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THE ASYMPTOTIC EXPANSION METHOD For HELIUMLIKE IONS.

by

RIDA EL-MEHDAWE

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Abstract

The aim of this work is to explore the range of validity of the asymptotic expansion method for a nuclear charge $Z \geq 3$. The asymptotic expansion method provides a simple analytical method to calculate the energies and properties of atoms with one electron in a highly excited state called a Rydberg state. The method was originally developed by Drachman from an expansion of the optical potential [7,8] for the Rydberg electron in powers of the perturbing potential and later reformulated by Drake based on a simple perturbation expansion for the total wave function. The method takes advantage of the fact that, with increasing angular momentum, the overlap of the Rydberg electron wave function with the core consisting of a $1s$ electron and the nucleus becomes vanishingly small. For a helium atom ($Z = 2$) with an angular momentum $L \geq 7$, the asymptotic method can be used as a high precession computational method, but for $Z \geq 3$ we have to increase the angular momentum to consider the asymptotic expansion as a high precession computational method as explained in chapter two. It provides a simple picture of the complex physics involved. This thesis extends the asymptotic expansion method to helium like ions for any value of Z and tests its accuracy against high precision variational calculations [31] for angular momentum L up to 7 and nuclear charge up to 18. For the exited states variational calculations become more difficult and the results' accuracy is inversely proportional with increasing angular momentum, in this case the asymptotic expansions take over variational calculations.

FOR THE HOPE OF MOST PEOPLE, FOR IMAM EL-MEHDI PEACE BE UP ON HIM

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Chapter 1

Introduction

The asymptotic expansion method is based on the physical picture of a single Rydberg electron moving in the field of a polarizable core consisting of the nucleus and the $1s$ electron. The Rydberg electron is moving in the effective field generated by the remaining two-body problem (hydrogenlike atom) see figure 1.1. This treats the outer electron as if it were a distinguishable particle so that both exchange effects and core penetration effects can be neglected. These approximations will be further discussed in the thesis. As a physical picture the Coulomb field of the Rydberg electron induces a shift in the charge distribution in the core, the positive charge of the core moves toward Rydberg electron at the same time the negative charge of the core moves away from the Rydberg electron. This will produce a diploe moment, and that diploe interacts with outer electron and shifts its energy downward. As a result the field experienced by the Rydberg electron can expanded asymptotically in the form [30]

$$V(x) = -\frac{(Z-1)}{x} - \frac{1}{2}\sum_{j=4}^{p} c_j x^{-j} \tag{1.1}$$

where Z is the nuclear charge of the nucleus, c_j some coefficients related to the multipole moments of the core, $p \leq 2L+2$, and x is the distance of the Rydberg electron from the nucleus. We can visualize the exited states as containing one electron in the

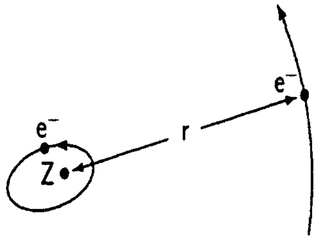


Figure 1.1: Shows the Rydberg electron moving in the field of the polarizable core

ground state $1s$ of a hydrogenlike atom but with nuclear charge Z, and the other electron in the exited state nL, n is the principal quantum number, and L is the orbital angular momentum quantum number, again of a hydrogenlike atom of nuclear charge $(Z-1)$ which is called the screened nuclear charge. Simply we have two electrons each of which belongs to a hydrogenlike atom, and since we know the energies of that kind of atoms, the total energy will be the sum of these two energies as follows

$$E_0 = -\frac{Z^2}{2} - \frac{(Z-1)^2}{2n^2} \tag{1.2}$$

the energy expressed in atomic units (a.u). With this trivial relation we can calculate the nonrelativistic energy for the state of 10G $E_0(10G) = -2.005$ a.u while the spin average variational results [31] for same state is $E_{av} = -2.005\,000\,112\,770$ a.u. We can see that the difference is only about one part in 10^7, while the difference in the singlet and triplet spin states of the two electrons is about one part in 10^{11} $E_{st} = 0.000\,000\,000\,012$ a.u, and rapidly becomes smaller with increasing L. These considerations lie behind the asymptotic expansion method. The central problem is to calculate the tiny difference between the exact E_{var} and hydrogenic value -2...5 a.u, from equation (2). We will show that a simple analytic picture involving core polarization provides a complete physical account of the correction -0.11277×10^{-6} a.u. In the next chapter we will develop perturbation expansion involving terms up to fourth order to account for the correction. A question maybe asked, if our visualize of the problem is right, why there is a difference between the two methods, to answer this question we would say that the picture is not that easy since the Rydberg electron has to spend some time close to the nucleus, and the other factor comes from the movement of the outer electron, during the time of establishing the diploe moment in the core, the Rydberg electron has moved from its initial position which reduces the effect of the diploe field. Considering factors like these will reduce the differences between the two results as we will see in the next chapter.

1.1 Asymptotic Expansion

When a function depends on a small parameter, and when the parameter appears as a multiplicative factor in a term in the governing equation, a power series solution is a possible approach. The resulting series need not converge for any value of the parameter; nevertheless the solution can be useful in approximating the function when the parameter is small. Computationally, a convergent series is not always useful, because convergence is a concept relating to the behavior of the terms in the series at the tail end. That a series converges says nothing about how rapidly the terms early in the series will decrease in magnitude. On the other hand, in asymptotic series, the terms will usually decrease rapidly for a sufficiently small parameter. Sometimes, they may begin to increase at some point after decreasing initially and then diverge. When the terms are decreasing rapidly, if we sum just the first few terms and we know that the error is of the order of the next term, we can get a good estimate of the sum. This is why asymptotic series are practically useful. We do not know how accurate the answer is, this is the main problem with asymptotic series. The results must be validated by comparison with some other representation of the expected answer (in our case we compare with variational calculations). Obtaining an analytical solution is often a difficult problem. We can define an asymptotic expansion for the function as a series of functions which has the property that truncating the series after a finite number of terms gives an accurate representation of the function being approximated, but which eventually diverges. This will provide (in most cases) an accepted approximation to the main function as the argument of the function tends towards a particular point. If we have a continuous function $f(x)$ on the domain of the asymptotic scale, then that function has an asymptotic expansion of order N with respect to the scale as a formal series.

$$\sum_{n=0}^{\infty} C_n \psi_n(x) \tag{1.3}$$

If

$$f(x) - \sum_{n=0}^{N-1} C_n \psi_n(x) = O(C_N \psi_N(x)) \tag{1.4}$$

Then we can say

$$f(x) \sim \sum_{n=0}^{N} C_n \psi_n(x) \tag{1.5}$$

In any place at the series we allowed to truncate, but if we are looking for the best approximation then we have to truncate at the smallest term of the series. This way of optimally truncating an asymptotic expansion is known as superasymptotics, and the error is thus less than any of the expansion terms. The potential that mentioned in equation 1.1 has to be truncated at the value of $p = 10$ because the series after that will diverge because the expectation values of $\langle \frac{1}{x^j} \rangle$ with respect to Rydberg electron will diverge for $j \geq 2L + 2$.

1.2 Helium and Heliumlike Ions

An introduction to some of the basic properties of helium and heliumlike ions (three-body atoms consisting of nucleus and two electrons) is necessary in order to understand the context of some of the calculations in this work. Helium and heliumlike ions represent the quantum analogue of the classical three-body problem and is the simplest system next to hydrogen. Unlike hydrogen, however, the helium and heliumlike ions problem is not separable and can not be solved exactly due to the correlated motion of the two electrons. As such, helium provided the first significant test of the new Quantum Theory initiated by Schro¨dinger in 1925.

1.3 Two Fundamental Approximate Methods

Since we are going to compare our asymptotic results with variational ones for all the three levels of energies (E_{nr}, E_{rel}, and, E_{QED}) the nonrelativistic, the relativistic, and the quantum electrodynamic energies respectively, so we need to briefly explain the method. At the same time we have to use the perturbation theory in our calculations, so it is a good place to explain both of the approximation methods. We need mathematical methods which will allow us to obtain approximate solutions of the Schrödinger equation. These methods are, the variational method and the perturbational approach.

1.3.1 Variational Principle

In quantum mechanics the variational method is one way of finding approximations to the lowest energy eigenstate (ground state), and some of the exited states. The basis of this method is the variational principle. The method consists of choosing a trial wave function depending on one or more parameters, and finding the values of these parameters for which the expectation value of the energy is the lowest possible. The expectation value of an operator in one of its eigenstates is the corresponding eigenvalue. So if the expectation value of the Hamiltonian for a bound particle is evaluated using the correct ground state eigenfunction, the result is the ground state energy E is

$$H \mid \Psi\rangle = E \mid \Psi\rangle. \tag{1.6}$$

Multiplying through by $\langle\Psi \mid$, and rearranging, gives the equation for energy,

$$\begin{aligned} \langle\Psi \mid H \mid \Psi\rangle &= \langle\Psi \mid E \mid \Psi\rangle \\ &= E\,\langle\Psi \mid \Psi\rangle \\ E &= \frac{\langle\Psi \mid H \mid \Psi\rangle}{\langle\Psi \mid \Psi\rangle} \end{aligned} \tag{1.7}$$

where the denominator is just a normalization factor, and

$$\langle\Psi \mid H \mid \Psi\rangle = \int \Psi^{*} H\ \Psi\ d\tau \tag{1.8}$$

If we replace the ground state eigenfunction Ψ by any other wave function (satisfying the correct boundary conditions), the expectation value must be greater than E, this is the basis for variational methods. Remember that a trial function approximating the exact wave function to arbitrary state of a particle can be expanded as a linear superposition of its energy eigenfunctions, so we may expand the wave function because we do not know the exact form of it and we are going to call it a trial function ψ_{tr}. In practice, we write a trial wave function in the form

$$\psi_{\mathrm{tr}} = \sum_{i=0}^{N} c_i \phi_i \tag{1.9}$$

where the basis set of functions ϕ_i becomes complete only when the summation is carried out over an infinite number of terms and the trial energy has form

$$E_{\mathrm{tr}} = \frac{\langle \Psi_{\mathrm{tr}} \mid H \mid \Psi_{\mathrm{tr}} \rangle}{\langle \Psi_{\mathrm{tr}} \mid \Psi_{\mathrm{tr}} \rangle} \tag{1.10}$$

To improve the result we have to write the trial wave function in terms of some parameters, then we have to differentiate E_{tr} with respect to each one of the parameters and set the derivatives to zero to minimize the energy. For example the set of coefficients C_i in equation (1.9) form a set of linear variational parameters.

1.3.2 Perturbation Theory

Let us start with the Hamiltonian H such that it can be written into two parts,

$$H = H_0 + V \tag{1.11}$$

where the $V = 0$ problem is solved and both the exact energy eigenfunctions $\mid \psi^{(0)} \rangle$ and the energy eigenvalues $E_n^{(0)}$ are known

$$H_0 \mid \psi^{(0)} \rangle = E_n^{(0)} \mid \psi^{(0)} \rangle. \tag{1.12}$$

Our goal to find approximate eigenfunctions and eigenvalues for the total Hamiltonian

$$(H_0 + V) \mid \psi \rangle = E_n \mid \psi \rangle. \tag{1.13}$$

where V is the perturbation part in the Hamiltonian. Let us consider the hydrogen atom in an external electric field. The unperturbed Hamiltonian H_0 is taken to be the kinetic energy $p^2/2m$ and the Coulomb potential due to the presence of the core e^2/r. Only that part of the potential due to the interaction with the external electric field is represented by the perturbation V. With the introduction of a real parameter λ can take values between 0 and 1, we can write the Schrödinger equation in the form

$$(H_0 + \lambda V) \mid \psi_n\rangle = E_n \mid \psi_n\rangle. \tag{1.14}$$

The parameter λ is introduced to keep track of the order of the perturbation. Setting λ to 1 will send the Hamiltonian back to the full-strength case. Thus λ controls the strength of the perturbation where setting λ to 0, is equivalent to imperturbation case, and setting it to 1 as mentioned will involve the full perturbation, so we can control the strength of the perturbation by controlling the value of λ. Now each eigenvalue and eigenfunction of the Hamiltonian H is expanded as a power series in λ

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \tag{1.15}$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + ... \tag{1.16}$$

Where $E_n^{(0)}$ is the nth eigenvalue of H (and is the zeroth-order approximation to the eigenvalues E_n of H). $E_n^{(1)}$, $E_n^{(2)}$, $E_n^{(3)}$, ... are the higher order corrections, the superscript denotes the order of the correction. Similarly $\psi_n^{(1)}$, $\psi_n^{(2)}$, $\psi_n^{(3)}$, ... are the first, second, third, ... order corrections to the zeroth-order approximation $\psi_n^{(0)}$ for the eigenfunction of the nth eigenstate. We substitute equations (1.15), and (1.16) in equation (1.14) and each side can be arrange as a power series in λ. Then, by equating the coefficients of successive power of λ we obtain

$$H_0 \mid \psi_0\rangle = E_0 \mid \psi_0\rangle. \tag{1.17}$$

$$(H_0 - E_0) \mid \psi_1\rangle + (V - E_1) \mid \psi_0\rangle = 0 \tag{1.18}$$

and

$$(H_0 - E_0) \mid \psi_2\rangle + (V - E_1) \mid \psi_1\rangle - E_2 \mid \psi_0\rangle = 0 \tag{1.19}$$

For the nth order we obtain

$$(H_0 - E_0) \mid \psi_n\rangle + (V - E_1) \mid \psi_{n-1}\rangle - E_2 \mid \psi_{n-2}\rangle + ... - E_n \mid \psi_0\rangle = 0 \tag{1.20}$$

1.4 Simple Examples

The hydrogen atom in an electric field (we can consider that field due to the Rydberg electron in the helium atom case) is a good example to explain the polarizability. An atom or molecule, when located in an electric field undergoes a deformation. We will show this in detail, taking the example of the hydrogen atom. We will consider a weak electric field, therefore the perturbation theory is applicable, this means just small corrections to the unperturbed situation. In our case the first-order correction to the wave function will be expanded in the series of hydrogenic wave functions

$$\begin{aligned} \mid \psi_0^{(1)}\rangle &= \frac{1}{E_0 - H_0}(V^{(l)} - E_1) \mid \psi_0\rangle \\ &= \sum_{j\neq 0} \frac{\langle \psi_j \mid V \mid \psi_0\rangle}{E_0 - E_j} \mid \psi_0\rangle \end{aligned} \tag{1.21}$$

where the unity has been used

$$1 = \sum_j \mid n\rangle\langle n \mid$$

Where $V^{(l)} = r^l P_l(cos\theta)$ (the multipole expansion), and $P_l(cos\theta)$ is Legendre polynomial. For the simplest case of $l = 1$, and the field points in z direction, then we need to sum over all the state. The hydrogen atom is in the ground state so $\mid \psi_0\rangle$ is the $\mid 1s\rangle$ state. The states we going to sum over for now are only $2S$, $2P_x$, $2P_y$, and $2P_z$, these represent $j = 1, 2, 3$, and 4 respectively, where $j = 0$ is the ground state itself. The contribution of the 2s is equal to zero, because $\langle 2s \mid z \mid 1s\rangle = 0$ due to the antisymmetry of the integrand with respect to reflection z goes to $-z$ (V changes its sign, while the orbital 1s and 2s do not). A similar argument excludes the $2p_y$ and $2p_x$ orbital. Hence, for the time being we have only a single candidate $2p_z$. This time the integral is not zero. If the candidates from the next shell ($n = 3$) are considered, similarly, the only nonzero contribution comes from $3p_z$. We will however stop our calculation at $n = 2$, because the goal is only to show how the machinery works. Thus we need to calculate $\langle 2p_z \mid z \mid 1s\rangle$ divided by $\frac{-1}{2} - \frac{-1}{8} = \frac{-3}{8}$ a.u. Calculating the integral gives us 0.7449, now we are ready to calculate the diploe polarizability

$$\alpha_1 = 2\frac{\langle 2p_z \mid z \mid 1s\rangle^2}{E_0 - E_1} \tag{1.22}$$

$\alpha_1 = 2.96$ a.u which is not bad compared to the exact value of 4.5 a.u. This result is expected to be off by not a small amount because of the simplicity of the perturbated wave function. Maple can sum over more sates, for example we let Maple to sum over the p states from $n = 2$ to $n = 500$ gives a value of 3.66 a.u for α_1, to get the exact number we need to sum over all the states. Graph 1.2 and table 1.1 show that the diploe polarizability components (in a.u) go to zero exponentially with n. The other method to calculate the polarizability is by solving Schrödinger equation (the first order perturbted wave function)

$$(E_0 - H_0)\psi_1 = V\psi_0 \tag{1.23}$$

Where $E_1 = 0$ (it will be explained in detail in the next chapter), see Appendix I for the solution of equation (1.23) .

$$\psi_1 = [\frac{1}{(l+1)Z}r + \frac{1}{lZ^2}]r^l P_l(cos\theta)\sqrt{\frac{Z^3}{\pi}}e^{-Zr} \tag{1.24}$$

This form of the perturbated wave function allows us to obtain a closed expression for the multipolar polarizabilities of the one electron atom or ions. It gives

$$\alpha_l = 2\langle\psi_0 \mid r^l P_l(cos\theta) \mid \psi_1\rangle$$

$$\alpha_l = 4\frac{(2l+1)!(l+2)}{l(2Z)^{2l+2}} \tag{1.25}$$

Equation 1.26 gives the exact value for α_l, and more than that it gives us $\alpha_l(Z)$ as a function of the nuclear charge Z, so we can use it for any value of Z as in the following equations

$$\alpha_1(Z) = \frac{9}{2Z^4}$$

$$\alpha_2(Z) = \frac{15}{Z^6}$$

$$\alpha_3(Z) = \frac{525}{4Z^8}$$

$$\alpha_4(Z) = \frac{8505}{4Z^{10}} \tag{1.26}$$

Now if we go back to equations (1.1), and (1.2) and using the results from equation

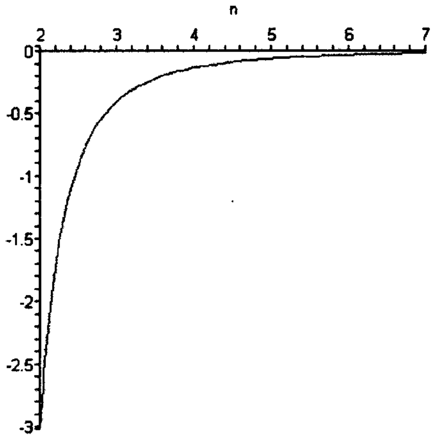


Figure 1.2: Shows contributions to the diploe polarizability and the principal quantum number n

Table 1.1: The components of the diploe polarizability α_{1c} in atomic units, vs the principal quantum number

n	$-\alpha_{1c}$(a.u)
2	-2.959621067
3	-.4004516551
4	-.1319413939
5	-0.06049628344
6	-0.03300617942
7	-0.02006648572
8	-0.01314116210
9	-0.009087430981
10	-0.006551851038

Table 1.2: The differences between the variational and asymptotic calculations, all the energies in (a.u)

State	E_{var}	δ_1	δ_2
10G	-2.005 000 112 770 661 0315	-1.13×10^{-7}	1.76×10^{-9}
10H	-2.005 000 039 214 405 9740	-3.92×10^{-8}	2.32×10^{-10}
10I	-2.005 000 016 086 516 2071	-1.61×10^{-8}	4.22×10^{-11}
10K	-2.005 000 007 388 375 8768	-7.39×10^{-9}	9.31×10^{-12}

(1.27) we can write the equation of the energy eigenvalues as below

$$E = -2 - \frac{(Z-1)^2}{2n^2} - \frac{1}{2}\sum_{l=1}^{4} \alpha_l \langle x^{-2l-2} \rangle \tag{1.27}$$

Where $\langle x^n \rangle$ is the mean value of the hydrogenic radius. Now let us show some improved results by programming equation (1.28) so we can see the differences in the energy eigenvalues between the spin average variational calculations and equation (1.28) as an asymptotic calculations. In table (1.2) E_{var} is the spin-averaged variational eigenvalue, $\delta_1 = E_{\text{var}} - E_0$, where E_0 is the energy calculated by equation 1.2, and $\delta_2 = E_{\text{var}} - E_2^{(0)}$, where $E_2^{(0)}$ is the energy calculated by equation (1.28). It is very clear to see that the differences between the two cases (δ_1, and δ_2) have been reduced about 100 times in the state of 10G, while the improvement in the state of 10K is about 1000 times, which means that the overlap of the Rydberg electron wave function with the core consisting of a 1s electron and the nucleus in the 10K state is much smaller than the 10G state. We can say as the angular momentum L increases the core penetration decreases see table (2.1), at the same time increasing L allow higher order terms in asymptotic expansion to contribute.

Chapter 2

Theory and Method of Calculations

In this chapter, we will describe the three-body Schrodinger equation which is can not be solved exactly, but there are available methods of successive approximations such that variational calculations, configuration interaction approach CI, and asymptotic expansion method. The asymptotic expansion method takes advantage of the face that, as the angular momentum of the Rydberg electron increases, the overlap of its wave function with the core electron becomes vanishingly small because of the positive term in the effective potential. The Rydberg electron can be treated as a distinguishable particle moving in the field of the polarizable core if we neglect the exchange and the short-range effects. The core becomes distorted as a consequence of the Rydberg electron movement, which results in the asymptotic potential expressed as an expansion in powers of $\frac{1}{x}$ as shown in equation (1.1). The potential acts asymptotically in both senses, physical and mathematical. From the physical point of view, increasing L causes the asymptotic behavior because of the centrifugal barrier. The mathematical point of view asymptotic expansions are well known and widely used for the calculation of special functions such as Bessel functions. In both cases, one must truncate the series after a finite number of terms in order to avoid a divergence. The history of asymptotic expansion for Rydberg states dates back to the early days of quantum mechanics, as summarized by Bethe and Salpeter [2] (1957, Section 29). The asymptotic potential has found wide applications in scattering problems, and in electron-nuclear coupling problems in molecules. Applications to energy level calculations in helium was revived by Deutsch(1970,1976) and refined in a series of papers by Drachman (1982, 1992) and Au et al (1991). The relativistic and relativistic recoil corrections were added by Drake and Yan [26](1992), and also QED corrections. There are two ways that have been used to derive the asymptotic expansion approach. The first approach by Drachman [28] is based on a Feshbach projection operator $P = | 1s\rangle\langle 1s |$ and expand the optical potential for the Rydberg electron in powers of the perturbing potential. The other approach by Drake [31] is based on a simple perturbation expansion for the total wave function. The later procedures is more transparent and the book keeping is more straight forward, they both lead to the same results.

At the end of this chapter we are going to compare our results with the variational calculation results and the CI results. The configuration-interaction CI method is based on a wave-function expansion in terms of sum of antisymmetrized products of functions of the electron radial coordinates r_i , and spherical harmonics $Y_l^m(\hat{r}_i)$ coupled to form states of the same total angular momentum L. For Rydberg states, great care must be taken to include all angular momentum couplings, for example for S-states ss', pp', dd' all contribute. Hylleraas-like expansions are usually used to express the wave function. The solution of the Schrodinger equation for a given angular momentum L and its projection M can be expressed as a sum over the product of the Sturmian functions S_{nl}^k for the two electrons

$$S_{nl}^k = N_{nl}^k r^{l+1} e^{-kr} L_{n-l-1}^{2l+1}(2kr)$$

where k is a nonlinear parameter, $L_{n-l-1}^{2l+1}(2kr)$ is the Laguerre polynomial, and N_{nl}^k is a normalization factor.

