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Simplified local-density theory of the cohesive energy of metals

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A simplified but accurate theory of the cohesive energy of metals has been developed from the density-functional formalism of Kohn and Sham. In this theory, the total energy of both the free atom and the solid is expressed as a sum of a core and a valence binding energy, and the cohesive energy is reduced (apart from a zero-point vibrational term) to a difference in binding energies. The free-atom binding energy is directly calculated, and accurately (to within 3%) matches the experimental ionization energy in nonrelativistic elements. The binding energy of the metal, on the other hand, is obtained by the generalized pseudopotential method developed previously by the author. This latter step permits all band-structure and self-consistent screening effects to be incorporated analytically. The calculated cohesive energy agrees well with both experiment (to about 20%) and heavy numerical computation (to about 10%) in simple as well as d-band metals. More importantly, the method permits the physical origins of the cohesion to be identified in each case, and these are discussed for 22 nontransition metals. It is found that band-structure effects are important in all nonalkali metals and, in particular, that *sd* hybridization contributes 30%–60% of the cohesion in the alkaline-earth and noble metals. In addition, the large relativistic energy shifts inherent in the binding energies of the heavy metals are seen to approximately cancel in the cohesive energy.

I. INTRODUCTION

The cohesive energy of a pure metal, E_{coh}, may be defined as the total energy of the isolated atom in its ground state minus the total free energy per atom of the solid at zero temperature and pressure. Even for a nonrelativistic metal, these total energies are on the order of 10^2–10^6 eV in magnitude, while their difference is only 1–10 eV. Understandably, most theories of the cohesive energy have tried to focus on the small set of presumed physical mechanisms responsible for the cohesion, rather than on accurate calculations of the total energies themselves. The most widely and successfully treated metals in this manner have been the alkalis, where the approximate 1-eV value of E_{coh} can be explained by the classic Wigner-Seitz formula[1]

$$E_{\text{coh}} = \epsilon_s - (E_\Gamma + \tfrac{3}{5}\epsilon_F)\,. \tag{1}$$

Here ϵ_s is the binding energy of the single valence s electron in the free atom, E_Γ is the energy of the bottom of the valence or conduction band in the metal, and ϵ_F is the free-electron Fermi energy. The simplicity of Eq. (1), however, arises from three unique features of the alkali metals: (i) only one electron per atom is involved in the cohesion, so ϵ_s is just (by Koopmans' theorem) the term value of the corresponding Hartree-Fock Hamiltonian and no distinction between one-electron eigenvalues and total or binding energies need be made; (ii) the potential which determines ϵ_s also adequately determines E_Γ with only the boundary condition on the wave function being changed (from vanishing at infinity in the free atom to a zero-slope condition at the Wigner-Seitz radius in the metal); and (iii) band-structure effects in the metal are negligible. None of these simplifications is available generally, and the historical consequence of this has been a legacy of uncertainty regarding the components of E_{coh} in other metals. Particularly elusive has been the precise role of d-state electrons in raising the cohesive energies of the alkaline-earth and noble metals above those in the alkalis.

Only in recent years, with the availability of high-speed computers, have systematic cohesive-energy studies on nonalkali metals begun to appear. The bulk of the renewed interest has been in the transition metals and there have been several attempts[2-4] to quantitatively analyze the origins of cohesion in these elements. In this regard, Gelatt *et al.*[3] have made approximate calculations on the components of E_{coh} for all of the $3d$ and $4d$ transition and noble metals, using the so-called renormalized-atom method[5] to treat the solid. At the same time, atomic and solid-state computational methods have advanced to the point where accurate calculations of E_{coh} from direct total-energy subtraction have also become possible.[6-8] In particular, the local-density formalism of Kohn and Sham[9] has been employed by Janak and co-workers[7,8] to self-consistently calculate the cohesive energy, equilibrium lattice constant, and bulk modulus of all metals with atomic number $Z_a < 50$. These calculations provide useful information regarding the applicability of the local-density theory, but unfortunately, they cannot be readily dissected to supply additional insight into the nature of metallic cohesion. The present work is an attempt both to improve this situation and to complement the recent transition-metal studies by providing a comparable analysis on all simple, alkaline-earth and noble metals. We derive in this paper a simplified local-density theory of the cohesive energy of metals which combines the benefits of the first-principles Kohn-Sham formalism with the insight offered by approximation techniques such as the renormalized-atom method.

Our simplified theory is developed on the basis of several systematic approximations. First, the total energies in both the free atom and the solid are carefully separated into core and valence contributions, with the atomic valence energy being identified as the negative of that required to remove Z valence electrons from the free atom. In nontransition metals Z is given by the column number of the element in the Periodic Table, although in pure transition metals a self-consistent definition would be required. For all d-band metals, however, the energy associated with the d bands in the solid can be advantageously partitioned between the core and valence energies and in the simplest cases the calculation of E_{coh} may be essentially reduced to a difference in valence binding energies.

