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Electron-Phonon Coupling and Pseudopotentials: The Mass Enhancements of the Noble Metals

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The first-principles form factors of Harrison and Moriarty (HM) and the empirical form factors of Fong and Cohen (FC) are investigated as a starting point for calculations of electron-phonon (EP) coupling in noble metals. A compact representation of Harrison's pseudopotential method for transition metals is presented. A theorem by Sham on the use of orthogonalized-plane-wave–based pseudopotentials for EP matrix elements is expressed in operator language and generalized to include a wide class of pseudopotentials, including Harrison's. With the underlying principles justified, single-plane-wave calculations of the EP mass enhancement and resistivity are presented. The FC form factors give results that are more nearly consistent with experimental knowledge than the HM form factors. The discrepancy is traced to the sign and magnitude of the d-wave interaction.

I. INTRODUCTION

There has been much recent interest[1-3] in the effect of electron-phonon (EP) interactions on the electronic properties of the noble metals. Because the Fermi-surface (FS) states contain relatively little d character, it is tempting to use for the noble metals the approximations that have been so successful for the nontransition metals.[4]

As a theoretical step in this direction, Harrison[5] has extended the orthogonalized-plane-wave (OPW) approach of Phillips and Kleinman (PK),[6] giving an energy- and angular-momentum-dependent pseudopotential with an $l=2$ resonance in the region of the d bands. From Harrison's formulation Moriarty[7] has calculated first-principles values of the form factor appropriate to scattering on the Fermi surface. We shall refer to these as the Harrison-Moriarty (HM) form factors. They differ from nontransition-metal form factors in having a hump due to the repulsive interaction above the $l=2$ resonance.

As an empirical step in the same direction, Fong and Cohen[8] have succeeded in adjusting a nonlocal model potential that reproduces experimental features of the band structure of copper, using a secular equation of 140 plane waves. Their model potential consisted of a local potential similar in shape and magnitude to nontransition-metal form factors, and a nonlocal d-wave term that is large in the region of the d bands, but very small for scattering between plane waves of wave vector equal to k_F. This d-wave term is attractive throughout phase space for elastic scattering, so the form factor looks rather different from that of HM. Preliminary results of similar calculations for silver and gold have been supplied.[9] The resulting form factors will be referred to as Fong-Cohen (FC) form factors.

The principal advantage of a pseudopotential formulation of energy bands is the possibility of using the pseudopotential to calculate other properties of the metal [such as electron-phonon (EP) coupling] in low-order perturbation theory. In this paper, such a calculation is attempted in the lowest order of approximation by using single plane waves as pseudo wave functions and neglecting the distortion of the Fermi surface from a sphere. Section III presents values of the mass enhancement λ and resistivity ρ that are determined by EP scattering on the Fermi surface. This type of calculation has been shown to be quite successful for nontransition metals. The application of these techniques to noble metals raises several questions. First is the question of whether in principle a pseudopotential that determines band structures is directly applicable to the EP problem. This question is explored in detail in Sec. II, where compact formulations are presented in operator language of Harrison's pseudopotential scheme and of Sham's theorem[10] on the use of pseudopotentials for EP coupling. The question is answered in the affirmative, provided that the potential and the pseudopotential are sufficiently localized. The second question is whether a single plane wave is an adequate pseudo wave function for the noble metals. This is related to the third question, namely, whether Fermi-surface distortions are crucial in calculating λ and ρ. Clearly ρ is more affected by this assumption than λ, since λ depends mainly on the average scattering matrix element, whereas ρ depends strongly on the scattering angle as well. The author thinks that Fermi-surface distortions should not have a major effect on the average matrix element, to within perhaps 50% accuracy or better. This study is most concerned with wave functions on the (approximately) spherical belly, where a single plane wave ought to provide a reasonable estimate. The results obtained for λ and ρ from the two different pseudopotentials differ by about a factor of 6, which lies considerably outside the estimated errors. Thus in Sec. IV some tentative conclusions are drawn about the different pseudopotential form factors.

