

Modified Augmented-Plane-Wave Method for Calculating Energy Bands*

LEONARD KLEINMAN AND ROBERT SHURTLEFF

Department of Physics, University of Texas, Austin, Texas 78712

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The orthogonalized-plane-wave (OPW) expansion converges poorly for ionic crystals and also for d -bands in transition metals even when modified by the addition of an atomiclike d function to the basis set. The augmented-plane-wave (APW) expansion converges rapidly, but requires the crystal potential to be approximated by an unphysical spherical muffin-tin potential. We here develop a modified APW expansion and compare its convergence with the other methods. The modified APW converges with the rapidity of the usual APW but, like the OPW, is applicable to nonspherical potentials.

I. INTRODUCTION

THE basic mathematical difficulty in calculating energy bands lies in finding a basis set in which an expansion of the crystal wave functions is rapidly convergent. The difficulty arises from the fact that near the lattice sites an expansion in atomic wave functions is appropriate, whereas in the interstitial regions a plane-wave expansion is rapidly convergent. Several methods of overcoming this dilemma are well known; all of them are closely related to one of two basic methods.¹ The augmented-plane-wave (APW) method^{2,3} was first proposed by Slater in 1937. It consists of an expansion in basis functions made up of a single plane wave in the interstitial region and of a sum of exact solutions to the Schrödinger equation in a spherical region about each atom with coefficients chosen to make the APW basis function continuous at the boundary of the sphere. This method seems to converge rapidly in most cases,⁴ whether used for simple metals, transition metals, semiconductors, or ionic crystals. Its major drawback is that the crystal potential must be approximated by a muffin tin, i.e., it must be spherical within the atomic spheres and constant outside them. It can be extended to the warped muffin-tin potential, which is spherical within the atomic spheres but not constant outside the spheres.^{5,6} Such a potential, however, is even less physical than the simple muffin tin (although it may lead to energy bands in better agreement with experiment), because it is not an analytic function.

The orthogonalized-plane-wave (OPW) method introduced by Herring⁷ in 1940 consists of expanding the valence wave functions in plane waves which have been orthogonalized to the occupied core states. This introduces the proper atomic character into the basis set, and convergence is fairly rapid for simple metals and

semiconductors. The OPW method (unlike the APW) is easily applied to nonspherical self-consistent crystal potentials. The convergence is worse for ionic crystals whose valence functions are poorly represented by plane waves. No convergence at all is obtained for the 3- d transition metals.⁸ This is because the 3- d functions are by symmetry automatically orthogonal to all the core functions, and the OPW expansion reduces to a simple plane-wave expansion. Following a suggestion in Herring's original paper,⁷ Callaway⁹ and Deegan and Twose¹⁰ modified the OPW expansion with the addition of atomic d functions which were made to vanish smoothly at the inscribed sphere. This modified OPW expansion (MOPW) converges, but not nearly as rapidly as the APW.

We introduce here a modified APW expansion (MAPW), which converges with nearly the rapidity of the old APW in all cases and yet is applicable to nonspherical crystal potentials. In Sec. II we derive the MAPW method for spherical muffin-tin potentials; in Sec. III we compare the convergence of the MAPW with the MOPW and the APW for nickel; and in Sec. IV we extend the MAPW method to nonspherical potentials.

II. MAPW METHOD

The MOPW method adds to the plane-wave basis set a set of atomic functions which are forced to go to zero smoothly at the inscribed sphere radius r_0 . Because of this they are not exact solutions to the Schrödinger equation within the inscribed sphere. Even if the atomic functions are exact solutions within some smaller sphere of radius r_{00} , the final crystal wave function obtained from an expansion using the atomic functions and a finite number of plane waves will not be exact within the r_{00} sphere. This is because any finite number of plane waves will give some additional contribution to the already exact wave function within the r_{00} sphere. The APW method avoids this difficulty by expanding in functions consisting of a plane wave outside the sphere joined continuously (but not smoothly) to an (in principle) infinite number of exact solutions inside

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¹ We are excluding from consideration all cellular methods.

² J. C. Slater, *Phys. Rev.* **51**, 846 (1937).

³ T. L. Loucks, *Augmented Plane Wave Method* (W. A. Benjamin, Inc., New York, 1967).

⁴ The transition metal dioxides and trioxides where the oxygen p 's hybridize with the metal d 's seem to be a case of slow convergence.

⁵ F. Belezny and M. J. Lawrence, *J. Phys.* **C1**, 1288 (1968).

⁶ H. Schlosser and P. M. Marcus, *Phys. Rev.* **131**, 2529 (1963).

⁷ C. Herring, *Phys. Rev.* **57**, 1169 (1940).