2.1 The Hamiltonian

The Schrödinger equation for heliumlike two-electron atomic system is defined by

$$H_{\mathrm{NR}}\psi = E\psi$$

The nonrelativistic Hamiltonian is

$$H_{\mathrm{NR}} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_{R_1}^2 - \frac{\hbar^2}{2m}\nabla_{R_2}^2 - \frac{Ze^2}{|\vec{R}-\vec{R}_1|} - \frac{Ze^2}{|\vec{R}-\vec{R}_2|} + \frac{e^2}{|\vec{R}_1-\vec{R}_2|} \tag{2.1}$$

where $\hbar$ is the Planck constant, e is the electronic charge, $\vec{R}$ is the position vector of the nucleus of mass M, $\vec{R_1}$ and $\vec{R_2}$ are the position vectors of the two electrons with mass m. We now make the standard transformation to scaled center-of-mass and relative coordinates defined by

$$\vec{X} = \frac{M\vec{R} + m\vec{R_1} + m\vec{R_2}}{(M+2m)a_\mu} \tag{2.2}$$

$$\vec{r_1} = \frac{\vec{R_1} - \vec{R}}{a_\mu} \tag{2.3}$$

$$\vec{r_2} = \frac{\vec{R_2} - \vec{R}}{a_\mu} \tag{2.4}$$

where $a_\mu = \frac{m}{\mu}a_0$ is reduced Bohr radius, $\mu = \frac{mM}{m+M}$ is the reduced electron mass, and $a_0 = \frac{\hbar^2}{me^2}$ is the Bohr radius. The center-of-mass $\vec{X}$ is an ignorable coordinate and the Schrödinger equation reduces to the dimensionless form

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\mu}{M}\vec{\nabla_1}\cdot\vec{\nabla_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\psi(r_1, r_2) = E_{\mathrm{NR}}\psi(r_1, r_2) \tag{2.5}$$

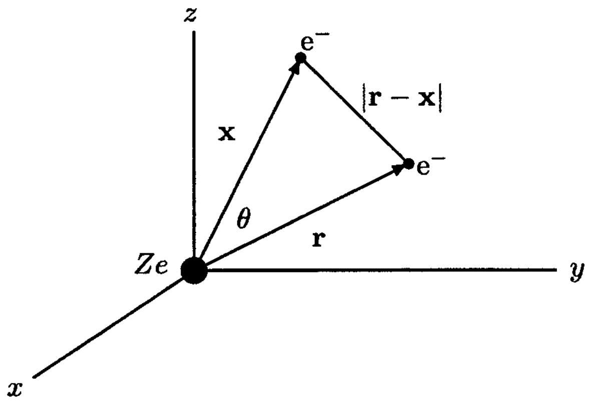
where $r_{12} = |\vec{r_1} - \vec{r_2}|$, $E_{\mathrm{NR}} = \frac{e^2}{a_\mu}E$ is the nonrelativistic energy. The unit of energy is $\frac{e^2}{a_\mu} = 2R_M$, where $R_M = \frac{\mu}{m}R_\infty$ is the reduced mass Rydberg, and $\frac{e^2}{a_0} = 2R_\infty$ is the atomic unit of energy. The mass polarization term $-\frac{\mu}{M}\vec{\nabla_1}\cdot\vec{\nabla_2}$ in Equation 2.6 produces the state-dependent special isotopic shift. If $\frac{\mu}{M} \ll 1$, then this term can be dropped to a first approximation. In this approximation, we obtain the Schrödinger equation for infinite nuclear mass

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\psi(r_1, r_2) = E_{NR}\psi(r_1, r_2) \tag{2.6}$$

with a change in notations more suitable for asymptotic expansions, Schrödinger equation becomes

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{2}\nabla_{\mathbf{x}}^2 - \frac{Z}{r} - \frac{Z}{x} + \frac{1}{|\,r-x\,|}\right]\Psi(\mathbf{r}, \mathbf{x}) = E\Psi(\mathbf{r}, \mathbf{x}). \tag{2.7}$$

Figure 2.1: Helium atom in internal and center-of-mass coordinate system.



Where r is the position vector for the inner electron, and x is the position vector for the Rydberg electron [30] as shown in figure 2.1. Now we can write the Hamiltonian as two parts

$$H(r,x) = H_0(r.x) + V(r,x) \tag{2.8}$$

where we add $1/x$ to H_0 and subtract it from $V(r,x)$ to obtain

$$\begin{aligned} H_0(r.x) &= -\frac{1}{2}\nabla_r^2 - \frac{Z}{r} - \frac{1}{2}\nabla_x^2 - \frac{(Z-1)}{x} \\ &= h_0(r,Z) + h_0(x,Z-1) \end{aligned} \tag{2.9}$$

where $h_0(r,Z)$ is a one electron hydrogenic Hamiltonian for the inner electron with full nuclear charge Z, and $h_0(x,Z-1)$ is the Hamiltonian for Rydberg electron with screened nuclear charge Z-1. The remanning perturbations is

$$V(r,x) = \frac{1}{\mid \vec{r} - \vec{x} \mid} - \frac{1}{x} \tag{2.10}$$

In the case where $x > r$, the potential $V(r,x)$ has the multipole expansion

$$V(r,x) = \frac{1}{x}\sum_{n=1}^{\infty}\left(\frac{r}{x}\right)^n P_n(cos\theta) \tag{2.11}$$

were θ is the angle between the two. The advantage gained is that the leading monopole term $n = 0$ no more appears. vectors r, and x. The solutions to the full Schrödinger equation

$$H(r,x)\Psi(r,x) = E\Psi(r,x) \tag{2.12}$$

will now be expanded as perturbation series with $V(r,x)$ as the perturbation according to

$$\Psi(r,x) = \Psi_0(r,x) + \Psi_1(r,x) + ... \tag{2.13}$$

$$E = E_0 + E_1 + ... \tag{2.14}$$

as explained in chapter (1) sec 1.3.2. Now

$$H_0\Psi_0(r,x) = E_0\Psi_0(r,x) \tag{2.15}$$

is the zero-order equation. The jth perturbation equation can be expressed as

$$(H_0 - E_0)\Psi_j + V\psi_{j-1} = \sum_{k=1}^{j} E_k\Psi_{j-k} \tag{2.16}$$

Our wave functions are normalized such that $\langle\Psi_j \mid \Psi_0\rangle = 0$ for $j \geq 1$, from equation (2.16) we can get the jth-order energy

$$E_j = \langle\Psi_0 \mid V \mid \Psi_{j-1}\rangle \tag{2.17}$$

and $E_1 = \langle\Psi_0 \mid V \mid \Psi_0\rangle \simeq 0$ since the monopole term is missing from equation (2.10) in the dominant region $x > r$, while the monopole is present for the region $r > x$ which is $V^{(0)} = \frac{1}{r} - \frac{1}{x}$. To calculate E_1 we have to integrate first over r from x to ∞

$$E_1 = \langle\phi_{1s}(r)\chi_{nL}(x) \mid V^{(0)} \mid \phi_{1s}(r)\chi_{nL}(x)\rangle$$

$$E_1 = -\langle\chi_{nL}(x) \mid (Z + \frac{1}{x})e^{-2Zx} \mid \chi_{nL}(x)\rangle \tag{2.18}$$

which goes to zero exponentially with increasing L. Table (2.1) shows some of the values of E_1. For angular momentum $L > 4$, E_1 can be neglected in comparison with spectroscopic accuracies, hence $E_1 \simeq 0$. Then the solution of equation 2.14 for the zero-order will be written as

$$\begin{aligned}\Psi_0(r,x) &= \phi_{1s}(r)\chi_{nL}(x)\\ &= \phi_0(r)\chi_0(x)\end{aligned} \tag{2.19}$$

Table 2.1: Energy shift E_1 in MHz due to penetration of the core

L	$n = 7$	$n = 8$	$n = 9$
3	-18.97	-13.69	-10.10
4	-5.39×10^{-2}	-4.33×10^{-2}	-3.42×10^{-2}
5	-7.07×10^{-5}	-7.06×10^{-5}	-6.32×10^{-5}
6	-3.46×10^{-8}	-5.70×10^{-8}	-6.48×10^{-8}
7		-1.80×10^{-11}	-3.45×10^{-11}
8			-7.43×10^{-15}

with neglect of exchange and the zero-order energy E_0 can be written as two hydrogenic parts

$$E_0 = \varepsilon_0 + e_0$$
$$E_0 = -\frac{Z^2}{2} - \frac{(Z-1)^2}{2n^2} \tag{2.20}$$

2.2 Recursion Relation for $\langle 1/x^p \rangle$

Since the early days of quantum mechanics the hydrogen atom and hydrogenic systems have been studied intensively because of their simplicity. Many interesting relations related to their wave functions have been used in different applications. One of these is the expectation values of the hydrogenic systems radii $\langle 1/x^p \rangle$ which are needed to calculate the energy shifts in our calculations for the Rydberg states of two-electron atoms. There are different methods to derive the recursion relation of $\langle 1/x^p \rangle$. One of the methods (which uses the hypervirial theorem) was derived by Killingbeck [23], and the other one by Drake and Swainson [15,20]. We may replace $\langle \frac{1}{x^j} \rangle$ by $f[j]$, the final form of the recursion relation obtained by Killingbeck

$$f[j] = \frac{4(Z-1)[(5-2j)f[j-1] - \frac{(Z-1)(3-j)}{n^2} f[j-2]]}{(2-j)(2L+j-1)(2L-j+3)} \tag{2.21}$$

To start using this recursion relation we need to know two terms, but if we start with $j = 3$ then the second term in the numerator of equation 2.21 will vanish, so all what we need to get $f[3]$ is $f[2]$ only

$$f[2] = \frac{2(Z-1)^2}{n^3(2L+1)} \tag{2.22}$$

so $f[3]$ will get the following form

$$f[3] = 2\frac{(Z-1)f[2]}{L(L+1)} = \frac{2(Z-1)^3}{n^3L(L+1)(2L+1)} \tag{2.23}$$

Feeding Maple version 9.5 with equations 2.21, and 2.22 we can get any jth term. we are going to stop the restriction at $j = 10$ because of the divergence in our series (see equation 1.1)

$$f[4] = 4\frac{(Z-1)^4\left(3n^2 - L^2 - L\right)}{n^5\,(L+1)\,L\,(2L+3)\,(4L^2-1)} \tag{2.24}$$

$$f[6] = 4\frac{(Z-1)^6\left(35\,n^4 - 30\,n^2L^2 - 30\,n^2L + 25\,n^2 + 3\,L^4 + 6\,L^3 - 3\,L^2 - 6\,L\right)}{n^7L\,(L+2)\,(2\,L+5)\,(4\,L^2-1)\,(L^2-1)\,(4\,L^2-9)} \tag{2.25}$$

$$f[7] = 4\frac{(Z-1)^7\left(63\,n^4 - 70\,n^2L^2 - 70\,n^2L + 105\,n^2 + 15\,L^4 + 30\,L^3 - 35\,L^2 - 50\,L + 12\right)}{n^7L\,(2\,L+5)\,(L+3)\,(4\,L^2-1)\,(L^2-1)\,(4\,L^2-9)\,(L^2-4)} \tag{2.26}$$

$$\begin{aligned} f[8] &= \frac{8(Z-1)^8(231n^6 - 315n^4L^2 - 315n^4L + 735n^4 + 105n^2L^4 + 210n^2L^3 - 420n^2L^2}{n^9L(L+3)(2L+7)(4L^2-1)(L^2-1)(4L^2-9)(L^2-4)(4L^2-25)} \\ &- 525n^2L + 294n^2 - 5L^6 - 15L^5 + 25L^4 + 75L^3 - 20L^2 - 60L) \end{aligned} \tag{2.27}$$

$$\begin{aligned} f[9] &= \frac{2048(Z-1)^9(2L-7)!}{(2L+8)!n^9} \\ &\times [429n^6 + [2310 - 693L(L+1)]n^4 \\ &+ [2121 + 315L(L+1)(L(L+1)-7)]n^2 \\ &- 35L^6 - 105L^5 + 280L^4 + 735L^3 - 497L^2 - 882L + 180] \end{aligned} \tag{2.28}$$

$$\begin{aligned} f[10] &= \frac{1024(L-1)^{10}(2L-8)!}{n^{11}(2L+9)!} \\ &\times \{6435n^8 + [54054 - 12012L(L+1)]n^6 \\ &+ 1155[6L^4 + 12L^3 - 50L^2 - 56L + 81]n^4 \\ &+ [-1260L^6 - 3780L^5 + 14490L^4 + 35280L^3 - 41118L^2 \\ &- 59388L + 27396]n^2 + \frac{35(L+4)!}{(L-4)!}\} \end{aligned} \tag{2.29}$$

all these results agree with Drake and swainson.

2.3 Polarizabilities

The response of atoms, and ions to external fields is important in the description of the interaction with each other and with other systems. This response is described by the changes in their properties, for example, multipole moments induced in them, which in turn interact with the sources which induce the multipole moments. The induced multipole moments and their interactions are given in terms of multipolar polarizabilities. Consider a spherically symmetric system S subjected to an external electric field ε in the z direction. this induces a diple moment p in S.

$$p = \alpha_1 \varepsilon \tag{2.30}$$

where α_1 is the diple polarizability of the system. The diple moment can also be written in terms of effective charges $\pm q$ separated by a distance of x as $p = qx$. The change in the energy of the system is then given by

$$\begin{aligned} \delta E &= -\int \varepsilon.(qdx) \\ \delta E &= -\int \varepsilon.\alpha_1 d\varepsilon \\ \delta E &= -\frac{1}{2}\alpha_1 \varepsilon^2 \end{aligned} \tag{2.31}$$

Thus the change in the energy of the system is given in terms of its diple polarizability α_1. Now consider the following perturbing potential

$$V^{(l)} = -\varepsilon r^l P_l(cos\theta)$$

for $l = 1$, V becomes

$$V^{(1)} = -\varepsilon r cos(\theta)$$

The second order energy shift is given by

$$E^{(2)} = \varepsilon^2 \sum_{n\neq 0}^{\infty} \frac{\langle \psi_0 \mid V^{(1)} \mid \psi_n \rangle \langle \psi_n \mid V^{(1)} \mid \psi_0 \rangle}{E_0 - E_n} \tag{2.32}$$

where the summation excludes the $n = 0$ term. Comparing this with equation (2.31) we can write the diple polarizabilty in the following form

$$\alpha_1 = -2 \sum_{n\neq 0}^{\infty} \frac{\langle \psi_0 \mid V^{(1)} \mid \psi_n \rangle \langle \psi_n \mid V^{(1)} \mid \psi_0 \rangle}{E_0 - E_n} \tag{2.33}$$

in more general form

$$\alpha_l = -2\sum_{n\neq 0}^{\infty} \frac{\langle\psi_0 \mid V^l \mid \psi_n\rangle\langle\psi_n \mid V^l \mid \psi_0\rangle}{E_0 - E_n} \tag{2.34}$$

The polarizability can also be written as

$$\alpha_l = 2\langle\psi_0 \mid V^l \mid \psi_l^{(1)}\rangle \tag{2.35}$$

where

$$\mid \psi_l^{(1)}\rangle = \sum_{n\neq 0}^{\infty} \frac{\mid \psi_n\rangle\langle\psi_n \mid V^l \mid \psi_0\rangle}{E_0 - E_n} \tag{2.36}$$

This can also be viewed as the solution to the first-order perturbation equation (see equation 1.18), and $E^{(1)} = 0$ if $\langle\psi_l^{(0)} \mid V^l \mid \psi_l^{(0)}\rangle = 0$

This problem is treated early by Dalgarno and Lewis [1] in a transparent way

$$E_2 = \sum_{n\neq 0}^{\infty} \frac{\langle 0 \mid V \mid n\rangle\langle n \mid V \mid 0\rangle}{\varepsilon_0 - \varepsilon_n} \tag{2.37}$$

where

$$\langle n \mid V \mid m\rangle = \int \psi_n^* V \psi_m d^3r \tag{2.38}$$

and

$$V = V(r,x) = \frac{1}{x}\sum_{l=1}^{\infty}\left(\frac{r}{x}\right)^l P_l(cos\theta) \tag{2.39}$$

which is the exact potential we are using for helium and heliumlike ions, but the summation over n is just a single complete set of quantum numbers. Since the wave function we are using for heliumlike ions can be expressed in form of simple product then the Hamiltonian can be written as a sum of two hydrogenic Hamiltonian. Now we can change notations to $\mid M\rangle$, where M represents two complete sets of quantum numbers m, and m' for the inner electron and Rydberg electron. Even the excitation energies at the denominator$(E_0 - E_n)$ similarly can be partitioned according to [30]

$$\Delta_M = D_m + d_{m'} = (\varepsilon_0 - \varepsilon_m) + (e_0 - e_{m'}) \tag{2.40}$$

where $\varepsilon_0 - \varepsilon_m$ represent a big excitation of the inner electron and $e_0 - e_{m'}$ represent a small excitation of the outer electron, see equation (2.20) for the definitions of the excitation energies. The summations are over all single and double excitations, including integrations over the continuum. Dalgarno and Lewis [1] found exact evaluation of the summation in equation (2.37) by eliminating the excitation energies from the denominator as below

$$\frac{\langle 0 \mid V \mid n\rangle}{E_0 - E_n} = \langle 0 \mid f \mid n\rangle \tag{2.41}$$

where f is a function related to V by the implicit definition $[H_0, f] = V$ and we have to find, then the summation will reach a simpler form

$$\begin{aligned} \sum_{n\neq 0}^{\infty} \frac{\langle 0 \mid V \mid n\rangle\langle n \mid V \mid 0\rangle}{E_0 - E_n} &= \sum_{n\neq 0}^{\infty} \langle 0 \mid f \mid n\rangle\langle n \mid V \mid 0\rangle \\ &= \langle 0 \mid Vf \mid 0\rangle \end{aligned} \tag{2.42}$$

Finally the 2^L-pole polarizability can be calculated from a single integral

$$\alpha_L = \langle 0 \mid V^L f \mid 0\rangle \tag{2.43}$$

The calculation of $f(r)$ for particular states described in Appendix I. Now let us go back to the excitation energies

$$\frac{1}{\Delta_M} = \frac{1}{D_m + d_{m'}} \tag{2.44}$$

The adiabatic approximation and corrections to it are obtained by assuming that $d_{m'} \ll D_m$ for $M \neq M_0$ and expanding

$$\frac{1}{\Delta_M} = \frac{1}{D_m}\left(1 - \frac{d_{m'}}{D_m} + \frac{d_{m'}^2}{D_m^2} - \dots\right) \tag{2.45}$$

The first term corresponds to the adiabatic approximation as already treated in the equations leading to (2.43) but if we consider the first correction term then we are getting an extra D_m in the denominator giving the leading nonadiabatic correction. Then it is necessary to insert f in both factors (using the Dalgarno-Lewis method two times) in the numerator, thus canceling both factors of D_m, and the integral we have to calculate looks like $\langle 0 \mid f^2 \mid 0\rangle$. We did see that $\alpha_L \propto \frac{1}{D_m}$ and it follows that

$$\beta_L \propto \frac{1}{D_m^2} \tag{2.46}$$

$$\gamma_L \propto \frac{1}{D_m^3} \tag{2.47}$$

$$\delta_L \propto \frac{1}{D_m^4} \tag{2.48}$$

where β_L, γ_L, and δ_L are the first, second, and third nonadiabatic corrections to α_L

2.4 The Second-Order Energy Shift E_2

Start with the excitation energies and keep in mind the nonadiabatic corrections due to the motion of the Rydberg electron. Now if we hold the Rydberg electron fixed (adiabatic approximation) then $d_{m'} = 0$, and so $\Delta_M = D_m$. The second-order energy is defined as

$$E_2 = \langle \Psi_0 \mid V \mid \Psi_1 \rangle \tag{2.49}$$

where

$$\mid \Psi_1 \rangle = \sum_M \frac{\mid M \rangle V_{M,0}}{\Delta_M} \tag{2.50}$$

For the adiabatic case the energy becomes

$$E_2 = \sum_M \frac{\langle 0 \mid V \mid M \rangle \langle M \mid V \mid 0 \rangle}{D_m}$$

The matrix elements $\langle 0 \mid V \mid M \rangle$ of V in equation (2.10) can be expressed as a sum of multipole [30]

$$V^{(l)} = \frac{r^l}{x^{l+1}} P_l(\hat{r}.\hat{x}) \tag{2.51}$$

where $l = 0$ for monopole (not included), $l = 1$ for diple etc ... If we use the spherical harmonic addition theorem to write

$$P_l(\hat{r}.\hat{x}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} (-1)^m Y_l^{-m}(\hat{r}) Y_l^m(\hat{x}) \tag{2.52}$$

then the matrix element of each multipole $V^{(l)}$ can be corrospondingly factorized according to

$$\langle M \mid V^{(l)} \mid N \rangle = \sum_\mu U_{m,n}^{l,\mu} u_{m',n'}^{l,\mu} \tag{2.53}$$

where

$$U_{m,n}^{l,\mu} = \sqrt{\frac{4\pi}{2l+1}} \langle \phi_m \mid r^l Y_l^\mu(\hat{r}) \mid \phi_n \rangle \tag{2.54}$$

for the inner electron

$$u^{l,\mu}_{m,n'} = \sqrt{\frac{4\pi}{2l+1}}\langle \chi_{m'} \mid x^{-l-1} Y_l^{\mu^*}(\hat{x}) \mid \chi_{n'} \rangle \tag{2.55}$$

for the outer electron The second-order energy E_2 can then be written as a summation of energies arising from each multipole rank

$$E_2 = \sum_l E_2^{(l)} \tag{2.56}$$

In the adiabatic approximation, the lth multipole contribution to E_2 is then

$$E_2^{(l)} = \sum_M \frac{V^{(l)}_{0,M} V^{(l)}_{M,0}}{D_m} \tag{2.57}$$

or, inserting the above factorization,

$$E_2^{(l)} = \sum_{m,\mu,\mu'} \frac{U^{(l,\mu)}_{0,m} U^{(l,\mu')}_{m,0}}{D_m} \sum_{m'} u^{(l,\mu)}_{0,m'} u^{(l,\mu')}_{m',0} \tag{2.58}$$

second summation (the summation over m') can be completed by closure resulting in

$$\begin{aligned} \sum_{m'} u^{(l,\mu)}_{0,m'} u^{(l,\mu')}_{m',0} &= \left(\frac{4\pi}{2l+1}\right) \langle \chi_0 \mid x^{-2l-2} Y_l^{\mu}(\hat{x}) Y_l^{\mu'}(\hat{x}) \mid \chi_0 \rangle \\ &= \left(\frac{4\pi}{2l+1}\right) (-1)^{\mu} \delta_{\mu,-\mu'} \langle \chi_0 \mid x^{-2l-2} |Y_l^{\mu}(\hat{x})|^2 \mid \chi_0 \rangle \end{aligned}$$

then the lth multipole contrbution to the energy becomes

$$E_2^{(l)} = \left(\frac{4\pi}{2l+1}\right) \sum_{m,\mu} \left((-1)^{\mu} \frac{U^{(l,\mu)}_{0,m} U^{(l,-\mu)}_{m,0}}{D_m} \langle \chi_0 \mid x^{-2l-2} |Y_l^{\mu}(\hat{x})|^2 \mid \chi_0 \rangle \right) \tag{2.59}$$

we can set μ to zero because the summation over magnetic quantum numbers for intermediate states is independent of μ as in the following equation

$$\sum_{\mu} |Y_l^{\mu}(\hat{x})|^2 = \frac{2l+1}{4\pi} \tag{2.60}$$

The final form of the energy will be

$$E_2^{(l)} = -\frac{1}{2}\alpha_l \langle \chi_0 \mid x^{-2l-2} \mid \chi_0 \rangle \tag{2.61}$$

where

$$\alpha_l = -2 \sum_m \frac{U^{(l)}_{0,m} U^{(l)}_{m,0}}{D_m} \tag{2.62}$$

is the 2^l-pole polarizability and

$$U_{0,m}^{(l)} = \langle \phi_0 \mid r^l P_l(cos\theta) \mid \phi_m \rangle \tag{2.63}$$

finally the second-order energy E_2 in the adiabatic approximation can be written as follows

$$\begin{aligned} E_2 &= -\frac{1}{2}\alpha_1\langle x^{-4}\rangle - \frac{1}{2}\alpha_2\langle x^{-6}\rangle - \frac{1}{2}\alpha_3\langle x^{-8}\rangle - \frac{1}{2}\alpha_4\langle x^{-10}\rangle \\ &= -\frac{1}{2}\left(\frac{9}{2}Z^{-4}\langle x^{-4}\rangle + 15Z^{-6}\langle x^{-6}\rangle + \frac{525}{4}Z^{-8}\langle x^{-8}\rangle + \frac{8505}{4}Z^{-10}\langle x^{-10}\rangle\right) \end{aligned} \tag{2.64}$$

where $\langle x^{-j}\rangle, j = 4, 6, 8,$ and 10 are defined in equations (2.24), (2.25), (2.27), and (2.29) respectively, and α_l are gicen in equations (2.103-2.105).

