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Different Types of Phase-Shift Pseudopotential with Application to the Alkali Metals and Copper

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The total pseudopotential in a metal can be expressed in many ways as a sum of atomic pseudopotentials. One way involves the usual "linear-screening" potential and another a "minimum-perturbation" potential. These different types of pseudopotential can be constructed by fitting experimental Fermi-surface data in terms of phase shifts within the formalism of the augmented-plane-wave method of band-structure calculation. An investigation is made of the effect of choosing different values of the "Fermi energy parameter" which defines the mean interstitial potential relative to the absolute Fermi level. Pseudopotential form factors calculated from the empirical phase shifts are presented for the alkali metals and copper.

I. INTRODUCTION

There has been a trend in recent years[1-6] to express the band structures of nearly free-electron solids in terms of scattering phase shifts η_l. This approach seems to be more effective than others when d-band effects are important, even in the alkali metals.[5] In particular, the Fermi surfaces of the alkali metals[5] and copper[6] have been fitted in this way by using the formalism of the augmented-plane-wave (APW) method[7] of band-structure calculation. The phase shifts describe the interaction of a conduction electron with the atom concerned, and, in order make use of this information to describe the electron-phonon interaction and a variety of physical properties, one needs to deduce the appropriate pseudopotential. The term pseudopotential is used here in its current wide sense,[7,8] and includes, for example, the APW form factor and the Korringa-Kohn-Rostoker-Ziman (KKRZ)[9] expression.

However, it is necessary to resolve one ambiguity first.[2,10,11] In fitting Fermi surfaces within the APW formalism, one has to choose a value of the Fermi energy parameter E_F, which is the measure of the Fermi energy relative to the muffin-tin constant. It is not a fitting parameter in the usual sense, because for any chosen E_F (within wide limits) one can obtain a corresponding set of phase shifts that reproduces the measured Fermi surface. The first purpose of this paper is to explore the effect of changing the E_F parameter and what it corresponds to physically. Secondly, we present phase-shift pseudopotentials for the alkali metals and copper. The calculation of various physical properties and comparison with other pseudopotentials is deferred to the following paper.

The nonuniqueness of E_F can be looked at from a physical point of view. Suppose one is given the total potential (or pseudopotential) $V(\vec{r})$ in a crystal. It can be expressed as a sum of atomic potentials $v(\vec{r}-\vec{R}_\alpha)$ associated with the sites $\vec{R}_\alpha$ in an infinite variety of ways (Fig. 1), and from Poisson's equation one can associate with each v a corresponding distribution of conduction electrons. In pseudopotential calculations the electrical neutrality is usually treated by linear-screening theory with overlapping charge clouds.[12-14] But this is not the only way to allocate the conduction electrons. Other formulations have appeared occasionally[4,15,16] and we think that there is a need to relate these to one another and also to the screening method. Thus by way of an extended introduction we try to classify these approaches in Sec. II. In particular, what we have called[11] the minimum-perturbation pseudopotential is stated more precisely than usual.

II. DEFINITION OF VARIOUS PSEUDOPOTENTIALS

We consider a system of N identical atoms at arbitrary positions $\vec{R}_\alpha$ in a volume $N\Omega$ with periodic boundary conditions applied at the surface of the box. The total pseudopotential $V(\vec{r})$ is expressed in

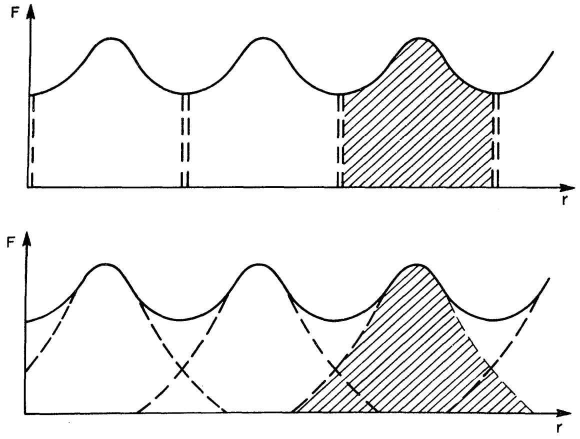

FIG. 1. Two ways of cutting up a periodic function $F(\vec r)$ into a sum of atomic contributions f (shown shaded). If one can subtract an arbitrary constant as in Eq. (2.1), that widens the range of choices further.

the form

$$V(\vec r) = A + \textstyle\sum_\alpha v(\vec r - \vec R_\alpha) \qquad (2.1)$$

$$= A' + \sum_{\vec q}{}' S(q)\, v(q)\, e^{i\vec q\cdot\vec r} , \qquad (2.2)$$

where

$$S(q) = N^{-1} \textstyle\sum_\alpha e^{-i\vec q\cdot\vec R_\alpha} , \qquad (2.3)$$

$$v(q) = \Omega^{-1} \int v(r)\, e^{-i\vec q\cdot\vec r}\, d^3\vec r . \qquad (2.4)$$

$\vec q$ runs over all wave vectors allowed by the size of the (large) box. We use the symbol $v(r)$ for the atomic pseudopotential in real space and $v(q)$ for its Fourier transform. Let each atom have z conduction electrons. In an infinite medium the constants A and A' have little physical significance. They contain, among other terms, the exchange and correlation contribution to the self-energy of an electron in a uniform gas of z electrons per volume Ω. They have a significance for the work function when there is a surface but we shall not consider that case. For our purposes it suffices to see that neither A nor A' is ordinarily equal to $v(0)$, defined as

$$v(0) = \lim_{q\to 0} v(q) . \qquad (2.5)$$

As already noted in Sec. I, there are many ways of dividing a given potential $V(\vec r)$ of the whole system into atomic contributions $v(r)$. The nonuniqueness is obvious for a crystal lattice: $V(\vec r)$ determines only $v(q)$ at the reciprocal-lattice vectors $\vec q = \vec g$ $(g \neq 0)$, and thus its interpolation and extrapolation from the smallest g towards $q \to 0$ is entirely at our disposal.

