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Pseudopotential and model potential calculation of zinc, cadmium and mercury.

Paul Joseph. Chevalier
University of Windsor

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PSEUDOPOTENTIAL AND MODEL POTENTIAL CALCULATIONS OF ZINC, CADMIUM AND MERCURY

by

(C) Paul Joseph Chevalier

A Thesis
submitted to the
Faculty of Graduate Studies and Research
through the
Department of Physics
in partial fulfillment
of the requirements for the
Degree of Master of Science
at the University of Windsor

Windsor, Ontario, Canada
1989
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ABSTRACT

Model potential and pseudopotential techniques to reduce computational complexity, in atomic and molecular calculations, are discussed and compared. Accurate model potentials and pseudopotentials, for the replacement of the cores of Zinc, Cadmium and Mercury, are found by fitting the calculated centre of gravity energies of Zn II, Cd II and Hg II to the experimental values. The Gaussian form of the pseudopotential gives more accurate results than does the form assumed for the model potentials. The spin-orbit interaction is included for both types of potentials. The model potential spin-orbit results are found to be more accurate than the pseudopotential spin-orbit results, due to the form assumed for the interaction. Model potential are also used to perform the two electron calculations of Zn I, Cd I and Hg I. Improvements and future work are also discussed.
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1 INTRODUCTION

One can usually divide the electrons in an atom or molecule into two distinct groupings. The first group being the core electrons, while the second group is the valence electrons. It is a well known fact that most physical properties of atoms and molecules are due to the valence electrons. In chemical reactions, it is the valence electrons that participate while the core electrons remain practically inert. These facts are what motivate the work herein.

Since only the valence electrons participate in the reactions, one is led to try to reduce the N-electron problem, where N is the total number of electrons in the atom or molecule, to an n-electron problem where n is the total number of valence electrons in the atom or molecule. A reduction such as this would lead to considerable computational simplification, especially if $n \ll N$. In an atom such as Hg, with $N=80$ and $n=2$, the reduction would decrease the complexity immensely. For example, in Hartree-Fock calculations one must solve a system of $N$ coupled differential equations. For Hg, the reduction would reduce a system of 80 coupled differential equations to a system of 2 coupled differential equations.

The pseudopotential and the model potential are two approaches used to reduce the N-electron problem to the n-electron problem. This thesis uses and compares both approaches to reduce the N-electron problem to the n-electron problem in Zinc, Cadmium and Mercury.
2 BACKGROUND

Hellmann (1935) was the first to reduce the N-electron problem to an n-electron problem for atoms with one electron in the outer valence shell. Hellmann used the Thomas-Fermi model to show that Pauli exclusion principle for the valence electron could be replaced by a nonclassical potential which he called "Abstossungspotential ", which has been renamed as the pseudopotential.

In atomic/molecular calculations, the valence orbitals are made orthogonal to the core electrons by giving the valence electrons the proper number of nodes. This is in essence the Pauli exclusion principle. In the pseudopotential method one replaces the orthogonality by the pseudopotential. It is the pseudopotential which keeps the valence electron out of the core. The valence electrons are only required to be orthogonal to the other valence orbitals.

Hellmann suggested a form for the total potential of a single valence electron as:

$$\bar{V}_H = -\frac{Z - N_c}{r} + \frac{A}{r} e^{-\beta r}.$$  \hspace{1cm} (2.1)

where Z is the atomic number and \(N_c\) is the number of electrons in the core. Both \(A\) and \(\beta\) were used as parameters which were adjusted so that \(\bar{V}_H\) would match the experimental energy spectrum of the lowest s, p and the first excited s-state of the valence electron. The first term in equation (2.1) corresponds to the electrostatic interaction between the valence electron and the shielded nucleus. The second term in equation (2.1) is the actual pseudopotential.

---

1 Pseudopotentials have also been employed successfully in describing the band structure of semiconductors and simple metals. These applications will not be discussed here.
The Schrödinger equation\(^2\) for the valence electron
\[
[-\nabla^2 + 2(V_\mu - E)]\psi = 0
\]
was then solved so that the ground state was nodeless and the excited states only had enough nodes to make them orthogonal to the lower unfilled valence states. Hellmann took the \(\psi\)'s to be parameterized hydrogenic wave functions.

For heavy atoms Ladanyi (1956) suggested that the potential should be changed from equation (2.1) to
\[
V = -\frac{Z - N_e}{r} + \frac{A}{r} e^{-\kappa r} + \frac{B}{r} e^{-\lambda r}
\]
with \(A, B, \kappa\) and \(\lambda\) all being adjustable parameters. He chose \(\kappa\) and \(\lambda\) arbitrarily and then used \(A\) and \(B\) to match the calculated energy with the experimental energy for the 1s and 2s states.

There were variations on the above which lead to slight improvements in accuracy over the Hellmann method, but the greatest improvement was due to Schwarz (1969). The form he chose was
\[
V = -\frac{Z - N_e}{r} + \sum_{l=0}^{\infty} \frac{A_l}{r} e^{-\kappa r} p^l
\]
where \(p^l\) is the angular momentum projection operator. Thus, the form of the potential is similar to the Hellmann form except that each \(l\) has a different potential and set of parameters associated with it. Schwarz only made fits to the lowest \(l\)-states with \(A_l\) arbitrarily chosen and \(\kappa\) used as an adjustable parameter. The Hellmann method found a potential that was averaged between the s and p-states, while the Schwarz method gives the s and p-states separately.

---

\(^2\) Atomic units are used throughout unless otherwise noted.
Bardsley (1970) made an improvement on the Schwarz formulation by including a polarization potential to take into account core-valence correlation. He adjusted the pseudopotential for each \( l \) so that the lowest two states were matched to experiment. Further modifications were made on the pseudopotential by changing the exponentials from Slaters into Gaussians (in order to do molecular calculations with greater ease).

Fock, Vesselow, and Petraschen (1940) were able to reduce the N-electron problem to a 2 electron problem for atoms with 2 electrons in their outer shells (see Szasz (1985)).

The Hellmann formulation, and the other variations on it, were also extended to atoms with 2 valence electrons. The basic assumption employed was that the addition of another valence electron does not distort the electronic configuration of the core. This is the frozen core approximation. The parameters of the pseudopotential are adjusted to match the experimental spectrum of the positive ion. The same pseudopotential is then used for both valence electrons. Thus the Hellmann Hamiltonian for the 2 valence system is

\[
H = \sum_{i=1}^{2} \left[ -\frac{1}{2} \nabla_i^2 - \frac{(Z - N_e)}{r_i} + \frac{A}{r_i^4} e^{-\beta r_i} \right] + \frac{1}{r_{12}} \tag{2.5}
\]

The Schrödinger equation for this Hamiltonian is then solved so that the ground state wave function is nodeless. Hellmann also extended his work to simple diatomic molecules.
3 MODEL POTENTIALS VS PSEUDOPOTENTIALS

There are two methods used to turn the N-electron problem into an n-electron problem. The first method, as described above, is the pseudopotential approach while the second method is the model potential approach. Both approaches are semi-emperical in nature, i.e. both types of potentials have parameters which are adjusted so that the energy spectrum of the valence electron(s) is reproduced.

The pseudopotential replaces the electronic core by a potential that takes into account the Pauli exclusion principle. The pseudopotential approach acts as if there were only valence electrons, i.e. there are no core electrons. The pseudopotential is repulsive in the core region in order to prevent the valence electron(s) from penetrating into the core. The pseudopotential becomes coulombic at long range as expected. Since there are no core orbitals, the ground state for the valence electron(s) is nodeless. The higher energy valence states are only orthogonal to the lower valence states.

The repulsive nature of the pseudopotential at short-range causes the pseudo-wave functions to have an incorrect short range form. The long-range coulombic nature \((- (Z - N_c)/r)\) of the pseudopotential gives the proper pseudo-wave function at long range. Hence for quantities that depend on small \(r\) (e.g. spin-orbit interaction) the pseudopotential leads to poor results. While quantities depending on the complete spectrum of \(r\) (e.g. total energy) are given quite accurately.

In the model potential approach, the interaction of the valence electron(s) with the electronic core is replaced by a potential. Thus, the actual states of the cores electrons do not matter. The existence of the core electrons is taken into account by the fact that the lowest energy valence
electron is located in the N-n+1 orbital. This is in contrast to the pseudopotential approach where the lowest energy valence electron occupies the lowest orbital. The model potential approach freezes the core electrons in such a manner that they do not come into play, except as discussed above. The model potential is attractive, for all r, and is coulombic at both long \( V \sim -(Z - N_e)/r \) and short-range \( V \sim -Z/r \). The nature of the model potential tends to make the model-wave functions more accurate than the pseudo-wave functions. Thus, the model-wave functions are capable of giving accurate results for quantities that depend on the short-range form of the wave functions as well as quantities depending on the long range form.

Thus for some calculations, the model potential approach is superior to the pseudopotential approach. For molecular calculations, the pseudopotential approach is preferred. Since there are no core electrons, (and more importantly no core states) in the pseudopotential approach, one only has to consider the valence electrons of the constituent atoms of the molecule. In contrast, the model potential has core orbitals and thus these orbitals must be taken into account in molecular calculations. This is performed by letting the basis set describing the valence electron(s) of the molecule include states describing the virtual bound states of the atomic cores. For atoms with large cores, the pseudopotential approach significantly simplifies the problem. The model-molecular potential must first calculate the virtual core orbitals and then put the valence electrons into the open valence orbitals. This requires almost the same amount of work as does a full electron calculation.

In this work both model potentials and pseudopotentials are considered. Model and pseudopotentials are calculated for the cores of Zn, Cd, and Hg. These three atoms consist
of cores of closed shell electrons with two valence electrons in the outer shell. The model potentials and the pseudopotentials are used to find the energies of the positive ions and the neutral atoms. The model potentials and the pseudopotentials may also be used to simplify calculations for diatomic molecules.
4 PSEUDOPOTENTIALS

The first method employed to reduce the N-electron problem to the n-electron problem is the pseudopotential technique. The pseudopotential is used to represent the cores of Zn, Cd and Hg. The pseudopotential takes into account the Pauli exclusion principle and hence it tends to be repulsive in the core region in order to keep the valence electron(s) out of the core. For a given atom, the pseudopotential is found by adjusting parameters in the pseudopotential until it reproduces the experimental energy spectrum of the positive ion.

In the first stage of the pseudopotential development, the pseudopotential is found by fitting (see chapter 8) the calculated terms of the positive, monovalent ions (i.e. Zn II, Cd II and Hg II) to the experimental values. The fine-structure is eliminated by performing a weighted average of the energy levels. This weighted average is the center of gravity for the energies and is calculated by

\[ E_{n,l} = \sum_{l=0}^{l_{max}}{E_{n,l,l-l+1/2}} \frac{P_l}{2l+1} \]  

(4.1)

The form of the pseudopotential is strictly radial in nature. This is due to the fact that the cores of Zn, Cd and Hg (and hence Zn II, Cd II and Hg II) are all closed shell and hence the potential representing them must not have any angular dependance. The pseudopotential is also made \( l \)-dependent (following Schwarz). The reason being that electrons with different values of \( l \) behave in a different manner and hence a more accurate form of the potential may be derived if one makes it \( l \)-dependent. The actual form of the pseudopotential is taken to be

\[ V_{p_s}(r) = \sum_{l=0}^{l_{max}} V_{p_s}^l(r) P_l \]  

(4.2)
where \( l_m \) is the largest value of \( l \) which occurs in the core, 
\[ P^l = \sum_m |lm><lm| \] is the projection operator,

\[ V_{ps}^l = \sum_{i=1}^{2} \zeta_{i,i} r^{|n_{i,i} - \alpha|} e^{-\beta_{i,i} r^2} + V_{pol}^l \quad \text{(4.3)} \]

and

\[ V_{pol}^l = -\frac{\alpha}{2r^4} \left( 1 - e^{-r^2/r_{i,i}^2} \right)^2 \quad \text{(4.4)} \]

\( V_{pol}^l \) is the polarization potential and \( \alpha \) is the dipole polarizability (see chapter 6).

