(\vec{r}_{B,i}\) is still very small, which means, that the matrix elements of the first few (lower order) terms will only slightly differ if we take the expanded version instead of the hybrid version (expanded terms + original ones outside of the radius of convergence). But in the hybrid version, they are the dominant contribution. Therefore, it is valid to only keep the first few terms and to use them in their fully expanded version\(^{17}\). The expansion is carried out below:

\(^{17}\)In fact, this discussion only tries to argue that it is reasonable to hope that we can get a feasible result by using perturbation theory. It is not difficult to see that the perturbation series can not possibly converge because the expanded operators are unbounded from below. Therefore we can not have a bound state.
will also assume in the following discussion, that this ground-state is non-degenerate on the perturbation to the ground state (i.e. both atoms are in their lowest energy states). We summarized in Appendix B)

With (2.28) we can now use time-independent perturbation theory (that mathematical tool is

different behaviour (i.e., a different dependence on \( |\vec{R}| \)) than derived in this section. We will elaborate more on that in (2.1.3) and give some references there.

\[
P_l \text{ are the Legendre polynomials as defined in (C.186). To perform the expansion the identity (C.188) was used. \( \vec{\mu}_A \) and \( \vec{\mu}_B \) are the electric dipole moments of the atoms A and B respectively. They are defined as:}
\[
\begin{align*}
\vec{\mu}_A := & \sum_{i=1}^{Z_A} e \vec{r}_{A,i} = \sum_{i=1}^{Z_A} \sqrt{\alpha \vec{r}_{A,i}} \\
\vec{\mu}_B := & \sum_{j=1}^{Z_B} e \vec{r}_{B,j} = \sum_{j=1}^{Z_B} \sqrt{\alpha \vec{r}_{B,j}}
\end{align*}
\]

This result can be interpreted as the interaction energy between two multipoles A and B (i.e. dipole-dipole, dipole-quadrupole, dipole-octopole, quadrupole-quadrupole and higher multipoles).

With (2.28) we can now use time-independent perturbation theory (that mathematical tool is summarized in Appendix B) \(^{18}\) to obtain corrections to the energy levels.

As atoms tend to be in the ground state due to the emission of photons, we will focus here only on the perturbation to the ground state (i.e. both atoms are in their lowest energy states). We will also assume in the following discussion, that this ground-state is non-degenerate\(^{19}\) (i.e. both

\(^{18}\)The applicability of perturbation theory has been proven in a rigorous way for two hydrogen atoms in [26]

\(^{19}\)This is the crucial ingredient for the proof in the Appendix A.2, that the terms arising from first order in perturbation theory (2.32) will vanish. Degenerate states and also states that are nearly degenerate might have a different behaviour (i.e., a different dependence on \( |\vec{R}| \)) than derived in this section. We will elaborate more on that in (2.1.3) and give some references there.
atoms are in an S-state). Let $|\psi_{00}^{AB}\rangle$ be the ground state of the unperturbed system and $\{|\psi_{\alpha,\beta}^{\alpha,\beta}\rangle\}$ be the complete set of (generalized) eigenfunctions of the Hamiltonian $\hat{H}_0$. (The eigenfunctions are given by (2.25)).

Then the corrections to the energy levels in first and second order of perturbation theory are given by (B.181),(B.185)

$$\epsilon_1 = \langle \psi_{00}^{00} | W | \psi_{00}^{00} \rangle$$

$$\epsilon_2 = \sum_{(\alpha,\beta): E_{\alpha,\beta} \neq E_{00}} \frac{|\langle \psi_{\alpha,\beta}^{\alpha,\beta} | W | \psi_{00}^{00} \rangle|^2}{E_{00} - E_{\alpha,\beta}}$$

$\sum$ means "sumation" over the complete set of eigenfunctions (including the continuous spectrum). Note, that we have two different expansions in inverse powers of $|\vec{R}|$. One is (2.28) and the other one is the perturbation expansion (2.30). Our goal is to find the leading non-vanishing order in inverse powers of $|\vec{R}|$. As derived in Appendix A.2 with the assumption of non-degeneracy of the ground state, $\epsilon_1$ is at least of order $O\left(|\vec{R}|^{-7}\right)$. This means, that it is negligible if we want to isolate the dominant contribution. Therefore, the leading non-vanishing correction is the correction due to the dipole-dipole term in second order perturbation theory $\epsilon_2$, which is $O\left(|\vec{R}|^{-6}\right)$. The energy correction therefore reads:

$$\Delta E = \epsilon_1 + \epsilon_2 = -\frac{1}{|\vec{R}|^6} \sum_{(\alpha,\beta): E_{\alpha,\beta} \neq E_{00}} \frac{|\langle \psi_{\alpha,\beta}^{\alpha,\beta} | \vec{\mu}_A \cdot \vec{\mu}_B - 3(\vec{R} / |\vec{R}|) \cdot (\vec{R} / |\vec{R}|) \cdot (\vec{R} / |\vec{R}|) | \psi_{00}^{00} \rangle|^2}{E_{\alpha,\beta} - E_{00}} + O\left(|\vec{R}|^{-7}\right)$$

$$:= -\frac{C}{|\vec{R}|^6} + O\left(|\vec{R}|^{-7}\right)$$

Note, that the sum is a positive quantity. The energy is therefore lowered, which can be classically interpreted as an attractive force. This $\frac{1}{|\vec{R}|^6}$ potential is called the London potential [2]. It is also interesting at which order in terms of $m_e$ and $\alpha$ we arrived. The dipole moment is of order $\sqrt{\alpha a_0} = \frac{e \alpha}{m_e}$, which implies that the numerator of the fraction inside the sum is of order $m_e^{-4} \alpha^{-2}$. Combining this with the fact that the denominator is of order $m_e^2 \alpha^2$ implies, that the whole energy term is of order:

$$\Delta E \sim -m_e^{-5} \alpha^{-4}$$

which gives together with the inequality (2.21):

$$m_e \alpha^5 \ll \Delta E \ll m_e \alpha^2$$

We can simplify the expression of the constant $C$, by using symmetry arguments. The precise

---

20This section gets some of its ideas from [27]
The mathematical argumentation is carried out in Appendix A.3. The result is:

\[
C = 6 \sum_{(\alpha, \beta): E_{\alpha, \beta} \neq E_{0,0}} \frac{|\langle \psi_{AB}^{\alpha, \beta} | \mu_{A,z} \mu_{B,z} | \psi_{AB}^{0,0} \rangle|^2}{E_{\alpha, \beta} - E_{0,0}}
\]

\[
= 6 \sum_{(\alpha, \beta): E_{\alpha, \beta} \neq E_{0,0}} \frac{|\langle \psi_{A}^{\alpha} | \mu_{A,z} | \psi_{A}^{0} \rangle|^2 |\langle \psi_{B}^{\beta} | \mu_{B,z} | \psi_{B}^{0} \rangle|^2}{E_{\alpha, \beta} - E_{0,0}}
\]

\[
= 6 \sum_{(\alpha, \beta): E_{\alpha, \beta} \neq E_{0,0}} \frac{(E_{\alpha}^{A} - E_{0}^{A})(E_{\beta}^{B} - E_{0}^{B})}{(E_{\alpha}^{A} - E_{0}^{A}) + (E_{\beta}^{B} - E_{0}^{B})} \frac{|\langle \psi_{A}^{\alpha} | \mu_{A,z} | \psi_{A}^{0} \rangle|^2}{E_{\alpha}^{A} - E_{0}^{A}} \frac{|\langle \psi_{B}^{\beta} | \mu_{B,z} | \psi_{B}^{0} \rangle|^2}{E_{\beta}^{B} - E_{0}^{B}}
\]

(2.35)

The two terms (a) and (b) look very much like the static polarizability obtained in (1.15). If we only consider bound states (which are the dominant contribution), then we can see, that (d) does not vary very much (for the hydrogen: \(\frac{3(2m_e^2\alpha^2)}{16} \leq (d) \leq \frac{2m_e^2\alpha^2}{4}\) holds). A. Unsöld therefore had the idea to consider this as an effective constant that can be put in front of the sum [28]. By convention we will call this constant \(\frac{I_{A}I_{B}}{I_{A} + I_{B}}\) and get for the energy correction:

\[
\Delta E \approx -\frac{3}{2} \frac{I_{A}I_{B}}{I_{A} + I_{B}} \frac{\alpha_{A} \alpha_{B}}{|\mathbf{R}|^6}
\]

(2.36)

With \(\alpha_{A}\) and \(\alpha_{B}\) being the static polarizability of the atoms A and B. This is exactly the result we expected from our physical discussion and the one obtained by London [2]. For two hydrogen atoms we get from (3.76) that \(\alpha_{A} = \alpha_{B} = \frac{5}{3}m_e^{-3}\alpha^{-3}\) and thus for the energy correction an approximate inequality:

\[
\sum_{25}^{7,59} \frac{3 \frac{2m_e^{-5}\alpha^{-4}}{|\mathbf{R}|^6}}{7,59} \leq \Delta E \leq \sum_{27}^{5,69} \frac{2 \frac{2m_e^{-5}\alpha^{-4}}{|\mathbf{R}|^6}}{5,69}
\]

(2.37)

which agrees well with the numerical result obtained in Section 2.1.4, which is \(-6.5 \frac{2m_e^{-5}\alpha^{-4}}{|\mathbf{R}|^6}\). Although this result contains all the important physics and outlines the importance of the static polarizability, it is still an (rough) approximation and is therefore not very valuable in precise predictions. Another possible way to rewrite the constant \(C\) is in terms of the dynamic polarizability. To see this we make use of the following mathematical identity, the proof of which can be done by a partial fraction expansion.

\[
\frac{1}{a + b} = \frac{2}{\pi} \int_{0}^{\infty} \frac{a}{a^2 + x^2} \frac{b}{b^2 + x^2} dx
\]

(2.38)

We identify (a) with \((E_{\alpha}^{A} - E_{0}^{A})\) and (b) with \((E_{\beta}^{B} - E_{0}^{B})\) in (2.35) and swap integration and summation, we get:

\[
C = 6 \sum_{\alpha: E_{\alpha}^{A} \neq E_{0}^{A}} \frac{(E_{\alpha}^{A} - E_{0}^{A})|\langle \psi_{A}^{\alpha} | \mu_{A,z} | \psi_{A}^{0} \rangle|^2}{(E_{\alpha}^{A} - E_{0}^{A})^2 + x^2} \sum_{\beta: E_{\beta}^{B} \neq E_{0}^{B}} \frac{(E_{\beta}^{B} - E_{0}^{B})|\langle \psi_{B}^{\beta} | \mu_{B,z} | \psi_{B}^{0} \rangle|^2}{(E_{\beta}^{B} - E_{0}^{B})^2 + x^2}
\]

(2.39)

The two terms in the integral are of the same form as the expression we obtained for the dynamic polarizability in (1.14) except for a sign in the denominator\(^{21}\). We therefore have an integral over

\(^{21}\)Note, that in this section we have \(\hbar = 1\)
the dynamic polarizabilities at imaginary frequencies. The Van der Waals constant can therefore be written as:

\[
C = \frac{3}{\pi} \int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega) d\omega
\]  

(2.40)

\(\alpha_A(\omega)\) and \(\alpha_B(\omega)\) are the dynamic polarizabilities of the atoms A and B, defined by (1.14).

### 2.1.2 Hydrogen-hydrogen interaction

We will use atomic units for the rest of the thesis.\(^{22}\)

In this section, we want to apply the results of the previous chapter to the case where we can solve the unperturbed problem in a closed form, namely two hydrogen atoms separated by a distance \(|\vec{R}|\). Furthermore, we will see that the potential is no longer of the form \(-\frac{C}{|\vec{R}|^6}\) if we address excited states (the situation is shown in Fig.2).

\[\text{Figure 2: Two hydrogen atoms}\]

The Hamiltonian therefore is a special case of (2.26) and reads:

\[
\hat{H} = \left[\frac{1}{2} \Delta \vec{r}_A - \frac{1}{|\vec{r}_A|}\right] + \left[\frac{1}{2} \Delta \vec{r}_B - \frac{1}{|\vec{r}_B|}\right] + \frac{1}{|\vec{R}|} \left[\frac{1}{|\vec{r}_B + \vec{R}|} - \frac{1}{|\vec{r}_A - \vec{R}|} + \frac{1}{|\vec{r}_B - \vec{r}_A + \vec{R}|}\right] \\
:= \hat{H}_A + \hat{H}_B + W(\vec{r}_A, \vec{r}_B)
\]

(2.41)

If we choose our coordinate system in a way, that \(\vec{R}\) points into the \(z\)-direction, we get for the energy correction of the ground state (special case of (2.32)):

\[^{22}\text{To remember: } \hbar = e = m_e = \frac{1}{4\pi e_0} = 1\]
\[ \Delta E = \epsilon_1 + \epsilon_2 = - \frac{1}{|R_0|} \sum_{(\alpha, \beta) : E_{\alpha, \beta} \neq E_{0,0}} \frac{|(\psi_{AB}^\alpha x_A x_B + y_A y_B - 2z_A z_B |\psi_{AB}^\beta|^2}{E_{\alpha, \beta} - E_{0,0}} \]  

(2.42)

2.1.3 Atoms in states with non-zero angular momentum

In chapter 2.1.1 we studied two atoms in their ground states and assumed that this state is non-degenerate if we neglect the spin. Equivalent to that statement is that both atoms are in an S state. Here we want to study the interaction between atoms in states that have a non-zero orbital angular momentum, which implies that these states are degenerate. We will do so by first considering the case of two hydrogen atoms in the first excited state and then give a more general discussion (multi-electron atoms) afterwards. We will be interested in the leading dependence on \( R \) of the potential between two atoms. We will see that this is not always \( R^{-6} \), as the London potential might be a subleading term in the case of states with \( l \neq 0 \).

Let us start with the case of two hydrogen atoms in the first excited state and then give a more general discussion (multi-electron atoms) afterwards. We will be interested in the leading dependence on \( R \) of the potential between two atoms. We will see that this is not always \( R^{-6} \), as the London potential might be a subleading term in the case of states with \( l \neq 0 \).

