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Non-Muffin-Tin Augmented-Plane-Wave Method for Diamond and Zinc-Blende Lattices

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The augmented-plane-wave method is adapted to the diamond and zinc-blende lattices by including both "nonflat" and "nonspherical" corrections to the usual "muffin-tin" potential. The former are treated exactly while the latter are treated perturbatively. The method is tested for silicon where "nonflat" corrections are as large as 3.4 eV with "nonspherical" corrections less than 0.4 eV. Plane wave convergence is superior to the orthogonalized-plane-wave method. The atomic-sphere radius was varied from $2.15a_0$ to $1.35a_0$ with energy changes of less than 0.03 eV. Nonflat matrix elements are easily computed by use of a spherical-harmonic expansion of the potential due to point charges. Multipole-lattice-sum coefficients are given for the fcc, diamond, and zinc-blende lattices.

I. INTRODUCTION

Until quite recently all calculations using the augmented-plane-wave (APW) method[1] assumed a potential of the "muffin-tin" form, namely constant outside touching atomic spheres and spherical inside. For materials with high coordination numbers this approximation should be quite good and the APW method has been very widely applied to such cases.

For materials with tetrahedral coordination the muffin-tin approximation is very poor and band-structure calculations have usually been done with the orthogonalized-plane-wave (OPW) method.[2]

It has always been recognized that the muffin-tin approximation was merely a computational convenience which was in no way essential to the APW method. Yet, it has been only in the past year that practical "non-muffin-tin" applications have been made. There are two separate contributions to the non-muffin-tin corrections: the "nonflat" part of the potential outside the atomic spheres and the "nonspherical" part of the potential within the spheres. The nonflat part of the problem involves computing plane-wave matrix elements of the potential over the region outside the atomic spheres. This is easily done for plane waves. However, a Fourier representation of the potential is too slowly convergent to be useful because of the Coulombic nature of the ionic potential. Hence the "obvious" approach to the nonflat problem cannot be made. The nonspherical part of the problem can be straightforwardly approached via perturbation theory but the number of terms which couple goes up very rapidly with the angular momentum.

The non-muffin-tin calculations which have appeared offer different solutions to the above problems. The most complete treatment of non-muffin-tin corrections is that of Rudge.[3] He makes a multipole expansion of the charge density inside the atomic spheres and computes the potential due to a lattice sum of multipoles by a "generalized Ewald method." He has evaluated the lattice sums for the body-centered lattice. Rudge treats the nonspherical part of the potential by perturbation theory. He applies his method to lithium for which he finds the non-muffin-tin corrections are not very important.

Koelling[4] has included non-muffin-tin corrections in his recent calculations on grey tin. He has found corrections of the order of 1 to 2 eV from the "nonflat" potential but has not explicitly calculated the nonspherical corrections which should be smaller.

Koelling's procedure for calculating the nonflat matrix elements of the potential involves computing the potential at a random set of points outside the atomic spheres and fitting to an expansion in terms of plane waves with spherical subtractions.

Kleinman and Shurtleff[5] have improved on Rudge's perturbation approach to the nonspherical corrections. They have given formulas for integration of the radial functions which include the nonspherical contributions to the potential.

They have also suggested a modified type of wave function in which they retain the plane-wave form inside the spheres but add terms which correct the low-l values of the spherical-harmonic expansion from spherical Bessel functions to accurate radial functions.

In this paper we adopt a procedure for treating non-muffin-tin corrections to the APW method which is very similar to that of Rudge.[3] We develop detailed formulas for the zinc-blende lattice and apply the results to silicon. We give the following brief outline of the paper. In Sec. II we give explicit expressions for the non-muffin-tin corrections to the APW method for the zinc-blende lattice. We divide the potential into valence and ionic (or core) contributions. The potential inside the atomic spheres is expressed as an expansion in spherical harmonics derived from a real-space lattice sum of the ionic potential and a plane-wave expansion of the valence potential. These representations permit a simple calculation of the nonflat matrix elements. By doing lattice sums only over the ionic potential which consists simply of monopoles on lattice sites we reduce the complexity of Rudge's multipole sums.

We treat the nonspherical potential by perturbation theory as Rudge has done. By limiting consideration to a selected class of terms with angular momenta $l \leq 4$ and using group theory we need only ten angular integrals for which we give explicit expressions.

In Sec. III we study the convergence and computational accuracy of the non-muffin-tin APW method as applied to silicon.

In terms of numbers of plane waves required we find convergence comparable to the empirical pseudopotential method and definitely better than the OPW method. In the spherical terms we have used l sums up to $l_{\max} = 9$ although $l_{\max} = 4$ gave differences of at most 0.05 eV.

We have found contributions as large as 3 eV due to the nonflat part of the potential whereas the nonspherical terms contribute at most 0.4 eV.

We are able to vary the sphere radius of the atomic spheres from $1.35a_0$ to $2.15a_0$ and find energies consistent to better than 0.03 eV. This gives a stringent test of the calculation involving most of the ingredients of the APW method.

In summary we believe that the approach to the non-muffin-tin APW corrections presented here provides an attractive alternative to the OPW method for band calculations in zinc-blende and diamond-type lattices.

We should note that A. R. Williams[6] has recently derived a generalization of the Green's-function method which permits the inclusion of non-muffin-tin corrections. Practical implementation appears to require a perturbation treatment of the nonflat terms which is not necessary in the APW method.

We should further note that a variety of attempts have been made to remedy some of the convergence difficulties of the OPW method by augmenting the basis set with functions of an atomic character.[6a] These methods have been a decided improvement on the unmodified OPW method. It would be interesting to see the convergence of these modifications compared directly with the APW method.

