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Linear augmented-Slater-type-orbital method for electronic-structure calculations

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The purpose of this paper is to explore the possibility of using augmented Slater-type orbitals (STO) as basis functions for electronic-structure calculations. STO's have a radial dependence given by $r^{n-1}\exp(-\zeta r)$ and as a result have a number of important advantages. They are localized about sites and have the same asymptotic form as actual atomic orbitals. They are regular at the origin and possess analytic Fourier transforms. The Fourier transform can be manipulated to yield an addition theorem, that is, a reexpansion formula for an STO about another site which is similar to the one used for spherical Bessel functions. Augmenting the STO's with numerical solutions of the Schrödinger equation within touching spheres leads to a small secular matrix since the numerical functions are orthogonal to all the core states and the STO's are only used in the interstitial region. The method has been applied to copper, silver, and palladium using Chodorow-type potentials and accounting for all relativistic effects except spin-orbit coupling. The results on copper are in good agreement with previous calculations and with experiments. The results on Pd and Ag are in better agreement with photoemission experiments than fully self-consistent local-density calculations.

I. INTRODUCTION

The purpose of this paper is to present a new method for solving Schrödinger's equation in crystals. The method can also be applied to films, chains, or molecules. It is a direct outgrowth of the linear muffin-tin orbital (LMTO) method[1–3] of Andersen and co-workers and the augmented spherical wave (ASW) method of Williams, Kübler, and Gelatt.[4] Both of these schemes are attractive because they resemble the traditional linear combination of atomic orbitals (LCAO) approach, hence lead in principle to easy interpretation of the resulting equations. However, as written, they have two disadvantages. One is that the basis functions have relatively long-range tails, decaying as $1/r^{l+1}$, which means more neighbors need to be considered than if a more localized basis set were used. Also, in the LMTO method the overlap matrix for two s functions diverges at the center of the Brillouin zone which then requires special treatment. The other problem is that it has proven difficult to include non-muffin-tin corrections in an exact way. They are handled by approximating integrals over the Wigner-Seitz cell by integrals over the sphere of equivalent volume (atomic sphere approximation). This must be an excellent approximation for close-packed structures, judging by the results, but is nevertheless not a well-controlled approximation. Also, for more open structures and particularly for surfaces it is not appropriate. These problems can be overcome to some extent by adding extra "empty" spheres.[5,6] Another approach, by Kasowski,[7] has been to use the standard LMTO basis but to perform integrations over the interstitial region by using fast Fourier transforms. The LMTO method has been applied to films by Krakauer and Cooper.[8]

Another point relevant to the LMTO method is the number of independent functions used. The impression one has is that there are two functions per angular-momentum quantum number, one, g, a numerical solution of the Schrödinger equation within the spheres and a second one, $\dot{g}$, the energy derivative of that function. In fact, there is only one energy-independent function per $\vec{k}$. This is because a particular linear combination of g and $\dot{g}$ is chosen by requiring that the log derivative of the combination be equal to the log derivative of a Bloch sum of tail functions. As noted by Harris and Painter[3] and more recently by Casula and Herman[9] one would often like to have more than one function per $\vec{k}$ in order to increase the variational freedom.

In this paper a different approach to these problems is proposed: the use of Slater-type orbitals as tail functions. These functions are given by[10]

$$\phi_{nlm}(\vec{r})=r^{n-1}\exp(-\zeta r)Y_{lm}(\vec{r}) , \tag{1}$$

where the Y_{lm}'s are standard spherical harmonics. They decay more rapidly at large distances than $1/r^{l+1}$ or spherical Neumann functions, so interactions should be limited to substantially fewer neighbors. Secondly, they are known to accurately represent atomic wave functions at large distances so they form an attractive basis set to understand the difference between atoms and solids. Thirdly, they are regular at the origin and have known Fourier transforms. This means that integrals over the unit cell can be performed by sums over the reciprocal lattice so that non-muffin-tin terms can be included in a practical way. As with the LMTO and ASW methods the STO's must be augmented within touching spheres surrounding each atom. Following Andersen[1] radial functions and their energy derivatives are chosen to represent the wave function within the spheres. Relativistic effects (except spin-orbit) are included by solving the "j-weighted-average" Dirac equation within the spheres following, for example, Koelling and Harmon.[11] This leads then to a linear augmented Slater-type orbital (LASTO) method which has the advantage that it has the same form as an LCAO or tight-binding formalism, but all interactions (i.e., all neighbors and all three-center terms) are included. The basis functions are short ranged so that Ewald techniques should not be necessary to evaluate the lattice sums which enter. On the other hand, since the Fourier transforms are known, Ewald techniques could be used if desired. The "screening constant" ζ is of the order of one atomic unit which is why the functions decay rapidly with distance. In the ASW method the tail functions also have an exponential cutoff but the screening constant is usually taken to be $\sim 0.1/a_0$,[4] where a_0 is the Bohr radius. One way to choose ζ is to require that the STO's match smoothly onto the numerical radial function inside the spheres. This gives

$$\frac{n-1}{R_s}-\zeta=\frac{g'}{g}\ , \tag{2a}$$

where g'/g is the logarithmic derivative of g. This is convenient because a second independent function can be chosen which matches smoothly onto $\dot{g}$. As an example, Andersen[12] has argued that the band center lies at the energy where the logarithmic derivative of g evaluated at the Wigner-Seitz radius is equal to $-(l+1)/R_{\mathrm{WS}}$. Applying this criterion to Eq. (2a) yields

$$\zeta=\frac{n+l}{R_{\mathrm{WS}}}\ . \tag{2b}$$

For example, for a $3d$ function in copper $\zeta=1.88/a_0$. This is in reasonable agreement with the shortest-ranged $3d$ function used in atomic calculations on copper with STO basis sets.[13,14]

