Dispersion forces in a four-component density functional theory framework

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The main purpose of this thesis is to implement the Gauss–Legendre quadrature for the dispersion coefficient. This has been done and can be now be made with different number of points. The calculations with this implementation has shown that the relativistic impact on helium, neon, argon and krypton is largest for krypton, that has the highest charge of its nucleus. It was also seen that the polarizability of neon as a function of the imaginary angular frequency decreases monotonically from a static value.

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To my parents
Abstract

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Chapter 1

Introduction

Atoms, ions and molecules can interact with each other in different ways. One interaction is achieved through covalent bonds and another through electrostatic forces between ions. Then there exists a third kind of interaction: the van der Waals force. This force is an interaction between molecules or atoms, that are either permanent dipoles or induced dipoles. The interaction can also be between a permanent dipole and an induced dipole. The van der Waals force is not a strong interaction compared to the two other interactions. However, it plays an important role in nature. There are some atoms that are called noble gases. Their outer shell of valence electrons is filled and because of that they do not tend to couple with other atoms or molecules with covalent bonds. Because of their structure, they do not become ions and consequently they cannot interact with other ions through electrostatic forces. If the van der Waals force did not exist neon atoms would not interact with each other. Because they do interact, the van der Waals force or the dispersion force is important for noble gases \[4\]. Without it there would not exist a solid state for neon. The dispersion force between the atoms depends on their ability to become induced dipoles. One way of inducing dipoles is to let an electric field act on the atoms. How the quantum mechanical electric dipole moment is affected by an acting field is described by something called polarizability. The polarizability is dependent on the frequency of the electric field. The interaction between the atoms implies that there is a potential and this one is called the Casimir–Polder potential. From this potential the dispersion coefficient is defined, which itself depends on the polarizabilities between the interacting atoms \[7\]. This thesis pays attention to the dispersion coefficients for helium, neon, argon and krypton, which are all noble gases. This thesis takes imaginary frequencies and relativistic effects into account. In order to calculate the polarizabilities the Hartree–Fock method is used. This method is needed to determine approximate wave functions, because the Schrödinger equation can in this case not be solved exactly. The dispersion forces might be useful for studying of protein folding.
Chapter 2

Theory

2.1 Hartree–Fock theory

A molecule is a many-electron system and therefore one of the needed basic concepts is many-electron wave functions. When dealing with many-electron systems a specific method, Hartree–Fock, is often used. This is a way to determine approximate wave functions, which is needed because the Schrödinger equation cannot always be solved exactly. A description of the method is found in the book Modern Quantum Chemistry by A. Szabo and N. S. Ostlund [14], which is the basis for this theory section.

First of all, attention is payed to some definitions and notation. An orbital is defined as a wave function for a single particle, that in the scope of this thesis is an electron. In the case of molecules the wave function of each electron is called a molecular orbital. This kind of wave function has a spatial part and also possesses the spin property and because of the fact that the Hamiltonian in the nonrelativistic case only acts on the spatial part of the wave function, the Hamiltonian can be viewed as a product of two functions. These two are the spatial orbital and the spin function respectively. The spatial orbital is denoted \( \psi_i(r) \) and depends on the position vector \( r \) and has the normal probabilistic interpretation. For the spin part the two spin functions \( \alpha(w) \) and \( \beta(w) \) for spin–up and spin–down are used. The product of a spatial orbital and a spin function defines a spin orbital that is written \( \chi(x) \) where \( x \) stands for space and spin coordinates. Due to the fact that there are two spin directions, one and the same spatial orbital can be a part of two different spin orbitals. These are

\[
\chi(x) = \begin{cases} 
\psi(r)\alpha(w), & \text{if spin–up} \\
\psi(r)\beta(w), & \text{if spin–down}
\end{cases}
\]  

(2.1)

It is necessary that the many-electron wave functions are antisymmetric. This is known as the Pauli exclusion principle and means that only a single electron can occupy each spin orbital. In order to achieve that, normalized Slater determinants are used. The simplest case is a two–electron system. A Slater determinant is
then denoted and written as follows

\[
\Psi(x_1, x_2) = |\psi_i \psi_j \rangle = \frac{1}{\sqrt{2}} (\chi_i(x_1) \chi_j(x_2) - \chi_j(x_1) \chi_i(x_2))
\]  

(2.2)

where a normalization constant has been introduced. It is now obvious that

\[
\Psi(x_1, x_2) = -\Psi(x_2, x_1)
\]  

(2.3)

For a \(N\)-electron system the Slater determinant can be generalized according to

\[
\Psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \chi_i(x_1) \chi_j(x_2) \ldots \chi_k(x_N)
\]  

(2.4)

As said in the beginning, the Hartree–Fock method uses approximations of wave functions. To get approximative wave functions the variation principle is used. The variation principle tells, that the energy of the ground state of an approximate wave function is always to high. Thus one measure of the quality of a wave function is its energy: the lower the energy, the better the wave function. The concept of the variation principle is to use a normalized trial function, which depends on certain parameters and vary these until the energy reaches a minimum. That is to minimize

\[
E = \langle 0 | \hat{H} | 0 \rangle
\]  

