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THE SCREENED COULOMB POTENTIALS IN SEMICONDUCTOR AND PLASMA PHYSICS

by

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Submitted in partial fulfillment
of
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To my father

Pah Ping Lam

and

the memory of my mother

Annie Chen

The Screened Coulomb Potentials in Semiconductor and Plasma Physics

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Abstract

This thesis presents a number of investigations on two- and three-particle systems in which the interaction between two particles can be represented by a screened Coulomb potential. Several types of screened potentials have been investigated, namely, the static screened Coulomb potential, the exponential cosine screened Coulomb potential, the Baer potential and the Hulthén potential. Bound states and their properties of two particles interacting via such potentials have been investigated. For the static screened Coulomb potential, three-body systems have also been studied. Two investigations dealing with H_2^+ and HeH^{2+}, respectively, are also included.

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Chapter 1. Introduction

In several areas of physics, Screened Coulomb Potentials play an important role. Such potentials can be generally written in the form

$$V(r) = -\frac{e^2}{r} f(\alpha r)$$

where f is a function of the screening parameter α and r. The major part of this thesis deals with such potentials. We summarize the investigations carried out in this thesis in the following.

The Static Screened Coulomb Potential (SSCP) :

$$V(r) = -\frac{e^2}{r} e^{-\alpha r}$$

where α is a screening parameter, is of interest in many areas of physics. In solid state physics, this potential represents the potential due to an ionized impurity; in plasma physics, this potential describes the ion-electron interaction and is commonly known as the Debye-Huckel potential. This potential (with e^2 replaced by another coupling constant) also occurs in nuclear physics, where it is known as the Yukawa potential. The significance of α in these different contexts is, of course, quite different. Chapter 2 of this thesis concerns itself with this potential. Perturbation and variational methods have been used to obtain the energies of 1s, 2s, 3s and 4s states. Several variational wave functions have been used; one of them gives highly accurate energies for the ground state. Also an approximate expression for the energy of any s state due to Ecker and Weizel is revised with a new identification of a quantity $\bar{r}$ occurring in this expression. The revised expression is shown to give

considerably better energies than the original one.

In a variational calculation, the energy eigenvalue obtained is only an upper bound to the true value of the ground state energy. Methods for obtaining the lower bound of the ground state have been developed by a number of authors, and the three best known ones are due to Weinstein (1934), Temple (1929) and Stevenson-Crawford (1938a, 1938b). Only a few numerical tests of these formulas have been reported. This fact can be attributed to the difficulty associated with the calculation of the integral $\langle HH \rangle$. A very satisfactory variational wave function that has been proposed in Chapter 2 for the ground state in the SSCP, is used in Chapter 3 to test the applicability and usefulness of these three lower bound formulas.

The potential

$$V(r) = - \frac{e^2}{\kappa r} e^{-qr} \cos(qr) ,$$

where κ is the dielectric constant and q is a screening parameter, is of importance in solid state physics. Under certain conditions it describes the potential between an ionized impurity and an electron in a metal. We shall call this potential the exponential cosine screened Coulomb (ECSC) potential. A number of properties of the bound eigenstates of an electron in an ECSC potential are studied in Chapter 4. Perturbation and variational methods are used to calculate the eigenvalues. Detailed results are presented for the first four s states.

For each state there is a critical value of the screening parameter δ_c above which no bound states with negative energy exist. The value of δ_c for the ground state is obtained from a two-parameter variational calculation. The total number of different energy levels is finite for any value of the screening parameter δ greater than zero, and is found to be approximately linear dependent on $1/\delta_c$. The square of the number of bound s states is also shown to be linear with $1/\delta_c$. Positive-energy states are also discussed.

The effective potential between a positive ion and an electron in a plasma has been a question of continuing interest. To a first approximation, it is customary to take this potential as the static screened Coulomb potential. At least at high temperature and low density, it is the correct asymptotic potential. However, the exact form of this potential is unclear and there has been controversy on this question (Nakayama and DeWitt 1964, and Jackson and Klein 1969, and Theimer and Kepple 1970). A few years ago, Baer (1970) derived the following expression for the screened potential around an ion:

$$\phi(r) = \frac{q^2}{2\epsilon n \times 2\pi r} (B_s e^{-q_s r} + B_o \cos q_o r)$$

where B_s, B_o, q_s and q_o are constants related to the electron density. The bound states for this potential are investigated in Chapter 5.

It is shown in Chapter 6 that the SSC, ECSC and Baer potentials can be considered to be special cases of a general screened Coulomb potential. The eigenstates in such a general potential are studied.

It is well known that in Ge- and Si-type semiconductors, there exist a bivalent impurity center (Glodeanu 1965, 1967, Gershenzon et al. 1971, and Godik et al. 1971). In a n-type semiconductor it is two electrons bound to a positive core and in a p-type semiconductor, two holes are associated with a negatively charged core. In n-type semiconductor, this kind of impurities arise from two situations (1) one additional electron attached to a neutral donor, in analogy to a H^- atom; (2) the substitutional impurity is a bivalent atom, in analogy to He To obtain the energy levels of this type of impurities, Glodeanu (1965, 1967) proposed a helium-like model in a single band approximation in which he used the free electron mass, instead of the effective mass, and the dielectric constant of the host crystal. Actually the interaction between the attached electrons or holes and the impurity center is not purely Coulombic. The existence of the free electrons weakens the interaction between these charged particles. In other words the Coulomb potential is screened by the free electrons. In Chapter 7, the binding energy of He-like atoms, in which the particles interact through a SSCP, has been obtained using the variational method.

In Chapter 8, the fine structure of excitonic lines in CuCl has been investigated. In the effective mass approximation, the non-relativistic electron-hole interaction operator is not purely Coulombic, and this leads to the fine structure of the excitonic lines (Haken 1962). For this effective electron-hole interaction, the Haken potential (1958) is chosen, which has the following form :

$$V(r) = -\frac{e^2}{\varepsilon_0 r} + V'(r)$$

$$V'(r) = -\frac{e^2}{2\varepsilon_0 r}\left(\frac{\varepsilon_0}{\varepsilon_\infty} - 1\right)\left(e^{-\frac{r}{\rho_e}} + e^{-\frac{r}{\rho_h}}\right)$$

where $\rho_{e,h} = (\hbar/2m^*_{e,h}\,\omega)^{\frac{1}{2}}$ is the polaron radius of the electron (the hole), $m^*_{e,h}$ the effective mass of the electron (the hole), ε_0 and ε_∞ are the static and optical dieletric constants respectively, and ω is the longitudinal circular frequency of the lattice. The non-Coulombic part $V'(r)$ is treated as a perturbation with respect to the Coulombic part and the energy difference between 2s and 2p levels is obtained by carrying out the calculation to the second order in the perturbation theory. The calculated value shows an improvement over an earlier result of Stebe and Certier (1972).

Chapter 9 deals with the binding energies of a positron to F and F' colour centers in alkali halides. Herlach and Heinrich (1970) investigated the 2γ-annihilation of positrons in additively coloured KCl crystals. They showed that the F-centers were the most important positron traps,

but the possible influence of complex (F'- and F- aggregate) colour centers on the annihilation characteristic was also noted. Berezin (1972) has given a theoretical treatment of the F_e^+ and $F'_e{}^+$ centers in terms of model potentials and has carried out calculations for these two systems for NaCl, KCl and KBr crystals. In Chapter 9, we have carried out the following calculations : (1) using Berezin's model, but employing a better variational wave function, the binding energy of positron to the F-center has been calculated for twenty alkali halides, and (2) the binding energy of positron to the F' center has been calculated for nine alkali halides.

The last three chapters of the thesis deal with two center problems. In Chapter 10, a two-parameter wave function for the $1s\sigma_g$ ground state of H_2^+ is proposed and is shown to give good results for the energy over a wide interval of the internuclear separation. Comparison is made with results obtained from several other wave functions.

The binding energy of an electron, bound to a donor atom in a doped semiconductor, relative to the conduction-band minima is usually calculated for a single impurity atom in the crystal. On the experimental side, it is known that the binding energy of the electron decreases as the number of donors increases until at some critical impurity concentration there is pratically no activation energy. The theoretical problems associated

with this phenomena can be conveniently discussed in terms of the potential of the singly charged donor screened by the conduction electrons, which is represented by a SSCP (Mott and Jones 1958, Mott 1961) The approximation that the electron is bound to a single ionized impurity is, however, no longer justified if there is considerable overlap between the wave functions of electrons bound to two neighboring impurity atoms. In such a situation an electron could be bound to two impurity atoms. In Chapter 11, the binding energy of an electron bound to two ionized impurity atoms is calculated as a function of the screening parameter δ, which occurs in the screened Coulomb potential. The binding energy is found to diminish with increase in δ, ultimately becoming zero at $\delta \simeq 1.254$. The role played by such a system in the Mott transition is discussed.

In Chapter 12, a geometric-mean type of variation function has been examined for the $1s\sigma$ state of HeH^{2+} and has been found to give very good results for the energy.

Unless otherwise indicated, we shall use atomic units throughout this thesis. The unit of length is $a_o = \hbar^2/m^*e^2$ and the unit of energy is equal to $-m^*e^4/\hbar^2$. Here m^* is the effective mass of an electron.

Chapter 2 - Bound Eigenstates of the Static Screened Coulomb Potential

2.1 Introduction

In this study, the potential

$$V(r) = \text{constant} \frac{e^{-\alpha r}}{r} \tag{2.1}$$

is called a Static Screened Coulomb Potential (SSCP), where α is a screening parameter. This potential enters several fields of physics. The significances of the constant and α are, of course, all different in the different contexts. In nuclear physics it is under the name of Yukawa potential, which describes the interaction between two nucleons. It is called the Debye-Hückel potential in plasma physics and it is used to account for a hydrogen-like atom in an ionized gas. In a semi-conductor or in a metal, this potential signifies an impurity atom in the sea of free charge carriers.

The problem of finding the energy levels of this potential has attracted a good number of authors. Since the Schrödinger equation of Eq.(2.1) is not analytically solvable, Harris (1962), Iafrate and Mendelsohn (1969), and Smith (1964) have employed perturbation theory, Harris (1962) and Krieger (1969) have used variational method and Bonch-Bruevich and Glasko (1962) and Rogers et al. (1970) have carried out the actual numerical integration of the differential equation of the Schrödinger equation. Of these, the results of Rogers et al. (1970), obtained by numerical techniques, are of high accuracy over a wide range of the screening parameter and cover 45 eigenstates.

In this study, we employed following calculations. For the purpose of comparison, we repeated the calculation of Smith (1964), who had used the Coulomb potential as the unperturbed potential. We then extended his calculation to the second order for the ground state by two different approaches — the series expansion and the F-factor technique. We made use of the fact that the Hulthèn potential (Appendix A) is a close approximation to the SSCP for not too large value of α. The energies of 1s-4s states were calculated by perturbation theory and variation method with the Hulthèn wave functions as the basic set. These types of calculations can be extented to any high s state without much difficulty. A new wave function for the ground state was proposed, which produced the energies identical to those quoted by Rogers et al. (1970) over the entire range of screening parameters. Finally we gave a new identification of $\bar{r}$ which appeared in the work of Ecker and Weizel (1956) in the same problem. With such a new identification the energy values were substantially improved. The comparison of all calculated results and some fine points were discussed in the last section.

In this chapter, we will write the SSCP in the following form

$$V(r) = \frac{e^{-\delta r}}{r} \tag{2.2}$$

2.2 Perturbation Calculation with the Coulomb Potential as an Unperturbed Potential

2.2.1 Introduction

Smith (1964) has calculated energy eigenvalues of the SSCP by using the Coulomb potential as an unperturbed potential. As shown in the Fig. 2.1, the Coulomb potential is not a good approximate potential to the SSCP but it has a simple form and its wave function of the Schrödinger equation is well developed.

Smith (1964) only quoted few calculated values of energy in his paper. Therefore it is necessary for us here to repeat his calculation in order to compare the energy eigenvalues of his method with the other calculations in a wide range of the screening parameter.

For the ground state we carried second order perturbation calculations by two different methods. These are the conventional series expansion method and a rarely used F-scalar factor technique (Hirschfelder et al. 1964). It has dual purposes for the second order calculations. First we want to show the importance of second order correction when the Coulomb potential is used as an unperturbed one; second we want to compare the accuracy of the second order calculations by two different methods.

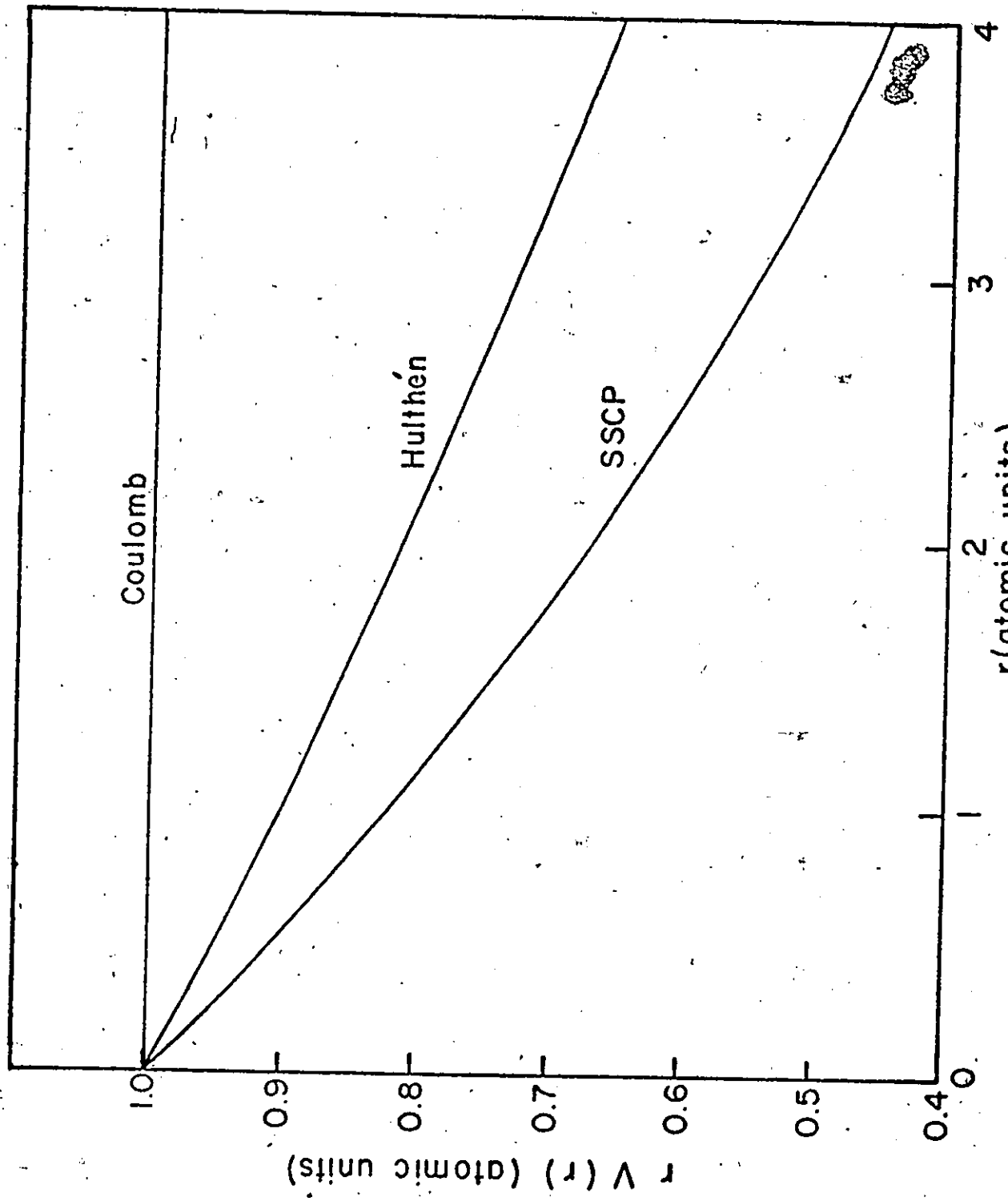

Fig. 2.1 : Product rV(r) as a function of r, for the Coulomb potential, the Hulthén potential and the SSCP for $\delta = 0,2$

2.2.2 First Order Perturbation Calculation

As Coulomb potential is considered as an unperturbed potential the SSCP can be written as

$$V(r) = \frac{1}{r} + \left(\frac{e^{-\delta r}}{r} - \frac{1}{r}\right)$$

$$= \frac{1}{r} + U(r) \qquad (2.3)$$

Now U(r) is treated as a perturbing potential. The unperturbed wave function or the hydrogenic function has the form

$$\psi_{n\ell}(r) = \frac{2^{\ell+1}}{n^{\ell+2}} \left[\frac{(n+\ell)!}{(n-\ell-1)!}\right]^{\frac{1}{2}} \frac{1}{(2\ell+1)!} e^{-\frac{r}{n}} r^{\ell+1}$$

$$\times {}_1F_1\left(-n+\ell+1,\ 2\ell+2;\ \frac{2r}{n}\right) \qquad (2.4)$$

where ${}_1F_1$ is the confluent hypergeometric function. And the unperturbed energy is

$$E_{no}^{(o)} = \frac{1}{2n^2} \qquad (2.5)$$

The first order energy correction is

$$\Delta E_{n\ell}^{(1)} = \langle \psi_{n\ell}(r) | U(r) | \psi_{n\ell}(r) \rangle$$

$$= \frac{2^{2\ell+2}}{n^{2\ell+4}} \frac{(n+\ell)!}{(n-\ell-1)!} \frac{1}{(2\ell+1)!} \frac{\delta^{2n-2\ell-2}}{\left(\frac{2}{n}+\delta\right)^{2n}}$$

$$\times {}_2F_1\left(-n+\ell+1,\ -n+\ell+1;\ 2\ell+2;\ \frac{4}{n^2\delta^2}\right) - \frac{1}{n^2} \qquad (2.6)$$

where ${}_2F_1$ is the hypergeometric function.

2.2.3 Second Order Perturbation Calculation - Series Expansion Method on the Ground State

The second order perturbation correction on the ground state energy is given by

$$\Delta E_{10}^{(2)} = \sum_{n=2}^{\infty} \frac{< \psi_{10} \mid U(r) \mid \psi_{no} >^2}{E_{no} - E_{10}} \tag{2.7}$$

where

$$< \psi_{10} \mid U(r) \mid \psi_{no} > = 4 \sqrt{n} \left[\frac{1}{(1+n+n\delta)^2} \, {}_2F_1 \left(-n+1, 2; 2; \frac{2}{1+n+n\delta}\right) - \frac{1}{(1+n)^2} \, {}_2F_1 \left(-n+1, 2; 2; \frac{2}{1+n}\right) \right]$$

2.2.4 Second Order Perturbation Calculation - F Operator Technique on the Ground State

The Hamiltonian of the system in the present case is

$$H = \frac{1}{2} \frac{d^2}{dr^2} + \frac{e^{-\delta r}}{r}$$

$$= H_o + U(r)$$

where $H_o = \frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{r}$, the unperturbed Hamiltonian or the system of a hydrogen-like atom. The first order perturbation equation is usually written in the following form

$$(H_o - E) \, \psi^{(1)} + (U - \Delta E^{(1)}) \, \Psi = 0 \tag{2.8}$$

where E and Ψ are respectively the energy and the wave function of the unperturbed Hamiltonian H_o, and $\Delta E^{(1)}$ and $\psi^{(1)}$ are respectively the first order energy correction and the first order wave function.

On the other hand the first order wave function can be written as

$$\psi^{(1)} = F\psi \tag{2.9}$$

where F is an undetermined scalar function of r. Note that

$$(H_o - E)F\psi = (H_oF - FH_o)\psi$$

Eq.(2.8) can be written as

$$(FH_o - H_oF)\psi = (U - \Delta E^{(1)})\psi$$

By replacing $H_o = \frac{1}{2}\frac{d^2}{dr^2} + \frac{1}{r}$ in the above equation, we have

$$(F\frac{d^2}{dr^2} - \frac{d^2}{dr^2}F)\psi = 2(U - \Delta E^{(1)})\psi$$

Assume all functions here being real, then

$$-\frac{d}{dr}(\psi^2\frac{dF}{dr}) = 2\psi(U - \Delta E^{(1)})\psi \tag{2.10}$$

The boundary conditions on the perturbed wave function are the same as those on the unperturbed-eigenfunction ψ. Thus on the boundaries at infinity the conditions on F are

$$F\psi = 0, \qquad \psi^2\frac{dF}{dr} = 0$$

This ensures the integral of the right-hand side of Eq.(2.10) vanishes. This leads the Eq.(2.10) to

$$\psi^2\frac{dF}{dr} = W(r) \tag{2.11}$$

where $W(r) = 2\int_o^r \psi^2(t)(U(t) - \Delta E^{(1)})dt$ (2.12)

For the ground state, the unperturbed wave function Ψ does not possess any nodes in the interval $(0, \infty)$, Eq.(2.11) may be integrated immediately to give

$$F(x) = F(a) + \int_0^x W(t)/\Psi^2(t)\, dt \qquad (2.13)$$

The additive constant F(a) is chosen such that the orthogonal condition

$$< \Psi \mid F\Psi > = 0$$

is satisfied.

In terms of F, the second order energy correction $\Delta E^{(2)}$ is therefore

$$\Delta E^{(2)} = < \Psi \mid U - \Delta E^{(1)} \mid F\Psi >$$

Substituting Ψ_{10} for Ψ, U(r) from Eq.(2.3) and $\Delta E^{(1)}$ from Eq.(2.6) in the Eq.(2.12), we have

$$W(r) = \frac{4}{(2+\delta)^2} e^{-2r} \{ 2 + 4r - (4+\delta)\delta r^2 - 2e^{-\delta r} [1 + (2+\delta)r] \}$$

therefore, $\Delta E^{(2)}$ can be integrated and results

$$\Delta E_{10}^{(2)} = \frac{2}{(2+\delta)^4} \left[- 8 - 4\delta(4+\delta) + \frac{8\delta(4+\delta)}{2+\delta} + \frac{\delta^2}{4}(4+\delta)^2 + \frac{2(2+\delta)^2}{1+\delta} - 8\ell n(1+\delta) + 16\ell n(2+\delta) - 16\ell n2 \right] \qquad (2.14)$$

Now instead of the series expansion form the second order energy correction is expressed in a closed form.

2.3 Perturbation Calculation with the Hulthén Potential as an Unperturbed Potential

The SSCP, Eq.(2.2) can be written as a Hulthén potential plus a perturbation U(r):

$$V(r) = \frac{\delta e^{-\delta r}}{1 - e^{-\delta r}} + \left(\frac{e^{-\delta r}}{r} - \frac{\delta e^{-\delta r}}{1 - e^{-\delta r}}\right)$$

$$= \frac{e^{-\delta r}}{1 - e^{-\delta r}} + U(r) \qquad (2.15)$$

Now U(r) is treated as a perturbing potential. In Fig. 2.1, we show the SSCP, the Hulthén potential and the Coulomb potential. Note that the choice of the Hulthén potential as the unperturbed potential is a better one than that of a Coulomb potential for the same.

From the Appendix A, the unperturbed energy eigenvalues and the unperturbed wave functions for s states are respectively

$$E_n^{(o)} = \frac{1}{8}\left(\frac{2}{n} - n\delta\right)^2 \qquad (2.16)$$

and

$$\Psi_n = \left[\frac{n}{4}\left(\frac{4}{n^2} - n^2\delta^2\right)\right]^{\frac{1}{2}} e^{-\frac{1}{2}\left(\frac{2}{n} - n\delta\right)r}$$

$$\times \sum_{k=1}^{n} C_k \left(1 - e^{-\delta r}\right)^k \qquad (2.17)$$

where

$$C_k = (-1)^{k-1} \binom{n-1}{k-1} \binom{k + \frac{2}{n\delta} - 1}{k}$$

In this section we only calculated the energies for the lowest four s states. The wave functions for the 1s-4s states can be deduced from the Eq.(2.17) and they are

$$\Psi_{1s} = \left(\frac{4}{\delta^2} - 1\right)^{\frac{1}{2}} (1 - e^{-\delta r})\, e^{-(1-\frac{\delta}{2})r} \tag{2.17a}$$

$$\Psi_{2s} = \frac{1}{2\delta^2}\left[\frac{1}{2}(1 - 4\delta^2)\right]^{\frac{1}{2}} (1 - e^{-\delta r})\left[- (1 - \delta)\, e^{-(\frac{1}{2}-\delta)r} + (1 + \delta)\, e^{-\frac{r}{2}}\right] \tag{2.17b}$$

$$\Psi_{3s} = \frac{1}{81\delta^3}\left[\frac{1}{3}(4 - 81\delta^2)\right]^{\frac{1}{2}} (1 - e^{-\delta r})\left[(1 - 3\delta)(2 - 3\delta)\, e^{-(\frac{1}{3}-\frac{3\delta}{2})r} - (4 - 9\delta^2)\, e^{-(\frac{1}{3}+\frac{\delta}{2})r} + (1 + 3\delta)(2 + 3\delta)\, e^{-(\frac{1}{3}+\frac{\delta}{2})r}\right] \tag{2.17c}$$

$$\Psi_{4s} = \frac{1}{768\delta^4} (1 - 64\delta^2)^{\frac{1}{2}} (1 - e^{-\delta r})\left[- (1 - 6\delta)(1 - 4\delta)(1 - 2\delta)\, e^{-(\frac{1}{4}-2\delta)r} + 3(1 - 4\delta)(1 - 4\delta^2)\, e^{-(\frac{1}{4}-\delta)r} - 3(1 + 4\delta)(1 - 4\delta^2)\, e^{-\frac{r}{4}} + (1 + 6\delta)(1 + 4\delta)(1 + 2\delta)\, e^{-(\frac{1}{4}+\delta)r}\right] \tag{2.17d}$$

When these equations are substituted into the following expression

$$E_n^{(1)} = \langle \Psi_n \mid U(r) \mid \Psi_n \rangle$$

$$= \langle \Psi_n \mid \frac{e^{-\delta r}}{r} \mid \Psi_n \rangle - \langle \Psi_n \mid \frac{\delta e^{-\delta r}}{1 - e^{-\delta r}} \mid \Psi_n \rangle \tag{2.18}$$

we can obtain the perturbation energy of the 1s-4s states. The integrals involved in the Eq.(2.18) can be analytically evaluated but are somewhat complicated. The complexity of calculation increases from 1s state to 4s state. The energy expression for a s state results from the integration of the Eq.(2.18) in conjunction with the Eq.(2.16). The expressions for the 1s to 4s states are as follows.

$$E_{1s} = -\frac{4-\delta^2}{8} + \frac{4-\delta^2}{\delta^2}\{2\,\ell n\,(1+\tfrac{\delta}{2}) - \ell n\,(1+\delta)\} \tag{2.19}$$

$$\begin{aligned} E_{2s} = -\frac{1-4\delta^2}{8} + \frac{1-4\delta^2}{8\delta^4}\{&-(1-\delta)^2\,\ell n\,(1-\delta) \\ &- 2(3-\delta^2)\,\ell n\,(1+\delta) - 4(1+\delta)\,\ell n\,(1+2\delta) \\ &- (1+\delta)^2\,\ell n\,(1+3\delta)\} \qquad (\delta < 1) \end{aligned} \tag{2.20}$$

$$\begin{aligned} E_{3s} = -\frac{4-81\delta^2}{72} + \frac{4-81\delta^2}{19683\delta^6}\{&-(1-3\delta)^2(2-3\delta)^2\,\ell n\,(1-3\delta) \\ &+ 6(1-3\delta)(2-3\delta)^2\,\ell n\,(1-\tfrac{3\delta}{2}) \\ &+ 2(4-9\delta^2)(10-9\delta^2)\,\ell n\,(1+\tfrac{3\delta}{2}) \\ &- 3(2+3\delta)(10+15\delta-18\delta^2)\,\ell n\,(1+3\delta) \\ &+ 6(2+3\delta)^2(1+3\delta)\,\ell n\,(1+\tfrac{9\delta}{2}) \\ &- (2+3\delta)^2(1+3\delta)^2\,\ell n\,(1+6\delta)\} \qquad (\delta < 1/3) \end{aligned} \tag{2.21}$$

$$E_{4s} = -\frac{1 - 64\delta^2}{32}$$

$$+ \frac{1 - 64\delta^2}{589824\delta^8} \{ - (1 - 6\delta)^2 (1 - 4\delta)^2 (1 - 2\delta)^2 \ln (1 - 6\delta)$$

$$+ 8(1 - 6\delta)(1 - 4\delta)^2 (1 - 2\delta)^2 \ln (1 - 4\delta)$$

$$- 4(1 - 4\delta)(1 - 2\delta)^2 (7 - 28\delta - 36\delta^2) \ln (1 - 2\delta)$$

$$- 2(1 - 2\delta)(1 + 2\delta)(35 - 380\delta + 576\delta^2) \ln (1 + 2\delta)$$

$$+ 8(1 - 2\delta)(1 + 2\delta)(1 + 4\delta)(7 + 14\delta - 6\delta^2) \ln (1 + 4\delta)$$

$$- 4(1 + 2\delta)^2 (1 + 4\delta)(7 + 28\delta - 36\delta^2) \ln (1 + 6\delta)$$

$$+ 8(1 + 2\delta)^2 (1 + 4\delta)^2 (1 + 6\delta) \ln (1 + 8\delta)$$

$$- (1 + 2\delta)^2 (1 + 4\delta)^2 (1 + 6\delta)^2 \ln (1 + 10\delta)\} \quad (\delta < 1/6) \qquad (2.22)$$

2.4 Variational Calculation with One Parameter Hulthén Function as a Trial Function

Harris (1962), Krieger (1969), and Margenau and Lewis (1959) have reported the energy eigenvalues of SSCP by variational calculation by using hydrogen-like wave functions as a basic set and exponential nuclear charge as a variational parameter. Of these, the best results are those of Harris by using the linear combination of 1s, 2s and 3s hydrogen-like wave functions as the trial function. In view of the fact that the Hulthén potential is a better approximation to the SSCP than the Coulomb potential, one anticipates that for the same number of parameters, the Hulthén wave functions would be a better choice for trial functions in this problem than the hydrogen-like wave functions.

From Eq.(2.17), it is seen that a s state Hulthén wave function only depends on the parameter δ. If one replaces it by μ, a variational parameter, one would have the trial function of the SSCP. Here we carried out the calculation for the lowest four s states. The trial functions of the 1s to 4s states are listed below.

$$\Psi_{1s} = \left(\frac{4}{\mu^2} - 1\right)^{\frac{1}{2}} \left(1 - e^{-\mu r}\right) e^{-\left(1 - \frac{\mu}{2}\right)r} \tag{2.23}$$

$$\Psi_{2s} = \frac{1}{2\mu^2}\left[\frac{1}{2}\left(1 - 4\mu^2\right)\right]^{\frac{1}{2}} \left(1 - e^{-\mu r}\right) \times \left[-(1 - \mu)\, e^{-\left(\frac{1}{2} - \mu\right)r} + (1 + \mu)\, e^{-\frac{r}{2}}\right] \tag{2.24}$$

$$\Psi_{3s} = \frac{1}{81\mu^3}\left[\frac{1}{3}(4 - 81\mu^2)\right]^{\frac{1}{2}} (1 - e^{-\mu r})$$
$$\times \left[(1 - 3\mu)(2 - 3\mu)\, e^{-(\frac{1}{3}-\frac{3\mu}{2})r} - (4 - 9\mu^2)\, e^{-(\frac{1}{3}-\frac{\mu}{2})r}\right.$$
$$\left. + (1 + 3\mu)(2 + 3\mu)\, e^{-(\frac{1}{3}+\frac{\mu}{2})r}\right] \qquad (2.25)$$

$$\Psi_{4s} = \frac{1}{768\mu^4} (1 - 64\mu^2)^{\frac{1}{2}} (1 - e^{-\mu r})$$
$$\times \left[-(1 - 6\mu)(1 - 4\mu)(1 - 2\mu)\, e^{-(\frac{1}{4}-2\mu)r}\right.$$
$$+ 3(1 - 4\mu)(1 - 4\mu^2)\, e^{-(\frac{1}{4}-\mu)r}$$
$$- 3(1 + 4\mu)(1 - 4\mu^2)\, e^{-\frac{1}{4}r}$$
$$\left. + (1 + 6\mu)(1 + 4\mu)(1 + 2\mu)\, e^{-(\frac{1}{4}+\mu)r}\right] \qquad (2.26)$$

The energy expression for a s state can be obtained from

$$E_n = \langle \Psi_n \mid \frac{1}{2}\frac{d^2}{dr^2} \mid \Psi_n \rangle + \langle \Psi_n \mid \frac{e^{-\delta r}}{r} \mid \Psi_n \rangle$$

All integrals involved in the calculation can be analytically evaluated and the results are shown below.

$$E_{1s} = (4/\mu^2 - 1) \times [-\mu^2/8 - \ell n\,(2 + \ell - \mu) + 2\,\ell n(2 + \delta)$$
$$- \ell n\,(2 + \delta + \mu)]$$
$$(\mu < 2 + \delta) \qquad (2.27)$$

$$E_{2s} = [(1 - 4\mu^2)/8\mu^4][-\mu^4 - (\mu - 1)^2 \ln (1 + \delta - 2\mu)$$
$$+ 4(1 - \mu) \ln (1 + \delta - \mu) - 2(3 - \mu^2) \ln (1 + \delta)$$
$$+ 4(1 + \mu) \ln (1 + \delta + \mu) - (1 + \mu)^2 \ln (1 + \delta + 2\mu)]$$

$$\mu < \tfrac{1}{2}(1 + \delta) \qquad (2.28)$$

$$E_{3s} = [(4 - 81\mu^2)/78732\mu^6][-2187\mu^6/2$$
$$- (2 - 6\mu)^2 (2 - 3\mu)^2 \ln (2 + 3\delta - 9\mu)$$
$$+ 12(2 - 6\mu)(2 - 3\mu)^2 \ln (2 + 3\delta - 6\mu)$$
$$- 12(2 - 3\mu)(10 - 15\mu - 18\mu^2) \ln (2 + 3\delta - 3\mu)$$
$$+ 8(4 - 9\mu^2)(10 - 9\mu^2) \ln (2 + 3\delta)$$
$$- 12(2 + 3\mu)(10 + 15\mu - 18\mu^2) \ln (2 + 3\delta + 3\mu)$$
$$+ 12(2 + 3\mu)^2 (2 + 6\mu) \ln (2 + 3\delta + 6\mu)$$
$$- (2 + 3\mu)^2 (2 + 6\mu)^2 \ln (2 + 3\delta + 9\mu)]$$

$$\mu < \tfrac{1}{9}(2 + 3\delta) \qquad (2.29)$$

$$E_{4s} = [(1 - 64\mu^2)/589824\mu^8] \times [-18432\mu^8$$
$$- (1 - 6\mu)^2 (1 - 4\mu)^2 (1 - 2\mu)^2 \ln (1 + 2\delta - 8\mu)$$
$$+ 8(1 - 6\mu)(1 - 4\mu)^2 (1 - 2\mu)^2 \ln (1 + 2\delta - 6\mu)$$
$$- 4(1 - 4\mu)(1 - 2\mu)^2 (7 - 28\mu - 36\mu^2) \ln (1 + 2\delta - 4\mu)$$
$$+ 8(1 - 4\mu^2)(1 - 4\mu)(7 - 14\mu - 24\mu^2) \ln (1 + 2\delta - 2\mu)$$
$$- 2(1 - 4\mu^2)(35 - 380\mu^2 + 576\mu^4) \ln (1 + 2\delta)$$
$$+ 8(1 - 4\mu^2)(1 + 4\mu)(7 + 14\mu - 24\mu^2) \ln (1 + 2\delta + 2\mu)$$
$$- 4(1 + 4\mu)(1 + 2\mu)^2 (7 + 28\mu - 36\mu^2) \ln (1 + 2\delta + 4\mu)$$
$$+ 8(1 + 6\mu)(1 + 4\mu)^2 (1 + 2\mu)^2 \ln (1 + 2\delta + 6\mu)$$
$$- (1 + 6\mu)^2 (1 + 4\mu)^2 (1 + 2\mu)^2 \ln (1 + 2\delta + 8\mu)]$$

$$\mu < \frac{1}{8}(2 + \delta) \qquad (2.30)$$

The energy of a state at a given value of δ is obtained by minimising E_n with respect to μ. The minimum of E is ensured by the zero of $\frac{\partial E_n}{\partial \mu}$. Therefore we have to work out the expressions for $\frac{\partial E_n}{\partial \mu}$. They are

$$\frac{\partial E_{1s}}{\partial \mu} = \frac{8}{\mu^3}\{\ell n(2+\delta-\mu) - 2\,\ell n(2+\delta) + \ell n(2+\delta+\mu)\}$$
$$+ \left(\frac{4}{\mu^2} - 1\right)\left(\frac{1}{2+\delta-\mu} - \frac{1}{2+\delta+\mu}\right) + \frac{\mu}{4}$$

$$\frac{\partial E_{2s}}{\partial \mu} = \frac{2\mu^2 - 1}{2\mu^5}\{-\mu^4 - (1-\mu)^2\,\ell n(1+\delta-2\mu)$$
$$+ 4(1-\mu)\,\ell n(1+\delta-\mu)$$
$$- 2(3-\mu^2)\,\ell n(1+\delta)$$
$$+ 4(1+\mu)\,\ell n(1+\delta+\mu)$$
$$- (1+\mu)^2\,\ell n(1+\delta+2\mu)\}$$
$$+ \frac{1-4\mu^2}{8\mu^4}\{-4\mu^3 + \frac{2(1-\mu)^2}{1+\delta-2\mu} - \frac{4(1-\mu)}{1+\delta-\mu}$$
$$+ \frac{4(1+\mu)}{1+\delta+\mu} - \frac{2(1+\mu)^2}{1+\delta+2\mu}$$
$$+ 2(1-\mu)\,\ell n(1+\delta-2\mu)$$
$$- 4\,\ell n(1+\delta-\mu)$$
$$+ 4\mu\,\ell n(1+\delta)$$
$$+ 4\,\ell n(1+\delta+\mu)$$
$$- 2(1+\mu)\,\ell n(1+\delta+2\mu)\}$$

$$\frac{\partial E_{3s}}{\partial \mu} = \frac{1}{78732\mu^6}\left(-\frac{24}{\mu^7}+\frac{324}{\mu^5}\right)\Big\{-\frac{2187}{2}\mu^6-(2-6\mu)^2(2-3\mu)^2\,\ell n(2+3\delta-9\mu)$$

$$+12(2-6\mu)(2-3\mu)^2\,\ell n(2+3\delta-6\mu)-12(2-3\mu)(10-15\mu-18\mu^2)\,\ell n(2+3\delta-3\mu)$$

$$+8(2-3\mu)(2+3\mu)(10-9\mu^2)\,\ell n(2+3\delta)-12(2+3\mu)(10+15\mu-18\mu^2)\,\ell n(2+3\delta+3\mu)$$

$$+12(2+3\mu)^2(2+6\mu)\,\ell n(2+3\delta+6\mu)-(2+3\mu)^2(2+6\mu)^2\,\ell n(2+3\delta+9\mu)\Big\}$$

$$+\frac{1}{78732\mu^6}(4-81\mu^2)\Big\{-6561\mu^5+\frac{9(2-6\mu)^2(2-3\mu)^2}{2+3\delta-9\mu}$$

$$-\frac{72(2-6\mu)(2-3\mu)^2}{2+3\delta-6\mu}+\frac{36(2-3\mu)(10-15\mu-18\mu^2)}{2+3\delta-3\mu}$$

$$-\frac{36(2+3\mu)(10+15\mu-18\mu^2)}{2+3\delta+3\mu}+\frac{72(2+3\mu)^2(2+6\mu)}{2+3\delta+6\mu}$$

$$-\frac{9(2+3\mu)^2(2+6\mu)^2}{2+3\delta+9\mu}$$

$$+36(2-6\mu)(2-3\mu)(1-2\mu)\,\ell n(2+3\delta-9\mu)$$

$$-72(2-3\mu)(4-9\mu)\,\ell n(2+3\delta-6\mu)$$

$$-72(-10+3\mu+27\mu^2)\,\ell n(2+3\delta-3\mu)$$

$$+288(-7\mu+9\mu^2)\,\ell n(2+3\delta)$$

$$-72(10+3\mu-27\mu^2)\,\ell n(2+3\delta+3\mu)$$

$$+72(2+3\mu)(4+9\mu)\,\ell n(2+3\delta+6\mu)$$

$$-36(2+3\mu)(2+6\mu)(1+2\mu)\,\ell n(2+3\delta+9\mu)\Big\}$$

$$\frac{\partial E_{4s}}{\partial \mu^s} = \frac{1}{73728}\left(\frac{48}{\mu^7} - \frac{1}{\mu^9}\right)\Big\{ - (1-6\mu)^2(1-4\mu)^2(1-2\mu)^2 \ln(1+2\delta-8\mu)$$
$$+ 8(1-6\mu)(1-4\mu)^2(1-2\mu)^2 \ln(1+2\delta-6\mu)$$
$$- 4(1-4\mu)(1-2\mu)^2(7-28\mu-36\mu^2) \ln(1+2\delta-4\mu)$$
$$+ 8(1-4\mu^2)(1-4\mu)(7-14\mu-24\mu^2) \ln(1+2\delta-2\mu)$$
$$- 2(1-4\mu^2)(35-380\mu^2+576\mu^4) \ln(1+2\delta)$$
$$+ 8(1-4\mu^2)(1+4\mu)(7+14\mu-24\mu^2) \ln(1+2\delta+2\mu)$$
$$- 4(1+4\mu)(1+2\mu)^2(7+28\mu-36\mu^2) \ln(1+2\delta+4\mu)$$
$$+ 8(1+6\mu)(1+4\mu)^2(1+2\mu)^2 \ln(1+2\delta+6\mu)$$
$$- (1+6\mu)^2(1+4\mu)^2(1+2\mu)^2 \ln(1+2\delta+8\mu)\Big\}$$
$$= \frac{1-64\mu^2}{589824\mu^8}\Big\{ \frac{8}{1+2\delta-8\mu}(1-6\mu)^2(1-4\mu)^2(1-2\mu)^2$$
$$- \frac{48}{1+2\delta-6\mu}(1-6\mu)(1-4\mu)^2(1-2\mu)^2$$
$$+ \frac{16}{1+2\delta-4\mu}(1-4\mu)(1-2\mu)^2(7-28\mu-36\mu^2)$$
$$- \frac{16}{1+2\delta-2\mu}(1-4\mu^2)(1-4\mu)(7-14\mu-24\mu^2)$$
$$+ \frac{16}{1+2\delta+2\mu}(1-4\mu^2)(1+4\mu)(7+14\mu-24\mu^2)$$
$$- \frac{16}{1+2\delta+4\mu}(1+4\mu)(1+2\mu)^2(7+28\mu-36\mu^2)$$
$$+ \frac{48}{1+2\delta+6\mu}(1+6\mu)(1+4\mu)^2(1+2\mu)^2$$
$$- \frac{8}{1+2\delta+8\mu}(1+6\mu)^2(1+4\mu)^2(1+2\mu)^2$$
$$+ 8(1-6\mu)(1-4\mu)(1-2\mu)(3-22\mu+36\mu^2) \ln(1+2\delta-8\mu)$$
$$-16(1-4\mu)(1-2\mu)(9-70\mu+120\mu^2) \ln(1+2\delta-6\mu)$$

$$+ 16(1 - 2\mu)(21 - 122\mu + 44\mu^2 + 360\mu^3)\ \ell n(1 + 2\delta - 4\mu)$$
$$- 16(21 - 4\mu - 396\mu^2 + 256\mu^3 + 960\mu^4)\ \ell n(1 + 2\delta - 2\mu)$$
$$+ 32\mu(65 - 524\mu^2 + 864\mu^4)\ \ell n(1 + 2\delta)$$
$$+ 16(21 + 4\mu - 396\mu^2 - 256\mu^3 + 960\mu^4)\ \ell n(1 + 2\delta + 2\mu)$$
$$- 16(1 + 2\mu)(21 + 122\mu + 44\mu^2 - 360\mu^3)\ \ell n(1 + 2\delta + 4\mu)$$
$$+ 16(1 + 4\mu)(1 + 2\mu)(9 + 70\mu + 120\mu^2)\ \ell n(1 + 2\delta + 6\mu)$$
$$- 8(1 + 6\mu)(1 + 4\mu)(1 + 2\mu)(3 + 22\mu + 36\mu^2)\ \ell n(1 + 2\delta + 8\mu)\Big\}$$
$$+ 4\mu$$

During the minimization of energy E, we first explored the behaviour of $\frac{\partial E_n}{\partial \mu}$ as well as E_n in a wide range of μ. Then the search for minimum E_n is restricted to a small interval of μ in which $\frac{\partial E_n}{\partial \mu} = 0$ happens. In practical the search was terminated as $\left| \frac{\partial E_n}{\partial \mu} \right| < 10^{-20}$ was satisfied. The calculations were carried in an IBM 370/168 in "Quadruple precision" (32 figures in accuracy).

2.5 Linear Variational Calculation on the Ground State

Here we will propose two linear variation functions. The first one is the combination of 1s and 2s one-parameter Hulthén wave functions. Harris (1962) has used the linear combination of 1s to 3s hydrogen-like wave functions to the ground state of the SSCP, and her results are quite satisfactory in a wide range of δ. We have indicated before that Hulthén potential is a better approximate potential than the Coulomb. With the same number of the parameter, the results from the one-parameter Hulthén wave function is much better than that from the Coulomb due to Krieger, but it is slightly poorer than the Harris's results. We want to see whether the result will be improved if one adds the 2s state Hulthén wave function to its 1s state wave function.

The second function is the linear combination of 1s state hydrogen-like wave function and 1s state two-parameter Hulthén wave function. For the weak screening, both the hydrogen-like and Hulthén are good approximate wave functions. The results of Ayrault and Langlois (1971) prove that the Hulthén two-parameter wave function is good for a fair wide range of δ. These lead us to the point that the linear combination of these two wave functions should yield the ground state energy, at least, not worse than either of the individual ones.

Now the suggested form of trial function is

$$\Psi = a_1\phi_1 + a_2\phi_2 \tag{2.31}$$

where a_1 and a_2 are the linear parameters, and ϕ_1 and ϕ_2 are the wave functions to be combined. The energy results from the lower root of the secular equation:

$$\begin{vmatrix} H_{11} - E & H_{12} - SE \\ H_{12} - SE & H_{22} - E \end{vmatrix} = 0 \tag{2.32}$$

where $H_{ij} = \langle \phi_i \mid \frac{1}{2}\frac{d^2}{dr^2} + \frac{e^{-\delta r}}{r} \mid \phi_j \rangle$

and $S = \langle \phi_i \mid \phi_j \rangle$

(a) Linear combination of 1s and 2s one-parameter Hulthén wave functions

$$\phi_1 = \left(\frac{4}{\mu^2} - 1\right)^{\frac{1}{2}} \left\{ e^{-(1+\frac{\mu}{2})r} - e^{-(1+\frac{\mu}{2})r} \right\} \tag{2.33a}$$

$$\phi_2 = \frac{1}{2\nu^2}\left\{\frac{1}{2}(1 - 4\nu^2)^{\frac{1}{2}}\left\{ - (1 - \nu)\, e^{-(\frac{1}{2}-\nu)r} + 2e^{-\frac{r}{2}} - (1 + \nu)\, e^{-(\frac{1}{2}+\nu)r} \right\}\right. \tag{2.33b}$$

$$H_{11} = \left(\frac{4}{\mu^2} - 1\right)\left\{ - \frac{\mu^2}{8} - \ell n(2 + \delta - \mu) + 2\ell n(2 + \delta) - \ell n(2 + \delta + \mu) \right\} \tag{2.33c}$$

$$H_{12} = \frac{1}{4\nu}\left\{\frac{1}{2}\left(\frac{4}{\mu^2} - 1\right)\left(\frac{1}{\nu^2} - 4\right)\right\}^{\frac{1}{2}}\left\{\frac{2\mu}{9 - \mu^2}\right.$$

$$- \frac{\mu(1 + \nu)(1 - 2\nu)^2}{(3 + 2\nu)^2 - \mu^2} - \frac{\mu(1 + \nu)(1 + 2\nu)^2}{(3 + 2\nu)^2 - \mu^2}$$

$$+ 2(1 - \nu)\ \ell n\ \frac{3 + 2\delta - \mu - 2\nu}{3 + 2\delta + \mu - 2\nu} - 4\ \ell n\ \frac{3 + 2\delta - \mu}{3 + 2\delta + \mu}$$

$$\left. + 2(1 + \nu)\ \ell n\ \frac{3 + 2\delta - \mu + 2\nu}{3 + 2\delta + \mu + 2\nu}\right\} \qquad (2.33d)$$

$$H_{22} = \frac{1 - 4\nu^2}{8\nu^2}\left\{-\nu^4 - (\nu - 1)^2\ \ell n(1 + \delta - 2\nu)\right.$$

$$+ 4(1 - \nu)\ \ell n(1 + \delta - \nu) - 2(3 - \nu^2)\ \ell n(1 + \delta)$$

$$\left. + 4(1 + \nu)\ \ell n(1 + \delta + \nu) - (1 + \nu)^2\ \ell n(1 + \delta + 2\nu)\right\} \qquad (2.33e)$$

$$S = \frac{2\mu}{\nu}\left\{\frac{1}{2}\left(\frac{4}{\mu^2} - 1\right)\left(\frac{1}{\nu^2} - 4\right)\right\}^{\frac{1}{2}}$$

$$\times\left\{\frac{2}{9 - \mu^2} - \frac{1 - \nu}{(3 - 2\nu)^2 - \mu^2} - \frac{1 + \nu}{(3 + 2\nu)^2 - \mu^2}\right\} \qquad (2.33f)$$

(b) Linear combination of 1s hydrogen-like wave function and 1s two-parameter Hulthén wave function

$$\phi_1 = \frac{1}{\mu}\left\{\nu\left(4\nu^2 - \mu^2\right)\right\}^{\frac{1}{2}}\left\{e^{-(\nu - \frac{\mu}{2})r} - e^{-(\nu + \frac{\mu}{2})r}\right\} \qquad (2.34a)$$

$$\phi_2 = 2\lambda^{\frac{3}{2}}\, r\, e^{-\lambda r} \qquad (2.34b)$$

$$H_{11} = -\frac{1}{8}(4\nu^2 - \mu^2) + \frac{\nu}{\mu^2}(4\nu^2 - \mu^2) - \ell n(\delta + 2\nu - \mu) + 2\,\ell n(\delta + 2\nu) - \ell n(\delta + 2\nu + \mu) \tag{2.34c}$$

$$H_{12} = 8\lambda^{\frac{3}{2}}\left[\nu(4\nu^2 - \mu^2)\right]^{\frac{1}{2}}\left\{-\frac{\lambda(4\nu^2 - \mu^2 + 4\nu\lambda)}{4(\lambda + \nu)^2 - \mu^2\,2} + \frac{1}{4(\delta + \lambda + \nu)^2 - \mu^2}\right\} \tag{2.34d}$$

$$H_{22} = -\frac{\lambda^2}{2} + \frac{4\lambda^3}{(\delta + 2\lambda)^2} \tag{2.34e}$$

$$S = 64\lambda^{\frac{3}{2}}\left[\nu(4\nu^2 - \mu^2)\right]^{\frac{1}{2}}\frac{\lambda + \nu}{\left[4(\lambda + \nu)^2 - \mu^2\right]^2} \tag{2.34f}$$

Upon optimizing the following equation, which is derived from Eq.(2.32),

$$E = \frac{H_{11} + H_{22} - 2SH_{12} \pm \sqrt{(H_{11}\ H_{22} - 2SH_{1s})^2 - 4(1 - S^2)(H_{11}\ H_{22} - H_{12}^{\ 2})}}{2(1 - S^2)} \tag{2.35}$$

The simplex method due to Nelder and Mead (1965) was used to mininize the expression (2.35) with respect to the variational parameters. The lower root corresponds to the energy eigenvalue of the SSCP. For the wave function (2.33) of the linear combination of the 1s and 2s Hulthén wave functions, the variation of energy with respect to ν associated with 2s Hulthén wave function is very insensitive. In order to ensure the global minimum of E with respect to both μ and ν, we have explored the behavious of the E in a large region of μ and ν.

