

Relativistic Electronic Structure in Crystals. I. Theory*

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A relativistic generalization of the augmented-plane-wave (APW) method is presented. The upper components of a Dirac plane wave are joined continuously on the Slater sphere to a linear expansion of central-field Dirac orbitals. The lower components of the functions in the two regions are discontinuous. A variational expression for the energy which is appropriate for this type of basis function is developed. The matrix elements between these relativistic APW's are derived and compared with the nonrelativistic case.

INTRODUCTION

AN increasing number of references in the current literature dealing with the electronic states in crystals have attempted to include relativistic effects. Most of these calculations begin with the two-component Hamiltonian which results from application of the Foldy-Wouthuysen transformation to the Dirac Hamiltonian.¹ This yields three relativistic correction terms to the nonrelativistic Hamiltonian: mass velocity, Darwin, and spin-orbit coupling. The spin-orbit term is the only one which mixes spinor components. The other two are radial functions which are simply corrections to the nonrelativistic crystal potential. By absorbing these radial terms in the Fourier coefficients of the pseudopotential, Anderson and Gold² were able to fit experimental de Haas-van Alphen data for lead by adjusting several parameters, one of which was the spin-orbit parameter. Herman, *et al.*^{3,4} have considered the corrections to the band structure of tetrahedrally bonded semiconductors due to all three of the relativistic corrections. Mattheiss and Watson⁵ have shown that the spin-orbit interaction term can (by an appropriate choice of the spin-orbit parameter) lead to band splitting in *W* which is of the same magnitude as determined experimentally by Walsh.⁶ Scop⁷ has included mass-velocity and spin-orbit perturbation corrections in an augmented-plane-wave (APW) calculation of the band structure of AgCl and AgBr.

Conklin, Johnson, and Pratt^{8,9} have used the relativistic Hamiltonian discussed above for lead telluride

with a linear variation function consisting of eigenfunctions determined from a nonrelativistic APW calculation. The first complete formulation of the relativistic theory for energy bands in crystals was reported recently by Soven.¹⁰ His approach was to generalize the orthogonalized-plane-wave method (OPW) by orthogonalizing four-component Dirac plane waves to the four-component central-field solutions of the core states. The results of this theory compare favorably with the experimental data available for thallium. More recently a theory of spin-orbit interaction in metals has been presented by Animalu.¹¹ It is essentially a generalization of the model potential of Heine and Abarenkov¹² which takes into account the observed spin-orbit splitting of atomic levels. This experimental information is used to evaluate quantities in the crystal theory which otherwise require a knowledge of the crystal potential near the core.

The theory presented here is the relativistic generalization of the Slater¹³ APW method. The basis function consists of an expansion of four-component central-field orbitals of the Dirac Hamiltonian inside the Slater sphere and a Dirac plane wave outside. The expansion coefficients are chosen such that the upper (large) components of the two functions in each region are continuous on the Slater sphere. As a result the lower (small) components of this relativistic APW (RAPW) are discontinuous on this boundary. A variational expression for the energy which is suitable for this type of function is developed.

Matrix elements between the states arising in a reciprocal lattice expansion of the wave function are evaluated. The resulting expression is very similar to the nonrelativistic APW theory. Using this method, relativistic calculations can be performed as easily as nonrelativistic calculations. Hence all of the advantages of the APW method are available with the added benefit that the procedure is completely relativistic. The size of the basis set is necessarily doubled by the inclusion of both spin states, but as Soven¹⁰ has pointed out in the relativistic OPW theory there are relations among the matrix elements which allow the triangularization procedure to be carried out for two rows simultaneously.

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⁴ F. Herman, *Physics of Semiconductors* (Dunod et Cie., Paris, 1964), p. 3.

⁵ L. F. Mattheiss and R. E. Watson, *Phys. Rev. Letters* **13**, 526 (1964).

⁶ W. M. Walsh, Jr., and C. C. Grimes, *Phys. Rev. Letters* **13**, 523 (1964).

