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Improved parametrization schemes for electronic energy bands

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In connection with semiempirical studies of electronic band structures we consider the development of parametrization schemes based mainly on the logarithmic derivatives L_l rather than exclusively on the tangent of the phase shifts, $\tan\eta_l$, as was done in an earlier study. Improvements over the earlier approach are sought in two different approaches considered here for the noble metals. In the first of these the logarithmic derivatives of the radial wave functions are exclusively treated as the fundamental quantities to be parametrized. For a comparable number of parameters, this scheme gives a small over-all improvement in the accuracy of fit to the results of several first-principles band calculations as compared to the fit obtained in the earlier $\tan\eta_l$ parametrization scheme. The second scheme gives significantly better fits to the first-principles band-calculation results. This approach obtains these improved results by adopting a hybrid technique which uses $\tan\eta_l$ parametrization to treat the resonant part of the d scattering contribution, while the residual d scattering and the complete s and p contributions are treated by parametrizing the logarithmic derivatives. The parametrization of the smoothly varying logarithmic derivatives is done in a uniform and systematic way in terms of square-well potentials. A simplified version of this scheme is also successful for a "simple" metal as demonstrated by an application to Al. An advantage of both schemes in an empirical application is that the goodness of fit is rather insensitive to the energy values used in evaluating the parameters. Finally, we discuss the relative advantages of the present scheme over others that have been proposed.

I. INTRODUCTION

In an earlier paper[1] (referred to as I hereafter) we have given the motivation for, and discussed the development of, a band-parametrization scheme based on the Green's-function method[2] (GFM) of Korringa, Kohn, and Rostoker (KKR). In the GFM, the dispersion relations for the electronic energy bands $E_n(\vec{k})$ are obtained from the determinantal equations

$$\det[B_{lj;l'j'}(\vec{k}, E) + E^{1/2}\cot\eta_l(E)\delta_{ll'}\delta_{jj'}] = 0\,, \qquad (1)$$

where the energy scale is such that the constant part of the muffin-tin potential V_c has the value zero. All information regarding the lattice structures is contained in the $B_{lj;l'j'}$, which can be calculated efficiently and to any desired degree of accuracy. On the other hand, all the dependence on the crystal potential is contained in the phase shifts $\eta_l(E)$. In contrast to the $B_{lj;l'j'}$, the effective crystal potential, and thus the $\eta_l(E)$, for a given metal is not accurately known. This is, in fact, the limiting factor in the accuracy of the calculation of $E(\vec{k})$. The aim of the parametrization scheme is to provide an effective empirical means for determining the $\eta_l(E)$ over a suitable range of energy.

The convergence of the GFM is sufficiently rapid so that the inclusion of $l > 2$ components in the trial wave function introduces only small shifts in the $E(\vec{k})$ of interest. These are negligible except for the p states.[3] For an empirical parametrization scheme, it appears to be both practical and desirable to include only the components for $l \leqslant 2$. The problem then is to accurately parametrize these three phase shifts with a small number of parameters. This is the aim of the present work. We test our schemes by comparing the $E(\vec{k})$ corresponding to the parametrized η_l against those calculated with the first-principles s, p, and d phase shifts.

In I, the $\tan\eta_l$ were chosen as the quantities to parametrize. Suitable functional forms having the characteristic energy dependences for these quantities for a family of elements, the noble metals, were set up; and as an application of the scheme, a semiempirical band structure was developed for silver.

The question was raised in I as to whether there would be an advantage in choosing the logarithmic derivatives of the radial wave functions,

$$L_l(E, r_i) \equiv R_l'/R_l \equiv \left(\frac{dR_l(r)}{dr}\bigg/ R_l(r)\right)\bigg|_{r=r_i}\,, \qquad (2)$$

as the fundamental quantities to parametrize rather than the $\tan\eta_l$'s. Here the R_l's are the radial wave functions, and the L_l's are related to the $\tan\eta_l$ by

$$\tan\eta_l = \frac{j_l'(E^{1/2}r) - j_l(E^{1/2}r)L_l}{n_l'(E^{1/2}r) - n_l(E^{1/2}r)L_l}\,. \qquad (3)$$

The $\tan\eta_l$ involves, in addition to the required information about the potential, the energy dependence of the Bessel and Neumann functions. The latter dominate the energy dependences for the range $E \sim V_c$, where the $\tan\eta_l$ are in fact not smooth. It seemed possible that without the E dependence due to the Bessel and Neumann functions a simpler and/or more accurate parametrization of the L_l might be possible than for the $\tan\eta_l$. The present paper discusses, on the basis of specific examples, whether this is the case.