2.6 Modification of the Approximate Calculation on the SSCP due to Ecker and Weizel

2.6.1 Introduction

The foregoing studies clearly show that either by perturbation method or by variational calculation fairly elaborate works were required to obtain an acceptable energy eigenvalue. However Ecker and Weizel (1956) have obtained a relatively simple expression for the energy eigenvalues of s states for any number of the principal quantum number. As the expression stands, it gives rather poor values of energy except in the weak screening case. Here we will interpret the quantity $\bar{r}$ entering in the Ecker-Weizel expression in a different way and will show that with this revised definition of $\bar{r}$, the Ecker-Weizel expression gives quite good values for the energy.

In the following sections, we will firstly outline the essential steps of the Ecker-Weizel derivation, then we will redefine the meaning of $\bar{r}$ in their expression for the energy.

2.6.2 Ecker and Weizel Approximate Expression for the s State Energy in the SSCP

The radial Schrödinger equation for s states in the SSCP is

$$\frac{1}{2}\frac{d^2\psi}{dr^2} + \left(\frac{e^{-\delta r}}{r} - E\right)\psi = 0 \tag{2.36}$$

The substitution of

$$\psi = e^{-\alpha_n r}\, v(r) \tag{2.37}$$

gives us

$$\frac{1}{2}\frac{d^2v}{dr^2} - \alpha_n \frac{dv}{dr} + \frac{e^{-\delta r}}{r} v = 0 \tag{2.38}$$

in which we have substituted

$$E_n = \frac{\alpha_n^2}{2} \tag{2.39}$$

Using the transformation

$$\delta r = -\ln(1 - x)$$

Eq.(2.38) becomes

$$\frac{\delta^2}{2}(1 - x)\frac{d^2v}{dx^2} - \beta_n \frac{\delta}{2}\frac{dv}{dx} - \frac{2}{\delta}\frac{x}{\ln(1 - x)} v = 0 \tag{2.40}$$

where

$$\beta_n = 1 + 2\frac{\alpha_n}{\delta} \tag{2.41}$$

The quantity $2x/\delta \ln(1 - x)$ is a slowly varying function in comparison with the other two terms; Ecker and Weizel (1956) assumed it to be constant to a first approximation and called it γ.

$$\gamma = \frac{2}{\delta^2} \frac{1 - e^{-\delta \bar{r}}}{\bar{r}} \tag{2.42}$$

where $\bar{r}$ represents some sort of a mean distance of the electron in the considered quantum state. With this approximation, Eq.(2.40) can be solved, and the solution of it is

$$v_n(x) = N_n \sum_{\nu=1}^{n} (-1)^{\nu-1} \binom{n-1}{\nu-1} \binom{n + \beta_n + \nu - 2}{\nu} x^{\nu} \tag{2.43}$$

The eigenvalues are given by

$$\gamma = n(\beta_n + n - 1) \tag{2.44}$$

Equation (2.44) in conjunction with the Eqs. (2.39) and (2.41) yields

$$E_n = \frac{1}{2}\left(\frac{\phi}{n} \frac{1 - e^{-\delta \bar{r}}}{\delta \bar{r}} - \frac{n\delta}{2}\right)^2 \tag{2.45}$$

This expression for the energy is valid for only such values of n for which α_n, that is the quantity inside the bracket is positive.

For small values of δ, Ecker and Weizel (1956) identified $\bar{r}$ with the expectation value of the radius, $< r >$,

$$\bar{r} = \frac{3}{2} n^2 \tag{2.46}$$

2.6.3 New Identification of $\bar{r}$

The energy eigenvalues obtained from Eq.(2.45) are rather poor if the condition (2.46) is imposed, except when δ is very small. For example, for the 1s state, at $\delta = 0.5$, Eq.(2.45) gives a value which is about 30% smaller than the correct value. Here we propose a different identification and identify $\bar{r}$ with the radius of the Bohr orbit for the quantum state in question. Thus

$$\bar{r} = n^2 \tag{2.47}$$

Our identification of $\bar{r}$ can be justified in two ways as follows:

(a) The foregoing procedure used in obtaining Eq.(2.45) is equivalent to solving the s-wave equation for the Hulthén potential (Appendix A), $V_0 e^{-\delta\bar{r}}/(1 - e^{-\delta\bar{r}})$, where V_0 is chosen such that this potential mimics $e^{-\delta\bar{r}}/r$. Because of the importance of the short range part of the potential, $\bar{r} = 1/\langle 1|r\rangle = n^2$ should be used.

(b) We may impose an asymptotic condition on Eq.(2.45) that for small values of δ, the leading correction term in δ, given by this equation, to the hydrogenic value should be identical with that obtained from the first order perturbation theory. Now for the small values of δ Eq.(2.45) can be written as

$$E_n = \frac{1}{2}\left(\frac{1}{n^2} - \delta\left(\frac{\bar{r}}{n^2} + 1\right) + O(\delta^2)\right) \tag{2.48}$$

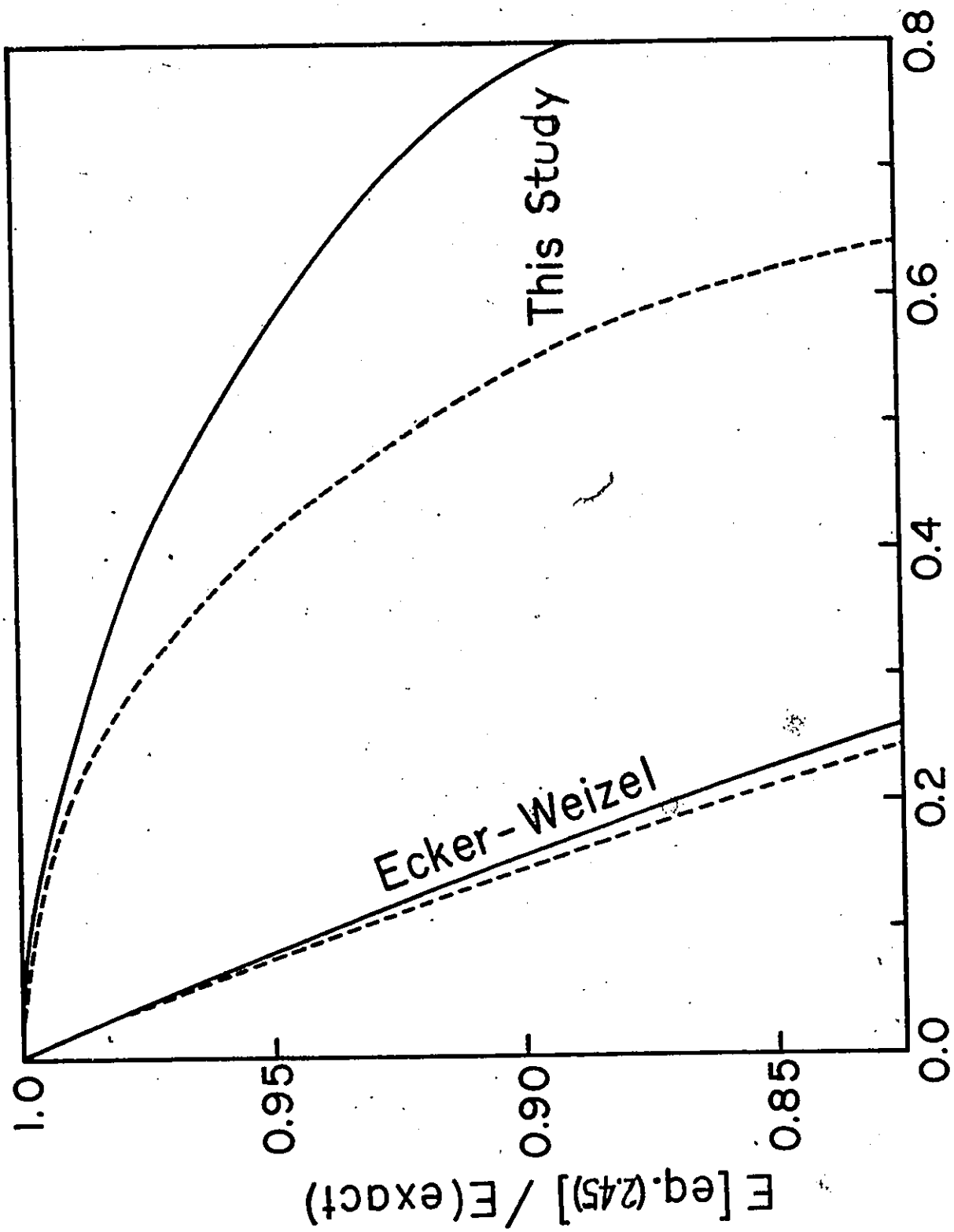

Fig. 2.2 : The ratio of the ground state energy calculated from Eq.(2.45) to the exact energy as the function of the reduced screening parameter δ/δ_c. The solid line curves are for the 1s state and the broken line ones for the 9s state.

Assuming the Coulomb potential to be the unperturbed potential, the correction to the energy obtained from the first order perturbation theory Eq.(2.6) is

$$\Delta E_n = -\delta + O(\delta^2) \tag{2.49}$$

Equating the correction terms in δ from Eqs. (2.48) and (2.49), we get Eq.(2.47).

In Fig. 2.2, we plot the results from Eq.(2.45) with two different identifications of $\bar{r}$, in which E (exact) is the energy values from Rogers et.al. (1970), and δ_c is the critical screening parameter. The solid-line curves are for the 1s state and the broken line ones for the 9s state. δ_c is equal to 1.1906 for the 1s state and 0.01567 for the 9s state. It will be noted from the Fig. 2.2 that the new identification of $\bar{r}$ gives a remarkable improvement in the energy. As an example, now, for the ground state at $\delta = 0.5$, the calculated energy is off from the exact value by only 2.7%. For the excited s states, as the value of n increases, the results obtained from Eq.(2.47) at the corresponding values of δ (i.e. the same values of δ/δ_c) tend to become poorer.

The expression (2.45) can, of course, also be used to determine the critical screening parameter. For δ_c one readily obtains the condition

$$1 - e^{-\delta_c n^2} - (\delta_c n^2)^2/2 = 0 \tag{2.50}$$

which can be solved to give

$$\delta_c n^2 = 1.176 \tag{2.51}$$

This gives δ_c = 1.176 for the ground state, which may be compared to the exact value 1.19. For excited states, a comparison of the results obtained from Eq.(2.51) with the exact results obtained by Rogers et al. (1970) shows that for these the results from Eq.(2.51) are slightly poorer than the one for the ground state.

2.7 Conclusion

Tables 2.1 - 2.6 show the results of the calculated energies of the ground state in the SSCP by various approximations. Table 2.1 actually is the calculation from the expression of the perturbation theory by Smith (1964). Table 2.2 is the results from the perturbation calculation by different approximate potentials and by different techniques. Up to five places of decimal, the four approximations give the identical results below δ = 0.06. Above this the accuracy of the calculations in the following order, F-scalar factor, Hulthén first order, Coulomb second order and the Coulomb first order. The F-scalar technique with the Coulomb potential as the approximate potential substantially improves the results from the conventional stationary perturbation theory. If one rounds off to four significant figures, the F-scalar factor technique results tally with those of Rogers et al. (1970) up to δ = 0.25. At high value of δ, the F-scalar technique results are, however, poor. For the two first order perturbation calculation, it is clear that the results from the Hulthén are better than those from the Coulomb over the whole

calculated range of δ, as anticipated. In comparison of the Hulthén first order calculation with the Coulomb second order, the latter is better than the former only in a region of $0.1 < \delta < 0.5$, and as $\delta > 0.5$, the second order results diminish with δ relatively faster in comparison with the Hulthén first order.

All ground state calculated energies by perturbation theory were carried in an IBM 360/65 in "double precision". In the stationary perturbation theory, the series was expanded to 55 terms, which is the limitation of the computer. However the high order terms do not contribute too much to the result if an accuracy of five significant figures is required.

Tables 2.3 - 2.5 show the results of variational calculation. For the one-parameter Hulthén wave function, we could accurately locate the real minimum of the energy expression by solving the equation $\frac{\partial E}{\partial \mu} = 0$. The optimized parameter μ is a monotonic increasing function of the screening parameter δ. Due to technical difficulties, we only computed the energy of a linear variation function in the region $\delta > 0.05$. For the trial function (2.33) of the linear combination of 1s and 2s Hulthén wave functions, both parameter μ associated with the 1s state Hulthén wave function and parameter ν associated with the 2s Hulthén wave function vary monotonically with the screening parameter δ. As mentioned before the parameter ν is very insensitive to the variation of E. We have examined a good number of cases in which as the value of ν increasing by a factor of 100, the energy only shows the change in the 8th or 9th places of decimal. The optimized parameters in the linear trial function (2.34) of the

two-parameter Hulthén 1s wave function and 1s hydrogen-like wave function increase with δ. Our experience on the Hulthén potential or Hulthén wave function indicates that at lower screening, due to the cancellation occurring in the logarithm terms, some significant figures may be lost in the computation. Although we have used "quadruple precision" in an IBM 370/168, this behavior may still happen when function minimization takes place as the variational parameters vary from one point to another point.

For the purpose of comparison, all ground state energies from different approximations along with the available exact values from Rogers et al.(1970) are listed in Table 2.7. Overall, the results from the variational calculation are better than those from the perturbation theory. One can find that the poorest results in the variational calculation, the Hulthén one-parameter wave function, are still better than the best results in the perturbation theory, the F-scalar technique. With an accuracy of four significant figures, the Eq.(2.34) yields the energies identical to the exact value over the whole range of δ . This is also true for all approximations when δ below 0.09, except the results from modified Ecker-Weizel approximation.

To seven places of decimal, the one-parameter Hulthén wave function (2.33) results the same values as the Eq.(2.34) does up to δ=0.1. Before our investigation on the SSCP, Harris' calculation (1962), by using three parameters from the linear combination of 1s to 3s hydrogen-like wave functions, was considered to be the best analytical values. With five figures in accuracy, the Eq.(2.23) compares very favorably with hers, and for δ up

to 0.25 both are identical. Above that her results are slightly better than the one from Eq.(2.23). In comparison with our three-parameter function of Eq.(2.34), her results only have the accuracy up to $\delta = 0.8$.

For the excited states, the Hulthén one-parameter wave functions give the results very close to the exact values. Our results here are slightly better than the Harris' three-parameter calculation in 2s state. And her calculations on 3s and 4s states by using only one parameter do not correspond the correct energy except in a very weak screening region. The energy values of an s state in SSCP from a corresponding s state hydrogen-like wave function are too deep to have practical value.

The results from the modified Ecker-Weizel calculation are still not very accurate. But it offers an alternative way to evaluate the energy values for the weak screening case and also a very rough estimate of the lower bound of the critical screening of an s state by Eq.(2.51). For the excited states it gives the upper bound of the energies.

It has been seen that the labor involved in obtaining the energy eigenvalues by the simple variation wave function (2.23) is much less than that from the linear variation wave functions. Another obvious advantage of having the wave function in a compact analytical form is that one can conveniently calculate other physical properties of the state. As an illustration, we can obtain the expectation value of the radius $< r >$ for the ground state from the Eq.(2.23). That is

$$< r > = \int \psi r \psi dr$$

$$= \frac{12 - \mu^2}{2(4 - \mu^2)} \qquad (2.52)$$

Fig. 2.3 shows the variation of $< r >$ with δ. In the vicinity of δ_c, the size of the system is seen to increase rapidly with δ. It is clear that beyond a certain value of δ the average radius would exceed one-half of the average internuclear separation. It means that the approximation of an electron bound to a single proton is no longer valid. One must take into account system of type $(S.C.)_2^+$, $(S.C.)_2$, etc.; here S.C. represents a neutral system (analogous to an H atom) in which the electron is bound in SSCP. This will be discussed in Chapter 11.

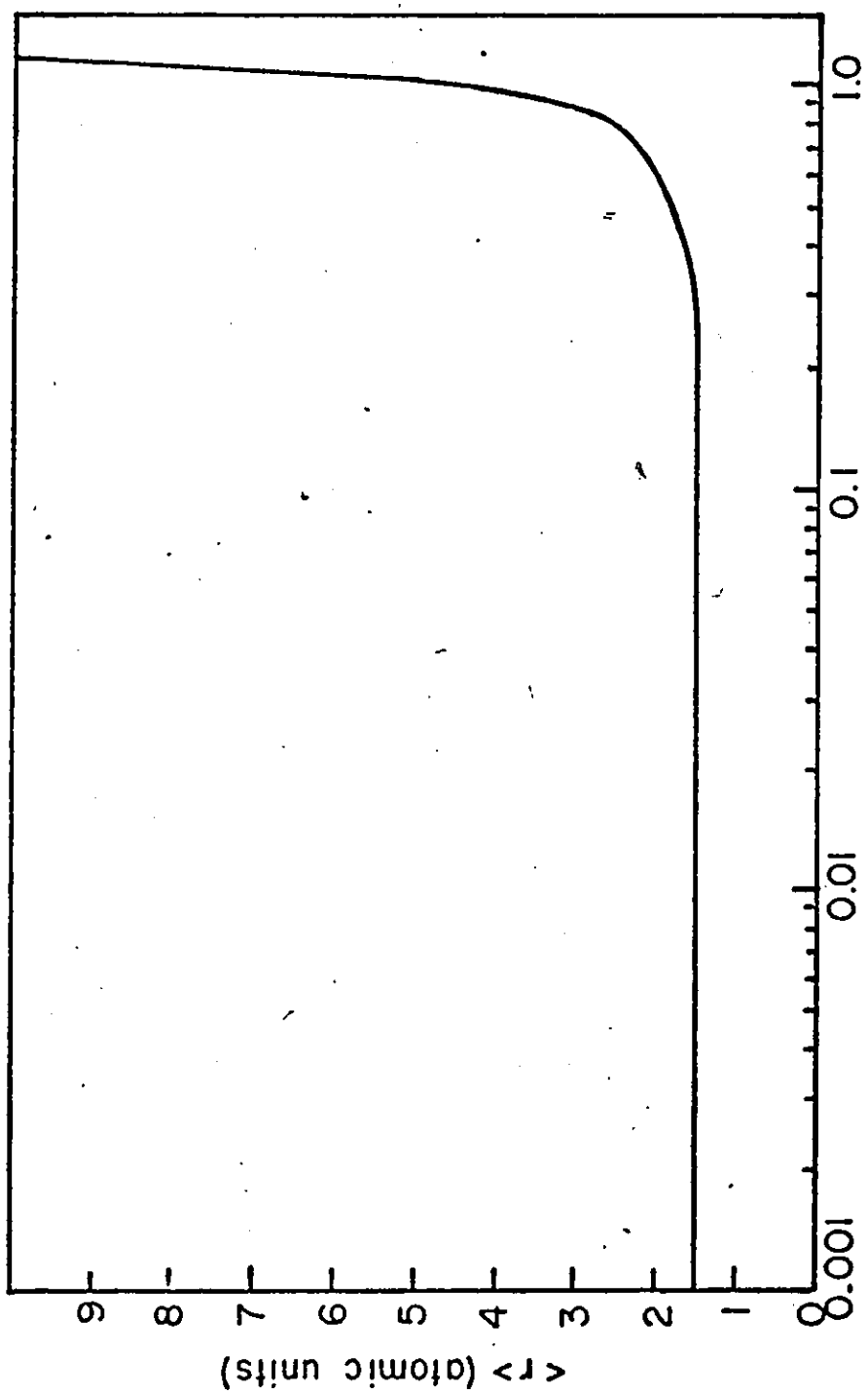

Fig. 2.3 : <r> as a function of screening parameter δ

Table 2.1 : Energies of the SSCP from perturbation calculation with Coulomb potential as an unperturbed potential

Screening parameter	Energy									
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
0.001	0.49900	0.12400	0.12400	0.05456	0.05456	0.05456	0.03026	0.03026	0.03026	0.03026
0.002	0.49800	0.12301	0.12301	0.05358	0.05358	0.05358	0.02930	0.02930	0.02929	0,02929
0.0025	0.49750	0.12252	0.12252	0.05310	0.05309	0.05309	0.02882	0.02882	0.02881	0.02881
0.003	0.49701	0.12203	0.12202	0.05262	0.05261	0.05260	0.02836	0.02835	0.02834	0.02833
0.004	0.49601	0.12105	0.12104	0.05166	0.05165	0.05164	0.02744	0.02743	0.02741	0.02739
0.005	0.49502	0.12007	0.12006	0.05072	0.05071	0.05068	0.02654	0.02653	0.02650	0.02647
0.006	0.49403	0.11911	0.11909	0.04979	0.04977	0.04974	0.02566	0.02564	0.02561	0.02556
0.007	0.49304	0.11814	0.11812	0.04887	0.04885	0.04881	0.02480	0.02478	0.02474	0.02467
0.008	0.49205	0.11719	0.11716	0.04797	0.04794	0.04788	0.02397	0.02394	0.02388	0.02380
0.009	0.49106	0.11624	0.11620	0.04708	0.04704	0.04697	0.02315	0.02311	0.02304	0.02294
0.01	0.49007	0.11529	0.11525	0.04620	0.04615	0.04606	0.02235	0.02231	0.02222	0.02209
0.02	0.48030	0.10615	0.10596	0.03800	0.03783	0.03750	0.01530	0.01515	0.01486	0.01442
0.025	0.47546	0.10177	0.10149	0.03429	0.03404	0.03353	0.01233	0.01211	0.01169	0.01105
0.03	0.47066	0.09752	0.09712	0.03080	0.03046	0.02977	0.00967	0.00938	0.00881	0.00796
0.04	0.46117	0.08938	0.08870	0.02447	0.02390	0.02277	0.00514	0.00469	0.00381	0.00252
0.05	0.45181	0.08170	0.08068	0.01888	0.01806	0.01644	0.00146	0.00085	-0.00034	-0.00209
0.06	0.44260	0.07445	0.07302	0.01393	0.01284	0.01070	-0.00155	-0.00232		
0.07	0.43351	0.06759	0.06572	0.00954	0.00817	0.00548				
0:08	0.42456	0.06111	0.05876	0.00564	0.00398	0.00074				
0.09	0.41573	0.05498	0.05211	0.00215	0.00021	-0.00358				

Table 2.1 (cont'd)

Screening parameter	Energy									
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
0.1	0.40703	0.04917	0.04575	-0.00096	-0.00320					
0.2	0.32645	0.00521	-0.00444							
0.25	0.29012	-0.00980								
0.3	0.25614									
0.4	0.19444									
0.5	0.14000									
0.6	0.09172									
0.7	0.04870									
0.8	0.01020									
0.9	-0.02438									

Table 2.1 (cont'd)

Screening parameter	Energy										
	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h
0.001	0.01902	0.01902	0.01902	0.01902	0.01901	0.01292	0.01291	0.01291	0.01291	0.01291	0.01291
0.002	0.01807	0.01807	0.01807	0.01806	0.01805	0.01199	0.01199	0.01199	0.01198	0.01197	0.01196
0.0025	0.01761	0.01761	0.01760	0.01760	0.01758	0.01155	0.01155	0.01154	0.01153	0.01152	0.01151
0.003	0.01716	0.01716	0.01715	0.01714	0.01712	0.01112	0.01111	0.01111	0.01109	0.01108	0.01106
0.004	0.01628	0.01628	0.01626	0.01624	0.01621	0.01029	0.01028	0.01027	0.01025	0.01022	0.01018
0.005	0.01544	0.01543	0.01540	0.01537	0.01533	0.00950	0.00949	0.00947	0.00944	0.00940	0.00934
0.006	0.01462	0.01461	0.01458	0.01453	0.01447	0.00875	0.00874	0.00871	0.00867	0.00861	0.00854
0.007	0.01384	0.01381	0.01377	0.01371	0.01363	0.00804	0.00803	0.00799	0.00793	0.00785	0.00776
0.008	0.01308	0.01305	0.01300	0.01292	0.01281	0.00737	0.00735	0.00730	0.00723	0.00713	0.00701
0.009	0.01235	0.01231	0.01225	0.01215	0.01202	0.00673	0.00670	0.00664	0.00655	0.00643	0.00629
0.01	0.01164	0.01160	0.01152	0.01140	0.01125	0.00612	0.00609	0.00602	0.00591	0.00577	0.00559
0.02	0.00579	0.00567	0.00542	0.00505	0.00456	0.00143	0.00133	0.00112	0.00082	0.00041	-0.00008
0.025	0.00354	0.00336	0.00302	0.00250	0.00182	-0.00020	-0.00034	-0.00062	-0.00103	-0.00157	
0.03	0.00163	0.00140	0.00095	0.00028	-0.00059						
0.04	-0.00140	-0.00173	-0.00239	-0.00334							

Table 2.1 (cont'd)

Screening parameter	Energy						
	7s	7p	7d	7f	7g	7h	7i
0.001	0.00924	0.00924	0.00924	0.00924	0.00924	0.00923	0.00923
0.002	0.00834	0.00834	0.00834	0.00833	0.00833	0.00832	0.00831
0.0025	0.00792	0.00792	0.00791	0.00790	0.00789	0.00788	0.00786
0.003	0.00751	0.00751	0.00750	0.00749	0.00747	0.00745	0.00743
0.004	0.00673	0.00673	0.00671	0.00669	0.00667	0.00663	0.00659
0.005	0.00601	0.00600	0.00598	0.00595	0.00591	0.00586	0.00580
0.006	0.00534	0.00532	0.00529	0.00525	0.00520	0.00513	0.00505
0.007	0.00471	0.00469	0.00465	0.00460	0.00453	0.00444	0.00434
0.008	0.00412	0.00410	0.00405	0.00399	0.00390	0.00379	0.00366
0.009	0.00357	0.00354	0.00349	0.00341	0.00331	0.00317	0.00302
0.01	0.00306	0.00303	0.00296	0.00287	0.00274	0.00259	0.00240
0.02	-0.00060	-0.00068	-0.00085	-0.00110	-0.00143	-0.00182	-0.00229

Table 2.1 (cont'd)

Screening parameter	Energy							
	8s	8p	8d	8f	8g	8h	8i	8k
0.001	0.00686	0.00686	0.00686	0.00686	0.00685	0.00685	0.00685	0.00685
0.002	0.00599	0.00599	0.00599	0.00598	0.00597	0.00597	0.00595	0.00594
0.0025	0.00559	0.00558	0.00558	0.00557	0.00556	0.00555	0.00553	0.00551
0.003	0.00520	0.00520	0.00519	0.00518	0.00516	0.00515	0.00512	0.00510
0.004	0.00448	0.00448	0.00446	0.00444	0.00442	0.00439	0.00435	0.00431
0.005	0.00383	0.00382	0.00380	0.00377	0.00373	0.00369	0.00363	0.00357
0.006	0.00323	0.00321	0.00319	0.00315	0.00310	0.00304	0.00296	0.00288
0.007	0.00268	0.00266	0.00263	0.00258	0.00252	0.00244	0.00234	0.00223
0.008	0.00217	0.00215	0.00211	0.00206	0.00198	0.00188	0.00176	0.00163
0.009	0.00171	0.00169	0.00164	0.00157	0.00148	0.00136	0.00122	0.00106
0.01	0.00129	0.00126	0.00121	0.00112	0.00101	0.00088	0.00072	0.00053
0.02	-0.00150	-0.00157	-0.00171	-0.00190	-0.00216	-0.00248	-0.00284	-0.00325

Table 2.1 (cont'd)

Screening parameter	Energy								
	9s	9p	9d	9f	9g	9h	9i	9k	9l
0.001	0.00523	0.00523	0.00523	0.00523	0.00523	0.00522	0.00522	0.00522	0.00521
0.002	0.00440	0.00439	0.00439	0.00439	0.00438	0.00437	0.00436	0.00435	0.00433
0.0025	0.00401	0.00401	0.00401	0.00400	0.00399	0.00397	0.00396	0.00394	0.00392
0.003	0.00365	0.00365	0.00364	0.00363	0.00362	0.00360	0.00358	0.00355	0.00353
0.004	0.00299	0.00299	0.00297	0.00296	0.00293	0.00290	0.00287	0.00283	0.00278
0.005	0.00240	0.00239	0.00238	0.00235	0.00232	0.00227	0.00222	0.00217	0.00210
0.006	0.00188	0.00186	0.00184	0.00181	0.00176	0.00170	0.00164	0.00156	0.00147
0.007	0.00140	0.00139	0.00136	0.00132	0.00126	0.00119	0.00110	0.00100	0.00089
0.008	0.00098	0.00096	0.00093	0.00087	0.00080	0.00072	0.00061	0.00049	0.00036
0.009	0.00060	0.00058	0.00054	0.00047	0.00039	0.00029	0.00017	0.00003	-0.00013
0.01	0.00026	0.00023	0.00018	0.00011	0.00002	-0.00010	-0.00024	-0.00040	
0.02	-0.00185	-0.00190	-0.00201	-0.00217	-0.00237				

Table 2.2 : Energies of 1s state of SSCP from Perturbation Calculations

Screening Parameter	1st order Hydrogen	1st order Hydrogen	F-scalar factor	1st order Hulthen	Exact
0.001	0.49900	0.49900	0.49900	0.49900	
0.002	0.49800	0.49800	0.49800	0.49800	0.4980
0.0025	0.49750	0.49750	0.49750	0.49750	
0.003	0.49701	0.49701	0.49701	0.49701	
0.004	0.49601	0.49601	0.49601	0.49601	
0.005	0.49502	0.49502	0.49502	0.49502	0.4950
0.006	0.49403	0.49403	0.49403	0.49403	
0.007	0.49304	0.49304	0.49304	0.49304	
0.008	0.49205	0.49205	0.49205	0.49205	
0.009	0.49106	0.49106	0.49106	0.49106	
0.01	0.49007	0.49007	0.49007	0.49007	0.4901
0.02	0.48030	0.48030	0.48030	0.48030	0.4803
0.025	0.47546	0.47546	0.47546	0.47546	0.4755
0.03	0.47066	0.47066	0.47066	0.47066	
0.04	0.46117	0.46117	0.46117	0.46117	
0.05	0.45182	0.45182	0.45182	0.45182	
0.06	0.44260	0.44260	0.44260	0.44260	
0.07	0.43351	0.43351	0.43352	0.43351	
0.08	0.42456	0.42456	0.42457	0.42456	
0.09	0.41573	0.41574	0.41575	0.41574	

Table 2.2 (cont'd)

Screening Parameter	1st order Hydrogen	1st order Hydrogen	F-scalar factor	1st order Hulthen	Exact
0.1	0.40703	0.40705	0.40706	0.40704	0.4071
0.2	0.32645	0.32667	0.32679	0.32658	0.3268
0.25	0.29012	0.29060	0.29086	0.29043	0.2909
0.3	0.25614	0.25700	0.25748	0.25674	
0.4	0.19444	0.19650	0.19776	0.19610	
0.5	0.14000	0.14387	0.14643	0.14358	0.1481
0.6	0.09172	0.09798	0.10242	0.09833	
0.7	0.04870	0.05787	0.06478	0.05968	
0.8	0.01020	0.02271	0.03266	0.02708	
0.9	-0.02438	-0.00821	0.00533	0.00009	
1.0			-0.01789	-0.02165	0.01029

Table 2.3 : Energies of 1s state of SSCP from one-parameter Hulthen wave function

Screening parameter	Optimized parameter	Energy	Exact
0.001	0.00494	0.4990007	
0.002	0.00570	0.4980030	0.4980
0.0025	0.00613	0.4975082	
0.003	0.00762	0.4970111	
0.004	0.00979	0.4960142	
0.005	0.01216	0.4950187	0.4950
0.006	0.01462	0.4940269	
0.007	0.01705	0.4930366	
0.008	0.01948	0.4920477	
0.009	0.02190	0.4910611	
0.01	0.02431	0.4900745	0.4901
0.02	0.04828	0.4802978	0.4803
0.025	0.06014	0.4754642	0.4755
0.03	0.07192	0.4706672	
0.04	0.09525	0.4611815	
0.05	0.11828	0.4518164	
0.06	0.14102	0.4426000	
0.07	0.16350	0.4335181	
0.08	0.18572	0.4245685	
0.09	0.20770	0.4157492	

Table 2.3 (cont'd)

Screening parameter	Optimized parameter	Energy	Exact
0.1	0.22944	0.4070580	0.4071
0.2	0.43576	0.3268078	0.3268
0.25	0.53269	0.2909176	0.2909
0.3	0.62628	0.2576341	
0.4	0.80516	0.1983616	
0.5	0.97503	-0.1480844	0.1481
0.6	1.13767	0.1060773	
0.7	1.29437	0.0717446	
0.8	1.44610	0.0445871	
0.9	1.59358	0.0241802	
1.0	1.73740	0.0101583	0.01029
1.05	1.80808	0.0054408	
1.10	1.87802	0.0022036	
1.15	1.94726	0.0004130	

Table 2.4 : Energies of 1s state of SSCP from the trial wave function Eq.(2.33)

Screening parameter	Optimized parameters μ	ν	Energy	Exact
0.05	0.11636	0.02983	0.4518164	
0.06	0.14905	0.03525	0.4426000	
0.07	0.16545	0.04076	0.4335181	
0.08	0.18773	0.04543	0.4245685	
0.09	0.21017	0.05031	0.4157492	
0.10	0.23241	0.05411	0.4070580	0.4071
0.20	0.44541	0.09107	0.3268082	0.3268
0.25	0.54685	0.08868	0.2909187	0.2909
0.30	0.63021	0.11321	0.2576375	
0.40	0.82313	0.16426	0.1983694	
0.50	1.01162	0.21532	0.1481037	0.1481
0.60	1.19338	0.26637	0.1061120	
0.70	1.39873	0.31743	0.0717984	
0.80	1.57712	0.36848	0.0446346	
0.90	1.60538	0.38541	0.0241812	
1.00	1.66625	0.39406	0.0102073	0.01029
1.05	1.75030	0.43795	0.0054924	
1.10	1.83721	0.44177	0.0022349	
1.15	1.94427	0.45185	0.0004334	

Table 2.5 : Energies of 1s state of SSCP from the trial wave function Eq.(2.34)

Screening parameter	Optimized parameters μ	ν	λ	Energy	Exact
0.05	0.11787	1.01100	1.03830	0.4518164	
0.06	0.13514	1.01333	1.04037	0.4426000	
0.07	0.15712	1.01429	1.04584	0.4335181	
0.08	0.17911	1.01524	1.05130	0.4245685	
0.09	0.20049	1.01745	1.05766	0.4157492	
0.1	0.22668	1.01998	1.06880	0.4070580	0.4071
0.2	0.47858	1.04677	1.17708	0.3268085	0.3268
0.25	0.60351	1.06197	1.23209	0.2909196	0.2909
0.3	0.71426	1.07218	1.27339	0.2576386	
0.4	0.91668	1.08592	1.34013	0.1983761	
0.5	1.10897	1.09695	1.40074	0.1481170	0.1481
0.6	1.29322	1.10598	1.45690	0.1061359	
0.7	1.47082	1.11346	1.50970	0.0718335	
0.8	1.64278	1.11972	1.55990	0.0447043	
0.9	1.80986	1.12501	1.60809	0.0243142	
1.0	1.97266	1.12951	1.65468	0.0102858	0.01029
1.05	2.05342	1.13191	1.67827	0.0055520	
1.10	2.13166	1.13336	1.70001	0.0022872	
1.15	2.20972	1.13501	1.72214	0.0004559	

Table 2.6 : s state energies of the SSCP from the modified Ecker-Weizel approximation

Screening parameter	Energy								
	1s	2s	3s	4s	5s	6s	7s	8s	9s
0.001	0.49900	0.12400	0.05456	0.03026	0.01902	0.01291	0.00924	0.00685	0.00523
0.002	0.49800	0.12301	0.05358	0.02929	0.01807	0.01198	0.00833	0.00598	0.00438
0.0025	0.49750	0.12252	0.05309	0.02882	0.01760	0.01153	0.00790	0.00557	0.00399
0.003	0.49701	0.12202	0.05261	0.02834	0.01715	0.01110	0.00749	0.00517	0.00362
0.004	0.49601	0.12104	0.05165	0.02742	0.01626	0.01026	0.00670	0.00444	0.00296
0.005	0.49502	0.12007	0.05070	0.02651	0.01540	0.00946	0.00596	0.00378	0.00237
0.006	0.49402	0.11910	0.04977	0.02562	0.01457	0.00870	0.00528	0.00318	0.00186
0.007	0.49303	0.11813	0.04884	0.02475	0.01377	0.00798	0.00465	0.00265	0.00142
0.008	0.49204	0.11717	0.04793	0.02391	0.01300	0.00730	0.00407	0.00217	0.00105
0.009	0.49105	0.11621	0.04703	0.02308	0.01226	0.00665	0.00353	0.00174	0.00074
0.01	0.49007	0.11526	0.04614	0.02227	0.01155	0.00605	0.00304	0.00137	0.00049
0.02	0.48027	0.10604	0.03783	0.01513	0.00577	0.00173	0.00022	0.00005	
0.025	0.47541	0.10162	0.03406	0.01218	0.00372	0.00061	0.00001		
0.03	0.47059	0.09731	0.03054	0.00960	0.00216	0.00007			
0.04	0.46105	0.08906	0.02418	0.00548	0.00035				
0.05	0.45164	0.08127	0.01871	0.00260	0.00006				
0.06	0.44236	0.07393	0.01404	0.00083					

Table 2.6 (cont'd)

Screening parameter	Energy 1s	2s	3s	4s	5s	6s	7s	8s	9s
0.07	0.43320	0.06701	0.01013	0.00005					
0.08	0.42416	0.06051	0.00692						
0.09	0.41525	0.05442	0.00437						
0.1	0.40646	0.04870	0.00244						
0.25	0.32510	0.01039							
0.4	0.28865	0.00218							
0.5	0.25485	0.00004							
0.4	0.19481								
0.5	0.14415								
0.6	0.10214								
0.7	0.06814								
0.8	0.04157								
0.9	0.02192								
1.0	0.00873								
1.05	0.00443								
1.10	0.00160								
1.15	0.00018								

Table 2.7 : Energies of 1s state of SSCP from various approximations

Screening Parameter	Perturbation Calculations: 1st order Hydrogen	2nd order Hydrogen	F-scalar factor	1st order Hulthen	Variational Calculations: one param Hulthen	1s Hulthen +2s Hulthen	1s Hydrogen +1s Hulthen	Ecker and Weizel	Exact
0.001	0.49900	0.49900	0.49900	0.49900	0.4990007			0.49900	
0.002	0.49800	0.49800	0.49800	0.49800	0.4980030			0.49800	0.4980
0.0025	0.49750	0.49750	0.49750	0.49750	0.4975082			0.49750	
0.003	0.49701	0.49701	0.49701	0.49701	0.4970111			0.49701	
0.004	0.49601	0.49601	0.49601	0.49601	0.4960142			0.49601	
0.005	0.49502	0.49502	0.49502	0.49502	0.4950187			0.49502	0.4950
0.006	0.49403	0.49403	0.49403	0.49403	0.4940269			0.49402	
0.007	0.49304	0.49304	0.49304	0.49304	0.4930366			0.49303	
0.008	0.49205	0.49205	0.49205	0.49205	0.4920477			0.49204	
0.009	0.49106	0.49106	0.49106	0.49106	0.4910611			0.49105	
0.01	0.49007	0.49007	0.49007	0.49007	0.4900745			0.49007	0.4901
0.02	0.48030	0.48030	0.48030	0.48030	0.4802978			0.48027	0.4803
0.025	0.47546	0.47546	0.47546	0.47546	0.4754642			0.47541	0.4755
0.03	0.47066	0.47066	0.47066	0.47066	0.4706672			0.47059	
0.04	0.46117	0.46117	0.46117	0.46117	0.4611815			0.46105	
0.05	0.45182	0.45182	0.45182	0.45182	0.4518164	0.4518164	0.4518164	0.45164	
0.06	0.44260	0.44260	0.44260	0.44260	0.4426000	0.4426000	0.4426000	0.44236	

Table 2.7 (cont'd)

Screening Parameter	Perturbation Calculations: 1st order Hydrogen	2nd order Hydrogen	F-scalar factor	1st order Hulthen	Variational Calculations: one param Hulthen	1s Hulthen +2s Hulthen	1s Hydrogen +1s Hulthen	Ecker and Weizel	Exact
0.07	0.43351	0.43351	0.43352	0.43351	0.4335181	0.4335181	0.4335181	0.43320	
0.08	0.42456	0.42456	0.42457	0.42456	0.4245685	0.4245685	0.4245685	0.42416	
0.09	0.41573	0.41574	0.41575	0.41574	0.4157492	0.4157492	0.4157492	0.41525	
0.1	0.40703	0.40705	0.40706	0.40704	0.4070580	0.4070580	0.4070580	0.40646	0.4071
0.2	0.32645	0.32667	0.32679	0.32658	0.3268078	0.3268082	0.3268085	0.32510	0.3268
0.25	0.29012	0.29060	0.29086	0.29043	0.2909176	0.2909187	0.2909196	0.28865	0.2909
0.3	0.25614	0.25700	0.25748	0.25674	0.2576341	0.2576375	0.2576386	0.25485	
0.4	0.19444	0.19650	0.19776	0.19610	0.1983616	0.1983694	0.1983761	0.19481	
0.5	0.14000	0.14387	0.14643	0.14358	0.1480844	0.1481037	0.1481170	0.14415	0.1481
0.6	0.09172	0.09798	0.10242	0.09833	0.1060773	0.1061120	0.1061359	0.10214	
0.7	0.04870	0.05787	0.06478	0.05968	0.0717446	0.0717984	0.0718335	0.06814	
0.8	0.01020	0.02271	0.03266	0.02708	0.0445871	0.0446346	0.0447043	0.04157	
0.9	-0.02438	-0.00821	0.00533	0.00009	0.0241802	0.0241812	0.0243142	0.02192	
1.0			-0.01789	-0.02165	0.0101583	0.0102073	0.0102858	0.00873	0.01029
1.05					0.0054[illegible]8	0.0054924	0.0055520	0.00443	
1.10					0.0022036	0.0022349	0.0022872	0.00160	
1.15					0.0004130	0.0004334	0.0004559	0.00018	

Table 2.8 : Energies of 2s - 4s states of the SSCP from perturbation calculation with Hulthen potential as an unperturbed potential

Screening parameter	Energy		
	2s	3s	4s
0.001	0.12400	0.05456	0.03026
0.002	0.12301	0.05358	0.02930
0.0025	0.12252	0.05310	0.02882
0.005	0.12007	0.05072	0.02654
0.01	0.11529	0.04620	0.02235
0.02	0.10615	0.03801	0.01533
0.025	0.10177	0.03430	0.01240
0.03	0.09753	0.03084	0.00980
0.04	0.08940	0.02456	0.00550
0.05	0.08173	0.01907	0.00223
0.06	0.07450	0.01430	-0.00015
0.07	0.06768	0.01017	
0.08	0.06125	0.00663	
0.09	0.05519	0.00361	
0.10	0.04948	0.00109	
0.20	0.00852		
0.25	-0.00306		

Table 2.9 : Energies of 2s state of the SSCP from Variational calculation

Screening parameter	Optimized parameter	Energy	Exact
0.001	0.0100	0.12400	
0.002	0.0100	0.12301	0.1230
0.005	0.0121	0.12007	0.1201
0.01	0.0240	0.11529	0.1153
0.02	0.0468	0.10615	0.1062
0.025	0.0579	0.10178	0.1018
0.03	0.0688	0.09753	
0.04	0.0900	0.08941	
0.05	0.1105	0.08177	0.08175
0.06	0.1304	0.07458	
0.07	0.1496	0.06782	
0.08	0.1684	0.06146	
0.09	0.1866	0.05551	
0.10	0.2044	0.04993	0.04993
0.20	0.3613	0.01208	0.01211
0.25	0.4283	0.00336	0.00339
0.30	0.4893	0.00008	

Table 2.10 : Energies of 3s state of the SSCP from variational calculation

Screening parameter	optimized parameter	Energy	Exact
0.001	0.0151	0.05456	
0.002	0.0151	0.05358	0.0536
0.005	0.0151	0.05072	0.0507
0.01	0.0234	0.04620	0.04620
0.02	0.0448	0.03802	0.03802
0.025	0.0549	0.03433	0.03433
0.03	0.0647	0.03089	
0.04	0.0834	0.02469	
0.05	0.1011	0.01935	0.01935
0.06	0.1178	0.01479	
0.07	0.1336	0.01095	
0.08	0.1486	0.00777	
0.09	0.1628	0.00520	
0.10	0.1763	0.00320	0.00321
0.11	0.1892	0.00172	
0.12	0.2012	0.00072	
0.13	0.2125	0.00016	

Table 2.11 : Energies of 4s state of the SSCP from variational calculation

Screening parameter	optimized parameter	Energy	Exact
0.001	0.0171	0.03026	0.03026
0.002	0.0171	0.02930	0.02930
0.0025	0.0171	0.02882	0.02883
0.005	0.0181	0.02654	0.02654
0.01	0.0231	0.02236	0.02236
0.02	0.0424	0.01538	0.01538
0.025	0.0515	0.01250	0.01251
0.03	0.0602	0.00999	
0.04	0.0763	0.00596	
0.05	0.0909	0.00309	0.00309
0.06	0.1041	0.00124	
0.07	0.1159	0.00025	

Chapter 3 - Lower Bounds of Variational Calculation

3.1 Introduction

In the variational calculation, the energy eigenvalue obtained is only an upper bound to the true value of the ground state energy. Methods for obtaining the lower bound of the ground state have been developed by a number of authors, and the three best known ones are due to Weinstein (1934), Temple (1929) and Stevenson-Crawford (1938a, 1938b). Weinstein bound is less practical because it yields the energy too deep to be of use. Kato (1949) states that Temple bound is the best of its type; and contradiction to this statement Walmsley (1967) proves that Stevenson-Crawford bound is better than the Temple bound. Only a few numerical tests of these formulas have been reported. This fact can be attributed to the difficulty associated with the calculation of the integral $< HH >$.

The variational wave function of Eq.(2.34) proposed for the ground state in the static screened Coulomb potential (SSCP) produces energy eigenvalues identical to those of the Rogers et al. (1970), who carried out the calculation by numerical integration of the Schrödinger equation, over the same range of screening parameters quoted in their work. The purpose of present study is to test the applicability and usefulness of the three lower bound formulas of the variational calculation by means of this wave function.

3.2 Calculation

The lower bound formulas of the variational calculation due to Weinstein (1934), Temple (1929) and Stevenson-Crawford (1938a, 1938b) have respectively the following forms:

$$E_W = \langle H \rangle + (\langle HH \rangle - \langle H \rangle^2)^{\frac{1}{2}} \tag{3.1}$$

$$E_T = \langle H \rangle - \frac{\langle HH \rangle - \langle H \rangle^2}{E_2 - \langle H \rangle} \tag{3.2}$$

and

$$E_S = \alpha + (\alpha^2 - 2\alpha\langle H \rangle + \langle HH \rangle)^{\frac{1}{2}} \tag{3.3}$$

where $\langle H \rangle = \int \psi H \psi dt$

$\langle HH \rangle = \int (H\psi)^2 \, dt$

and α is any parameter such that $\alpha \leq \frac{1}{2}(E_1 + E_2)$. Here E_1 and E_2 are respectively the exact energies of the ground state and the first excited state of the same symmetry. The best choice of α is that $\alpha = \frac{1}{2}(E_1 + E_2)$. If the wave function has the form of Eq.(2.31), that is

$$\psi = \phi_1 + a\phi_2$$

where

$$\phi_1 = \frac{1}{\mu} \left[\nu(4\nu^2 - \mu^2)\right]^{\frac{1}{2}} \left[e^{-(\nu - \frac{\mu}{2})r} - e^{-(\nu + \frac{\mu}{2})r}\right]$$

$$\phi_2 = 2\lambda^{\frac{3}{2}} r \, e^{-\lambda r}$$

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<H> has been shown in the Eq.(2.35) and <HH> will take the following form

$$\langle HH\rangle = \frac{\left(\langle HH\rangle_{11} + 2a\langle HH\rangle_{12} + a^2\langle HH\rangle_{22} \right)}{1 + a^2 + 2aS}$$

in which

$$S = \int \phi_1 \phi_2 dt$$

$$= 64\lambda^{\frac{3}{2}} \left[\nu(4\nu^2 - \mu^2)\right]^{\frac{1}{2}} \frac{\lambda + \nu}{\left[4(\lambda + \nu)^2 - \mu^2\right]^2}$$

$$\langle HH\rangle_{11} = \int (H\phi_1)^2 \, dt$$

$$= \frac{\nu}{\mu^2}(4\nu^2 - \mu^2)\left\{\frac{1}{64}\left[(2\nu - \mu)^3 - \frac{(4\nu^2 - \mu^2)^2}{\nu} + (2\nu + \mu)^3\right]\right.$$

$$+ \frac{1}{4}\left[(2\nu - \mu)^2 \ell n \frac{\delta + 2\nu}{\delta + 2\nu - \mu} - (2\nu + \mu)^2 \ell n \frac{\delta + 2\nu + \mu}{\delta + 2\nu}\right]$$

$$+ (2\delta + 2\nu - \mu) \ell n(2\delta + 2\nu - \mu) - 4(\delta + \nu) \ell n(2\delta + 2\nu)$$

$$\left. + (2\delta + 2\nu + \mu) \ell n(2\delta + 2\nu + \mu)\right\}$$

$$\langle HH\rangle_{12} = \int (H\psi_1)(H\psi_2) \, dt$$

$$= \frac{\lambda^{\frac{3}{2}}}{\mu}\left[\nu(4\nu^2 - \mu^2)\right]^{\frac{1}{2}} \left\{ - \frac{\lambda}{2}\left[\frac{(2\nu - \mu)^2}{2\lambda + 2\nu - \mu} - \frac{(2\nu + \mu)^2}{2\lambda + \nu + \mu}\right]\right.$$

$$\frac{\lambda^2}{2}\left[\frac{(2\nu - \mu)^2}{(2\lambda + 2\nu - \mu)^2} - \frac{(2\nu + \mu)^2}{(2\lambda + 2\nu + \mu)^2}\right]$$

$$- 2\lambda \ell n \frac{2\delta + 2\lambda + 2\nu + \mu}{2\delta + 2\lambda + 2\nu - \mu} + 2 \ell n \frac{4\delta + 2\lambda + 2\nu + \mu}{4\delta + 2\lambda + 2\nu - \mu}$$

$$+ 2\lambda^2\left[\frac{1}{2\delta + 2\lambda + 2\nu - \mu} - \frac{1}{2\delta + 2\lambda + 2\nu + \mu}\right]$$

$$\left. + \frac{1}{2}\left[\frac{(2\nu - \mu)^2}{2\delta + 2\lambda + 2\nu - \mu} - \frac{(2\nu + \mu)^2}{2\delta + 2\lambda + 2\nu + \mu}\right]\right\}$$

and

$$\langle HH\rangle_{22} = \int (H\phi_2)^2 \, dt$$

$$= \lambda^3 \left[\frac{5}{4}\lambda - \frac{4\lambda(2\delta + 3\lambda)}{(\delta + 2\lambda)^2} + \frac{2}{\delta + \lambda} \right]$$

The ground state energy lower bounds are obtained by substituting the optimized parameters a, μ, ν and λ corresponding to the minimum $\langle H\rangle$ into the respective lower bound formulas (3.1) to (3.3). Table 3.1 shows the results. For E_1 and E_2 we have used the values by Rogers et al. (1970). In some cases interpolated values were used, interpolation being made for difference [E(Rogers) - E(variational)]. Lower bound of E_2, i.e. $E_2 = 0$, was used when the bound state of the excited state does not exist.

