PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Pseudopotential Form Factors for Copper, Silver, and Gold*

JOHN A. MORIARTY
Department of Applied Physics, Stanford University, Stanford, California 94305

(Received 25 August 1969)

Using the generalized pseudopotential formalism given by Harrison, form factors have been calculated for copper, silver, and gold at both liquid and solid densities. All quantities entering in the form factors have been calculated from first principles, including the position of the d resonance. The full nonlocal character of both the ordinary pseudopotential terms and the additional hybridization terms is included without approximation. To first order, the orthogonalization hole has also been treated exactly. The Kohn-Sham approximation is used for the conduction band-core exchange, while exchange among conduction electrons is included through a modified dielectric function. The effects of electron correlation and crystal-field splitting are neglected. The calculated form factors are used to estimate the band gap at the L point and to calculate the resistivity of the liquid metal with good results. It is expected that the form factors will be useful in further calculations of the electronic properties of the noble metals.

I. INTRODUCTION

THE reformulation and generalization of the pseudopotential method to include the d-band metals has recently been discussed by Harrison.[1] Exactly as for simple metals, one may transform the Schroedinger equation to an equivalent pseudopotential equation in which the ordinary potential is replaced by a weak effective pseudopotential, W. Plane-wave matrix elements $\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle$ appear quite naturally in the approximate solution of the new pseudopotential equation and hence also appear in the calculation of physical properties. For a metal with a reasonably spherical Fermi surface, a particularly important set of these matrix elements connect plane waves on the corresponding free electron sphere. Apart from the usual structure factor, these matrix elements are the form factors and they enter in the calculation of electronic properties in the same way as do the form factors for simple metals. Of those d-band metals for which we might like to calculate a form factor, the easiest to treat theoretically are those having a completely empty or filled d-band. These are the alkaline-earths and the noble metals. Transition metals of interest, like nickel, for instance, require special treatment and will be considered elsewhere. In this paper we choose to confine our attention to one of the two remaining groups: the noble metals. In the succeeding sections of this paper, we will discuss the calculation and application of the form factors for these metals.

II. GENERALIZED PSEUDOPOTENTIAL METHOD

The essence of the generalized pseudopotential method is to abandon the small core approximation for the d-states. It is recognized that the atomic d states, ϕ_d, are not exact eigenstates of the crystal Hamiltonian and that they form bands of nonzero width which hybridize with the s-p conduction band. These facts are taken into account by consistently retaining the extra potential seen by a d electron in the metal, $-\delta V$. In the Harrison formulation, this extra potential appears in the hybridization parameter Δ:

$$\Delta=\delta V-\langle\phi_d|\delta V|\phi_d\rangle. \tag{1}$$

The quantity Δ together with an ordinary pseudopotential W_0 are then the key ingredients which make up the new effective pseudopotential W.[2]

The new pseudopotential equation may be written quite generally as

$$(T+W)|\Phi_{\mathbf{k}}\rangle=E_{\mathbf{k}}|\Phi_{\mathbf{k}}\rangle, \tag{2}$$

where T is the kinetic energy operator, $\Phi_{\mathbf{k}}$ is the pseudowave function, and $E_{\mathbf{k}}$ is the exact eigenvalue for the state $\mathbf{k}$. The exact form of W is, of course, not unique. In ordinary pseudopotential theory one usually uses the optimized form of Cohen and Heine[3] which is constructed to give the "smoothest" pseudo-wave function. This is also the pseudopotential which is obtained by approximating the Phillips-Kleinman form consistently in perturbation theory. In the new method, Harrison has uniquely specified W by simply generalizing the latter procedure. The resulting plane wave matrix elements of W may be written

$$\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle=S(\mathbf{q})\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle, \tag{3}$$

where we have defined a structure factor,

$$S(\mathbf{q})=\frac{1}{N}\sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i}, \tag{4}$$

and the form factor is given by

$$\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle=\langle\mathbf{k}+\mathbf{q}|w_0|\mathbf{k}\rangle+\sum_d\frac{\langle\mathbf{k}+\mathbf{q}|\Delta|\phi_d\rangle\langle\phi_d|\Delta|\mathbf{k}\rangle}{(k^2-E_d)}, \tag{5}$$

---

* Research supported by the National Science Foundation through Grant No. GP-6775.

[1] W. A. Harrison, Phys. Rev. **181**, 1036 (1969).

[2] The nomenclature here differs slightly from that in Ref. 1. The quantity we denote as W_0 is what Harrison labels W and calls the "transition metal pseudopotential." Our effective pseudopotential W includes this term plus Harrison's "hybridization term."

[3] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

where

$$\begin{aligned}\langle\mathbf{k}+\mathbf{q}|w_0|\mathbf{k}\rangle\\ =\langle\mathbf{k}+\mathbf{q}|v|\mathbf{k}\rangle+\sum_{\alpha=c,d}(k^2+\langle\mathbf{k}|w_0|\mathbf{k}\rangle-E_\alpha)\\ \times\langle\mathbf{k}+\mathbf{q}|\phi_\alpha\rangle\langle\phi_\alpha|\mathbf{k}\rangle+\sum_d(\langle\mathbf{k}+\mathbf{q}|\Delta|\phi_d\rangle\langle\phi_d|\mathbf{k}\rangle\\ +\langle\mathbf{k}+\mathbf{q}|\phi_d\rangle\langle\phi_d|\Delta|\mathbf{k}\rangle).\quad(6)\end{aligned}$$

(We have set $\hbar=2m=e^2/2=1$ throughout. In these atomic units distances are in Bohr radii and energies are in Rydbergs.) In Eqs. (5) and (6) $|\mathbf{k}+\mathbf{q}\rangle$ and $|\mathbf{k}\rangle$ are plane waves normalized in the atomic volume Ω_0. For our purposes, both $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$ are taken to have a magnitude equal to the free-electron wave number k_F. The quantity v is the contribution to the total self-consistent potential (V) arising from a single ion site and is calculated entirely within the framework of the theory. The ϕ_c and ϕ_d are atomic core states and atomic d states, respectively. The corresponding expectation values of the crystal Hamiltonian, $\langle\phi_\alpha|T+V|\phi_\alpha\rangle$, are E_c and E_d. To lowest order, E_d is just the position of the d resonance in the metal. The sums in the above equations run over core states, c, and d states, d, on a single ion site. In the denominator of the last term in Eq. (3) the zero of energy has been taken such that $E_F=k_F^2$. We note finally that in the limit $\Delta\rightarrow 0$ the form factor $\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle$ reduces to the Cohen-Heine optimized form for simple metals.