Two different approaches involving parametrization of the logarithmic derivatives were investigated, and will be discussed here. In the first of these the parametrization is exclusively in terms of the logarithmic derivatives. The second scheme obtains improved results by adopting a hybrid technique which uses $\tan\eta_l$ parametrization to treat the resonant part of the d scattering contribution, while the residual d scattering and the complete s and p contributions are treated by parametrizing the logarithmic derivatives. This combines the advantages of parametrizing the d-resonance behavior in terms of $\tan\eta_2$ with the advantages of parametrizing the logarithmic derivatives, which vary smoothly with energy, in the nonresonant regimes of behavior. [It is worth according special treatment to the $\tan\eta_2$ in the d-band region where the $E(\vec{k})$ is very sensitive to the d phase shift. For example, the shift in the lower L_1 level produced by a given percentage change in $\tan\eta_l$ is about twenty times larger for the d than for the s component.] The parametrization of the smoothly varying logarithmic derivatives is done in a systematic way in terms of square-well potentials. The well depths prove to be smooth functions of energy and are readily parametrized.

It should be noted that while the primary effort in this paper is directed to the noble metals, the conclusions reached are not limited to that family of elements. An approach applicable to the noble metals is also applicable to the d transition metals (in the paramagnetic state), the bands of which are rather similar. It would also be applicable *a fortiori* to "simple" metals as we will illustrate with Al.

There has been much interest in recent years in the development of parametrization schemes for describing the energy band structures. Efforts in this area can be divided into two categories. In one the effort is restricted to fitting the electronic structures at the Fermi energy.[4] In the other,[5-9] to which the present work belongs, the goal is to fit the energy bands across a substantial energy range typically about 1 Ry. We believe that the present scheme offers advantages over the other schemes in this category in a number of respects. These will be enumerated in the conclusion where a brief comparison will be made.

II. A PARAMETRIZATION SCHEME FOR LOGARITHMIC DERIVATIVES

Figure 1 shows the logarithmic derivative of the radial wave functions for the copper "Chodorow" potential (as used in Segall's[10] first-principles band calculation), as well as the logarithmic derivatives of the spherical Bessel functions, with $l = 0$, 1, and 2. In finding appropriate parametric forms of the R_l'/R_l, we were guided both by the behavior shown in Fig. 1 and by the parametric forms developed for the $\tan\eta_l$ in I.

It is clear from Fig. 1 that L_1 and the free-electron counterpart (i.e., j_1'/j_1) are quite similar to each other. This led us to adopt a form

$$L_1(\epsilon) = P_1 + P_2(j_1'/j_1) . \qquad (4)$$

In Eq. (4) and hereafter we use dimensionless[2] quantities r and ϵ, with r in units of the lattice parameter a and $\epsilon = (a/2\pi a_0)^2 E$, where a_0 is the Bohr radius and E is in rydbergs.

For L_0, there is reasonably close agreement with j_0'/j_0 for the lower-ϵ part of the ϵ range of interest, but the agreement at higher ϵ is sufficiently poor to suggest that we not use a form analogous to Eq. (4). On the other hand, one can use a form similar to the $\tan\eta_0$ given in Eq. (14) of I. It is