As in chapter 2.1.2 we will use the Hamiltonian:

\[
\hat{H} = \left[ -\frac{1}{2} \Delta \hat{r}_A - \frac{1}{|\hat{r}_A|} \right] + \left[ -\frac{1}{2} \Delta \hat{r}_B - \frac{1}{|\hat{r}_B|} \right] =: \hat{H}_A + \hat{H}_B
\]

and we will treat the interaction-function \( W \) as a perturbation on the non-interacting system described by the Hamiltonian \( \hat{H}_0 = \hat{H}_A + \hat{H}_B \). Due to 2.26 we have (we denote the eigenstates of \( \hat{H}_A \) and \( \hat{H}_B \) as \( |n_A, l_A, m_A⟩ \) and \( |n_B, l_B, m_B⟩ \) and the combined (multiplied) state as \( |n_A, l_A, m_A; n_B, l_B, m_B⟩ \))

\[
\hat{H}_0 |n_A, l_A, m_A; n_B, l_B, m_B⟩ = -\frac{1}{2} \left( \frac{1}{n_A^2} + \frac{1}{n_B^2} \right) |n_A, l_A, m_A; n_B, l_B, m_B⟩
\]

(2.44)

Thus the first excited state has an energy eigenvalue \( -\frac{1}{2} \left( \frac{1}{n_A^2} + \frac{1}{n_B^2} \right) \) and it is eight times degenerate. These degenerate eigenvectors are:

\[
\begin{align*}
|1, 0, 0; 2, 0, 0⟩ & := |1⟩ \\
|1, 0, 0; 2, 1, -1⟩ & := |2⟩ \\
|1, 0, 0; 2, 1, 0⟩ & := |3⟩ \\
|1, 0, 0; 2, 1, 1⟩ & := |4⟩ \\
|2, 0, 0; 1, 0, 0⟩ & := |5⟩ \\
|2, 1, -1; 1, 0, 0⟩ & := |6⟩ \\
|2, 1, 0; 1, 0, 0⟩ & := |7⟩ \\
|2, 1, 1; 1, 0, 0⟩ & := |8⟩
\end{align*}
\]

(2.45)

In order to get the eigenvectors and the eigenvalues in zeroth and first order of time-independent perturbation theory, one needs to diagonalize an 8x8 matrix (see also section B). Fortunately, due

\[\text{footnote}{\text{23}}\text{It was pointed out to me, that a similar discussion about the first excited state of the hydrogen-hydrogen interaction has also been also done in [29].}}\]
to the selection rules most of the terms in this matrix are zero. One can see that by looking at relations (C.193), (C.200) and (C.201). If we denote the eigenstates as in (2.45) by |1⟩, |2⟩, |3⟩ ... we need to solve the following finite-dimensional eigenvalue problem:

\[
\begin{pmatrix}
|1⟩ W |1⟩ & |2⟩ W |1⟩ & ... & |7⟩ W |1⟩ & |8⟩ W |1⟩ \\
|1⟩ W |2⟩ & |2⟩ W |2⟩ & ... & |7⟩ W |2⟩ & |8⟩ W |2⟩ \\
... & ... & ... & ... & ...
\end{pmatrix}
\begin{pmatrix}
|v_1⟩ \\
|v_2⟩ \\
... \\
|v_7⟩ \\
|v_8⟩
\end{pmatrix} = \epsilon_1
\]

The matrix elements can explicitly be calculated by using the relations above and (C.224). Explicitly the matrix is as follows:

\[
\begin{pmatrix}
0 & D \\
D & 0
\end{pmatrix}
\]  

with a diagonal 4x4 matrix D

\[
D = \frac{1}{|R|^4} \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & \frac{2^{15}}{3^{15}} & 0 & 0 \\
0 & 0 & -\frac{2^{16}}{3^{17}} & 0 \\
0 & 0 & 0 & \frac{2^{15}}{3^{17}}
\end{pmatrix}
\]

One can easily check that the eigenvalues and eigenvectors are given as:

<table>
<thead>
<tr>
<th>Eigenvalue $\epsilon_1$</th>
<th>Eigenvector</th>
<th>Eigenvalue $\epsilon_1$</th>
<th>Eigenvector</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\frac{1}{\sqrt{2}}(</td>
<td>1⟩ +</td>
<td>5⟩)$</td>
</tr>
<tr>
<td>$\frac{1}{</td>
<td>R</td>
<td>^3} \frac{2^{15}}{3^{15}}$</td>
<td>$\frac{1}{\sqrt{2}}(</td>
</tr>
<tr>
<td>$\frac{1}{</td>
<td>R</td>
<td>^3} \frac{2^{15}}{3^{15}}$</td>
<td>$\frac{1}{\sqrt{2}}(</td>
</tr>
<tr>
<td>$-\frac{1}{</td>
<td>R</td>
<td>^3} \frac{2^{16}}{3^{17}}$</td>
<td>$\frac{1}{\sqrt{2}}(</td>
</tr>
</tbody>
</table>

It is remarkable that the eigenvalues are both positive as well as negative. This corresponds to repulsive and attractive forces. It is very interesting that it is state dependent if there is an attractive force or a repulsive one. Furthermore, we also see that the eigenvalues are still zero if we combine S-states. This fits well with the physical intuition that S-states should not have a permanent dipole moment because they are spherically symmetric. We also see that the energy correction is dependent on $R^{-3}$ instead of $R^{-6}$. We must, therefore, conclude that we cannot expect that the term proportional to $R^{-6}$, arising from the dipole-dipole interaction in the second order, is the dominant contribution if the atoms are not in S-states.

We want to discuss now the circumstances that cause the interaction potential to have a different dependence on R than $R^{-6}$.\textsuperscript{24} The discussion applies to multi-electron atoms. As the total angular momentum operator commutes with the Hamiltonian operator (2.23), talking about states with a definite angular momentum is meaningful.\textsuperscript{25} For S-states we have proven in Appendix A.2 that the dominant contribution arises from the dipole-dipole interaction in the second order of perturbation theory.\textsuperscript{26}

\textsuperscript{24} A discussion similar to the following one can also be found in [30].

\textsuperscript{25} Clearly this means, that the states are eigenstates of $J^2$ and $J_z$, where $J$ is to total angular momentum operator.

\textsuperscript{26} One might thus consider reading that section first.
which arguments still apply and which do not, for atoms in states with a total angular momentum \((l \neq 0)\). Unfortunately, there are several cases one needs to deal with separately. Although the study of the hydrogen-hydrogen system outlines that the dependence on \(R\) can be different from \(R^{-6}\), this system is a very special case. It is special because the energy levels are degenerate with respect to the azimuthal quantum number \(l\), which is typically not the case for other atoms\(^{27}\). Thus not all degenerate states have the same behaviour with respect to parity transformation. It is also special because it is a system of two atoms of the same kind. In the multipole-expansion (2.28) there are three terms that have a lower order than \(R^{-6}\). These terms are the dipole-dipole term \(W_2 (R^{-3})\), the dipole-quadrupole term \(W_3 (R^{-4})\) and the term accounting for the quadrupole-quadrupole and the dipole-octupole interaction \(W_4 (R^{-6})\). A formal definition of these terms is given in (A.154). If any of these terms does not vanish in the first order of perturbation theory, then the dependence of the interaction potential on \(R\) will be different from \(R^{-6}\). Recall, that in the first order of perturbation theory one needs to diagonalize a matrix. This matrix consists of matrix elements of all degenerate states. We say that some term vanishes in the first order of perturbation theory, if and only if all matrix elements are zero. Let us first consider two atoms of different kinds and let us also assume that there is no degeneracy with respect to the quantum number \(l\). The latter assumption ensures that all eigenfunctions of the degenerate energy level will have the same behaviour under a parity transformation. In this setup all matrix elements of the terms \(W_2\) and \(W_3\), which we have to evaluate in first order of perturbation theory, vanish due to parity\(^{28}\), regardless of the initial states. This is remarkable as it implies that there is no permanent dipole-dipole interaction \((R^{-3})\) between two atoms of different kinds. Furthermore if at least one of the two atoms is in an S-state, also all the matrix elements of \(W_4\) will vanish\(^{29}\) and we will have the usual \(R^{-6}\) dependence. This is obvious physically as S-states are spherically symmetric and will not have any permanent multipole-moment. For the case where both atoms are in states with a non-zero total angular momentum, the matrix elements of the \(W_4\) term will not vanish and will account for the leading order contribution\(^{30}\) \((R^{-5})\). For two atoms of the same kind, the discussion is different. This is because, for two atoms of the same kind, an additional degeneracy occurs because of exchange symmetry. For example, if one atom, we call it atom A, is in an S-state and the atom B is in a P-state then the configuration where the atom A is in a P-state and the atom B is in an S-state has the same energy. We thus also have to evaluate the matrix elements between states with different quantum numbers \(l\). Typically one would call them transition matrix elements. (In the hydrogen-hydrogen calculation the matrix element \((2 | W | 6)\) is of that kind.) If these states have different parity\(^{31}\), then it is possible that the dipole-dipole term has a contribution. This is indeed the case in our present calculation of the hydrogen-hydrogen system. To conclude: if we have two different atoms and at least one of them is in an S-state, then we will have an interaction potential of the \(R^{-6}\) form. In all other cases, the lowest order contribution will be \(R^{-5}\), which is due to the quadrupole-quadrupole interaction. This changes for two atoms of the same kind, where also a potential of the \(R^{-3}\) form is possible.

\(^{27}\)For the real hydrogen system there is also spin-orbit coupling which causes the fine-structure. In case one includes these relativistic effects, the energy levels are nearly degenerate. This implies that we have to change the perturbation procedure as the electrostatic interaction between the atoms is no longer small compared to the splitting of the energy levels.

\(^{28}\)In the language of the Appendix the operators needed to formally prove this are \(\hat{P}_A\), \(\hat{P}_B\) and \(\hat{P}_{AB}\).

\(^{29}\)The rigorous proof of this statement is based on the invariance of the S-state wavefunction with respect to transformations with the \(S^{(3)}_N\) operator. This operator is defined in (A.142). The proof then reduces to some elementary algebra, starting at the explicit expression for \(W_4\) (A.156).

\(^{30}\)We are not interested in the asymptotic behaviour \((R \to \infty)\) of the interaction potential but in the form of the potential for typical values of \(R\) in the London regime. In this range, the contribution arising from the dipole-dipole term in second order often dominates the contribution of the \(W_4\) term in the first order. Still, this needs to be shown in every specific case. For a case study see [31].

\(^{31}\)This is the case if the azimuthal quantum number of the first state is even and the one of the second state is odd. Furthermore due to the selection rules these quantum numbers cannot differ by more than 1.
2.1.4 Numerical evaluation

In this section we are going to calculate the Van der Waals constant $C$ as given in equation (2.35) for the special case of two hydrogen atoms. For this special case this equation reads:

$$C = 6 \sum_{(\alpha,\beta): E_{\alpha,\beta} \neq E_{0,0}} \frac{|\langle \psi^{\alpha,\beta}_{AB} | z_{AB} | \psi^{0,0}_{AB} \rangle|^2}{E_{\alpha,\beta} - E_{0,0}}$$  \hspace{1cm} (2.49)

We are going to achieve a very high accuracy and will give the first 15 digits of this number. Given, that the Hamiltonian, this formula is derived from, is also an approximation, this large number of digits has no physical significance. But we think it is still valuable to compare this result to other very accurate calculations [32]. The way we are going to calculate this constant is direct which means that we are, in fact, just going to sum up the series. To do so, we need an explicit representation of the eigenfunctions $|\psi^{\alpha,\beta}_{AB}\rangle := |\psi^{\alpha}_{A}\rangle |\psi^{\beta}_{B}\rangle$.

$|\psi^{\alpha}_{A}\rangle$ and $|\psi^{\beta}_{B}\rangle$ are the well-known eigenfunctions of the hydrogen atom. The spectrum of hydrogen has both a discrete as well as a continuous part.

We will label the discrete eigenfunctions by three integers $n, l, m$ The eigenfunctions to eigenvalue equation $\hat{H}_0 \Phi_{n,l,m} = -\frac{1}{2m} \Phi_{n,l,m}$ are given as:

$$\Phi_{n,l,m} := R_{nl}(r) \cdot Y_{lm}(\theta, \phi) \text{ with } n \in \mathbb{N}^*, 0 \leq l \leq n - 1, -l \leq m \leq l$$ \hspace{1cm} (2.50)

A detailed definition is given by (C.203). The continuous part will be labeled by a non-negative real number $k$ and two integers $l, m$. The eigenvalue equation is $\hat{H}_0 \tilde{\Phi}_{k,l,m} = \frac{k^2}{2} \tilde{\Phi}_{k,l,m}$ and the eigenfunctions are:

$$\tilde{\Phi}_{n,l,m} := \tilde{R}_{kl}(r) \cdot Y_{lm}(\theta, \phi) \text{ with } k \in \mathbb{R}^+, 0 \leq l \leq \infty, -l \leq m \leq l$$ \hspace{1cm} (2.51)

A detailed definition is given by (C.220). These eigenfunctions satisfy a completeness relation on the Hilbertspace of square-integrable functions on the three dimensional space. With the formal completeness relation [30]:

$$\delta(\vec{r} - \vec{r}') = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} R_{nl}(r) Y_{lm}(\theta, \phi) \cdot R_{nl}^*(r') Y_{lm}^*(\theta', \phi')$$  \hspace{1cm} (2.52)

$$+ \int_0^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \tilde{R}_{kl}(r) Y_{lm}(\theta, \phi) \cdot \tilde{R}_{kl}^*(r') Y_{lm}^*(\theta', \phi') \frac{dk}{2\pi}$$  \hspace{1cm} (2.53)

We are now almost ready to write (2.49) explicitly in terms of sums and integrals. We have to sum up the quantity

$$\frac{|\langle \psi^{\alpha,\beta}_{AB} | z_{AB} | \psi^{0,0}_{AB} \rangle|^2}{E_{\alpha,\beta} - E_{0,0}} = \frac{|\langle \psi^{\alpha}_{A} | z | \Phi_{1,0,0} \rangle|^2 |\psi^{\beta}_{B} | z | \Phi_{1,0,0} \rangle|^2}{E_{\alpha,\beta} + 1}$$ \hspace{1cm} (2.54)

If $\psi^{\alpha}_{A}$ is a discrete eigenfunction we define:

$$|\langle \psi^{\alpha}_{A} | \Phi_{1,0,0} \rangle|^2 := T^2(n_A, l_A, m_A)$$ \hspace{1cm} (2.55)

and if it is an eigenfunction of the continuum we define:

$$|\langle \psi^{\alpha}_{A} | \Phi_{1,0,0} \rangle|^2 := \tilde{T}^2(k_A, l_A, m_A)$$ \hspace{1cm} (2.56)

22
The same definition is clearly also suitable for $B$ as these are the same eigenfunctions. We are now able to write down (2.49) explicitly:

$$C = \frac{1}{6} \sum_{n,A=1}^{\infty} \sum_{l_A=0}^{n_A-1} \sum_{m_A=-l_A}^{l_A} \sum_{n_B=1}^{\infty} \sum_{l_B=0}^{n_B-1} \sum_{m_B=-l_B}^{l_B} (1 - \delta_{n_A,1} \delta_{n_B,1}) \frac{I^2(n_A, l_A, m_A) I^2(n_B, l_B, m_B)}{1 - \frac{1}{2} \left( \frac{1}{n_A^2} + \frac{1}{n_B^2} \right)}$$

$$+ \sum_{n,A=1}^{\infty} \sum_{l_A=0}^{n_A-1} \sum_{m_A=-l_A}^{l_A} \int_0^\infty \sum_{l_B=0}^{n_B-1} \sum_{m_B=-l_B}^{l_B} \frac{I^2(n_A, l_A, m_A) I^2(k_B, l_B, m_B)}{1 - \frac{1}{2} (\frac{1}{n_A^2} - k_B^2)} \, dk_B$$

$$+ \int_0^\infty \sum_{l_A=0}^{n_A-1} \sum_{m_A=-l_A}^{l_A} \sum_{n_B=1}^{\infty} \sum_{l_B=0}^{n_B-1} \sum_{m_B=-l_B}^{l_B} \frac{I^2(n_B, l_B, m_B) I^2(k_A, l_B, m_B)}{1 - \frac{1}{2} (\frac{1}{n_B^2} - k_A^2)} \, dk_A$$

$$+ \int_0^\infty \sum_{l_A=0}^{n_A-1} \sum_{m_A=-l_A}^{l_A} \int_0^\infty \sum_{l_B=0}^{n_B-1} \sum_{m_B=-l_B}^{l_B} \frac{I^2(k_A, l_A, m_A) I^2(k_B, l_B, m_B)}{1 + \frac{1}{2} (\frac{1}{k_A^2} + k_B^2)} \, dk_B \, dk_A$$

$$I^2(n, l, m)$$ can be further evaluated to be:

$$I^2(n, l, m) = \left[ \int_0^\infty r^3 R_{n}^* R_{10} \right]^2 \frac{\delta_{l,0} \delta_{m,0}}{3}$$

with $I^2_R(n)$ given by (C.224) as:

$$I^2_R(n) = \frac{2^8 n^7}{(n^2 - 1)^5} \cdot \left( \frac{n - 1}{n + 1} \right)^{2n}$$

Similarly $\tilde{I}^2(k, l, m)$ is:

$$\tilde{I}^2(k, l, m) = \left[ \int_0^\infty r^3 \tilde{R}_{n}^* \tilde{R}_{10} \right]^2 \frac{\delta_{l,0} \delta_{m,0}}{3}$$

and $\tilde{I}^2_R(k)$ is given by (C.225) as:

$$\tilde{I}^2_R(k) = \frac{32 \pi \cdot 24^2 k}{9(1 - e^{-\frac{2 \pi}{3}}) \cdot (1 + k^2)^4} \left| \frac{1}{2} F_1 \left( \frac{i}{k}, 2, 5, 4; \frac{2i k}{1 + i k} \right) \right|^2$$

with $\frac{1}{2} F_1$ being the Hypergeometric function defined by (C.218). By using (2.58) and (2.60), equation (2.57) simplifies to be:

$$C = \frac{2}{3} \left\{ \sum_{n_A=2}^{\infty} \sum_{n_B=2}^{\infty} \frac{I^2_R(n_A) I^2_R(n_B)}{1 - \frac{1}{2} \left( \frac{1}{n_A^2} + \frac{1}{n_B^2} \right)} + \sum_{n=2}^{\infty} \int_0^\infty \frac{I^2_R(n) \tilde{I}^2_R(k)}{1 + \frac{k^2}{2} - \frac{1}{2 \pi^2}} dk \right\} + \int_0^\infty \int_0^\infty \frac{\tilde{I}^2_R(k_A) \tilde{I}^2_R(k_B)}{1 + \frac{k_A^2}{2} + \frac{k_B^2}{2} \pi^2} \, dk_A \, dk_B$$

This is now suitable for a direct evaluation.
First recall the Taylor formula from elementary calculus, which states, that for an \( N+1 \) times continuously differentiable function \( f(x) \) there exists a real value \( \xi \) between \( x \) and \( x_0 \) such that:

\[
f(x) = \sum_{i=0}^{N} \frac{f^{(i)}(x_0)}{i!} (x - x_0)^i + \frac{f^{(N+1)}(\xi)}{(N+1)!} (x - x_0)^{N+1}
\]

\( := R_N \) (2.63)

The residual term \( R_N \) is called the Lagrange form.