(2.5)

where \( \langle 0 \rangle \) is a Slater determinant, which describes the ground state of an \(N\)-electron system and \( \hat{H} \) is the electronic Hamiltonian. In this context atomic units are used. In atomic units the mass of an electron, the elementary charge, the reduced Planck’s constant and the Bohr radius is set to 1. In these units the electronic Hamiltonian looks like

\[
\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_A \frac{1}{r_iA} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}
\]  

(2.6)

The second term is the potential that arises, when the nuclei of the molecule interact with the electrons. The third term is the potential that depends on the interaction between electrons. When using the variation principle, the spin orbitals can be varied. The point is to find the optimal spin orbitals. The result will be an eigenvalue equation named the Hartree–Fock equation. It looks like

\[
\hat{f} \chi_i(x_i) = \varepsilon_i \chi_i(x_i)
\]  

(2.7)

The complicated many-electron problem is now reduced to a one-electron problem. The operator \( \hat{f} \) is named the Fock operator and it takes the form

\[
\hat{f} = -\frac{1}{2} \nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{|r - R_A|} + \hat{H}^{\text{HF}}(r)
\]  

(2.8)
2.1 Hartree–Fock theory

where $\hat{\psi}^{HF}(\mathbf{r})$ is the average potential due to the other electrons acting on the $i$th electron and it is named the Hartree–Fock potential. It can be expressed as

$$\hat{\psi}^{HF} = \sum_{b=1}^{N} (\hat{J}_{b}(i) - \hat{K}_{b}(i))$$  \hspace{1cm} (2.9)$$

where $N$ is the number of occupied spin orbitals. If the $j$th electron acts on the $i$th, the average potential for electron $i$ at position $\mathbf{r}_i$ can be calculated. This is achieved through defining the Coulomb operator as follows

$$\hat{J}_{b}(i) = \int \frac{\lvert \chi_{b}(i) \rvert^2}{r_{ij}} d\mathbf{x}_j$$  \hspace{1cm} (2.10)$$

If then $\hat{J}_{b}(i)$ is summed over all occupied $b$ except $b = a$, the result will be the total averaged potential for electron $i$ at position $\mathbf{r}_i$, which is the potential by virtue of interaction from all the electrons other than the $i$th acting on the $i$th electron. Furthermore, there is another interaction between the electrons. That is the exchange interaction and it is because of the antisymmetric nature of the Slater determinant and it has no classical counterpart. The operator, $\hat{K}_{b}(i)$, is defined by how it acts on a spin orbital, $\chi_{a}(i)$

$$\hat{K}_{b}(i)\chi_{a}(i) = \left[ \int \frac{\chi_{b}^{*}(j)\chi_{b}(j)dx'}{r_{ij}} \right] \chi_{b}(i)$$  \hspace{1cm} (2.11)$$

Like the Coulomb operator the exchange operator can be summed over all $b$ except $b = a$, in order to get the total exchange potential. It is now easy to realize that

$$\left[ \hat{J}_{a}(i) - \hat{K}_{a}(i) \right] \chi_{a}(i) = 0$$  \hspace{1cm} (2.12)$$

Because of Eq. (2.12) the terms from $b = a$ can be included in the sum in Eq. (2.9). Eq. (2.7) is nonlinear and it must be solved iteratively. The reason for the equation being nonlinear is that the average potential depends on the spin orbitals of the other electrons. One of the steps that is done, in order to solve the equation, is to eliminate the spin from the Hartree–Fock equation. That is done by integrating out the spin functions and the result will be the following equation

$$\hat{f}(\mathbf{r}_i)\psi_i(\mathbf{r}_i) = \varepsilon_i\psi_i(\mathbf{r}_i)$$  \hspace{1cm} (2.13)$$

where the Fock operator will be

$$\hat{f}(1) = \hat{h}(1) + \frac{N}{2} \left[ 2\hat{J}_{a}(1) - \hat{K}_{a}(1) \right]$$  \hspace{1cm} (2.14)$$

and

$$\hat{h}(1) = -\frac{1}{2\overline{\mathbf{r}}^2} - \sum_{A=1}^{M} \frac{Z_A}{\overline{\mathbf{r}}_{iA}}$$  \hspace{1cm} (2.15)$$
The number of occupied spatial orbitals, which are closed shelled. Next step in the process of solving the equation is to introduce a set of \( K \) known spatial basis functions \( \{ \phi_\mu(r) \} \), where \( \mu = 1, 2, \ldots, K \). Then the unknown molecular orbitals are expanded as a linear combination of the basis set

\[
\psi_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu \quad i = 1, 2, \ldots, K
\]  

(2.16)

If the basis set were complete, the expansion would be exact, but due to practical computational reasons a finite set is used. Different sets give different accuracy of the expansion of the molecular orbitals. The problem that now is needed to be solved, is to determine the expansion coefficients \( C_{\mu i} \). With Eq. (2.16) in Eq. (2.13), the equation beneath is hereby obtained.

\[
\hat{f}^{(1)} \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu^{(1)} = \varepsilon_i \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu^{(1)}
\]

(2.17)

Last equation can be turned to a matrix equation and is then called the Roothan equations. The solution will consists of a set \( \{ \chi_k \} \) of orthonormal Hartree–Fock spin orbitals with orbital energies \( \{ \varepsilon_k \} \). The \( N \) spin orbitals with the lowest energies are chosen to be occupied. If a Slater determinant is formed from these, it yields the Hartree–Fock ground state wave function in the given basis set.