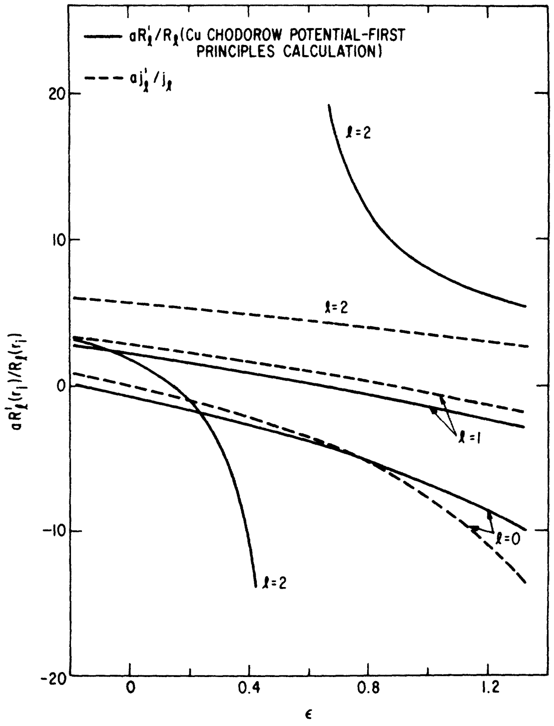

FIG. 1. Logarithmic derivatives of the radial wave functions as a function of ϵ for the Cu Chodorow potential and for a free electron. The dimensionless quantities plotted are given by the lattice constant a times the L_l defined by Eq. (2).

only necessary to remove the $\epsilon^{1/2}$ factor which comes from the low-ϵ behavior of the Bessel functions

$$L_0(\epsilon) = (S_1 - S_2\epsilon)/(1 + S_3\epsilon) . \qquad (5)$$

In fact, this trial form gives quite satisfactory results for the entire ϵ range of interest.

From Fig. 1 it can be seen that the presence of the singularity corresponding to the d-band "resonance" complicates the comparison to j_2'/j_2. Since the important d-band states lie in the energy region around the singularity of L_2, we instead consider the reciprocal, $1/L_2$, which behaves smoothly around the singularity. Of course, one "pays" for this by transforming the zero of L_2 into a singularity of $1/L_2$. However, as there are fewer important d states around the zero of L_2, that region is not as crucial as that around the singularity. As a trial form, we examined whether R_2/R_2' could be given by the appropriately scaled reciprocal logarithmic derivative for the free-electron wave function, with a correction for the presence of the singularity in R_2/R_2'. This led us to try and to adopt a form,

$$1/L_2(\epsilon) = -D_1/(\epsilon - D_2) + D_3(j_2/j_2') + D_4 . \qquad (6)$$

The parameters in Eqs. (4)-(6) have been evaluated for two copper[10] and two silver[11] potentials (i.e., the same potentials treated in I): for L_1 by fitting the first-principles result at one energy at each end of the range of interest, for L_0 by fitting at one energy at each end and one energy in the middle of the range of interest, and for $1/L_2$ by fitting at one energy at each end and one energy in the middle of the range of interest, as well as taking D_2 given by the zero of the first-principles L_2. Because one is fitting smooth curves (except near the singularity of $1/L_2$) the evaluation of parameters and goodness of fit is less sensitive to the choice of particular ϵ used for the fitting than was the case for the $\tan\eta_l$ scheme developed in I.

The values of the parameters giving L_0, L_1, and L_2 for these four potentials are given in Table I. The band-energy deviations with this scheme at some high-symmetry points for three of the potentials are shown in Table II. We note that while the present L_l scheme gives only a modest reduction in the number of parameters required (9 instead of the 10 employed in I), it also leads to a small overall improvement in the accuracy of fit to the first-principles results.

TABLE I. Parameters entering expressions for $R_l'(r_l)/R_l(r_l)$ given by Eqs. (4)-(6) of the text.

	S_1	S_2	S_3	P_1	P_2
Cu (Chodorow)	−0.720	4.184	−0.274	−0.878	1.085
Cu (l dependent)[a]	0.403	3.816	−0.171	0.186	0.939
Ag (Hartree)	−0.992	4.092	−0.258	−0.846	1.050
Ag (Hartree-Fock)	−0.646	4.094	−0.250	0.167	0.902
	D_1	D_2	D_3	D_4	
Cu (Chordow)	0.062	0.144	0.520	0.046	
Cu (l dependent)	0.076	0.224	0.531	0.038	
Ag (Hartree)	0.078	−0.038	0.288	0.079	
Ag (Hartree-Fock)	0.083	−0.305	0.360	0.071	

[a] For Cu with the l-dependent potential, additional parameters were needed for R_0'/R_0 and R_1'/R_0 because of discontinuities in the $l=0$, 1 potentials, introduced in the original first-principles calculation. The parametric expressions used were $L_0(\epsilon) = (S_1 - S_2\epsilon)/(1 + S_3\epsilon) + 0.4\delta$, $L_1(\epsilon) = P_1 + P_2(j_1'/j_1) - 0.06\delta$, with $\delta = 0$ for $\epsilon < 0.5$, $\delta = 1$ for $\epsilon > 0.5$.

