MULTIPLIET SEPARATIONS IN 3p AND 3d ELECTRON ATOMS

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Part</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part I</td>
<td>Many Body Problem</td>
<td>1</td>
</tr>
<tr>
<td>1-</td>
<td>Central Field Approximation</td>
<td>1</td>
</tr>
<tr>
<td>2-</td>
<td>Determinantal Wave Functions</td>
<td>5</td>
</tr>
<tr>
<td>3-</td>
<td>Perturbation Method</td>
<td>6</td>
</tr>
<tr>
<td>4-</td>
<td>Two Theorems on the Matrix Components of Energy</td>
<td>9</td>
</tr>
<tr>
<td>Part II</td>
<td>One-Electron Wave Functions</td>
<td>13</td>
</tr>
<tr>
<td>1-</td>
<td>Analytic One-electron Radial Wave Functions</td>
<td>13</td>
</tr>
<tr>
<td>2-</td>
<td>Evaluation of the Matrix Components of Energy</td>
<td>16</td>
</tr>
<tr>
<td>Part III</td>
<td>Ground State Multiplet Separations for Filled Shells Plus:</td>
<td>20</td>
</tr>
<tr>
<td>1-</td>
<td>(3p)_2, Si I</td>
<td>21</td>
</tr>
<tr>
<td>2-</td>
<td>(3p)_3, P I and K I</td>
<td>26</td>
</tr>
<tr>
<td>3-</td>
<td>(3d)_2, Ti I, V II, Cr III, Mn IV, Fe V</td>
<td>29</td>
</tr>
<tr>
<td>4-</td>
<td>(3d)_3, V I, Cr II, Mn III, Fe IV, Co V</td>
<td>32</td>
</tr>
<tr>
<td>5-</td>
<td>(3d)_7 (4s)_2, Co I; (3d)_5 (4s)_2 N I</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Summary of Results</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Appendix I</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Appendix II</td>
<td>46</td>
</tr>
</tbody>
</table>
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I would like to express my sincere gratitude to Prof. J. C. Slater for his encouragement and excellent guidance in investigating this problem. My appreciation is also extended to the members of the Solid State and Molecular Theory Group for their stimulating discussions. I am truly grateful for this opportunity to be associated with the group.
The solution of the many body central field problem forms a convenient basis for consideration of the total energy of an atom in a given state.\(^{(1)}\)

The central field problem describes \(N\) electrons moving about a nucleus of charge \(Ze\). The forces considered are the coulomb forces of attraction due to the nuclear charge and the mutual electrostatic repulsion of the electrons. The electron distribution has been averaged out over the wavefunctions to give a spherically symmetrical charge distribution and thus a purely radial field. Each electron is assumed to move in this averaged field due to all of the other electrons.

The Hamiltonian of the system may be written:

\[
H = \sum_{i=1}^{N} \left\{ \frac{\vec{p}_i^2}{2m} + U(\vec{r}_i) \right\}
\] \(^{(1)}\)

To solve the problem in a Schrödinger representation, the classical Hamiltonian is transformed to the quantum mechanical operator by introducing the operators:

\[
\vec{p}_i \rightarrow \frac{\hbar}{2\pi r_i} \hat{V}_i
\]

\[
\vec{r}_i \rightarrow \vec{r}_i
\]

where \(\vec{r}_i\) is a notation for the space coordinates of the

\(^{(1)}\) J. C. Slater, Phys. Rev. 34, 1293 (1929).
\( i^{th} \) electron and \( \mathbf{\nabla}_{i} \) is the gradient with respect to these coordinates.

Thus:

\[
\mathcal{H}^{o} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{8\pi^2 m} \mathbf{\nabla}_{i}^2 + U(\mathbf{r}_i) \right\}
\]  

For convenience we transform to atomic units such that the unit of energy is \( \hbar c = \frac{2\pi^2}{(4\pi\epsilon_0)^2} \hbar^2 \), and the unit of distance is \( a_0 = \frac{\hbar^2}{(4\pi\epsilon_0)}/4\pi^2me^2 \).

Schrödinger's equation for the problem becomes:

\[
\left[ \sum_{i=1}^{N} \left\{ -\nabla_{i}^2 + U(\mathbf{r}_i) \right\} \right] \psi = E \psi
\]  

Since the Hamiltonian contains no terms which depend upon the coordinates of more than one electron, the solution may be written as a product of functions, each depending solely upon the coordinates of a single electron. Thus the equation is separable and the wave function may be written:

\[
\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \cdots \cdots \psi_N(\mathbf{r}_N)
\]

Upon introducing this wave function into Eq. (4), a set of \( N \) equations results, each of the form:

\[
\left\{ -\nabla_{i}^2 + U(\mathbf{r}_i) \right\} \psi_{i}(\mathbf{r}_i) = E_{i} \psi_{i}(\mathbf{r}_i)
\]

This is just the form of the Schrödinger equation for the motion of a single particle in the potential \( U(\mathbf{r}) \).
Since $U(r_i)$ is spherically symmetric due to the averaging procedure which was described above, $U$ is a function of $|r_i|$. The solution may be carried out by again using the separation of variables scheme. The well known solution is of the form:

$$u_i^s(r_i) = R_{nj_i}(r_i)Y_{nj_i}^m(\theta_i, \varphi_i)$$  \hspace{1cm} (7)

where $R_{nj_i}(r_i)$ is a function of the radius of the $i^{th}$ electron, and $Y_{nj_i}^m(\theta_i, \varphi_i)$, the spherical harmonics.

At this point we must also include consideration of the spin dependence of the wave function. There exists a great deal of physical evidence that another coordinate is needed to describe an electronic state in the one electron approximation. This may be mathematically described by introducing a two valued variable $s$, or spin, which can considered similar to an angular momentum coordinate. The spin momentum may have a component of $\pm \frac{1}{2}$ unit in the $z$ direction. This spin portion of the wave function may be written as a function of spin alone, similar to the $R_{nj}(r)$ and $Y_{nj}(\theta, \varphi)$ functions and denoted as $\sigma(s)$. Since there are only two allowed values of $m_s$, or the $z$ component of the spin, these functions are written as $\alpha(s)$ and $\beta(s)$, denoting a function with $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ respectively. These functions are summarized by:

$$\alpha\left(\frac{1}{2}\right) = 1 \quad \alpha\left(-\frac{1}{2}\right) = 0$$

$$\beta\left(\frac{1}{2}\right) = 0 \quad \beta\left(-\frac{1}{2}\right) = 1$$
The one-electron wave function is now:

\[ u_i^\circ(x_i) = R_{n_i l_i}^\circ(r_i) Y_{l_i}^{m_i}(\theta_i, \phi_i) \left\{ \alpha(s_i) \right\} \]

(8)

depending upon whether the electron has + 1/2 or - 1/2 component of spin. \( u_1 \) is now a function of three space coordinates and one spin coordinate, the aggregate being denoted by the symbol \( x_1 \).

The solution of the many body problem becomes:

\[ u_i^\circ(x_1, x_2 \ldots \ldots x_N) = \prod_{i=1}^{N} R_{n_i l_i}^\circ(r_i) Y_{l_i}^{m_i}(\theta_i, \phi_i) \]

(9)

There are many other solutions to Eq. (4) of this same form. Since the Hamiltonian operator is a symmetric function of the coordinates, that is, the electrons are identical dynamically, the Hamiltonian may be written in a new form by permuting the coordinates of the several electrons and thus the solution will be of the same form as Eq. (8) but the identification of certain electrons with certain sets of quantum numbers will be interchanged. Since each of these permuted wavefunctions is a solution of Eq. (4), a linear combination of these solutions must also be a solution since the equation is linear. Thus:

\[ \Psi^\circ(x_1, x_2 \ldots \ldots x_N) = \sum_{k=1}^{N!} A_k u_k^\circ(x_1, x_j, \ldots \ldots) \]

(10)

where \( A_k \) is the constant of combination.

Another condition is to be satisfied by these wavefunctions. It is the following: the wave function must be
antisymmetric with respect to the interchange of the co-
ordinates of any two electrons. This is known as the Pauli
Exclusion Principle and restricts the choice of coefficients
in Eq. (10).

Slater has shown a convenient representation of a
linear combination of these permuted wave functions satisfy-
ing this condition. Consider arraying the one electron wave
functions in a determinant:

\[ \Psi^0 = \frac{1}{\sqrt{N!}} \begin{bmatrix}
  u_1^*(x_1) & u_1^*(x_2) & \cdots & u_1^*(x_N) \\
  u_2^*(x_1) & u_2^*(x_2) & \cdots & u_2^*(x_N) \\
  \ddots & \ddots & \cdots & \ddots \\
  u_N^*(x_1) & u_N^*(x_2) & \cdots & u_N^*(x_N)
\end{bmatrix} \] (11)

Interchanging the coordinates of any two electrons is ef-
fected by interchanging two columns of the determinant and
as a result the value of the determinant changes sign. If
two one-electron functions are identical, then two rows are
equal and the determinant vanishes. This determinantal
wave function is normalized if the one-electron wave func-
tions are assumed to be normalized.