II. NON-MUFFIN-TIN CORRECTIONS TO THE APW METHOD

The general method we adopt is very similar to that of Rudge.[3] Our application is to the zinc-blende and diamond lattices whereas Rudge applied his results to the bcc lattice. There are many other points of difference so we will repeat the derivation in detail.

We introduce the conventional composite APW wave function

$$\psi(\vec{r}) = \sum\nolimits_n b_n |\vec{k}_n\rangle, \quad \rho_1, \rho_2 > R \tag{2.1}$$

$$\psi(\vec{r}) = \sum_{lj\alpha} c^m_{lj\alpha} u^m_l(\rho_m, E) K^l_{j\alpha}(\hat{\vec{\rho}}_m), \qquad \rho_m \leq R, \quad m = 1, 2 \tag{2.2}$$

$$\vec{\rho}_1 = \vec{r} + \tfrac{1}{2}\vec{\tau}, \quad \vec{\rho}_2 = \vec{r} - \tfrac{1}{2}\vec{\tau} , \tag{2.3}$$

$$\vec{\tau} = (\tfrac{1}{4}a, \tfrac{1}{4}a, \tfrac{1}{4}a) , \tag{2.4}$$

$$|\vec{k}_n\rangle = e^{i(\vec{k}+\vec{K}_n)\cdot\vec{r}} \;. \tag{2.5}$$

We choose the origin of $\vec{r}$ to be midway between atoms 1 and 2; the origin of $\vec{\rho}_m$ is atom m. a is the lattice constant. $\vec{K}_n$ is a reciprocal-lattice vector.

The $K^l_{j\alpha}(\hat{\vec{\rho}})$ are cubic harmonics as defined by Von der Lage and Bethe[7] except that we use the normalization

$$\int d\hat{\vec{\rho}}\,[K^l_{j\alpha}(\hat{\rho})]^2 = 1 \;, \tag{2.6}$$

where the integration is over the unit sphere. The superscript l refers to the angular momentum of the spherical representation while $j\alpha$ denote, respectively, the representation and partner function of the cubic group O_h. We use Koster's notation.[8]

The radial functions $u^m_l(\rho_m, E)$ are determined by a numerical solution of the radial Schrödinger equation

$$\left[-\frac{1}{2}\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d}{d\rho}\right)+\frac{l(l+1)}{2\rho^2}+V^m_0(\rho)-E\right]u^m_l(\rho,E)=0 \;. \tag{2.7}$$

$V^m_0(\rho)$ is the spherical part of the potential around atom m. For the diamond lattice $V^m_0(\rho)$ does not depend on m. We use atomic units where $e=\hbar=m_0=1$ and energy is in double rydbergs. $a_0=1$ is the Bohr radius

The b_n in Eq. (2.1) are arbitrary coefficients which will be determined variationally to minimize the energy. In the usual way this leads to the APW secular equation.

The $c^m_{lj\alpha}$ are coefficients which are completely determined in terms of the b_n's by the requirement that the wave function be continuous on the sphere boundaries, $\rho_m = R$. It is conventional to make each plane wave $|\vec{k}_n\rangle$ continuous with a set of spherical waves. This overspecification is clearly not required. The secular equation is the same in either case.

To obtain the $c^m_{lj\alpha}$ in terms of the b_n we make the usual spherical harmonic expansion of the plane waves

$$|\vec{k}_n\rangle = 4\pi\varphi_m(-\vec{k}_n)\sum_{l=0}^{\infty} i^l j_l(k_n\rho_m)\sum_{j\alpha}K^l_{j\alpha}(\hat{\vec{k}}_n)K^l_{j\alpha}(\hat{\vec{\rho}}_m) \;, \tag{2.8}$$

$$\varphi_1(\vec{k}_n)=e^{i\vec{k}_n\cdot\vec{\tau}/2}, \quad \varphi_2(\vec{k}_n)=e^{-i\vec{k}_n\cdot\vec{\tau}/2} \;; \tag{2.9}$$

we have used the identity

$$\sum_{j\alpha}K^l_{j\alpha}(\hat{\vec{k}})K^l_{j\alpha}(\hat{\vec{\rho}})=\sum_m Y^*_{lm}(\hat{\vec{k}})\,Y_{lm}(\hat{\vec{\rho}}) \;, \tag{2.10}$$

which follows from the unitarity of the transformation from spherical to cubic harmonics. The cubic harmonics are real. The m in (2.10) is not to be confused with the atom index m in (2.8).

Substituting (2.8) in (2.1) and equating coefficients of $K_{j\alpha}(\hat{\vec{\rho}}_m)$ in (2.1) and (2.2) gives the relations

$$c^m_{lj\alpha}=\frac{4\pi i^l}{u^m_l(R,E)}\sum_{\vec{k}_n} b_n\,\varphi_m(-\vec{k}_n)\,j_l(k_nR)\,K^l_{j\alpha}(\hat{\vec{k}}_n) \;. \tag{2.11}$$

We write the total Hamiltonian as a sum of three parts

$$H=H_0+P_{\text{EXT}}V+(1-P_{\text{EXT}})V^{\text{NS}} \;, \tag{2.12}$$

$$H_0=T+(1-P_{\text{EXT}})V^{\text{SPH}} \;, \tag{2.13}$$

$$V^{\text{SPH}}(\vec{r})=V^m_0(\rho_m), \qquad \rho_m\le R$$

where T is the kinetic-energy operator. We have

$$\begin{aligned} P_{\text{EXT}} &= 1, & \rho_{1,2} &> R \\ &= 0, & \rho_1 \le R &\text{ or } \rho_2 \le R \end{aligned} \tag{2.14}$$

$$V(\vec{r})=(4\pi)^{1/2}\sum_{l=0}^{\infty}V^m_l(\rho_m)K^l_j(\hat{\vec{\rho}}_m), \quad \rho_m\le R \tag{2.15}$$

$$V(\vec{r})=V^{\text{NS}}(\vec{r})+V^m_0(\rho_m), \qquad \rho_m\le R. \tag{2.16}$$

