

## Density-functional formulation of the generalized pseudopotential theory

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The generalized pseudopotential theory of  $d$ -band metals is rederived using the self-consistent-field equations of Kohn and Sham as the starting point. The basic features of the original theory are recovered, but a number of important and unifying refinements are achieved. Central to the development is the careful approximation of the total exchange and correlation potential in the form of a constant plus a sum of overlapping, but structure-independent, intra-atomic potentials. This result, combined with our previously introduced zero-order-pseudoatom technique of defining core and  $d$  states, permits an accurate first-principles evaluation of all matrix elements entering the theory, including direct  $d$ -state overlap integrals. In addition, the structure dependence of the hybridization potential, which has been previously ignored or only spherically averaged, is now treated explicitly. As a result, new second-order terms in the total energy are uncovered, leading to a modified energy-wave-number characteristic and  $d$ -state overlap potential. Also derived is a moderately simple, but very accurate (to within 3%), formula for the binding energy of the metal. Partial application to copper and full application to nineteen other simple and  $d$ -band metals are discussed.

### I. INTRODUCTION

There are two principal ingredients in the present work. The first is the Kohn-Sham density-functional formalism<sup>1</sup> as applied to the case of a pure metal. In this theory, the electron density  $n(\vec{r})$  is isolated as the basic variable of the system and both  $n$  and the total ground-state energy  $E_{\text{tot}}$  can be expressed (exactly in principle) in terms of the solutions of a set of one-electron self-consistent-field equations. When  $n(\vec{r})$  is sufficiently slowly varying or sufficiently large, the effective exchange-correlation potential  $\mu_{xc}$  entering these equations is well approximated by the local functional

$$\mu_{xc}(n) = \frac{d}{dn} [n\epsilon_{xc}(n)], \quad (1)$$

where  $\epsilon_{xc}(n)$  is the total exchange and correlation energy of a free-electron gas of density  $n$ . In the case of solids, Kohn and Sham proposed the use of Eq. (1) for the entire system, and in this form the scheme has enjoyed wide-spread popularity and considerable success in calculations on both simple and  $d$ -band metals.

The second ingredient here is the generalized pseudopotential theory,<sup>2-8</sup> formulated for  $d$ -band metals by Harrison<sup>2</sup> and the present author<sup>3</sup> and developed by the latter in a series of papers.<sup>4-8</sup> As in the Kohn-Sham formalism, the electron density and the total energy play fundamental roles in this theory. One seeks an analytic decomposition of  $n$  into a sum of uniform, core, and oscillatory terms<sup>3,9</sup>

$$n(\vec{r}) = n_{\text{unif}} + \sum_i n_{\text{core}}(\vec{r} - \vec{r}_i) + \sum_{\vec{q}}' S(\vec{q}) \delta n_{\text{val}}(q) e^{i\vec{q} \cdot \vec{r}}. \quad (2)$$

The quantity  $n_{\text{core}}$  includes the contributions from localized core and (filled)  $d$  states, while  $\delta n_{\text{val}}(q)$  represents the remaining orthogonalization hole and self-consistent screening contributions of the valence electrons. The density  $\delta n_{\text{val}}$  is developed as a simultaneous expansion in a pseudopotential  $w_0$  and a hybridization potential  $\Delta$ . To first order in  $w_0$  and  $\Delta^2$ , both  $n_{\text{core}}$  and  $\delta n_{\text{val}}$  are independent of the positions of the nuclei,  $\vec{r}_i$ , and all structure dependence is explicit in Eq. (2) through the summation over  $i$  and the structure factor

$$S(\vec{q}) = N^{-1} \sum_i e^{-i\vec{q} \cdot \vec{r}_i}.$$

A similar decomposition of  $E_{\text{tot}}$  into volume, electrostatic, band structure, and  $d$ -state overlap terms yields<sup>3,5,9</sup>

$$E_{\text{tot}} = E_0 + E_{\text{es}} + N \sum_{\vec{q}}' |S(\vec{q})|^2 F(q) + \frac{1}{2} \sum_{i,j}' v_{\text{ol}}(|\vec{r}_i - \vec{r}_j|), \quad (3)$$

where to second order in  $w_0$  and  $\Delta^2$ , the characteristic functions  $E_0$ ,  $F(q)$ , and  $v_{\text{ol}}(r)$  are also independent of structure. In the limit  $\Delta \rightarrow 0$ , the generalized pseudopotential formalism reduces to conventional nonlocal pseudopotential theory,

so that both simple and  $d$ -band metals are covered by Eqs. (2) and (3).

For any metal, the characteristic functions  $n_{\text{core}}$ ,  $\delta n_{\text{val}}$ ,  $E_0$ ,  $F(q)$ , and  $v_{\text{oi}}(r)$  all depend on the precise nature of the total self-consistent potential  $V(\vec{r})$  in the solid. Of particular importance here are the structure dependence of  $V(\vec{r})$  and the approximations made for exchange and correlation. The central objective of this paper is to reformulate the generalized pseudopotential theory using the Kohn-Sham equations as the starting point. The result will be a refined and highly unified version of the theory with several important new features.

The rigorous separation of  $n$  and  $E_{\text{tot}}$  into volume and structure terms requires that the total potential be expressible in the form

$$V(\vec{r}) = \sum_i v(\vec{r} - \vec{r}_i), \quad (4)$$

where  $v(\vec{r})$  is independent of structure. In Sec. II, we show that, in spite of its nonlinear dependence on  $n$ , the exchange-correlation potential  $\mu_{xc}(n)$  is well approximated in metals as a constant plus a sum of overlapping potentials as in Eq. (4). The most remarkable feature of this result is that it remains true even when there is significant overlap between neighboring cores, as in  $d$ -band metals with filled  $d$  states. This leads to a formally simplified set of Kohn-Sham equations consistent with Eq. (2)–(4).

In Sec. III, we begin to systematically develop the generalized pseudopotential theory from the simplified Kohn-Sham equations by first introducing a zero-order pseudoatom, as we did in Ref. 8 (hereafter referred to as paper I). The zero-order pseudoatom precisely defines core and  $d$  states, and their energy eigenvalues, and permits accurate evaluation of all matrix elements of both the pseudopotential  $w_0$  and the hybridization potential  $\Delta$ . Particular attention is paid here to the structure dependence of  $\Delta$ , which has previously been neglected<sup>2-7</sup> or only partly averaged.<sup>8</sup> Then, in Sec. IV, the generalized pseudopotential theory is rederived and it is shown that the structure-dependent parts of  $\Delta$  lead to new second-order terms, and hence, a modified energy-wave-number characteristic  $F(q)$  and overlap potential  $v_{\text{oi}}(r)$ . We also derive in Sec. IV a relatively simple yet very accurate formula for the binding energy of the metal. Application of the refined formalism to 19 metals is discussed in Sec. V and concluding remarks are given in Sec. VI.

## II. SIMPLIFIED KOHN-SHAM EQUATIONS

For a metal of atomic number  $Z_a$  the Kohn-Sham equations may be written as follows. The

one-electron Schrödinger equation, to be solved self-consistently for occupied states  $\alpha$ , is

$$[T + V(\vec{r})]\psi_\alpha(\vec{r}) = E_\alpha \psi_\alpha(\vec{r}), \quad (5)$$

where  $T$  is the kinetic-energy operator and

$$V(\vec{r}) = - \sum_i \frac{Z_a e^2}{|\vec{r} - \vec{r}_i|} + \int \frac{e^2 n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \mu_{xc}(n(\vec{r})). \quad (6)$$

The nuclear term involving  $Z_a$  in Eq. (6) is the applied external potential in the general Kohn-Sham formalism.<sup>1</sup> In terms of  $\psi_\alpha(\vec{r})$  and  $E_\alpha$ , the electron density and total ground-state energy are given by

$$n(\vec{r}) = \sum_\alpha \psi_\alpha^*(\vec{r}) \psi_\alpha(\vec{r}) \quad (7)$$

and

$$E_{\text{tot}} = \frac{1}{2} \sum_{i,j} \frac{(Z_a e)^2}{|\vec{r}_i - \vec{r}_j|} + \sum_\alpha E_\alpha - \frac{1}{2} \int \frac{e^2 n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \int n(\vec{r}) [\epsilon_{xc}(n(\vec{r})) - \mu_{xc}(n(\vec{r}))] d\vec{r}. \quad (8)$$

The functional  $\mu_{xc}(n)$  entering Eqs. (6) and (8) can be separated into an exchange and a correlation potential:

$$\mu_{xc}(n) = \mu_x(n) + \mu_c(n), \quad (9)$$

where the exchange potential is<sup>1</sup>

$$\mu_x(n) = -2e^2(3n/8\pi)^{1/3}. \quad (10)$$

The correlation potential does not have simple analytic representation, but accurate interpolation formulas, valid in the range of metallic densities, have been obtained by fitting to computed values of  $\epsilon_{xc}(n)$  and using Eq. (1). One such formula has been developed by Hedin and Lundqvist<sup>10</sup> using the correlation-energy results of Singwi *et al.*<sup>11</sup>:

$$\mu_c(n) = -\mu_0 \ln[1 + \gamma_0 (\frac{4}{3}\pi n)^{1/3}], \quad (11)$$

where  $\mu_0 = 0.045$  Ry and  $\gamma_0 = 21$  a.u.

The precise details of  $\mu_x(n)$  and  $\mu_c(n)$ , however, will not affect our manipulations of Eqs. (5)–(8) and only Eq. (1) linking  $\epsilon_{xc}$  and  $\mu_{xc}$  need to be assumed. In this regard, closely related treatments of exchange and correlation, such as in Slater's  $X\alpha$  method,<sup>12</sup> will also be covered by our formal results. In the  $X\alpha$  scheme, the correlation potential is omitted and the exchange potential is taken in the form  $\frac{3}{2}\alpha\mu_x(n)$ , where  $\alpha$  is a constant to be determined separately.

To develop the desired approximation for  $V(\vec{r})$ , we first decompose the electron density as in Eq.

(2). We then add and subtract a term  $\mu_{xc}(n_{\text{val}})$  from  $\mu_{xc}(n)$ :

$$\mu_{xc}(n) = \mu_{xc}(n_{\text{val}}) + \mu_{xc}\left(n_{\text{val}} + \sum_i n_{\text{core}}^i\right) - \mu_{xc}(n_{\text{val}}), \quad (12)$$

where

$$n_{\text{val}} = n_{\text{unif}} + \delta n_{\text{val}} \quad (13)$$

and we have introduced the shorthand notation  $n_{\text{core}}^i \equiv n_{\text{core}}(\vec{r} - \vec{r}_i)$  and

$$\delta n_{\text{val}} \equiv \sum_{\vec{q}}' S(\vec{q}) \delta n_{\text{val}}(q) e^{i\vec{q} \cdot \vec{r}}.$$

The term  $\mu_{xc}(n_{\text{val}})$  plays the role of a valence-electron exchange-correlation potential. Since  $\delta n_{\text{val}}$  is a small (first-order) quantity, one can expand this potential as

$$\begin{aligned} \mu_{xc}(n_{\text{val}}) &= \mu_{xc}(n_{\text{unif}}) + \frac{d\mu_{xc}(n_{\text{unif}})}{dn} \delta n_{\text{val}} \\ &+ \frac{1}{2} \frac{d^2\mu_{xc}(n_{\text{unif}})}{dn^2} (\delta n_{\text{val}})^2 + \dots \end{aligned} \quad (14)$$

The last two terms in Eq. (12), on the other hand, together play the dual role of a core-electron and a valence-core exchange-correlation potential. To remove the summation over  $i$  from inside the argument of the first of these terms, we consider the region of space where  $n_{\text{core}}^i \ll n_{\text{val}}$ , i.e., outside the core  $i$ , and expand in powers of  $\sum_i n_{\text{core}}^i / n_{\text{val}}$ . Then we isolate all core overlap terms and analytically continue the result to the whole solid by resumming the remaining terms. This yields

$$\begin{aligned} \mu_{xc}\left(n_{\text{val}} + \sum_i n_{\text{core}}^i\right) - \mu_{xc}(n_{\text{val}}) &= \sum_i [\mu_{xc}(n_{\text{val}} + n_{\text{core}}^i) - \mu_{xc}(n_{\text{val}})] \\ &+ \frac{1}{2} \frac{d^2\mu_{xc}(n_{\text{val}})}{dn^2} \sum_{i,j}' n_{\text{core}}^i n_{\text{core}}^j + \dots \end{aligned} \quad (15)$$

If the cores do not overlap, then the first term on the right-hand side of Eq. (15) represents an exact result, as is physically obvious. For small first-order overlap, the leading correction to this result is formally second order. The accuracy of the linear superposition represented by the first term is illustrated in Fig. 1. Here we compare this term with the left-hand side of Eq. (15) along a nearest-neighbor direction in the fcc lattice for copper and for zinc, with  $\delta n_{\text{val}} = 0$  in both cases. In zinc, the error is about 5% at the point of maximum overlap, where  $\sum_i n_{\text{core}}^i \sim \frac{1}{3} n_{\text{unif}}$ . In the extreme case of copper  $\sum_i n_{\text{core}}^i \sim \frac{3}{2} n_{\text{unif}}$  at this point, yet the error is still only 15% owing to the slowly varying nature of  $\mu_{xc}(n)$ . The latter