III. CALCULATION OF SELF-CONSISTENT POTENTIAL

We will now proceed to discuss the calculation of the various components which make up the right-hand side of Eq. (5). We begin with the self-consistent potential. This calculation proceeds in the usual way. One first calculates the total charge density in the metal in terms of the potential by perturbation theory or some other means. Self-consistency is achieved by using Poisson's equation to eliminate the charge density in favor of the potential and then solving the resulting equation for the potential. In practice, of course, it is most convenient to perform these manipulations in terms of Fourier transforms. This also always permits us to separate out a structure factor and to talk in terms of the potential and the charge density associated with a single ion site.

We write the Fourier transform of the total electron density associated with one ion site, $n_\mathbf{q}$, as a sum of four terms:

$$n_\mathbf{q}=n_\mathbf{q}{}^{\text{core}}+n_\mathbf{q}{}^{d}+n_\mathbf{q}{}^{\text{cond}}+n_\mathbf{q}{}^{\text{ex}}.\quad(7)$$

The core electron density $n_\mathbf{q}{}^{\text{core}}$ and the d-state electron density $n_\mathbf{q}{}^{d}$ are calculated directly from the wave functions for the free ion or atom:

$$n_\mathbf{q}{}^{\text{core}}+n_\mathbf{q}{}^{d}=\frac{1}{\Omega_0}\sum_{\alpha=c,d}\langle\phi_\alpha|e^{-i\mathbf{q}\cdot\mathbf{r}}|\phi_\alpha\rangle.\quad(8)$$

In all our numerical work we take the ϕ_α's from the Herman-Skillman tables for the free atom.[4] These were calculated in the Hartree-Fock-Slater approximation.

The third term in Eq. (7) represents the remaining electron density calculated in the Hartree approximation. This quantity may be divided into two parts:

$$n_\mathbf{q}{}^{\text{cond}}=n_\mathbf{q}{}^{\text{oh}}+n_\mathbf{q}{}^{\text{sc}}.\quad(9)$$

The first term is the Fourier transform of the orthogonalization hole density, $n^{\text{oh}}(\mathbf{r})$, which may be written to first order as

$$\begin{aligned}n^{\text{oh}}(\mathbf{r})=-\frac{2\Omega_0}{(2\pi)^3}\int_{k<k_F}d^3\mathbf{k}(\langle\mathbf{r}|P|\mathbf{k}\rangle\langle\mathbf{k}|\mathbf{r}\rangle\\ +\langle\mathbf{r}|\mathbf{k}\rangle\langle\mathbf{k}|P|\mathbf{r}\rangle-\langle\mathbf{r}|P|\mathbf{k}\rangle\langle\mathbf{k}|P|\mathbf{r}\rangle),\quad(10)\end{aligned}$$

where we have defined a projection operator,

$$P=\sum_{\alpha=c,d}|\phi_\alpha\rangle\langle\phi_\alpha|.\quad(11)$$

The quantity $n^{\text{oh}}(\mathbf{r})$ results from the orthogonalization of the pseudo-wave-function to the core and d states to obtain the true wave function. In all our calculations the orthogonalization hole is included exactly through Eq. (10). In previous pseudopotential calculations, $n^{\text{oh}}(\mathbf{r})$ has usually been approximated in one way or another. We have found that such approximations usually overestimate its effect and we believe that it is important to treat this term correctly.

The last term in Eq. (7) is the so-called screening electron density which brings in the self-consistency of the calculation. For the case of a completely full or empty d band Harrison has computed $n_\mathbf{q}{}^{\text{sc}}$ with a careful use of perturbation theory. The result for a full d band may be written

$$\begin{aligned}n_\mathbf{q}{}^{\text{sc}}=\frac{4}{(2\pi)^3}\int_{k<k_F}^{d^3\mathbf{k}}\frac{\langle\mathbf{k}+\mathbf{q}|w_0|\mathbf{k}\rangle}{(k^2-|\mathbf{k}+\mathbf{q}|^2)}-\frac{4}{(2\pi)^3}\\ \times\int_{k>k_F}^{d^3\mathbf{k}}\sum_d\Bigg[\frac{\langle\mathbf{k}+\mathbf{q}|\Delta|\phi_d\rangle\langle\phi_d|\Delta|\mathbf{k}\rangle}{(k^2-|\mathbf{k}+\mathbf{q}|^2)(k^2-E_d)}\\ +\frac{\langle\phi_d|e^{-i\mathbf{q}\cdot\mathbf{r}}|\phi_d\rangle\langle\mathbf{k}|\phi_d\rangle\langle\phi_d|\Delta|\mathbf{k}\rangle-\langle\mathbf{k}+\mathbf{q}|\phi_d\rangle\langle\phi_d|\Delta|\mathbf{k}\rangle}{(k^2-E_d)}\\ +\frac{\langle\phi_d|e^{-i\mathbf{q}\cdot\mathbf{r}}|\phi_d\rangle\langle\mathbf{k}|\Delta|\phi_d\rangle\langle\phi_d|\Delta|\mathbf{k}\rangle}{2(k^2-E_d)^2}\Bigg].\quad(12)\end{aligned}$$

For future convenience we rewrite Eq. (12) as follows. We take out $\langle\mathbf{k}+\mathbf{q}|v|\mathbf{k}\rangle$ from $\langle\mathbf{k}+\mathbf{q}|w_0|\mathbf{k}\rangle$ and note that it does not depend upon $\mathbf{k}$. (This simplification would not be allowed if we were to include exchange as an operator, i.e., in the Hartree-Fock approximation.)