The determinantal wave function is a result of neglect-
ing the terms in the Hamiltonian which depend upon the co-
ordinates of more than one electron. Because of this approxi-
mation, further steps must be taken to get a good representa-
tion of the true wave function. The energy given by the sum
of the one-electron energies is also a poor approximation to
the energy associated with an exact solution of the Schrödinger problem for the real Hamiltonian.

An expression for the Hamiltonian of the many body problem neglecting spin-orbit coupling is:

\[ H = \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m} - \frac{Ze_i^2}{r_i} \right\} + \sum_{i,j, \text{pairs}} \frac{e^2}{r_{ij}} \]  \hspace{1cm} (12)

or transforming to the operator form in atomic units:

\[ H = \sum_{i=1}^{N} \left\{ -\nabla_i^2 - \frac{Ze_i^2}{r_i} \right\} + \sum_{i,j, \text{pairs}} \frac{2}{r_{ij}} \]  \hspace{1cm} (13)

where \( r_{ij} \) is the separation distance of electrons \( i \) and \( j \).

The Schrödinger equation for the problem is thus:

\[ \left\{ \sum_{i=1}^{N} \left(-\nabla_i^2 - \frac{Ze_i^2}{r_i} \right) + \sum_{i,j, \text{pairs}} \frac{2}{r_{ij}} \right\} \psi = E \psi \]  \hspace{1cm} (14)

where \( E \) is the total energy of the electron configuration.

Since our determinantal wavefunctions were approximations to the exact eigenfunctions of the Hamiltonian, (14), it would seem reasonable to attempt to expand the eigenfunction of this Hamiltonian operator in a series of determinantal wave functions. One may regard the determinantal wavefunctions as vectors in a many dimensional space. If the one electron functions composing a set of determinantal wave functions are mutually orthogonal, it follows that the determinantal wave functions are also mutually orthogonal. Thus an eigenfunction of \( Ea. \) (14) may be considered as a vector in function space and the determinantal wave
functions as defining a set of orthogonal axes in a sub-
space. If the components of this eigenfunction are small
along any axis in function space other than the axes de-
defined in the sub-space, then a linear combination of the
determinants will be a good representation of

If we define:

$$\psi_n = \sum_m S_{mn} \psi_m^*$$  \hspace{1cm} (15)

then:

$$H \sum_m S_{mn} \psi_m^* = E_n \sum_m S_{mn} \psi_m^*$$  \hspace{1cm} (16)

The problem thus reduces to finding the expansion coeffi-
cients $S_{mn}$. Using the orthogonality property of the
the following set of linear homogenous equations is ob-
tained:

$$(H_n - E_n) S_{1n} + H_{12} S_{2n} + H_{13} S_{3n} = 0$$

$$H_{21} S_{1n} + (H_{22} - E_n) S_{2n} + H_{23} S_{3n} = 0$$

$$H_{31} S_{1n} + H_{32} S_{2n} + (H_{33} - E_n) S_{3n} = 0$$  \hspace{1cm} (17)

where the number of equations equals the number of deter-
mminants used in the expansion and the coefficients are
defined by:

$$H_{km} = \int \psi_k^* \psi_m^* d\chi_1 d\chi_2 \cdots d\chi_n$$  \hspace{1cm} (18)

The integration is to be performed by integrating over the
coordinates of all the electrons and summing over all spins.

The matrix components, $H_{km}$, have been worked out by Prof. J. C. Slater\(^{(2)}\) and we shall merely quote the results. The Hamiltonian is divided into two parts, one having terms which contain coordinates of a single electron, the other being composed of terms which come from the mutual electrostatic repulsion of the electrons and depend upon the coordinates of two electrons. Thus:

$$H = \sum_{i=1}^{N} (-\nabla_i^2 - \frac{Z^2}{r_i^3}) + \sum_{i \neq j, \text{pairs}} \frac{1}{r_{ij}} \equiv \sum_{i=1}^{N} f_i + \sum_{i \neq j, \text{pairs}} g_{ij}$$  \hspace{1cm} (19)

The diagonal matrix components are given by:

$$H_{mm} = \sum_{i=1}^{N} (i|f|/i) + \sum_{i \neq j, \text{pairs}} \{ (i|g|/i) - (i|g|/i) \}$$  \hspace{1cm} (20)

where:

$$(i|f|/j) = \int u_i^*(\mathbf{r}_i) f_i u_j(\mathbf{r}_j) \, d\mathbf{r}_i$$

if $\text{spin } i = \text{spin } j$

and $i|f|/j = 0$ if $\text{spin } i \neq \text{spin } j$  \hspace{1cm} (21)

and:

$$(i|g|/ij) = \int \int u_i^*(\mathbf{r}_i) u_j^*(\mathbf{r}_j) u_k^*(\mathbf{r}_k) u_l^*(\mathbf{r}_l) \, d\mathbf{r}_i \, d\mathbf{r}_j$$

if $\text{spin } i = \text{spin } k$ and $\text{spin } j = \text{spin } l$  \hspace{1cm} (22)

and $i|g|/ij = 0$ otherwise

\( x_1 \) and \( x_2 \) represent the dummy variable space coordinates.

The non-diagonal components are given as follows:

a). If the determinantal wave functions differ from each other by having one of the one electron functions \( u_1 \) replaced by \( u_1' \):

\[
H_{kn} = (i|f|i') + \sum_{j \neq i} \{(ij|g|ij') - (ij|g|jj')\}
\]  
(23)

b). If the determinantal wave functions differ from each other by having two of the one electron functions \( u_1 \) and \( u_j \) replaced by \( u_1' \) and \( u_j' \):

\[
H_{kn} = (ij|g|ij') - (ij|g|jj')
\]  
(24)

c). If the determinantal wave functions differ by more than two one electron functions, the non-diagonal component vanishes. The various integrals are defined in Eqns. (21) and (22).

We now ask for what values of \( E \) does the set of equations (17) possess a solution. It is well known that a solution exists only if the determinant of the coefficients is zero.

\[
\begin{bmatrix}
H_{11} - E_1 & H_{12} & H_{13} & \cdots \\
H_{12} & H_{22} - E_2 & H_{23} & \cdots \\
\vdots & \vdots & \ddots & \ddots \\
H_{31} & H_{32} & H_{33} & \cdots
\end{bmatrix} = 0
\]  
(25)

Fortunately, two general theorems simplify the solution of this problem considerably. The first states that there exist no matrix components of energy between states
of different $M_L$, the $z$ component of the total orbital angular momentum of the electronic system. The second that there exist no matrix components of energy between states of different $M_S$, the $z$ component of the total electronic spin.

The Hamiltonian operator was assumed to exclude the spin-orbit coupling, $L \cdot S$. Because of this fact the operator $M_L = \sum_i m_i$ will commute with the Hamiltonian. That is, the result of operating on the wave function by these operators is independent of the order of operation.

That this is the case may be seen by considering the spherical symmetry of $H$. $M_L$ is easily seen to be $-i \sum_{i=1}^{N} \frac{\partial}{\partial \varphi i} \Psi_i$ where $\varphi_i$ is the $\varphi$ spherical coordinate of the $i^{th}$ electron. But such an operation effectively rotates the system through an infinitesimal angle $\varphi$ because:

$$\frac{\partial}{\partial \varphi} f(\varphi) d\varphi \approx f(\varphi + d\varphi)$$

Thus:

$$-i \sum_{i=1}^{N} \frac{\partial}{\partial \varphi i} H \Psi_n = -i \left[ \sum_{i=1}^{N} \frac{\partial}{\partial \varphi i} H \right] \Psi_n + H \left[ -i \sum_{i=1}^{N} \frac{\partial}{\partial \varphi i} \Psi_n \right]$$

Due to the spherical symmetry of $H$, $\sum_{i=1}^{N} \frac{\partial}{\partial \varphi i} H = 0$,

and, $\sum_{i=1}^{N} m_{Li} H \Psi_n = H \sum_{i=1}^{N} m_{Li} \Psi_n$

or:

$$H M_L - M_L H = 0 \quad \text{(26)}$$

It is obvious that the spin operator $M_S$ commutes because
the Hamiltonian does not include any terms depending upon
the spin and in this sense is a constant operating upon
the spin of $\Psi_n$.
Thus:

$$HM_S - M_S H = 0$$  \hspace{1cm} (27)