2.5 The Third-Order Energies E_3

To derive the third-order energy we have to start with equation 2.16 for $j = 3$

$$E_3 = \langle \Psi_0 \mid V \mid \Psi_2 \rangle \tag{2.65}$$

This term is derived by Drake [32], by using equation (2.15) for $j = 2$, and multiplying both sides of the equation by $\langle \Psi_1 \mid$ from the left, we get

$$\langle \Psi_1 \mid H_0 \mid \Psi_2 \rangle + \langle \Psi_1 \mid V \mid \Psi_1 \rangle = 0 \tag{2.66}$$

Next we have to use same equation (2.15) but for $j = 1$, and multiply both sides of the equation by $\langle \Psi_2 \mid$ from the left, we get

$$\langle \Psi_2 \mid H_0 \mid \Psi_1 \rangle + \langle \Psi_2 \mid V \mid \Psi_0 \rangle = 0 \tag{2.67}$$

the third-order energy can be expressed as

$$E_3 = \langle \Psi_0 \mid V \mid \Psi_2 \rangle = \langle \Psi_1 \mid V \mid \Psi_1 \rangle \tag{2.68}$$

In the adiabatic approximation the energy becomes

$$E_3 = \sum_M \sum_N \frac{\langle 0 \mid V \mid N \rangle \langle N \mid V \mid M \rangle \langle M \mid V \mid 0 \rangle}{D_m D_n} \tag{2.69}$$

We next follow the same steps we used for $E_2^{(l)}$ (see equation 2.57), except that there will be three spherical harmonic terms instead of two. In this case we are going to use so called the Wigner 3-j symbols instead of the orthogonality [28]

$$\int_0^{\pi}\int_0^{2\pi} Y_{l_1}^{m1}(\hat{x})Y_{l_2}^{m2}(\hat{x})Y_{l_3}^{m3}(\hat{x})\sin\theta d\theta d\phi =$$

$$\sqrt{\frac{(2l'+1)(2l''+1)(2l+1)}{4\pi}}\begin{pmatrix} l' & l'' & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & l'' & l \\ m' & m'' & m \end{pmatrix} \tag{2.70}$$

This expression will vanish unless l', l'', and l satisfy two conditions. First they have to satisfy the triangular inequality $(l' + l'' \geq l)$, and second the sum of $l' + l'' + l = p$ must be an even integer. Therefore $p = 4$ will be the first term with $l = l' = 1$ and $l'' = 2$ and this corresponds to $\langle x^{-7}\rangle$ (see equation 2.26). The second term (which is the last for this case) is $p = 6$, which comes from (222), or (123) indices corresponding to $\langle x^{-9}\rangle$ (see equation 2.28). Now we can write the third-order energy for the adiabatic approximation as follows

$$E_3 = \sum_{ll'l''} E_3^{(ll'l'')} \tag{2.71}$$

and the nonvanishing terms are

$$E_3 = E_3^{(112)} + E_3^{(123)} + E_3^{(222)} \tag{2.72}$$

and in terms of the polarizability coefficients

$$\begin{aligned} E_3 &= \frac{1}{2}\eta\langle x^{-7}\rangle + \frac{1}{2}\kappa\langle x^{-9}\rangle + \frac{1}{2}\lambda\langle x^{-9}\rangle \\ &= \frac{1}{2}\left(\frac{213}{2}Z^{-8}\langle x^{-7}\rangle + 1620Z^{-10}\langle x^{-9}\rangle + 153Z^{-10}\langle x^{-9}\rangle\right) \end{aligned} \tag{2.73}$$

where η (defined in equation 2.74), κ, and λ are calculated by using the Dalgarno-Lewis method [1], details for their calculation will be explained in section (2.7).

$$\eta = 2\sum_{m,n}\sum_{l,l',l''}\frac{U_{0,m}^{(l)}U_{m,n}^{(l')}U_{n,0}^{(l'')}}{D_m D_n} \tag{2.74}$$

The superscrips (112) belong to η , similarly κ, and λ have the same form as η, but with two different indices (123), and (222) respectively.

2.6 The Fourth-Order Energies E_4

This is term derived by Drake also [30], by starting employing equation (2.16) for $j = 4$ and the fourth-order energy can be written as

$$E_4 = \langle \Psi_0 \mid V \mid \Psi_3 \rangle \tag{2.75}$$

This can be simplified in the same way we did for E_3 again by using equation (2.15) but for $j = 3$, and multiplying both sides of the equation from the left by $\langle \Psi_1 \mid$ we get

$$\langle \Psi_1 \mid H_0 \mid \Psi_3 \rangle + \langle \Psi_1 \mid V \mid \Psi_2 \rangle = E_2 \langle \Psi_1 \mid \Psi_1 \rangle \tag{2.76}$$

Next we have to use equation 2.16 for $j = 1$, and multiply both sides of the equation by $\langle \Psi_3 \mid$ from the left, we get

$$\langle \Psi_3 \mid H_0 \mid \Psi_1 \rangle + \langle \Psi_3 \mid V \mid \Psi_0 \rangle = 0 \tag{2.77}$$

and the fourth-order of energy can be expressed as

$$E_4 = \langle \Psi_1 \mid V \mid \Psi_2 \rangle - E_2 \langle \Psi_1 \mid \Psi_1 \rangle \tag{2.78}$$

where

$$\mid \Psi_2 \rangle = \sum_M \sum_N \frac{\mid N \rangle \langle N \mid V \mid M \rangle \langle M \mid V \mid 0 \rangle}{\Delta_M \Delta_N} \tag{2.79}$$

in more detail the energy become

$$\begin{aligned} E_4 &= \sum_M \sum_N \sum_P \frac{\langle 0 \mid V \mid P \rangle \langle P \mid V \mid N \rangle \langle N \mid V \mid M \rangle \langle M \mid V \mid 0 \rangle}{\Delta_M \Delta_N \Delta_N \Delta_P} \\ &- E_2 \sum_M \sum_N \frac{\langle 0 \mid V \mid N \rangle \langle N \mid M \rangle \langle M \mid V \mid 0 \rangle}{\Delta_M \Delta_N} \end{aligned} \tag{2.80}$$

for the adiabatic approximation the energy becomes

$$\begin{aligned} E_4 &= \sum_M \sum_N \sum_P \frac{\langle 0 \mid V \mid P \rangle \langle P \mid V \mid N \rangle \langle N \mid V \mid M \rangle \langle M \mid V \mid 0 \rangle}{D_m D_n D_n D_p} \\ &- E_2 \sum_M \sum_N \frac{\langle 0 \mid V \mid N \rangle \langle N \mid M \rangle \langle M \mid V \mid 0 \rangle}{D_m D_n} \end{aligned} \tag{2.81}$$

The normalization term and the second-order correction (e_2) to the energy of the Rydberg electron due to part of Ψ_2 will be added later. As we did in the previous section we can write the fourth-order energy in terms of its components

$$E_4^{(ll'l''l''')} = \sum_{M,N,P} \frac{V_{0,M}^{(l)} V_{M,N}^{(l')} V_{N,P}^{(l'')} V_{P,0}^{(l''')}}{D_m D_n D_p} \tag{2.82}$$

we can write it explicitly in terms of the two summations (the inner electron sum and the Rydberg electron sum)

$$\begin{aligned} E_4^{(ll'l''l''')} &= \sum_{m,n,p} \sum_{\mu,\mu',\mu'',\mu'''} \frac{U_{0,m}^{(l,\mu)} U_{m;n}^{(l',\mu')} U_{n,p}^{(l'',\mu'')} U_{p,0}^{(l''',\mu''')}}{D_m D_n D_p} \\ &\times \sum_{m',n',p'} u_{0,m'}^{(l,\mu)} u_{m',n'}^{(l',\mu')} u_{n',p'}^{(l'',\mu'')} u_{p',0}^{(l''',\mu''')} \end{aligned} \tag{2.83}$$

the last sum over m', n', and p' can be completed by closure, and following the same steps we did for E_2

$$E_4^{(ll'l''l''')} = \sum_{m,n,p} \frac{U_{0,m}^{(l)} U_{m,n}^{(l')} U_{n,p}^{(l'')} U_{p,0}^{(l''')}}{D_m D_n D_p} \langle x^{-8} \rangle \tag{2.84}$$

which is the only term corresponding to $\langle x^{-8} \rangle$ where all the indices have the same value $l = l' = l'' = l''' = 1$, and there are two successive cases of (1113), and (1122) both correspond to $\langle x^{-10} \rangle$. The total fourth-order energy in the adiabatic approximation is

$$E_4 = E_4^{(1111)} + E_4^{(1113)} + E_4^{(1122)} \tag{2.85}$$

where the adiabatic coefficients are defined as below

$$\epsilon = \sum_{m,n,p} \frac{U_{0,m}^{(l)} U_{m,n}^{(l')} U_{n,p}^{(l'')} U_{p,0}^{(l''')}}{D_m D_n D_p} \tag{2.86}$$

similarly ρ, and σ have the same form as ϵ does but with different indices (1113), and (1212) respectively as shown in the following section. By calculating the integrals we get

$$\epsilon = \frac{4329}{32} Z^{-10} \tag{2.87}$$

$$\rho = \frac{4905}{2} Z^{-12} \tag{2.88}$$

$$\sigma = \frac{98511}{16} Z^{-12} \tag{2.89}$$

2.7 Dalgarno-Lewis Method

So far we used the adiabatic approximation for the energy shifts. In this section we are going to explain the Dalgarno-Lewis method [1] that we used to calculate the polarizabilities. Let us start with 2^l-pole polarizability

$$\alpha_l = -2 \sum_m \frac{U^{(l)}_{0,m} U^{(l)}_{m,0}}{D_m} \tag{2.90}$$

this can be written explicitly as

$$\alpha_l = -2 \sum_m \frac{\langle \phi_0 \mid r^l P_l(cos\theta) \mid \phi_m \rangle \langle \phi_m \mid r^l P_l(cos\theta) \mid \phi_0 \rangle}{(E_0 - E_m)} \tag{2.91}$$

our aim is to eliminate the excitation energy in the denominator, by interducing a corrosponing term in the numenator such that

$$(E_m - E_0) \langle \phi_m \mid f \mid \phi_0 \rangle = \langle \phi_m \mid [f, H_0] \mid \phi_0 \rangle = \langle \phi_m \mid r^l P_l(cos\theta) \mid \phi_0 \rangle \tag{2.92}$$

where ϕ_0 is the $1s$ state for the inner electron with nuclear charge Z, $f = f(r)$ is the function we are looking for, and H_0 is the Hamiltonian for the inner electron only, because we already sperate the inner electron terms from the Rydberg electron terms. The advantage gained is that the sum over m can be complited by closure. Letting the Hamiltonian acts to the right first and to the left for the second time, then we get

$$(E_0 - E_m) \langle \phi_m \mid f \mid \phi_0 \rangle = \langle \phi_m \mid r^l P_l(cos\theta) \mid \phi_0 \rangle \tag{2.93}$$

The summation over m (excludes the ground state) can be then completed by a closure

$$\alpha_l = -2 \langle \phi_0 \mid f \;\; r^l P_l(cos\theta) \mid \phi_0 \rangle \tag{2.94}$$

now we have to solve the differential equation to find $f(r)$, it is easy to see that $f(r)$ must be equal to $g(r) \;\; P_l(cos\theta)$ otherwise $\langle 0 \mid fV \mid 0 \rangle$ will vanish, where $g(r)$ is an arbitrary function we have to fined. Let the commutator act on the ground state

$$[f, H_0] \phi_0 = r \;\; P_1(cos\theta) \phi_0 \tag{2.95}$$

then we get

$$(E_0 - H_0) g(r) \;\; P_1(cos\theta) \phi_0 = r \;\; P_1(cos\theta) \phi_0 \tag{2.96}$$

which is the same as the first-order perturbation equation (see equations 1.24 and 2.16) and the differential equation for $g(r)$ will be

$$\frac{d^2}{dr^2}g(r) + 2(\frac{1}{r} - Z)\frac{d}{dr}g(r) - \frac{2}{r^2}g(r) = 2r \tag{2.97}$$

with a solution of

$$g(r) = -\frac{r}{Z^2} - \frac{r^2}{2Z} \tag{2.98}$$

as shown in Appendix I. Thus

$$f(r) = -P_1(cos\theta)\left[\frac{r}{Z^2} + \frac{r^2}{2Z}\right] \tag{2.99}$$

now we are ready to calculate the polarizability

$$\begin{aligned} \alpha_1 &= -2\langle 1s \mid f_1 V^{(1)} \mid 1s\rangle \\ &= -\int d^3 r e^{-2Zr}\left[\frac{2r^2}{Z^2} + \frac{r^3}{Z}\right][\ P_1(cos\theta)]^2 \\ &= -\frac{9}{2}Z^{-4} \end{aligned} \tag{2.100}$$

To solve for α_2, α_3, and α_4 we need to consider the cases of $l = 2$, 3, and 4 for both $V^{(l)}$ and $f_l(r)$, so the more general form for the differential equation is

$$\frac{d^2}{dr^2}g_l(r) + 2(\frac{1}{r} - Z)\frac{d}{dr}g_l(r) - \frac{l(l+1)}{r^2}g_l(r) = 2r^l \tag{2.101}$$

and its solution is [28]

$$g_l(r) = -\frac{r^l}{Z^2 l} - \frac{r^{l+1}}{Z(l+1)} \tag{2.102}$$

By solving a similar integral we did for α_1 we can get the other polarizabilities

$$\alpha_2 = -15Z^{-6} \tag{2.103}$$

$$\alpha_3 = -\frac{525}{4}Z^{-8} \tag{2.104}$$

$$\alpha_4 = -\frac{8505}{4}Z^{-10} \tag{2.105}$$

Now for the third-order energy E_3 we have two terms in the denominator which is not a problem, all what we have to do is just to apply the Dalgano function two times, and the coefficients we are going to solve have the form

$$\eta = 2\sum_{m,n}\sum_{l,l',l''}\frac{U^{(l)}_{0,m}U^{(l')}_{m,n}U^{(l'')}_{n,0}}{D_m D_n} \tag{2.106}$$

the sum can be simplified to

$$\sum_{m,n} \langle 0 \mid f^{l} \mid m\rangle\langle m \mid V^{l'} \mid n\rangle\langle n \mid f^{l''} \mid 0\rangle \tag{2.107}$$

Completing the summations over m and n by two closures we get

$$\langle 0 \mid f^{l} V^{l'} f^{l''} \mid 0\rangle \tag{2.108}$$

and the integral we have to calculate is

$$\begin{aligned} &\frac{Z^3}{\pi}\int_0^\infty dr e^{-2Zr} r^2 \left[\frac{r^l}{Z^2 l} + \frac{r^{l+1}}{Z(l+1)}\right] 2r^{l'} \left[\frac{r^{l''}}{Z^2 l''} + \frac{r^{l''+1}}{Z(l''+1)}\right] \\ &= \frac{4(p+2)!}{(2Z)^{p+4}\pi}\left[\frac{1}{ll''} + \frac{p+3}{2}\left(\frac{1}{l[l''+1]} + \frac{1}{l''[l+1]}\right) + \frac{(p+3)(p+4)}{4(l+1)(l''+1)}\right] \end{aligned} \tag{2.109}$$

where $p = l + l' + l''$. Now all that we have to do is just to subsittute the values of the indices to get final forms for the polarizability coefficients

$$\eta^{(112)} = \frac{213}{2} Z^{-8} \tag{2.110}$$

$$\kappa^{(123)} = 1620 Z^{-10} \tag{2.111}$$

$$\lambda^{(222)} = 153 Z^{-10} \tag{2.112}$$

The calculation of fourth-order energy E_4 has a problem comeing from the three different energy denominators, and the Dalgarno method cannot handle this problem directly because the coefficients have the following form

$$\epsilon = \sum_{m,n,p} \frac{U^{(l)}_{0,m} U^{(l')}_{m,n} U^{(l'')}_{n,p} U^{(l''')}_{p,0}}{D_m D_n D_p} \tag{2.113}$$

where the first and the last energy denominators (D_m, and D_p) can be eliminated in same way as we did before, but the the middle one D_n causes a problem. After eliminating the two energies, the sum simplifies to

$$\sum_{n} \frac{\langle 0 \mid fV \mid n\rangle\langle n \mid fV \mid 0\rangle}{D_n} \tag{2.114}$$

To eliminate the third energy denominator and summing over n by closure we have to solve another Dalgarno equation $F(r)$ which can be done by following the same way we got $f(r)$, but the inhomogeneous term in this case will be more complicated

$$[F, H_0] \mid 0\rangle = Vf \mid 0\rangle \tag{2.115}$$

After the commutator acts on the ground state to get

$$D_n\langle n \mid F \mid 0\rangle = \langle n \mid Vf \mid 0\rangle \tag{2.116}$$

by using the results of the last equation, the sum can be simplified to

$$\langle 0 \mid fV \mid (1- \mid 0\rangle\langle 0 \mid) \mid F \mid 0\rangle \tag{2.117}$$

yielding the final form

$$\langle 0 \mid fVF \mid 0\rangle - \langle 0 \mid fV \mid 0\rangle\langle 0 \mid F \mid 0\rangle \tag{2.118}$$

We have only one set (1111) of indices for the case of $p = 4$ which is expressed by ϵ, and for $p = 6$ cases we have two sets (1113) that is for ρ, and the last set for σ (1212) as follows

$$\epsilon^{(1111)} = \frac{329}{32}Z^{-10} \tag{2.119}$$

$$\rho^{(1113)} = \frac{4905}{2}Z^{-12} \tag{2.120}$$

$$\sigma^{(1212)} = \frac{98511}{16}Z^{-12} \tag{2.121}$$

These are the adiabatic fourth-order contributions to the energy, but it does not include the term that comes from the normalization of the perturbed wave function. That term will be discussed in the next sections. The adiabatic corrections for the second-order and third-order are fully completed at this point.

2.8 Nonadiabatic Corrections

Now we consider the motion of Rydberg electron and let us start with an expansion form of the perturbed wave function of the form

$$\mid \Psi_1\rangle = \sum_M \frac{\mid M\rangle V_{M,0}}{D_m}\left[1 - \frac{d_{m'}}{D_m} + \frac{d^2_{m'}}{D^2_m} - \frac{d^3_{m'}}{D^3_m} + \dots\right] \tag{2.122}$$

which include the nonadiabatic corrections. In order to have a means to complete the sum over m', we first define $h = h_0(x, Z-1) - e_0$ where e_0 is defined in equation (2.40). Then we can make the replacement

$$-d_{m'} \mid m'\rangle \to \hat{h} \mid m'\rangle \tag{2.123}$$

to obtain equation (2.122) in the form

$$\mid \Psi_1\rangle = \sum_M \left[1 + \frac{\hat{h}_{m'}}{D_m} + \frac{\hat{h}^2_{m'}}{D^2_m} + \frac{\hat{h}^3_{m'}}{D^3_m} + \ldots\right] \frac{\mid M\rangle V_{M,0}}{D_m} \tag{2.124}$$

The second term in the parentheses represents the first nonadiabatic correction correspond to β_l (to be calculated below). The third and the fourth terms in the same parentheses represent the second and the third nonadiabatic corrections respectively (see equations 2.47 and 2.48). The following commutation relation will be used to calculate the nonadiabatic corrections by simplifying $\mid \psi_1\rangle$

$$[\hat{h}, u^{(l,-\mu)}] = -\nabla u^{(l,-\mu)}.\nabla \tag{2.125}$$

using $\hat{h} \mid \chi_0\rangle = 0$, and following the same technique we did in section 2.4 then we can express the leading nonadiabatic correction as

$$\begin{aligned} \Delta E_2^{(l)} &= \sum_m \frac{U^{(l)}_{0,m} U^{(l)}_{m,0}}{D^2_m} \sum_{m',\mu} (u^{l,\mu}\hat{h})_{0,m'} u^{l,-\mu}_{m',0} \\ &= \beta_l \sum_\mu \langle \chi_0 \mid u^{(l,\mu)} \hat{h} u^{(l,-\mu)} \mid \chi_0\rangle \end{aligned} \tag{2.126}$$

where β_l, is the leading nonadiabatic correction to the diple polarizability α_l

$$\beta_l = \sum_m \frac{U^{(l)}_{0,m} U^{(l)}_{m,0}}{D^2_m} \tag{2.127}$$

Letting the operator $\hat{h}$ act to the right in equation 2.126 and integrating by part, then the first nonadiabatic correction can be written as

$$\begin{aligned} \Delta E_2^{(l)} &= \frac{1}{4}\beta_l \langle \nabla^2 (\chi^{-2l-2})\rangle \\ &= \frac{1}{4}\beta_l (2l+1)(2l+2)\langle \chi^{-2l-4}\rangle \end{aligned} \tag{2.128}$$

Next we calculate nonadiabatic polarizability coefficient β_l by using again Dalgarno-Lewis method

$$\begin{aligned} \beta_l &= \sum_m \frac{\langle 0 \mid V \mid m\rangle\langle m \mid V \mid 0\rangle}{D^2_m} \\ &= \sum_m \langle 0 \mid f \mid m\rangle\langle m \mid f \mid 0\rangle \\ &= \langle 0 \mid f(1- \mid 0\rangle\langle 0 \mid) f \mid 0\rangle \\ &= \langle 0 \mid f^2 \mid 0\rangle \end{aligned} \tag{2.129}$$

Performing the integral gives [28]

$$\beta_l = \frac{16(2l-1)!(2l^4+11l^3+18l^2+10l+2)}{(2Z)^{2l+4}l(l+1)} \tag{2.130}$$

Now let us go to the second nonadiabatic correction. In this case the denominator has the third power of energies D_m^3, and nominator involving $\hat{h^2}$

$$\begin{aligned} \Delta E_2^{(l)} &= \sum_m \frac{U_{0,m}^{(l)}U_{m,0}^{(l)}}{D_m^3} \sum_{m',\mu} (u^{l,\mu}\hat{h^2})_{0,m'} u_{m',0}^{l,-\mu} \\ &= \gamma_l \sum_\mu \langle \chi_0 \mid u^{(l,\mu)}\hat{h^2} u^{(l,-\mu)} \mid \chi_0 \rangle \end{aligned} \tag{2.131}$$

By using the same steps we did for the first nonadiabatic corrections we can get [32]

$$\Delta E_2^{(l)} = 2\gamma_l(l+1)^2 \left[\frac{2(Z-1)}{(2l+3)}\langle x^{-2l-5}\rangle - (l+2)(2l+1)\left(1+\frac{L(L+1)}{(l+1)(2l+3)}\right)\langle x^{-2l-6}\rangle\right] \tag{2.132}$$

As we did with β_l use the Dalgarno-Lewis method to calculate γ_l (the second nonadiabatic correction)

$$\begin{aligned} \gamma_l &= -\frac{1}{2}\sum_m \frac{\langle 0 \mid V \mid m\rangle\langle m \mid V \mid 0\rangle}{D_m^3} \\ &= -\frac{1}{2}\sum_m \langle 0 \mid f \mid m\rangle\langle m \mid F \mid 0\rangle \\ &= -\frac{1}{2}\langle 0 \mid f(1- \mid 0\rangle\langle 0 \mid)F \mid 0\rangle \\ &= -\frac{1}{2}\langle 0 \mid fF \mid 0\rangle \end{aligned} \tag{2.133}$$

Performing the integral gives

$$\gamma^{(11)} = \frac{319}{48}Z^{-8} \tag{2.134}$$

for $l = l' = 1$, and

$$\gamma^{(22)} = \frac{2399}{192}Z^{-10} \tag{2.135}$$

for $l = l' = 2$

The third nonadiabatic correction for E_2 can be calculated by following the same steps as we did for the first and second corrections

$$\begin{aligned} \Delta E_2^{(l)} &= \sum_m \frac{U_{0,m}^{(l)}U_{m,0}^{(l)}}{D_m^4} \sum_{m',\mu} (u^{l,\mu}\hat{h^3})_{0,m'} u_{m',0}^{l,-\mu} \\ &= \delta_l \sum_\mu \langle \chi_0 \mid u^{(l,\mu)}\hat{h^3} u^{(l,-\mu)} \mid \chi_0 \rangle \end{aligned} \tag{2.136}$$

where

$$
\begin{aligned}
\delta_l &= \sum_m \frac{\langle 0 \mid V \mid m\rangle\langle m \mid V \mid 0\rangle}{D_m^4} \\
&= \sum_m \langle 0 \mid F \mid m\rangle\langle m \mid F \mid 0\rangle \\
&= \langle 0 \mid F(1- \mid 0\rangle\langle 0 \mid)F \mid 0\rangle \\
&= \langle 0 \mid F^2 \mid 0\rangle - \langle 0 \mid F \mid 0\rangle^2 \qquad (2.137)
\end{aligned}
$$

performing the two integrals gives

$$
\delta^{(11)} = \frac{9673}{1152} Z^{-10} \qquad (2.138)
$$

We have now completed calculation of the nonrelativistic second-order energy corrections including the nonadiabatic terms. The final result can be summarized by

$$
\begin{aligned}
E_2 &= -\frac{1}{2}\left[\alpha_1\langle x^{-4}\rangle + \alpha_2\langle x^{-6}\rangle + \alpha_3\langle x^{-8}\rangle + \alpha_4\langle x^{-10}\rangle\right] \\
&+ \frac{1}{2}\left[6\beta_1\langle x^{-6}\rangle + 15\beta_2\langle x^{-8}\rangle + 28\beta_3\langle x^{-10}\rangle\right] \\
&+ \gamma_1\left[\frac{5}{8}(Z-1)\langle x^{-7}\rangle - 36\left(1+\frac{L(L+1)}{10}\right)\langle x^{-8}\rangle\right] \\
&+ 18\gamma_2\left[\frac{1}{7}(Z-1)\langle x^{-9}\rangle - 10\left(1+\frac{L(L+1)}{21}\right)\langle x^{-10}\rangle\right] \\
&- 8\delta_1\left[\frac{51}{7}(Z-1)\langle x^{-9}\rangle - 90\left(1+\frac{3L(L+1)}{14}\right)\langle x^{-10}\rangle\right] \qquad (2.139)
\end{aligned}
$$

We are ready to program equation (2.139) and define $\delta_3 = E_{\text{var}} - E_2^{(2)}$ where $E_2^{(2)}$ ($E_2^{(2)} = E_2^{(1)} + E_2^{(0)}$) is the sum of equations (1.2), and (2.139). Table 2.2 shows the improvement in the energies after adding the polarizability corrections. We can see that the improvement is approximately eight times compared to equations (1.28) for 10G state, and for 10K state the improvement is 66 times which shows the dramatic improvement that results from increasing the angular momentum L from 4 to 7. We next calculate the nonadiabatic corrections for the third-order energy shift E_3 by following the same steps we did for the second-order energy corrections E_2 and considering only the first nonadiabatic correction corresponding to $\frac{h}{D_m}$ term, the

Table 2.2: The differences between the variational and asymptotic calculations, all the energies in (a.u) δ_1 and δ_2 are the same as in table 1.2, and δ_3 is defined by $\delta_3 = E_{\text{var}} - E_2$

State	E_{var}	δ_1	δ_2	δ_3	δ_2/δ_3
10G	-2.0050001127706610315	-1.13×10^{-7}	1.76×10^{-9}	2.35×10^{-10}	8
10H	-2.0050000392144059740	-3.92×10^{-8}	2.32×10^{-10}	1.79×10^{-11}	13
10I	-2.0050000160865162071	-1.61×10^{-8}	4.22×10^{-11}	1.11×10^{-12}	38
10K	-2.0050000073883758768	-7.39×10^{-9}	9.31×10^{-12}	1.41×10^{-13}	66

polarizability coefficient can be written as

$$\begin{aligned} \xi &= \sum_{m,n}\sum_{l,l',l''} \frac{U^{(l)}_{0,m}U^{(l')}_{m,n}U^{(l'')}_{n,0}}{D^2_m D_n} \\ &= \sum_{m,n} \frac{\langle 0 \mid V \mid m\rangle\langle m \mid V \mid n\rangle\langle n \mid V \mid 0\rangle}{D_n D^2_m} \\ &= \sum_{m,n} \frac{\langle 0 \mid f \mid m\rangle\langle m \mid V \mid n\rangle\langle n \mid f \mid 0\rangle}{D_m} \\ &= \sum_{m,n} \langle 0 \mid F \mid m\rangle\langle m \mid V \mid n\rangle\langle n \mid f \mid 0\rangle \\ &= \langle 0 \mid F^{(1)}V^{(1)}f^{(2)} \mid 0\rangle \end{aligned} \tag{2.140}$$

Performing the integral we get

$$\xi^{(112)} = \frac{28491}{8}Z^{-10} \tag{2.141}$$

and the correction term is

$$\Delta E^{(112)}_3 = -\xi^{(112)}\langle x^{-9}\rangle \tag{2.142}$$

The third-order energy shift then becomes

$$E_3 = \frac{1}{2}\eta\langle x^{-7}\rangle + \frac{1}{2}\eta(-\xi+\kappa+\lambda)\langle x^{-9}\rangle \tag{2.143}$$

where the η, κ and λ terms are the adiabatic terms, and ξ is the nonadiabatic correction. For convenience we lump all four together to see the explicit improvement achieved by adding these terms. By defining $\delta_{23} = E_{\text{var}} - (E_2 + E_3)$ table 2.3 shows the improvement is about 23 times for 10G state and 104 times for 10K state.