---

[4] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, N. J., 1963).

We can then do the corresponding integration over $\mathbf{k}$ immediately and obtain

$$n_{\mathbf{q}}^{\mathrm{sc}}=-\frac{q^2}{8\pi}(\epsilon(\mathbf{q})-1)v_{\mathbf{q}}+n_{\mathbf{q}}^{R}, \tag{13}$$

where we have set $v_{\mathbf{q}}=\langle\mathbf{k}+\mathbf{q}|v|\mathbf{k}\rangle$ and let $n_{\mathbf{q}}^{R}$ equal all the remaining terms in Eq. (12). The quantity $\epsilon(\mathbf{q})$ is just the familiar Hartree dielectric function.

The last term in Eq. (5) represents the exchange hole seen by a conduction electron in the metal. We divide this quantity into two parts:

$$n_{\mathbf{q}}^{\mathrm{ex}}=n_{\mathbf{q}}^{\mathrm{ex\text{-}core},d}+n_{\mathbf{q}}^{\mathrm{ex\text{-}cond}}. \tag{14}$$

The first term represents the exchange hole due to the core and d-state electron density. We do not actually calculate this quantity directly, but instead we use the free electron exchange approximation to calculate the corresponding exchange potential. We obtain

$$-\frac{4}{\Omega_0}\int d^3\mathbf{r}e^{-i\mathbf{q}\cdot\mathbf{r}}\left[\frac{3}{8\pi}\sum_{\alpha=c,d}\langle\mathbf{r}|\phi_\alpha\rangle\langle\phi_\alpha|\mathbf{r}\rangle\right]^{1/3}. \tag{15}$$

For this contribution we have used the Kohn-Sham coefficient rather than the Slater coefficient. This seems appropriate here since we are specifically interested in the potential seen by an electron on the Fermi surface. However, the choice is important due to the large exchange contribution from the d states. For $q=2k_F$, the difference between Slater and Kohn-Sham exchange is approximately 0.1 Ry for the case of copper.

The second contribution to $n_{\mathbf{q}}^{\mathrm{ex}}$ comes from the conduction electron density $n_{\mathbf{q}}^{\mathrm{cond}}$. This quantity we calculate in the spirit of the Hubbard self-consistent exchange approximation.[5,6] We write

$$n_{\mathbf{q}}^{\mathrm{ex\text{-}cond}}=-G(\mathbf{q})n_{\mathbf{q}}^{\mathrm{cond}}. \tag{16}$$

Hubbard noted that at short wavelengths the exchange contribution should cancel half of the direct interaction, so that $G(\mathbf{q})$ should go to $\frac{1}{2}$ as $q\rightarrow\infty$. He postulated the very approximate form

$$G(\mathbf{q})=\tfrac{1}{2}q^2/(q^2+k_F^2). \tag{17}$$

In recent years various other approximate forms for $G(\mathbf{q})$ have been proposed.[7-9] All of these involve interpolations between small and large values of q and none of them are unlike Eq. (17). Quite recently, Singwi *et al.*[10] have reformulated this problem and have found an analytic expression for $G(\mathbf{q})$:

$$G(\mathbf{q})=\frac{9}{32}\left(\frac{q}{k_F}\right)^2\left\{\frac{2}{105}\left[24\left(\frac{k_F}{q}\right)^2+44+\left(\frac{q}{k_F}\right)^2\right]\right.$$
$$-2\frac{k_F}{q}\left[\frac{8}{35}\left(\frac{k_F}{q}\right)^2-\frac{4}{15}+\frac{1}{6}\left(\frac{q}{k_F}\right)^2\right]\ln\left|\frac{q+2k_F}{q-2k_F}\right|$$
$$\left.+\left(\frac{q}{k_F}\right)^2\left[\frac{1}{210}\left(\frac{q}{k_F}\right)^2-\frac{2}{15}\right]\ln\left|\frac{q^2-4k_F^2}{q^2}\right|\right\}. \tag{18}$$

Although algebraically complicated, the result is still qualitatively similar to Eq. (17). For comparison, five different $G(\mathbf{q})$'s are plotted in Fig. 1. Besides those of Hubbard and Singwi *et al.*, we include the forms used in model potential calculations by Heine and Abarenkov[8] and by Shaw and Pynn.[9] In our calculations we use the new expression, Eq. (18). Since conduction-electron exchange does not make a large contribution to the calculated form factor, it is probably not too important which form of $G(\mathbf{q})$ we actually choose.

To the electron density we must finally add the nuclear density $n_{\mathbf{q}}^{\mathrm{nuc}}$, which is simply

$$n_{\mathbf{q}}^{\mathrm{nuc}}=\frac{\text{atomic number}}{\Omega_0}=(Z/\Omega_0+n_0^{\mathrm{core}}+n_0^{d}), \tag{19}$$

where Z is the valence (which is 1 for the noble metals). We are then ready to use Poisson's equation, which we may take in the form

$$v_{\mathbf{q}}=\frac{8\pi}{q^2}(n_{\mathbf{q}}^{\mathrm{el}}-n_{\mathbf{q}}^{\mathrm{nuc}}). \tag{20}$$

Using Eqs. (7), (9), (13), (14), (16), and (19) in Eq. (20)

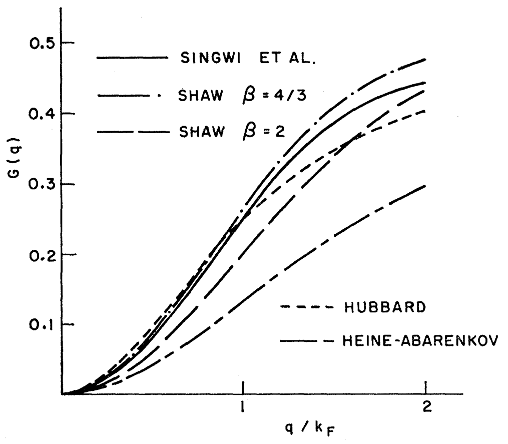

FIG. 1. The function $G(\mathbf{q})$ as used by various authors.