II. THEORY OF MATRIX ELEMENT

The usual (PK) pseudopotential approach begins by choosing as a basis set the plane waves augmented by atomic core functions, in the hope of improving convergence. The resulting wave functions ψ can be split into the part φ arising from plane waves (called the pseudo wave function) and the remainder, arising from core functions. But for conduction bands, ψ is orthogonal to core functions, so ψ and φ are related by

$$\psi = (1 - P_c)\varphi \ , \tag{1}$$

where P_c is the projection operator onto core states The Schrödinger equation for ψ can be transformed into a pseudo Schrödinger equation for φ:

$$(T + V + V_R)\varphi = E\varphi \ , \tag{2}$$

where $V + V_R$ is the pseudopotential and V_R is given by

$$V_R = (E - \mathcal{H})P_c \ , \tag{3}$$

where $\mathcal{H}$ is the "real" Hamiltonian $T + V$. For transition metals, however, this scheme is inadequate to yield rapid convergence for the d bands. Harrison[5] suggested adding a set of atomic d functions to the basis set in order to improve convergence. The pseudo wave function φ is still defined as the plane-wave part of ψ; however, Eq. (1) no longer holds since ψ is not orthogonal to the atomic d states. Harrison's analysis at this point becomes somewhat intricate and we will not repeat it. His conclusions, however, can be expressed rather simply in operator language. We define an operator

$$P_H = P(E - \mathcal{H}_{\text{at}})^{-1}(E - \mathcal{H}) \ , \tag{4}$$

where P is the projection operator onto core states plus atomic d states, which are all eigenfunctions of $\mathcal{H}_{\text{at}}$. P_H has the same effect as P_c when operating on core states since $\mathcal{H}$ and $\mathcal{H}_{\text{at}}$ are assumed to be identical in the core region, and similar enough elsewhere that

$$\langle d|\mathcal{H}|d\rangle = \langle d|\mathcal{H}_{\text{at}}|d\rangle = E_d \tag{5}$$

holds for the atomic d state $|d\rangle$. Then the wave function and the pseudo wave function are related by

$$\psi = (1 - P_H)\varphi \tag{6}$$

and the pseudo Schrödinger equation is the same as Eq. (2), with the V_R given by

$$\begin{aligned} V_R &= (E - \mathcal{H})P_H \\ &= (E - \mathcal{H})(E - \mathcal{H}_{\text{at}})^{-1/2} P (E - \mathcal{H}_{\text{at}})^{-1/2}(E - \mathcal{H}) \ , \end{aligned} \tag{7}$$

where in the second line, V_R is written in an explicitly Hermitian form by using the fact that P and $\mathcal{H}_{\text{at}}$ commute. Note that V_R has a resonance at $E = E_r$ (in practice, $E_r = E_d$), where E_r is any eigenvalue of $\mathcal{H}_{\text{at}}$ that does not coincide with an eigenvalue of $\mathcal{H}$. We are now in a position to investigate electron-phonon coupling. The approach is identical to that of Sham,[10] except that by using operator language a simpler and more general proof is obtained. We start by reformulating relations (1) and (6) between ψ and φ into the form

$$\psi = [1 - (E - \mathcal{H})^{-1} V_R]\varphi \ . \tag{8}$$

This form is valid not only for the particular pseudopotentials of PK and Harrison, but more generally for any problem in continuum physics in which we want to know the eigenfunction ψ (of energy E) of a Hamiltonian $\mathcal{H} = T + V$ and we are given the eigenfunction φ (of the same energy) of a Hamiltonian $T + V + V_R$. Thus in particular it applies to any pseudopotential.

Now we are interested in the electron-phonon matrix element[11]

$$\vec{I} = \langle \psi' | \vec{\nabla} v | \psi \rangle \ . \tag{9}$$

We are going to specialize to the case of elastic scattering (for example, the states ψ and ψ' are both on the Fermi surface). The difficulty comes from the fact that v is the localized potential of a single atom, whereas we have dealt previously with the total crystal potential

$$V = \textstyle\sum_{\vec{l}} v(\vec{r} - \vec{l}) \ . \tag{10}$$

If we were dealing with the total potential [∇V in place of ∇v in Eq. (9)], we could use the identity

$$\vec{\nabla} V = [\vec{\nabla}_{\text{op}} , \mathcal{H}] \tag{11}$$

(∇_{op} is $i\vec{p}/\hbar$, where $\vec{p}$ is the momentum operator) to reduce $\vec{I}$ to a simple expression, namely, zero for elastic scattering. Incidentally, this is consistent with the deformation-potential theorem, which states that at long wavelengths (equivalent to displacing the whole crystal) the scattering must go to zero.