Compared to Gaussian-type orbitals[15,16] STO's should be better at describing regions of low charge density such as that outside a metal surface. It is often noted that GTO's do not satisfy the "cusp condition," i.e., they do not have a finite slope at the nuclei in contrast to actual atomic wave functions. STO's do, of course, satisfy this condition, but because they are not used inside the spheres this is of no special advantage. In fact, Batra and coworkers[17] have advocated using augmented Gaussians in the same spirit as Slaters are used in this paper which eliminates the cusp problem completely.

In common with all the augmented schemes, including the augmented-plane-wave method, the numerical functions used inside the spheres are orthogonal to all the core states so the size of the secular matrix is determined by the valence orbitals only. However, in contrast to pseudopotential methods the core states can be explicitly calculated and allowed to adjust to the crystalline environment.

Finally, since the Fourier transforms of the STO's are known functions, Poisson's equation can be solved along the lines suggested by Weinert and Hamann.[18,19]

The remainder of this paper is organized as follows. In Sec. II the method is derived in detail and the form of the basis functions given. In Sec. III the secular matrix is derived. In Sec. IV results for calculated energy bands for copper, silver, and palladium are given, and in Sec. V there is a discussion. Appendix A gives the Fourier transforms of STO's and Appendix B the formulas for reexpanding an STO about another site.

II. LASTO METHOD

In this section the equations for the LASTO method are written in a way which mirrors tight binding as closely as possible. The wave function is expanded as

$$\psi(\vec{r})=\sum_{n,l,m}A_{nlm}\psi_{nlm}(\vec{r})\ , \tag{3}$$

with

$$\psi_{nlm}(\vec{r})=\frac{1}{\sqrt{N_c}}\sum_i \exp(i\vec{k}\cdot\vec{R}_i)\phi_N(\vec{r}-\vec{R}_i)\ , \tag{4}$$

where N_c is the number of sites in the crystal and the ϕ_N are Slater-type orbitals centered at site R_i. Upper case N is a composite index implying n,l,m. It is assumed that there is one atom per unit cell, but the generalization to more is straightforward as is the inclusion of more than one orbital of given N at a site.

The Bloch sum of STO's [Eq. (4)] is used only in the interstitial region, between touching "muffin-tin" spheres. Within spheres the function is replaced by a linear combination of numerical functions to which it matches smoothly. The numerical functions are $g_l(r)$ and $\dot{g}_l(r)$, the energy derivative of g_l as usual in the LMTO method except that relativistic effects other than spin-orbit are included. Then, within the ith sphere,

$$\psi_N(\vec{r})=\frac{1}{\sqrt{Nc}}\sum_{L'}\exp(i\vec{k}\cdot\vec{R}_i)[\beta_{N,L'}g_{l'}(r_i) + \alpha_{N,L'}\dot{g}_{l'}(r_i)]Y_L(\hat{r}_i)\ . \tag{5}$$

The g's are normalized within the spheres,

$$\int_0^{R_s} r^2 g_l^2(r)dr=1\ , \tag{6}$$

and g_l and $\dot{g}_l$ are orthogonal. They satisfy the radial equations

$$h_r g_l=\epsilon g_l \tag{7}$$

and

$$h_r\dot{g}_l=\epsilon\dot{g}_l+g_l\ , \tag{8}$$

where h_r is the scalar relativistic Hamiltonian,

$$h_r=-\frac{\hbar^2}{2M}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right] -\frac{\hbar^2}{2M}\frac{1}{2Mc^2}\frac{dV}{dr}\frac{d}{dr}+V\ , \tag{9}$$

as discussed by Koelling and Harmon.[11] In Eq. (9)

$$M=m\left[1+\frac{\epsilon-V}{2mc^2}\right]$$

and the other symbols have their usual meaning. Notice that as $c\rightarrow\infty$, Eq. (9) reduces to the usual nonrelativistic radial Schrödinger Hamiltonian.