3.3 Conclusion

If one only considers the values of energy lower bounds, the Weinstein bound is the lowest over the complete calculated range of screening parameter δ, except when δ is close to the critical screening, and the Temple bound and the Stevenson-Crawford bounds are identical to six places of decimal up to $\delta = 0.8$ and above it the Temple bound is slightly higher than the Stevenson-Crawford bound. It is therefore in agreement with the Walmsley's statement that the Weinstein formula is the worst and the Stevenson-Crawford formula is the best among the three.

We have confirmed that for $\delta \leq 1$, the energy obtained by the wave function (2.31) has at least four figures accuracy. For $\delta > 1$, it appears reasonable to estimate that they are correct to at least three significant figures at $\delta = 1.05$ and $\delta = 1.10$, at least two significant figures for $\delta = 1.15$. A satisfactory lower bound formula should help us to "bracket" the energy in the next or higher significant figures. With this criterion in mind we find that the Weinstein formula is not very helpful. At lower values of δ, it does help to bracket the energy in the fifth significant figure but there is an increasing divergence between $\langle H \rangle$ and E_W with δ, and at high value of δ the Weinstein lower bound is of little practical value.

Both the Temple and Stevenson-Crawford formulas help us to estimate energy eigenvalues to an accuracy, at least, 4×10^{-5} below $\delta = 0.7$, if we consider the results of Rogers et al. (1970) as the true ground state energies of the SSCP. The slightly increasing discrepancy between <H> and E_T or E_S with δ is mainly caused by the approximate values of E_2 in these two formulas. It is suggested here that when both the values of E_1 and E_2 are available, the lower bound formula of either Temple or Stevenson-Crawford is very helpful to estimate the accuracy of the ground state energy of a variational calculation.

Table 3.1 : Lower bounds to the ground state energy from the formulas of Weinstein, Temple and Stevenson-Crawford

Screening parameter	Energy Eq.(2.34)	Lower Bounds Weinstein	Temple	Stevenson
0.05	0.4518164	0.4518164	0.4518164	0.4518164
0.06	0.4426000	0.4426031	0.4426000	0.4426000
0.07	0.4335181	0.4335206	0.4335181	0.4335181
0.08	0.4245685	0.4245752	0.4245685	0.4245685
0.09	0.4157492	0.4157591	0.4157492	0.4157492
0.10	0.4070580	0.4070704	0.4070580	0.4070580
0.20	0.3268085	0.3268572	0.3268085	0.3268085
0.25	0.2909196	0.2909644	0.2909196	0.2909196
0.30	0.2576386	0.2576975	0.2576386	0.2576386
0.40	0.1983761	0.1985238	0.1983762	0.1983762
0.50	0.1481170	0.1484004	0.1481176	0.1481176
0.60	0.1061359	0.1065936	0.1061379	0.1061379
0.70	0.0718335	0.0724860	0.0718395	0.0718395
0.80	0.0447043	0.0455442	0.0447201	0.0447201
0.90	0.0243142	0.0253048	0.0243546	0.0243545
1.00	0.0102858	0.0113347	0.0103928	0.0103917
1.05	0.0055520	0.0065555	0.0057334	0.0057278
1.10	0.0022872	0.0031975	0.0026495	0.0026052
1.15	0.0004559	0.0011361	0.0014709	0.0009454

Chapter 4 - Bound Eigenstates of the Exponential Cosine Screened Coulomb Potential

4.1 Introduction

The potential

$$V(r) = -\frac{e^2}{kr} e^{-\alpha r} \cos(\alpha r) \qquad (4.1)$$

where k is the dielectric constant and α is a screened parameter, is of importance in solid state physics. In a metal when the energy due to plasma oscillation is greater than four times its Fermi energy, Bonch-Bruevich and Glasko (1958, 1959), Hall (1962), McIrvine (1960) and Takimoto (1959) described it as the potential between an electron and an ionized impurity. When $r \ll 1/k_o$ where $k_o = (2m^* kT)^{\frac{1}{2}}/\hbar$ for the non-degenerate case and $k_o = (3\pi^2 n)^{1/3}$ in the fully degenerate case, Bonch-Bruevich and Kogan (1960) and Bonch-Bruevich and Tyablikov (1962) used it to represent the ionized impurity-electron potential in a semi-conductor. Prokop'ev (1967) used it to describe the electron-positron interaction in a positronium atom in a solid. The potential in this study is called the Exponential Cosine Screened Coulomb (ECSC) potential.

At the time we carried out the study of this potential, the only investigation on the bound state was due to Bonch-Bruevich and Glasko (1958, 1959), who had determined a few eigenvalues for the 1s state in the high screening region by numerical method and had also determined the critical screening parameter.

In this study, we have carried out a perturbation calculation with the Coulomb potential as an unperturbed potential. This calculation enables us to investigate several properties of the ECSC potential, such as energy variation with the screening parameter for many states, critical screening parameters for these states, number of bound states, etc. For s states, we used the Hulthén wave functions as the basis set and carried out the calculation by virtue of perturbation theory and variational method. To determine the critical screening parameter of the ground state, we employed a variational calculation by using two-parameter Hulthen wave function as a trial function. Some fine points about the ECSC potential are discussed in the last section.

In this chapter we use atomic units, where the unit of length is $a_0 = \hbar^2/m^*e^2$ and the unit of energy is equal to $-m^*e^4/\kappa^2\hbar^2$. Here m^* is the effective mass and $\delta = qa_0$. In these units the ECSC potential (4.1) can be written as

$$V(r) = \frac{e^{-\delta r}}{r} \cos(\delta r) \qquad (4.2)$$

4.2 Perturbation Calculation with the Coulomb Potential as an Unperturbed Potential

As a first approximation, we take the Coulomb potential as the unperturbed potential. Then the perturbation U(r) is given be

$$U(r) = \frac{e^{-\delta r}}{r} \cos \delta r - \frac{1}{r} \tag{4.3}$$

The unperturbed wave function has the form

$$\Psi_{n\ell}(r) = \frac{2^{\ell+1}}{n^{\ell+2}} \left[\frac{(n+\ell)!}{(n-\ell-1)!}\right]^{1/2} \frac{1}{(2\ell+1)!} e^{-\frac{r}{n}} r^{\ell+1} {}_1F_1(-n+\ell+1,\ 2\ell+2;\ \frac{2r}{n})$$

where ${}_1F_1$ is the confluent hypergeometric function. And the corresponding unperturbed energy is

$$E_n^{(o)} = \frac{1}{2n^2} \tag{4.4}$$

The first order energy shift is

$$\Delta E_{n\ell} = \langle \Psi_{n\ell}(r) | U(r) | \Psi_{n\ell}(r) \rangle$$

$$= \frac{2^{2\ell+2}}{n^{2\ell+4}} \frac{(n+\ell)!}{(n-\ell-1)!} \frac{1}{(2\ell+1)!} \frac{\delta^{2n-2\ell-2}}{\left(\frac{4}{n^2} + \frac{4\delta}{n} + 2\delta^2\right)^{2n}}$$

$$\times \mathrm{Re}\left[(1-i)^{2n-2\ell-2} \left(\frac{2}{n} + \delta + i\delta\right)^{2n} \times {}_2F_1\left(-n+\ell+1,\ -n+\ell+1;\ 2\ell+2;\ \frac{2i}{n^2\delta^2}\right)\right]$$

$$- \frac{1}{n^2} \tag{4.5}$$

where Re[ ] means the real part of the complex number in the square bracket and ${}_2F_1$ is the hypergeometric function.

The energy eigenvalues $E_{n\ell}$ is the sum of Eqs. (4.4) and (4.5).

The calculated values of energies for the 1s, 2s, 3s, and 4s states, obtained on an IBM 360/65 in "double precision" are shown in Tables 4.1 - 4.4. Results for some further states are presented in Table 4.7.

4.3 Perturbation Calculation with the Hulthén Potential as an Unperturbed Potential

For small values of δr the behaviour of the Hulthén potential (Appendix A)

$$V(r) = \frac{\delta e^{-\delta r}}{1 - e^{-\delta r}} \tag{4.6}$$

is quite similar to that of the ECSC potential. For s states ($\ell = 0$), the Schrödinger equation is analytically solvable for the potential (4.6). The eigenvalue is given by

$$E_n^{(o)} = \frac{1}{8}\left(\frac{2}{n} - n\delta\right)^2 \tag{4.7}$$

and the normalized eigenfunction is

$$\psi_n(r) = \frac{n}{4}\left(\frac{4}{n^2} - n^2\delta^2\right)^{\frac{1}{2}} e^{-\frac{1}{2}\left(\frac{2}{n} - n\delta\right)r} \sum_{k=1}^{n} C_k (1 - e^{-\delta r})^k \tag{4.8}$$

where

$$C_k = (-1)^{k-1} \binom{n-1}{k-1} \binom{k + \frac{2}{n\delta} - 1}{k}$$

In Fig. 4.1, we show the ECSC, the Hulthén and the Coulomb potentials. It will be noticed that the choice of the Hulthén potential as the unperturbed potential is a better one than that of a Coulomb potential for the same.

The perturbation U(r) can be then written as

$$U(r) = \frac{1}{r} e^{-\delta r} \cos \delta r - \frac{\delta e^{-\delta r}}{1 - e^{-\delta r}} \tag{4.9}$$

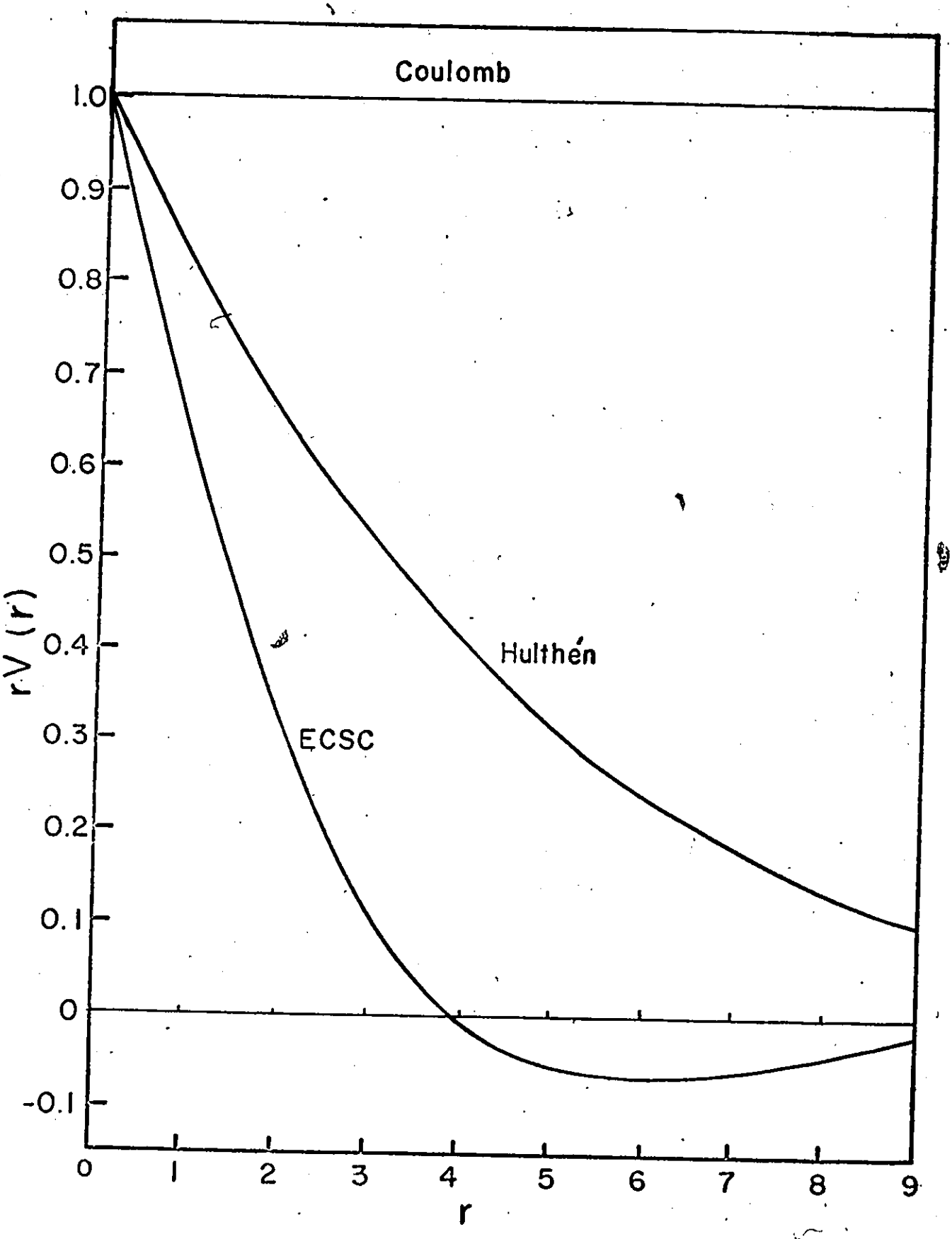

Fig. 4.1 : The product rV(r) as function of r, for the Coulomb potential, the Hulthén potential and the ECSC potential for $\delta = 0.4$

In the following we will only show the calculation for the 1s-4s states. However this calculation can be extended to any s states. The wave functions of the 1s-4s states are of the forms of Eqs. (2.17a) - (2.17d). The first order perturbation energy can be obtained by substituting Ψ_n in the following equation.

$$\Delta E_n^{(1)} = \langle \Psi_n \mid U(r) \mid \Psi_n \rangle$$

$$= \langle \Psi_n \mid \frac{e^{-\delta r}}{r} \cos(\delta r) \mid \Psi_n \rangle - \langle \Psi_n \mid \frac{\delta e^{-\delta r}}{1 - e^{-\delta r}} \mid \Psi_n \rangle$$

The complexity of calculation increases as the principal quantum number n increases. But all integrals involved can be analytically solved. Following are the results of the energy expressions for the 1s-4s states.

$$E_{1s} = -\frac{1}{8}(4 - \delta^2) + \frac{4 - \delta^2}{2\delta^2}\left[-\ell n(\delta^2 + 4) + 2\ell n(2\delta^2 + 4\delta + 4) - \ell n(5\delta^2 + 8\delta + 4)\right] \qquad (4.10)$$

$$E_{2s} = -\frac{1}{8}(1 - 4\delta^2) + \frac{1 - 4\delta^2}{16\delta^4}\left[-(1-\delta)^2 \ell n(2\delta^2 - 2\delta + 1) + 4(1-\delta)\ell n(\delta^2 + 1) - 2(3 - \delta^2)\ell n(2\delta^2 + 2\delta + 1) + 4(1+\delta)\ell n(5\delta^2 + 4\delta + 1) - (1 + \delta)^2 \ell n(10\delta^2 + 6\delta + 1)\right]$$

$$(\delta \gtrsim 1) \qquad (4.11)$$

$$E_{3s} = -\frac{1}{72}(4 - 81\delta^2)$$

$$+ \frac{4-81\delta^2}{39366\delta^6}\Big[-(1 - 3\delta)^2 (2 - 3\delta)^2 \ln (45\delta^2 - 24\delta + 4)$$

$$+ 6(1 - 3\delta) (2 - 3\delta)^2 \ln (18\delta^2 - 12\delta + 4)$$

$$- 3(2 - 3\delta) (10 - 15\delta - 18\delta^2) \ln (9\delta^2 + 4)$$

$$+ 2(4 - 9\delta^2) (2 - 9\delta^2) \ln (18\delta^2 + 12\delta + 4)$$

$$- 3(2 + 3\delta) (10 + 15\delta - 18\delta^2) \ln (45\delta^2 + 24\delta + 4)$$

$$+ 6(1 + 3\delta) (2 + 3\delta)^2 \ln (90\delta^2 + 36\delta + 4)$$

$$- (1 + 3\delta)^2 (2 + 3\delta)^2 \ln (153\delta^2 + 48\delta + 4)\Big].$$

$$(\delta \leq \tfrac{1}{3}) \qquad (4.12)$$

$$E_{4s} = -\frac{1}{32}(1 - 64\delta^2)$$

$$+ \frac{1-64\delta^2}{1179648\delta^8}\Big[-(1 - 2\delta)^2 (1 - 4\delta)^2 (1 - 6\delta)^2 \ln (40\delta^2 - 12\delta + 1)$$

$$+ 8(1 - 2\delta)^2 (1 - 4\delta)^2 (1 - 6\delta) \ln (20\delta^2 - 8\delta + 1)$$

$$- 4(1 - 2\delta)^2 (1 - 4\delta) (7 - 28\delta - 36\delta^2) \ln (8\delta^2 - 4\delta + 1)$$

$$+ 8(1 - 4\delta) (1 - 4\delta^2) (7 - 14\delta - 24\delta^2) \ln (4\delta^2 + 1)$$

$$- 2(1 - 4\delta^2) (35 - 380\delta^2 + 576\delta^4) \ln (8\delta^2 + 4\delta + 1)$$

$$+ 8(1 + 4\delta) (1 - 4\delta^2) (7 + 14\delta - 24\delta^2) \ln (20\delta^2 + 8\delta + 1)$$

$$- 4(1 + 2\delta)^2 (1 + 4\delta) (7 + 28\delta - 36\delta^2) \ln (40\delta^2 + 12\delta + 1)$$

$$+ 8(1 + 2\delta)^2 (1 + 4\delta)^2 (1 + 6\delta) \ln (68\delta^2 + 16\delta + 1)$$

$$- (1 + 2\delta)^2 (1 + 4\delta)^2 (1 + 6\delta)^2 \ln (104\delta^2 + 20\delta + 1)\Big]$$

$$(\delta \leq \tfrac{1}{6}) \qquad (4.13)$$

The calculated energy values from the above expressions are shown in Tables 4.1 - 4.4. We may note here that when δ is small there are large cancellations between the terms occurring in Eqs. (4.10) - (4.13), and a 16-significant-figure accuracy is not adequate. Most of the recorded results were obtained on an IBM 370/168 in "quadruple precision" (32-figure accuracy).

4.4 Variational Calculation with One Parameter Hulthén type Wave Function as a Trial Function

The similarity in the behavior of the ECSC and the Hulthén potentials for small values of δr suggested that it would be appropriate to employ Hulthén type wave functions for a variational calculation. The trial wave functions for the 1s to 4s states are chosen by replacing δ with μ, a variational parameter. They have the exactly the same form as those used for the SSCP, i.e. Eqs. (2.23) - (2.26). By substituting these equations into

$$E_n = \langle \Psi_n \mid \frac{1}{2}\frac{d^2}{dr^2} \mid \Psi_n \rangle + \langle \Psi_n \mid \frac{e^{-\delta r}}{r} \cos(\delta r) \mid \Psi_n \rangle$$

we have the energy expressions of 1s to 4s states:

$$E_{1s} = \frac{1}{2\mu^2}(4 - \mu^2)\left\{-\frac{\mu^2}{4} - \ell n\left[\delta^2 + (2 + \delta - \mu)^2\right] + 2\,\ell n\left[\delta^2 + (2 + \delta)^2\right] - \ell n\left[\delta^2 + (2 + \delta + \mu)^2\right]\right\} \qquad (\mu < 2 + \delta) \qquad (4.14)$$

$$E_{2s} = \frac{1}{16\mu^4}(1 - 4\mu^2)\left\{-2\mu^4 - (1 - \mu)^2\,\ell n\left[\delta^2 + (1 + \delta - 2\mu)^2\right] + 4(1 - \mu)\,\ell n\left[\delta^2 + (1 + \delta - \mu)^2\right] - 2(3 - \mu^2)\,\ell n\left[\delta^2 + (1 + \delta)^2\right] + 4(1 + \mu)\,\ell n\left[\delta^2 + (1 + \delta + \mu)^2\right] - (1 + \mu)^2\,\ell n\left[\delta^2 + (1 + \delta + 2\mu)^2\right]\right\}$$

$$(2\mu < 1 + \delta) \qquad (4.15)$$

$$E_{3s} = \frac{1}{39366\mu^6}(4 - 81\mu^2) \times \Big\{ -\frac{2187}{4}\mu^6$$
$$- (1 - 3\mu)^2 (2 - 3\mu)^2 \ln [9\delta^2 + (2 + 3\delta - 9\mu)^2]$$
$$+ 6(1 - 3\mu) (2 - 3\mu)^2 \ln [9\delta^2 + (2 + 3\delta - 6\mu)^2]$$
$$- 3(2 - 3\mu) (10 - 15\mu - 18\mu^2) \ln [9\delta^2 + (2 + 3\delta - 3\mu)^2]$$
$$+ 2(4 - 9\mu^2) (10 - 9\mu^2) \ln [9\delta^2 + (2 + 3\delta)^2]$$
$$- 3(2 + 3\mu) (10 + 15\mu - 18\mu^2) \ln [9\delta^2 + (2 + 3\delta + 3\mu)^2]$$
$$+ 6(1 + 3\mu) (2 + 3\mu)^2 \ln [9\delta^2 + (2 + 3\delta + 6\mu)^2]$$
$$- (1 + 3\mu)^2 (2 + 3\mu)^2 \ln [9\delta^2 + (2 + 3\delta + 9\mu)^2] \Big\}$$

$(9\mu < 2 + 3\delta)$ (4.16)

$$E_{4s} = \frac{1}{1179648\mu^8}(1 - 64\mu^2) \times \Big\{ - 36864\mu^8$$
$$- (1 - 2\mu)^2 (1 - 4\mu)^2 (1 - 6\mu)^2 \ln [4\delta^2 + (1 + 2\delta - 8\mu)^2]$$
$$+ 8(1 - 2\mu)^2 (1 - 4\mu)^2 (1 - 6\mu) \ln [4\delta^2 + (1 + 2\delta - 6\mu)^2]$$
$$- 4(1 - 2\mu)^2 (1 - 4\mu) (7 - 28\mu - 36\mu^2) \ln [4\delta^2 + (1 + 2\delta - 4\mu)^2]$$
$$+ 8(1 - 4\mu) (1 - 4\mu^2) (7 - 14\mu - 24\mu^2) \ln [4\delta^2 + (1 + 2\delta - 2\mu)^2]$$
$$- 2(1 - 4\mu^2) (35 - 380\mu^2 + 576\mu^4) \ln [4\delta^2 + (1 + 2\delta)^2]$$
$$+ 8(1 + 4\mu) (1 - 4\mu^2) (7 + 14\mu - 24\mu^2) \ln [4\delta^2 + (1 + 2\delta + 2\mu)^2]$$
$$- 4(1 + 2\mu)^2 (1 + 4\mu) (7 + 28\mu - 36\mu^2) \ln [4\delta^2 + (1 + 2\delta + 4\mu)^2]$$
$$+ 8(1 + 2\mu)^2 (1 + 4\mu)^2 (1 + 6\mu) \ln [4\delta^2 + (1 + 2\delta + 6\mu)^2]$$
$$- (1 + 2\mu)^2 (1 + 4\mu)^2 (1 + 6\mu)^2 \ln [4\delta^2 + (1 + 2\delta + 8\mu)^2] \Big\}$$

$(8\mu < 1 + 2\delta)$ (4.17)

The energies of these four states were obtained by minimizing each with respect to μ separately. The minimum of the energy is guaranteed by $\left|\frac{\partial E}{\partial \mu}\right| < 10^{-8}$. The values of μ thus obtained are shown in Table 4.5, and the corresponding energies are shown in Tables 4.1 - 4.4. The calculations were carried out on an IBM 370/168 in "quadruple precision"; however, even this accuracy was not enough for $\delta = 0.0001$, for which satisfactory results could not be obtained and are not shown. We may note here that the wave functions for 2s, 3s, and 4s states with the given values of μ are not exactly orthogonal to the eigenfunctions of the corresponding lower states, but they are close to it, except when δ is large.

4.5 Ground State Energy by Variational Calculation with a Two-Parameter Hulthén Function as a Trial Function

In the previous section, the 1s state wave function is chosen such that the two independent parameters in the Hulthén potential are set to be equal (Appendix A). In order to determine the energy more precisely, we introduce the two-parameter Hulthén type wave function for the ground state of the ECSC potential. If μ and ν stand for the optimized parameters, the wave function has the form of

$$\Psi_{1s}(r) = \left[\nu\left(\frac{4\nu^2}{\mu^2} - 1\right)\right]^{\frac{1}{2}} \left[e^{-(\nu - \frac{\mu}{2})r} - e^{-(\nu + \frac{\mu}{2})r}\right]$$

For this wave function we derive

$$E_{1s} = -\frac{\mu^2}{8}\left(\frac{4\nu^2}{\mu^2} - 1\right) + \frac{\nu}{2}\left(\frac{4\nu^2}{\mu^2} - 1\right)\left\{-\ell n\left[\delta^2 + (\delta + 2\nu - \mu)^2\right] + 2\,\ell n\left[\delta^2 + (\delta + 2\nu)^2\right] - \ell n\left[\delta^2 + (\delta + 2\nu + \mu)^2\right]\right\}$$

$$(\mu - 2\nu < \delta) \qquad (4.18)$$

We have used the direct search method of Hooke and Jeeves (1961), (see also Wilde (1964), and Kawalik and Osborne (1968) to determine the optimized parameters μ and ν at which the energy is at the minimum. The energy from the Eq.(4.18) are listed in the Table 4.1 and the corresponding optimized values of the parameters in the Table 4.6.

4.6 The Critical Screening and the Number of Bound States

One of the important physical quantity for a screening potential is to calculate its critical screening. It is the value of δ_c at which the energy is zero. For the ground state energy, the two-parameter Hulthén wave function provides a precise way to determine it. According to the definition of the critical screening, we have

$$E(\delta, \mu, \nu) = 0$$

From Eq.(4.17), it gives

$$\mu = 2\nu \tag{4.19}$$

In addition, E has to satisfy the basic assumption of the variational calculation, i.e.

$$\frac{\partial E(\delta, \mu, \nu)}{\partial \nu} = 0 \quad \left(\text{or } \frac{\partial E(\delta, \mu, \nu)}{d\mu} = 0\right) \tag{4.20}$$

Setting condition (4.19) in Eq.(4.18), Eq.(4.20) becomes

$$\frac{\partial E}{\partial \nu} = 0$$

$$= -\nu - \ell n(2\delta^2) + 2\,\ell n\left[\delta^2 + (\delta + 2\nu)^2\right]$$

$$- \ell n\left[\delta^2 + (\delta + 4\nu)^2\right] \tag{4.21}$$

By using bisectional iterations, we determined

$$\delta_c = 0.7115 \quad \text{at} \quad \nu = 1.238 \tag{4.22}$$

Although the perturbed Coulomb potential treatment does not yield very accurate values, it has the advantage to obtain the energy for any state. We have calculated the energies and critical screening parameters of states up to n = 15 by this method. This enables us to examine the total number of bound states n* at a given δ. In Fig. 4.2 we plotted n* against $1/\delta_c$. A linear relationship is seen to hold between them, and linear regression yielded the following result:

$$n^* = 0.4425 + 0.2919/\delta_c \qquad (4.23)$$

Another quantity of interest is the maximum bound principal quantum number g*, or the number of bound s states. The quantity $(g^*)^2$ is also plotted against $1/\delta_c$ in Fig. 4.2, and is seen to exhibit a linear dependance on $1/\delta_c$. From the linear regression, we obtained

$$(g^*)^2 = 0.040 + 0.6078/\delta_c \qquad (4.24)$$

For a given value of δ, the perturbed Coulomb potential treatment gives binding energies which are too small. In other words, for a given value of δ, the number of bound states obtained from this method is smaller than the actual one. Thus the coefficients 0.2919 and 0.6078 in Eqs. (3.23) and (3.24) respectively should be considered as a lower bound in the two cases. The intercepts at $1/\delta_c = 0$ are quite small in both cases, and within the accuracy of these results, may be considered to be practically zero.

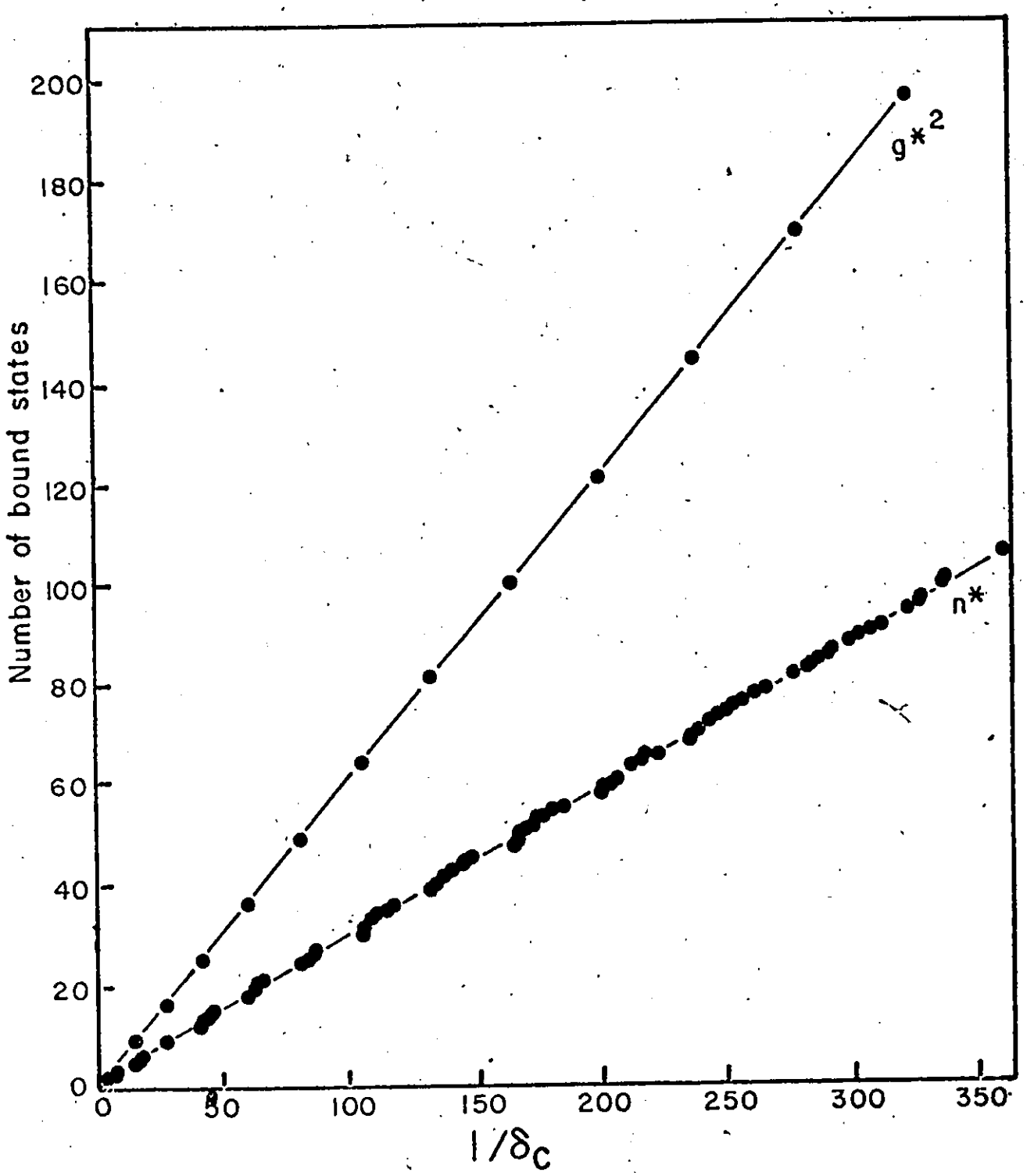

Fig. 4.2 : Number of bound states n* and the square of the maximum bound principal quantum number g*, as a function of the critical screening length $1/\delta_c$.

4.7 Comparison of Results

It will be noticed from Table 4.1 that for the ground state, for low values of $\delta (\lesssim 0.05)$, there is little difference between the four sets of results. Up to six significant figures, the energies obtained from the two-parameter Hulthén wave function do not show any difference from those obtained from the one-parameter wave function for $\delta \lesssim 0.1$. In general, as δ increases the accuracy of results improves in the following order: perturbation (Coulomb), perturbation (Hulthén), one-parameter variational calculation, two-parameter variational calculation. The last named results are the most accurate.

The only other investigation with which we can compare our results is that of Bonch-Bruevich and Glasko (1956, 1959), who obtained their results by numerical methods. These authors have used a special set of units; when their results are converted into atomic units, we find that in most cases their results are close to ours. For example, at $\delta = 0.4793$, they get $E = 0.0287$, while our two-parameter variational result is 0.02877. At $\delta = 0.5298$, their value is $E = 0.0149$, compared to 0.01496 obtained from Eq. (4.17). Bonch-Bruevich and Glasko's results leads to $\delta_c = 0.72$, as compared to 0.7115 obtained in the last section.

The pattern of the results for the excited s states (Tables 4.2 - 4.4) is quite similar to that of the ground state. The Hulthén perturbation results are better than the Coulomb perturbation ones and the variational results are the best of the three.

4.8 Some Fine Points

The oscillating shape of the ECSC potential gives rise to some interesting properties which we now consider. In Fig. 4.3 we show the qualitative behavior of the ECSC potential; we shall find it convenient for our discussion. We wish to emphasize that it is only a qualitative diagram, in reality the amplitudes of the crests and troughs diminish much more rapidly than what is shown in the diagram. The positions of the maxima and minima can be obtained by putting the first derivative of Eq. (4.2) equal to zero, which leads to

$$1 + \frac{1}{\delta R} + \tan \delta R = 0 \qquad (4.25)$$

Equation (4.25) has, of course, multiple solutions; the first five of these are δR = 2.1712, 5.4134, 8.5844, 11.740 and 14.890. The potential barrier at R_1 can enable levels with positive energies to exist on its left side. The phenomenon is similar to that found in diatomic molecules where levels, above the dissociation limit, are known to exist for large values of the rotational quantum number, because of the potential hill created due to the rotational term $J(J + 1)/r^2$. So far, in our case, we have considered only those bound levels which have negative energies with respect to the dissociation limit. We must now consider these positive energy levels. In principle, a dissociation of the system can take place from these positive energy states by tunneling through the potential hill, and this will also lead to a broadening of the discrete levels. However,

these effects are expected to be important for only those levels which lie near the top of the potential hill. It is obvious that even for $\delta > \delta_c$, a given level can exist as a positive energy level till its energy becomes equal to the height of the first maximum. This final value of δ beyond which no levels can exist (with negative or positive energies) shall be denoted by δ_f. Our two-parameter variational wave function is not satisfactory for obtaining positive energy states and thus δ_f. However, by a graphical comparison of the two-parameter variational results with those from the Hulthén perturbation, we estimate $\delta_f = 0.8$ for the ground state.

The ECSC potential has numerous minima (at R_2, R_4, ... etc.) and if the depths of these wells is sufficiently large, metastable states can be formed in these. To obtain the precise location of these levels would require the application of some refined numerical techniques, for example, the work due to Kolos and Wolniewicz (1969). However, some order of magnitude estimates can be carried out by approximate means. The shape of these minima is similar to that of the potential energy curve of a diatomic molecule in the neighborhood of its minimum, and it would be legitimate to estimate the position of the first level by calculating the zero-point energy from the second derivative of the potential. In this way we find that the zero-point energy at the first minimum is given by

$$\frac{1}{2}\hbar\omega = \delta^{3/2} \{4e^{-\delta R_2} (\delta R_2)^{-3} (\delta R_2 + 1) \cos(\delta R_2) + \delta R_2 \sin(\delta R_2) \}^{1/2} \qquad (4.26)$$

The depth of this well, E_d, is given by the energy difference between the first minimum and the second maximum;

$$E_d = \frac{e^{-\delta R_2}}{R_2} \cos(\delta R_2) - \frac{e^{-\delta R_3}}{R_3} \cos(\delta R_3) \qquad (4.27)$$

In Fig. 4.4 we show some numerical results for the first minimum at R_2. It will be noticed that from Eqs. (4.26) and (4.27) that the ratio $\frac{1}{2}\hbar\omega/E_d$ is a function of δ alone. We find from this ratio that $\frac{1}{2}\hbar\omega < E_d$ only when $\delta < 9.46 \times 10^{-4}$. Similarly for the second well at R_4, we find that $\frac{1}{2}\hbar\omega < E_d$ when $\delta < 9 \times 10^{-7}$. From these results it would be reasonable to infer that for $\delta > 1 \times 10^{-3}$ bound states do not exist in these wells. However, the possible existence of levels for $\delta < 1 \times 10^{-3}$ is a somewhat surprising conclusion from this analysis; it is possible that our method of estimating the zero point energy in such shallow wells is not satisfactory. A definite conclusion on this point can only be obtained by a numerical integration of the Schrödinger equation for the ECSC potential.

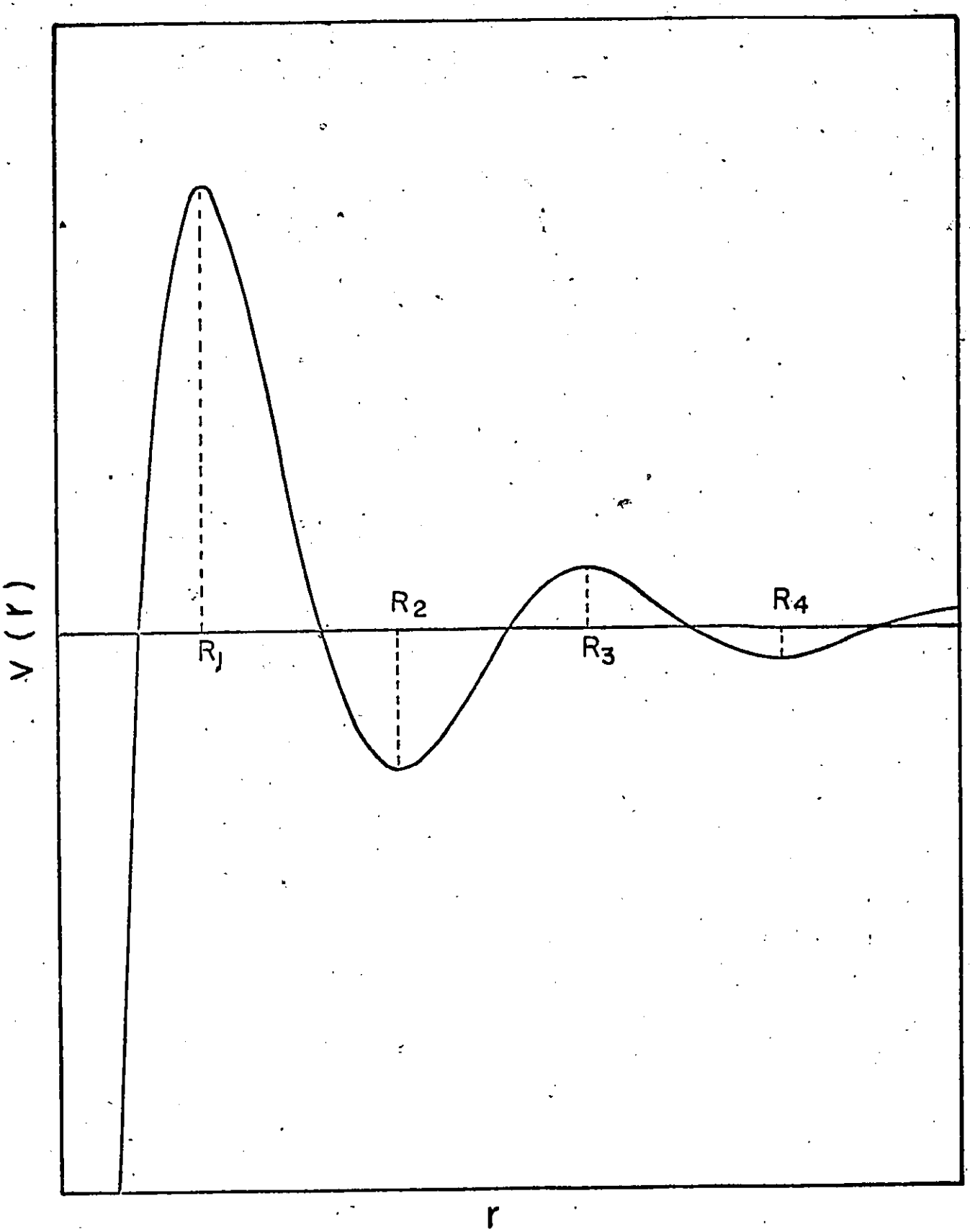

Fig. 4.3 : Schematic diagram of the behavior of the ECSC potential as a function of r. As an aid to the eye, the relative strength of oscillations have been exaggerated, for example, in reality $|V(R_2)/V(R_1)| \simeq 0.02$ rather than what is shown in the diagram.

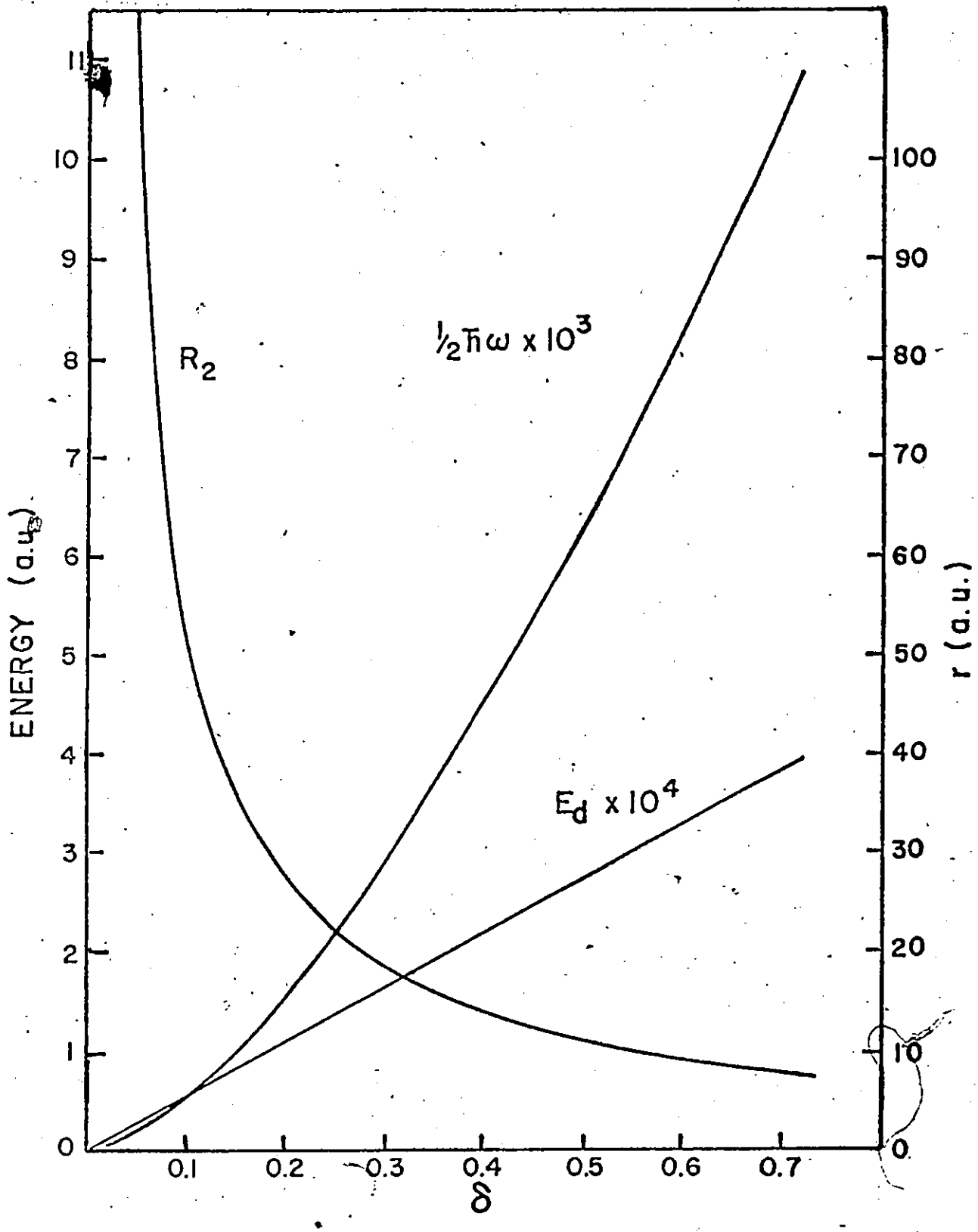

Fig. 4.4 : Parameters of the first minimum : its position R_2, depth E_d and the zero-point energy $\frac{1}{2}\hbar\omega$ as a function of δ

Table 4.1: Energy eigenvalues as a function of screening parameter for the 1s-state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one-parameter)	Variational (two-parameter)
0.0001	0.499900	0.499900	--	
0.0002	0.499800	0.499800	0.499800	
0.0005	0.499500	0.499500	0.499500	
0.0010	0.499000	0.499000	0.499000	
0.0015	0.498500	0.498500	0.498500	
0.0020	0.498000	0.498000	0.498000	
0.0025	0.497500	0.497500	0.497500	
0.0030	0.497000	0.497000	0.497000	
0.0035	0.496500	0.496500	0.496500	
0.0040	0.496000	0.496000	0.496000	
0.0045	0.495500	0.495500	0.495500	
0.0050	0.495000	0.495000	0.495000	
0.0060	0.494000	0.494000	0.494000	
0.0070	0.493000	0.493000	0.493000	
0.0080	0.492001	0.492001	0.492001	
0.0090	0.491001	0.491001	0.491001	
0.010	0.490001	0.490001	0.490001	
0.015	0.485003	0.485003	0.485003	
0.020	0.480008	0.480008	0.480008	
0.025	0.475015	0.475015	0.475015	

Table 4.1 (cont'd)

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one-parameter)	Variational (two-parameter)
0.030	0.470026	0.470026	0.470026	
0.035	0.465041	0.465041	0.465041	
0.040	0.460061	0.460061	0.460061	
0.045	0.455086	0.455086	0.455086	
0.050	0.450117	0.450117	0.450117	
0.060	0.440200	0.440201	0.440201	
0.070	0.430314	0.430315	0.430315	
0.080	0.420463	0.420464	0.420464	
0.090	0.410651	0.410653	0.410653	
0.10	0.400883	0.400884	0.400885	0.400885
0.20	0.306235	0.306298	0.306332	0.306334
0.25	0.261452	0.261630	0.261761	0.261766
0.30	0.218619	0.219028	0.219399	0.219411
0.40	0.139153	0.140595	0.142375	0.142418
0.50	0.068047	0.071714	0.077481	0.077606
0.60	0.004987	0.012585	0.027708	0.028031
0.70	-0.050624	-0.036908	0.000184	0.000614

Table 4I2 : Energy eigenvalues as function of screening parameter for the 2s-state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one-parameter)
0.0001	0.124900	0.124900	
0.0002	0.124800	0.124800	0.124800
0.0005	0.124500	0.124500	0.124500
0.0010	0.124000	0.124000	0.124000
0.0015	0.123500	0.123500	0.123500
0.0020	0.123000	0.123000	0.123000
0.0025	0.122500	0.122500	0.122500
0.0030	0.122000	0.122000	0.122000
0.0035	0.121501	0.121501	0.121501
0.0040	0.121001	0.121001	0.121001
0.0045	0.120501	0.120501	0.120501
0.0050	0.120002	0.120002	0.120002
0.0060	0.119003	0.119003	0.119003
0.0070	0.118005	0.118005	0.118005
0.0080	0.117007	0.117007	0.117007
0.0090	0.116010	0.116010	0.116010
0.010	0.115013	0.115013	0.115013
0.015	0.110045	0.110045	0.110045
0.020	0.105104	0.105104	0.105104

Table 4.12 (cont'd)

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one-parameter)
0.025	0.100198	0.100198	0.100198
0.030	0.095336	0.095336	0.095337
0.035	0.090523	0.090524	0.090525
0.040	0.085765	0.085768	0.085769
0.045	0.081068	0.081073	0.081075
0.050	0.076436	0.076445	0.076449
0.060	0.067385	0.067408	0.067421
0.070	0.058640	0.058687	0.058721
0.080	0.050222	0.050310	0.050384
0.090	0.042147	0.042299	0.042445
0.10	0.034425	0.034668	0.034935
0.20	-0.023671	-0.019323	

Table 413:: Energy eigenvalues as a function of screening parameter for the 3s-state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one-parameter)
0.0001	0.055456	0.055456	
0.0002	0.055356	0.055356	0.055356
0.0005	0.055056	0.055056	0.055056
0.0010	0.054556	0.054556	0.054556
0.0015	0.054056	0.054056	0.054056
0.0020	0.053556	0.053556	0.053556
0.0025	0.053057	0.053057	0.053057
0.0030	0.052557	0.052557	0.052557
0.0035	0.052058	0.052058	0.052058
0.0040	0.051560	0.051560	0.051560
0.0045	0.051062	0.051062	0.051062
0.0050	0.050564	0.050564	0.050564
0.0060	0.049570	0.049570	0.049570
0.0070	0.048578	0.048578	0.048578
0.0080	0.047589	0.047589	0.047589
0.0090	0.046602	0.046602	0.046602
0.010	0.045619	0.045619	0.045619
0.015	0.040761	0.040761	0.040762
0.020	0.036022	0.036024	0.036025

Table 4.3 (cont'd).