A Gaussian form for the pseudopotential is assumed in order to export the results to molecular calculations. Gaussians make multi-centre molecular calculations much easier. Slater type exponentials would introduce complicated angular dependencies into the molecular calculations. The Gaussians simplify the form of the angular dependence in the multi-centre integrals.

The total potential seen by the valence electron is

\[ V = -\frac{Z - N_c}{r} + V_{ps} \quad \text{(4.5)} \]

where \( Z \) is the atomic number and \( N_c \) is the number of electrons in the core of the atom. The term added to the pseudopotential is the electrostatic potential of the nucleus acting on the valence electron. It is a screened function due to the electronic core shielding the nucleus. The probability of finding the valence electron in the core region is much smaller than the probability of finding the electron outside the core region (due to the potential barrier).

Thus, in general the electron will be acted on by a shielded nucleus.
The parameters of the pseudopotential were varied so that the calculated centre of gravity energies were fitted to as many of the low lying experimental states as possible (using a least squares fit, chapter 8). For example, the \(l=0\) pseudopotential, representing the Zn II core, was matched to the six lowest experimental centre of gravity energies with \(l=0\). Once the centre of gravity energies have been matched adequately, the fine structure energy separations will be included, see chapter 7.
5 Model Potentials

The second approach used to reduce the $N$-electron problem into an $n$-electron problem is the model potential. The model potential is used to represent the interaction between the valence electron(s) and the electronic core. Since the model potential does not take into account the Pauli exclusion principle, the ground state wave function has the proper number of nodes and the model potential is attractive in the everywhere. The model potential, as in the pseudopotential case, is found by adjusting parameters to fit the experimental energy spectrum of the positive, monovalent ions (see chapter 8). As in the pseudopotential approach, the fine-structure is eliminated by fitting the model potential to the centre of gravity energies.

The form of the model potential is strictly radial in nature since all the core electrons reside in closed shells. The model potential is taken to be $l$ dependent for a better fit. The general form for the model potential is

$$V_M(r) = \sum_{l=0}^{l_m} V_M^l(r) P^l$$  \hspace{1cm} (5.1)

where $l_m$ is the largest value of $l$ which occurs in the core, $P^l = \sum_m |lm><lm|$ is the projection operator and

$$V_M^l(r) = V_{ss}^l(r) + V_x^l(r) + V_{pol}^l(r)$$  \hspace{1cm} (5.2)

with

$V_{ss}^l$ - Electrostatic potential

$V_x^l$ - Exchange potential

$V_{pol}^l$ - Polarization potential.
5.1 Electrostatic potential

The electrostatic interaction consists of two parts, 1) nuclear attraction and 2) interaction of the valence electron with the core electrons (in closed shells). Thus

\[ V_{es} = V_N + V_v \]

where \( V_N \) is the nuclear attraction and \( V_v \) is the interaction between the valence electron and the electronic core.

The nuclear attraction between the nucleus with charge +Z and the valence electron with charge -1 is given by

\[ V_N = -Z/r. \quad (5.3) \]

The interaction between the valence electron and the electronic core is derived from basic electrostatics (see for example Zahn (1979)). Assume that the density of the core electrons is given by \( \rho_c(r) \). Thus the radial density of the core electrons is \( D(r) = 4\pi r^2 \rho_c(r) \).

The potential due to a spherical charge density \( \rho_c \) is given by:

\[ V(r) = 4\pi \int_0^\infty \frac{\rho_c(r')}{r} r'^2 dr' + 4\pi \int_r^\infty \rho_c(r') r' dr'. \]

Letting \( D(r) = 4\pi r^2 \rho_c(r) \) leads to

\[ V(r) = \int_0^r \frac{D(r')}{r} dr' + \int_r^\infty \frac{D(r')}{r'} dr'. \quad (5.4) \]

where \( R \) is the radial extent of the charge density.

If the charge density is replaced by the electronic core of an atom then \( R \to \infty \), since the core volume extends out to infinity. Thus the electrostatic potential due to the core is
\[ V_\ast (r) = \int_0^r \frac{D(r')}{r} dr' + \int_r^\infty \frac{D(r')}{r'} dr' \]
\[ = \frac{1}{r} \int_0^r D(r') dr' - \int_r^\infty D(r') \left( \frac{1}{r'} - \frac{1}{r} \right) dr' \quad \text{(5.5)} \]

The charge enclosed in a sphere of radius \( r \) is
\[ Q(r) = \int_0^r D(r') dr' \quad \text{(5.6)} \]

Letting \( r \to \infty \) gives
\[ Q = \int_0^\infty D(r') dr' \]

which is the number of electrons in the core, i.e. \( N_c \).

Therefore the total electrostatic interaction is found by combining equations (5.3), (5.5) and (5.6)
\[ V_\ast(r) = -\frac{(Z-N_c)}{r} - \int_r^\infty D(r') \left( \frac{1}{r'} - \frac{1}{r} \right) dr' \quad \text{(5.7)} \]
\[ \Rightarrow r V_\ast(r) = -(Z-N_c) - \int_r^\infty D(r') \left( 1 - \frac{r}{r'} \right) dr' \quad \text{(5.7a)} \]

\section{5.1.1 Limiting forms of the electrostatic interaction}

Examine \( V_\ast \), equation (5.7) to see the form it takes at long and short range

1) \( r \to \infty \):
\[ r V_\ast(r) \to -(Z-N_c) - \lim_{r \to \infty} \int_r^\infty D(r') \left( 1 - \frac{r}{r'} \right) dr' \]
\[ = -(Z-N_c) \]

Therefore at long range the valence electron sees a shielded nucleus and the interaction potential is
\[ V_\ast(r) = -\frac{(Z-N_c)}{r} \]
as would be expected.

2) as \( r \to 0 \):

\[
\alpha r V_{es}(r) \to -(Z - N_c) - \int_0^\infty D (r') dr' = -(Z - N_c) - N_c = -Z
\]

Thus at short range the valence electron sees a bare nucleus and the interaction potential is

\[
V_{es}(r) = -\frac{Z}{r}.
\]

The actual form of the electrostatic potential can be seen from the following graph of the electrostatic potential of Zn II. The radial density was found by using the Dirac-Fock program of Desclaux (1975), see Appendix E. The electrostatic interaction is attractive everywhere and, as expected, follows the asymptotic forms stated above.

Fig. 1 Model Electrostatic Potential of Zn II
5.1.2 Integration Technique

The integration technique to evaluate equation (5.7a) is the extended Lagrange Integration (see Appendix A). The extended Lagrange integration requires an equal step size. The radial density $D(r)$ was found using a logarithmic grid (see Appendix C). Thus a change of coordinates is required. The starting integral is

$$I = -\int_{r}^{\infty} D(r') \left( 1 - \frac{r}{r'} \right) dr'$$

let $r' = e^y$ thus $dr' = r'dy$ and

$$I = -\int_{\ln r}^{\infty} D(r')(r' - r) dy$$

which has equal an equal step size, and the extended Lagrange integration may be employed.

5.2 Exchange Potential

The exchange potential between the electronic core and the valence electron(s) is based upon the work of Slater (1951). Slater developed a local approximation to the non-local exchange potential by using a free-electron gas (of constant density) model. He found the exchange potential to be

$$V_x = -2\kappa \rho^{1/3} F(\eta),$$

where $\kappa = (3/\pi)^{1/3}$, $\rho$ is the total electronic density of the atomic or ionic electrons,

$$F(\eta) = \frac{1}{2} \left( \ln \frac{1 + \eta}{1 - \eta} \right) \left[ \frac{1 - \eta^2}{\eta} \right],$$

and $\eta = p/p_f$, where $p$ is the single electron momentum and $p_f$ is the Fermi momentum of the electronic distribution, which is given by $p_f = \pi \kappa \rho^{1/3}$. 
Slater found that \( F(\eta) = \frac{3}{4} \) by averaging the momentum over the Fermi sphere. Kohn and Sham (1965) took \( F(\eta) = \frac{1}{2} \) based on energy minimization procedures.

The present treatment uses a variation of the Slater method (Migdalek and Baylis, 1980). The total density \( \rho \) was replaced by the electronic core density \( \rho_c \), since the only the exchange between the valence electron and the core electrons is included in the model potential.

In the free-electron gas model, the interaction between the valence electron (with momentum \( p \)) and electronic distribution (with Fermi momentum \( p_f \) and density \( \rho_f \)), is dependent on \( \eta = p/p_f \). The averaging that Slater did over the Fermi sphere was an average over \( p \) in the range \( 0 < p < p_f \). The momentum of the valence electron is larger than the Fermi momentum. Thus, \( \eta = 1 \) at \( r = 0 \) and it increases as \( r \) increases. \( F(\eta = 1) = \frac{1}{2} \) and it decreases rapidly with increasing energy (i.e. increasing \( \eta \)). The free-electron gas model implies that equation (5.8) overestimates the exchange potential between the valence electron and the electronic core. This overestimation occurs mostly for large \( r \), thus Migdalek and Baylis (1980) replaced \( F(\eta) \) by a cut-off function of the form \( F(\eta) = \frac{1}{2} e^{-\lambda r} \), where \( \lambda \) was an adjustable parameter.

Thus the exchange potential used in the calculation of the model potential for the ions was an \( \eta \)-dependent potential of the form:

\[
V_x(r) = -\left(\frac{3}{\pi}\right)^{1/3} \rho_c^{1/3} e^{-\lambda r} .
\] (5.10)

Using \( D(r) = 4\pi r^2 \rho_c \) gives

\[
V_x(r) = -\left(\frac{3}{\pi}\right)^{1/3} \left(\frac{D(r)}{4\pi r^2}\right)^{1/3} e^{-\lambda r} .
\] (5.11)
The Slater exchange potential for the interaction between the valence electron and the core of Zn II has the following form:

\[ V_{\text{Model Exchange}} = \rho(r) \]

![Graph showing the model exchange potential vs r](graph.png)

**Fig. 2** Model Exchange Potential for Zn II

### 5.3 Polarization potential

The form of the polarization potential used in the model potential is the same form as used in the pseudopotential, equation (4.4), i.e.

\[ V_{\text{pot}} = -\frac{a}{2r^4} \left( 1 - e^{-r^2/r_{c1}^2} \right)^2 \]

See the chapter 6.

Thus the total model potential used to represent the interaction between the electronic core and the valence electron is given by
\[ V_\mu(r) = \sum_{l=0}^{l_{\text{max}}} V_\mu^l P^l = -\frac{Z - N}{r} - \int_r^\infty D(r') \left( \frac{1}{r} - \frac{1}{r'} \right) dr' \]

\[ -\sum_{l=0}^{l_{\text{max}}} \left\{ \left( \frac{3}{\pi} \right)^{1/3} \left( \frac{D(r)}{4\pi r^2} \right)^{1/3} e^{-\lambda_1 r} - \frac{\alpha}{2 e^{r^2/2}} \right\} P^l. \] (5.12)

The parameters \( \lambda_1 \) and \( r_{c,1} \) are adjusted, so that the lowest calculated centre of gravity energy levels are fitted to the experimental values using a least square fit (see chapter 8). Once the match is satisfactory, the fine structure is included (see chapter 7).
6 POLARIZATION POTENTIAL

The pseudopotential and model potential approaches involve representing the atomic cores of atoms/ions/molecules by potentials. The pseudopotential approach replaces the atomic cores completely, while in the model potential approach, the electronic cores are frozen and the interaction between the valence electron(s) and the cores is replaced. One then solves the Schrödinger (or Dirac) equation for the valence electron(s). In both cases the frozen core approximation is employed, i.e. the cores are assumed to be fixed in space. In reality the core is distorted by the valence electron(s). This core distortion is the principal contribution the valence-core correlation.