The first part of (2.62) is very slowly converging. This can be changed by using the Taylor formula for the denominator, stop the sum at some \( S \) and use the binomial theorem afterwards:

\[
\sum_{n_A=2}^{\infty} \sum_{n_B=2}^{\infty} \frac{I_R(n_A)I_R(n_B)}{1 - \frac{1}{n_A^2} + \frac{1}{n_B^2}} = \sum_{n_A=2}^{\infty} \sum_{n_B=2}^{\infty} \sum_{k=0}^{S} \frac{I_R(n_A)I_R(n_B)\left(\frac{1}{n_A^2} + \frac{1}{n_B^2}\right)^k}{2^k} \\
+ \sum_{n_A=2}^{\infty} \sum_{n_B=2}^{\infty} R_S I_R(n_A)I_R(n_B) \quad := \Delta_{DD} \tag{2.64}
\]

\[
= \sum_{k=0}^{S} \sum_{l=0}^{k} \frac{1}{2^k} \left(\frac{k}{l}\right) Q(l)Q(k-l) + \Delta_{DD}
\]

with \( Q(m) \) defined as:

\[
Q(m) := \sum_{n=2}^{\infty} \frac{I_R(n)}{n^{2m}} \tag{2.65}
\]

and \( R_S \) being the remainder which can explicitly be written in the Lagrange form as:

\[
R_S = \frac{1}{(1-\xi)^{S+2}} \left[ \frac{1}{2} \left( \frac{1}{n_A^2} + \frac{1}{n_B^2} \right) \right]^{S+1} \tag{2.66}
\]

with \( \xi \in [0, \frac{1}{2} \left( \frac{1}{n_A^2} + \frac{1}{n_B^2} \right) \] . This can be estimated as \(^{32}\)

\[
|R_S| \leq 4 \left( \frac{1}{3} \right)^{S+1} \leq \left( \frac{1}{3} \right)^S \tag{2.67}
\]

and therefore:

\[
\Delta_{DD} \leq \frac{Q^2(0)}{3^S} \tag{2.68}
\]

where we used \( Q(0) \geq Q(1) \geq Q(2) \ldots \)

This proves that the double sum can be evaluated to a large number of digits if one knows the \( Q(m) \) function well enough. However, this is just a single sum instead of a double sum and therefore much simpler. With the standard technique (Euler-Mclaurin summation) this sum can be evaluated to about 30 digits in reasonable time. Writing down the first 15 digits of the double sum: 5.885325168831455

\(^{32}\)Using \( \frac{4}{3} \left( \frac{1}{n_A^2} + \frac{1}{n_B^2} \right) \leq \frac{1}{4} \)
Let us have a look at the second term in (2.62). In order to perform a low number of numerical integrations we will also expand the mixed term (the expansion is in the small parameter \( \frac{1}{2n^2} \)). By using the Tailor formula again and stopping the summation at some integer \( T \) we get:

\[
2 \sum_{n=2}^{\infty} \int_0^\infty \frac{I_R^2(n) \tilde{I}_R^2(k)}{1 + \frac{k^2}{2} - \frac{1}{2n^2}} \frac{dk}{2\pi} = 2 \sum_{n=2}^{T} \int_0^\infty \frac{I_R^2(n) \tilde{I}_R^2(k)}{(1 + \frac{k^2}{2})^{T+1}} \frac{dk}{2\pi} + 2 \sum_{n=2}^{\infty} \int_0^\infty \frac{\tilde{R}_T(n) \tilde{I}_R^2(k)}{(1 + \frac{k^2}{2})^{T+1}} \frac{dk}{2\pi} \equiv \Delta_{DC}
\]

with \( U(l) \) defined as:

\[
U(l) := \int_0^\infty \frac{I_R^2(k)}{(1 + \frac{k^2}{2})^{l+1}} \frac{dk}{2\pi}
\]

The absolute value of \( \Delta_{DC} \) also obeys an inequality, which can be derived in the same way as (2.68)

\[
|\tilde{R}_T| \leq \frac{8}{7} \left( \frac{1}{7} \right)^{T+1} \left( \frac{1}{7} \right)^T \leq \left( \frac{1}{7} \right)^T
\]

\[
\Rightarrow |\Delta_{DC}| \leq \frac{2U(0)Q(0)}{7^T}
\]

We can therefore again obtain a very accurate result by using only a few terms. The first 15 digits of the result are: 3.351770564933760

The last part to evaluate is the double integral:

\[
\int_0^\infty \int_0^\infty \frac{\tilde{I}_R^2(k_A) \tilde{I}_R^2(k_B)}{1 + \frac{1}{2} ( k_A^2 + k_B^2 )} \frac{dk_A dk_B}{2\pi^2}
\]

We have evaluated this double integral using two different algorithms\(^\text{33}\). They both reported an estimated error of about \( 10^{-28} \). The first 15 digits of the result are: 0.51144324343543

Adding these results gives a final value for \( C \) which is:

\[
C = 6.499026705405839
\]

This number is exactly equivalent to the result obtained in [32].

\(^{33}\)Gauss-Legendre and Sinh-Tanh method
3 Methods to calculate the polarizability of the hydrogen atom

As seen with the Van der Waals problem the electrostatic polarizability occurs in many physical problems. It is, therefore, useful to have an elementary expression for it. This can be achieved for the hydrogen atom in an arbitrary bound state. We will discuss here two methods to obtain this general result. One follows the method in papers [33],[34] and is based on finding particular solutions to a partial differential equation. The other method is used for the same purpose in [35] and relies on an identity for the Coulomb Greens function.

The problem can be formally defined as to compute the following sum, which indeed is the definition of the static polarizability found in (1.15):

$$\alpha_{n,l,m} := -2 \sum_{\{k \colon E_k \neq E_n\}} \frac{|\langle k | z | n,l,m \rangle|^2}{E_n - E_k}$$ (3.75)

where $|k\rangle$ denotes the eigenstates of the hydrogen atom (discrete as well as continuous).

The solution which we will derive in two different ways is:

$$\alpha_{n,l,m} = \frac{n^4}{16} \left\{ \frac{l^2 - m^2}{4l^2 - 1} (n^2(28 - 20l) + 20 - 76l + 60l^2 - 12l^3) \right. \\
+ \frac{(l + 1)^2 - m^2}{(2l + 1)(2l + 3)} (n^2(48 + 20l) + 168 + 232l + 96l^2 + 12l^3) \left. \right\}$$ (3.76)

It is interesting, that this formula has a very strong dependence on the principal quantum number $n$, which physically means, that highly excited states are much more polarizable than the ground state and will, therefore, interact much stronger.

3.1 Differential equation approach

Let us start with the approach based on differential equations [33]. If we look carefully at (3.75) we can notice that it is very similar to the expression one gets in second order of perturbation theory (when calculating the quadratic Stark-effect) where one expands the first order eigenvector correction into eigenstates of the unperturbed operator.$^{34}$ In order for the differential equation (B.178)$^{35}$ to have a normalizable and therefore expandable solution the perturbative operator needs to be diagonal with respect to the zeroth order states. This is not the case for the operator $z$ and the states $|n,l,m\rangle$. As we want to keep the states fixed we need to change the perturbation operator. The operator is obviously diagonal if one subtracts its projection on the other states with same energy. Mathematically this can be expressed that we can obtain the polarizability by solving

$$(E_n - \hat{H}_0) |\Psi_1\rangle = z |n,l,m\rangle - \sum_{l' = 0}^{n-1} \sum_{m'} \langle n, l', m' | z | n, l, m \rangle | n, m', l' \rangle$$ (3.77)

$^{34}$ $z$ is the perturbation operator and $\hat{H}_0$ is the usual hamiltonian of the hydrogen atom
$^{35}$ $\lambda^4$ equation
for $|\Psi_1\rangle$ and performing the integral:

$$\alpha_{n,l,m} = - 2 \langle n, l, m | z | \Psi_1 \rangle \quad (3.78)$$

under the side condition

$$\langle n, l', m' | \Psi_1 \rangle = 0 \text{ for all } l', m' \quad (3.79)$$

**Proof:**

We assume $|\Psi_1\rangle$ to be expandable as:

$$|\Psi_1\rangle = \sum \sum \langle k | \Psi_1 \rangle | k \rangle \quad (3.80)$$

and therefore

$$\langle n, l, m | z | \Psi_1 \rangle = \sum \sum \langle k | \Psi_1 \rangle \langle n, l, m | z | k \rangle$$

$$= \sum \sum \langle k | \Psi_1 \rangle \langle n, l, m | z | k \rangle + \sum \sum \langle k | \Psi_1 \rangle \langle n, l', m' | z | n, l', m' \rangle$$

$$\quad \sum \sum \langle k | \Psi_1 \rangle \langle n, l, m | z | k \rangle \quad (3.81)$$

Where we used (3.79) for the last equal sign.

By multiplying (3.77) from the right with $\langle k | \Psi_1 \rangle$, we get:

$$\langle k | \Psi_1 \rangle = \frac{\langle k | z | n, l, m \rangle}{E_n - E_k} \quad (3.82)$$

and therefore

$$\langle n, l, m | z | \Psi_1 \rangle = \sum \sum \frac{|\langle k | z | n, l, m \rangle|^2}{E_n - E_k} \quad (3.83)$$

which is what we wanted to prove.

This also defines the procedure, to solve (3.77) by an appropriate ansatz first and then obtain $\alpha_{n,l,m}$ by integration.

The right hand side of (3.77) can be simplified by using (C.193) and $z = r \cdot \cos(\theta)$

$$z | n, l, m \rangle - \sum_{l'=0}^{n-1} \sum_{m'= -l'}^{l'} \langle n, l', m' | z | n, l, m \rangle | n, m', l' \rangle$$

$$= r | n, l \rangle \left( C_{l+1,m} | l+1, m \rangle + C_{l,m} | l-1, m \rangle \right)$$

$$- C_{l+1,m} \langle n, l+1 | r | n, l \rangle | n, l+1, m \rangle - C_{l,m} \langle n, l-1 | r | n, l \rangle | n, l-1, m \rangle$$

$$= C_{l+1,m} \left[ r | n, l \rangle - \langle n, l+1 | r | n, l \rangle | n, l+1 \rangle \right] | l+1, m \rangle$$

$$+ C_{l,m} \left[ r | n, l \rangle - \langle n, l-1 | r | n, l \rangle | n, l-1 \rangle \right] | l-1, m \rangle \quad (3.84)$$

---

This is mathematically correct as the solution needs to be normalizable to be expandable, which can easily be checked a posteriori.
With $C_{l,m}$ being defined as $C_{l,m} := \sqrt{(2l-m-\alpha)}$

The inhomogenous part of the equation is therefore a sum of two terms with different angular states. As the equation is linear they can be treated separately and the solution will be the sum of the two solutions. As we expect to obtain the generalized Laguerre equation, we perform the ansatz:

$$\Psi_l = g(\rho)e^{l+1}e^{-\frac{\rho}{2}}Y_{l+1,m} + f(\rho)e^{l-1}e^{-\frac{\rho}{2}}Y_{l-1,m}$$ (3.85)

and do the calculation, where we use $h_{\pm}$ as generic function for $g$ and $f$.

$$E_n - \hat{H}_0 = -\frac{1}{2n^2} + \frac{1}{2} \Delta + \frac{1}{r} = -\frac{1}{2n^2} + \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{L^2}{2r^2} + \frac{1}{r}$$

(3.86)

$$\implies (E_n - \hat{H}_0)(h_{\pm}(\rho)e^{l+1}e^{-\frac{\rho}{2}}Y_{l\pm,1,m}) = 2\rho^{l\pm1} e^{-\frac{\rho}{2}}Y_{l\pm,1,m}\bullet$$

$$\bullet \left( \rho \frac{\partial^2 h_{\pm}(\rho)}{\partial \rho^2} + (2(l \pm 1) + 1 + 1 - n) \frac{\partial h_{\pm}(\rho)}{\partial \rho} + (n - (l \pm 1) - 1)h_{\pm}(\rho) \right)$$

:= $L_{n,\pm}$ Generalized Laguerre equation (C.215)

Solving equation (3.77) can therefore be split into solving\(^{37}\)

$$\left( \rho \frac{\partial^2}{\partial \rho^2} + ([2(l+1)+1] + 1 - \rho) \frac{\partial}{\partial \rho} + (n - (l+1) - 1) \right) g$$

$$= \frac{n^2C_{l+1,m}}{2} e^{\frac{\rho}{2}} \rho^{l+1} \left[ rR_{nl} + (-) \langle n,l+1 \mid r \mid n,l \rangle R_{n,l+1} \right]$$ (3.88)

and

$$\left( \rho \frac{\partial^2}{\partial \rho^2} + ([2(l-1)+1] + 1 - \rho) \frac{\partial}{\partial \rho} + (n - (l-1) - 1) \right) f$$

$$= \frac{n^2C_{l,m}}{2} e^{\frac{\rho}{2}} \rho^{l+2} \left[ rR_{nl} + (-) \langle n,l-1 \mid r \mid n,l \rangle R_{n,l-1} \right]$$ (3.89)

When looking at identity (C.217) it is a good idea to write these equations in a form where the right sides only contain Laguerre polynomials with $\alpha = 2(l \pm 1) + 1$ respectively because one can then immediately find $f$ and $g$ as linear combinations of Laguerre polynomials and their coefficients by comparison.