⁸ We have used 4279 plane waves in an expansion of the Γ_{12} level of Ni without any sign of convergence.

⁹ J. Callaway, *Phys. Rev.* **97**, 933 (1955); **99**, 500 (1955).

¹⁰ R. A. Deegan and W. D. Twose, *Phys. Rev.* **164**, 993 (1967).

the sphere. These exact solutions are of the form $\psi_{lm} = f_l(r)Y_{lm}(\hat{r})$, where Y_{lm} is a spherical harmonic and

$$[-\nabla_r^2 + V(r) + l(l+1)/r^2 - E_0]f_l(r) = 0. \quad (1)$$

In practice,³ the maximum value of l used is about 12, giving 169 different ψ_{lm} . Thus, if the potential within the inscribed sphere were to be nonspherical, then instead of 12 uncoupled differential equations one would have 169 coupled differential equations to solve numerically. This is beyond the capability of present day computers and is the reason why the APW method has been limited to spherical muffin-tin potentials.

We therefore propose a modified APW basis function,

$$\chi_k = (N\Omega)^{-1/2} \left(e^{i\mathbf{k} \cdot \mathbf{r}} - 4\pi \sum_{\text{val } l} \sum_{m=-l}^l \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} r_l \right. \\ \left. \times [j_l(kr_n) - f_l(r_n)j_l(kr_0)/f_l(r_0)] \right. \\ \left. \times Y_{lm}^*(\hat{k})Y_{lm}(\hat{r}_n)\Theta(r_0 - r_n) \right), \quad (2)$$

where j_l is a spherical Bessel function, $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$ with \mathbf{R}_n a lattice vector,¹¹ and Θ is a unit step function. This MAPW basis function differs from the APW in that only l values corresponding to atomic valence states¹² are summed over; in the APW method all values of l are summed over.¹³ Like the APW, the MAPW basis function is continuous at the inscribed sphere, but has a discontinuous normal derivative. Although in the remainder of this section we shall use the spherical muffin-tin potential, one can already see that by reducing the l sum to valence states we have removed the major obstacle to extending the APW method to nonspherical potentials. In Sec. III we shall see that we have done this without incurring any appreciable loss of convergence.

Schlosser and Marcus⁶ have derived the following variational expression for the energy E_v when two separate basis sets are used, one in an inner volume Ω_i bounded by a surface S and the other in the outer volume Ω_o of the unit cell:

$$E_v \int_{\Omega_i + \Omega_o} \psi^* \psi d\Omega = \text{Re} \left(\int_{\Omega_i + \Omega_o} \psi^* H \psi d\Omega \right. \\ \left. + \int_S (\psi_o^* \partial_n \psi_i - \psi_i^* \partial_n \psi_o) dS \right). \quad (3)$$

¹¹ For simplicity we assume one atom per unit cell. The extension to more complicated crystal structures is trivial.

¹² In cases where there are occupied core levels with l values not found in the valence, one should include those core l values in the valence l sum lest the expansion converge to that core level. For example, in a calculation involving Br or its ion one would include $l=2$ along with the valence $l=0$ and 1 in the sum.

¹³ In standard APW calculations one takes $\chi_k^{\text{out}} = (N\Omega)^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}}$ and $\chi_k^{\text{in}} = (N\Omega)^{-1/2} 4\pi \sum_{n,l,m} e^{i\mathbf{k} \cdot \mathbf{R}_n} j_l(kr_0) Y_{lm}^*(\hat{k}) Y_{lm}(\hat{r}_n) f_l(r_n)/f_l(r_0)$, which is identical to Eq. (2) only when the sum over l is actually infinite. Since the sum in practice must be finite, the standard APW basis functions are actually slightly discontinuous.

The surface integral reduces to $\int_S \psi^* (\partial_n \psi_i - \partial_n \psi_o) dS$ in the present case of continuous functions. The E_0 in Eq. (1) should be taken to be the variational energy E_v . However, Eq. (3) is variationally correct¹⁴ even when $E_0 \neq E_v$, thus accelerating the iterative process of making $E_0 = E_v$.