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one-parameter)
0.025	0.031429	0.031436	0.031439
0.030	0.027003	0.027019	0.027028
0.035	0.022758	0.022791	0.022816
0.40	0.018707	0.018768	0.018822
0.045	0.014857	0.014960	0.015068
0.050	0.011211	0.011376	0.011574
0.060	0.004538	0.004903	0.005454
0.070	-0.001328	-0.000629	0.000722

Table 4.4 : Energy eigenvalues as a function of screening parameter for the 4s-state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one-parameter)
0.0001	0.031150	0.031150	
0.0002	0.031050	0.031050	0.031050
0.0005	0.030750	0.030750	0.030750
0.0010	0.030250	0.030250	0.030250
0.0015	0.029751	0.029751	0.029751
0.0020	0.029252	0.029252	0.029252
0.0025	0.028753	0.028753	0.028753
0.0030	0.028256	0.028256	0.028256
0.0035	0.027759	0.027759	0.027759
0.0040	0.027263	0.027263	0.027263
0.0045	0.026768	0.026768	0.026768
0.0050	0.026275	0.026275	0.026275
0.0060	0.025293	0.025293	0.025293
0.0070	0.024317	0.024317	0.024317
0.0080	0.023348	0.023349	0.023349
0.0090	0.022388	0.022389	0.022389
0.010	0.021436	0.021437	0.021437
0.015	0.016835	0.016840	0.016842
0.020	0.012539	0.012557	0.012572
0.025	0.008587	0.008640	0.008693
0.030	0.005000	0.005119	0.005270
0.035	0.001782	0.002014	0.002374
0.040	-0.001079	-0.000670	0.000118

Table 4.5: Best values of the parameter μ for the one-parameter variational results.

Screening parameter δ	Parameter μ			
	1s	2s	3s	4s
0.0002	0.00001	0.00008	0.00020	0.00060
0.0005	0.00004	0.00010	0.00030	0.00062
0.0010	0.00013	0.00024	0.00035	0.00074
0.0015	0.00024	0.00044	0.00064	0.00088
0.0020	0.00037	0.00068	0.00098	0.00128
0.0025	0.00052	0.00095	0.00136	0.00177
0.0030	0.00069	0.00124	0.00179	0.00232
0.0035	0.00087	0.00157	0.00225	0.00291
0.0040	0.00106	0.00191	0.00274	0.00354
0.0045	0.00127	0.00228	0.00326	0.00420
0.0050	0.00149	0.00267	0.00381	0.00489
0.0060	0.00195	0.00350	0.00497	0.00637
0.0070	0.00246	0.00439	0.00624	0.00794
0.0080	0.00301	0.00535	0.00756	0.00960
0.0090	0.00358	0.00636	0.00897	0.01134
0.010	0.00419	0.00743	0.01043	0.01315
0.015	0.00767	0.01345	0.01860	0.02303
0.020	0.01175	0.02039	0.02781	0.03400
0.025	0.01633	0.02806	0.03781	0.04586
0.030	0.02136	0.03634	0.04844	0.05866

Table 4.5c (contd)

Screening parameter δ	Parameter μ 1s	2s	3s	4s
0.035	0.02678	0.04513	0.05962	0.07279
0.040	0.03255	0.05437	0.07130	0.08996
0.045	0.03864	0.06398	0.08348	
0.050	0.04503	0.07394	0.09621	
0.060	0.05859	0.09476	0.12385	
0.070	0.07309	0.11662	0.15761	
0.080	0.08841	0.13943		
0.090	0.10446	0.16315		
0.10	0.12116	0.18780		
0.20	0.31348			
0.25	0.42167			
0.30	0.53586			
0.40	0.78141			
0.50	1.05482			
0.60	1.37679			
0.70	1.90443			

Table V4.6: The best values of parameters μ and ν for the 1s-state two-parameter wavefunction.

Screening parameter δ	Parameters μ	ν
0.10	0.18036	1.00241
0.20	0.35729	1.00458
0.25	0.47331	1.00729
0.30	0.59516	1.01058
0.40	0.86749	1.02148
0.50	1.17700	1.03919
0.60	1.57150	1.07610
0.70	2.26080	1.18811

Table 4.7: Energy eigenvalues as a function of screening parameter for the 2p, 3p, 3d, 4p, 4d, 4f and 5s-8k states.

state \ δ	0.0001	0.0002	0.0005	0.0010	0.0020	0.0050	0.0100	0.0200	0.0500	0.1000
2p	0.124900	0.124800	0.124500	0.124000	0.123000	0.120001	0.115010	0.105075	0.076049	0.032042
3p	0.055456	0.055356	0.055056	0.054556	0.053556	0.050563	0.045611	0.035965	0.010588	
3d	0.055456	0.055356	0.055056	0.054556	0.053556	0.050561	0.045595	0.035849	0.009292	
4p	0.031150	0.031050	0.030750	0.030250	0.029252	0.026273	0.021424	0.012454		
4d	0.031150	0.031050	0.030750	0.030250	0.029251	0.026270	0.021397	0.012283		
4f	0.031150	0.031050	0.030750	0.030250	0.029251	0.026264	0.021357	0.012019		
5s	0.019900	0.019800	0.019500	0.019001	0.018004	0.015059	0.010419	0.002663		
5p	0.019900	0.019800	0.019500	0.019000	0.018004	0.015056	0.010401	0.002559		
5d	0.019900	0.019800	0.019500	0.019000	0.018003	0.015051	0.010364	0.002350		
5f	0.019900	0.019800	0.019500	0.019000	0.018003	0.015043	0.010309	0.002028		
5g	0.019900	0.019800	0.019500	0.019000	0.018002	0.015032	0.010233	0.001583		
6s	0.013789	0.013689	0.013389	0.012890	0.011897	0.009004	0.004673			
6p	0.013789	0.013689	0.013389	0.012890	0.011897	0.009001	0.004651			
6d	0.013789	0.013689	0.013389	0.012890	0.011896	0.008994	0.004605			
6f	0.013789	0.013689	0.013389	0.012890	0.011895	0.008983	0.004537			
6g	0.013789	0.013689	0.013389	0.012890	0.011894	0.008968	0.004443			

Table 4.7 (cont'd)

state \ δ	0.0001	0.0002	0.0005	0.0010	0.0020	0.0050	0.0100	0.0200	0.0500	0.1000
6h	0.013789	0.013689	0.013389	0.012889	0.011893	0.008950	0.004324			
7s	0.010104	0.010004	0.009704	0.009206	0.008219	0.005406	0.001494			
7p	0.010104	0.010004	0.009704	0.009206	0.008218	0.005401	0.001468			
7d	0.010104	0.010004	0.009704	0.009206	0.008218	0.005392	0.001417			
7f	0.010104	0.010004	0.009704	0.009206	0.008217	0.005379	0.001339			
7g	0.010104	0.010004	0.009704	0.009206	0.008215	0.005361	0.001232			
7h	0.010104	0.010004	0.009704	0.009205	0.008214	0.005337	0.001096			
7i	0.010104	0.010004	0.009704	0.009205	0.008211	0.005310	0.000929			
8s	0.007713	0.007613	0.007313	0.006816	0.005837	0.003134				
8p	0.007713	0.007613	0.007313	0.006816	0.005837	0.003128				
8d	0.007713	0.007613	0.007313	0.006816	0.005836	0.003118				
8f	0.007713	0.007613	0.007313	0.006815	0.005834	0.003102				
8g	0.007713	0.007613	0.007313	0.006815	0.005833	0.003080				
8h	0.007713	0.007613	0.007313	0.006815	0.005830	0.003053				
8i	0.007713	0.007613	0.007313	0.006814	0.005828	0.003020				
8k	0.007713	0.007613	0.007313	0.006814	0.005825	0.002981				

Table 4.8 : The critical screening lengths ($X\ 10^{-5}$) of 105 states of the ECSC potentail, obtained by perturbation calculation with the Coulomb potential as an unperturbed potential

n\ℓ	0	1	2	3	4	5	6	7	8	9	10	11	12	13
1	60845													
2	15204	14264												
3	6760	6560	6218											
4	3805	3739	3619	3465										
5	2436	2409	2357	2287	2206									
6	1690	1679	1653	1618	1575	1527								
7	1244	1236	1220	1200	1178	1149	1119							
8	950	946	937	926	911	893	874	854						
9	750	750	742	735	725	714	701	688	673					
10	610	606	602	600	591	583	575	565	555	545				
11	502	501	500	495	490	485	480	472	465	457	450			
12	422	421	420	417	413	410	405	400	395	390	383	377		
13	360	360	360	355	353	350	347	343	340	335	331	326	321	
14	310	310	310	307	305	303	303	300	295	291	290	284	281	277

Chapter 5 - Energies of s States of the Baer Potential

5.1 Introduction

The effective potential between a positive ion and an electron in a plasma has been a question of continuing interest. To a first approximation, it is customary to take this potential as the static screened Coulomb potential. At least at high temperature and low density, it is the correct asymptotic potential. However, the exact form of this potential is unclear and there has been controversy on this question (Nakayama and DeWitt 1964, Jackson and Klein 1969, and Theimer and Kepple 1970).

A few years ago, Baer (1970) derived the following expression for the screened potential around an ion:

$$\phi(r) = \frac{q^2 kT}{2en \times 2\pi r} (B_s e^{-q_s r} + B_o \cos q_o r) \qquad (5.1)$$

where

$$B_s = \frac{q_s^2 + q^2}{q_s^2 + q_o^2}, \quad B_o = \frac{q_o^2 - q^2}{q_s^2 + q_o^2}$$

in which

$$q_s = (\sqrt{3} + 1)^{\frac{1}{2}} q$$

$$q_o = (\sqrt{3} - 1)^{\frac{1}{2}} q$$

the Debye length q being equal to $(4\pi ne^2/kT)^{\frac{1}{2}}$.

Eq. (5.1) leads to the following expression for the ion-electron interaction:

$$V(r) = - \frac{\sqrt{3} + 2}{2\sqrt{3}} \frac{e^2}{kr} [e^{-q_s r} - (7 - 4\sqrt{3}) \cos q_o r] \qquad (5.2)$$

This potential consists of a sum of two terms: an exponentially decaying Coulomb term (or SSCP in the previous study) and an oscillatory Coulomb term. Because the amplitude of the screened Coulomb term is greater than that of the oscillatory term (indeed it is 14 times greater), one may expect that at moderately large distances the SSCP is dominant and obscures the presence of the oscillatory term, and the oscillatory term becomes important at very large distances. Hence, it behaves like the static screened Coulomb potential when qr is small and oscillates like the exponential cosine screened potential when qr is large.

To evaluate the partition function of a plasma, one requires data on the energy eigenvalues of the ion-electron system. In this study, we shall employ variational calculation to estimate the energy eigenvalues of s states. Our main interest is in the ground state,

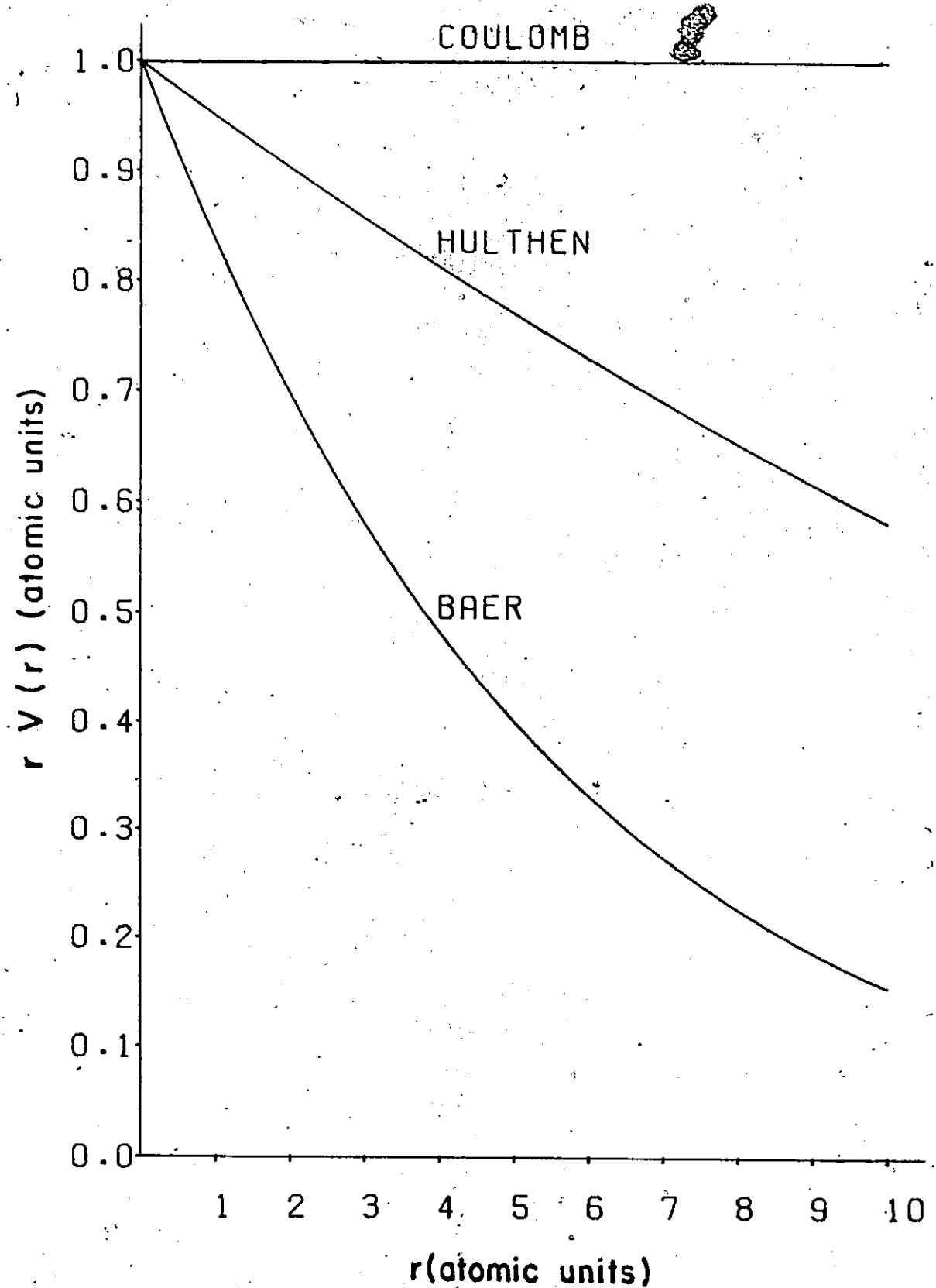

Fig. 5.1 : Product rV(r) as a function of r, for the Coulomb potential, the Hulthén potential and the Baer potential for $\delta = 0.1$

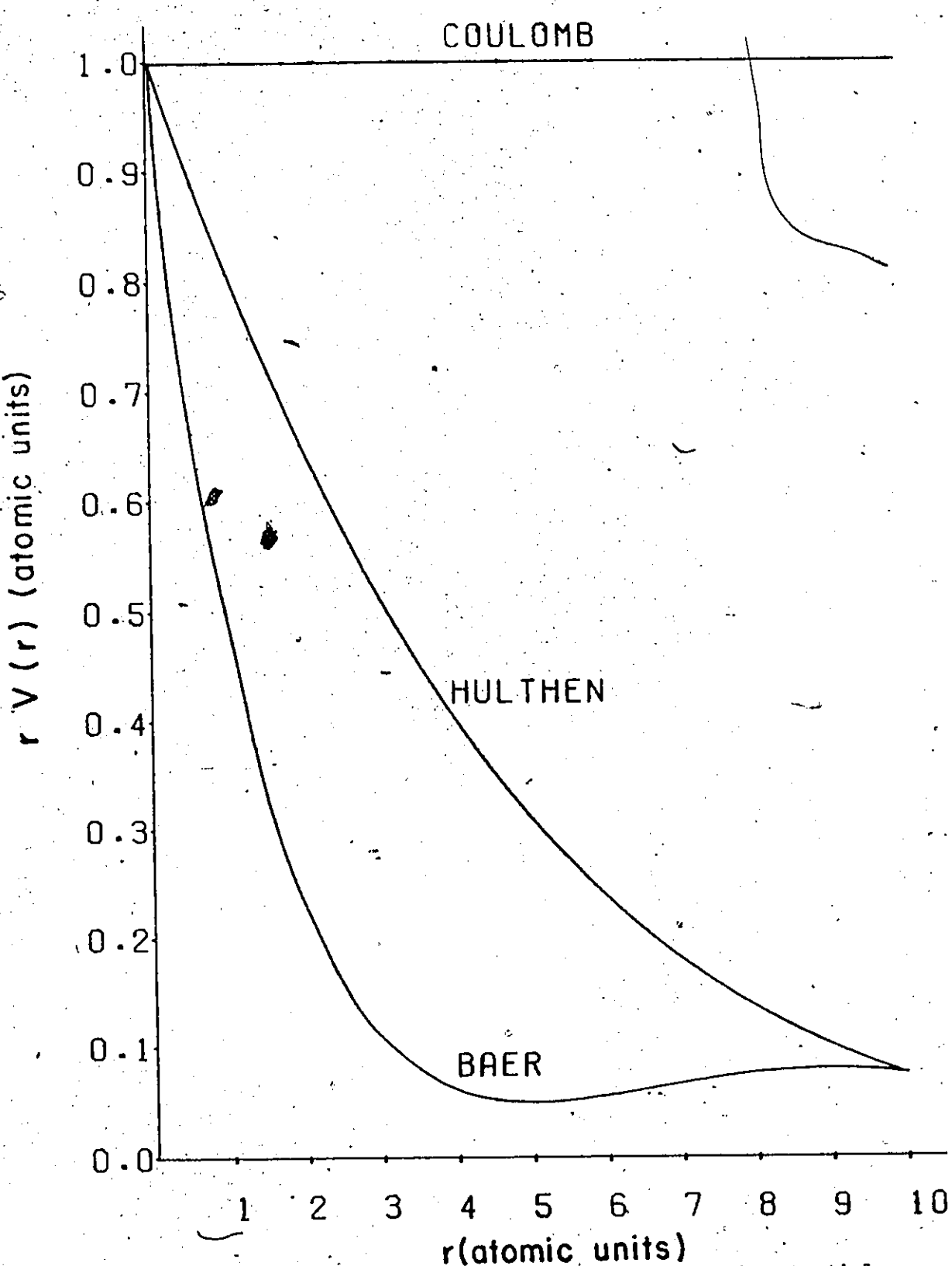

Fig. 5.2 : Product rV(r) as a function of r, for the Coulomb potential, the Hulthén potential and the Baer potential for $\delta = 0.4$

for which we have used seven different variational functions. For the excited states only Hydrogenic and Hulthen type wave functions are used.

In atomic units, if the dimensionless quantities δ, δ_s and δ_o correspond to q, q_s and q_o respectively, the Baer potential takes the form of

$$V(r) = \frac{\sqrt{3}+2}{2\sqrt{3}} \frac{1}{r} [e^{-\delta_s r} - (7 - 4\sqrt{3}) \cos \delta_o r] \tag{5.3}$$

where

$$\delta_s = (\sqrt{3}+1)^{\frac{1}{2}} \delta$$
$$\tag{5.4}$$
$$\delta_o = (\sqrt{3}-1)^{\frac{1}{2}} \delta$$

5.2 Variational Calculation on the Ground State Energy of the Baer Potential

The Baer potential behaves both like the static screened Coulomb potential and the exponential cosine screened Coulomb potential when δr is small. As the first attempt to obtain the energy eigenvalues, we will use the wave functions or the combinations of the wave functions, which we have proposed for the SSC and ECSC potentials, and of which some produce satisfactory results over a wide range of δ.

There are seven wave functions and they can be classified into two categories: the simple variation functions and the linear variation functions. In the following sections, we list the proposed wave functions and the corresponding energy expressions.

5.2.1 Simple Variation Functions

For a simple wave function, the energy expression is given by

$$E = \langle\psi|\frac{1}{2}\frac{d^2}{dr^2}|\psi\rangle + \langle\psi|V(r)|\psi\rangle$$

$$= \frac{1}{2}\langle\psi|\frac{d^2}{dr^2}|\psi\rangle$$

$$+ \frac{\sqrt{3}+2}{2\sqrt{3}}\langle\psi|\frac{1}{r}[e^{-\delta_s r} - (7-4\sqrt{3})\cos\delta_o r]|\psi\rangle \qquad (5.5)$$

The wave functions proposed and the corresponding energy expressions are:

(a) Hydrogen-like wave function

$$\psi_a = 2\mu^{\frac{3}{2}} re^{-\mu r} \qquad (5.6)$$

$$E_a = -\frac{\mu^2}{2} + \frac{2(\sqrt{3}+2)}{\sqrt{3}}\mu^3\left[\frac{1}{(2\mu+\delta_s)^2} - (7-4\sqrt{3})\frac{\cos\left(2tg^{-1}\frac{\delta_o}{2\mu}\right)}{\delta_o^2+4\mu^2}\right] \tag{5.7}$$

where μ is the variational parameter.

(b) One parameter Hulthén type wave function

$$\psi_b = \left(\frac{4}{\mu^2}-1\right)^{\frac{1}{2}}\left[e^{-(1-\frac{\mu}{2})r} - e^{-(1+\frac{\mu}{2})r}\right] \tag{5.8}$$

$$E_b = -\frac{1}{8}(4-\mu^2) + \frac{\sqrt{3}+2}{4\sqrt{3}}\,\frac{4-\mu^2}{\mu^2}\Big(-2\ell n\,(\delta_s+2-\mu)$$

$$+ 4\ell n(\delta_s+2) - 2\ell n\,(\delta_s+2+\mu)$$

$$-(7-4\sqrt{3})\{-\ell n[\delta_o^2+(2-\mu)^2] + 2\ell n(\delta_o^2+4)$$

$$-\ell n[\delta_o^2+(2+\mu)^2]\}\Big) \qquad (\mu < 2) \tag{5.9}$$

where μ is the variational parameter.

(c) Two parameter Hulthen type wave function

$$\psi_c = \left[\nu\left(\frac{4\nu^2}{\mu^2}-1\right)\right]^{\frac{1}{2}}\left[e^{-(\nu-\frac{\mu}{2})r} - e^{-(\nu+\frac{\mu}{2})r}\right] \tag{5.10}$$

$$E_c = -\frac{1}{8}(4\nu^2 - \mu^2) + \frac{\sqrt{3}+2}{4\sqrt{3}}\frac{\nu(4\nu^2-\mu^2)}{\mu^2}\Big(-2\ell n(\delta_s + 2\nu - \mu)$$

$$+ 4\ell n(\delta_s + 2\nu) - 2\ell n(\delta_s + 2\nu + \mu)$$

$$- (7 - 4\sqrt{3})\{-\ell n[\delta_o{}^2 + (2\nu - \mu)^2]$$

$$+ 2\ell n(\delta_o{}^2 + 4\nu^2) - \ell n[\delta_o{}^2 + (2\nu + \mu)^2]\}\Big)$$

$$(2\nu - \mu > 0) \qquad (5.11)$$

where μ and ν are the variational parameters.

5.2.2 Linear Variation Functions

The linear variation function that we are considering here has the form

$$\Psi = a_1\phi_1 + a_2\phi_2 \qquad (5.12)$$

where a_1 and a_2 are constants, and ϕ_1 and ϕ_2 are simple variational wave functions. Furthermore, the functions listed below can be classified into two groups. One is that in which the basic function ϕ_i is the ith state of a known potential. For instance, ϕ_1 and ϕ_2 are respectively the 1s and 2s hydrogen-like wave functions. This type of variation functions have been used for the SSCP by Harris, who employed hydrogen wave functions as the basic set and the ith state wave function is the linear combination of the three consecutive wave

functions commencing from i with the same angular momentum ℓ. The other one is the arbitrary combination of two 1s state wave functions of some known potentials. Usually the basic function itself produces some satisfactory results over a certain range of δ.

For normalized wave functions ϕ_i, the energy is obtained by solving the secular equation

$$\begin{vmatrix} H_{11} - E & H_{12} - SE \\ H_{12} - SE & H_{22} - E \end{vmatrix} = 0 \tag{5.13}$$

The quantities H_{ij} and S are defined as

$$H_{ij} = \int \phi_i H \phi_j dt \tag{5.14}$$

$$S = \int \phi_i \phi_j dt \tag{5.15}$$

where H is the Hamiltonian operator.

$$H = \frac{1}{2}\frac{d^2}{dr^2} + V(r) \tag{5.16}$$

From Eq. (5.13) we derive

$$E = \frac{H_{11} + H_{22} - 2SH_{12} \pm (H_{11} + H_{22} - 2SH_{12})^2 - 4(1 - S^2)(H_{11}H_{22} - H_{12}^2)}{2(1 - S^2)} \tag{5.17}$$

The lower root of the Eq. (5.17) corresponds to the expected energy value.

(d) Linear combination of 1s and 2s state hydrogen-like wave functions

$$\phi_1 = \psi_a$$

$$\phi_2 = \frac{\nu^{\frac{3}{2}}}{\sqrt{8}} e^{-\frac{\nu r}{2}} r(2 - \nu r)$$

$$S = \frac{64\mu^{\frac{3}{2}} \nu^{\frac{3}{2}} (\mu - \nu)^4}{\sqrt{2}(2\mu + \nu)^4}$$

$$H_{11} = E_a$$

$$H_{22} = -\frac{\nu^2}{8} + \frac{\sqrt{3} + 2}{8\sqrt{3}} \nu^3 \{\frac{2\delta_s^2 + \nu^2}{(\delta_s + \nu)^4}$$

$$- (7 - 4\sqrt{3}) [\frac{2 \cos (2 \tan^{-1} \frac{\delta_o}{\nu})}{\delta_o^2 + \nu^2}$$

$$- \frac{4\nu \cos (3 \tan^{-1} \frac{\delta_o}{\nu})}{(\delta_o^2 + \nu^2)^{\frac{3}{2}}} + \frac{3\nu^2 \cos (4 \tan^{-1} \frac{\delta_o}{\nu})}{(\delta_o^2 + \nu^2)^2}]\}$$

$$H_{12} = \frac{8\mu^{\frac{5}{2}}\nu^{\frac{5}{2}}}{\sqrt{2}} \frac{(\nu - 4\mu)}{(2\mu + \nu)^4}$$

$$+ \frac{4(\sqrt{3} + 2)}{\sqrt{6}} \mu^{\frac{3}{2}} \nu^{\frac{3}{2}} \{\frac{2\delta_s + 2\mu - \nu}{(2\delta_s + 2\mu + \nu)^3}$$

$$- (7 - 4\sqrt{3}) [\frac{\cos (2 \tan^{-1} \frac{2\delta_o}{2\mu + \nu})}{4\delta_o^2 + (2\mu + \nu)^2} - \frac{2\nu \cos(3 \tan^{-1} \frac{2\delta_o}{2\mu + \nu})}{[4\delta_o^2 + (2\mu + \nu)^2]^{3/2}}]\}$$

(e) Linear combination of 1s and 2s state one-parameter Hulthen type wave functions

$$\phi_1 = \psi_b$$

$$\phi_2 = \frac{1}{2\nu} [\frac{1}{2} (\frac{1}{\nu^2} - 4)]^{\frac{1}{2}} [e^{-(\frac{1}{2} - \nu)r} - e^{-\frac{1}{2}r}]$$

$$x [- (1 - \nu) + (1 + \nu) e^{-\nu r}]$$

$$S = \frac{2\mu}{\nu} [\frac{1}{2} (\frac{4}{\mu^2} - 1) (\frac{1}{\nu^2} - 4)]^{\frac{1}{2}}$$

$$x [\frac{2}{9 - \mu^2} - \frac{1 - \nu}{(3 - 2\nu)^2 - \mu^2} - \frac{1 + \nu}{(3 + 2\nu)^2 - \mu^2}$$

$$H_{11} = E_b$$

$$H_{22} = -\frac{1}{8}(1 - 4\nu^2)$$

$$+ \frac{\sqrt{3} + 2}{2\sqrt{3}} \frac{1 - 4\nu^2}{16\nu^4} \Big(\{ - 2(1 - \nu)^2 \ln(1 + \delta_s - 2\nu)$$

$$+ 8(1 - \nu) \ln(1 + \delta_s - \nu) - 4(3 - \nu^2) \ln(1 + \delta_s)$$

$$+ 8(1 + \nu) \ln(1 + \delta_s + \nu) - 2(1 + \nu)^2 \ln(1 + \delta_s + 2\nu)$$

$$- (7 - 4\sqrt{3}) \{ - (1 - \nu)^2 \ln[\delta_o{}^2 + (1 - 2\nu)^2]$$

$$+ 4(1 - \nu) \ln[\delta_o{}^2 + (1 - \nu)^2] - 2(3 - \nu^2) \ln(\delta_o{}^2 + 1)$$

$$+ 4(1 + \nu) \ln[\delta_o{}^2 + (1 + \nu)^2] - (1 + \nu)^2 \ln[\delta_o{}^2 + (1 + 2\nu)^2] \} \Big)$$

$$H_{12} = \frac{\mu}{4\nu}\left[\frac{1}{2}\left(\frac{4}{\mu^2} - 1\right)\left(\frac{1}{\nu^2} - 4\right)\right]^{\frac{1}{2}}$$

$$\times \left[\frac{2}{9 - \mu^2} - \frac{(1 - \nu)(1 - 2\nu)^2}{(3 - 2\nu)^2 - \mu^2} - \frac{(1 + \nu)(1 + 2\nu)^2}{(3 + 2\nu)^2 - \mu^2}\right]$$

$$+ \frac{\sqrt{3} + 2}{8\sqrt{3}} \frac{1}{\nu}\left[\frac{1}{2}\left(\frac{4}{\mu^2} - 1\right)\left(\frac{1}{\nu^2} - 4\right)\right]^{\frac{1}{2}}$$

$$\times \{2(1 - \nu) \ln \frac{3 + 2\delta_s - \mu - 2\nu}{3 + 2\delta_s + \mu - 2\nu} - 4\ln \frac{3 + 2\delta_s - \mu}{3 + 2\delta_s + \mu}$$

$$+ 2(1 + \nu) \ln \frac{3 + 2\delta_s - \mu + 2\nu}{3 + 2\delta_s + \mu + 2\nu}$$

$$- (7 - 4\sqrt{3})\left[(1 - \nu) \ln \frac{4\delta_o^2 + (3 - \mu - 2\nu)^2}{4\delta_o^2 + (3 + \mu - 2\nu)^2}\right.$$

$$- 2\ln \frac{4\delta_o^2 + (3 - \mu)^2}{4\delta_o^2 + (3 + \mu)^2}$$

$$\left. + (1 + \nu) \ln \frac{4\delta_o^2 + (3 - \mu + 2\nu)^2}{4\delta_o^2 + (3 + \mu + 2\nu)^2}\right]\}$$

(f) Linear combination of one-parameter 1s state Hulthen wave function and 1s state hydrogen-like wave function

$$\phi_1 = \psi_b$$

Replacing μ by ν in Eq. (5.6)

$$\phi_2 = \psi_a$$

$$S = 64\nu^{\frac{3}{2}} \left(\frac{4}{\mu^2} - 1\right)^{\frac{1}{2}} \frac{\mu(1+\nu)}{[4(1+\nu)^2 - \mu^2]^2}$$

$$H_{11} = E_b$$

Replacing μ by ν in Eq. (5.7)

$$H_{22} = E_a$$

$$H_{12} = -8\mu\nu^{\frac{5}{2}} \left(\frac{4}{\mu^2} - 1\right)^{\frac{1}{2}} \frac{(4 + 4\nu - \mu^2)}{[4(1+\nu)^2 - \mu^2]^2}$$

$$+ \frac{2(\sqrt{3}+2)}{\sqrt{3}} \nu^{\frac{3}{2}} \left(\frac{4}{\mu^2} - 1\right)^{\frac{1}{2}} \left(\frac{2\mu}{4(1+\delta_s+\nu)^2 - \mu^2} \right.$$

$$\left. - (7 - 4\sqrt{3}) \left\{ \frac{\cos\left(\tan^{-1} \frac{2\delta_o}{2 + 2\nu - \mu}\right)}{[4\delta_o^2 + (2 + 2\nu - \mu)^2]^{\frac{1}{2}}} - \frac{\cos\left(\tan^{-1} \frac{2\delta_o}{2 + 2\nu + \mu}\right)}{[4\delta_o^2 + (2 + 2\nu + \mu)^2]^{\frac{1}{2}}} \right\} \right)$$

(g) Linear combination of two-parameter 1s state Hulthen wave function and 1s state hydrogen-like wave function

$$\phi_1 = \psi_c$$

Replacing μ by ρ in Eq. (5.6)

$$\phi_2 = \psi_a$$

$$S = 64\mu\rho^{\frac{3}{2}} \left[\nu\left(\frac{4\nu^2}{\mu^2} - 1\right)\right]^{\frac{1}{2}} \frac{\rho + \nu}{\left[4(\rho + \nu)^2 - \mu^2\right]^2}$$

$$H_{11} = E_c$$

Replacing μ by ρ in Eq. (5.7)

$$H_{22} = E_a$$

$$H_{12} = -\,8\mu\rho^{\frac{5}{2}} \left[\nu\left(\frac{4\nu^2}{\mu^2} - 1\right)\right]^{\frac{1}{2}} \frac{(4\nu^2 - \mu^2 + 4\nu\rho)}{\left[4(\rho + \nu)^2 - \mu^2\right]^2}$$

$$+ \frac{2(\sqrt{3} + 2)}{\sqrt{3}}\, \rho^{\frac{3}{2}} \left[\nu\left(\frac{4\nu^2}{\mu^2} - 1\right)\right]^{\frac{1}{2}} \left(\frac{2\mu}{4(\delta_s + \rho + \nu)^2 - \mu^2} - (7 - 4\sqrt{3})\right.$$

$$\left. \times \left\{\frac{\cos\left(\tan^{-1}\frac{2\delta_o}{2\rho + 2\nu - \mu}\right)}{\left[4\delta_o^2 + (2\rho + 2\nu - \mu)^2\right]^{\frac{1}{2}}} - \frac{\cos\left(\tan^{-1}\frac{2\delta_o}{2\rho + 2\nu + \mu}\right)}{\left[4\delta_o^2 + (2\rho + 2\nu + \mu)^2\right]^{\frac{1}{2}}}\right\}\right)$$

5.3 Excited s States

It is usually difficult to estimate the energy of an excited state by means of a variational calculation. As pointed out earlier, the Baer potential has certain characteristics common with the SSC and ECSC potentials. For the latter two potentials, hydrogen-like wave functions and Hulthén wave functions have been found to give reasonable results. Hence for the Baer potential also we have used these two types of wave functions. Here we have only carried the calculations for the 2s, 3s and 4s states, but these can be extended to any higher s state through some lengthy calculation.

5.3.1 Hydrogenic Wave Function

The trial wave functions and their corresponding energy expressions of the 2s, 3s and 4s states are shown below.

2s state:

$$\psi_{2s} = \frac{\mu^{\frac{3}{2}}}{\sqrt{8}} e^{-\frac{\mu r}{2}} r(2 - \mu r) \qquad (5.38)$$

$$E_{2s} = -\frac{\mu^2}{8} + \frac{\sqrt{3}+2}{8\sqrt{3}}\mu^3\left\{\frac{2\delta_s^2+\mu^2}{(\delta_s+\mu)^4} - (7-4\sqrt{3})\right.$$

$$\left.\times\left[\frac{2\cos(2\theta)}{\delta_o^2+\mu^2} - \frac{4\mu\cos(3\theta)}{(\delta_o^2+\mu^2)^{\frac{3}{2}}} + \frac{3\mu^2\cos(4\theta)}{(\delta_o^2+\mu^2)^2}\right]\right\} \qquad (5.19)$$

where

$$\theta = \tan^{-1}\frac{\delta_o}{\mu}$$

3s state:

$$\psi_{3s} = \frac{2\mu}{81}\left(\frac{\mu}{3}\right)^{\frac{1}{2}} r\,(27 - 18\mu r + 2\mu^2 r^2)\, e^{-\frac{\mu r}{3}} \qquad (5.20)$$

$$E_{3s} = -\frac{\mu^2}{18} + \frac{2(\sqrt{3}+2)}{9\sqrt{3}}\mu^3\left\{\frac{243\delta_s^2 + 216\delta_2^2\mu^2 + 16\mu^4}{(3\delta_s+2\mu)^6}\right.$$

$$-(7-4\sqrt{3})\left[\frac{3\cos(2\theta)}{9\delta_o^2+4\mu^2} - \frac{24\mu\cos(3\theta)}{(9\delta_o^2+4\mu^2)^{\frac{3}{2}}}\right.$$

$$\left.\left.+\frac{96\mu^2\cos(4\theta)}{(9\delta_o^2+4\mu^2)^2} - \frac{192\mu^3\cos(5\theta)}{(9\delta_o^2+4\mu^2)^{\frac{5}{2}}} + \frac{160\mu^4\cos(6\theta)}{(9\delta_o^2+4\mu^2)^3}\right]\right\} \qquad (5.21)$$

where

$$\theta = \tan^{-1}\frac{3\delta_o}{2\mu}$$

4s state:

$$\psi_{4s} = \frac{\mu^{\frac{3}{2}}}{768} e^{-\frac{\mu}{4}r} r(192 - 144\mu r + 24\mu^2 r^2 - \mu^3 r^3) \qquad (5.22)$$

$$E_{4s} = -\frac{\mu^2}{32} + \frac{\sqrt{3}+2}{32\sqrt{3}}\mu^3 \{\frac{256\delta_s^6 + 288\delta_s^4\mu^2 + 48\delta_s^2\mu^4 + \mu^6}{(2\delta_s + \mu)^8}$$

$$- (7 - 4\sqrt{3})\left[\frac{4\cos(2\theta)}{4\delta_o^2 + \mu^2} - \frac{24\mu\cos(3\theta)}{(4\delta_o^2 + \mu^2)^{\frac{3}{2}}} + \frac{78\mu^2\cos(4\theta)}{(4\delta_o^2 + \mu^2)^2}\right.$$

$$- \frac{152\mu^3\cos(5\theta)}{(4\delta_o^2 + \mu^2)^{\frac{5}{2}}} + \frac{180\mu^4\cos(6\theta)}{(4\delta_o^2 + \mu^2)^3} - \frac{120\mu^5\cos(7\theta)}{(4\delta_o^2 + \mu^2)^{\frac{7}{2}}}$$

$$\left. + \frac{35\mu^6\cos(8\theta)}{(4\delta_o^2 + \mu^2)^4}\right]\} \qquad (5.23)$$

where

$$\theta = \frac{2\delta_o}{\mu}$$

5.3.2 Hulthén Type Wave Function

The trial wave functions and their corresponding energy expressions of the 2s, 3s and 4s states are shown below.

2s state:

$$\Psi_{2s} = \frac{1}{2\mu^2}\left[\frac{1}{2}(1 - 4\mu^2)\right]^{\frac{1}{2}}(1 - e^{-\mu r})\left[-(1 - \mu)\, e^{-(\frac{1}{2} - \mu)r} + (1 + \mu)\, e^{-\frac{r}{2}}\right] \tag{5.24}$$

$$\begin{aligned} E_{2s} = &-\frac{1}{8}(1 - 4\mu^2) + \frac{\sqrt{3} + 2}{16\sqrt{3}}\,\frac{(1 - 4\mu^2)}{\mu^4}\Big\{-(1 - \mu)^2 \ln(\delta_s + 1 - 2\mu) \\ &+ 4(1 - \mu)\ln(\delta_s + 1 - \mu) - 2(3 - \mu^2)\ln(\delta_s + 1) \\ &+ 4(1 + \mu)\ln(\delta_s + 1 + \mu) - (1 + \mu)^2 \ln(\delta_s + 1 + 2\mu) \\ &= \frac{1}{2}(7 - 4\sqrt{3})\Big((-(1 - \mu)^2 \ln[\delta_o^2 + (1 - 2\mu)^2] \\ &+ 4(1 - \mu)\ln[\delta_o^2 + (1 - \mu)^2] - 2(3 - \mu^2)\ln(\delta_o^2 + 1) \\ &+ 4(1 + \mu)\ln[\delta_o^2 + (1 + \mu)^2] - (1 + \mu)^2 \ln[\delta_o^2 + (1 + 2\mu)^2]\Big)\Big\} \end{aligned}$$

$$(\mu < \tfrac{1}{2}) \tag{5.25}$$

3s state:

$$\Psi_{3s} = \frac{1}{81\mu^3}\left[\frac{1}{3}(4 - 81\mu^2)\right]^{\frac{1}{2}} (1 - e^{-\mu r})\left[(1 - 3\mu)(2 - 3\mu)\, e^{-(\frac{1}{3} - \frac{3\mu}{2})r}\right.$$

$$\left. - (4 - 9\mu^2)\, e^{-(\frac{1}{3} - \frac{\mu}{2})r} + (1 + 3\mu)(2 + 3\mu)\, e^{-(\frac{1}{3} + \frac{\mu}{2})r}\right] \tag{5.26}$$

$$E = -\frac{1}{72}(4 - 81\mu^2)$$

$$+ \frac{\sqrt{3} + 2}{39366\sqrt{3}} \frac{(4 - 81\mu^2)}{\mu^6}\Big\{ - (1 - 3\mu)^2 (2 - 3\mu)^2 \ln(3\delta_s + 2 - 9\mu)$$

$$+ 6(1 - 3\mu)(2 - 3\mu)^2 \ln(3\delta_s + 2 - 6\mu)$$

$$- 3(2 - 3\mu)(10 - 15\mu - 18\mu^2) \ln(3\delta_s + 2 - 3\mu)$$

$$\pm 2(4 - 9\mu^2)(10 - 9\mu^2) \ln(3\delta_s + 2)$$

$$- 3(2 + 3\mu)(10 + 15\mu - 18\mu^2) \ln(3\delta_s + 2 + 3\mu)$$

$$+ 6(1 + 3\mu)(2 + 3\mu)^2 \ln(3\delta_s + 2 + 6\mu)$$

$$- (1 + 3\mu)^2 (2 + 3\mu)^2 \ln(3\delta_s + 2 + 9\mu)$$

$$- \frac{1}{2}(7 - 4\sqrt{3})\Big(- (1 - 3\mu)^2 (2 - 3\mu)^2 \ln[9\delta_o^2 + (2 - 9\mu)^2]$$

$$+ 6(1 - 3\mu)(2 - 3\mu)^2 \ell n[9\delta_0^2 + (2 - 6\mu)^2]$$

$$- 3(2 - 3\mu)(10 - 15\mu - 18\mu^2) \ell n[9\delta_0^2 + (2 - 3\mu)^2]$$

$$+ 2(4 - 9\mu^2)(10 - 9\mu^2) \ell n[9\delta_0^2 + 4]$$

$$- 3(2 + 3\mu)(10 + 15\mu - 18\mu^2) \ell n[9\delta_0^2 + (2 + 3\mu)^2]$$

$$+ 6(1 + 3\mu)(2 + 3\mu)^2 \ell n[9\delta_0^2 + (2 + 6\mu)^2]$$

$$- (1 + 3\mu)^2 (2 + 3\mu)^2 \ell n[9\delta_0^2 + (2 + 9\mu)^2]\Big)\Big\}$$

$$(\mu < \tfrac{2}{9}) \qquad (5.27)$$

4s state:

$$\Psi_{4s} = \frac{1}{768\mu^4} (1 - 64\mu^2)^{\frac{1}{2}} (1 - e^{-\mu r})$$

$$[- (1 - 6\mu)(1 - 4\mu)(1 - 2\mu)\, e^{-(\frac{1}{4} - 2\mu)r}$$

$$+ 3(1 - 4\mu)(1 - 4\mu^2)\, e^{-(\frac{1}{4} - \mu)r}$$

$$= 3(1 + 4\mu)(1 - 4\mu^2)\, e^{-\frac{1}{4}r}$$

$$+ (1 + 6\mu)(1 + 4\mu)(1 + 2\mu)\, e^{-(\frac{1}{4} + \mu)r} \qquad (5.28)$$

$$E_{4s} = \frac{\sqrt{3}+2}{1179648\sqrt{3}} \frac{1-64\mu^2}{\mu^8}$$

$$\Big\{ -(1-2\mu)^2 (1-4\mu)^2 (1-6\mu)^2 \ln(2\delta_s + 1 - 8\mu)$$

$$+ 8(1-2\mu)^2 (1-4\mu)^2 (1-6\mu) \ln(2\delta_s + 1 - 6\mu)$$

$$- 4(1-2\mu)^2 (1-4\mu)(7 - 28\mu - 36\mu^2) \ln(2\delta_s + 1 - 4\mu)$$

$$+ 8(1-4\mu)(1-4\mu^2)(7 - 14\mu - 24\mu^2) \ln(2\delta_s + 1 - 2\mu)$$

$$- 2(1-4\mu^2)(35 - 380\mu^2 + 576\mu^4) \ln(2\delta_s + 1)$$

$$+ 8(1+4\mu)(1-4\mu^2)(7 + 14\mu - 24\mu^2) \ln(2\delta_s + 1 + 2\mu)$$

$$- 4(1+2\mu)^2 (1+4\mu)(7 + 28\mu - 36\mu^2) \ln(2\delta_s + 1 + 4\mu)$$

$$+ 8(1+2\mu)^2 (1+4\mu)^2 (1+6\mu) \ln(2\delta_s + 1 + 6\mu)$$

$$- (1+2\mu)^2 (1+4\mu)^2 (1+6\mu)^2 \ln(2\delta_s + 1 + 8\mu)$$

$$
\begin{aligned}
&-\frac{1}{2}(7-4\sqrt{3})\\
&\Big\{-(1-2\mu)^2(1-4\mu)^2(1-6\mu)^2\,\ell n[4\delta_o{}^2+(1-8\mu)^2]\\
&+8(1-2\mu)^2(1-4\mu)^2(1-6\mu)\,\ell n[4\delta_o{}^2+(1-6\mu)^2]\\
&-4(1-2\mu)^2(1-4\mu)(7-28\mu-36\mu^2)\,\ell n[4\delta_o{}^2+(1-4\mu)^2]\\
&+8(1-4\mu)(1-4\mu^2)(7-14\mu-24\mu^2)\,\ell n[4\delta_o{}^2+(1-2\mu)^2]\\
&-2(1-4\mu^2)(35-380\mu^2+576\mu^4)\,\ell n[4\delta_o{}^2+1]\\
&+8(1+4\mu)(1-4\mu^2)(7+14\mu-24\mu^2)\,\ell n[4\delta_o{}^2+(1+2\mu)^2]\\
&-4(1+2\mu)^2(1+4\mu)(7+28\mu-36\mu^2)\,\ell n[4\delta_o{}^2+(1+4\mu)^2]\\
&+8(1+2\mu)^2(1+4\mu)^2(1+6\mu)\,\ell n[4\delta_o{}^2+(1+6\mu)^2]\\
&-(1+2\mu)^2(1+4\mu)^2(1+6\mu)^2\,\ell n[4\delta_o{}^2+(1+8\mu)^2]\Big)\Big\}
\end{aligned}
$$

$$(\mu < \tfrac{1}{8}) \qquad (5.29)$$

5.4 Results and Discussion

The energy eigenvalues of 1s to 4s states of the Baer potential can be determined by optimizing the energy expressions with respect to the variational parameters. In the case of one parameter trial wave functions, the minimum of energy is accurately obtained by bisectional method, in which the location of the minimum is determined at a value of μ such that $\frac{dE}{d\mu} \leq 10^{-10}$. In the case of multi-parameter trial wave functions in the ground state, the direct search method due to Hooke and Jeeves (1961) (also see Wilde 1964, and Kawalik and Osborne 1968) was employed for the same purpose. In Tables 5.1-5.7, the results from the seven respective approximate wave functions for the ground state are shown. For the purpose of comparison, we list energy values from these approximate wave functions in Table 5.8. Tables 5.9-5.14 show the results for excited states.

The ground state energies listed in the Tables 5.1-5.8 are only the upper bound of the true energy in the Baer potential. To five places of decimal all seven calculations yield identical results below $\delta = 0.025$. If the complete range of screening is considered, the two-parameter Hulthén type trial wave function is the best in the simple wave function group and the calculation (g) of the linear combination of the hydrogen-like 1s wave function and the two-parameter Hulthén wave function is the best of all seven calculations.

Hydrogen-like wave functions (case (a) and (d)) give poor results. Below $\delta = 0.25$, all other five calculations involving Hulthén type trial wave function produce the identical energies. The calculation (c) of the two-parameter Hulthén wave function places highly in the third behind the calculations (f) and (g). However the effort of getting the results from a simple variational wave function is much less than those from a linear variation wave function.

The calculation (c) using the two-parameter Hulthén wave function provides a simple way to determine the critical screening of the Baer potential. By definition of the critical screening, $E_c = 0$. From Eq. (5.12) this results $\mu = 2\nu$. But we know $\frac{\partial E_c}{\partial \nu} = 0$ for a variational calculation. Taking the derivative from Eq. (5.11) and then substituting $\mu = 2\nu$, we have

$$\frac{\partial E_c}{\partial \nu} = 0$$

$$= -\nu + \frac{2(\sqrt{3}+2)}{\sqrt{3}} \{ -2\ell n\delta_s + 4\ell n(\delta_s + 2\nu)$$

$$- 2\ell n(\delta_s + 4\nu) - (7 - 4\sqrt{3}) [-\ell n\delta_o^2$$

$$+ 2\ell n(\delta_o^2 + 4\nu^2) - \ell n(\delta_o^2 + 16\nu^2)] \} \qquad (5.30)$$

By alternate iterations with respect to δ and ν, we obtained

$$\delta_c = 0.7212 \qquad \text{at} \qquad \nu = 0.718 \tag{5.31}$$

This value of δ_c may be considered as a lower limit of the critical screening.