---

[5] J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1958).

[6] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966), Chap. 8.

[7] L. J. Sham, Proc. Roy. Soc. (London) **A283**, 33 (1965).

[8] V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

[9] R. W. Shaw, Jr., and R. Pynn, J. Phys. C **2**, 2071 (1969).

[10] K. S. Singwi, M. P. Tose, R. H. Land, and A. Sjölander, Phys. Rev. **176**, 589 (1968).

and solving for $v_{\mathbf{q}}$ leads to the result

$$v_{\mathbf{q}}=\frac{8\pi}{q^2\epsilon^*(\mathbf{q})}\Big[-Z/\Omega_0+(n_{\mathbf{q}}^{\text{core}}-n_0^{\text{core}})+(n_{\mathbf{q}}^{d}-n_0^{d})+n_{\mathbf{q}}^{\text{ex-core},d}+(1-G(\mathbf{q}))(n_{\mathbf{q}}^{\text{oh}}+n_{\mathbf{q}}^{R})\Big], \quad (21)$$

where we have defined a new dielectric function

$$\epsilon^*(\mathbf{q})=\epsilon(\mathbf{q})-G(\mathbf{q})(\epsilon(\mathbf{q})-1). \quad (22)$$

We have discussed all of the terms in Eq. (21) except $n_{\mathbf{q}}^{R}$. In order to calculate this term we first need to evaluate the quantities $\langle\mathbf{k}|w_0|\mathbf{k}\rangle$, E_d, and Δ. All of these require special detailed consideration which we delay until Sec. IV. We do note that in our calculations we have chosen to ignore crystal-field splitting in the solid. We use the average value of E_d for all d states instead of the two crystal-field-split values which actually occur for the fcc lattice structure of the noble metals. Although the splitting itself may be rather large (0.05 Ry for copper), its effect on the form factor is probably small. The reason is as follows. In all terms where E_d appears we sum over all d states. The extra contributions to the sum from the levels lying above the average always tend to be cancelled by the extra contributions from the levels lying below the average. The net effect is a tendency for the sum to reflect only the average position of E_d.

The neglect of crystal-field splitting is not strictly necessary, but it does simplify the details of the calculation. The approximation implies, for instance, that the potential v (and hence Δ) will be spherically symmetric. Furthermore, it allows us to consider the special case of the liquid metal by changing only one number, the atomic volume Ω_0. No additional approximations are involved in computing $n_{\mathbf{q}}^{R}$ and the full nonlocal character of all terms is included exactly.

IV. CALCULATION OF $\langle k|w_0|k\rangle-E_\alpha$, δV, Δ, AND E_d

The term $\langle\mathbf{k}|w_0|\mathbf{k}\rangle$ may be obtained by setting $\mathbf{q}=0$ in Eq. (6). After a small amount of manipulation and noting that $\langle\mathbf{k}|v|\mathbf{k}\rangle=\langle\mathbf{k}|V|\mathbf{k}\rangle$, we obtain the result

$$\langle\mathbf{k}|w_0|\mathbf{k}\rangle-E_\alpha=\langle\mathbf{k}|V|\mathbf{k}\rangle-E_\alpha+\frac{\sum_{\alpha=c,d}\{[k^2+\langle\mathbf{k}|V|\mathbf{k}\rangle-E_\alpha]\langle\mathbf{k}|\phi_\alpha\rangle\langle\phi_\alpha|\mathbf{k}\rangle\}+\sum_d\{\langle\mathbf{k}|\Delta|\phi_d\rangle\langle\phi_d|\mathbf{k}\rangle+\langle\mathbf{k}|\phi_d\rangle\langle\phi_d|\Delta|\mathbf{k}\rangle\}}{1-\sum_{\alpha=c,d}\langle\mathbf{k}|\phi_\alpha\rangle\langle\phi_\alpha|\mathbf{k}\rangle}. \quad (23)$$

We have thus reduced the calculation of $\langle\mathbf{k}|w_0|\mathbf{k}\rangle-E_\alpha$ to a calculation of $\langle\mathbf{k}|V|\mathbf{k}\rangle-E_\alpha$ and of Δ. We need only compute the potential to lowest order in these terms since they always appear in first-order quantities. To do this we simply use the zero-order electron distribution in the metal. This is the electron density from the atomic core states, the atomic d states, and the orthogonalization hole centered on each site, plus a uniform electron density of magnitude

$$Z^*/\Omega_0=Z/\Omega_0-\frac{1}{\Omega_0^2}\int d^3\mathbf{r}\,n^{\text{oh}}(\mathbf{r}). \quad (24)$$

The quantity Z^*-Z is the magnitude of the orthogonalization hole. Strictly speaking, the orthogonalization hole must be considered a first-order quantity, but it is customary to include it with zero-order terms since its effect can be significant. Using this charge distribution, we can systematically write down the contributions to $\langle\mathbf{k}|V|\mathbf{k}\rangle-E_\alpha$:

(a) The average potential seen by an electron in a lattice of point ions of charge Z^* and a compensating uniform background. The calculation of this quantity is easily done and is discussed in Harrison's book.[6]

(b) A correction to (a) resulting from the finite size of the orthogonalization hole:

$$\bar{V}^*=\frac{1}{\Omega_0}\int d^3\mathbf{r}\left[v^{\text{oh}}(\mathbf{r})+\frac{2(Z^*-Z)}{r}\right], \quad (25)$$

where $v^{\text{oh}}(\mathbf{r})$ is the exact potential due to the electron density $n^{\text{oh}}(\mathbf{r})$.