Suppose we have two commuting operators, $A$ and $B$, with:

$$A u(a,n) = a u(a,n)$$  \hspace{1cm} (28)

The eigenfunction, $u(a,n)$, corresponds to the eigenvalue
$a$, and is the $n^{th}$ degenerate eigenfunction of this eigen-
value. Then:

$$AB u(a,n) = \sum_{a',n'} A' u(a',n')(a',n'/B|a,n)$$  \hspace{1cm} (29)

where the result of operating on $u(a,n)$ by $B$ has been ex-
panded in the eigenfunctions of $A$, $(a',n'/B|a,n)$ being the expansion coefficients. Also:

$$BA u(a,n) = a \sum_{a',n'} u(a',n')(a',n'/B|a,n)$$  \hspace{1cm} (30)

But because the operators commute, the two expressions
must be identical.

$$(a-a')(a',n'/B|a,n) = 0$$  \hspace{1cm} (31)

Either $a = a'$ or the matrix component $(a',n'/a,n) = 0$.
Since $H$ and $M_L$ commute, either $H_{ij} = 0$ or $(M_L)_{jj} = (M_L)_{11}$,
establishing the important result that there exist no matrix components of energy between states of different $M_L$. A similar proof holds for $M_3(3)$.

The determinant, Eq. (25), is now factored into sub-determinants, each being characterized by a value of $M_1$ and $M_3$. In many cases the eigenvalues of energy, $E_n$, may be easily obtained by the use of the diagonal sum rule. This states that the sum of the diagonal components of the perturbed Hamiltonian is equal to the sum of the eigenvalues, $E_n$. This result may be seen by expanding the determinant in descending powers of $E$, and comparing this with the factored form of the solution of the determinant. Thus:

$$\sum_i H_{ii} = \sum_n E_n$$

(32)

If by some means we know all but one solution of the determinant, we can easily find the remaining one by using this rule. Specific examples of this method will be discussed later.

The complexity of evaluating the matrix components of energy is directly related to the form of the one electron wave functions which are used. Since the angular part of the one electron wave function is well known, the radial part is of prime interest. The self consistent field solutions which have been worked out by D. R. Hartree and others,\(^{(4)}\) exist in tabulated form and require numerical methods for performing the integrations. Several authors have attempted to obtain analytic forms of these single electron functions.\(^{(5)}\)

Prof. J. C. Slater\(^{(6)}\) has given rules for setting up a nodeless radial wave function in terms of shielding constants. These constants were fixed merely by adjusting them to get agreement with the empirical values of the stripped atom and x-ray energy levels, size, etc. Prof. P. M. Morse and others\(^{(7)}\) have done a variation calculation to determine the best parameters. Their method consists of

\(^{(4)}\) D. R. Hartree, Reports Prog. Phys. 11, 113 (1946-47).
\(^{(5)}\) J. C. Slater, Phys. Rev. 36, 57 (1930).
\(^{(7)}\) C. Zener, Phys. Rev. 36, 51 (1930).
\(^{(6)}\) P. Löwdin, Studies of Atomic Self-Consistant Fields.
\(^{(7)}\) J. C. Slater, Phys. Rev. 36, 57 (1930).
\(^{(7)}\) P. M. Morse, L. A. Young and E. S. Haurwitz, Phys. Rev. 48, 948 (1935).
expressing the energy of a configuration in terms of several parameters and varying these parameters to get the lowest possible energy.

Because of the simplicity of Prof. Slater's wave functions and the relatively wide range of quantum states for which these wave functions are given, we will use them as a basis for calculations of multiplet separations.

The form of the radial part of the one electron function is:

\[ R_{\eta}^{n}(r) = r^{n+1} e^{-[(Z-S)/\pi^{n}]} r \]  \hspace{1cm} (33)

The rules for \( n \) and \( S \) are simply stated.

1.) \( n^{*} \) is assigned by the following table, in terms of the real principal quantum number \( n \):

For \( n = 1, 2, 3, 4, 5, 6 \)

\( n^{*} = 1, 2, 3, 3.7, 4.0, 4.2 \)

2.) For determining \( S \), the electrons are divided into the following groups, each having a different shielding constant:

1s; 2s, 2p; 3s, 3p; 3d; 4s, 4p; etc.

3.) The shielding constant \( S \) is formed, for any group of electrons, from the following contributions:
a). Nothing from any shell outside the one considered.
b). An amount 0.35 from each other electron in the group considered (except in the 1s group, where 0.30 is used instead).
c). If the shell is an s, p shell, an amount 0.85 from each electron with total quantum number less by one, and an amount 1.00 from each electron still further in; but if the shell is a d or f, an amount 1.00 from every electron inside it.

The radial wave functions set up in this way are not orthogonal to each other. Since the method of writing down the matrix components assumed orthogonal one-electron wave functions, an orthogonalization procedure must be carried out. Wave functions of different $l$ or $m_l$ need not be adjusted since they are automatically orthogonal over the angular portion. However, wave functions of the same $l$ and $m_l$ can be made orthogonal by taking the new radial function to be a linear combination of radial functions of the several non-orthogonal functions. Thus, if we wish to make the 3p function orthogonal to the 2p, we take: $u_{2p}' = u_{2p}$

$$u_{3p}' = au_{2p} + bu_{3p}$$

where $a$ and $b$ are determined from the orthogonality of $u_{2p}'$ and $u_{3p}'$, and by normalization of $u_{3p}'$. 
The following notation shall be introduced for the radial parts of the one-electron functions.

\[ R_{1S} = C_1 e^{-Z_1r} \]
\[ R_{2S} = C_2 e^{-Z_1r} + C_3 r e^{-Z_2r} \]
\[ R_{2p} = C_4 r e^{-Z_2r} \]
\[ R_{3S} = C_5 e^{-Z_1r} + C_6 r e^{-Z_2r} + C_7 r^2 e^{-Z_3r} \]
\[ R_{3p} = C_8 r^2 e^{-Z_2r} + C_9 r e^{-Z_3r} \]
\[ R_{3d} = C_{10} r^2 e^{-Z_4r} \]

(34)

It will be noticed that certain simplifications arise due to the shielding constants being the same for an s and a p electron with the same total quantum number.

Consider evaluating an integral \((i/f/i)\) using these orthogonalized wave functions. If we denote a general radial function of the form above by:

\[ R_{\ell l}(r) = \sum_k C_k r^k e^{-Z_k r} \]

(35)

then:

\[ \langle i/f/i \rangle = \int \sum_i C_i r^m_i e^{-Z_{ij} r} Y_{\ell_i}^{m_i}(\theta, \phi) \left[ - \nabla^2 - 2Z/r \right] \sum_k C_k r^m_k e^{-Z_k r} Y_{\ell_i}^{m_i}(\theta, \phi) \cdot r^2 dr \sin \theta d\theta d\phi \]

(36)

Expanding we get:

\[ u_i \nabla^2 u_i = \left[ R_{\ell_i l_i} \frac{\partial^2}{\partial r^2} (r R_{\ell_i l_i}) - l_i (l_i + 1) \frac{R_{\ell_i l_i}}{r^2} \right] Y_{\ell_i}^{m_i}(\theta, \phi) Y_{\ell_i}^{m_i}(\theta, \phi) \]

(37)

\[ \frac{\partial^2}{\partial r^2} \frac{2Z}{r} u_i = \frac{2Z}{r} R_{\ell_i l_i} Y_{\ell_i}^{m_i}(\theta, \phi) Y_{\ell_i}^{m_i}(\theta, \phi) \]
Thus: 
\[
(i/f/l) = \int_0^\infty \frac{R_{ni,l}(r)}{r} \frac{2^2}{2n^2} \left( r R_{ni,l}(r) + \frac{\ell(l+\ell)}{r^2} r^2 R_{ni,l}^2(r) \right) r^2 dr \tag{38}
\]

If we define: 
\[
D_{njn_k}(z_j, z_k, z, l) = \int_0^\infty r^{n_j} e^{-Z_j r} \left[ -\frac{1}{r^2} \frac{\partial^2}{\partial r^2} r^{n_k+1} e^{-Z_k r} + \frac{\ell(l+\ell)}{r^2} r^{n_k-2} e^{-Z_k r} \right] r^2 dr \tag{39}
\]

Then:
\[
(i/f/l) = \sum_{j,k} C_j C_k D_{njn_k}(z_j, z_k, z, l) \tag{40}
\]

The various D's may be evaluated from D^{00} by differentiation with respect to the parameters \(a_j\) and \(a_k\).