The right side of (3.88) can be manipulated with identities (C.207) and (C.211) and using (C.226) for $A$. It yields

$$\frac{n}{2} e^{\frac{\rho}{2}} \rho^{-l+1} R_{nl} = \frac{n}{2} N_{nl} R^{(2l+1)} = \frac{n}{2} N_{nl} \left[ 2n \L^{(2l+1)}_{n-l-1} - (n + l) \L^{(2l+1)}_{n-l-2} - (n - l) \L^{(2l+1)}_{n-l} \right]$$

(3.90)

$$= \frac{n}{2} N_{nl} \left[ (l - n) \L^{(2l+3)}_{n-l} + 2(2n - l) \L^{(2l+3)}_{n-l-1} - 6n \L^{(2l+3)}_{n-l-2} \right] + 2(2n + l) \L^{(2l+3)}_{n-l-3} - (n + l) \L^{(2l+3)}_{n-l-4}$$

\(^{37}\)By combining equations (3.84) and (3.87)

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and
\[
A e^{\frac{2}{3} \rho^{-1}} R_{n,l+1} = AN_{n,l+1} \rho L^{(2l+3)}_{n-l-2}
\]
\[
= \frac{n}{2} N_{nl} \left[ 6n L^{(2l+3)}_{n-l-2} - 3(n + l + 1)L^{(2l+3)}_{n-l-3} - 3(n - l - 1)L^{(2l+3)}_{n-l-1} \right]
\] (3.91)

which is finally combined:
\[
\left( \rho \frac{\partial^2}{\partial \rho^2} + \left[ 2(l + 1) + 1 - \rho \right] \frac{\partial}{\partial \rho} + (n - (l + 1) + 1) \right) g
\]
\[
= I \left[ (l - n)L^{(2l+3)}_{n-l} + (n + l + 3)L^{(2l+3)}_{n-l-1} + (n - l - 3)L^{(2l+3)}_{n-l-3} - (n + l)L^{(2l+3)}_{n-l-4} \right]
\] (3.92)

with \( I := \frac{n^3 C_{l+1,n} N_{nl}}{4} \)

We can now make the ansatz:
\[
g(\rho) := \sum_{i=0}^{4} \gamma_{n-l-i} L^{(2l+3)}_{n-l-i}(x)
\] (3.93)

which determines together with (C.217) the constants to be:
\[
\gamma_{n-l} = \frac{I}{2} (n - l) \quad \gamma_{n-l-3} = I(n - l - 3) \quad \gamma_{n-l-4} = -\frac{I}{2} (n + l)
\]

Note that \( \gamma_{n-l-2} \) is not determined yet. It will be used later on to satisfy condition (3.79)

Similarly we will now manipulate the right side of (3.89). We will use the same identities (C.207), (C.211) and (C.226) as before in a slightly different form and get:
\[
\frac{n}{2} e^{\frac{2}{3} \rho^{-1+3}} R_{nl} = \frac{n}{2} N_{nl} \rho^3 L^{(2l+1)}_{n-l-1} = \frac{n}{2} N_{nl} \left[ \rho^3 L^{(2l+2)}_{n-l-1} - \rho^3 L^{(2l+2)}_{n-l-2} \right]
\]
\[
= \frac{n}{2} N_{nl} \left[ - (n + l)(n + l - 1)(n + l - 2)L^{(2l-1)}_{n-l-2} + 2(2n - l - 1)(n + l)(n + l - 1)L^{(2l-1)}_{n-l-1} \right.
\]
\[
- 6(n - l)(n + l) L^{(2l-1)}_{n-l-1} + 2(2n + l + 1)(n - l)(n - l - 1)L^{(2l-1)}_{n-l+1}
\]
\[
- (n - l + 2)(n - l + 1)(n - l) L^{(2l-1)}_{n-l+2} \right]
\] (3.94)

and
\[
B e^{\frac{2}{3} \rho^{-1+2}} R_{n,l-1} = BN_{n,l-1} \rho L^{(2l-1)}_{n-l} = \left( \frac{n}{2} (n + l)(n - l) N_{nl} \right) \bullet
\]
\[
\bullet \left[ 6n L^{(2l-1)}_{n-l} - 3(n + l - 1)L^{(2l-1)}_{n-l-1} - 3(n - l + 1)L^{(2l-1)}_{n-l+1} \right]
\] (3.95)
which combined is:

\[
\left( \frac{\partial^2}{\partial \rho^2} + \left( [2(l - 1) + 1] + 1 - \rho \right) \frac{\partial}{\partial \rho} + (n - (l - 1) - 1) \right) f
\]

\[= D \left[ -(n + l)(n + l - 1)(n + l - 2) + (n + l)(n - 1)(n + l - 2) + (n - l + 2)(n - l + 1)(n - l) \right]
\]

with \( D := \frac{n^3 C_{lm} N_{nl}}{4} \)

The ansatz should therefore be:

\[ f(\rho) := \sum_{i=-2}^{2} \sigma_{n-l+i} L_{n-l+i}^{(2l-1)}(\rho) \]  \hspace{1cm} (3.97)

which again determines four constants:

\[ \sigma_{n-l-2} = -\frac{D}{2} (n + l)(n + l - 1)(n + l - 2) \quad \sigma_{n-l-1} = -2\sigma_{n-l-2} \]

\[ \sigma_{n-l+2} = \frac{D}{2} (n - l)(n - l + 1)(n - l + 2) \quad \sigma_{n-l+1} = -2\sigma_{n-l+2} \]

With the last coefficients \( \sigma_{n-l} \) and \( \gamma_{n-l-2} \) we can now satisfy condition (3.79). In the following we will make extensive use of the orthogonality relation (C.208).

\[ 0 = \langle n, l', m' | \Psi l \rangle = \delta_{l', l+1} \delta_{m', m} \int_{0}^{\infty} r^2 \left[ R_{n,l+1} g(\rho) \rho^{l+1} e^{-\frac{\rho}{2}} \right] dr 
\]

\[+ \delta_{l', l-1} \delta_{m', m} \int_{0}^{\infty} r^2 \left[ R_{n,l-1} f(\rho) \rho^{l-1} e^{-\frac{\rho}{2}} \right] dr \]

to satisfy this equation both integrals must vanish.

This yields:

\[ 0 = \int_{0}^{\infty} r^2 \left[ R_{n,l+1} g(\rho) \rho^{l+1} e^{-\frac{\rho}{2}} \right] dr = \frac{n^3}{8} N_{n,l+1} \int_{0}^{\infty} e^{-\rho} \rho^{2l+3} g(\rho) p L_{n-l-2}^{(2l+3)} d\rho 
\]

\[= \int_{0}^{\infty} e^{-\rho} \rho^{2l+3} g(\rho) \left[ 2n L_{n-l-2}^{(2l+3)} - (n + l + 1) L_{n-l+1}^{(2l+3)} - (n - l + 1) L_{n-l-1}^{(2l+3)} \right] d\rho 
\]

\[= 2n \left( \frac{n + l + 1)!}{(n - l - 2)!} \right) \gamma_{n-l-2} - \left( \frac{n + l + 1)!}{(n - l - 3)!} \right) \gamma_{n-l-3} - \left( \frac{n + l + 2)!}{(n - l - 2)!} \right) \gamma_{n-l-1} 
\]

\[\Rightarrow \gamma_{n-l-2} = -\frac{I(2l + 5)}{} \]  \hspace{1cm} (3.98)
and
\[
0 = \int_0^\infty r^2 \left[R_{n,l-1}(f(r)\rho^{l-1}e^{-\frac{r}{\rho}})\right] dr = \frac{n^3}{8} N_{n,l-1} \int_0^\infty e^{-\rho} \rho^{2l-1} f(\rho) L_{n-l}^{(2l-1)} d\rho
\]
\[
= \int_0^\infty e^{-\rho} \rho^{2l-1} f(\rho) \left[2n L_{n-l}^{(2l-1)} - (n+l-1) L_{n-l-1}^{(2l-1)} - (n-l+1) L_{n-l+1}^{(2l-1)} \right] d\rho
\]
\[
= 2n \left(\frac{(n+l-1)!}{(n-l-1)!} \right) \sigma_{n-l} - \left(\frac{(n+l)!}{(n-l-1)!} \right) \sigma_{n-l-1} - \left(\frac{(n+l)!}{(n-l)!} \right) \sigma_{n-l+1}
\]
\[
\Rightarrow \sigma_{n-l} = D(n^2 - l^2)(2l - 3)
\] (3.99)

This completely determines the function \(\Psi_1\). As the last step one needs to do the integral (3.78).

\[
-2 \langle n, l, m | r \cos(\theta) | \Psi_1 \rangle = -2 \langle l, m | \cos(\theta) | l + 1, m \rangle \int_0^\infty R_{nl} r^3 g(\rho) \rho^{l+1} e^{-\frac{r}{\rho}} dr
\]
\[
-2 \langle l, m | \cos(\theta) | l - 1, m \rangle \int_0^\infty R_{nl} r^3 f(\rho) \rho^{l-1} e^{-\frac{r}{\rho}} dr
\] (3.100)

\[
= -\frac{n^4 N_{nl}}{8} \left[ C_{l+1,m} \int_0^\infty \rho^{2l+3} e^{-\rho} g(\rho) L_{n-l-1}^{(2l+1)} d\rho + C_{l,m} \int_0^\infty \rho^{2l-1} e^{-\rho} f(\rho) L_{n-l-1}^{(2l+1)} d\rho \right]
\] (3.101)

The calculation is now exactly the same as in (3.94) and (3.90) with the orthogonality relation (C.208) one gets:

\[
\alpha_{n,l,m} = -\frac{n^4 N_{nl}}{8} \left[ C_{l+1,m} \left[ -\frac{(n+l+3)!}{(n-l-1)!} \gamma_{n-l} + \frac{2(2n-l)(n+l+2)!}{(n-l-1)!} \gamma_{n-l-1} \right. \right.
\]
\[
\left. - \frac{6n(n+l+1)!}{(n-l-2)!} \gamma_{n-l-2} + \frac{2(2n+l)(n+l)!}{(n-l-3)!} \gamma_{n-l-3} - \frac{(n+l)!}{(n-l-4)!} \gamma_{n-l-4} \right]
\]
\[
- \frac{n^4 N_{nl}}{8} \left[ C_{l,m} \left[ -\frac{(n+l+1)!}{(n-l-1)!} \sigma_{n-l+2} + \frac{2(2n+l+1)(n+l)!}{(n-l-1)!} \sigma_{n-l+1} \right. \right.
\]
\[
\left. - \frac{6n(n+l)!}{(n-l-1)!} \sigma_{n-l} + 2(2n-l-1) - \frac{(n+l)!}{(n-l-2)!} \sigma_{n-l-1} - \frac{(n+l)!}{(n-l-2)!} \sigma_{n-l-2} \right]
\] (3.102)

Note that from the last step one can easily extract a lot of integrals (just by inserting arbitrary \(\gamma\) and \(\sigma\) - we will make use of this in the next section). After simplifying this expression we finally arrive at:

\[
\alpha_{n,l,m} = \frac{n^4}{16} \left\{ \frac{l^2 - m^2}{4l^2 - 1} (n^2(28 - 20l) + 20 - 76l + 60l^2 - 12l^3) \right. 
\]
\[
+ \frac{(l+1)^2 - m^2}{(2l+1)(2l+3)} (n^2(48 + 20l) + 168 + 232l + 96l^2 + 12l^3) \right\}
\] (3.103)

### 3.2 Approach involving the Coulomb Greens function

This section follows the way presented in the Appendix C of [35]. It uses a special representation of the Coulomb Greens function. The Greens function is defined through the following distributional
equation:

\[(\hat{H}_0 - E)G(\vec{x}, \vec{y}, E) = \delta^3(\vec{x} - \vec{y})\]  (3.104)

where \(\hat{H}_0\) is the Hamiltonian of the Coulomb problem (hydrogen atom)

\[\hat{H}_0 = -\frac{1}{2}\Delta_x - \frac{1}{|\vec{x}|}\]  (3.105)

and \(E\) is an arbitrary number. For our purpose though \(E\) will be a negative real number. There are various representations for this function. The one that is useful for our purpose is its expansion into the so called Coulomb-Sturmian functions, which form a discrete basis of the \(L^2(\mathbb{R}^3)\) Hilbertspace. They are defined as follows: [36]

\[S_{nlm}(\vec{r}) = S_{nml}(r, \theta, \phi) = \sqrt{(2k)^2n!} \frac{(2n+2l+1)!}{2kr} L_n^{(2l+1)}(2kr)e^{-kr}Y_{lm}(\theta, \phi)\]  (3.106)

Where \(k\) is an arbitrary parameter which we will choose conveniently later on to be \(\sqrt{-2E}\). The proof of the completeness of these functions is difficult, but is done in [37]. The completeness can be written in a formal way as:

\[\delta^3(\vec{x} - \vec{y}) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} S_{nlm}(\vec{x})S^*_{nlm}(\vec{y}) \frac{1}{|\vec{y}|}\]  (3.107)

This means that every function \(f(\vec{r})\) in \(L^2(\mathbb{R}^3)\) can be expanded with respect to the \(L^2\) Norm as:

\[f(\vec{r}) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} S_{nlm}(\vec{r}) \langle S_{nlm}(\vec{v}) | f(\vec{v}) \rangle \frac{1}{|\vec{v}|}|\vec{v}|\]  (3.108)

\[\langle S_{nlm}(\vec{v}) | f(\vec{v}) \rangle = \int_{\mathbb{R}^3} S^*_{nlm}(\vec{v}) * f(\vec{v}) \frac{1}{|\vec{v}|} d^3\vec{v}\]  (3.109)

The Greens function \(G(\vec{x}, \vec{y}, E)\) can therefore be expanded in these functions as:

\[G(\vec{x}, \vec{y}, E) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} S_{nlm}(\vec{x}) \langle S_{nlm}(\vec{v}) | G(\vec{v}, \vec{y}, E) \rangle \frac{1}{|\vec{v}|} \]  (3.110)

Plugging (3.110) and (3.107) into (3.104) while using the symmetry of the delta function \(\delta^3(\vec{x} - \vec{y}) = \delta^3(\vec{y} - \vec{x})\) yields:

\[\sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \beta_{nlm}(\vec{y}, E)(\hat{H}_0 - E)S_{nlm}(\vec{r}) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{|\vec{r}|}S_{nlm}(\vec{r})S^*_{nlm}(\vec{y})\]  (3.111)

By using (3.105) and relation (C.217) it can be carried out that:

\[(\hat{H}_0 - E)S_{nlm}(r, \theta, \phi) = k \left(n + l + 1 - \frac{1}{k}\right) \frac{S_{num}(r, \theta, \phi)}{r}\]  (3.112)
where we put \( k = \sqrt{-2E} \). The coefficients \( \beta_{n l m}(\vec{y}, E) \) can therefore be determined by factor-comparison which leads with (3.110) to the final expression:

\[
G(\vec{x}, \vec{y}, E) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{S_{n l m}(\vec{x}) S_{n l m}^*(\vec{y})}{k(n + l + 1 - \frac{1}{2})} \left( \frac{4kn!}{(n + 2l + 1)! (n + l + 1 - \frac{1}{2})} (2kx)^l L_n^{(2l+1)}(2kx)e^{-kx} \right) \left( 2ky \right)^l L_n^{(2l+1)}(2ky)e^{-ky} \cdot 
\]

(3.113)

Note, that this would be singular if \( E \) were equal to an energy eigenvalue of \( \hat{H}_0 \).

Now that we have this expression we will go over to actually calculate the polarizability: (3.75)

\[
\alpha_{n,l,m} := -2 \sum \int |\langle k | z | n, l, m \rangle|^2 \frac{E_n - E_k}{E_k - E_n} (3.114)
\]

If we introduce an additional parameter \( \lambda \) in this expression such that (3.114) is no longer singular if we also sum over states \( |k \rangle \) with \( E_k = E_n \). This requires that \( \lambda \) is smaller than the difference between \( E_n \) and its closest energy eigenvalue.

\[
\alpha_{n,l,m}(\lambda) := +2 \sum \int |\langle k | z | n, l, m \rangle|^2 \frac{E_k - (E_n + \lambda)}{E_k - E_n} (3.115)
\]

we can see, that this is a continuous function of lambda and it therefore holds, that:

\[
\alpha_{n,l,m} = \lim_{\lambda \to 0} [\alpha_{n,l,m}(\lambda)] (3.116)
\]

When defining \( E := E_n + \lambda \) we can write:

\[
\alpha_{n,l,m}(\lambda) = +2 \sum \int |\langle k | z | n, l, m \rangle|^2 \frac{E_k - E}{E_k - E_n} \left( \sum \int |\langle k | z | n, l, m \rangle|^2 \frac{E_k - E}{E_k - E_n} \right) (3.117)
\]

The operator in brackets is nearly the inverse of the operator \( \hat{H}_0 - E \) except that the summation is not over energy states with \( E_k = E_n \). With the definition of the projector on the subspace of energy-eigenstates with eigenvalue \( E_n \),

\[
P_n := \sum_{\{k : E_k = E_n\}} |k \rangle \langle k| (3.118)
\]

we can write (3.117) as:

\[
\alpha_{n,l,m}(\lambda) = +2 \langle n, l, m | \frac{1 - P_n}{\hat{H}_0 - E} z | n, l, m \rangle (3.119)
\]

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For $\lambda \neq 0$ neither the term with the projector nor without it is singular. We can therefore treat them separately and take the limit in the end.