(c) The average direct potential due to the remaining charge density. This we may write as

$$\bar{V}^{\text{core},d}=\frac{1}{\Omega_0}\lim_{q\to0}\left[\frac{8\pi}{q^2}(n_{\mathbf{q}}^{\text{core}}+n_{\mathbf{q}}^{d}-n_0^{\text{core}}-n_0^{d})\right]$$
$$=-\frac{4\pi}{3\Omega_0}\sum_{\alpha=c,d}\langle\phi_\alpha|r^2|\phi_\alpha\rangle. \quad (26)$$

(d) The average exchange potential due to the zero-order charge density, $\bar{V}^{\text{ex}}$. Here we use a free-electron-exchange approximation with the Slater rather than the Kohn-Sham coefficient. We have found that the Slater exchange leads to a much more realistic value for the position of the resonance, E_d. That calculation is discussed below. The probable reason that Slater exchange works better here is that in another contribution to $\langle\mathbf{k}|V|\mathbf{k}\rangle-E_\alpha$ we use atomic term values $E_\alpha{}^a$ which have been calculated in the Hartree-Fock-Slater approxima-

TABLE I. Relevant parameters for the noble metals (in a.u.).

Element	Phase	E_F	k_F	Ω_0	R_{WS}	Z^*	E_F-E_d
Cu	solid	0.5169	0.7189	79.68	2.669	1.1937	0.1877
Cu	liquid	0.4782	0.6915	89.54	2.775	1.1688	0.1795
Ag	solid	0.4045	0.6360	115.1	3.018	1.2345	0.4293
Ag	liquid	0.3717	0.6097	130.7	3.148	1.2025	0.4240
Au	solid	0.4061	0.6372	114.4	3.012	1.2971	0.4519
Au	liquid	0.3774	0.6143	127.7	3.124	1.2610	0.4330

tion. [See (e) below.] Since the average exchange potential in the free-electron approximation does not depend linearly on the position of the ions, this potential is only properly calculated by integrating the actual charge density in the metal over one Wigner-Seitz cell. In our calculations we have replaced the cell by a sphere of equal volume and have neglected overlap from the neighboring ions in computing the charge density in the cell. The latter approximation was verified to be a good one for the case of copper. It also removes any slight dependence of the form factor on the position of the ions.

(e) $E_\alpha{}^a$, the atomic term value: We use the Hartree-Fock-Slater values calculated by Herman and Skillman.[4]

(f) $\langle\phi_\alpha|\delta V|\phi_\alpha\rangle$: The calculation of this term is discussed below. The inherent constant in this term exactly cancels the constant from contribution (a).

These contributions may be added to give the net result

$$\langle\mathbf{k}|V|\mathbf{k}\rangle-E_\alpha=-(18/5)Z^*/R_{\mathrm{WS}}+\bar{V}^*+\bar{V}^{\mathrm{core},d}+\bar{V}^{\mathrm{ex}}+|E_\alpha{}^a|+\langle\phi_\alpha|\delta V|\phi_\alpha\rangle, \quad (27)$$

where R_{WS} is the radius of the Wigner-Seitz cell. Equation (27) may then be used directly in Eq. (23) to calculate $\langle\mathbf{k}|w_0|\mathbf{k}\rangle-E_\alpha$.

Next we consider the calculation of δV. We recall that δV is defined as the difference in potential seen by an electron in the free atom and an electron in the vicinity of an ion site in the metal. Again we only need to calculate this term using the zero-order charge distribution in the metal. We divide the contributions to δV into four parts:

(a) The direct potential from the valence s electron in the atom, $v_{\mathrm{dir}}{}^s(\mathbf{r})$, minus the direct potential from the free electron gas in the metal.

(b) The direct potential from the orthogonalization hole, $v^{\mathrm{oh}}(\mathbf{r})$, on the site in question.

(c) The exchange potential seen by an electron in the free atom minus the exchange potential seen by an electron in the metal.

(d) The potential due to the charge distributions of the neighboring ions in the metal.

We retain contributions (a) and (b) and calculate them exactly by integrating Poisson's equation using the appropriate charge densities. The spatial variation of contribution (c) is assumed to be small (i.e., at least first-order) and we approximate this term as a constant. The quantity (d) gives rise to crystal-field splitting. Since we have chosen to ignore this effect in our calculations, we consider only a spherical average of this term which then contributes just a constant to the potential. The resulting δV is simply

$$\delta V=v_{\mathrm{dir}}{}^s(\mathbf{r})+Z^*r^2/R_{\mathrm{WS}}{}^3-v^{\mathrm{oh}}(\mathbf{r})+\mathrm{const}. \quad (28)$$

The calculation of $\langle\phi_\alpha|\delta V|\phi_\alpha\rangle$ and of Δ is now quite a straightforward matter. We note the important fact that any constant potential makes no contribution to $\langle\mathbf{k}|w_0|\mathbf{k}\rangle-E_\alpha$ nor to Δ and hence we need never evaluate the constant in Eq. (28).