The second major simplification we introduce is the calculation of the valence binding energy of the metal by means of the generalized pseudopotential theory.[10,11] This approach offers some significant advantages in the study of cohesion and the appropriate density-functional version of the theory has recently been developed by the author.[11] The usual cumbersome procedure of band-structure generation, summation over occupied states, and iteration to self-consistency in the metal is bypassed entirely in this technique, as all band-structure and self-consistent-screening effects are incorporated analytically. Thus, the valence binding energy may be readily broken down into its component parts and the effect of each on the cohesive energy quantitatively assessed. On the other hand, the implementation of the generalized pseudopotential theory becomes increasingly complex as one proceeds from simple metals to metals with empty, filled, and partially-filled d bands, respectively. Only in the former three cases has the full quantitative machinery needed to calculate E_{coh} been developed, and for this reason we will confine the bulk of our attention to nontransition metals. This provides ample overlap (15 metals) with the work of Janak and co-workers[7,8] but only a minimum of overlap (3 metals) with the renormalized-atom calculations.[3]

Lastly, and as a matter of convenience only, we have ultilized two further simplifications in our development. First, the free atom is handled in the spirit of the original Kohn-Sham formalism,[9] with spin-polarization effects[12,13] neglected. This introduces a small quantitative error for elements with odd values of Z, but the magnitude of the error is systematic and has been well studied in the nontransition free atoms.[7,13] Second, the equilibrium atomic volume of the metal, Ω_0, is taken as the observed volume rather than that which minimizes the total energy, as done by Janak and co-workers.[7,8] This greatly reduces the computational effort required to obtain E_{coh}, without significantly affecting the interpretation of the results. Our external input into the calculation of the cohesive energy thus consists of Z and Ω_0 in addition to the atomic number Z_a.

In Sec. II we consider in detail the separation of the total energy into core and valence contributions, and the valence binding energies of 27 free atoms are compared with experiment. Then in Sec. III our simplified theory for E_{coh} is fully developed and applied to 22 metals, including 7 heavy metals not previously treated in either the renormalized-atom or local-density studies.

II. VALENCE BINDING ENERGY

The separation of a valence binding energy from the total electronic energy per atom, E_{tot}, is conceptually similar in both the free atom and the metal. One begins by defining the core energy E_{core} as equal to the total energy of an isolated free ion (with net charge Ze) whose electron density is exactly the same as that of the free-atom (or metal) core. A precise definition of the valence binding energy is then simply

$$E_{\text{bind}} = E_{\text{tot}} - E_{\text{core}} . \tag{2}$$

In practice the binding energy will be on the order of 5–100 eV in magnitude for nonrelativistic elements and still typically an order of magnitude larger than E_{coh}. Moreover, E_{bind} remains a complicated quantity, so that considerable care must be exercised in its approximate evaluation. In the context of the Kohn-Sham local-density formalism, part of this complexity arises from the fact that the exchange and correlation energy is a nonlinear function of the *total* electron density of the system. It is advantageous, and in the case of the metal necessary, to treat the exchange and correlation terms in an approximate manner. This introduces a small quantitative error (at most a few percent) into E_{bind}, but by applying the same approximation technique to both the free atom and the solid the bulk of the error can be made to cancel in E_{coh}.

A. Free atom

We first derive an appropriate expression for the free-atom binding energy. The total electronic energy of an atom in the local-density formalism may be written[9]

$$E_{\rm tot}^{\rm atom}=\sum_{\alpha}E_{\alpha}-\frac{1}{2}\iint\frac{e^2 n(\vec{r})\,n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,' + \int n(\vec{r})\left[\epsilon_{xc}(n(\vec{r}))-\mu_{xc}(n(\vec{r}))\right]d\vec{r}\,, \qquad (3)$$

where E_α is the eigenvalue of the self-consistent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Z_a e^2}{r}+\int\frac{e^2 n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' + \mu_{xc}(n(\vec{r}))\right)\psi_\alpha(\vec{r})=E_\alpha\psi_\alpha(\vec{r})\,, \qquad (4)$$

$n(\vec{r})$ is the total electron density of the system,

$$n(\vec{r})=\sum_{\alpha}\psi_\alpha^*(\vec{r})\,\psi_\alpha(\vec{r})\,, \qquad (5)$$

$\epsilon_{xc}(n)$ is the total exchange and correlation energy (per electron) of a free-electron gas of density n, and $\mu_{xc}(n)$ is the corresponding exchange-correlation potential:

$$\mu_{xc}(n)=\frac{d}{dn}\left[n\epsilon_{xc}(n)\right]\,. \qquad (6)$$

The sums in Eqs. (3) and (5) are, of course, over all occupied states of the free atom in its ground state.