The term without the projector can be rewritten in position-space using the Greens function:

$$\alpha_{\text{red}} := 2 \langle nlm | z(\hat{H}_0 - E)^{-1} z | nlm \rangle = 2 \iint \langle nlm | | x \rangle \langle \hat{H}_0 - E)^{-1} | y \rangle \langle x | z | nlm \rangle d^3\tilde{x}d^3\tilde{y}$$

$$= 2 \iint \Phi^*_{nlm}(\tilde{x})z_G(\tilde{x}, \tilde{y}; E)z_y \Phi_{nlm}(\tilde{y})d^3\tilde{x}d^3\tilde{y}$$

(3.120)

By substituting (3.113) for $G(\tilde{x}, \tilde{y}; E)$ (using $\nu, \mu, \Lambda$ for $n, m, l$) and (C.203) for $\Phi_{nlm}$ and separation of angular and radial integration yields:

$$\alpha_{\text{red}} = \sum_{\nu=0}^{\infty} \sum_{\lambda=0}^{\Lambda} \sum_{\mu=-\Lambda}^{\Lambda} \frac{8k\nu! N^2_{nl} \nu + 2\Lambda + 1}{(\nu + \Lambda + 1 - 1/t)} (\langle \Lambda, \mu | \cos(\theta) \rangle [n, l])^2 \cdot$$

$$\cdot \left( \int_0^\infty \xi^3 (2k_0\xi)^l L^{(2l+1)}_{n-l-1}(2k_0\xi)(2k\xi) L^{(2\Lambda+1)}(2k\xi)e^{-(k+k_0)\xi}d\xi \right)^2$$

(3.121)

with $k_0 := \sqrt{-2E_n} = \frac{1}{\tilde{n}}$. It is convenient to define:

$$I_\lambda(\nu, \Lambda) := \frac{1}{8k_0} \int_0^\infty (2k_0\xi)^{l+3} L^{(2l+1)}_{n-l-1}(2k_0\xi)(2k\xi) L^{(2\Lambda+1)}(2k\xi)e^{-(k+k_0)\xi}d\xi$$

(3.122)

By using identity (C.193) on equation (3.121) we get:

$$\alpha_{\text{red}} = \sum_{\nu=0}^{\infty} \sum_{\nu \neq (n-l-2)} \frac{8\nu! N^2_{nl} C^{l+1,m}_{l+1,m}}{n(\nu + 2l + 3)! (\nu + 2l + n)} I_0^2(\nu, l + 1)$$

(3.123)

$$+ \frac{8k(n-l-2)! N^2_{nl} C^{l+1,m}_{l+1,m}}{(n+l+1)! (n-1)} I_0^2(n-l-2, l+1)$$

(3.124)

$$+ \sum_{\nu=0}^{\infty} \sum_{\nu \neq (n-l)} \frac{8\nu! N^2_{nl} C^{l+1,m}_{l+1,m}}{n(\nu + 2l + 1)! (\nu + l-n)} I_0^2(\nu, l - 1)$$

(3.125)

$$+ \frac{8k(n-l)! N^2_{nl} C^{l+1,m}_{l+1,m}}{(n+l+1)! (n-1)} I_0^2(n-l, l-1)$$

(3.126)

where we have separated the singular part (for $\lambda \to 0$) of the sum and performed the limit $\lambda \to 0$ for the regular parts, which means $k \to \frac{1}{\tilde{n}}$.

For the non-singular part we can notice (by looking at relations (C.207), (C.208), (C.210)) that $I_0$ has only a few non-vanishing terms. These are $\nu \in \{(n-l), (n-l-1), (n-l-3), (n-l-4)\}$ for $I_0(\nu, l+1)$ and $\nu \in \{(n-l-2), (n-l-1), (n-l+1), (n-l+2)\}$ for $I_0(\nu, l-1)$. It seems now a bit messy to do these eight integrals. However we can notice, that we have already done the essential parts of the whole summation, including the integration in section 3.1. Namely the step from equation (3.101) to (3.102) is nothing else than evaluating these integrals with arbitrary coefficients $38\gamma$ and $\sigma$. In fact, this is not an accident, there should be an exact matching of each

$38$ Recall that $g(\rho) := \sum_{n=0}^{4} \gamma_{n-l-1} L^{(2l+3)}_{n-l-1}(x)$ and $f(\rho) := \sum_{l=2}^{4} \sigma_{n-l-1} L^{(2l+1)}_{n-l-1}(x)$.
term if both methods are correct - this is indeed the case. Doing the algebra leads to:

$$\alpha_{\text{red}} = C_{l+1,m}^2 \frac{n^4}{16} (n^2 (44l + 108) - 12l^3 - 12l^2 + 88l + 108)$$

$$+ \frac{8k(n - l - 2)! N_{nl}^2 C_{l+1,m}^2}{(n + l + 1)! (n - \frac{1}{2})} I_3^2(n - l - 2, l + 1)$$

$$+ C_{l,m}^2 \frac{n^4}{16} (n^2 (44l + 108) + 12l^3 + 24l^2 - 76l + 20)$$

$$+ \frac{8k(n - l)! N_{nl}^2 C_{l,m}^2}{(n + l - 1)! (n - \frac{1}{2})} I_3^2(n - l, l - 1)$$

(3.127)

In order to obtain the contribution of the singular part, we also need to evaluate the missing term with the projector. That term can be written as:

$$\alpha_{\text{pro}} := 2 \langle nlm | \frac{P_n}{H_0 - E} | nlm \rangle$$

(3.128)

using that for a state $|k\rangle$ with energy $E_n, \frac{1}{H_0 - E} |k\rangle = \frac{1}{H_0 - (E_n + \lambda)} |k\rangle = -\frac{1}{\lambda} |k\rangle$. This can be rewritten in position-space as:

$$\alpha_{\text{pro}} = - \frac{2}{\lambda} \int \int \int (nlm) |x\rangle \langle y| |z\rangle |nlm\rangle d^3\vec{x} d^3\vec{y}$$

$$= - \frac{2}{\lambda} \sum_{\lambda=0}^{n-1} \sum_{\lambda=0}^{n} \int \int \Phi_{nlm}^*(\vec{x}) z \Phi_{n,\lambda\mu}(\vec{y}) \Phi_{n,\lambda\mu}(\vec{y}) z \Phi_{nlm}(\vec{y}) d^3\vec{x} d^3\vec{y}$$

$$= - \frac{2}{\lambda} \left[ N_{n,l}^2 N_{n,l+1}^2 C_{l+1,m}^2 I_3^2(n - l - 2, l + 1) + N_{n,l}^2 N_{n,l-1}^2 C_{l,m}^2 I_3^2(n - l, l - 1) \right]$$

(3.129)

In order to finish the calculation we have to perform the limit $\lambda \to 0$ for $\alpha_{\text{red}} - \alpha_{\text{pro}}$. Beside the terms where the limit has been performed earlier, the two terms are:

$$s_1(\lambda) := \frac{8k(n - l - 2)! N_{nl}^2 C_{l+1,m}^2}{(n + l + 1)! (n - \frac{1}{2})} I_3^2(n - l - 2, l + 1) + 2 \frac{N_{n,l}^2 N_{n,l+1}^2 C_{l+1,m}^2}{\lambda} I_0^2(n - l - 2, l + 1)$$

$$= N_{n,l}^2 N_{n,l+1}^2 C_{l+1,m}^2 \left[ \frac{2kn^4}{n - \frac{1}{2}} I_3^2(n - l - 2, l + 1) + 2 \frac{I_0^2}{\lambda} (n - l - 2, l + 1) \right]$$

(3.130)

and:

$$s_2(\lambda) := \frac{8k(n - l)! N_{nl}^2 C_{l,m}^2}{(n + l - 1)! (n - \frac{1}{2})} I_3^2(n - l, l - 1) + 2 \frac{N_{n,l}^2 N_{n,l-1}^2 C_{l,m}^2}{\lambda} I_0^2(n - l, l - 1)$$

$$= N_{n,l}^2 N_{n,l-1}^2 C_{l,m}^2 \left[ \frac{2kn^4}{n - \frac{1}{2}} I_3^2(n - l, l - 1) + 2 \frac{I_0^2}{\lambda} (n - l, l - 1) \right]$$

(3.131)

To work out these limits, first note that:

$$\lim_{\lambda \to 0} \frac{2kn^4}{n - \frac{1}{2}} = 2n^4 \lim_{\lambda \to 0} \frac{\lambda k^2}{n + k - 1} = 2n^4 \lim_{\lambda \to 0} \frac{\lambda (\frac{1}{\sqrt{\pi}} - 2\lambda)}{n \sqrt{\frac{1}{\pi} - 2\lambda - 1}} = 2n^4 \lim_{\lambda \to 0} \frac{\lambda^2 - 4\lambda}{n \sqrt{\frac{1}{\pi} - 2\lambda}} = -2$$

(3.132)
where we used the L’Hôpital’s rule for the second last equal sign. This proves, that \( \lim_{\lambda \to 0} \lambda s_1(\lambda) = \lim_{\lambda \to 0} \lambda s_2(\lambda) = 0 \) We can therefore again employ L’Hôpital’s rule for the complete term and get:

\[
\lim_{\lambda \to 0} s_1(\lambda) = \frac{ds_1}{d\lambda} \bigg|_{\lambda=0} = 2N^2 n_{n,l} N^2_{n,l+1} C^2_{l+1,m} \left( I^2_0(n - l - 2, l + 1) + \frac{d}{d\lambda} [I^2_0(n - l - 2, l + 1)]_{\lambda=0} \right)
\]

(3.133)

Evaluating this is a bit messy. We will first compute \( \frac{d}{d\lambda} [I_0(\nu, \Lambda)] \). To do so we apply relations (C.214, C.211, C.207) we get:

\[
\frac{d}{d\lambda} [I_0(\nu, \Lambda)] = \frac{n^2}{2} \left( (2\Lambda + 2\nu + 1)I_0(\nu, \Lambda) + (2\Lambda + \nu + 1)I_0(\nu - 1, \Lambda) + (\nu + 1)I_0(\nu + 1, \Lambda) \right)
\]

(3.134)

Applying the chain rule and noting that the integrals were again implicitly done in (3.102) yields:

\[
S_1(0) = \frac{n^4}{16} (24l^3 + 108l^2 + 144l + 60 - n^2(60 + 24l))
\]

(3.135)

\[
S_2(0) = \frac{n^4}{16} (n^2(24l - 36) - 24l^3 + 36l^2)
\]

(3.136)

combining this yields the same result for the polarizability again:

\[
\alpha_{n,l,m} = \frac{n^4}{16} \left\{ \frac{l^2 - m^2}{4l^2 - 1} \left( n^2(28 - 20l) + 20 - 76l + 60l^2 - 12l^3 \right) \\
+ \frac{(l + 1)^2 - m^2}{(2l + 1)(2l + 3)} \left( n^2(48 + 20l) + 168 + 232l + 96l^2 + 12l^3 \right) \right\}
\]

(3.137)
4 Conclusion

In this thesis, we studied the Van der Waals interactions within the electromagnetic framework. The physical origin of Van der Waals interactions are dipole-fluctuations, which can only be understood quantum mechanically and are the result of the fact that the Hamiltonian operator does not commute with the dipole operator.

We have seen that a system of two atoms has two independent (time) scales.

1. The time $T$ it takes the atom to develop a fluctuation, which is related to the typical binding energy of an atom $m_e \alpha^2$ via $\frac{1}{T} \sim m_e \alpha^2$.

2. The time $t_\gamma$ it takes a photon to travel between the atoms, which is related to the distance $R$ between the atoms via $t_\gamma = R$.

Depending on the ratio of these quantities two different regimes, with different interaction potentials emerge. The short range regime is characterized by $t_\gamma \ll T$ and has an attractive interaction potential, typically of the form $-\frac{C}{R^6}$ while the long range regime is characterized by $t_\gamma \gg T$. The interaction potential, in that case, changes to $-\frac{C'}{R^7}$.

We have seen that the short-range interaction potential is not always of the form $-\frac{C}{R^6}$ and studied the circumstances that cause this change. The conclusion was that for two different atoms we will have the $R^{-6}$ potential if and only if at least one of the atoms is in an S-state. Otherwise, the leading order of the potential is $R^{-5}$. For two atoms of the same kind, also an $R^{-3}$ dependence is possible. We have illustrated that by an explicit calculation of the interaction in the first excited state of the hydrogen-hydrogen system.

For the case of two hydrogen atoms, we have also numerically evaluated the constant $C$ to a very high precision of 15 decimal places. To achieve that we needed explicit expressions for the matrix elements involved, as well as some numerical techniques to speed up the convergence of the series that we have encountered.

We also found that the constant $C$ is related to the polarizabilities of the atoms. More precisely $C$ is proportional to the product of the polarizabilities of the atoms. The polarizability is, therefore, the quantity of interest when one wants to study Van der Waals interactions. It is interesting that an analogue quantity also exists in the theory of strong interactions and accounts for so-called gluonic Van der Waals interactions. As polarizabilities have complicated mathematical forms, methods are needed to calculate them. One of the main goals of this thesis was, therefore, to study methods to evaluate the expression for the polarizability that arises in the electromagnetic theory. We, therefore, discussed methods to analytically evaluate expressions arising in perturbation theory and used them to calculate the polarizability of the hydrogen atom in arbitrary bound states.

A further question would be, whether the methods we used to derive an expression for the polarizability of the hydrogen atom can be extended to find an exact expression for the constant $C$ of the London potential between two ground-state hydrogen atoms. Trying the differential equation approach (Section 3.1) in a naive way, unfortunately, does not work, as unlike in the calculation of the polarizability of hydrogen one does not end up with a finite number of terms but with a very complicated series.

A more ambitious project is to extend the systematic study of the electromagnetic Van der Waals
interactions, which has been achieved through EFTs [23], to strong interactions, to achieve a better understanding of gluonic-Van der Waals interactions.

Acknowledgements

I would like to thank Prof. Dr. Nora Brambilla for offering this, highly interdisciplinary, topic to me and also for here patience when some relatively simple things took me a long time. I also want to thank Dr. Jaume Tarrús Castellà for helpful discussions and very useful hints. Last but not least, I want to thank Lotte Usar for helping me with the English and my family and girlfriend for their patience.
A Mathematical considerations for the London force

A.1 On symmetries of the unperturbed London-Hamiltonian

In section 2.1 we said that the Hamiltonian (2.24) completely described the system. To go on in perturbation theory we have considered the unperturbed system (non-interacting system) to be described by the Hamiltonian

\[ \hat{H}_0 = \sum_{i=1}^{Z_A} \left[ -\frac{1}{2} \Delta_{\vec{r}_{A,i}} - \frac{Z_A}{|\vec{r}_{A,i}|} + \sum_{j=1}^{Z_A} \frac{1}{|\vec{r}_{A,i} - \vec{r}_{A,j}|} \right] \]

\[ := \hat{H}_A \]

\[ + \sum_{i=1}^{Z_B} \left[ -\frac{1}{2} \Delta_{\vec{r}_{B,i}} - \frac{Z_B}{|\vec{r}_{B,i}|} + \sum_{j=1}^{Z_B} \frac{1}{|\vec{r}_{B,i} - \vec{r}_{B,j}|} \right] \]

\[ := \hat{H}_B \]

(A.138)

This section is about the symmetries of this Hamiltonian and their consequences for matrix elements.

For our purpose it is important that the Hamiltonians \( \hat{H}_A \) and \( \hat{H}_B \) have a certain symmetry, which means, that they commute with the following operators which are hereby defined as:

\[ \hat{O}_A(M)\Psi(\{\vec{r}_{A,i}\}) := \Psi(M \cdot \vec{r}_{A,i}, \vec{r}_{A,1}, \vec{r}_{A,2}, ..., \vec{r}_{A,Z_A}, \{\vec{r}_{B,i}\}) \] (A.139)

\[ \hat{O}_B(M)\Psi(\{\vec{r}_{B,i}\}, \vec{r}_{B,1}, \vec{r}_{B,2}, ..., \vec{r}_{B,Z_B}) := \Psi(\{\vec{r}_{A,i}\}, M \cdot \vec{r}_{B,1}, M \cdot \vec{r}_{B,2}, ..., M \cdot \vec{r}_{B,Z_B}) \] (A.140)

where \( M \) is an element of the orthogonal group \( O(3) \) (i.e. \( M \) is a 3x3 matrix with \( M^TM = I \), \( I \) being the identity matrix) and \( \Psi \) is an arbitrary state. Note that this is just a unified way to say, that both \( \hat{H}_A \) and \( \hat{H}_B \) are invariant under rotations and certain parity-like operation which we will define later on.