The value of E_d may now be inferred from the above results. We note that we can write

$$E_F-E_d=k_F{}^2+\langle\mathbf{k}_F|w_0|\mathbf{k}_F\rangle+|E_d{}^a|+\langle\phi_d|\delta V|\phi_d\rangle. \quad (29)$$

If the zero of energy is chosen such that $E_F=k_F{}^2$, then we simply have for E_d

$$E_d=-[|E_d{}^a|+\langle\phi_d|\delta V|\phi_d\rangle+\langle\mathbf{k}_F|w_0|\mathbf{k}_F\rangle]. \quad (30)$$

The values of E_F-E_d calculated from Eq. (29) are listed in Table I. The results for solid copper and silver compare favorably with existing band structure calculations.[11] The situation for gold, however, is unclear because of the scarcity of theoretical work on this metal.

V. FORM FACTORS AND THEIR APPLICATION

To finally compute the form factor, we simply need to add the remaining terms in Eq. (5) to the self-consistent potential, Eq. (21). Since these extra terms do not introduce any new quantities, the problem has been reduced to one of translating the existing formulas to forms which may be readily evaluated numerically. For the simple metals this procedure has been considered in detail.[6] For the noble metals the process is necessarily more lengthy and involved, but it is sufficiently similar that only a few brief comments are in order. We note that two principal types of integrals appear in the form factors. The first of these have forms like $\langle\mathbf{k}|\phi_\alpha\rangle$, $\langle\mathbf{k}|\Delta\phi_\alpha\rangle$, and $\langle\phi_\alpha|e^{-i\mathbf{k}\cdot\mathbf{r}}|\phi_\alpha\rangle$. By symmetry these all reduce to radial integrals of some or all of the following: a spherical Bessel function, a simple power of r, a tabulated radial wave function, and a previously calcu-

---

[11] For example, for Cu: B. Segall, Phys. Rev. **125**, 109 (1962); E. C. Snow, *ibid.* **171**, 785 (1968); for Ag: B. Segall (unpublished) and E. C. Snow, Phys. Rev. **172**, 708 (1968).

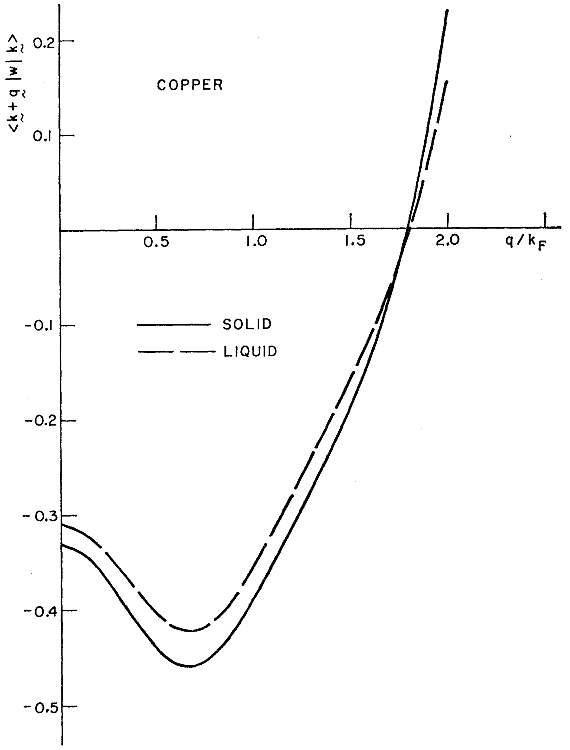

FIG. 2. The computed form factor for copper in Ry at both solid and liquid densities.

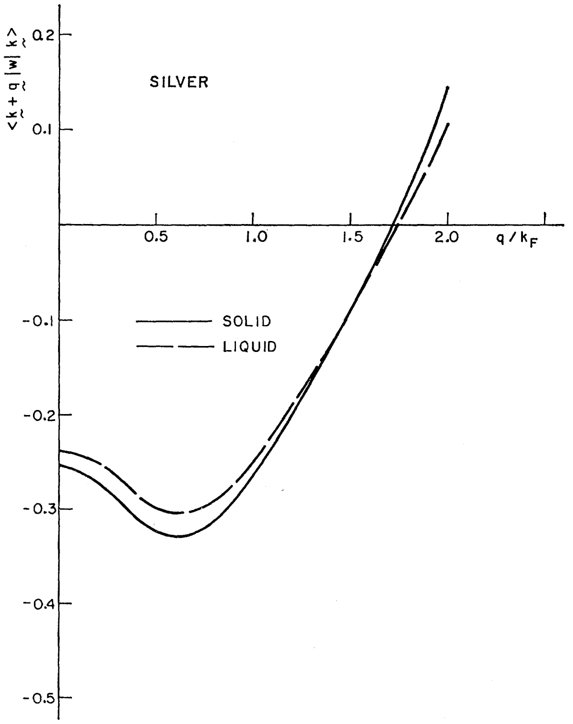

FIG. 3. The computed form factor for silver in Ry at both solid and liquid densities.

lated function of r such as $v^{\mathrm{oh}}(\mathbf{r})$. These are easily evaluated as a function of k and needed values may be obtained by interpolation. The second principal type of integral involves a triple integration of some combination of these latter quantities over $\mathbf{k}$ either inside or outside the Fermi sphere. These integrals are the terms in $n_{\mathbf{q}}^{R}$ appearing in Eq. (12). Those involving a factor of $[k^2-|\mathbf{k}+\mathbf{q}|^2]$ in the denominator must be handled as principal-value integrals. A simple but accurate Simpson-like integration procedure is used to calculate these. This involves replacing the integrand by its first derivative at the singularity. The integrations outside the Fermi sphere are found to converge rapidly. This is largely because the matrix element $\langle\mathbf{k}|\Delta|\phi_d\rangle$ turns out to be a rather sharply peaked function of k around $k=k_F$. In all cases it was found that these integrations need only be taken out to $k=4k_F$ to obtain four-place accuracy.

