THE

PHYSICAL REVIEW

*A journal of experimental and theoretical physics established by E. L. Nichols in 1893*

SECOND SERIES, VOL. **188**, NO. 3 15 DECEMBER 1969

# Symmetrized Relativistic Augmented-Plane-Wave Method: Gray Tin and the Warped Muffin-Tin Potential[*]

DALE DEAN KOELLING[†]
*Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
*and*
*Magnetic Theory Group, Physics Department, Northwestern University, Evanston, Illinois 60201*

(Received 30 June 1969)

A symmetrized form of the relativistic augmented-plane wave (RAPW) method is described. This symmetrized relativistic APW technique (SRAPW) uses the double-space-group projection operators to greatly reduce the size of the Hamiltonian matrix that must be dealt with on symmetry points and lines. This enables one to obtain better convergence than can be obtained with the unsymmetrized RAPW technique and identifies the symmetry properties of the states found. The technique has also been generalized to include the effects of a nonconstant potential outside the muffin-tin spheres. The SRAPW method is then applied to gray tin to test a number of potential approximations, including non-self–consistency and the treatment of exchange as well as the various features of the muffin-tin approximation to the model potential. The results show that, of the terms left out of the muffin-tin approximation to the model potential, the additional warping of the potential outside the muffin-tin spheres has the most significant effect.

## I. INTRODUCTION

THE relativistic formulation of the aumented plane wave method[1] (APW) by Loucks[2] has been used with much success by many workers. This relativistic (RAPW) method was obtained by using the relativistic basis functions and rewriting the variational quantity that gave the nonrelativistic method to use the Dirac single-particle equation. The approach has yielded such good results that the RAPW technique has become the most frequently used *ab initio* technique for energy-band calculations of high-$Z$ materials.

There are, however, three good reasons for reformulating the technique to make use of the additional crystal symmetry as was done for the nonrelativistic technique.[3] The first and most obvious reason is the reduction in size of the basis set. This is not only economically desirable—cutting down computation time by over an order of magnitude—but necessary for accuracy and convergence. Second, one can quickly and correctly indentify states, since one knows the transformation properties of the basis functions, and thus of the trial function. The third reason is that the secular determinants will have only first-order roots, which are more widely separated in energy and, hence, easier to locate—a feature that can only be fully appreciated by those who have actually done an RAPW calculation. These advantages of the symmetrized RAPW technique (SRAPW) will exist whenever there exists the additional crystal symmetry, i.e., on the symmetry points, lines, and planes.

The symmetrized relativistic APW (SRAPW) method has been developed using a modified, but equivalent, form of the RAPW matrix elements. This symmetrization is greatly facilitated by the realization that the same RAPW technique can also be obtained by using Pauli spinors in the region outside the muffin-tin spheres in a Foldy-Wouthusen transformed Dirac formalism. (See Appendix A.) The SRAPW method has also been extended to include a more general "warped muffin-tin" potential approximation which requires only that one spherically average the model potential out to

---

[*] Part of this work represents a thesis submitted to the Physics Department, MIT, in partial fulfillment of the requirements for the Ph.D. degree, 1968. Part of this work was supported by the National Science Foundation and Kennecott Copper Corp.

[†] Supported in part by the Advanced Research Projects Agency through the Northwestern University Materials Research Center.

[1] J. C. Slater, Phys. Rev. **92**, 603 (1937).

[2] T. L. Loucks, Phys. Rev. **139**, 1333 (1965); *Augmented Plane Wave Method* (W. A. Benjamin, Inc., New York, 1967).

[3] J. H. Wood, Phys. Rev. **126**, 517 (1962).

the muffin-tin sphere radius.[4] This SRAPW method and its extension to the warped muffin-tin potential is developed in Sec. II.

As a severe test of the SRAPW method, we study the energy-band structure of gray tin. Gray tin has a diamond structure which is nonsymmorphic, so that one is dealing with a more general case than the fcc of bcc materials. Further, the muffin-tin approximation is inadequate for the diamond structure, so that one can study the effects of the various approximations made for the model potential in addition to the various ways of constructing it. This is only possible because the energy-band structure is reasonably well known from experimental data. Groves and Paul[5] first combined successfully the data available to them to create a model band structure into which additional data has fit well.[6] Filling in the positions of the bands away from the Fermi energy bands by using the optical data of Cardona and Pollack,[7] one can set up a set of energy bands to be identified as the experimental data. To fill in any gaps that cannot be assigned directly from experiment, one also has the extensive work of the Herman group[8] using orthogonalized plane-wave techniques.

In all *ab initio* energy-band calculations, the first and most significant problem is the question of what model potential is to be used. It is here that a great deal of the physics is to be included (or omitted), so the approximations used to construct the model potential should be constantly reviewed. The approximation used for constructing the model potential that is currently receiving the most attention is the Slater $\rho^{1/3}$ (Thomas-Fermi) exchange term.[9] The one other approximation which is widely used (and which has not received quite as much attention) is the omission of the self-consistency requirement. This omission leaves one with uncertainties in what atomic configuration should be used to set up the model potential. In this paper, the model potential constructed by overlapping free-atom potentials and charge densities[10] and then using the $\rho^{1/3}$ exchange approximation are adhered to. Other prescriptions do exist, but they are primarily of use for transition metals.[11] Within the model potential prescription used, there are two "parameters" which can be varied; namely, the exchange scale factor and the configuration. (Of course, for gray tin one would expect to find the $sp^3$ configuration to be the "best" choice.) The various calculations done as a result of invoking these choices are described in Table I.

TABLE I. Description of calculations. Lattice constant $a = 12.26664$ a.u. APW sphere radius $R = 2.636227$ a.u.

| Name | Configuration used | Exchange scaling factor |
|---|---|---|
| *SN*1 | $5s\,5p_{1/2}^2\,5p_{3/2}$ | $\frac{2}{3}$ |
| *SN*3 | $5s\,5p_{1/2}^2\,5p_{3/2}$ | 1 |
| *SN*6 | $5s^2\,5p_{1/2}^2$ | 1 |

The other approximations to be dealt with are the two parts of the muffin-tin approximation to the model potential: (a) the use of the constant potential in the region outside the muffin-tin spheres, and (b) the spherical averaging in the inside region. This approximation is usually, but not always,[12,13] used in APW calculations. For the fcc and bcc lattices with a low-$Z$ material, it works very well. However, for diamond-structured materials such as gray tin, the situation is very different. Since two-thirds of the volume in the unit cell is ***outside*** the muffin-tin spheres for this structure, the use of a muffin tin looks like a nearly free-electron model calculation. For example, Kweon[14] had to use the muffin-tin height as a disposable parameter in his calculation for diamond to get the right band gap. The situation is, in fact, much better in diamond than in gray tin, since the lower $Z$ of diamond implies that the outer electrons are more tightly bound to the nucleus and so remain more inside the muffiin-tin spheres. With so much volume outside the muffin-tin spheres, an intermediate approximation between the muffin-tin approximation and the use of the full model potential can be tried. This warped muffin-tin approximation keeps the spherical averaging within the muffin-tin spheres but uses the actual model potential in the region between the spheres. The calculations for the various potentials in both the muffin-tin and the warped muffin-tin approximation are described in Sec. III.

For the diamond-structured gray tin, the warped muffin tin is seen to be not quite adequate, although

---

[4] The term warped muffin tin has been introduced to distinguish between the addition of the correction terms outside the spheres and the "nonspherical" correction terms inside the spheres. Outside the spheres, one is dealing with plane waves and Fourier analyses, whereas inside the spheres one is dealing with spherical harmonic decompositions. Thus, only inside the spheres should the term nonspherical be applied.

[5] S. Groves and W. Paul, in the *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965); Phys. Rev. Letters **11**, 194 (1963).

[6] The newer data has been discussed in a recent paper by A. W. Ewald [Helv. Phys. Acta **41**, 795 (1968)].

[7] M. Cardona, K. L. Shaklee, and F. H. Pollack, Phys. Rev. **154**, 696 (1967); M. Cardona, P. McElroy, F. H. Pollack, and K. L. Shaklee, Solid State Commun. 4, 319 (1966).