Prof. Slater\(^{(3)}\) has shown that the integrals \((ij/g/lj)\) and \((ij/g/ji)\) may be evaluated by expanding \(1/r_{ij}\) in spherical harmonics and the resulting sum of integrals expressed as:
\[
(ij/g/lj) = \sum_k a^k(lm'j, l'mj') F^k(nj, n'l') \tag{41}
\]

where:
\[
F^k(nj, n'l') = 2 \int_0^\infty \int_0^\infty R^2_{nj}(r) R^2_{n'l'}(r) \frac{r^k(a)}{r^{k+b}(b)} r^2 r'^2 dr dr' \tag{42}
\]

and by definition \(r(a)\) is the smaller and \(r(b)\) is the larger

\(^{(3)}\) J. C. Slater, Phys. Rev. 34, 1293 (1929)
of \( r \) and \( r' \), the dummy variables of integration:

Similarly:

\[
\langle i j | g | i j \rangle = \sum_k b^k(\lambda \mu_i; \lambda' \mu_j) \, G^k(\nu \lambda; \nu' \lambda')
\]  \hspace{1cm} (43)

where:

\[
G^k(\nu \lambda; \nu' \lambda') = 2 \int_0^\infty \rho_\nu(\rho) \, \rho_{\nu'}(\rho') \, \rho_{\lambda}(\rho) \, \rho_{\lambda'}(\rho') \, \frac{r^k(a)}{r^{k+}(b)} \, \frac{1}{r^2 \, r'^2} \, dr \, dr'
\]  \hspace{1cm} (44)

Upon introduction of the expressions for the orthogonalized wave functions, \( F^k(n \ell; n' \ell') \) becomes:

\[
\sum_{s \ell u v} c_s c_u c_v c_v \int_0^\infty \int_0^\infty \rho_\nu(\rho) \, \rho_{\nu'}(\rho') \, \rho_{\lambda}(\rho) \, \rho_{\lambda'}(\rho') \, \frac{r^k(a)}{r^{k+}(b)} \, \frac{1}{r^2 \, r'^2} \, dr \, dr'
\]  \hspace{1cm} (45)

If we define:

\[
k^2 \langle i j | (a, b) = \int_0^\infty \int_0^\infty \, e^{-a \frac{r^k(a)}{r^{k+}(b)}} \, e^{-b \frac{r' (a)}{r^{k+}(b)}} \, r^2 \, r'^2 \, dr \, dr'
\]  \hspace{1cm} (46)

Then:

\[
F^k(n \ell; n' \ell') = \sum_{s \ell u v} c_s c_u c_v c_v \, k^{n_\nu + \ell_\mu v, n_{\nu'} + \ell_{\nu'} v} (s_\lambda + \ell_\lambda, s_{\nu} + \ell_{\nu})
\]  \hspace{1cm} (47)

Also:

\[
k^2 \langle i j | (a, b) = (-1)^{i+j} \frac{\partial^2}{\partial a^i \partial b^j} \{ k^{00} \langle i j | (a, b) \}
\]  \hspace{1cm} (48)

\( G^k(n \ell; n' \ell') \) may be expanded in a similar manner.

The integrals may thus be written in terms of the \( L \) functions which are given in Appendix I for \( i, j \) and \( k \) going from one to four. With this table it is possible to evaluate any integral involving electrons up to the 3d shell.
with wave functions of the form of Eq. (34), without performing any integrations. The formulae for the constants, $C_k$, are given in Appendix II.

There exists some question with regard to the normalization convention used for the one electron functions. Here we have used the convention that each portion of the function is separately normalized over its own portion of the volume element. Specifically:

$$\int_0^\infty \int_0^{\pi} \int_0^{\pi} \sum_{\ell=0}^\infty \int_0^{2\pi} \sum_{\ell=0}^\infty \sum_{m=-\ell}^\ell \int_0^\infty R_{n\ell m}^2(r) r^2 dr \, Y_{\ell m}^{*}(\theta, \varphi) Y_{\ell m}(\theta, \varphi) \, \sin \theta \, d\theta \, d\varphi = 1$$

With this convention, the numerical factor preceding the integral in the expressions for $F^k$ and $G^k$ is 2, while Prof. Slater's convention gives $32 \pi^2$. However, the tables for $a^k$ and $b^k$ as derived by Prof. Slater(9) are correct for either convention and may be used directly in Eq. (41) and Eq. (43).

(9) J. C. Slater, Phys. Rev. 34, 1293 (1929).
The ground state configuration multiplet separations for some of the elements in the first row of the periodic table have been worked out by a variation calculation. However, when the number of electrons increases appreciably, this computation becomes arduous.

If the separations are calculated by the perturbation method discussed thus far, the computations are relatively easy. This is particularly true if one assumes the radial part of a one-electron function to be the same for all multiplets of a given configuration and configuration interaction to be negligible. To compute the energy separation of two multiplets, one must evaluate the total energy of the atom in each of the multiplet states and take the difference of these results. These two energy expressions generally have many terms in common which cancel upon subtraction. Thus the separation energy is expressed as a sum of relatively few integrals compared to the energy of a single multiplet.

The method of writing down the matrix components is straightforward. A table is made which tabulates all the possible combinations of \( m_l \) and \( m_s \) for the electrons of the atom considered. Since closed shells do not introduce

(10) P. M. Morse, L. A. Young and E. S. Haurwitz, Phys. Rev. 48, 948 (1935)
any new states, they will not be included in the table. The expressions for the matrix components, Eq. (20) is then employed, considering only diagonal components and non-diagonal components between states of the same \( M_L \) and the same \( M_S \), since it was shown that all other matrix components vanish.

The ground state of silicon will be considered as an example of this procedure. Silicon has a ground state configuration:

\[(1s)^2 \ (2s)^2 \ (2p)^6 \ (3s)^2 \ (3p)^2 \ 3p\]

A table is constructed considering the two \( 3p \) electrons in various states. The sub-scripts 1 and 2 in the column heads refer to the first and second \( 3p \) electrons. The spins repeat in each set of four states, as indicated in 1-4. The orbital angular momentum is the same in all four states of a set. The table continues in a similar fashion for \( M_L = -1, -2 \). However no new information is obtained.

The vector model would indicate that two \( p \) electrons would lead to the following multiplets: \(^1(S \ P \ D), \ 3(S \ P \ D)\). By studying the table we notice that state one is not allowed because of the exclusion principle, since two electrons have the same set of quantum numbers and thus the wave function vanishes. The same is true about state four. States two and three are equivalent since the electrons are indistin-
guishable. States nine through twelve are equivalent to

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<th>( M_S )</th>
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</tbody>
</table>

**TABLE I**

five through eight. Similar facts are true about the states with \( M_L = 0 \) and the table, after renumbering, reduces to:

<table>
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<tr>
<th></th>
<th>( m_{l_1} )</th>
<th>( m_{l_2} )</th>
<th>( M_L )</th>
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<th>( m_{s_2} )</th>
<th>( M_S )</th>
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</tr>
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<td>( -\frac{1}{2} )</td>
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<td></td>
</tr>
</tbody>
</table>

**TABLE II**
The diagonal energy of state one must be the $^1D$ energy since the $^3D$ has been excluded by the exclusion principle and there exist no non-diagonal components with this state. By similar reasoning the $^3P$ energy is the diagonal energy of state two. States seven, eight and nine must lead to the energies of a $^1D$, a $^3P$ and a $^1S$. The $^1S$ energy may be obtained by the diagonal sum rule since the determinant factors and the solution of this sub-determinant must give these three energies.

The energy matrix is shown for the states tabulated above.

```
\[
\begin{pmatrix}
H_{11} & E & & & & \\
& H_{22} & E & & & \\
& & H_{33} & E & H_{34} & \\
& & H_{43} & H_{44} & E & \\
& & & H_{55} & E & \\
& & & & H_{66} & E \\
& & & & & \vdots \\
& & & & & H_{77} & E & H_{78} & H_{79} \\
& & & & & H_{87} & H_{88} & H_{89} & E \\
& & & & & H_{97} & H_{98} & H_{99} & E \\
& & & & & & & \vdots \\
& & & & & & & H_{1010} & E \\
\end{pmatrix}
\]
```

The matrix has been blocked off such that each block bordered by dashes contains components from states of a single $M_L$. The dots similarly represent states of a single $M_S$. 
Thus:

\[ E_{1D} = ^1D = H_{11} \]
\[ E_{3P} = ^3P = H_{22} \]
\[ E_{1S} = ^1S = H_{77}H_{88} + H_{99} - ^3P - ^1D = H_{77}H_{88} + H_{99} - H_{11} - H_{22} \]

(50)

It is obvious that if the separation, \(^3P - ^1D\), is computed, \((i/f/1)\) for the two states will cancel as well as the integrals between electrons in the closed shells, since these integrals are independent of \(m_l\) and \(m_s\) of the outer electrons. It is also true that the integrals involving the interaction of an outer electron with a closed shell will cancel and we are merely left with the integrals between electrons in the uncompleted outer shell.