For the three calculated excited states, the hydrogen-like wave functions yield energies deeper than that of the Hulthén values. The accuracy of the calculation for an excited state here can be justified as follows:

(1) The orthogonality of the wave functions with the given optimized parameters - both hydrogen-like and Hulthen type excited state wave functions are not orthogonal respectively to their eigenfunctions of the corresponding lower states, but the Hulthén type wave functions are more closer to being orthogonal than the hydrogen-like wave functions are.

(2) In Fig. 5.1 and 5.2, we show the variations of Coulomb potential, Hulthén potential and Baer potential with r for $\delta = 0.1$ and $\delta = 0.4$. It is obvious that Hulthén potential is a closer approximation to the Baer potential than the Coulomb potential.

(3) As an indirect justification, in the case of the SSCP, the hydrogen-like wave function also produces deeper energy values of an excited state than the Hulthén values. With the help of the numerical

values from Rogers et al. (1970), we have shown that the Hulthén wave function is the better one between the two.

Therefore, it would be reasonable to infer that the Hulthén type wave function yields better energy values for an excited state for the Baer potential. Of course, a definite answer on this can only be obtained by the exact values of energies from the numerical solution of the Schrödinger equation.

Table 5.1 : Energy eigenvalues of the ground state of the Baer potential from the trial wave function (a)

Screening parameter	Optimized parameter	Energy
0.001	1.00000	0.4982215
0.002	0.99999	0.4964475
0.0025	0.99999	0.4955622
0.003	0.99998	0.4946780
0.004	0.99996	0.4929129
0.005	0.99994	0.4911522
0.006	0.99992	0.4893960
0.007	0.99989	0.4876442
0.008	0.99986	0.4858968
0.009	0.99982	0.4841538
0.01	0.99978	0.4824152
0.02	0.99914	0.4652664
0.025	0.99866	0.4568515
0.03	0.99809	0.4485408
0.04	0.99667	0.4322262
0.05	0.99489	0.4163116
0.06	0.99276	0.4007864
0.07	0.99031	0.3856409
0.08	0.98753	0.3708659
0.09	0.98445	0.3564528

Table 5.1 (cont'd)

Screening parameter	Optimized parameter	Energy
0.1	0.98106	0.3423936
0.2	0.93217	0.2197683
0.25	0.89795	0.1696162
0.3	0.85695	0.1262115
0.4	0.74986	0.0583144
0.5	0.58057	0.0014846
0.6	0.22918	-0.0007053

Table 5.2 : Energy eigenvalues of the ground state of the Baer potential from the trial wave function (b)

Screening parameter	Optimized parameter	Energy
0.001	0.00010	0.4982215
0.002	0.00010	0.4964475
0.0025	0.01043	0.4955622
0.003	0.01266	0.4946780
0.004	0.01687	0.4929129
0.005	0.02108	0.4911522
0.006	0.02527	0.4893960
0.007	0.02945	0.4876442
0.008	0.03362	0.4858968
0.009	0.03778	0.4841538
0.01	0.04193	0.4824152
0.02	0.08292	0.4652666
0.025	0.10309	0.4568518
0.03	0.12306	0.4485414
0.04	0.16243	0.4322279
0.05	0.20108	0.4163155
0.06	0.23908	0.4007941
0.07	0.27647	0.3856546
0.08	0.31330	0.3708882
0.09	0.34962	0.3564869

Table 5.2 (cont'd)

Screening parameter	Optimized parameter	Energy
0.1	0.38545	0.3424433
0.2	0.72380	0.2203173
0.25	0.88382	0.1707741
0.3	1.04071	0.1283275
0.4	1.35125	0.0637165
0.5	1.63882	0.0247700
0.6	1.83660	0.0060622
0.7	1.98416	0.0000573

Table 5.3 : Energy eigenvalues of the ground state of the Baer potential from the trial wave function (c)

Screening parameter	Optimized parameter μ	ν	Energy
0.001	0.00571	1.00000	0.4982215
0.002	0.00762	1.00000	0.4964475
0.0025	0.00981	1.00000	0.4955622
0.003	0.01243	1.00000	0.4946780
0.004	0.01682	1.00000	0.4929129
0.005	0.02103	1.00000	0.4911522
0.006	0.02521	1.00000	0.4893960
0.007	0.02937	1.00000	0.4876442
0.008	0.03352	1.00000	0.4858968
0.009	0.03766	1.00000	0.4841538
0.01	0.04178	1.00000	0.4824152
0.02	0.08235	0.99998	0.4652666
0.025	0.10221	0.99997	0.4568518
0.03	0.12183	0.99995	0.4485414
0.04	0.16031	0.99989	0.4322279
0.05	0.19784	0.99978	0.4163155
0.06	0.23456	0.99965	0.4007941
0.07	0.27058	0.99947	0.3856546
0.08	0.30593	0.99925	0.3708882
0.09	0.34067	0.99898	0.3564870

Table 5.3 (cont'd)

Screening parameter	Optimized parameter μ	Optimized parameter ν	Energy
0.1	0.37486	0.99868	0.3424435
0.2	0.69483	0.99349	0.2203217
0.25	0.84606	0.98987	0.1707837
0.3	0.99567	0.98613	0.1283435
0.4	1.29790	0.97977	0.0637406
0.5	1.54933	0.96049	0.0248235
0.6	1.57526	0.87646	0.0062897
0.7	1.46369	0.74757	0.0001717

Table 5.4 : Energy eigenvalues of the ground state of the Baer potential from the trial wave function (d)

Screening parameter	Optimized parameter μ	ν	Energy
0.001	1.00000	1.52219	0.4982215
0.002	1.00000	1.52300	0.4964475
0.0025	1.00000	1.52336	0.4955622
0.003	1.00000	1.52340	0.4946780
0.004	1.00000	1.52391	0.4929129
0.005	1.00000	1.52435	0.4911522
0.006	1.00002	1.56542	0.4893960
0.007	1.00002	1.55563	0.4876442
0.008	1.00002	1.54928	0.4858968
0.009	1.00004	1.56251	0.4841538
0.01	1.00005	1.55633	0.4824152
0.02	1.00031	1.59955	0.4652666
0.025	1.00041	1.58680	0.4568518
0.03	1.00053	1.58037	0.4485413
0.04	1.00085	1.57451	0.4322278
0.05	1.00199	1.60811	0.4163153
0.06	1.00289	1.61082	0.4007937
0.07	1.00254	1.57740	0.3856536
0.08	1.00563	1.62137	0.3708870
0.09	1.00776	1.63033	0.3564854

Table 5.4 (cont'd)

Screening parameter	Optimized parameter μ	ν	Energy
0.1	1.01914	1.71532	0.3424423
0.2	1.09700	1.77223	0.2203223
0.25	1.09216	1.67378	0.1707823
0.3	1.07578	1.55855	0.1283334
0.4	1.00922	1.28631	0.0636564
0.5	0.90715	1.01074	0.0246484
0.6	0.80000	0.82903	0.0061579

Table 5.5 : Energy eigenvalues of the ground state of the Baer potential from the trial wave function (e)

Screening parameter	Optimized parameter μ	Optimized parameter ν	Energy
0.001	0.01156	0.37952	0.4982215
0.002	0.01179	0.37950	0.4964475
0.0025	0.01184	0.37967	0.4955622
0.003	0.01298	0.37975	0.4946780
0.004	0.01700	0.38414	0.4929129
0.005	0.02105	0.37569	0.4911522
0.006	0.02522	0.38269	0.4893960
0.007	0.02944	0.39344	0.4876442
0.008	0.03362	0.39397	0.4858968
0.009	0.03777	0.39185	0.4841538
0.01	0.04195	0.39828	0.4824152
0.02	0.08299	0.38787	0.4652666
0.025	0.11034	0.38244	0.4568518
0.03	0.14322	0.38170	0.4485414
0.04	0.16264	0.40184	0.4322279
0.05	0.20140	0.39322	0.4163155
0.06	0.23949	0.40356	0.4007941
0.07	0.27701	0.40446	0.3856546
0.08	0.31398	0.40537	0.3708882
0.09	0.35042	0.39206	0.3564869

Table 5.5 (cont'd)

Screening parameter	Optimized parameter μ	ν	Energy
0.1	0.38637	0.37412	0.3424433
0.2	0.72592	0.42021	0.2203178
0.25	0.88627	0.42212	0.1707750
0.3	1.04320	0.43554	0.1283286
0.4	1.35377	0.45140	0.0637178
0.5	1.64263	0.48533	0.0247743
0.6	1.82976	0.39726	0.0061351
0.7	1.97503	0.48030	0.0001160

Table 5.6 : Energy eigenvalues of the ground state of the Baer potential from the trial wave function (f)

Screening parameter	Optimized parameter μ	ν	Energy
0.001	0.29861	1.00000	0.4982215
0.002	0.29480	1.00000	0.4964475
0.0025	0.30626	1.00000	0.4955622
0.003	0.29820	1.00000	0.4946780
0.004	0.29573	1.00000	0.4929129
0.005	0.30017	1.00000	0.4911522
0.006	0.30528	1.00000	0.4893960
0.007	0.30029	1.00000	0.4876442
0.008	0.29933	1.00000	0.4858968
0.009	0.30007	1.00000	0.4841538
0.01	0.30173	0.99999	0.4824152
0.02	0.29081	0.99997	0.4652666
0.025	0.29044	0.99994	0.4568518
0.03	0.29017	0.99990	0.4485414
0.04	0.28955	0.99976	0.4322279
0.05	0.28919	0.99950	0.4163155
0.06	0.28861	0.99883	0.4007941
0.07	0.30271	0.99724	0.3856546
0.08	0.33337	0.99511	0.3708882
0.09	0.35482	0.98685	0.3564870

Table 5.6 (cont'd)

Screening parameter	Optimized parameter μ	Optimized parameter ν	Energy
0.1	0.41102	0.99188	0.3424435
0.2	0.62851	1.01271	0.2203229
0.25	0.80584	1.02944	0.1707859
0.3	1.01053	0.64362	0.1283455
0.4	1.30435	0.41387	0.0637421
0.5	1.57840	0.28107	0.0248855
0.6	1.77672	0.21999	0.0067108
0.7	1.96652	0.18685	0.0003367

Table 5.7 : Energy eigenvalues of the ground state of the Baer potential from the trial wave function (g)

Screening parameter	Optimized parameter μ	ν	ρ	Energy
0.001	0.34723	1.00515	1.00000	0.4982215
0.002	0.34534	1.00083	1.00000	0.4964475
0.0025	0.34128	0.99929	1.00000	0.4955622
0.003	0.31171	1.00023	1.00000	0.4946780
0.004	0.32684	0.99956	1.00000	0.4929129
0.005	0.32609	0.99948	1.00000	0.4911522
0.006	0.32546	0.99954	1.00000	0.4893960
0.007	0.32398	0.99943	1.00000	0.4876442
0.008	0.31075	0.99958	1.00000	0.4858968
0.009	0.31023	0.99958	1.00000	0.4841538
0.01	0.31306	0.99960	1.00000	0.4824152
0.02	0.34777	0.99935	0.99999	0.4652666
0.025	0.35010	0.99949	0.99997	0.4568518
0.03	0.34521	0.99959	0.99994	0.4485414
0.04	0.37492	1.00104	0.99953	0.4322279
0.05	0.30165	0.99125	1.00509	0.4163155
0.06	0.24788	0.99957	1.00022	0.4007941
0.07	0.27153	0.99945	1.00344	0.3856546
0.08	0.33214	0.99984	0.99586	0.3708882
0.09	0.37770	1.00045	0.99251	0.3564870

Table 5.7 (cont'd)

Screening parameter	Optimized parameter μ	ν	ρ	Energy
0.1	0.39199	1.03451	0.89605	0.3424436
0.2	0.65538	1.06637	0.74047	0.2203230
0.25	0.79396	1.06112	0.65588	0.1707860
0.3	0.86031	1.08673	0.58152	0.1283457
0.4	1.29210	0.99883	0.38878	0.0637422
0.5	1.57158	1.05405	0.26894	0.0248963
0.6	2.01740	1.11593	0.24257	0.0067656
0.7	2.15404	1.09281	0.19271	0.0003442

Table 5.8 : Energy eigenvalues of the ground state of the Baer potential from the approximate wave function (a) - (g)

Screening parameter	Energy (a)	(b)	(c)	(d)	(e)	(f)	(g)
0.001	0.4982215	0.4982215	0.4982215	0.4982215	0.4982215	0.4982215	0.4982215
0.002	0.4964475	0.4964475	0.4964475	0.4964475	0.4964475	0.4964475	0.4964475
0.0025	0.4955622	0.4955622	0.4955622	0.4955622	0.4955622	0.4955622	0.4955622
0.003	0.4946780	0.4946780	0.4946780	0.4946780	0.4946780	0.4946780	0.4946780
0.004	0.4929129	0.4929129	0.4929129	0.4929129	0.4929129	0.4929129	0.4929129
0.005	0.4911522	0.4911522	0.4911522	0.4911522	0.4911522	0.4911522	0.4911522
0.006	0.4893960	0.4893960	0.4893960	0.4893960	0.4893960	0.4893960	0.4893960
0.007	0.4876442	0.4876442	0.4876442	0.4876442	0.4876442	0.4876442	0.4876442
0.008	0.4858968	0.4858968	0.4858968	0.4858968	0.4858968	0.4858968	0.4858968
0.009	0.4841538	0.4841538	0.4841538	0.4841538	0.4841538	0.4841538	0.4841538
0.01	0.4824152	0.4824152	0.4824152	0.4824152	0.4824152	0.4824152	0.4824152
0.02	0.4652664	0.4652666	0.4652666	0.4652666	0.4652666	0.4652666	0.4652666
0.025	0.4568515	0.4568518	0.4568518	0.4568518	0.4568518	0.4568518	0.4568518
0.03	0.4485408	0.4485414	0.4485414	0.4485413	0.4485414	0.4485414	0.4485414
0.04	0.4322262	0.4322279	0.4322279	0.4322278	0.4322279	0.4322279	0.4322279
0.05	0.4163116	0.4163155	0.4163155	0.4163153	0.4163155	0.4163155	0.4163155
0.06	0.4007864	0.4007941	0.4007941	0.4007937	0.4007941	0.4007941	0.4007941

Table 5.8 (cont'd)

Screening parameter	Energy (a)	(b)	(c)	(d)	(e)	(f)	(g)
0.07	0.3856409	0.3856546	0.3856546	0.3856536	0.3856546	0.3856546	0.3856546
0.08	0.3708659	0.3708882	0.3708882	0.3708870	0.3708882	0.3708882	0.3708882
0.09	0.3564528	0.3564869	0.3564870	0.3564854	0.3564869	0.3564870	0.3564870
0.1	0.3423936	0.3424433	0.3424435	0.3424423	0.3424433	0.3424435	0.3424436
0.2	0.2197683	0.2203173	0.2203217	0.2203223	0.2203178	0.2203229	0.2203230
0.25	0.1696162	0.1707741	0.1707837	0.1707823	0.1707750	0.1707859	0.1707860
0.3	0.1262115	0.1283275	0.1283435	0.1283334	0.1283286	0.1283455	0.1283457
0.4	0.0583144	0.0637165	0.0637406	0.0636564	0.0637178	0.0637421	0.0637422
0.5	0.0014846	0.0247700	0.0248235	0.0246484	0.0247743	0.0248855	0.0248963
0.6	-0.0007053	0.0060622	0.0062897	0.0060579	0.0061351	0.0067108	0.0067656
0.7		0.0000573	0.0001717		0.0001160	0.0003367	0.0003442

Table 5.9 : Energies of 2s state of the Baer potential from variational calculation with hydrogenic wave function as the trial function

Screening parameter	Optimized parameter	Energy
0.001	0.99996	0.1232282
0.002	0.99986	0.1214742
0.0025	0.99978	0.1206039
0.003	0.99968	0.1197379
0.004	0.99944	0.1180189
0.005	0.99913	0.1163172
0.006	0.99876	0.1146325
0.007	0.99832	0.1129647
0.008	0.99782	0.1113136
0.009	0.99726	0.1096791
0.01	0.99664	0.1080610
0.02	0.98729	0.0927491
0.025	0.98061	0.0856597
0.03	0.97268	0.0789289
0.04	0.95323	0.0664942
0.05	0.92908	0.0553603
0.06	0.90016	0.0454588
0.07	0.86618	0.0367351
0.08	0.82652	0.0291473
0.09	0.78011	0.0226662
0.1	0.72501	0.0172775
0.2	0.33297	0.0036501

Table 5.10 : Energies of 2s state of the Baer potential from variational calculation with Hulthen wave function as the trial function

Screening parameter	Optimized parameter	Energy
0.001	0.00802	0.1232282
0.002	0.01099	0.1214742
0.0025	0.01099	0.1206039
0.003	0.01099	0.1197379
0.004	0.01661	0.1180189
0.005	0.02081	0.1163172
0.006	0.02488	0.1146325
0.007	0.02892	0.1129647
0.008	0.03294	0.1113136
0.009	0.03693	0.1096790
0.01	0.04089	0.1080609
0.02	0.07919	0.0927472
0.025	0.09755	0.0856552
0.03	0.11545	0.0789198
0.04	0.15003	0.0664673
0.05	0.18325	0.0552979
0.06	0.21532	0.0453354
0.07	0.24649	0.0365162
0.08	0.27695	0.0287878
0.09	0.30696	0.0221085
0.1	0.33681	0.0164481
0.2	0.49615	0.0000215

Table 5.11 : Energies of 3s state of the Baer potential from variational calculation with hydrogenic wave function as the trial function

Screening parameter	Optimized parameter	Energy
0.001	0.99982	0.0537949
0.002	0.99929	0.0520738
0.0025	0.99890	0.0512277
0.003	0.99843	0.0503912
0.004	0.99726	0.0487465
0.005	0.99577	0.0471388
0.006	0.99398	0.0455673
0.007	0.99191	0.0440313
0.008	0.98956	0.0425301
0.009	0.98694	0.0410632
0.01	0.98404	0.0396298
0.02	0.94132	0.0270342
0.025	0.91080	0.0218383
0.03	0.87389	0.0173239
0.04	0.77717	0.0102348
0.05	0.63191	0.0056572
0.06	0.40331	0.0036615
0.07	0.34580	0.0030331
0.08	0.34231	0.0025340
0.09	0.34775	0.0020261
0.1	0.35490	0.0014899

Table 5.12 : Energies of 3s state of the Baer potential from variational calculation with Hulthen wave function as the trial function

Screening parameter	Optimized parameter	Energy
0.001	0.00867	0.0537948
0.002	0.01008	0.0520732
0.0025	0.01295	0.0512276
0.003	0.01438	0.0503911
0.004	0.01495	0.0487464
0.005	0.02038	0.0471386
0.006	0.02433	0.0455669
0.007	0.02817	0.0440307
0.008	0.03198	0.0425291
0.009	0.03573	0.0410616
0.01	0.03945	0.0396276
0.02	0.07452	0.0270045
0.025	0.09088	0.0217716
0.03	0.10664	0.0171950
0.04	0.13682	0.0098703
0.05	0.16631	0.0048243
0.06	0.19617	0.0020036
0.07	0.20933	0.0009202
0.08	0.21375	0.0004116
0.09	0.21704	0.0001329
0.1	0.22080	0.0000076

Table 5.13 : Energies of 4s state of the Baer potential from variational calculation with hydrogenic wave function as the trial function

Screening parameter	Optimized parameter	Energy
0.001	0.99944	0.0295015
0.002	0.99782	0.0278286
0.0025	0.99663	0.0270155
0.003	0.99520	0.0262188
0.004	0.99166	0.0246731
0.005	0.98722	0.0231893
0.006	0.98194	0.0217655
0.007	0.97584	0.0204000
0.008	0.96894	0.0190911
0.009	0.96126	0.0178375
0.01	0.95281	0.0166376
0.02	0.82347	0.0073767
0.025	0.71844	0.0044790
0.03	0.55266	0.0027092
0.04	0.33168	0.0017537
0.05	0.33721	0.0012497
0.06	0.34840	0.0006903

Table 5.14 : Energies of 4s state of the Baer potential from variational calculation with Hulthen wave function as the trial function

Screening parameter	Optimized parameter	Energy
0.001	0.01706	0.0295013
0.002	0.01606	0.0278263
0.0025	0.01706	0.0270131
0.003	0.02000	0.0262169
0.004	0.01901	0.0246717
0.005	0.02075	0.0231881
0.006	0.02376	0.0217636
0.007	0.02722	0.0203967
0.008	0.03084	0.0190857
0.009	0.03433	0.0178291
0.01	0.03778	0.0160254
0.02	0.06965	0.0072278
0.025	0.08440	0.0041452
0.03	0.09911	0.0020468
0.04	0.11877	0.0005390
0.05	0.12123	0.0001795
0.06	0.12357	0.0000140

Chapter 6 - General Expressions in the Perturbation and Variational Calculations for the General Screened Coulomb Potential

6.1 Introduction

We have studied the static screened Coulomb potential (SSCP), the exponential cosine screened Coulomb potential (ECSC) and the Baer potential in the previous chapters. In atomic units they have the forms respectively

$$V(r) = \frac{e^{-\delta r}}{r} \tag{6.1}$$

$$V(r) = \frac{e^{-\delta r}}{r} \cos \delta r \tag{6.2}$$

$$V(r) = \frac{\sqrt{3}+2}{2\sqrt{3}} \frac{1}{r} [e^{-\delta_s r} - (7 - 4\sqrt{3}) \cos \delta_o r] \tag{6.3}$$

where

$$\delta_s = (\sqrt{3} + 1)^{\frac{1}{2}}$$

$$\delta_o = (\sqrt{3} - 1)^{\frac{1}{2}}$$

It is interesting to note that all three potentials contain a screening factor δ. In Figs. 6.1 and 6.2, we have plotted the variation of these potentials with r at $\delta = 0.1$ and $\delta = 0.4$ respectively. They all decay with δr. The SSCP shows the monotonically decreasing with

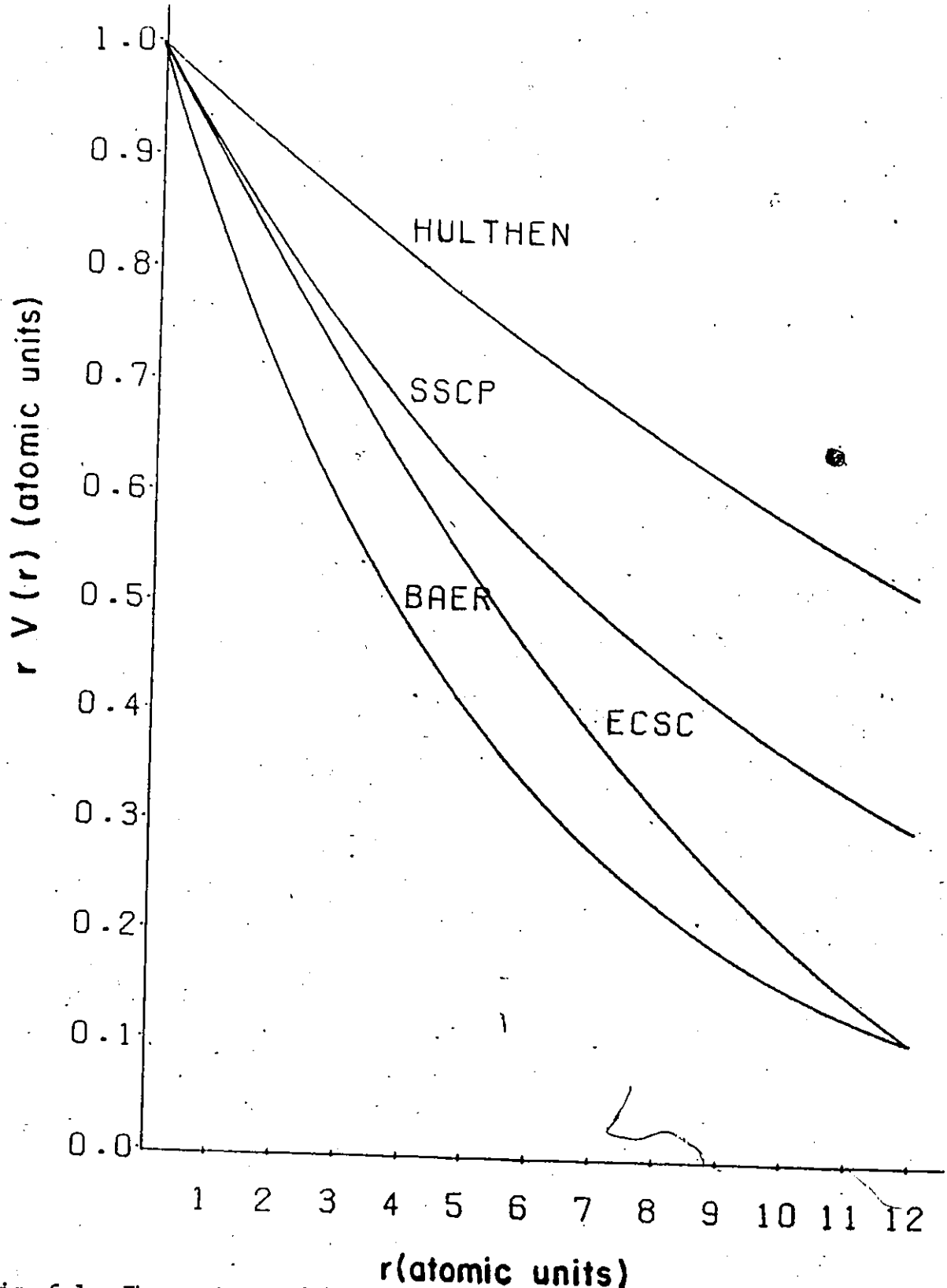

Fig. 6.1 : The product rV(r) as a function of r for the Hulthén potential, the SSCP, the ECSC potential and the Baer potential for $\delta = 0.1$

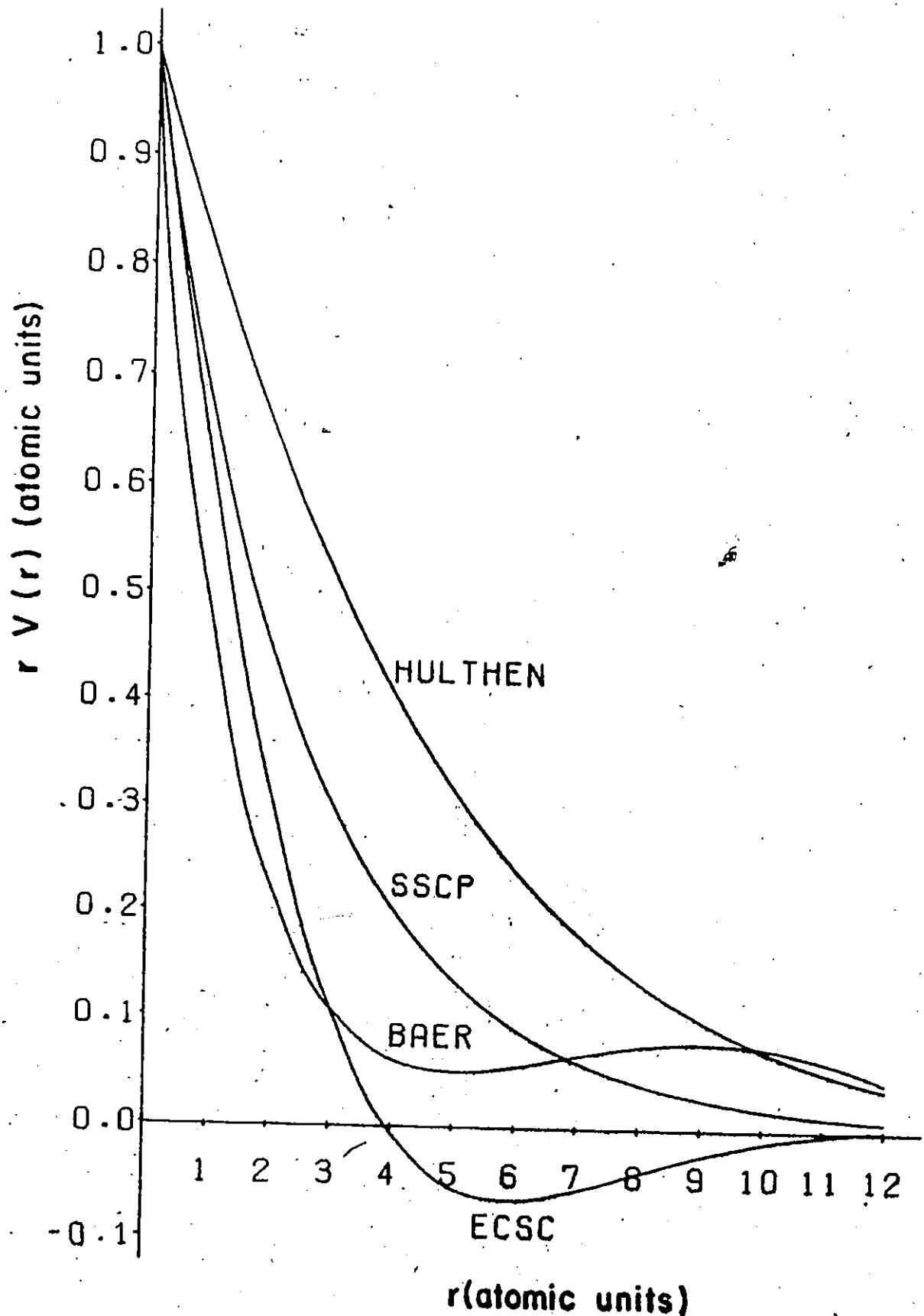

Fig. 6.2 : The product rV(r) as a function of r, for the Hulthén potential, the SSCP, the ECSC potential and the Baer potential for $\delta = 0.4$

δr while the ECSC and Baer potentialsshave the oscillatory behavior at large δr. In the limiting case of $\delta \to 0$, they all tend to a Coulomb potential. In this chapter we write them in a general form,

$$V(r) = c_1 \frac{e^{-a_1 \delta r}}{r} + c_2 \frac{e^{-a_2 \delta r}}{r} \cos a_2 \delta r \qquad (6.4)$$

and call it a general screened Coulomb potential. For a particular potential in Eq. (6.1) to Eq. (6.3), the constants a's and c's can be determined by comparing Eq. (6.4) with the one in the problem. For instance, for the SSCP we should have $c_1 = 1$, $a_1 = 1$ and $c_2 = a_2 = 0$.

It is our intention to develop some general expressions for the energy of s states with Hulthén potential as a first approximation. In this chapter we shall carry out perturbation calculation in section 2 and variational calculation with one-parameter and two-parameter Hulthén type wave functions in section 3. The discussion in section 4 concludes this chapter.

6.2 Perturbation Calculation

When Hulthén potential is chosen as an unperturbed potential, the perturbation to the general screened Coulomb potential takes the form of

$$U(r) = c_1 \frac{e^{-a_1 \delta r}}{r} + c_2 \frac{e^{-a_2 \delta r}}{r} \cos a_2 \delta r - \frac{e^{-\delta r}}{1 - e^{-\delta r}} \qquad (6.5)$$

The unperturbed energy eigenvalues for s states (Appendix A) are given by

$$E_n^{(o)} = \frac{1}{8}\left(\frac{2}{n} - n\delta\right)^2 \tag{6.6}$$

and the unperturbed eigenfunctions for s states (Appendix A) are

$$\Psi_n(r) = \left[\frac{n}{4}\left(\frac{4}{n^2} - n^2\delta^2\right)\right]^{\frac{1}{2}} e^{-\frac{1}{2}\left(\frac{2}{n} - n\delta\right)r} \sum_{k=1}^{n} f_k \left(1 - e^{-\delta r}\right)^k \tag{6.7}$$

where

$$f_k = (-1)^{k-1} \binom{n-1}{k-1} \binom{k + \frac{2}{n\delta} - 1}{k}$$

The first order energy correction are

$$\Delta E_n^{(1)} = \langle \Psi_n(r) | U(r) | \Psi_n(r) \rangle$$

$$= c_1 \langle \Psi_n(r) | \frac{e^{-a_1\delta r}}{r} | \Psi_n(r) \rangle + c_2 \langle \Psi_n(r) | \frac{e^{-a_2\delta r}}{r} \cos a_2\delta r | \Psi_n(r) \rangle$$

$$+ \langle \Psi_n(r) | \frac{e^{-\delta r}}{1 - e^{-\delta r}} | \Psi_n(r) \rangle$$

By substituting Eq. (6.7) into the above integrals and after some lengthy calculations, we have the final expression for the perturbation energy of a s state

$$\Delta E_n^{(1)} = \frac{c_1 n}{4}\left(\frac{4}{n^2} - n^2 a_1^2 n^2\right)$$

$$\times \sum_{i=1}^{2n-1} d_i \left\{ \sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \left[\ell n\left(\frac{2}{n} - n a_1 \delta + j a_1 \delta + a_1 \delta\right) \right.\right.$$

$$\left.\left. - \ell n\left(\frac{2}{n} - n a_1 \delta + j a_1 \delta\right)\right]\right\}$$

$$+ \frac{c_2 n}{8}\left(\frac{4}{n^2} - n^2 a_2^2 \delta^2\right)$$

$$\times \sum_{i=1}^{2n-1} d_i \left\{ \sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \left(\ell n\left[a_2^2 \delta^2 + \left(\frac{2}{n} + a_2 \delta - n a_2 \delta + j a_2 \delta\right)^2\right] \right.\right.$$

$$\left.\left. - \ell n\left[a_2^2 \delta^2 + \left(\frac{2}{n} - n a_2 \delta + j a_2 \delta\right)^2\right]\right)\right\}$$

$$- \frac{n\delta}{4}\left(\frac{4}{n^2} - n^2 \delta^2\right) \sum_{i=1}^{2n-1} d_i \left[\sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \frac{1}{\frac{2}{n} - n\delta + j\delta} \right] \tag{6.8}$$

with

$$\delta \leq \frac{2}{n(n-1)\min(a_1, a_2)}$$

where

$$d_i = \sum_{k=1}^{i} f_k \, f_{1+i-k}$$

In conjunction with Eq. (6.6), this gives the energy eigenvalues of a s state due to perturbation calculation. The compact expression Eq. (6.8) generalizes the perturbation calculations, which we have carried out for the SSCP, the ECSC and the Baer potential, with the Hulthén potential as the unperturbed one.

6.3 Variational Calculation

6.3.1 One-Parameter Hulthen Type Wave Function

One-parameter Hulthen type wave function for a variational calculation is the result of replacing δ by μ in Eq. (6.7), that is

$$\psi_n(r) = \left[\frac{n}{4}\left(\frac{4}{n^2} - n^2\mu^2\right)\right]^{\frac{1}{2}} e^{-\frac{1}{2}\left(\frac{2}{n} - n\mu\right)r} \sum_{k=1}^{n} f_k (1 - e^{-\mu r})^k \qquad (6.9)$$

where

$$f_k = (-1)^{k-1} \binom{n-1}{k-1} \binom{k + \frac{2}{n\mu} - 1}{k}$$

The energy of s states is obtained from

$$E_n = \langle\psi_n|\frac{1}{2}\frac{d^2}{dr^2} + c_1 \frac{e^{-a_1\delta r}}{r} + c_2 \frac{e^{-a_2\delta r}}{r} \cos a_2\delta r|\psi_n\rangle$$

$$= \langle\psi_n|\frac{1}{2}\frac{d^2}{dr^2}|\psi_n\rangle$$

$$+ \langle\psi_n|c_1 \frac{e^{-a_1\delta r}}{r} + c_2 \frac{e^{-a_2\delta r}}{r} \cos a_2\delta r|\psi_n\rangle \qquad (6.10)$$

The first integral in the right hand side of the Eq. (6.10) is not easy to be solved directly, but it can be integrated in an indirect way as follows

$$\langle\Psi_n|\frac{1}{2}\frac{d^2}{dr^2}|\Psi_n\rangle = \langle\Psi_n|\frac{1}{2}\frac{d^2}{dr^2} + \frac{\mu e^{-\mu r}}{1 - e^{-\mu r}}|\Psi_n\rangle$$

$$- \langle\Psi_n|\frac{\mu e^{-\mu r}}{1 - e^{-\mu r}}|\Psi_n\rangle \qquad (6.11)$$

Now the first integral in the right hand side of the Eq. (6.11) is trivial — it is the eigen-energy of the potential $\frac{\mu e^{-\mu r}}{1 - e^{-\mu r}}$. And the second integral of Eq. (6.11) can be done without much difficulty. The final energy expression is then obtained to be

$$E_n = \frac{1}{8}(\frac{2}{n} - n\mu)^2 - \frac{n}{4}(\frac{4\mu}{n^2} - n^2\mu^2) \sum_{i=1}^{2n-1} d_i [\sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \frac{1}{\frac{2}{n} - n\mu + j\mu}]$$

$$+ \frac{c_1 n}{4}(\frac{4}{n^2} - n^2\mu^2) \sum_{i=1}^{2n-1} d_i \Big\{ \{\sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} [\ell n(\frac{2}{n} + a_1\delta - n\mu + j\mu)$$

$$- \ell n(\frac{2}{n} + a_1\delta - n\mu + j\mu - \mu)]\} \Big\}$$

$$+ \frac{c_2 n}{8}(\frac{4}{n^2} - n^2\mu^2) \sum_{i=1}^{2n-1} d_i \Big\{ \{\sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \Big(\ell n[a_2{}^2\delta^2 + (\frac{2}{n} - n\mu + j\mu + a_2\delta)^2]$$

$$- \ell n[a_2{}^2\delta^2 + (\frac{2}{n} - n\mu + j\mu - \mu + a_2\delta)^2] \Big) \} \Big\} \qquad (6.12)$$

with

$$\mu < \frac{1}{n}\left(\frac{2}{n} + a\delta\right)$$

in which

$$a = \min(a_1, a_2)$$

and

$$d_i = \sum_{k=1}^{i} f_k \, f_{1+i-k}$$

The energy of s state is the result of the minimization of Eq. (6.12) with respect to μ by setting appropriate values of a's and c's for the problem of interest.

6.3.2 Two-Parameter Hulthén Type Wave Function

The two-parameter Hulthen wave function has the form

$$\psi_n(r) = \left[\frac{n}{4\nu}\left(\frac{4\nu^2}{n^2} - n^2\mu^2\right)\right]^{\frac{1}{2}} e^{-\frac{1}{2}\left(\frac{2\nu}{n} - n\mu\right)r} \sum_{k=1}^{n} f_k \left(1 - e^{-\mu r}\right)^k \tag{6.13}$$

where

$$f_k = (-1)^{k-1} \binom{n-1}{k-1} \binom{k + \frac{2\nu}{n\mu} - 1}{k}$$

μ and ν are variational parameters.

The integral $\langle\Psi_n|\frac{d^2}{dr^2}|\Psi_n\rangle$ is rewritten in the following way

$$\langle\Psi_n|\frac{d^2}{dr^2}|\Psi_n\rangle = \langle\Psi_n|\frac{1}{2}\frac{d^2}{dr^2} + \frac{ve^{-\mu r}}{1 - e^{-\mu r}}|\Psi_n\rangle$$

$$- \langle\Psi_n|\frac{ve^{-\mu r}}{1 - e^{-\mu r}}|\Psi_n\rangle \qquad (6.14)$$

It now becomes the difference of the eigen-energy of the Hulthén potential $\frac{ve^{-\mu r}}{1 - e^{-\mu r}}$ and the $\langle\Psi_n|\frac{ve^{-\mu r}}{1 - e^{-\mu r}}|\Psi_n\rangle$. Both integrals in Eq. (6.14) can be analytically solved. The result of Eq. (6.10) in this calculation is

$$E_n = \frac{1}{8}(\frac{2v}{n} - n\mu)^2 - \frac{n\mu}{4}(\frac{4v^2}{n^2} - n^2\mu^2) \sum_{i=1}^{2n-1} d_i \left[\sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \frac{1}{\frac{2v}{n} - n\mu + j\mu}\right]$$

$$\frac{c_1 n}{4v}(\frac{4v^2}{n^2} - n^2\mu^2) \sum_{i=1}^{2n-1} d_i \left\{\sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \left[\ell n(\frac{2v}{n} + a_1\delta - n\mu + j\mu)\right.\right.$$

$$\left.\left. - \ell n(\frac{2v}{n} + a_1\delta - n\mu + j\mu - \mu)\right]\right\}$$

$$+ \frac{c_2 n}{8v}(\frac{4v^2}{n^2} - n^2\mu^2) \sum_{i=1}^{2n-1} d_i \left\{\sum_{j=1}^{i+1} (-1)^{j-1} \binom{i}{j-1} \left(\ell n[a_2{}^2\delta^2 + (\frac{2v}{n} - n\mu + j\mu + a_2\delta)^2]\right.\right.$$

$$\left.\left. - \ell n[a_2{}^2\delta^2 + (\frac{2v}{n} - n\mu + j\mu - \mu + a_2\delta)^2]\right)\right\} \qquad (6.15)$$

with

$$n\mu - \frac{2v}{n} < a\delta$$

where

$$a = \min (a_1, a_2)$$

and

$$d_i = \sum_{k=1}^{i} f_k \, f_{1+i-k}$$

Upon optimizing Eq. (6.15) with respect to μ and ν, one can obtain the energy of the general screened Coulomb potential by setting appropriate values of a's and c's.

6.4 Conclusion

We have obtained expressions for the eigenvalue for a screened Coulomb potential by using Hulthén potential as a first approximation, in a compact form. These compact expressions, namely Eqs. (6.8), (6.12) and (6.15), contain all calculations that we have done on the energy eigenvalues of the SSCP, ECSC potential and Baer potential with Hulthén wave functions as a basis set.

On the practical side, the use of these compact expressions to compute the s-state energy values is limited. We have made several attempts to do so, by programming these expressions in quadruple precision (32 figures in accuracy) in an IBM 370/168 machine and double precision (29 figures in accuracy) in a CYBER 74 computer,

but we failed to obtain an energy values in the lower screening region for the ground state and hardly anything for an excited state. An examination of these expressions shows that the complexity of the computation increases with μ and also that there are large cancellation between terms and the most significant portion of a number may be lost during the computation. We have experienced the same kind of problem when we carried the calculation on the energies of the SSCP or ECSC potential or Baer potential when δ is small in the previous chapters. For obtaining the energies from these compact expressions, a very high precision computer (with more than 32 significant figures in accuracy) is required.

Chapter 7 - Energy Levels of a Helium - Like Atom with a Static Screened Coulomb Potential

7.1 Introduction

It is well known that in Ge-and Si-type semiconductors, there exist a bivalent impurity centre (Glodeanu 1965, 1967, Gershenzon et al. 1971, and Godik et al. 1971). In a n-type semiconductor it is two electrons bound to a positive core and in a p-type semiconductor, two holes are associated with a negatively charged core. In a n-type semiconductor, this kind of impurities arise from (1) one additional electron attached to a neutral donor, in analogye to a H^- atom; (2) the substitutional impurity is a bivalent atom, in analogye to He atom. To obtain the energy-levels of this type of impurities, Glodeanu (1965, 1967) proposed a helium-like model in a single band approximation in which he used the free electron mass, instead of the effective mass, and the dielectric constant of the host crystal.

Here we attempt to approach the problem in a different way. Actually the interaction between the attached electrons of holes and the impurity centre is not purely Coulombic. The existence of the free electrons weakens the interaction between these charged particles. In other words the Coulomb potential is screened by the free electrons.

In the following sections we shall evaluate the binding energy of He-like atoms with a SSCP using by the variational method.

7.2 Calculation

The Hamiltonian of the helium-like atom in atomic unit is

$$H = \frac{1}{2}\nabla_1^2 + \frac{Ze^{-\delta r_1}}{r_1} + \frac{1}{2}\nabla_2^2 + \frac{Ze^{-\delta r_2}}{r_2} - \frac{e^{-\delta r_{12}}}{r_{12}} \qquad (7.1)$$

where δ is the screening parameter, r_i is the coordinate of the i-th electron with respect to the impurity centre of charge Ze and r_{12} is the distance between two electrons. The type of the trial wave functions which will be employed in the following is of the form

$$\psi = f(r_1) \times f(r_2) \times g(r_1, r_2, r_{12}) \qquad (7.2)$$

where $f(r_i)$ is the hydrogen-like wave function and $g(r_1, r_2, r_{12})$ is a correlation factor. This type of the wave functions has been widely used for helium-like systems, such as H^-, He, Li^+ etc. (Green et al. 1958a, 1958b). Recently ground state wave functions of very high accuracy have been obtained for a number of helium-like atoms. These wave functions have been of the form of Eq. (7.2) with a large number of terms in the function g. However in our present investigation, we are dealing with a slightly different system. We shall restrict ourselves to relatively simple forms of g. The wave functions used by us are

$$\psi = e^{-a(r_1 + r_2)} \qquad (7.3)$$

$$\psi = e^{-a(r_1 + r_2)} (1 + br_{12})^{\frac{1}{2}} \qquad (7.4)$$

$$\psi = e^{-a(r_1 + r_2)} (1 + br_{12}) \tag{7.5}$$

$$\psi = e^{-a(r_1 + r_2)} e^{br_{12}} \tag{7.6}$$

$$\psi = e^{-a(r_1 + r_2)} \; 1 + br_{12} + c(r_1 - r_2)^2 \tag{7.7}$$

The energy is obtained from

$$E = \langle \psi | H | \psi \rangle$$

The energy associated with the kinetic energy operator ∇_i^2 and the potential energy operator $\frac{e^{-\delta r_i}}{r_i}$ can be integrated without much difficulty. The integration associated with the interaction between two electrons is carried in a different way. The integrand $\frac{e^{-\delta r_{12}}}{r_{12}}$ has to be expanded in terms of the coordinates r_1 and r_2. To obtain this, we use the fact that

$$\frac{e^{ikr_{12}}}{r_{12}} = k j_0 (kr_<) \, h_0^{(+)} (kr_>)$$

$$= k \frac{\sin kr_<}{kr_<} \frac{e^{ikr_>}}{kr_>}$$

where j_0 is the Bessel function and $h_0^{(+)}$ is the Hankel function of the first kind. $r_<$ stands for the smaller of the lengths r_1 and r_2, and $r_>$ stands for the larger of the lengths r_1 and r_2. If we write $k = i\delta$, it follows

$$\frac{e^{-\delta r_{12}}}{r_{12}} = -\frac{i}{\delta}\frac{\sin i\delta r_<}{r_<}\frac{e^{-\delta r_>}}{r_>}$$

Because $\sin i\delta r_< = i \sinh(\delta r_<) = i\,\frac{e^{\delta r_<} - e^{-\delta r_<}}{2}$

therefore $$\frac{e^{-\delta r_{12}}}{r_{12}} = \frac{1}{2\delta}\frac{e^{\delta r_<} - e^{-\delta r_<}}{r_<}\frac{e^{-\delta r_>}}{r_>}$$

The energy expressions for the wave functions (7.3) to (7.7) are respectively listed below.

$$E = -\frac{a^2}{2(2a+\delta)^4}\left[2(2a+\delta)^4 + a(\delta^2 + 8a\delta + 20a^2)\right] + \frac{8Za^3}{(2a+\delta)^2} \quad (7.8)$$

$$\begin{aligned} E = {} & \frac{1}{24b^2(16a+35b)}(-8a^3 + 16a^2b + 80ab^2 + 165b^3) \\ & - \frac{a^3}{3b^4(16a+35b)}(6a^2 - 7ab + 3b^2)\, e^{\frac{2a}{b}} E_i\left(-\frac{2a}{b}\right) \\ & + \frac{32Za^2}{(4a+\delta)^2(2a+\delta)^3(16a+35b)}\Big[2a(4a+\delta)^2(2a+\delta) \\ & + b(120a^3 + 100a^2\delta + 30a\delta^2 + 3\delta^3)\Big] \\ & - \frac{4a^3}{(2a+\delta)^5(16a+35b)}\Big[(20a^2 + 8a\delta + \delta^2)(2a+\delta) \\ & + 2b(32a^2 + 10a\delta + \delta^2)\Big] \end{aligned} \quad (7.9)$$

where $E_i(-x)$ is an exponential integral.

$$E = (8a^2 + 35ab + 48ac + 48b^2 + 154bc + 288c^2)^{-1}$$

$$+ \{\tfrac{1}{4}(8a^2 + 25ab + 32b^2 + 48ac + 480c^2 + 146bc)$$

$$+ \frac{32a^2\Sigma}{(4a + \delta)^2 (2a + \delta)^4}\Big[(4a + \delta)^2 (2a + \delta)^2 a^2$$

$$+ ab(2a + \delta)(120a^3 + 100a^2\delta + 30a\delta^2 + 3\delta^3)$$

$$+ 3b^2(4a + \delta)^2 (6a^2 + 4a\delta + \delta^2)\Big]$$

$$+ \frac{384a^3c\Sigma}{(2a + \delta)^4} (2a^2 + 2a\delta + \delta^2)$$

$$+ \frac{64a^2bc\Sigma}{(4a + \delta)^2 (2a + \delta)^5} (1120a^5 + 2128a^4\delta + 1960a^3\delta^4$$

$$+ 876a^2\delta^2 + 186a\delta^4 + 15\delta^5)$$

$$+ \frac{192a^2c^2\Sigma}{(2a + \delta)^6} (96a^4 + 192a^3\delta + 192a^2\delta^2 + 80a\delta^3 + 15\delta^4)\Big]$$

$$- \frac{2a^4}{(2a + \delta)^6}\Big[(2a + \delta)^2 (20a^2 + 8a\delta + \delta^2)$$

$$+ 4b(2a + \delta)(32a^2 + 10a\delta + \delta^2) + 2b^2(140a^2 + 36a\delta + 3\delta^2)\Big]$$

$$+ \frac{16a^5c}{(2a + \delta)^6} (36a^2 + 12a\delta + \delta^2)$$

$$+ \frac{64a^5bc}{(2a + \delta)^7} (48a^2 + 14a\delta + \delta^2)$$

$$+ \frac{192a^6c^2}{(2a + \delta)^8} (52a^2 + 16a\delta + \delta^2)\} \qquad (7.10)$$

$$E = \frac{(a-b)}{4a^2(8a^2 - 5ab + b^2)} (8a^3 \# 7a^2b + 4ab^2 - b^3)$$

$$+ \frac{32\sharp a^2(a - b)^2}{(4a + \delta)^2 (2a - 2b + \delta)^2 (8a^2 - 5ab + b^2)} \left[\delta^2 + 48(2a - b) \right.$$

$$\left. + 4(a - b)(4a - b)\right]$$

$$= \frac{2(a - b)^5}{a(2a - 2b + \delta)^4 (8a^2 - 5ab + b^2)} \left[20a^2 + 8a(\delta - 2b) + (\delta - 2b)^2\right] \tag{7.11}$$

$$E = \frac{8a^2 + 25ab + 32b^2}{4(8a^2 + 35ab + 48b^2)}$$

$$+ \frac{32\sharp a^2}{(4a + \delta)^2 (2a + \delta)^4 (8a^2 + 35ab + 48b^2)} \left[(4a + \delta)^2 (2a + \delta)^2 a^2 \right.$$

$$+ ab(2a + \delta)(120a^3 + 100a^2\delta + 30a\delta^2 + 3\delta^3)$$

$$\left. + 3b^2(4a + \delta)^2 (6a^2 + 4a\delta + \delta^2)\right]$$

$$- \frac{2a^4}{(2a + \delta)^6 (8a^2 + 35ab + 48b^2)} \left[(20a^2 + 8a\delta + \delta^2) (2a + \delta)^2 \right.$$

$$+ 4b(32a^2 + 10a\delta + \delta^2) (2a + \delta)$$

$$\left. + 2b^2(140a^2 + 36a\delta + 3\delta^2)\right] \tag{7.12}$$

2,3 Discussion

Upon optimizing the expressions (7.8) to (7.12) with respect to the variational parameters by the method of "pattern search" due to Hooke and Jeeves (1961) (also see Wilde 1964, and Kawalik and Osborne 1968), energy eigenvalues are obtained. Tables 7.1 to 7.5 showed the energies of H^- atom and Tables 7.6 to 7.10 showed the energies of He atom, as a function of screening parameter δ. Also showed in the Tables are the optimized parameters.