[8] F. Herman, R. F. Kortum, C. D. Kuglin, and R. A. Short, *Quantum Theory of Atoms, Molecules, and the Solid State: A Tribute to J. C. Slater* (Academic Press Inc., New York, 1966); J. Phys. Soc. Japan Suppl. **21**, (1966); J. P. Van Dyke and F. Herman, Bull. Am. Phys. Soc. **13**, 413 (1968); and (private communications). F. Herman has kindly made the relativistic OPW data available.

[9] J. C. Slater, Phys. Rev. **81**, 385 (1951); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965); R. Gaspar, Acta Phys. Acad. Sci. Hung. 3, 263 (1954).

[10] D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. **137**, 27 (1965). We are grateful to J. Waber for making all the atomic data available.

[11] S. Wakoh and J. Yamashita, J. Phys. Soc. Japan **21**, 1712 (1966); S. Asana and J. Yamashita, *ibid.* **23**, 714 (1967).

[12] P. D. DeCicco, Phys. Rev. **153**, 931 (1967).

[13] W. E. Rudge, MIT Solid State and Molecular Theory Group, Quarterly Progress Report No. 68, p. 2 (unpublished); Phys. Rev. (to be published).

[14] R. Keown, Phys. Rev. **150**, 568 (1966).

much better than the muffin-tin approximation. As the remaining corrections are small, several adjustment procedures are explored as an alternative to including the nonspherical terms within the muffin-tin spheres (at which point one would be using the full model potential). These calculations are discussed in detail in Sec. IV. Finally, Sec. V discusses the conclusions of this work as it applies to work presently in progress.

## II. METHOD OF CALCULATION

The SRAPW method is based on the use of the full crystal symmetry to form the basis set in a relativistic APW calculation. To formulate the procedure, it is convenient to start with a modified form of the unsymmetrized relativistic APW matrix elements obtained by Loucks[2] for a muffin-tin potential and then add a nonflat potential outside the APW spheres to correct the muffin-tin approximation.[15] The modified form of the matrix elements for the muffin-tin potential problem can be obtained by a Bessel function identity[16] and some recombining of the $\kappa$-sum terms to get a sum on $l$. The matrix elements then take the form

$$
\begin{aligned}
M(\mathbf{k}'s';\mathbf{k}s) &\equiv \langle \mathbf{k}'s' | H-E | \mathbf{k}s\rangle ,\\
&= \langle s' | s\rangle M^{NR}(\mathbf{k}';\mathbf{k}) + \langle s' | M^{SO}(\mathbf{k}';\mathbf{k}) | s\rangle ,\\
M^{NR}(\mathbf{k}';k) &= (\mathbf{k}'\cdot\mathbf{k}-E)U(\mathbf{k}-\mathbf{k}') + (4\pi R^2/\Omega)S(\mathbf{k}-\mathbf{k}')\\
&\quad \times \sum_l P_l(\hat{k}'\cdot\hat{k})j_l(kR)j_l(k'R)\xi_l(E) ,\\
M^{SO}(k';k) &= (i4\pi R^2/\Omega)S(\mathbf{k}-\mathbf{k}')\\
&\quad \times \sum_l P_l'(\hat{k}'\cdot\hat{k})j_l(kR)j_l(k'R)\eta_l(E)\\
&\quad \otimes(\hat{k}'\times\hat{k})\cdot\boldsymbol{\sigma} ,\\
S(\mathbf{k}-\mathbf{k}') &= \sum_t \exp i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{t} ,\\
U(\mathbf{k}-\mathbf{k}') &= \delta_{kk'} - (4\pi R^2/\Omega)S(\mathbf{k}-\mathbf{k}')\\
&\quad \times [j_l(|\mathbf{k}-\mathbf{k}'|R)/|\mathbf{k}-\mathbf{k}'|] ,\\
\xi_l(E) &= l[cf_2(R,E)/g_l(R,E)]\\
&\quad +(l+1)[cf_{-l-1}(R,E)/g_{l-1}(R,E)] ,\\
\eta_l(E) &= cf_l(R,E)/g_l(R,E)\\
&\quad -cf_{-l-1}(R,E)/g_{-l-1}(R,E)-(2l+1)/R .
\end{aligned}
$$

In these expressions, $\Omega$ is the volume of the unit cell, $R$ is the radius of the APW spheres, $\mathbf{t}$ is the position of the atoms within the unit cell, $g_l$ is the large-component radial function, and $f_l$ is the small-component radial function. The expression is written for more than one atom per unit cell of the same species and muffin-tin environment. Thus the $\xi_l$ and $\eta_l$ are the same for each site, and only the structure factor $S$ appears. Thus, for one atom per unit cell, $S=1$.

Writing the matrix elements in this form has a number of advantages. First, the nonrelativistic limit is immediately obvious since $M^{NR}$ is exactly the nonrelativistic matrix element as $c\rightarrow\infty$, because $\xi_l$ becomes $(2l+1)$ times the logarithmic derivative, as it is just a $j$-weighted sum of the spin-up and spin-down logrithmic derivatives. For $c$ finite, $M^{NR}$ contains all the relativistic effects *except* the spin-orbit coupling obtained in the second term. Second, the evaluation of the matrix elements is easier since it has reduced the number of quantities that one must have the computer calculate. The most important result for symmetrization is that the spin factors $\eta_l$ are within the noise of the numerical integration for $l>4$, even for uranium. This allows the truncation of the spin-orbit sum at $l=2$ for tin, resulting in a great savings of array space when symmetry elements are used. Further, the $\xi_l$ can well be represented by a linear fit

$$\xi_l = A_l - Eb_l$$

for $l\geq 4$, since the radial functions are very nearly the Bessel functions, $j_l[r(E+V_0)^{1/2}]$ in their small argument region. In fact, the value of $\xi_l$ for a Bessel function,

$$
\begin{aligned}
A_l &= (2l+1)l/R - [(2l+1)/(2l+3)]RV_0 - \cdots ,\\
b_l &= [(2l+1)/(2l+3)]R - \cdots ,
\end{aligned}
$$

could be used directly. The ability to use a linear fit for $\xi_l$ means that the symmetry elements need not be stored for $l>4$. (The sum was carried out to $l=12$, although $l=6$ was probably sufficient—after all, it required almost no extra computer time.)

The modification of the RAPW matrix elements to include the warping is a very simple task, since they are merely a Fourier analysis in an incomplete space. The potential is now written

$$V(\mathbf{r}) = V_m(\mathbf{r}) + V_1(\mathbf{r}) ,$$

where $V_m$ is the muffin-tin potential and $V_1$ is a correction to the muffin potential which is defined to be zero inside the APW spheres. It is convenient to Fourier expand $V_1$ making explicit use of the knowledge that $V_1$ must be invariant under the transformations that send the crystal into itself, so that

$$
\begin{aligned}
V(\mathbf{r}) &= \sum_n c_n s_n(\mathbf{r}) ,\\
s_n(\mathbf{r}) &= \frac{U(\mathbf{r})}{g}\sum_\alpha \exp i\alpha\mathbf{K}_n\cdot(\mathbf{r}-\boldsymbol{\tau}_\alpha) ,
\end{aligned}
$$

where $\alpha$ indicates a rotation operation from the point

---

[15] The integral techniques used by L. F. Mattheis, Phys. Rev. **133**, 1399 (1964), have been used to set up the muffin-tin potential instead of the differential techniques of Loucks. It should be pointed out that Loucks, in determining the muffin-tin floor by averaging between the muffin-tin and atomic volume radii, makes a small error by including part of the adjacent muffin-tin spheres. This is unnecessary as it is just as easy to average over the true Wigner-Seitz cell.

[16] J. O. Dimmock (private communication); L. F. Mattheis, Phys. Rev. **151**, 1450 (1966).

group of the crystal, $g$ is the order of the point group, and $\boldsymbol{\tau}_\alpha$ is any nonprimitive translation associated with the rotation $\alpha$. The primitive translations are taken care of by the fact that $\mathbf{K}_n$ is a reciprocal lattice vector. The function $U(\mathbf{r})$ is a step function which is zero inside the APW spheres and one outside. It already has the proper symmetry and so need not be symmetrized. There is no conflict in the use of $U$ here and in the expression for RAPW matrix elements, since $U(\mathbf{K})$ is the Fourier transform of $U(\mathbf{r})$.