Table 2.3: The differences between the variational and asymptotic calculations, all the energies in (a.u)

State	E_{var}	δ_1	δ_2	δ_{23}	δ_2/δ_{23}
10G	-2.0050001127706610315	-1.13×10^{-7}	1.76×10^{-9}	7.72×10^{-11}	23
10H	-2.0050000392144059740	-3.92×10^{-8}	2.32×10^{-10}	-1.28×10^{-12}	181
10I	-2.0050000160865162071	-1.61×10^{-8}	4.22×10^{-11}	-4.24×10^{-13}	100
10K	-2.0050000073883758768	-7.39×10^{-9}	9.31×10^{-12}	-8.99×10^{-14}	104

For E_4 there is one nonadiabatic term comes from considering the factor of $\frac{\hat{h}}{D_m}$ which is similar to the one corresponds to the third-order energy E_3. The first nonadiabatic correction to the adiabatic polarizability coefficient ϵ (see equation 2.85) can be calculated as below

$$\begin{aligned}
\theta^{(1111)} &= \sum_{m,n,p} \frac{U^{(l)}_{0,p} U^{(l')}_{p,m} U^{(l'')}_{m,n} U^{(l'')}_{n,0}}{D_n^2 D_p D_m} \\
&= \sum_{m,n,p} \frac{\langle 0 \mid V \mid p\rangle\langle p \mid V \mid m\rangle\langle m \mid V \mid n\rangle\langle n \mid V \mid 0\rangle}{D_n^2 D_p D_m} \\
&= \sum_{m,n,p} \frac{\langle 0 \mid f \mid p\rangle\langle p \mid V \mid m\rangle\langle m \mid V \mid n\rangle\langle n \mid F \mid 0\rangle}{D_m} \\
&= \sum_{m} \frac{1}{D_m}\{[\langle 0 \mid fV \mid m\rangle - \langle 0 \mid f \mid 0\rangle\langle 0 \mid V \mid m\rangle][\langle m \mid VF \mid 0\rangle - \langle m \mid V \mid 0\rangle\langle 0 \mid F \mid 0\rangle]\} \\
&= \langle 0 \mid gfVVF \mid 0\rangle - \langle 0 \mid gfV \mid 0\rangle\langle 0 \mid VF \mid 0\rangle - \langle 0 \mid fVf \mid 0\rangle \qquad (2.144)
\end{aligned}$$

Performing the three integrals gives

$$\theta^{(1111)} = \frac{791313}{128} Z^{-12} \qquad (2.145)$$

and for the term corresponding to the Rydberg electron we let $\hat{h}$ act to the right as we did in equation (2.61), then we get a factor of ∇_x^2, which gives $\langle x^{-10}\rangle$ term, and finally the nonadiabatic correction becomes

$$\Delta E_4^{(1111)} = \frac{1}{2}\theta^{(1111)}\langle x^{-10}\rangle \qquad (2.146)$$

Now let us go back and calculate the normalization term which is the second term in the fourth-order energy shift E_4, considering both terms, the adiabatic and the nonadiabatic contributions. Let us start with the adiabatic corrections

$$E_2\langle\Psi_1 \mid \Psi_1\rangle = \sum_{M,N,P} \frac{\langle 0 \mid V \mid M\rangle\langle M \mid V \mid 0\rangle\langle 0 \mid V \mid N\rangle\langle N \mid P\rangle\langle P \mid V \mid 0\rangle}{D_n D_p D_m} \tag{2.147}$$

where Ψ_1 is already defined in equation 2.123, and E_2 in equation 2.49. We again use the same steps we did in section 2.4 to separate the two summations

$$\begin{aligned} E_2\langle\Psi_1 \mid \Psi_1\rangle &= \sum_{m,n} \frac{U^{(l)}_{0,m}U^{(l)}_{m,0}U^{(l')}_{0,n}U^{(l')}_{n,0}}{D_m D_n^2} \sum_{m',n'} u^{(l)}_{0,m'}u^{(l)}_{m',0}u^{(l')}_{0,n'}u^{(l')}_{n',0} \\ &= \alpha_l\beta_{l'}\langle x^{-2l-2}\rangle\langle x^{-2l'-2}\rangle \end{aligned} \tag{2.148}$$

we have three successive sets $(l = l' = 1)$. This set corresponds to an $\langle x^{-8}\rangle$ term, and two sets of $(l = 1, l' = 2)$ and $(l = 2, l' = 1)$ corresponding to an $\langle x^{-10}\rangle$. By following the same steps we already did for both adiabatic and nonadiabatic corrections the fourth-order energy shift becomes

$$\begin{aligned} E_4 &= \frac{1}{2}[-\epsilon\langle x^{-8}\rangle + (\theta - \rho - \sigma)\langle x^{-10}\rangle + \alpha_1\beta_1\langle x^{-4}\rangle^2 \\ &+ (\alpha_1\beta_2 + \alpha_2\beta_1 - 12\alpha_1\gamma_1 - 6\beta_1^2)\langle x^{-4}\rangle\langle x^{-6}\rangle] \end{aligned} \tag{2.149}$$

Note that equation (2.149) does not include the second order energy $e_2 = \langle\Psi_1 \mid V \mid \phi_0\chi_0^{(1)}\rangle$ contained in equation (2.79). This will be calculated in detail in the following section.

2.9 Second-Order Correction e_2 due to $\mid \phi_0\chi_0^{(1)}\rangle$

In this section we calculate the additional second-order term contained in equation (2.79) due to $\mid \phi_0\chi_0^{(1)}\rangle$ where $\chi_0^{(1)}$ satisfies the first-order perturbation (equation 1.18). Let us recall the definition

$$\mid \Psi_2\rangle = \sum_{M,N,N\neq N_0} \frac{\mid N\rangle\langle N \mid V \mid M\rangle\langle M \mid V \mid 0\rangle}{D_m D_n} \left[1 - \frac{d_{m'}}{D_m} - \frac{d_{n'}}{D_n} + \ldots\right] + \mid \phi_0\chi_0^{(1)}\rangle \tag{2.150}$$

where

$$\mid \phi_0\chi_0^{(1)}\rangle = \sum_{M,N_0} \frac{\mid N_0\rangle\langle N_0 \mid V \mid M\rangle\langle M \mid V \mid 0\rangle}{D_m d_{n'}} \left[1 - \frac{d_{m'}}{D_m} + \frac{d_{m'}^2}{D_m^2} - \ldots\right] \tag{2.151}$$

Table 2.4: Adiabatic and nonadiabatic coefficients

Coef	Value	l	l'	Coef	Value	l	l'	l''	l'''
α_1	$\frac{9}{2}Z^{-4}$	1	1	δ_1	$\frac{9673}{1152}Z^{-10}$	1	1		
α_2	$15Z^{-6}$	2	2	η	$\frac{213}{2}Z^{-8}$	1	1	2	
α_3	$\frac{525}{4}Z^{-8}$	3	3	ζ	$\frac{28491}{8}Z^{-10}$	1	1	2	
α_4	$\frac{8505}{4}Z^{-10}$	4	4	κ	$1620Z^{-10}$	1	2	3	
β_1	$\frac{43}{8}Z^{-6}$	1	1	λ	$153Z^{-10}$	2	2	2	
β_2	$\frac{107}{8}Z^{-8}$	2	2	ϵ	$\frac{4329}{32}Z^{-10}$	1	1	1	1
β_3	$\frac{3265}{32}Z^{-10}$	3	3	θ	$\frac{791313}{128}Z^{-12}$	1	1	1	1
γ_1	$\frac{319}{48}Z^{-8}$	1	1	ρ	$\frac{4905}{2}Z^{-12}$	1	1	1	3
γ_2	$\frac{2399}{192}Z^{-10}$	2	2	σ	$\frac{98511}{16}Z^{-12}$	1	2	1	2

The adiabatic part of $\mid \phi_0\chi_0^{(1)}\rangle$ corresponds to the leading term

$$\mid \phi_0\chi_0^{(1)}\rangle = -\frac{1}{2}\sum_l \alpha_l \mid \phi_0\rangle \sum_{n'} \frac{\mid \chi_{n'}\rangle\langle\chi_{n'} \mid x^{-2l-2} \mid \chi_0\rangle}{d_{n'}} \tag{2.152}$$

and the nonadiabatic corrections are negligible. Summing over M in equation (2.155) is the same as that leading to equation (2.61) for $E_2^{(l)}$. The sum over $n' \neq 0$ define the solution to the perturbation equation

$$\hat{h}w^{(2l+2)}(x) = (\langle x^{-2l-2}\rangle - x^{-2l-2})\chi_0(x) \tag{2.153}$$

where $\hat{h}$ is defined in equation (2.124) and thus

$$\mid \chi_0^{(1)}\rangle = -\frac{1}{2}\sum_l \alpha_l \mid w^{(2l+2)}\rangle + \text{nonadiabatic corrections} \tag{2.154}$$

Equation (2.157) can be solved analytically (Drake and Swainson 1991) [18]. The leading two adiabatic parts of $e_2 = \langle\Psi_1 \mid V \mid \phi_0\chi_0^{(1)}\rangle$ can be written in the form $e_{2,0} = e_{2,0}^{(1,1)} + e_{2,0}^{(1,2)}$, where

$$e_{2,0}^{(j,k)} = \frac{1}{4}(2 - \delta_{j,k})\alpha_j\alpha_k\langle\chi_0 \mid x^{-2j-2} \mid w^{(2k+2)}\rangle \tag{2.155}$$

We can write the two energies as functions of n, and L (Swainson and Drake 1992) [24] as

$$e_{2,0}^{(1,1)}(n, L) = -\frac{1}{4}\alpha_1^2 S_{2,2}(n, L) \tag{2.156}$$

and

$$e_{2,0}^{(1,2)}(n,L) = -\frac{1}{2}\alpha_1\alpha_2 S_{2,4}(n,L) \tag{2.157}$$

where

$$S_{p_1,p_2}(n,L) = \langle nl \mid r^{-p_1-2}\hat{G}(n)r^{-p_2-2} \mid nl\rangle \tag{2.158}$$

and $\hat{G}(n)$ is the reduced Schrödinger-Couloumb-Green function, defined by its spectral representation

$$\hat{G}(n) = \sum \frac{\mid n'l'm'\rangle\langle n'l'm' \mid}{E_{n'} - E_n} \tag{2.159}$$

the term $n = n'$ is omitted. The results for the two cases $p_1 = p_2 = 2$, and $p_1 = 2, p_2 = 4$ are [24]

$$\begin{aligned} e_{2,0}^{(1,1)}(n,L) &= -\frac{1}{4}\alpha_1^2\frac{2^7}{n^3}\left[\frac{(2l-2)!}{(2l+3)!}\right]^2 \Bigg(\frac{2^4(2l-4)!}{(2l+5)!}\{[9(f_1-2)-6n^{-2}f_2](45+623f_1+3640f_2 \\ &\quad +560f_3)n^{-4}f_1^2f_2(3+40f_1+240f_2)\} + 27n^{-1} - 30n^{-3}f_1 + 7n^{-5}f_1^2\Bigg) \end{aligned} \tag{2.160}$$

and

$$\begin{aligned} e_{2,0}^{(1,2)}(n,L) &= -\frac{1}{2}\alpha_1\alpha_2\frac{2^9(2l-2)!(2l-4)!}{n^3(2l+3)!(2l+5)!}\{\frac{2^6(2l-6)!}{(2l+7)!}[-21(94500+122850f_1-1126125f_2 \\ &- 18931770f_3 - 11171160f_4 - 1029600f_5 - 18304f_6) \\ &- 15n^{-2}(94500 - 444150f_1 + 7747425f_2 + 337931880f_3 + 375290190f_4 \\ &+ 66518760f_5 + 2880416f_6 + 29568f_7) + 9n^{-4}f_1(90300 - 177450f_1 \\ &+ 1738450f_2 + 133125575f_3 + 160040870f_4 + 29322216f_5 + 1293600f_6 + 13440f_7) \\ &+ 2n^{-6}f_1f_2f_3(45 + 252f_1 - 1680f_2 - 2240f_3)] \\ &+ 315n^{-1} + 125n^{-3}(3-5f_1) - 7n^{-5}f_1(43-39f_1) - 27n^{-7}f_1f_2\} \end{aligned} \tag{2.161}$$

where

$$f_n(l) = \frac{(l+n)!}{(l-n)!} \tag{2.162}$$

Adding e_2 to equation (2.149) gives

$$\begin{aligned} E_4 &= \frac{1}{2}[-\epsilon\langle x^{-8}\rangle + (\theta-\rho-\sigma)\langle x^{-10}\rangle + \alpha_1\beta_1\langle x^{-4}\rangle^2 \\ &+ (\alpha_1\beta_2 + \alpha_2\beta_1 - 28\alpha_1\gamma_1 - 10\beta_1^2)\langle x^{-4}\rangle\langle x^{-6}\rangle] \\ &+ e_{2,0}^{(1,1)} + (1-6\beta_1/\alpha_2)e_{2,0}^{(1,2)} \end{aligned} \tag{2.163}$$

Table 2.5: Adiabatic second-order energies $e^{(1,1)}_{2,0}(n, L)$ calculated from equation 2.160 in (MHz)

Z	10G	10H	10I	10K	10L	10M
2	-0.206399	-0.019208	-0.002640	-0.000468	-0.000098	-0.000023
3	-0.515461	-0.047970	-0.006594	-0.001168	-0.000244	-0.000056
4	-0.587799	-0.054702	-0.007520	-0.001332	-0.000279	-0.000064
5	-0.554101	-0.051566	-0.007089	-0.001255	-0.000263	-0.000061
6	-0.491588	-0.045748	-0.006289	-0.001114	-0.000233	-0.000054
7	-0.427677	-0.039801	-0.005471	-0.000969	-0.000203	-0.000047
8	-0.370565	-0.034486	-0.004741	-0.000839	-0.000176	-0.000041
9	-0.321807	-0.029948	-0.004117	-0.000729	-0.000153	-0.000035
10	-0.280836	-0.026135	-0.003593	-0.000636	-0.000133	-0.000031
11	-0.246522	-0.022942	-0.003154	-0.000558	-0.000117	-0.000027
12	-0.217723	-0.020262	-0.002785	-0.000493	-0.000103	-0.000024
13	-0.193437	-0.018002	-0.002475	-0.000438	-0.000092	-0.000021
14	-0.172836	-0.016085	-0.002211	-0.000392	-0.000082	-0.000019
15	-0.155252	-0.014448	-0.001986	-0.000352	-0.000074	-0.000017
16	-0.140148	-0.013043	-0.001793	-0.000317	-0.000066	-0.000015
17	-0.127095	-0.011828	-0.001626	-0.000288	-0.000060	-0.000014
18	-0.115748	-0.010772	-0.001481	-0.000262	-0.000055	-0.000013

Tables (2.5) and (2.6) show the adiabatic second-order energies expressed in MHz and KHz respectively.

Table 2.6: Adiabatic second-order energies $e_{2,0}^{(1,2)}(n, L)$ calculated from equation 2.161 in (KHz)

Z	10G	10H	10I	10K	10L	10M
2	-7.011397	-0.208526	-0.011786	-0.000968	-0.000098	-0.000011
3	-31.129340	-0.925819	-0.052330	-0.004296	-0.000436	-0.000047
4	-44.927034	-1.336176	-0.075524	-0.006200	-0.000629	-0.000068
5	-48.186530	-1.433117	-0.081003	-0.006649	-0.000675	-0.000073
6	-46.386940	-1.379595	-0.077978	-0.006401	-0.000650	-0.000070
7	-42.695174	-1.269798	-0.071772	-0.005892	-0.000598	-0.000064
8	-38.551085	-1.146549	-0.064806	-0.005320	-0.000540	-0.000058
9	-34.549913	-1.027550	-0.058080	-0.004768	-0.000484	-0.000052
10	-30.909628	-0.919284	-0.051960	-0.004265	-0.000433	-0.000047
11	-27.683873	-0.823347	-0.046538	-0.003820	-0.000388	-0.000042
12	-24.858971	-0.739331	-0.041789	-0.003430	-0.000348	-0.000037
13	-22.396063	-0.666082	-0.037649	-0.003091	-0.000314	-0.000034
14	-20.249859	-0.602252	-0.034041	-0.002794	-0.000284	-0.000030
15	-18.376723	-0.546543	-0.030892	-0.002536	-0.000257	-0.000028
16	-16.737357	-0.497786	-0.028136	-0.002310	-0.000234	-0.000025
17	-15.297762	-0.454971	-0.025716	-0.002111	-0.000214	-0.000023
18	-14.028926	-0.417235	-0.023583	-0.001936	-0.000196	-0.000021

2.10 Total Nonrelativistic Energies

We have all the energy shifts for terms up to $\langle x^{-10}\rangle$ except the mass polarization (which will be calculated in the next chapter). The complete expression for the asymptotic expansions energy for the helium atom (Z=2) can be expressed in the form

$$E_\infty = -2 - \frac{1}{2n^2} + \Delta E_\infty \tag{2.164}$$

where

$$\begin{aligned}
\Delta E_\infty &= E_2 + E_3 + E_4 \\
&= \frac{1}{2}\{-\alpha_1\langle x^{-4}\rangle - (\alpha_2 - 6\beta_1)\langle x^{-6}\rangle + [\eta + \frac{16}{5}(Z-1)\gamma_1] + \langle x^{-7}\rangle \\
&+ \left[-\alpha_3 + 15\beta_2 - \epsilon + \alpha_1\beta_1 - 72\gamma_1\left(1 + \frac{L(L+1)}{10}\right)\right]\langle x^{-8}\rangle \\
&+ [-\zeta + \kappa + \lambda + \frac{36}{7}(Z-1)\gamma_2 - \frac{816}{7}(Z-1)\delta_1]\langle x^{-9}\rangle \\
&+ [-\alpha_4 + 28\beta_3 + \theta - \rho - \sigma + \alpha_1\beta_2 + \alpha_2\beta_1 - 28\alpha_1\gamma_1 \\
&- 10\beta_1^2 - 360\gamma_2\left[1 + \frac{L(L+1)}{21}\right] \\
&+ 1440\delta_1\left(1 + \frac{3L(L+1)}{14}\right)]\langle x^{-10}\rangle\} \\
&+ e_{2,0}^{(1,1)} + (1 - 6\beta_1/\alpha_2)e_{2,0}^{(1,2)} + O(\langle x^{-11}\rangle)
\end{aligned} \tag{2.165}$$

Now equation (2.164) is ready to be compared with the nonrelativistic variational calculations (see table 2.7), and for higher angular momentum L see tables (2.8, 2.9, and 2.10) which compare our results [46] with the CI results [38]. Recently G. Lagmago Kamta, B. Piraux, and A. Scrinzi [38] performed what they claimed were high precision CI calculations. However, our asymptotic expansions showed that not even the leading diple correction term proportional to $\alpha\langle x^{-4}\rangle$ was contained correctly in their calculation (see tables 2.9 and 2.10). We proposed that there is an important class of configurations missing from the CI calculations, subsequent calculations by them verified that this is indeed the case. Table (2.12) shows the contributions to the nonrelativistic energy eigenvalue for the helium atom at a state of 10M, where half of the contribution correspond to $\langle x^{-10}\rangle$ term is the uncertainty in our calculations. The important point is that the first two entries in table 2.12 $-Z^2/2 - 1/2n^2$ are independent of L, they therefore cancel exactly for transitions between states with the same

n but different L. Thus a CI calculation that does not get the leading dipole polarization correction correct will give grossly incorrect results for transition frequencies with $\triangle n = 0$.

Table 2.7: The differences between the variational and asymptotic calculations, all the energies in (a.u)

State	E_{var}	E_{AE}	$E_{\text{var}} - E_{\text{AE}}$
10G	-2.005 000 112 770 661 0315	-2.005 000 112 524 976 2383	-2.5×10^{-10}
10H	-2.005 000 039 214 405 9740	-2.005 000 039 213 856 1930	-5.5×10^{-13}
10I	-2.005 000 016 086 516 2071	-2.005 000 016 086 511 5598	-4.6×10^{-15}
10K	-2.005 000 007 388 375 8768	-2.005 000 007 388 375 8121	-6.5×10^{-17}

Table 2.8: shows the energy eigenvalues for ($L = 7$) states for helium atom, E_1 is our results by using the asymptotic expansion method [46], E_2 is the CI results obtained by [36] (CI method), $E_1' = E_1 - 2 - \frac{1}{2n^2}$, $E_2' = E_2 - 2 - \frac{1}{2n^2}$, Δ is the difference between our and the CI results, and δ is the uncertainty in our results

n	$-E_1$	$-E_1'$	$-E_2'$	$\Delta \times 10^{16}$	$\delta \times 10^{16}$
8	2.007 812 512 570 229 3	0.000 000 012 570 2293	0.000 000 012 570 227	2.	1.
9	2.006 172 849 096 329 8	0.000 000 009 590 1569	0.000 000 009 590 156	1.	2.
10	2.005 000 007 388 375 8	0.000 000 007 388 3758	0.000 000 007 388 375	1.	2.
11	2.004 132 237 176 715 3	0.000 000 005 771 7567	0.000 000 005 771 758	2.	2.
12	2.003 472 226 797 270 3	0.000 000 004 575 0481	0.000 000 004 575 059	11.	2.
13	2.002 958 583 559 214 5	0.000 000 003 677 5577	0.000 000 003 677 554	3.	2.
14	2.002 551 023 402 909 7	0.000 000 002 994 7464	0.000 000 002 994 744	3.	1.
15	2.002 222 224 690 046 0	0.000 000 002 467 8238	0.000 000 002 467 821	3.	1.
16	2.001 953 127 055 667 0	0.000 000 002 055 6670	0.000 000 002 055 667	0.	1.
17	2.001 730 105 535 420 0	0.000 000 001 729 1916	0.000 000 001 729 190	2.	1.