If we write $\psi = \sum_k A_k \chi_k$, where the sum is over all \mathbf{k} differing by a reciprocal lattice vector from a given \mathbf{k} within the Brillouin zone, Eq. (3) becomes

$$\text{Re} \sum_{\mathbf{k}\mathbf{k}'} A_{\mathbf{k}}^* A_{\mathbf{k}'} (H_{\mathbf{k}\mathbf{k}'} + S_{\mathbf{k}\mathbf{k}'} - E_v D_{\mathbf{k}\mathbf{k}'}) = 0 \quad (4)$$

or

$$\sum_{\mathbf{k}\mathbf{k}'} A_{\mathbf{k}}^* A_{\mathbf{k}'} (H_{\mathbf{k}\mathbf{k}'} + H_{\mathbf{k}'\mathbf{k}}^* \\ + S_{\mathbf{k}\mathbf{k}'} + S_{\mathbf{k}'\mathbf{k}}^* - 2E_v D_{\mathbf{k}\mathbf{k}'}) = 0, \quad (5)$$

where $D_{\mathbf{k}\mathbf{k}'}$, $H_{\mathbf{k}\mathbf{k}'}$, and $S_{\mathbf{k}\mathbf{k}'}$ are the overlap, Hamiltonian, and surface integrals of Eq. (3), and where we have used the fact that $D_{\mathbf{k}\mathbf{k}'}^* = D_{\mathbf{k}'\mathbf{k}}$. Because the first-order variation of E_v vanishes when a first-order variation of any $A_{\mathbf{k}}^*$ is made,⁶ a set of linear equations for the $A_{\mathbf{k}}$ are obtained which lead to the secular equation

$$\det |H_{\mathbf{k}\mathbf{k}'} + H_{\mathbf{k}'\mathbf{k}}^* + S_{\mathbf{k}\mathbf{k}'} + S_{\mathbf{k}'\mathbf{k}}^* - 2E_v D_{\mathbf{k}\mathbf{k}'}| = 0. \quad (6)$$

The matrix elements in Eq. (6) are easily evaluated:

$$D_{\mathbf{k}'\mathbf{k}} = \delta_{\mathbf{k}\mathbf{k}'} - \frac{4\pi}{\Omega} \sum_l (2l+1) P_l(\cos \theta_{\mathbf{k}\mathbf{k}'}) \\ \times \left(\int_0^{r_0} j_l(kr) j_l(k'r) r^2 dr \right. \\ \left. - \int_0^{r_0} f_l^2 r^2 dr j_l(kr_0) \frac{j_l(k'r_0)}{f_l^2} \right), \quad (7)$$

¹⁴ We question the validity of Eq. (3) when ψ is discontinuous. Schlosser and Marcus (Ref. 6) argue that the exact solution to which one is converging is continuous, and that their variational procedure involves integrations over the inner and outer volumes, but not over the discontinuity itself. This, we believe, is an incorrect limiting procedure. The fact remains that the final wave function, if expanded in a finite number of discontinuous functions, will contain a small discontinuity. This results in a "small" infinity in the kinetic energy of that function. We have applied Eq. (3) to the Γ_{12} level of Ni, expanding in $\psi_d(\mathbf{r}_n)\Theta(r_0 - r_n)$, where $\psi_d(\mathbf{r}_n)$ is the exact solution within the inscribed sphere, plus a set of $\psi_k = (N\Omega)^{-1/2} [e^{i\mathbf{k} \cdot \mathbf{r}} + 4\pi \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} j_2(kr_n) Y_{20}^*(\hat{k}) Y_{20}(\hat{r}_n) \Theta(r_0 - r_n)]$. The dd matrix element of Eq. (6) contained no surface contribution and was just $2(E_0 - E_v)$. The dk matrix elements consisted purely of surface terms and caused E_v to drop below the value E_0 obtained from the 1×1 determinant. Because of the nonorthogonality and discontinuity of the ψ_k , spurious eigenvalues (whose eigenvectors contained almost no ψ_d component) developed. We list the lowest nonspurious, as well as the spurious, eigenvalues for various sizes of secular determinants: (1×1) 0.2832; (2×2) 0.2773; (3×3) 0.2755; (4×4) -76.15, 0.2769; (6×6) -328.04, 0.2766; (8×8) -2361.58, -15.37, 0.2770.

$$H_{\mathbf{k}'\mathbf{k}} = k^2 \delta_{\mathbf{k}\mathbf{k}'} + V(\mathbf{k}-\mathbf{k}') - \frac{4\pi}{\Omega} \sum_l^{\text{val}} (2l+1) P_l(\cos\theta_{\mathbf{k}\mathbf{k}'})$$

$$\times \left(\int_0^{r_0} V(r) j_l(k'r) j_l(kr) r^2 dr \right.$$

$$+ k^2 \int_0^{r_0} j_l(k'r) j_l(kr) r^2 dr$$

$$\left. - E_0 \int_0^{r_0} f_l^2 r^2 dr j_l(kr_0) \frac{j_l(k'r_0)}{f_l^2} \right), \quad (8)$$