The repulsive part of the pseudopotential V_R is also a sum of localized terms:

$$V_R = \sum_{\vec{l}} v_R(\vec{r} - \vec{l})$$

(which is true for the PK and HM forms because the projection operators are sums of projections onto individual atoms.) This fact enables us to take partial advantage of Eq. (11). Pseudo wave functions φ' and φ are introduced by using Eq. (8) in Eq. (9). Then expanding we get

$$\vec{I} = \langle \varphi' | \vec{\nabla} v | \varphi \rangle + \vec{a} + \vec{b} + \cdots , \tag{12}$$

where $\vec{a}$, $\vec{b}$, etc., are a series of terms that all involve the localized product $v_R | \varphi \rangle$ or $(v_R | \varphi \rangle)^*$ summed over atomic sites $\vec{l}$. We now make the assumption that v and v_R are sufficiently localized that we may drop all terms except those in which v and v_R occur on the same site. By the same assumption we may now replace $\nabla \vec{v}$ by $\nabla \vec{V}$ in these same terms, and use the identity (11). A convenient way of dividing the terms $\vec{a}$, $\vec{b}$, ..., is

$$\begin{aligned} \vec{a} &= \langle \varphi' | (1 - V_R^\dagger (E - \mathcal{H})^{-1}) \mathcal{H} \vec{\nabla}_{\text{op}} (E - \mathcal{H})^{-1} v_R | \varphi \rangle , \\ -\vec{b} &= \langle \varphi' | v_R^\dagger (E - \mathcal{H})^{-1} \vec{\nabla}_{\text{op}} \mathcal{H} (1 - (E - \mathcal{H})^{-1} V_R) | \varphi \rangle , \\ \vec{c} &= \langle \varphi' | v_R^\dagger (E - \mathcal{H})^{-1} \mathcal{H} \vec{\nabla}_{\text{op}} | \varphi \rangle , \\ -\vec{d} &= \langle \varphi' | \vec{\nabla}_{\text{op}} \mathcal{H} (E - \mathcal{H})^{-1} v_R | \varphi \rangle . \end{aligned} \tag{13}$$

Note that in $\vec{a}$ and $\vec{b}$ we have kept a term containing V_R instead of v_R (which is permissible because an over-all factor v_R multiplies it). This was done intentionally so that the complete wave function ψ' (or ψ) would appear on the left-hand side (right-hand side) in $\vec{a}$ ($\vec{b}$). Because ψ appears, $\mathcal{H}$ may be replaced by E. Finally the terms in $\vec{a}$ and $\vec{b}$ that are bilinear in v_R cancel, and the linear terms can be added to $\vec{c}$ and $\vec{d}$, which causes further cancellations. The result is

$$\vec{a} + \vec{b} + \vec{c} + \vec{d} = \langle \varphi' | \nabla_{\text{op}} v_R - v_R^\dagger \nabla_{\text{op}} | \varphi \rangle . \tag{14}$$

We can go no further unless v_R is Hermitian. This is true for the PK and HM pseudopotentials although not true for the more general form of Austin, Heine, and Sham.[12] Assuming Hermiticity, the desired theorem

$$\vec{I} = \langle \psi' | \vec{\nabla} v | \psi \rangle = \langle \varphi' | \vec{\nabla}(v + v_R) | \varphi \rangle \tag{15}$$

has been proved.

We emphasize that the result (15) requires three conditions, viz., elastic scattering, Hermiticity of v_R, and nonoverlap of v and v_R. Only the last criterion presents any problem for our case. The size of v_R is determined by the size of the core and atomic d functions. Thus the theorem (15) is on slightly weaker grounds for transition metals than for nontransition metals, where there are no d functions near the Fermi level, and v_R is determined by the well-localized core functions. Numerical estimates of the magnitude of this error are presented in the Appendix. For copper the error in Eq. (15) should be less than 5%.