The most important factor, when talking about basis sets, is the number of functions to be used. The smallest number of functions possible is a minimal basis set. Only enough functions are employed to contain all the electrons of the neutral atom \( \text{H} \). Some commonly used type of basis functions are the Gaussian Type Orbitals. They take the functional form

\[
\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{2n-2-l}e^{-\zeta r^2}
\]

(2.18)

\( N \) is a normalization constant and \( Y_{l,m} \) are spherical harmonic functions. The parameter \( \zeta \) is called Gaussian orbital exponent.

### 2.2 Polarizability

When a molecule is subjected to a time-dependent electric field, the field can in many circumstances be treated as a perturbation. If the electric field takes the form,

\[
F_j(t) = \sum_{k=-N}^{N} F_j^{\omega k} e^{-i\omega_k t}, k \neq 0
\]

(2.19)

and for real fields it is valid that

\[
(F^{\omega_k})^* = F^{-\omega_k} = F^{\omega_{-k}}
\]

(2.20)
2.2 Polarizability

the electric dipole moment, $\mu_i(t)$, is now

$$\mu_i(t) = \mu_i^0 + \sum_k \alpha_{ij}(\omega_k)F_j \omega_k e^{-i\omega_k t} + \ldots \quad (2.21)$$

where

$$\mu_i(t) = \langle \Psi(t)|\hat{\mu}_i|\Psi(t)\rangle \quad (2.22)$$

and

$$\mu_i^0 = \langle 0|\hat{\mu}_i|0\rangle \quad (2.23)$$

where $\hat{\mu}_i$ is the electric dipole operator. The purpose of this part is to find an expression for $\alpha_{ij}$, which is called polarizability. This section is based on an article [13]. The wave function will be time developed and that is ruled by the time-dependent Schrödinger equation with the Hamiltonian

$$\hat{H} = \hat{H}_0 - \hat{\mu}_i F_i(t) = \hat{H}_0 - \hat{V}(t) \quad (2.24)$$

A parametrization of the time dependence is

$$|\Psi(t)\rangle = e^{-\hat{P}(t)}|0\rangle \quad (2.25)$$

$|0\rangle$ is the time-independent ground state. $\hat{P}(t)$ is an anti-Hermitian operator and is defined

$$\hat{P}(t) = \sum_{n>0} [P_n(t)|n\rangle\langle 0| - P_n^*(t)|0\rangle\langle n|] \quad (2.26)$$

$$= \sum_{n>0} [P_n(t)\hat{\Omega}_n - P_n^*(t)\hat{\Omega}_n^\dagger]$$

When $\hat{P}(t)$ is anti-Hermitian, $e^{-\hat{P}}$ is unitary. It is now interesting to develop $P_n$ in time. For doing this, Ehrenfest’s theorem is applicable. This is valid for any time-independent operator $\hat{\Omega}$. The reader should be familiar with this, but it is given here

$$\frac{d}{dt} \langle \hat{\Omega} \rangle = \frac{1}{\hbar i} \langle \Psi(t)|[\hat{\Omega}, \hat{H}]|\Psi(t)\rangle \quad (2.27)$$

$P_n(t)$ is expanded to first order in the perturbation and that together with Ehrenfest’s theorem with $\hat{\Omega}_n^\dagger$ as time-independent operator give a first order equation which reads

$$\frac{d}{dt} \langle 0|[\hat{P}^{(1)}(t), \hat{\Omega}_n^\dagger]|0\rangle = \frac{1}{\hbar i} \left[\langle 0|\hat{P}^{(1)}(t)|\hat{\Omega}_n^\dagger, \hat{H}_0\rangle \right]|0\rangle + \langle 0|\hat{\Omega}_n^\dagger, \hat{V}(t)|0\rangle \right] \quad (2.28)$$

After derivation and some algebra the following differential equation for $\hat{P}^{(1)}_n$ is received

$$\hat{P}^{(1)}(t) + i\omega_n \eta_n \hat{P}^{(1)}(t) = -\frac{1}{\hbar i} \langle n|\hat{V}(t)|0\rangle \quad (2.29)$$

where

$$\hbar \omega_n = (E_n - E_0) \quad (2.30)$$
In order to get a solution of Eq. (2.29), $P^{(1)}_n(t)$ is expanded in its Fourier series according to

$$P^{(1)}_n(t) = \sum_{k=-N}^{N} P^{(1)}_n(\omega_k)e^{-i\omega_k t}$$  \hspace{1cm} (2.31)

Eq. (2.31) is put in Eq. (2.29) and after derivation of the Fourier series of $P^{(1)}_n(t)$, some calculation and remembering the expression for $\hat{V}(t)$, $P^{(1)}_n(t)$ is given as

$$P^{(1)}_n(t) = \frac{1}{\hbar} \sum_{k=-N}^{N} \langle n|\hat{\mu}_i|0\rangle \omega_k \omega_{n0} e^{\omega_k t}$$  \hspace{1cm} (2.32)