Table 2.9: shows the energy eigenvalues for ($L = 10$) states, note that Δ is multiplied by 10^{-11} (a.u) while δ is multiplied by 10^{-19}(a.u) which is 10^8 times smaller

n	$-E_1$	$-E_1'$	$-E_2'$	$\Delta \times 10^{11}$	$\delta \times 1$
11	2.004 132 232 280 227 0202	0.000 000 000 875 268 3426	0.000 000 000 417 089	45	11
12	2.003 472 222 943 200 2286	0.000 000 000 720 978 0063	0.000 000 000 343 625	37	18
13	2.002 958 580 477 370 6029	0.000 000 000 595 713 7981	0.000 000 000 283 955	31	22
14	2.002 551 020 903 322 9573	0.000 000 000 495 159 6920	0.000 000 000 236 054	25	23
15	2.002 222 222 636 741 5704	0.000 000 000 414 519 3482	0.000 000 000 197 624	21	23
16	2.001 953 125 349 602 6708	0.000 000 000 349 602 6708	0.000 000 000 166 681	18	22
17	2.001 730 104 103 256 0302	0.000 000 000 297 027 6565	0.000 000 000 141 623	15	21
18	2.001 543 210 130 691 8405	0.000 000 000 254 148 6306	0.000 000 000 121 186	13	20
19	2.001 385 041 770 166 6786	0.000 000 000 218 920 1413	0.000 000 000 104 390	11	18
20	2.001 250 000 189 764 7724	0.000 000 000 189 764 7724	0.000 000 000 090 496	09	16

Table 2.10: shows the energy eigenvalues for ($L = 11$) states

n	$-E_1$	$-E_1'$	$-E_2'$	$\Delta \times 10^{11}$	$\delta \times 1$
12	2.003 472 222 647 669 7866	0.000 000 000 425 447 5644	0.000 000 000 203 585	22	18
13	2.002 958 580 238 056 9723	0.000 000 000 356 400 1676	0.000 000 000 170 565	18	30
14	2.002 551 020 707 350 0718	0.000 000 000 299 186 8065	0.000 000 000 143 197	15	37
15	2.002 222 222 474 545 3235	0.000 000 000 252 323 1013	0.000 000 000 120 776	13	40
16	2.001 953 125 214 026 3817	0.000 000 000 214 026 3817	0.000 000 000 102 446	11	41
17	2.001 730 103 988 891 1831	0.000 000 000 182 662 8094	0.000 000 000 087 441	09	41
18	2.001 543 210 033 406 7279	0.000 000 000 156 863 5180	0.000 000 000 075 090	08	39
19	2.001 385 041 686 770 4310	0.000 000 000 135 523 8936	0.000 000 000 064 880	07	37
20	2.001 250 000 117 766 8599	0.000 000 000 117 766 8599	0.000 000 000 056 391	06	34
21	2.001 133 786 950 972 6642	0.000 000 000 102 900 1018	0.000 000 000 049 265	05	32

Table 2.11: shows the nonrelativistic energy eigenvalues E calculated by the asymptotic method for states of angular momentum L up to 14, δ is the uncertainty expressed in atomic units (e^2/a_ν)

L	n	E	$\delta \times 10^{16}$
7	8	-2.007 812 512 570 229 299 6	11
	9	-2.006 172 849 096 329 752 3	16
	10	-2.005 000 007 388 375 834 1	18
	11	-2.004 132 237 176 715 328 1	18
	12	-2.003 472 226 797 270 345 7	16
	13	-2.002 958 583 559 214 483 1	15
	14	-2.002 551 023 402 909 675 7	13
	15	-2.002 222 224 690 046 023 8	11
	16	-2.001 953 127 055 667 037 9	10
	17	-2.001 730 105 535 419 983 7	8

L	n	E	$\delta \times 10^{17}$
8	9	-2.006 172 844 174 560 382 3	8
	10	-2.005 000 003 675 244 488 0	12
	11	-2.004 132 234 317 414 120 4	14
	12	-2.003 472 224 554 125 183 7	14
	13	-2.002 958 581 769 974 758 1	14
	14	-2.002 551 021 954 497 073 0	12
	15	-2.002 222 223 502 038 818 3	11
	16	-2.001 953 126 069 770 014 6	10
	17	-2.001 730 104 708 628 242 2	9
	18	-2.001 543 210 644 174 526 8	8

L	n	E	$\delta \times 10^{18}$
9	10	-2.005 000 001 934 675 380 5	8
	11	-2.004 132 232 966 556 319 2	13
	12	-2.003 472 223 488 347 173 1	15
	13	-2.002 958 580 916 242 012 5	16
	14	-2.002 551 021 261 123 416 3	16
	15	-2.002 222 222 931 854 517 1	15
	16	-2.001 953 125 595 605 870 9	14
	17	-2.001 730 104 310 311 145 0	12
	18	-2.001 543 210 306 503 563 9	11
	19	-2.001 385 041 920 650 045 0	10

L	n	E	$\delta \times 10^{19}$
10	11	-2.004 132 232 280 227 020 2	11
	12	-2.003 472 222 943 200 228 6	18
	13	-2.002 958 580 477 370 602 9	22
	14	-2.002 551 020 903 322 957 3	23
	15	-2.002 222 222 636 741 570 4	23
	16	-2.001 953 125 349 602 670 8	22
	17	-2.001 730 104 103 256 030 2	21
	18	-2.001 543 210 130 691 840 5	20
	19	-2.001 385 041 770 166 678 6	18
	20	-2.001 250 000 189 764 772 4	16

L	n	E	$\delta \times 10^{20}$
11	12	-2.003 472 222 647 669 786 64	18
	13	-2.002 958 580 238 056 972 34	30
	14	-2.002 551 020 707 350 071 78	37
	15	-2.002 222 222 474 545 323 49	40
	16	-2.001 953 125 214 026 381 70	41
	17	-2.001 730 103 988 891 183 07	41
	18	-2.001 543 210 033 406 727 88	39
	19	-2.001 385 041 686 770 430 98	37
	20	-2.001 250 000 117 766 859 86	34
	21	-2.001 133 786 950 972 664 17	32

L	n	E	$\delta \times 10^{21}$
12	13	-2.002 958 580 101 207 765 823	35
	14	-2.002 551 020 594 708 187 804	59
	15	-2.002 222 222 380 947 857 240	74
	16	-2.001 953 125 135 545 320 024	83
	17	-2.001 730 103 922 521 924 511	86
	18	-2.001 543 209 976 832 911 265	86
	19	-2.001 385 041 638 190 382 080	83
	20	-2.001 250 000 075 766 338 519	80
	21	-2.001 133 786 914 431 440 619	75
	22	-2.001 033 057 909 639 997 850	70

L	n	E	$\delta \times 10^{21}$
13	14	-2.002 551 020 527 347 779 222 9	7
	15	-2.002 222 222 324 721 558 026 7	13
	16	-2.001 953 125 088 231 855 907 1	16
	17	-2.001 730 103 882 396 195 792 2	19
	18	-2.001 543 209 942 549 970 092 4	20
	19	-2.001 385 041 608 695 107 822 7	20
	20	-2.001 250 000 050 224 898 230 4	20
	21	-2.001 133 786 892 179 758 170 9	19
	22	-2.001 033 057 890 145 057 526 6	18
	23	-2.000 945 179 618 584 203 280 2	17

L	n	E	$\delta \times 10^{22}$
14	15	-2.002 222 222 289 793 953 536 6	20
	16	-2.001 953 125 058 721 907 548 7	33
	17	-2.001 730 103 857 288 827 819 4	43
	18	-2.001 543 209 921 042 675 294 9	49
	19	-2.001 385 041 590 151 707 230 9	52
	20	-2.001 250 000 034 138 563 390 0	53
	21	-2.001 133 786 878 144 252 243 7	53
	22	-2.001 033 057 877 832 623 732 1	52
	23	-2.000 945 179 607 728 619 807 7	50
	24	-2.000 868 055 576 592 020 687 4	48

Table 2.12: Breakdown of contributions to the nonrelativistic energy for the n=10, L=9 state of helium.

Quantity	value in (a.u)
$-Z2/2$	-2.000 000 000 000 000 000
$-1/2n2$	0.005 000 000 000 000 000 0
$c_4\langle x^{-4}\rangle/2$	-0.000 000 001 934 984 520 1
$c_6\langle x^{-6}\rangle/2$	0.000 000 000 000 309 060 0
$c_7\langle x^{-7}\rangle/2$	0.000 000 000 000 008 175 5
$c_8\langle x^{-8}\rangle/2$	-0.000 000 000 000 004 669 5
$c_9\langle x^{-9}\rangle/2$	-0.000 000 000 000 000 011 1
$c_{10}\langle x^{-10}\rangle/2$	0.000 000 000 000 000 016 5
Second order	-0.000 000 000 000 003 431 8
Uncertainty	0.000 000 000 000 000 008 25
Total	-2.005 000 001 934 675 380 5

Chapter 3

Mass Polarization Corrections

In this chapter we will calculate the mass polarization term that we postponed in chapter (2). As for the total energy itself, an asymptotic expansion method can be developed to obtain the mass polarization correction. The key point is to introduce Jacobi coordinates to treat the motion of the nucleus in the center-of-mass frame. The center-of-mass and relative coordinates transformation equation (2.4) generates a mass polarization term $-y\nabla_1.\nabla_2$ where $y = \mu/M$ (μ is the reduced mass, and M is the mass of the nucleus). For the asymptotic expansion method we use Jacobi coordinates instead of the center-of-mass and relative coordinates, the Jacobi coordinates give us advantages which eliminate the mass polarization term in the main Hamiltonian, but with an extra term in the potential $V(r, x)$.

Even though and extra term has been added in the potential, $V(r, x)$ still has the simple multipole expansion form (see equation 3.10)

3.1 The Jacobi coordinates

Jacobi coordinates can be defined as

$$r = (R_1 - R_0)/a_\mu \tag{3.1}$$

$$x = \Lambda[R_2 - R_0 - y(R_1 - R_0)]/a_\mu \tag{3.2}$$

$$X = \Lambda[R_0 + y(R_1 + R_2 - R_0)]/a_\mu \tag{3.3}$$

where $\Lambda = 1/(1-y^2)$. The derivatives transform according to

$$\nabla_{R_1} = a_\mu^{-1}(\nabla_r - \Lambda y \nabla_x + \Lambda y \nabla_X) \tag{3.4}$$

$$\nabla_{R_2} = a_\mu^{-1}(\Lambda \nabla_x + \Lambda y \nabla_X) \tag{3.5}$$

$$\nabla_{R_0} = -a_\mu^{-1}(\nabla_r + \Lambda \nabla_x - \Lambda y \nabla_X) \tag{3.6}$$

X is the ignorable coordinate in the center-of-mass frame, the Hamiltonian becomes

$$H = \left[-\frac{1}{2}\nabla_r^2 - \frac{Z}{r}\right] + \Lambda\left[-\frac{1}{2}\nabla_x^2 - \frac{Z-1}{x}\right] + V(r,x) \tag{3.7}$$

In terms of a single electron Hamiltonian

$$H = h_r + \Lambda h_x + V(r,x) \tag{3.8}$$

where

$$V(r,x) = \Lambda\left[\frac{Z-1}{x} - \frac{Z}{|x + \Lambda y r|} + \frac{1}{|x - \Lambda(1-y)r|}\right] \tag{3.9}$$

which has the following multipole expansion

$$V(r,x) = \frac{1}{x}\sum_{l=1}^{\infty} C_l \left(\frac{r}{x}\right)^l P_l(\hat{r}.\hat{x}) \tag{3.10}$$

with

$$C_l = \frac{[(1-y)^l - Z(-y)^l]}{(1-y^2)^{l+1}} \tag{3.11}$$

Each coefficient in equation (2.168) is multiplied by combinations of C_l factors according to the combinations of multipolarities that contribute. For example, the 2^l-pole polarizability α_l is quadratic in C_l and so it is replaced by $C_l^2\alpha_l$. The same is true for β_l and γ_l. The C_l can be expanded according to

$$\begin{aligned} C_1 &= 1 + (Z-1)y + 2y^2 + \ldots \\ C_2 &= 1 - 2y + (4-Z)y^2 + \ldots \\ C_3 &= 1 - 3y + 7y^2 + + \ldots \\ C_4 &= 1 - 4y + 11y^2 + + \ldots \end{aligned} \tag{3.12}$$

The leading term $-\alpha_1\langle x^{-4}\rangle/2$ in equation 2.168 becomes $-\alpha_1 C_1^2\langle x^{-4}\rangle/2$. The leading mass polarization terms can be calculated by finding the differences between the infinite mass and finite mass Hamiltonian, for the above term this will be $-\alpha_1(C_1^2 - 1)\langle x^{-4}\rangle/2$.

3.2 The Mass Polarization Energy Coefficients

Adding the mass polarization corrections to the energy in equation (2.169) the total nonrelativistic energy becomes

$$E_M = E_\infty + y\varepsilon_M^{(1)} + y^2\varepsilon_M^{(2)} + y^3\varepsilon_M^{(3)} + y^4\varepsilon_M^{(4)} \tag{3.13}$$

The expansion in (3.12) causes the first and the second-order contributions to the corresponding mass polarization energy coefficients $\varepsilon_M^{(1)}$ and $\varepsilon_M^{(2)}$ to be separated (second term corresponds to $\varepsilon_M^{(1)}$, and third term corresponds to $\varepsilon_M^{(2)}$).

There is another contribution which comes from expanding Λ ($\Lambda = 1/(1-y^2)$) in the screened hydrogenic energies

$$\varepsilon_0 + e_0 = -\frac{Z^2}{2} - \frac{(Z-1)^2}{2n^2}(1 + y^2 + y^4 + \ldots) \tag{3.14}$$

Collecting the preceding contributions, and defining

$$\begin{aligned} Z_1 &= 4 + (Z-1)^2 \\ Z_{11} &= 2[7 + 3Z(Z-2)] \\ Z_\eta &= 13 + Z(Z-7) \\ Z_{12} &= -11 + (Z-6)^2 \end{aligned} \tag{3.15}$$

for the y^2 coefficients of C_1^2, C_1^4, $C_1^2C_2$, and $C_1^2C_2^2$, respectively, the final results are

$$
\begin{aligned}
\varepsilon_M^{(1)} &= -(Z-1) - \alpha_1\langle x^{-4}\rangle + [2\alpha_2 + 6(Z-1)\beta_1]\langle x^{-6}\rangle \\
&+ [(Z-2)\eta + \frac{16}{5}(Z-1)^2\gamma_1]\langle x^{-7}\rangle \\
&+ \{3\alpha_3 - 30\beta_2 + 2(Z-1)(\alpha_1\beta_1 - \epsilon) \\
&- 72(Z-1)\gamma_1\left[1 + \frac{L(L+1)}{10}\right]\}\langle x^{-8}\rangle \\
&+ [-(Z-2)\zeta + \frac{1}{2}(Z-6)\kappa - 3\lambda \\
&- \frac{72}{7}(Z-1)\gamma_2 - \frac{816}{7}(Z-1)^2\delta_1]\langle x^{-9}\rangle \\
&+ [4\alpha_4 - 84\beta_3 + 2(Z-1)(\theta - 28\alpha_1\gamma_1 - 10\beta_1^2) \\
&- \frac{3}{2}(Z-2)\rho + (Z-3)(-\sigma + \alpha_1\beta_2 + \alpha_2\beta_1) \\
&+ 720\gamma_2\left(1 + \frac{L(L+1)}{21}\right) + 1440(Z-1)\delta_1\left(1 + \frac{3L(L+1)}{14}\right)]\langle x^{-10}\rangle \\
&+ 4(Z-1)e_{2,0}^{(1,1)} + 2[Z-3 \\
&- 12(Z-1)\beta_1/\alpha_2]e_{2,0}^{(1,2)} + O(\langle x^{-11}\rangle) \qquad (3.16)
\end{aligned}
$$

$$
\begin{aligned}
\varepsilon_M^{(2)} &= -\frac{1}{2}(Z-1)^2 n^{-2} - \frac{1}{2}Z_1\alpha_1\langle x^{-4}\rangle + [(Z-6)\alpha_2 \\
&+ 3Z_1\beta_1]\langle x^{-6}\rangle + \left[\frac{1}{2}Z_\eta\eta + \frac{8}{5}(Z-1)Z_1\gamma_1\right]\langle x^{-7}\rangle \\
&+ \{-23\alpha_3/2 - 15(Z-6)\beta_2 + \frac{1}{2}Z_{11}(\alpha_1\beta_1 - \epsilon) \\
&- 36Z_1\gamma_1\left(1 + \frac{L(L+1)}{10}\right)\}\langle x^{-8}\rangle \\
&+ \{-Z_\eta\zeta - 3(Z-4)\kappa/2 - \frac{3}{2}(Z-8)\lambda - \frac{36}{7}(Z-1)(Z-6)\gamma_2 \\
&- \frac{408}{7}(Z-1)Z_1\delta_1\}\langle x^{-9}\rangle + \{-19\alpha_4 + 322\beta_3 \\
&+ \frac{1}{2}Z_{11}(\theta - 28\alpha_1\gamma_1 - 10\beta_1^2) - \frac{1}{2}[25 + 3Z(Z-5)]\rho \\
&+ \frac{1}{2}Z_{12}(-\sigma + \alpha_1\beta_2 + \alpha_2\beta_1) \\
&- 360(Z-6)\gamma_2\left(1 + \frac{L(L+1)}{21}\right) \\
&+ 72Z_1\delta_1\left(1 + \frac{3L(L+1)}{14}\right)\}\langle x^{-10}\rangle \\
&+ Z_{11}e_{2,0}^{(1,1)} + (Z_{12} - 6Z_{11}\beta_1/\alpha_2)e_{2,0}^{(1,2)} + O(\langle x^{-11}\rangle) \qquad (3.17)
\end{aligned}
$$

$$\varepsilon_M^{(3)} = -4(Z-1)\alpha_1\langle x^{-4}\rangle + O(\langle x^{-6}\rangle) \tag{3.18}$$

and

$$\varepsilon_M^{(4)} = -\frac{1}{2}(Z-1)^2 n^{-2} + O(\langle x^{-4}\rangle) \tag{3.19}$$

Tables (3.1) and (3.2) show a comparison between the asymptotic and variational methods for the first and second-order mass polarization coefficients. From the two tables, the comparison at 5G state shows that the asymptotic results are sufficient to replace the variational calculations, because the uncertainty in the asymptotic expansion result is in the range of the difference between the two calculations. As the angular momentum L goes higher we can see that the differences between the variational and asymptotic methods can be neglected.

Table 3.1: Comparison between variational (calculated by Drake) and asymptotic (equation 3.16) for the first-order mass polarization coefficient, units in 10^{-3}a.u

State	Variational	Asymptotic	Diferences
4F	-0.0098469545(2)	-0.0101(4)	0.0003(4)
5F	-0.0055553923(6)	-0.0057(3)	0.002(3)
6F	-0.003375358(7)	-0.0035(2)	0.0001(2)
7F	-0.00218629(5)	-0.0023(1)	0.0001(1)
8F	-0.00149097(1)	-0.00155(9)	0.00006(9)
9F	-0.001059809(2)	-0.00110(7)	0.00004(7)
10F	-0.000779184(9)	-0.00081(5)	0.00003(5)
5G	-0.00140420744(5)	-0.0014037(9)	-0.0000005(9)
6G	-0.000898352(1)	-0.000898(1)	-0.000000(1)
7G	-0.000598201(1)	-0.0005978(8)	-0.0000004(8)
8G	-0.00041484720(5)	-0.0004146(6)	-0.0000002(6)
9G	-0.0002981435(1)	-0.0002979(5)	-0.0000002(5)
10G	-0.000220883(3)	-0.0002207(4)	-0.0000002(4)
6H	-0.0002903469081(3)	-0.000290348(3)	0.000000001(2)
7H	-0.00020109752(3)	-0.000201098(3)	0.000000001(3)
8H	-0.0001426489(4)	-0.000142650(3)	0.000000001(3)
9H	-0.00010400205(2)	-0.000104003(3)	0.000000001(3)
10H	-0.00007780645(4)	-0.000077807(2)	0.000000001(2)
7I	-0.000077775523(4)	-0.00007777554(3)	0.00000000002(3)
8I	-0.00005693591(2)	-0.00005693594(5)	0.00000000003(5)
9I	-0.00004231360(6)	-0.00004231367(5)	0.00000000006(8)
10I	-0.0000320589(3)	-0.00003205900(5)	0.0000000000(3)
8K	-0.000025111331651(1)	-0.000025111332(1)	0.000000000001(1)
9K	-0.0000191516196(3)	-0.000019151621(2)	0.000000000002(2)
10K	-0.0000147514111(7)	-0.000014751390(2)	-0.000000000021(7)

Table 3.2: Comparison between variational (calculated by Drake) and asymptotic (equation 3.17) for the second-order mass polarization coefficient, units in 10^{-3}a.u

State	Variational	Asymptotic	Diferences
4F	-31.276 164(4)	-31.276 1(1)	-0.000 0(1)
5F	-20.015 030(7)	-20.014 96(9)	-0.000 07(9)
6f	-13.898 10(3)	-13.898 05(6)	-0.000 05(7)
7F	-10.209 9(4)	10.210 04(4)	0.000 1(4)
8f	-7.816 5(3)	-7.816 57(3)	0.000 1(3)
9F	-6.175 61(1)	-6.175 74(2)	0.000 13(3)
10f	-5.000 55(3)	-5.002 14(2)	0.000 06(2)
5G	-20.003 562 72(7)	-20.003 568(3)	0.000 005(3)
6G	-13.891 18(1)	-13.891 183(3)	0.00 00(1)
7G	-10.205 61(7)	-10.205 613(2)	0.000 00(7)
8G	-7.813 566(3)	-7.813 564(2)	-0.000 002(3)
9G	-6.173 586(4)	-6.173 605(1)	0.000 019(5)
10G	-5.000 55(3)	-5.000 568(1)	0.000 02(3)
6H	-13.889 619 02(4)	-13.889 619 36(7)	0.000 000 34(8)
7H	-10.204 589(2)	-10.204 588 4998)	-0.000 000(2)
8H	-7.812 857(6)	-7.812 859 93(7)	0.000 003(6)
9H	-6.173 103(3)	-6.173 102 12(6)	-0.000 000(3)
10H	-5.000 081(1)	-5.000 196 56(5)	0.000 003 1(2)
7I	-10.204 276 76(2)	-10.204 276 794(4)	0.000 000 04(2)
8I	-7.812 642 91(4)	-7.812 642 992(5)	0.000 000 08(4)
9I	-6.172 945 9(2)	-6.172 945 836(5)	-0.000 000 1(2)
10I	-5.000 081(1)	-5.000 196 56(5)	-0.000 000(1)
8K	-7.812 563 02(1)	-7.812 563 0145(4)	-0.000 000 01(1)
9K	-6.172 887 59(1)	-6.172 887 5893(5)	-0.000 000 00(1)
10K	-5.000 036 88(5)	-5.000 037 0503(5)	0.000 000 17(5)

Chapter 4

Relativistic and QED Corrections

In this chapter we need to find nonrelativistic operators whose expectation values with respect to nonrelativistic solutions to the Schrodinger equation are equal to the corresponding relativistic operators from the Dirac equation evaluated with respect to relativistic wave functions. The matrix elements will be calculated with respect to $\psi_{\rm NR}$ satisfying the nonrelativistic Schrodinger equation. All the relativistic corrections are going to be separated into terms of lowest order α^2, relativistic reduced-mass corrections of order $y\alpha^2$, $(y = \mu/M)$ and anomalous magnetic moment corrections of order α^3 [2, 26, 32]. This corresponds to the expansion

$$E = E_{\rm NR} + \alpha^2 E^{(2,0)}_{\rm rel} + \alpha^3 E^{(3,0)}_{\rm anom} + \alpha^2 \frac{\mu}{M} E^{(2,1)}_{\rm rel} + \alpha^3 E^{(3,0)}_{\rm QED} \tag{4.1}$$

4.1 Lowest-Order Relativistic Corrections

The lowest order $O(\alpha^2)$ relativistic correction is

$$E^{(2,0)}_{\rm rel} = \langle \psi_{\rm NR} | H_{\rm rel} | \psi_{\rm NR} \rangle \tag{4.2}$$

$\psi_{\rm NR}$ is the nonrelativistic two-electron wave function, where $H_{\rm rel} = \sum_{i=1}^{6} B_i$, and $\{B_i\}$ are Breit operators

$$B_1 = -\frac{\alpha^2}{8}(\nabla_1^4 + \nabla_2^4) \tag{4.3}$$

$$B_2 = \frac{\alpha^2}{2}\left[\frac{1}{r_{12}}\vec{\nabla}_1 \cdot \vec{\nabla}_2 + \frac{1}{r_{12}^3}\vec{r_{12}}(\vec{r_{12}} \cdot \vec{\nabla}_1)\vec{\nabla}_2\right] \tag{4.4}$$

$$\begin{aligned} B_3 \;=\; & \frac{\alpha^2}{2r_{12}^3}\left[(\vec{r_2} - \vec{r_1}) \times \vec{P_1} \cdot (\vec{s_1} + 2\vec{s_2}) + (\vec{r_1} - \vec{r_2}) \times \vec{P_2} \cdot (\vec{s_2} + 2\vec{s_1})\right] \\ & + \frac{Z\alpha^2}{2}\left[\frac{1}{r_1^3}\vec{r_1} \times \vec{P_1} \cdot \vec{s_1} + \frac{1}{r_2^3}\vec{r_2} \times \vec{P_2} \cdot \vec{s_2}\right] \end{aligned} \tag{4.5}$$

$$B_4 = \frac{1}{2}\pi\alpha^2 Z\left[\delta(\vec{r_1}) + \delta(\vec{r_2})\right] \tag{4.6}$$

$$B_5 = \alpha^2\left[\frac{1}{r_{12}^3}\vec{s_1} \cdot \vec{s_2} - \frac{3}{r_{12}^5}(\vec{s_1} \cdot \vec{r_{12}})(\vec{s_2} \cdot \vec{r_{12}})\right] \tag{4.7}$$

$$B_6 = -\frac{8}{3}\pi\alpha^2\delta(\vec{r_{12}})\vec{s_1} \cdot \vec{s_2} \tag{4.8}$$

Here B_1 is the relativistic correction due to the variation of mass with velocity. B_2 corresponds to the classical relativistic orbit-orbit interaction between the electrons. B_3 describes the spin-other-orbit interaction and the spin-orbit interaction between the two electrons. B_4 represents the contact terms. B_5 represents the interaction between the spin magnetic diple moments of the two electrons. B_6 represents the spin-spin contact term which accounts for the interaction of the spin magnetic moments of two electrons. It only affects singlet states since $\langle\delta(r_{12})\rangle = 0$ for triplet states. The one-electron parts B_1, B_4, and the spin-orbit interaction come directly from a nonrelativistic reduction of the Dirac equation, and the remaining two-electron terms from the relativistic Breit operator (see Araki) [48].