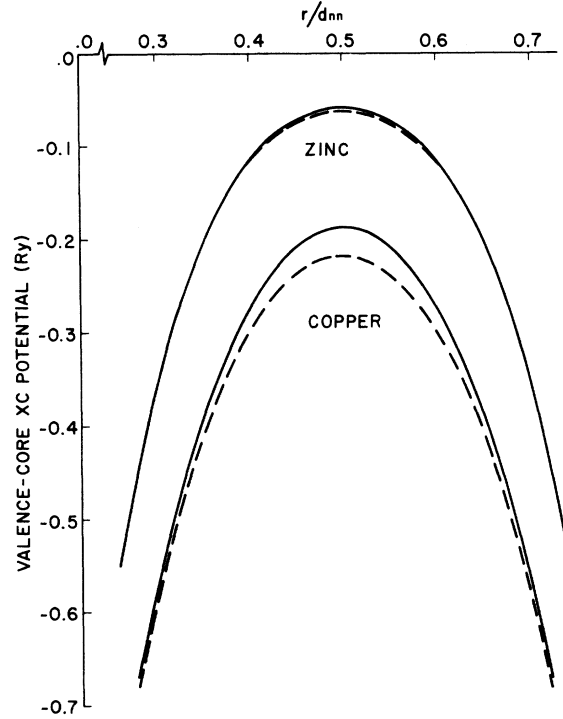


FIG. 1. Valence-core exchange-correlation potential for zinc and for copper along a [110] direction in the fcc lattice, where  $d_m$  is the nearest-neighbor distance. The solid lines represent the left-hand side of Eq. (15) and the dashed lines the linear-superposition approximation given by the first term on the right-hand side of that equation. In both cases  $n_{\text{val}}$  has been set equal to  $n_{\text{unif}}$  and the  $d$  states used to compute  $n_{\text{core}}$  are the same as those employed in Table II.

error is tolerable for computing most properties, although the  $d$ -state matrix elements and characteristic functions in copper are sensitive to the choice of exchange-correlation potential.

In the usual way,<sup>3-6</sup> calculation of the electron density to first order and the total energy to second order only requires a knowledge of  $V(\vec{r})$  and hence  $\mu_{xc}(n)$  to first order. We may thus drop the second-order terms in Eqs. (14) and (15). As a practical matter, it is also convenient to make the decoupling approximation  $\delta n_{\text{val}} = 0$  in Eq. (15). This removes completely any nonlinear dependence of  $\mu_{xc}(n)$  on structure and also permits the self-consistency of the core and valence states to be handled separately. This approximation becomes an exact result in both the limits  $n_{\text{core}}^i \rightarrow 0$  and  $n_{\text{core}}^i \rightarrow \infty$ , and since  $n_{\text{unif}} \gg \delta n_{\text{val}}$ , it should be a good approximation everywhere in the metal. We are thus led to an exchange-correlation potential with the desired linear dependence on structure

$$\mu_{xc}(n) = \mu_{xc}(n_{\text{unif}}) + \frac{d\mu_{xc}(n_{\text{unif}})}{dn} \delta n_{\text{val}} + \sum_i v_{xc}^i, \quad (16)$$

where

$$v_{xc}^i = \mu_{xc}(n_{unif}^i + n_{core}^i) - \mu_{xc}(n_{unif}), \quad (17)$$

with  $v_{xc}^i \equiv v_{xc}(\vec{r} - \vec{r}_i)$ . Equation (17) has the same form as the valence-core exchange-correlation potential introduced by the author previously,<sup>6-8</sup> but the fact that such potentials can be directly

superimposed in the case of overlapping cores is an important new result.

The final exchange-correlation terms in Eq. (8) for  $E_{tot}$  can be handled in an analogous manner. Developing  $n\epsilon_{xc}(n)$  to second order in powers of  $\delta n_{val}$  and  $n_{core}^i$  and using Eq. (1), then subtracting off  $n\mu_{xc}(n)$  as given by Eqs. (2) and (16) and re-summing leads to

$$n[\epsilon_{xc}(n) - \mu_{xc}(n)] = n_{unif}[\epsilon_{xc}(n_{unif}) - \mu_{xc}(n_{unif})] - \frac{1}{2} \frac{d\mu_{xc}(n_{unif})}{dn} (\delta n_{val})^2 + \sum_i n_{core}^i [\epsilon_{xc}(n_{core}^i) - \mu_{xc}(n_{unif}) - \frac{d\mu_{xc}(n_{unif})}{dn} \delta n_{val} - v_{xc}^i] - \frac{1}{2} \sum_{i,j}' n_{core}^i v_{xc}^j. \quad (18)$$

This result is again consistent with the dependence on structure assumed in Eq. (3).

The use of Eqs. (2), (16), and (18) in Eqs. (6) and (8) yields the formally simplified results for  $V(\vec{r})$  and  $E_{tot}$  we desire. The total self-consistent potential can now be written

$$V(\vec{r}) = V_{unif} + \sum_i (v_{nuc}^i + v_{core}^i + v_{xc}^i) + \delta V_{val} + \frac{d\mu_{xc}(n_{unif})}{dn} \delta n_{val} + \mu_{xc}(n_{unif}), \quad (19)$$

where  $v_{nuc}^i \equiv -Z_a e^2 / |\vec{r} - \vec{r}_i|$  and  $V_{unif}$ ,  $v_{core}^i$ , and  $\delta V_{val}$  are the direct Coulomb potentials arising from  $n_{unif}$ ,  $n_{core}^i$ , and  $\delta n_{val}$ , respectively. To similarly

express  $E_{tot}$ , on the other hand, also requires the sum over one-electron energies  $\sum_\alpha E_\alpha$ . We may anticipate from Eqs. (2) and (5) that this sum will have the form

$$\sum_\alpha E_\alpha = T(n_{unif}) + n_{unif} V + \sum_i [T(n_{core}^i) + n_{core}^i V] + \sum_\alpha \delta E_\alpha, \quad (20)$$

where  $T(n)$  is the kinetic energy of the density  $n$  and where we have introduced the further shorthand notation  $nV \equiv \int n(\vec{r})V(\vec{r})d\vec{r}$ . Using Eq. (20) together with the above results, one can combine the principal electrostatic and exchange-correlation terms to obtain without further approximation

$$E_{tot} = n_{unif} \left\{ \frac{3}{5} \epsilon_F + \epsilon_{xc}(n_{unif}) + \sum_i \left[ \left( \frac{Z_a - Z}{Z_a} \right) v_{nuc}^i + v_{core}^i + v_{xc}^i \right] \right\} + \sum_i E_{core}^i + \sum_\alpha \delta E_\alpha + E_{es}(Z) - \frac{1}{2} \delta n_{val} \left( \delta V_{val} + \frac{d\mu_{xc}(n_{unif})}{dn} \delta n_{val} \right) + \frac{1}{2} \sum_{i,j}' n_{core}^i \left[ \left( \frac{Z_a - Z}{Z_a} \right) v_{nuc}^j + v_{core}^j + v_{xc}^j \right] + \frac{1}{2} \sum_{i,j}' \left( \frac{Z_a + Z}{Z_a} \right) n_{nuc}^i \left[ \left( \frac{Z_a - Z}{Z_a} \right) v_{nuc}^j + v_{core}^j \right], \quad (21)$$

where we have defined a structure-independent core energy

$$E_{core}^i = T(n_{core}^i) + n_{core}^i \left[ v_{nuc}^i + \frac{1}{2} v_{core}^i + \epsilon_{xc}(n_{core}^i) \right] \quad (22)$$

and an Ewald or electrostatic energy

$$E_{es}(Z) = \frac{1}{2} n_{unif} V_{unif} + \frac{Z}{Z_a} n_{unif} \sum_j v_{nuc}^j + \frac{1}{2} \left( \frac{Z}{Z_a} \right)^2 \sum_{i,j}' n_{nuc}^i v_{nuc}^j \quad (23)$$

of point ions of charge  $Ze$  immersed in the uniform background

$$n_{unif} = Z / \Omega_0. \quad (24)$$

The quantities  $Z$ ,  $\Omega_0$ , and  $\epsilon_F$  are just the valence, atomic volume, and free-electron Fermi energy of the metal, respectively. Also note that  $n_{nuc}^i \equiv -Z_a \delta(\vec{r} - \vec{r}_i)$  and that the last group of terms in Eq. (21) is identically zero unless the core density  $n_{core}^i$  overlaps a neighboring nucleus  $j$ . Such

terms are most naturally included in the overlap potential of Eq. (3), and the term involving  $n_{\text{nuc}}^i v_{\text{nuc}}^j$  insures that  $v_{o1}(r) \rightarrow +\infty$  as  $r \rightarrow 0$ . Near the equilibrium lattice spacing of any common structure, however, this last group of terms is entirely negligible.

There are three novel features in Eqs. (19) and (21). The first we have already mentioned, namely, the direct superposition of the potentials  $v_{xc}^i$  in  $V$ . The second related feature is the appearance of the exchange-correlation overlap term  $n_{\text{core}}^i v_{xc}^j$  in  $E_{\text{tot}}$ . This term is entirely new and has not been previously anticipated in this form. From Eqs. (10) and (11) it is clear that  $n_{\text{core}}^i v_{xc}^j$  is an inherently negative quantity which subtracts from  $v_{o1}$ , although it will only contribute significantly if  $n_{\text{core}}^i$  includes filled  $d$  states.

The final new feature is the form of the valence exchange-correlation potential. In the usual notation, one can write

$$\delta V_{\text{val}} + \frac{d\mu_{xc}(n_{\text{unif}})}{dn} \delta n_{\text{val}} = \sum_{\vec{q}} \frac{4\pi e^2}{q^2} S(\vec{q}) [1 - G(q)] \delta n_{\text{val}}(q) e^{i\vec{q} \cdot \vec{r}}, \quad (25)$$

with

$$G(q) = -\frac{q^2}{4\pi e^2} \frac{d\mu_{xc}(n_{\text{unif}})}{dn}. \quad (26)$$

Equation (26) for  $G(q)$  has been previously noted for simple metals by Hedin and Lundqvist<sup>10</sup> among others, although this form has not been used in practice. Instead, various external  $G(q)$  have been put into the right-hand side of Eq. (25) in a slightly *ad hoc* fashion. Most of the forms used have been

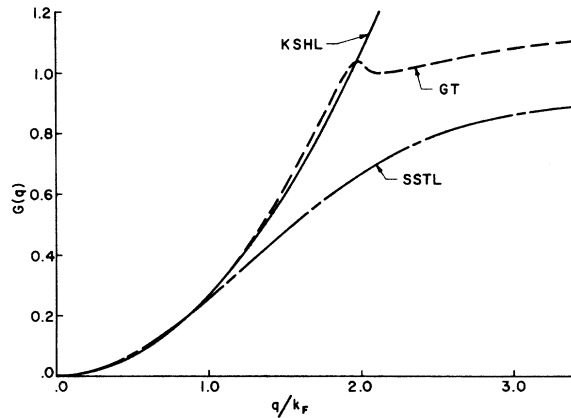


FIG. 2. Valence exchange-correlation function  $G(q)$  as given by the density-functional formalism [KSHL, Eqs. (10), (11), and (26) of the text] and as determined by Geldart and Taylor (GT, Ref. 13) and Singwi *et al.* (SSTL, Ref. 11). All results correspond to the valence electron density in aluminum.

inferred from independent studies on the interacting electron gas. In Fig. 2 compare Eq. (26) with both the Singwi *et al.* (SSTL) function,<sup>11</sup> which we have used in most of our previous applications,<sup>5-8</sup> and with the Geldart and Taylor (GT) function<sup>13</sup> at an electron density corresponding to aluminum. The latter  $G(q)$  arises from a full many-body treatment of the electron gas and would seem to represent the most rigorous form yet obtained. Note that Eq. (26) and the GT  $G(q)$  are virtually identical for  $q < 2k_F$ , but unlike Eq. (26) the latter approaches a constant as  $q \rightarrow \infty$ . The agreement at small  $q$  is quite satisfying since Eq. (26) is presumably exact<sup>14</sup> in the long-wavelength limit  $q \rightarrow 0$ . The correct behavior of  $G(q)$  at large  $q$ , however, is not well established even by the work of Geldart and Taylor. Fortunately, this uncertainty has little consequence in practice, as we will demonstrate in Sec. V below.