$$S_{\mathbf{k}'\mathbf{k}} = -\frac{4\pi}{\Omega} r_0^2 \sum_l^{\text{val}} (2l+1) P_l(\cos\theta_{\mathbf{k}\mathbf{k}'}) j_l(k'r_0) j_l(kr_0)$$

$$\times [k j_l'(kr_0)/j_l(kr_0) - f_l'(r_0)/f_l(r_0)], \quad (9)$$

where $P_l(\cos\theta_{\mathbf{k}\mathbf{k}'})$ is the Legendre polynomial of the cosine of the angle between \mathbf{k} and \mathbf{k}' , $V(\mathbf{r})$ is the potential which here must be either a flat or warped muffin tin,

$$V(K) = \Omega^{-1} \int_{\Omega_i + \Omega_0} V(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}} d^3\mathbf{r},$$

and the prime on $j_l'(kr_0)$ and $f_l'(r_0)$ indicates differentiation with respect to the arguments kr and r evaluated at $r=r_0$. The relative simplicity of the matrix elements is due to the fact that $e^{i\mathbf{k} \cdot \mathbf{r}} - 4\pi i^l \sum_m j_l(kr) Y_{lm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}})$ is orthogonal to $Y_{lm}(\hat{\mathbf{r}})$; thus, no cross terms involving $f_l(r)$ appear in Eqs. (7)–(9). All the matrix elements are obviously real. Although $H_{\mathbf{k}'\mathbf{k}}$ and $S_{\mathbf{k}'\mathbf{k}}$ are not individually symmetric, it can be shown³ that their sum is; thus Eq. (6) reduces to $\det |H_{\mathbf{k}\mathbf{k}'} + S_{\mathbf{k}\mathbf{k}'} - E_v D_{\mathbf{k}\mathbf{k}'}| = 0$.

III. CONVERGENCE

Because our desire was merely to test the convergence properties of various expansions, we chose a rather simple muffin-tin potential for nickel. The potential was generated using the Slater¹⁵ exchange approximation from a self-consistent d^9s^1 atomic configuration, using the program of Herman and Skillman¹⁶ and starting from their d^8s^2 configuration. A constant was subtracted from the potential in order to make it vanish at the inscribed sphere, $r_0=2.3500$ a.u.¹⁷ In spite of its simplicity, this potential is no worse than that used for most so-called first principles APW calculations. All calculations were done for the partner of the two-fold degenerate representation Γ_{12} whose d projection contains only the $m=0$ spherical harmonic.

¹⁵ J. C. Slater, Phys. Rev. **81**, 385 (1951).

¹⁶ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

¹⁷ This is the largest inscribed sphere commensurate with a mesh point of our numerical integration. The maximum inscribed sphere for the lattice constant $a_0=3.3293$ a.u. is $r_0=2.3542$ a.u.

TABLE I. Convergence of MOPW method for three different cutoff factors.

No. of PW	Matrix size	Energy (Ry)		
		$\alpha=2.0430$	$\alpha=3.1093$	$\alpha=4.1757$
15	2×2	0.3839295	0.4882709	0.5980045
65	5×5	0.3380652	0.3789099	0.4186325
169	10×10	0.3013187	0.3301688	0.3709477
259	15×15	0.2968527	0.3146819	0.3423550
379	20×20	0.2964055	0.3118600	0.3334954
555	25×25	0.2943814	0.3084479	0.3301247
705	30×30	0.2916657	0.3015888	0.3189393
813	35×35	0.2898656	0.2961349	0.3078040
989	40×40	0.2891362	0.2937418	0.3022876
1205	45×45	0.2885806	0.2917862	0.2972336
1373	50×50	0.2884777	0.2913704	0.2959369
2083	69×69	0.2883423	0.2910817	0.2954741

In the MOPW expansion we took the basis functions χ_i ($1 \leq i \leq n$) to be symmetrized combinations of plane waves and

$$\chi_0(\mathbf{r}) = \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} f_d(\mathbf{r}_n) e^{-\alpha(r_{00}-r_n)^2} Y_{20}(\theta, \varphi), \quad r_n > r_{00}$$

$$= \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} f_d(\mathbf{r}_n) Y_{20}(\theta, \varphi), \quad r_n < r_{00} \quad (10)$$

where $f_d(r)$ is the solution to the $l=2$ Schrödinger equation (1) with E_0 chosen to be the eigenenergy we are calculating. We need not have used the eigenenergy since, because of the cutoff factor $e^{-\alpha(r_{00}-r)^2}$, χ_0 is not an eigenfunction of the Hamiltonian, and therefore the convergence is not sensitive to small discrepancies between E_0 and the eigenenergy. The value of r_{00} is arbitrary, but should be chosen to be considerably larger than that value of r for which $f_d(r)$ is a maximum and yet much less than r_0 ; α is then chosen to make $\chi_0(r_0) < 10^{-3}$ so that overlap integrals involving $f_d(\mathbf{r}_n) f_d(\mathbf{r}_m)$ are negligible. The calculation of the secular determinant $\langle \chi_i | H - E | \chi_j \rangle$ is straightforward; the determination of the eigenvalue E and the eigenfunction $\psi_{12} = \sum_{i=0}^n A_i \chi_i$ is somewhat complicated by the fact that E occurs in the off-diagonal $0i$ matrix elements, but is still straightforward.¹⁸