III. HYBRID SCHEME INVOLVING SQUARE-WELL PARAMETRIZATION OF NONRESONANT PHASE SHIFTS

The parametrization scheme developed in Sec. II can be improved upon in some respects. While the goal of an 0.01 Ry maximum error in the $E(\vec{k})$ has been achieved, one can seek even greater accuracy for a comparable number of parameters. [The accuracies in fitting the three L_l's are not uniform. The principal contribution to the deviations in $E(\vec{k})$ comes from the $l=2$ component which appears to be difficult to fit accurately over a wide range of ϵ with only four parameters.] Also, the approach of Sec. II lacks uniformity, being different for each l value.

We, therefore, sought another and more systematic means of relating the $L_l(\epsilon)$ to relatively smooth functions of ϵ. A possibility for such functions which occurred to us are the logarithmic derivatives for the square-well potentials.[12]

$$\begin{aligned} V_l(\epsilon, r) &= -v_l(\epsilon), \quad r < r_l \\ V_l &= 0, \quad r > r_l . \end{aligned} \qquad (7)$$

The logarithmic derivatives $L_l(\epsilon)$ for these square-well potentials are obtained from Eq. (2) where,

$$R_l(r) = j_l(K_l r) \quad \text{for } r < r_l , \qquad (8a)$$

with

$$K_l = (2\pi/a)(\epsilon + v_l)^{1/2} . \qquad (8b)$$

The procedure for fitting to the first-principles logarithmic derivatives, then, is to exactly transform the first-principles L_l to the equivalent square-well potential via Eqs. (2) and (8). The ϵ dependence of this "exact" square-well potential is then parametrized.

Figure 2 shows the $v_l(\epsilon)$ for $l=0$, 1, and 2, corresponding to one Cu and two Ag potentials. The magnitude of $v_l(\epsilon)$ reflects the scattering strength for the lth partial wave. It can be seen that v_0 and v_1 for the three potentials are very weak and are very smooth functions of ϵ, so that they can easily be parametrized. Over the energy range of interest

TABLE II. Deviations of $E(\vec{k})$ (in 10^{-3} Ry) with respect to the first-principles results for the different parametrization schemes. The tan, L, and v label, respectively, the $\tan\eta_l$ scheme in I, the L_l scheme in Sec. II, and the hybrid square-well scheme in Sec. III of the present paper.

	Cu (Chodorow)			Ag (Hartree)			Ag (Hartree-Fock)			Al	
	tan	L	v	tan	L	v	tan	L	v	tan	v
Γ_1	0	1	0	−5	0	1	−6	1	0	0	0
Γ_{25}	6	−3	0	2	−3	0	10	0	0	⋯	⋯
Γ'_{12}	7	−4	0	0	−5	0	1	−3	0	⋯	⋯
L_1^{lower}	−9	−5	0	−3	0	0	4	0	0	⋯	⋯
L_3^{lower}	4	−3	0	−6	−2	0	1	−1	0	⋯	⋯
L_3^{upper}	5	−5	0	1	−6	1	2	−4	1	⋯	⋯
L'_2	−3[a]	−2	1	4	0	−1	−2	4	2	−4[a]	−1
L_1^{upper}	5	1	0	0	2	2	0	4	0	−2	0
X_1^{lower}	−10	−5	0	−6	−1	0	10	−1	2	⋯	⋯
X_3	−9	−1	1	−4	−1	−1	9	1	2	⋯	⋯
X_2	3	−4	0	0	−6	1	−5	−3	0	⋯	⋯
X_5	1	−3	0	0	−6	0	−3	−4	1	⋯	⋯
X'_4	1[a]	−1	1	−1	1	2	1	4	2	−2[a]	−1
X_1^{upper}	4	0	1	0	1	0	−6	1	2	−3	0

[a] These values differ from those quoted in I where the comparison was made with the first principles results which included the effect[3] of $l \geq 3$ components.