Neglecting all integrals except those between the 3p electrons the energies are:

\[ ^1D = F^0 (3p,3p) + 1/25F^2 (3p,3p) \]
\[ ^3P = F^0 (3p,3p) - 5/25F^2 (3p,3p) \]
\[ ^1S = F^0 (3p,3p) + 10/25F^2 (3p,3p) \]

(51)

The expression for \(^3P\) simplified because \(F's\) and \(G's\) of the same indices are equal. The separations are:

\[ ^1D - ^3P = 6/25F^2 (3p,3p) \]
\[ ^1S - ^1D = 9/25F^2 (3p,3p) \]

(52)

If wave functions of the form Eq. (34) are used, then
the integral may be expanded as in Eq. (45).

\[ F^2(3p,3p) = C_8^4 z^{22}(2Z_2,2Z_2) + 4C_8^2 C_9^4 z^{33}(Z_2+Z_3, Z_2+Z_3) + C_9^4 z^{44}(2Z_3, 2Z_3) + 4C_8^3 C_9 z^{32}(Z_2+Z_3, 2Z_2) + 2C_8^2 C_9 z^{42} \]

\[ (2Z_3, 2Z_2) + 4C_8^3 C_9^3 z^{43}(2Z_3, Z_2+Z_3) \] (53)

where the various \( L \)'s are given in Appendix I.

Reference to Appendix I shows that if the arguments of an \( L \) function are equal, the result can be written as a constant divided by a certain power of the argument. In this case:

\[ z^{22}(2Z_2, 2Z_2) = 50.625/(2Z_2)^9 \]

\[ z^{33}(Z_2+Z_3, Z_2+Z_3) = \frac{1102.50}{(Z_2+Z_3)^9} \]

\[ z^{44}(2Z_3, 2Z_3) = 35,319.2/(2Z_3)^{13} \] (54)

keeping six figure accuracy.

The other \( L \)'s must be evaluated numerically in terms of the values of \( Z_2 \) and \( Z_3 \). The \( Z \)'s are calculated directly from Prof. Slater's rules for atomic shielding coefficients. (11)

Thus for silicon, \( Z_2 = 4.93 \) and \( Z_3 = 1.38 \). \( C_8 \) and \( C_9 \) must be evaluated from the formulae given in Appendix II.

(11) J.C. Slater, Phys. Rev. 36, 57 (1930)

These rules are summarized on page of this paper.
The result of this calculation is:

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<th></th>
<th>Calc.</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1D - ^3P$</td>
<td>10,285.5 cm$^{-1}$</td>
<td>6,198.66 cm$^{-1}$</td>
</tr>
<tr>
<td>$^1S - ^1D$</td>
<td>15,428.2 cm$^{-1}$</td>
<td>9,095.42 cm$^{-1}$</td>
</tr>
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</table>

The experimental value of $^1D - ^3P$ was gotten by averaging the differences in energies of the $^1D$ and $^3P$ levels. This appears to be a reasonable procedure since to compute the $^3P$ splittings, the spin-orbit interaction is introduced as a perturbation to these degenerate states, and it is well known that the center of gravity of such a group of states remains unaltered. The ratio of the splittings from Eq. (52) is while experimentally, 1.461, in good agreement.

\[
\frac{^1S - ^1D}{^1D - ^3P} = 1.5
\]

The next example is that of neutral phosphorous. It has a ground state configuration $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3\ ^4S$. This configuration gives rise to three multiplets, $^4S, ^2D, \ ^2P$. A table similar to table I is constructed for the three 3p electrons since they are the only electrons which can enter into the multiplet structure. After ruling out the states which violate the exclusion principle and combining the equivalent states, the table reduces to the one shown below.
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<td>-1</td>
<td>0</td>
<td>-1/2</td>
<td>-1/2</td>
<td>1/2</td>
<td>-1/2</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-1/2</td>
<td>-3/2</td>
</tr>
</tbody>
</table>

**TABLE III**

Since there exist no non-diagonal components with states one or two, these must be the \(^2\text{D}\) states and the energy is given by \(H_{11} = H_{22}\). States four and five give a \(^2\text{D}\) plus a \(^2\text{F}\) energy, and the \(^2\text{F}\) may be obtained by the diagonal sum rule as \(H_{44} + H_{55} - H_{11}\). The \(^4\text{S}\) energy is given directly by the diagonal energy of state seven, because neither the \(^2\text{D}\) nor the \(^2\text{F}\) can have \(M_S = 3/2\). It might be noted that the \(^4\text{S}\) energy could have been gotten in several other ways, namely by using the diagonal sum rule on the states with \(M_L = 0\) and \(M_S\) either \(1/2\) or \(-1/2\). Also the diagonal energy of state fourteen would give the \(^4\text{S}\) energy. Using Eq. (20), and neglecting all integrals except those between the 3p electrons, we get:
\[ 4S = 3P^0(3p,3p) - 15/25P^2(3p,3p) \]
\[ 2D = 3P^0(3p,3p) - 6/25P^2(3p,3p) \]
\[ 2F = 3P^0(3p,3p) \]

and:
\[ 2D - 4S = 9/25P^2(3p,3p) \]
\[ 2F - 2D = 6/25P^2(3p,3p) \]

Again the separations depend upon the \( P^2 \) integral as expressed in Eq. (54). With the exponents \( Z_2 = 5.245 \) and \( Z_3 = 1.6 \), the separations become:

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2D - 4S )</td>
<td>17,179.0 cm(^{-1})</td>
<td>11,369.1 cm(^{-1})</td>
</tr>
<tr>
<td>( 2F - 2D )</td>
<td>11,452.6 cm(^{-1})</td>
<td>7,366.1 cm(^{-1})</td>
</tr>
</tbody>
</table>

The multiplet separations for the ground state of potassium \( V \), which has the same electron configuration as phosphorous I, were calculated. It was felt that this calculation would give some indication of the relative exactness of the wave functions as a function of atomic number. It must be realized, however, that the radial parts of the one-electron functions really depend upon the individual multiplet considered, and the terms which are considered to cancel when a separation is calculated, actually do contribute to the separation energy. The exponents for \( K V \) are \( Z_2 = 7.425 \) and \( Z_3 = 2.933 \).
<table>
<thead>
<tr>
<th>Transition</th>
<th>Calculated (cm(^{-1}))</th>
<th>Observed (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2D - 4S)</td>
<td>20,914.6</td>
<td>24,118.5</td>
</tr>
<tr>
<td>(2P - 2D)</td>
<td>13,831.2</td>
<td>15,786.0</td>
</tr>
<tr>
<td>(2D - 4S) (2P - 2D)</td>
<td>1.50000</td>
<td>1.57860</td>
</tr>
</tbody>
</table>

The separations appear to improve somewhat, however the error is over corrected. If the separations are considered to be given by Eq. (56), then the above results are an indication of the exactness of the 3p wavefunction independent of the other one-electron functions of the problem. The effect of other nearby levels of the same symmetry will tend to invalidate this indication because of configuration interaction, which has been neglected.

The next configuration considered is 3d\(^2\) with closed shells. Titanium I has the ground state configuration:

\[
(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^2 (4s)^2 \quad 3P
\]

The addition of the 4s electrons will have no effect on the computations since Prof. Slater's shielding coefficients are independent of electrons outside the shell considered. The separations are expressed as functions of the F's by the method illustrated in the previous problems. For two equivalent d electrons the separations are:

\[(12)\]

\[(12)\] J. C. Slater, Phys. Rev. 34, 1293 (1929)
\[ {}^3F - {}^3F = \frac{135}{441}F^2 \quad (3d, 3d) - \frac{75}{441}F^4 \quad (3d, 3d) \]
\[ {}^3F - {}^1G = \frac{108}{441}F^2 \quad (3d, 3d) + \frac{10}{441}F^4 \quad (3d, 3d) \]
\[ {}^3F - {}^1D = \frac{45}{441}F^2 \quad (3d, 3d) + \frac{45}{441}F^4 \quad (3d, 3d) \]  \(57\)
\[ {}^3F - {}^1S = \frac{198}{441}F^2 \quad (3d, 3d) + \frac{135}{441}F^4 \quad (3d, 3d) \]

Since the 3d radial function is given by a single term expression, only one \( L \) function is needed for each \( F \).
\[ F^2 \quad (3d, 3d) = 2c_{10}^4 L_{44}^{44} \quad (2Z_4, 2Z_4) = \text{const.} \times Z_4 \]
\[ F^4 \quad (3d, 3d) = 2c_{10}^4 L_{44}^{44} \quad (2Z_4, 2Z_4) = \text{const.} \times Z_4 \]  \(58\)

In this case the separations can be written in a simple form directly as a function of the atomic number, a rather unique circumstance. The separations for Titanium I are:

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^3F - {}^3F)</td>
<td>7,099.07</td>
<td>8,324.80</td>
</tr>
<tr>
<td>(^3F - {}^1G)</td>
<td>9,443.96</td>
<td>11,932.79</td>
</tr>
<tr>
<td>(^3F - {}^1D)</td>
<td>6,131.07</td>
<td>7,069.62</td>
</tr>
<tr>
<td>(^3F - {}^1S)</td>
<td>23,588.4</td>
<td></td>
</tr>
</tbody>
</table>

To the authors knowledge, the \(^1S\) level in Ti II has not been observed.