4.2 Relativistic Reduced Mass and Recoil Corrections

The relativistic reduced mass correction comes from the reduced mass scaling of the above B_i terms upon the replacement $r \to \frac{m}{\mu}r$ together with additional terms Δ_2 and

$\triangle_3$, generated by the transformation of the Breit interaction to center-of-mass and relative coordinates [2]. There are three sources of relativistic terms of order $\alpha^2\mu/M$.

1. Reduced mass scaling corretions to the Breit operators B_1 to B_6
2. New operators genrated by transformation the Breit operators to center-of-mass plus relative coordinates (same as in chapter 2 section 1)
3. relativistic recoil corrections due to changes in the wave function $\psi_{\rm NR}$ due to the $-\frac{\mu}{M}\nabla_1.\nabla_2$ term

$$\langle E_{RR}\rangle_M = \sum_{i=1}^{6}\langle B_i^M\rangle \tag{4.9}$$

in units of $\frac{e^2}{a_\mu}$, where

$$B_1^M = -3\frac{\mu}{M}B_1 \tag{4.10}$$

$$B_2^M = -2\frac{\mu}{M}B_2 + \triangle_2 \tag{4.11}$$

$$B_3^M = -2\frac{\mu}{M}B_{3e} + \triangle_3 \tag{4.12}$$

$$B_i^M = -2\frac{\mu}{M}B_i,\ \ i = 4,5,6 \tag{4.13}$$

$$\begin{aligned}\triangle_2 \ &= \ \frac{1}{2}Z\alpha^2\frac{\mu}{M}\sum_{j=1}^{2}\left\{\frac{1}{r_j^3}\vec{r_j}\cdot\left[\vec{r_j}\cdot(\vec{\nabla}_1+\vec{\nabla}_2)\vec{\nabla}_j\right]\right\} \\ &\quad +\frac{1}{2}Z\alpha^2\frac{\mu}{M}\sum_{j=1}^{2}\left\{\frac{1}{r_j}(\vec{\nabla}_1+\vec{\nabla}_2)\cdot\vec{\nabla}_j\right\}\end{aligned} \tag{4.14}$$

$$\triangle_3 = Z\alpha^2\frac{\mu}{M}\left[\frac{1}{r_1^3}\vec{r_1}\times\vec{P_2}\cdot\vec{s_1}+\frac{1}{r_2^3}\vec{r_2}\times\vec{P_1}\cdot\vec{s_2}\right] \tag{4.15}$$

The recoil correction arises from second-order cross terms between B_i and the mass polarization operator $-\frac{\mu}{M}\nabla\cdot\nabla$ denoted by

$$\langle E_{RR}\rangle_X = \sum_{i=1}^{6}\langle B_i^X\rangle \tag{4.16}$$

where

$$\langle B_i^X\rangle = -2\frac{\mu}{M}\sum_{k\neq n}\frac{\langle\psi_{\rm NR}^{(n)}|\vec{\nabla}_1\cdot\vec{\nabla}_2|\psi_{\rm NR}^{(k)}\rangle\langle\psi_{\rm NR}^{(k)}|B_i|\psi_{\rm NR}^{(n)}\rangle}{E_n-E_k} \tag{4.17}$$

4.3 Spin-Dependent Anomalous Magnetic Moment Corrections

The spin-dependent parts of the anomalous magnetic moment correction to B_i can be included by replacing each spin factor s_i by $\frac{1}{2}g_i s_i$, where $g_i \simeq 2(1+\frac{\alpha}{2\pi})$. The result is expressed as

$$\langle E_{\mathrm{anom}} \rangle = \langle B_3^A \rangle + \langle B_5^A \rangle + \langle B_6^A \rangle \tag{4.18}$$

where

$$B_3^A = \frac{\alpha}{2\pi} B_3 \tag{4.19}$$

$$B_5^A = \frac{\alpha}{2\pi} B_5 \tag{4.20}$$

$$B_6^A = \frac{\alpha}{\pi} B_6 \tag{4.21}$$

4.4 The Singlet-triplet Mixing Term

E_{ST} is due to the singlet-triplet mixing caused by the spin-dependent Breit operators, the anomalous magnetic moment, and finite mass corrections providing off-diagonal singlet-triplet coupling terms. It is the difference between the energies of state $n\ {}^1L_J$ before diagonalization and after diagonalization of the Hamiltonian matrix in the two-dimensional basis sets of LS-coupled states with the same n, L, and J.

4.5 Quantum Electrodynamics Corrections

To order α^3, the total QED energy shift can be written as the sum of an electron-nucleus correction and an electron-electron correction as derived by Kabir and Salpeter so that

$$E_{\mathrm{QED}}^{(3,0)} = E_{L,1} + E_{L,2} \tag{4.22}$$

4.5.1 Electron-Nucleus QED Correction

The general form of the electron-nucleus part denoted as $E_{L,1}$ for helium is simply obtained from the corresponding hydrogenic case by inserting the correct electron density at the nucleus in place of the hydrogenic matrix element $\langle\delta(\vec{r})\rangle = \frac{Z^3}{(\pi n^3)}$, and the correct two-electron value of the Bethe logarithm. The lowest-order QED shift is

$$E_{L,1} = \frac{4\alpha^3 Z}{3}\langle\delta(\vec{r_1}) + \delta(\vec{r_2})\rangle\left[\ln(Z\alpha)^{-2} + 19/30 - \beta(1snl)\right], \tag{4.23}$$

where $\beta(nls)$ is the two-electron Bethe logarithm term defined by

$$\beta(1snl) = \frac{\sum_{i\neq 0}|\langle\psi^{(0)}_{\mathrm{NR}}|\vec{p_1}+\vec{p_2}|\psi^{(i)}\rangle|^2(E_i - E_0)\ln|\mathrm{E_i} - \mathrm{E_0}|}{\sum_{i\neq 0}|\langle\psi^{(0)}_{\mathrm{NR}}|\vec{p_1}+\vec{p_2}|\psi^{(i)}\rangle|^2(E_i - E_0)} \tag{4.24}$$

4.5.2 Electron-Electron QED Correction

Araki and Sucher [48] derived the electron-electron QED shift as

$$E_{L,2} = \alpha^3\left[\frac{14}{3}\ln(\alpha) + \frac{164}{15}\right]\langle\delta(\vec{r_{12}})\rangle - \frac{14}{3}\alpha^3 Q, \tag{4.25}$$

where

$$Q = \frac{1}{4\pi}\lim_{\varepsilon\to 0}\langle r_{12}^{-3}(\varepsilon) + 4\pi(\gamma + \ln(\varepsilon))\delta(\mathrm{r}_{12})\rangle \tag{4.26}$$

γ is Euler's constant, and ε is the radius of a sphere centered about r_{12} that is excluded from the range of integration.

4.5.3 Correction Due to Finite Nuclear Size

The lowest-order correction due to finite nuclear size is

$$E_{\mathrm{nuc}} = \frac{2\pi Z}{3}\left(\frac{R}{a_0}\right)^2\langle\delta^3(\vec{r_1}) + \delta^3(\vec{r_2})\rangle, \tag{4.27}$$

where R is the root-mean-square (rms) radius of the nuclear charge distribution and a_0 is the Bohr radius.

4.6 Total Energy

Accounting for the relativistic corrections and QED corrections, the total energy [22, 23, 26] for state ${}^{2S+1}L_J$ may be expressed as

$$\begin{aligned} E_{\rm tot} &= E_{\rm NR} + E_M^{(1)} + E_M^{(2)} + E_{\rm REL} + (E_{RR})_M + (E_{RR})_X + \\ & E_{\rm ANOM} + E_{L,1} + E_{L,2} + E_{\rm NU} + E_{\rm ST}, \end{aligned} \tag{4.28}$$

where

$$E_M^{(1)} = -\frac{\mu}{M}\varepsilon_M^{(1)} \tag{4.29}$$

$$E_M^{(2)} = \left(\frac{\mu}{M}\right)^2 \varepsilon_M^{(2)}. \tag{4.30}$$

The asymptotic form of $E_{\rm rel}$ is

$$E_{\rm rel} \sim h_1(nL) + B_1(\alpha_{rel}) + B_1(\phi_1) + \langle B_2 \rangle \tag{4.31}$$

after lengthy derivations given by Drake and Yan [26] with the result

$$h_1(nL) = \frac{\alpha^2(Z-1)^4}{2n^3}\left[\frac{3}{4n^2} - \frac{1}{L+\frac{1}{2}}\right], \tag{4.32}$$

$$\triangle B_1(\alpha_{rel}) = \frac{1}{2}(Z\alpha)^2[\alpha_{1,rel}\langle x^{-4}\rangle + (\alpha_{2,rel} - 6\beta_{1,rel})\langle x^{-6}\rangle + \ldots], \tag{4.33}$$

$$\begin{aligned} \triangle B_1(\phi_1) &= \frac{1}{2}\alpha^2\alpha_1\{3\left(\frac{Z-1}{n}\right)^2\langle x^{-4}\rangle - (Z-1)\langle x^{-5}\rangle \\ &- 4\frac{(2L-2)!}{(2L+3)!}[4\left(\frac{Z-1}{n}\right)^6\left(n + \frac{9n^2-5f_1}{2L+1}\right) \\ &+ (Z-1)^2\langle x^{-4}\rangle\left(\frac{40f_2+70f_1-3}{2L+1}\right)]\}, \end{aligned} \tag{4.34}$$

$$\langle B_2 \rangle = \frac{\alpha^2}{Z^2}\left(\langle x^{-4}\rangle + \frac{3(Z-1)}{Z^2}\langle x^{-5}\rangle - \frac{1}{Z^2}\left[\frac{51}{4} - \frac{27(Z-1)}{2Z} + \frac{3L(L+1)}{4}\right]\langle x^{-6}\rangle\right), \tag{4.35}$$

$\alpha_{1,rel} = \frac{14}{3Z^4}$, $\alpha_{2,rel} = \frac{879}{40Z^6}$, and $\beta_{1,rel} = \frac{2063}{288Z^6}$.

The asymptotic form of $E_{\rm anom}$ is

$$E_{\rm anom} \sim 2\gamma_e\{Z - 2 + (2+\gamma_e)S_L(J) - y[Z - 2 + 4S_L(J)]\}T_{nL}(J) \tag{4.36}$$

where

$$\begin{aligned} S_L(J) &= 1, \mathrm{for J = L} \\ &= \pm\frac{1}{2J+1}\mathrm{for J = L \pm 1} \end{aligned} \tag{4.37}$$

and

$$\begin{aligned} T_{nL}(L-1) &= -\frac{\alpha^2}{4}(L+1)\langle x^{-3}\rangle \\ T_{nL}(L) &= -\frac{\alpha^2}{4}\langle x^{-3}\rangle \\ T_{nL}(L+1) &= \frac{\alpha^2}{4}L\langle x^{-3}\rangle \end{aligned} \tag{4.38}$$

E_{st} is the singlet-triplet mixing term obtained by diagonalizing all other contributions in the $n\ {}^3L_L$, $n\ {}^1L_L$ two-dimensional subset of states. The asymptotic form of the off-diagonal matrix element of B_{tot} is

$$\langle n\ {}^3L_L \mid B_{tot} \mid n\ {}^1L_L\rangle \sim (Z+1-2y+2\gamma_e Z-2\gamma_e yZ)[L(L+1)]^{1/2}T_{nL}(J) \tag{4.39}$$

and the diagonal matrix element is

$$2\kappa = \left[1+\left(\frac{3}{2L-1}\right)^{1/2}\right]\pi\langle\delta(r_{12})\rangle_{\mathbf{singlet}} \tag{4.40}$$

where

$$\begin{aligned} \pi\langle\delta(r_{12})\rangle &= \frac{1}{2}\int_0^{\mathrm{NR}} |R_{1s}(r,Z)|^2|R_{nL}(r,Z-1)|^2 r^2 dr \\ &= \frac{2Z^3(n+1)!}{(2L+1)!(n-L-1)!}\left[\frac{Z-1}{nZ}\right]^{2L+4}\left[\frac{ZL+1}{Z-1}\right]e^{-2(Z-1)/Z} \end{aligned} \tag{4.41}$$

$(E_{RR})_M$ asymptotically goes to

$$\begin{aligned} (E_{RR})_M \sim &- 3y[h_1(nL)+\Delta B_1(\alpha_{rel})+\Delta B_1(\phi_1)] + y\left[Zh_2(nL)+\frac{235}{16Z^2}\alpha^2[1+(Z-2)/6]\langle x^{-4}\rangle\right] \\ &+ y\alpha^2\left[-\frac{31}{4Z^2}\langle x^{-4}\rangle+\frac{1447}{32Z^4}\langle x^{-6}\rangle\right] - 2y\{\langle b_2\rangle+[Z-3+1+2S_L(J)]T_{nL}(J)\delta_{S,1}\} \end{aligned} \tag{4.42}$$

where

$$h_2(nL) = \frac{\alpha^2(Z-1)^3}{n^3}\left[\frac{1}{n}-\frac{3}{2(L+\frac{1}{2})}\right] \tag{4.43}$$

$$\begin{aligned}(E_{RR})_X \quad &\sim \quad y\alpha^2\left[Z^2(Z-1)\alpha_{1,rel}-\frac{20}{9Z^2}+\frac{25}{16Z^2}\right]\langle x^{-4}\rangle - yh_2(nL)\\ &+ \quad 2y(Z-1)\Delta B_1(\phi_1)-(4\pm 1)y\alpha^2\langle x^{-6}\rangle - 2yT_{nL}(J)\\ &+ \quad y^2\left[-\frac{5}{12}\left(\frac{\alpha Z(Z-1)}{n}\right)^2+4h_1(nL)\right]+\frac{1}{6}y^2\left[\frac{\alpha Z(Z-1)}{n}\right]^2\end{aligned} \tag{4.44}$$

$$E_{nuc}\sim\frac{2}{3}(R/a_0)^2\left[-\frac{31}{2Z^2}\langle x^{-4}\rangle+\frac{1447}{16Z^4}\langle x^{-6}\rangle\right] \tag{4.45}$$

Where R is the rms nuclear radius.

$$\begin{aligned}E_{L,1} \quad \sim \quad &\frac{4\alpha^3 Z}{3\pi}\{(Z^3-\frac{31}{2}Z^{-3}\langle x^{-4}\rangle+\frac{1447}{16}Z^{-5}\langle x^{-6}\rangle)\times\\ &[\ln(\mathrm{Z}\alpha)^{-2}+\frac{19}{30}-\beta_{1\mathrm{s}}-\left[\frac{\mathrm{Z}-1}{\mathrm{Z}}\right]^4\mathrm{n}^{-3}\beta_{\mathrm{nL}}-0.31626\mathrm{Z}^{-6}\langle \mathrm{x}^{-4}\rangle\\ &+2.296\pi\alpha Z+O(\alpha^2Z^2)+yC_M]\}-\Delta E_L(1s)\end{aligned} \tag{4.46}$$

Where the β_{nL} are hydrogen-atom Bethe logarithms, the finite mass corrections denoted by yC_M, and $\Delta E_L(1s)$ is the He$^+$(1s) Lamb shift.

Finally the electron-electron QED energy shift

$$E_{L,2}(nLS)=\alpha^3(\frac{14}{3}\ln\alpha+\frac{164}{15})\langle\delta(\mathrm{r}_{12})\rangle-\frac{14}{3}\alpha^3\mathrm{Q} \tag{4.47}$$

Where

$$Q=\frac{1}{2\pi}(\langle x^{-3}\rangle+3Z^{-2}\langle x^{-5}\rangle) \tag{4.48}$$

and $\langle\delta(r_{12})\rangle$ can be neglected, since it decreases exponentially with L.

Chapter 5

Results and Conclusion

In this thesis we have studied the comparison between the predictions of the asymptotic expansion method and the results of high precision variational calculations for a range of values of nuclear charge. We have found that the asymptotic expansion method is not useful for small values of angular momentum L, because of the divergence of the series for inverse powers of x beyond $1/x^{2j+2}$ (see equation 1.1) and because of exchange and core penetration effects. Only the first one or two terms can be included in the asymptotic series, which is not enough to obtain high precision in comparison with other methods such that the variational or configuration interaction (CI)[36] methods. Howaver,there is a rapid improvement with increasing angular momentum L for the nonrelativistic energies (see below for further discussion). For purposes of comparison with experiment, the asymptotic expansions become very accurate for $L \geq 7$ and it is sufficient to replace the variational calculations (see fig 5.1) for the case of helium atom $Z = 2$, and for lithium ion Li^{+} the angular momentum $L \geq 8$, and for all other nuclear charge $Z \geq 4$ the asymptotic expansions can replace variational calculations if $L \geq 9$ (see fig 5.2) .

Recently G. Lagmago Kamta, B. Piraux, and A. Scrinzi [36] performed what they claimed were high precision CI calculations. However, our asymptotic expansions showed that not even the leading diploe correction term proportional to $\alpha_l \langle x^{-4} \rangle$ was contained correctly in their calculation. For example, table 2.12 shows a detailed breakdown of contributions for $n = 15$, $L = 10$.

We proposed that there is an important class of configurations missing from the CI calculations. Subsequent calculations by them verified that this is indeed the case. As L increases the uncertainty in our calculations decreases rapidly. For example when $L = 7$ the uncertainty is 15×10^{-16} a.u and when $L = 14$ the uncertainty decreases by over a million to 40×10^{-22} a.u (see table 2.11).

We next consider the errors resulting from neglecting exchange and core penetration, with increasing nuclear charge Z for the nonrelativistic energies. For same values of angular momentum L the error increasing with increasing nuclear charge Z (see figures 5.2), that come from neglecting the exchange corrections and the core penetration (see figures 5.9 and 5.15). The core penetration correction for $n = 8$ is 13.69 MHz and 0.0433 MHz for $L = 3$ and $L = 4$ respectively, which cannot be neglected, but for $L = 7$ this correction becomes 1.8×10^{-11} MHz which is negligible for experiment purposes. The short-range corrections rapidly become insignificant as the angular momentum increases, although they may not be negligible for lower values of L. For the leading relativistic corrections the differences between the asymptotic and variational calculations oscillate when Z increases. Although there is oscillation, for practical purposes, it is negligible. Computing the energies and properties of Rydberg states for heliumlike ions can be done more simply using the asymptotic methods rather than employing the more difficult variational calculations.

5.1 Total Energies

Tables 5.1 to 5.3 collect together all the finite nuclear mass ($E_M^{(1)}$, $E_M^{(2)}$) relativistic (E_{REL}), anomalous magnetic moment (E_{ANOM}), singlet-triplet mixing (E_{ST}), relativistic recoil ($(E_{RR})_M$), $(E_{RR})_X$), finite nuclear size (E_{NUC}), and QED ($E_{L,1}$, $E_{L,2}$) corrections from chapters 2, 3, and 4 in order to get total energies that can be compared with experiment for the case of helium. Figure 5.1 presents a comparison with the high precision measurement of Lundeen [47]. For the 4-5 transition, the difference between theory and experiment is much less than the uncertainty of ±0.5MHz. For all the other transitions, the differences are well within the combined theoretical and experimental error bars. The result of this thesis allow similar tables to be constructed for the heliumlike ions. A general purpose program has been written to produce tables of this type for any n, L, and Z. The next two figures show a comparison between the asymptotic expansions and variational calculations as a function of Z for the 10K state. The quantity plotted is the fractional difference (A-V)/A. It can be seen that the differences increase rapidly with Z up to $Z = 7$, and then start decreasing again. To understand this behavior, it is instructive to write equation (2.9) in Z-scaled atomic units with distances in units of a_0/Z and energies in units of Z^2e^2/a_0 with the result

$$H_0(r.x) = -\frac{1}{2}\nabla_r^2 - \frac{1}{r} - \frac{1}{2}\nabla_x^2 - \left[\frac{(Z-1)}{Z}\right]\frac{1}{x}$$

and

$$V(r,x) = \frac{1}{Z}\left[\frac{1}{|r-x|} - \frac{1}{x}\right]$$

For large Z, the electron-electron interaction represented by $V(r,x)$ becomes negligible compared to electron-nucleus interaction, and so the difference ultimately decrease as $1/Z$. For small Z the polarization model gets worse with increasing Z because the expansion parameter is $\frac{Z-1}{Z}$, and this increases with increasing Z. For example, $\alpha_l\langle\frac{1}{x^4}\rangle$ scales as $\left(\frac{Z-1}{Z}\right)^4$. The behavior of the corresponding relativistic corrections as a function of Z is shown in figures 5.4 to 5.7, These similarly show relatively large deviations that fluctuate in sign with increasing Z but that ultimately tend to zero for $Z > 10$.

For the singlet-triplet splittings in the nonrelativistic energies, figure 5.8 shows that the splittings go to zero exponentially fast with increasing L, verifying that electron exchange effects become negligible for large L. Figure 5.9 shows one example of the behavior of the nonrelativistic singlet-triplet splittings as a function of Z for the 10H state. As expected, they increase linearly with Z, while the total energies increase in proportion to Z^2. The final singlet-triplet splittings are the result of diagonolizing the 2×2 matrix, including also the off-diagonal spin-orbit and spin-other-orbit interactions given by equation (4.39). Figure 5.10 compares the variational and asymptotic results for the final diagonolized energies. There are similar oscillations for small Z, with the differences ultimately decreasing for large Z. Figures 5.11 to 5.14 present similar comparisons for the first and second-order mass polarizations, E_{M}^{1} and E_{M}^{2}, the relativistic recoil correction E_{RRX} and the electron-nucleus QED correction E_{L1}. They all show a similar pattern of oscillations for small Z with differences alternately decreasing for large Z. Finally, figure 5.15 shows the calculated energy shift due to core penetration for the 8H state as a function of Z as estimated from equation (2.18). The first entry 0.000071 MHz agrees with the value for n=8, L=5 in table 2.1. The extended results in figure 5.15 show that this effect, which is not included in the asymptotic expansion, increases linearly with Z for large Z, and so L must be correspondingly bigger for this effect to be negligible.

Thus, by including all of these effects, we can get accurate total energies for all n and L, provided that $L > 8$ for $Z = 3$ and $L > 9$ for $Z \geq 4$.