In Table I we show the convergence of the eigenvalue (for $r_{00}=0.8805$, $E_0=0.2831952$ Ry, and three different values of α) as a function of the number of plane waves used and the dimensionality of the secular matrix. Each plane wave (PW) is counted once, whether it appears in zero, one, or more than one symmetrized combinations of plane waves (SCPW's).¹⁹ Thus the 2×2 matrix has as basis functions χ_0 and the (2,0,0) SCPW. The 15 PW's are the six (2,0,0) plus the eight (1,1,1) and the (0,0,0), which do not occur in Γ_{12} SCPW's. The convergence is seen to be very slow when compared with

¹⁸ I. Goroff and L. Kleinman, Phys. Rev. **164**, 1100 (1967), Sec. II.

¹⁹ Plane waves of the form (a,b,c) and $(a,b,0)$ each occur in two Γ_{12} SCPW's.

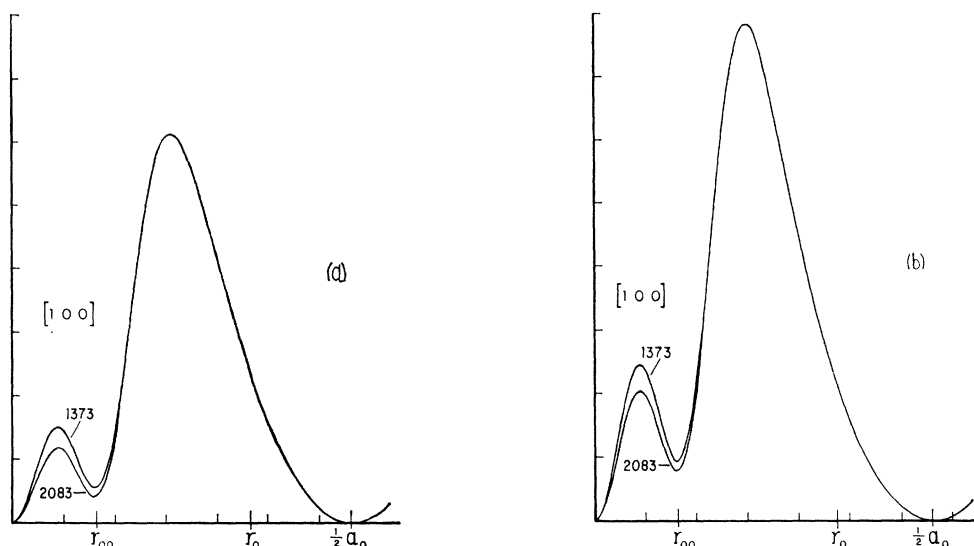


FIG. 1. PW contribution to Γ_{12} wave function in the $[100]$ direction for 1373 and 2083 MOPW expansions with (a) $\alpha = 2.0430$ and (b) $\alpha = 3.1093$.

the APW results of Table II. Furthermore, even though the drop in energy incurred going from a 1373 to a 2083 PW expansion is only 0.0001 Ry (for the smallest α), a further drop of 0.005 Ry must occur before convergence to the eigenvalue found by the APW method. The reason for this slow convergence becomes obvious when one looks at Fig. 1, in which we plot the PW contribution to Ψ_{12} in the $[100]$ direction for $\alpha = 2.0430$ and 3.1093. For $r < r_{00}$ where χ_0 by itself is the exact eigenfunction, the PW contribution should be zero; we see, however, that it is fairly large in the $r < r_{00}$ region.

Note that there is very little difference between the 1373 and 2083 PW expansions in the $r > r_{00}$ region, but that the 2083 PW expansion has a noticeably smaller amplitude in the $r < r_{00}$ region. Thus, the very slow convergence of 0.006 Ry which occurs after the first 1000 PW's is due almost entirely to the PW's canceling one another in the $r < r_{00}$ region. Note also that for the larger α not only is the over-all PW contribution larger (because the larger α makes χ_0 smaller), but that the amplitude in the $r < r_{00}$ region is disproportionately larger. Thus, when using the MOPW method, it is important to keep the cutoff factor as large as possible consistent with the nonoverlapping of wave functions on different sites. In Fig. 2(a) we show the PW contribution to ψ_{12} in the $[110]$ direction for $\alpha = 2.0430$, and in 2(b) we add this to χ_0 to obtain the total ψ_{12} wave function.