At this point, the present formulation differs in approach from the calculations of De Cicco[12] and Rudge[13] who do a numerical Fourier analysis. Instad of attempting a numerical integration, the model potential is calculated at a large number of points throughout the unit cell and the $c_n$'s determined by a least-squares-fit procedure. This would amount to a Monte Carlo calculation were sufficient $s_n$'s used. Between 200 and 500 points were used to determine the potential. For gray tin, an additional set of basis functions were added to aid convergence. This is discussed in Appendix B.

To get the proper modification of the matrix elements, we make use of the knowledge that the RAPW matrix element form used can be obtained more easily by working in a Foldy-Wouthusen transformed Dirac formalism. (See Appendix A.) In this way, the region outside the APW spheres is dealt with using a Schrödinger equation and Pauli spinor plane waves. Thus, one merely adds to the muffin-tin matrix elements the plane-wave matrix elements of $V_1$:

$$\langle k's' | V_1 | ks\rangle = \langle s' | s\rangle V_1(\mathbf{k}-\mathbf{k}'),$$

$$V_1(\mathbf{k}-\mathbf{k}') = \frac{1}{g} \sum_{n,\alpha} c_n U(\mathbf{k}-\mathbf{k}'+\alpha\mathbf{K}_n) \exp i\alpha\mathbf{K}_n\cdot\boldsymbol{\tau}_\alpha .$$

These matrix elements are given in Appendix B. As can be seen, they are small, but not negligibly so. One should note that when this term is added into the matrix elements, one is doing a variational calculation with a basis set restricted only by its finite size. It is not perturbation theory that is being applied.

With this modified form of the RAPW method, the inclusion of the additional symmetry can be accomplished straightforwardly by carefully applying projection operator techniques. The Foldy-Wouthusen transformed Dirac formalism is again useful, since we can symmetrize Pauli spinors in the region outside the APW spheres. This was, of course, checked with the results of using the Dirac formalism and then making approximations of the matrix elements. The results were identical, although much harder to obtain. The region inside the APW spheres need not be explicitly dealt with here because the matching condition of the APW basis set takes care of maintaining the symmetry in that region, provided the functions is properly symmetrized in the outside region. Thus one can focus on the transformation properties of Pauli plane-wave spinors. For this spinor

$$\exp i\mathbf{k}\cdot\mathbf{r} \quad |s\rangle,$$

$$|\tfrac{1}{2}\rangle = \begin{pmatrix}1\\0\end{pmatrix} \quad |-\tfrac{1}{2}\rangle = \begin{pmatrix}0\\1\end{pmatrix},$$

the projection operator $P$ is defined as

$$P(\mathbf{k}jpg) = \frac{1}{N}\left(\frac{n_j}{2h}\right)^{1/2} \sum_{H_\mathbf{k}} \Gamma_j{}^*(R)_{pg} R .$$

$H_\mathbf{k}$ indicates the entire subgroup of the space group which leaves the vector $\mathbf{k}$ invariant to within a reciprocal lattice vector. $N$ is the number of unit cells in the crystal—so the translation subgroup in $H_\mathbf{k}$ cancels this factor. $2h$ is the order of the double point group of $H_\mathbf{k}$, $n_j$ is the dimension of the $j$th representation $\Gamma_j(R_\alpha)$. The operator $R_\alpha$ is written

$$R_\alpha = \{\alpha | \mathbf{a}\} D_{1/2}(\alpha),$$

$$D_{1/2}(\alpha) = \exp(-i\tfrac{1}{2}\theta_\alpha \hat{n}_\alpha\cdot\boldsymbol{\sigma}),$$

so its effect on the Pauli plane-wave spinor is

$$R_\alpha' \exp i\mathbf{k}\cdot\mathbf{r} | s\rangle = \exp i\alpha\mathbf{k}\cdot(\mathbf{r}-\mathbf{a}) D_{1/2}(\alpha) | s\rangle .$$

Then the symmetrized spinor is

$$\| ksjpg\rangle = P \exp i\mathbf{k}\cdot r | s\rangle$$

$$= \frac{1}{2N}\left(\frac{n_j}{h}\right)^{1/2} \sum_{H_\mathbf{k}} \Gamma_j{}^*(R_\alpha) \exp i\alpha\mathbf{k}\cdot(\mathbf{r}-\mathbf{a}) \otimes D_{1/2}(\alpha) | s\rangle .$$

The projection operator has been constructed so that it commutes with the Hamiltonian, and it is easily shown using the results of representation theory that

$$P^+ = P \text{ (Hermiticity)},$$

$$P(\mathbf{k},j,p,q) P(\mathbf{k},j',p',q') = \delta_{jj'}\delta_{pp'} \frac{1}{2N} \sum_{H_\mathbf{k}} \Gamma_j(R)_{qq'}{}^* R .$$

This permits the matrix elements for two SRAPW's to be written

$$M^{\mathrm{sym}}(kjpqs; k'j'p'q's') = \delta_{jj'}\delta_{pp'} \frac{1}{2N} \sum_{H_\mathbf{k}} \Gamma_j(R)_{qq'}{}^* \otimes M^{\mathrm{unsym}}[\mathbf{k},s; \alpha\mathbf{k}',(D_{1/2}s)] .$$

Since $k$ and $k'$ must be related by a reciprocal lattice vector to get a nonzero result, the sum on the translation subgroup of $H_\mathbf{k}$ merely cancels the $1/N$ factor, and the operation together with its negative cancel the $\frac{1}{2}$ factor. Thus it becomes obvious that the choice of constants in the projection operator $P$ has been designed to make the matrix element expression as simple as possible. There is no reason not to do this, since the normalization of the basis functions is not needed (or known at this point) to perform the calculation. The possible requirement for $q' \neq q$ can be eliminated by properly choosing the list of vectors to generate one's basis functions so the $q = q'$ matrix elements are the only ones that must appear. In the nonrelativistic SAPW method,[3] the possible appearance of $q' \neq q$ was considered, instead of readjusting the vector list. This would be much less convenient in the relativistic case, since it would interfere with the technique used to deal with several complications caused by the presence of spin.

A further simplification can be included by specializing to crystals with an inversion site and locating our origin at that site. By commuting the symmorphic inversion (or parity) operation with any operation, one finds that all nonprimitive translations are half some primitive translations so that writing

$$\Gamma_j(\{\alpha|\mathbf{a}\}) = \gamma_j(\alpha) \exp(-i\mathbf{a}\cdot\mathbf{k}_{\text{red}}),$$

one can write

$$M^{\text{sym}}(ks;k's') = \sum \gamma_j^*(\alpha)_{qq}\tau(\alpha k')M^{\text{unsym}} \times[\mathbf{k}s;\alpha\mathbf{k}'(D_{1/2}(\alpha)s')],$$

$$\tau(\alpha k') = \exp i\mathbf{a}\cdot(\alpha\mathbf{k}' - \mathbf{k}_{\text{red}}) = \pm 1.$$

In this expression, the sum is over the *single point group* of $H_{\mathbf{k}}$, and the indices $j = j'$, $p = p'$, and $q = q'$ have been suppressed. $\mathbf{k}_{\text{red}}$ is the reduced $\mathbf{k}$ vector (i.e., in the first Brillouin zone), so $\alpha\mathbf{k}' - \mathbf{k}_{\text{red}}$ must be a reciprocal lattice vector. Note that the spin-state of the initial RAPW is used to label the projected SRAPW. This is a useful but arbitrary convention, since the projection operator in general mixes RAPW's with different spins. Some difficulty is encountered due to the existence of this index, since one must check whether one gets 0, 1, or 2 linearly independent functions by projection from the two RAPW's with the same $k$ vector but different spins.