Consider an atom or ion with a core of closed-shell electrons and an open shell of valence electrons. Assume that \( r_i \gg r_0 \), where the \( r_i \) are the positions of the valence electrons and \( r_0 \) is the radius of the electronic core distribution. The valence electrons will set up an electric field \( \vec{E} \). This field will induce a dipole moment \( \vec{d} = \alpha \vec{E} \), where \( \alpha \) is the dipole polarizability of the core. The potential associated with this dipole is

\[
V_{pot} = -\frac{\alpha}{2} \vec{E} \cdot \vec{E} .
\]

For large \( r_i \), the form of the electric field is

\[
\vec{E} \approx \sum_i \frac{\vec{r}_i}{r_i^3} .
\]

since the valence electrons act as distant point charges. This whole treatment ignores higher order effects such as the quadrupole interaction (Bottcher 1971 and Norcross 1974).
Born and Heisenberg (1924) and Van Vleck and Whitelaw (1933) took the long range form of the electric field, equation (6.2), to be the field for all \( r \). This leads to a dipole moment

\[
\vec{d} = -\alpha \sum_i \frac{\vec{r}_i}{r_i^3} .
\]  

(6.3)

Using the fact that the electric field due to a dipole of strength \( \mu \) along its axis is \( 2\mu/r^3 \), they found that

\[
V_{pol} = -\frac{\alpha}{2} \sum_i \frac{1}{r_i^3} .
\]  

(6.4)

This holds well for \( r_i > r_0 \), but it is unbounded as \( r_i \to 0 \). Thus the form of the electric field must be modified by the inclusion of a cut-off function.

Baylis (1977) chose the form of the electric field to be

\[
\vec{E} = \sum_i \vec{E}_i = -\sum_i \frac{\vec{r}_i}{(r_i^2 + r_0^2)^{3/2}}
\]  

(6.5)

this leads to a polarization potential

\[
V_{pol} = -\frac{\alpha}{2} \left( \sum_i \vec{E}_i \right)^2 = -\frac{\alpha}{2} \sum_i \frac{r_i^2}{(r_i^2 + r_0^2)^3}
\]

\[
\quad -\alpha \sum_{i<j} \frac{\vec{r}_i \cdot \vec{r}_j}{(r_i^2 + r_0^2)^{3/2} (r_j^2 + r_0^2)^{3/2}} .
\]  

(6.6)

The first term is the direct term and the second term is the dielectric term or cross term, first introduced by Chisholm and Opik (1964). The dielectric term takes into account the fact that the polarization of the core by one valence electron affects the potential experienced by the other valence electrons. For 1 electron this reduces to

\[
V_{pol}(r) = -\frac{\alpha}{2} \frac{r^2}{(r^2 + r_0^2)^{3/2}} .
\]  

(6.7)
This potential has the proper long range form, i.e. \(-\frac{a}{2r^4}\), and it also remains finite for \(r \rightarrow 0\). The value for \(r_0\) was taken to be approximately the rms value of \(r\) for the outermost orbital of the core.

There have been numerous suggestions for the form of \(\vec{E}\) and hence for \(V_{po}\). Müller et al (1984) suggested the following as the electric field

\[
\vec{E} = \sum_i \vec{E}_i = -\sum_i \frac{\vec{r}_i}{r_i^3} C(r_i, r_c)
\]

(6.8)

Where \(C(r_i, r_c)\) is the cut-off function and \(r_c\) is the cut-off parameter. Müller et al (1984) considered various forms for \(C(r_i, r_c)\). They argued that since it is difficult to know what the form of the potential is at close range, it is wise to choose a form for the cut-off function that makes integrations easier. Since Gaussian-type basis functions are used in molecular calculations and Gaussians are also used in the pseudopotential presented here, a Gaussian form for the cut-off function is used. This is the reason for choosing Müller's form for the polarization potential over the form used by Baylis. Müller et al (1984) claimed that although a Gaussian form may be the most useful the exact form of the Gaussian cut-off function is not very critical since all of the forms they tested lead to similar results.

The form of the cut-off function used, is the one employed by Fuentealba et al. (1982, 1985) which was originally derived by Müller et al (1984). The cut-off function is

\[
C(r_i, r_c) = \left(1 - e^{-r_i^2/r_c^2}\right)
\]

(6.9)

Thus the electric field becomes
\[ \mathbf{E} = \sum_i \mathbf{E}_i = \frac{\mathbf{r}_i}{r_i^3} \left( 1 - e^{-r_i^2/r_i^2} \right) . \]  
(6.10)

Which leads to a polarization potential

\[ V_{\text{pol}} = -\frac{\alpha}{2} \sum_i \frac{1}{r_i^3} \left( 1 - e^{-r_i^2/r_i^2} \right)^2 - \alpha \sum_{i<j} \frac{r_i \cdot r_j}{r_i r_j^3} \left( 1 - e^{-r_i^2/r_j^2} \right) \left( 1 - e^{-r_j^2/r_i^2} \right) \]  
(6.11)

for 1 electron

\[ V_{\text{pol}} = -\frac{\alpha}{2r_1^4} \left( 1 - e^{-r_1^2/r_1^2} \right)^2 . \]  
(6.12)

and for 2 electrons

\[ V_{\text{pol}} = -\frac{\alpha}{2r_1^4} \left( 1 - e^{-r_1^2/r_1^2} \right)^2 - \frac{\alpha}{2r_2^4} \left( 1 - e^{-r_2^2/r_2^2} \right)^2 - \alpha \frac{r_1 \cdot r_2}{r_1 r_2^3} \left( 1 - e^{-r_1^2/r_2^2} \right) \left( 1 - e^{-r_2^2/r_1^2} \right) . \]  
(6.13)

This polarization potential has been included in an \( l \) - dependent pseudopotential and also in an \( l \) - dependent model potential with \( r_c \) as an adjustable parameter for the one electron case. Thus the form of the polarization potential used in the centre of gravity calculations for the positive ions is

\[ V_{\text{pol}} = -\frac{\alpha}{2r_1^4} \left( 1 - e^{-r_1^2/r_1^2} \right)^2 , \]  
(6.14)

as discussed above, in chapters 4 and 5.

The polarization potential for the two-electron problem is given by

\[ V_{\text{pol}} = -\frac{\alpha}{2r_1^4} \left( 1 - e^{-r_1^2/r_1^2} \right)^2 - \frac{\alpha}{2r_2^4} \left( 1 - e^{-r_2^2/r_2^2} \right)^2 - \alpha \frac{r_1 \cdot r_2}{r_1 r_2^3} \left( 1 - e^{-r_1^2/r_2^2} \right) \left( 1 - e^{-r_2^2/r_1^2} \right) . \]  
(6.15)

and will be employed in chapter 11.
7 SPIN-ORBIT INTERACTION

The spin-orbit interaction is due to the relativistic orbital motion of an electron with spin through an electric field set up by the nuclear charge. It is the largest term added to the Hamiltonian after the residual electrostatic term.

Since an electron has spin, it also has a magnetic moment (see Capri 1985) given by

\[ \vec{\mu} = \frac{ge}{2mc} \vec{s} = g \mu_B \vec{s} \]  \hspace{1cm} (7.1)

where \( \mu_B = \alpha / 2 \) is the Bohr Magneton, \( g \) is the gyromagnetic ratio \( \approx 2 \).

When one views the electric field due to the nucleus in the rest frame of the electron, the electric field

\[ \vec{E} = -\frac{\partial \vec{V}}{\partial r} \]  \hspace{1cm} (7.2)

acquires a magnetic component

\[ \vec{B} = -\frac{\vec{v}}{c} \times \vec{E} \]  \hspace{1cm} (7.3)

Therefore the spin-orbit interaction is given by

\[ V_{s.o.} = -\vec{\mu} \cdot \vec{B} = \frac{g}{2c^2} \vec{s} \cdot (\vec{v} \times \vec{E}) \]

\[ = \frac{g}{2c^2} \vec{s} \cdot (\vec{p} \times \vec{E}) \]  \hspace{1cm} (7.4)

The interaction must be adjusted by a factor of 1/2 due to the Thomas precession of the spin vector. Thus the actual spin-orbit interaction is given by

\[ V_{s.o.} = -\frac{g}{4c^2} \vec{s} \cdot (\vec{p} \times \vec{r}) \]  \hspace{1cm} (7.5)
Letting \( g = 2 \) leads to

\[
V_{s.o.} = -\frac{1}{2c^2} \vec{s} \cdot (\vec{E} \times \vec{p}) .
\]  

(7.6)

Using equation (7.2) the electrostatic potential of the nucleus gives an electric field

\[
\vec{E} = -\frac{1}{r} \frac{dV(r)}{dr} \vec{r}
\]

therefore

\[
V_{s.o.} = \frac{1}{2c^2} \frac{dV(r)}{dr} \vec{r} \cdot (\vec{r} \times \vec{p})
\]

\[
= \frac{1}{2c^2} \frac{dV(r)}{dr} \vec{s} \cdot \vec{l} .
\]  

(7.7)

Taking \( \vec{j} = \vec{l} + \vec{s} \) we find that

\[
\vec{j}^2 = (\vec{l} + \vec{s})^2 = \vec{l}^2 + \vec{s}^2 + 2\vec{s} \cdot \vec{l}
\]

\[
\therefore \quad \vec{s} \cdot \vec{l} = \frac{1}{2} \{ j(j+1) - l(l+1) - s(s+1) \} .
\]  

(7.8)

Without the spin-orbit interaction, the terms are degenerate with respect to \( j \). The inclusion of the spin-orbit interaction removes this degeneracy. For a single electron in the outer shell the terms of a given \( l \) value are split into 2 levels (excluding the \( l=0 \) states, where \( \vec{s} \cdot \vec{l} = 0 \)), one corresponding to the \( j = l + 1/2 \) and the other corresponding to \( j = l - 1/2 \).

For \( j = l + 1/2 \)

\[
\vec{s} \cdot \vec{l} = \frac{1}{2} l
\]
For $j = l - 1/2$

\[ \vec{s} \cdot \vec{l} = -\frac{1}{2}(l+1) \]

Therefore the spin-orbit interaction is represented by

\[
V_{s.o.} = \frac{1}{2c^2r} \frac{dV(r)}{dr} \left\{ \begin{array}{ll}
\frac{1}{2}l, & j = l + 1/2 \\
-\frac{1}{2}(l+1), & j = l - 1/2
\end{array} \right. \tag{7.9}
\]

$V(r)$ is the electrostatic potential, due to the nucleus, which acts on the valence electron. At long range, the electron experiences a potential due to a nucleus shielded by the electronic core. Thus at long range

\[
V(r) = -\frac{(Z-N_e)}{r} \tag{7.10}
\]

where $Z$ is the atomic number and $N_e$ is the number of electrons in the core. For singly charged positive ions (i.e. Zn II, Cd II and Hg II) $Z-N_e = 2$, in both the model and pseudopotential approaches. Therefore at long range

\[
\frac{1}{r} \frac{dV(r)}{dr} = -\frac{2}{r^3} \tag{7.11}
\]

At short range, the electron will experience a bare nucleus and hence

\[
V(r) = -\frac{Z}{r} \Rightarrow \frac{1}{r} \frac{dV(r)}{dr} = \frac{Z}{r^3} \tag{7.12}
\]

To ensure the proper form of the potential at intermediate range, let $Z \rightarrow Z + (Z_{eff} - Z)e^{-r/a^2}$, where $Z_{eff}$ and $\alpha$ are used as adjustable parameters. The parameter $\alpha$ corresponds to a cut-off parameter for the core. The parameter $Z_{eff}$ compensates for the fact that while the electron is in the core it does not always see a bare nucleus. The electron sees a shielded nucleus.
Thus, the spin-orbit interaction gives

$$V_{s.o.} = \frac{1}{2c^2r^3}\{-(Z'_{eff} - 2)e^{-r^2/\alpha^2} + 2\} \hat{s} \cdot \hat{l}$$  \hspace{1cm} (7.13)$$

From first order perturbation theory, the energy shifts due to the spin-orbit interaction given by:

$$\Delta E = \langle \psi_0 | V_{s.o.} | \psi_0 \rangle$$

where $\psi_0$ is the wave function for the centre of gravity term. These shifts give energy levels above and below the centre of gravity, depending on the value of $\hat{s} \cdot \hat{l}$.