It is now time to introduce the useful Baker–Campbell–Hausdorf formula

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n\hat{B}$$ \hspace{1cm} (2.33)

$\hat{A}$ is called superoperator and is defined by

$$\hat{A}\hat{B} = [\hat{A}, \hat{B}]$$ \hspace{1cm} (2.34)
2.3 Casimir–Polder potential and the energy difference method

The first order of $\mu_i(t)$ can now be written

$$\mu_i(t) = \langle 0 | \hat{E} \hat{\mu}_i e^{-\hat{H}t} | 0 \rangle$$

$$= \langle 0 | \hat{\mu}_i | 0 \rangle + \langle 0 | \left[ \hat{P}^{(1)}, \hat{\mu}_i \right] | 0 \rangle$$

$$= \mu_i^0 + \sum_{n>0} \left[ P_n^{(1)}(t) \langle n \vert \hat{\mu}_i \vert 0 \rangle + P_n^{(1)}(t) \langle 0 \vert \hat{\mu}_i \vert n \rangle \right]$$

$$= \mu_i^0 + \frac{1}{\hbar} \sum_{n>0} \sum_{k=-N}^N \left[ \langle 0 \vert \hat{\mu}_j \vert n \rangle F_{kj} e^{i \omega_k t} \langle n \vert \hat{\mu}_i \vert 0 \rangle + \frac{\langle n \vert \hat{\mu}_j \vert 0 \rangle}{\omega_{n0} - \omega_k} F_{kj} e^{i \omega_k t} \langle 0 \vert \hat{\mu}_i \vert n \rangle \right]$$

$$= \mu_i^0 + \frac{1}{\hbar} \sum_{k=-N}^N \left[ \sum_{n>0} \left( \frac{\langle 0 \vert \hat{\mu}_j \vert n \rangle \langle n \vert \hat{\mu}_j \rangle}{\omega_{n0} - \omega_k} + \frac{\langle 0 \vert \hat{\mu}_j \vert n \rangle \langle n \vert \hat{\mu}_i \rangle}{\omega_{n0} + \omega_k} \right) \right] F_{kj} e^{i \omega_k t}$$

(2.35)

If the last expression is compared to Eq. (2.21), the goal to find the polarizability is finally reached

$$\alpha_{ij}(\omega_k) = \frac{1}{\hbar} \sum_{n>0} \left[ \frac{\langle 0 \vert \hat{\mu}_j \vert n \rangle \langle n \vert \hat{\mu}_j \rangle}{\omega_{n0} - \omega_k} + \frac{\langle 0 \vert \hat{\mu}_j \vert n \rangle \langle n \vert \hat{\mu}_i \rangle}{\omega_{n0} + \omega_k} \right]$$

(2.36)

Figure 2.1 shows how the polarizability for a water molecule depends on the photon energy. The polarizability will be divergent when $\omega_k$ gets close to $\omega_{n0}$, i.e. the resonance energies. Figure 2.2 shows the orientation in space of the water molecule.

2.3 Casimir–Polder potential and the energy difference method

The interactions between atoms or molecules with dipole moments can be classified into two categories: short range and long range [3]. Short range interactions occur
when molecules are so close to each other, that their electronic wave functions overlap. If they not are so close to each other, the overlap will be negligible and that is characterised as a long range interaction. Interactions between induced dipoles are called induced dipole-dipole dispersion interactions.

The most general form of long-range interaction is the Casimir-Polder force. The van der Waals force is a special case of the Casimir–Polder force, that is the interaction in the entire long-range region. To have van der Waals interaction, the separation must be intermediate. From here on, attention is only paid to long range interactions and especially in the van der Waals region. For the Casimir–Polder region, which includes the van der Waals region, the interaction energy or potential can be calculated from the polarizabilities of the interacting objects. The Casimir–Polder potential is expressed as the following integral \[3\], where \(A\) stands for an atom or molecule and \(B\) is another atom or molecule.

\[
V_{CP}(r) = -\frac{\hbar}{4\pi r^6} \int_0^\infty d\omega \bar{\alpha}^A(i\omega)\bar{\alpha}^B(i\omega)e^{-2\omega r/c} [3 + 6(\omega r/c) + 5(\omega r/c)^2 + 2(\omega r/c)^3 + (\omega r/c)^4]
\]

(2.37)

Here \(\bar{\alpha}^A\) and \(\bar{\alpha}^B\) represent the isotropic average polarizability and it is defined as

\[
\bar{\alpha}^A = \frac{1}{3}[\alpha_{xx}^A + \alpha_{yy}^A + \alpha_{zz}^A]
\]

(2.38)

The integral in Eq. (2.37) is further reduced, when only the van der Waals region is concerned

\[
V_{vdW}(r) = -\frac{3\hbar}{4\pi r^6} \int_0^\infty d\omega \bar{\alpha}^A(i\omega)\bar{\alpha}^B(i\omega)
\]