⁷ P. M. Scop, Massachusetts Institute of Technology, Quarterly Progress Report No. 54, SSMTG, 1964 (unpublished).

⁸ J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., *Phys. Rev.* **137**, A1282 (1965).

⁹ J. B. Conklin, Jr., Massachusetts Institute of Technology, Technical Report No. 1, 1964 (unpublished).

¹⁰ P. Soven, *Phys. Rev.* **137**, A1706 (1965).

¹¹ A. O. E. Animalu (to be published).

¹² V. Heine and I. Abarenkov, *Phil. Mag.* **9**, 451 (1964).

¹³ J. C. Slater, *Phys. Rev.* **51**, 846 (1937).

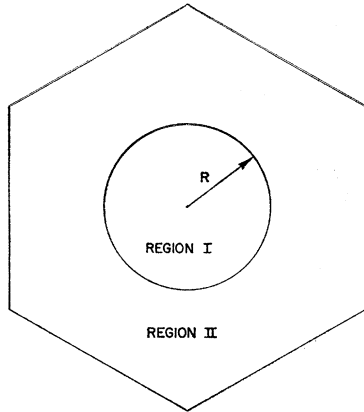


FIG. 1. Unit cell in crystal showing Slater sphere.

In this paper only the theory will be presented. Although the calculations for tungsten are nearly completed, it was felt that the method itself should be made available as soon as possible so that others could take advantage of its relative ease of application. The preliminary results for tungsten are very encouraging, however, since it has been possible to perform *ab initio* calculations which predict the observed spin-orbit splitting of the energy bands. The complete relativistic calculation of the Fermi surface of tungsten will be presented in a later companion article.

THEORY

Form of the RAPW

Let us consider a unit cell which contains only one Slater sphere (Fig. 1). Our results can easily be generalized to more than one sphere. In region II the potential is zero and the wave function in this region is

$$\Psi_{nm}^{\text{II}} = \left(\frac{k_n^* + 1}{2k_n^*} \right)^{1/2} \begin{pmatrix} \chi(m) \\ \sigma \cdot \mathbf{k}_n \\ k_n^* + 1 \end{pmatrix} e^{i\mathbf{k}_n \cdot \mathbf{r}} \quad (m = \pm \frac{1}{2}). \quad (1)$$

The normalization is one particle per unit volume.¹⁴ $k_n^* = (k_n^2 + 1)^{1/2}$. \mathbf{k}_n is the reciprocal space vector, $\mathbf{k} + \mathbf{K}_n$. σ is the usual notation for the Pauli matrices, and $\chi(\pm \frac{1}{2})$ are the Pauli spinors.¹ The Dirac Hamiltonian is

$$H = \alpha \cdot \mathbf{p} + \beta + V. \quad (2)$$

For zero potential the eigenvalue equation is

$$H \Psi_{nm}^{\text{II}} = k_n^* \Psi_{nm}^{\text{II}}. \quad (3)$$

In region I the wave function is a linear combination of the central field orbitals¹⁵:

$$\Psi_{nm}^{\text{I}} = \sum_{\kappa\mu} A_{\kappa\mu}{}^{nm} \begin{pmatrix} g_{\kappa}(r) & \chi_{\kappa}{}^{\mu} \\ i f_{\kappa}(r) & \chi_{-\kappa}{}^{\mu} \end{pmatrix}. \quad (4)$$

¹⁴ Units are $m = c = \hbar = 1$. Later in the paper we will convert to atomic units with $e^2 = 2$, $m = \frac{1}{2}$, and $\hbar = 1$.

¹⁵ The subscripts nm are in anticipation of the joining requirement which will be discussed.

TABLE I. C coefficients $C(l\frac{1}{2}j; m - m_2, m_2)$.