### III. ZERO-ORDER PSEUDOATOMS AND HYBRIDIZATION

The total external input to our proposed solution of the Kohn-Sham equations will consist of three numbers: the atomic number  $Z_a$ , the valence  $Z$ , and the atomic volume  $\Omega_0$ . In terms of Eqs. (2) and (21), this leaves three principal quantities to be determined:  $n_{\text{core}}$ ,  $\delta n_{\text{val}}$ , and  $\sum_{\alpha} \delta E_{\alpha}$ . By construction,  $n_{\text{core}}$  is to be defined and  $\delta n_{\text{val}}$  and  $\sum_{\alpha} \delta E_{\alpha}$  will depend self-consistently on the definition through the pseudopotential  $w_0$  and the hybridization potential  $\Delta$ . The general objective is to optimize  $w_0$  and  $\Delta$  so that a first-order calculation of  $\delta n_{\text{val}}$  and a second-order calculation of  $\sum_{\alpha} \delta E_{\alpha}$  is as accurate as possible. As demonstrated in paper I, this can be accomplished very systematically by introducing a neutral pseudoatom whose electron density is just the zero-order density in the metal. This zero-order pseudoatom is defined by the self-consistent Schrödinger equation

$$[T + v_{\text{pa}}(\vec{r}) + v_{\text{loc}}(\vec{r})] \varphi_{\alpha}(\vec{r}) = E_{\alpha}^{\text{pa}} \varphi_{\alpha}(\vec{r}), \quad (27)$$

where the total pseudoatom potential is

$$v_{\text{pa}}(\vec{r}) = v_{\text{unif}}(\vec{r}) + v_{\text{nuc}}(\vec{r}) + v_{\text{core}}(\vec{r}) + v_{\text{xc}}(\vec{r}) \quad (28)$$

and  $v_{\text{unif}}$  is the Coulomb potential arising from that part of  $n_{\text{unif}}$  contained within  $\Omega_0$

$$v_{\text{unif}}(\vec{r}) = \frac{1}{2} Z e^2 (3 - r^2/R_{\text{WS}}^2)/R_{\text{WS}}, \quad r < R_{\text{WS}}, \\ = Z e^2/r, \quad r > R_{\text{WS}}, \quad (29)$$

with  $\Omega_0 = \frac{4}{3} \pi R_{\text{WS}}^3$ . For convenience, the constant  $\mu_{xc}(n_{\text{unif}})$  is omitted in the definition of  $v_{\text{pa}}$  [and also in  $V$  in Eq. (31) below]. This places the zero of energy in Eq. (27) at the bottom of the free-electron valence band in the metal and, of course,

has no effect on the wave functions  $\varphi_\alpha(\vec{r})$ . The localization potential  $v_{1oc}$  is an applied potential which is designed to shape the tails of the localized states  $\varphi_\alpha$  in some optimum way. These states then define the core density:

$$n_{core}(\vec{r}) = \sum_{\alpha} \varphi_{\alpha}^*(\vec{r}) \varphi_{\alpha}(\vec{r}); \quad (30)$$

where the sum is over occupied core and  $d$  states. Equation (27) also defines any required unoccupied states, such as the  $d$  states of metals with empty  $d$  bands just above the Fermi level.

The difference in potential seen by an electron in our zero-order pseudoatom (centered at site  $i=0$ ) and in the metal is then exactly

$$\begin{aligned} \delta V(\vec{r}) &= v_{1oc}(\vec{r}) + v_{pa}(\vec{r}) - V(\vec{r}), \\ &= v_{1oc}(\vec{r}) - \sum_{i \neq 0} v_{pa}(\vec{r} - \vec{r}_i) + \sum_{\vec{q}} S(\vec{q}) \frac{4\pi e^2}{q^2} \\ &\quad \times \{n_{unif}(q) - [1 - G(q)] \delta n_{val}(q)\} e^{i\vec{q} \cdot \vec{r}}, \end{aligned} \quad (31)$$

where  $(4\pi e^2/q^2)n_{unif}(q)$  is the Fourier transform of  $v_{unif}(\vec{r})$ :

$$n_{unif}(q) = \frac{3j_1(qR_{ws})}{qR_{ws}} \frac{Z}{\Omega_0}, \quad (32)$$

with  $j_1$  the familiar  $l=1$  spherical Bessel function. The last form of  $\delta V$  given in Eq. (31) has been obtained by using Eqs. (19), (25), and (28) and then subtracting and adding  $\sum_i v_{unif}(\vec{r} - \vec{r}_i)$ . The term involving  $n_{unif}(q)$  arises from the distinction between  $v_{unif}$  and  $V_{unif}$ , the latter being the potential associated with the whole electron gas.

The inner-core electrons are very tightly bound by  $v_{pa}$  alone, and in the absence of any localization potential the effective strength of  $\delta V(\vec{r})$  is negligibly small for these states. Setting  $v_{1oc}(\vec{r}) = \delta V(\vec{r}) = 0$  is a small-core approximation, in which the  $\varphi_\alpha$  (or more properly Block sums of the  $\varphi_\alpha$ ) become exact eigenstates of the metal Hamiltonian. For the  $d$  states of  $d$ -band metals, on the other hand,  $\delta V(\vec{r})$  becomes very significant. In this case, the  $d$  states  $\varphi_d(\vec{r})$  are only weakly bound (if bound at all) by  $v_{pa}$ , and such states are generally not good eigenstates nor even useful basis states. A strong (formally zero order) localization potential is implicitly required to obtain a  $\varphi_d$  and a hybridization potential

$$\Delta = \delta V - \langle \varphi_d | \delta V | \varphi_d \rangle \quad (33)$$

with the properties required in the generalized pseudopotential theory.

Two of the most important optimization criteria in selecting  $v_{1oc}$  are that (the square of) the plane-wave hybridization matrix element  $\langle \vec{k} | \Delta | \varphi_d \rangle$  and the  $d$ -state overlap matrix element  $\langle \varphi_d^i | \Delta | \varphi_d^j \rangle$  be

small, i.e., first-order quantities. A general form for  $v_{1oc}$  which accomplishes this goal is the barrier potential

$$\begin{aligned} v_{1oc}(\vec{r}) &= 0, \quad r < R_0 \\ &= f(r), \quad r > R_0 \end{aligned} \quad (34)$$

where  $R_0 \geq R_{ws}$  and  $f(r) > 0$  as  $r \rightarrow \infty$ . The atomic character of  $\varphi_d(\vec{r})$  inside  $\Omega_0$  is essentially unaffected by this potential, while the tails of these states can be contracted such that the effective strength of  $\Delta$  is minimized. In the vicinity of this minimum, there will be considerable insensitivity in the matrix elements of  $\Delta$ , and consequently in  $n$  and  $E_{tot}$ , to the precise nature of  $f(r)$ . This is because the  $v_{1oc}$  added to the pseudoatom potential to define  $\varphi_d$  is subtracted from the metal potential in the definition of  $\Delta$ . If one were to calculate  $n$  and  $E_{tot}$  to all orders in  $w_0$  and  $\Delta$ , the results should be exactly independent of  $v_{1oc}$  and  $f(r)$ .

For the low-order expansions we seek here, a near-optimum form for  $f(r)$  now appears to be

$$f(r) = V_0 (r/R_0 - 1)^2, \quad (35)$$

where the constants  $V_0$  and  $R_0$  taken as a pair depend primarily on the number of  $d$  electrons in the zero-order pseudoatom. For finite  $V_0$  and  $R_0$ , Eq. (35) leads to Gaussian-like tails for the  $d$  states, because the total potential in Eq. (27) varies as  $+r^2$  as  $r \rightarrow \infty$ . In the limit  $V_0 \rightarrow \infty$ , applying  $v_{1oc}$  to the  $d$  states is equivalent to imposing the boundary condition

$$\varphi_d(\vec{R}_0) = 0. \quad (36)$$

This type of localization was introduced and used successfully by us in paper I. Its principal advantage is that it leads to an exact analytic form for the pseudoatom portion of the hybridization matrix element

$$\begin{aligned} \langle \vec{k} | \Delta_{pa} | \varphi_d \rangle &= \langle \vec{k} | v_{1oc} - \langle \varphi_d | v_{1oc} | \varphi_d \rangle | \varphi_d \rangle \\ &= -4\pi \Delta_{pa}(k) Y_{2m}(\vec{k}), \end{aligned} \quad (37)$$

with

$$\Delta_{pa}(k) = -\frac{1}{\Omega_0^{1/2}} R_0 \frac{dP_d(R_0)}{dr} j_2(kR_0), \quad (38)$$

where  $P_d(r)/r$  is the radial part of  $\varphi_d(\vec{r})$  and  $j_2$  and  $Y_{2m}$  are the usual  $l=2$  spherical Bessel function and spherical harmonic, respectively. As can be inferred from our studies in paper I, the optimum value of  $R_0/R_{ws}$  in this case is near 1.0 for metals with empty  $d$  bands and in the range 1.25–1.75 for metals with filled  $d$  bands. In the latter range the radial wave function  $P_d(r)$  is very close to that of the corresponding free atom for  $r < R_{ws}$  (see Fig. 8 of paper I). The long-range tail of  $\Delta_{pa}(k)$ , which falls off only as  $\text{sink}R_0/k$  at large

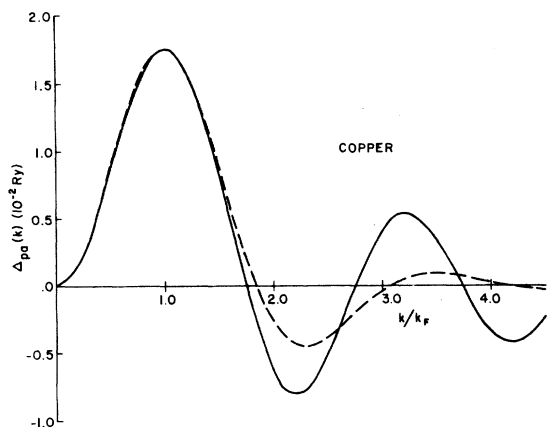


FIG. 3. Hybridization function  $\Delta_{pa}(k)$  for copper based on two different types of  $d$ -state localization potential. The solid line corresponds to the set of parameters  $V_0 = \infty$  and  $R_0/R_{WS} = 1.72$  and the dashed line to  $V_0 = 4.0$  Ry and  $R_0/R_{WS} = 1.0$ .

$k$ , can be made to decay more rapidly without affecting  $\Delta_{pa}(k)$  at small  $k$  by using a finite value of  $V_0$  and a smaller value  $R_0$  in  $f(r)$ . For example, replacing the set of parameters  $V_0 = \infty$  and  $R_0/R_{WS} = 1.72$  by  $V_0 = 4.0$  (Ry) and  $R_0/R_{WS} = 1.0$  does this very nicely, as shown in Fig. 3 for copper.

For any spherically symmetric localization potential, solving Eq. (27) becomes a straightforward atomic self-consistent-field problem and can be handled by standard techniques, as discussed in Paper I. Once the  $\varphi_\alpha(\vec{r})$  and  $E_\alpha^{pa}$  of interest have been found, all of the relevant matrix elements of the generalized pseudopotential theory can be obtained. Of particular interest here are the consequences of the exact structure dependence of  $\delta V$ , which we have obtained in Eq. (31). One important consequence is a simple unambiguous formula for the  $d$ -state overlap matrix element:

$$\begin{aligned} \Delta_d^{ij} &\equiv \langle \varphi_d^i | \Delta | \varphi_d^j \rangle \\ &= \int \varphi_d^* (\vec{r} - \vec{r}_i) [v_{loc}(\vec{r} - \vec{r}_j) - v_{pa}(\vec{r} - \vec{r}_i)] \\ &\quad \times \varphi_d(\vec{r} - \vec{r}_j) d\vec{r} + \dots, \end{aligned} \quad (39)$$

where the dots represent second-order terms. The second-order terms in Eq. (39) lead to negligible third-order contributions in both  $n$  and  $E_{tot}$  and may always be dropped. The remaining first-order integral is the analog of the familiar two-center transfer integral in tight-binding theory. In the usual notation the  $m=0, 1$ , and 2 components of  $\Delta_d^{ij}$  (evaluated at the nearest-neighbor distance) are denoted as  $-dd\sigma$ ,  $-dd\pi$ , and  $-dd\delta$ , respectively. This identification permits one to make a direct check on the accuracy of Eq. (39). The total  $d$ -band-width of an fcc metal like copper is approximately<sup>15</sup>

$$4 \left( \frac{12}{5} \right)^{1/2} [(dd\sigma)^2 + (dd\pi)^2 + (dd\delta)^2]^{1/2}. \quad (40)$$

For a given treatment of exchange and correlation, the combined prediction of Eqs. (39) and (40) may be compared against the result of a full self-consistent band-structure calculation. We do this in Table I for copper using three different choices of exchange and correlation potential and two choices of localization potential in defining  $\varphi_d$ . The insensitivity of the results to  $v_{loc}$  is clearly evident here. For both a moderate and a strong localization potential we obtain a quantitatively accurate estimate of the  $d$ -band width, and hence of  $\Delta_d^{ij}$ , for each treatment of exchange and correlation.