III. CALCULATION OF λ AND ρ

The details of this calculation have been published often enough before and do not warrant repeating. The interested reader may consult the paper of Allen and Cohen[13] for details of the method and a review of much of the earlier work. A few points should be mentioned, however. In addition to the single-plane-wave and spherical-Fermi-surface approximations mentioned earlier, the phonon spectra have been approximated by spherical symmetric functions $\omega(|\vec{q}|)$ chosen to represent closely the data obtained from inelastic neutron scattering in symmetry directions. The unrenormalized density of states was determined by dividing the specific heat mass by $(1+\lambda)$ in a self-consistent fashion. This has the effect of raising the theoretical λ in the FC case for Cu, and lowering the values for all the metals (especially Ag) in the HM case, with respect to the value obtained with a free-electron density of states. Thus it tends to make the theoretical calculations more similar than would be the case if a constant value of $N(0)$ had been used.

The HM pseudopotential form factors were taken directly from Moriarty's calculation for the Harrison first-principles potential. The procedure for extracting the pseudopotential matrix element for scattering on the Fermi surface from the FC empirical potential is unambiguous for the nonlocal part of their potential, which turns out to be small on the Fermi surface. To obtain the local part, one must extrapolate from the known values $V(G)$ down to the region $0 < q < 2k_F$. This was done by requiring the *total* potential to have the Fermi-Thomas shape $[-4\pi e^2/(q^2 + k_s^2)]$ at small q, and drawing a smooth curve inbetween. The form factors obtained in this way are shown in Fig. 1.

The data used in the calculation and the results are given in Table I. Neither form factor gives results that compare well with experimental values of ρ. As mentioned earlier, ρ should be more sensitive to Fermi-surface distortions than λ, and in fact distortions should have the effect of increasing ρ by increasing the effective scattering angle of scatterings mediated by low-$\vec{q}$ phonons. Thus the FC form factors, which underestimate ρ, seem more realistic than the HM form factors, which

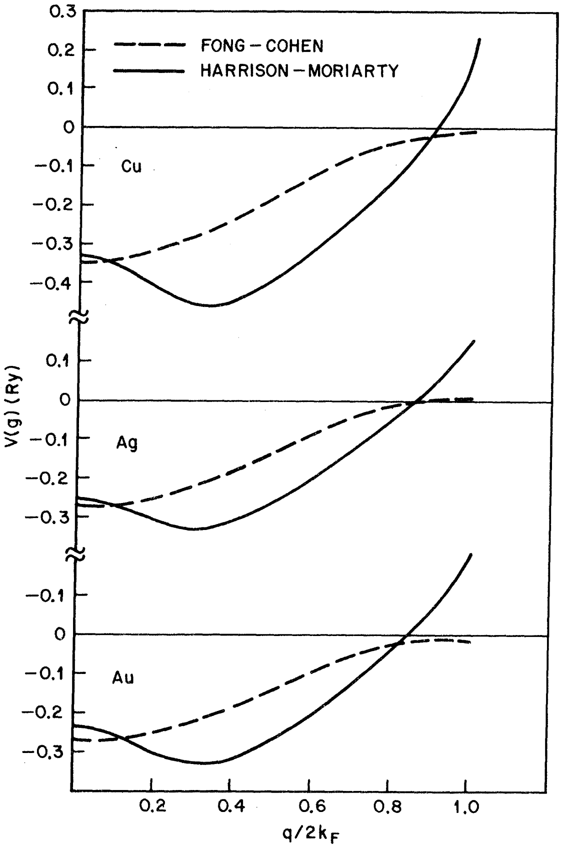

FIG. 1. Form factors $V(q)$ in rydbergs plotted vs $q/2k_F$ for the noble metals. The Fong-Cohen form factors for Ag and Au are preliminary; however, future alterations are expected to be small for scattering on the Fermi surface.

overestimate it.