Table 5.1: Contributions to the energies of ^{4}He, relative to He$^+$(1s) in MHz (9L state) [26]

Term	$9\ ^1L_8$	$9\ ^3L_7$	$9\ ^3L_8$	$9\ ^3L_9$
ΔE_{nr}	-30.712 304	-30.712 304	-30.172 304	30.712 304
$\Delta E_{\mathrm{M}}(1)$	-0.008 414	-0.008 414	-0.008 414	-0.008 414
$\Delta E_{\mathrm{M}}(2)$	-0.763 037	-0.763 037	-0.763 037	-0.763 037
ΔE_{rel}	-8.235 266(9)	-6.232 928(9)	-8.431 574(9)	-9.640 416(9)
ΔE_{anom}	0.000 000	0.000 547	-0.000 911	0.000 384
ΔE_{st}	4.906 83(2)	0.000 000	-4.906 83(2)	0.000 000
$(\Delta E_{\mathrm{RR}})_{\mathrm{M}}$	-0.005 219	-0.006 252	-0.005 219	-0.004 403
$(\Delta E_{\mathrm{RR}})_{\mathrm{X}}$	0.004 225	0.004 709	0.004 279	0.003 795
ΔE_{nuc}	-0.000 001	-0.000 001	-0.000 001	-0.000 001
$\Delta E_{\mathrm{L,1}}$	-0.000 722(3)	-0.000 722(3)	-0.000 722(3)	-0.000 722(3)
$\Delta E_{\mathrm{L,2}}$	-0.002 128	-0.002 128	-0.002 128	-0.002 128
Total	-34.816 03(2)	-37.720 53(1)	-44.826 87(2)	-41.127 25(1)

Table 5.2: Contributions to the energies of ^{4}He, relative to He$^+$(1s) in MHz (10L state) [26]

Term	$9\ ^1L_8$	$9\ ^3L_7$	$9\ ^3L_8$	$9\ ^3L_9$
ΔE_{nr}	-24.178 633	-24.178 633	-24.178 633	-24.178 633
$\Delta E_{\mathrm{M}}(1)$	-0.006 623	-0.006 623	-0.006 623	-0.006 623
$\Delta E_{\mathrm{M}}(2)$	-0.618 060	-0.618 060	-0.618 060	-0.618 060
ΔE_{rel}	-7.462 659(8)	-6.002 954(8)	-7.605 767(8)	-8.487 013(8)
ΔE_{anom}	0.000 000	0.000 398	0.000 664	0.000 280
ΔE_{st}	3.577 08(1)	0.000 000	-3.577 08(1)	0.000 000
$(\Delta E_{\mathrm{RR}})_{\mathrm{M}}$	-0.004 271	-0.005 025	-0.004 271	-0.003 677
$(\Delta E_{\mathrm{RR}})_{\mathrm{X}}$	0.003 607	0.003 960	0.003 646	0.003 293
ΔE_{nuc}	0.000 000	0.000 000	0.000 000	0.000 000
$\Delta E_{\mathrm{L,1}}$	-0.000 557(3)	-0.000 557(3)	-0.000 557(3)	-0.000 557(3)
$\Delta E_{\mathrm{L,2}}$	-0.001 551	-0.001 551	-0.001 551	-0.001 551
Total	-28.691 67(2)	-30.809 045(9)	-35.989 56(2)	-33.292 541(9)

Table 5.3: Contributions to the energies of ^{4}He, relative to He$^+$(1s) in MHz (10M state) [26]

Term	$9\ ^1L_8$	$9\ ^3L_7$	$9\ ^3L_8$	$9\ ^3L_9$
$\triangle E_{\rm nr}$	-12.727 808	-12.727 808	-12.727 808	-12.727 808
$\triangle E_{\rm M}(1)$	-0.003 488	-0.003 488	-0.003 488	-0.003 488
$\triangle E_{\rm M}(2)$	-0.618 059	-0.618 059	-0.618 059	-0.618 059
$\triangle E_{\rm rel}$	-5.297 028(3)	-4.152 161(3)	-5.399 463(3)	-6.131 145(3)
$\triangle E_{\rm anom}$	0.000 000	0.000 280	0.000 475	0.000 204
$\triangle E_{\rm st}$	2.868 615(6)	0.000 000	-2.868 615(6)	0.000 000
$(\triangle E_{\rm RR})_{\rm M}$	-0.003 380	-0.003 975	-0.003 380	-0.002 898
$(\triangle E_{\rm RR})_{\rm X}$	0.002 715	0.002 995	0.002 743	0.002 462
$\triangle E_{\rm nuc}$	0.000 000	0.000 000	0.000 000	0.000 000
$\triangle E_{\rm L,1}$	-0.000 285(2)	-0.000 285(2)	-0.000 285(2)	-0.000 285(2)
$\triangle E_{\rm L,2}$	-0.001 110	-0.001 110	-0.001 110	-0.001 110
Total	-15.779 827(7)	-17.503 610(3)	-21.619 941(7)	-19.482 127(3)

$L \to L'$	Theory	Experiment	Exp-Theory
$4 \to 5$	490 9566 ± 521	491 0052 ± 0005	0.0486 ± 521
$5 \to 6$	157 0499 ± 0059	157 0524 ± 0002	0 0025 ± 0059
$6 \to 7$	60 8148 ± 00014	60 8159 ± 0002	0 0011 ± 0002
$7 \to 8$	27 17502	27 1747 ± 0005	-0 0003 ± 0005

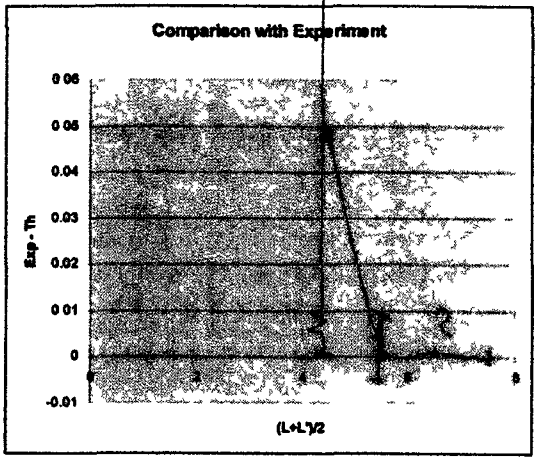


Figure 5.1: The theoretical energy differences in MHz in the n=10 manifold, with Z=2 by Ref [28], are compared with the accurate measurements of Ref [47]

Asymptotic	Unce	Variational	z	Ratio	Uncer/A
-2.00500000738837581	1.90E-15	-2.005000007388370	2	3.23E-17	-9.48E-16
-4.52000002333936401	3.30E-14	-4.52000002333936743	3	7.57E-16	-7.30E-15
-8.04500003737463989	1.10E-13	-8.04500003737465520	4	1.90E-15	-1.37E-14
-12.58000004837439498	2.10E-13	-12.58000004837442925	5	2.72E-15	-1.67E-14
-18.12500005694804600	3.10E-13	-18.12500005694810280	6	3.13E-15	-1.71E-14
-24.68000006373520308	4.10E-13	-24.68000006373528346	7	3.26E-15	-1.66E-14
-32.24500006921029243	5.00E-13	-32.24500006921039599	8	3.21E-15	-1.55E-14
-40.82000007370662461	5.90E-13	-40.82000007370675022	9	3.08E-15	-1.45E-14
-50.40500007745851279	6.70E-13	-50.40500007745865904	10	2.90E-15	-1.33E-14
-61.00000008063323079	7.40E-13	-61.00000008063339616	11	2.71E-15	-1.21E-14
-72.60500008335250072	8 00E-13	-72.60500008335268374	12	2.52E-15	-1.10E-14
-85.22000008570661993	8.60E-13	-85.22000008570681922	13	2.34E-15	-1.01E-14
-98.84500008776380035	9.20E-13	-98.84500008776401463	14	2.17E-15	-9.31E-15
-113.48000008957643595	9.60E-13	-113.48000008957666406	15	2.01E-15	-8.46E-15
-129.12500009118538556	1.00E-12	-129.12500009118562576	16	1.86E-15	-7.74E-15
-145.78000009262294977	1.00E-12	-145.78000009262320208	17	1.73E-15	-6.86E-15
-163.44500009391498714	1.10E-12	-163.44500009391525034	18	1.61E-15	-6.73E-15

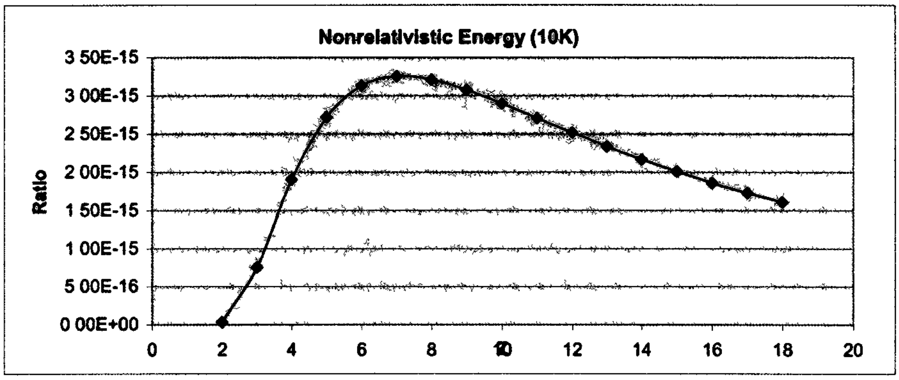
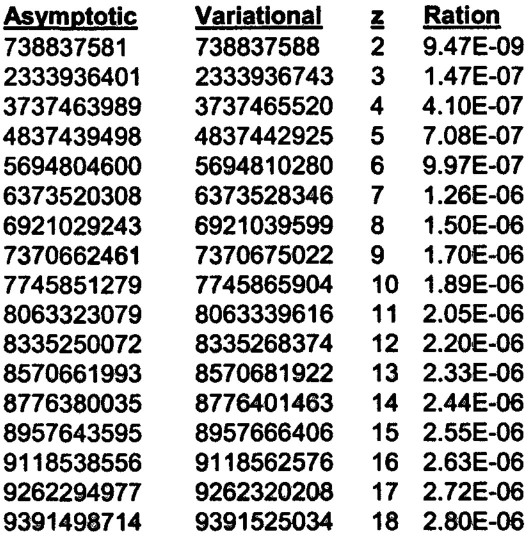


Figure 5.2: Comparison between variational and asymptotic calculations for $\triangle E_{\rm nr}$ for the 10K state for different values of the nuclear charge Z. The Ratio is defined by R= (A-V)/A.



Asymptotic	Variational	z	Ration
738837581	738837588	2	9.47E-09
2333936401	2333936743	3	1.47E-07
3737463989	3737465520	4	4.10E-07
4837439498	4837442925	5	7.08E-07
5694804600	5694810280	6	9.97E-07
6373520308	6373528346	7	1.26E-06
6921029243	6921039599	8	1.50E-06
7370662461	7370675022	9	1.70E-06
7745851279	7745865904	10	1.89E-06
8063323079	8063339616	11	2.05E-06
8335250072	8335268374	12	2.20E-06
8570661993	8570681922	13	2.33E-06
8776380035	8776401463	14	2.44E-06
8957643595	8957666406	15	2.55E-06
9118538556	9118562576	16	2.63E-06
9262294977	9262320208	17	2.72E-06
9391498714	9391525034	18	2.80E-06

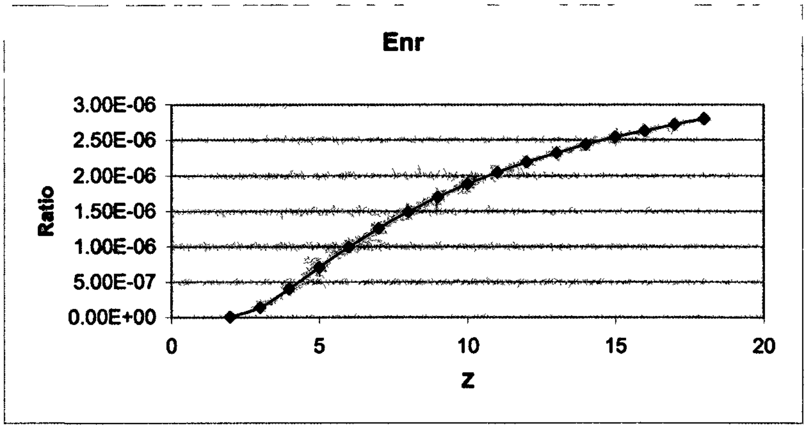


Figure 5.3: Comparison between variational and asymptotic calculations for $\triangle E_{\mathrm{nr}}$ (10K state) without the trivial part (the n dependent term)

Asymototic	Variational	Unce	Z	Ratio	Unce/A
-16.89923924	-16.89923297	3.00E-08	2	3.71E-07	-1.78E-09
-270.79685788	-270.79416129	1.00E-08	3	9.96E-06	-3.69E-11
-1371.58271201	-1371.60496557	1.00E-06	4	-1.62E-05	-7.29E-10
-4335.97256540	-4335.99419919	6.00E-06	5	-4.99E-06	-1.38E-09
-10587.27668343	-10587.28413881	1.50E-05	6	-7.04E-07	-1.42E-09
-21955.51430094	-21955.57814746	2.00E-05	7	-2.91E-06	-9.11E-10
-40677.61154111	-40677.58780925	3.50E-05	8	5.83E-07	-8.60E-10
-69396.58832003	-69396.84568925	4.90E-05	9	-3.71E-06	-7.06E-10
-111163.04171337	-111163.11991249	3.50E-05	10	-7.03E-07	-3.15E-10
-169433.10676348	-169433.71879641	5.80E-05	11	-3.61E-06	-3.42E-10
-248070.68807110	-248071.45179052	1.21E-04	12	-3.08E-06	-4.88E-10
-483935.99547129	-483937.10837268	1.30E-04	14	-2.30E-06	-2.69E-10
-650924.29300731	-650925.60224924	3.10E-04	15	-2.01E-06	-4.76E-10
-857800.04843885	-857801.56723791	4.80E-04	16	-1.77E-06	-5.60E-10
-1415213.43825382	-1415215.41248365	6.00E-04	18	-1.40E-06	-4.24E-10

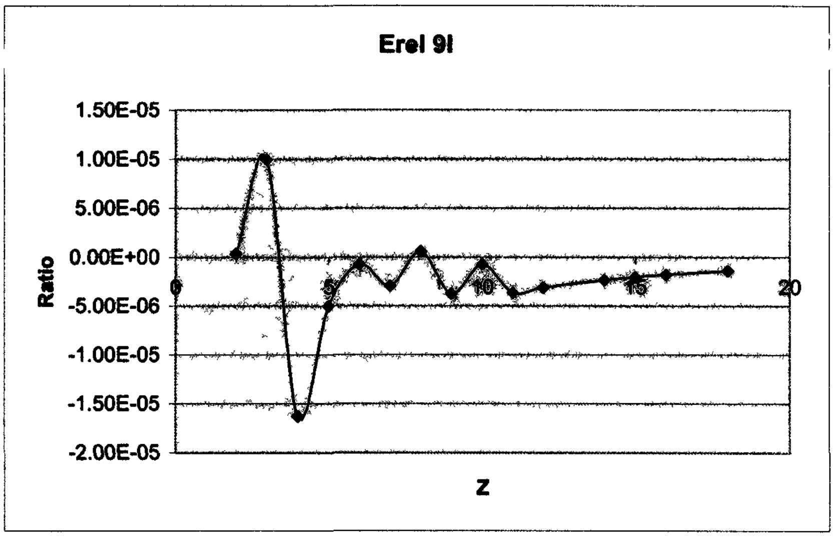


Figure 5.4: Comparison between variational and asymptotic calculations for $\triangle E_{rel}$ (9I state) the Ratio= (A-V)/A for different values of nuclear charge Z

Asymptotic	Variational	Z	Ratio
-11.99423963	-11.99423716	2	2.06E-07
-192.09977239	-192.09573757	3	2.10E-05
-972.80647352	-972.81288039	4	-6.59E-06
-3075.06481374	-3075.05698267	5	2.55E-06
-7508.13363626	-7508.09476750	6	5.18E-06
-15569.66408160	-15569.63672102	7	1.76E-06
-28845.84073108	-28845.71509297	8	4.36E-06
-49210.80530125	-49210.83508843	9	-6.05E-07
-78827.70867273	-78827.55964553	10	1.89E-06
-120147.26490040	-120147.43494802	11	-1.42E-06
-175909.33371398	-175909.54364963	12	-1.19E-06
-249142.15005341	-249142.40307990	13	-1.02E-06
-343161.30469024	-343161.60332193	14	-8.70E-07
-461572.33941118	-461572.68582846	15	-7.51E-07
-608267.30003646	-608267.69573766	16	-6.51E-07
-1003526.8301358	-1003527.3261312	18	-4.94E-07

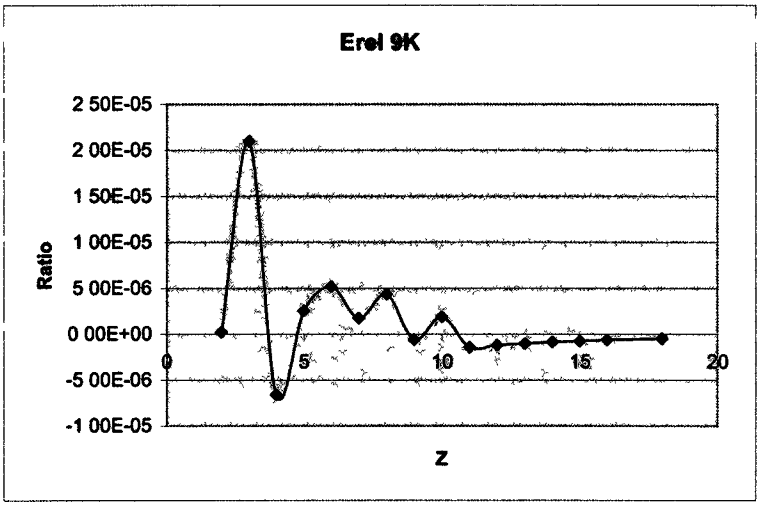


Figure 5.5: Comparison between variational and asymptotic calculations for $\triangle E_{rel}$ (9K state) the Ratio= (A-V)/A for different values of nuclear charge Z

Asymptotic	Variational	Z	Ratio
-13.77802353	-13.77801933	2	3.05E-07
-220.75934061	-220.75713722	3	9.98E-06
-1118.10338295	-1118.12146411	4	-1.62E-05
-3534.59206031	-3534.60947370	5	-4.93E-06
-8630.44374589	-8630.44941163	6	-6.56E-07
-17897.40718652	-17897.45851233	7	-2.87E-06
-33158.92301179	-33158.90253348	8	6.18E-07
-56569.46099063	-56569.66946017	9	-3.69E-06
-90615.72924563	-90615.79106482	10	-6.82E-07
-138115.01199173	-138115.50836672	11	-3.59E-06
-202216.98865033	-202217.60788898	12	-3.06E-06
-286402.84816145	-286403.60286080	13	-2.64E-06
-394484.11713595	-394485.01941975	14	-2.29E-06
-530605.64315903	-530606.70450400	15	-2.00E-06
-699241.63228248	-699242.86315089	16	-1.76E-06
-905200.32469883	-905201.73593008	17	-1.56E-06
-1153620.30566485	-1153621.90605657	18	-1.39E-06

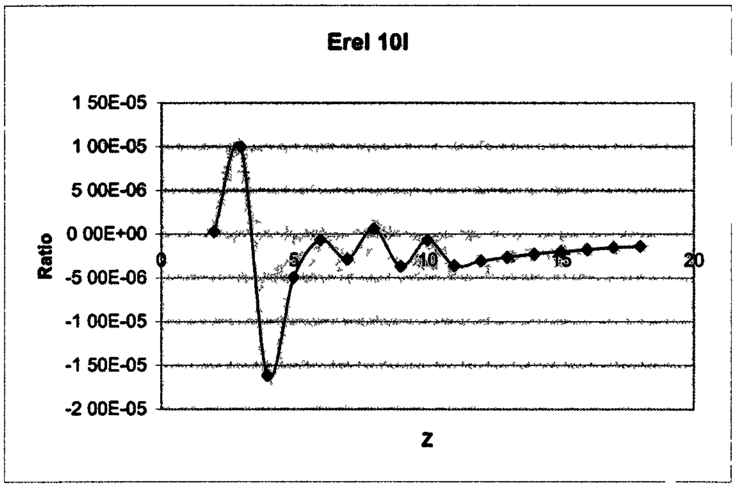


Figure 5.6: Comparison between variational and asymptotic calculations for $\triangle E_{rel}$ (10I state) the Ratio= (A-V)/A for different values of nuclear charge Z

Variational	Asymptotic	Z	Ratio
-10.202700	-10.202702	2	2.0583E-07
-163.388848	-163.392251	3	2.0827E-05
-827.40995	-827.404383	4	-6.7283E-06
-2615.40197	-2615.408365	5	2.4447E-06
-6385.7466	-6385.779179	6	5.1013E-06
-13242.1468	-13242.16928	7	1.6995E-06
-24533.523	-24533.62872	8	4.3096E-06
-41854.142	-41854.11509	9	-6.4225E-07
-67043.2635	-67043.38824	10	1.8605E-06
-102185.928	-102185.7805	11	-1.4397E-06
-149611.725	-149611.5425	12	-1.2162E-06
-211896.407	-211896.1882	13	-1.0334E-06
-291859.887	-291859.6275	14	-8.8737E-07
-392568.674	-392568.3737	15	-7.6397E-07
-517332.954	-517332.6117	16	-6.6239E-07
-669710.045	-669709.6576	17	-5.7777E-07
-853501.66	-853501.2288	18	-5.0524E-07

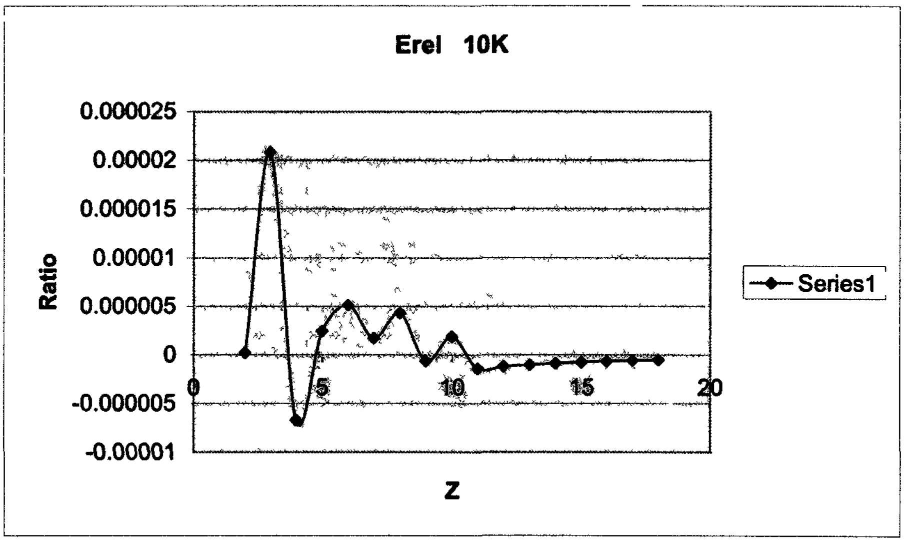
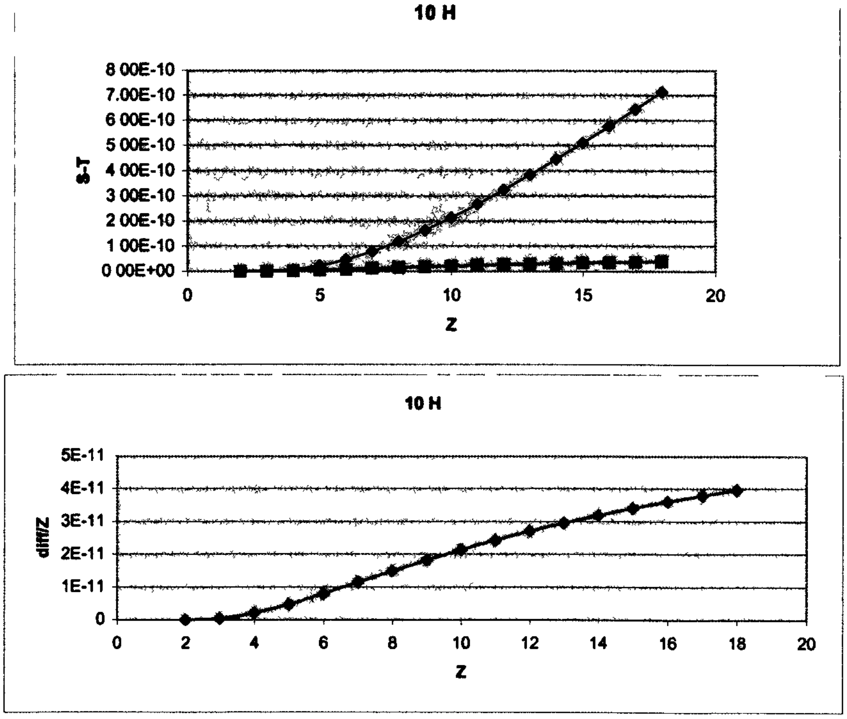


Figure 5.7: Comparison between variational and asymptotic calculations for $\triangle E_{rel}$ (9K state) the Ratio= (A-V)/A for different values of nuclear charge Z

State	Energy	S-T splitting ($\times 10^3$)
10 ^1S	−2.005 142 991 747 992 6(1)[a]	
10 ^3S	−2.005 310 794 915 611 3(1)	0.167 803 167 618 7
10 ^1P	−2.004 987 983 802 217 9(26)	
10 ^3P	−2.005 068 805 497 706 7(30)	0.080 821 695 488 8
10 ^1D	−2.005 002 071 654 256 81(75)	
10 ^3D	−2.005 002 818 080 228 84(53)	0.000 746 425 972 0
10 ^1F	−2.005 000 417 564 668 80(11)	
10 ^3F	−2.005 000 421 686 604 88(26)	0.000 004 121 936 08[a]
10 ^1G	−2.005 000 112 764 318 746(22)	
10 ^3G	−2.005 000 112 777 003 317(21)	0.000 000 012 684 571
10 ^1H	−2.005 000 039 214 394 532(17)	
10 ^3H	−2.005 000 039 214 417 416(17)	0.000 000 000 022 884
10 ^1I	−2.005 000 016 086 516 194 7(3)	
10 ^3I	−2.005 000 016 086 516 219 4(3)	0.000 000 000 000 025
10 ^1K	−2.005 000 007 388 375 876 9(0)	
10 ^3K	−2.005 000 007 388 375 876 9(0)	0.000 000 000 000 000

Figure 5.8: Variational energies and singlet-triplet (S-T) splittings for the $n = 10$ states of helium. Units are atomic units.