(2.39)

A new constant \(C_{6,AB}\) is now introduced, so that Eq. (2.39) is written

\[
V_{vdW}(r) = -\frac{C_{6,AB}}{r^6}
\]

(2.40)

The constant is called induced dipole-dipole dispersion coefficient. Another method for calculation of the interaction energy is the energy difference method. The principle of this method is to subtract the energy for each isolated dipole from the energy of the system, in which the separated dipoles interact with each other. If the dipoles are A and B this can be written as

\[
\Delta E(R) = E(R) - [E_A + E_B]
\]

(2.41)

The energy can be calculated with different methods. One is the Hartree–Fock method, but this method lacks electronic correlation and gives a potential that differs much from the one obtained from calculations with Eq. (2.55). A method that takes care of electronic correlation is the second order Møller–Plesset method, where the electronic correlation is included in a pertubative way. It is also called MP2 \[13\]. Figure 2.3 shows the potential, when two neon atoms interact. This figure shows the potential with the energy difference method with both Hartree–Fock and MP2 method, whose points come from an article on the subject \[10\].
2.4 Relativistic quantum mechanics

The Schrödinger equation can be applied for non-relativistic cases. When the velocities of the particles that are described are large, the phenomena described will be affected by relativistic effects and because of that the Schrödinger equation will not give a correct description. For electrons that have spin 1/2, another equation namely the Dirac equation can be applied. Here is a short description with the book Quantum Mechanics by B. H. Brandsen and C. J. Joachain as source [2].

Dirac wanted his wave equation to have the same form as the Schrödinger equation. That form is

$$i\hbar \frac{d}{dt}\Psi = \hat{H}\Psi$$

(2.42)

The wave function for spin 1/2 has four components and it is called a four-
component spinor. It can be written as

\[ \Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} \]  

(2.43)

In the case of the free particle, the Hamiltonian looks like

\[ \hat{h}_D = c\hat{\alpha} \cdot \hat{p} + \beta mc^2 \]  

(2.44)

\[ = c \sum_k \hat{\alpha}_k \hat{p}_k + \beta mc^2, k = x, y, z \]

where

\[ \hat{p} = -i\hbar \nabla \]  

(2.45)

and \((\hat{p})_k\) stands for the Cartesian components of \(\hat{p}\). The Dirac equation can now be expressed as

\[ i\hbar \frac{d}{dt} \Psi = -i\hbar c\hat{\alpha} \cdot \nabla \Psi + \beta mc^2 \Psi \]  

(2.46)

It should be emphasized that the equation is a matrix equation and therefore the components \((\alpha_x, \alpha_y, \alpha_z)\) of \(\hat{\alpha}\) and \(\beta\) are matrices. When the spin is 1/2, the matrices will be \(4 \times 4\) matrices. They will be

\[ \hat{\alpha}_k = \begin{pmatrix} 0 & \hat{\sigma}_k \\ \hat{\sigma}_k & 0 \end{pmatrix} \]  

(2.47)

\[ \hat{\beta} = \begin{pmatrix} \hat{I} & 0 \\ 0 & -\hat{I} \end{pmatrix} \]  

(2.48)

\(\sigma_k\) and \(I\) are \(2 \times 2\) matrices and \(\sigma_k\) stands for the three Pauli spin matrices \((\sigma_x, \sigma_y, \sigma_z)\).

In order to treat the motion of electrons in a molecule, the interaction with an external field must be described. The Dirac Hamiltonian for an electron will in atomic units take the form

\[ \hat{h}_D = \hat{V} + c\hat{\alpha} \cdot [\hat{p} - \hat{A}] + \beta c^2 \]  

(2.49)

\(\hat{V}\) and \(\hat{A}\) is the external scalar potential respectively the vector potential. The external field includes the interaction between the electron and the nuclei. To fully describe the motion of electrons in a molecule, a many-electron Hamiltonian that also treats interaction between the electrons is needed. A way to describe the interaction between the electrons, is to use the nonrelativistic Coulomb operator

\[ \hat{g}(i, j) = \frac{1}{r_{ij}} \]  

(2.50)

Now, the Hamiltonian for an \(N\)-electron system can finally be expressed. This one is called the Dirac-Coulomb-Breit Hamiltonian

\[ \hat{H} = \sum_{i=1}^{N} \hat{h}_D + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i, j) \]  

(2.51)
2.5 Gauss–Legendre quadrature

For the integration that is needed, in order to calculate the dispersion coefficient, a numeric integration method called Gauss–Legendre quadrature is used. The variable $x$ is integrated from $-1$ to $1$ and the quadrature is a sum. Only a few values of the function of $x$ are calculated and included in the sum. These values are called abscissas. The abscissas are not randomly chosen, but decided by the method. In the sum there is also a weight for each abscissa. The quadrature formula is given below where $a_i$ is the weight for each abscissa $x_i$

$$\int_{-1}^{1} f(x)dx \approx \sum_{i=1}^{n} a_i f(x_i) \quad (2.52)$$

The integral to which this formula will be applied, is the Casimir–Polder potential in the van der Waals region (Eq. (2.39)). Because the calculation of the Casimir–Polder potential and the dispersion coefficient is an integration from $0$ to $\infty$, a variable substitution must be made. One substitution that can be made for imaginary angular frequencies is given in [12]. This is