The most common method of constructing the potential is to start with a free-electron gas, and replace the positive background charge by positive ions at arbitrary positions $\vec R_\alpha$. The screening redistribution of the electrons is calculated by perturbation theory, and yields[12] (ST stands for screening theory)

$$v_{\mathrm{ST}}(0) = -\tfrac{2}{3} E_{\mathrm{F}0} , \qquad (2.6)$$

where

$$E_{\mathrm{F}0} = \hbar^2 k_{\mathrm{F}}^2 / 2m \qquad (2.7)$$

is the free-electron Fermi energy. The limit (2.6) derives from the screening of the ionic charge and is otherwise independent of the nature of the pseudopotential. A more general formula[17] is $-[n(E_{\mathrm{F}})]^{-1}$, where $n(E_{\mathrm{F}})$ is the density of states at the Fermi level, and includes exchange and correlation corrections and the band effective mass. But these niceties are irrelevant to the present discussion. The perturbation theory leading to (2.6) is valid for a reasonably uniform density of atoms. Thus it is an exact result[17] for the electron-phonon interaction in the limit of a long-wavelength density fluctuation of small amplitude. Equation (2.6) expresses the fact that each ion in a metal drags a neutralizing charge $-ze$ with it in any such fluctuation. Similarly, if an additional impurity of charge $z'e$ is placed in the metal, its pseudopotential after screening has the limit

$$v_{\mathrm{imp}}(0) = -\tfrac{2}{3} E_{\mathrm{F}0}(z'/z) . \qquad (2.8)$$

Many pseudopotentials $v(q)$ are formulated in this way with the limit (2.6). When Fourier transformed back into real space $v(r)$, they constitute Ziman's neutral pseudo-atoms.[18] Phase shifts $\eta_l\,(E_{\mathrm{F}})$ can be calculated for $v(r)$, which we would expect to yield a Friedel sum[7]

$$\mathcal{F} = (2/\pi) \textstyle\sum_l (2l+1)\, \eta_l , \qquad (2.9)$$

with

$$\mathcal{F}_{\mathrm{LS}} = z \qquad (2.10)$$

because $v(r)$ is the pseudopotential of an ion that has attracted z screening electrons. $\mathcal{F}$ will not equal z exactly since perturbation theory has been used in $v(q)$. The $v(r)$ extends outside the atomic cell and overlaps considerably with its neighbors.[14]

However there is another approach to constructing the pseudopotential which is attractively simple, but more limited in its usefulness.[4,19] For this reason, it is less well documented in the literature. Consider a perfect crystal of a close-packed metal, divided into atomic polyhedra. For simplicity of discussion, we shall approximate these by atomic spheres of radius R_a that are electrically neutral and hence have zero potential outside R_a. Inside we have the ionic pseudopotential v_{ion} together with the potential[20]

$$v_e(r) = (e/R_a)\left[\tfrac{3}{2} - \tfrac{1}{2}(r/R_a)^2\right] \qquad (2.11)$$

from a uniform distribution of electrons (ignoring the radial wiggles in the wave function). The latter can be visualized conveniently as the very simple Ashcroft form[13]

$$v_{\text{ion}}(r) = -ze/r\,, \quad r > R_c$$
$$= 0\,, \qquad r < R_c \tag{2.12}$$

with an empty core of radius R_c, but other forms will serve as well or better. We shall refer to the total potential as the atomic-sphere potential[11]

$$v_{\text{AS}}(r) = v_e(r) + v_{\text{ion}}(r)\,, \quad r < R_a$$
$$= 0\,, \qquad r > R_a\,. \tag{2.13}$$

When we add these up for all the atoms, we get a good model of the total potential $V(\vec{r})$ in the metal, and the constant A in (2.1) is zero, aside from the mean exchange and correlation hole in the electron gas.[20] Otherwise this potential has few interesting properties beyond its simplicity.

We need to take one step further in the spirit of the coherent potential approximation[21] and subtract a constant B inside R_a to obtain the minimum-perturbation potential[11,16] (Fig. 2)

$$v_{\text{MP}}(r) = v_e(r) + v_{\text{ion}}(r) - B\,, \quad r < R_a$$
$$= 0\,, \qquad r > R_a\,. \tag{2.14}$$

B is chosen so that the mean value of v_{MP} is zero:

$$v_{\text{MP}}(0) \equiv \langle v_{\text{MP}}(r) \rangle = 0\,, \tag{2.15}$$

where by $v(0)$ we mean strictly the diagonal $\vec{k}_F$, $\vec{k}_F$ matrix element of $v(r)$ and ignore the nonlocal variation with k. Adding the constant potential B inside every atomic cell (we still ignore the difference between cell and sphere) only corresponds to a shift $-B$ in the zero of energy without affecting bandgaps, etc. Thus in Fig. 2 the horizontal line outside R_a represents the mean potential in all the other atoms. From (2.15) it is the energy of the bottom of the band (in first-order perturbation theory). Thus in v_{MP} we have a representation of $V(\vec{r}) - B$ with zero net attractive or repulsive strength. Each cell as set up has the correct number of z electrons and v_{MP} does not attract any more. Therefore we expect the corresponding Friedel sum[17] to be nearly zero:

$$\mathfrak{F}_{\text{MP}} = 0\,. \tag{2.16}$$

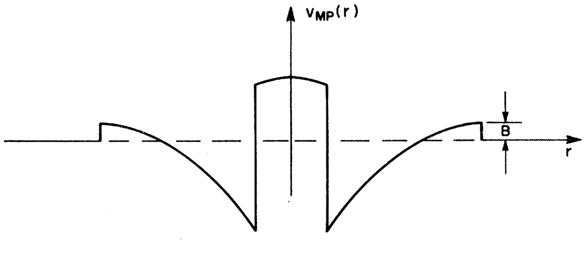

FIG. 2. The minimum-perturbation pseudopotential. The central positive region represents the repulsive pseudopotential of the core as in Eq. (2.12).