To account for time reversal symmetry, it is convenient to introduce an operator $Q$ which is the product of the time reversal operator and the inversion (or parity) operator. The operator $Q$ is an anti-unitary four-dimensional inversion operator which can be called the spin-flip operator, since its effect is to "reverse" the spin of a state. Thus we have

$$\langle s|Q|s\rangle = 0.$$

Using the properties of $Q$, it is possible to show for the definite spin functions such as RAPW's that

$$\langle\uparrow|\uparrow\rangle = \langle\downarrow|\downarrow\rangle^*,$$

$$\langle\downarrow|\uparrow\rangle = -\langle\uparrow|\downarrow\rangle^*.$$

Since $Q$ commutes with the Hamiltonian, its matrix elements have the same symmetry, giving rise to the Kramers degeneracy.[17]

This, however, is not the form that the degeneracy takes when working with SRAPW's. The results required to discuss the form of the Kramer's degeneracy are obtained by showing that

$$QP = P^x Q$$

$$\langle\uparrow|P|\downarrow\rangle = \langle\downarrow|P^x|\downarrow\rangle^*,$$

$$\langle\uparrow|P|\downarrow\rangle = -\langle\downarrow|P^x|\uparrow\rangle^*,$$

where $P^x$ is the projection operator obtained from the representation

$$\Gamma_j^x(\{\alpha|a\}) = \gamma_j^*(\alpha) \exp(-i\alpha\mathbf{k}_{\text{red}}\cdot\mathbf{a}),$$

and all basis vector indices have been suppressed except the spin index. These relations are obtained by a straightforward manipulation. The resulting form of $\Gamma^x$ is a consequence of choosing an inversion site as the origin. Otherwise, a phase factor depending on the nonprimitive translation of the inversion and the operation considered appears.

There are three cases which occur. The first is that $\gamma$ is real, or can be made so. This is the case at a general $k$ point or when dealing with RAPW's. This case does not appear on the symmetry lines or points thus far considered.[18] But if it did, it would have to be handled in the same way as the unsymmetrized RAPW's. The second is that $\gamma^*$ is inequivalent to $\gamma$. This is implied by having a representation with complex characters. These two representations are then time reversal (or spin-flip) degenerate and are usually one-dimensional. One handles this case merely by doing calculations for one of the two representations. The third and predominant case is tke $\gamma$ be equivalent to $\gamma^*$, but impossible to make real. A good example of this case is the $D_{1/2}$ representation. In this case, there is no additional degeneracy due to time reversal. This case requires no special handling.

## III. STRAIGHTFORWARD CALCULATIONS

A large number of gray-tin calculations have been done for the symmetry points $\Gamma$, $L$, and $X$. The results are shown in Table II. These calculations are generated

TABLE II. Unadjusted calculations (units are mRy).

| Level | *SN*1 | *SN*3 | *SN*6 | *SN*1MT | *SN*3MT | *SN*6MT |
|---|---|---|---|---|---|---|
| $\Gamma_7^+$ | −55 | −57 | −55 | −57 | −60 | −58 |
| $\Gamma_7^-$ | −85 | −125 | −113 | −181 | −228 | −213 |
| $\Gamma_8^{+a}$ | ... | ... | ... | ... | ... | ... |
| $\Gamma_6^-$ | 116 | 138 | 113 | 76 | 86 | 81 |
| $\Gamma_8^-$ | 155 | 174 | 154 | 115 | 129 | 123 |
| $L_6^-$ | −123 | −115 | −118 | −130 | −123 | −124 |
| $L_4^-$ | −88 | −78 | −83 | −96 | −85 | −87 |
| $L_6^+$ | −12 | −31 | −30 | −122 | −122 | −126 |
| $L_6^+$ | 226 | 243 | 216 | 157 | 174 | 165 |
| $L_4^+$ | 246 | 269 | 238 | 174 | 195 | 185 |
| $X_5$ | −196 | −176 | −189 | −220 | −202 | −207 |
| $X_5$ | +80 | 116 | 64 | −66 | −38 | −51 |

[a] The $\Gamma_8^+$ has been chosen as the zero of energy.

---

[17] P. Soven [Phys. Rev. **137**, 170 (1965)] has shown how to handle the computational problems of the double roots resulting from the occurrence of the degeneracy. It is, in fact, possible to calculate the factor which when squared becomes the determinant. Loucks (Ref. 2) discusses this in his book in some detail.

[18] SRAPW has also been used with fcc, bcc, hcp, white tin, and $\alpha$-uranium structures and only on two lines of $\alpha$-U has this situation occurred. However, on planes of symmetry, it does occur more frequently. See Bull. Am. Phys. Soc. **13**, 413 (1968); **14**, 28 (1969); **14**, 360 (1969).

by choosing (1) the configuration, (2) the exchange scale factor, and (3) whether the muffin-tin or the warped muffin-tin approximation is applied. These choices were given in Table I except for the distinction between the muffin-tin and the warped muffin-tin approximations. The muffin-tin approximation is identified by adding an MT to the end of the identification for the calculation.

The calculations discussed in this section have no adjustments. That is, once the choices described have been made, the calculation is straightforwardly carried through to the end. In Sec. IV, two types of trimming adjustments are discussed.

These calculations are to be compared with the following results from the Groves-Paul model and Cardona-Pollack $\mathbf{k}\cdot\mathbf{p}$ interpretation of their electroreflectance data: (1) the $\Gamma_7^-$ should lie between the $\Gamma_7^+-\Gamma_8^+$ spin-orbit split states, (2) the $L_6^+$ should lie 0.006 Ry above the $\Gamma_8^+$, and (3) the $\Gamma_8^+$ should be the point of contact between the valence and conduction bands. (In particular, one $X_5$ should lie above and the other below the $\Gamma_8^+$.)

If one first looks at the straight muffin-tin calculations one sees that the situation is very bad. The calculation makes gray tin a metal with electrons at both $L$ and $X$. In fact, the $L_6^+$ which should lie above $\Gamma_8^+$ is now the *bottom* of the band. Furthermore, the $\Gamma_7^-$ lies 0.12–0.15 Ry below the $\Gamma_7^+$.

If one goes to the warped muffin-tin calculations, the situation is much improved. There is no longer the pocket of electrons at $X$. In fact, the $X_5$–$X_5$ separation agrees well with the electroreflectance result of 0.275 Ry. The $L_6^+$ still lies below the $\Gamma_8^+$ but now it is only 0.03–0.07 Ry below it. Thus, one can say that the inclusion of the potential variations outside the spheres has greatly improved the calculation, but it has not made it agree with experiment. The bands for the best calculations (*SN*1) are shown in Fig. 1 for the lines $L$-$\Gamma$-$X$. The most interesting feature of these bands are the distortions occurring near $\Gamma$ because the $\Gamma_7^-$ is still too low in energy. The local nature of this distortion is most impressive.

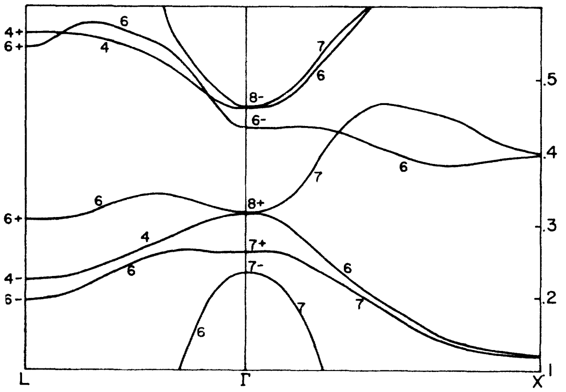

FIG. 1. Straightforward calculation for *SN*1.

One other feature of Table II should be pointed out. If one compares *SN*3MT with *SN*6MT, one sees that these two results are extremely similar. Since these two calculations differ only in the configuration initially chosen, one would be inclined to say that configuration was unimportant. But if one then looks at the *SN*3-*SN*6 calculations, the differences are more noticeable, especially in the upper bands. This would, of course, be an even more pronounced effect for the Kohn-Sham exchange, since the potential would be less attractive and thus more sensitive to the outer regions.