The maximum value of $V_{s.o.}$ (equation (7.13)) is found by letting $\alpha \to \infty$, and leads to

$$V_{s.o.} = \frac{Z'_{eff} \hat{s} \cdot \hat{l}}{2c^2r^3}.$$  \hspace{1cm} (7.14)$$

Thus, using first order perturbation theory and equation (7.8), the maximum energy difference between the $j = l+1/2$ and $j = l-1/2$ levels is (using (7.14))

$$\Delta E = \frac{Z'_{eff}}{2c^2} (l + 1/2) \langle \psi_0 | r^{-3} | \psi_0 \rangle.$$  \hspace{1cm} (7.15)$$

where $\psi_0$ is the centre of gravity wave function. This was evaluated by using both centre of gravity model-wave functions and pseudo-wave functions. It was evaluated in order to determine if equation (7.13) was acceptable or if it needed adjustment. The energy difference between the $4d^{10}5p^2P_{3/2}$ and the $4d^{10}5p^2P_{1/2}$ levels, in Cd II, was calculated for the model-potential approach as well as for the pseudopotential approach. These results were then compared with the actual experimentally derived differences. The results were as follows.
Table 1 Spin-orbit Compatibility

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{1/2} - E_{3/2}$ a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>1.13E-02</td>
</tr>
<tr>
<td>Model Potential</td>
<td>2.94E-02</td>
</tr>
<tr>
<td>Pseudopotential</td>
<td>2.61E-04</td>
</tr>
</tbody>
</table>

These are the maximum shifts that can be calculated. Thus, equation (7.13) is applicable in the model potential case, but not in the pseudopotential case. The reason is that the pseudo-wave functions are very unrealistic for small $r$, they tend to get very small upon entering the core region and they do not oscillate in the core region. The integral $\langle \psi_0 | r^{-3} | \psi_0 \rangle$ is highly dependent on the form of $\psi_0$ for small $r$ and thus the pseudo-wave functions will give values for this integral that are too small.

In order to accommodate the splittings in the pseudopotential approach, a new form for the spin-orbit interaction must be used. Since the pseudo-wave functions are unrealistic in the core region, a different form of the spin-orbit interaction is assumed in order to achieve accurate fits. The spin-orbit interaction is assumed to be a perturbation of the centre of gravity potential. The total $l$-dependent pseudopotential acting on the valence electron is

$$V(r) = -\frac{Z - N_e}{r} + \sum_{l=0}^{l_{max}} V_{ps}^l(r) \times \Gamma_{s.o.}^l(r) P^l$$ (7.16)

where

$$\Gamma_{s.o.}^l(r) = 1 + A \frac{z^2}{a^2} e^{-r^2/a^2}$$ (7.17)
This form of the spin-orbit interaction may not have the correct form for the theoretical spin-orbit interaction, but it does lead to satisfactory results (see chapter 10).

The total potential acting on the valence electron in the model potential case is given by equation (5.12) with the spin-orbit term added on, i.e.

\[ V(r) = \sum_{l=0}^{l_{\text{max}}} \left( V^l_{\mu}(r) + V^l_{s.o.}(r) \right) P^l \]  \hspace{1cm} (7.18)

where \( V^l_{s.o.} \) is given by equation (7.13), with the parameters being \( l \)-dependent.
8 ENERGY FITTING PROCEDURE

The fitting of the energies (for both the model and pseudopotentials) was carried out by a Fortran program based upon a minimization algorithm developed by Baylis and Pradhan (1984), see appendix E. The program minimizes the sum of the squares of the differences between the actual energies and the calculated energies. Thus the problem is a least squares problem in that the function

$$\phi = \sum_{i=1}^{n} (E_{\text{exp},i} - E_{\text{calc},i})^2$$

(8.1)

is to be minimized. The value of \( n \) \((\leq 10)\) is taken to be as large as possible so that as much of the valence electron spectra as possible is used. This should lead to more realistic potentials.

The calculated eigenenergies, used in equation (8.1) are found by solving the Schrödinger equation

$$H \psi_i = E_i \psi_i$$

where \( H \) is the Hamiltonian of the valence electron:

$$H = -\frac{1}{2} \nabla^2 + V(r)$$

with \( V \) given by either equation (4.2) or (5.12), \( \psi_i \) is the wave function of the valence electron and \( E_i \) is the energy.

The solution of the Schrödinger equation is found by setting up the potential and then integrating the wave function using the Numerov method (see appendix B). The energies found by solving the Schrödinger are then used in equation (8.1). The parameters in the potentials are varied to make the value of \( \phi \) as small as possible.
The method of minimization is an extension of the Levenberg-Marquardt minimization procedure. The procedure combines both the curvature method and the gradient method. Instead of the usual unconstrained search for a minimum, the method confines the search to a circle with a fixed radius. Once the minimum is found in this circle then the point of minimization becomes the new centre of the circle and the search continues. A discussion of the procedure may be found in Appendix E.
9 CENTRE OF GRAVITY RESULTS

The centre of gravity results for both pseudopotentials and model potentials are given. Centre of gravity is the elimination of the fine-structure by performing a weighted average of the energies as in equation (4.1), i.e.

\[ E_{n,l} = \frac{lE_{n,l-1} + (l+1)E_{n,l+1}}{2l+1} \]  \hspace{1cm} (4.1)

The parameters and graphs for the pseudopotentials and model potentials of the cores of Zn II, Cd II and Hg II are given, as well as the energies of various states of Zn II, Cd II and Hg II.

9.1 Pseudopotentials

9.1.1 Pseudopotential Parameters

The parameters for the pseudopotential, defined by equations (4.2) - (4.4), are \( c_{l,1} \), \( \beta_{l,1} \) and \( r_{c,1} \). Thus for a given \( l \) value there are 5 parameters. The parameters calculated for Zn II, Cd II and Hg II are given in the following charts.
Table 2  Pseudo-parameters for the C. of G. – Zn II states

For Zn II: $\alpha_\text{II} = 2.296 \alpha_\text{e}^3$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>s</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
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<td>$\beta_2$</td>
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<tr>
<td>$r_\text{c}$</td>
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</tr>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$n_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 3  Pseudo-parameters for the C. of G. - Cd II states

For Cd II: $\alpha_d = 4.971 \ a_0^3$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>s</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
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<td>$c_1$</td>
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<td>$r_c$</td>
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<td>$n_1$</td>
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<tr>
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Table 4  Pseudo-parameters for the C. of G. - Hg II states

For Hg II: \( \alpha_0 = 8.106 \alpha_0^2 \)

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<td>-0.2554356</td>
<td>0.3105169</td>
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<tr>
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<td>-0.1472885</td>
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<td>( \beta_1 )</td>
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<td>1.2789905</td>
<td>0.1135141</td>
</tr>
<tr>
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<td>1.5977620</td>
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</tr>
<tr>
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<td>0</td>
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<tr>
<td>( n_2 )</td>
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<td>0</td>
</tr>
</tbody>
</table>
9.1.2 Pseudopotential Graphs

Plots of the pseudopotentials for all \( l \) occurring in the cores of Zn II, Cd II and Hg II are given below.

![Graph showing pseudopotential plots for Zn II, Cd II, and Hg II.]

**Fig. 3** Pseudopotentials for Zn II
Fig. 4 Pseudopotentials for Cd II

Fig. 5 Pseudopotentials for Hg II
9.1.2.1 Discussion

All of the above graphs show the repulsive nature of the pseudopotential. The long range (the screen nucleus) form of all of the pseudopotentials is exhibited. These graphs represent the cores of Zn II, Cd II and Hg II for the s, p and d states, along with the f-states of Hg II. A discussion of all of the above plots is given below.

The first set of plots give the pseudopotentials representing the s, p and d core states of Zn II. These plots indicate that the pseudopotential representing the s-electrons is more repulsive than the ones representing the p and d-electrons. The reason for this is that, the s-electrons are more penetrating than the p and d-electrons and thus they must be more effectively repulsed than the p and d-electrons. The pseudopotential representing the d-electrons is attractive at close range and then becomes repulsive. The reason being that, there is only one shell of d-electrons in the core (the 3d shell). The d-electrons only have to be repulsed at long range since the 3d shell is the outermost core shell. Inside the 3d shell the electrons are only acted on by the nucleus and hence the potential is attractive. The pseudopotential acting on the p-electrons is somewhere in between the s and the d-electrons. The p-electrons are not as penetrating as the s-electrons and so they are not repulsed as strongly as the s-electrons are. The p-electrons are distributed throughout the core and thus the pseudopotential must have the same general form as the pseudopotential representing the s-electrons (which are also distributed throughout the core).

The second set of plots represents the pseudopotentials used to represent the s, p and d states of the Cd II core. The Cd II core has 2 shells of d-electrons (3d and 4d). The furthermore shell is the 4d shell with the 3d shell a little
farther in. A d valence electron would see two large filled d shells when it tries to penetrate into the core. This is the reason for the large potential barrier representing the core d-electrons. The pseudopotential representing the s-electrons in the core is similar to the pseudopotential representing the s-electrons in the core of Zn II, i.e. the pseudopotential has to keep the penetrating s-electrons out of the core. Since there are more s-electrons in the Cd II core than in the Zn II core, the pseudopotential representing the s-electrons in the Cd II core must be slightly larger than the one used in the Zn II case. Once again the pseudopotential representing the p-electrons in the Cd II core must be repulsive to keep out the penetrating p-electrons, but not as repulsive as the pseudopotential representing the s-electrons.

The last set of graphs, shows the pseudopotentials used to replace the core electrons in Hg II, are similar to those found for the Cd II case. There are now 3 full d shells (3d, 4d and 5d). Thus the pseudopotential representing the d-electrons must be very repulsive in order to ensure that the d-valence electron does not penetrate into these shells. The pseudopotential representing the s core electrons is larger in the Hg II case than in the Cd II case since there is now an extra s shell (5s). The pseudopotential representing the p-electrons is a little smaller than pseudopotentials found in the Zn II and the Cd II cases. There is not any obvious explanations for this except for the fact, that the pseudopotentials representing the p-electrons in all three cases were much less accurate than the pseudopotentials used to represent the s and d-electrons. The inaccuracies could mask differences in the pseudopotentials. The f-pseudopotential is attractive at short range and becomes repulsive further out. The 4f shell in the Hg II core is one
of the outermost shells. Thus the pseudopotential representing it only has to be repulsive at long range and can be attractive at short range, similar to the d-pseudopotential of Zn II.