Before proving that symmetry we want to make a comment on the notation. In this chapter it is not necessary to distinguish between \( A \) or \( B \) most of the time. We thus write the subscript \( X \) for all these quantities. One can substitute \( A, B \) for \( X \)

Proof:

We just plug into the equation:

\[ \hat{O}_X(M)\hat{H}_X\Psi(\{\vec{r}_{A,i}\}) = \hat{O}_X(M) \sum_{i=1}^{Z_X} \left[ -\frac{1}{2} \Delta_{\vec{r}_{X,i}} - \frac{Z_X}{|\vec{r}_{X,i}|} + \sum_{j=1}^{Z_X} \frac{1}{|\vec{r}_{X,i} - \vec{r}_{X,j}|} \right] \Psi(\{\vec{r}_{A,i}\}) \]

\[ = \sum_{i=1}^{Z_X} \left[ -\frac{1}{2} \Delta_{M \vec{r}_{X,i}} - \frac{Z_X}{|M \vec{r}_{X,i}|} + \sum_{j=1}^{Z_X} \frac{1}{|M \vec{r}_{X,i} - M \vec{r}_{X,j}|} \right] \Psi(\{M \vec{r}_{A,i}\}) \]

\[ = \sum_{i=1}^{Z_X} \left[ -\frac{1}{2} \Delta_{\vec{r}_{X,i}} - \frac{Z_X}{|\vec{r}_{X,i}|} + \sum_{j=1}^{Z_X} \frac{1}{|\vec{r}_{X,i} - \vec{r}_{X,j}|} \right] \hat{O}_X(M)\Psi(\{\vec{r}_{A,i}\}) \]

\[ = \hat{H}_X \hat{O}_X(M)\Psi(\{\vec{r}_{A,i}\}) \] (A.141)
By definition absolute value of a vector is invariant under transformation with \( M \). Also the Laplace operator is invariant. One can see this by using the chain rule.

Several special cases of the general operator \( \hat{O}_X(M) \) are defined below.

\[
\hat{P}_X^{(i)} := \hat{O}_X \begin{bmatrix}
(-1)^{\delta_{i1}} & 0 & 0 \\
0 & (-1)^{\delta_{i2}} & 0 \\
0 & 0 & (-1)^{\delta_{i3}}
\end{bmatrix}
\]  
(A.142)

\[
\hat{P}_X := \hat{P}_X^{(x)} \hat{P}_X^{(y)} \hat{P}_X^{(z)}
\]  
(A.143)

\[
\hat{P}_{AB} := \hat{P}_A \hat{P}_B
\]  
(A.144)

\[
\hat{S}_X^{(i,j)} := \hat{O}_X \begin{bmatrix}
(1 - \delta_{ij}) \cdot (1 - \delta_{j1}) + \delta_{ij} & \delta_{i1} \delta_{j2} + \delta_{i2} \delta_{j1} & \delta_{i1} \delta_{j3} + \delta_{i3} \delta_{j1} \\
\delta_{i1} \delta_{j2} + \delta_{i2} \delta_{j1} & (1 - \delta_{i1}) \cdot (1 - \delta_{j2}) + \delta_{ij} & \delta_{i2} \delta_{j3} + \delta_{i3} \delta_{j2} \\
\delta_{i1} \delta_{j3} + \delta_{i3} \delta_{j1} & \delta_{i2} \delta_{j3} + \delta_{i3} \delta_{j2} & (1 - \delta_{i1}) \cdot (1 - \delta_{j3}) + \delta_{ij}
\end{bmatrix}
\]  
(A.145)

These should be read as parity-like transformations (i.e. \( x \to -x \)), combinations of them and a swap operation \( \hat{S}_X^{(i,j)} \) (i.e. \( x \leftrightarrow y, y \leftrightarrow z, x \leftrightarrow z \)). Note, that applying any of these operators twice results in the identity operation. This implies that the eigenvalues of these operators must be +1 or -1.

In general if an operator \( \hat{O} \) commutes with the Hamiltonian it follows that a state also has these symmetries, if this state is non-degenerate. This means, that a non-degenerate eigenstate to \( \hat{H} \), which we call \( |\Psi\rangle \), is also an eigenstate to \( \hat{O} \), with eigenvalue \( \Omega \). One can easily see this as:

\[
\hat{H}(|\Psi\rangle) = \hat{O}\hat{H}|\Psi\rangle = E(\hat{O}|\Psi\rangle)
\]
\[
\Rightarrow \hat{O}|\Psi\rangle = \Omega |\Psi\rangle
\]  
(A.146)

This in fact proves, that \( |\Psi\rangle \) and \( \hat{O}|\Psi\rangle \) are in the same subspace (which is the subspace with energy eigenvalue \( E \)). If this subspace is one-dimensional (non-degenerate) they must, therefore, be proportional.

We now want to find out consequences of these symmetries for the computation of matrix elements. Let \( |\psi_{\alpha,\beta}^{0,0}\rangle \) be a non-degenerate eigenstate of \( \hat{H}_0 := \hat{H}_A + \hat{H}_B \) with eigenvalue \( E_\alpha + E_\beta \). It is thus simultaneously an eigenstate to the operator \( \hat{O}_X(M) \) with eigenvalue \( \Omega \). By doing substitutions like \( \vec{r} \to M\vec{r} \) in the integral and by using the fact that \( \text{det}(M) = 1 \), we can see, that for an operator \( \hat{D}(\{\vec{r}_{A,i}\}, \{\vec{r}_{B,i}\}) \) the following identity holds:

\[
\langle \psi_{AB}^{0,0} | \hat{D} | \psi_{AB}^{0,0} \rangle = |\Omega|^2 \langle \psi_{AB}^{0,0} | \hat{O}(M) \hat{D} | \psi_{AB}^{0,0} \rangle
\]  
(A.147)

With the property, the eigenvalues of the special operators above are 1, one finds:

\[
\langle \psi_{AB}^{\alpha,\beta} | \hat{D} | \psi_{AB}^{\alpha,\beta} \rangle = \langle \psi_{AB}^{\alpha,\beta} | \hat{P}_X^{(i)} \hat{D} | \psi_{AB}^{\alpha,\beta} \rangle = \langle \psi_{AB}^{\alpha,\beta} | \hat{S}_X^{(i,j)} \hat{D} | \psi_{AB}^{\alpha,\beta} \rangle
\]  
(A.148)

It therefore follows, that the expectation value of an operator \( \hat{D} \) in a non-degenerate state vanishes, if:

\[
\hat{P}_X^{(i)} \hat{D} = -\hat{D}
\]  
(A.149)

\[
\hat{S}_X^{(i,j)} \hat{D} = -\hat{D}
\]  
(A.150)
Another consequence is the following: Recall, that the set of eigenvectors of $\hat{H}_0$ to an eigenvalue $E$ form a subspace. We will assume, that this subspace has a finite dimension $d$. Let $\{ |\Psi^{(i)}\rangle \}$ ($i = 1, 2 \cdots d$) be an orthonormal basis of this subspace, and $\hat{O}_X(M)$ an operator which commutes with $\hat{H}_0$ and $(\hat{O}_X(M))^2 = 1$ then:

$$\sum_{i=1}^{d} \hat{O}_X(M) |\Psi^{(i)}\rangle \langle \Psi^{(i)}| \hat{O}_X(M) = \sum_{i=1}^{d} |\Psi^{(i)}\rangle \langle \Psi^{(i)}|$$  \hfill (A.151)

Proof:
Due to (A.146) $\hat{O}_X(M) |\Psi^{(i)}\rangle$ is still in the same subspace. We can therefore expand it in this basis:

$$\sum_{i=1}^{d} \hat{O}_X(M) |\Psi^{(i)}\rangle \langle \Psi^{(i)}| \hat{O}_X(M) =$$

$$= \sum_{i,j,k} |\Psi^{(j)}\rangle \langle \Psi^{(j)}| \hat{O}_X(M) |\Psi^{(i)}\rangle \langle \Psi^{(i)}| \hat{O}_X(M) |\Psi^{(k)}\rangle \langle \Psi^{(k)}|$$

$$= \sum_{j,k} |\Psi^{(j)}\rangle \langle \Psi^{(j)}| \hat{O}_X(M) \sum_{i=1}^{d} |\Psi^{(i)}\rangle \langle \Psi^{(i)}| \hat{O}_X(M) |\Psi^{(k)}\rangle \langle \Psi^{(k)}|$$

$$= \sum_{j,k} |\Psi^{(j)}\rangle \langle \Psi^{(j)}| \hat{O}_X(M) \hat{O}_X(M) |\Psi^{(k)}\rangle \langle \Psi^{(k)}|$$

$$= \sum_{j,k} |\Psi^{(j)}\rangle \langle \Psi^{(j)}| |\Psi^{(k)}\rangle \langle \Psi^{(k)}|$$

$$= \sum_{i=1}^{d} |\Psi^{(i)}\rangle \langle \Psi^{(i)}|$$  \hfill (A.152)

### A.2 Evaluation of first order perturbation theory

In this section we want to prove that the $\epsilon_1$ term in (2.30) is at least of order $O \left( |\vec{R}|^{-7} \right)$. The main point in this chapter is to explicitly write down the relevant terms of lower order and to use symmetry arguments to prove that they do vanish. Note that one needs to be very careful in proving this, because as pointed out in [38], this statement is not true if one considers the Coulomb problem in two dimensions.\(^{39}\) The argument, therefore, depends not only on symmetry but also on the dimension of space.

From $\hat{S}^{(i,j)}$ it follows that:

$$\langle \psi^{0,0}_{AB} | x^2 | \psi^{0,0}_{AB} \rangle = \langle \psi^{0,0}_{AB} | y^2 | \psi^{0,0}_{AB} \rangle = \langle \psi^{0,0}_{AB} | z^2 | \psi^{0,0}_{AB} \rangle = \frac{1}{2} \langle \psi^{0,0}_{AB} | \vec{r}^2 | \psi^{0,0}_{AB} \rangle$$  \hfill (A.153)

Notice, that for the last equal sign the dimension of space is important.

\(^{39}\)In fact the relevant matrix elements do only vanish in 3 and 5 dimensions [38]
The only remaining term is now of order $O\left(\frac{1}{|R|^{l+1}}\right)$ with $l \geq 1$ is given by (2.28) as:

$$W_l := \frac{1}{|R|} \cdot \sum_{i,j} P_l \left( \frac{\vec{r}_{A,i} - \vec{r}_{B,j}}{|\vec{r}_{A,i} - \vec{r}_{B,j}||R|} \right) \left( \frac{|\vec{r}_{A,i} - \vec{r}_{B,j}|}{|R|} \right)^l$$

$$- \sum_{i,j} \left\{ P_l \left( \frac{\vec{r}_{A,i} \cdot \vec{R}}{|\vec{r}_{A,i}||R|} \right) \left( \frac{|\vec{r}_{A,i}|}{|R|} \right)^l + P_l \left( \frac{-\vec{r}_{B,j} \cdot \vec{R}}{|\vec{r}_{B,j}||R|} \right) \left( \frac{|\vec{r}_{B,j}|}{|R|} \right)^l \right\} \right\} \tag{A.154}$$

By using (C.187) it follows that $\hat{P}_{AB} W_l = (-1)^l W_l$ and therefore $\langle \psi_{AB}^0 | W_l | \psi_{AB}^0 \rangle = 0$ for odd $l$.

The dipole-dipole term

$$W_2 = \frac{\vec{\mu}_A \cdot \vec{\mu}_B - 3(\vec{R} \cdot \vec{\mu}_A)(\vec{R} \cdot \vec{\mu}_B)}{|R|^3} \tag{A.155}$$

transforms as $\hat{P}_A W_2 = -W_2$ which again implies $\langle \psi_{AB}^0 | W_2 | \psi_{AB}^0 \rangle = 0$.

The only remaining term is now of order $O\left(\frac{1}{|R|^5}\right)$. We will now explicitly write this term down whereby we set $\vec{R} := |\vec{R}| \vec{e}_z$ with $\vec{e}_z$ being the unit vector in $z$ direction and dropping terms which have odd parity (Note, that $P_4(x) = \frac{35x^4 - 30x^2 + 3}{8}$)

$$8W_4|\vec{R}|^5 = \sum_{i,j} \left[ (z_{A,i} - z_{B,j})^4 - z_{A,i}^4 - z_{B,j}^4 \right] + 3 \left[ |\vec{r}_{A,i} - \vec{r}_{B,j}|^4 - |\vec{r}_{A,i}|^4 - |\vec{r}_{B,j}|^4 \right]
- 30 \left[ (z_{A,i} - z_{B,j})^2 |\vec{r}_{A,i} - \vec{r}_{B,j}|^2 - z_{A,i}^2 |\vec{r}_{A,i}|^2 - z_{B,j}^2 |\vec{r}_{B,j}|^2 \right]
= \sum_{i,j} 2 \left[ 2z_{A,i}^2 z_{B,j}^2 - 30 \left( z_{A,i}^2 \vec{r}_{A,i}^2 + z_{B,j}^2 \vec{r}_{B,j}^2 + 4z_{A,i} z_{B,j} \right) \right]
+ 6 \left[ \vec{r}_{A,i} \cdot \vec{r}_{B,j} + 2(x_{A,i} x_{B,j} + y_{A,i} y_{B,j} + z_{A,i} z_{B,j}) \right] + \text{odd parity terms} \tag{A.156}$$

Using relation(A.153) and some counting yields:

$$\langle \psi_{AB}^0 | W_4 | \psi_{AB}^0 \rangle = \frac{1}{8|\vec{R}|^5} (210 - 300 + 90) \langle \psi_{AB}^0 | \sum_{i,j} z_{A,i} z_{B,j} | \psi_{AB}^0 \rangle = 0 \tag{A.157}$$

### A.3 Proof of identity (2.35)

Here we want to prove that:

$$C = \sum_{(\alpha,\beta): E_{\alpha,\beta} \neq E_{0,0}} \frac{|\langle \psi_{AB}^{\alpha,\beta} | \vec{\mu}_A \cdot \vec{\mu}_B - 3(\vec{R} \cdot \vec{\mu}_A)(\vec{R} \cdot \vec{\mu}_B) | \psi_{AB}^{0,0} \rangle|^2}{E_{\alpha,\beta} - E_{0,0}} \tag{A.158}$$

$$= 6 \sum_{(\alpha,\beta): E_{\alpha,\beta} \neq E_{0,0}} \frac{|\langle \psi_{AB}^{\alpha,\beta} | \vec{\mu}_{A,z} \vec{\mu}_{B,z} | \psi_{AB}^{0,0} \rangle|^2}{E_{\alpha,\beta} - E_{0,0}}$$

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when we define $\tilde{R}$ to point into the $z$-direction. Thus:

$$C = \frac{1}{|R|^6} \sum_{(\alpha, \beta): E_{\alpha, \beta} \neq E_{0,0}} \left| \langle \psi_{AB}^\alpha | \mu_{A, x} \mu_{B, x} + \mu_{A, y} \mu_{B, y} - 2 \mu_{A, z} \mu_{B, z} | \psi_{AB}^0 \rangle \right|^2$$  \hspace{1cm} \text{(A.159)}$$

by performing the multiplication of the square we get:

$$C = \sum_{(\alpha, \beta): E_{\alpha, \beta} \neq E_{0,0}} \frac{|M_{xy}^\alpha|^2 + |M_{yz}^\alpha|^2 + 4|M_{xy}^\alpha|^2 + 2\Re \{M_{xy}^\alpha - 2M_{yz}^\alpha - 2M_{yz}^\alpha\}}{E_{\alpha, \beta} - E_{0,0}}$$  \hspace{1cm} \text{(A.160)}$$

where we defined:

$$M_{xy}^\alpha := \langle \psi_{AB}^\alpha | \mu_{A, x} \mu_{B, x} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.161)}$$

$$M_{yz}^\alpha := \langle \psi_{AB}^\alpha | \mu_{A, y} \mu_{B, y} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.162)}$$

$$M_{xz}^\alpha := \langle \psi_{AB}^\alpha | \mu_{A, z} \mu_{B, z} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.163)}$$

$$M_{xy}^\alpha := \langle \psi_{AB}^\alpha | \mu_{A, x} \mu_{B, x} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.164)}$$

$$M_{yz}^\alpha := \langle \psi_{AB}^\alpha | \mu_{A, y} \mu_{B, y} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.165)}$$

$$M_{xz}^\alpha := \langle \psi_{AB}^\alpha | \mu_{A, z} \mu_{B, z} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.166)}$$