(roughly 1 Ry) they can be accurately approximated by

$$v_0(\epsilon) = s_0 + s_1\epsilon + s_2\epsilon^2 ,$$
$$v_1(\epsilon) = p_0 + p_1\epsilon . \tag{9}$$

The situation is different for v_2. Its magnitude is large and the variation is great in the region around the resonance energy. This behavior reflects the strong d-resonance scattering that is important in these materials. Though the energy dependence of $v_2(\epsilon)$ is not too radical, we have been unable with a moderate effort to fit it with a suitable functional form involving only a reasonable number of parameters (four or less) which would yield d-band energies to the same accuracy (i.e., deviations $\leq 2\times10^{-3}$ Ry) as that achieved for the sp states by Eq. (9). An important point is that the d-band energies are very sensitive to v_2—even more than they are to $\tan\eta_2$. For example, to achieve deviations from the first-principles result of 0.001 Ry for a typical d state, v_2 must be fitted to an accuracy of $\frac{1}{4}\%$ while a 1% accuracy sufficies for $\tan\eta_2$.

At this point it is useful to consider the physical nature of the $l = 2$ component. It can be described as involving two different aspects: the strong resonance scattering and a "residual"—or nearly-free-electron-like—contribution similar to that expected in a "simple" metal. It is natural to expect that the latter would be considerably weaker and smoother than v_2. Now, as was found in I, the strong resonant scattering contribution can successfully be represented in the $\tan\eta_2(\epsilon)$ by the well-known resonant-pole form[13] $\Gamma(\epsilon)/(\epsilon_d - \epsilon)$. It thus appears useful to retrench somewhat on the proposal to base our approach entirely on the logarithmic derivatives. That is, we propose to use the resonance pole form for the resonant contribution to $\tan\eta_2$ and the square-well-potential approach for the remainder. To this end we split the $\tan\eta_2$ into a resonance and a residual part as follows:

$$\tan\eta_2(\epsilon) = \frac{\Gamma_0}{\epsilon_d - \epsilon}\left(\frac{K}{K_d}\right)\left(\frac{j_2(Kr_i)}{j_2(K_d r_i)}\right)^2 + \tan\eta'_2(\epsilon), \tag{10}$$

where $K \equiv 2\pi\epsilon^{1/2}$. We note that the ϵ dependence of $\Gamma(\epsilon)$ has been changed from the low-ϵ form $\sim\epsilon^{5/2}$ (i.e., K^5) used in I to the $K[j_2(Kr_i)]^2$ form suggested by Pettifor,[14] which gives the same low-ϵ behavior, but which is more reasonable at large ϵ.

In the present calculations, ϵ_d is taken as the ϵ value for the zero of the $\cot\eta_2$ from the first-principles calculations; and the width parameter Γ_0 is obtained from $\Gamma_0 = \lim_{\epsilon\to\epsilon_d}(\epsilon - \epsilon_d)\tan\eta_2$. Once ϵ_d and Γ_0 are determined, $\tan\eta'_2$ is obtained from Eq. (10). The logarithmic derivative $L'_2(\epsilon)$ and the square-well-potential depth $v'_2(\epsilon)$ corresponding to $\tan\eta'_2$ are then readily obtained from Eqs. (3) and (8). The v'_2 thus obtained for the three potentials are

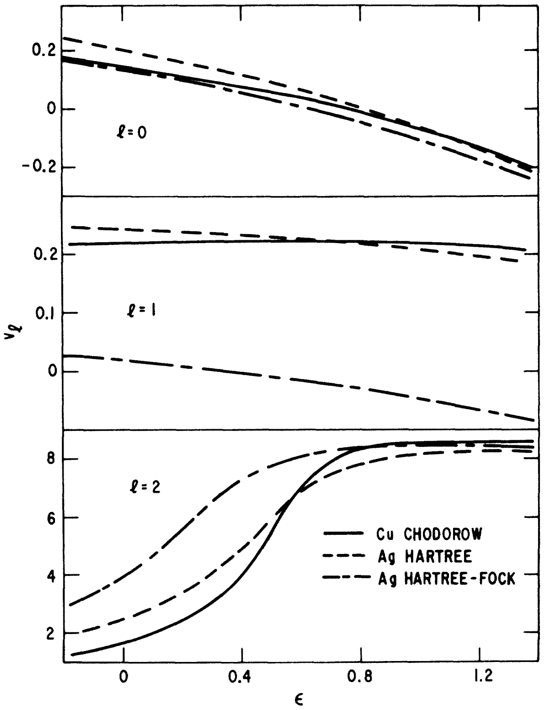

FIG. 2. Depths of the square-well potentials $v_l(\epsilon)$ for the Cu Chodorow, Ag Hartree, and Ag Hartree-Fock potentials used by Segall (Refs. 10 and 11) in the first-principles band calculations. The v_l in this and the subsequent figures are given in the same dimensionless units as ϵ.