## IV. ADJUSTED CALCULATIONS

It is clear what is missing from the warped muffin-tin potential calculations. These potentials have the spherical averaging out to a given muffin-tin radius $R_I$. If one looks at a spherical harmonic expansion of the model potential inside these spheres, one finds the $l=0$ term, which is the muffin-tin term, and then $l=3$, $l=4$, etc., terms. The $l=4$ term enters for all cubic systems, but the $l=3$ term results from the tetrahedral coordination of the diamond structure. The $l=4$ term can couple $d$ components with each other, but no lower $l$ components. Thus it is relatively unimportant for gray tin where the bands are $s$-$p$ in character. But this is not the case for the $l=3$ term. It can couple the $p$ component to the $d$ bands above and below the energy range of interest. That this is indeed so is greatly supported by the observation that as the warping of the muffin tin is turned on, the $\Gamma_7^-$ and $L_6^+$ levels remain almost stationary, while the other levels lower significantly. As these two levels have no $d$ character, their immobility indicates that the interaction with $d$ states is the primary feature being misrepresented in the muffin-tin approximation.

As evidence that it is the approximation to the model potential and not the model potential itself which is responsible for the discrepancy, one can cite the fact that the relativistic OPW calculations[8] do not show this discrepancy. These calculations were done using the $sp^3$ configuration and Kohn-Sham exchange. They are thus a version of *SN*1.

Since the remaining effects are rather small, it is natural to ask whether or not they can be mocked up by an adjustment of the calculation. (One might even say by a pseudopotential.) The adjustment of the muffin-tin constant potential originally suggested by Scop[19] was tried, although it must be reinterpreted as a movement of the logarithmic derivatives (or phase shifts), since there is no longer a constant potential in the warped muffin tin. This amounts to adding a constant potential $V_{Sh}$ to the potential inside the spheres. The results of performing such an adjustment are shown in Table III. As can be seen, the $\Gamma_7^-$ can be moved to its correct position, but the $L_6^+$ has not been adequately moved

---

[19] P. Scop, Phys. Rev. **139**, A934 (1965).

and the rest of the band structure has been degraded. This is obviously not a very successful approach.

But from the observation that it is the interaction with the low-lying $d$ states that is influencing the problem, and from the lack of $d$ bands in the immediate region of interest, one sees a more natural adjustment: the shift of the $d$ component of the logarithmic derivatives (and spin factors) alone. This is easily done since $\xi_2 = 3.506 - 2.7606E$ and $\eta_2 = -0.0201 + 0.00954E$ with a very small rms error. Thus one merely changes the constant to the appropriate value to shift the logarithmic derivative and spin factor. As can be seen from Table III, this is a great deal more successful. It is also most consistent with the nature of the potential effect that we are trying to mock up. What is being done can be viewed as follows: Since the interaction with the $d$ bands has been weakened, the $d$ bands have just been moved nearer by shifting the logarithmic derivatives.

The resulting adjusted band structure is shown in Fig. 2. One interesting result is that as the $\Gamma_7^-$ moves into place, the $\Gamma_7^+ - \Gamma_8^+$ is reduced to a value which more nearly agrees with the results of Herman.

TABLE III. Adjusted calculations (units are mRy).

| REP. ID. | MT shifted by 0.05 Ry | 0.25 Ry | 0.1 Ry | $d$'s shifted by 0.3 Ry | 0.6 Ry | 0.8 Ry |
|---|---|---|---|---|---|---|
| $\Gamma_7^+$ | $-54$ | $-49$ | $-54$ | $-53$ | $-50$ | $-48$ |
| $\Gamma_7^-$ | $-73$ | $-33$ | $-77$ | $-65$ | $-43$ | $-25$ |
| $\Gamma_8^{+a}$ | ... | ... | ... | ... | ... | ... |
| $\Gamma_6^-$ | 109 | 80 | 115 | 113 | 111 | 112 |
| $\Gamma_8^-$ | 148 | 112 | 154 | 151 | 148 | 148 |
| $L_6^-$ | $-124$ | $-132$ | $-119$ | $-112$ | $-99$ | $-189$ |
| $L_4^-$ | $-90$ | $-101$ | $-84$ | $-27$ | $-65$ | $-54$ |
| $L_6^+$ | $-12$ | $-24$ | $-6$ | $-2$ | 5 | 11 |
| $L_6^+$ | 217 | 176 | 221 | 211 | 194 | 183 |
| $L_4^+$ | 236 | 189 | 240 | 229 | 210 | 196 |
| $X_5$ | $-201$ | $-223$ | $-190$ | $-179$ | $-160$ | $-145$ |
| $X_5$ | 69 | 13 | 80 | 74 | 75 | 59 |

[a] The $\Gamma_8^+$ has been chosen as the zero of energy.

## V. CONCLUSION

The formalism required to symmetrize the RAPW technique has been developed. It proves to be a straightforward application of projection operator techniques to Pauli spinors once the RAPW has been reformulated as the result of a Foldy-Wouthusen transformed Dirac formalism. This alternate formulation of the RAPW technique has also reduced the problem of generalizing the RAPW technique for a warped muffin-tin potential to the same problem as occurs in the nonrelativistic technique. Computer codes have been written for the SRAPW technique and applied to gray tin, which was chosen as a very severe test of the technique. Having an atomic number of 50, gray tin requires the relativistic formalism and, in addition, it has the diamond structure which is both nonsymmorphic and far from the applicable region of the muffin-tin approximation. In this way, we have been able to examine the efficiency of using the additional symmetrization while experimenting with the various parameters and approximations in the construction of the potentials. With an eye towards future applications, the computer codes also print out the SRAPW expansion of the trail function whenever an eigenvalue is found sufficiently accurately. Another small code exists to reanalyze these SRAPW expansions into RAPW expansions so that one can find wave functions as well as eigenvalues.

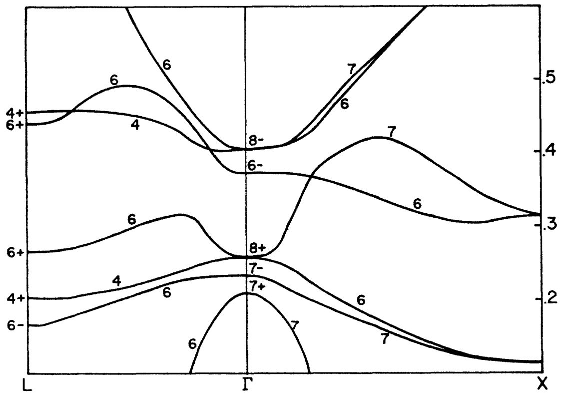

FIG. 2. Adjusted calculation for $SN1$.

Once set up, SRAPW is much faster and a great deal more convenient to operate than the unsymmetrized method. This increase in speed is accomplished in several ways. There is, of course, the reduction in size of the secular matrix which is the major factor producing the increased speed. But the fact that all roots of the secular equation are of first order and separated according to symmetry type also allows one to locate the eigenvalues more quickly, as one can search on a wider energy mesh and look only for sign changes. This is in contrast to the very inconvenient dips that would occur for roots of even order.

The technique of using a least-squares fit with plane waves to the model potential in the region outside the muffin-tin spheres is very rapidly convergent for all the structures that have been investigated except the diamond structure.[20] For the fcc and bcc structures (Pt and $\gamma$-$U$), the expansion is well converged (to about one part in $10^4$ for the matrix elements) by the time one has reached the fifth star. Further, one has at each stage a good estimate of the errors involved in the fit. And once the fit is obtained, the matrix elements are then evaluated analytically so that the errors involved are defined much better than for the numerical procedures.

The reason for the good (if not complete) success of the warped muffin-tin potential for gray tin is seen from an inspection of the errors relative to the model potential. The region outside the muffin-tin spheres has been corrected to coincide with the model potential, since

---

[20] SRAPW has successfully been used with a warped muffin-tin potential to the fcc, bcc, and white tin structures.

this region is the larger portion of the volume of the crystal (roughly $\frac{2}{3}$). In this large region, the use of a constant muffin-tin potential would make an rms error of 0.25 Ry. Within the smaller region enclosed by the spheres, spherical averaging is still applied. This yields a maximum rms error of 0.1 Ry at the sphere surface, and this error drops off rapidly as one moves into the sphere. Thus, one is now accounting for a large part of the muffin-tin errors, but not for all of them.