We will organize the summation so that we sum the states with the same energy first and sum over all energy eigenvalues then:

$$\sum_{E} \sum_{(\alpha, \beta): E_{\alpha, \beta} = E} \frac{|M_{xy}^\alpha|^2 + |M_{yz}^\alpha|^2 + 4|M_{xy}^\alpha|^2 + 2\Re \{M_{xy}^\alpha - 2M_{yz}^\alpha - 2M_{yz}^\alpha\}}{E_{\alpha, \beta} - E_{0,0}}$$  \hspace{1cm} \text{(A.167)}$$

We can thus write the factor $\frac{1}{E_{\alpha, \beta}}$ in front of the inner sum and get a summation over the individual elements $M$. We will argue that the inner sum over the mixed terms $(M_{xy}^\alpha, M_{yz}^\alpha, M_{xz}^\alpha)$ is zero and that the sum has the same value for $M_{xy}^\alpha, M_{yz}^\alpha, M_{xz}^\alpha$. To see this we write, for example, the sum over $M_{xy}^\alpha$ as\footnote{Taking the real part does not matter, because summation over real and imaginary part is independent}:

$$U_{xy} := \sum_{(\alpha, \beta): E_{\alpha, \beta} = E} M_{xy}^\alpha = \sum_{(\alpha, \beta): E_{\alpha, \beta} = E} \langle \psi_{AB}^0 | \mu_{A, x} \mu_{B, x} | \psi_{AB}^\alpha \rangle \langle \psi_{AB}^\alpha | \mu_{A, y} \mu_{B, y} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.168)}$$

$$= \langle \psi_{AB}^0 | \mu_{A, x} \mu_{B, x} \sum_{(\alpha, \beta): E_{\alpha, \beta} = E} | \psi_{AB}^\alpha \rangle \langle \psi_{AB}^\alpha | | \mu_{A, y} \mu_{B, y} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.169)}$$

We perform a substitution $x_A \rightarrow -x_A$ in the outer scalar-product which of course is an integral and get (as $\mu_{A, x} \rightarrow -\mu_{A, x}$):

$$U_{xy} = \langle \psi_{AB}^0 | P^{(z)}_A | \mu_{A, x} \mu_{B, x} \sum_{(\alpha, \beta): E_{\alpha, \beta} = E} | \psi_{AB}^\alpha \rangle \langle \psi_{AB}^\alpha | \mu_{A, y} \mu_{B, y} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.170)}$$

$$= -\langle \psi_{AB}^0 | \mu_{A, x} \mu_{B, x} P^{(z)}_A \sum_{(\alpha, \beta): E_{\alpha, \beta} = E} | \psi_{AB}^\alpha \rangle \langle \psi_{AB}^\alpha | P^{(z)}_A | \mu_{A, y} \mu_{B, y} | \psi_{AB}^0 \rangle$$  \hspace{1cm} \text{(A.171)}$$

By employing (A.151) we arrive at:

$$U_{xy} = -U_{xy}$$  \hspace{1cm} \text{(A.172)}$$

And therefore $U_{xy} = 0$. The same argument applies to all mixed terms. In exactly the same way but using the swap operator $\hat{S}_{x}^{(ij)}$ defined in (A.142) instead of $P^{(z)}_A$ gives that the sums over $M_{xy}^\alpha, M_{yz}^\alpha$ and $M_{xz}^\alpha$ are the same. We therefore get the result (A.158).


\section*{B Time independent perturbation theory}

As it is not included in every introductory quantum mechanics course, we introduce perturbation theory for energy eigenstates. It is called time independent perturbation theory - in contrast to the time-dependent perturbation theory of quantum dynamics. We want to (approximately) solve the following eigenvalue problem:

\[ \hat{H} \ket{\Psi} = E \ket{\Psi} \] 

(B.173)

with the Hamiltonian \( \hat{H} \), the eigenstate \( \ket{\Psi} \) and the real energy eigenvalue \( E \). When working in position-space, this is a differential equation most of the time, which cannot be solved in a closed form. However, in many cases it turns out that the Hamiltonian can be written as:

\[ \hat{H} = \hat{H}_0 + V \] 

(B.174)

with \( \hat{H}_0 \) being the Hamiltonian of an exactly solvable problem and \( V \) being small perturbation. Small means that at least

\[ \left| \frac{\langle \Psi_0 | V | \Psi \rangle}{E_n - E_k} \right| \ll 1 \] 

42 holds, with \( \Psi_0 \) being the unperturbed state.

The unperturbed operator \( \hat{H}_0 \) has a complete set of (generalized) eigenstates \( \ket{n} \) which fulfill:

\[ \hat{H}_0 \ket{n} = E_n \ket{n} \] 

(B.175)

If we introduce a parameter \( \lambda \), both the eigenvalue \( E \) as well as the eigenfunction \( \ket{\Psi} \) are functions of \( \lambda \)

\[ (\hat{H}_0 + \lambda V) \ket{\Psi (\lambda)} = E(\lambda) \ket{\Psi} \] 

(B.176)

If we now assume that both can be expanded into a power series (with the size of the radius convergence being at least 1) in \( \lambda \) we get:

\[ (\hat{H}_0 + \lambda V) (\omega_0 + \lambda \omega_1 + \cdots) = (\epsilon_0 + \lambda \epsilon_1 + \lambda^2 \epsilon_2 + \cdots) (\omega_0 + \lambda \omega_1 + \cdots) \] 

(B.177)

If that series converges, then terms on the left and right hand side must be identical in each power of \( \lambda \). This is:

\[ \lambda^0 : \hat{H}_0 \ket{\Psi_0} = \epsilon_0 \ket{\Psi_0} \]

\[ \lambda^1 : \hat{H}_0 \ket{\Psi_1} + V \ket{\Psi_0} = \epsilon_0 \ket{\Psi_1} + \epsilon_1 \ket{\Psi_0} \]

\[ \lambda^2 : \hat{H}_0 \ket{\Psi_2} + V \ket{\Psi_1} = \epsilon_0 \ket{\Psi_2} + \epsilon_1 \ket{\Psi_1} + \epsilon_2 \ket{\Psi_0} \]

\[ \lambda^m : \hat{H}_0 \ket{\Psi_m} + V \ket{\Psi_{m-1}} = \sum_{i=0}^m \epsilon_i \ket{\Psi_{m-i}} \]

(B.178)

If we set \( \lambda = 0 \) we can see that \( \epsilon_0 = E_n \), if we considered the perturbation to the state with energy \( E_n \). If that energy level is non-degenerate this equation determines \( \ket{\Psi_0} \) up to a normalization constant. However, this is not necessarily the case. In addition, we now assume, that the eigenvalue

\[ \text{The Hamiltonian can always be written that way, but not necessarily with the condition of } V \text{ being small.} \]

\[ \text{This is a necessary not a sufficient condition!} \]

\[ \text{This is the main assumption, which is in not fulfilled in general. However we might obtain a suitable result anyway as this can be an asymptotic series.} \]

\[ \text{The other assumption is that each of the states } \ket{\Psi_i} \text{ is properly normalizable} \]
$E_n$ has only finite degeneracy $D$ and label these (normalized) eigenfunctions $|n^{(i)}\rangle \ i = 1, 2, \cdots D$. As the eigenfunctions to a specific eigenvalue form a subspace, we can write:

$$|\Psi_0\rangle = \sum_{i=1}^{D} \alpha_i |n^{(i)}\rangle \quad \text{(B.179)}$$

If we substitute this into the first order equation followed by a multiplication with $\langle n^{(i)}|$ and use the fact, that $\langle n^{(i)}| \hat{H}_0 |\Psi_1\rangle = \langle \hat{H}_0 n^{(i)}| |\Psi_1\rangle = \epsilon_0 \langle n^{(i)}| |\Psi_1\rangle$ we get\footnote{In this step it is important that we assumed $|\Psi_1\rangle$ to be normalizable. I.e. all scalar products have a finite value. This is important as the differential equation may also have other solutions (exponentially growing ones for example).}

$$\sum_{i=1}^{D} \alpha_i \langle n^{(i)}| V |n^{(i)}\rangle = \epsilon_1 \sum_{i=1}^{D} \alpha_i \langle n^{(i)}| n^{(i)}\rangle = \alpha_1 \langle n^{(i)}| n^{(i)}\rangle$$

This set of equations can alternatively be written in the more familiar matrix form:

$$\begin{pmatrix} \langle n^{(1)}| V |n^{(1)}\rangle & \langle n^{(1)}| V |n^{(2)}\rangle & \cdots & \langle n^{(1)}| V |n^{(D)}\rangle \\ \langle n^{(2)}| V |n^{(1)}\rangle & \ddots & \vdots & \langle n^{(2)}| V |n^{(D)}\rangle \\ \vdots & \ddots & \ddots & \vdots \\ \langle n^{(D)}| V |n^{(1)}\rangle & \cdots & \cdots & \langle n^{(D)}| V |n^{(D)}\rangle \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_D \end{pmatrix} = \epsilon_1 \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_D \end{pmatrix} \quad \text{(B.181)}$$

This is the familiar eigenvalue problem on a finite dimensional vector space with a Hermitian matrix which of course can be orthogonally diagonalized. If this is done we get the eigenstates in zeroth order and the first order correction in energy levels. Note, that (B.180) reduces to $\epsilon_1 = \langle n| V |n\rangle$ if the energy level is non-degenerate.

Let us have a quick look at the normalization of the state, which is not completely determined by the equations above: The probability interpretation of QM requires that $\langle \Psi(\lambda)| \Psi(\lambda)\rangle = 1$. This reads in expanded form:

$$1 = \langle \Psi(\lambda)| \Psi(\lambda)\rangle = (\langle \Psi_0| + \lambda \langle \Psi_1| + \cdots)(\langle \Psi_0| + \lambda \langle \Psi_1| + \cdots)$$

$$= \sum_{k=0}^{\infty} \lambda^k \left( \sum_{l=0}^{k} \langle \Psi_l| \Psi_{k-l}\rangle \right) \quad \text{(B.182)}$$

This implies $\langle \Psi_0| \Psi_0\rangle = 1$.

Let us now turn to the second order correction to the energy. We do assume in the following that the finite dimensional eigenvalue problem (B.181) leads to different energy eigenvalues. Otherwise $\Psi_0$ would still not be completely determined, which would result in finite dimensional eigenvalue problems again and again - we will not discuss this case here.

If we multiply the $\lambda^2$ equation in (B.178) by $\langle \Psi_0|$ we get:

$$\epsilon_2 = \langle \Psi_0| V |\Psi_1\rangle - \epsilon_1 \langle \Psi_0| \Psi_1\rangle \quad \text{(B.183)}$$

Therefore, if we know the first order correction to the states we can find the second order energy correction simply by integrating. If the equation (B.178) ($\lambda^1$) is solvable for $|\Psi_1\rangle$ we are done. If it is not, we can still try to expand $\Psi_1$ into eigenfunctions of the unperturbed system and end up with an infinite series. We will derive the expression for that case now: As the term $\langle k| \Psi_1\rangle$
will appear in the following we will first derive a different expression for that. We do that by multiplying (B.178) \((\lambda^1)\) by \(\langle k|\) and obtain:

\[
(\epsilon_0 - E_k) \langle k| \Psi_1 \rangle = \langle k| V |\Psi_0 \rangle - \epsilon_1 \langle k| \Psi_0 \rangle \tag{B.184}
\]

If \(|k\rangle\) is in the subspace with equal energy as \(|\Psi_0\rangle\) we will not get any further information. In the other case we obtain \(\langle k| \Psi_1 \rangle\) by division threw \((\epsilon_0 - E_k)\). We will, therefore, split the expansion into two sums: one over all states that are in that subspace and one over the rest. Combining (B.183) and (B.184) yields:

\[
\epsilon_2 = \sum_{|k|: E_k \neq \epsilon_0} \langle \Psi_0| V |k\rangle \langle k| \Psi_1 \rangle + \sum_{|k|: E_k = \epsilon_0} \left( (\langle \Psi_0| V |k\rangle - \epsilon_1) \langle k| \Psi_1 \rangle \right) = 0
\]

\[
\epsilon_2 = \sum_{|k|: E_k \neq \epsilon_0} \frac{|\langle \Psi_0| V |k\rangle|^2}{\epsilon_0 - E_k} \tag{B.185}
\]

The second term is zero, as we constructed \(\Psi_0\) to be an eigenvector with eigenvalue \(\epsilon_1\) in that particular subspace. Using the same principle one can find expressions in terms of series also for higher order corrections. As second order is sufficient for the Van der Waals interaction we will not elaborate on that any further.
C Relations on special functions

This chapter uses [39] and [30] as references.

C.1 Legendre polynomials

The Legendre polynomials for a non-negative integer \( l \) can be defined by their Rodrigues formula:

\[
P_l(x) := \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l
\]

From this definition one can immediately see:

\[
P_l(-x) = (-1)^l P_l(x)
\]

An important property is their generating function \( \frac{1}{\sqrt{1-2xt+t^2}} \), which means

\[
\frac{1}{\sqrt{1-2xt+t^2}} = \sum_{l=0}^{\infty} P_l(x)t^l
\]

for \( |x| < 1 \) and \( |t| < 1 \)

C.2 Associated Legendre polynomials

The associated Legendre polynomials for an integer \( m \) and a non-negative integer \( l \) can be defined by their Rodrigues formula:

\[
P_{l}^{m}(x) := \begin{cases} 
\left(\frac{-1}{2^{l}n}ight)^{m} (1 - x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l & |m| \leq l \\
0 & |m| > l
\end{cases}
\]

This can be extended to negative integer values of \( l \) by defining

\[
P_{l}^{m}(x) = P_{-l-1}^{m}(x)
\]

Also note, that by definition the "ordinary" Legendre polynomials are a special case:

\[
P_l(x) = P_{0}^{l}(x)
\]

C.3 Spherical harmonics

\[
Y_{l,m}(\theta, \phi) := \frac{K_{l,m} P_{l}^{m}(\cos(\theta)) e^{im\phi}}{\sqrt{2\pi}}
\]

\[
K_{l,m} := \sqrt{\frac{2l + 1 (l - m)!}{2 (l + m)!}}
\]
Note, that this is only well defined if \( |m| \leq l \) for the other cases we hereby define \( Y_{l,m} := 0 \)

Here the following identity is derived:

\[
\cos(\theta) \cdot Y_{l,m} = \sqrt{\frac{(l + 1)^2 - m^2}{(2l + 1) \cdot (2l + 1)}} \cdot Y_{l+1,m} + \sqrt{\frac{l^2 - m^2}{(2l + 1) \cdot (2l - 1)}} \cdot Y_{l-1,m} \quad \text{(C.193)}
\]

Proof:
It is done by using the recurrence relation for associated Legendre polynomials.

\[
xP_l^{(m)}(x) = \frac{l + m}{2l + 1} P_l^{(m)}(x) + \frac{l - m + 1}{2l + 1} P_{l+1}^{(m)}(x) \quad \text{(C.194)}
\]

and the definition of the spherical harmonics (C.192)

\[
\cos(\theta)Y_{l,m}(\theta, \phi) := \frac{K_{l,m}}{\sqrt{2\pi}} P_l^{(m)}(\cos(\theta))e^{im\phi}
\]

\[
= \frac{K_{l,m}}{\sqrt{2\pi}} \left[ \frac{l + m}{2l + 1} P_{l-1}^{(m)}(\cos(\theta)) + \frac{l - m + 1}{2l + 1} P_{l+1}^{(m)}(\cos(\theta)) \right]
\]

\[
= \frac{(l + m)K_{l,m} - K_{l-1,m}}{(2l + 1)K_{l-1,m}} P_{l-1}^{(m)}(\cos(\theta))e^{im\phi}
+ \frac{(l - m + 1)K_{l,m} - K_{l+1,m}}{(2l + 1)K_{l+1,m}} P_{l+1}^{(m)}(\cos(\theta))e^{im\phi}
\quad \text{(C.195)}
\]

\[
= \sqrt{\frac{(l + 1)^2 - m^2}{(2l + 1) \cdot (2l + 1)}} \cdot Y_{l+1,m}(\theta, \phi)
+ \sqrt{\frac{l^2 - m^2}{(2l + 1) \cdot (2l - 1)}} \cdot Y_{l-1,m}(\theta, \phi)
\]