The energies of these atoms are a monotonic decreasing function of the screening parameter δ and eventually diminish at the critical screenings. The parameter a in the wave functions (7.3) to (7.7) are practically a constant value below $\delta = 0.02$ and are monotonically decreasing with δ as $\delta > 0.02$ for both atoms. The parameter b, which have different meanings in different wave functions of (8.4) to (8.7), with δ in the same manner as the parameter a does. The parameter c of the wave function (7.7) increases with δ in the He atom and it increases to $\delta = 0.6$ and then decreases in the H^- atom.

In Eq. (7.3) g is set to 1. It is simply the product of two hydrogenic wave functions and does not contain any expressions involving r_{12}. The reason that we include it here is to show how effectively the calculated energies of H^- and He in the screening situation are improved by introducing $g(r_1, r_2, r_{12})$. For instance, at low screening case,

δ = 0.0001, the improvement over Eq. (7.3) by Eq. (7.4) is 6.7%, by Eq. (7.5) is 7.1%, by Eq. (7.6) is 6.9%, and by Eq. (7.7) is 10.0% in H^- and by the order of the Eqs. they are respectively improved by 0.83%, 1.5%, 1.45% and 1.89% in He. The improvement is more substantial near the critical screening. At δ = 0.8, the improvements of Eq. (7.4) to Eq. (7.7) over Eq. (7.3) in H^- are respectively 50%, 52%, 53% and 77%; at δ = 1.8 in He the improvements are respectively 23%, 44%, 48% and 77%. The importance of the factor $g(r_1, r_2, r_{12})$ is therefore quite obvious. From the results shown in the Table 7.11, Table 7.12 and some statistics shown above, by all means the three-parameter trial function of Eq. (7.7) is the best among all five functions listed here. The improvement from the two-parameter trial functions to the three-parameter trial function is substantial at high screening case. Among three two-parameter wave functions, the Eq. (7.4) is the poorest. The results show that below δ = 0.7 in H^- and δ = 0.8 in He the Eq. (7.5) is slightly better than the Eq. (7.6) and the opposite is true when $\delta \geq$ 0.7 in H^- and $\delta >$ 0.8 in He. If one expands $e^{-br_{12}}$ and retains the terms up to the first order of br_{12} in Eq. (7.6), Eq. (7.5) is immediately followed. The improvement of Eq. (7.5) over Eq. (7.6) is quite small (less than 1%) in the low screening region but the opposite is relatively large. Near the critical screening an improvement about 3% is recorded in H^- and 7% in He. Overall Eq. (7.6) is the best among the two-parameter trial functions.

We cannot accurately determine the critical screening parameter of either atoms with the static screened Coulomb potential. Our calculation only suggests that the lower bounds for the H^- and He are respectively 0.9 and 2.0.

Table 7.1 : Energies of H^- with the SSCP from the trial wave function (7.3)

Screening parameter	Optimized parameter	Energy
0.0	0.6875	0.47266
0.0001	0.6875	0.47256
0.0002	0.6875	0.47246
0.0005	0.6875	0.47216
0.001	0.6875	0.47166
0.002	0.6875	0.47066
0.0025	0.6875	0.47016
0.005	0.6875	0.46767
0.01	0.6875	0.46272
0.02	0.6875	0.45289
0.025	0.6870	0.44803
0.05	0.6865	0.42413
0.1	0.6835	0.37853
0.2	0.6710	0.29587
0.25	0.6620	0.25866
0.3	0.6510	0.22409
0.4	0.6235	0.16254
0.5	0.5890	0.11065
0.6	0.5455	0.06793
0.7	0.4910	0.03403
0.8	0.4175	0.00886

Table 7.2 : Energies of H^- with the SSCP from the trial wave function (7.4)

Screening parameter	Optimized parameter a	b	Energy
0.0	0.7965	2.5647	0.50659
0.0001	0.7965	2.5647	0.50649
0.0002	0.7965	2.5647	0.50639
0.0005	0.7965	2.5647	0.50609
0.001	0.7965	2.5647	0.50559
0.002	0.7965	2.5647	0.50459
0.0025	0.7965	2.5647	0.50409
0.005	0.7965	2.5647	0.50160
0.01	0.7965	2.5647	0.49664
0.02	0.7965	2.5647	0.48679
0.025	0.7965	2.5647	0.48189
0.05	0.7955	2.5615	0.45781
0.1	0.7925	2.5202	0.41153
0.2	0.7800	2.4024	0.32662
0.25	0.7715	2.3299	0.28796
0.3	0.7595	2.2329	0.25179
0.4	0.7310	2.0614	0.18677
0.5	0.6940	1.8460	0.13117
0.6	0.6480	1.6330	0.08463
0.7	0.5910	1.4184	0.04688
0.8	0.5170	1.1684	0.01779
0.9	0.4050	0.8505	-0.00227

Table 7.3 : Energies of H^- with the SSCP from the trial wave function (7.5)

Screening parameter	Optimized parameter a	b	Energy
0.0	0.8525	0.2251	0.50790
0.0001	0.8525	0.2251	0.50780
0.0002	0.8520	0.2249	0.50770
0.0005	0.8520	0.2249	0.50740
0.001	0.8520	0.2249	0.50690
0.002	0.8520	0.2249	0.50590
0.0025	0.8520	0.2249	0.50540
0.005	0.8520	0.2249	0.50291
0.01	0.8520	0.2249	0.49794
0.02	0.8520	0.2249	0.48808
0.025	0.8520	0.2249	0.48318
0.05	0.8510	0.2247	0.45904
0.1	0.8470	0.2219	0.41257
0.2	0.8315	0.2145	0.32724
0.25	0.8190	0.2080	0.28843
0.3	0.8060	0.2031	0.25216
0.4	0.7720	0.1899	0.18707
0.5	0.7310	0.1769	0.13157
0.6	0.6805	0.1620	0.08525
0.7	0.6195	0.1462	0.04776
0.8	0.5435	0.1283	0.01890
0.9	0.4325	0.1021	-0.00110

Table 7.4 : Energies of H^- with the SSCP from the trial wave function (7.6)

Screening parameter	Optimized parameter a	b	Energy
0.0	0.8255	0.4936	0.50878
0.0001	0.8255	0.4936	0.50868
0.0002	0.8255	0.4936	0.50858
0.0005	0.8255	0.4936	0.50828
0.001	0.8255	0.4936	0.50778
0.002	0.8255	0.4936	0.50678
0.0025	0.8255	0.4936	0.50628
0.005	0.8255	0.4936	0.50379
0.01	0.8255	0.4936	0.49883
0.02	0.8255	0.4936	0.48896
0.025	0.8255	0.4936	0.48407
0.05	0.8245	0.4914	0.45995
0.1	0.8210	0.4827	0.41355
0.2	0.8070	0.4568	0.32829
0.25	0.7965	0.4397	0.28945
0.3	0.7840	0.4218	0.25311
0.4	0.7525	0.3838	0.18779
0.5	0.7130	0.3451	0.13197
0.6	0.6640	0.3028	0.08530
0.7	0.6040	0.2597	0.04747
0.8	0.5275	0.2131	0.01834
0.9	0.4135	0.1563	-0.00179

Table 7.5 : Energies of H^- with the SSCP from the trial wave function (7.7)

Screening parameter	Optimized parameter a	b_b	c	Energy
0.0	0.7685	0.3194	0.0819	0.52531
0.0001	0.7685	0.3194	0.0819	0.52521
0.0002	0.7685	0.3194	0.0819	0.52511
0.0005	0.7685	0.3189	0.0818	0.52481
0.001	0.7685	0.3189	0.0818	0.52431
0.002	0.7685	0.3189	0.0818	0.52331
0.0025	0.7685	0.3189	0.0818	0.52281
0.005	0.7685	0.3189	0.0818	0.52032
0.01	0.7685	0.3189	0.0818	0.51536
0.02	0.7685	0.3189	0.0818	0.50551
0.025	0.7680	0.3181	0.0819	0.50062
0.05	0.7670	0.3160	0.0819	0.47658
0.1	0.7625	0.3073	0.0820	0.43044
0.2	0.7455	0.2806	0.0828	0.34605
0.25	0.7330	0.2637	0.0833	0.30776
0.3	0.7195	0.2482	0.0839	0.27201
0.4	0.6850	0.2137	0.0851	0.20787
0.5	0.6445	0.1811	0.0856	0.15303
0.6	0.5985	0.1530	0.0857	0.10689
0.7	0.5480	0.1295	0.0844	0.06883
0.8	0.4910	0.1093	0.0812	0.03834
0.9	0.4255	0.0928	0.0755	0.01503
1.0	0.3355	0.0766	0.0654	-0.00113

Table 7.6 : Energies of He with the SSCP from the trial wave function (7.3)

Screening parameter	Optimized parameter	Energy
0.0	1.6875	2.84766
0.0001	1.6875	2.84736
0.0002	1.6875	2.84706
0.0005	1.6875	2.84616
0.001	1.6875	2.84466
0.002	1.6875	2.84166
0.0025	1.6875	2.84016
0.005	1.6875	2.83268
0.01	1.6875	2.81777
0.02	1.6875	2.78810
0.025	1.6875	2.77336
0.05	1.6865	2.70044
0.1	1.6845	2.55862
0.2	1.6755	2.29031
0.25	1.6690	2.16343
0.3	1.6615	2.04118
0.4	1.6435	1.80991
0.5	1.6210	1.59540
0.6	1.5950	1.39668
0.7	1.5650	1.21292
0.8	1.5310	1.04338
0.9	1.4940	0.88739

Table 7.6 (cont'd)

Screening parameter	Optimized parameter	Energy
1.0	1.4530	0.74439
1.1	1.4080	0.61385
1.2	1.3590	0.49532
1.3	1.3055	0.38841
1.4	1.2465	0.29279
1.5	1.1810	0.20820
1.6	1.1080	0.13448
1.7	1.0235	0.07160
1.8	0.9210	0.01982
1.9	0.7775	-0.01991

Table 7.7 : Energies of He with the SSCP from the trial wave function (7.4)

Screening parameter	Optimized parameter a	b	Energy
0.0	1.8770	3.0633	2.87159
0.0001	1.8770	3.0633	2.87129
0.0002	1.8770	3.0633	2.87099
0.0005	1.8770	3.0633	2.87009
0.001	1.8770	3.0633	2.86859
0.002	1.8770	3.0633	2.86559
0.0025	1.8770	3.0633	2.86410
0.005	1.8770	3.0633	2.85662
0.01	1.8770	3.0633	2.84170
0.02	1.8770	3.0633	2.81203
0.025	1.8765	3.0624	2.79728
0.05	1.8760	3.0616	2.72432
0.1	1.8735	3.0576	2.58236
0.2	1.8640	3.0420	2.31354
0.25	1.8570	3.0269	2.18632
0.3	1.8485	3.0094	2.06366
0.4	1.8285	2.9731	1.83148
0.5	1.8040	2.9261	1.61594
0.6	1.7750	2.8720	1.41612
0.7	1.7420	2.8116	1.23120
0.8	1.7050	2.7416	1.06047
0.9	1.6640	2.6691	0.90329

Table 7.7 (cont'd)

Screening parameter	Optimized parameter a	b	Energy
1.0	1.6635	2.6616	0.75910
1.1	1.5690	2.5041	0.62740
1.2	1.5150	2.4119	0.50772
1.3	1.4560	2.3092	0.39970
1.4	1.3905	2.1970	0.30300
1.5	1.3190	2.0787	0.21735
1.6	1.2380	1.9437	0.14260
1.7	1.1455	1.7939	0.07870
1.8	1.0345	1.6138	0.02584
1.9	0.8835	1.3747	-0.01515

Table 7.8 : Energies of He with the SSCP from the trial wave function (7.5)

Screening parameter	Optimized parameter a	b	Energy
0.0	1.8565	0.2525	2.88962
0.0001	1.8565	0.2525	2.88932
0.0002	1.8565	0.2525	2.88902
0.0005	1.8565	0.2525	2.88812
0.001	1.8565	0.2525	2.88662
0.002	1.8565	0.2525	2.88362
0.0025	1.8565	0.2525	2.88212
0.005	1.8565	0.2525	2.87464
0.01	1.8565	0.2525	2.85973
0.02	1.8565	0.2525	2.83001
0.025	1.8565	0.2525	2.81530
0.05	1.8560	0.2524	2.74235
0.1	1.8560	0.2561	2.60042
0.2	1.8465	0.2548	2.33168
0.25	1.8395	0.2539	2.20451
0.3	1.8315	0.2527	2.08191
0.4	1.8120	0.2501	1.84985
0.5	1.7875	0.2467	1.63441
0.6	1.7595	0.2428	1.43466
0.7	1.7270	0.2383	1.24978
0.8	1.6930	0.2370	1.07903
0.9	1.6530	0.2314	0.92176

Table 7.8 (cont'd)

Screening parameter	Optimized parameter a	b	Energy
1.0	1.6110	0.2288	0.77740
1.1	1.5650	0.2254	0.64543
1.2	1.5140	0.2210	0.52539
1.3	1.4585	0.2159	0.41687
1.4	1.3970	0.2096	0.31954
1.5	1.3290	0.2020	0.23311
1.6	1.2545	0.1957	0.15738
1.7	1.1690	0.1870	0.09227
1.8	1.0680	0.1773	0.03788
1.9	0.9370	0.1630	-0.00523

Table 7.9 :- Energies of He with the SSCP from the trial wave function (7.6)

Screening parameter	Optimized parameter a	b	Energy
0.0	1.8500	0.3663	2.89112
0.0001	1.8500	0.3663	2.89082
0.0002	1.8500	0.3663	2.89052
0.0005	1.8500	0.3663	2.88962
0.001	1.8500	0.3663	2.88812
0.002	1.8500	0.3663	2.88513
0.0025	1.8500	0.3663	2.88363
0.005	1.8500	0.3663	2.87615
0.01	1.8500	0.3663	2.86123
0.02	1.8500	0.3663	2.83156
0.025	1.8495	0.3662	2.81681
0.05	1.8490	0.3661	2.74385
0.1	1.8465	0.3656	2.60188
0.2	1.8370	0.3637	2.33303
0.25	1.8290	0.3585	2.20578
0.3	1.8210	0.3569	2.08309
0.4	1.8015	0.3531	1.85081
0.5	1.7770	0.3447	1.63512
0.6	1.7485	0.3392	1.43509
0.7	1.7165	0.3330	1.24991
0.8	1.6800	0.3226	1.07884
0.9	1.6400	0.3149	0.92126

Table 7.9 (cont'd)

Screening parameter	Optimized parameter a	b	Energy
1.0	1.5965	0.3065	0.77657
1.1	1.5475	0.2940	0.64428
1.2	1.4955	0.2841	0.52393
1.3	1.4385	0.2733	0.41512
1.4	1.3765	0.2643	0.31751
1.5	1.3075	0.2510	0.23083
1.6	1.2315	0.2389	0.15490
1.7	1.1440	0.2219	0.08963
1.8	1.0410	0.2061	0.03515
1.9	0.9065	0.1831	-0.00792

Table 7.10 : Energies of He with the SSCP from the trial wave function (7.7)

Screening parameter	Optimized parameter a	b	c	Energy
0.0	1.8170	0.2929	0.0360	2.90243
0.0001	1.8170	0.2929	0.0360	2.90213
0.0002	1.8170	0.2929	0.0360	2.90183
0.0005	1.8170	0.2929	0.0360	2.90093
0.001	1.8170	0.2929	0.0360	2.89943
0.002	1.8170	0.2929	0.0360	2.89644
0.0025	1.8170	0.2929	0.0360	2.89494
0.005	1.8170	0.2929	0.0360	2.88746
0.01	1.8170	0.2929	0.0360	2.87255
0.02	1.8155	0.2912	0.0359	2.84289
0.025	1.8155	0.2912	0.0359	2.82814
0.05	1.8145	0.2907	0.0363	2.75524
0.1	1.8120	0.2899	0.0366	2.61350
0.2	1.8005	0.2841	0.0378	2.34549
0.25	1.7920	0.2799	0.0387	2.21882
0.3	1.7835	0.2768	0.0400	2.09682
0.4	1.7600	0.2668	0.0426	1.86620
0.5	1.7315	0.2549	0.0454	1.65253
0.6	1.6980	0.2418	0.0486	1.45486
0.7	1.6610	0.2289	0.0522	1.27233
0.8	1.6200	0.2155	0.0561	1.10421
0.9	1.5745	0.2015	0.0598	0.94981

Table 7.10 (cont'd)

Screening parameter	Optimized parameter a	b	c	Energy
1.0	1.5255	0.1876	0.0641	0.80851
1.1	1.4715	0.1733	0.0683	0.67973
1.2	1.4135	0.1589	0.0724	0.56294
1.3	1.3525	0.1463	0.0768	0.45764
1.4	1.2870	0.1338	0.0811	0.36335
1.5	1.2170	0.1222	0.0852	0.27963
1.6	1.1430	0.1120	0.0889	0.20604
1.7	1.0635	0.1029	0.0921	0.14220
1.8	0.9785	0.0961	0.0947	0.08776
1.9	0.8840	0.0903	0.0962	0.04247
2.0	0.7750	0.0866	0.0956	0.00630
2.1	0.6195	0.0834	0.0901	-0.02010

Table 7.11 : Energy eigenvalues of H^- with the SSCP from various approximate trial wave functions

Screening parameter	Energy				
	Eq.(7.3)	Eq.(7.4)	Eq.(7.5)	Eq.(7.6)	Eq.(7.7)
0.0	0.47266	0.50659	0.50878	0.50790	0.52531
0.0001	0.47256	0.50649	0.50868	0.50780	0.52521
0.0002	0.47246	0.50639	0.50858	0.50770	0.52511
0.0005	0.47216	0.50609	0.50828	0.50740	0.52481
0.001	0.47166	0.50559	0.50778	0.50690	0.52431
0.002	0.47066	0.50459	0.50678	0.50590	0.52331
0.0025	0.47016	0.50409	0.50628	0.50540	0.52281
0.005	0.46767	0.50160	0.50379	0.50291	0.52032
0.01	0.46272	0.49664	0.49883	0.49794	0.51536
0.02	0.45289	0.48679	0.48896	0.48808	0.50551
0.025	0.44803	0.48189	0.48407	0.48318	0.50062
0.05	0.42413	0.45781	0.45995	0.45904	0.47658
0.1	0.37853	0.41153	0.41355	0.41257	0.43044
0.2	0.29587	0.32662	0.32829	0.32724	0.34605
0.25	0.25866	0.28796	0.28945	0.28843	0.30776
0.3	0.22409	0.25179	0.25311	0.25216	0.27201
0.4	0.16254	0.18677	0.18779	0.18707	0.20787
0.5	0.11065	0.13117	0.13197	0.13157	0.15303
0.6	0.06793	0.08463	0.08530	0.08525	0.10689
0.7	0.03403	0.04688	0.04747	0.04776	0.06883
0.8	0.00886	0.01779	0.01834	0.01890	0.03834
0.9		-0.00227	-0.00179	-0.00110	0.01503
1.0					-0.00113

Table 7.12 : Energy eigenvalues of He with the SSCP from various approximate trial wave functions

Screening parameter	Energy				
	Eq.(7.3)	Eq.(7.4)	Eq.(7.5)	Eq.(7.6)	Eq.(7.7)
0.0	2.84766	2.87159	2.89112	2.88962	2.90243
0.0001	2.84736	2.87129	2.89082	2.88932	2.90213
0.0002	2.84706	2.87099	2.89052	2.88902	2.90183
0.0005	2.84616	2.87009	2.88962	2.88812	2.90093
0.001	2.84466	2.86859	2.88812	2.88662	2.89943
0.002	2.84166	2.86559	2.88513	2.88362	2.89644
0.0025	2.84016	2.86410	2.88363	2.88212	2.89494
0.005	2.83268	2.85662	2.87615	2.87464	2.88746
0.01	2.81777	2.84170	2.86123	2.85973	2.87255
0.02	2.78810	2.81203	2.83156	2.83001	2.84289
0.025	2.77336	2.79728	2.81681	2.81530	2.82814
0.05	2.70044	2.72432	2.74385	2.74235	2.75524
0.1	2.55862	2.58236	2.60188	2.60042	2.61350
0.2	2.29031	2.31354	2.33303	2.33168	2.34549
0.25	2.16343	2.18632	2.20578	2.20451	2.21882
0.3	2.04118	2.06366	2.08309	2.08191	2.09682
0.4	1.80991	1.83148	1.85081	1.84985	1.86620
0.5	1.59540	1.61594	1.63512	1.63441	1.65253
0.6	1.39668	1.41612	1.43509	1.43466	1.45486
0.7	1.21292	1.23120	1.24991	1.24978	1.27233
0.8	1.04338	1.06047	1.07884	1.07903	1.10421
0.9	0.88739	0.90329	0.92126	0.92176	0.94981

Table 7.12 (cont'd)

Screening parameter	Energy				
	Eq.(7.3)	Eq.(7.4)	Eq.(7.5)	Eq.(7.6)	Eq.(7.7)
1.0	0.74439	0.75910	0.77657	0.77740	0.80851
1.1	0.61385	0.62740	0.64428	0.64543	0.67973
1.2	0.49532	0.50772	0.52393	0.52539	0.56294
1.3	0.38841	0.39970	0.41512	0.41687	0.45764
1.4	0.29279	0.30300	0.31751	0.31954	0.36335
1.5	0.20820	0.21735	0.23083	0.23311	0.27963
1.6	0.13448	0.14260	0.15490	0.15738	0.20604
1.7	0.07160	0.07870	0.08963	0.09227	0.14220
1.8	0.01982	0.02584	0.03515	0.03788	0.08776
1.9	-0.01991	-0.01515	-0.00792	-0.00523	0.04247
2.0					0.00630
2.1					-0.02010

Chapter 8 - Fine Structure of Excitonic Lines in CuCl

8.1 Introduction

Stebe and Certier (1972) presented a quantitative study on the fine structure of excitonic lines due to ionic polarization, in the case of an intermediate polaron-lattice coupling and have applied it to CuCl.

In the effective mass approximation, the non-relativistic electron-hole interaction operator is not purely Coulombic, and this leads to the fine structure of the excitonic lines (Haken 1962). For this effective electron-hole interaction, Stebe and Certier (1972) chose the Haken potential (1958), which has the following form:

$$V(r) = -\frac{e^2}{\varepsilon_0 r} + V'(r) \tag{8.1}$$

$$V'(r) = -\frac{e^2}{2\varepsilon_0 r}\left(\frac{\varepsilon_0}{\varepsilon_\infty} - 1\right)\left(e^{-\frac{r}{\rho_e}} + e^{-\frac{r}{\rho_h}}\right) \tag{8.2}$$

where $\rho_{e,h} = (h/2m^*_{e,h}\,\omega)^{1/2}$ is the polaron radius of the electron (the hole), $m^*_{e,h}$ the effective mass of the electron (the hole), ε_0 and ε_∞ are the static and optical dielectric constants respectively, and ω is the longitudinal circular frequency of the lattice.

Stebe and Certier (1972) have considered the non-Coulombic part $V'(r)$ as a perturbation with respect to the Coulombic part and have obtained the energy difference between the 2s and 2p levels from the first order

Perturbation energy. Their calculated result is 29 cm^{-1}, as compared to the experimental value of 50 cm^{-1} for CuCl at $4^{o}K$.

In Fig. 8.1, we show the unperturbed Coulomb potential and the perturbation V'(r) as a function of r for the case of CuCl. It is noticed that the perturbation is substantial and if we view this in light of the considerable difference between the theoretical and experimental values of $\Delta E(2s - 2p)$, we are led to inquire the effect of higher order terms in the perturbation theory.

In the following sections, we will present the results for the splitting $\Delta E(2s - 2p)$ when the calculation is carried out to the second order in the perturbation theory.

8022 Calculation

The energy of a state to the second order correction in the perturbation calculation is given by

$$E_{nl} = E_n + \Delta E_{nl}^{(1)} + \Delta E_{nl}^{(2)} \tag{8.3}$$

where

$$\Delta E_{nl}^{(1)} = H_{nn} \tag{8.4}$$

$$\Delta E_{nl}^{(2)} = \sum_{\substack{m \\ m \neq n}} \frac{|H_{nm}|^2}{E_n - E_m} \tag{8.5}$$

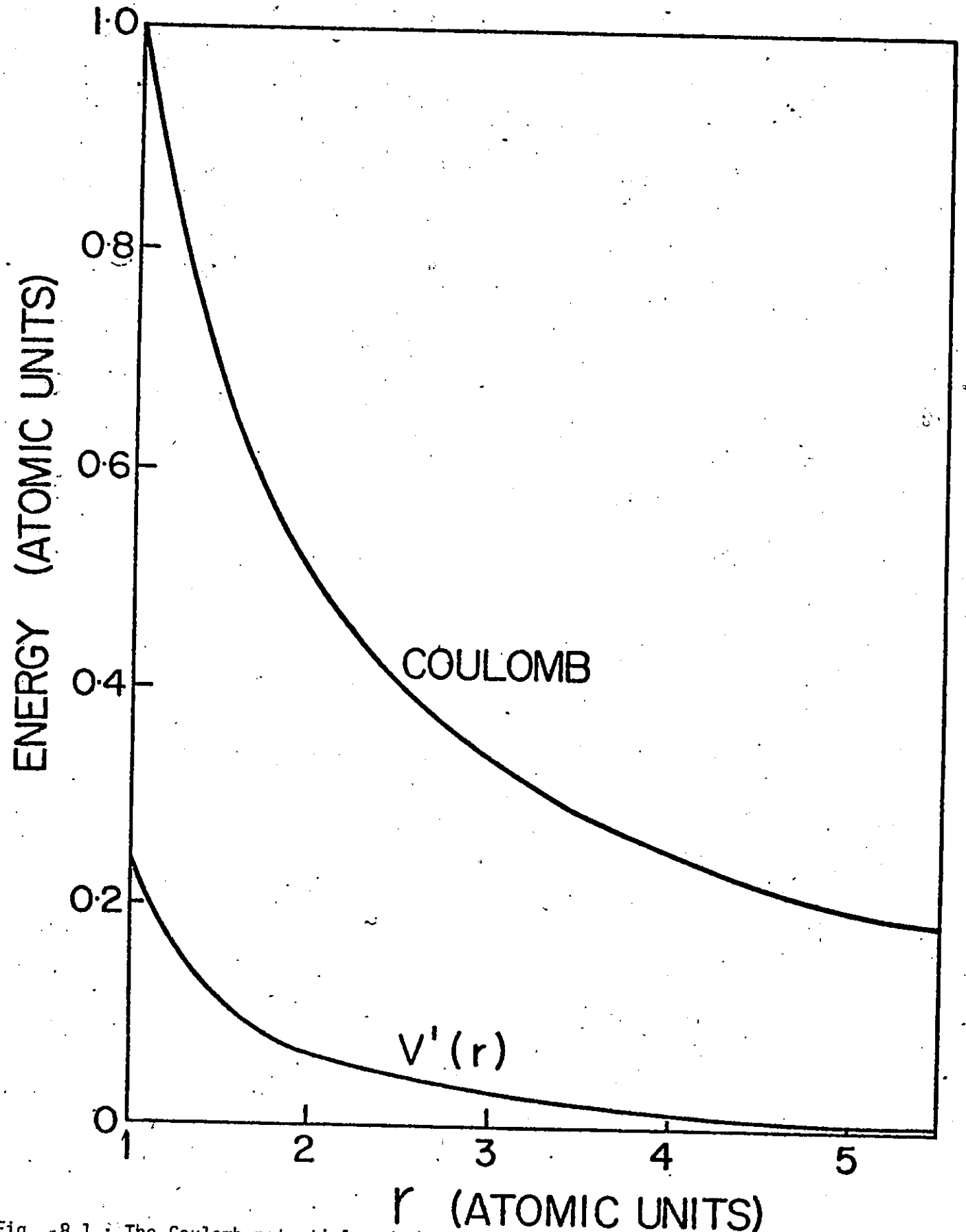

Fig. -8.1 : The Coulomb potential and the perturbation V'(r) as a function of r

where

$$H_{nm} = \int \phi_{n\ell} V'(r) \phi_{m\ell} \, dt \tag{8.6}$$

The atomic units as adapted to solid state physics are used here. They are $a_o = \varepsilon_o h^2/\mu^* e^2$ for the unit of length and $\mu^{**} e^4/\varepsilon_o^2 h^2$ for the unit of energy, where $\mu^* = m_e^* m_h^*/(m_e^* + m_h^*)$. The Haken potential is then

$$V(r) = \frac{1}{r} + \frac{1}{2r}\left(\frac{\varepsilon_o}{\varepsilon_\infty} - 1\right)\left(e^{-\delta_e r} + e^{-\delta_h r}\right) \tag{8.7}$$

where

$$\delta_{e,h} = a_o/\rho_{e,h}$$

The unperturbed wave function is

$$\phi_{n\ell} = \frac{2^{\ell+1}}{n^{\ell+2}}\left[\frac{(n+\ell)!}{(n-1-\ell)!}\right]^{\frac{1}{2}} \frac{1}{(2\ell+1)!} e^{\frac{-r}{n}} r^{\ell+1}$$

$$\cdot {}_1F_1\left(-n+\ell+1,\ 2\ell+2,\ \frac{2r}{n}\right)$$

where ${}_1F_1$ is the confluent hypergeometric function.

Substitution of this wave function in Eq. (8.6) gives the following expression for H_{nm}.

$$H_{nm} = \left(\frac{\varepsilon_o}{\varepsilon_\infty} - 1\right) \frac{2^{2\ell+1}}{(2\ell+1)!} \frac{1}{n^{\ell+2}\, m^{\ell+2}} \left[\frac{(n+1)!}{(n-\ell-1)!} \frac{(m+1)!}{(m-\ell-1)!}\right]^{\frac{1}{2}}$$

$$\times \left\{ \frac{1}{\left(\delta_e - \frac{1}{n} + \frac{1}{m}\right)^{-n+\ell+1}} \frac{1}{\left(\delta_e + \frac{1}{n} - \frac{1}{m}\right)^{-m+\ell+1}} \frac{1}{\left(\delta_e + \frac{1}{n} + \frac{1}{m}\right)^{n+m}} \right.$$

$$\times {}_2F_1\left(-n+\ell+1, -m+\ell+1, 2\ell+2; \frac{4mn}{(\delta_e mn - m + n)(\delta_e mn + m - n)}\right)$$

$$+ \frac{1}{\left(\delta_h - \frac{1}{n} + \frac{1}{m}\right)^{-n+\ell+1}} \times \frac{1}{\left(\delta_h + \frac{1}{n} - \frac{1}{m}\right)^{-m+\ell+1}} \times \frac{1}{\left(\delta_h + \frac{1}{n} + \frac{1}{m}\right)^{n+m}}$$

$$\left. \times {}_2F_1\left(-n+\ell+1, -m+\ell+1, 2\ell+2; \frac{4mn}{(\delta_h mn - m + n)(\delta_h mn + m - n)}\right) \right\}$$

where ${}_2F_1$ is the hypergeometric function.

Eq. (8.3) in conjunction with Eqs. (8.4) and (8.8) can be used to calculate the fine structure of any given excitonic state.

To allow for the ionic polarization, we have also used the polaron masses, as has been done in the work of Stebe and Certier (1972), which are connected to Frohlich's polaron coupling constant (1963) by

$$\alpha_{e,h} = \frac{1}{2}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_o}\right) \frac{e^2}{\hbar\omega} \frac{1}{\rho_{e,h}}$$

For weak or intermediate coupling

$$m^{**}_{e,h} = m^{*}_{e,h} \left(1 + \frac{\alpha_{e,h}}{6}\right)$$

and for strong coupling limit, characterized by $\alpha_{e,h} > 6$, they used the following relation due to Allcock (1963):

$$m^{**}_{e,h} = m^{*}_{e,h}\left[\frac{16}{81\pi^2}\alpha^4_{e,h} + O(\alpha^2)\right]$$

For CuCl, we have taken following values:

$m^*_e/m_o = 0.5$

$m^*_h/m_o = 13.5$

$\varepsilon_o = 7.5$

$\varepsilon_\infty = 4.84$

$\alpha_e = 1.17$

$\alpha_h = 6.1$

and $\omega = 216\ cm^{-1}$

8.3 Result

Our calculation were carried out in an IBM 360/65 computer. Because of the computer limitation on the function n!, we were only able to take 52 terms in obtaining the contribution of the second order term. The contribution of the higher order terms in Eq. (8.5) is quite small and can be neglected.

We find that the total contribution of the first and the second order terms in the perturbation theory gives:

$$\Delta E(2s - 2p) = 33.9 \text{ cm}^{-1} \quad \text{for CuCl}$$

which is a 17% improvement over the first order result.

Chapter 9 - Binding Energies of Positron to F and F' Colour Centres in Alkali Halides

9.1 Introduction

The possible role of lattice defects in positron trapping was discussed by several workers (Gol'danski and Prokopiev 1964 and Vorobiev et al. 1967) in the mid-sixties. Herlach and Heinrich (1970) investigated the 2γ-annihilation of positrons in additively coloured KCl crystals. They showed that the F-centres were the most important positron traps, but the possible influence of complex (F'- and F-aggregate) colour centres on the annihilation characteristics was also noted.

Berezin and Evarestov (1971) have investigated the bound state of the F_e+ centre, i.e. the system of a positron trapped by the F-centre. Berezin (1972) has considered the bound state of the F'_e+ centre, i.e. the system of a positron trapped by an F'-centre. Berezin (1972) has given a theoretical treatment of the F_e+ and F'_e+ centres in terms of model potentials and has carried out calculations for these two systems for NaCl, KCl and KBr crystals.

In the present study we have carried out the following calculations:

(a) using Berezin's model, but employing a better variational wave function, the binding energy of positron to the F-centre has been calculated for twenty alkali halides, and

(b) the binding energy of positron to the F' centre has been calculated for nine alkali halides. Atomic units are used throughout the chapter except where otherwise indicated. The necessary experimental data (Dawson and Pooley 1969 and Lynch and Robinson 1968) used in the calculations are given in Table 9.1.

9.2 Ground State Energy of the F_{e^+} Centre

In a F_{e^+} centre, an electron and a positron are moving in the Coulomb field of the anion vacancy. The effective potential of the free anion vacancy has the approximate form (Berezin 1970 and 1972).

$$V(r) = \delta/r \tag{9.1}$$

in which

$$\delta = \sqrt{\frac{8}{3} E^F_{abs}}, \tag{9.2}$$

where E^F_{abs} is the energy in the maximum of the F-absorption band. The Hamiltonian of the system can be written as

$$H = \frac{1}{2} \nabla_1^2 + \frac{1}{2} \nabla_2^2 - V(r_1) + V(r_2) + \frac{1}{|r_1 - r_2|} \tag{9.3}$$

where the subscripts, 1 and 2, are used to distinguish the quantities referring to the electron and the positron respectively.

The variational wave function (unnormalized) that we have used is

$$\psi = e^{-\alpha r_1} e^{-\beta r_2} [1 - \epsilon r_{12} + \eta(r_1 - r_2)^2] \tag{9.4}$$

where α, β, ϵ and η are variational parameters. The energy of the system is

$$E = \frac{1}{N} (T + V_1 + V_2) \tag{9.5}$$

where

$$T = \frac{1}{2} \langle \psi | \nabla_1^2 + \nabla_2^2 | \psi \rangle$$

$$V_1 = \delta \langle \psi | \frac{1}{r_1} - \frac{1}{r_2} | \psi \rangle$$

$$V_2 = \langle \psi | \frac{1}{|r_1 - r_2|} | \psi \rangle$$

and

$$N = \langle \psi | \psi \rangle$$

The calculations are carried out in elliptical coordinates. By decomposition and simplification of the integrations in N, T, V_1 and V_2, all integrals involved can have the following unique form

$$I(\ell, m, n) = \int_0^\infty s^\ell e^{-(\alpha + \beta)s} ds \int_0^s u^m du \int_{-u}^{u} e^{-(\alpha - \beta)t} t^n dt \tag{9.6}$$

in which s, u and t are the elliptical coordinates (Appendix B), and in terms of r_1, r_2 and r_{12}, they are

$$s = r_1 + r_2,$$

$$t = r_1 - r_2,$$

and $u = r_{12}$.

The above integral can be analytically evaluated. After some lengthy algebric procedures (see Appendix C), the following result is obtained.

$$I(\ell, m, n) = -\frac{n!\ell!}{(\alpha+\beta)^{\ell+1}(\alpha-\beta)^{n+m+2}}\sum_{k=0}^{n}\frac{(k+m)!}{k!}$$

$$-\frac{(-1)^m n!\ell!}{(\alpha+\beta)^{\ell+1}(\alpha-\beta)^{n+m+2}}\sum_{k=0}^{n}\frac{(k+m)!}{k!}$$

$$+\frac{n!}{2^{\ell+1}\alpha^{\ell+1}(\alpha-\beta)^{n+m+2}}\sum_{k=0}^{n}\frac{(k+m)!}{k!}\left(\sum_{j=0}^{k+m}\frac{(\ell+j)!}{j!}\left(\frac{\alpha-\beta}{2\alpha}\right)^j\right)$$

$$+\frac{(-1)^m n!}{2^{\ell+1}\beta^{\ell+1}(\alpha-\beta)^{n+m+2}}\sum_{k=0}^{n}\frac{(k+m)!}{k!}\left(\sum_{j=0}^{k+m}\frac{(-1)^j(\ell+j)!}{j!}\left(\frac{\alpha-\beta}{2\beta}\right)^j\right) \tag{9.7}$$

The expressions for N, T, V_1 and V_2 are respectively as follows:

$$N = \pi^2 \{I(2, 1, 0) - I(0, 1, 2) - 2\varepsilon [I(2, 2, 0) - I(0, 2, 2)] +$$
$$+ \varepsilon^2 [I(2, 3, 0) - I(0, 3, 2)] + 2\eta [I(2, 1, 2) - I(0, 1, 4)]$$
$$- 2\varepsilon\eta [I(2, 2, 2) - I(0, 2, 4)] + \eta^2 [I(2, 1, 4) - I(0, 1, 6)]\}$$

$$T = \pi^2 (\alpha^2 + \beta^2) \{I(2, 1, 0) - I(0, 1, 2) - 2\varepsilon [I(2, 2, 0) - I(0, 2, 2)]$$
$$+ \varepsilon^2 [I(2, 3, 0) - I(0, 3, 2)] + 2\eta [I(2, 1, 2) - I(0, 1, 4)]$$
$$- 2\varepsilon\eta [I(2, 2, 2) - I(0, 2, 4)] + \eta^2 [I(2, 1, 4) - I(0, 1, 6)]$$
$$+ 4\pi^2\eta^2 [I(2, 1, 2) - I(0, 1, 4)]$$
$$- 4\pi^2\beta\eta \{I(2, 1, 1) - I(0, 1, 3)$$
$$- \varepsilon [I(2, 2, 1) - I(0, 2, 3)] + \eta [I(2, 1, 3) - I(0, 1, 5)]$$
$$+ \pi^2\varepsilon^2 [I(2, 1, 0) - I(0, 1, 2)]$$
$$+ 2\pi^2\alpha\varepsilon \{I(1, 2, 0) - I(1, 0, 2)$$
$$- \varepsilon [I(1, 3, 0) - I(1, 1, 2)] + \eta [I(1, 2, 2) - I(1, 0, 4)]\}$$
$$+ 2\pi^2\beta\varepsilon \{I(2, 0, 1) - I(0, 2, 1)$$
$$- \varepsilon [I(2, 1, 1) - I(0, 3, 1)] + \eta [I(2, 0, 3) - I(0, 2, 3)]$$
$$- 4\pi^2\varepsilon\eta [I(2, 0, 2) - I(0, 2, 2)]\}$$

$$V_1 = 4\pi^2 a [I(0, 1, 1) - 2\varepsilon I(0, 2, 1) + \varepsilon^2 I(0, 3, 1)$$
$$+ 2\eta I(0, 1, 3) - 2\varepsilon\eta I(0, 2, 3) + \eta^2 I(0, 1, 5)]$$

$$W_2 = -\pi^2 \{I(2, 0, 0) - I(0, 0, 2) - 2\varepsilon [I(2, 1, 0) - I(0, 1, 2)]$$

$$+ \varepsilon^2 [I(2, 2, 0) - I(0, 2, 2)] + 2\eta [I(2, 0, 2) - I(0, 0, 4)]$$

$$- 2\varepsilon\eta [I(2, 1, 2) - I(0, 1, 4)] + \eta^2 [I(2, 0, 4) - I(0, 0, 6)]\}$$

The ground state energy of the F_e^+ centre is the optimum value of $\langle\Psi|H|\Psi\rangle$ with respect to the parameters α, β, ε and η. The binding energy (E_B) of the F_e^+ centre (i.e. the positron affinity of a F-centre) may be defined as the difference between the ground state energy of the optical electron of the F centre and the ground state energy of the F_e^+ centre. Table 9.2 shows the values of the optimized parameters, the ground state energies of F_e^+ and F centres, and $E_B(F_e^+)$.

9.3 Ground State Energy of the $F_e'^+$ Centre

The F' centre in alkali halides is the bound state of an extra electron with an F-centre and it is analogous to the negative hydrogen ion H^-. The potential experienced by an electron in the field of a hydrogen atom can be approximated (Tietz 1961 and Obyedkov 1969) by the Hulthēn potential (Appendix A).

$$V(r) = \frac{be^{-\delta r}}{1 - e^{-\delta r}} \qquad (9.8)$$

where δ and b are parameters. Berezin (1971) adopts this potential for

the field of an F-centre. The eigenvalue of the 1s state of the Hulthén potential is given by

$$E = \frac{1}{8}\left(\frac{2b}{\delta} - \delta\right)^2 \qquad (9.9)$$

We write $\gamma = \frac{b}{\delta} - \frac{\delta}{2}$, then $E = \frac{\gamma^2}{2}$ and $b = \delta\gamma + \frac{\delta^2}{2}$. If we assume the electron binding energy in the potential (9.8) is equal to the experimental value of the binding energy for the F' centre, then

$$\gamma = \sqrt{2\hbar\omega_0} \qquad (9.10)$$

$\hbar\omega_0$ being the long-wavelength edge of the photoionization absorption band of the F'-centre.

The F'_e+ centre is formed when a positron is trapped by an F' centre. In other words, a positron and an electron are bound to a neutral F centre. The Hamiltonian of the system has the same form as eq. (9.3), except that now V(r) is given by eq. (9.8). Berezin (1972) calculated the ground state energy of the F'_e+ centre for three alkali halides - NaCl, KCl and KBr, by the variational method. Here we extend his calculations to nine alkali halides, using more recent data to determine the constants δ and b.

The trial wave function is the product of two ground state Hulthén type wave functions,

$$\Psi = \phi_1(r_1)\,\phi_2(r_2) \qquad (9.11)$$

where

$$\phi_i(r_i) = \frac{\sqrt{2\alpha_i(\delta + \alpha_i)(\delta + 2\alpha_i)}}{\delta} e^{-\alpha_i r_i} (1 - e^{-\delta r_i}) \qquad (9.12)$$

in which the α_i's are variational parameters. The ground state energy can be expressed as

$$E = \langle\Psi|H|\Psi\rangle$$

$$= \frac{1}{2}\langle\Psi|\nabla_1^2|\Psi\rangle + \frac{1}{2}\langle\Psi|\nabla_2^2|\Psi\rangle$$

$$- \langle\Psi|V(r_1)|\Psi\rangle + \langle\Psi|V(r_2)|\Psi\rangle + \langle\Psi|\frac{1}{|r_1 - r_2|}|\Psi\rangle \qquad (9.13)$$

in which

$$\langle\Psi|\nabla_i^2|\Psi\rangle = -\alpha_i(\delta + \alpha_i) \qquad (9.14)$$

and

$$\langle\Psi|V(r_i)|\Psi\rangle = \frac{\alpha_i b}{\delta} \qquad (9.15)$$

$$\langle\Psi|\frac{1}{|r_1 - r_2|}|\Psi\rangle = \frac{4\alpha_1\alpha_2}{\delta^4}(\delta + \alpha_1)(\delta + \alpha_2)(\delta + 2\alpha_1)(\delta + 2\alpha_2)$$

$$\times \{\frac{1}{2}(\frac{1}{\alpha_1} + \frac{1}{\alpha_2})[\ell n(2\alpha_1 + 2\alpha_2) - 2\ell n(\delta + 2\alpha_1 + 2\alpha_2) + \ell n(2\delta + 2\alpha_1 + 2\alpha_2)]$$

$$- 2(\frac{1}{\delta + 2\alpha_1} + \frac{1}{\delta + 2\alpha_2})[\ell n(\delta + 2\alpha_1 + 2\alpha_2) - 2\ell n(2\delta + 2\alpha_1 + 2\alpha_2)$$

$$+ \ell n(3\delta + 2\alpha_1 + 2\alpha_2)]$$

$$+ \frac{1}{2}(\frac{1}{\delta + \alpha_1} + \frac{1}{\delta + \alpha_2})[\ell n(2\delta + 2\alpha_1 + 2\alpha_2) - 2\ell n(3\delta + 2\alpha_1 + 2\alpha_2)$$

$$+ \ell n(4\delta + 2\alpha_1 + 2\alpha_2)]$$

$$- \frac{\delta^2}{2\alpha_1(\delta + \alpha_1)(\delta + 2\alpha_1)}[\ell n\, 2\alpha_2 - 2\ell n(\delta + 2\alpha_2) + \ell n(2\delta + 2\alpha^2)]$$

$$- \frac{\delta^2}{2\alpha_2(\delta + \alpha_2)(\delta + 2\alpha_2)}[\ell n\, 2\alpha_1 - 2\ell n(\delta + 2\alpha_1) + \ell n(2\delta + 2\alpha_1)]\} \qquad (9.16)$$

The values of δ, b and γ are shown in Table 9.1. The ground state energy of the F'_e+ centre was determined by minimizing eq. (9.13) with respect to α_1 and α_2. The values of α_1 and α_2 thus obtained together with the corresponding energies are given in Table 9.3. The ground state energy of the F' centre is shown in column 5 of Table 9.3, and

the binding energy (E_B) of the F'_e+ centre in column 6. The ground state energy of the F' centre is given by $\gamma^2/2$.

9.4 Discussion

It will be noticed from Table 9.2 that the positron affinity of the F-centre lies between 0.77 and 2.31 eV for the various alkali halides. For NaCl, KCl and KBr, Berezin (1972) obtained $E_B(F_e+)$ = 1.39, 1.57, and 1.67 eV respectively. The wave function used by us improves on these values; the new values being 1.72, 1.96, and 2.10 eV respectively.

Table 9.3 shows an interesting result; the positron affinity of the F' centre is practically the same for all the nine alkali halides for which we have carried out the calculations. Also a comparison of the last columns of Tables 9.2 and 9.3 shows that the F' centre is a more efficient positron trap than the F centre. The relative importance of the two, however, depends on the individual alkali halide.