$$i\omega = i\omega_0 \frac{(1 - x)}{1 + x} \quad (2.53)$$

If the derivative of $\omega$ with respect to $x$ is taken, this will yield

$$d\omega = -\omega_0 \frac{2dx}{(1 + x)^2} \quad (2.54)$$

The result, if the substitution is made and if only the dispersion coefficient and not the potential is considered, will be

$$C_{6,AB} = \frac{6\hbar\omega_0}{\pi} \int_{-1}^{1} \frac{dx \tilde{\alpha}^A(x) \tilde{\alpha}^B(x)}{(1 + x)^2} \quad (2.55)$$

The values of the polarizabilities for which the integral should be evaluated, is given by Eq. (2.53) with the restriction $-1 \leq x \leq 1$. Furthermore, if a dimer with two atoms of the same kind is considered, the following will be valid

$$\tilde{\alpha}^A(x) = \tilde{\alpha}^B(x) = \tilde{\alpha}(x) \quad (2.56)$$

For a dimer Eq. (2.55) can be written with the dispersion coefficient denoted only with $C_6$

$$C_6 = \frac{6\hbar\omega_0}{\pi} \int_{-1}^{1} \frac{dx \tilde{\alpha}^2(x)}{(1 + x)^2} \quad (2.57)$$

It is now time to conclude this section with its main result, which is given by approximating the last integral with a Gauss–Legendre quadrature. Here atomic
units are used and therefore $\hbar$ equals 1. The quadrature formula Eq. (2.52) with the integral in Eq. (2.57) gives

$$C_6 = \frac{6\omega_0}{\pi} \int_{-1}^{1} \frac{dx}{[1 + x]^2} \approx \frac{6}{\pi} \sum_{i=1}^{n} a_i \frac{\bar{\alpha}^2(x_i)}{[1 + x_i]^2}$$

(2.58)

### 2.6 The London approximation

In contrast to the previous section, where a numerical way was used to evaluate the dispersion coefficient, Eq. (2.5) contains an analytical method. This method is called the London approximation. The dispersion coefficient is here given without indices as

$$C_6 = \frac{3h}{\pi} \int_{0}^{\infty} d\omega \bar{\alpha} A(i\omega) \bar{\alpha} B(i\omega)$$

(2.59)

First the polarizability is approximated with a function, namely

$$\bar{\alpha}(i\omega) = \frac{\bar{\alpha}(0)}{1 + (\omega/\omega_1)}$$

(2.60)

$\omega_1$ is here an effective angular frequency. If now Eq. (2.60) is put in Eq. (2.59) the resulting integral can be evaluated analytically. The following relation will then be obtained

$$C_6 = \frac{3\omega_1}{4} \bar{\alpha}_A(0) \bar{\alpha}_B(0)$$

(2.61)

If $C_6$ happens to be known, the effective angular frequency can be calculated according to

$$\omega_1 = \frac{4C_6}{3} \frac{1}{\bar{\alpha}_A(0) \bar{\alpha}_B(0)}$$

(2.62)
Chapter 3
Results and Discussion

3.1 Computational details

First, all calculations are carried out in atomic units. Consequently, computed values in this result chapter are also in atomic units. The reason for the choice of using atomic units is because it is convenient, when the focus is on electrons and electronic properties. Atomic units in the calculations means for example that $\hbar$ in the implementations of Eq. (2.36) and Eq. (2.58) are set to one. In addition, as mentioned before the electronic Hamiltonian is in atomic units.

Second, the softwares being used consists of two programs, namely Dalton [1] and Dirac [5]. These two are made for quantum chemical calculations. The main difference between them is that Dalton is nonrelativistic and Dirac relativistic. For calculations of the dispersion coefficient Dirac has been locally modified. This means that Eq. (2.58) has been implemented in Dirac. For the Gauss–Legendre quadrature 6, 8, 10, 12, 14 or 16 number of points can be selected. However, an error remains to be fixed in the Dirac code, so the computations of the polarizability does not always converge. This has also effects on the convergence of the dispersion coefficient.

Third, the calculations that are based on Hartree–Fock theory are computed with four different basis sets. These are aug-cc-pVDZ(augmented correlation consistent polarized Valence Double Zeta), daug-cc-pVDZ(doubly augmented correlation consistent polarized Valence Double Zeta), taug-cc-pVTZ(triply augmented correlation consistent polarized Valence Triple Zeta) and qaug-cc-pVQZ(quadruply augmented correlation consistent polarized Valence Quadruple Zeta)[8][15][16][17]. They were here ordered in their size and they are all Gaussian basis sets. Double Zeta means a doubling of all basis functions of the minimal basis. Triple Zeta means that the basis contains three times as many functions as the minimal basis and Quadruple Zeta means four times as many functions as the minimal basis set. To augment the basis sets is to extend them with one or many extra functions, so called diffuse functions, that better describe the long range behaviour. In this context that is done with one, two, three or four extra functions.