Another useful identity is:

\[
\sin(\theta)e^{i\phi}Y_{l,m} = \sqrt{\frac{(l - m)(l - m - 1)}{(2l + 1)(2l - 1)}} \cdot Y_{l-1,m+1} - \sqrt{\frac{(l + m + 2)(l + m + 1)}{(2l + 1)(2l + 3)}} \cdot Y_{l+1,m+1}
\quad \text{(C.196)}
\]

where we define:

\[
Q(l,m) := \sqrt{\frac{(l - m)(l - m - 1)}{(2l + 1)(2l - 1)}}
\quad \text{(C.197)}
\]

Proof:
We use the following identity about Associated Legendre polynomials:

\[
\sqrt{1 - x^2} P_l^{(m)}(x) = \frac{1}{2l + 1} \left[ P_{l+1}^{(m+1)}(x) - P_{l-1}^{(m+1)}(x) \right]
\quad \text{(C.198)}
\]
and the definition of spherical harmonics (C.192):

\[
\sin(\theta) e^{i\phi} Y_{l,m} = \frac{K_{l,m}}{\sqrt{2\pi}} \sqrt{1 - \cos^2(\theta) P_l^{(m)}(\cos(\theta))} e^{i(m+1)\phi}
\]

\[
= \frac{1}{2l+1} \frac{K_{l,m}}{\sqrt{2\pi}} e^{i(m+1)\phi} \left[ P^{m+1}_{l-1}(\cos(\theta)) - P^{m+1}_{l+1}(\cos(\theta)) \right]
\]

\[
= \frac{1}{2l+1} \left[ \frac{K_{l,m}}{K_{l-1,m+1}} Y_{l-1,m+1} - \frac{K_{l,m}}{K_{l+1,m+1}} Y_{l+1,m+1} \right]
\]

\[
= \sqrt{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}} Y_{l-1,m+1} - \sqrt{\frac{(l+m+2)(l+m+1)}{(2l+1)(2l+3)}} Y_{l+1,m+1}
\]

(C.199)

From this it follows after a short calculation that:

\[
\sin(\theta) \sin(\phi) Y_{l,m} = \frac{1}{2l+1} \left[ Q(l,m) Y_{l-1,m+1} - Q(l+1, -(m+1)) Y_{l+1,m+1} 
\right.
\]

\[
+ Q(l,-m) Y_{l-1,m-1} - Q(l+1, m-1) Y_{l+1,m-1}
\]

\]

\[
= \frac{1}{2l+1} \left[ Q(l,m) Y_{l-1,m+1} - Q(l+1, -(m+1)) Y_{l+1,m+1} 
\right.
\]

\[
- Q(l,-m) Y_{l-1,m-1} + Q(l+1, m-1) Y_{l+1,m-1}
\]

(C.200)

and:

\[
\sin(\theta) \cos(\phi) Y_{l,m} = \frac{1}{2l+1} \left[ Q(l,m) Y_{l-1,m+1} - Q(l+1, -(m+1)) Y_{l+1,m+1} 
\right.
\]

\[
- Q(l,-m) Y_{l-1,m-1} + Q(l+1, m-1) Y_{l+1,m-1}
\]

(C.201)

### C.4 Generalized Laguerre polynomials

The Generalized Laguerre polynomials for an integer \( n \) can be defined as

\[
L^{(\alpha)}_n(x) := \begin{cases} 
\frac{e^x - x^{-\alpha} \frac{d^n}{dx^n} (e^{-x} x^{n+\alpha})}{n!} & n \geq 0 \\
0 & n < 0 
\end{cases}
\]

(C.202)

The eigenfunctions of the Coulomb problem are given as:

\[
\Phi_{n,l,m} = R_{n,l}(r) Y_{l,m}(\theta, \phi)
\]

\[
R_{n,l} = N_{n,l} \cdot \rho L_{2(l-1)}^{(2l+1)}(\rho) e^{-\frac{\rho}{2}}
\]

\[
\rho := 2r \cdot N_{n,l} := \sqrt{\frac{4(n-l-1)!}{n^2(n+l)!}}
\]

(C.203) \hspace{1cm} (C.204) \hspace{1cm} (C.205)

\( Y_{l,m} \) denote the spherical harmonics and \( L^{(\alpha)}_k(\rho) \) the generalized Laguerre polynomials

From the references we get:

\[
L^{(\alpha)}_k = L^{(\alpha+1)}_k - L^{(\alpha+1)}_{k-1}
\]

(C.206)
Repeated substitution yields
\[ L_k^{(\alpha)}(x) = L_k^{(\alpha+1)}(x) - L_{k-1}^{(\alpha+1)}(x) \]
\[ = L_k^{(\alpha+2)}(x) - 2L_{k-1}^{(\alpha+2)}(x) + L_{k-2}^{(\alpha+2)}(x) \]
\[ = L_k^{(\alpha+3)}(x) - 3L_{k-1}^{(\alpha+3)}(x) + 3L_{k-2}^{(\alpha+3)}(x) - L_{k-3}^{(\alpha+3)}(x) \]  \hspace{1cm} (C.207)
\[ = \sum_{i=0}^{n} (-1)^i \binom{n}{i} L_{k-i}^{(\alpha+n)}(x) \]

There is also an orthogonality relation for generalized Laguerre polynomials:
\[ \int_0^{\infty} x^n e^{-x} L_n^{(\alpha)}(x) \cdot L_m^{(\alpha)}(x) \, dx = \frac{\Gamma(n + \alpha + 1)}{n!} \delta_{nm} \]  \hspace{1cm} (C.208)
with \( \Gamma(z) \) being the usual gamma-function.

Also:
\[ x^k \cdot L_n^{(\alpha)}(x) = k! \sum_{i=0}^{k} (-1)^i \binom{n + i}{i} \binom{n + \alpha}{k-i} L_{n+i}^{(\alpha-k)}(x) \]  \hspace{1cm} (C.209)
\[ x^k L_n^{(\alpha)}(x) = \sum_{i=-k}^{k} \binom{k}{i} \sum_{l=i}^{\min(k,|i|)} (-1)^l a_{i,k} \cdot L_{n+i}^{(\alpha)}(x) \]  \hspace{1cm} (C.210)
\[ a_{i,k} := \left\{ \begin{array}{ll}
\sum_{l=0}^{k-|i|} \binom{n+l+i}{i} \binom{n+\alpha}{k-l-i} \binom{k}{l} & 0 \leq i \leq k \\
\sum_{l=0}^{k-|i|} \binom{n+i}{i} \binom{n+\alpha}{k} \binom{k}{l} & -l \leq i \leq 0
\end{array} \right. \]

A special case of this formula is:
\[ xL_n^{(\alpha)}(x) = (\alpha + n)L_n^{(\alpha-1)}(x) - (n + 1)L_{n+1}^{(\alpha-1)}(x) \]  \hspace{1cm} (C.211)
\[ = (\alpha + n)L_n^{(\alpha)}(x) - (\alpha + n)L_{n-1}^{(\alpha)}(x) - (n + 1)L_{n+1}^{(\alpha)}(x) \]  \hspace{1cm} (C.212)
\[ = (2n + \alpha + 1)L_n^{(\alpha)}(x) - (\alpha + n)L_{n-1}^{(\alpha)}(x) - (n + 1)L_{n+1}^{(\alpha)}(x) \]  \hspace{1cm} (C.213)

The derivative of a generalized Laguerre polynomial is a generalized Laguerre polynomial with the following identity:
\[ \frac{d^k}{dx^k} L_n^{(\alpha)}(x) = (-1)^k L_{n-k}^{(\alpha+k)}(x) \]  \hspace{1cm} (C.214)

An important aspect is the connection between the generalized Laguerre polynomials and the generalized Laguerre equation:
\[ x \frac{d^2 f}{dx^2} + (\alpha + 1 - x) \frac{df}{dx} + n f := L_{\alpha,n} f \]  \hspace{1cm} (C.215)

It holds that:
\[ \hat{L}_{\alpha,n} L_k^{(\beta)}(x) = (n - k) \cdot L_k^{(\beta+1)}(x) + [(\beta - \alpha) + (k - n)] \cdot L_{k-1}^{(\beta+1)}(x) \]  \hspace{1cm} (C.216)
Note, that for the case where \( \alpha = \beta \) this is:

\[
\hat{L}_{\alpha,n} L^{(\alpha)}_k(x) = (n-k)L^{(\alpha)}_k(x) \tag{C.217}
\]

Proof:
Here the formulas (C.207) and (C.214) are used.

\[
\hat{L}_{\alpha,n} L^{(\beta)}_k(x) := x \frac{d^2}{dx^2} L^{(\beta)}_k(x) + (\alpha + 1 - x) \frac{d}{dx} L^{(\beta)}_k(x) + nL^{(\beta)}_k(x)
\]

\[
= xL^{(\beta+2)}_k(x) - (\alpha + 1)L^{(\beta+1)}_k(x) + xL^{(\beta+1)}_k(x) + nL^{(\beta)}_k(x)
\]

\[
= (k + \beta)L^{(\beta+1)}_{k-2}(x) - (k + 1)L^{(\beta+1)}_{k-1}(x) - (\alpha + 1)L^{(\beta+1)}_{k-1}(x) + (n-k)L^{(\beta+1)}_{k-1}(x) + (n-k)\cdot L^{(\beta+1)}_{k-1}(x)
\]

C.5 (Confluent-)Hypergeometric function

We define the Hypergeometric function \( {}_2F_1(a, b, c, x) \) as:

\[
{}_2F_1(a, b, c, x) := \sum_{k=0}^{\infty} \frac{\Gamma(a+k)\Gamma(b+k)\Gamma(c)}{\Gamma(a)\Gamma(b)\Gamma(c+k)} \frac{x^k}{k!} \tag{C.218}
\]

and the confluent hypergeometric function \( {}_1F_1(a, b, x) \) as:

\[
{}_1F_1(a, c, x) := \sum_{k=0}^{\infty} \frac{\Gamma(a+k)\Gamma(c)}{\Gamma(a)\Gamma(c+k)} \frac{x^k}{k!} \tag{C.219}
\]

The radial wavefunctions of the continuum of the hydrogen problem can be written in terms of the confluent hypergeometric function.

\[
\hat{R}_{k,l}(r) = \left[ \sqrt{\frac{8\pi k}{1-e^{-2\pi r/c}}} \prod_{s=1}^{l} \frac{1}{s^2 + \frac{1}{k^2}} \right] \frac{1}{(2l+1)!} (2kr)^l e^{-ikr} {}_1F_1\left( \frac{l}{2}, \frac{l+1}{2}, 2l+2, 2ikr \right) \tag{C.220}
\]

Also note, that there is a connection to the generalized Laguerre polynomials for integers \( n \) and \( m \), which can be derived by applying the Leibniz rule to their definition:

\[
L^{(m)}_n(x) = (-1)^m \frac{(n!)^2}{m!(n-m)!} {}_1F_1(-n-m, m+1, x) \tag{C.221}
\]

If the following integral exists then following identity is true:

\[
\int_0^{\infty} x^\beta e^{-\lambda x} {}_1F_1(a, c, x)dx = \frac{\Gamma(\beta+1)}{\lambda^{\beta+1}} {}_2F_1(a, \beta+1, c, \lambda^{-1}) \tag{C.222}
\]
Now due to the orthogonality relation (C.208) only two summands do not vanish when integrated with these identities, the binomial theorem and some elementary algebra one can derive:

\[ \int_0^\infty x^\beta e^{-\lambda x} F_1(a, c, x) dx = \int_0^\infty x^\beta e^{-\lambda x} \sum_{k=0}^\infty \frac{\Gamma(a+k)\Gamma(c) x^k}{\Gamma(a)\Gamma(c+k) k!} dx \]

\[ = \sum_{k=0}^\infty \frac{\Gamma(a+k)\Gamma(c)}{\Gamma(a)\Gamma(c+k)} \frac{x^{k+\beta}}{k!} \]

\[ = \frac{\Gamma(\beta+1)}{\lambda^{\beta+1}} \sum_{k=0}^\infty \frac{\Gamma(a+k)\Gamma(b+k)\Gamma(c) x^k}{\Gamma(a)\Gamma(b)\Gamma(c+k) k!} \]

With these identities, the binomial theorem and some elementary algebra one can derive:

\[ I_R^2(n) := \left[ \int_0^\infty r^3 R_{n,1}(r) R_{1,0}(r) dr \right]^2 = \frac{2^8 n^7}{(n^2 - 1)^5} \left( \frac{n - 1}{n + 1} \right)' \]

(C.224)

and

\[ \tilde{I}_R^2(k) := \left[ \int_0^\infty r^3 \tilde{R}_{k,1}(r) R_{1,0}(r) dr \right]^2 = \frac{32\pi \cdot 24^2 k^2}{9(1 - e^{-\frac{2\pi k}{k}})(1 + k^2)^4} |F(i\frac{k}{k} + 2, 5, 4, 1 + i k)|^2 \]

(C.225)

### C.6 Evaluation of radial matrix elements

Here the matrix-elements \( \langle nl \pm 1 | r | nl \rangle \) are evaluated. The results are:

\[ \langle nl + 1 | r | nl \rangle = -N_{n,l+1} N_{n,l} \cdot n^5 \frac{3 \cdot (n + l + 1)!}{8 \cdot (n - l - 2)!} \]

\[ \langle nl - 1 | r | nl \rangle = -N_{n,l-1} N_{n,l} \cdot n^5 \frac{3 \cdot (n + l)!}{8 \cdot (n - l - 1)!} \]

(C.226)

Proof:

Let’s start with the definition of the matrix-element, substitute \( \rho := \frac{2\pi k}{k} \) in the integral, and use the relations (C.207)

\[ \langle n, l + 1 | r | n, l \rangle = N_{n,l+1} N_{n,l} \int_0^\infty r^3 [e^{\frac{2\pi k}{k} \rho} \rho^{l+1} L_{n+1}^{(2l+3)}(\rho)] \cdot [e^{\frac{2\pi k}{k} \rho} L_{n-l-1}^{(2l+1)}(\rho)] dr \]

\[ = \frac{n^4 \cdot N_{n,l+1} N_{n,l}}{16} \int_0^\infty \rho^{2l+4} e^{-\rho} L_{n+1}^{(2l+3)}(\rho) \cdot L_{n-l-1}^{(2l+1)}(\rho) d\rho \]

\[ = \frac{n^4 \cdot N_{n,l+1} N_{n,l}}{16} \int_0^\infty \rho^{2l+4} e^{-\rho} [L_{n-l-2}^{(2l+4)}(\rho) - L_{n-l-4}^{(2l+4)}(\rho)] \cdot [L_{n-l-1}^{(2l+3)}(\rho) - 3L_{n-l-2}^{(2l+4)}(\rho) - 3L_{n-l-2}^{(2l+4)}(\rho) - L_{n-l-4}^{(2l+4)}(\rho)] d\rho \]

(C.227)

Now due to the orthogonality relation (C.208) only two summands do not vanish when integrated which yields

\[ \langle n, l + 1 | r | n, l \rangle = -3 \frac{n^4 \cdot N_{n,l+1} N_{n,l}}{16} \left[ \frac{(2l + 4 + n - l - 2)!}{(n - l - 2)!} + \frac{(2l + 4 + n - l - 3)!}{(n - l - 3)!} \right] \]

\[ = -N_{n,l+1} N_{n,l} \cdot n^5 \frac{3 \cdot (n + l + 1)!}{8 \cdot (n - l - 2)!} \]

(C.228)
The second relation can be obtained by simply substituting $l \rightarrow l - 1$. This is valid because the radial wavefunction is real.
References