A slightly different alternative determination of B would be to satisfy (2.16) exactly. A third possibility would be to set the forward-scattering amplitude

$$f(0) = k_F^{-1} \textstyle\sum_l (2l+1)\, e^{i\eta_l} \sin\eta_l \tag{2.17}$$

equal to zero. If we do an expansion to lowest order in η_l, then $v(0)$, $\mathfrak{F}$, and $f(0)$ become identical, apart from simple multiplicative constants, so that the three conditions (2.15), (2.16), and (2.17) are virtually the same.

The idea of a minimum-perturbation potential has of course occurred to other people but we think that our prescription is more precise. Thus Meyer and Young[4] discuss what they term a minimal-muffin-tin potential, which is essentially equivalent to our minimum-perturbation potential. However, the low-q limit of their potential satisfies $V_{\text{mt}}(0) \approx 0$, whereas our potential is constructed to set the low-q limit (2.15) exactly equal to zero. Ball[15] defines a neutral potential corresponding to our v_{AS} and then obtains (2.15) by linear-screening theory. However we think that a weaker potential is obtained by shifting the zero of energy as in our formulation (2.14). Physically it means that we take as our zero-order model a free-electron gas with the bottom of the band at $A_{\text{AS}} - B$, and apply v_{MP} (with mean zero) as a fluctuation about that. At that stage we can screen the minimum-perturbation potential by the electron gas and thus render it even weaker, as can be calculated by linear-screening theory.

How useful is v_{MP}? Its minimum-perturbation properties of course make it superficially very attractive. However it cannot be used where there are long-range density fluctuations, such as with a low-q phonon or a liquid metal. In such situations the mean potential and the muffin-tin constant, i.e., the potential midway between atoms, both fluctuate according to $-\frac{2}{3}E_{F0}\Delta$, where Δ is the local dilatation, as was recognized long ago by Ziman.[19] It is then essential to use a formulation with limit (2.6) that expresses physically that each ion drags a neutralizing charge with it, no matter what the structure.

The application of v_{MP} to pure metals is therefore confined on theoretical grounds to reasonably close-packed perfect crystals without thermal or other density fluctuations. Its practical utility in such a situation has not yet been tested widely. Ball[15] has considered the band structures of sodium and lithium, but only at the bottom of the band, well away from the band gap. Shively[16] obtained reasonable results (as good as most *a priori* calculations) for the band gaps in aluminum. In the case of the alkali metals and copper we have obtained a highly accurate fitting of the shapes of Fermi surfaces with sets of phase shifts satisfying (2.15), as shown in Sec. III. Incidentally, in all our discussion thus far we have equated the atomic polyhedron with the atomic sphere. In actual calculations from first principles the non-negligible difference has to be corrected for, as can easily be done,[16] but in fitting calculations it is all already included in the fitting parameters. In either case, a correction must be made when transferring pseudopotentials between different structures.

Of course v_{MP} is just a precise statement of what we neglect when we approximate a metal by a free-electron gas. Its greatest use may lie in alloy theory. There the value of B differs for two different types of atom X and Y so that one cannot express it simply as a shift in the zero of energy. Instead one must add and subtract B in each cell, yielding the potential in the form

$$v_{\mathrm{AS}}(r) = v_{\mathrm{MP}}(r) + B\,. \qquad (2.18)$$

The first term is then negligible in a zeroth approximation and the difference $B_X - B_Y$ in the second term scatters the electrons as in the calculation of Mott and Jones[22] of the resistivity of alloys of the noble metals with one another. We effectively replace each atom by a small piece of free-electron gas with the bottom of the band at $-B$. Such a simple model of an atom is not without application. It gives satisfactory zeroth-order values of cohesion and atomic radius for the pure elements,[23] and may yet find a greater didactic role. For most purposes, however, the $v_{\mathrm{MP}}(r)$ must then be applied as a further perturbation.

We conclude that pseudopotentials with limit $v(0)$ effectively zero and Friedel sum $\mathfrak{F}$ zero correspond to the minimum-perturbation type of potential v_{MP}. We have set up a simple model of v_{MP} in (2.14), and have shown that it is conceptually not quite the same as the neutral atomic-sphere potential v_{AS} (2.13), which is more closely related to the absolute scale of energy. In both of these potentials, the electrical neutrality is treated in a fundamentally different way from the usual linear-screening theory.