The projection operator P_{EXT} serves to divide the unit cell into regions external and internal to the atomic spheres. In the internal region the potential is given in terms of a spherical-harmonic expansion in Eq. (2.15). $V^m_0(\rho_m)$ is the totally symmetric term in the expansion while $V^{\text{NS}}(\vec{r})$ is the sum of all other terms, i.e., the nonspherical part of the potential. Because of the tetrahedral site symmetry only the cubic representations $j\alpha = 1+$ and $j\alpha = 2-$ contribute in Eq. (2.15). Only even (odd) l are compatible with $1+$ $(2-)$. Hence we don't need a $j\alpha$ label on $V^m_l(\rho_m)$.

The spherical potential $V^m_0(\rho_m)$ is used in Eq. (2.7) to generate the radial functions $u^m_l(\rho, E)$ which are used in the composite wave function of Eq. (2.2). The nonspherical potential $V^{\text{NS}}(\vec{r})$ is treated perturbatively in the manner of Rudge.[3]

In the muffin-tin approximation the external potential is replaced by its average value

$$\overline{V}_{\text{EXT}}=\int P_{\text{EXT}}V\,d\vec{r}\Big/\int P_{\text{EXT}}\,d\vec{r} \;\;. \tag{2.17}$$

Equation (2.12) can then be written

$$H=H^{\text{MT}}+P_{\text{EXT}}(V-\overline{V}_{\text{EXT}})+(1-P_{\text{EXT}})V^{\text{NS}} \;, \tag{2.18}$$

$$H^{\text{MT}}=H_0+P_{\text{EXT}}\,\overline{V}_{\text{EXT}} \;. \tag{2.19}$$

The right-hand side of (2.18) then consists of the muffin-tin Hamiltonian, the nonflat potential, and the nonspherical potential. In muffin-tin papers it is conventional to set $\overline{V}_{\text{EXT}}=0$. However, we use a different choice of 0 so we will retain this term explicitly.

A. Muffin-Tin Terms

We treat the muffin-tin Hamiltonian H^{MT} in the standard manner.[1] In order to avoid orthonormality problems it is conventional to calculate matrix elements of $(H-E)$.

For the zinc-blende lattice we have

$$\langle\psi|H^{\mathrm{MT}}-E|\psi\rangle=\sum_{n,n'}b_{n'}^{*}b_n\left\{\left(\tfrac{1}{2}k_n^2+\overline{V}_{\mathrm{EXT}}-E\right)\delta_{nn'}+\frac{4\pi R^2}{\Omega}\left[2\cos\tfrac{1}{2}(\vec{\mathrm{Q}}\cdot\vec{\tau})[E-\overline{V}_{\mathrm{EXT}}-\tfrac{1}{2}(\vec{\mathrm{k}}_n\cdot\vec{\mathrm{k}}_{n'})]\frac{j_1(QR)}{Q}\right.\right.$$
$$\left.\left.+\frac{1}{2}\sum_{l=0}^{l_{\max}}(2l+1)P_l(\cos\theta_{nn'})j_l(k_{n'}R)j_l(k_nR)\sum_{m=1}^{2}\varphi_m(\vec{\mathrm{Q}})\left(\frac{d\ln u_l^m(\rho,E)}{d\rho}\right)_{\rho=R}\right]\right\},\tag{2.20}$$

$$\vec{\mathrm{Q}}=\vec{\mathrm{k}}_{n'}-\vec{\mathrm{k}}_n,\quad \cos\theta_{n'n}=\vec{\mathrm{k}}_{n'}\cdot\vec{\mathrm{k}}_n/k_nk_{n'}\ ,\tag{2.21}$$

where φ_m is defined in Eq. (2.9) and Ω is the volume of the unit cell.

Energies are computed in the usual way by calculating the value of the secular determinant versus energy and interpolating to zero. Quadratic interpolation was used with three points spaced 0.002 a.u. apart.

B. Nonflat Potential

If the potential V is expressed in a Fourier series, the matrix elements of $P_{\mathrm{EXT}}V$ are easily expressed in terms of the relation

$$\int P_{\mathrm{EXT}}e^{i\vec{\mathrm{Q}}\cdot\vec{\mathrm{r}}}d\vec{\mathrm{r}}/v$$
$$=\delta_{\vec{\mathrm{Q}},0}-(8\pi R^2/\Omega)\cos(\tfrac{1}{2}\vec{\mathrm{Q}}\cdot\vec{\tau})\,j_1(QR)/Q\ .\tag{2.22}$$

A Fourier series representation is not an appropriate scheme for treating the ionic contribution to the potential because of its slow convergence. It is a good method for treating the valence-electron contribution, however. We write

$$V^{\mathrm{val}}(\vec{\mathrm{r}})=\sum_{\vec{\mathrm{K}}_n\neq0}\tilde{V}^{\mathrm{val}}(\vec{\mathrm{K}}_n)e^{i\vec{\mathrm{K}}_n\cdot r}\ .\tag{2.23}$$