In order to effect the matching at a given sphere it is necessary to expand an STO about a site other than the one on which it is centered. This is a problem which has been considered by many authors.[20–27] In practice the expression given by Silverstone[22] is convenient because it resembles closely the more familiar one for spherical Bessel and Neuman functions. Silverstone's result (with indices reordered) is

$$\phi_{nlm}(\vec{r}-\vec{R})=\sum_{L',L''}4\pi I(L,L',L'')V^n_{ll'l''}(r,R)\times Y_{L'}(\hat{r})Y_{L''}(\hat{R})\,, \tag{10}$$

where I is the Gaunt integral

$$I(L,L',L'')=\int Y_L^*(\hat{r})Y_{L'}(\hat{r})Y_{L''}(\hat{r})d^2r, \tag{11}$$

and, for $R>r$,

$$V^n_{ll'l''}(r,R)=\left[-\frac{d}{d\zeta}\right]^{n-l}\left[\zeta^{-1}\frac{d}{d\zeta}\right]^{l}\zeta^{l+1}i_{l'}(\zeta r)k_{l''}(\zeta R)\,. \tag{12}$$

The i's and k's are modified spherical Bessel functions of the first and third kinds, respectively.[28] They are polynomials in $(1/x)$ times $\exp(\pm\zeta x)$ (see Appendix B). For the (nonphysical) case $n=0$, $l=0$, $m=0$, Eq. (10) is called Gegenbauer's addition theorem. In order to actually compute V it is convenient to expand Eq. (12) into elementary functions as advocated by Sharma[23] and by Jones and Weatherford.[24,25] Using Eq. (12) and standard representations for $i_{l'}$ and $k_{l''}$ it is shown in Appendix B that

$$V^n_{ll'l''}(r,R)=\frac{1}{\zeta^{n-1}}\sum_{n'=-l'}^{n}\sum_{n''=-l''}^{n}V^n_{ll'l''}(n',n'')(\zeta r)^{n'-1}[e^{\zeta r}+(-1)^{l'+n'-1}e^{-\zeta r}](\zeta R)^{n''-1}e^{-\zeta R}\,. \tag{13}$$

It can be anticipated therefore that the band problem will involve "structure constants" which are defined as

$$D_{nL}(\vec{k})\equiv\sum_{i\neq 0}(\zeta R_i)^{n-1}\exp(i\vec{k}\cdot\vec{R}_i-\zeta R_i)Y_L(\hat{R}_i)\,. \tag{14}$$

These structure constants are the analogs of those appearing in the LMTO, KKR, or ASW methods. But note that they are well behaved. The sum over i converges for all values of $\vec{k}$ (including $\vec{k}=0$).

With the use of these expansion formulas it is possible to match at the ith sphere in the following way:

$$\beta_{nL\,L'}g_{l'}(r)+\alpha_{nL,\,L'}\dot{g}_{l'}(r)=r^{n-1}\exp(-\zeta r)\delta_{LL'}+\sum_{i\neq 0}\exp(i\vec{k}\cdot\vec{R}_i)\sum_{l''}4\pi I(L,L',L'')V^n_{ll'l''}(r,R_i)Y_{L''}(\hat{R}_i) \tag{15}$$

for $r=R_s$. It is also required that the radial derivative of this equation be satisfied for $r=R_s$ which yields two equations for the two unknowns, β and α.

All of these expansions have been carried out in real space. Alternatively, they can be done in reciprocal space. The Bloch sum of STO's has a reciprocal-lattice representation given by

$$\chi_{nlm}(\vec{r})=\frac{1}{\sqrt{N_c}}\frac{N_c}{V_c}\sum_{\vec{g}}e^{i(\vec{k}+\vec{g})\cdot\vec{r}}\tilde{\phi}_{nlm}(\vec{k}+\vec{g})\,, \tag{16}$$

where V_c/N_c is the volume of the unit cell, the $\vec{g}$'s are reciprocal-lattice vectors, and $\tilde{\phi}$ is the Fourier transform of ϕ (see Appendix A). The series, Eq. (16), converges fairly quickly because the ϕ's are relatively slowly varying in space. To match at the ith sphere requires

$$\beta_{nL,L'}g_{l'}(r)+\alpha_{nL,L'}\dot{g}_{l'}(r)=\sum_{\vec{g}}\frac{N_c}{V_c}4\pi i^{l'}j_{l'}(qr)Y^*_{L'}(\hat{q})\tilde{\phi}_{nlm}(\vec{q})\,, \tag{17}$$

where $\vec{q}=\vec{k}+\vec{g}$. Energy bands for copper have been calculated using both real-space and reciprocal-space methods [Eqs. (15) and (17)] with the same results.

III. HAMILTONIAN AND OVERLAP MATRICES

A. Sphere terms

From the matrices β and α defined by Eq. (15) the contribution to the overlap and Hamiltonian matrices can be obtained straightforwardly. The overlap matrix is

$$S_{NN'}=\int d^3r\,\psi^*_{nlm}(\vec{r})\psi_{n'l'm'}(\vec{r})\,, \tag{18}$$

and the contribution from the spheres is

$$S^1_{NN'}=\sum_{L''}\beta^*_{nL,\,L''}\beta_{n'L',\,L''}+\alpha^*_{nL,\,L''}\alpha_{n'L',\,L''}\langle\dot{g}_{l''}\,|\,\dot{g}_{l''}\rangle\,, \tag{19}$$

where

$$\langle\dot{g}\,|\,\dot{g}\rangle=\int_0^{R_s}r^2dr\,\dot{g}^2\,. \tag{20}$$

Notice that $\langle g\,|\,g\rangle=1$ and $\langle g\,|\,\dot{g}\rangle=0$. In a similar way, and using Eq. (8), one finds

$$H^1_{N,N'}=\epsilon S^1_{N,N'}+\sum_{L''}\beta^*_{nL,\,L''}\alpha_{n'L',\,L''}\,. \tag{21}$$