III. APW FORM FACTORS

The measured shapes of the Fermi surfaces[5,6,24] of the alkali metals and copper have been fitted by solving a secular equation of the APW type,[7] expressed in terms of the phase shifts η_l (modulo π) of the atomic scattering potential, which are treated as adjustable parameters. The elements of the equation can be viewed[7,8] as scattering matrix elements $v(q)$ of a pseudopotential from plane-wave state $\vec{k}$ to $\vec{k}\,' = \vec{k} + \vec{q}$:

$$v(q) \equiv v_{\mathrm{APW}}(\vec{k}, \vec{k}\,')$$

$$= \frac{4\pi R_s^2}{\Omega}\left[\left(E - \frac{\hbar^2}{2m}\,\vec{k}\cdot\vec{k}\,'\right)\frac{j_1(|\vec{k}-\vec{k}\,'|R_s)}{|\vec{k}-\vec{k}\,'|} + \frac{\hbar^2}{2m}\sum_l (2l+1)P_l(\cos\theta_{\vec{k}\vec{k}\,'})\,j_l(kR_s)\,j_l(k'R_s) \times\left(\frac{j_l'(\kappa r) - \tan\eta_l(E)\,y_l'(\kappa r)}{j_l(\kappa r) - \tan\eta_l(E)\,y_l(\kappa r)}\right)_{r=R_s}\right], \qquad (3.1)$$

where R_s is the muffin-tin radius, Ω is the volume of the primitive unit cell, $E \equiv \hbar^2\kappa^2/2m$ is the energy of the electron state measured with respect to the interstitial potential, θ is the angle between the wave vectors $\vec{k}$ and $\vec{k}\,'$, $\eta_l(E_F)$ are the phase shifts that describe the scattering of conduction electrons by the ion cores, the primes on the spherical Bessel functions denote derivatives with respect to r, and the notation for the spherical Bessel functions is that used by Abramowitz and Stegun[25] [i.e., $y_l(0) = -\infty$]. While only those elements with $\vec{q}$ equal to a reciprocal-lattice vector $\vec{g}$ occur for a perfect solid, our physical interpretation of the matrix elements allows us to treat q as a continuous variable to generate a pseudopotential "form factor" $v(q)$ that is applicable to a wider range of situations, including electron-phonon coupling, etc. For purposes of tabular and graphical display, we follow the usual custom[26] of placing $|\vec{k}| = k_F$ on the free-electron sphere, and $\vec{k}+\vec{q}$ on the free-electron sphere if $q \leq 2k_F$, or, in the direction opposite to $\vec{k}$, if $q \geq 2k_F$.

The experimental data on the Fermi surfaces and the numerical method of fitting to them have been reported elsewhere, as have a few of the pseudopotentials.[5,6,24] In that work, the range of the E_F parameter was chosen more or less at random, and it remains to select the sets of phase shifts that correspond to the physical models discussed in Sec. II.

With the APW and KKRZ[9] methods it is usual, though not necessary, to set the potential equal to a constant (the muffin-tin constant) outside a chosen radius R_s, and this constant forms a convenient zero of energy for calculations. We have followed that practice in our discussion. Usually R_s is chosen to be not greater than the radius R_I of a sphere inscribed in the atomic polyhedron. To do otherwise introduces several complications when solving a band structure from first principles, but there is no need for this restriction in the present context. Indeed we shall abandon it, at least temporarily, in order to make a connection with the pseudo-atoms corresponding to (2.6), which overlap considerably.[12] The matrix elements of the APW, KKRZ, and other phase-shift formulations correspond to well-defined pseudopotentials in real space.[8,27,28] For example, the KKRZ formula can be derived by taking plane-wave matrix elements of a model potential consisting of δ functions

TABLE I. Variation of best set of phase shifts and Friedel sum $\mathfrak{F}$ with radius of APW sphere for Cu. The Fermi energy parameter is taken to be $E_F = 0.180$ Ry. $R_a = 2.66$ a.u.

R_s (a.u.)	η_0	η_1	η_2	$\mathfrak{F}$
2.207	1.070	0.1939	−0.0097	1.0208
2.407 (R_I)	1.061	0.1936	−0.0098	1.0142
2.607	1.063	0.1939	−0.0101	1.0149
2.807	1.116	0.1938	−0.0101	1.0483
3.007	1.035	0.1908	−0.0098	0.9924
3.207	1.012	0.1877	−0.0098	0.9694
3.407	1.122	0.1721	−0.0112	1.0074

on the surface of a sphere of radius R_s,[27] and there is no mathematical reason why these should not be allowed to overlap as do other potentials. The phase shifts derived from Fermi-surface data for the alkali and noble metals are remarkably insensitive to the choice of R_s. This is illustrated by tables of phase shifts for sodium and copper for different values of R_s that have been published elsewhere.[5,6] Phase shifts for copper over an extended range of R_s are presented in Table I. It will be seen that consistent results can be obtained with R_s ranging from less than R_I to $R = 3.4$ a.u., which is approximately the distance to the farthest corner of the atomic polyhedron. The phase shifts were fitted independently at each R_s by the method already described,[5,6,24] and the remaining, rather random, variation presumably arises from neglect of higher η_l and other compromises in the formalism.

It should be clear from Sec. II that there is considerable difficulty in relating the muffin-tin constant to an absolute scale of potential. We have not explored this question, and indeed it is probably impossible in principle to deduce anything about the position of the whole band on an absolute energy scale from the shape of the Fermi surface.

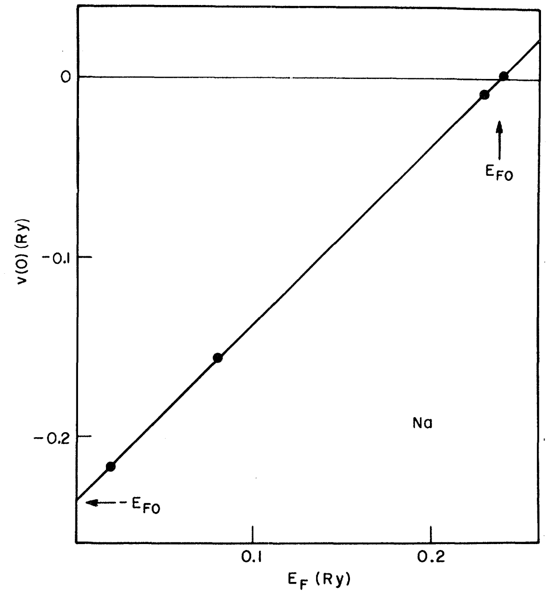

FIG. 3. Values of $v(0)$ for sodium for various values of the parameter E_F. Points are from Eq. (3.1) with sets of η_l fitted to the Fermi surface with $R_s = R_I$. The line is the theoretical relationship (3.2b).