9.1.3 Pseudo-wave Functions

As discussed earlier, the pseudo-wave function does not have the proper number of nodes, i.e. \( \text{nodes} = n - l - 1 \) where \( n \) is the principle quantum number and \( l \) is the angular momentum quantum number. Instead the pseudo-wave function is nodeless for the ground state and has the proper number of nodes for the excited states, with respect to the ground state. The following graph shows the pseudopotential used to model the core of Cd II and the ground state pseudo-wave function of Cd II.
Fig. 6 Ground state pseudo-wave function of Cd II

From the above graph, it is clear that the pseudopotential is constructed in order to keep the valence electron out of the core region. The pseudopotential is repulsive in the core region and attractive outside the core (as described earlier). The maximum of the pseudo-wave function lies outside of the core and, as expected, the pseudo-wave function dies down rapidly in the core. Both the pseudopotential and the pseudo-wave function have the correct coulombic form outside of the core (i.e. $r \sim 2 \text{ a.u.}$).
9.2 Model Potentials

9.2.1 Model Potential Parameters

The form of the model potential is given by equation (5.12). The first parameter $\lambda$ is found in the correction to the exchange term, equation (5.11), and the second parameter $r_c$ is found in the polarization term, equation (4.4). These parameters are varied for each value of $l$ that is found in the core. The values of the parameters were found to be:

Table 5 Model-parameters for the C. of G. - Zn II states

For Zn II: $\alpha = 2.296 \alpha^3$

<table>
<thead>
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<th>Parameters</th>
<th>s</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.9810030</td>
<td>1.3304082</td>
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<tr>
<td>$r_c$</td>
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<td>0.9651951</td>
<td>0.7726923</td>
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</table>

Table 6 Model-parameters for the C. of G. - Cd II states

For Cd II: $\alpha = 4.971 \alpha^3$

<table>
<thead>
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<th>Parameters</th>
<th>s</th>
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<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.7008376</td>
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<tr>
<td>$r_c$</td>
<td>1.2183091</td>
<td>1.2546035</td>
<td>1.7503494</td>
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</tbody>
</table>
Table 7  Model-parameters for the C. of G. - Hg II states

For Hg II: \( \alpha = 8.106 \alpha_o^3 \)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
</tr>
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<tr>
<td>( \lambda )</td>
<td>0.7415970</td>
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<td>( r_\varepsilon )</td>
<td>1.0360743</td>
<td>2.6982495</td>
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<td>27.2205967</td>
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</table>
9.2.2 Model Potential Graphs

Plots of the model potentials for the cores of Zn II, Cd II and Hg II are given for \( l = 0 \).

\[ V_{\text{model}} \times r \text{ vs } r \]

Fig. 7 Model Potential for Zn II
Fig. 8 Model Potential for Cd II

Fig. 9 Model Potential for Hg II
9.2.2.1 Discussion

Only s-model potentials, representing the interactions between the valence electrons and the cores of Zn II, Cd II and Hg II were plotted, since for each ion the plots (for all l values) were all very similar. All of the plots, for all of the states, followed the same pattern. The model potentials are attractive for all r. The potentials go as \(-Z/r\) for small r and as \(-(Z-N_e)/r\) for large r. The plots are very similar in nature to the electrostatic potentials, since the electrostatic interaction dominates over the polarization and the exchange potential. The exchange potential is a small correction (as compared to the electrostatic interaction) at small r and it dies off rapidly due to the exponential term. The polarization potential is very small for small r and it dies off as \(r^{-4}\), for large r, which is much quicker than the \(r^{-1}\) form of the electrostatic potential. The exchange and polarization potentials make the model potential deeper and more spread out, as compared to the electrostatic interaction.

9.2.3 Model-wave Functions

As discussed earlier the model-wave functions have the same form as full electron calculations do. The model-wave functions have the proper number of nodes, i.e.

\[ \text{nodes} = n - l - 1 \]

where \(n\) is the principal quantum number and \(l\) is the angular quantum number. The model-wave functions have the proper short range form since the model potential is attractive in the core. This is in stark contrast to the pseudopotential method. At long range the model potential as well as the model-wave function have the correct coulombic form. The following graph gives the model potential and the model-wave function for the ground state of Cd II on the same axis.
Fig. 10 Ground state model-wave function for Cd II

The forms of the model and pseudo-wave functions are easily shown with the following graph of the model and pseudo-wave functions vs r. The coulombic form for both wave functions at long range is clearly seen. The wave functions match each other outside of the core ($r - 2 \ a.u.$). The pseudo-wave function dies off quickly inside the core, while the model-wave function oscillates.
Fig. 11  Ground state Model & pseudo-wave functions for Cd II
### 9.3 Energies

The experimental centre of gravity, equation (4.1), energies (Moore 1971) and the calculated eigenenergies are given in the following charts. All energies are given in atomic units. In the following charts

\[ \text{Dev} = \text{Square Deviations of the Energies} \]

\[ = \sum_{i=1}^{6} (E_{\text{expi}} - E_{\text{calc}})^2. \]

(9.1)

where \( E_{\text{calc}} \) is either \( E_{\text{model}} \) or \( E_{\text{pseudo}} \)

#### The Zn II states

**Table 8 Centre of Gravity Energies for Zn II s-states**

<table>
<thead>
<tr>
<th>state</th>
<th>(-E_{\text{expi}})</th>
<th>(-E_{\text{pseudo}})</th>
<th>(-E_{\text{model}})</th>
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</thead>
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Table 9  Centre of Gravity Energies for Zn II p-states

<table>
<thead>
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<th>state</th>
<th>$-E_{\text{expt.}}$</th>
<th>$-E_{\text{pseudo}}$</th>
<th>$-E_{\text{model}}$</th>
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Table 10  Centre of Gravity Energies for Zn II d-states

<table>
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<th>$-E_{\text{pseudo}}$</th>
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<tr>
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The Cd II states

Table 11 Centre of Gravity Energies for Cd II s-states

<table>
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Table 12 Centre of Gravity Energies for Cd II p-states

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Table 13  Centre of Gravity Energies for Cd II d-states

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</table>
The Hg II states

Table 14 Centre of Gravity Energies for Hg II s-states

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<th>$-E_{\text{psudo}}$</th>
<th>$-E_{\text{model}}$</th>
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Table 15 Centre of Gravity Energies for Hg II p-states

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</tr>
<tr>
<td>11p</td>
<td>0.0374334</td>
<td>0.0374635</td>
<td>0.0373143</td>
</tr>
<tr>
<td>Dev</td>
<td>5.28E-08</td>
<td>4.23E-06</td>
<td></td>
</tr>
</tbody>
</table>
Table 16  Centre of Gravity Energies for Hg II d-states

<table>
<thead>
<tr>
<th>state</th>
<th>(-E_{exp})</th>
<th>(-E_{pseudo})</th>
<th>(-E_{model})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6d</td>
<td>0.2094143</td>
<td>0.2094140</td>
<td>0.2094160</td>
</tr>
<tr>
<td>7d</td>
<td>0.1175702</td>
<td>0.1175785</td>
<td>0.1175647</td>
</tr>
<tr>
<td>8d</td>
<td>0.0758012</td>
<td>0.0757619</td>
<td>0.0757671</td>
</tr>
<tr>
<td>9d</td>
<td>0.0529092</td>
<td>0.0529646</td>
<td>0.0529739</td>
</tr>
<tr>
<td>10d</td>
<td>0.0391404</td>
<td>0.0391308</td>
<td>0.0391396</td>
</tr>
<tr>
<td>11d</td>
<td>0.0301218</td>
<td>0.0300966</td>
<td>0.0301040</td>
</tr>
<tr>
<td>12d</td>
<td>0.0238660</td>
<td>0.0238693</td>
<td>0.0238752</td>
</tr>
<tr>
<td>13d</td>
<td>0.0193800</td>
<td>0.0193942</td>
<td>0.0193989</td>
</tr>
<tr>
<td>Dev</td>
<td>5.62E-09</td>
<td>6.14E-09</td>
<td></td>
</tr>
</tbody>
</table>

Table 17  Centre of Gravity Energies for Hg II f-states

<table>
<thead>
<tr>
<th>state</th>
<th>(-E_{exp})</th>
<th>(-E_{pseudo})</th>
<th>(-E_{model})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5f</td>
<td>0.1276591</td>
<td>0.1276591</td>
<td>0.1276843</td>
</tr>
<tr>
<td>6f</td>
<td>0.0819011</td>
<td>0.0819098</td>
<td>0.0819090</td>
</tr>
<tr>
<td>7f</td>
<td>0.0568580</td>
<td>0.0568616</td>
<td>0.0568160</td>
</tr>
<tr>
<td>8f</td>
<td>0.0416962</td>
<td>0.0416877</td>
<td>0.0416662</td>
</tr>
<tr>
<td>9f</td>
<td>0.0318508</td>
<td>0.0318509</td>
<td>0.0318428</td>
</tr>
<tr>
<td>10f</td>
<td>0.0251126</td>
<td>0.0251206</td>
<td>0.0251186</td>
</tr>
<tr>
<td>Dev</td>
<td>1.49E-10</td>
<td>3.41E-09</td>
<td></td>
</tr>
</tbody>
</table>
9.3.1 Comparison with McGinn's Results

McGinn (as reported by Szasz 1985) found energy levels for the centre of gravity states, for Zn II by using the Philips-Kleinman form of the pseudopotential (see Szasz 1985). His results compared with the results calculated here are tabulated in the following (where Dev is as in equation (9.1)):

Table 18 Comparison with McGinn's results for Zn II

<table>
<thead>
<tr>
<th>states</th>
<th>Model Dev</th>
<th>Pseudo Dev</th>
<th>McGinn Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>3.05E-10</td>
<td>1.83E-11</td>
<td>2.68E-03</td>
</tr>
<tr>
<td>p</td>
<td>3.51E-06</td>
<td>3.51E-06</td>
<td>1.05E-03</td>
</tr>
<tr>
<td>d</td>
<td>1.46E-08</td>
<td>1.20E-11</td>
<td>2.85E-05</td>
</tr>
</tbody>
</table>

As can be seen the results found using the pseudopotential and model potential approach are much more accurate than the results presented by McGinn. The results for both the model potential and the pseudopotential are highly accurate and could be used in molecular calculations.
9.4 Discussion of Results

The calculated centre of gravity energies were compared with the experimental values (Moore, 1971). The values of the eigenenergies for Zn II were also compared with those found by McGinn (as reported by Szasz, 1985). The results derived here were many orders of magnitude more accurate than those of McGinn. In general the calculated values were highly accurate with the exception of the Zn II, Cd II and Hg II p-states. This was found to be true for both the model potential and the pseudopotential approaches.

An energy level diagram for the p-states of Zn II clearly shows the major reason for the disagreement between calculation and experiment. The error seems to be caused by the interference of an excited core state $3d^9 + s^4p$, labelled as $\frac{1}{2}p$. This core state tends to raise the $8p$ level and lower the $7p$ level. The nature of both the model and pseudopotentials prevents the inclusion of this excited core state. Both approaches consist of frozen cores and hence the core states are not involved. Numerous attempts were made to artificially include this excited core state into the pseudopotential, but none were successful. One would have to include all the electrons in the $3d$ shell as valence electrons, in order to shift the levels to those observed. Another source of error could be the fine structure inversion found in the $7p$ level. This inversion implies that the first order perturbation theory for the spin-orbit splittings does not hold. Since the centre of gravity is only constant for the first order perturbation, there is no reason to expect the centre of gravity energies to remain constant.
The Cd II p-states results are very similar to those of the Zn II p-states. There is an excited core state $4d^23s3p$ which lies between the $10p$ and the $11p$ energies. This state tends to push the $10p$ state lower while raising up the $11p$ state. Two other excited core states are found to lie between $6p$-$7p$ and $7p$-$8p$. These core states do not seem to cause a noticeable shift in the energies. There is also a fine structure inversion in the $10p$ state. This could also lead to a shift in the centre of gravity.
There do not seem to be any excited core states in Hg II that could effectively take into account the energy differences, even though there are excited core states lying between 6p-7p and 7p-8p states. These excited core states do not seem to shift the energies. The major factor leading to the energy discrepancies would probably be due to large fine structure splittings. The fine structure splittings are very large in Hg and hence could lead to a breakdown in the centre of gravity approximation.