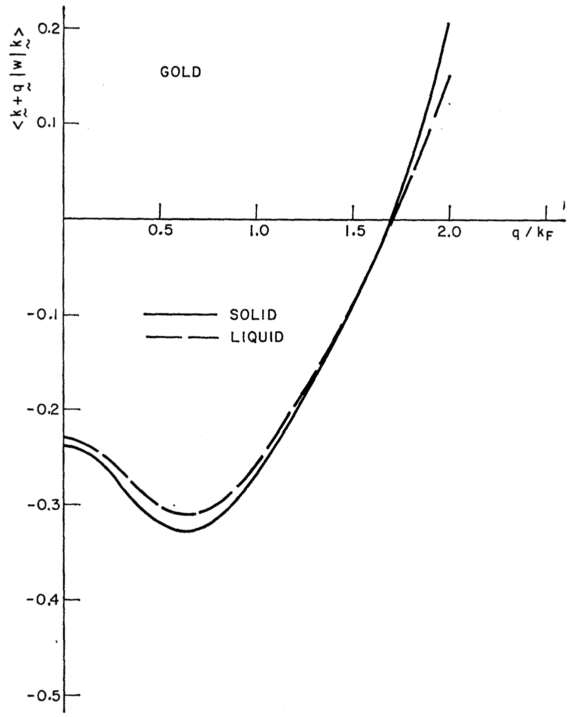

FIG. 4. The computed form factor for gold in Ry at both solid and liquid densities.

FORTRAN IV computer programs have been written to perform the above intergrations and to calculate the form factors as a function of q/k_F from 0 to 2 at both liquid and solid densities. The results are plotted in Figs. 2–4 for copper, silver, and gold, respectively. The corresponding numerical values of the form factors are listed in Table II. The density of the solid was inferred from the room-temperature lattice constants, while the density of the liquid metal was taken from experimental measurements made at the temperature at which

TABLE II. Form factors in Rydbergs for the noble metals at liquid and solid densities.

q/k_F	Cu (solid)	Cu (liquid)	Ag (solid)	Ag (liquid)	Au (solid)	Au (liquid)
0.0	−0.3319	−0.3105	−0.2546	−0.2385	−0.2379	−0.2301
0.1	−0.3392	−0.3167	−0.2595	−0.2425	−0.2437	−0.2351
0.2	−0.3578	−0.3327	−0.2713	−0.2525	−0.2575	−0.2471
0.3	−0.3866	−0.3574	−0.2903	−0.2686	−0.2810	−0.2669
0.4	−0.4158	−0.3828	−0.3077	−0.2840	−0.3009	−0.2848
0.5	−0.4420	−0.4059	−0.3228	−0.2975	−0.3198	−0.3016
0.6	−0.4566	−0.4193	−0.3285	−0.3035	−0.3271	−0.3089
0.7	−0.4588	−0.4217	−0.3260	−0.3024	−0.3264	−0.3088
0.8	−0.4459	−0.4103	−0.3130	−0.2919	−0.3141	−0.2982
0.9	−0.4213	−0.3874	−0.2927	−0.2745	−0.2948	−0.2807
1.0	−0.3878	−0.3552	−0.2659	−0.2507	−0.2689	−0.2566
1.1	−0.3499	−0.3178	−0.2349	−0.2226	−0.2385	−0.2279
1.2	−0.3105	−0.2781	−0.2009	−0.1914	−0.2043	−0.1953
1.3	−0.2705	−0.2379	−0.1651	−0.1585	−0.1681	−0.1608
1.4	−0.2299	−0.1983	−0.1282	−0.1247	−0.1299	−0.1249
1.5	−0.1852	−0.1573	−0.0896	−0.0897	−0.0887	−0.0868
1.6	−0.1337	−0.1134	−0.0498	−0.0542	−0.0447	−0.0472
1.7	−0.0704	−0.0631	−0.0076	−0.0176	+0.0046	−0.0044
1.8	+0.0080	−0.0039	+0.0376	+0.0204	0.0605	+0.0422
1.9	0.1061	+0.0679	0.0880	0.0612	0.1266	0.0953
2.0	0.2286	0.1557	0.1463	0.1067	0.2070	0.1580

structure factor data had also been recorded. The corresponding atomic volumes are listed in Table I.

To test the usefulness of our form factors we have made two simple calculations. The first is a *rough* estimate of the band gap at the L point in the Brillouin zone of the solid. In perturbation theory this band gap is given by $2\langle -\mathbf{G}/2|w|\mathbf{G}/2\rangle$, where $\mathbf{G}$ is a reciprocal lattice vector equal to twice the Γ to L vector in the Brillouin zone. The gap is roughly estimated by the backscattering form factor ($\mathbf{q}=-2\mathbf{k}=-2\mathbf{k}_F$), the difference being that the ΓL distance is about 10% greater than k_F. In Table III we give the estimated band gaps for copper, silver, and gold. For comparison, we also list experimental values inferred from optical measurements as well as values taken directly from band structure calculations.

The second calculation we have performed is of the resistivity of the liquid metal. This calculation involves an integration of the form factor squared times the experimentally measured intensity function (the structure factor squared) over the Fermi sphere. The results are listed in Table IV together with those of experiment. We have found it important to use the liquid density form factors and other liquid parameters in this calculation to obtain the best results. Use of the solid density counterparts roughly doubles the calculated resistivity for copper and silver.

A detailed comparison between our theoretical calculations and experiment is neither intended nor of particular significance here. In the case of the band gap, for instance, we have not concerned ourselves with the exact relationship between the number we calculate and the quantities to which we compare it. The resistivity calculation, on the other hand, suffers from the well-known sensitivity of the answer to the details of the form factor used. Although we have established the importance of using liquid density parameters in such a calculation, it is clear that comparable variations in the form factor due to other sources (e.g., the use of a different conduction band-core exchange approximation) could be equally as important. For this reason, close agreement between theory and experiment, such as in the case of liquid copper, must be viewed as fortuitous.