In Sec. II we saw that the same total pseudopotential $V(\vec{r})$ can be expressed in various ways in terms of atomic pseudopotentials v, each with a different mean value $v(q=0)$. In a phase-shift analysis these different pseudopotentials are generated by choosing different values for the Fermi energy parameter E_F, which measures the Fermi energy relative to the muffin constant.[10,11] For let us start with zero potential everywhere and the Fermi level equal to the free-electron value E_{F0} (2.7). Then turning on the pseudopotential pulls the whole band down by an amount $v(0)$ in first-order perturbation theory, and the Fermi energy with respect to the muffin constant becomes

$$E_F = E_{F0} + v(0) , \tag{3.2a}$$

so that

TABLE II. Phase-shift and pseudopotential parameters for the alkali metals, all for radius R_I.

	E_{F0}(Ry)	E_F(Ry)	η_0	η_1	η_2	η_3	$v_{APW}(0)$	$\mathfrak{F}$
Li	0.3492	0.0902	0.8528	0.1240	−0.0007	0	−0.2327	0.777
		0.3190	−0.1854	0.1289	−0.0242	0	0.0000	0.051
Na	0.2384	0.0770	0.9753	0.1013	0.0019	0	−0.1589	0.821
		0.2370	−0.1449	0.0325	0.0100	0.0002	0.0000	0.003
K	0.1559	0.0486	0.6889	0.0932	0.0062	0	−0.1039	0.637
		0.1551	−0.1064	0.0007	0.0237	0	0.0000	0.009
Rb	0.1364	0.0421	0.7636	0.0812	0.0066	0	−0.0909	0.662
		0.1346	−0.0688	−0.0230	0.0334	0	0.0000	0.019
Cs	0.1165	0.0338	0.7883	0.0657	0.0070	0	−0.0777	0.650
		0.1122	−0.0639	−0.0420	0.0506	0	0.0000	0.040

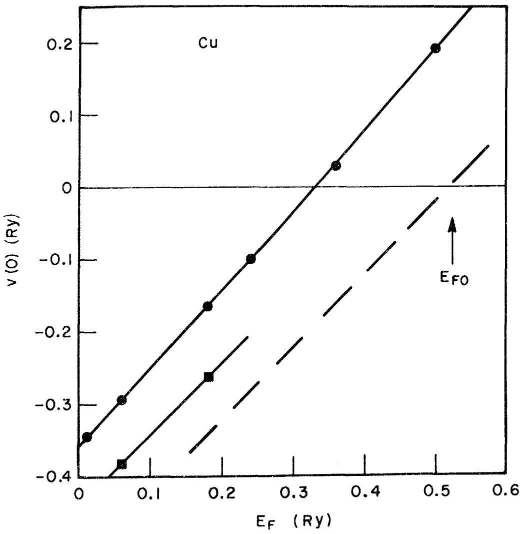

FIG. 4. Values of $v(0)$ for copper for various values of the parameter E_F fitted to the Fermi surface. Circles are for $R_s = R_I = 2.407$ a.u.; squares are for $R_s = 2.707$ a.u. The theoretical relation (3.2b) is shown as the broken line.

$$v(0) = E_F - E_{F0} \ . \tag{3.2b}$$

In conformity with experience,[5,6] E_F is not a fitting parameter in the usual sense of being optimized to obtain the best fit to the Fermi surface. We find that equally good results[29] can be obtained by choosing it at any value within reasonable limits, e.g., $0 - E_{F0}$.

Equation (3.2) turns out to be well obeyed for all the alkali metals, particularly Na, as illustrated in Fig. 3. Some values of E_F and $v(0)$ for the alkali metals are given in Table II. For Cu the situation is more complicated than (3.2). Figure 4 shows a plot of $v(0)$ versus E_F for two values of R_s. We find to a good approximation

$$v(0) = E_F - C(R_s) \ , \tag{3.3}$$

where C is independent of E_F but dependent on the chosen R_s (Fig. 4). The breakdown of (3.2) in Cu reflects the nonlocality of the potential due to the proximity of the d band. The degree of nonlocality is evident from the variation of $v(0)$ around the Fermi surface. By $v(0)$ we mean throughout our tables the diagonal $\vec{k}$, $\vec{k}$ matrix element with $|\vec{k}| = k_F$ and this is spherically symmetric by definition. Values of $v(0)$ with $\vec{k}$ on the actual Fermi surface of Cu (instead of the free-electron sphere) are 0.33 and 0.10 Ry along the (100) and (110) directions and 0.46 Ry on the side of the neck.

However it is interesting that the relation (3.3) is still linear in E_F. Indeed we have found that the whole $v(q)$ varies very nearly linearly with E_F, which allows one to interpolate $v(q)$ for any desired E_F from the two sets of results in Tables II and III. The nearly linear variation arises from the fact that E enters (3.1) linearly in the first term. The only other E dependence is through κ in the last term within large parentheses in (3.1), which is just the logarithmic derivative of the wave function.[7] In an *ab initio* band-structure calculation it would be determined by the position of the Fermi level relative to the potential inside the atom and would not depend explicitly on the potential in the interstitial region. We are therefore not surprised that the term in square brackets does not vary very much with E, and that what variation there is can be approximated as linear.