We have calculated the APW eigenvalues using the standard procedure,³ except that we take $Hf_i(r) = E_0 f_i(r)$ rather than assume $Hf_i(r) = E_r f_i(r)$. The final value of E_0 used was 0.2831952 Ry, which is sufficiently

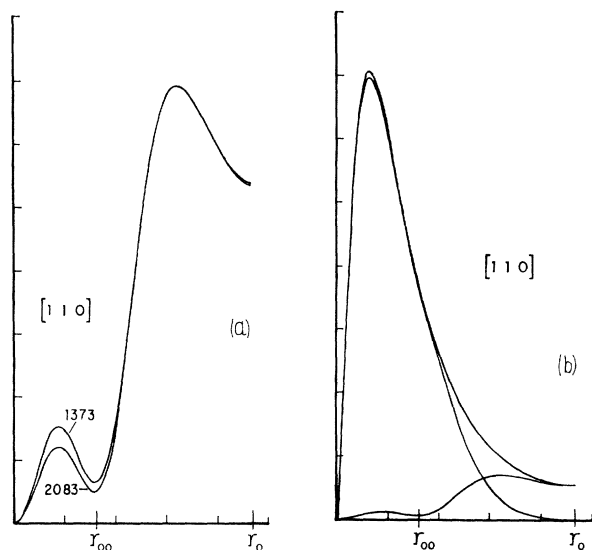


FIG. 2. (a) PW contribution to Γ_{12} wave function in the $[110]$ direction for 1373 and 2083 MOPW expansions with $\alpha = 2.0430$ (same scale as Fig. 1). (b) 2083 MOPW expansion of (a) added to χ_0 to give total Γ_{12} wave function in the $[110]$ direction.

TABLE II. Comparison of convergence of MAPW with APW method.

Size of matrix	No. of PW	APW			MAPW
		$l_{\max} = 6$	$l_{\max} = 12$	$l_{\max} = 18$	
1×1	15	0.2881819	0.2882095	0.2882095	0.2898665
2×2	27	0.2852193	0.2853354	0.2853354	0.2855048
3×3	51	0.2832355	0.2833480	0.2833480	0.2835035
5×5	89	0.2830794	0.2832323	0.2832324	0.2832481
7×7	113	0.2830645	0.2831952	0.2831957	0.2832029
9×9	169	0.2830600	0.2831922	0.2831927	0.2831940
12×12	229	0.2830314	0.2831921	0.2831926	0.2831935
14×14	259	0.2830067	0.2831919	0.2831925	0.2831933
20×20	387	0.2829934	0.2831918	0.2831925	0.2831932

close to $E_v = 0.2831932$ Ry that no further change in E_v will occur as E_0 is made to equal E_v . Because the sum over f_l is finite, the APW's are always slightly discontinuous. This causes the APW expansion to converge to a result slightly *below* the correct eigenvalue. This can be seen in Table II where we compare the APW convergence for the three cases of $l_{\max} = 6, 12$, and 18 with the MAPW method. All even l 's except zero appear in Γ_{12} ; thus, the sum over valence l 's in the MAPW method contains only $l=2$. It is seen that the APW method converges only very slightly more rapidly than the MAPW. To obtain convergence to within 0.0005 Ry (which is about what one would want for a very accurate band calculation) one needs a 3×3 matrix for Γ_{12} in either case. This convergence is not obtained with a 69×69 matrix in the MOPW method.

IV. NONSPHERICAL POTENTIALS

We will discuss here the application of the MAPW method to transition metals in either the fcc or bcc crystal structures. Because of the partially filled d bands we expect the potential to be highly nonspherical within the inscribed spheres as well as far from constant outside. Let us assume that we know the crystal potential both in terms of its Fourier expansion and in terms of an expansion in Kubic harmonics²⁰ (and hence spherical harmonics as well) about a lattice point,

$$V(\mathbf{r}) = \sum_L V_L(\mathbf{r}) K_L^{\Gamma_1}(\hat{r}) = \sum_L V_L(\mathbf{r}) \sum_M \alpha_{LM} Y_{LM}(\hat{r}), \quad (11)$$

where the Γ_1 superscript on the K_L indicates that it transforms with the full cubic symmetry. The exact solution within the inscribed sphere will be of the form

$$\psi_{\text{in}}(\mathbf{r}) = \sum_{l=0}^2 \sum_t \bar{f}_{lt}(\mathbf{r}) K_{lt}(\hat{r}) + \sum_{l=3}^{\infty} \sum_m \bar{f}_{lm}(\mathbf{r}) Y_{lm}(\hat{r}), \quad (12)$$

where the bar over the f 's indicates that they contain the proper amplitude factor so that $\psi(\mathbf{r})$ is correctly normalized, and the subscript l represents which partner of which ($k=0$) irreducible representation K transforms like.²¹ The reason for using both Kubic and spherical harmonics in the same expansion will become clear shortly.