Multiplet separations for the configuration
\((1s)^2 \quad (2s)^2 \quad (2p)^6\quad (3s)^2 \quad (3p)^6 \quad (3d)^2\)
were computed as a function of atomic number. This is the
configuration of Ti I lacking the 4s electrons. These separations are plotted in graph I. The graph shows rather poor agreement between the experimental values and the calculated values directly, however, the experimental values lie quite close to a straight line, in agreement with Eq. (58). The slopes of the observed and calculated curves show definite correlation. The observed separations for Ti I show a marked difference from the other data. This is due to the fact that the two 4s electrons really do shield the 3d electrons to a certain extent. The energy shift is toward smaller separations in all cases. This is consistent with Eq. (58) because $Z_4$ is decreased when the shielding constant becomes larger. An estimate of the shielding effect of these electrons may be gotten from graph I. If the separations are considered to be linear in the atomic number, the experimental curves can be extrapolated to a value of Z such that the separation agrees with the experimental value for Ti I. This value of Z is the atomic number minus the shielding due to the 4s electrons. Thus the addition to the shielding constant is just the true atomic number minus the extrapolated value of Z from the experimental curve. The three separations give the 4s shielding as 0.90 to 1.05 units. The rather large errors in the calculated values of separation shown in graph I are possibly due to the shielding constant being too large. Since the atomic number is of the order of the shielding constant, small errors in the latter would be reflected in relatively
large errors in the separations. The graphs indicate that if the errors are to be explained in this manner, the shielding constants must be dependant upon the multiplet considered. This may be seen by subtracting the true atomic number from the value of Z obtained by extrapolating the theoretical curve to the point where the theoretical and observed separations agree. For example, the differences taken from the graph I for chromium are:

\[
\begin{align*}
\Delta \text{Shielding Constant} &= \left\{ \begin{array}{l}
3^P - 1^D = 1.85 \\
3^P - 3^P = 2.15 \\
3^P - 1^G = 2.35
\end{array} \right.
\]

However, if the shielding constants depend upon the specific multiplet considered, we are not justified in assuming the terms common to both total energy expressions cancel when a separation is computed. It therefore appears there is an element of truth in both explanations for the difference between the calculated and observed separations.

To obtain another check upon the amount of shielding the 4s electrons contribute, the $^4P - ^4P$ separation for a series of elements having a (3d)$^3$ configuration was computed. Vanadium I is similar to Ti I in that it has two 4s electrons. Graph II shows the same characteristics as seen in graph I. The separations are linear in the atomic number and V I departs considerably from the extrapolated experimental curve. The 4s shielding proves to be about 1.0 in this case. The effective shielding constant is indicated to be about 2 units smaller than the one used.
Again this is no indication of the value of the shielding constant to be used if the radial wave function is considered to change from multiplet to multiplet, thus it appears necessary to consider such changes if the separations are to be computed accurately.

The expressions for the multiplet separations for the configurations (3d)$^7$ and (3d)$^8$ turn out to be the same as for the $^3F - ^3P$ separation of (3d)$^2$. Separations were calculated for cobalt I and nickel I.

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co I</td>
<td>(3d)$^7$</td>
<td>(4s)$^2$ $^4F - ^4P$</td>
</tr>
<tr>
<td>Ni I</td>
<td>(3d)$^8$</td>
<td>(4s)$^2$ $^5F - ^3P$</td>
</tr>
</tbody>
</table>

These computations were made with Prof. Slater's shielding constants which neglect outer shielding. The separations for Co III and Ni III having (3d)$^7$ and (3d)$^8$ configurations respectively, give another indication of the shielding introduced by the 4s electrons. If it is assumed that the $^4F - ^4P$ and the $^3F - ^3P$ separations are linear functions of atomic number, and the slope of these curves is the theoretically derived slope, the 4s shielding can be obtained directly. These assumptions seem reasonable because of the close agreement in the observed end theoretical values of slope and the linearity of the separations shown in graphs I and II. The observed separations are:

- Co III (3d)$^7$ $^4F - ^4P = 14,440.7$ cm.$^{-1}$
- Ni III (3d)$^8$ $^5F - ^3P = 15,746.6$ cm.$^{-1}$
From graph III, the 4s shielding is seen to be 0.825 for Co I and 0.75 for Ni I. This method of evaluating the 4s shielding was chosen because the spectra of ions with these electron configurations have not been published and experimental extrapolation is impossible. The 4s shielding tends to decrease as the number of 3d electrons increase.

The apparent accuracy in calculating the separations for Co I and Ni I is somewhat accidental. In this case, neglecting the 4s shielding decreased the shielding constant by almost the amount required to get agreement with experiment, however, it has been shown in previous examples that such a balance does not generally occur.
CONCLUSIONS

A summary of results is given in table IV. The greatest error in the calculated separations occurs for the 3p electron configurations. A source of this error is that Eq. (34) is not a good representation of the wave function. The exponent in the first term of $R_{3p}$ is assumed to be equal to the exponent in $R_{2p}$. Prof. Slater's later paper \(^{(13)}\) shows that these exponents must vary from each other to obtain a good approximation to the Hartree functions. Also, the single exponential in each term should be replaced by a linear combination of exponentials. Multiplet dependance of the radial one-electron functions and configuration interaction also contribute to the error, as previously stated.

The 3d configurations exhibit somewhat better agreement. Since the 3d function has a single maximum, it turns out that the one term expression for the radial function gives a fair representation of this function. Graphs I and II show that the expression is quite exact, in that, linearity is found in the separations as a function of atomic number. The shielding constant appears to be too large, accounting for the translation of the theoretical curve. As pointed out, the error is also indicated to be due to the multiplet dependance of the shielding constants.