The constant term in (2.23) is taken to be 0. We should note at this point that the purpose of the Fourier expansion of (2.23) is primarily to calculate the plane-wave matrix elements of $P_{\mathrm{EXT}}V$ with the use of (2.22). Obviously, the behavior of $V(r)$ inside the atomic spheres is irrelevant for this purpose and it is undoubtedly possible to utilize a pseudo-$V(r)$ with better Fourier convergence which does not reproduce the short-wavelength charge-density fluctuations deep in the core but which does accurately describe the potential in the region external to the atomic spheres. We have one further degree of freedom in hastening the Fourier convergence of (2.23), namely, we need not insist that the ionic charge be integral. In this way some of the valence charge deep in the atom core which leads to high Fourier components in $V(r)$ could be incorporated in the ionic potential. In the interest of simplicity we will not incorporate any of this flexibility in our formalism. We will continue to assume that $V^{\mathrm{val}}(\vec{\mathrm{r}})$ represents the complete effective potential of the valence-valence interaction both inside and outside the atomic spheres.

It is convenient to divide the total potential into a sum of three parts:

$$V(\vec{\mathrm{r}})=V^{\mathrm{val}}(\vec{\mathrm{r}})+V^{\mathrm{pc}}(\vec{\mathrm{r}})+(1-P_{\mathrm{EXT}})V^{\mathrm{core}}(\vec{\mathrm{r}}),\tag{2.24}$$

$$V^{\mathrm{pc}}(\vec{\mathrm{r}})=\sum_{m,n}\frac{-Z_m}{|\vec{\mathrm{r}}-\vec{\mathrm{R}}_n^m|}+V_u,\quad m=1,2\tag{2.25}$$

$$\langle V^{\mathrm{pc}}(\vec{\mathrm{r}})\rangle=0\ ,\tag{2.26}$$

$$V^{\mathrm{core}}(\rho_m)=V_m^{\mathrm{ion}}(\rho_m)+Z_m/\rho_m,\quad \rho_m\leq R\ .\tag{2.27}$$

The point-charge potential V^{pc} is a sum of point charges Z_m on the two fcc lattices $m=1,2$. V_u is the potential of a uniform electron gas of charge density $-(Z_1+Z_2)/\Omega$ sufficient to give charge neutrality. V_u is also understood to include a constant term of such a magnitude that (2.26) holds, i.e., the average point-charge potential is 0.

In Eq. (2.27) the core potential $V^{\mathrm{core}}(\rho_m)$ is defined in such a way as to correct the atom-site potential from the simple point-charge value to the ion-core value $V_m^{\mathrm{ion}}(\rho_m)$. It is assumed that the ion-core potential is accurately Coulombic outside the atomic spheres.

In the Appendix we show that the point-charge potential can be expressed in a spherical-harmonic expansion inside the atomic spheres as follows:

$$V^{\mathrm{pc}}(\vec{\rho}_m)=-\frac{Z_m}{\rho_m}+\frac{Z_m}{a}A_0^c+\frac{Z_{m'}}{a}A_0^t-\frac{8\pi}{3}\frac{(Z_1+Z_2)}{a^3}\rho_m^2$$
$$+\sum_{l=3,7}(-1)^{m+1}\frac{Z_{m'}A_l^t\rho_m^lK_{2-}^l(\hat{\vec{\rho}}_m)}{a^{l+1}}$$
$$+\sum_{l=4,6,8}\frac{(Z_mA_l^c+Z_{m'}A_l^t)}{a^{l+1}}\rho_m^lK_{1+}^l(\hat{\vec{\rho}}_m),\quad \rho_m\leq R\ .\tag{2.28}$$

Z_m is the point charge on site m, and $Z_{m'}$ is the point charge on the "other" site, i.e., $(m=1, m'=2)$ or $(m=2, m'=1)$. The structure constants A_l^c and A_l^t are given numerically in Table I.

With the help of (2.28) it is then possible to calculate the Fourier components of $P_{\mathrm{EXT}}V^{\mathrm{pc}}(\vec{\mathrm{r}})$ using the identity $P_{\mathrm{EXT}} = 1-(1-P_{\mathrm{EXT}})$. Using also the plane-wave expansion of (2.8), we have

$$\int P_{\mathrm{EXT}}V^{\mathrm{pc}}(\vec{\mathrm{r}})e^{-i\vec{\mathrm{Q}}\cdot\vec{\mathrm{r}}}d\vec{\mathrm{r}} = \sum_{m=1}^{2} -\frac{4\pi\varphi_m(\vec{\mathrm{Q}})Z_m}{Q^2\Omega} + \frac{\varphi_m(\vec{\mathrm{Q}})}{\Omega}\Bigg(4\pi Z_m B_z - 4\pi R^2\frac{j_1(QR)}{Qa}(Z_mA_0^c + Z_{m'}A_0^t) + \frac{32\pi^2(Z_1+Z_2)}{3a^3}B_2$$

$$+\sum_{l=3,7}(-1)^{m+1}\frac{Z_{m'}A_l^t 4\pi i^l K_{2-}^l(\hat{\vec{\mathrm{Q}}})}{a^{l+1}}B_{l+1} - \sum_{l=4,6,8}\frac{Z_mA_l^c + Z_{m'}A_l^t}{a^{l+1}}4\pi i^l K_{1+}^l(\hat{\vec{\mathrm{Q}}})B_{l+1}\Bigg), \tag{2.29}$$

$$B_z = (1-\cos QR)/Q^2\,, \tag{2.30}$$

$$B_2 = R^3[QRj_1(QR) - 2j_2(QR)]/Q^2\,, \tag{2.31}$$

$$B_l = Q^{-1}R^{l+1}j_l(QR), \quad l \geq 3\,. \tag{2.32}$$

In deriving (2.32) we have used the identity

$$\int_0^R \rho^{l+2}j_l(\rho)d\rho = R^{l+2}j_{l+1}(R)\,. \tag{2.33}$$

C. Nonspherical Potential

In Eqs. (2.15) and (2.16) the nonspherical potential $V^{\mathrm{NS}}(\vec{\mathrm{r}})$ is defined in terms of a spherical-harmonic expansion. Using the decomposition of the potential into point-charge, core, and valence contributions [as in (2.24)] we note that Eq. (2.29) gives us the expansion we require for the point-charge potential. The analogous expansion for the valence potential is easily obtained by expanding the Fourier series of (2.23) according to Eq. (2.8).