Grimvall[3] has used the resistivity data to derive approximate lower bounds of 0.07, 0.05, and 0.07 for λ in Cu, Ag, and Au. These lower bounds are very close to the values computed from the FC form factors. From the observed absence of superconductivity, Grimvall[3] has derived approximate upper bounds on λ of 0.24, 0.25, and 0.26. The values of λ obtained from the HM form factors equal or exceed these numbers. Lee[1] has analyzed cyclotron resonance data for Cu and derived values of λ which are quite anisotropic, varying from 0.04 to 0.21 for various points in the belly. The isotropic value 0.083 calculated from the FC form factors is not inconsistent with Lee's results, whereas the value 0.45 from the HM form factor is much too large. Christensen[2] has calculated cyclotron resonance masses for Au. Comparison with experiment yields renormalization parameters λ equal to 0.1 and 0.13 for (100) and (111) belly orbits, respectively, and 0.2 for the (111) neck orbit. Also he has calculated the density of states. Comparison with the specific heat yields an average mass enhancement λ equal to 0.08, in fair agreement with the value 0.056 calculated from the FC form factors, but much smaller than the value 0.34 from the HM form factors. It seems reasonable to conclude that the HM form factors disagree with experiment by an amount that is outside the severe limitations of the calculation, while the FC form factors give results that agree within these limitations.

IV. DISCUSSION

It is interesting that the theoretical values of λ and ρ from the two sets of form factors deviate from experiment in opposite directions. This fact can be correlated with the strength of the $l=2$ potential in each case. For insights in this direction it is useful to decompose the pseudopotential V_p in terms of effective phase shifts φ_l defined by

$$V_p(q)=(2/\pi)V_p(0)\textstyle\sum_l(2l+1)P_l(\cos\theta)\varphi_l\ , \qquad (16)$$

where P_l is the Legendre polynomial for the scattering angle θ between initial and final plane-wave states $\vec{k}$ and $\vec{k}'$ on the Fermi surface. Approximate values of φ_l for l up to 2 are given in Table II. In the case of the HM form factors, the values of φ_2 are all negative (repulsive interaction), which arises naturally from the fact that the Fermi surface lies above a d-wave resonance. The FC form factors have positive values of φ_2, which arises

TABLE I. Data used in calculating λ [C and W stand for velocity and maximum frequency of the modes L (longitudinal) and T (transverse)] and results of calculations.

	m^*	r_s	C_L (10^{+5} cm/sec)	C_T (10^5 cm/sec)	W_L (meV)	W_T (meV)
Cu	1.38^a	2.67	4.69^b	2.40^b	30.3^b	20.9^b
Ag	1.00^a	3.02	3.17^c	1.62^c	20.5^c	14.1^c
Au	1.09^a	3.01	2.36^d	1.21^d	15.3^d	10.5^d

	Pseudopotential	$\rho(T=295)$ ($\mu\,\Omega$ cm) Meas	$\rho(T=295)$ ($\mu\,\Omega$ cm) Calc	λ
Cu	FC^e	1.70^f	0.42	0.083
	HM^g		5.03	0.45
Ag	FC^e	1.61^f	0.24	0.046
	HM^g		4.27	0.25
Au	FC^e	2.20^f	0.40	0.056
	HM^g		6.75	0.34

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TABLE II. Approximate phase shifts φ_l for various form factors, as defined by Eq. (16).

Metal	Potential	φ_0	φ_1	φ_2	$V(0)$
Cu	FC	0.50	0.24	0.06	−0.345
Cu	HM	0.96	0.52	−0.08	−0.330
Ag	FC	0.43	0.26	0.07	−0.270
Ag	HM	0.74	0.52	−0.04	−0.253
Au	FC	0.50	0.25	0.07	−0.271
Au	HM	0.74	0.60	−0.07	−0.238

partly from their choice of an attractive nonlocal d-wave interaction, and partly from the somewhat *ad hoc* (but perfectly natural) fashion in which the local part of their potential was extrapolated to $q=0$.