shown in Fig. 3. It is seen that these quantities are, as expected, quite small and smoothly varying with ϵ. We note that if ϵ_d and Γ_0 are not accurately determined, the $v_2'(\epsilon)$ will not in fact be very smooth in the vicinity of the resonance as is the case for one of the curves for Ag in Fig. 3. This is not significant in a practical computation since the resonance term completely dominates the $\tan\eta_2$ for ϵ near ϵ_d. In fact, v_2' is only important for ϵ significantly greater than ϵ_d. It thus suffices to represent v_2' by

$$v_2'(\epsilon) = d_0 + d_1\epsilon \, . \qquad (11)$$

The seven parameters in Eqs. (9) and (11) along with the resonance parameters ϵ_d and Γ_0 for the three potentials are listed in Table III. It should be noted that this scheme uses the same number of parameters (a total of 9) as used in the approach of Sec. II. However, there has been considerable gain in accuracy. This can be seen from Table II, where the deviations of band energies at high-symmetry points are compared for the different schemes. We see that the hybrid square-well scheme gives the best results by far, with deviations no greater than 0.002 Ry. The agreement is so good that for all practical purposes we can almost consider the resulting phase shifts to be exact. We note, in fact, that the accuracy far surpasses the goal we set in I of a maximum deviation of 0.01 Ry.

As noted earlier, an approach which is successful for the noble metals should be applicable to a "simple" metal. The only change involved is the simplification effected by the elimination of the d-resonance contribution. The approach thus reduces completely to the square-well scheme. We have tested this assertion using logarithmic derivatives from a calculation[15] for Al. The resulting v_l for $l = 0$, 1, and 2 are shown in Fig. 4. With a view toward encompassing the bands from the bottom of the conduction band (Γ_1) to above the Fermi energy, we have used the forms for $v_l(\epsilon)$ given by Eqs. (9) and (11). The seven parameters used are given in Table III; while Table II lists the deviations of the resulting energies for some high-symmetry states from those for the first-principles calculation. The agreement again is excellent with maximum deviations no larger than 0.001 Ry.

As indicated in the introduction, the inclusion of the $l \geq 3$ components lowers the p-like L_2' and X_4' levels.[3] If we were to adjust the parameters of the present scheme so as to fit the energies, as would be done in an empirical application, the effective $l = 1$ logarithmic derivatives [and thus $v_1(\epsilon)$] would be slightly modified for relatively high ϵ. For the Cu Chodorow potential, for example, the $l = 1$ well depth is increased by 0.006 and 0.015 at the L_2' ($\epsilon = 0.602$) and X_4' ($\epsilon = 0.833$) energies, respectively. The $v_1(\epsilon)$ curves are thus slightly flattened (and thus easier to fit), although their shape is essentially unaffected.

IV. SUMMARY AND CONCLUSION

Two different schemes based mainly on the logarithmic derivatives are considered in this paper.

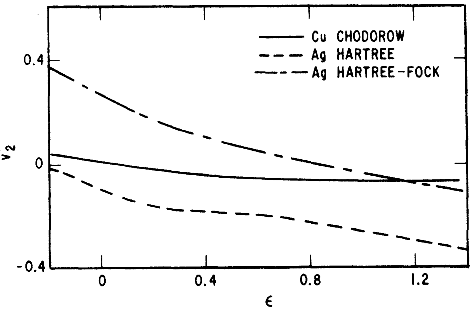

FIG. 3. Depths of the square-well potentials v_2' corresponding to the "residual" scattering described by the $\tan\eta_2'$ in Eq. (10) for the three potentials considered in Fig. 2. The values of ϵ_d and Γ_0 used to remove the resonance contribution are listed in Table III.

TABLE III. Parameters for the square-well scheme given by Eqs. (9)–(11).