The generalized secular equation,

$$HA=\lambda SA\,, \tag{22}$$

may now be solved to give the eigenvalues and eigenvectors. Making use of Eq. (21) this can be rewritten to obtain an effective Hamiltonian without overlap:

$$H_{\text{eff}}=\epsilon+S^{-1}[\beta^*\alpha] \tag{23}$$

(note that $[\beta^*\alpha]$ is a matrix). This bears a close resemblance to the LCAO procedure of Anderson and Bullett[29] except that a very flexible basis set has been used to construct H_{eff}. A similar procedure has been advocated by Andersen.[30]

B. Intersphere terms

In order to evaluate the integrals over the region between spheres the STO's are integrated over all space and the contributions from the spheres are subtracted out. Since the STO's are regular at the origin, this integration is well defined and presents no special problems. Further, since the Fourier transforms of STO's are known the integration can be evaluated using either real- or reciprocal-space techniques. The method will be dictated by the form chosen for the potential in the interstitial region. The reciprocal-space version is given here. A Bloch sum of STO's has a reciprocal-space representation given by Eq. (16). Consequently, the integral over all space is given by

$$\int \chi_N^*(\vec{r})\chi_{N'}(\vec{r})d^3r = \frac{N_c}{V_c}\sum_{\vec{g}} \tilde{\phi}_N^*(\vec{k}+\vec{g})\tilde{\phi}_{N'}(\vec{k}+\vec{g}) \ . \quad (24)$$

The integral over the interstitial region is then obtained by subtracting from Eq. (24) the integral of the χ's over the spheres. The integral over the spheres can be obtained using the expansion formula, Eq. (10) (although some care must be taken with the limit $r \rightarrow 0$). In the current work this integral was not evaluated explicitly. Instead the atomic sphere approximation was used and only integrals over the Wigner-Seitz sphere (volume equal to the unit-cell volume) were computed.

IV. APPLICATION TO Cu, Pd, AND Ag

In order to test the LASTO method bulk band-structure calculations were performed for fcc copper, palladium, and silver. The overlap integrals were evaluated in the atomic sphere approximation:[1] That is, the integrals were carried out over a sphere with volume equal to the unit-cell volume (Wigner-Seitz sphere) and the interstitial region was not included. The lattice constants were taken to be Cu, 3.61 Å; Pd, 3.89 Å; and Ag, 4.09 Å.

For copper the potential was taken from Burdick[31] (the Chodorow potential) except that it was interpolated onto a logarithmic mesh (using four-point Lagrange interpolation). For palladium and silver a Hartree-Fock-Wigner-Seitz (HFWS) potential[32,33] was used. This potential (which is also known as a renormalized-atom potential) is essentially a Chodorow potential since Chodorow used a similar procedure to obtain his famous potential for the d electrons in copper. For the atoms treated here a Dirac-Fock calculation was performed and the potential was taken to be the j-weighted average of the $d_{5/2}$ and $d_{3/2}$ potentials, and this was used when integrating for wave functions of all l of interest. The configuration was $4d^95s$ for Pd and $4d^{10}5s$ for Ag. This potential, while not self-consistent, is known to accurately represent bulk band structures. In fact, the Chodorow potential is in better agreement with photoemission data for these metals than self-consistent local-density approximations.

In each case a "minimal basis" was chosen of $3d$, $4s$, and $4p$ functions for the Cu and $4d$, $5s$, and $5p$ functions for Pd and Ag. This leads to the diagonalization of 9×9 matrices. The ζ's were chosen according to Andersen's criterion as given in Eq. (2). The energy parameter used in evaluating the radial functions was set to -0.33 H (H indicates hartree, which is equal to 27.2116 eV) close to the d resonance in copper. The "internal summation" in Eq. (15) was extended to $l'=3$. The structure constants [Eq. (14)] were calculated by summing over five shells of neighbors in the fcc lattice.