	$m_2 = +\frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j = l + \frac{1}{2}$	$\left(\frac{l + m + \frac{1}{2}}{2l + 1} \right)^{1/2}$	$\left(\frac{l - m + \frac{1}{2}}{2l + 1} \right)^{1/2}$
$j = l - \frac{1}{2}$	$-\left(\frac{l - m + \frac{1}{2}}{2l + 1} \right)^{1/2}$	$\left(\frac{l + m + \frac{1}{2}}{2l + 1} \right)^{1/2}$

The spin-angular functions $\chi_{\kappa}{}^{\mu}$ are

$$\chi_{\kappa}{}^{\mu} = \sum_{m = \pm \frac{1}{2}} C(l\frac{1}{2}j; \mu - m, m) Y_{l}{}^{\mu - m}(\hat{r}) \chi(m) \quad (5)$$

and they have the properties

$$(\sigma \cdot \mathbf{l} + 1) \chi_{\kappa}{}^{\mu} = -\kappa \chi_{\kappa}{}^{\mu}, \quad (6)$$

$$\sigma \cdot \hat{r} \chi_{\kappa}{}^{\mu} = -\chi_{-\kappa}{}^{\mu}. \quad (7)$$

These functions are orthonormal in the sense that

$$\int \chi_{\kappa}{}^{\mu \dagger} \chi_{\kappa'}{}^{\mu'} \sin \theta d\theta d\phi = \delta_{\mu\mu'} \delta_{\kappa\kappa'}. \quad (8)$$

The C coefficients as given by Rose¹ are reproduced in Table I for completeness. Notice that they satisfy

$$\sum_{m_2 = \pm \frac{1}{2}} C^2(j) = 1. \quad (9)$$

The radial functions are solutions of the following coupled linear differential equations:

$$\frac{df}{dr} = \frac{(\kappa - 1)f}{r} - (W - 1 - V)g, \quad (10)$$

$$\frac{dg}{dr} = (W - V + 1)f - \frac{(\kappa + 1)g}{r}. \quad (11)$$

The expansion coefficients $A_{\kappa\mu}{}^{nm}$ are chosen such that the upper components of Ψ_{nm}^{I} and Ψ_{nm}^{II} are equal on the Slater sphere. This is easily done if the plane wave is expanded in terms of the spin-angular functions. The result is¹

$$\Psi_{nm}^{\text{II}} = \sum_{\kappa\mu} a_{\kappa\mu}{}^{nm} \begin{pmatrix} j_l(k_n r) \chi_{\kappa}{}^{\mu} \\ \frac{ik_n S_{\kappa}}{k_n^* + 1} j_{l'}(k_n r) \chi_{-\kappa}{}^{\mu} \end{pmatrix}, \quad (12)$$

where

$$a_{\kappa\mu}{}^{nm} = 4\pi i^l \left(\frac{k_n^* + 1}{2k_n^*} \right)^{1/2} C(l\frac{1}{2}j; \mu - m, m) Y_{l}{}^{\mu - m}(\hat{k}_n). \quad (13)$$

$j_l(x)$ is a spherical Bessel function. S_{κ} means "sign of κ ." The κ summation is over all positive and negative integers (not zero). j , l , and l' are specified by κ ac-

cording to the rules

$$\begin{aligned} l = \kappa, \quad j = l - \frac{1}{2}, \quad l' = \kappa - 1 \quad (\kappa > 0), \\ l = -\kappa - 1, \quad j = l + \frac{1}{2}, \quad l' = -\kappa \quad (\kappa < 0). \end{aligned} \quad (14)$$

For fixed κ , the μ summation is between j and $-j$.

The expansion coefficient is taken to be

$$A_{\kappa\mu}{}^{nm} = a_{\kappa\mu}{}^{nm} [j_l(k_n R) / g_\kappa(R)], \quad (15)$$

which establishes the desired continuity of the upper components. The lower components, however, are discontinuous on the Slater sphere. Before forming matrix elements between the RAPW's, it is necessary to consider the appropriate variational expression for the energy.