	Cu (Chodorow)	Ag (Hartree)	Ag (Hartree-Fock)	Al
s_0	0.1513	0.2014	0.1344	0.3512
s_1	-0.1341	-0.1809	-0.1610	-0.8901×10^{-1}
s_2	-0.8652×10^{-1}	-0.8201×10^{-1}	-0.7759×10^{-1}	-0.7774×10^{-1}
p_0	-0.2279	0.2529	0.2952×10^{-1}	0.4504
p_1	-0.9114×10^{-2}	-0.4479×10^{-1}	-0.7912×10^{-1}	0.6989×10^{-1}
d_0	-0.4979×10^{-1}	-0.8419×10^{-1}	0.1960	0.4972
d_1	-0.1544×10^{-1}	-0.1790	-0.2299	0.1195
Γ_0	0.9190×10^{-2}	0.625×10^{-2}	0.2492×10^{-4}	•••
ϵ_d	0.3519	0.2503	0.2419×10^{-1}	•••

Both schemes required one less parameter and gave better agreement with first-principles calculations than did the scheme used in I based completely on the $\tan\eta_l$. It turns out that the scheme providing the considerably better agreement is, in fact, a partial compromise between the L_l and $\tan\eta_l$ approaches in that the strong d-resonance scattering contribution is treated by the resonant pole contribution to $\tan\eta_2$. For the remainder of the $l=2$ and the complete $l=0$ and 1 contribution square-well potentials of depths $v_l(\epsilon)$ are defined which yield the required logarithmic derivatives. The resulting smooth $v_l(\epsilon)$ functions prove to be quantities which are readily and accurately parametrized. The accuracy achieved with this scheme is excellent. With nine parameters a maximum deviation in $E(\vec{k})$ of only 0.002 Ry is found for three different noble metal potentials over a roughly 1-Ry energy range.

Another virtue of both schemes considered here, which is important in an empirical or semiempirical application and which follows from the smoothness of v_0, v_1, and v_2' (and their corresponding L_l's), is the relative insensitivity of the results to the E's used to determine the parameters. Indeed the virtues of the hybrid square-well scheme strongly indicate that this scheme could provide an excellent basis for an empirical or semiempirical determination of the electronic structure of the noble and transition metals. Such an application is in progress by two of us.[16]

It was also shown by a study of Al, that with a suitable simplification the hybrid square-well scheme can be successfully applied to a "simple" metal. The simplification consists of the elimination of the d-resonance contribution (a reduction of two parameters) with the consequence that the results are given entirely by the well depths v_l.

In the present study, high accuracy over a large energy range was stressed. This ultimately affected the number of parameters required. Clearly there is some flexibility in this matter. Some reduction in the number of parameters would result from reducing the range of E considered and/or the accuracy demanded. We note that the uncertainties associated with the presently available empirical information, e.g., energy gaps obtained from optical measurements, is at best 0.1 eV, which is substantially larger than the maximum deviations achieved by the second scheme.

It is useful to briefly compare the present results with those of several other parametrization schemes that have been proposed for the noble and transition metals. One which has received much attention is the nearly-free-electron–tight-binding (NFE-TB) interpolation scheme proposed by Hodges *et al.*[5] and by Mueller.[6] The number of adjustable parameters that were employed to determine the 9×9 model Hamiltonian for Cu was 14 and 11, respectively. We also note that the accuracy of those calculations were not as good as the present one.[17] Another approach which has been applied to Fe and Cr by Connolly[7] is the linear-combination-of-atomic-orbitals (LCAO) interpolation method. To achieve an accuracy comparable to that obtained by the present scheme for Cu and Ag, it was necessary for him to employ 27 parameters.

A pseudopotential scheme which also utilizes a nonlocal d-wave potential has been proposed by Fong and Cohen and was applied to Cu[8] and NbN.[9] The advantage of this scheme appears to be that it requires a relatively small number of parameters, essentially the same number as in the present

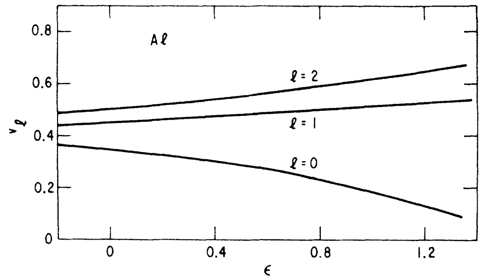

FIG. 4. Depths of the square-well potentials $v_l(\epsilon)$ for the Al potential used by Segall (Ref. 15).

work.[18] Since a comparison with a first-principle calculation such as we presented here was not made in their Cu calculation, a measure of the scheme's accuracy for the noble metals is not available. However, such a comparison was made in their NbN study[9] and the deviations from the first-principles results were found to be quite large. A practical difficulty with the application of their scheme is that it involves the solution of high-dimension determinental equations (e.g., corresponding to matrices larger than 100×100 for Cu). Finally we also note that a satisfactory explanation has not been given for why the scheme with the damped energy-independent nonlocal potential should be successful.[19]

It is worth noting that in contrast to the other schemes, the present scheme parametrizes quantities, namely the L_l and the $\tan\eta_l$, which have a simple and basic physical significance. The determination of these quantities provides useful information about the effective potential.