The constant $\omega_0$ in Eq. (2.58) is taken from an article [12], which suggests
$\omega_0 = 0.3$ atomic units.

3.2 Calculations on neon

In this thesis the noble gases and especially neon has attracted the most attention. The noble gases have their outer shell of valence electrons filled and because of that, they are not very reactive. An interaction that are important for them is the van der Waals interaction. On account of that fact, they are interesting to study. Why neon is chosen is because it is not too heavy and that the calculations by virtue of that do not require to much computer power. The atomic number for neon is 10.

First the behaviour of the polarizability depending on the imaginary angular frequency was studied. Eq. (2.36) was already implemented in Dalton with an iterative method. The basis set for the calculation was aug-cc-pVTZ, which because it is the second best, ensures relatively well converged results. In Figure 3.1, the polarizability as a function of the imaginary angular frequency, $\alpha(i\omega)$, is plotted.

![Figure 3.1. Polarizability of neon.](image)

The polarizability decreases monotonically from its static value, called the static polarizability, towards zero. The static polarizability is in other words the
3.2 Calculations on neon

polarizability at the angular frequency zero. For the dispersion coefficient the calculations were made with imaginary angular frequencies and they were calculated with an implementation of Eq. (2.58).

Table 3.1. Nonrelativistic static polarizability and dispersion coefficients of neon for different basis sets.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>$\alpha(0)$</th>
<th>$C_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVDZ</td>
<td>1.831</td>
<td>4.121</td>
</tr>
<tr>
<td>daug-cc-pVDZ</td>
<td>2.353</td>
<td>5.461</td>
</tr>
<tr>
<td>taug-cc-pVTZ</td>
<td>2.375</td>
<td>5.536</td>
</tr>
<tr>
<td>qaug-cc-pVQZ</td>
<td>2.380</td>
<td>5.538</td>
</tr>
</tbody>
</table>

Table 3.2. $C_6$ for neon calculated with Gauss–Legendre with different number of points.

<table>
<thead>
<tr>
<th>Number of points</th>
<th>$C_6$ with Dalton</th>
<th>$C_6$, analytic $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 points</td>
<td>5.523588</td>
<td>5.075460</td>
</tr>
<tr>
<td>8 points</td>
<td>5.535445</td>
<td>5.054295</td>
</tr>
<tr>
<td>10 points</td>
<td>5.535607</td>
<td>5.056596</td>
</tr>
<tr>
<td>12 points</td>
<td>5.535602</td>
<td>5.056360</td>
</tr>
<tr>
<td>14 points</td>
<td>5.535452</td>
<td>5.056383</td>
</tr>
<tr>
<td>16 points</td>
<td>5.535484</td>
<td>5.056380</td>
</tr>
<tr>
<td>Analytic</td>
<td></td>
<td>5.056381</td>
</tr>
</tbody>
</table>

Thereafter the effects of different kinds of basis sets were studied. According to theory, a larger set would render better converged results. To see that, the dispersion coefficient was calculated with a 12 points Gauss–Legendre quadrature. This calculation was based on the polarizabilities, that were calculated for each abscissa. This procedure was done four times. Every time a different basis set was used to generate the values. Table 3.1 shows the results of the calculations. The last row contains experimental data. To calculate more converged values not only better basis sets are needed, but improved methods.

The experimental values of the static polarizability and the dispersion coefficient come from [11] and there many different methods are used. The article suggests that experimental methods are better than the theoretical ones and therefore the experimental values are here seen as reference values. The values of the different basis sets are here computed with the Hartree–Fock method. The most significant change of the values is between the basis set aug-cc-pVDZ and daug-cc-pVTZ. It can also be seen that the values converge towards the experimental values as the basis sets get better.

As said before, the Gauss–Legendre quadrature could be made with different numbers of points. In order to try the quadrature with a varied number of points for neon, the polarizabilities in the basis set taug-cc-pVTZ was calculated for a different number of points. Thereafter the dispersion coefficient was calculated.
Besides, the polarizabilities were computed analytically with the London approximation i.e. Eq. (2.60). With these, the dispersion coefficients with a Gauss–Legendre quadrature with different number of points were calculated. Table 3.2 contains the results of these computations. With Eq. (2.61) $C_6$, was also analytically computed. It is obvious that the values converges towards a value as the number of points increases. For $C_6$ with the analytic polarizabilities, the values really do converge towards the analytic $C_6$. The number of points that is needed for the quadrature depends on the requested accuracy, but it can be seen that already ten points will give three significant digits.

### 3.3 Calculations on noble gases

To compare relativistic effects with nonrelativistic, the polarizabilities and dispersions coefficients for four noble gases were computed. The four noble gases were the first four elements in the group: helium, neon, argon and krypton. They have the atomic numbers 2, 10, 18 and 36. The polarizability was calculated with the basis set aug-cc-pVTZ. Once it was calculated with Dalton and twice with Dirac, once with a nonrelativistic Hamiltonian and the other time with a relativistic Hamiltonian. The implementation of the Gauss–Legendre quadrature calculation of the dispersion coefficient works well, but because the calculations of the polarizabilities do not always converge except for the static polarizability, the dispersion coefficients will not always be correct. Table 3.3 shows the results of the calculations.