Writing $n(\vec{r})$ as a sum of a valence and a core density,

$$n(\vec{r})=n_{\rm val}(\vec{r})+n_{\rm core}(\vec{r})\,, \qquad (7)$$

the core energy entering Eq. (2) may be taken as

$$E_{\rm core}=T(n_{\rm core})+\int n_{\rm core}(\vec{r})\left(-\frac{Z_a e^2}{r}+\frac{1}{2}\int\frac{e^2 n_{\rm core}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' + \epsilon_{xc}(n_{\rm core})\right)d\vec{r}\,, \qquad (8)$$

where $T(n_{\rm core})$ is the kinetic energy of the core electrons. Subtracting Eq. (8) from Eq. (3) gives one exactly

$$E_{\rm bind}^{\rm atom}=\sum_{\alpha={\rm val}}E_{\alpha}-\frac{1}{2}\iint\frac{e^2 n_{\rm val}(\vec{r})\,n_{\rm val}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,' + \int n_{\rm val}(\vec{r})\left[\epsilon_{xc}(n)-\mu_{xc}(n)\right]d\vec{r} + \int n_{\rm core}(\vec{r})\left[\epsilon_{xc}(n)-\epsilon_{xc}(n_{\rm core})\right]d\vec{r}\,, \qquad (9)$$

where the sum in the first term is now restricted to occupied valence states. The approximation we wish to introduce to this result involves the final two integrals. To simplify these terms we note that physically the valence electron density tends to be excluded from the core such that

$$(n_{\rm val}\,n_{\rm core})^{1/2}\ll n_{\rm val}+n_{\rm core} \qquad (10)$$

everywhere in the system.[14] For small valence-core overlap the integrand of the final term in Eq. (9) can be approximated by expanding $\epsilon_{xc}(n)$ in powers of $n_{\rm val}$ and using Eq. (6):

$$n_{\rm core}\left[\epsilon_{xc}(n_{\rm core}+n_{\rm val})-\epsilon_{xc}(n_{\rm core})\right] = n_{\rm core}\left(n_{\rm val}\frac{d\epsilon_{xc}(n_{\rm core})}{dn}+O(n_{\rm val}^2)\right) \cong n_{\rm val}\left[\mu_{xc}(n_{\rm core})-\epsilon_{xc}(n_{\rm core})\right]\,. \qquad (11)$$

The final two integrals in Eq. (9) can then be combined as

$$\int n_{\rm val}(\vec{r})\left\{\left[\epsilon_{xc}(n_{\rm core}+n_{\rm val})-\epsilon_{xc}(n_{\rm core})\right] - \left[\mu_{xc}(n_{\rm core}+n_{\rm val})-\mu_{xc}(n_{\rm core})\right]\right\}d\vec{r} \cong \int n_{\rm val}(\vec{r})\left[\epsilon_{xc}(n_{\rm val})-\mu_{xc}(n_{\rm val})\right]d\vec{r}\,. \qquad (12)$$

The free-atom binding energy is thus reduced to

$$E_{\rm bind}^{\rm atom}=\sum_{\alpha={\rm val}}E_{\alpha}-\frac{1}{2}\iint\frac{e^2 n_{\rm val}(\vec{r})\,n_{\rm val}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,' + \int n_{\rm val}(\vec{r})\left[\epsilon_{xc}(n_{\rm val})-\mu_{xc}(n_{\rm val})\right]d\vec{r}\,. \qquad (13)$$

This result becomes exact in the limit of no valence-core overlap where the left-hand side of Eq. (10) vanishes. Alternatively, Eq. (13) can be viewed as the exact total energy of a system of electrons of density $n_{\rm val}(\vec{r})$ in the presence of an external ionic potential

$$v_{\rm ion}(\vec{r})=-\frac{Z_a e^2}{r}+\int\frac{e^2 n_{\rm core}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' + \mu_{xc}(n_{\rm val}+n_{\rm core})-\mu_{xc}(n_{\rm val})\,. \qquad (14)$$

In either case, $-E_{\rm bind}^{\rm atom}$ is physically the energy required to remove the Z valence electrons from the free atom, assuming no significant relaxation of the core.

It should also be pointed out that the derivation of Eq. (13) requires no specific knowledge of the exchange-correlation functional $\epsilon_{xc}(n)$. The result thus applies to any closely related treatment of exchange and correlation satisfying Eq. (6). In particular, the popular $X\alpha$ method due to Slater[15] is encompassed by our formal results.