To treat the structure dependence of  $\langle \vec{k} | \Delta | \varphi_d \rangle$ , it is convenient to divide the hybridization potential into pseudoatom, overlap, and screening plus orthogonalization-hole contributions. The pseudoatom matrix element  $\langle \vec{k} | \Delta_{pa} | \varphi_d \rangle$  is defined by Eq. (37), while the overlap contribution to the hybridization is derived from the second term in Eq. (31)

TABLE I. Width of the  $d$  bands in copper as calculated from Eqs. (39) and (40) and as inferred from full self-consistent band-structure calculations, in Ry. The notation KSHL refers to the Kohn-Sham exchange potential, Eq. (10), and the Hedin-Lundqvist correlation potential, Eq. (11). The quantity  $V_0$  relates to the  $d$ -state localization potential defined by Eqs. (34) and (35); in both cases  $R_0/R_{WS} = 1.0$ .

Exchange-correlation potential	Present work		Self-consistent band calculation
	$V_0 = 4.0$ Ry	$V_0 = 25.0$ Ry	
KSHL	0.270	0.268	0.260 <sup>a</sup>
$X\alpha$ ( $\alpha = \frac{5}{8}$ )	0.234	0.231	0.229 <sup>a</sup>
$X\alpha$ ( $\alpha = 1.0$ )	0.195	0.191	0.189 <sup>b</sup>

<sup>a</sup> Reference 16.

<sup>b</sup> E. C. Snow, Phys. Rev. **171**, 785 (1968).

$$\sum_{i \neq 0} \langle \vec{k} | \Delta_{oi}^i | \varphi_d \rangle, \quad (41)$$

where  $\Delta_{oi}^i \equiv \Delta_{oi}(\vec{r} - \vec{r}_i)$  and

$$\Delta_{oi}(\vec{r} - \vec{r}_i) = -v_{pa}(\vec{r} - \vec{r}_i) + \langle \varphi_d | v_{pa}(\vec{r} - \vec{r}_i) | \varphi_d \rangle. \quad (42)$$

Similarly, the screening and orthogonalization-hole portion of the hybridization is

$$\sum_{\vec{q}} S(\vec{q}) \frac{4\pi e^2}{q^2} \{ n_{unif}(q) - [1 - G(q)] \delta n_{val}(q) \} \\ \times [\langle \vec{k} - \vec{q} | \varphi_d \rangle - \langle \varphi_d | e^{i\vec{q} \cdot \vec{r}} | \varphi_d \rangle \langle \vec{k} | \varphi_d \rangle]. \quad (43)$$

The key to treating the explicit structure dependence in Eqs. (41) and (43) will be to assign these quantities one higher order of smallness than  $\langle \vec{k} | \Delta_{pa} | \varphi_d \rangle$ . In the screening and orthogonalization hole contribution this is clearly valid since  $\delta n_{val}(q)$  is first order and  $n_{unif}(q)$  at nonzero reciprocal-lattice vectors also behaves as a first-order quantity. The size of the overlap contribution, on the other hand, is variable, but in principle it can be

made as small as necessary with a sufficiently contracted  $d$  state.

The magnitude of  $\langle \vec{k} | \Delta_{pa} | \varphi_d \rangle$  near  $k = k_F$  may be directly checked if the width  $W_d$  and position  $E_d$  of the  $l=2$  resonance of the corresponding band-structure potential are known. To lowest order<sup>3-5</sup>

$$W_d/E_d^{5/2} = 2\Omega_0 [\Delta_{pa}(k_d)/E_d^{pa}]^2 \quad (44)$$

in Rydberg atomic units<sup>18</sup> where  $E_d^{pa} = k_d^2$ . The form given in Eq. (44) is especially convenient because both sides of the equation are approximately independent of the choice of the zero of energy. Using our previously obtained values of  $W_d$  and  $E_d$  for the Chodorow potential of copper,<sup>15</sup> we calculate 0.335 for  $W_d/E_d^{5/2}$ . For the range of exchange-correlation and localization potentials given in Table I, we obtain values varying between 0.303 and 0.352 for the right-hand side of Eq. (44).

Another simple test on the magnitude of  $\langle \vec{k}_F | \Delta_{pa} | \varphi_d \rangle$  comes through the total occupied valence-band width in the metal. To first-order in  $w_0$  and  $\Delta_{pa}^2$  this width is

$$\epsilon_F + \langle \vec{k}_F | w_0 | \vec{k}_F \rangle - \langle 0 | w_0 | 0 \rangle + \sum_d \frac{\langle \vec{k}_F | \Delta_{pa} | \varphi_d \rangle \langle \varphi_d | \Delta_{pa} | \vec{k}_F \rangle}{\epsilon_F - E_d^{pa}} \\ = \epsilon_F + \sum_{\alpha=c,d} [(\epsilon_F - E_\alpha^{pa}) \langle \vec{k}_F | \varphi_\alpha \rangle \langle \varphi_\alpha | \vec{k}_F \rangle + E_\alpha^{pa} \langle 0 | \varphi_\alpha \rangle \langle \varphi_\alpha | 0 \rangle] \\ + \sum_d \left( \langle \vec{k}_F | \Delta_{pa} | \varphi_d \rangle \langle \varphi_d | \vec{k}_F \rangle + \text{c.c.} + \frac{\langle \vec{k}_F | \Delta_{pa} | \varphi_d \rangle \langle \varphi_d | \Delta_{pa} | \vec{k}_F \rangle}{\epsilon_F - E_d^{pa}} \right), \quad (45)$$

TABLE II. Total occupied valence-band width of four metals as calculated from Eq. (45) and as given by band-structure calculations, in Ry. The without hybridization column refers to the limit  $\varphi_d = 0$  for metals with empty  $d$  bands (K and Ca) and to the limit  $\Delta_{pa} = 0$  for metals with filled  $d$  bands (Cu and Zn). The calculations both with and without hybridization relate to the Kohn-Sham-Hedin-Lundqvist (KSHL) treatment of exchange and correlation, as discussed in the text, and  $d$ -state localization parameters  $V_0 = \infty$  and  $R_0/R_{WS} = 1.0$  for K and Ca, = 1.72 for Cu and = 1.50 for Zn. The quantity  $\epsilon_F$  is the free-electron Fermi energy.

Metal	$\epsilon_F$	Present work		Band calculation
		Without hybridization	With hybridization	
K	0.156	0.168	0.163	0.157 <sup>a</sup>
Ca	0.343	0.352	0.296	0.296 <sup>b</sup>
Cu	0.517	0.537	0.718	0.690 <sup>c</sup>
Zn	0.693	0.720	0.760	0.780 <sup>d</sup>

<sup>a</sup> M. J. Lawrence, J. Phys. F **1**, 836 (1971). Self-consistent  $X\alpha$  ( $\alpha = 1.0$ ) calculation.

<sup>b</sup> Reference 17. Self-consistent  $X\alpha$  ( $\alpha = \frac{2}{3}$ ) calculation.

<sup>c</sup> Reference 16. Self-consistent KSHL calculation.

<sup>d</sup> G. E. Juras, B. Segall, and C. B. Sommers, Solid State Commun. **10**, 427 (1972). Non-self-consistent  $X\alpha$  ( $\alpha = \frac{5}{6}$ ) calculation.



where the sum over  $\alpha$  includes a sum over both core and  $d$  states, either occupied or unoccupied. Like Eqs. (39) and (44), this result is a function only of the parameters of the zero-order pseudo-atom. The net hybridization contribution to the total bandwidth depends on the magnitude and sign of  $\epsilon_F - E_d^{pa}$  as well as the magnitude of  $\langle \vec{k} | \Delta_{pa} | \varphi_d \rangle$ . In Table II, we compare Eq. (45), both with and without hybridization contributions, with the results of band-structure calculations for several metals. Note that in the limit of no hybridization the shift away from  $\epsilon_F$  is always small and positive. When hybridization is included, however, the shift can be either positive (K, Cu, and Zn) or negative (Ca) and small (K), moderate (Ca and Zn) or large (Cu), in complete accord with the band-structure calculations.

#### IV. GENERALIZED PSEUDOPOTENTIAL THEORY

We now proceed to obtain the quantities  $\delta n_{\text{val}}$  and  $\sum_{\alpha} \delta E_{\alpha}$  as explicit functions of  $w_0$ ,  $\Delta_{pa}$ , and the other parameters defined above. The initial steps in this development are identical to our original analysis in Ref. 3. The one-electron Schrödinger equation (5) is transformed exactly to an equivalent pseudo-Schrödinger equation. A pseudo-Green's-function  $G_{\alpha\alpha'}$  is then introduced for the latter and is expanded in a basis set  $|\alpha\rangle$  of plane waves  $|\vec{k}\rangle$  and localized  $d$  states  $|\varphi_d\rangle$ . The resulting pseudo-Green's-function equations may be readily decoupled and solved in terms of total pseudopotential and hybridization potentials  $W_0$  and  $\Delta$ , respectively. By analytically integrating the appropriate functions of  $G_{\alpha\alpha'}(E)$  over energy, one may obtain the sum of one-electron energies [for example, Eqs. (83)–(86) of Ref. 3] and the total electron density [for example, Eqs. (100)–(105)] in terms of  $W_0$  and  $\Delta$ . This latter step is only completely straightforward, however, in the cases of empty or filled  $d$  bands where certain simplifications are possible. For this reason, we shall now confine our attention to these cases specifically. We may then infer the general forms of  $\delta n_{\text{val}}$  and  $\sum_{\alpha} \delta E_{\alpha}$  directly from our previous results.<sup>19</sup>

At this point, however, both  $W_0$  and  $\Delta$  still contain an implicit structure dependence. In the case of the hybridization potential, we have already seen above how this dependence can be extracted explicitly in the matrix elements  $\langle \vec{k} | \Delta | \varphi_d \rangle$  and  $\langle \varphi_d^i | \Delta | \varphi_d^j \rangle$ . Similarly, one can write (for an optimized choice of  $W_0$ )

$$\langle \vec{k} + \vec{q} | W_0 | \vec{k} \rangle = S(\vec{q}) \langle \vec{k} + \vec{q} | w_0 | \vec{k} \rangle + \dots, \quad (46)$$

where the dots represent second-order terms, and where  $\langle \vec{k} + \vec{q} | w_0 | \vec{k} \rangle$  is the structure-independent

matrix element [as in Eq. (45)]

$$\langle \vec{k} + \vec{q} | w_0 | \vec{k} \rangle = v(q) + \sum_{\alpha=c,d} (\epsilon_{\vec{k}} - E_{\alpha}^{pa}) \langle \vec{k} + \vec{q} | \varphi_{\alpha} \rangle \langle \varphi_{\alpha} | \vec{k} \rangle + \sum_d (\langle \vec{k} + \vec{q} | \Delta_{pa} | \varphi_d \rangle \langle \varphi_d | \vec{k} \rangle + \text{c.c.}), \quad (47)$$

with  $\epsilon_{\vec{k}} = \hbar^2 k^2 / 2m$ . The remaining task is to treat the second-order terms in Eq. (46) and the structure-dependent parts of  $\Delta$  fully and explicitly in  $\delta n_{\text{val}}$  and  $\sum_{\alpha} \delta E_{\alpha}$ .