Variational Expression for the Energy

The Dirac Hamiltonian has been shown by Swirles¹⁶ to yield a variational expression for the energy if an infinite region is considered. Schlosser and Marcus¹⁷ have developed variational expressions which apply to nonrelativistic trial wave functions which are discontinuous on a surface inside the unit cell. We will consider the combined situation of a relativistic trial function discontinuous on the Slater sphere.

From the divergence theorem we have

$$\int_{\Omega} \nabla \cdot (\phi^\dagger \alpha \Psi) d\tau = \int_S \phi^\dagger \alpha \cdot \hat{n} \Psi d\sigma. \quad (16)$$

The volume integration is over regions I and II of the unit cell. In region I the outward unit normal \hat{n} is equal to \hat{r} . In region II it is in the opposite direction. The surface integration in both cases is over the Slater sphere. Expanding the integrand of the left-hand side, it is easy to show that

$$\int_{\Omega} \phi^\dagger \alpha \cdot \nabla \Psi d\tau = - \int_{\Omega} (\Psi^\dagger \alpha \cdot \nabla \phi)^* d\tau + \int_S \phi^\dagger \alpha \cdot \hat{n} \Psi d\sigma. \quad (17)$$

Setting $\hat{p} = -i\nabla$ and using the Hermiticity of $\beta + V$, we find

$$\int_{\Omega} \phi^\dagger H \Psi d\tau = \int_{\Omega} (\Psi^\dagger H \phi)^* d\tau - i \int_S \phi^\dagger \alpha \cdot \hat{n} \Psi d\sigma. \quad (18)$$

A comparison of the above surface term and the analogous term in the nonrelativistic theory¹⁷ leads us to assume the following form for the energy:

$$\begin{aligned} W \int_{\Omega} \Psi^\dagger \Psi d\tau = \int_{\Omega} \Psi^\dagger H \Psi d\tau - (i/2) \\ \times \int_S (\Psi^{\text{II}} + \Psi^{\text{I}})^\dagger \alpha \cdot \hat{r} (\Psi^{\text{II}} - \Psi^{\text{I}}) d\sigma, \end{aligned} \quad (19)$$

where Ψ^{I} and Ψ^{II} are the forms of the trial function in regions I and II, respectively. It is implied that in the volume integrations the appropriate form of Ψ is to be used in each region. It is not difficult to show that this expression has the desired properties: W is both variational and real for arbitrary trial functions Ψ^{I} and Ψ^{II} . In the following section the matrix elements between RAPW's corresponding to different wave vectors and different spin states will be determined using the above variational expression.

RAPW Matrix Elements

If we expand the crystal wave function in a linear combination of RAPW's (a reciprocal lattice expansion), then the secular equation is

$$\begin{aligned} \left| M \begin{pmatrix} NM \\ nm \end{pmatrix} \right| \\ = \left| H \begin{pmatrix} NM \\ nm \end{pmatrix} - W Q \begin{pmatrix} NM \\ nm \end{pmatrix} - S \begin{pmatrix} NM \\ nm \end{pmatrix} \right| = 0, \end{aligned} \quad (20)$$

where

$$H \begin{pmatrix} NM \\ nm \end{pmatrix} = \int_{\Omega} \Psi_{nm}^\dagger H \Psi_{NM} d\tau, \quad (21)$$

$$Q \begin{pmatrix} NM \\ nm \end{pmatrix} = \int_{\Omega} \Psi_{nm}^\dagger \Psi_{NM} d\tau, \quad (22)$$

$$\begin{aligned} S \begin{pmatrix} NM \\ nm \end{pmatrix} = (i/2) \int_S (\Psi_{nm}^{\text{II}} + \Psi_{nm}^{\text{I}})^\dagger \alpha \cdot \mathbf{r} \\ \times (\Psi_{NM}^{\text{II}} - \Psi_{NM}^{\text{I}}) d\sigma. \end{aligned} \quad (23)$$

We consider first the Hamiltonian and overlap matrix elements. For convenience the energy parameter W in the central-field orbital equations [Eqs. (10) & (11)] is identified with the crystal eigenvalue in the secular equation. This simplifies the expression for the matrix elements because the volume integration of $(H - W)$ over region I is identically zero. However, the price we pay is that the final form of the matrix elements will have an implicit dependence on the energy parameter.