To keep the notation simple we write the result in general and understand that we wish to apply it to V^{val}:

$$V(\vec{\mathrm{r}}) = (4\pi)^{1/2}\textstyle\sum_l V_l^m(\rho_m)K_j^l(\hat{\vec{\rho}}_m)\,, \tag{2.34}$$

$$V(\vec{\mathrm{r}}) = \textstyle\sum_{\vec{\mathrm{Q}}}\tilde{V}(\vec{\mathrm{Q}})e^{i\vec{\mathrm{Q}}\cdot\vec{\mathrm{r}}}\,, \tag{2.35}$$

$$V_l^m(\rho_m) = (4\pi)^{1/2}i^l\textstyle\sum_{\vec{\mathrm{Q}}}\varphi_m(-\vec{\mathrm{Q}})\,\tilde{V}(\vec{\mathrm{Q}})K_j^l(\hat{\vec{\mathrm{Q}}})j_l(Q\rho_m)\,. \tag{2.36}$$

$j = 1+$ or $2-$ because of the tetrahedral site symmetry. We can use symmetry to sum over the star of $\vec{\mathrm{Q}}_0$, $\vec{\mathrm{Q}} = \tilde{R}\vec{\mathrm{Q}}_0$, where $\tilde{R}$ is a cubic operation. We require irreducibly transforming functions. For the potential we define $\tilde{V}_j(Q)$:

$$\begin{aligned}\tilde{V}_{1+}(\vec{\mathrm{Q}}) &= \tfrac{1}{2}[\tilde{V}(\vec{\mathrm{Q}}) + \tilde{V}(-\vec{\mathrm{Q}})],\\ \tilde{V}_{2-}(\vec{\mathrm{Q}}) &= \tfrac{1}{2}[\tilde{V}(\vec{\mathrm{Q}}) - \tilde{V}(-\vec{\mathrm{Q}})]\,,\end{aligned} \tag{2.37}$$

where $\tilde{V}_{1+}$ is symmetric under inversion about the origin while $\tilde{V}_{2-}$ is antisymmetric. Naturally $\tilde{V}_{2-}$ is zero in the diamond lattice.

The function $\varphi_m(\vec{\mathrm{Q}})$ of Eq. (2.9) is decomposed into $\varphi_{mj}(\vec{\mathrm{Q}})$:

$$\begin{aligned}\varphi_m(\vec{\mathrm{Q}}) &= \varphi_{m1+}(\vec{\mathrm{Q}}) + \varphi_{m2-}(\vec{\mathrm{Q}})\,,\\ \varphi_{m1+}(\vec{\mathrm{Q}}) &= \cos(\vec{\mathrm{Q}}\cdot\vec{\tau}/2)\,,\\ \varphi_{m2-}(\vec{\mathrm{Q}}) &= i(-1)^{m+1}\sin(\vec{\mathrm{Q}}\cdot\vec{\tau}/2)\,.\end{aligned} \tag{2.38}$$

The sum over the star of $\vec{\mathrm{Q}}_0$ in (2.36) can then be easily performed:

$$V_l^m(\rho_m) = (4\pi)^{1/2}i^l\sum_{\vec{\mathrm{Q}}_0, j1}N(\vec{\mathrm{Q}}_0)\,\varphi_{mj2}(-\vec{\mathrm{Q}}_0)$$

$$\times\tilde{V}_{j1}(\vec{\mathrm{Q}}_0)K_j^l(\hat{\vec{\mathrm{Q}}}_0)j_l(Q_0\rho_m)\,, \tag{2.39}$$

$$j2 = j1\times j\,, \tag{2.40}$$

where $N(\vec{\mathrm{Q}}_0)$ is the number of elements in the star of $\vec{\mathrm{Q}}_0$. The product of the representations in (2.40) is easily given as $j\times j = 1+$, $(1+)\times(2-) = 2-$.

Following Rudge,[3] we compute the matrix elements of the nonspherical potential using Eq. (2.2) with the radial functions determined from the spherical potential as in Eq. (2.7). This is roughly equivalent to treating the nonspherical potential by first-order perturbation theory. We find that in silicon the nonspherical contribution to the valence energies are at most 0.4 eV so that Rudge's treatment should be good whenever energy gaps between states of the same symmetry considerably

TABLE I. Dimensionless lattice-sum coefficients for the fcc, diamond, and zinc-blende lattices.

l	A_l^c	A_l^t
0	4.5848620	0.8019360
3	0	−106.29
4	11.644	153.838
5	0	0
6	74.0677	−867.311
7	0	1836.76
8	−97.2070	−1345.33

exceed this value.

If this correction becomes serious the present approach can be easily extended to include the computation and diagonalization of V^{NS} as a small submatrix connecting the unperturbed bands. Because of the small value of V^{NS} the size of the submatrix will always be quite small.