The SRAPW technique can be modified with very little conceptual difficulty (although a great deal of computer coding) to include the nonspherical terms within the spheres—as has been done for the nonrelativistic method.[12,13] There will be a great deal more Clebsch-Gordon coefficients to calculate as one also has spin to consider. (It may well be, though, that one would be wiser to use the plane-wave angular functions $X_\kappa^s$ instead.) However, because the nonspherical terms of the potential expansion within the muffin-tin spheres do have much smaller effects,[21] it may be much wiser to seek an approximate technique for their inclusion. A modification of a suggestion by DeCicco[22] to use the plane-wave matrix elements of these terms is particularly attractive, since the deviations from spherical symmetry occur principally near the muffin-tin sphere surface where the APW's are most like the plane waves to which they are joined. These considerations become more and more crucial as one attempts to do calculations in the lower symmetry crystals where such terms are more important.

For structures more appropriate to an APW calculation, one would expect that the warped muffin-tin approximation would work quite well.[21] In high-$Z$ fcc and bcc materials, a great deal of charge is to be found outside the muffin-tin spheres. Thus, one suspects that the warping could be significant although the nonspherical terms inside the spheres are not. One solid where the warped muffin-tin approximation must be applicable is white tin; here, the rms deviations are as large in the region outside spheres as for gray tin, but the deviations from spherical symmetry inside the spheres are less than half the size. Another class of materials for consideration are those with the hcp and double hexagonal structures. For these materials, a great deal of charge is also found outside the muffin-tin radius, so that the warping could easily be important. Furthermore, one can make the observation that the logarithmic derivatives are the same for the hcp and dhcp crystals. This means that the only difference to be found for these two structures in the muffin-tin approximation is due to the different structure factors $S(\mathbf{k}-\mathbf{k}')$. However, the remaining parts of the model potential are radically changed. Thus, one could suggest a second look at all the hexagonal materials to see what has been missed, although it might be necessary to go beyond the warped muffin-tin potential.

The RAPW method has proven itself to be a very useful technique in actual practice. With the use of the additional symmetry and generalizations to include non-muffin-tin potentials, it has become an even more useful technique and should be used extensively in the future. The procedure is already being used to provide the band structure data for several efforts in which the author is involved and other applications are in the planning stage.

## ACKNOWLEDGMENTS

The author expresses his gratitude to his thesis adviser G. F. Koster for suggesting the energy-band structures of tin as a thesis problem, and to him and A. J. Freeman for continued support and encouragement. The many useful discussions with P. DeCicco, A. J. Freeman, R. Gilmore, F. Mueller, and W. Rudge while working on this problem are gratefully acknowledged. The author enjoyed the hospitality of the Metallurgy Division, Argonne National Laboratory at a crucial state of this project.

## APPENDIX A: RAPW METHOD FORMULATED USING FOLDY-WOUTHUSEN TRANSFORMATION

It is clear that throughout most of the solid, the nonrelativistic approximation is quite adequate. Only near the nuclei does this approximation break down. Thus, it is appealing to break up the volume of the solid into a relativistic region and a nonrelativistic region. The relativistic region is to coincide with the muffin-tin spheres, and the nonrelativistic region is the remaining volume outside the spheres. This is precisely what results from using the Foldy-Wouthusen (FW) transformed Dirac formalism.

The FW transformation[23] proceeds in steps, with each step reducing the relative size of the small component by a factor on the order of the kinetic energy over $mc^2$. We use two transformations so that they are reduced to third order. Thus,

$$H=e^{iW_2}e^{iW_1}H_De^{iW_1}e^{iW_2},$$

$$\phi=e^{iW_2}e^{iW_1}\Psi_D,$$

$$W_1=(-i/2m)\beta\boldsymbol{\alpha}\cdot\mathbf{p},$$

$$W_2=(-i/6m^3)p^2\boldsymbol{\alpha}\cdot\mathbf{p},$$

$$\boldsymbol{\alpha}=\begin{pmatrix}0 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0\end{pmatrix},$$

$$\beta=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

---

[21] P. DeCicco and J. C. Slater, MIT Solid State and Molecular Theory Group, Quarterly Progress Report No. 50, p. 46, 1963 (unpublished).

[22] P. DeCicco (private communication).

[23] M. E. Rose, *Relativistic Electron Theory* (Wiley-Interscience Inc., New York, 1961).

In these expressions, a $D$ subscript indicates the Dirac form so

$$H_D=\boldsymbol{\alpha}\cdot\mathbf{p}+m(\beta-1)+V\,,$$

where the rest mass energy has been subtracted out of the Hamiltonian. The units $\hbar=c=1$ have been adopted here with $m$ retained explicity since $\langle E\rangle/m$ is the expansion variable. The transformation cannot be carried out exactly when there is a potential present, so it is written as an expansion in commutators to the accuracy to which the small components vanish. Such an expansion yields

$$\begin{aligned}H=m(\beta-1)+\beta p^2/2m+V&\\ -\tfrac{1}{2}m^2\beta\{\nabla V\cdot\nabla+i\boldsymbol{\sigma}\cdot\nabla V\times\nabla\}&+O(1/m^2)\,.\end{aligned}$$

This expansion converges sufficiently rapidly in the outside region so that only the kinetic energy and potential terms need be retained. Inside the spheres, the transformation is only needed at the sphere surface, and thus this is more than adequate.

The transformation on the basis functions becomes

$$\phi=[1+(1/2m)\beta\boldsymbol{\alpha}\cdot\mathbf{p}]\Psi_D+O(1/m^2)\Psi_D\,,$$

which is

$$\phi=\begin{pmatrix}U_D\\0\end{pmatrix}+\frac{E-V}{2m}\beta\Psi_D+O\left(\frac{1}{m^2}\right)\Psi_D\,.$$

For the region outside the spheres where $(E-V)/m$ is of order $10^{-5}$, the remaining small component is quite negligible. Since we need not worry about normalization at this point, one can use

$$\phi^{\text{out}}=\begin{pmatrix}\chi^s\\0\end{pmatrix}e^{i\mathbf{k}\cdot\mathbf{r}}\,,$$

and an equivalent Hamiltonian

$$H=p^2/2m+V$$

in the outside region. This is just the Schrödinger equation and Pauli spinor formulation.

For the discussion of the region inside the spheres, it is convenient to define the functions

$$\begin{aligned}X_\kappa{}^s\equiv 4\pi\sum C(\kappa,\mu,s)\chi_\kappa{}^\mu(\hat{r})Y_{l(\kappa)}{}^{m-s*}&\\ =\begin{pmatrix}D_\kappa(\hat{r}+\frac{1}{2};\hat{k}s)\\D_\kappa(\hat{r}-\frac{1}{2};\hat{k}s)\end{pmatrix}&\quad\text{for}\quad\kappa\gtrless 0\,.\end{aligned}$$

In these expressions, $C$ is a Clebsh-Gordan coefficient, $\kappa$ is the relativistic quantum number satisfying the relationships

$$\begin{aligned}&|\kappa|=j+\tfrac{1}{2}\,,\\ &|\kappa|=l\quad\text{and}\quad j=l-\tfrac{1}{2}\quad\text{for }\kappa>0\,,\\ &|\kappa|=l-1\quad\text{and}\quad j=l+\tfrac{1}{2}\quad\text{for }\kappa<0\,,\end{aligned}$$

and $D_\kappa$ is the quantity defined by Loucks.[2] It can most conveniently be written in a matrix formulation as

$$D_\kappa(\hat{r};\hat{k})=|\kappa|P_l(\hat{k}\cdot\hat{r})1+iS_kP_l{}'(\hat{k}\cdot\hat{r})(\hat{r}\times\hat{k})\cdot\boldsymbol{\sigma}\,,$$

where $P_l$ is the Legendre polynomial and $S_\kappa$ is the sign of $\kappa$. These functions satisfy the relation that

$$\int d^2\hat{r}X_\kappa{}^{s_i}(\hat{k}_i,\hat{r})^\dagger X_\kappa{}^{s_j}(\hat{k}_j,\hat{r})=4\pi\delta_{\kappa\gamma}D_\kappa(\hat{k}_is_i;\hat{k}_js_j)\,,$$

which are used later.