A. Copper

The results for copper are listed in Table I for the points Γ, X, and L in the Brillouin zone. The first column gives the results of Burdick's APW calculation except[31] that the eigenvalues were shifted to an absolute-energy scale by adding the muffin-tin zero -0.470 H. To compare with the APW calculation which was not relativistic the standard trick of setting $c^{-1}=0$ was used. The scalar relativistic eigenvalues are given in the third column. The errors in the LASTO eigenvalues generally increase as the distance of the eigenvalue from the energy used to evaluate radial functions (-0.33 H). This is to be expected for a linear method. The relativistic corrections are expected to be about 10 mH based on Herman and Skillman's tables.[34] The d and s levels all have corrections which are close to this value. The p levels are substantially larger, but this is probably related to the fact that they are too high in energy to be well described by $\epsilon=-0.33$ H. In order to investigate the effect of the various parameters on the calculation the expansion energy, the ζ's, the l convergence, and the shell-by-shell convergence were studied for copper. Changing the expansion energy ϵ from -0.33 to -0.40 H caused the s and d levels at Γ to shift by less than 1 mH. This is consistent with similar results for this potential using the linear APW method.[35] The p level had a much larger shift, 56 mH, which again reflects the high energy of that state. The ζ values [Eq. (2b)] for the $3d$ and $4s$ levels were 1.8755 and 1.5004, respectively. Varying the ζ_{3d} from 1.6 to 2.1 produced shifts up to 0.6 mH and varying ζ_{4s} from 1.00 to 1.5 produced shifts of 0.2 mH. Changing the l' sum in Eq. (15) to 2 instead of 3 caused changes of 0.1 mH in the s and d levels and 50—60 mH in the p level. Finally, including only the first shell of neighbors in the structure constants caused shifts in the d levels of 1—4 mH while for the more delocalized s level the shift was 50 mH. This indicates that using nearest neighbors only may be useful for model calculations. Notice that this approximation does include three center terms which would be excluded in the more usual "tight-binding" parametrizations. Increasing the sum from the fifth to the eighth shell caused a shift in the d levels which was less than 0.01 mH but for the s and p levels it was ~ 0.3 mH.

In order to compare with other calculations and with experiment[36] three characteristic eigenvalues at the X point are plotted in Fig. 1. The energy zero is Γ_1, "the bottom of the s band." The values shown are usually labeled $X_{4'}$, X_5, and X_3. In the case that the z axis is along the X direction and using the minimal basis set, $X_{4'}$ is pure p_z, X_5 is $d_{xz,yz}$, and X_3 is pure d_{xy}. If spin-orbit coupling is included X_5 is split. X_5-X_3 is a good measure of the d-band width while $X_{4'}-\Gamma_1$ is a measure of the s-band width.

TABLE I. LASTO method bulk band-structure calculations for fcc copper.

	APW	LASTO (nonrelativistic)	LASTO (scalar relativistic)	Label	
Γ	0.711	0.866	0.849	Γ_{15}	$p_{x,y,z}$
	-0.291	-0.290	-0.298	Γ_{12}	$d_{x^2-y^2,z^2}$
	-0.320	-0.316	-0.324	$\Gamma_{25'}$	$d_{xy,yz,zx}$
	-0.520	-0.519	-0.532	Γ_1	s
X	0.301	0.311	0.303	$X_{5'}$	$p_{x,y}$
	0.076	0.058	0.036	X_1	s,d_{z^2}
	-0.118	-0.110	-0.117	$X_{4'}$	p_z
	-0.264	-0.262	-0.271	X_5	$d_{xz,yz}$
	-0.270	-0.270	-0.279	X_2	$d_{x^2-y^2}$
	-0.370	-0.363	-0.369	X_3	d_{xy}
	-0.388	-0.381	-0.388	X_1	s,d_{z^2}
L	0.596	0.650	0.638		
	-0.047	-0.020	-0.040		
	-0.215	-0.193	-0.200		
	-0.269	-0.269	-0.277		
	-0.321	-0.320	-0.327		
	-0.388	-0.380	-0.388		

In the case of copper, where careful comparisons with experiment have been made[36] the Chodorow potential is known to agree better than the best self-consistent local-density calculations. This is illustrated in Fig. 1, where it can be seen that the s- and d-band widths are about the same in the two calculations but the d bands lie too high by $\sim$40 mH$\simeq$1 eV. This conclusion has of course been reached before.[36–38]

B. Palladium and silver

The bands for Pd and Ag are shown in Figs. 2 and 3 and compared with other calculations[38–40] at the X point in Fig. 4. The results labeled SP for "standard potential" are from Christensen who overlapped the atomic charge density from atomic Dirac-Slater calculations and used full Slater exchange. The calculations are not self-consistent, but they do include spin-orbit coupling which is why two levels are shown for X_5.

The same general conclusions apply for these metals as for copper. The d bands lie higher in the self-consistent local density approximation (LDA) calculations than they do in the non-self-consistent calculations, although in Pd the scale of this discrepancy is less than it is in Cu or Ag. The HFWS calculations are roughly in agreement with the non-self-consistent $X\alpha$ calculations of Christensen. Since Christensen's bands have been found to roughly agree with experiment[41–44] the HFWS results may be presumed to be in better agreement with experiment as well. In particular, for Ag the bandwidth is narrower by about 30 mH ($\sim$0.8 eV) while experimentally it is narrower by about 15 mH. This contrasts with copper where the bandwidths are roughly correct. There has been one self-consistent HFWS calculation[33] (for nickel) in which it was found that the d-band width narrowed relative to the non-self-