In computing the nonspherical contributions we have used only the $l=3$ and $l=4$ contributions to the potential. Higher terms should be much smaller. Calling these terms V_3 and V_4 we have

$$\langle\psi|V_l|\psi\rangle = \sum_{m,l_1,j,\alpha,l_2} c^{m*}_{l_1 j\alpha}\, c^{m}_{l_2\tilde{j}\tilde{\alpha}}\, \langle u^m_{l_1}(\rho_m)|V^m_l(\rho_m)|u^m_{l_2}(\rho_m)\rangle \times\{l_1 l_2 l\}_{j\alpha}, \quad l=3,4 \qquad (2.41)$$

$$\{l_1 l_2 3\}_{j\alpha} = (4\pi)^{1/2}\int d\hat{\vec{\rho}}\, K^{l_1}_{j\alpha}(\hat{\vec{\rho}})K^{3}_{2-}(\hat{\vec{\rho}})K^{l_2}_{\tilde{j}\tilde{\alpha}}(\hat{\vec{\rho}}), \qquad (2.42)$$

$$\{l_1 l_2 4\}_{j\alpha} = (4\pi)^{1/2}\int d\hat{\vec{\rho}}\, K^{l_1}_{j\alpha}(\hat{\vec{\rho}})K^{4}_{1+}(\hat{\vec{\rho}})K^{l_2}_{j\alpha}(\hat{\vec{\rho}}) . \qquad (2.43)$$

In (2.42), $\Gamma_{\tilde{j}\tilde{\alpha}}$ is the outer product of the representations $\Gamma_{2-}\times\Gamma_{j\alpha}$. These cubic Clebsch-Gordan coefficients are given in Koster's group-theory tables.[8] The integrals over cubic harmonics given in (2.42) and (2.43) can be expressed in terms of spherical Clebsch-Gordan coefficients but for our needs it is just as easy to calculate them directly. Cubic rotational invariance requires that $\{l_1 l_2 3\}_{j\alpha}$ and $\{l_1 l_2 4\}_{j\alpha}$ are independent of α.

We have included all possible couplings of $l_1=0, 1, 2$ with $l_2=0, 1, 2, 3, 4$ in Eq. (2.41) but have ignored couplings of $l_1=3, 4$ with $l_2=3, 4$ as well as coupling of all higher-l values.

With these restrictions there are just four values of $\{l_1 l_2 3\}_j$ and six of $\{l_1 l_2 4\}_j$ which are required. For convenience, these quantities are listed in Table II.

TABLE II. Cubic-harmonic coupling integrals $\{l_1 l_2 l\}_j$. See Eqs. (2.42) and (2.43). j is a cubic representation in the notation of Ref. 8.

$\{033\}_{1+}=1$

$\{123\}_{4-}=\sqrt{3}/\sqrt{7}$

$\{143\}_{4-}=2/\sqrt{7}$

$\{323\}_{4-}=-\frac{2}{3}$

$\{044\}_{1+}=1$

$\{134\}_{4-}=\frac{2}{3}$

$\{224\}_{3+}=\sqrt{3}/\sqrt{7}$

$\{224\}_{5+}=-2/\sqrt{21}$

$\{244\}_{3+}=\frac{20}{11}/\sqrt{7}$

$\{244\}_{5+}=-\frac{10}{11}/\sqrt{7}$

TABLE III. Energy levels at Γ in eV. Lowest valence levels of the indicated symmetry in Koster's notation and the standard band notation.

Γ_{5+}	14.41	$\Gamma_{25'}$
Γ_{4-}	17.61	Γ_{15}
Γ_{2-}	18.17	$\Gamma_{2'}$

III. CONVERGENCE AND COMPUTATIONAL ACCURACY

We have applied the method of Sec. II to the study of the band structure of silicon. We have used the valence-electron charge density given by Brinkman and Goodman.[9] We have also used their results for the Slater approximation to exchange involving the valence electrons. We have treated the interaction with the ionic core by fitting to the atomic term levels of Si^{3+} in a manner similar to Heine and Abarenkov.[10] Our results for the important levels at the Γ point are given in Table III in eV. Because of our different method of treating the core interactions we differ by as much as 0.7 eV from Brinkman and Goodman's results. We discuss the potential and band structure of silicon at length in another publication.[11] For the present we are interested in the convergence properties and computational accuracy of our method. We do not expect these results to depend sensitively

TABLE IV. Convergence of energy levels at Γ as a function of the number of plane waves n in the secular equation. Energies in double Ry. Atomic sphere radius is 2.15 Bohr radii. Numbers in parentheses are OPW values of Ref. 12.

n	$\Gamma_{2-}(n) - \Gamma_{2-}(339)$	$\Gamma_{5+}(n)-\Gamma_{5+}(307)$	$\Gamma_{4-}(n) - \Gamma_{4-}(307)$
9			
15	0.001 02	0.027 5	
27		0.013 5, (0.058)	0.009 72
51	0.000 923	0.005 21	0.006 32
59	0.000 061	0.001 04, (0.019)	0.001 35
65			0.001 31
89	0.000 022	0.000 505	0.000 299
113	0.000 021	0.000 157	
137	0.000 013	0.000 057, (0.0040)	0.000 126
145	0.000 005		0.000 044
169		0.000 029	
181			0.000 013
229	−0.000 008		
253		0.000 006, (0.0015)	0.000 001
259	−0.000 030		
283			
307		0.000 000	0.000 000
331			
339	0.000 000		

on the choice of potential.