Lastly we consider the work of Pettifor[14,20] who showed that the NFE-TB model Hamiltonian can be obtained from the GFM by suitable approximations and transformations. As a consequence, all parameters entering the model Hamiltonian can be obtained from the $\tan\eta_l$ (or L_l) and, in principle, can be parametrized by the present scheme. However, the $\tan\eta_l$ appear in relatively complicated summations; and, as a result, an application of this approach is less convenient than one (such as ours) based on the standard GFM where the potential dependent terms are neatly separated out. Furthermore, the approximations made to obtain the model Hamiltonian from the GFM unavoidably reduces the accuracy. Some evidence for this is apparent in the excited bands (e.g., the upper X_1 and L_1 states) in Pettifor's[14] Fe and Cu calculations.

In conclusion, it appears that the present parametrization scheme in conjunction with the GFM is superior to the other proposed schemes because of its combination of simplicity and accuracy. It promises to be a useful tool in the empirical and semiempirical studies of electronic structure.

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[1] B. R. Cooper, E. L. Kreiger, and B. Segall, Phys. Rev. B 4, 1734 (1971). (Referred to as I throughout.) There are two typographical errors in this paper that may confuse the reader. On p. 1739, in the seventh line of the second column, ϵ^2 should be ϵ^3. In Eq. (20), B_{1111} should be B_{1010}. Also it should be pointed out that in the semiempirical phase-shift parametrization calculation of the band structure of silver reported in I, the value of the lattice constant used for silver was about 2% greater than the best current experimental value at low temperature. This was done to maintain consistency with the original calculation by Segall [i.e., Segall's band calculations for an Ag potential derived from Hartree-Fock ionic wave functions as reported in B. Segall, General Electric Research Laboratory Report No. 61-RL-2785G, 1961 (unpublished)], which was modified to obtain the semiempirical band structure. We would like to thank Dr. P. T. Coleridge for bringing to our attention the fact that we had neglected to mention this point.

[2] For a review of the Green's-function method, see B. Segall and F. S. Ham, in *Method in Computational Physics*, *Energy Bands of Solids*, edited by B. Alder, S. Fernback, and M. Rotenberg (Academic, New York, 1968), Vol. 8, Chap. 7. The suggestion of using the GFM as a parametrization scheme was made in this paper.

[3] For example, the addition of the $l=3$ component lowers the L_2' levels in Cu and Al by approximately 0.002 Ry and the higher energy X_4' levels by approximately 0.006 Ry.

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[8] C. Y. Fong and M. L. Cohen, Phys. Rev. Lett. 24, 306 (1970).

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[10] B. Segall, Phys. Rev. 125, 109 (1962).

[11] B. Segall (unpublished).

[12] Square-well potentials v_l were also used by V. Heine and I. Abarenkov [Philos. Mag. 9, 451 (1964); Philos. Mag. 12, 529 (1965)] in a pseudopotential context. We note that their v_l's were used to reproduce the effect of the "core" of atomic potentials while those in the present work mimic the effect of the complete muffin-tin crystal potential.

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[14] D. G. Pettifor, J. Phys. C 2, 1051 (1969).

[15] B. Segall, Phys. Rev. 124, 1797 (1961).

[16] A. B. Chen and B. Segall (unpublished).

[17] rms errors of 0.008 and 0.006 Ry and maximum errors of 0.025 and 0.013 Ry in band energies of Cu were quoted in Refs. 4 and 5, respectively.

[18] Fong and Cohen state that 8 parameters are needed for Cu, but in addition, two cutoff parameters (E_1 and E_2) are employed, the choice of which may well effect the results and the value of other parameters.

[19] L. Kleinman, Phys. Rev. B 5, 4198 (1972).

[20] D. G. Pettifor, J. Phys. C 5, 97 (1972).