We now wish to find the differential equation satisfied by the f_{lt} . Substituting Eq. (12) into the Schrödinger equation, multiplying through by K_{lt} , and integrating over the solid angle, one obtains

$$[-\nabla_r^2 + l(l+1)/r^2 + V_0(r) + A_{2l} \delta_{2,l} V_4(r) - E_0] f_{lt}(r) = - \sum_{l'=3}^{\infty} \sum_{m'} V_L(r) f_{l'm'}^{(0)}(r) \int K_{lt} K_L^{\Gamma_1} Y_{l'm'} d\Omega, \quad (13)$$

where the superscript on $f_{l'm'}$ indicates that it is taken from the previous iteration. Because the lowest nonzero spherical harmonic in the expansion of a cubic potential is $L=4$, the only mixing of the valence states $l=0, 1$, and 2 is d with d . By using Kubic harmonics this mixing is uncoupled and the left-hand side of (13) contains only a single valence f_{lt} . The right-hand side contains all nonvalence $\bar{f}_{l't'}$; because they are expected to be small compared to the valence \bar{f}_{lt} , the iterative procedure should converge rapidly. The coefficient of the V_4 term is

$$A_{2l} = \int (K_{2l})^2 K_4^{\Gamma_1} d\Omega, \quad (14)$$

which yields $A_{2\Gamma_{12}} = \sqrt{(21)}/7$, $A_{2\Gamma_{25}} = -\sqrt{(21)}/42$. The integral on the right-hand side of (13) is easily evaluated by writing the Kubic harmonics in terms of spherical harmonics and by using the well-known formula for integrals of three spherical harmonics. The solution to Eq. (13) is $f_{lt} = f_{lt}^{\text{homo}} + \bar{f}_{lt}^{\text{inho}}$, where the magnitude of the solution to the homogeneous equation f_{lt}^{homo} is to be fixed by the condition

$$\int_0^{r_0} |f_{lt}^{\text{homo}} + \bar{f}_{lt}^{\text{inho}}|^2 r^2 dr = \int_0^{r_0} |\bar{f}_{lt}|^2 r^2 dr = \int_0^{r_0} |\bar{f}_{lt}^0|^2 r^2 dr. \quad (15)$$

Writing $K_{lt} = \sum_m \alpha_{lm} Y_{lm}$, one easily obtains the $f_{lm}(\mathbf{r}) = \sum_t \alpha_{lm}^t f_{lt}(\mathbf{r})$ which are to be entered²² into the MAPW basis function χ_k identical with that given by Eq. (2), except that the f_l are replaced by f_{lm} . From this one calculates the matrix elements to be entered into the secular equation (6):

$$D_{k'k} = \delta_{kk'} - \frac{4\pi}{\Omega} \sum_l^{\text{val}} \left[(2l+1) P_l(\cos \theta_{kk'}) \int_0^{r_0} j_l(kr) j_l(k'r) r^2 dr - 4\pi \sum_m \left(\int_0^{r_0} [f_{lm}(r)]^2 r^2 dr \frac{j_l(kr_0) j_l(k'r_0)}{[f_{lm}(r_0)]^2} \right) Y_{lm}^*(\hat{k}) Y_{lm}(\hat{k}') \right], \quad (16)$$

$$S_{k'k} = -\frac{(4\pi)^2}{\Omega} r_0^2 \sum_l^{\text{val}} j_l(k'r_0) j_l(kr_0) \sum_{m=-l}^l \left(\frac{k j_l'(kr_0)}{j_l(kr_0)} - \frac{f_{lm}'(r_0)}{f_{lm}(r_0)} \right) Y_{lm}(k') Y_{lm}^*(k), \quad (17)$$

²⁰ F. C. Von der Lage and H. Bethe, Phys. Rev. **71**, 612 (1947).

²¹ If ψ is at a general point of the Brillouin zone, all partners of all irreducible representations will contribute to the sum.