The "figure of merit" for a band-structure calculation is generally considered to be the size of the secular equation which must be manipulated in order to obtain the eigenvalues. For the OPW and APW methods this is the number of "plane waves" used. In Table IV we tabulate this convergence for the lowest valence levels at Γ of the indicated symmetry. The number of plane waves n is the value which would be required without making use of symmetry. By comparing these results to the recent OPW study of silicon by Stukel and Euwema[12] it can be seen that the APW method is significantly more rapidly convergent. This result is to be expected because of the much better treatment of the wave function inside the atomic spheres. The plane-wave expansion is only called on to represent the wave function outside the spheres.

The Korringa-Kohn-Rostoker (KKR)[13] method requires a secular equation which is even smaller than the APW method. However, this method requires a muffin-tin approximation in the usual treatments. See Ref. 6, however. We have tested the muffin-tin approximation for silicon and have found it to be quite unsatisfactory. The changes in the energy levels at Γ and the indirect gap E_G owing to making the muffin-tin approximation are shown in Table V. The most serious change is in the indirect gap which is shifted by 3.4 eV. The shifts due to the nonspherical parts of the potential inside the atomic spheres are also noted in Table V. These are seen to be much smaller than the muffin-tin errors but still are not negligible. Since the shifts are less than 0.4 eV we felt that our perturbative method of calculation is satisfactory. When bands of the same symmetry come close in energy it would be desirable to treat the anisotropy corrections more accurately by diagonalizing a small submatrix.

In performing the l sum in Eq. (2.20) we have gone up to $l_{\max}=9$. The difference between $l_{\max}=9$ and $l_{\max}=4$ was at most 0.05 eV so we feel that $l_{\max}=9$ is more than adequately large.

TABLE V. Numbers in the right-hand column give the energy shift of the principal levels at Γ and the indirect gap E_G due to the nonspherical potential inside the atomic spheres. Left-hand column gives the muffin-tin shifts due to the nonspherical potential plus the nonflat-potential outside the atomic spheres. Energies in eV.

	E(non-muffin-tin) $-E$(muffin-tin)	E(anisotropy) $-E$(spherical)
$\delta\Gamma_{5+}$	-1.16	-0.392
$\delta\Gamma_{4-}$	0.582	0.210
$\delta\Gamma_{2-}$	0.577	0.218
δE_G	3.43	0.128

TABLE VI. Energy shifts of the principal levels at Γ due to changing the atomic sphere radius R. R in Bohr radii, energy in eV.

	$E(R=2.15)$ $-E(R=1.75)$	$E(R=2.15)$ $-E(R=1.35)$
$\delta\Gamma_{5+}$	0.020	0.013
$\delta\Gamma_{4-}$	0.0095	0.0049
$\delta\Gamma_{2-}$	0.017	0.032

The use of a non-muffin-tin method permits us to vary the atomic sphere radius R. The maximum possible value where the spheres touch is $R_{\max}=\frac{1}{8}\sqrt{3}\,a$. For silicon where $a=10.263a_0$, $R_{\max}=2.22a_0$. We have generally used $R=2.15$ Bohr radii. We have also tested our results for smaller values of R and have found the expected result that for smaller values of R the number of plane waves required for convergence is greater. Hence it appears that the largest value of R is best for computational purposes. The change in the principal levels at Γ in going from $R=2.15$ to 1.75 and 1.35 are given in Table VI. The maximum variation is 0.03 eV. At the present time we are not sure of the source of this discrepancy. The anisotropy corrections should be very small for $R=1.35$. Hence this calculation gives a limit on the error in our method of treating these nonspherical corrections. It also provides a useful check on the calculation in general since many of the details depend on the size of the sphere radius.

Table IV indicates that in order to achieve 0.03-eV accuracy 60 plane waves are needed. In order to reduce the matrix size as much as possible without losing accuracy we make a Löwdin transformation.[14] This transformation divides states into two classes: i,j in class A and J in class B. Interactions between states in A and states in B are treated perturbatively while interactions between states in A are treated exactly. The matrix element h_{ij} then is renormalized to

$$h_{ij}\rightarrow h_{ij}+\sum_{J\,\mathrm{in}\,B}\frac{h_{iJ}h_{Jj}}{h_{JJ}-E}\;. \tag{3.1}$$

In our calculations we have divided the APW plane waves into sets A and B by the inequalities

$$\begin{aligned}&(a/2\pi)^2k_i^2\leq 9, &&k_i \text{ in } A\\ 9<&(a/2\pi)^2k_J^2\leq 19.5, &&k_J \text{ in } B\;.\end{aligned} \tag{3.2}$$

For this choice of A and B we estimate the convergence error in the APW method to be ≤ 0.03 eV.

The convergence is quite comparable to the empirical pseudopotential method. The difference is that the matrix elements of the Hamiltonian are much easier to compute in the empirical pseudopotential approach.

IV. SUMMARY

A. Broad Summary

To summarize, we have presented a practical scheme for treating the non-muffin-tin corrections to the APW method for the zinc-blende lattice. We have tested the method on silicon. The convergence in terms of plane waves is significantly better than the OPW method and is comparable to the empirical pseudopotential method. The non-muffin-tin corrections are of two types: "nonflat" and "nonspherical." The nonflat corrections may be as large as 3.4 eV while the nonspherical corrections are less than 0.4 eV. The latter are treated by first-order perturbation theory while the former are treated exactly. Sixty plane waves lead to results accurate to ~ 0.03 eV for a sphere radius $R = 2.15 a_0$. The number of plane waves required for convergence increases as R decreases. The converged results are independent of sphere radius for R between $2.15 a_0$ and $1.35 a_0$ with an accuracy of better than 0.03 eV.