##### A. Electron density, self-consistent potential, and form factor

As usual, it is convenient to divide  $\delta n_{\text{val}}$  into separate orthogonalization hole and screening contributions:

$$\delta n_{\text{val}} = \delta n_{\text{oh}} + \delta n_{\text{scr}}. \quad (48)$$

The former can be written as a background density plus a localized hole density  $n_{\text{oh}}^i$  at each site:

$$\delta n_{\text{oh}} = \frac{Z^* - Z}{Z} n_{\text{unif}} + \sum_i n_{\text{oh}}^i, \quad (49)$$

where  $n_{\text{oh}}^i \equiv n_{\text{oh}}(\vec{r} - \vec{r}_i)$  and

$$n_{\text{oh}}(\vec{r}) = -\frac{2\Omega_0}{(2\pi)^3} \int_{k < k_F} [\langle \vec{r} | p | \vec{k} \rangle \langle \vec{k} | \vec{r} \rangle + \text{c.c.}] - \langle \vec{r} | p | \vec{k} \rangle \langle \vec{k} | p | \vec{r} \rangle d\vec{k}, \quad (50)$$

with

$$p = \sum_{\alpha=c,d} |\varphi_{\alpha}\rangle \langle \varphi_{\alpha}|.$$

The effective valence  $Z^*$  is

$$Z^* = Z - \int n_{\text{oh}}(\vec{r}) d\vec{r} = Z + \frac{2\Omega_0}{(2\pi)^3} \int_{k < k_F} \langle \vec{k} | p | \vec{k} \rangle d\vec{k}. \quad (51)$$

The total electron density is thus from Eqs. (2) and (49)

$$n(\vec{r}) = \frac{Z^*}{Z} n_{\text{unif}} + \sum_i [n_{\text{core}}(\vec{r} - \vec{r}_i) + n_{\text{oh}}(\vec{r} - \vec{r}_i)] + \sum_{\vec{q}} S(\vec{q}) n_{\text{scr}}(q) e^{i\vec{q} \cdot \vec{r}}. \quad (52)$$

The screening component  $n_{\text{scr}}(q)$  may be obtained to first order from our previous results<sup>3</sup> by setting  $\Delta = \Delta_{pa}$  and using Eq. (46):

$$n_{\text{scr}}(q) = \frac{4}{(2\pi)^3} \left[ \int_{k < k_F} \frac{w_0(\vec{k}, \vec{q})}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}} d\vec{k} \mp \int_{k \approx k_F} \left( \frac{h_1(\vec{k}, \vec{q})}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}} + h_2(\vec{k}, \vec{q}) \right) d\vec{k} \right], \quad (53)$$

where we have set  $w_0(\vec{k}, \vec{q}) \equiv \langle \vec{k} + \vec{q} | w_0 | \vec{k} \rangle$  and have further defined

$$h_1(\vec{k}, \vec{q}) = \sum_d \frac{\langle \vec{k} + \vec{q} | \Delta_{pa} | \varphi_d \rangle \langle \varphi_d | \Delta_{pa} | \vec{k} \rangle}{\epsilon_{\vec{k}} - E_d^{pa}} \quad (54)$$

and

$$h_2(\vec{k}, \vec{q}) = \sum_d \frac{\langle \vec{k} | \varphi_d \rangle \langle \varphi_d | e^{-i\vec{q}\cdot\vec{r}} | \varphi_d \rangle \langle \varphi_d | \Delta_{pa} | \vec{k} \rangle - \langle \vec{k} + \vec{q} | \varphi_d \rangle \langle \varphi_d | \Delta_{pa} | \vec{k} \rangle}{\epsilon_{\vec{k}} - E_d^{pa}} + \frac{\langle \vec{k} | \Delta_{pa} | \varphi_d \rangle \langle \varphi_d | e^{-i\vec{k}\cdot\vec{r}} | \varphi_d \rangle \langle \varphi_d | \Delta_{pa} | \vec{k} \rangle}{2(\epsilon_{\vec{k}} - E_d^{pa})^2}. \quad (55)$$

The second integration in Eq. (53) is outside the Fermi sphere with a minus sign if  $E_d^{pa} < \epsilon_F$  (filled  $d$  bands) and inside the Fermi sphere with a plus sign if  $E_d^{pa} > \epsilon_F$  (empty  $d$  bands).

The Fourier component of the self-consistent potential  $v(q)$  is obtained in the usual way<sup>4-6</sup> from Eqs. (19), (25), (47), and (53). This now takes the form

$$v(q) = \left[ \frac{4\pi e^2}{q^2} \left( \frac{-Z_a}{\Omega_0} + n_{\text{core}}(q) + [1 - G(q)][n_{\text{oh}}(q) + n_R(q)] \right) + v_{xc}(q) \right] [\epsilon^*(q)]^{-1}, \quad (56)$$

with

$$n_R(q) = n_{\text{scr}}(q) + \frac{q^2}{4\pi e^2} [\epsilon(q) - 1] v(q),$$

and where  $\epsilon^*(q)$  is related to the Hartree dielectric function  $\epsilon(q)$  by

$$\epsilon^*(q) = \epsilon(q) - G(q)[\epsilon(q) - 1]. \quad (57)$$

In Eqs. (47) and (56), as in Eq. (32), the Fourier transform of  $t(\vec{r})$  is understood to be

$$t(q) = \Omega_0^{-1} \int t(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} d\vec{r}.$$

In all cases of interest  $t(\vec{r})$  is spherically symmetric and the result depends only on the magnitude of  $\vec{q}$ .

An additional nice feature of the Kohn-Sham formalism is that  $\mu_{xc}$  is the appropriate exchange and correlation potential seen by an electron at the Fermi level. Thus, in addition to  $n(\vec{r})$  and  $E_{\text{tot}}$ , one may rigorously construct the pseudopotential form factor

$$w(q) = w_0(\vec{k}_F, \vec{q}) + h_1(\vec{k}_F, \vec{q}), \quad (58)$$

with  $q \leq 2k_F$ , for the calculation of electronic properties, as we have done previously.<sup>4-6,8</sup>

## B. Components of the total energy

The completion of the total energy calculation is somewhat more difficult because one must obtain the result to second order. From Eq. (83)–(86) of Ref. 3 one may infer the general relationship

$$\sum_{\alpha} \delta E_{\alpha} = N \frac{2\Omega_0}{(2\pi)^3} \left( \int_{k < k_F} (\langle \vec{k} | W_0 - V | \vec{k} \rangle + \langle \vec{k} | W_0 | \vec{k} \rangle \langle \vec{k} | P | \vec{k} \rangle) d\vec{k} + \int_{k > k_F} \sum_d \frac{\langle \vec{k} | \Delta | \varphi_d \rangle \langle \varphi_d | \Delta | \vec{k} \rangle}{\epsilon_{\vec{k}} - E_d} d\vec{k} \right) + \dots, \quad (59)$$

where the dots again represent second-order terms. The second-order terms in Eq. (59) will go over to their final form directly by using Eq. (46) and the replacement  $\Delta = \Delta_{pa}$ , as in Eq. (53). The terms involving  $W_0$  may be exactly manipulated<sup>20</sup> into the form

$$N \frac{2\Omega_0}{(2\pi)^3} \int_{k < k_F} \langle \vec{k} | w_0^{pa} | \vec{k} \rangle [1 + \langle \vec{k} | p | \vec{k} \rangle] d\vec{k} - n_{\text{unif}} \sum_i \left( v_{\text{unif}}^i + \frac{Z}{Z_a} v_{\text{nuc}}^i \right) - n_{\text{unif}} \sum_i \left[ \left( \frac{Z_a - Z}{Z_a} \right) v_{\text{nuc}}^i + v_{\text{core}}^i + v_{xc}^i \right] + \delta n_{\text{oh}} V - \sum_i \left( \frac{Z^* - Z}{Z} n_{\text{unif}}^i + n_{\text{oh}}^i \right) v_{pa}^i, \quad (60)$$

using Eqs. (19), (28), (31), (50), and (51). The pseudopotential  $w_0^{pa}$  denotes  $w_0$  with  $v$  replaced by  $v_{pa}$  in Eq. (47). The second group of terms in Eq. (60) is just  $N(\bar{v}_{\text{unif}} + \bar{v}_{\text{nuc}}) = N \frac{3}{10} (Ze)^2 / R_{WS}$ , using Eq. (29), while the third group of terms exactly cancels that in the total energy, Eq. (21).

The final orthogonalization hole terms in Eq. (60) are most conveniently grouped into four separate contributions. The terms involving  $\delta n_{\text{val}}$  are readily combined with those in Eq. (21) to give

$$[\delta n_{\text{oh}} - \frac{1}{2}\delta n_{\text{val}}] \left( \delta V_{\text{val}} + \frac{d\mu_{\text{xc}}(n_{\text{unit}})}{dn} \delta n_{\text{val}} \right) = \frac{1}{2}\delta n_{\text{oh}} \left( \delta V_{\text{oh}} + \frac{d\mu_{\text{xc}}(n_{\text{unit}})}{dn} \delta n_{\text{oh}} \right) - \frac{1}{2}\delta n_{\text{scr}} \left( \delta V_{\text{scr}} + \frac{d\mu_{\text{xc}}(n_{\text{unit}})}{dn} \delta n_{\text{scr}} \right). \quad (61)$$

The exchange-correlation and screening terms in Eq. (61) may be absorbed into the band-structure energy in the usual way.<sup>5,6</sup> The term  $\frac{1}{2}\delta n_{\text{oh}}\delta V_{\text{oh}}$  plus the remaining orthogonalization hole terms in Eq. (60) may then be exactly rearranged into: (i) structure-independent contributions  $-\frac{9}{10}N(Ze)^2/R_{\text{WS}}$  and  $NE_{\text{oh}}$ , where

$$E_{\text{oh}} = -\frac{9}{10} \frac{(Z^* - Z)^2 e^2}{R_{\text{WS}}} + \frac{1}{2} \int_0^\infty u_{\text{oh}}(r) \left( v_{\text{oh}}(r) - \frac{(Z^* - Z)e^2 r^2}{R_{\text{WS}}^3} \right) dr + \frac{1}{2} \int_{R_{\text{WS}}}^\infty u_{\text{oh}}(r) Z e^2 \left( \frac{3}{R_{\text{WS}}} - \frac{r^2}{R_{\text{WS}}^3} - \frac{2}{r} \right) dr, \quad (62)$$

with  $u_{\text{oh}}(r) = 4\pi r^2 n_{\text{oh}}(r)$ ; (ii) electrostatic contributions which can be combined with  $E_{\text{es}}(Z)$  to give the second-order structure-dependent energy

$$NE_{\text{es}}^{\text{struc}} = E_{\text{es}}(Z^*) + \frac{9}{10}N(Z^*e)^2/R_{\text{WS}}, \quad (63)$$

where  $E_{\text{es}}(Z^*)$  is the electrostatic energy of point charges  $Z^*e$  in a uniform compensating background; and (iii) an overlap contribution

$$\sum_{i,j}' \left\{ n_{\text{oh}}^i \left[ \left( \frac{Z_a - Z}{Z_a} \right) v_{\text{nuc}}^j + v_{\text{core}}^j + v_{\text{xc}}^j \right] + \frac{1}{2} \left( n_{\text{oh}}^i + \frac{Z^* + Z}{Z_a} n_{\text{nuc}}^i \right) \left( v_{\text{oh}}^j - \frac{Z^* - Z}{Z_a} v_{\text{nuc}}^j \right) \right\}. \quad (64)$$

The overlap terms have been previously neglected and are obtained here for the first time.

The implicit structure dependence of the first-order hybridization term in Eq. (59) can be extracted by using the results of Sec. III and noting from Eq. (31) that

$$E_d = \langle \varphi_d | T + V | \varphi_d \rangle = E_d^{\text{pa}} - \langle \varphi_d | v_{\text{pa}} - V | \varphi_d \rangle, \quad (65)$$

where we have now conveniently subtracted off the tiny structure-independent constant  $\langle \varphi_d | v_{\text{loc}} | \varphi_d \rangle$  in the definition of  $E_d^{\text{pa}}$ . [This subtraction has been done implicitly in Eqs. (44)–(63) above.] We then expand  $(\epsilon_{\vec{k}} - E_d)^{-1}$  in powers of  $(\epsilon_{\vec{k}} - E_d^{\text{pa}})^{-1}$  and use Eqs. (31), (41) and (43) to obtain, in addition to  $h_1(\vec{k}, 0)$ , the second-order structure-dependent term

$$\pm N \sum_{\vec{q}}' |S(\vec{q})|^2 \frac{4\pi e^2}{q^2} \{ n_{\text{unit}}(q) - [1 - G(q)][n_{\text{scr}}(q) + n_{\text{oh}}(q)] \} \left( \frac{2\Omega_0}{(2\pi)^3} \int_{k \approx k_F} h_2(\vec{k}, \vec{q}) d\vec{k} \right) + \text{c.c.}, \quad (66)$$

which can be readily absorbed into the band-structure energy, and

$$\mp \sum_{i,j}' \left[ \frac{2\Omega_0}{(2\pi)^3} \int_{k \approx k_F} \sum_d \left( \frac{\langle \vec{k} | \Delta_{\text{pa}} | \varphi_d \rangle \langle \varphi_d | \Delta_{\text{ol}}^j | \vec{k} \rangle + \text{c.c.}}{\epsilon_{\vec{k}} - E_d^{\text{pa}}} + \frac{\langle \vec{k} | \Delta_{\text{pa}} | \varphi_d \rangle \langle \varphi_d | v_{\text{pa}}^j | \varphi_d \rangle \langle \varphi_d | \Delta_{\text{pa}} | \vec{k} \rangle}{(\epsilon_{\vec{k}} - E_d^{\text{pa}})^2} \right) d\vec{k} \right], \quad (67)$$

which can be readily absorbed into the overlap energy. In Eq. (67) both  $\Delta_{\text{pa}}$  and  $\varphi_d$  are centered on the site  $\vec{r}_i$ .