Table 9.1 : Experimental data for E^F_{abs} and $\hbar\omega_o$, and the constants δ , γ , and b^a

Crystal	E^F_{abs} (ev)	$\hbar\omega_o$ (ev)	δ (at.unit)	γ (at.unit)	b (at.unit)
LiF	5.083		0.7059		
LiCl	3.256		0.5650		
LiBr	2.767		0.5208		
LiI	3.176		0.5580		
NaF	3.702	1.85	0.6024	0.3688	0.4037
NaCl	2.746	1.72	0.5189	0.3556	0.3191
NaBr	2.345		0.4795		
NaI	2.063		0.4497		
KF	2.873		0.5307		
KCl	2.295	0.90	0.4743	0.2572	0.2345
KBr	2.059	0.65	0.4493	0.2186	0.1992
KI	1.874	0.70	0.4286	0.2269	0.1891
RbF	2.409		0.4860		
RbCl	2.036		0.4468	0.2169	0.1967
RbBr	1.851		0.4260		
RbI	1.705	0.55	0.4088	0.2011	0.1658
CsF	1.876		0.4289		
CsCl	2.169		0.4611		
CsBr	1.951	0.54	0.4373	0.1993	0.1828
CsI	1.718	0.55	0.4104	0.2011	0.1667

Table 9.2 : The binding energy of the Fe^+ center. All values, except those in the last column, are in atomic units

Crystal	α	β	ε	η	Ground state energy Fe^+ center	Ground state energy Fe^+ center	Binding energy Fe^+ center (ev)
LiF	0.7040	0.1270	0.0400	0.0003	0.27744	0.24918	0.77
LiCl	0.5722	0.1610	0.0560	0.0006	0.21383	0.15962	1.47
LiBr	0.5351	0.1703	0.0598	0.0006	0.19862	0.13565	1.71
LiI	0.5670	0.1626	0.0563	0.0005	0.21131	0.15573	1.51
NaF	0.6055	0.1529	0.0524	0.0005	0.22840	0.18147	1.28
NaCl	0.5335	0.1707	0.0599	0.0006	0.19798	0.13462	1.72
NaBr	0.5030	0.1786	0.0624	0.0006	0.18617	0.11497	1.94
NaI	0.4801	0.1843	0.0646	0.0007	0.17821	0.10114	2.10
KF	0.5437	0.1683	0.0587	0.0006	0.20185	0.14421	1.57
KCl	0.4992	0.1796	0.0627	0.0006	0.18473	0.11251	1.96
KBr	0.4797	0.1843	0.0648	0.0007	0.17809	0.10094	2.10
KI	0.4654	0.1884	0.0657	0.0007	0.17304	0.09188	2.21
RbF	0.5072	0.1772	0.0624	0.0007	0.18801	0.11810	1.90
RbCl	0.4780	0.1848	0.0648	0.0007	0.17746	0.09982	2.11
RbBr	0.4637	0.1889	0.0657	0.0006	0.17243	0.09076	2.22
RbI	0.4519	0.1921	0.0666	0.0006	0.16854	0.08359	2.31
CsF	0.4657	0.1883	0.0656	0.0006	0.17310	0.09198	2.21
CsCl	0.4889	0.1821	0.0638	0.0006	0.18116	0.10633	2.04
CsBr	0.4717	0.1867	0.0651	0.0006	0.17513	0.09565	2.16
CsI	0.4530	0.1918	0.0665	0.0006	0.16888	0.08423	2.30

Table 9.3 : The binding energy of the Fe^+ center. All values, except those in the last column, are in atomic units

Crystal	α_1	α_2	Ground state energy Fe^+ center	Ground state energy Fe center	Binding energy Fe^+ center (ev)
NaF	0.4537	0.1036	0.17785	0.06801	2.99
NaCl	0.4432	0.1101	0.17200	0.06323	2.96
KCl	0.3745	0.1199	0.14231	0.03308	2.97
KBr	0.3501	0.1250	0.13263	0.02389	2.96
KI	0.3555	0.1269	0.13413	0.02574	2.95
RbCl	0.3491	0.1254	0.13221	0.02352	2.96
RbI	0.3402	0.1313	0.12811	0.02022	2.93
CsBr	0.3386	0.1278	0.12822	0.01986	2.95
CsI	0.3402	0.1311	0.12814	0.02022	2.94

Chapter 10 - Wave Functions for the Hydrogen Molecular Ion

10.1 Introduction

The Schrodinger equation for the hydrogen molecular ion, H_2^+, has been solved exactly by Bates, Ledsham and Stewart (1953). However, often in practical applications, analytical wave functions, although approximate, are more convenient to use. A number of wave functions have been proposed for the $1s\sigma$ state of H_2^+ (for a partial listing, see Geller et al. 1962). In the two-parameter category, the following wave functions (unnormalized) can be analytically treated to give relatively good results for the energy in the neighborhood of the minimum of the potential energy curve.

James (1935):

$$\Psi = e^{-\alpha\mu} (1 + \beta\nu^2) \tag{10.1}$$

Guillemin and Zener (1929):

$$\Psi = e^{-\alpha\mu} \cosh (\beta\nu) \tag{10.2}$$

and geometric-mean function (Radel et al. 1969):

$$\Psi = e^{-\alpha\mu} \left[\cosh (\alpha\nu) + \beta\right] \tag{10.3}$$

The Eq. (10.3) is a special case of the Dalgarno-Poots (1954) wave function. Here μ and ν are confocal elliptic coordinates

$$\mu = (r_a + r_b)/R \tag{10.4}$$

$$\nu = (r_a - r_b)/R \tag{10.5}$$

R is the distance between two nuclei, α and β are variational parameters, different for different wave functions.

Rothstein (1971) has suggested a Padé type variational wave function:

$$\psi = \frac{(1 + c(a)\ \mu)}{(d(a) + a\mu)}\ e^{-a\mu}\ \cosh(b\nu)$$

where

$$c(a) \equiv \frac{R}{a(3 - \sigma)}$$

$$d(a) \equiv \frac{a(3 + \sigma)}{(1 - \sigma)}$$

$$\sigma \equiv \frac{R}{a} - 1$$

and a and b are variational parameters.

Amongst two-parameter wave functions, as far as we are aware, the Rothstein function gives the best energy at the potential minimum, with the geometric-mean at the second place. However, as will be seen later (Fig. 10.1), Rothstein results are poorer than the geometric-mean results above R > 4 atomic units.

In this study we proposed a function of the following form:

$$\psi = e^{-\alpha\mu}\ \left[\cosh(\beta\nu) + \cosh(2\beta\nu)\right] \qquad (10.6)$$

These functions have one feature in common. They are formed by $e^{-\alpha\mu}$ multiplied by a suitable function of ν. It seemed appropriate to make a comparative study of these functions.

To obtain the energy of the uppermost vibrational levels, it is necessary to determine the potential energy curve over a wide interval of R. These uppermost levels are of importance, for example, in determining the probability of field dissociation. Here we lay stress on the aspect of variational results. Kim et al. (1965) have reported results from the Guillemin-Zener function in the range R=0 to R=10 a.u. Patel (1967) has carried out calculations on the James function in the range R=0 to R=6 a.u. For the Geometric-mean wave function, Radel et al. (1969) have given energies for the range R=0 to R=20 a.u. However, the R values at which results have been reported by these authors do not have a sufficient number of common points. With a view to carry out the comparison over a wide range of R (R=0 to 40 a.u.) and to have the energy values from the four functions, Eq. (10.1), Eq. (10.2), Eq. (10.3) and Eq. (10.6), for the same values of R, a recalculation for the wave functions (10.1), (10.2) and (10.3) is necessary, in addition to the calculation on the function (10.6). No new calculations were made for the Rothstein function, as these involve gaussian quadrature.

For simplicity the following abbreviations are used: GZ for Guillemin-Zener and GM for the Geometric-mean.

10.2 Calculation

The Schrodinger equation for a hydrogen molecular ion is

$$\frac{1}{2}\nabla^2\Psi + \left(\frac{1}{r_a} + \frac{1}{r_b} - \frac{1}{R}\right)\Psi = E\Psi$$

In confocal elliptical coordinates, energy of the system is given by

$$E = \frac{1}{2}\langle\Psi|\nabla^2|\Psi\rangle + \frac{2}{R}\langle\Psi|\frac{1}{\mu+\nu}|\Psi\rangle + \frac{2}{R}\langle\Psi|\frac{1}{\mu-\nu}|\Psi\rangle - \frac{1}{R} \qquad (10.7)$$

where

$$\nabla^2 = \frac{4}{R^2}\frac{1}{\mu^2-\nu^2}\left\{\frac{\partial}{\partial\mu}\left[(\mu^2-1)\frac{\partial}{\partial\mu}\right] + \frac{\partial}{\partial\nu}\left[(1-\nu^2)\frac{\partial}{\partial\nu}\right]\right\}$$

$$+ \frac{4}{R}\frac{1}{(\mu^2-1)(1-\nu^2)}\frac{\partial^2}{\partial\phi^2}$$

Energy results by substituting the wave function into the Eq. (10.7). The evaluations of integrals in most cases here are quite complex but all can analytically be carried out (see Appendix D). The final expressions are shown below.

From the James function:

$$E = -\frac{1}{R} - \frac{14\alpha}{R^2}\frac{1}{4\alpha^2(35+14\beta+3\beta^2)+7(2\alpha+1)(15+10\beta+3\beta^2)}$$

$$\times\left[(2\alpha+1)(15+10\beta+3\beta^2)(\alpha-2R)+16\alpha\beta^2\right] \qquad (10.8)$$

From the Guillemin-Zener function:

$$E = -\frac{1}{R} - \frac{16\alpha}{R^2}\left[\frac{4}{3} + \frac{2}{\alpha} + \frac{1}{\alpha^2} + \frac{1}{\alpha\beta}\sinh(2\beta)\right.$$

$$\left. + \frac{1}{2\alpha^2\beta}\sinh(2\beta) - \frac{1}{2\beta^3}\sinh(2\beta) + \frac{1}{\beta^2}\cosh(2\beta)\right]^{-1}$$

$$\times \left\{\frac{1}{4} + \frac{1}{8\alpha} - \frac{\beta^2}{6\alpha} + \frac{1}{8\beta}\sinh(2\beta) + \frac{1}{8\alpha}\cosh(2\beta)\right.$$

$$\left. - \frac{R}{4\alpha}\left[\frac{\sinh(2\beta)}{\beta} + \frac{\sinh(2\beta)}{2\alpha\beta} + \frac{1}{\alpha}\right]\right\} \qquad (10.9)$$

From the Geometric-mean function:

$$E = \frac{1}{R} + \frac{8\alpha^3}{R^2}\left[2e^{-2\alpha} + 16\beta e^{\alpha} + 16\beta\cosh(\alpha)\right.$$

$$\left. - \frac{24\beta}{\alpha}\sinh(\alpha) + \frac{2}{3}(1 + 2\beta^2)(4\alpha^2 + 6\alpha + 3)\right]^{-1}$$

$$\times \left\{-\frac{1}{2\alpha}e^{2\alpha} - \frac{4\beta}{\alpha}\sinh(\alpha) - \frac{2\beta}{\alpha^2}\sinh(\alpha)\right.$$

$$+ \frac{2}{3}\alpha + \frac{1}{2\alpha^2}(1 + 2\alpha)(1 + 2\beta^2)(\alpha + 2R)$$

$$\left. + \frac{(1 + 2\alpha)R}{\alpha^2}\left[\frac{1}{2}\sinh(2\alpha) + \frac{4\beta}{\alpha}\sinh(\alpha)\right]\right\} \qquad (10.10)$$

From the Eq. (10.6):

$$E = -\frac{1}{R} + \frac{8\alpha}{R^2}\left\{\frac{4}{3} + \frac{2}{\alpha} + \frac{1}{\alpha^2} - \frac{4}{\beta^3}\left[\sinh(\beta) - \beta\cosh(\beta)\right]\right.$$

$$- \frac{1}{4\beta^3}\left[\sinh(2\beta) - 2\beta\cosh(2\beta)\right] - \frac{4}{27\beta^3}\left[\sinh(3\beta) - 3\beta\cosh(3\beta)\right]$$

$$- \frac{1}{32\beta^3}\left[\sinh(4\beta) - 4\beta\cosh(4\beta)\right]$$

$$+ \left(\frac{1}{\alpha^2} + \frac{2}{\alpha}\right)\left[\frac{\sinh(\beta)}{\beta} + \frac{\sinh(2\beta)}{4\beta} + \frac{\sinh(3\beta)}{3\beta} + \frac{\sinh(4\beta)}{4\beta}\right]\Big\}^{-1}$$

$$\times \left\{\frac{1}{4\alpha}\left[-1 - 2\alpha + \frac{10}{3}\beta^2 - \left(\frac{9}{\beta} + \frac{2\alpha}{\beta}\right)\sinh(\beta) - \frac{\alpha}{2\beta}\sinh(2\beta)\right.\right.$$

$$+ \left(\frac{1}{27\beta} + \frac{2\alpha}{3\beta}\right)\sinh(3\beta) - \frac{\alpha}{4\beta}\sinh(4\beta) - 8\cosh(\beta)$$

$$- \frac{1}{2}\cosh(2\beta) - \frac{8}{9}\cosh(3\beta) - \frac{1}{2}\cosh(4\beta)\Big]$$

$$+ \frac{R(1+2\alpha)}{48\alpha^2\beta}\left[24\beta + 24\sinh(\beta) + 6\sinh(2\beta)\right.$$

$$\left.\left.\left. + 8\sinh(3\beta) + 3\sinh(4\beta)\right]\right\} \qquad (10.11)$$

The energy of a hydrogen molecular ion at a given internuclear separation R is obtained by minimizing these expressions with respect to α and β. Table 10.1 shows the energies calculated here at various internuclear distance R along with the exact energy values due to Wind (1965) and Peek (1965). Table 10.2 gives the optimized values of parameters α and β.

10.3 Summary of Results and Discussion

Table 10.2 shows that the α's of the four functions are monotonically increasing function of R and below R=6 a.u.; these are very close to each other. Above R=6 a.u., α (James) shows an increasing departure from the other three α's. The significance of β is different in different functions and here no similarity is expected or found. β (James), β (GZ) and β (here) show an increase with R while β(GM) decreases with R. At large R β(James) assumes very large values.

It will be noticed from the Table 10.1 that the results from the James function are the poorest of the four, especially at large R. The James function does not lead to the correct wave function in the limit of large internuclear distances and its poor performance at large R, is therefore, understandable.

To compare the performance of the other four functions, in Fig. 10.1, we show the behavior of $\left[E(\text{cal}) - E(\text{exact}) \right]$ for these wave functions as a function of R. Here E(cal) represents the energy calculated from the wave function in question.

Below R=1, the results from the GZ, GM and Eq. (10.6) are identical to seven significant figures. It will be noticed from the Table 10.1 and Fig. 10.1 that our results are better than the GM ones above R=1. Our results are better than the GZ ones between R=1 and R≈9.8. Between R≈9.8 and R≈16, GZ results are slightly better than ours and above R≈16, the

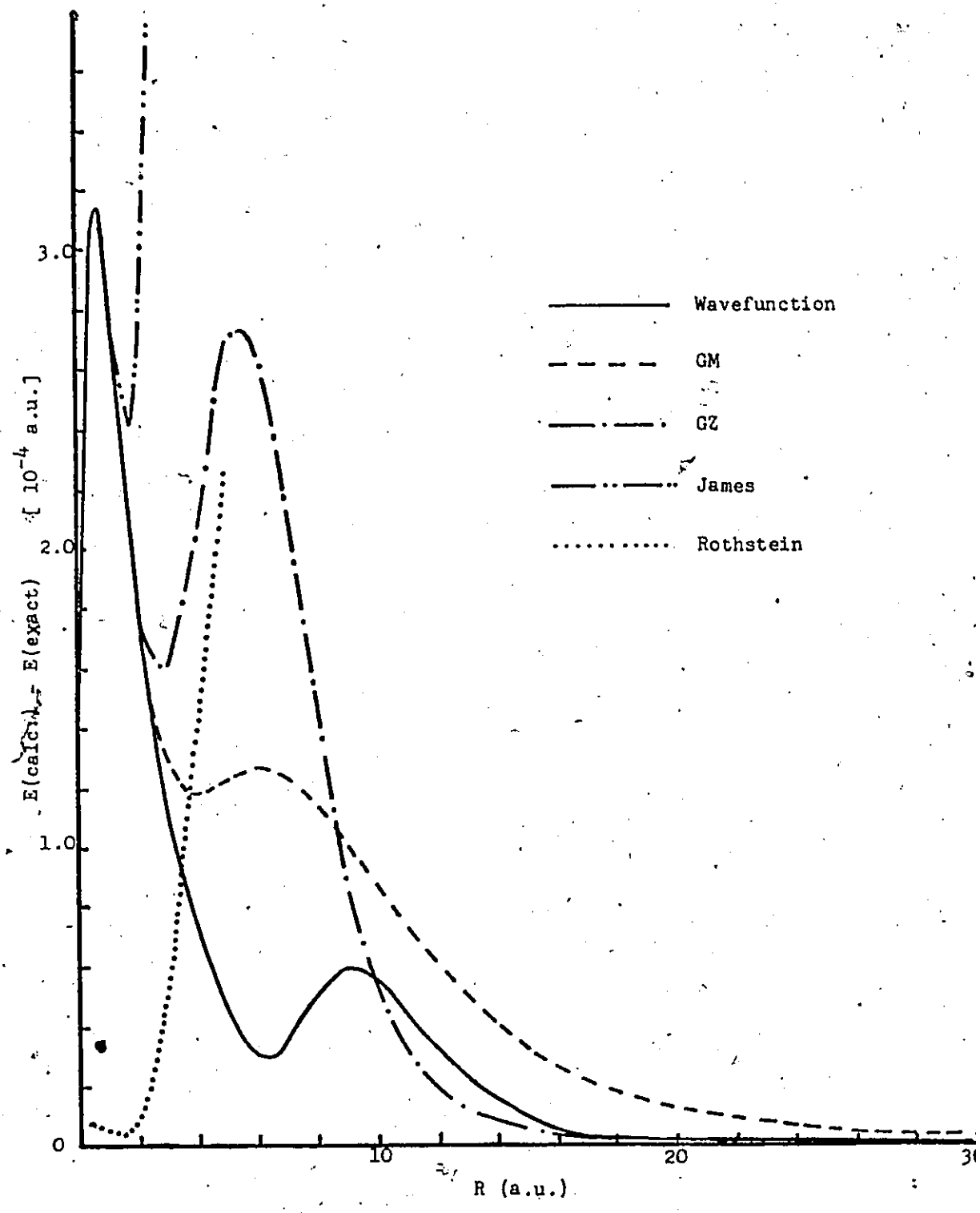

Fig. 10:1 : E(calc) - E(exact) against internuclear separation R for various wave functions

two give practically identical results. Rothstein (1971) results are better than ours below R=3.5, but above this the reverse is true. We may also note here that for the wave function (10.6), all the required integrals can be evaluated analytically, while for the Rothstein function, guassian quadrature has to be resorted to.

The minimum in the potential energy curve from our wave function (10.6) is obtained by minimizing the Eq. (10.11) with respect to α, β and R simultaneously. It happens at R=1.9988 a.u. and the total energy at this point is -0.602451 a.u. These results may be compared with the exact values of 1.99719 a.u. (Bishop 1971) and -0.602346 a.u. for the equilibrium internuclear separation R_e and E respectively.

Another quantity of interest is R_c. It is value of R, less than R_e, at which the total energy has the same value as at infinite separation. In determining it from the Eq. (10.11), we first assume that E varies with $R-R_c$ quadratically. In other words R_c can be approximated by three points in the neighborhood of R_c. Then minimization of E with respect to α and β is carried out. This procedure is continued until the E obtained is within the required accuracy. Here we obtained R_c = 1.110 a.u. which is in satisfactory agreement with the experimental value of 1.12 a.u. of Stevenson (1951) (see also Frost and Musulin 1954).

In Fig. 10.1 the GM results are seen to be better than the GZ ones below R ≈ 8.6; but above this the reverse is true. The Rothstein energies

are seen to be very good at low R, but these become rapidly poor as R increases. A comparison of the results from the Rothstein function with those from the functions (10.2), (10.3) and (10.6) leads us to conjecture that if one wishes to improve the latter functions at small R(< 2) then one should multiply them by a suitable function of μ. This function should be such that it rapidly assumes a constant value beyond R ≈ 2.

In conclusion, we find that there is no single function which gives the "best" energy values for all R values. All functions quoted here are adequate approximate wave function in R ≤ 2 a.u. The wave function (10.6) proposed here does provide a good 'compromise' description.

Table 10.1: Optimized parameters for various wave functions at various internuclear separations (R).

Internuclear separation R	James		Guillemin-Zener		Geometric-mean		Wave-function (10.6)	
	α	β	α	β	α	β	α	β
0.2	0.19383	0.00645	0.19383	0.11353	0.19382	1.9007	0.19383	0.07018
0.4	0.36802	0.02431	0.36802	0.22012	0.36803	1.8598	0.36800	0.13904
0.6	0.52415	0.05148	0.52415	0.31970	0.52414	1.7214	0.52410	0.20194
0.8	0.66622	0.08661	0.66622	0.41364	0.66622	1.6443	0.66620	0.26103
1.0	0.79740	0.12895	0.79740	0.50331	0.79742	1.5803	0.79740	0.31728
1.2	0.92007	0.17828	0.92007	0.58982	0.92002	1.5151	0.92010	0.37140
1.4	1.0359	0.23455	1.0359	0.67401	1.0359	1.4701	1.0359	0.42389
1.6	1.1462	0.29795	1.1462	0.75659	1.1461	1.4203	1.1462	0.47509
1.8	1.2520	0.36892	1.2520	0.83812	1.2519	1.3768	1.2520	0.52544
2.0	1.3540	0.44796	1.3540	0.91907	1.3539	1.3330	1.3540	0.57531
2.2	1.4530	0.53582	1.4530	0.99984	1.4527	1.2909	1.4530	0.62460
2.4	1.5491	0.63308	1.5494	1.0807	1.5490	1.2499	1.5494	0.67380
2.6	1.6434	0.74106	1.6437	1.1620	1.6433	1.2124	1.6438	0.72300
2.8	1.7361	0.86054	1.7364	1.2440	1.7357	1.1740	1.7365	0.77221
3.0	1.8270	0.99278	1.8277	1.3269	1.8266	1.1357	1.8278	0.82170
3.2	1.9172	1.1395	1.9180	1.4109	1.9163	1.0977	1.9180	0.87141
3.4	2.0063	1.3024	2.0075	1.4961	2.0053	1.0621	2.0076	0.92148
3.6	2.0947	1.4830	2.0964	1.5827	2.0938	1.0291	2.0965	0.97178

Table 10.1 (cont'd)

Internuclear separation R	James		Guillemin-Zener		Geometric-mean		Wave-function(10.6)	
	α	β	α	β	α	β	α	β
3.8	2.1823	1.6838	2.1849	1.6708	2.1819	0.99630	2.1851	1.0226
4.0	2.2697	1.9073	2.2733	1.7605	2.2690	0.96077	2.2735	1.0739
4.2	2.3569	2.1567	2.3616	1.8519	2.3565	0.92862	2.3620	1.1254
4.4	2.4442	2.4346	2.4501	1.9449	2.4438	0.89703	2.4505	1.1775
4.6	2.5312	2.7458	2.5388	2.0397	2.5316	0.86807	2.5390	1.2297
4.8	2.6178	3.0945	2.6278	2.1362	2.6188	0.83664	2.6282	1.2823
5.0	2.7047	3.4859	2.7172	2.2343	2.7068	0.80852	2.7178	1.3350
5.2	2.7914	3.9270	2.8071	2.3339	2.7956	0.78399	2.8077	1.3878
5.4	2.8783	4.4265	2.8974	2.4351	2.8839	0.75618	2.8981	1.4410
5.6	2.9650	4.9930	2.9884	2.5376	2.9731	0.73226	2.9891	1.4938
5.8	3.0521	5.6389	3.0798	2.6414	3.0629	0.71034	3.0805	1.5466
6.0	3.1388	6.3803	3.1718	2.7462	3.1533	0.68964	3.1728	1.5995
6.5	3.3544	8.7937	3.4041	3.0118	3.3806	0.64056	3.4045	1.7304
7.0	3.5696	12.468	3.6394	3.2805	3.6105	0.59765	3.6403	1.8598
7.5	3.7828	18.617	3.8774	3.5501	3.8459	0.57587	3.8781	1.9869
8.0	3.9932	30.766	4.1175	3.8190	4.0799	0.54096	4.1180	2.1125
8.5	4.2015	65.703	4.3593	4.0861	4.3196	0.53205	4.3597	2.2357
9.0	4.4064	917.91	4.6025	4.3512	4.5588	0.51601	4.6026	2.3571
9.5	4.6072	4.975×10^5	4.8466	4.6140	4.8003	0.50901	4.8469	2.4776

Table 10.1 (cont'd)

Internuclear separation R	James		Guillemin-Zener		Geometric-mean		Wave-function (10.6)	
	α	β	α	β	α	β	α	β
10.0	4.8033	5.167×10^5	5.0915	4.8749	5.0440	0.51778	5.0911	2.5977
11.0	5.1812	9.009×10^5	5.5832	5.3921	5.5339	0.55015	5.5826	2.8349
12.0	5.5418	1.026×10^6	6.0765	5.9046	6.0264	0.60758	6.0769	3.0722
13.0	5.8889	1.236×10^6	6.5710	6.4139	6.5181	0.61242	6.5712	3.3093
14.0	6.2225	1.498×10^6	7.0662	6.9214	7.0141	0.70157	7.0660	3.5477
15.0	6.5443	1.506×10^6	7.5621	7.4274	7.5107	0.80306	7.5620	3.7868
16.0	6.8560	1.564×10^6	8.0585	7.9326	8.0093	1.0524	8.0580	4.0280
17.0	7.1573	1.615×10^6	8.5552	8.4369	8.5074	1.2591	8.5551	4.2695
18.0	7.4507	1.678×10^6	9.0523	8.9406	9.0050	1.3419	9.0524	4.5132
19.0	7.7356	1.738×10^6	9.5497	9.4441	9.5042	1.7305	9.5495	4.7576
20.0	8.0133	1.797×10^6	10.047	9.9470	10.003	1.9949	10.047	5.0023
25.0	9.3073	2.083×10^6	12.538	12.458	12.500	1.9952	12.538	6.2402
30.0	10.478	2.358×10^6	15.032	14.966	15.000	2.1953	15.032	7.4861
35.0	11.553	2.588×10^6	17.528	17.470	17.500	2.3953	17.529	8.7363
40.0	12.555	2.803×10^6	20.025	19.974	20.000	2.5954	20.023	9.9877

Table 10.2 : Energy for $1s\sigma$ ground state of H_2^+ as obtained from the various wave functions. Energies given in the table do not include nuclear-nuclear repulsive energy 1/R. E(exact) is from Wind(1965) and Peek(1965)

R	Energy				
	James	Guillemin -Zener	Geometric -mean	Wave function (10.6)	Exact
0.2	1.928538	1.928538	1.928538	1.928538	1.928620
0.4	1.800525	1.800525	1.800525	1.800525	1.800754
0.6	1.671185	1.671185	1.671185	1.671185	1.671485
0.8	1.554166	1.554166	1.554166	1.554166	1.554480
1.0	1.451483	1.451485	1.451485	1.451485	1.451786
1.2	1.362025	1.362029	1.362029	1.362030	1.362308
1.4	1.284007	1.284016	1.284016	1.284017	1.284269
1.6	1.215689	1.215707	1.215708	1.215710	1.215937
1.8	1.155567	1.155600	1.155602	1.155605	1.155809
2.0	1.102386	1.102443	1.102447	1.102451	1.102634
2.2	1.055115	1.055207	1.055214	1.055219	1.055385
2.4	1.012910	1.013052	1.013063	1.013070	1.013220
2.6	0.975075	0.975287	0.975302	0.975312	0.975449
2.8	0.941033	0.941339	0.941361	0.941374	0.941499
3.0	0.910306	0.910736	0.910765	0.910781	0.910896

Table 10.2 (cont'd)

R	Energy				
	James	Guillemin -Zener	Geometric -mean	Wave function (10.6)	Exact
3.2	0.882488	0.883078	0.883117	0.883137	0.883243
3.4	0.857236	0.858029	0.858080	0.858104	0.858202
3.6	0.834258	0.835305	0.835367	0.835396	0.835487
3.8	0.813300	0.814659	0.814734	0.814769	0.814853
4.0	0.794141	0.795878	0.795967	0.796008	0.796085
4.2	0.776587	0.778777	0.778879	0.778927	0.778997
4.4	0.760467	0.763191	0.763307	0.763362	0.763426
4.6	0.745628	0.748976	0.749104	0.749166	0.749224
4.8	0.731935	0.736002	0.736140	0.736210	0.736262
5.0	0.719265	0.724151	0.724298	0.724374	0.724422
5.2	0.707508	0.713317	0.713471	0.713553	0.713594
5.4	0.696566	0.703405	0.703562	0.703650	0.703687
5.6	0.686350	0.694327	0.694484	0.694577	0.694610
5.8	0.676780	0.686003	0.686157	0.686253	0.686284
6.0	0.667785	0.678359	0.678509	0.678607	0.678636
6.5	0.647412	0.661808	0.661935	0.662032	0.662062
7.0	0.629439	0.648232	0.648327	0.648416	0.648451
7.5	0.613267	0.636946	0.637007	0.637083	0.637126
8.0	0.598467	0.627427	0.627456	0.627520	0.627570

Table 10.2 (cont'd)

R	Energy				
	James	Guillemin -Zener	Geometric -mean	Wave function (10.6)	Exact
8.5	0.584732	0.619282	0.619286	0.619338	0.619394
9.0	0.571848	0.612221	0.612206	0.612248	0.612307
9.5	0.559494	0.606024	0.605996	0.606031	0.606089
10.0	0.547424	0.600529	0.600493	0.600524	0.600579
11.0	0.524277	0.591179	0.591137	0.591164	0.591208
12.0	0.502562	0.583484	0.583443	0.583470	0.583502
13.0	0.482294	0.577015	0.576978	0.577005	0.577027
14.0	0.463419	0.571489	0.571458	0.571484	0.571498
15.0	0.445855	0.566710	0.566683	0.566707	0.566716
16.0	0.429503	0.562532	0.562510	0.562531	0.562536
17.0	0.414266	0.558848	0.558830	0.558848	0.558852
18.0	0.400049	0.555575	0.555560	0.555576	0.555578
19.0	0.386764	0.552647	0.552634	0.552648	0.552649
20.0	0.374329	0.550013	0.550002	0.550013	0.550014
25.0	0.322560	0.540005	0.540000	0.540005	0.540006
30.0	0.283569	0.533336	0.533333	0.533336	0.533336
35.0	0.253179	0.528573	0.528571	0.528573	
40.0	0.228825	0.525001	0.525000	0.525001	

Chapter 11. Electron Shielding in Doped Semiconductors

11.1 Introduction

The binding energy of an electron, bound to a donor atom in a doped semiconductor, relative to the conduction-band minima is usually calculated for a single impurity atom in the crystal (Kohn and Luttinger 1955, and Kohn 1957). On the experimental side, it is known that the binding energy of the electon decreases as the number of donors increases until at some critical impurity concentration there is pratically no activation energy (Pearson and Bardeen 1949, and Debye and Conwell 1954).

The theoretical problems associated with this phenomena can be conveniently discussed in terms of the potential of the singly charged donor screened by the conduction electrons (Mott and Jones 1958, and Mott 1961) :

$$V(r) = - \frac{e^2}{\kappa r} e^{-qr}$$

where κ is the static dielectric constant and q is the Mott screening parameter defined by $q^2 = 4m^* e^2 n^{1/3}/(\kappa h^2)$, n being the free-electron density.

The approximation that the electron is bound to a single ionized impurity is, however, no longer justified if there is considerable overlap between the wave functions of electrons bound to two neighboring impurity atoms. The occurrence of such a situation is governed by three factors : the static dielectric constant κ, the effective mass m*, and the free-electron density n. The effect of κ and of m* can be seen from the expression of the Bohr radius, $a_0 = \kappa \hbar^2 / m^* e^2$; since in semiconductor, $\kappa > 1$ and $m^* < m$, this means a greater radius than that in the free space. An increase in

the doping concentration acts in two ways : First, it decreases the average distance between impurities, and second, it increases the value of q, which in its turn leads to an increase in the average distance <r> between the electron and nucleus of the impurity atom (See Chapter 2). An appropriate combination of these factors can leads to the situation such that $\langle r \rangle \simeq \frac{1}{2}d$, where d is the average distance between impurities, We may note here that such a condition can sometimes exist at fairly low impurity concentrations, e.g., for InSb it occurs at an impurity concentration of $\sim 10^{14}/cm^3$. As this limit is approached, there will be an increasing concentration of systems in which two or more impurity atoms are participating. In this study we investigate the stability of the simplest of these systems, consisting of two ionized impurity atoms and an electron. We shall represent this system by Im_2^+ in analogy with H_2^+.

11.2 Calculation

Fig. 11.1 shows the electron bound to two impurity atoms A and B. In the present case the potential V includes the various charge interactions. They are the interaction between the electron and the impurity atom A, $-e^{-\delta r}\ a/r_a$, the interaction between the electron and the impurity atom B, $-e^{-\delta r}\ b/r_b$, and the mutual interaction between the impurity atoms, $e^{-\delta R}/R$, where δ is the screening parameter. The choice of the same δ between two positive ion cores has been established by the works of Lazarus (1960), Alfred and March (1957), and Corless and March (1961).

The Hamiltonian of the system is

$$H = \frac{1}{2}\nabla^2 + \frac{e^{-\delta r_a}}{r_a} + \frac{e^{-\delta r_b}}{r_b} - \frac{e^{-\delta R}}{R} \tag{11.1}$$

We will try to obtain the energy of this system by variational method. We will make use the wave functions which are frequently used for the H_2^+. In the following there are four two-parameter wave functions, in unnormalized form,

$$\psi = e^{-\alpha\mu}\ (1 + \beta\nu^2) \tag{11.2}$$

$$\psi = e^{-\alpha\mu}\ \cosh(\beta\nu) \tag{11.3}$$

$$\psi = e^{-\alpha\mu}\ \left[\cosh(\alpha\nu) + \beta\right] \tag{11.4}$$

$$\psi = e^{-\alpha\mu}\ \left[\cosh(\beta\nu) + \cosh(2\beta\nu)\right] \tag{11.5}$$

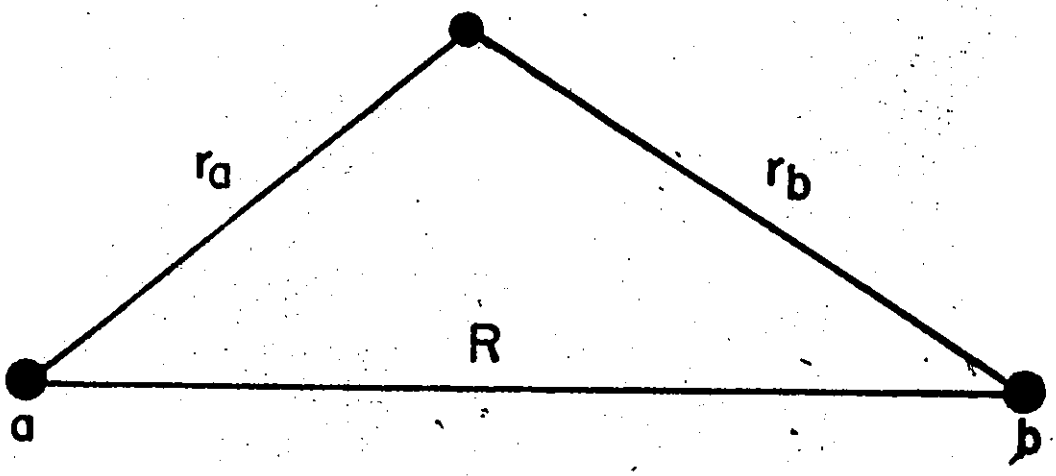

Fig. 11.1 : Coordinates used for Im_2^+

where α and β are variational parameters, different for different functions. Eq. (11.5) is a new function proposed by us which has been proved a good wave function over a wide range of internuclear distances R. The variables μ and ν are in confocal elliptical coordinates. By substituting these functions into the equation $\langle\Psi|H|\Psi\rangle$, energy expressions corresponding to the wave functions (11.2) - (11.5) are respectively

$$E = -\frac{e^{-\delta R}}{R} - \frac{840}{R^2}\frac{\alpha^3}{4\alpha^2(35+14\beta^2+3\beta^2)+7(2\alpha+1)(15+10\beta+3\beta^2)} \times \left\{\frac{1}{60\alpha}\left[(2\alpha+1)(15+10\beta+3\beta^2)+16\beta^2\right] - \frac{2Re^{-\frac{\delta R}{2}}}{\delta R+4\alpha}\left[B_1(\tfrac{\delta R}{2})+2\beta B_3(\tfrac{\delta R}{2})+\beta^2 B_5(\tfrac{\delta R}{2})\right]\right\} \qquad (11.6)$$

where

$$B_n(m) = \int_{-1}^{1} \nu^n e^{-m\nu}\, d\nu$$

$$E = -\frac{e^{-\delta R}}{R} - \frac{16\alpha}{R^2}\left[\frac{4}{3}+\frac{2}{\alpha}+\frac{1}{\alpha^2}+\frac{1}{\alpha\beta}\sinh(2\beta)+\frac{1}{2\alpha^2\beta}\sinh(2\beta) - \frac{1}{2\beta^3}\sinh(2\beta)+\frac{1}{\beta^2}\cosh(2\beta)\right]^{-1} \times \left(\frac{1}{4}+\frac{1}{8\alpha}-\frac{\beta^2}{6\alpha}+\frac{1}{8\alpha}\sinh(2\beta)\right.$$
$$+\frac{1}{8\alpha}\cosh(2\beta) - \frac{2Re^{-\frac{\delta R}{2}}}{\delta R+4\alpha}\left\{\frac{1}{\delta R+4\beta}\left[\sinh(\tfrac{\delta R}{2}+2\beta)\right.\right.$$
$$\left.+\cosh(\tfrac{\delta R}{2}+2\beta) - \frac{8(\alpha-\beta)}{(\delta R+4\alpha)(\delta R+4\beta)}\sinh(\tfrac{\delta R}{2}+2\beta)\right]$$
$$+\frac{1}{\delta R-4\alpha}\left[\sinh(\tfrac{\delta R}{2}-2\beta)+\cosh(\tfrac{\delta R}{2}-2\beta) - \frac{8(\alpha+\beta)}{(\delta R+4\alpha)(\delta R-4\beta)}\sinh(\tfrac{\delta R}{2}-2\beta)\right]$$
$$\left.\left.+\frac{2}{\delta R}\left[\sinh(\tfrac{\delta R}{2})+\cosh(\tfrac{\delta R}{2}) - \frac{8\alpha}{\delta R(\delta R+4\alpha)}\sinh(\tfrac{\delta R}{2})\right]\right\}\right) \qquad (11.7)$$

$$E = -\frac{e^{-\delta R}}{R} + \frac{8\alpha^3}{R^2}\left[2e^{2\alpha} + 16\beta e^{\alpha} + 16\beta \cosh(\alpha) - \frac{24\beta}{\alpha}\sinh(\alpha) \right.$$

$$\left. + \frac{2}{3}(1 + 2\beta^2)\ (4\alpha^2 + 6\alpha + 3)\right]^{-1}$$

$$\times \left\{ -\frac{1}{2\alpha} e^{2\alpha} - \frac{4\beta}{\alpha} e^{\alpha} - \frac{2\beta}{\alpha^2}\sinh(\alpha) + \frac{2\alpha}{3} - (1 + 2\beta^2)\ \left(\frac{1}{2\alpha} + 1\right) \right.$$

$$+ \frac{8e^{-\frac{\delta R}{2}}}{4\alpha + \delta R}\left[\frac{R}{4\alpha + \delta R} e^{\frac{4\alpha + \delta R}{2}} - \frac{R}{4\alpha - \delta R} e^{\frac{4\alpha - \delta R}{2}} \right.$$

$$\left. + \frac{4\beta R}{2\alpha + \delta R} e^{\frac{2\alpha + \delta R}{2}} - \frac{4\beta R}{2\alpha - \delta R} e^{\frac{2\alpha - \delta R}{2}} \right.$$

$$\left. + \frac{2(1 + 2\beta^2)}{\delta} e^{\frac{\delta R}{2}} \right.$$

$$+ \frac{16\alpha R}{(4\alpha + \delta R)(4\alpha - \delta R)}\sinh\left(\frac{4\alpha - \delta R}{2}\right)$$

$$- \frac{16\alpha\beta R}{(4\alpha + \delta R)(2\alpha + \delta R)^2}\sinh\left(\frac{2\alpha + \delta R}{2}\right)$$

$$+ \frac{48\alpha\beta R}{(4\alpha + \delta R)(2\alpha - \delta R)^2}\sinh\left(\frac{2\alpha - \delta R}{2}\right)$$

$$\left. \left. - \frac{16\alpha(1 + 2\beta^2)}{(4\alpha + \delta)\ \delta^2 R}\sinh\left(\frac{\delta R}{2}\right)\right]\right\} \qquad (11.8)$$

$$E = -\frac{e^{-\delta R}}{R} + \frac{8\alpha}{R^2}\left\{\frac{4}{3} + \frac{2}{\alpha} + \frac{1}{\alpha^2} - \frac{4}{\beta^3}\left[\sinh(\beta) - \beta\cosh(\beta)\right]\right.$$

$$- \frac{1}{4\beta^3}\left[\sinh(2\beta) - 2\beta\cosh(2\beta)\right] - \frac{4}{27\beta^3}\left[\sinh(3\beta) - 3\beta\cosh(3\beta)\right]$$

$$- \frac{1}{32\beta^3}\left[\sinh(4\beta) - 4\beta\cosh(4\beta)\right]$$

$$\left. + \left(\frac{1}{\alpha^2} + \frac{2}{\alpha}\right)\left[\frac{\sinh(\beta)}{\beta} + \frac{\sinh(2\beta)}{4\beta} + \frac{\sinh(3\beta)}{3\beta} + \frac{\sinh(4\beta)}{8\beta}\right]\right\}^{-1}$$

$$\times \left\{\frac{1}{4\alpha}\left[-1 - 2\alpha + \frac{10}{3}\beta^2 - \left(\frac{9}{\beta} + \frac{2\alpha}{\beta}\right)\sinh(\beta) - \frac{\alpha}{2\beta}\sinh(2\beta)\right.\right.$$

$$- \left(\frac{1}{27\beta} + \frac{2\alpha}{3\beta}\right)\sinh(3\beta) - \frac{\alpha}{4\beta}\sinh(4\beta) - 8\cosh(\beta)$$

$$\left.\left. - \frac{1}{2}\cosh(2\beta) - \frac{8}{9}\cosh(3\beta) - \frac{1}{2}\cosh(4\beta)\right]\right.$$

$$+ \frac{Re^{-\frac{\delta R}{2}}}{\delta R + 4\alpha}\left[\frac{2}{\delta R - 8\beta}\left\{\sinh\left(\frac{\delta R}{2} - 4\beta\right) + \cosh\left(\frac{\delta R}{2} - 4\beta\right)\right\}\right.$$

$$- \frac{16(\alpha + 2\beta)}{(\delta R + 4\alpha)(\delta R - 8\beta)^2}\sinh\left(\frac{\delta R}{2} - 4\beta\right)$$

$$+ \frac{4}{\delta R - 6\beta}\left\{\sinh\left(\frac{\delta R}{2} - 3\beta\right) + \cosh\left(\frac{\delta R}{2} - 3\beta\right)\right\}$$

$$- \frac{16(2\alpha + 3\beta)}{(\delta R + 4\alpha)(\delta R - 6\beta)^2}\sinh\left(\frac{\delta R}{2} - 3\beta\right)$$

$$+ \frac{2}{\delta R - 4\beta}\left\{\sinh\left(\frac{\delta R}{2} - 2\beta\right) + \cosh\left(\frac{\delta R}{2} - 2\beta\right)\right\}$$

$$- \frac{16(\alpha + \beta)}{(\delta R + 4\alpha)(\delta R - 4\beta)^2}\sinh\left(\frac{\delta R}{2} - 2\beta\right)$$

$$\left. + \frac{4}{\delta R - 2\beta}\left\{\sinh\left(\frac{\delta R}{2} - \beta\right) + \cosh\left(\frac{\delta R}{2} - \beta\right)\right\}\right.$$

$$- \frac{16(2\alpha + \beta)}{(\delta R + 4\alpha)(\delta R - 2\beta)^2} \sinh\left(\frac{\delta R}{2} - \beta\right)$$

$$+ \frac{8}{\delta R} \left\{\sinh\left(\frac{\delta R}{2}\right) + \cosh\left(\frac{\delta R}{2}\right)\right\} - \frac{64\alpha}{(\delta R + 4\alpha)\ \delta^2 R^2} \sinh\left(\frac{\delta R}{2}\right)$$

$$+ \frac{4}{\delta R + 2\beta} \left\{\sinh\left(\frac{\delta R}{2} + \beta\right) + \cosh\left(\frac{\delta R}{2} + \beta\right)\right\}$$

$$- \frac{16(2\alpha - \beta)}{(\delta R + 4\alpha)(\delta R + 2\beta)^2} \sinh\left(\frac{\delta R}{2} + \beta\right)$$

$$+ \frac{2}{\delta R + 4\beta} \left\{\sinh\left(\frac{\delta R}{2} + 2\beta\right) + \cosh\left(\frac{\delta R}{2} + 2\beta\right)\right\}$$

$$- \frac{16(\alpha - \beta)}{(\delta R + 4\alpha)(\delta R + 4\beta)^2} \sinh\left(\frac{\delta R}{2} + 2\beta\right)$$

$$+ \frac{4}{\delta R + 6\beta} \left\{\sinh\left(\frac{\delta R}{2} + 3\beta\right) + \cosh\left(\frac{\delta R}{2} + 3\beta\right)\right\}$$

$$- \frac{16(2\alpha - 3\beta)}{(\delta R + 4\alpha)(\delta R + 6\beta)^2} \sinh\left(\frac{\delta R}{2} + 3\beta\right)$$

$$+ \frac{2}{\delta R + 8\beta} \left\{\sinh\left(\frac{\delta R}{2} + 4\beta\right) + \cosh\left(\frac{\delta R}{2} + 4\beta\right)\right\}$$

$$- \frac{16(\alpha - 2\beta)}{(\delta R + 4\alpha)(\delta R + 8\beta)^2} \sinh\left(\frac{\delta R}{2} + 4\beta\right)\Bigg]\Bigg\} \qquad (11.9)$$

For a value of screening parameter δ, the energy of the system is the optimum value of the energy expression with respect to the parameters α and β, as well as the internuclear separation R. This optimum value is determined by the direct search due to Hooke and Jeeves (1961) (see also Wilde, 1964, and Kawalik and Osborne, 1968). Tables 11.1 to 11.4 show the energy along with the parameters at the equilibrium internuclear

distance R. Also shown in the Tables is the 'dissociation' energy D, given by

$$D = E(Im_2^+) - E(Im) \qquad (11.10)$$

for the dissociation

$$Im_2^+ \longrightarrow Im + Im^+$$

Values of E(Im) were taken from the results of our variational calculation of the three-parameter trial function in Chapter 2.

11.3 Discussion

The term $e^{-\alpha\mu}$ in all wave functions is simply the product of two 1s state hydrogenic wave functions with the atomic number Z as a variational parameter. The terms, respectively attached to it in Eqs. (11.2) to (11.5), $(1 + \beta\nu^2)$, $\cosh(\beta\nu)$, $[\cosh(\alpha\nu) + \beta]$ and $[\cosh(\beta\nu) + \cosh(2\beta\nu)]$, can be considered as a correction factor to it. These correction factors improve the results remarkably. Although we did not report the calculation of the trial function $e^{-\alpha\mu}$ here, for the sake of proving the above statement, we would show few energy eigenvalues here. At a weak screening $\delta = 0.001$, $e^{-\alpha\mu}$ gives $E = 0.58127$ and it is 3.49% higher in comparison with 0.60229 from Eq. (11.2), 3.50% higher in comparison with 0.60234 from Eq. (11.3) and 3.50% higher in comparison with 0.60235 from the Eqs. (11.4) and (11.5). This wave function yields unbound energy at $\delta = 1.20$ while all two-parameter wave functions here still produce bound energy values.

The James function of Eq. (11.2) is a special case of the Guillemin and Zener's function of Eq. (11.3). If one expands the hyperbolic cosine function in the Eq. (11.3) and retains only the power up to ν^2, Eq. (11.2) immediately follows. Eq. (11.5) is an extension of the Eq. (11.3) by adding $\cosh(2\beta\nu)$ in the correction term. So it is not hard to explain why the James function records the poorer results than the Guillemin-Sener's function and the Eq. (11.5). However in the weak screening region, the James function is a fairly good approximate wave function.

Below $\delta = 0.2$, Eqs. (11.3), (11.4) and (11.5) all give the same values of energy to the fifth place of decimal. This happens up to $\delta = 0.9$ for the wave functions (11.4) and (11.5). Overall the results obtained from Eq. (11.5) are the best. Thereafter, the discussion, if numerical values are involved in an electron bound to two impurity centres, will be reference to the Eq. (11.5).

The binding energy is seen to diminish with increase in δ, and ultimately becomes zero at $\delta = 1.254$, obtained from Eq. (11.5). The trial function (11.5) is known to give very good results for H_2^+ (0.017% accuracy in E), and it would be reasonable to assume that for low values of δ our results are satisfactory. However, it is difficult to estimate the accuracy of our results at high screening case. In view of this, the critical value of δ quoted here is, more accurately, only a lower limit.

It is of interest to note that in the case of an electron bound to a single impurity centre, the critical value of δ at which the ionization energy becomes zero is 1.19 (Rogers et al. 1970), thus there is a narrow region between $\delta = 1.19$ and 1.254 in which an electron cannot be bound to one ionized impurity, but it can be bound to two.

The results obtained here have a bearing on the nature of the Mott transition in semiconductors (1961, see also Mott and Twose 1961). Fritzsche (1958) has measured the resistivity of germanium at 2.5^{o}K with

different impurity concentrations. Antimony-doped and gallium-doped samples were used. His results are frequently quoted in support of the Mott transition in semiconductors and these are reproduced in Fig. 11.2. The dotted lines indicate the approximate borders between the three concentration ranges in which the resistivity showed a different behaviour. The low C region is what we have investigated in Chapter 2 of the static screened Coulomb potential. In this region resistivity decreases with the increase of electron concentration. The valence electron in this region is well localized in the ionized impurity centre to form a bound state so that at absolute zero it will not be free to move through the crystal and carry a current. The dotted line at the right-most of the low C is the limit at which the binding energy of the electron bound to the single ionized impurity of the static screening Coulomb potential is zero. Mott took the approximate value of $\delta = 1.0$ (1958, 1961); the same value was obtained by Krieger (1969) from a simple hydrogenic wave function. Here we take it 1.19, the result of Rogers et al. (1970) obtained by numerical technique.

In the high C region, resistivity is quite small and crystal shows metallic property. Mott and Jones (1958) explained it as follows. In this region the electron concentration is high enough to prevent the formation of electron - ionized impurity pair. Hence the localized state of the electron no longer exists. Even at absolute zero, there are still a large number of free electrons in the crystal and the conductivity is a finite value.