The pseudopotential results tend to be somewhat more accurate than the model potential results. One would expect the model potential results to be more accurate due to the more realistic form of the wave functions. The model potential is based on the density of the core of the ion in question. This density was calculated using a Dirac-Fock program (Desclaux 1975). Since the density is numerically calculated and not experimentally derived, there could inaccuracies introduced into the model potential. It is possible that the valence-core correlation is not being handled as well as it should when the densities are being calculated. The pseudopotential form tends to be more flexible than does the model potential form. This could lead to better energy fittings which may or may not mean that it is a better form to use.
10 SPIN-ORBIT RESULTS

10.1 Model Potential Results

For the model potential, the form of the spin-orbit interaction is taken to be

\[ V_{s.o.}(r) = \frac{1}{2e^2 r^3} [(Z_{eff, i} - 2)e^{-r^2/\alpha_i^2} + 2] \cdot \frac{s \cdot l}{r} \]  (7.13)

where \( Z_{eff, i} \) and \( \alpha_i \) are adjustable parameters. The total model potential for the valence electron is given by:

\[ V(r) = \sum_{l=0}^{l=m} (V_{M}^l(r) + V_{s.o.}^l(r)) \cdot \frac{l}{r} \]  (7.18)

where \( V_{s.o.}^l \) is given by equation (7.13) and \( V_{M}^l \) is given by equation (5.2).

In order to achieve an accurate fit to the energy levels for both the \( j = l + \frac{1}{2} \) and \( j = l - \frac{1}{2} \) energy levels, the parameters in the centre of gravity potential were varied along with \( Z_{eff, i} \) and \( \alpha_i \) in the spin-orbit term. The varying of parameters in the centre of gravity term was performed in order to accommodate the shifts in the centre of gravity. As discussed in the results for the centre of gravity, it appears that the first order perturbation theory does not hold well for all for the states of Zn II, Cd II and Hg II. It is hoped that the centre of gravity shift is small for the model calculations, and in most cases this is observed.
10.1.1 Parameters for the Energy Splittings

Table 19 Model Parameters for the Spin-orbit in Zn II

<table>
<thead>
<tr>
<th>state</th>
<th>$\lambda$</th>
<th>$r_e$</th>
<th>$Z_{eff}$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>1.240735</td>
<td>0.993928</td>
<td>34.45383</td>
<td>0.102914</td>
</tr>
<tr>
<td>d</td>
<td>1.393426</td>
<td>0.965499</td>
<td>16.14342</td>
<td>3.500000</td>
</tr>
</tbody>
</table>

Table 20 Model Parameters for the Spin-orbit in Cd II

<table>
<thead>
<tr>
<th>state</th>
<th>$\lambda$</th>
<th>$r_e$</th>
<th>$Z_{eff}$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>0.887952</td>
<td>1.225703</td>
<td>25.50943</td>
<td>3.500000</td>
</tr>
<tr>
<td>d</td>
<td>0.480174</td>
<td>1.719693</td>
<td>28.35970</td>
<td>0.646931</td>
</tr>
</tbody>
</table>

Table 21 Model Parameters for the Spin-orbit in Hg II

<table>
<thead>
<tr>
<th>state</th>
<th>$\lambda$</th>
<th>$r_e$</th>
<th>$Z_{eff}$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
<td>1.062073</td>
<td>1.563291</td>
<td>15.32599</td>
<td>3.500000</td>
</tr>
<tr>
<td>d</td>
<td>0.540913</td>
<td>1.585192</td>
<td>22.54108</td>
<td>1.356075</td>
</tr>
</tbody>
</table>
10.2 Pseudopotential Results

The form of the spin-orbit interaction, in the pseudopotential case, varies from the form used in the model case. As was shown earlier, the form for the spin-orbit chosen for the model potential case can not possibly work in the pseudopotential case. The form of the spin-orbit potential was assumed so that the total potential acting on the valence electron is

\[ V(r) = -\frac{Z - N}{r} + \sum_{l=0}^{l_m} V_{ps}^l(r) \times F_{s.o.}^l(r) \]  

(7.16)

where \( V_{ps}^l \) is given by (4.3) and

\[ F_{s.o.}^l(r) = 1 + \alpha \hat{s} \cdot \hat{r} e^{-r^2/\alpha^2} \]  

(7.17)

The parameters in the centre of gravity potential and the parameters from the spin-orbit potential, \( A_i \) and \( \alpha_i \) were varied to achieve a proper fit to the experimental energies. It was hoped that the centre of gravity parameters would require only small adjustments, but this was not the case. The parameters for the splittings are given in the following charts.
10.2.1 Parameters for the Fine-structure Splittings

Table 22  Pseudo-parameters for the Spin-orbit in Zn II

<table>
<thead>
<tr>
<th>Parameters</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>-6.588363</td>
<td>2.149917</td>
</tr>
<tr>
<td>$c_2$</td>
<td>69.11465</td>
<td>-2.839331</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>1.735304</td>
<td>0.573202</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>2.870501</td>
<td>1.951258</td>
</tr>
<tr>
<td>$r_e$</td>
<td>1.177768</td>
<td>0.614344</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.282251</td>
<td>0.383613</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.000000</td>
<td>1.218760</td>
</tr>
</tbody>
</table>
Table 23  Pseudo-parameters for the Spin-orbit in Cd II

<table>
<thead>
<tr>
<th>Parameters</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>-5.335712</td>
<td>0.383854</td>
</tr>
<tr>
<td>$c_2$</td>
<td>60.16706</td>
<td>86.95222</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>0.933687</td>
<td>0.252986</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>1.669138</td>
<td>1.551324</td>
</tr>
<tr>
<td>$r_c$</td>
<td>1.083880</td>
<td>1.078060</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>1.105573</td>
<td>0.896759</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.970809</td>
<td>1.000000</td>
</tr>
</tbody>
</table>

Table 24  Pseudo-parameters for the Spin-orbit in Hg II

<table>
<thead>
<tr>
<th>Parameters</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>195.0651</td>
<td>4.094692</td>
</tr>
<tr>
<td>$c_2$</td>
<td>212.5451</td>
<td>-5.570775</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>2.604491</td>
<td>0.412595</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>2.605415</td>
<td>2.523742</td>
</tr>
<tr>
<td>$r_c$</td>
<td>0.741605</td>
<td>0.807566</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>3.290643</td>
<td>1.408788</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.891897</td>
<td>1.389857</td>
</tr>
</tbody>
</table>
10.3 Energy Splittings

The spin-orbit energy shifts for various states of Zn II, Cd II and Hg II were calculated using the above data. The calculated values for the energy shifts are tabulated along with the experimental energy shifts in the following tables. The shifts, both calculated and experimental (in a.u.), are found by:

\[
\Delta E = E_{j=\frac{3}{2}} - E_{j=\frac{1}{2}}
\]

10.3.1 Tables 25 & 26 - Zn II Spin-orbit Splittings

<p>| p-states |</p>
<table>
<thead>
<tr>
<th>state</th>
<th>$-\Delta E_{\text{expt.}} \times 10^{-3}$</th>
<th>$-\Delta E_{\text{pseudo}} \times 10^{-3}$</th>
<th>$-\Delta E_{\text{model}} \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4p</td>
<td>3.9814</td>
<td>3.9035</td>
<td>3.9490</td>
</tr>
<tr>
<td>5p</td>
<td>1.1186</td>
<td>1.2477</td>
<td>1.1304</td>
</tr>
<tr>
<td>6p</td>
<td>0.3239</td>
<td>0.5580</td>
<td>0.4885</td>
</tr>
</tbody>
</table>

<p>| d-states |</p>
<table>
<thead>
<tr>
<th>state</th>
<th>$-\Delta E_{\text{expt.}} \times 10^{-4}$</th>
<th>$-\Delta E_{\text{pseudo}} \times 10^{-4}$</th>
<th>$-\Delta E_{\text{model}} \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4d</td>
<td>2.3100</td>
<td>2.3060</td>
<td>2.3330</td>
</tr>
<tr>
<td>5d</td>
<td>1.1020</td>
<td>1.1180</td>
<td>1.0500</td>
</tr>
<tr>
<td>6d</td>
<td>0.6014</td>
<td>0.5961</td>
<td>0.5510</td>
</tr>
<tr>
<td>7d</td>
<td>0.3600</td>
<td>0.3512</td>
<td>0.3230</td>
</tr>
<tr>
<td>8d</td>
<td>0.2324</td>
<td>0.2232</td>
<td>0.2051</td>
</tr>
</tbody>
</table>
### 10.3.2 Tables 27 & 28 - Cd II Spin-orbit Splittings

#### p-states

<table>
<thead>
<tr>
<th>state</th>
<th>$-\Delta E_{\text{expt.}} \times 10^{-4}$</th>
<th>$-\Delta E_{\text{pseudo}} \times 10^{-4}$</th>
<th>$-\Delta E_{\text{model}} \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5p</td>
<td>113.11</td>
<td>109.87</td>
<td>119.87</td>
</tr>
<tr>
<td>6p</td>
<td>30.675</td>
<td>33.764</td>
<td>33.024</td>
</tr>
<tr>
<td>7p</td>
<td>5.8930</td>
<td>15.174</td>
<td>14.335</td>
</tr>
<tr>
<td>8p</td>
<td>4.2246</td>
<td>8.1261</td>
<td>7.5497</td>
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<tr>
<td>9p</td>
<td>1.4321</td>
<td>4.8539</td>
<td>4.4674</td>
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</table>

#### d-states

<table>
<thead>
<tr>
<th>state</th>
<th>$-\Delta E_{\text{expt.}} \times 10^{-4}$</th>
<th>$-\Delta E_{\text{pseudo}} \times 10^{-4}$</th>
<th>$-\Delta E_{\text{model}} \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5d</td>
<td>7.0410</td>
<td>6.7960</td>
<td>7.2310</td>
</tr>
<tr>
<td>6d</td>
<td>3.3490</td>
<td>3.5950</td>
<td>3.0570</td>
</tr>
<tr>
<td>7d</td>
<td>1.7893</td>
<td>2.0299</td>
<td>1.5809</td>
</tr>
<tr>
<td>8d</td>
<td>1.0570</td>
<td>1.2396</td>
<td>0.9232</td>
</tr>
<tr>
<td>9d</td>
<td>0.6767</td>
<td>0.8072</td>
<td>0.5857</td>
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</tbody>
</table>
### 10.3.3 Tables 29 & 30 - Hg II Spin-orbit Splittings

#### p-states

<table>
<thead>
<tr>
<th>state</th>
<th>$-\Delta E_{\text{expt.}}$ $\times 10^{-3}$</th>
<th>$-\Delta E_{\text{pseudo}}$ $\times 10^{-3}$</th>
<th>$-\Delta E_{\text{model}}$ $\times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6p</td>
<td>41.575</td>
<td>42.201</td>
<td>43.668</td>
</tr>
<tr>
<td>7p</td>
<td>16.730</td>
<td>12.331</td>
<td>10.895</td>
</tr>
<tr>
<td>8p</td>
<td>3.8866</td>
<td>5.4759</td>
<td>4.6475</td>
</tr>
<tr>
<td>9p</td>
<td>1.6494</td>
<td>2.9169</td>
<td>2.4322</td>
</tr>
<tr>
<td>10p</td>
<td>0.9158</td>
<td>1.7370</td>
<td>1.4344</td>
</tr>
</tbody>
</table>

#### d-states

<table>
<thead>
<tr>
<th>state</th>
<th>$-\Delta E_{\text{expt.}}$ $\times 10^{-4}$</th>
<th>$-\Delta E_{\text{pseudo}}$ $\times 10^{-4}$</th>
<th>$-\Delta E_{\text{model}}$ $\times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6d</td>
<td>25.515</td>
<td>24.429</td>
<td>25.167</td>
</tr>
<tr>
<td>7d</td>
<td>11.574</td>
<td>11.212</td>
<td>11.656</td>
</tr>
<tr>
<td>8d</td>
<td>6.1971</td>
<td>6.6452</td>
<td>6.3692</td>
</tr>
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<td>9d</td>
<td>3.0983</td>
<td>3.9868</td>
<td>3.8485</td>
</tr>
<tr>
<td>10d</td>
<td>2.2554</td>
<td>2.5662</td>
<td>2.4966</td>
</tr>
</tbody>
</table>
10.4 Discussion of Results

As seen above, the fine-structure splittings were calculated for the p and d-states of Zn II, Cd II and Hg II. The s-states do not have any fine structure associated with them, since $\Sigma \cdot \Lambda = 0$ for s-states. Five different splittings were calculated for each $\ell$ of Zn II, Cd II and Hg II, except for the p-states of Zn II. Only three splittings were calculated for the p-states of Zn II. The reason for this is that the $3d^{10}7\rho$ term has an inversion in the fine-structure. The theory used here can not take into account fine-structure inversion. In order to do so, one would have to go to higher order perturbations, or include other effects.