The total energy  $E_{\text{tot}}$  can now be put in the form of Eq. (3). If one identifies  $E_{\text{es}}$  in that equation as the second-order structure-dependent electrostatic energy  $NE_{\text{es}}^{\text{struc}}$ , then the structure-independent contribution can be written

$$E_0 = NE_{\text{fe}} + \sum_i E_{\text{core}}^i, \quad (68)$$

where the free-electron energy (per atom)  $E_{\text{fe}}$  is, from Eqs. (21), (59), (60), and (62), and Eq. (83) of Ref. 3,

$$E_{\text{fe}} = \frac{3}{5} Z \epsilon_F + Z \epsilon_{\text{xc}}(n_{\text{unit}}) - \frac{3}{5} \frac{(Ze)^2}{R_{\text{WS}}} + E_{\text{oh}} + \frac{2\Omega_0}{(2\pi)^3} \left[ \int_{k < k_F} w_0^{\text{pa}}(\vec{k}, 0) [1 + p(\vec{k})] d\vec{k} \mp \int_{k \approx k_F} h_1(\vec{k}, 0) \left( 1 + p(\vec{k}) - \frac{w_0^{\text{pa}}(\vec{k}, 0) + h_1(\vec{k}, 0)}{\epsilon_{\vec{k}} - E_d^{\text{pa}}} \right) d\vec{k} \right], \quad (69)$$

with  $p(\vec{k}) \equiv \langle \vec{k} | p | \vec{k} \rangle$ . This result is now exact to second order, and as we shall see below, considerably more accurate than our previous approximate formulas.<sup>5,6</sup>

From Eqs. (61) and (66), and Eq. (85) of Ref. 3, the energy-wave-number characteristic now takes the form

$$\begin{aligned}
F(q) = & \frac{2\Omega_0}{(2\pi)^3} \left[ \int_{\mathbf{k} < k_F} \frac{[w_0(\vec{k}, \vec{q})]^2}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}} d\vec{k} \right. \\
& \mp \int_{\mathbf{k} > k_F} \left( \frac{2h_1(\vec{k}, \vec{q})w_0(\vec{k}, \vec{q}) + [h_1(\vec{k}, \vec{q})]^2}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}} - \frac{8\pi e^2}{q^2} \{n_{\text{unif}}(q) - [1-G(q)][n_{\text{scr}}(q) + n_{\text{oh}}(q)]\} h_2(\vec{k}, \vec{q}) \right) d\vec{k} \left. \right] \\
& - \frac{2\pi e^2 \Omega_0}{q^2} \{G(q)[n_{\text{oh}}(q)]^2 + [1-G(q)][n_{\text{scr}}(q)]^2\}, \tag{70}
\end{aligned}$$

which is again exact to second order. The principal new feature of this result is the group of terms involving  $h_2(\vec{k}, \vec{q})$ , which arises from the structure dependence of  $\langle \vec{k} | \Delta | \varphi_d \rangle$ . The effect of these terms on  $F(q)$  will be discussed in Sec. V.

Finally, using Eqs. (21), (64), and (67), and Eq. (86) of Ref. 3, the overlap potential may be written

$$\begin{aligned}
v_{\text{ol}}(|\vec{r}_i - \vec{r}_j|) = & \sum_d \left\{ 4S_d^{ij} \Delta_d^{ji} \Theta(\epsilon_F - E_d^{\text{pa}}) - \frac{4\Omega_0}{(2\pi)^3} \left[ \int_{\mathbf{k} < k_F} \{S_d^{ij}[(\epsilon_{\vec{k}} - E_d^{\text{pa}})h_3^{ji}(\vec{k}) + 2h_4^{ji}(\vec{k})] + \Delta_d^{ij}h_3^{ji}(\vec{k})\} d\vec{k} \right. \right. \\
& \left. \left. + \int_{\mathbf{k} > k_F} \left( S_d^{ij}h_1^{ji}(\vec{k}) + \frac{\Delta_d^{ij}[2h_4^{ji}(\vec{k}) + h_1^{ji}(\vec{k})]}{\epsilon_{\vec{k}} - E_d^{\text{pa}}} - h_5^{ij}(\vec{k}) \right) d\vec{k} \right] \right\} \\
& + (n_{\text{core}}^i + 2n_{\text{oh}}^i) \left[ \left( \frac{Z_a - Z}{Z_a} \right) v_{\text{nuc}}^j + v_{\text{core}}^j + v_{\text{zc}}^j \right] + n_{\text{oh}}^i \left[ v_{\text{oh}}^j - \frac{Z^* - Z}{Z_a} v_{\text{nuc}}^j \right], \tag{71}
\end{aligned}$$

where

$$\begin{aligned}
S_d^{ij} & \equiv \langle \varphi_d^i | \varphi_d^j \rangle, \\
h_1^{ji}(\vec{k}) & = \frac{\langle \varphi_d^j | \Delta_{\text{pa}} | \vec{k} \rangle \langle \vec{k} | \Delta_{\text{pa}} | \varphi_d^i \rangle}{(\epsilon_{\vec{k}} - E_d^{\text{pa}})}, \\
h_3^{ji}(\vec{k}) & = \langle \varphi_d^j | \vec{k} \rangle \langle \vec{k} | \varphi_d^i \rangle, \\
h_4^{ji}(\vec{k}) & = \langle \varphi_d^j | \vec{k} \rangle \langle \vec{k} | \Delta_{\text{pa}} | \varphi_d^i \rangle,
\end{aligned}$$

and

$$h_5^{ij}(\vec{k})$$

denotes the two terms in large parens in Eq. (67). The  $\Theta$  function in the first term of Eq. (71) has its usual meaning: it is plus one for  $\epsilon_F > E_d^{\text{pa}}$  and zero for  $\epsilon_F < E_d^{\text{pa}}$ . Also, as a matter of convenience only, we have dropped from Eq. (71) the utterly negligible terms involving  $n_{\text{nuc}}^i$  from Eqs. (21) and (64). The result (71) for  $v_{\text{ol}}$  is again otherwise exact to second order.

### C. Binding energy

The total energy may also be written as

$$E_{\text{tot}} = NE_{\text{bind}} + \sum_i E_{\text{core}}^i, \tag{72}$$

where  $E_{\text{bind}}$  is the binding energy per atom of the  $Z$  valence electrons:

$$E_{\text{bind}} = E_{\text{te}} + E_{\text{es}}^{\text{struc}} + \sum_q' |S(\vec{q})|^2 F(q) + \frac{1}{2} \sum_{i \neq 0} v_{\text{ol}}(r_i). \tag{73}$$

The primary quantities of interest in this result are, of course, the final three second-order structure-dependent terms. But to the extent that  $E_{\text{core}}^i$  differs insignificantly in the solid from its corresponding value in the free atom,  $E_{\text{bind}}$  can be directly compared to the cohesive energy plus the energy required to ionize the  $Z$  valence electrons in the free atom. This comparison is physically meaningful for nontransition metals, where  $Z$  is clearly the same in the free atom as in the solid. In principle, one should use free-atom  $d$  states (through an appropriate choice of the localization potential  $v_{\text{loc}}$ ) in computing  $E_{\text{bind}}$  for such a comparison, but this is not crucial. The zero-order terms in  $E_{\text{bind}}$  are, of course, independent of the  $d$  states and the residual dependence on  $v_{\text{loc}}$  comes indirectly through the hybridization and  $d$ -state overlap matrix elements. To the extent that the latter quantities depend weakly on  $v_{\text{loc}}$ , one expects Eq. (73) to reflect the accuracy of a Kohn-Sham calculation of the binding energy.

### V. APPLICATIONS

We have made a full application of the density-functional version of the generalized pseudopotential theory to nineteen simple and  $d$ -band metals. This study complements that presented in Paper I and we shall discuss here only selected results, with emphasis on the effect of the refinements introduced above on typical metals. In this regard, it is convenient to discuss separately simple metals, metals with empty  $d$  bands, and metals with filled  $d$  bands, as was done in paper I.

TABLE III. Various quantities of interest for aluminum computed with the four valence exchange-correlation functions  $G(q)$  discussed in the text. The quantities  $\rho_L$  and  $\nu_q$  are, respectively, the resistivity of the liquid metal and the fcc phonon frequencies at Brillouin-zone boundaries in the solid, computed as in Ref. 8. The quantities  $E_{fcc}$ ,  $E_{bcc}$ , and  $E_{hcp}$  denote the (minimum) total energies of the fcc, bcc, and hcp structures, while  $E_{bind}$  is the binding energy computed for the (observed) stable structure. All energies are in Ry,  $\rho_L$  is in  $\mu\Omega\text{cm}$ , and the  $\nu_q$  are in  $10^{12}\text{Hz}$ .

$G(q)$	0.0	SSTL	KSHL	GT	Experiment
$w(G_{111})$	0.011	0.010	0.010	0.010	0.018 <sup>a</sup>
$w(G_{200})$	0.044	0.050	0.052	0.053	0.056 <sup>a</sup>
$w(2k_F)$	0.058	0.063	0.067	0.067	
$\rho_L$	15.0	19.0	20.6	20.9	24.2 <sup>b</sup>
$F_N(2k_F)$	0.006 00	0.007 17	0.008 00	0.007 92	
$F_N(5k_F)$	0.000 15	0.000 29	0.001 21	0.000 33	
$F_N(8k_F)$	0.000 02	0.000 03	0.000 21	0.000 03	
$E_{bind}$	-4.170	-4.175	-4.192	-4.177	-4.166 <sup>c</sup>
Stable structure	fcc	fcc	fcc	fcc	fcc <sup>d</sup>
$E_{bcc}-E_{fcc}$	0.005 58	0.007 08	0.007 56	0.008 18	
$E_{hcp}-E_{fcc}$	0.001 37	0.001 67	0.001 85	0.002 14	
$\nu_q$ :					
$L[100]$	13.35	10.85	10.87	10.74	9.67 <sup>e</sup>
$T[100]$	8.01	7.19	7.08	6.92	5.81
$L[111]$	13.89	10.82	10.92	10.82	9.64
$T[111]$	5.16	5.03	5.09	4.95	4.18

<sup>a</sup> Reference 21, p. 184. Values inferred from the measured Fermi surface. The quantities  $G_{111}=1.54k_F$  and  $G_{200}=1.77k_F$  are the magnitudes of the (111) and (200) reciprocal-lattice vectors.

<sup>b</sup> At melting temperature of the metal from Reference 22.

<sup>c</sup> Reference 23.

<sup>d</sup> Reference 24.

<sup>e</sup> Measured at 80 °K by R. Stedman and G. Nilsson, Phys. Rev. **145**, 492 (1966); and quoted from M. A. Coulthard, J. Phys. C **3**, 820 (1970).

#### A. Simple metals

*A priori* we include in the category of simple metals only those elements with no  $d$  states of interest to consider. These are lithium, sodium, beryllium, magnesium, and aluminum. To these we might add the metals in which the calculated hybridization effects turn out to be very small, for instance, the group-III A and IV A metals. The simple-metal limit of our formalism is obtained by setting  $\varphi_d(\mathbf{r})=0$  for empty  $d$  bands and  $\Delta=v_{oi}(r)=0$  for filled  $d$  bands. In these limits there is only one difference in the form factor  $w(q)$  and energy wave-number characteristic  $F(q)$  obtained from the present formalism and from that given in paper I for simple metals. This is in the choice of the valence exchange-correlation function  $G(q)$ . In Table III we compare various calculated properties of aluminum for  $G(q)=0$  and for the three  $G(q)$  functions plotted in Fig. 2. Although including valence exchange and correlation is clearly

important, there is little to choose among the three nonzero  $G(q)$  functions based on comparison with experiment. The primary disadvantage of using Eq. (26) for  $G(q)$  (the KSHL function) is that it leads to a relatively long-range tail in the normalized energy-wave-number characteristic

$$F_N(q) = -(q^2\Omega_0/4\pi Z^*)F(q). \quad (74)$$

Replacing Eq. (26) with the Geldart-Taylor (GT) function<sup>13</sup> appears to be an acceptable solution to this problem, and we have done this implicitly in all the calculations discussed below.

The relationship among the four sets of theoretical results given in Table III is fairly typical of all the simple metals. The Singwi *et al.* (SSTL) function<sup>11</sup> was used in the calculations of paper I, and the results presented for the simple metals in Tables I, II, and VII of that paper remain representative of the refined theory developed here.

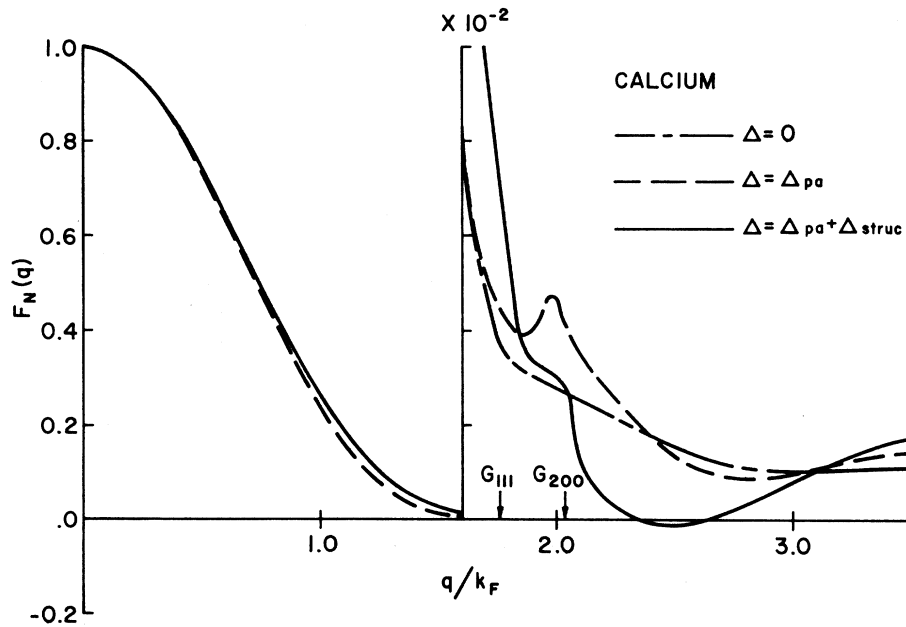


FIG. 4. Normalized energy-wave-number characteristic for calcium computed in three hybridization limits (with  $V_0 = \infty$  and  $R_0/R_{WS} = 1.0$ ), as discussed in the text. The small arrows on the horizontal scale indicate the magnitudes of the  $G_{111}$  and  $G_{200}$  reciprocal-lattice vectors in the observed fcc structure.