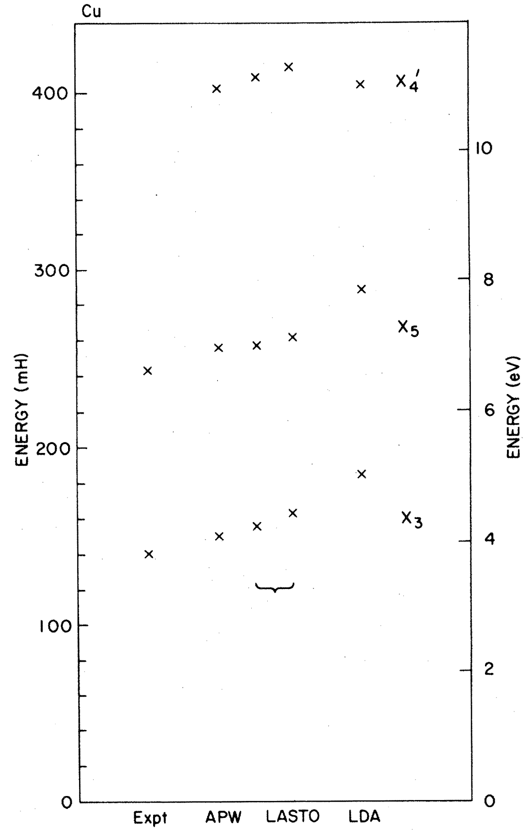

FIG. 1. Comparison of band energies of copper at the X point relative to Γ_1. Experimental points are from Ref. 36. APW is from Burdick (Ref. 31). LASTO refers to the present results both nonrelativistic and scalar relativistic. LDA is a self-consistent local-density calculation of Jepsen *et al.* (Ref. 37).

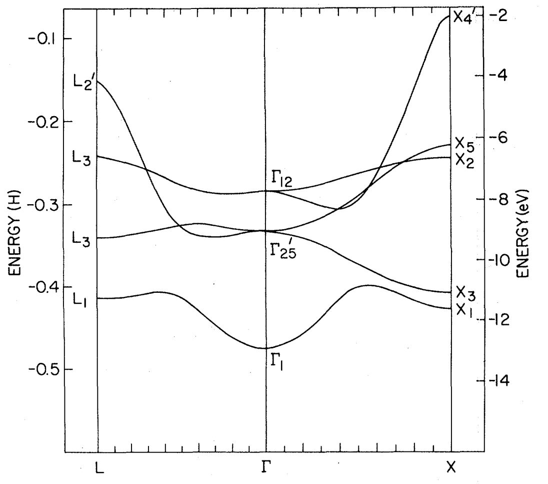

FIG. 2. Calculated energy bands of palladium using HFWS potential and atomic sphere approximation.

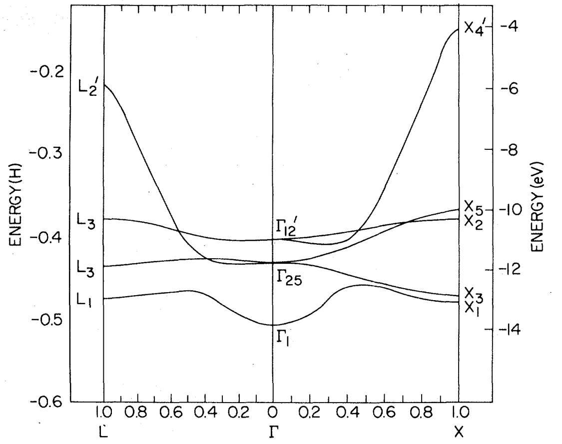

FIG. 3. Calculated energy bands of silver using HFWS potential and atomic sphere approximation.

consistent result (in contrast to the LDA where it broadens on going to self-consistency). It would be interesting to apply the self-consistent HFWS method to Cu, Pd, and Ag as well.

V. CONCLUSION

The purpose of this paper was to explore the possibility of using augmented Slater-type orbitals as basis functions for electronic-structure calculations. It has been found that the main requirement, the ability to expand an STO centered on one site about another site can be accomplished straightforwardly. The calculated energy bands are in reasonable agreement with previous results for the Chodorow potential. The remaining discrepancies are probably due to the use of the atomic sphere approximation, which can easily be improved upon in future work. Calculations on Pd and Ag using a Chodorow-type potential (actually a Hartree-Fock-Wigner-Seitz or renormalized-atom potential) further illustrate the use of