In the outer region the eigenvalue of the Hamiltonian is k_N^* . The first two terms in the secular equation can therefore be written

$$H \begin{pmatrix} NM \\ nm \end{pmatrix} - W Q \begin{pmatrix} NM \\ nm \end{pmatrix} = (k_N^* - W) Q^{\text{II}} \begin{pmatrix} NM \\ nm \end{pmatrix}, \quad (24)$$

where the superscript indicates that the volume integration is only over region II. It can be shown using Ψ^{II}

¹⁶ B. Swirles, Proc. Roy. Soc. (London) **152**, 625 (1935).

¹⁷ H. Schlosser and P. M. Marcus, Phys. Rev. **131**, 2529 (1963).

from Eq. (1) that

$$Q^{\text{II}}\left(\begin{matrix} NM \\ nm \end{matrix}\right) = \Omega \delta_{nN} \delta_{mM} - 4\pi R^2 \frac{j_1(|\mathbf{k}_N - \mathbf{k}_n| R)}{|\mathbf{k}_N - \mathbf{k}_n|} \left(\frac{k_n^* + 1}{2k_n^*}\right)^{1/2} \\ \times \left(\frac{k_N^* + 1}{2k_N^*}\right)^{1/2} \left\{ \left[1 + \frac{\mathbf{k}_N \cdot \mathbf{k}_n}{(k_n^* + 1)(k_N^* + 1)} \right] \delta_{mM} \right. \\ \left. + \frac{i \mathbf{k}_n \times \mathbf{k}_N \cdot \langle m | \boldsymbol{\sigma} | M \rangle}{(k_n^* + 1)(k_N^* + 1)} \right\}, \quad (25)$$

where Ω is the volume of the unit cell. The spin-matrix elements are given by

$$\langle \pm | \boldsymbol{\sigma} | \pm \rangle = \pm \hat{e}_z, \quad \langle \pm | \boldsymbol{\sigma} | \mp \rangle = \hat{e}_x \pm i \hat{e}_y. \quad (26)$$

The integration in the surface term of Eq. (23) is over the Slater sphere: $d\sigma = R^2 \sin\theta d\theta d\phi$. Hence all the radial functions are evaluated at $r=R$. We use Ψ^{I} given in Eq. (4) [with A_{κ}^{nm} from Eq. (15)] and Ψ^{II} from Eq. (12). Operating $\boldsymbol{\alpha} \cdot \hat{r}$ on $\Psi^{\text{II}} - \Psi^{\text{I}}$ and performing the angular integrations yields

$$S\left(\begin{matrix} NM \\ nm \end{matrix}\right) = 4\pi R^2 \left(\frac{k_n^* + 1}{2k_n^*}\right)^{1/2} \left(\frac{k_N^* + 1}{2k_N^*}\right)^{1/2} \\ \times \sum_{\kappa} D_{\kappa} \left(\begin{matrix} NM \\ nm \end{matrix}\right) j_{\nu}(k_n R) \left\{ \left(\frac{k_N S_{\kappa}}{k_N^* + 1}\right) j_{\nu}(k_N R) \right. \\ \left. - j_{\nu}(k_n R) \frac{f_{\kappa}(R)}{g_{\kappa}(R)} \right\}, \quad (27)$$

where

$$D_{\kappa} \left(\begin{matrix} NM \\ nm \end{matrix}\right) = 4\pi \sum_{\mu} C(l\frac{1}{2}j; \mu - m, m) C(l\frac{1}{2}j; \mu - M, M) \\ \times Y_{l}^{(\mu - M)\dagger}(\hat{k}_N) Y_{l}^{\mu - m}(\hat{k}_n). \quad (28)$$