TABLE IV. Various quantities of interest for calcium computed in the simple-metal limit of no hybridization ( $\Delta = 0$ ), in the limit of a purely volume-dependent hybridization potential ( $\Delta = \Delta_{pa}$ ), and finally, including the full structure dependence of the hybridization ( $\Delta = \Delta_{pa} + \Delta_{struc}$ ). The quantities  $T_c$  and  $E_{ph}^0$  are, respectively, the fcc-bcc phase transition temperature (in °K) and the zero-point vibrational energy (in Ry), computed as in Ref. 7. The notation and units are otherwise the same as in Table III.

$\Delta$	0	$\Delta_{pa}$	$\Delta_{pa} + \Delta_{struc}$	Experiment
$w(G_{111})$	0.011	0.014	0.014	0.021 <sup>a</sup>
$w(G_{200})$	+0.003	-0.056	-0.056	-0.056 <sup>a</sup>
$w(2k_F)$	+0.004	-0.052	-0.052	
$\rho_L$	9.8	31.5	31.5	33.0 <sup>b</sup>
$E_{bind}$	-1.430	-1.475	-1.478	-1.458 <sup>c</sup>
Stable structure	hcp (1.63)	fcc	fcc	fcc <sup>d</sup>
$E_{bcc} - E_{fcc}$	0.000 34	0.001 67	0.001 75	
$E_{hcp} - E_{fcc}$	-0.000 31	0.000 80	0.000 90	
$E_{ph}^0$	0.001 71	0.001 75	0.001 60	0.001 64 <sup>e</sup>
$T_c$	195	660	590	721 <sup>f</sup>
$\nu_q$ :				
L[100]	5.91	5.92	5.37	
T[100]	3.99	4.24	3.88	
L[111]	5.92	5.77	5.22	
T[111]	2.43	2.57	2.36	

<sup>a</sup> Inferred from the self-consistent  $X\alpha$  ( $\alpha = \frac{2}{3}$ ) band calculation of Ref. 17. The first band gap at the  $L$  point in the Brillouin zone is approximately  $|2w(G_{111})|$ , while that at the  $X$  point is approximately  $|2w(G_{200})|$ . The quantities  $G_{111} = 1.76k_F$  and  $G_{200} = 2.03k_F$  are the magnitudes of the (111) and (200) reciprocal-lattice vectors.

<sup>b</sup> At the melting temperature of the metal from J. B. Van Zytveld, J. E. Enderby, and E. W. Collings, *J. Phys. F* **2**, 73 (1972).

<sup>c</sup> Reference 23.

<sup>d</sup> Reference 24.

<sup>e</sup> Inferred from the observed Debye temperature  $T_D = 230$  °K by the Debye formula  $E_{ph}^0 = \frac{3}{8} k_B T_D$ .

<sup>f</sup> A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **132**, 1620 (1963).

### B. Metals with empty $d$ bands

The metals with empty  $d$  bands just above the Fermi level are the heavy alkalis: potassium, rubidium, and cesium, and the heavy alkaline earths: calcium, strontium, and barium. In these metals one may conveniently work with nonoverlapping  $d$  states, corresponding to  $V_0 = \infty$  and  $R_0/R_{WS} = 1.0$  in Eq. (35), as discussed in paper I. Then, just as for simple metals,  $v_{oi}(r) = 0$  in the total energy and the form factor  $w(q)$  is modified only by the choice of  $G(q)$ . The energy-wave-number characteristic, on the other hand, is now altered by the structure dependence of the hybridization as well as the choice of  $G(q)$ . In Fig. 4, we plot  $F_N(q)$  for calcium in the limits  $\varphi_d = \Delta = 0$  (the simple-metal limit),  $\Delta = \Delta_{pa}$  (as in paper I) and

$$\Delta = \Delta_{pa} + \Delta_{struc}, \quad (75)$$

where the structure-dependent term  $\Delta_{struc}$  represents the new screening and orthogonalization-hole contributions considered above. A corresponding set of calculated physical properties is given in Table IV. From Fig. 4 we see that the effect of both  $\Delta_{pa}$  and  $\Delta_{struc}$  on  $F_N(q)$  is most significant in the important region  $1.5 < q/k_F < 3.0$ , where the first few nonzero reciprocal lattice vectors of all the common crystal structures lie. The prominent peak near  $q = 2k_F$  found in the limit  $\Delta = \Delta_{pa}$  is smoothed into a shoulder with a relatively deep minimum to its right when  $\Delta_{struc}$  is included. The net effect of  $\Delta_{struc}$  on the calculated properties given in Table IV, however, tends to be only 10% or less. In particular, the stability of the fcc crystal structure is only modestly affected by the structure dependence of the hybridization. In both hybridization limits the theoretical predictions match up very well with experiment, in sharp contrast to the simple-metal limit of no hybridization.

The effects of  $\Delta_{pa}$  and  $\Delta_{struc}$  in strontium and barium turn out to be very similar to those in calcium. (Compare Table IV, here, with Table V of paper I.) In the heavy alkalis, on the other hand, the effect of both  $\Delta_{pa}$  and  $\Delta_{struc}$  is quantitatively small, as can be appreciated by comparing Table IV of paper I with Table IV above.

### C. Metals with filled $d$ bands

In our final category are the metals with filled  $d$  bands below the Fermi level. These include the noble metals and all metals to their right in the Periodic Table. In practice, however, the strength of the  $d$ -state hybridization potential decreases very rapidly as one moves away from the noble metals, and beyond zinc, cadmium, and mercury the hy-

bridization is essentially negligible.

As discussed in paper I and above, an essential feature of metals with filled  $d$  bands is the need for spatially overlapping  $d$  states. In this case, all three characteristic functions— $w(q)$ ,  $F(q)$ , and  $v_{oi}(r)$ —are affected by our explicit treatment of the structure-dependent terms in the hybridization potential. The potential  $\Delta_{struc}$  now represents overlap contributions which modify  $v_{oi}(r)$  as well as the screening and orthogonalization hole contributions which alter  $F(q)$ . In addition, it is  $\Delta_{pa}$  alone, rather than a spherically averaged  $\Delta$  as in paper I, which appears in the plane-wave hybridization matrix element.

In Fig. 5, we plot  $F_N(q)$  for zinc in the same hybridization limits as in Fig. 4 for calcium, but with  $d$ -state localization parameters  $V_0 = 25.0$  Ry and  $R_0/R_{WS} = 1.0$  in each case. Again both  $\Delta_{pa}$  and  $\Delta_{struc}$  have a large effect on  $F_N(q)$  in the vicinity of  $q = 2k_F$ . Note, however, that the latter effect tends to be of opposite sign from that in calcium. The corresponding overlap potential is shown in Fig. 6 both in the limits  $\Delta = \Delta_{pa}$  and  $\Delta = \Delta_{pa} + \Delta_{struc}$ . The contribution of  $\Delta_{struc}$  to  $v_{oi}(r)$  is clearly very large for  $r < 2R_{WS}$  with the sign of the function and its first two derivatives being changed as  $r$  is decreased below  $2R_{WS}$ . This behavior reflects the rapid increase in magnitude of the matrix element  $\langle \varphi_d | \Delta_{oi}^j | \vec{k} \rangle$  as  $|\vec{r}_i - \vec{r}_j|$  is decreased. Also shown in Fig. 6 is the contribution of exchange and correlation to  $v_{oi}(r)$  in the two limits. Note that roughly one-half of the effect of  $\Delta_{struc}$  comes in the form of exchange and correlation terms.

The importance of  $\Delta_{struc}$  to calculated physical properties of zinc is illustrated in Table V. As in the case of calcium, the net effect of  $\Delta_{struc}$  on such properties is generally less than on the characteristic functions themselves. One very interesting result which does occur, however, is that the predicted stable structure is found to be hcp with an axial ratio very near the observed value when  $\Delta_{struc}$  is taken into account. Furthermore, this result is rather insensitive to the particular choice of  $d$  state. The latter is very satisfying and in sharp contrast to the sensitivity found in paper I, where  $\Delta_{struc}$  was effectively ignored. Both the large peak in  $F_N(q)$  near  $q = 2k_F$  and the positive slope of  $v_{oi}(r)$  for  $r < 2R_{WS}$  resulting from  $\Delta_{struc}$  appear to favor the distortion of the ideal hcp structure toward one with high  $c/a$  axial ratio.

The calculated results for cadmium and mercury are, as in paper I, similar to those for zinc. In particular, the observed stable structure of hcp ( $c/a = 1.89$ ) in cadmium is well explained by the present calculations. With  $V_0 = \infty$  and  $R_0/R_{WS} = 1.40$ , we obtain hcp (1.85), and with  $V_0 = 25.0$  Ry and  $R_0/R_{WS} = 1.0$ , we find hcp (1.86).

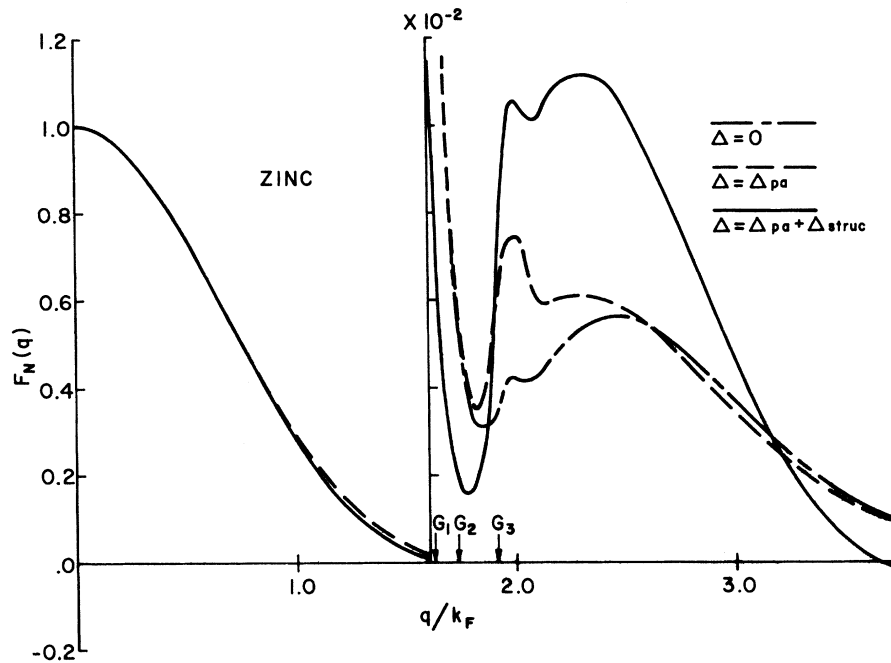


FIG. 5. Normalized energy-wave-number characteristic for zinc computed in three hybridization limits (with  $V_0 = 25.0$  and  $R_0/R_{WS} = 1.0$ ), as discussed in the text. The small arrows on the horizontal scale indicate the magnitudes of the shortest three reciprocal-lattice vectors in the observed hcp ( $c/a = 1.86$ ) structure.

TABLE V. Various quantities of interest for zinc computed in the same hybridization limits as in Table IV and with three choices of the  $d$ -state localization parameters  $V_0$  and  $R_0$ . The notation and units are otherwise the same as in Table III.