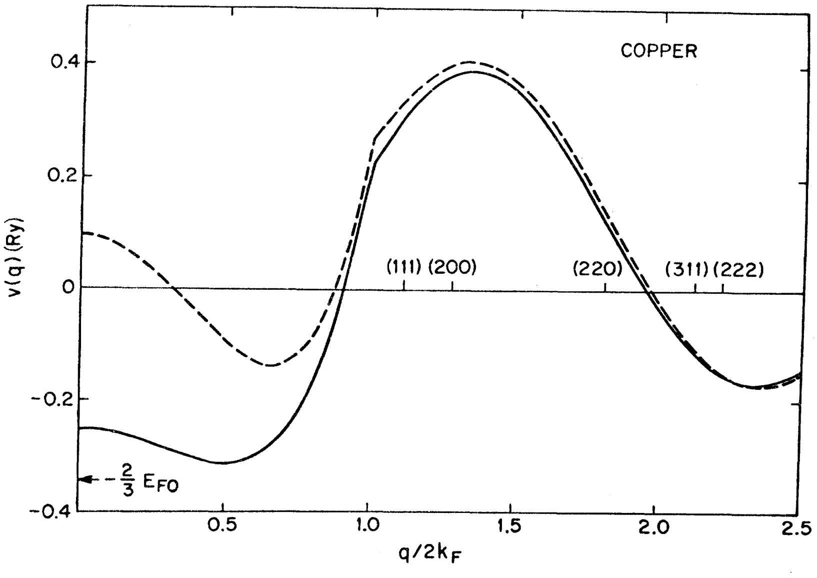

FIG. 5. APW-pseudopotential form factors for copper. The broken curve is for $E_F \approx E_F^0$, whereas the solid curve corresponds to $E_F \approx \frac{1}{3} E_F^0$. For copper, $v(0)$ depends sensitively on the muffin-tin radius (see Fig. 3). In the calculations shown here we have set this parameter equal to the Wigner-Seitz radius ($R_a = 2.6602$ a.u.) rather than the inscribed sphere radius as in our calculations for the alkali metals. The other parameters were as follows (phase shifts in radians): $E_F = 0.18$ Ry, $\eta_0 = 1.059$, $\eta_1 = 0.1933$, $\eta_2 = -0.0098$, $\eta_3 = 0$ (solid curve), and $E_F = 0.52$ Ry, $\eta_0 = 0.1133$, $\eta_1 = 0.1468$, $\eta_2 = -0.1037$, $\eta_3 = 0.0009$ (broken curve).

TABLE III. $v(q)$ in rydbergs calculated with APW matrix elements from both sets of parameters in Table II and with KKRZ matrix elements using the first set of parameters for each element in Table II. The last four rows refer to the reciprocal-lattice vectors of the bcc structure.

$q/2k_F$	Li(APW)	Li(APW)	Li(KKRZ)	Na(APW)	Na(APW)	Na(KKRZ)	K(APW)	K(APW)
0.000	−0.232 71	0.000 00	−0.210 12	−0.158 93	0.000 00	−0.145 85	−0.103 93	0.000 00
0.100	−0.230 37	−0.000 54	−0.207 88	−0.156 75	0.000 49	−0.143 73	−0.101 80	0.000 41
0.200	−0.223 23	−0.001 98	−0.201 09	−0.150 28	0.001 93	−0.137 56	−0.095 53	0.001 58
0.300	−0.211 06	−0.003 72	−0.189 47	−0.139 78	0.004 19	−0.127 27	−0.085 56	0.003 37
0.400	−0.193 45	−0.004 82	−0.172 61	−0.125 62	0.007 09	−0.113 55	−0.072 59	0.005 54
0.500	−0.169 79	−0.003 90	−0.149 89	−0.108 38	0.010 36	−0.096 84	−0.057 59	0.007 74
0.600	−0.139 36	0.000 76	−0.120 55	−0.088 76	0.013 69	−0.077 85	−0.041 82	0.009 53
0.700	−0.101 21	0.011 29	−0.083 63	−0.067 65	0.016 68	−0.057 44	−0.026 84	0.010 36
0.800	−0.054 28	0.030 21	−0.038 01	−0.046 06	0.018 92	−0.036 61	−0.014 47	0.009 61
0.900	0.002 71	0.060 40	0.017 61	−0.025 20	0.019 95	−0.016 54	−0.006 80	0.006 53
1.000	0.071 20	0.105 17	0.084 68	−0.006 40	0.019 32	0.001 44	−0.006 22	0.000 29
1.100	0.094 79	0.108 34	0.113 12	0.005 30	0.014 72	0.016 37	−0.005 24	−0.003 56
1.200	0.110 03	0.107 42	0.131 96	0.013 58	0.009 64	0.027 06	−0.006 08	−0.007 22
1.300	0.116 52	0.103 27	0.140 40	0.018 40	0.004 48	0.033 25	−0.008 25	−0.010 39
1.400	0.114 53	0.093 41	0.138 49	0.019 99	−0.000 39	0.035 03	−0.011 17	−0.012 83
1.500	0.104 92	0.081 06	0.127 07	0.018 81	−0.004 62	0.032 82	−0.014 25	−0.014 36
1.600	0.089 03	0.066 11	0.107 69	0.015 45	−0.007 94	0.027 33	−0.016 93	−0.014 86
1.700	0.068 63	0.049 49	0.082 43	0.010 62	−0.010 17	0.019 49	−0.018 77	−0.014 33
1.800	0.045 69	0.032 27	0.053 76	0.005 05	−0.011 23	0.010 34	−0.019 44	−0.012 85
1.900	0.022 22	0.015 51	0.024 23	−0.000 55	−0.011 13	0.000 92	−0.018 77	−0.010 56
2.000	0.000 15	0.000 24	−0.003 67	−0.005 56	−0.009 99	−0.007 77	−0.016 76	−0.007 69
2.100	−0.018 86	−0.012 67	−0.027 74	−0.009 49	−0.008 00	−0.014 93	−0.013 55	−0.004 51
2.200	−0.033 55	−0.022 57	−0.046 30	−0.012 01	−0.005 44	−0.019 93	−0.009 43	−0.001 28
2.300	−0.043 11	−0.029 04	−0.058 23	−0.012 99	−0.002 59	−0.022 45	−0.004 78	0.001 73
2.400	−0.047 24	−0.031 96	−0.063 07	−0.012 45	0.000 26	−0.022 42	−0.000 02	0.004 27
2.500	−0.046 13	−0.031 49	−0.061 06	−0.010 58	−0.002 84	−0.020 02	0.004 42	0.006 16
1.140	0.101 90	0.108 47	0.121 84	0.009 02	0.012 73	0.021 16	−0.005 38	−0.005 06
1.612	0.086 79	0.064 19	0.104 92	0.014 93	−0.008 27	0.026 50	−0.017 21	−0.014 85
1.974	0.005 59	0.003 97	0.003 23	−0.004 36	−0.010 37	−0.005 66	−0.014 70	−0.008 47
2.280	−0.041 61	−0.028 01	−0.056 37	−0.012 92	−0.003 18	−0.022 15	−0.005 74	0.001 15