\(^{(13)}\) J. C. Slater, Phys. Rev. 42, 33 (1932)
### SUMMARY OF RESULTS

<table>
<thead>
<tr>
<th>Multiplet Separation</th>
<th>Calculated Separation</th>
<th>Observed Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon I (3p)²</td>
<td>3_F - 1_D</td>
<td>10,285.5 cm⁻¹</td>
</tr>
<tr>
<td>Phosphorus I (3p)³</td>
<td>4_S - 2_D</td>
<td>17,179.0</td>
</tr>
<tr>
<td></td>
<td>2_D - 2_P</td>
<td>11,452.6</td>
</tr>
<tr>
<td>Potassium V (3p)³</td>
<td>4_S - 2_D</td>
<td>20,914.6</td>
</tr>
<tr>
<td></td>
<td>4_S - 2_D</td>
<td>34,857.8</td>
</tr>
<tr>
<td>Titanium I (3d)²(4s)²</td>
<td>3_F - 1_D</td>
<td>6,131.02</td>
</tr>
<tr>
<td></td>
<td>3_F - 3_P</td>
<td>7,099.02</td>
</tr>
<tr>
<td></td>
<td>3_F - 1_G</td>
<td>9,443.88</td>
</tr>
<tr>
<td>Vanadium IV (3d)²</td>
<td>3_F - 1_D</td>
<td>7,810.79</td>
</tr>
<tr>
<td></td>
<td>3_F - 3_P</td>
<td>9,044.00</td>
</tr>
<tr>
<td></td>
<td>3_F - 1_G</td>
<td>12,031.3</td>
</tr>
<tr>
<td>Chromium V (3d)²</td>
<td>3_F - 1_D</td>
<td>9,490.51</td>
</tr>
<tr>
<td></td>
<td>3_F - 3_P</td>
<td>10,988.9</td>
</tr>
<tr>
<td></td>
<td>3_F - 1_G</td>
<td>14,618.7</td>
</tr>
<tr>
<td>Manganese VI (3d)²</td>
<td>3_F - 1_D</td>
<td>11,170.3</td>
</tr>
<tr>
<td></td>
<td>3_F - 3_P</td>
<td>12,933.9</td>
</tr>
<tr>
<td></td>
<td>3_F - 1_G</td>
<td>17,206.1</td>
</tr>
<tr>
<td>Iron VII (3d)²</td>
<td>3_F - 1_D</td>
<td>12,850.0</td>
</tr>
<tr>
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<td>3_F - 3_P</td>
<td>14,878.8</td>
</tr>
<tr>
<td></td>
<td>3_F - 1_G</td>
<td>19,793.5</td>
</tr>
<tr>
<td>Vanadium I (3d)³(4s)²</td>
<td>4_F - 4_P</td>
<td>8,363.25</td>
</tr>
<tr>
<td>Chromium IV (3d)³</td>
<td>4_F - 4_P</td>
<td>10,308.2</td>
</tr>
<tr>
<td>Manganese V (3d)³</td>
<td>4_F - 4_P</td>
<td>12,253.2</td>
</tr>
<tr>
<td>Multiplet Separation</td>
<td>Calculated Separation</td>
<td>Observed Separation</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Iron VI (3d)³ 4F - 4F</td>
<td>14,198.1 cm⁻¹</td>
<td>18,169. cm⁻¹</td>
</tr>
<tr>
<td>Cobalt VII (3d)³ 4F - 4F</td>
<td>16,143.1</td>
<td>20,271.</td>
</tr>
<tr>
<td>Cobalt I (3d)⁷(4s)² 4F - 4P</td>
<td>13,420.1</td>
<td>13,068.98</td>
</tr>
<tr>
<td>Nickel I (3d)⁸(4s)² 3F - 3P</td>
<td>14,684.4</td>
<td>14,604.17</td>
</tr>
</tbody>
</table>

The "observed separations" were gotten in all cases by averaging the fine structure splittings in the levels concerned. The experimental data was taken from:

GRAPH II
MULTIPLET SEPARATION ENERGIES
FOR 3d\(^n\) CONFIGURATION
APPENDIX I

The \( L \) functions are defined by:

\[
L_{ij}^{k}(a,b) = \int_0^{\infty} \int_0^{\infty} r_i e^{-ar} \frac{r(a) e^{-br}}{r(b)^{k+1}} \left[ e^{-br'} r^2 \left( \frac{r}{r'} \right)^{k+1} \right] dr \, dr'
\]

where by definition \( r(a) \) is the larger and \( r(b) \) the smaller of \( r \) and \( r' \). They have been computed for values of \( i, j \) and \( k \) from one to four. This was done with the hope that it would facilitate future atomic calculations which employ radial one-electron functions of the form:

\[
R_{nl}(r) = \sum_k C_k r^k e^{-Zkr}
\]

It will be noted that some combinations of \( i, j \) and \( k \) have not been computed because of the fact and specific properties of the \( a^k \)'s and \( b^k \)'s coupled with the wavefunctions of Eq. (34).

\[
L_{ij}^{00}(a,b) = \frac{2}{a^2 b^3} - \frac{2}{(a+b)^3 b^2} - \frac{2}{(a+b)^2 b^3}
\]

\[
L_{ij}^{10} = \frac{4}{a^3 b^3} - \frac{6}{(a+b)^4 b^2} - \frac{4}{(a+b)^3 b^3}
\]

\[
L_{ij}^{20} = \frac{312}{a^4 b^3} - \frac{41}{(a+b)^5 b^2} - \frac{312}{(a+b)^4 b^3}
\]

\[
L_{ij}^{30} = \frac{412}{a^5 b^3} - \frac{51}{(a+b)^6 b^2} - \frac{412}{(a+b)^5 b^3}
\]
\[ 0L^{40} = \frac{512}{a^6b^3} - \frac{6!}{(a+b)^7b^2} - \frac{5!2}{(a+b)^6b^3} \]

\[ 0L^{11} = \frac{312}{a^3b^4} - \frac{6!}{(a+b)^5b^2} - \frac{5!}{(a+b)^4b^3} - \frac{312}{(a+b)^3b^4} \]

\[ 0L^{21} = \frac{313!}{a^4b^5} - \frac{5!}{(a+b)^6b^2} - \frac{4!4}{(a+b)^5b^3} - \frac{3!3!}{(a+b)^4b^4} \]

\[ 0L^{31} = \frac{413!}{a^3b^6} - \frac{6!}{(a+b)^7b^2} - \frac{5!4}{(a+b)^6b^3} - \frac{4!3!}{(a+b)^5b^4} \]

\[ 0L^{41} = \frac{513!}{a^2b^7} - \frac{7!}{(a+b)^8b^2} - \frac{6!4}{(a+b)^7b^3} - \frac{5!3!}{(a+b)^6b^4} \]

\[ 0L^{22} = \frac{413!}{a^3b^5} - \frac{6!}{(a+b)^7b^2} - \frac{6!}{(a+b)^6b^3} - \frac{4!18}{(a+b)^5b^4} - \frac{4!3!}{(a+b)^4b^5} \]

\[ 0L^{32} = \frac{414!}{a^2b^6} - \frac{7!}{(a+b)^8b^2} - \frac{6!6}{(a+b)^7b^3} - \frac{5!18}{(a+b)^6b^4} - \frac{4!4!}{(a+b)^5b^5} \]

\[ 0L^{42} = \frac{514!}{a^5b^5} - \frac{8!}{(a+b)^9b^2} - \frac{7!6}{(a+b)^8b^3} - \frac{6!18}{(a+b)^7b^4} - \frac{5!4!}{(a+b)^6b^5} \]

\[ 0L^{33} = \frac{514!}{a^5b^6} - \frac{8!}{(a+b)^9b^2} - \frac{8!}{(a+b)^8b^3} - \frac{6!36}{(a+b)^7b^4} - \frac{5!14!}{(a+b)^6b^5} - \frac{5!4!}{(a+b)^5b^6} \]

\[ 0L^{43} = \frac{515!}{a^6b^6} - \frac{9!}{(a+b)^10b^2} - \frac{8!8}{(a+b)^9b^3} - \frac{7!36}{(a+b)^8b^4} - \frac{6!14!}{(a+b)^7b^5} \]

\[ 0L^{44} = \frac{515!}{a^7b^7} - \frac{10!}{(a+b)^11b^2} - \frac{9!10}{(a+b)^10b^3} - \frac{8!60}{(a+b)^9b^4} - \frac{7!5!2}{(a+b)^8b^5} \]