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic</th>
<th>Relativistic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dalton</td>
<td>Dirac</td>
</tr>
<tr>
<td>$\alpha(0)$</td>
<td>$C_6$ $\Delta$</td>
<td>$\alpha(0)$ $C_6$ $\Delta$</td>
</tr>
<tr>
<td>Helium</td>
<td>1.322 1.378 conv.</td>
<td>1.322 1.378 conv.</td>
</tr>
<tr>
<td>Neon</td>
<td>2.375 5.536 conv.</td>
<td>2.375 5.526 conv.</td>
</tr>
<tr>
<td>Argon</td>
<td>10.54 62.01 conv.</td>
<td>10.54 61.49 0.52</td>
</tr>
<tr>
<td>Krypton</td>
<td>16.46 128.1 conv.</td>
<td>16.46 127.2 3.0</td>
</tr>
</tbody>
</table>

The converge problem in the response solver does not occur except for the calculation of the static polarizability and therefore the static polarizabilities between the nonrelativistic calculations with Dalton and Dirac can be compared with the relativistic result with the Dirac calculations. In Table 3.3 ”conv.” means that the result is converged in the sense that all figures are significant.

In order to compare Gauss–Legendre integration with the London approximation, the following where done. First the $w_1$ for each noble gas according to Eq. (2.62) with the nonrelativistic computed dispersion coefficient and static polarizability from Dalton were calculated. Based on the result of that, $C_6$ according
3.3 Calculations on noble gases

Table 3.4. Effective angular frequency and relativistic dispersion coefficient based on the London approximation.

<table>
<thead>
<tr>
<th></th>
<th>$\omega_1$</th>
<th>$C^6_{\text{rel}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>1.051</td>
<td>1.381</td>
</tr>
<tr>
<td>Neon</td>
<td>1.308</td>
<td>5.550</td>
</tr>
<tr>
<td>Argon</td>
<td>0.7435</td>
<td>62.13</td>
</tr>
<tr>
<td>Krypton</td>
<td>0.6201</td>
<td>125.2</td>
</tr>
</tbody>
</table>

To Eq. (2.61) was calculated with the relativistic static polarizability given from Dirac. Table 3.4 shows the result.
Chapter 4

Conclusions

The first conclusion is already drawn in the result section and that is that the polarizability of neon as a function of the imaginary angular frequency decreases monotonically from the static value of the polarizability. As the imaginary angular frequency tends toward infinity, the polarizability tends to zero.

When doing a calculation not only the method is important, but also the choice of basis set. The example studied with neon and the four basis sets, indicates that aug-cc-pVDZ is not a sufficiently good basis set, when the focus is on getting converged results. There is a large discrepancy between the results given with that basis set and the next, daug-cc-pVDZ. The gap between results obtained with daug-cc-pVDZ and the other two is not as large compared with the first gap. It seems like that augmentation with more than one function, that better describe the long range behaviour, is critical for an accurate description of the polarizability. The basis set aug-cc-pVTZ has shown to give well converged results and because of that, it was used in the calculations. In the case studied the results did not totally match the experimental values and that is because the method used was not the best. If better converged result is the goal, there has to be improvements or a change of method. An improvement could be to use a method that take care of electron correlation.

One of the main goals with the work of this thesis was to implement the Gauss–Legendre quadrature for the dispersion coefficient for imaginary angular frequencies. This has been done in the Dirac code. This implementation can be run nonrelativistically and relativistically with 6, 8, 10, 12, 14 or 16 points. The calculation has been checked and the implementation works with all number of points. When it comes to convergence, it can be said that the calculations converge towards a value, when the number of points increases. In the second case, Column 2 in Table 3.2 the value, which the values for different number of points converge towards, is given. With 10 points there are four correct significant digits, with 12 there are 5 and with 16 there are 6. So the choice of number of points has only to do with what is required. For instance for the work of this thesis four significant digits were enough and to ensure that a quadrature with 12 points was selected. With the first column of Table 3.2 it is harder to study
the relation between the number of points in the quadrature and the number of
significant digits, but it seems that is at least five or could possibly be 6 significant
digits with 16 points.

Then it comes to the study of the relativistic effects. For the static polarizabil-
ity this could be done without any problems, because with these all the values are
converged. First it can be seen that relativistic effects has impact on the static
polarizability. It can be seen that the effects are largest for krypton, that has the
largest charge of its nucleus.

When it comes to the dispersion coefficients, conclusions could not be drawn
for krypton, because there are too few of significant digits. For the other no-
bles gases something could be concluded, because the accuracy is good enough.
The conclusion is that the relativistic effects depend on the charge of the noble
gas. A larger charge means that the relativistic effects are larger, but there is
no tendency. When the nonrelativistic results are compared with the relativistic,
calculated with Dirac and the London approximation, it seems that the relativistic
effects are larger for a noble gas with a larger charge. The results between the
relativistic calculations of the dispersion coefficients and the ones with the London
approximation could not be compared with each other, on account of the fact that
there are no reference values to compare with.
Bibliography