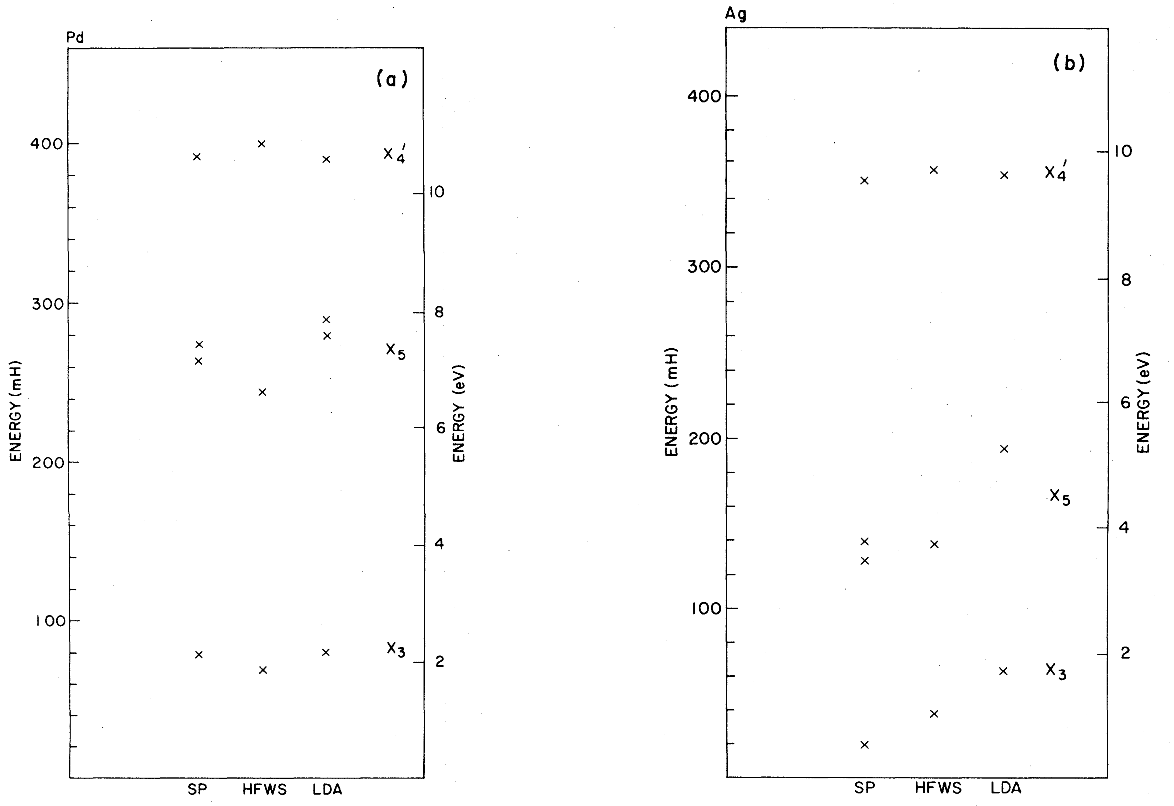

FIG. 4. (a) Comparison of energy bands at X point for Pd. SP refers to the non-self-consistent RAPW calculation of Christensen (Ref. 40) using the "standard potential." LDA is the self-consistent local-density result of MacDonald *et al.* (Ref. 38). (b) Same for silver except LDA is from Jepsen *et al.* (Ref. 37).

the method. As with previous non-self-consistent calculations the HFWS results are in better agreement with photoemission experiments than fully self-consistent local-density calculations.

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APPENDIX A: FOURIER TRANSFORMS

Collected here, for convenience, are results useful for reciprocal space. They are all implicit in the work of Silverstone.[22]

First the Fourier transform of an STO is given by

$$\tilde{\phi}_{nlm}(\vec{q}) = \int d^3r\, e^{-i\vec{q}\cdot\vec{r}}\phi_{nlm}(\vec{r}) \ , \tag{A1}$$

$$\tilde{\phi}_{nlm}(\vec{q}) = 4\pi(-i)^l Y_L(\hat{q}) \int_0^\infty dr\, j_l(qr) r^{n+1}\exp(-\zeta r) \ , \tag{A2}$$

where j is the usual spherical Bessel Function

$$j_l(qr) = (\pi/2qr)^{1/2} J_{l+1/2}(qr) \ . \tag{A3}$$

The integral is known:

$$I = \left[\frac{\pi}{2q}\right]^{1/2} \left[\frac{q}{2\zeta}\right]^{l+1/2} \frac{\Gamma(l+n+2)}{\zeta^{n+3/2}\Gamma(l+\frac{3}{2})} \times \frac{f_{nl}(q^2/\zeta^2)}{(1+q^2/\zeta^2)^{n+1}} \ , \tag{A4}$$

and f_{nl} is a hypergeometric function given by[28]

$$f_{nl}(q^2/\zeta^2) = F(-(n-l)/2, -(n-l-1)/2, l+\tfrac{3}{2}, -q^2/\zeta^2) \tag{A5}$$

and

$$F(\alpha,\beta,\gamma,x) = 1 + \frac{\alpha\beta}{\gamma}x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{\gamma(\gamma+1)}\frac{x^2}{2!} + \cdots \tag{A6}$$

since either $-(n-l)/2$ or $-(n-l-1)/2$ is a negative integer the series always terminates. An alternative representation can be found by using the relation

$$j_l(x) = x^l \left[-\frac{1}{x}\frac{d}{dx}\right]^l \frac{\sin x}{x} \ . \tag{A7}$$

Then the integral in Eq. (A2) can be written

$$(-1)^n \left[\frac{\partial}{\partial\zeta}\right]^{n-l} q^l \left[\frac{1}{q}\frac{d}{dq}\right]^l \times \left[\frac{1}{q}\int_0^\infty \exp(-\zeta r)\sin(qr)dr\right] \ . \tag{A8}$$

The integral is just $1/(q^2+\zeta^2)$ and

$$q^l \left[\frac{1}{q}\frac{d}{dq}\right]^l \frac{1}{q^2+\zeta^2} = \left[\frac{1}{\zeta}\frac{d}{d\zeta}\right]^l \frac{q^l}{q^2+\zeta^2} \ , \tag{A9}$$

so

$$\tilde{\phi}_{nlm}(\vec{q}) = 4\pi(-i)^l Y_L(\hat{q})\Phi_{nl}(q)$$

where

$$\Phi_{nl}(q) = (-1)^n \left[\frac{\partial}{\partial\zeta}\right]^{n-l} \left[\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right]^l \frac{q^l}{q^2+\zeta^2} \ . \tag{A10}$$