The coefficients D_{κ} are evaluated using the addition theorem for spherical harmonics:

$$(2l+1) P_l(\hat{N} \cdot \hat{n}) = 4\pi \sum_{m=-l}^{m=l} Y_l^{m\dagger}(\hat{N}) Y_l^m(\hat{n}). \quad (29)$$

In some instances the necessary expressions are found by applying the orbital-angular-momentum operators to the addition theorem. The results are

$$D_{\kappa} \left(\begin{matrix} N+ \\ n+ \end{matrix}\right) = |\kappa| P_l(\hat{N} \cdot \hat{n}) - i S_{\kappa} (\hat{N} \times \hat{n})_z P_l'(\hat{N} \cdot \hat{n}), \quad (30)$$

$$D_{\kappa} \left(\begin{matrix} N- \\ n+ \end{matrix}\right) = -S_{\kappa} P_l'[(\hat{N} \times \hat{n})_y + i(\hat{N} \times \hat{n})_x], \quad (31)$$

$$D_{\kappa} \left(\begin{matrix} N- \\ n- \end{matrix}\right) = D_{\kappa}^* \left(\begin{matrix} N+ \\ n+ \end{matrix}\right), \quad (32)$$

$$D_{\kappa} \left(\begin{matrix} N+ \\ n- \end{matrix}\right) = -D_{\kappa}^* \left(\begin{matrix} N- \\ n+ \end{matrix}\right). \quad (33)$$

This completes the derivation of the matrix elements. In the next section various simplifications will be considered, and the procedure for the relativistic calculation will be compared to the nonrelativistic APW method.

DISCUSSION

Our results to this point are expressed in relativistic units: $m=c=\hbar=1$. Let us now convert to atomic units with $e^2=2$, $m=\frac{1}{2}$ and $\hbar=1$. The energy will be expressed in the form $W=E+mc^2$, where E is the energy measured with respect to the rest mass in the region of zero potential energy. If we agree to neglect terms of the order $(137)^{-2}$ as compared to unity, the expression for the matrix elements becomes

$$M\left(\begin{matrix} NM \\ nm \end{matrix}\right) = (k_N^2 - E) \Omega_{nN} \delta_{mM} + 4\pi R^2 \\ \times \sum_{\kappa} D_{\kappa} \left(\begin{matrix} NM \\ nm \end{matrix}\right) j_{\nu}(k_n R) \left\{ j_{\nu}(k_N R) \right. \\ \left. \times \left(\frac{c f_{\kappa}(R, E)}{g_{\kappa}(R, E)}\right) - j_{\nu}(k_n R) k_N S_{\kappa} \right\}, \quad (34)$$

where

$$\Omega_{nN} = \Omega \delta_{nN} - 4\pi R^2 \frac{j_1(|\mathbf{k}_N - \mathbf{k}_n| R)}{|\mathbf{k}_N - \mathbf{k}_n|}. \quad (35)$$

In our present units $c=2/\alpha$, where $\alpha \approx 1/137$ is the fine-structure constant. Of course, lengths are in Bohr radii and energies in rydbergs.

By considering the divergence theorem for the case of plane waves in region II, it can be shown that

$$\Omega_{nN} \delta_{mM} (k_N^2 - k_n^2) \\ = 4\pi R^2 \sum_{\kappa} S_{\kappa} D_{\kappa} \left(\begin{matrix} NM \\ nm \end{matrix}\right) \\ \times \{ k_N j_{\nu}(k_n R) j_{\nu}(k_N R) - k_n j_{\nu}(k_N R) j_{\nu}(k_n R) \}. \quad (36)$$