We should note that band calculations on tetrahedrally bonded II-VI compounds have obtained better results using the muffin-tin potential[15] than might have been expected from the results reported here. However, recent results of Walter and Cohen[16] show that the bond charge in II-VI compounds is significantly smaller than in the purely covalent column IV compounds. For this reason, it seems reasonable to expect that the muffin-tin potential will become a better approximation as we move from covalent to more ionic materials.

B. Detailed Summary

In Eq. (2.18) we have broken up the Hamiltonian into muffin-tin, nonflat, and nonspherical contributions. For reference, the muffin-tin secular equation is given in Eq. (2.20). To treat the nonflat potential we simply add the plane-wave matrix elements of the potential outside the atomic spheres. This is easily obtained from Eq. (2.22) for a single Fourier component. Fourier expansion is a good way to treat the valence-electron contribution but it converges slowly for the ionic potential.

In Eq. (2.28) we give a spherical-harmonic representation of the point-charge potential V^{pc} which is used in (2.29) to give the Hamiltonian matrix elements.

The nonspherical potential is treated by perturbation theory using the radial functions computed from the spherical potential in Eq. (2.7). We use the $l = 3$ and $l = 4$ components of the nonspherical potential which are obtained from Eq. (2.28) for the point-charge potential and Eq. (2.36) or (2.39) for the valence-charge potential. The matrix elements of the nonspherical perturbation are given in Eq. (2.41). The spherical-harmonic coefficients $c^m_{lj\alpha}$ are given in terms of the plane-wave coefficients b_n in Eq. (2.11). The angular integrals $\{l_1 l_2 l\}_j$ are given in Table II. The radial integrals must be obtained numerically.

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APPENDIX: MULTIPOLE EXPANSION OF THE POINT-CHARGE POTENTIAL ENERGY

We are interested in the potential energy due to an array of point charges located on the zinc-blende lattice, namely,

$$V^{\mathrm{pc}}(\vec{\rho}_m) = -\sum_{\vec{\mathrm{R}}^m_n} \frac{Z_m}{|\vec{\rho}_m - \vec{\mathrm{R}}^m_n|} - \sum_{\vec{\mathrm{R}}^{m'}_n} \frac{Z_{m'}}{|\vec{\rho}_m - \vec{\mathrm{R}}^{m'}_n|} + V_U , \tag{A1}$$

where V_U is the potential of a uniform distribution of electronic charge sufficient to guarantee charge neutrality, plus a constant such that the average value of $V^{\mathrm{pc}}(\vec{\mathrm{r}})$ is zero.

The sums in Eq. (A1) are over the two interpenetrating fcc lattices which constitute the zinc-blende lattice. The sum on $\vec{\mathrm{R}}^m_n$ is over the fcc lattice which includes lattice site m. This lattice has full cubic symmetry with respect to rotations about lattice site m. The sum on $\vec{\mathrm{R}}^{m'}_n$ is over the fcc lattice which is tetrahedrally oriented with respect to lattice site m.

By using a multipole expansion of the form

$$\frac{1}{|\vec{\rho} - \vec{\mathrm{R}}|} = 4\pi \sum_{l,j,\alpha} \frac{\rho^l}{R^{l+1}} \frac{K^l_{j\alpha}(\hat{\vec{\rho}}) K^l_{j\alpha}(\hat{\vec{\mathrm{R}}})}{(2l+1)} , \quad \rho < R \tag{A2}$$

we can express Eq. (A1) in the form

$$V^{\mathrm{pc}}(\vec{\rho}_m) = -\frac{Z_m}{\rho_m} + \frac{Z_m}{a} A^c_0 + \frac{Z_{m'}}{a} A^t_0 - \frac{8\pi}{3} \frac{(Z_1 + Z_2)}{a^3} \rho^2_m + \sum_{l,j,\alpha} \frac{\rho^l}{a^{l+1}} \{Z_m A^c_l + Z_{m'} A^t_l\} K^l_{j\alpha}(\hat{\vec{\rho}}_m) , \tag{A3}$$

$$A^c_l = -4\pi \sum_{\vec{\mathrm{R}}^m_n} \frac{K^l_{j\alpha}(\hat{\vec{\mathrm{R}}}^m_n)}{(2l+1)(R^m_n/a)^{l+1}} , \tag{A4}$$

with an exactly analogous formula for A^t_l with $\vec{\mathrm{R}}^{m'}_n$ substituted for $\vec{\mathrm{R}}^m_n$.

Because of the cubic symmetry only $K^l_{1+}(\hat{\vec{\mathrm{R}}}^m_n)$ contributes to A^c_l. A^t_l receives contributions from $K^l_{1+}(\hat{\vec{\mathrm{R}}}^{m'}_n)$ and $K^l_{2-}(\hat{\vec{\mathrm{R}}}^{m'}_n)$, which are both totally symmetric under the tetrahedral group. These lattice sums are easily evaluated numerically by direct summation. Optimum convergence is obtained by summing over lattice shells which form the closest possible approximation to a sphere since a truly spherical shell would make a zero contribution. The values are tabulated in Table I.

The term in ρ^2 comes from the electron gas and corresponds to a uniform charge density of $-(Z_1+Z_2)/\Omega$. This can be checked by computing $\nabla^2 V$. The terms A_0^c and A_0^t can be expressed in terms of the potential in a simple-cubic lattice which has been computed by Takahasi and Sakamoto using an Ewald method.[17] In terms of their functions ψ and $\bar{\psi}$ we have

$$A_0^c = \bar{\psi}(0) + 3\psi(\tfrac{1}{2}, \tfrac{1}{2}, 0),$$
$$A_0^t = 4\psi(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}) . \qquad (A.5)$$

These values are also included in Table I.

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