APPENDIX B: ADDITION THEOREM

A derivation is given of the expression in Eq. (10) for the expansion of a Slater-type orbital about another site. Such expansions are generally called addition theorems:

$$\phi_{nlm}(\vec{r}) = r^{n-1}\exp(-\zeta r) Y_L(\hat{r}) \ , \tag{B1}$$

$$\phi_{nlm}(\vec{r}-\vec{R}) = \int \frac{d^3q}{(2\pi)^3} e^{i\vec{q}\cdot(\vec{r}-\vec{R})}\tilde{\phi}_{nlm}(\vec{q}) \ . \tag{B2}$$

The strategy is to expand the exponential and use the form for $\tilde{\phi}$ given in (A10) as follows:

$$\phi_{nlm}(\vec{r}-\vec{R}) = \sum_{L',L''} 4\pi i^{l'-l''-l} Y_{L'}(\hat{r}) Y_{L''}(\hat{R}) \frac{2}{\pi} \int d^3q\, Y^*_{L'}(\hat{q}) Y^*_{L''}(\hat{q}) Y_L(\hat{q}) j_{l'}(qr) j_{l''}(qR) \Phi_{nl}(q) \ . \tag{B3}$$

The angular integral is the Gaunt integral $I(L,L',L'')$. So comparing with Eq. (10) and using Eq. (A10)

$$V^n_{ll'l''}(r,R) = \frac{2}{\pi} i^{l'-l''-l}(-1)^n \left[\frac{\partial}{\partial\zeta}\right]^{n-l} \left[\frac{1}{\zeta}\frac{\partial}{\partial\zeta}\right]^l \int_0^\infty dq\, q^2 \frac{q^l}{q^2+\zeta^2} j_{l'}(qr) j_{l''}(qR) \ . \tag{B4}$$

The integral in Eq. (B4) can be evaluated as a contour integral. There are poles at $q = \pm i\zeta$; hence one naturally obtains modified spherical Bessel functions. The exact form is given in Eq. (12) (for $R > r$). The V coefficients in Eq. (13) were evaluated with the expansion

$$i_{l'}(\zeta r) = \sum_{i=0}^{l'} \frac{(l'+i)!}{i!(l'-i)!}[(-1)^i\exp(\zeta r) - (-1)^{l'}\exp(-\zeta r)]\frac{1}{(2\zeta r)^{i+1}} \tag{B5}$$

and the corresponding expression for $k_{l''}(\zeta R)$.[28] It is then a straightforward, although somewhat tedius matter, to obtain the V's by repeated application of the differential operator

$$\left[\frac{d}{d\zeta}\right]^{n-l}\left[\zeta^{-1}\frac{d}{d\zeta}\right]^{l} . \tag{B6}$$

Explicitly,

$$\begin{aligned} V^{n}_{ll'l''}(r,R)=(-1)^{n-l}\frac{1}{\zeta^{n-1}} \sum_{i=0}^{l'} \frac{\Gamma(l'+i+1)}{\Gamma(i+1)\Gamma(l'-i+1)} \\ \times\sum_{j=0}^{l''}\frac{\Gamma(l''+j+1)}{\Gamma(j+1)\Gamma(l''-j+1)}\frac{1}{2^{i+j+1}} \\ \times\sum_{k=0}^{n}a_k^{nl}(l-i-j-1)\sum_{k'=0}^{k}\frac{\Gamma(k+1)}{\Gamma(k-k'+1)\Gamma(k'+1)}(\zeta r)^{k-k'-i-1}(-1)^{i} \\ \times[\exp(\zeta r)+(-1)^{l'+k-k'-i-1}\exp(-\zeta r)] \\ \times(-1)^{k'}(\zeta R)^{k'-j-1}\exp(-\zeta R) , \end{aligned} \tag{B7}$$

where Γ is the Gamma function

$$\Gamma(n+1)=n! ,$$

and $a_k^{nl}(p)$ is defined by

$$\left[\frac{d}{dx}\right]^{n-l}\left[\frac{1}{x}\frac{d}{dx}\right]^{l}x^{p}\exp(x)=\left[\sum_{k=0}^{n}a_k^{nl}(p)x^{k}\right]x^{p-n-l}\exp(x) . \tag{B8}$$

A computer program was written which performs these sums and collects terms with given powers of r and R along the lines suggested by Jones and Weatherford.[24,25]

A few explicit examples of the $V^{n}_{ll'l''}(n',n'')$ are

$$V^{1}_{000}(n',n'')=\frac{1}{2}\begin{bmatrix} 1 & 1 \\ -1 & 0 \end{bmatrix} , \tag{B9}$$

$$V^{4}_{000}(n',n'')=\frac{1}{2}\begin{bmatrix} 24 & 24 & 12 & 4 & 1 \\ -24 & -24 & -12 & -4 & 0 \\ 12 & 12 & 6 & 0 & 0 \\ -4 & -4 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} . \tag{B10}$$

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