For the Zn II splittings, the values derived for the p-states were fairly good for the 4p and 5p levels, but the 6p results were very poor. The magnitude of the splitting for the 6p term is 1/10 that of the 4p term. The minimization procedure (see chapter 8) minimizes the square of the absolute difference between the actual energies and the calculated energies and not the relative difference. Thus, if the energy splitting of one doublet is much smaller in magnitude than another, then the smaller state will not be fitted with as high an (relative) accuracy as would the larger. The first two splittings (i.e. 4p and 5p) were fit much better than the 6p due to the fact that they are much larger in size.

A similar trend is noticed in the d-states of Zn II. The first few states are fit more accurately than the last few states. The effect is not quite as drastic as in the p-states because the d-states do not have any excited core states or fine-structure inversions. The excited core states in the p-states may affect more than just the higher order states. The $4\rho'$ state shifts the 7p state downwards and this shifting of the 7p state may affect the 6p state.
The p-states of the Cd II gave the poorest results. The fine-structure is fairly large and the values of the splittings range over 2 orders of magnitude. Thus, if the calculated 5p state is in agreement with the calculated 5p state (as it is) then the states with splittings that are many times smaller shall problem not agree very well. This does seem to be the case in the 7p, 8p and 9p states. There are also excited cores states lying between the 6p and 7p states as well as between the 7p and 8p states. These excited core states do not seem to affect the centre of gravity calculations, but it is possible that they could affect the fine-structure splittings. The differences between calculation and experiment may indicate an improper r dependence in the potentials. The Cd II d-states give results which are similar to the Zn II d-states. The range in the magnitudes between the largest fine-structure splitting to the smallest in just over one order of magnitude. This leads to errors that are within reason.

The fine-structure splitting for the Hg II p-states is the largest of all the states considered. The accuracy for the Hg II p-states is similar to the accuracy in finding the splittings for the Cd II p-states. The 6p state splittings is matched to experiment fairly well, but then the other states are in poor agreement. The splitting for the 6p state is about 45 times larger than the splitting for the 10p state. This leads to inaccuracies the higher states. There are excited core states between the 6p and 7p states as well as between the 7p and 8p states. It is possible that these excited core states could interfere with the fine-structure splitting. The difference in the magnitude between the largest fine-structure splitting in Hg II d-states and the
smallest splitting is about a factor of 10. This makes one expect that the accuracy for these levels should be much higher than for the p-states. This is actually seen.

In general the model potential calculations for the fine-structure splittings Zn II, Cd II and Hg II are better than the pseudopotential calculations. This is due to the form of the pseudopotential and its wave-functions. As discussed earlier, the pseudo-wave functions do not describe the short range interaction very well. The ideal form for the spin-orbit interaction had to be changed to a perturbation like term. Thus the inclusion of the spin-orbit interaction for the pseudopotential method is completely unnatural and thus should not be expected to lead to accurate results.
11 TWO ELECTRON CALCULATIONS

Two-electron calculations were performed for Zn, Cd and Hg. The calculations were performed using a modified relativistic Dirac-Fock program, see Desclaux (1975). The modification consisted of replacing the electronic core with the calculated centre of gravity model potentials, so that each electron experienced a potential based on its \( l \) value. Electrons with differing \( l \) values experienced differing core potentials. The dielectric polarization term, described above, was included in the calculations. Ground state energies for Zn, Cd and Hg were calculated and compared with a full electron Dirac-Fock calculation and with the actual experimental results. The spin-orbit interaction was not included in the model potential calculations since the Desclaux program, being a relativistic calculation, naturally calculates the splitting.

11.1 Ground State Results

<table>
<thead>
<tr>
<th>State</th>
<th>(-E_{model})</th>
<th>(-E_{DF})</th>
<th>(-E_{exp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Zn} ) ([Ar]3d^{10},4s^2)</td>
<td>0.33472531</td>
<td>0.29861675</td>
<td>0.34521899</td>
</tr>
<tr>
<td>( \text{Cd} ) ([Kr]4d^{10}5s^2)</td>
<td>0.33021833</td>
<td>0.28147463</td>
<td>0.33051114</td>
</tr>
<tr>
<td>( \text{Hg} ) ([Xe]4f^{14}5d^{10}6s^2)</td>
<td>0.47563269</td>
<td>0.32836530</td>
<td>0.38357104</td>
</tr>
</tbody>
</table>

11.2 Discussion

The values for the ground states for the Dirac-Fock method are all too high. This is due to the fact that polarization has not been properly taken into account. The dif-
ference between the model energies and the experimental energies is smaller than the difference between the Dirac-Fock energies and the experimental energies for both Zn and Cd. The major source of error in the model calculations is the improper accounting of relativistic effects. The model potentials were calculated by using the non-relativistic Schrödinger equation. Thus, the model potential is inherently nonrelativistic. The model potential is then used in a relativistic program to calculate the energies. Thus, the interaction between the valence electron(s) and the core electrons may not be properly accounted. For large elements the relativistic effects are much more noticeable than in small atoms. Hg is a large atom and hence the relativistic effects should make a large contribution. The model potential fit for the Hg core is also not as accurate as the fits for both the Cd and the Zn cores. The value found for the ground state of Zn shows that the relativistic effects do not contribute as much as in the Hg case. This makes sense since Zn is a much smaller atom than Hg. The energy value for the ground state of Cd is very accurate. The model potential fit for the Cd core was the most accurate of the three atoms. This may have helped the results. One would expect fairly large anomalies due to relativistic effects, but none were noticed.

Two-electron calculations were not performed using the centre of gravity pseudopotentials. The pseudopotential form is too unrealistic for the Dirac-Fock program to calculate the energies. The Dirac-Fock program expects that the potential will be coulombic near the origin, while the pseudopotential is repulsive near the origin.
12 IMPROVEMENTS AND FUTURE WORK

It has been shown that the forms assumed by the model potential and the pseudopotential lead to accurate results in the centre of gravity case. These results are of sufficient accuracy to be used in complex molecular calculations. The results found for the p-states of Zn II, Cd II and Hg II were inferior to those found in the other cases. As discussed in chapter 9, the results could be improved upon if the excited core states were included in the calculations. Instead of just one valence electron, as in the ionic case, there would now be eleven valence electrons. If these ten extra valence electrons were included in the calculations, then the results for the p-state calculations would probably be greatly improved. It is not clear that the improvement in accuracy would justify the increase in computational complexity due to the inclusion of ten extra electrons.

The results from the inclusion of the spin-orbit term were not as accurate as those from the centre of gravity results. The results showed that the forms chosen for the potentials (especially for the pseudopotential) need to be changed. The major error involved in the calculation of the fine structure splitting is due to the method of calculation. The method uses a least squares fit of the differences between the experimental energies and the calculated energies to find the potentials. Thus to improve on the results, the method used should be altered so that the square of the relative energies differences is used instead of the square of the absolute energy differences. This way all of the energies would have approximately the same weights.

Another, easier, way to improve on the spin-orbit results would be to use the centre of gravity forms of the
model potential and pseudopotential to fit each component of the doublet. A centre of gravity result could be derived using a weighted average of the parameters.

More work needs to be done on the two electron problem. Solutions to the model-two electron problem for excited states should be calculated and compared to the experimental energies. Two electron calculations should also be performed using the pseudopotentials derived here. The Dirac-Fock program is not able to perform pseudopotential calculations due to the non-coulombic form of the pseudopotential at short-range and so a different method should be employed. Once the pseudopotential-two electron calculations are complete, these pseudopotentials should be used in molecular calculations in order to verify their accuracy and to aid in the molecular calculations.
APPENDIX A. EXTENDED LAGRANGE INTEGRATION

The problem is to numerically integrate an indefinite integral of the form:

\[ l = \int_{y_0}^{y_n} f(y) dy. \]  \hspace{1cm} (A.1)

where \( y \) and \( f(y) \) are discrete functions. This integral is found in the model-electrostatic potential of chapter 5.

The Method

Using Lagrange Integration (see Hildebrand (1937)) leads to

\[ \int_{y_m}^{y_n} f(y) dy = h \sum_k a_k(m)f(y_k) \]  \hspace{1cm} (A.2)

where the \( a_k(m) \) are the Lagrange coefficients (see Abrahamowitz and Stegun (1966)).
Choose \( n = 10 \) (order of Lagrange Integration), hence

\[
\int_{\gamma_0}^{\gamma_1} f(y) dy = h(a_{-4} f_{-4} + a_{-3} f_{-3} + \cdots + a_0 f_0 + \cdots + a_5 f_5) \quad (A.3)
\]

and

\[
\int_{\gamma_1}^{\gamma_2} f(y) dy = h(a_{-4} f_{-4} + a_{-3} f_{-3} + \cdots + a_0 f_1 + \cdots + a_5 f_5) \quad (A.4)
\]

where

| \( \alpha_{-4} = \alpha_5 \) | 2497/D |
| \( \alpha_{-3} = \alpha_4 \) | -28939/D |
| \( \alpha_{-2} = \alpha_3 \) | 162680/D |
| \( \alpha_{-1} = \alpha_2 \) | -641776/D |
| \( \alpha_0 = \alpha_1 \) | 4134338/D |
| \( D \) | 7257600 |

and \( f_i = f(\gamma_0 + ih) \).

The integration formula for a function \( f(y) \) ranging from \( y = \gamma_0 \) to \( y = \infty \) is given by:

\[
\int_{\gamma_0}^{\gamma_n} f(y) dy = \int_{\gamma_0}^{\gamma_1} f(y) dy + \int_{\gamma_1}^{\gamma_2} f(y) dy + \cdots + \\
+ \cdots + \int_{\gamma_{m-1}}^{\gamma_m} f(y) dy + \cdots . \quad (A.5)
\]

using the above gives
\[
\int_{y_0}^{y} f(y) dy = h \left[ a_{-1} f_{-1} + (a_{-2} + a_{-4}) f_{-2} + \cdots + a_0 + \cdots + a_{-4} f_0 + \cdots + a_5 + \cdots + a_{-4} f_5 + \cdots + a_{m} + \cdots \right] \tag{A.6}
\]

or

\[
\int_{y_0}^{y} f(y) dy = \frac{h}{B} \left[ 2.497 f_{-4} - 2641 f_{-3} + 136238 f_{-2} - 505538 f_{-1} + 362880 f_0 + 776138 f_1 + 7121362 f_2 + 7284042 f_3 + 7255103 f_4 + 7257600 f_5 + 7257600 f_6 + \cdots + 7257600 f_m + \cdots \right] \tag{A.7}
\]

rearranging gives

\[
\int_{y_0}^{y} f(y) dy = h \left( \sum_{n=1}^{4} b_n [f(y_0 - nh) - f(y_0 + nh)] + Trap \right) \tag{A.8}
\]

where

\[
Trap = \frac{1}{2} f(y_0) + \sum_{n=1}^{z} f(y_0 + nh) \tag{A.9}
\]

is the trapezoidal approximation to the integral,
and

Table 33 Parameters for the Extended Lagrange Integration

<table>
<thead>
<tr>
<th>$b_{-4} = -b_4$</th>
<th>2497/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_{-3} = -b_3$</td>
<td>-26442/D</td>
</tr>
<tr>
<td>$b_{-2} = -b_2$</td>
<td>136238/D</td>
</tr>
<tr>
<td>$b_{-1} = -b_1$</td>
<td>-505538/D</td>
</tr>
<tr>
<td>$b_0$</td>
<td>3628800/D</td>
</tr>
<tr>
<td>$D$</td>
<td>7257600</td>
</tr>
</tbody>
</table>
APPENDIX B. NUMEROV METHOD

The method of solution of the Schrödinger equation used in chapter 8 is the Numerov method. It was originally derived by B. Numerov (1933). The method solves 2nd order differential equations of the form

\[
\frac{d^2 \phi(x)}{dx^2} = F(x, \phi(x)) \tag{B.1}
\]

The Schrödinger equation is given by equation C.2, and fits the form of equation (B.1) if

\[
F(x, \phi(x)) = \{2x^2(V(x) - E) + (l + 1/2)^2\} \phi(x) \tag{B.2}
\]

The actual method of solution used is the Predictor-corrector method of Baylis and Peel (1982). This method is chosen since only two starting points are required (these two starting points are found using Bates-Damgaard wave functions, see Bates and Damgaard (1949)) and the solution varies from the actual solution in the sixth order, at most.