(The text continues with annotations and corrections)
\[
\begin{align*}
1^{00} & = 3! \left[ \frac{1}{a^4 b^4} - \frac{1}{(a+b)^2 b^2} - \frac{1}{(a+b)^3 b^3} - \frac{1}{(a+b)^4 b^4} \right] \\
1^{10} & = 3! \left[ \frac{1}{a^2 b^4} - \frac{3}{(a+b)^4 b^2} - \frac{2}{(a+b)^3 b^3} - \frac{1}{(a+b)^2 b^4} \right] \\
1^{11} & = 3! \left[ \frac{4}{a^2 b^5} - \frac{4}{2(a+b)^5 b^2} - \frac{3}{2(a+b)^4 b^3} - \frac{8}{(a+b)^3 b^4} - \frac{4}{(a+b)^2 b^5} \right] \\
1^{21} & = 3! \left[ \frac{8}{a^3 b^5} - \frac{5}{2(a+b)^6 b^2} - \frac{4}{(a+b)^5 b^3} - \frac{4}{(a+b)^4 b^4} - \frac{8}{(a+b)^3 b^5} \right] \\
1^{31} & = 3! \left[ \frac{4}{a^4 b^5} - \frac{6}{2(a+b)^7 b^2} - \frac{5}{(a+b)^6 b^3} - \frac{4}{(a+b)^5 b^4} - \frac{4}{(a+b)^4 b^5} \right] \\
1^{41} & = 3! \left[ \frac{4}{a^5 b^5} - \frac{7}{2(a+b)^8 b^2} - \frac{6}{(a+b)^7 b^3} - \frac{5}{(a+b)^6 b^4} - \frac{4}{(a+b)^5 b^5} \right] \\
1^{22} & = 3! \left[ \frac{40}{a^3 b^6} - \frac{6}{2(a+b)^7 b^2} - \frac{5}{(a+b)^6 b^3} - \frac{5}{(a+b)^5 b^4} - \frac{5}{(a+b)^4 b^5} \right] \\
1^{32} & = 3! \left[ \frac{5}{a^4 b^6} - \frac{7}{(a+b)^8 b^2} - \frac{6}{(a+b)^7 b^3} - \frac{5}{(a+b)^6 b^4} - \frac{5}{(a+b)^5 b^5} \right] \\
1^{42} & = 3! \left[ \frac{5}{a^5 b^6} - \frac{8}{2(a+b)^9 b^2} - \frac{7}{(a+b)^8 b^3} - \frac{6}{(a+b)^7 b^4} - \frac{5}{(a+b)^6 b^5} \right] \\
1^{33} & = 3! \left[ \frac{6}{a^4 b^7} - \frac{8}{2(a+b)^9 b^2} - \frac{7}{(a+b)^8 b^3} - \frac{6}{(a+b)^7 b^4} - \frac{5}{(a+b)^6 b^5} \right]
\end{align*}
\]
\[ \begin{align*}
L^{43} &= 3! \left[ \frac{6}{a_5^5 b_7^7} \frac{9}{2(a+b)^{10} b_2^2} - \frac{8}{(a+b)^9 b_3^3} - \frac{7}{(a+b)^8 b_4^4} - \frac{6}{(a+b)^7 b_5^5} \right] \\
&\quad - \frac{5}{(a+b)^6 b_6^6} - \frac{4}{(a+b)^5 b_7^7} \\
L^{44} &= 3! \left[ \frac{7}{a_5^5 b_8^8} - \frac{10}{2(a+b)^{11} b_2^2} - \frac{9}{(a+b)^{10} b_3^3} - \frac{8}{(a+b)^9 b_4^4} - \frac{8}{(a+b)^8 b_5^5} - \frac{7}{(a+b)^7 b_6^6} - \frac{6}{(a+b)^6 b_7^7} - \frac{5}{(a+b)^5 b_8^8} \right] \\
L^{22} &= 6! \left[ \frac{1}{a_2^2 b_7^7} - \frac{5}{(a+b)^7 b_2^2} - \frac{4}{(a+b)^6 b_3^3} - \frac{3}{(a+b)^5 b_4^4} - \frac{2}{(a+b)^4 b_5^5} - \frac{1}{(a+b)^3 b_6^6} \right] \\
L^{32} &= 6! \left[ \frac{2}{a_3^3 b_7^7} - \frac{35}{(a+b)^8 b_2^2} - \frac{30}{(a+b)^7 b_3^3} - \frac{20}{(a+b)^6 b_4^4} - \frac{12}{(a+b)^5 b_5^5} - \frac{6}{(a+b)^4 b_6^6} - \frac{2}{(a+b)^3 b_7^7} \right] \\
L^{42} &= 6! \left[ \frac{6}{a_4^4 b_7^7} - \frac{280}{(a+b)^9 b_2^2} - \frac{210}{(a+b)^8 b_3^3} - \frac{120}{(a+b)^7 b_4^4} - \frac{60}{(a+b)^6 b_5^5} - \frac{24}{(a+b)^5 b_6^6} - \frac{6}{(a+b)^4 b_7^7} \right] \\
L^{33} &= 7! \left[ \frac{2}{a_3^3 b_8^8} - \frac{35}{(a+b)^9 b_2^2} - \frac{40}{(a+b)^8 b_3^3} - \frac{30}{(a+b)^7 b_4^4} - \frac{20}{(a+b)^6 b_5^5} - \frac{12}{(a+b)^5 b_6^6} - \frac{6}{(a+b)^4 b_7^7} - \frac{2}{(a+b)^3 b_8^8} \right] \\
L^{43} &= 7! \left[ \frac{6}{a_4^4 b_8^8} - \frac{320}{(a+b)^{10} b_2^2} - \frac{320}{(a+b)^9 b_3^3} - \frac{210}{(a+b)^8 b_4^4} - \frac{120}{(a+b)^7 b_5^5} - \frac{60}{(a+b)^6 b_6^6} - \frac{24}{(a+b)^5 b_7^7} - \frac{6}{(a+b)^4 b_8^8} \right] \\
L^{44} &= 8! \left[ \frac{6}{a_4^4 b_9^9} - \frac{450}{(a+b)^{11} b_2^2} - \frac{450}{(a+b)^{10} b_3^3} - \frac{330}{(a+b)^9 b_4^4} - \frac{210}{(a+b)^8 b_5^5} - \frac{120}{(a+b)^7 b_6^6} - \frac{60}{(a+b)^6 b_7^7} - \frac{24}{(a+b)^5 b_8^8} - \frac{6}{(a+b)^4 b_9^9} \right] \\
\end{align*} \]
\[ 3^L_{33} = 8! \left[ \frac{1}{a^2 b^9} - \frac{7}{(a+b)^9 b^2} - \frac{7}{(a+b)^8 b^3} - \frac{5}{(a+b)^7 b^4} - \frac{5}{(a+b)^6 b^5} \right. \\
\left. \frac{4}{(a+b)^5 b^6} - \frac{3}{(a+b)^4 b^7} - \frac{2}{(a+b)^3 b^8} - \frac{1}{(a+b)^2 b^9} \right] \]

\[ 3^L_{43} = 8! \left[ \frac{2}{a^3 b^9} - \frac{63}{(a+b)^6 b^2} - \frac{56}{(a+b)^5 b^3} - \frac{42}{(a+b)^4 b^4} - \frac{30}{(a+b)^3 b^5} \right. \\
\left. \frac{20}{(a+b)^2 b^6} - \frac{12}{(a+b)^3 b^7} - \frac{6}{(a+b)^4 b^8} - \frac{2}{(a+b)^5 b^9} \right] \]

\[ 3^L_{44} = 9! \left[ \frac{2}{a^3 b^{10}} - \frac{70}{(a+b)^9 b^2} - \frac{70}{(a+b)^8 b^3} - \frac{56}{(a+b)^7 b^4} - \frac{42}{(a+b)^6 b^5} \right. \\
\left. \frac{30}{(a+b)^5 b^6} - \frac{20}{(a+b)^4 b^7} - \frac{12}{(a+b)^3 b^8} - \frac{6}{(a+b)^2 b^9} - \frac{2}{(a+b) b^{10}} \right] \]

\[ 4^L_{44} = 10! \left[ \frac{1}{a^2 b^{11}} - \frac{9}{(a+b)^{10} b^2} - \frac{9}{(a+b)^9 b^3} - \frac{8}{(a+b)^8 b^4} - \frac{7}{(a+b)^7 b^5} \right. \\
\left. \frac{6}{(a+b)^6 b^6} - \frac{5}{(a+b)^5 b^7} - \frac{4}{(a+b)^4 b^8} - \frac{3}{(a+b)^3 b^9} - \frac{2}{(a+b)^2 b^{10}} - \frac{1}{(a+b) b^{11}} \right] \]
APPENDIX II

The constants $c_k$ from Eq. (34) are determined from orthogonality and normalization conditions upon the radial parts of the one-electron wave functions.

\[
c_1^2 = 4z_1^3
\]

\[
c_2/c_3 = -\frac{(z_1 + z_2)^4}{3(2z_1)^3}
\]

\[
c_2^2 = \frac{1}{\left[ \frac{8(z_1 + z_2)^8}{3(2z_2)^5(2z_1)^6} - \frac{2}{(2z_1)^3} \right]}
\]

\[
c_4^2 = \frac{(2z_2)^5}{24}
\]

\[
c_5^2 = \frac{1}{\left[ -\frac{240}{(z_2 + z_3)} \frac{b c d^2}{(ce-br)^2} + 24 \frac{c_2^2 \ d^2}{(2z_2)^5(ce-br)^2} + \frac{720}{(2z_3)^7(ce-br)^2} \ - \frac{1}{(2z_1)^3} \right]}
\]

\[
b = \frac{24c_3}{(2z_2)^5} \quad \frac{6c_2}{(z_1 + z_2)^4} \quad \quad c = \frac{24c_2}{(z_1 + z_3)^5} \quad \frac{120 c_3}{(z_1 + z_2)^4} \quad \quad d = \frac{1}{c_1^2} \quad e = \frac{6}{(z_1 + z_2)^4} \quad f = \frac{24}{(z_1 + z_3)^5}
\]
\[ c_6 = \frac{-cd}{ce-bf} c_5 \]

\[ c_7 = \frac{bd}{ce-bf} c_5 \]

\[ c_8 = \frac{1}{24 \left[ \frac{6(z_2+z_3)^{12}}{5(z_2)^5(z_3)^7} - 1 \right]} \]

\[ c_9 = \frac{1}{720(z_3)^7 - \frac{600(z_2)^5}{(z_2+z_3)^{12}}} \]

\[ c_{10} = \frac{8}{45} z_4^7 \]