S	T	Z	diff	Z	diff/Z
-0.00500003921439	-0.00500003921442	2	2.29E-14	2	1.1E-14
-0.02000012369369	-0.02000012369507	3	1.38E-12	3	4.6E-13
-0.04500019794286	-0.04500019795119	4	8.32E-12	4	2.1E-12
-0.08000025610632	-0.08000025613007	5	2.38E-11	5	4.8E-12
-0.12500030143063	-0.12500030147869	6	4.81E-11	6	8E-12
-0.18000033730504	-0.18000033738543	7	8.04E-11	7	1.1E-11
-0.24500036624021	-0.24500036635983	8	1.20E-10	8	1.5E-11
-0.32000038999917	-0.32000039016378	9	1.65E-10	9	1.8E-11
-0.40500040982101	-0.40500041003542	10	2.14E-10	10	2.1E-11
-0.50000042659027	-0.50000042685848	11	2.68E-10	11	2.4E-11
-0.60500044095057	-0.60500044127595	12	3.25E-10	12	2.7E-11
-0.72000045337940	-0.72000045376477	13	3.85E-10	13	3E-11
-0.84500046423748	-0.84500046468524	14	4.48E-10	14	3.2E-11
-0.98000047380188	-0.98000047431408	15	5.12E-10	15	3.4E-11
-1.12500048228868	-1.12500048286708	16	5.78E-10	16	3.6E-11
-1.28000048986873	-1.28000049051485	17	6.46E-10	17	3.8E-11
-1.44500049667880	-1.44500049739396	18	7.15E-10	18	4E-11



all Z.pdf

Figure 5.9: nuclear charge Z vs the difference between singlet and triplet energies (upper), dividing the differences by Z (lower)

Variational	Asymptotic	Z	ratio
4.584763	4.584728	2	-7.68E-06
48.377698	48.379558	3	3.84E-05
202.766372	202.765997	4	-1.85E-06
574.254742	574.26009	5	9.31E-06
1304.458657	1304.473432	6	1.13E-05
2570.12788	2570.143102	7	5.92E-06
4583.11764	4583.15578	8	8.32E-06
7590.42089	7590.434019	9	1.73E-06
11874.09054	11874.14119	10	4.27E-06
17751.40906	17751.43078	11	1.22E-06
25574.62934	25574.65781	12	1.11E-06
35731.30437	35731.36398	13	1.67E-06
48643.8891	48643.96412	14	1.54E-06
64770.21373	64770.25822	15	6.87E-07
84602.92837	84602.98273	16	6.43E-07
108670.147990	108670.2065	17	5.39E-07

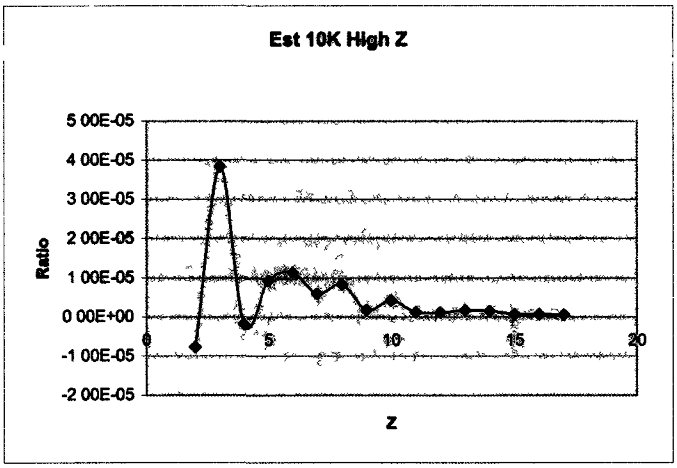


Figure 5.10: Comparison between variational and asymptotic calculations for $\triangle E_{st}$ (10K state) the Ratio= (A-V)/A for different values of nuclear charge Z

Asymptotic	Variational	Z	Ratio
-0.013303	-0.0133026	2	3.01E-05
-0.047948	-0.0479340	3	2.92E-04
-0.089636	-0.0896300	4	6.69E-05
-0.126626	-0.1266150	5	8.69E-05
-0.170954	-0.1709380	6	9.36E-05
-0.19675	-0.1967300	7	1.02E-04
-0.218221	-0.2182000	8	9.62E-05
-0.223605	-0.2235800	9	1.12E-04
-0.251221	-0.2512000	10	8.36E-05
-0.252683	-0.2526600	11	9.10E-05
-0.275409	-0.2753800	12	1.05E-04
-0.274613	-0.2745900	13	8.38E-05
-0.293806	-0.2937800	14	8.85E-05
-0.291687	-0.2916700	15	5.83E-05
-0.305307	-0.3053000	17	2.29E-05

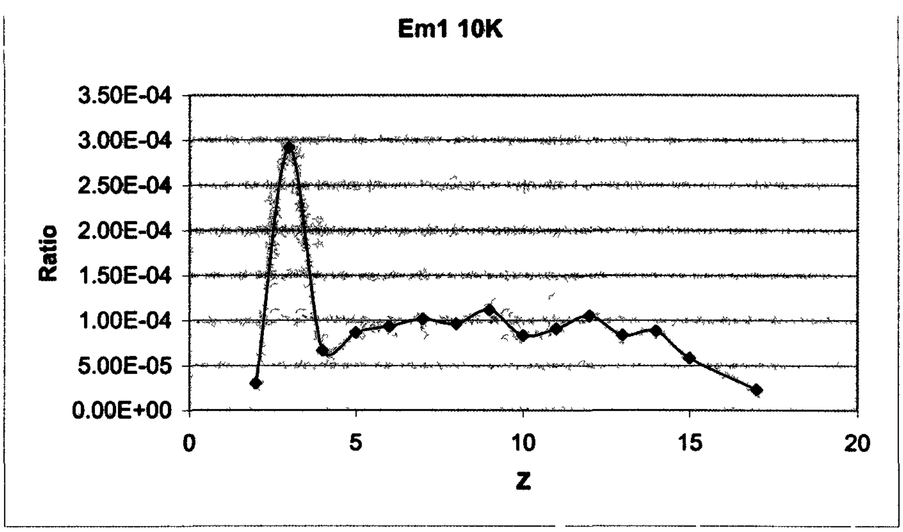


Figure 5.11: Comparison between variational and asymptotic calculations for $\triangle E_{\mathrm{M}}(1)$ (10K state) the Ratio= (A-V)/A for different values of nuclear charge Z

Asymptotic	Variational	Z	Ratio
-0.618063	-0.6180626	2	6.47183E-07
-0.804735	-0.8047130	3	2.73382E-05
-1.097422	-1.0974230	4	-9.1123E-07
-1.307421	-1.3074100	5	8.41351E-06
-1.719573	-1.7195580	6	8.7231E-06
-1.818462	-1.8184600	7	1.09983E-06
-1.897103	-1.8970900	8	6.85255E-06
-1.75629	-1.7562900	9	0
-2.007341	-2.0073300	10	5.47989E-06
-1.874083	-1.8740800	11	1.60078E-06
-2.083421	-2.0834200	12	4.7998E-07
-1.959278	-1.9592800	13	-1.0208E-06
-2.138766	-2.1387700	14	-1.8702E-06
-2.023661	-2.0236600	15	4.94154E-07
-2.073721	-2.0737200	17	4.82225E-07

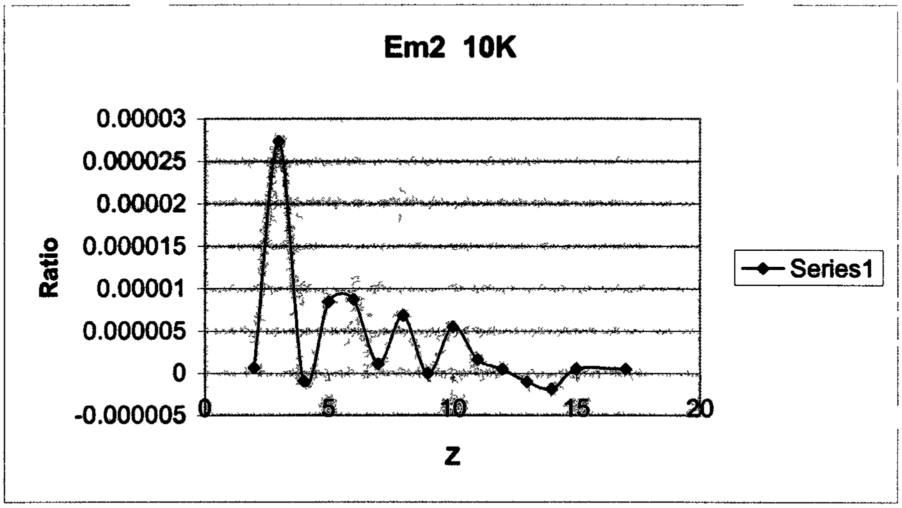


Figure 5.12: Comparison between variational and asymptotic calculations for $\triangle E_{\mathrm{M}}(2)$ (10K state) the Ratio= (A-V)/A for different values of nuclear charge Z

Asymptotic	Variational	Z	Ratio
0.004738	0.004738	2	0.000021
0.021741	0.013927	3	0.359424
0.057641	0.057176	4	0.008067
0.116428	0.110998	5	0.046638
0.160326	0.198828	6	-0.240148
0.259868	0.294520	7	-0.133345
0.330228	0.409540	8	-0.240173
0.493082	0.514980	9	-0.044410
0.610633	0.696600	10	-0.140783
0.837750	0.802483	11	0.042097
1.068611	1.025797	12	0.040065
1.232934	1.147874	13	0.068990
1.511244	1.410542	14	0.066635
1.704036	1.650724	15	0.031286
2.029221	1.967702	16	0.030317
2.249977	2.187445	17	0.027792
2.351526	2.359402	18	-0.003349

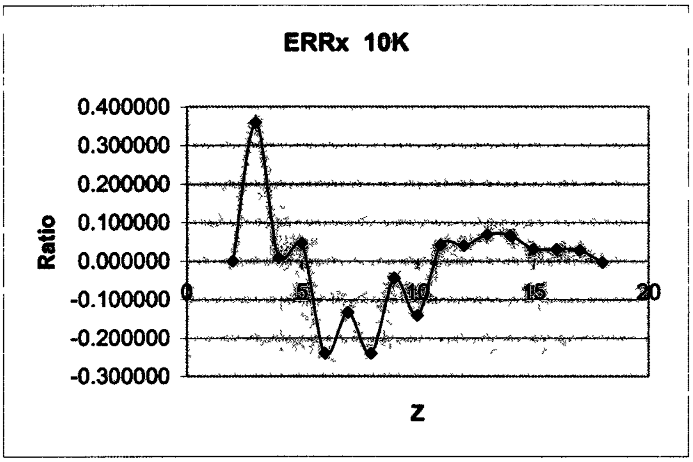
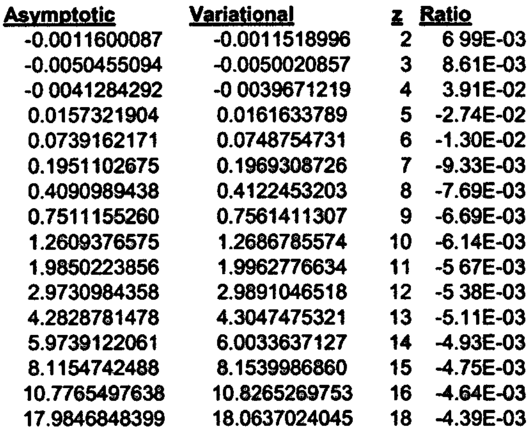


Figure 5.13: Comparison between variational and asymptotic calculations for $(\triangle E_{\mathrm{RR}})_{\mathrm{X}}$ (10K state) the Ratio= (A-V)/A for different values of nuclear charge Z



Asymptotic	Variational	z	Ratio
-0.0011600087	-0.0011518996	2	6 99E-03
-0.0050455094	-0.0050020857	3	8.61E-03
-0 0041284292	-0 0039671219	4	3.91E-02
0.0157321904	0.0161633789	5	-2.74E-02
0.0739162171	0.0748754731	6	-1.30E-02
0.1951102675	0.1969308726	7	-9.33E-03
0.4090989438	0.4122453203	8	-7.69E-03
0.7511155260	0.7561411307	9	-6.69E-03
1.2609376575	1.2686785574	10	-6.14E-03
1.9850223856	1.9962776634	11	-5 67E-03
2.9730984358	2.9891046518	12	-5 38E-03
4.2828781478	4.3047475321	13	-5.11E-03
5.9739122061	6.0033637127	14	-4.93E-03
8.1154742488	8.1539986860	15	-4.75E-03
10.7765497638	10.8265269753	16	-4.64E-03
17.9846848399	18.0637024045	18	-4.39E-03

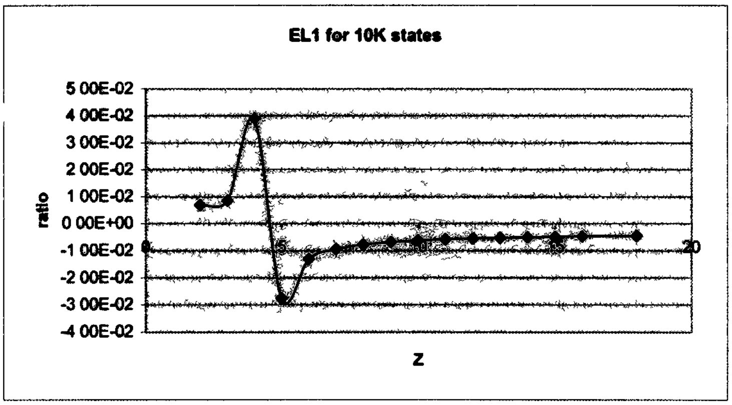


Figure 5.14: Comparison between variational and asymptotic calculations for the ΔE_{L1} (10K state) the Ratio= (A-V)/A for different values of nuclear charge Z

Z	E	Z	E/Z
2	0.000071	2	0.000036
3	0.003190	3	0.001063
4	0.016700	4	0.004175
5	0.043900	5	0.008780
6	0.084000	6	0.014000
7	0.135000	7	0.019286
8	0.195000	8	0.024375
9	0.262000	9	0.029111
10	0.335000	10	0.033500
11	0.413000	11	0.037545
12	0.494000	12	0.041167
13	0.579000	13	0.044538
14	0.667000	14	0.047643
15	0.756000	15	0.050400
16	0.849000	16	0.053063
17	0.942000	17	0.055412
18	1.040000	18	0.057778
19	1.133000	19	0.059632
20	1.230000	20	0.061500
21	1.328000	21	0.063238
22	1.427000	22	0.064864
25	1.729000	25	0.069160
30	2.241000	30	0.074700
35	2.762000	35	0.078914
40	3.288000	40	0.082200
45	3.819000	45	0.084867
50	4.352000	50	0.087040
55	4.887000	55	0.088855
65	5.961000	65	0.091708
75	7.040000	75	0.093867

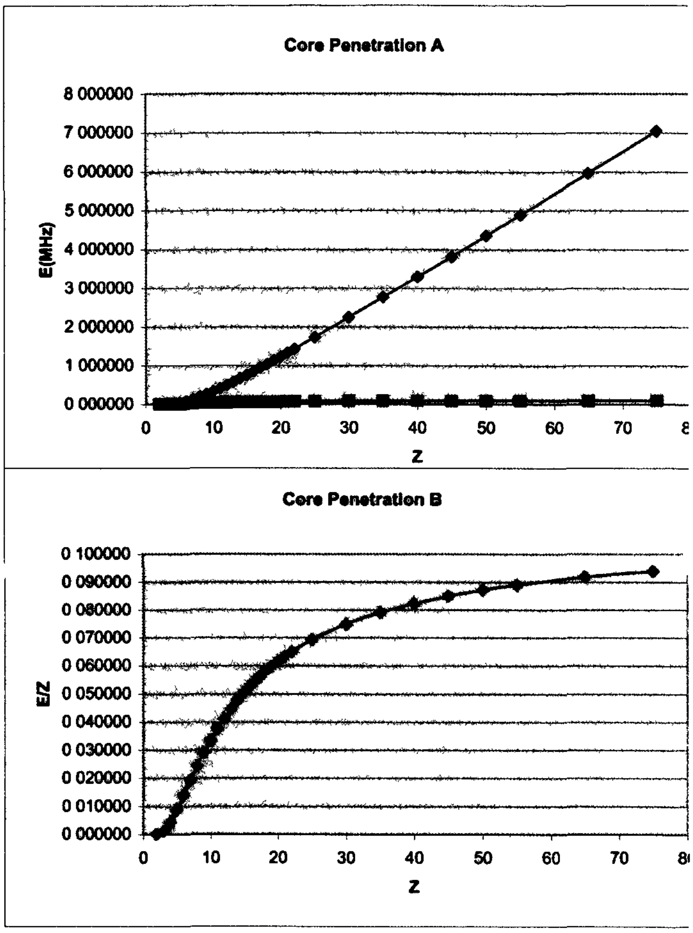


Figure 5.15: Core penetration correction for 8H state vs nuclear charge (upper), dividing the corrections by Z (lower)

Chapter 6

Future Work

The asymptotic methods can be used to calculate the energies of Rydberg states of lithium-like ions [34] consisting of a core (a core consisting of a nucleus with two electrons in the ground state in spherically symmetric orbits) and Rydberg electron (third electron) with high angular momentum. As we did with heliumlike ions, we consider the core and Rydberg electron as distinguishable particles. The variational calculations give us precise results for the core Li^+. The polarizabilities discussed for heliumlike ions can be used for the lithiumlike ions as well. Using the asymptotic technique to solve a four-body problem is much easier than solving the same system using variational calculation. We simplify the four-body problem to a three-body problem plus a distinguishable outer electron, thereby making a simple two-body system. The three-body problem is already treated by variational calculations with high precision. There are no difficulties in solving a two-body problem (hydrogen-like ions). The only concern is the polarizabilities of the core due to the Redberg electron. The next step would involve increasing the nuclear charge Z from 3 to 18 as we did with heliumlike ions and see how the accuracy varies with respect to Z [34].

Chapter 7

Appendix

7.1 Appendix I

There are more than one method for solving the function $f(r)$, where $f(r)$ is a function related to V by the implicit definition

$$[f, H_0]\phi_{1s} = V\phi_{1s} \tag{7.1}$$

where

$$V = V(r, x) = \frac{1}{x}\sum_{l=1}^{\infty}\left(\frac{r}{x}\right)^l P_1(\hat{r}.\hat{x}) \tag{7.2}$$

$$H_0 = -\frac{1}{2}\nabla_r^2 - \frac{Z^2}{r} \tag{7.3}$$

and

$$\phi_{1s} = \frac{1}{\sqrt{\pi}}e^{-r} \tag{7.4}$$

for $l = 1$ we have

$$[f, H_0]\phi_{1s} = \frac{r}{x^2}P_1(\hat{r}.\hat{x})\phi_{1s} \tag{7.5}$$

it is clear to see that $f(r) = g(r)P_1(\hat{r}\hat{x})/x^2$, otherwise $\langle\phi_{1s} \mid Vf \mid \phi_{1s}\rangle$ will vanish because of orthogonality, and the commutator equation for $f(r)$ becomes a simple differential equation for $g(r)$

$$\frac{d^2g}{dr^2} + 2\left(\frac{1}{r} - Z\right)\frac{dg}{dr} - \frac{2g}{r} = 2r \tag{7.6}$$

by using Frobenius method

$$g(r) = -\frac{r}{Z^2} - \frac{r^2}{2Z} \tag{7.7}$$

Variational method also can be used, starting from the commutator

$$[f, H_0]\phi_{1s} = V\phi_{1s} \tag{7.8}$$

let the commutator act

$$E_0 f\phi_{1s} - H_0 f\phi_{1s} = V\phi_{1s} \tag{7.9}$$

let $\psi_1 = f\phi_{1s}$, then the trial wave function can be defined as

$$\psi_{\text{tri}} = \sum_i C_i r^i V\phi_{1s} \tag{7.10}$$

substitute equation (7.10) in equation (7.9) and write it in matrix representation

$$\begin{pmatrix} A_{1,1} & A_{1,2} & \cdots & A_{1,j} \\ A_{2,1} & A_{2,2} & \cdots & A_{2,j} \\ \vdots & \vdots & \ddots & \vdots \\ A_{i,1} & A_{i,2} & \cdots & A_{i,j} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_i \end{pmatrix} = \begin{pmatrix} B_1 \\ B_2 \\ \vdots \\ B_i \end{pmatrix}$$

where $A_{ij} = \langle \phi_i \mid E_0 - H_0 \mid \phi_j \rangle$, $B_i = \langle \phi_i \mid V \mid \phi_{1s} \rangle$, and $\phi_i = r^i V\phi_{1s}$. For 2 by 2 matrix and for $l = 1$ we get

$$A_{ij}^{-1} = \begin{pmatrix} 6 & -2 \\ -2 & 1 \end{pmatrix}$$

and

$$B_i = \begin{pmatrix} 1 \\ \frac{5}{2} \end{pmatrix}$$

which give the following coefficients

$$C_i = \begin{pmatrix} 1 \\ \frac{1}{2} \end{pmatrix}$$

We can do the same for $l = 2, 3, \ldots$ and the general form for $f_l(r)$ will be

$$f_l(r) = \left(-\frac{r^l}{Z^2 l} - \frac{r^{l+1}}{Z(l+1)}\right) P_1(\hat{r}.\hat{x})/x^{l+1} \tag{7.11}$$

Bibliography

[1] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London Ser. **A 233**, 70 (1955). 868 (1963)

[2] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of one- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).

[3] Charles Schwartz, Phys. Rev. **123**, 5 (1961).

[4] R.J. Drachman, Phys. Rev. **132**, 374(1963).

[5] R.J. Drachman and S. K. HOUSTON, Phys. Rev. A **12**, 885 (1975),

[6] Y. Accad, C.L. Pekeris, and B. Schiff, Phys. Rev. A **11**, 1479 (1975).

[7] R.J. Drachman, Phys. Rev. A **26**,1228 (1982).

[8] R.J. Drachman, Phys. Rev. A **31**, 1253 (1985),

[9] R.J. Drachman, Phys. Rev. A **33**,2782 (1986).

[10] E. A. Hinds, J. D. Prestage, and F. M. J. Pichanick Phys. Rev. A **33**, 68 (1986)

[11] G.W.F. Drake ,Phys. Rev. Lett. **59**, 1549 (1987)

[12] R.J. Drachman, Phys. Rev. A **37**, 1 (1988),

[13] R.J. Drachman, Phys. Rev. A **38**, 1659 (1988),

[14] G.W.F. Drake ,Phys. Rev. Lett. **65**, 2769 (1990)

[15] G. W. F. Drake and R. A. Swainson , *Phys. Rev. A*, **42**, 1123, (1990).

[16] G.W.F. Drake and R. A. Swainson, Phys. Rev. A **41**, 1243 (1990).

[17] G. W. F. Drake, *Phys. Rev. A*, **41**, 70, (1991).

[18] G.W.F. Drake and R. A. Swainson, Phys. Rev. A **44**, 5448 (1991).

[19] G.W.F. Drake, Phys. Rev. A **43**,3325 (1991).

[20] G.W.F. Drake and R. A. Swainson, Phys. Rev. A **43**, 3168(E) (1991).

[21] J. Killingbech ,Phys. Lett. A **65**, 87 (1978)

[22] S. P. Goldman and G.W.F. Drake ,Phys. Rev. Lett. **68**, 1683 (1992)

[23] G.W.F. Drake, Phys. Rev. A **45**, 70 (1992).

[24] R. A. Swainson and G.W.F. Drake, Can. J. Phys. **70**, 187 (1992).

[25] A. K. BHATIA and R.J. Drachman, Phys. Rev. A **45**, 7752 (1992),

[26] G.W.F. Drake and Z.-C. Yan, Phys. Rev. A **46**, 2378 (1992).

[27] R.J. Drachman, Phys. Rev. A **47**, 1 (1992).

[28] R.J. Drachman, in *Long Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, Edited by F.S. Levin and D. Micha (Plenum, New York, 1993), pp. 219–272.

[29] G.W.F. Drake, Adv. At. Mol. Opt. Phys. **31**, 1 (1993).

[30] G.W.F. Drake, Adv. At. Mol. Opt. Phys. **32**, 93 (1993).

[31] G. W. F. Drake, in *Long Range Casimir Forces: Theory and Recent Experiments on Atomic Systems*, Edited by F.S. Levin and D. Micha (Plenum, New York, 1993), pp. 107-217.

[32] G. W. F. Drake in *Adv. At.Mol and Optical Physics.* edited by Sir David Bates and Benjamin Bederson V 31 (Academic Press. INC 1993)

[33] F. Marin, F. Minardi, F. S. Pavone, M. Inguscio, and G. W. F. Drake Z. Phys. D **32**, 285 (1995)

[34] Richard. J. Drachman and A. K. Bhatia, Phys. Rev. A **51**,5 (1995).

[35] A. K. Bhatia and Richard J. Drachman, Phys. Rev. A **55**, 3 (1996).

[36] G.D. Stevens and S.R. Lundeen, Phys. Rev. A **60**, 4379 (1999).

[37] G.W.F. Drake and S.P. Goldman, Can. J. Phys. **77**, 835 (1999).

[38] G. Lagmago Kamta, B. Piraux, and A. Scrinzi, *Phys. Rev. A*, **63**, 040502-1, (2001).

[39] S.R. Lundeen, Ad. At. Mol. Opt. Phys. **52**, 161 (2005).

[40] C. Schwartz, Int. J. Mod. Phys. E, **15**, 877 (2006)

[41] G. W. F. Drake and D. C. Morton, Ap. J. Sup. Ser. **170**, 251 (2007)

[42] H. Nakashima and H. Nakatsuji, J. Chem. Phys., **127**, 224104 (2007).

[43] I. A. Sulai, Qixue Wu, M. Bishof, G. W. F. Drake, Z.-T. Lu, P. Mueller, R. Santra, Phys. Rev. Lett. **101**, 173001 (2008)

[44] H. Nakashima, Y. Hijikata, and H. Nakatsuji, J. Chem. Phys., **128**, 154108 (2008).

[45] G.W.F. Drake and Zong-Chao Yan, Can. J. Phys. **86**, 45 (2008).

[46] Rida El-Wazni and G. W. F. Drake, Phys. Rev. A **80**, 064501 (2009).

[47] E. A. Hessels, F. J. Deck, P. W. Arcuni and S. R. Lundeen, Phys. Rev. Lett. **65**, 2765 (1990)

[48] H. Araki, Prog. Theor. Phys. **17**, 619 (1957)

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