**Predictor-Corrector Numerov Method**

The equation to be solved is:

\[
\phi''(x) = F(x, \phi(x))
\]

where \( F \) is given by equation B.2. Expanding \( \phi \) in a Taylor series about \( x = x_0 \) gives

\[
\phi = \phi_0 + h \phi_0' + \frac{h^2}{2!} \phi_0'' + \frac{h^3}{3!} \phi_0''' + \cdots \tag{B.3}
\]

and

\[
\phi = \phi_0 - h \phi_0' + \frac{h^2}{2!} \phi_0'' - \frac{h^3}{3!} \phi_0''' + \cdots \tag{B.4}
\]

where \( \phi_0 = \phi(x_0) \), \( \phi_+ = \phi(x_0 + h) \), \( \phi_- = \phi(x_0 - h) \) and \( h \) is the step size. Adding B.3 and B.4 leads to
\[
\phi_+ + \phi_ - = 2\phi_0 + h^2 \phi_0^{(2)} + \frac{h^4}{12} \phi_0^{(4)} + 2 \frac{h^6}{6!} \phi_0^{(6)} + O(h^8) \quad (B.5)
\]

similarly for 
\[
F_+ = 2F_0 - F_ - + h^2 F_0^{(2)} + \frac{h^4}{12} F_0^{(4)} + O(h^6) \quad (B.6)
\]

therefore, using B.5, B.6 and the fact that \( \phi_0^{(2)} = F_0 \) gives
\[
\phi_ - = 2\phi_0 - \phi_ + h^2 F_0 + \frac{h^4}{12} [F_+ + F_- - 2F_0] - \frac{h^6}{240} \phi_0^{(4)} + O(h^8) \quad (B.8)
\]

As a first approximation to the actual solution, \( \phi_+ \),

\[
\phi_+^{(p)} = 2\phi_0 - \phi_ + h^2 F_0 . \quad (B.9)
\]

This is the predictor solution to the problem. The difference between the predictor solution and the actual solution is
\[
\phi_+ - \phi_+^{(p)} = \frac{h^4}{12} F_0^{(4)} + O(h^6) \quad (B.10)
\]

Thus the error is 4th order in \( h \). Once \( \phi_+^{(p)} \) is known, it may be used to find
\[
F_+^{(p)} = F(x_0 + h, \phi_+^{(p)}). \]

The difference between \( F_+^{(p)} \) and \( F_+ \) is also of 4th order.

The corrector to the actual solution is taken to be
\[
\phi_+^{(c)} = \phi_+^{(p)} + \frac{h^2}{12} [F_+^{(p)} + F_- - 2F_0] \quad (B.11)
\]

The difference between the actual solution and the corrector solution is sixth order and is given by
\[
\phi_+ - \phi_+^{(c)} = \frac{h^6}{240} \phi_0^{(6)} + \frac{h^2}{12} [F_+^{(p)} - F_+] \quad (B.12)
\]
As in the predictor case a new approximation to \( F \) may be found by using the new approximation to \( \phi \) (i.e. \( \phi^{(c)} \)). Thus, \( F^{(c)} = F(x_0 + h \cdot \phi^{(c)}) \). \( \phi^{(c)} \) has a sixth order error with respect to \( \phi \).

The final approximation to the actual solution \( \phi \) is given by a combination of the predictor and corrector solutions.

\[
\phi^{(f)} = \phi^{(c)} + \frac{h^2}{30} [F^{(c)} - F^{(p)}].
\]  

(\( B.13 \))

this also varies from the actual solution by a sixth order term. Baylis and Peel found that if \( F(x, \phi(x)) \) varies linearly with \( x \) and \( \phi(x) \) then the error drops to eighth order in \( h \). Even if they do not vary linearly, Baylis and Peel found that the error in \( \phi^{(f)} \) was generally smaller than the error in \( \phi^{(c)} \) for a smoothly varying \( F \). The latter is the case for the form of \( F \) given by equation B.2.
APPENDIX C. LOGARITHMIC GRID

The time-independent Schrödinger equation is to be solve (i.e. the nonrelativistic case),

$$
\hat{H}\Psi = E\Psi
$$

where $\hat{H}$ is the Hamiltonian, $E$ is the Eigenenergy of the Hamiltonian, and $\Psi$ is the wave function.

This equation may be broken up into radial and angular equations (see for example Merzbacher (1970)). The angular solution is given by the spherical harmonics. The radial equation is not as easy to solve. The radial equation is given by

$$
\left[ \frac{d^2}{dr^2} \frac{l(l+1)}{r^2} + 2(E - V(r)) \right] u(r) = 0. \quad (C.1)
$$

where $l$ is the angular momentum, $V(r)$ is the potential energy, and $u(r)$ is the solution of the radial equation.

This is to be solved numerically for a given $V(r)$. Numerically it is easier to solve the equation for equally spaced grid points. For an accurate representation in a region where the function is rapidly changing the points must be close together. The solutions of the Schrödinger equation tend to vary more rapidly with $r$ near the origin than they do further out. Hence a grid with closely spaced points near the origin and more distantly spaced points further out is desired.

If the grid is changed from $r$ to $\rho = \ln r$ the desired form is arrived upon. It is also desirable to keep the same form of the radial Schrödinger equation (i.e. no first derivatives). Thus not only must the independent variable $r$ need to be changed to $\rho$, but the dependent variable must also be changed from $u(r)$ to $\tilde{u}(\rho) = u(r)/r^{1/2}$. 
The Schrödinger equation under these transformations gives:

$$\left[ \frac{\partial^2}{\partial \rho^2} + 2r \frac{\partial}{\partial r} [E - V(r)] - (l + 1/2)^2 \right] \bar{u}(\rho) = 0 \quad (C.2)$$

This is the radial Schrödinger equation on a logarithmic grid, which is used by the minimization program (see chapter 8).
APPENDIX D. RADIAL DENSITIES

The following are the radial densities for Zn III, Cd III, and Hg III. Thus they give the core densities of Zn II, Zn I, Cd II, Cd I, Hg II, and Hg I. The densities were found by using the Relativistic Hartree-Fock method implemented by Desclaux (1975). The total densities \( \rho \) are calculated by

\[
\rho(r) = \sum_A q_A [P_A^2 + Q_A^2]
\]

where \( P \) is the large component of the wave function and \( Q \) is the small component. \( q_A \) gives the number of electrons in the shell labeled by \( A \).

The radial densities are derived from the total densities using:

\[
D(r) = 4\pi r^2 \rho.
\]

The core of Zn (i.e. Zn III) is given by:

\[1s^22s^22p^63s^23p^63d^{10}\]

**Fig. 13** Radial Density of the Zn core
The core of Cd (i.e. Cd III) is given by:

\[ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} \]

**Fig. 14** Radial Density of the Cd core

The core of Hg (i.e. Hg III) is given by:

\[ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} \]

**Fig. 15** Radial Density of the Hg core
APPENDIX E. MINIMIZATION ALGORITHM

The minimization method of Baylis and Pradhan (1984) is summarized below. The problem is to find the minimum of a surface $\Phi(\vec{x})$ where $\vec{x}$ is an $N$-dimensional vector. $\Phi(\vec{x})$ may be expanded in a Taylor series as

$$
\Phi(\vec{x}) = \Phi(\vec{x}_0) + \vec{g}' \delta + \delta' \kappa \delta + O(\delta^3)
$$

$$
= \phi^{(2)}(\vec{x}) + O(\delta^3)
$$

(E.1)

where $\vec{g}$ is the gradient, $\kappa$ is the curvature tensor and $\delta = \vec{x} - \vec{x}_0$ is the displacement.

Let $U$ be an orthogonal matrix which diagonalizes $\kappa$, i.e. $U' \kappa U = K$, where $K$ is a diagonal matrix of the eigenvalue of $\kappa$. $U$ gives a transformation from the basis of eigenvectors to the original coordinates. Thus, the gradient and displacement in the original coordinates are related to the gradient and displacement in the eigenvector coordinates by

$$
\delta = U \Delta \quad \& \quad \vec{g} = U \vec{c}
$$

therefore

$$
\phi^{(2)}(\vec{x}) = \phi(\vec{x}_0) + \vec{c}' \Delta + \Delta' \kappa \Delta
$$

$$
= \phi(\vec{x}_0) + \left( \sum \frac{\kappa_{nn}}{\Delta_n} \Delta_n \right) (E.2)
$$

Combining the condition

$$
d \Phi = 0 = \sum \frac{\partial \Phi}{\partial \Delta_n} d \Delta_n = \sum (G_n + 2K_{nn} \Delta_n) d \Delta_n
$$

along with the constraint

$$
\delta^2 = \Delta^2 = \delta_0^2 \quad \Rightarrow \quad d \Delta^2 = 2 \sum \Delta_n d \Delta_n = 0
$$

gives

$$
G_n + (2K_{nn} + \lambda) \Delta_n = 0
$$

(E.3)
for all \( n \leq N \) and \( \lambda \) is a Lagrange multiplier. \( \lambda \) is chosen (see Baylis and Pradhan (1984)) to satisfy

\[
\delta_0^2 = \sum_n \Delta_n^2
\]

where \( \Delta_n \) is given by equation (E.3). There is generally more than one value of \( \lambda \) that satisfies the above. One of the values will make \( \Phi^{(2)} \) a minimum in the circle \( |\vec{x} - \vec{x}_0| = \delta_0 \) and another will make it a maximum. Taking \( \Delta_n \) from equation (E.3) and putting it into \( \Phi^{(2)} \), one finds that

\[
\Phi^{(2)}(\vec{x}) - \Phi(\vec{x}_0) = -\frac{1}{2} \lambda \delta_0^2 - \frac{1}{2} \sum_n \frac{G_n^2}{2K_{nn} + \lambda}
\]  

(E 4)

In order to make sure that equation (E.4) is a minimum, choose \( \lambda \) in the range

\[
\frac{|G_n|}{\delta_0} - 2K_{mm} < \lambda < \frac{G}{\delta_0} - 2K_{mm}
\]

where \( K_{mm} \) is the lowest eigenvalue of \( K \) with a nonvanishing gradient.

If \( \lambda < 0 \) then 1) all of the eigenvalues of \( K \) are greater than zero and 2) the usual curvature method (i.e. \( \delta = -1/2\kappa^{-1} \)) will find the minimum inside the circle and hence the curvature method should be employed. Thus, \( \lambda \) is always taken to be greater or equal to zero. \( \delta_0 \) should be taken small enough that \( \Phi^{(2)} \) is a reasonable approximation to the surface. But, it should taken large enough so that convergence is rapid. The actual minimum of the whole surface is found when all of the eigenvalues are positive and \( \delta \) is small in comparison to distances over which \( \Phi \) varies significantly.
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