$\Delta$	0	$\Delta_{pa}$	$\Delta_{pa} + \Delta_{struct}$	Experiment		
$V_0$ (Ry)	25.0	25.0	$\infty$	$\infty$		
$R_0/R_{WS}$	1.0	1.0	1.25	1.50		
$w(G_1)$	-0.021	-0.040	-0.040	-0.044	-0.038	-0.022 <sup>a</sup>
$w(G_3)$	0.043	0.068	0.068	0.071	0.067	0.063 <sup>a</sup>
$w(2k_F)$	0.058	0.105	0.105	0.111	0.103	
$\rho_L$	18.3	38.9	38.9	42.8	37.5	37.4 <sup>b</sup>
$E_{bind}$	-2.142	-2.128	-2.139	-2.178	-2.154	-2.111 <sup>c</sup>
Stable structure	hcp (1.64)	hcp (1.72)	hcp (1.94)	hcp (1.89)	hcp (1.92)	hcp (1.86) <sup>d</sup>
$E_{bcc} - E_{fcc}$	0.003 11	0.005 46	0.005 60	0.006 36	0.005 39	
$E_{hcp} - E_{fcc}$	-0.000 52	-0.001 09	-0.002 20	-0.002 52	-0.001 86	
$E_{ph}^0$ <sup>e</sup>	0.001 50	0.001 58	0.001 22	0.001 36	0.001 23	
$\nu_q$ <sup>e</sup>						
$L[100]$	4.83	5.33	3.89	4.27	3.98	
$T[100]$	3.55	3.48	2.77	3.14	2.78	
$L[111]$	4.77	5.55	4.03	4.39	4.13	
$T[111]$	2.62	2.77	2.53	2.84	2.50	

<sup>a</sup> Reference 21, p. 183. Values inferred from the measured optical spectrum and Fermi surface. The quantities  $G_1 = 1.62k_F$  and  $G_3 = 1.91k_F$  are the magnitudes of the (0002) and (1011) reciprocal lattice vectors.

<sup>b</sup> At melting temperature of the metal from Ref. 22.

<sup>c</sup> Reference 23.

<sup>d</sup> Reference 24. The  $c/a$  axial ratio is in parentheses.

<sup>e</sup> Computed for the fcc structure.



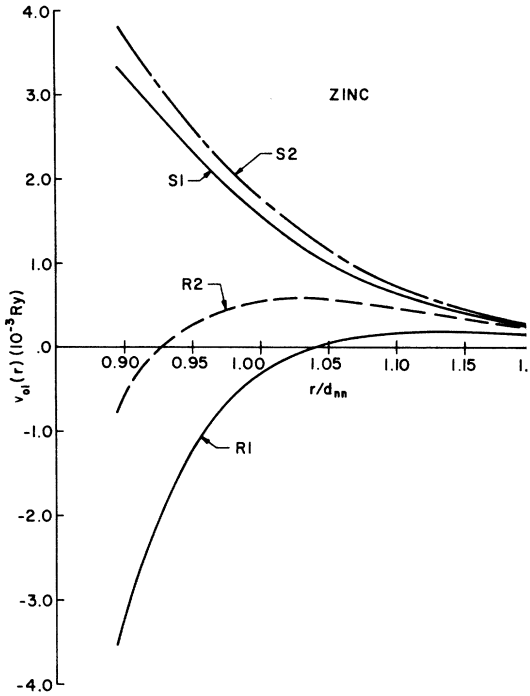


FIG. 6. Overlap potential for zinc computed in several limits (with  $V_0=25.0$  and  $R_0/R_{WS}=1.0$ ), where  $d_{nn}$  is the nearest-neighbor distance in the ideal hcp or fcc structures. The curves labeled S1 and R1 refer to the hybridization limits  $\Delta=\Delta_{pa}$  and  $\Delta=\Delta_{pa}+\Delta_{struc}$ , respectively, as discussed in the text. In the corresponding curves S2 and R2 all explicit exchange-correlation terms in the overlap potential have been set to zero. (Note,  $2R_{WS}=1.105d_{nn}$ ).

#### D. Binding energy

Lastly, we have used the equations of Sec. IV to compute the binding energy  $E_{bind}$  for the 19 metals considered above. The results are listed in Table VI together with the experimental values of  $E_{bind}$ . The agreement with experiment is within 3%, except in the three very heavy metals, mercury, thallium, and lead, where neglected relativistic effects are undoubtedly important. The theoretical results given in Table VI take full account of hybridization in the heavy alkali and alkaline-earth metals (with  $V_0=\infty$  and  $R_0/R_{WS}=1.0$ ) and in zinc, cadmium, and mercury (with  $V_0=25.0$  and  $R_0/R_{WS}=1.0$ ). From Tables IV and V, however, one can see that the net effect of the hybridization on  $E_{bind}$  is very small. This is in agreement with our previous conclusions for  $d$ -band metals,<sup>5,6</sup> but the absolute agreement with experiment is now decidedly better.

It is also rather instructive to decompose the binding energy as

$$E_{bind} = E_{fe}^0 + E_{vol} + E_{struc}, \quad (76)$$

TABLE VI. Binding energy  $E_{bind}$  and its free-electron ( $E_{fe}^0$ ), volume ( $E_{vol}$ ) and structure ( $E_{struc}$ ) components, as described in the text, for nineteen metals, in Ry.

Metal	$E_{fe}^0$	$E_{vol}$	$E_{struc}^a$	$E_{bind}$	$E_{bind}^{expt}{}^b$
Li	-0.520	+0.020	-0.018	-0.517	-0.516
Na	-0.466	-0.006	-0.001	-0.474	-0.460
K	-0.406	+0.012	0.000	-0.394	-0.388
Rb	-0.387	+0.016	0.000	-0.371	-0.370
Cs	-0.366	+0.028	-0.001	-0.338	-0.345
Be	-1.952	-0.146	-0.121	-2.219	-2.269
Mg	-1.670	-0.117	-0.009	-1.796	-1.779
Ca	-1.466	0.000	-0.011	-1.478	-1.458
Sr	-1.384	+0.039	-0.008	-1.353	-1.356
Ba	-1.351	+0.153	-0.018	-1.216	-1.259
Zn	-1.798	-0.320	-0.021	-2.139	-2.111
Cd	-1.693	-0.224	-0.009	-1.925	-1.990
Hg	-1.673	-0.215	+0.008 <sup>c</sup>	-1.880	-2.196
Al	-3.681	-0.457	-0.040	-4.177	-4.166
Ga	-3.579	-0.735	-0.097 <sup>d</sup>	-4.411	-4.419
In	-3.387	-0.506	-0.055 <sup>d</sup>	-3.948	-4.060
Tl	-3.311	-0.456	-0.048	-3.815	-4.281
Sn	-5.691	-0.992	-0.163 <sup>d</sup>	-6.846	-7.085
Pb	-5.542	-0.868	-0.141	-6.550	-7.261

<sup>a</sup> Computed in the observed crystal structure except where noted.

<sup>b</sup> Reference 23.

<sup>c</sup> Computed for the hcp ( $c/a=1.9$ ) structure.

<sup>d</sup> Computed for the fcc structure.

where  $E_{fe}^0$  represents the first three terms in the free-electron energy:

$$E_{fe}^0 = \frac{3}{5}Z\epsilon_F + Z\epsilon_{xc}(n_{unif}) - \frac{3}{5}(Ze)^2/R_{WS}; \quad (77)$$

$E_{vol}$  is the remaining volume-dependent energy

$$E_{vol} = E_{fe} - E_{fe}^0; \quad (78)$$

and  $E_{struc}$  is the sum of the three structure-dependent terms in Eq. (73). When written in this way, the binding energy is very roughly approximated by Eq. (77) alone

$$E_{bind} \sim E_{fe}^0 \quad (79)$$

as can be seen from Table VI. The first two terms in  $E_{fe}^0$  are the familiar kinetic energy and exchange-correlation energy contributions, but the third term is somewhat nontrivial. This latter term is exactly  $\frac{2}{3}$  of the electrostatic energy of a point ion of charge  $Ze$  immersed in a compensating sphere of uniform electron gas. This energy is also a rough measure of the position of the bottom of the valence energy bands with respect to vacuum.

It must be stressed, however, that only in the alkali metals, where all contributions to  $E_{vol}$  and  $E_{struc}$  are small, is Eq. (79) quantitatively reliable. In the remaining metals  $E_{vol}$  is generally significant, although the net orthogonalization hole contribution  $E_{oh}$  is always negligible and accidental

cancellation of large terms can occur, such as calcium and strontium. Equation (79) is also slightly misleading because it implies that the equilibrium atomic volume  $\Omega_0$  (determined by  $dE_{\text{bind}}/d\Omega=0$ ) depends only on the valence  $Z$ . Even in the alkali metals this is quite wrong and  $E_{\text{vol}}$  must be considered.

## VI. CONCLUSIONS

Careful consideration of the Kohn-Sham equations has allowed us to incorporate a number of significant refinements into the generalized pseudopotential theory. At the heart of this development has been the approximation of the full exchange-correlation potential as a constant plus a sum of structure-independent intra-atomic potentials, which we accomplished in Eq. (16). This result has permitted us to define and treat very precisely the structure dependence of the hybridization potential at all points in the theory, leading to important modifications in both the energy-wave-number characteristic and the overlap potential. We have not addressed here the question of the adequacy of the local Kohn-Sham theory itself, but it seems likely that more general treatments of exchange and correlation, which encompass non-local effects, can be handled in a similar manner.

Although the total external input to this formalism consists of only three numbers: the atomic number, the valence, and the atomic volume,<sup>25</sup>

reliable calculation of a wide range of properties seems to be at hand for many simple and  $d$ -band metals. Particularly satisfying in this regard is the accuracy of Eq. (39) for the  $d$ -state overlap matrix elements  $\Delta_d^{ij}$  and Eq. (73) for the binding energy, as well as the invariant prediction of the high  $c/a$  axial ratios in zinc and cadmium. All of these calculations have been very uncertain in the past. Moreover, it seems clear that the zero-order pseudoatom construction, and hence the determination of the basic governing quantities  $E_d^{\text{pa}}$ ,  $\Delta_{\text{pa}}(k)$ ,  $\Delta_d^{ij}$ , and  $w_0^{\text{pa}}(\vec{k}, \vec{q})$ , can be directly extended to transition metals.

Full application of the generalized pseudopotential theory to the noble and transition metals, however, entails many additional considerations. In transition metals one must deal with the fundamental complications that arise in the calculation of the screening electron density and the total energy.<sup>3</sup> In the case of the noble metals, the equations of Sec. IV apply directly, but the question of optimization, both with respect to the choice of  $d$ -state localization potential and the treatment of exchange and correlation, appears to be very important in the calculation of the characteristic functions. In contrast to the metals studied in Sec. V, more precise optimization criteria for determining  $V_0$  and  $R_0$  may be required in the noble and transition metals. These problems have not been fully resolved and are currently under study.

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<sup>9</sup>Throughout this paper, we shall use the standard notation  $\sum_{\vec{q}}$  and  $\sum_{i,j}$  to denote the omission of the  $\vec{q}=0$  and  $i=j$  terms, respectively, from the summation.

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<sup>14</sup>The Geldart-Taylor  $G(q)$  is exactly given by Eq. (26) in the limit  $q \rightarrow 0$  and in general depends on the choice of  $\mu_c$ . In this paper, we calculate the Geldart-Taylor

$G(q)$  consistent with the Hedin-Lundqvist correlation potential, Eq. (11).

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<sup>18</sup>In Rydberg atomic units  $\hbar = 2m = \frac{1}{2}e^2 = 1$ . Energies are in Rydbergs and distances are in Bohr radii.

<sup>19</sup>In this regard, two typographical errors in the first paper of Ref. 3 should be pointed out. In Eq. (86) of that paper the range of summation on the third and fifth sums should be  $k \geq k_F$  instead of  $k \leq k_F$ . In Eq. (102) the term  $\langle \vec{F} | P^d | \vec{F} \rangle$  should be  $\langle \vec{F} | P^d | \vec{k} \rangle \langle \vec{k} | P^d | \vec{F} \rangle$ .

<sup>20</sup>Interestingly, this manipulation is most straightforward if one starts with a full expression for  $\sum_{\alpha} \delta E_{\alpha}$  in which the small-core approximation has not been made and the core states appear in  $W_0$  in formally the same manner as the  $d$  states. The terms in Eq. (60) involving  $n_{\alpha}^i$  are obtained exactly from a careful consideration of the term

$$\sum_{\alpha \neq c,d} [-E_{\alpha} \langle \vec{k} | \varphi_{\alpha} \rangle \langle \varphi_{\alpha} | \vec{k} \rangle + (\langle \vec{k} | \varphi_{\alpha} \rangle \langle \varphi_{\alpha} | \Delta | \vec{k} \rangle + \text{c.c.})] \text{ in } \langle \vec{k} | W_0 | \vec{k} \rangle.$$

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- <sup>22</sup>N. E. Cusack, *Rep. Prog. Phys.* **26**, 361 (1963).
- <sup>23</sup>The experimental binding energy is equal to the cohesive energy plus the energy required to ionize the  $Z$  valence electrons in the free atom. The experimental cohesive energies were taken from C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 74. The experimental ionization energies were taken from *Handbook of Chemistry and Physics*, 56th ed. (Chemical Rubber, Cleveland, 1975), p. E-68.
- <sup>24</sup>W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (Pergamon, New York, 1967).
- <sup>25</sup>In principal, the input of the atomic volume  $\Omega_0$  could be eliminated by minimizing the total energy with respect to volume, although this is only profitable in practice when the lattice constant and the compressibility are the quantities of direct interest.