Using these functions one can write the (not quite normalized) Dirac plane wave as

$$\Psi^{\text{out}}(\mathbf{k},\mathbf{r},s)=(N\Omega^{-1/2})\sum_\kappa i^l\begin{pmatrix}j_l(kr)X_\kappa{}^s(\hat{k},\hat{r})\\-ij_{l'}(kr)\sigma_rX_\kappa{}^s(\hat{k},\hat{r})\end{pmatrix},$$

$$l'=\begin{Bmatrix}\kappa-1, & \kappa>0\\ |\kappa|\;, & \kappa<0\end{Bmatrix},\quad\kappa\gtrless 0\,,$$

$$\sigma_r=\hat{r}\cdot\boldsymbol{\sigma}\,.$$

$\Omega$ is the volume of the unit cell, and $N$ is the number of unit cells. This requires the function

$$\Psi^{\text{in}}(\mathbf{k},\mathbf{r},s)=\sum_\kappa il\frac{j_l(kR)}{g_x(R,E)}\begin{pmatrix}g_\kappa(r,E)X_\kappa{}^s(\hat{k},\hat{r})\\-if_\kappa(r,E)\sigma_rX_\kappa{}^s(\hat{k},\hat{r})\end{pmatrix}e^{i\mathbf{k}\cdot\mathbf{t}}$$

to join the large components continuously, as required for the sphere centered at the point $\mathbf{t}$. As the functions inside the muffin-tin spheres are required to satifsy the radial Dirac equation for the energy under consideration, the only place the actual FW transformed equation is required is at the sphere surface. There, the first terms of the expansion are quite adequate. In fact, the only term that is needed is the first term—which consists of taking the Dirac spinor and ignoring the lower components. Again we are back to Pauli spinors.

One must be careful now in the formulation of the variational principle since the basis functions formed from $\Psi^{\text{in}}$ and $\Psi^{\text{out}}$ do not have a continuous small component—or derivative of the large component—as one crosses the muffin-tin sphere surface. There is also the further difficulty that the FW transformation as well as the Hamiltonian involves differential operators. This nonphysical difficulty can be eliminated by excluding a spherical shell of thickness $\epsilon$, and then allowing $\epsilon$ to approach zero. However, if this is done, the differential operators are no longer Hermitian. It is then most convenient to add in a term which makes the variational quantity Hermitian and vanishes as the trial function approaches continuity. This is the origin of the surface integral in the APW methods as well as the uncertainties in the actual variational quantities used.[24,25] The most convenient and physical term to include is

---

[24] R. S. Leigh, Proc. Phys. Soc. (London) **A69**, 388 (1956).

[25] P. M. Marcus, J. Quant. Chem. **1**, 567 (1967).

one which is a finite-increment evaluation of the integration over the thin shell.[26]
The resulting variational quantity is

$$K_E(1,2)=\langle\phi_1|U(\mathbf{r})(H-E)|\phi_2\rangle+Q(1,2)\,,$$

$$Q(1,2)=\frac{1}{2m}\int_{\text{surface}} d^2\mathbf{r}\{\boldsymbol{\phi}_1{}^{\text{in}\dagger}\beta\hat{r}\cdot\boldsymbol{\nabla}\boldsymbol{\phi}_2{}^{\text{in}}-\boldsymbol{\phi}_1{}^{\text{out}\dagger}\hat{r}\cdot\boldsymbol{\nabla}\boldsymbol{\phi}_2{}^{\text{out}}\}\,.$$

The matrix integration for $(H-E)$ has the step function in it because the basis functions have already been required to satisfy the Hamiltonian equation for the energy $E$ inside the muffin-tin spheres. Thus it is seen that one only needs to evaluate the transformed function at the sphere surface. The operator $\hat{r}\cdot\boldsymbol{\nabla}$ appears in the surface integral instead of the operator $\hat{r}\cdot\boldsymbol{\alpha}$ that appears in the straight Dirac formulation[2] because

$$W_2W_1\boldsymbol{\alpha}W_1{}^{+}W_2{}^{+}=\boldsymbol{\alpha}+\beta\mathbf{p}/m+O(1/m^2)\,.$$

The $\boldsymbol{\alpha}$ operating on the transformed basis functions would give a term of order $(1/m^2)$ and so need not be included. The presence of the $\beta$ in these expressions is not significant, as the lower components are to be neglected. Again we are back to a nonrelativistic operator.

The variation of the quantity $K_E$ is done by expanding the trial function in the FW transformed basis functions and doing a Rayleigh-Ritz variation. When this is done, one gets a secular equation involving the basis-function matrix elements of $K_E$:

$$\det K_E(i,j)=0\,.$$

This is the only reason that the two indices were included in the definition of $K_E$, since the quantity varied is its diagonal matrix element with the trial function.

It remains only to evaluate the matrix elements and the procedure is complete. The warping terms have been discussed in the text and Appendix B, so that only the muffin-tin potential terms need be dealt with here. The volume integration can be done immediately:

$$\langle k_is_i|U(\mathbf{r})(H-E)|k_js_j\rangle=(k_j{}^2-E)\langle s_i|s_j\rangle U(\mathbf{k}_j-\mathbf{k}_i)\,.$$

Note that this term is *not* Hermitian as mentioned. The term in the surface integral obtained from the outside limit is also easily evaluated:

$$\sum_{\mathbf{R}}\int d^2\mathbf{r}\boldsymbol{\phi}_1{}^{\text{out}}\hat{r}\cdot\boldsymbol{\nabla}\boldsymbol{\phi}_2{}^{\text{out}}$$

$$=\frac{4\pi R^2}{\Omega}S(\mathbf{k}_j-\mathbf{k}_i)\frac{(k_j{}^2-\mathbf{k}_i\cdot\mathbf{k}_j)j_1(|\mathbf{k}_j-\mathbf{k}_i|R)}{|k_j-k_i|}\langle s_i|s_j\rangle\,,$$

leaving only the first term to be evaluated. The logarithmic derivative involved in that term is evaluated using the radial Dirac equation

$$[1/g_\kappa(R,E)](d/dr)g_\kappa(R,E)$$
$$=(2m+E-V)f_\kappa(R,E)/g(R,E)-(\kappa+1)/R$$

and its solutions as obtained from a radial integration.[2] This is the actual mechanism for the appearance of the relativistic effects and is found via the FW transformation. Having already obtained the surface integrals for the $X_\kappa{}^s$'s, the integral can be evaluated leading to the matrix elements

$$K_E(\mathbf{k}_is_i;\,\mathbf{k}_js_j)=\left(\frac{1}{2m}\mathbf{k}_i\cdot\mathbf{k}_j-E\right)U(\mathbf{k}_j-\mathbf{k}_i)\langle s_i|s_j\rangle$$
$$+S(\mathbf{k}_j-\mathbf{k}_i)\frac{4\pi R^2}{2m\Omega}\sum_k D_\kappa(k_is_i;\,k_js_j)$$
$$\times j_l(k_iR)j_l(k_jR)\frac{1}{g_\kappa(R,E)}\frac{d}{dr}g_\kappa(R,E)\,,$$

which is the same matrix element as that obtained by Loucks[2]—although somewhat rearranged. It is only necessary to combine the $\kappa=l$ and $\kappa=(l+1)$ terms of the summation and switch to atomic units to get the matrix elements used in Sec. II.