Theoretical scattering arguments make Harrison's repulsive d-wave interaction seem more realistic than Fong and Cohen's attractive interaction. However, there is no question that the repulsive d-wave terms are what causes the HM form factors to overestimate λ and ρ. This can be seen by using a representation for λ given by McMillan[14]:

$$\lambda \cong \frac{1.51}{r_s}\,\frac{\langle v^2\rangle}{\langle \omega_q{}^2/\Omega_p{}^2\rangle}\,, \tag{17}$$

where r_s is the dimensionless electron-gas parameter (radius of the volume per electron) and $\langle v^2\rangle$ is a dimensionless average of the pseudopotential over the Fermi surface

$$\langle v^2\rangle \equiv \frac{\int_0^{2k_F} dq\, q^3 V_p{}^2(q)}{\int_0^{2k_F} dq\, q^3 V_p{}^2(0)}\quad . \tag{18}$$

Equations (17) and (18) can be thought of as defining $\langle \omega_q{}^2/\Omega_p{}^2\rangle$, which is an average of the square phonon frequency $\omega_q{}^2$ normalized to the ionic plasma frequency $\Omega_p{}^2$. The average contains the pseudopotential as a weight factor, but it is not particularly sensitive to the details of the pseudopotential. (It is more sensitive for monovalent metals than for polyvalent metals, however.) At any rate, (17) provides an approximate way of separating out the effect of the pseudopotential on λ.

Using Eq. (16), we can derive an explicit expression for $\langle v^2\rangle$ in Eq. (18) in terms of the phase shifts φ_l:

$$\langle v^2\rangle = (2/\pi)^2 \textstyle\sum_l \left[(2l+1)\varphi_l{}^2 - (2l+2)\varphi_l\varphi_{l+1}\right]\,. \tag{19}$$

Now the phase shifts φ_l are not all independent. Equation (16) implies that they must satisfy the Friedel sum rule

$$\textstyle\sum_l (2l+1)\varphi_l = \frac{1}{2}\pi\,. \tag{20}$$

If we assume that the expansion (16) terminates at a finite number of terms, then the value of $\langle v^2\rangle$ must be greater than some minimum value. If only s and p phase shifts are allowed, the minimum value is $\frac{1}{9}$, obtained if $\varphi_0:\varphi_1::3:2$. The small size of the observed λ's for noble metals implies that $\langle v^2\rangle$ is not much larger than $\frac{1}{9}$. If we now turn on a small φ_2, this will act to lower or raise $\langle v^2\rangle$, depending on whether φ_2 has the same or the opposite sign as φ_0 and φ_1. (If arbitrary values of φ_0, φ_1, and φ_2 are allowed, there is a minimum value $\langle v^2\rangle = \frac{1}{36}$ obtained when $\varphi_0:\varphi_1:\varphi_2::6:5:3$.)

Similar arguments can be applied to ρ, which will scale approximately according to $\langle v_{\mathrm{tr}}{}^2\rangle$, which is given by

$$\begin{aligned}\langle v_{\mathrm{tr}}{}^2\rangle &= \langle v^2(1-\cos\theta)\rangle \\ &= 2\left(\frac{2}{\pi}\right)^2 \sum_l \left(\frac{(2l+1)(3l^2+3l-2)}{(2l-1)(2l+3)}\,\varphi_l{}^2\right. \\ &\qquad \left. -(2l+2)\,\varphi_l\varphi_{1+1} + \frac{(l+1)(l+2)}{(2l+3)}\,\varphi_l\varphi_{l+2}\right)\cdot\end{aligned} \tag{21}$$

For s and p phase shifts, $\langle v_{\mathrm{tr}}{}^2\rangle$ has a minimum value of $\frac{1}{12}$ when $\varphi_0:\varphi_1::3:1$; with d phase shifts as well, the minimum is $\frac{1}{75}$ when $\varphi_0:\varphi_1:\varphi_2::20:15:7$. A small d-wave phase shift of the same (or opposite) sign as φ_0 and φ_1 will lower (or raise) $\langle v_{\mathrm{tr}}{}^2\rangle$.