²² The $f_{lm}(\mathbf{r})$ of course depend on the point in the Brillouin zone because of the inhomogeneous term in Eq. (13).

$$\begin{aligned}
H_{\mathbf{k}'\mathbf{k}} = & k^2 \delta_{\mathbf{k}\mathbf{k}'} + V(\mathbf{k}-\mathbf{k}') - \frac{4\pi}{\Omega} \sum_l^{\text{val}} \left[(2l+1) P_l(\cos\theta_{\mathbf{k}\mathbf{k}'}) \left(\int_0^{r_0} V_0(r) j_l(k'r) j_l(kr) r^2 dr + k^2 \int_0^{r_0} j_l(k'r) j_l(kr) r^2 dr \right) \right. \\
& - 4\pi \sum_{m=-l}^l Y_{lm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{k}}') \frac{j_l(kr_0) j_l(k'r_0)}{[f_{lm}(r_0)]^2} \int_0^{r_0} f_{lm}(r) \left(-\nabla_r^2 + \frac{l(l+1)}{r^2} + V_0(r) \right) f_{lm}(r) r^2 dr \Big] \\
& + \frac{(4\pi)^2}{\Omega} \sum_{m,m'=-2}^2 Y_{2m}^*(\hat{\mathbf{k}}) Y_{2m'}(\hat{\mathbf{k}}') \left(\frac{j_2(kr_0) j_2(k'r_0)}{f_{2m}(r_0) f_{2m'}(r_0)} \int_0^{r_0} f_{2m}(r) f_{2m'}(r) V_4(r) r^2 dr - \int_0^{r_0} j_2(kr) j_2(k'r) V_4(r) r^2 dr \right) \\
& \times \int Y_{2m}(\hat{\mathbf{r}}) Y_{2m'}^*(\hat{\mathbf{r}}) K_4(\hat{\mathbf{r}}) d\Omega + \frac{(4\pi)^2}{\Omega} \sum_{l=3}^{\infty} \sum_{m=-l}^l \sum_{l'=0}^2 \sum_{m'=-l'}^{l'} \sum_{L=4}^{\infty} (i)^{l+l'} \\
& \times \left[(-1)^l Y_{lm}(\hat{\mathbf{k}}') Y_{l'm'}^*(\hat{\mathbf{k}}) \int_0^{r_0} \left(\frac{j_{l'}(kr_0)}{f_{l'm'}(r_0)} f_{l'm'}(r) - j_{l'}(kr) \right) V_L(r) j_l(k'r) r^2 dr \int Y_{lm}^*(\hat{\mathbf{r}}) Y_{l'm'}(\hat{\mathbf{r}}) K_L(\hat{\mathbf{r}}) d\Omega \right. \\
& \left. + (-1)^{l'} Y_{lm}^*(\hat{\mathbf{k}}) Y_{l'm'}(\hat{\mathbf{k}}') \int_0^{r_0} \left(\frac{j_{l'}(k'r_0)}{f_{l'm'}(r_0)} f_{l'm'}(r) - j_{l'}(k'r) \right) V_L(r) j_l(kr) r^2 dr \int Y_{lm}(\hat{\mathbf{r}}) Y_{l'm'}^*(\hat{\mathbf{r}}) K_L(\hat{\mathbf{r}}) d\Omega \right]. \quad (18)
\end{aligned}$$

Once the secular equation is solved for $\psi = \sum_{\mathbf{k}} A_{\mathbf{k}} \chi_{\mathbf{k}}$, one may use the spherical-harmonic expansion of plane waves to obtain $\psi_{\text{in}}(r)$ (Eq. 12) and thence the $f_{l'm'}^0$ which enter Eq. (13).

Many so-called first-principles APW calculations, in order to better fit experiment, use a discontinuous muffin-tin potential, the constant potential between spheres being treated as an adjustable parameter. This is equivalent to a "core shift" in an OPW calculation,²³ and while it shifts the d levels relative to the s and p , it has very little effect on the splitting of the d bands, which is controlled by the V_4 terms in Eqs. (13) and (18).

²³ P. J. Lin and J. C. Phillips, *Advan. Phys.* **14**, 215 (1965).

After this work was completed we became aware of Rudge's²⁴ APW calculation for Li with a nonspherical potential. Rudge calculates his $f_{lm}(r)$ from a spherical potential (so that the m subscript may be dropped), but then uses the full nonspherical potential to compute the matrix elements. If the potential within the inscribed sphere is not too far from spherical, and if only s and p waves are important (as should be the case for Li), the small errors introduced into $f_l(r)$ by the spherical approximation should (by the variational principle) lead to negligible errors in the eigenvalues E_v . On the other hand, the neglect of the V_4 term in Eq. (13) will probably lead to significant errors in the transition metals.

²⁴ W. E. Rudge, *Phys. Rev.* **181**, 1033 (1969).