$q/2k_F$	K(KKRZ)	Rb(APW)	Rb(APW)	Rb(KKRZ)	Cs(APW)	Cs(APW)	Cs(KKRZ)
0.000	−0.095 11	−0.090 93	0.000 00	−0.083 14	−0.077 67	0.000 00	−0.070 69
0.100	−0.093 02	−0.089 08	0.000 40	−0.081 33	−0.076 01	0.000 45	−0.069 07
0.200	−0.086 89	−0.083 64	0.001 53	−0.076 00	−0.071 16	0.001 73	−0.064 32
0.300	−0.077 13	−0.075 01	0.003 22	−0.067 56	−0.063 49	0.003 63	−0.056 82
0.400	−0.064 45	−0.063 83	0.005 18	−0.056 64	−0.053 64	0.005 79	−0.047 20
0.500	−0.049 81	−0.051 01	0.007 01	−0.044 14	−0.042 49	0.007 71	−0.036 34
0.600	−0.034 47	−0.037 71	0.008 17	−0.031 22	−0.031 18	0.008 75	−0.025 37
0.700	−0.019 96	−0.025 36	0.008 04	−0.019 29	−0.021 10	0.008 12	−0.015 67
0.800	−0.008 10	−0.015 64	0.005 84	−0.010 02	−0.013 89	0.004 92	−0.008 86
0.900	−0.000 97	−0.010 48	0.000 72	−0.005 33	−0.011 44	−0.001 94	−0.006 84
1.000	−0.000 94	−0.012 08	−0.008 32	−0.007 41	−0.015 90	−0.013 67	−0.011 73
1.100	0.002 16	−0.011 07	−0.012 03	−0.004 55	−0.015 77	−0.017 93	−0.010 00
1.200	0.002 91	−0.011 41	−0.015 22	−0.003 50	−0.016 53	−0.021 43	−0.009 57
1.300	0.001 63	−0.012 69	−0.017 63	−0.003 99	−0.017 78	−0.023 87	−0.010 16
1.400	−0.001 18	−0.014 43	−0.019 06	−0.005 65	−0.019 11	−0.025 04	−0.011 43
1.500	−0.004 96	−0.016 18	−0.019 37	−0.008 01	−0.020 12	−0.024 83	−0.012 99
1.600	−0.009 06	−0.017 51	−0.018 56	−0.010 60	−0.020 49	−0.023 26	−0.014 47
1.700	−0.012 90	−0.018 09	−0.016 69	−0.012 94	−0.019 98	−0.020 44	−0.015 51
1.800	−0.015 96	−0.017 71	−0.013 92	−0.014 65	−0.018 48	−0.016 60	−0.015 84
1.900	−0.017 82	−0.016 26	−0.010 49	−0.015 43	−0.016 00	−0.012 06	−0.015 31
2.000	−0.018 25	−0.013 80	−0.006 67	−0.015 13	−0.012 66	−0.007 17	−0.013 84
2.100	−0.017 18	−0.010 48	−0.002 77	−0.013 67	−0.008 68	−0.002 31	−0.011 50
2.200	−0.014 70	−0.006 57	0.000 90	−0.011 20	−0.004 37	0.002 16	−0.008 44
2.300	−0.011 06	−0.002 39	0.004 08	−0.007 92	−0.000 07	0.005 92	−0.004 91
2.400	−0.006 63	0.001 69	0.006 54	−0.004 13	0.003 88	0.008 71	−0.001 20
2.500	−0.001 85	0.005 32	0.008 13	−0.000 18	0.007 17	0.010 41	0.002 37

TABLE III. (*Continued*)

$q/2k_F$	K(KKRZ)	Rb(APW)	Rb(APW)	Rb(KKRZ)	Cs(APW)	Cs(APW)	Cs(KKRZ)
1.140	0.002 73	−0.011 07	−0.013 38	−0.003 93	−0.015 99	−0.019 43	−0.009 69
1.612	−0.009 55	−0.017 62	−0.018 29	−0.010 90	−0.020 48	−0.022 98	−0.014 62
1.974	−0.018 28	−0.014 52	−0.007 67	−0.015 31	−0.013 59	−0.008 44	−0.014 31
2.280	−0.011 88	−0.003 24	0.003 49	−0.008 64	−0.000 93	0.005 22	−0.005 65

The second point of interest about (3.3) and Fig. 4 is that $C(R_s)$ approaches the value E_{F0} expected in (3.2b) as R_s becomes larger. (It equals $0.944E_{F0}$ at $R = 3.4$ a.u.) We believe the reason to be that the over-all potential $V(\vec{r})$ in the metal becomes more uniform on the gross scale as the potentials that are equivalent[27, 28] to the APW matrix elements overlap more. Thus the perturbation theory inherent in (3.2a) is a better approximation.