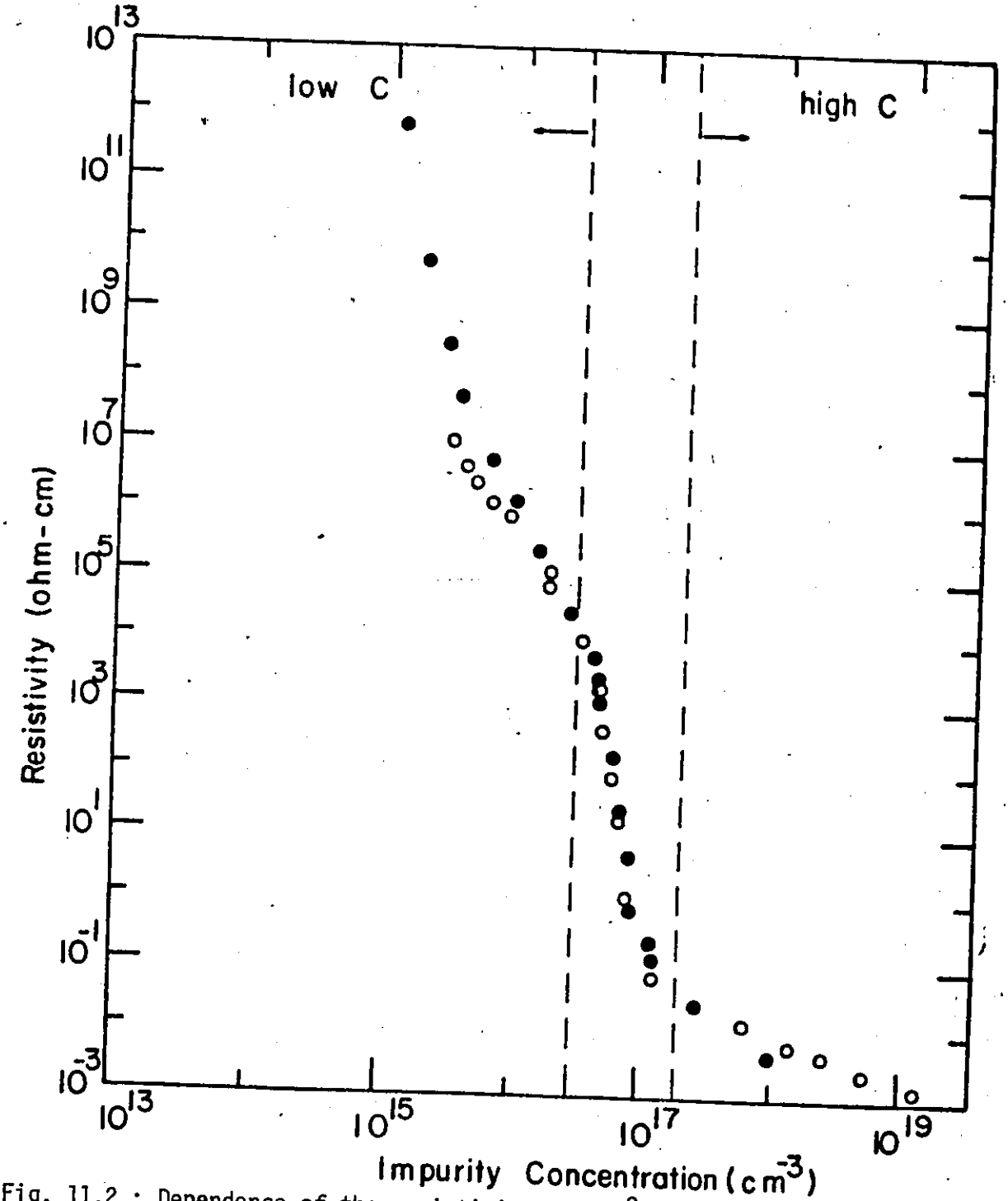

Fig. 11.2 : Dependence of the resistivity at 2.5°K on the impurity concentration (from Fritzsche 1958). Dots : n-type germanium, antimony doped; circles : p-type germanium, gallium doped.

Now what is happening between two dotted lines, in Fig. 11.2, in which resistivity shows a sharp drop? Our results clearly show that as $\delta > 1.19$ the electron will not be completely delocalized. There will be Im_2^+ system at least up to $\delta = 1.254$. As mentioned earlier, the value 1.254 is only a lower limit, probably $\delta = 1.27$ would be a better value. Furthermore, the results suggest that probably a more complex system, such as, Im_2 (two ionized impurities and two electrons), Im_3^{+2}, Im_4^+ (one electron in the field of three or four neighboring impurities) etc. might have a finite binding energy even for $\delta > 1.27$. For the foregoing discussions, we are led to the following picture: In the region $\delta = 1.19$ to 1.4 (a very approximate value), the electrons are no longer localized around individual impurities, but many of these partially localized. This region corresponds to the transition region between two dotted lines in Fig. 11.2.

Table 11.1 : Binding energy and optimized parameters as a function of screening parameter (Eq.(11.2))

Screening parameter	Internuclear separation	Optimized parameter α	β	E	D
0.0001	1.997	1.3522	0.4466	0.60229	0.10239
0.0002	1.997	1.3522	0.4466	0.60219	0.10239
0.0005	1.997	1.3522	0.4466	0.60189	0.10239
0.001	1.997	1.3522	0.4466	0.60139	0.10239
0.002	1.997	1.3522	0.4466	0.60039	0.10239
0.0025	1.997	1.3522	0.4466	0.59989	0.10238
0.005	1.997	1.3522	0.4466	0.59740	0.10238
0.01	1.997	1.3522	0.4466	0.59245	0.10238
0.02	1.997	1.3519	0.4467	0.58265	0.10235
0.025	1.997	1.3517	0.4467	0.57779	0.10233
0.03	1.997	1.3515	0.4468	0.57297	0.10231
0.04	1.997	1.3510	0.4470	0.56342	0.10225
0.05	1.997	1.3503	0.4472	0.55399	0.10217
0.06	1.997	1.3495	0.4474	0.54468	0.10208
0.07	1.998	1.3486	0.4477	0.53549	0.10197
0.08	1.998	1.3476	0.4480	0.52642	0.10185
0.09	1.998	1.3464	0.4483	0.51746	0.10171

Table 11.1 (cont'd)

Screening parameter	Internuclear separation	Optimized parameter α	Optimized parameter β	E	D
0.1	1.999	1.3451	0.4486	0.50861	0.10155
0.2	2.005	1.3269	0.4533	0.42594	0.09913
0.25	2.010	1.3145	0.4563	0.38828	0.09736
0.3	2.016	1.3007	0.4595	0.35287	0.09524
0.4	2.033	1.2690	0.4666	0.28834	0.08998
0.5	2.056	1.2330	0.4740	0.23153	0.08345
0.6	2.087	1.1933	0.4815	0.18177	0.07569
0.7	2.126	1.1503	0.4887	0.13852	0.06678
0.8	2.178	1.1036	0.4953	0.10132	0.05673
0.9	2.244	1.0526	0.5010	0.06979	0.04561
1.0	2.333	0.9961	0.5052	0.04360	0.03344
1.05	2.389	0.9650	0.5066	0.03243	0.02699
1.10	2.456	0.9312	0.5073	0.02253	0.02033
1.15	2.539	0.8938	0.5073	0.01387	0.01346
1.20	2.648	0.8509	0.5061	0.00648	0.00607
1.25	2.803	0.7984	0.5031	0.00040	0.00040

Table 11.2. Binding energy and optimized parameters as a function of screening parameter. (Eq. (11.3))

Screening parameter	Internuclear separation	α	β	Energy	D
0.0001	1.998	1.353	0.9182	0.60234	0.10245
0.0002	1.998	1.353	0.9182	0.60224	0.10245
0.0005	1.998	1.353	0.9182	0.60194	0.10245
0.001	1.998	1.353	0.9183	0.60144	0.10245
0.002	1.998	1.353	0.9183	0.60045	0.10245
0.0025	1.998	1.353	0.9183	0.59995	0.10245
0.005	1.998	1.353	0.9183	0.59746	0.10244
0.01	1.998	1.353	0.9183	0.59251	0.10244
0.02	1.998	1.353	0.9184	0.58271	0.10241
0.025	1.998	1.353	0.9184	0.57785	0.10239
0.03	1.998	1.352	0.9185	0.57303	0.10237
0.04	1.998	1.352	0.9186	0.56348	0.10231
0.05	1.999	1.351	0.9188	0.55405	0.10223
0.06	1.999	1.350	0.9190	0.54474	0.10214
0.07	1.999	1.349	0.9193	0.53555	0.10203
0.08	2.000	1.348	0.9196	0.52647	0.10190
0.09	2.000	1.347	0.9199	0.51751	0.10176
0.1	2.000	1.346	0.9203	0.50867	0.10161
0.2	2.007	1.328	0.9248	0.42600	0.09919
0.25	2.012	1.315	0.9277	0.38834	0.09742
0.3	2.018	1.302	0.9309	0.35293	0.09530
0.4	2.035	1.270	0.9376	0.28841	0.09005

Table 11.2 (cont'd)

0.5	2.058	1.234	0.9447	0.23160	0.08352
0.6	2.088	1.194	0.9518	0.18184	0.07576
0.7	2.129	1.151	0.9587	0.13859	0.06685
0.8	2.180	1.105	0.9650	0.10140	0.05681
0.9	2.247	1.054	0.9704	0.06986	0.04568
1.0	2.336	0.9972	0.9745	0.04367	0.03351
1.05	2.393	0.9662	-0.9761	0.03251	0.02707
1.10	2.459	0.9323	-0.9768	0.02260	0.02040
1.15	2.543	0.8949	-0.9769	0.01394	0.01353
1.20	2.651	0.8522	-0.9761	0.00654	0.00650
1.25	2.807	0.7998	-0.9737	0.00045	0.00045
1.30	3.102	0.7208	-0.9673	-0.00418	

Table 11.3. Binding energy and optimized parameters as a function of screening parameter (Eq. (11.4))

Screening parameter	Internuclear separation	α	β	Energy	D
0.0001	1.998	1.354	1.334	0.60235	0.10245
0.0002	1.998	1.354	1.334	0.60225	0.10245
0.0005	1.998	1.354	1.334	0.60195	0.10245
0.001	1.998	1.354	1.334	0.60145	0.10245
0.002	1.998	1.354	1.334	0.60045	0.10245
0.0025	1.998	1.354	1.334	0.59995	0.10245
0.005	1.998	1.354	1.334	0.59746	0.10244
0.01	1.998	1.354	1.333	0.59251	0.10244
0.02	1.998	1.354	1.332	0.58271	0.10241
0.025	1.998	1.354	1.331	0.57785	0.10239
0.03	1.998	1.353	1.330	0.57303	0.10237
0.04	1.999	1.353	1.327	0.56348	0.10231
0.05	1.999	1.352	1.324	0.55405	0.10223
0.06	1.999	1.351	1.320	0.54474	0.10214
0.07	1.999	1.350	1.315	0.53555	0.10203
0.08	2.000	1.349	1.309	0.52648	0.10191
0.09	2.000	1.347	1.302	0.51752	0.10177
0.1	2.000	1.346	1.296	0.50867	0.10161
0.2	2.007	1.323	1.203	0.42600	0.09919
0.25	2.012	1.308	1.143	0.38835	0.09743
0.3	2.018	1.290	1.077	0.35294	0.09531
0.4	2.035	1.248	0.9358	0.28842	0.09006

Table 11.3 (cont'd)

0.5	2.058	1.199	0.7870	0.23161	0.08353
0.6	2.089	1.143	0.6358	0.18185	0.07577
0.7	2.129	1.082	0.4869	0.13861	0.06687
0.8	2.180	1.013	0.3400	0.10141	0.05682
0.9	2.247	0.9380	0.1959	0.06987	0.04569
1.0	2.336	0.8541	0.05311	0.04367	0.03351
1.05	2.392	0.8082	-0.01719	0.03251	0.02707
1.10	2.459	0.7584	-0.09180	0.02259	0.02039
1.15	2.542	0.7044	-0.1670	0.01393	0.01352
1.20	2.651	0.6430	-0.2473	0.00653	0.00649
1.25	2.805	0.5702	-0.3370	0.00044	0.00044
1.30	3.098	0.4667	-0.4530	-0.00419	

Table 11.4. Binding energy and optimized parameters as a function of screening paramter (Eq. (11.5))

Screening parameter	Internuclear separation	α	β	Energy	D
0.0001	1.998	1.353	0.5747	0.60235	0.10245
0.0002	1.998	1.353	0.5747	0.60225	0.10245
0.0005	1.998	1.353	0.5747	0.60195	0.10245
0.001	1.998	1.353	0.5747	0.60145	0.10245
0.002	1.998	1.353	0.5747	0.60045	0.10245
0.0025	1.998	1.353	0.5747	0.59995	0.10245
0.005	1.998	1.353	0.5747	0.59747	0.10245
0.01	1.998	1.353	0.5749	0.59252	0.10245
0.02	1.998	1.353	0.5749	0.58271	0.10241
0.025	1.998	1.353	0.5749	0.57786	0.10240
0.03	1.998	1.353	0.5750	0.57304	0.10238
0.04	1.998	1.352	0.5750	0.56348	0.10231
0.05	1.999	1.351	0.5751	0.55406	0.10224
0.06	2.000	1.351	0.5755	0.54475	0.10215
0.07	2.000	1.350	0.5755	0.53556	0.10204
0.08	2.000	1.349	0.5758	0.52648	0.10191
0.09	2.000	1.347	0.5758	0.51752	0.10177
0.1	2.001	1.346	0.5761	0.50867	0.10161
0.2	2.007	1.328	0.5789	0.42600	0.09919
0.25	2.012	1.316	0.5807	0.38835	0.09743
0.3	2.018	1.301	0.5824	0.35294	0.09531
0.4	2.035	1.270	0.5867	0.28842	0.09006

Table 11.4 (Cont'd)

0.5	2.056	1.234	0.5910	0.23161	0.08353
0.6	2.089	1.194	0.5954	0.18185	0.07577
0.7	2.130	1.152	0.5998	0.13861	0.06687
0.8	2.181	1.105	0.6035	0.10141	0.05682
0.9	2.247	1.054	0.6068	0.06987	0.04569
1.0	2.337	0.9975	0.6095	0.04369	0.03353
1.05	2.393	0.9664	0.6104	0.03252	0.02708
1.10	2.461	0.9328	0.6111	0.02261	0.02041
1.15	2.544	0.8954	0.6112	0.01396	0.01355
1.20	2.653	0.8525	0.6107	0.00656	0.00652
1.25	2.808	0.8002	0.6093	0.00047	0.00047
1.30	3.102	0.7213	0.6054	-0.00416	

Table 11.5 : Binding energies of the hydrogen molecular ion with the SSCP from various approximate trial wave functions

Screening parameter	Binding energy Eq.(11.2)	Eq.(11.3)	Eq.(11.4)	Eq.(11.5)
0.0001	0.60229	0.60234	0.60235	0.60235
0.0002	0.60219	0.60224	0.60225	0.60225
0.0005	0.60189	0.60194	0.60195	0.60195
0.001	0.60139	0.60144	0.60145	0.60145
0.002	0.60039	0.60045	0.60045	0.60045
0.0025	0.59989	0.59995	0.59995	0.59995
0.005	0.59740	0.59746	0.59746	0.59747
0.01	0.59245	0.59251	0.59251	0.59252
0.02	0.58265	0.58271	0.58271	0.58271
0.025	0.57779	0.57785	0.57785	0.57786
0.03	0.57297	0.57303	0.57303	0.57304
0.04	0.56342	0.56348	0.56348	0.56348
0.05	0.55399	0.55405	0.55405	0.55406
0.06	0.54468	0.54474	0.54474	0.54475
0.07	0.53549	0.53555	0.53555	0.53556
0.06	0.52642	0.52647	0.52648	0.52648
0.09	0.51746	0.51751	0.51752	0.51752

Table 11.5 (cont'd)

Screening parameter	Binding energy Eq.(11.2)	Eq.(11.3)	Eq.(11.4)	Eq.(11.5)
0.1	0.50861	0.50867	0.50867	0.50867
0.2	0.42594	0.42600	0.42600	0.42600
0.25	0.38828	0.38834	0.38835	0.38835
0.3	0.35287	0.35293	0.35294	0.35294
0.4	0.28834	0.28841	0.28842	0.28842
0.5	0.23153	0.23160	0.23161	0.23161
0.6	0.18177	0.18184	0.18185	0.18185
0.7	0.13852	0.13859	0.13861	0.13861
0.8	0.10132	0.10140	0.10141	0.10141
0.9	0.06979	0.06986	0.06987	0.06987
1.0	0.04360	0.04367	0.04367	0.04369
1.05	0.03243	0.03251	0.03251	0.03252
1.10	0.02253	0.02260	0.02259	0.02261
1.15	0.01387	0.01394	0.01393	0.01396
1.20	0.00648	0.00654	0.00653	0.00656
1.25	0.00040	0.00045	0.00044	0.00047
1.30	-0.00423	-0.00418	-0.00419	-0.00416

Chapter 12 - Geometric-Mean Wave Function for HeH^{2+}

12.1 Introduction

Radel, Gorman, Cutler and Kahn (1969) have proposed a two parameter variation function for the $1s\sigma$ ground state of the hydrogen molecular ion. Their function, which builds up the probability density at intermediate distances by the addition of a geometric-mean term to the well known Finkelstein-Horowitz function, is expressed as follows:

$$\psi(\text{unnormalized}) = (\psi_{1sa} + \psi_{1sb}) + \beta(\psi_{1sa} \times \psi_{1sb})^{\frac{1}{2}} \qquad (12.1)$$

where $\psi = e^{-Zr}$, and Z and β are the variational parameters.

This function gives very good results for the energy at all internuclear distances. It is of interest to examine the applicability of such a function to more complex systems. In the present study, we have applied a variation wave function similar to Eq. (12.1) to the $1s\sigma$ state of HeH^{2+}. One of the aim of the investigation is to find if the accuracy achieved using certain types of approximate wave function is affected by the lack of nuclear symmetry.

The HeH^{2+} molecular ion was first treated by Beach (1936). Coulson and Duncanson (1938) employed five different methods, including a calculation at two values of the internuclear distance by an exact treatment in spherical coordinates. Bates and Carson (1956) have

obtained exact energies and wave functions for several states of HeH^{2+}. Other contributions to the problem are those of Dalgarno and Stewart (1956), Moiseiwitsch and Stewart (1956), Harris and Frost (1965), Matcha et al. (1965), Wilson and Gallup (1966), Cohen et al. (1967), Combs and Runnels (1968), Horak and Siskova (1973), and Combs and Miller (1976).

12.2 Calculation

The electronic energy of this complex molecular ion results from the integration of:

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{12.2}$$

where

$$H = \frac{1}{2}\nabla^2 + \frac{1}{r_a} + \frac{2}{r_b} \tag{12.3}$$

where r_a and r_b are the distances of the electron from the H^+ and He^{++} nuclei respectively. The wave function of Eq. (12.1) has the following explicit form.

$$\Psi = e^{-\alpha r_a} + \lambda e^{-\gamma r_b} + \beta(e^{-\alpha r_a} - \gamma r_b)^{\frac{1}{2}} \tag{12.4}$$

where α, β, γ and λ are variational parameters. The integrations are carried on confocal elliptical coordinates (Appendix B) by defining

$$\mu = \frac{1}{R}(r_a + r_b)$$

$$\nu = \frac{1}{R}(r_a - r_b)$$

in which R is the distance between two nuclei.

After some lengthy calculations, the final results for

$$E = \frac{1}{N}\,(E_k + E_p)$$

are that

$$N = \frac{4}{\alpha} + \frac{4\lambda^2}{\gamma 3}$$

$$+ \frac{32(\beta^2 + 2\lambda)}{\alpha^2 - \gamma^2}\, e^{-R(\alpha+\gamma)/2} \left\{ - \frac{8\gamma}{R(\alpha^2 - \gamma^2)^2} \sinh\left[\frac{R}{2}(\alpha - \gamma)\right] \right.$$

$$\left. + \frac{1}{\alpha + \gamma} \sinh\left[\frac{R}{2}(\alpha - \gamma)\right] + \frac{1}{\alpha - \gamma} \cosh\left[\frac{R}{2}(\alpha - \gamma)\right] \right\}$$

$$+ \frac{512\beta}{9\alpha^2 - \gamma^2}\, e^{-R(3\alpha+\gamma)/4} \left\{ - \frac{48\alpha\gamma}{R(9\alpha^2 - \gamma^2)^2} \sinh\left[\frac{R}{4}(3\alpha - \gamma)\right] \right.$$

$$\left. + \frac{1}{3\alpha + \gamma} \sinh\left[\frac{R}{4}(3\alpha - \gamma)\right] + \frac{1}{3\alpha - \gamma} \cosh\left[\frac{R}{4}(3\alpha - \gamma)\right] \right\}$$

$$+ \frac{512}{\alpha^2 - 9\gamma^2}\, e^{-R(\alpha+3\gamma)/4} \left\{ - \frac{48\alpha\gamma}{R(\alpha^2 - 9\gamma^2)^2} \sinh\left[\frac{R}{4}(\alpha - 3\gamma)\right] \right.$$

$$\left. + \frac{1}{\alpha + 3\gamma} \sinh\left[\frac{R}{4}(\alpha - 3\gamma)\right] - \frac{1}{\alpha - 3\gamma} \cosh\left[\frac{R}{4}(\alpha - 3\gamma)\right] \right\}$$

$$E_k = \frac{2}{\alpha} + \frac{2\lambda^2}{\gamma}$$

$$+ \frac{32\lambda\gamma}{\alpha^2 - \gamma^2} e^{-R(\alpha + \gamma)/2} \left\{ \left[\frac{4\alpha(\alpha^2 + \gamma^2)}{R(\alpha^2 - \gamma^2)^2} \sinh \left[\frac{R}{2} (\alpha - \gamma) \right] \right. \right.$$

$$\left. \left. + \frac{\alpha}{\alpha + \gamma} \sinh \left[\frac{R}{2} (\alpha - \gamma) \right] - \frac{\alpha}{\alpha - \gamma} \cosh \left[\frac{R}{2} (\alpha - \gamma) \right] \right] \right\}$$

$$+ \frac{4\beta^2}{\alpha^2 - \gamma^2} e^{-R(\alpha + \gamma)/2} \left\{ \left[(\alpha + \gamma) \sinh \left[\frac{R}{2} (\alpha - \gamma) \right] \right. \right.$$

$$\left. \left. + (\alpha - \gamma) \cosh \left[\frac{R}{2} (\alpha - \gamma) \right] \right] \right\}$$

$$+ \frac{128\alpha\beta}{9\alpha^2 - \gamma^2} e^{-R(3\alpha + \gamma)/4} \left\{ \left[\frac{8\gamma(3\alpha^2 + \gamma^2}{R(9\alpha^2 - \gamma^2)^2} \sinh \left[\frac{R}{4} (3\alpha - \gamma) \right] \right. \right.$$

$$\left. \left. + \frac{\alpha + \gamma}{3\alpha - \gamma} \sinh \left[\frac{R}{4} (3\alpha - \gamma) \right] + \frac{\alpha - \gamma}{3\alpha - \gamma} \cosh \left[\frac{R}{4} (3\alpha - \gamma) \right] \right] \right\}$$

$$+ \frac{128\alpha\beta\gamma\lambda}{\alpha^2 - 9\gamma^2} e^{-R(\alpha + 3\gamma)/4} \left\{ \left[\frac{8\alpha(\alpha^2 + 3\gamma^2)}{R(\alpha^2 - 9\gamma^2)^2} \sinh \left[\frac{R}{4} (\alpha - 3\gamma) \right] \right. \right.$$

$$\left. \left. + \frac{\alpha + \gamma}{\alpha + 3\gamma} \sinh \left[\frac{R}{4} (\alpha - 3\gamma) \right] - \frac{\alpha - \gamma}{\alpha - 3\gamma} \cosh \left[\frac{R}{4} (\alpha - 3\gamma) \right] \right] \right\}$$

And

$$E_p = -\frac{4}{\alpha^2} e^{-\alpha R}\left[\frac{4}{\alpha R}\sinh(\alpha R) + 3\sinh(\alpha R) - \cosh(\alpha R)\right]$$

$$-\frac{4\lambda^2}{\gamma^2} e^{-\gamma R}\left[\frac{2}{\gamma R}\sinh(\gamma R) + 3\sinh(\gamma R) + \cosh(\gamma R)\right]$$

$$-\frac{16(\beta^2 + 2\lambda)}{\alpha^2 - \gamma^2} e^{-R(\alpha+\gamma)/2}\left\{\frac{4(2\alpha - \gamma)}{R(\alpha^2 - \gamma^2)}\sinh\left[\frac{R}{2}(\alpha - \gamma)\right]\right.$$

$$\left. + 3\sinh\left[\frac{R}{2}(\alpha - \gamma)\right] - \cosh\left[\frac{R}{2}(\alpha - \gamma)\right]\right\}$$

$$-\frac{128\beta}{9\alpha^2 - \gamma^2} e^{-R(3\alpha - \gamma)/4}\left\{\frac{8(6\alpha - \gamma)}{R(9\alpha^2 - \gamma^2)}\sinh\left[\frac{R}{4}(3\alpha - \gamma)\right]\right.$$

$$\left. + 3\sinh\left[\frac{R}{4}(3\alpha - \gamma)\right] - \cosh\left[\frac{R}{4}(3\alpha - \gamma)\right]\right\}$$

$$-\frac{128\lambda\beta}{\alpha^2 - 9\gamma^2} e^{-R(\alpha + 3\gamma)/4}\left\{\frac{8(2\alpha - 3\gamma)}{\alpha R(\alpha - 9\gamma^2)}\sinh\left[\frac{R}{4}(\alpha - 3\gamma)\right]\right.$$

$$\left. + 3\sinh\left[\frac{R}{4}(\alpha - 3\gamma)\right] - \cosh\left[\frac{R}{4}(\alpha - 3\gamma)\right]\right\}$$

12.3 Conclusion

The optimized values of the parameters α, β, γ and λ are shown in the Table 12.1 at various internuclear distances. Table 12.2 compares the electronic energies and electronic potential energies calculated here with the exact values. It will be noticed that E values obtained from the function (12.4) are quite close to the exact ones. The average percent difference between the two is 0.015% with a maximum difference of 0.023% (occurring at R = 2.5). This may be compared with an average

difference of 0.016%, over a comparable range of R, between the results of Radel et al. and the exact values of H_2^+. Our values for V are also in good accord with the exact values.

The kinetic energy T, the potential energy V' = V + 2/R, and the total energy E' = E + 2/R of the $1s\sigma$ state as a function of R are shown in Fig. 12.1. T has a shallow minimum at R ≈ 1.5; a similar result was found by Moiseiwitsch and Stewart (1956).

In conclusion, we find that the results obtained by a geometric-mean type of variation function for HeH^{2+} are of a comparable accuracy to those obtained by a similar function for H_2^+.

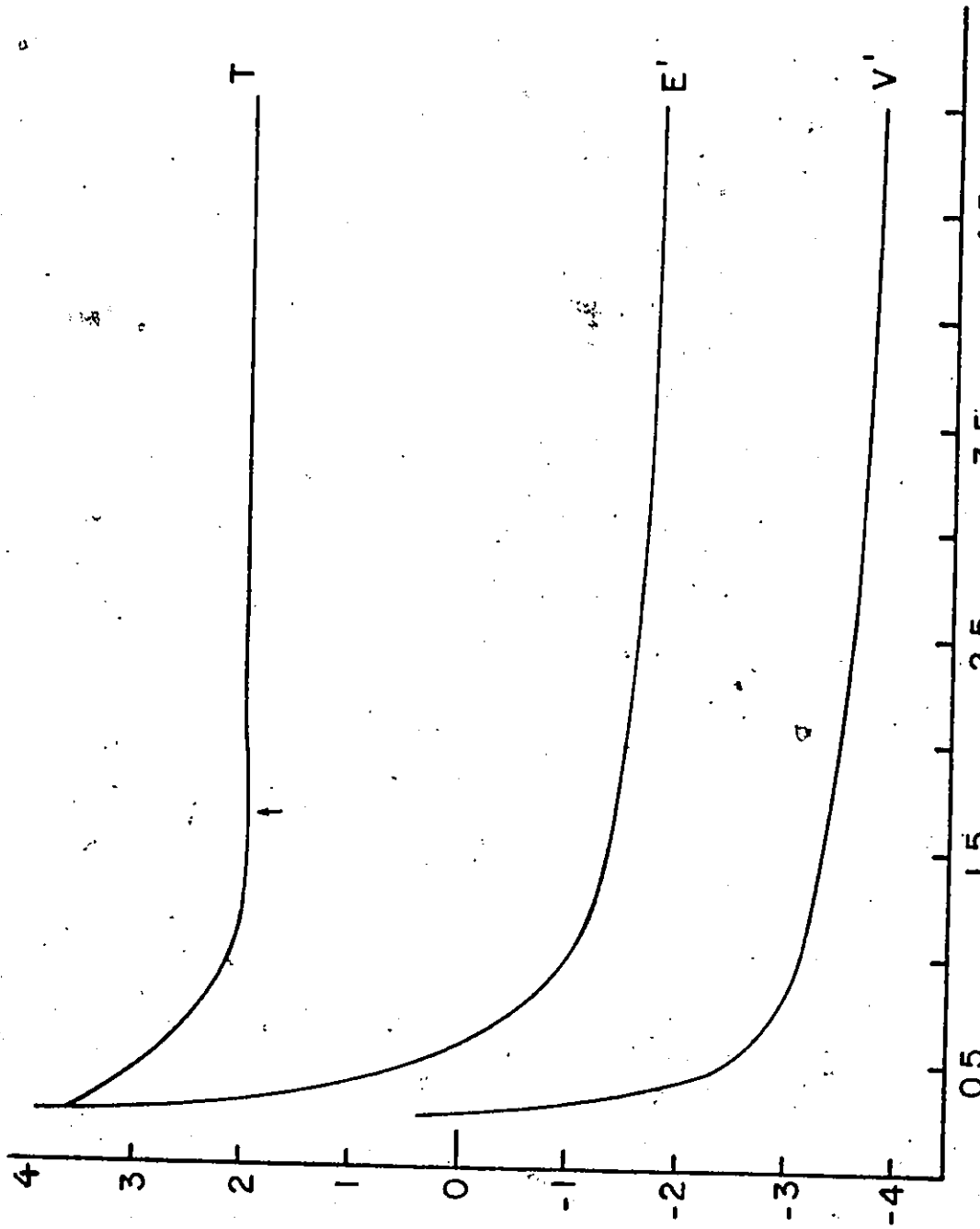

Fig. 12.2 : V', T and E' as function of internuclear separation R for the $1s\sigma$ state. The arrow indicates the position of the minimum in T.

Table 12.1 : Optimized parameter at various internuclear separations (R)

R	α	β	γ	λ
0.25	2.739	18.85	2.832	12.33
0.50	2.562	17.03	2.593	14.05
0.75	2.408	17.93	2.427	18.04
1.00	2.293	22.21	2.309	26.68
1.5	2.111	33.95	2.168	61.10
2.0	2.030	84.49	2.091	219.5
2.5	1.953	377.9	2.051	1361.
3.0	1.924	718.1	2.018	3351.
3.5	1.916	895.8	2.016	4906.
4.0	1.901	988.4	2.009	5941.
4.5	1.887	1272.	2.008	7844.
5.0	1.860	1399.	2.005	8476.

Table 12.2 : Total electronic energies (-E) and electronic potential (-V) energies of the $1s\sigma$ state as obtained here compared with the exact values. The exact values of E are from Bates and Carson (1956) and those of V from Moiseiwitsch and Stewart (1956)

R	-E this study	-E exact	-V this study	-V exact
0.25	4.13327	4.13365	7.767	
0.50	3.66500	3.66554	6.491	6.50
0.75	3.30088	3.30137	5.665	
1.0	3.03291	3.03335	5.154	5.13 55133
1.5	2.69499	2.69546	4.660	
2.0	2.51164	2.51219	4.478	4.48
2.5	2.40433	2.40489	4.388	
3.0	2.33499	2.33549	4.328	4.33
3.5	2.28640	2.28679	4.283	
4.0	2.25031	2.25060	4.249	4.25
4.5	2.22237	2.22259	4.222	
5.0	2.20008	2.20023	4.200	4.20

Appendix A. The Hulthén Potential

For our problem, we write the Hulthén potential (1942), in atomic units, in the form

$$V(r) = \frac{\eta e^{-\delta r}}{1 - e^{-\delta r}} \tag{A.1}$$

It is possible to solve the Schrödinger equation for the potential (A.1) for $\ell = 0$. In the following we adapt Hulthén treatment to our problem.

The radial Schrödinger equation for $\ell = 0$ for the potential (A.1) is

$$\left(\frac{1}{2}\frac{d^2}{dr^2} + \frac{\eta e^{-\delta r}}{1 - e^{-\delta r}} - E\right) \psi_n(r) = 0 \tag{A.2}$$

By substituting

$$E = \frac{1}{2} a_n^2 \delta^2 \tag{A.3}$$

and making the following transformation

$$\psi_n(r) = e^{-a_n \delta r} \phi_n(r)$$

$$y = 1 - e^{-\delta r}$$

Eq. (A.2) becomes

$$y(1 - y)\frac{d^2\phi_n}{dy^2} - (1 + 2a_n)y\frac{d\phi_n}{dy} + \frac{2\eta}{\delta^2}\phi_n = 0 \tag{A.4}$$

The solution of the differential equation (A.4) has the form

$$\phi_n(y) = y^\rho \sum_{\nu=0}^{\infty} c_\nu y^\nu = \sum_{\nu=0}^{\infty} c_\nu y^{\nu+\rho}$$

Substituting it in Eq. (A.4), we get the following recursion relation for c_ν's:

$$c_{\nu+1} = \frac{\nu(\nu-1) + (1+2a_n)\nu - \frac{2\eta}{\delta^2}}{\nu(\nu+1)} c_\nu \qquad (\nu \geq 1)$$

To have physical meaning, the wave function $\phi(r)$ must be finite, so that the infinite series should terminate somewhere — say, at $\nu = n$ — to become a polynomial; thus $c_\nu = 0$ for $\nu > n$. This gives

$$n(n-1) + (1+2a_n)n - \frac{2\eta}{\delta^2} = 0$$

or

$$a_n = \frac{1}{2}\left(\frac{2\eta}{n\delta^2} - n\right) \qquad (A.5)$$

In conjunction with (A.3), this gives the eigenvalues.

The normalized eigenfunction is found to be

$$\psi_n(r) = \left[\frac{2\delta\, a_n(a_n+n)}{2a_n+n}\right]^{\frac{1}{2}} e^{-a_n\delta r} \times \sum_{\nu=1}^{n} (-1)^{\nu-1} \binom{n-1}{\nu-1} \binom{n+2a_n+\nu-1}{\nu} (1-e^{-\delta r})^\nu \qquad (A.6)$$

When two parameters, n and δ, are set to be equal, Eq. (A.5) becomes

$$a_n = \frac{1}{2}\left(\frac{2}{n\delta} - n\right) \tag{A.7}$$

and the eigenvalues (A.3) and the eigenfunction (A.6) respectively become

$$E_n = \frac{1}{8}\left(\frac{2}{n} - n\delta\right)^2 \tag{A.8}$$

and

$$\Psi_n(r) = \frac{n}{4}\left(\frac{4}{n^2} - n^2\delta^2\right) \frac{1}{2} e^{-\frac{1}{2}\left(\frac{2}{n} - n\delta\right)r} \times \sum_{\nu=1}^{n} (-1)^{-1} \binom{n-1}{\nu-1} \binom{\nu + \frac{2}{n\delta} - 1}{\nu} (1 - e^{-\delta r})^{\nu} \tag{A.9}$$

Appendix B. Outlines of Confocal Elliptical Coordinates

The variables μ and ν in confocal elliptical coordinates relate to r_a and r_b in spherical coordinates by

$$\mu = \frac{r_a + r_b}{R} ; \qquad \nu = \frac{r_a - r_b}{R} \tag{B.1}$$

The volume element in this coordinates is

$$dt = \frac{R^3}{8} (\mu^2 - \nu^2)\, d\mu\, d\nu\, d\phi \tag{B.2}$$

with

$$1 \leq \mu < \infty$$

$$-1 \leq \nu \leq 1$$

$$0 \leq \phi \leq 2\pi$$

The operator ∇^2 is given by

$$\nabla^2 = \frac{4}{R^2} \frac{1}{\mu^2 - \nu^2} \left\{ \frac{\partial}{\partial \mu} \left[(\mu^2 - 1) \frac{\partial}{\partial \mu} \right] + \frac{\partial}{\partial \mu} \left[(1 - \nu^2) \frac{\partial}{\partial \nu} \right] \right\}$$

$$+ \frac{4}{R} \frac{1}{(\mu^2 - 1)(1 - \nu^2)} \frac{\partial^2}{\partial \phi 2} \tag{B.3}$$

Appendix C. Derivation of the Integral $I_1(\ell,m,n)$ in Chapter 9

$$\int_0^{\infty} s^{\ell} e^{-xs}\, ds \int_0^{s} u^{m}\, du \int_{-u}^{u} e^{-yt}\, t^{n}\, dt$$

$$I_1 = \int_0^{u} e^{-yt}\, t^{n}\, dt$$

$$= \int_0^{u} e^{-yt}\, t^{n}\, dt + \int_{-u}^{0} e^{-yt}\, t^{n}\, dt$$

$$= \int_0^{u} e^{-yt}\, t^{n}\, dt + (-1)^{n} \int_0^{u} e^{yt}\, t^{n}\, dt$$

$$= \frac{n!}{y^{n+1}} - e^{-yu} \sum_{R=0}^{n} \frac{n!}{k!} \frac{u^{k}}{y^{n-k+1}}$$

$$+ (-1)^{n}\, (-1)^{n+1} \left\{ \frac{n!}{y^{n+1}} - e^{yu} \sum_{k=0}^{n} (-1)^{k} \frac{n!}{k!} \frac{u^{k}}{y^{n-k+1}} \right\}$$

$$= \frac{n!}{y^{n+1}} - e^{-yu} \sum_{k=0}^{n} \frac{n!}{k!} \frac{u^{k}}{y^{n-k+1}}$$

$$- \frac{n!}{y^{n+1}} + e^{yu} \sum_{k=0}^{n} (-1)^{k} \frac{n!}{k!} \frac{u^{k}}{y^{n-k+1}}$$

$$= - \frac{n!}{y^{n+1}} e^{-yu} \sum_{k=0}^{n} \frac{y^{k}}{k!} u^{k} + \frac{n!}{y^{n+1}} e^{yu} \sum_{k=0}^{n} \frac{(-1)^{k}}{k!} y^{k}\, u^{k}$$

$$I_2 = \int_0^s u^m \, du \int_{-u}^{u} e^{-yt} \, tn \, dt$$

$$= - \frac{n!}{y^{n+1}} \sum_{k=0}^{n} \frac{y^k}{k!} \int_0^s e^{-yu} \, u^{k+m} \, du + \frac{n!}{y^{n+1}} \sum_{k=0}^{n} \frac{(-1)^k y^k}{k!} \int_0^s e^{yu} \, u^{k+m} \, du$$

$$= - \frac{n!}{y^{n+1}} \sum_{k=0}^{n} \frac{y^k}{k!} \left\{ \frac{(k+m)!}{y^{k+m+1}} - e^{-ys} \sum_{j=0}^{k+m} \frac{(k+m)!}{j!} \frac{s^j}{y^{k+m-j+1}} \right\}$$

$$+ \frac{n!}{y^{n+1}} \sum_{k=0}^{n} \frac{(-1)^k y^k}{k!} (-1)^{k+m+1} \left\{ \frac{(k+m)!}{y^{k+m+1}} - e^{ys} \sum_{j=0}^{k+m} (-1)^j \frac{(k+m)!}{j!} \frac{s^j}{y^{k+m-j+1}} \right\}$$

$$= - \frac{n!}{y^{n+1}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} \frac{1}{y^{m+1}} - \frac{(k+m)!}{k!} \frac{1}{y^{m+1}} e^{-ys} \sum_{j=0}^{k+m} \frac{y^j}{j!} s^j \right\}$$

$$+ \frac{(-1)^{m+1} n!}{y^{n+1}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} \frac{1}{y^{m+1}} - \frac{(k+m)!}{k!} \frac{1}{y^{m+1}} e^{ys} \sum_{j=0}^{k+m} (-1)^j \frac{y^j}{j!} s^j \right\}$$

$$= - \frac{n!}{y^{n+m+2}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} - \frac{(k+m)!}{k!} e^{-ys} \sum_{j=0}^{k+m} \frac{y^j}{j!} s^j \right\}$$

$$+ \frac{(-1)^{m+1} n!}{y^{n+m+2}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} - \frac{(k+m)!}{k!} e^{ys} \sum_{j=0}^{k+m} (-1)^j \frac{y^j}{j!} s^j \right\}$$

$$I(\ell,m,n)$$

$$= \int_0^\infty s^\ell e^{-xs}\, ds \int_0^s u^m\, du \int_{-n}^n e^{-yt}\, t^n\, dt$$

$$= -\frac{n!}{y^{n+m+2}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} \int_0^\infty s^\ell e^{-xs}\, ds \right.$$

$$\left. - \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{y^j}{j!} \int_0^\infty s^{\ell+j} e^{-(x+y)s}\, ds \right\}$$

$$+ \frac{(-1)^{m+1} n!}{y^{n+m+2}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} \int_0^\infty s^\ell e^{-xs}\, ds \right.$$

$$\left. - \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{(-1)^j y^j}{j!} \int_0^\infty s^{\ell+j} e^{-(x-y)s}\, ds \right\}$$

$$= -\frac{n!}{y^{n+m+2}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} \frac{\ell!}{x^{\ell+1}} - \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{y^j}{j!} \frac{(\ell+j)!}{(x+y)^{\ell+j+1}} \right\}$$

$$+ \frac{(-1)^{m+1} n!}{y^{n+m+2}} \sum_{k=0}^{n} \left\{ \frac{(k+m)!}{k!} \frac{\ell!}{x^{\ell+1}} - \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{(-1)^j y^j}{j!} \frac{(\ell+j)!}{(x-y)^{\ell+j+1}} \right\}$$

$$= -\frac{n!\ell!}{x^{\ell+1} y^{n+m+2}} \sum_{k=0}^{n} \frac{(k+m)!}{k!} + \frac{(-1)^{m+1} n!\ell!}{x^{\ell+1} y^{n+m+2}} \sum_{k=0}^{n} \frac{(k+m)!}{k!}$$

$$+ \frac{n!}{y^{n+m+2}} \sum_{k=0}^{n} \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{y^j}{j!} \frac{(\ell+j)!}{(x+y)^{\ell+j+1}}$$

$$- \frac{(-1)^{m+1} n!}{y^{n+m+2}} \sum_{k=0}^{n} \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{(-1)^j y^j}{j!} \frac{(\ell+j)!}{(x-y)^{\ell+j+1}}$$

$$= - \frac{n!\,\ell!}{x^{\ell+1}\,y^{n+m+2}} \sum_{k=0}^{n} \frac{(k+m)!}{k!}$$

$$- \frac{(-1)^m\, n!\,\ell!}{x^{\ell+1}\,y^{n+m+2}} \sum_{k=0}^{n} \frac{(k+m)!}{k!}$$

$$+ \frac{n!}{y^{n+m+2}\,(x+y)^{\ell+1}} \sum_{k=0}^{n} \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{(\ell+j)!}{j!} \left(\frac{y}{x+y}\right)^j$$

$$+ \frac{(-1)^m\, n!}{y^{n+m+2}\,(x-y)^{\ell+1}} \sum_{k=0}^{n} \frac{(k+m)!}{k!} \sum_{j=0}^{k+m} \frac{(-1)^j\,(\ell+j)!}{j!} \left(\frac{y}{x-y}\right)^j$$

Appendix D. Integrals Used in Chapters 10 and 11

There are some integrals which are repeatedly used in the calculations of hydrogen molecular ion in the Chapters 10 and 11. Two main ones are

$$A_n(m) = \int_1^\infty \mu^n e^{-m\mu} d\mu \tag{D.1}$$

$$B_n(m) = \int_{-1}^{1} \nu^n e^{-m\nu} d\nu \tag{D.2}$$

The integral $B_n(m)$ has the following properties:

$$\begin{aligned} B_{2n}(-m) &= B_{2n}(m) \\ B_{2n+1}(-m) &= -B_{2n+1}(m) \end{aligned} \tag{D.3}$$

Relating to $B_n(m)$, following integrals have been used in the calculation.

$$\begin{aligned} \int_{-1}^{1} \nu^n \cosh(m\nu)\, d\nu &= \frac{1}{2}\int_{-1}^{1} \nu^n \left(e^{m\nu} + e^{-m\nu}\right) d\nu \\ &= \frac{1}{2}\left[B_n(-m) + B_n(m)\right] \\ &= \begin{cases} B_n(m) & \text{if } n \text{ even} \\ 0 & \text{if } n \text{ odd} \end{cases} \end{aligned} \tag{D.4}$$

$$\int_{-1}^{1} \nu^n \sinh(m\nu)\, d\nu = \begin{cases} 0 & \text{if } n \text{ even} \\ -B_n(m) & \text{if } n \text{ odd} \end{cases} \tag{D.5}$$

$$\int_{-1}^{1} \nu^n \sinh(a\nu) \sinh(b\nu)\, d\nu$$

$$= \int_{-1}^{1} \nu^n \frac{e^{a\nu} - e^{-a\nu}}{2} \frac{e^{b\nu} - e^{-b\nu}}{2}\, d\nu$$

$$= \frac{1}{4} \int_{-1}^{1} \nu^n \left[e^{(a+b)\nu} + e^{-(a+b)\nu} - e^{(a-b)\nu} - e^{-(a-b)\nu} \right] d\nu$$

$$= \begin{cases} \frac{1}{2} B_n(a+b) - \frac{1}{2} B_n(a-b) & \text{if } n \text{ even} \\ 0 & \text{if } n \text{ odd} \end{cases} \qquad (D.6)$$

$$\int_{-1}^{1} \nu^n \cosh(a\nu) \cosh(b\nu)\, d\nu$$

$$= \begin{cases} \frac{1}{2} B_n(a+b) + \frac{1}{2} B_n(a-b) & \text{if } n \text{ even} \\ 0 & \text{if } n \text{ odd} \end{cases} \qquad (D.7)$$

$$\int_{-1}^{1} \nu^n \sinh(a\nu) \cosh(b\nu)\, d\nu$$

$$= \begin{cases} 0 & \text{if } n \text{ even} \\ -\frac{1}{2} B_n(a+b) - \frac{1}{2} B_n(a-b) & \text{if } n \text{ odd.} \end{cases} \qquad (D.8)$$

For some particular values of n, the expressions for $A_n(m)$ and $B_n(m)$ are listed below:

$$A_0(m) = \frac{1}{m} e^{-m}$$

$$A_1(m) = \frac{1}{m} e^{-m} \left(1 + \frac{1}{m}\right)$$

$$A_2(m) = \frac{1}{m} e^{-m} \left(1 + \frac{2}{m} + \frac{2}{m^2}\right)$$

$$B_0(m) = \frac{e^m}{m}(1 - e^{-2m}) = \frac{2}{m}\sinh(m)$$

$$B_1(m) = \frac{e^m}{m^2}\left[1 - e^{-2m} - m(1 + e^{-2m})\right]$$

$$= \frac{2}{m^2}\left[\sinh(m) - m\cosh(m)\right]$$

$$B_2(m) = \frac{2e^m}{m^3}\left[1 - e^{-2m} - m(1 + e^{-2m}) + \frac{m^2}{2}(1 - e^{-2m})\right]$$

$$= \frac{4}{m^3}\left[\sinh(m) - m\cosh(m) + \frac{m^2}{2}\sinh(m)\right]$$

$$B_3(m) = \frac{6e^m}{m^4}\left[1 - e^{-2m} - m(1 + e^{-2m}) + \frac{m^2}{2}(1 - e^{-2m}) - \frac{m^3}{6}(1 + e^{-2m})\right]$$

$$= \frac{12}{m^4}\left[\sinh(m) - m\cosh(m) + \frac{m^2}{2}\sinh(m) - \frac{m^3}{6}\cosh(m)\right]$$

$$B_4(m) = \frac{24e^m}{m^5}\left[1 - e^{-2m} - m(1 + e^{-2m}) + \frac{m^2}{2}(1 - e^{-2m})\right.$$

$$\left. - \frac{m^3}{6}(1 + e^{-2m}) + \frac{m^4}{24}(1 - e^{-2m})\right]$$

$$= \frac{48}{m^5}\left[\sinh(m) - m\cosh(m) + \frac{m^2}{2}\sinh(m)\right.$$

$$\left. - \frac{m^3}{6}\cosh(m) + \frac{m^4}{24}\sinh(m)\right]$$

$$B_5(m) = \frac{120e^m}{m^6}\left[1 - e^{-2m} - m(1 + e^{-2m}) + \frac{m^2}{2}(1 - e^{-2m})\right.$$

$$\left. - \frac{m^3}{6}(1 + e^{-2m}) + \frac{m^4}{24}(1 - e^{-2m}) - \frac{m^5}{120}(1 + e^{-2m})\right]$$

$$= \frac{240}{m^6}\left[\sinh(m) - m\cosh(m) + \frac{m^2}{2}\sinh(m)\right.$$

$$\left. - \frac{m^3}{6}\cosh(m) + \frac{m^4}{24}\sinh(m) - \frac{m^5}{120}\cosh(m)\right]$$

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Appendix G : Publications

Co-author with Y. P. Varshni in the following publications

1. "Energies of s Eigenstates in a Static Screened Coulomb Potential ", 1971, Phys. Rev. A, 4, 1875.

2. "Electron Shielding in Doped Semiconductors", 1971, Phys. Rev. B, 4, 4452.

3. "Geometric-Mean Wave Function for HeH ", 1972, Can. J. Phys. 50, 666.

4. "Wavefunction for the Hydrogen Molecular Ion", 1972, J. Phys. B, 5, 1833.

5. "Bound Eigenstates of the Exponential Cosine Screened Coulomb Potential", 1972, Phys. Rev. A, 6, 1391.

6. "Fine Structure of Excitonic Lines in CuCl", 1974, Phys. Stat. Sol. b61, K23.

7. "Laser Action in Stellar Envelopes", 1976, Astrophys. Space Sci. 45, 87.

8. "Bound s-States Energies for the Static Screened Coulomb Potential", 1976, Phys. Letters, 59A, 363.

Epilogue

My appreciation to my parents cannot be expressed here with my knowledge of English language. My sisters and I were brought up by them through several political systems. In their most difficult time, they had to work over 18 hours a day to suuport the family. However they never allowed their children to quit from school to help them. They felt that the completion of university education for their children was their duty. At this point, we all did not disappoint them. Last October when I was writing the last portion of this thesis, my mother was seriously ill. She wanted to see me complete this thesis, but I did not. She left me forever in January. If I had worked harder for my thesis during the last few years, I would have made her expectation to be reality. This leaves me with much regret.

I also want to express my deep appreciation to my grand-father-in-law, the late Mr. Pak-kong Chen, who had helped my parents and had supported my education expenses for years.

At this very end of the thesis, I enclose a peom which was written by my grand-uncle, Professor Te-fung Leung, at the time that I left Hong Kong for Canada. Throughout the years of my graduate studies, I kept it on my desk. In brief, it tells : "facing the problems, overcoming the difficulties and never saying impossible ".

May 1978

壯志淩雲日貫虹騰飛萬里向前衝沉舟
破釜等閒事縛取蒼龍一唉中　窮書卷
引凋弓移山倒海古今同冷看天壑如無
物莫讓張騫去鑿空
歲月催人可奈何學窮書圃幾曾過登天
蜀道休回顧不辭通神任折磨　思不盡
日無多尋激索隱莫蹉跎驪龍探穴訣何
易記取愚公日荷鉏一賦鴟鴞天二闋

戊申十月書示振幸孫　太素