TABLE III. Band gap at the L point in Rydbergs. For the present estimate the backscattering value of the form factor ($\mathbf{q}=-2\mathbf{k}=-2\mathbf{k}_F$) is used. The experimental values listed are those inferred from optical measurements.

Element	$2\langle \mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle$	Experimental	Band-structure calculations
Cu	0.46	0.35[a]	0.44[b]
Ag	0.29	0.28[c]	0.33[d]
Au	0.41	0.30[a]	0.37[e]

[a] G.P. Pells and M. Shiga, J. Phys. C2, 1835 (1969).
[b] B. Segall, Phys. Rev. **125**, 109 (1962).
[c] From table in J. F. Cornwall, Phil. Mag. **6**, 727 (1961).
[d] B. Segall (unpublished).
[e] R. L. Jacobs, J. Phys. C **1**, 1296 (1968).

TABLE IV. Resistivity of the liquid metal in μΩ cm.

Element	Experimental[a]	Theoretical	Temperature (°C)
Cu	21.5	21.6[b]	1125
Ag	18.1	28.2[b]	1050
Au	32.0	∼52.1[c]	1120

[a] From table in N. E. Cusack, Rept. Progr. Phys. **26**, 361 (1963).
[b] Structure factor data taken from C. N. J. Wagner, H. Ocken, and M. L. Joshi, Z. Naturforsch. **20A**, 325 (1965).
[c] No tabulated structure factor data on gold are available in the literature. From the plotted x-ray data of H. Hendus [Z. Naturforsch. **2A**, 505 (1947)] and O. Pfannenschmid [*ibid.* **15A**, 603 (1960)], however, we were able to infer that the intensity function (structure factor squared) for gold is about the same as that for silver and we have used the latter in this calculation.

Nonetheless, the over-all qualitative picture suggests that there is no particular mystery in understanding the properties we calculate in terms of the theory we use. We are, therefore, generally encouraged by the results of these calculations. We hope that our form factors will prove useful in future studies on the noble metals. With the computed form factors it may now be possible to do systematic quantitative calculations of the electronic properties of these metals just as has been done for the simple metals.

ACKNOWLEDGMENT

The author is grateful to Professor W. A. Harrison for supplying the results of his paper prior to publication and for encouragement and helpful discussions during the course of this work.

PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Electronic Properties of Liquid Metals*

N. W. Ashcroft and W. Schaich†
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 20 May 1969)

It is shown that an approximation for the n-body ionic correlation permits the generalization of nearly free-electron formulas for some of the electronic properties of liquid metals. The electrical resistivity is considered in detail and it is shown that a result identical in form to that due to Ziman can be obtained, but in terms of an effective potential involving both the electron-ion potential and the static structure factor. Some further assumptions are necessary for this effective potential to be approximately evaluated. The numerical work strongly indicates that the effective potential differs little from the commonly used pseudopotentials. Finally, generalized expressions are obtained for the electrical resistivity and Knight shift for liquid metal alloys.

I. INTRODUCTION

THIS work is concerned with an extension of the nearly free-electron model for the electronic properties of liquid metals. The specific property we discuss is the electrical resistivity, ρ. The well-known Ziman formula for ρ is the lowest-order result and yields[1]

$$\rho=\frac{m^2}{12Ze^2n_e\hbar^3\pi^3}\Omega^2\int_0^{2k_F} q^3dq\,S(q)\,|\langle\mathbf{k}|v|\mathbf{k}+\mathbf{q}\rangle|^2, \quad (1)$$

where n_e is the number density of electrons, Z is the nominal valence, k_F is the Fermi wavevector, and Ω is the total volume of the system. In (1) it is understood that

$$|\mathbf{k}|=|\mathbf{k}+\mathbf{q}|=k_F \quad (2)$$

and

$$n_e/Z=n_i=\text{density of ions}=N/\Omega. \quad (3)$$

The potential matrix element is defined by

$$\Omega\langle\mathbf{k}|v|\mathbf{k}'\rangle=v(\mathbf{k}-\mathbf{k}')=\int d\mathbf{r}\,e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}v(r), \quad (4)$$

where v is a pseudopotential describing the interaction between an electron and a single self-consistently screened ion. $S(q)$ represents the liquid structure factor and is defined by

$$S(q)=1/N\langle\langle\rho_\mathbf{q}\rho_{-\mathbf{q}}\rangle\rangle-N\delta_{\mathbf{q},0}, \quad (5)$$

with

$$\rho_\mathbf{q}=\sum_{i=1}^{N}e^{-i\mathbf{q}\cdot\mathbf{R}_i}, \quad (6)$$

where $\mathbf{R}_i$ gives the instantaneous position of the ith ion. In (5) the brackets denote an ensemble average over ionic configurations. The liquid structure factor $S(q)$ is readily obtained from either x-ray or neutron-diffraction experiments or may be sufficiently well represented by the hard-core structure factor for a suitable choice of parameters.[2]

The derivation of (1) may be made clear if we rewrite the result as

$$\rho=m/n_ee^2\tau, \quad (7)$$

with

$$\frac{1}{\tau}=\left\langle\left\langle\frac{2\pi}{\hbar}\frac{1}{\Omega}\int\frac{d\mathbf{k}'}{(2\pi)^3}|v(\mathbf{k}-\mathbf{k}')\rho_{\mathbf{k}-\mathbf{k}'}|^2 \times(1-\cos\theta_{\mathbf{k},\mathbf{k}'})\delta(E_F-E_{k'})\right\rangle\right\rangle, \quad (8)$$

where

$$E_{k'}=\hbar^2k'^2/2m,$$

and

$$E_F=\hbar^2k_F{}^2/2m. \quad (9)$$

---

* Work supported by the National Science Foundation under Grant No. GP-9402.

† National Science Foundation Predoctoral Fellow.

[1] J. M. Ziman, Phil. Mag. 6, 1013 (1961).

[2] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).