From (3.2) it is clear that the choice

$$E_F = \tfrac{1}{3}E_{F0} \tag{3.4}$$

yields a $v(q)$ corresponding approximately to the linear-screening model of Sec. II with the limit (2.6) for $v(0)$. Similarly,

$$E_F = E_{F0} \tag{3.5}$$

gives a pseudopotential approximately of the minimum-perturbation type with the limit (2.15).

Our final sets of phase shifts for the alkali metals are contained in Table II. They have been chosen to satisfy the $v(0)$ limits (2.6) and (2.15) exactly. As expected, the Friedel sums (2.10) and (2.16) and the E_F values (3.4) and (3.5) are fulfilled approximately. The corresponding $v_{APW}(q)$ are given in Table III. While the two $v(q)$ for an element differ substantially at low q, they are approximately equal at large q around the reciprocal lattice vectors g, as one would expect from the fact that they give the same shape of Fermi surface. This is also true for copper,[30] as shown by Fig. 5. The fractional difference between the pseudo-atom and minimum-perturbation form factors is largest for sodium but is comparable to the other elements in absolute magnitude.

Finally Table III gives $v(q)$ calculated from the KKRZ formula for the first set of phase shifts for each element in Table II. The results differ a little from $v_{APW}(q)$ and the limit (2.6) is no longer exactly satisfied, but for the perfect crystal the KKRZ matrix elements must[27, 28] give the same Fermi surfaces as the APW ones if each calculation is carried to convergence.

While we have concentrated on (3.4) and (3.5), corresponding to two particular pseudopotentials in Sec. II, any other value of E_F is equally legitimate and it is interesting to derive the variation of $\mathfrak{F}$.[5] Figure 6 suggests that we consider the metal as an electron gas of $z(E_F/E_{F0})^{3/2}$ electrons per atom forming a free electron band from the muffin constant to E_F. The remaining

$$\mathfrak{F} = z - z(E_F/E_{F0})^{3/2} \tag{3.6}$$

electrons, which would extend the free-electron band to E_{F0}, have instead been pulled below the Fermi level by that attractive center. To the extent that the potential can be regarded as a weak-scattering center, this number must correspond to the Friedel sum, as anticipated in the notation of

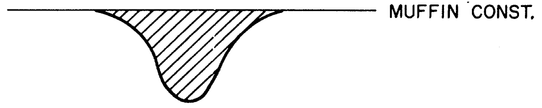

FIG. 6. Attractive potential $v(r)$ (shaded) lowers the Fermi level from E_{F0} to E_F.

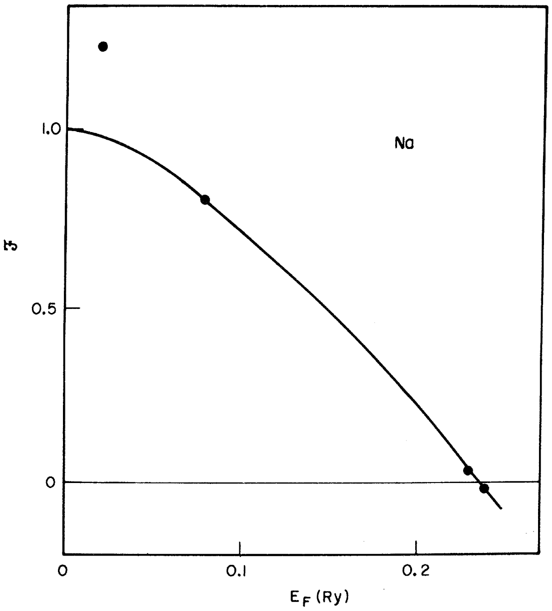

FIG. 7. The Friedel sum of the best set of phase shifts for sodium as a function of the parameter E_F. Circles are from sets of phase shifts fitted to the Fermi surface. Curve is the theoretical expression (3.6).

(3.6). Figure 7 shows that for sodium Eq. (3.6) is well obeyed for both the minimum-perturbation and the pseudo-atom phase shifts, and that it fails only for very small values of E_F.

IV. CONCLUSIONS

Our purpose has been to discuss the relationship between various types of pseudopotential that differ only in the way in which electrical neutrality is taken into account. We have described two especially important examples, the minimum-perturbation and the pseudo-atom pseudopotential. The former corresponds to a model of the metal in which the ionic potential in each atomic cell is totally screened by the conduction charge within that cell. The latter corresponds to screening of overlapping atomic potentials by extended distributions of conduction charge. We have emphasized that, whereas any of these pseudopotentials can be used to describe the electronic structures of metals and alloys, only the pseudo-atom pseudopotential can be used to describe the interaction of conduction electrons with thermal or other density fluctuations.

We have shown how these different types of pseudopotential can be constructed by appropriate choice of the Fermi-energy parameter in a phase-shift analysis of experimental Fermi-surface data, and have presented minimum-perturbation and pseudo-atom form factors for the alkali metals and copper. An analysis of the electronic properties of the alkali metals in terms of phase-shift pseudopotentials will be presented in the following paper.[31]

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