All this has now led us to a very simple result. One could get the matrix elements for the RAPW by first writing down the variational quantity in the Dirac form; then, observing that all integrals are in a nonrelativistic region, one uses the nonrelativistic operators and Pauli spinors to evaluate them *except* that the logarithmic derivatives are evaluated using the radial Dirac equation.[27]

## APPENDIX B: WARPING POTENTIAL $V_1$ AND ITS MATRIX ELEMENTS

The warping potential is

$$V_1(\mathbf{r})=U(\mathbf{r})\{\sum_{\mathbf{R}}V_{\text{at}}(|\mathbf{r}-\mathbf{R}|)$$
$$+\alpha C[\sum_{\mathbf{R}}\rho(|\mathbf{r}-\mathbf{R}|)]^{1/3}-V_0\}\,,$$
$$C=-6(3/8\pi)^{1/3}\,,$$

where $V_0$ is the muffin-tin potential adjustment. $U(r)$ is included because this potential is nonzero only outside the muffin-tin spheres. $V_{\text{at}}(r)$ is the atomic Coulomb potential, and $\rho(r)$ is the atomic charge density. The sum is over all lattice sites. This potential is calculated for a set of points distributed randomly in the outside region and put in a large array. This array is then a function to be fit with a set of basis functions. The natural set of functions for an expansion of $V_1(\mathbf{r})$ are the reciprocal-lattice vector plane waves. The basis set must have the $\Gamma_1$ symmetry, so the plane waves are

---

[26] R. Gilmore, MIT Solid State and Molecular Theory Group, Quarterly Progress Report No. 60, p. 24, 1966 (unpublished).

[27] D. D. Koelling, MIT Solid State and Molecular Theory Group, Quarterly Progress Report No. 68, p. 36, 1968 (unpublished).

TABLE IV. Warping potential $V_1(\mathbf{R})$ coefficients.

| | | | Coefficient[a] |
|---|---|---|---|
| | $h_0$ | | −18.8209 |
| | $h_1$ | | −2.23815 |
| $K_x$ | $K_y$ | $K_z$[b] | |
| 0 | 0 | 0 | 0.492529 |
| 2 | 2 | 2 | 0.269096 |
| 4 | 4 | 0 | 0.127321 |
| 6 | 2 | 2 | −0.088075 |
| 4 | 4 | 4 | 0.144225 |
| 6 | 6 | 2 | −0.153114 |
| 8 | 0 | 0 | 0.099502 |
| 8 | 4 | 4 | −0.038026 |
| 6 | 6 | 6 | −0.001710 |
| 10 | 2 | 2 | 0.012310 |
| 8 | 8 | 0 | 0.016318 |
| 10 | 6 | 2 | −0.072102 |
| 8 | 8 | 4 | 0.011729 |
| 12 | 4 | 0 | −0.010546 |
| 10 | 6 | 6 | 0.000017 |
| 12 | 4 | 4 | 0.010181 |
| 8 | 8 | 8 | 0.001550 |

[a] Units are Ry.
[b] Reciprocal-lattice vectors are in units of $\pi/a$.

combined to the symmetrized functions:

$$s_n(\mathbf{r})=U(\mathbf{r})\frac{1}{24}\sum_{i=1}^{24}\cos[\alpha_i\mathbf{K}_n\cdot(\mathbf{r}-\boldsymbol{\tau}_i)].$$

Obviously one should take only one $\mathbf{K}_n$ from each star to get a linear independent set of functions. Furthermore, $s_n$ is zero for some stars, since this is a nonsymmorphic crystal structure. This set, however, does not converge conveniently rapidly, so we define another set of functions to aid the convergence:

$$h_n(\mathbf{r})=U(\mathbf{r})\sum_{\mathbf{R}}|\mathbf{r}-\mathbf{R}|^{n-1}\exp(-|\mathbf{r}-\mathbf{R}|);\quad n=0,1,\cdots.$$

The first two of these functions fits $V_1$ with an rms error of 0.03 Ry, but adding more functions does nothing to reduce the rms error. The best fit for $SN1$ was accomplished by using $h_0$, $h_1$, and the first 16 nonzero $s_n$ to yield an rms error of 0.0005 Ry. The coefficients of this fit are shown in Table IV. It should be noted that the inclusion of the $h_n$'s is a convenient crutch for the diamond structure, whereas for other structures it is not needed (for example, white tin).

Once one has a fit for $V_1(\mathbf{r})$, one can then calculate analytically the required quantity $V_1(\mathbf{K})$:

TABLE V. $V_1(\mathbf{K})$.

| Simple cubic vectors | | | | | bcc vectors | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $n$[a] | $K_x$ | $K_y$ | $K_z$[b] | $V_1(\mathbf{K})$[c] | $n$[d] | $K_x$ | $K_y$ | $K_z$[b] | $V_1(\mathbf{K})$[c] |
| 2 | 4 | 4 | 0 | −27.66 | 1* | 2 | 2 | 2 | 52.13 |
| 3 | 4 | 4 | 4 | 25.90 | 2 | 6 | 2 | 2 | −19.54 |
| 4 | 8 | 0 | 0 | 13.57 | 3* | 0 | 0 | 0 | 48.52 |
| 6 | 8 | 4 | 4 | −6.00 | 4 | 6 | 6 | 2 | −3.76 |
| 8 | 8 | 8 | 0 | 2.03 | 5* | 6 | 6 | 6 | −4.87 |
| 9 | 8 | 8 | 4 | 0.54 | 6 | 10 | 2 | 2 | −3.05 |
| 10 | 12 | 4 | 0 | 4.86 | 10 | 10 | 6 | 6 | −3.87 |
| 11 | 12 | 4 | 4 | 1.56 | 11* | 10 | 10 | 2 | −5.21 |
| 12 | 8 | 8 | 8 | −7.38 | 12 | 14 | 2 | 2 | 6.15 |
| 14 | 12 | 8 | 4 | −6.97 | 13* | 10 | 10 | 6 | −5.10 |
| 16 | 16 | 0 | 0 | 5.49 | 14 | 14 | 6 | 2 | −4.13 |
| 17 | 12 | 8 | 8 | −0.59 | 16 | 14 | 6 | 6 | −2.88 |
| 18 | 16 | 4 | 4 | −2.32 | 17* | 18 | 6 | 6 | 1.27 |
| 19 | 12 | 12 | 4 | 0.17 | 18 | 10 | 10 | 10 | 0.71 |
| 20* | 12 | 12 | 0 | −1.79 | 19* | 18 | 2 | 2 | −0.40 |
| 21 | 16 | 8 | 4 | 0.39 | 20 | 14 | 10 | 6 | 0.54 |
| 22 | 12 | 12 | 8 | 0.12 | 23* | 14 | 10 | 10 | 0.22 |
| 24 | 16 | 8 | 8 | 0.96 | 24 | 14 | 14 | 2 | 1.07 |

[a] Except for the element marked with an asterisk, this indexing is $|K|^2/16$.
[b] Reciprocal-lattice vectors are in units of $\pi/a$.
[c] Units are mRy.
[d] Except for the element marked with an asterisk, this indexing is $(|K|^2-12)/16$.

$$V_1(\mathbf{K})\equiv\frac{1}{N\Omega}\int_{\text{crystal}}d^3\mathbf{r}\,V_1(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}}.$$

The result for the $s_n$ was given in Sec. II, but the $h_n$'s present a somewhat more difficult problem. By noting that the integral is actually a faltung of the step function with a lattice sum of spherically symmetric functions, one can immediately write down the relation

$$h_n(\mathbf{K})=\frac{4\pi}{\Omega}\sum_{K'}S(\mathbf{K}')U(\mathbf{K}+\mathbf{K}')(-1)^n\frac{d^n}{dp^n}\left[\frac{1}{p^2+K'^2}\right]\Bigg|_{p=1}.$$

The sum for $h_n(\mathbf{K})$ is very slowly converging, so it is necessary to tabulate and store the $V_1(\mathbf{K})$. This is readily accomplished by observing that one needs only the value of $V_1(\mathbf{K})$ for one vector of the star. $V_1(\alpha\mathbf{K})$ equals $V_1(\mathbf{K})$ in magnitude, although it may be of opposite sign. However, the look-up procedure and prescription for determining whether a sign change should occur are merely programming details[28] which can be given to anyone who is sufficiently interested. The values of $V_1(\mathbf{K})$ are tabulated in Table V.

---

[28] D. D. Koelling, Ph.D. thesis, 1968 (unpublished).