This can be substituted into Eq. (34) to yield an index-symmetric form for the matrix elements:

$$M\left(\begin{matrix} NM \\ nm \end{matrix}\right) = \left(\frac{k_N^2 + k_n^2}{2} - E\right) \delta_{mN} \Omega_{nN} + 4\pi R^2 \sum_{\kappa} D_{\kappa} \left(\begin{matrix} NM \\ nm \end{matrix}\right) \\ \times \left\{ j_{\nu}(k_n R) j_{\nu}(k_N R) \left(\frac{c f_{\kappa}(R, E)}{g_{\kappa}(R, E)}\right) \right. \\ \left. - \frac{1}{2} S_{\kappa} [k_N j_{\nu}(k_n R) j_{\nu}(k_N R) \right. \\ \left. + k_n j_{\nu}(k_N R) j_{\nu}(k_n R)] \right\}. \quad (37)$$

It is interesting to compare the above expression with the nonrelativistic APW matrix elements¹³:

$$\text{APW} \binom{N}{n} = (\mathbf{k}_N \cdot \mathbf{k}_n - E) \Omega_{nN} + 4\pi R^2 \sum_{l=0}^{\infty} (2l+1) P_l(\hat{N} \cdot \hat{n}) \times j_l(k_n R) j_l(k_N R) \frac{u_l'(R, E)}{u_l(R, E)}. \quad (38)$$

Instead of a single sum over atomic orbitals labeled by l , we have the double sum over κ which includes both possible orientations of the spin. In place of the logarithmic derivative of the radial wave function u , it is necessary to evaluate the ratio of the two central-field functions f and g . These satisfy Eqs. (10) and (11), which are repeated here in a convenient form:

$$\frac{d(cf)}{dr} = \left(\frac{\kappa-1}{r} \right) cf - (E-V)g, \quad (39)$$

$$\frac{dg}{dr} = \left(\frac{E-V}{c^2} + 1 \right) cf - \frac{(\kappa+1)}{r} g. \quad (40)$$

The following comparison can be made in the non-relativistic limit:

$$\lim_{c \rightarrow \infty} cf/g = (\kappa+1)/r + u'/u. \quad (41)$$

Methods for solving the coupled equations have been discussed by Hartree¹⁸ and by Rose.¹ For numerical work the Runge-Kutta method and the Milne method are applicable.

The last term on the right-hand side of Eq. (37) does not appear in the nonrelativistic theory, but it increases the necessary computing only trivially because the spherical Bessel functions must also be determined for the preceding term in the expression. Hence the only significant complication which the relativistic theory imposes on the matrix elements is in the coefficients D_κ . Because these are complex one must use complex algebra in triangularizing the secular determinant. Here again, however, the additional computing requirements are negligible.

There is a significant increase in computing time which results from the spin-doubling of the basis set. However, this can be substantially reduced because of the relations between matrix elements indicated in Eqs. (32) and (33). It is found that if the matrix elements are ordered according to the following scheme¹⁰

$$n_{1+}, n_{1-}, n_{2+}, n_{2-}, \text{ etc.}, \quad (42)$$

it is necessary to apply the triangularization procedure only to the odd rows. If $M(i, j)$ is the matrix element as determined by either Eq. (34) or (37), the operation necessary to triangularize the determinant can be written

$$M(i, j) \rightarrow M(i, j) - \sum_{\nu \text{ odd}}^{i-2} \frac{[M^*(\nu, i)M(\nu, j) + (-1)^{j+1}M^*(\nu, j) + (-1)^{i+1}M(\nu, i+1)]}{M(\nu, \nu)}. \quad (43)$$

Because the even rows are not needed, there are gaps in the machine storage of the matrix. It has been found convenient to store the real parts and the imaginary parts each in vectors. There is a one-to-one relation between matrix elements (I, J) in the odd rows (above and including the main diagonal) and the vector component KV , where

$$KV = \frac{(I-1)}{2} \left(N+2 - \left(\frac{I+1}{2} \right) \right) + J - I + 1; \quad (44)$$

N is the dimension of the matrix (two times the number of reciprocal lattice vectors included in the expansion).

The maximum storage locations required for the complex matrix elements using this identification is $2[N(N+2)/4-1]$.

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¹⁸ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).