These arguments lead to the conclusion that a single-plane-wave scattering model for the noble metals cannot be consistent with known information about λ and ρ unless the d-wave interaction at the Fermi surface is attractive (as in the FC form factors) or at least much less repulsive than in the HM form factors. Possibly the latter calculation has underestimated the screening of the d-wave interaction.

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APPENDIX

We want to estimate the errors involved in approximating the terms $\vec{a}$, $\vec{b}$, ..., in Eq. (12) by omitting all terms $v_R(\vec{r}-\vec{l})$ except the terms $\vec{l}=0$ and then replacing $v(\vec{r})$ by the sum over all sites of $v\,(\vec{r}-\vec{l})$. A typical term is (in exact form)

$$\langle \vec{k}'\,|\textstyle\sum_{\vec{l}} v_R{}^\dagger(\vec{r}-\vec{l})(E-\mathcal{H})^{-1}\vec{\nabla}v(\vec{r})\,|\,\vec{k}\rangle\,, \tag{A1}$$

which we want to compare with the approximate form

$$\langle \vec{k}'\,|\,v_R{}^\dagger(\vec{r})(E-\mathcal{H})^{-1}\textstyle\sum_{\vec{l}}\vec{\nabla}\,v(\vec{r}-\vec{l})\,|\,\vec{k}\rangle\,. \tag{A2}$$

It is adequate to consider single-plane-wave matrix elements instead of pseudo wave function matrix elements.

For the purposes of numerical comparison, let us consider a simpler overlap integral

$$A = \sum_{\vec{l} \neq 0} \langle \vec{k}' | v_R{}^{\dagger}(\vec{r}) v(\vec{r}+\vec{l}) | \vec{k} \rangle , \tag{A3}$$

which we want to compare with the single-site matrix element

$$B = \langle \vec{k}' | v_R{}^{\dagger}(\vec{r}) v(\vec{r}) | \vec{k} \rangle . \tag{A4}$$

Finally, for simplicity consider only the special case $\vec{k}' = \vec{k}$. We will approximate the real potential $v(\vec{r})$ by a screened Coulomb potential. For the repulsive potential we use an unscreened Coulomb potential, cutoff at the core radius r_c. If we keep only the nearest neighbors in the sum over sites in (A3), the ratio of A to B is

$$A/B = c(e^{-k_s a}/k_s a)\, e^{k_s r_c/2} \sinh(k_s r_c/2) , \tag{A5}$$

where c is the coordination number (12 for fcc structure), k_s is the Thomas-Fermi screening wave vector, and a is the nearest-neighbor distance. The ratio A/B represents the approximate fractional error incurred in omitting the $l \neq 0$ terms from (A1) or from (A2).

Let us evaluate (A5) for copper. If we consider only one s electron per atom, $k_s a$ has the value 4.61. Fong and Cohen[8] used for the d-wave part of v_R a well truncated at $r_c = 0.814$ Å. These parameters give a fractional error $A/B = 4\%$. For the Harrison-Moriarty potential, a slightly larger value of r_c is appropriate. If we choose r_c to be the radius at which the atomic wave function $r^2 |\Psi_{3d}|^2$ decays to 10% of its maximum value, we find from Hermann and Skillman's tables[15] a value $r_c = 1.06$ Å. This yields a fractional error $A/B = 7\%$.

The expression (A5) involves many approximations, and we can argue that the errors of (4–7)% are probably overestimates. For example, by translational invariance it is clear that the error made in dropping the $\vec{l} \neq 0$ terms from (A1) exactly cancels the error in adding them to (A2), if the wave vectors $\vec{k}'$ and $\vec{k}$ are equal. Thus, when $\vec{k}' = \vec{k}$ the exact error is 0%, not (4–7)%. When $\vec{k}' \neq \vec{k}$ this cancellation of errors does not occur. However, (A5) will still be an overestimate, because we can expect the contributions from the 12 different nearest neighbors in Eq. (A3) to start adding out of phase. The parameter c in Eq. (A5) should decrease from 12 as $\vec{k}'$ moves away from $\vec{k}$.

These considerations lead to the conclusion that the "theorem" of Eq. (15) is probably valid to better than 5% for pseudopotentials for copper.

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