We have performed atomic self-consistent field calculations on 27 elements from groups IA, IIA, IB, IIB, IIIA and IVA in the Periodic Table. The exchange-correlation potential defined by Eq. (6) was taken in the form

$$\mu_{xc}(n)=\mu_x(n)+\mu_c(n)\,, \qquad (15)$$

where $\mu_x(n)$ is the familiar Kohn-Sham exchange potential,[9]

$$\mu_x(n)=-2e^2(3n/8\pi)^{1/3}\,, \qquad (16)$$

and $\mu_c(n)$ is the Hedin-Lundquist correlation potential[16]

$$\mu_c(n)=-\mu_0\ln[1+r_0(\tfrac{4}{3}\pi n)^{1/3}]\,, \qquad (17)$$

with $\mu_0=0.045$ Ry and $r_0=21$ a.u. The valence eigenvalues and wave functions obtained from solving Eq. (4) were then used in Eq. (13) to obtain the free-atom binding energy in each case. These results are given in Table I together with the corresponding experimental ionization energies.[17] The agreement with experiment is clearly very good with all trends for the nonrelativistic atoms given correctly. Except for the special case of hydrogen, Eq. (13) for the light elements ($Z_a\leqslant 38$) is accurate to within 3%. For the intermediate elements ($47\leqslant Z_a\leqslant 56$) the error ranges from 2% to 6%, while for the heavy elements ($Z_a\geqslant 79$) the error becomes 10%–22%. The latter is a reflection of the importance of relativistic effects, which, of course, are not included in Eq. (13). Interestingly, however, the relativistic energy shifts appear to cancel out in the cohesive energy, as shown in Sec. III, suggesting that such shifts are largely volume independent.

The 1.4-eV error in $E_{\rm bind}^{\rm atom}$ for the case of hydrogen is a direct consequence of our neglect of spin polarization. The local-density theory given above implicitly assumes that all spins are paired, so that spin-up and spin-down electron densities are identical:

$$n_\uparrow(\vec{r})=n_\downarrow(\vec{r})=\tfrac{1}{2}n(\vec{r})\,. \qquad (18)$$

This obviously is not true in a free atom with an odd value of Z, and with only one electron present in hydrogen the error is particularly large. Proper account of the spin polarization in hydrogen[13] lowers $E_{\rm bind}^{\rm atom}$ by about 1.1 eV and brings the result close to the observed value of −13.6 eV. Spin polarization always lowers the total energy and consequently increases $|E_{\rm bind}^{\rm atom}|$, but the magnitude of the effect falls off dramatically in multielectron atoms to 0.3–0.4 eV in Li, Na, and Al to less than 0.3 eV for elements with $Z_a\geqslant 19$.[7,13] In this regard, note that our calculated $|E_{\rm bind}^{\rm atom}|$ is less than experiment for all odd-Z elements except Cu.

B. Metal

We now turn to the corresponding treatment of the valence binding energy in the metal, $E_{\rm bind}^{\rm metal}$. The derivation of an approximate expression for this quantity is necessarily more complicated than in the free atom, but all of the pertinent details have been given previously in Ref. 11. We shall only briefly summarize here the essential features of the development which are relevant to the cohesive energy.

The total electron density in the metal is broken down into a sum of uniform, oscillatory, and localized-core contributions:

$$n(\vec{r})=n_{\rm unif}+\delta n_{\rm val}(\vec{r})+\sum_i n_{\rm core}(\vec{r}-\vec{R}_i)\,, \qquad (19)$$

where $n_{\rm unif}$ is the free-electron density

TABLE I. Valence binding energy of 27 free atoms, in eV. The theoretical values represent $-E_{\rm bind}^{\rm atom}$ as obtained from Eq. (13), while the experimental values are the measured ionization energies from Ref. 17.

Element	Theory	Experiment	Element	Theory	Experiment
H	12.21	13.60	Zn	27.70	27.35
Li	5.23	5.39	Cd	24.98	25.90
Na	5.08	5.14	Hg	24.66	29.18
K	4.28	4.34			
Rb	4.08	4.18	B	70.41	71.36
Cs	3.73	3.89	Al	53.12	53.25
			Ga	57.18	57.27
Be	27.15	27.53	In	51.00	52.68
Mg	22.82	22.68	Tl	49.46	56.33
Ca	18.06	17.98			
Sr	16.69	16.72	C	145.8	148.0
Ba	14.92	15.21	Si	102.3	103.1
			Ge	102.7	102.7
Cu	7.83	7.72	Sn	90.33	93.18
Ag	7.11	7.57	Pb	86.49	96.68
Au	7.21	9.22			

$$n_{\mathrm{unif}} = Z/\Omega_0 , \tag{20}$$

$n_{\mathrm{core}}(\vec{r} - \vec{R}_i)$ is the core density of the ith nucleus in the metal, and $\delta n_{\mathrm{val}}(\vec{r})$ represents the remaining valence (screening plus orthogonalization hole) density. In d-band metals the total d-electron density can be conveniently partitioned between δn_{val} and n_{core} such that in nontransition elements n_{core} is formally the same as the core density in the free atom. Identifying $n_{\mathrm{unif}} + \delta n_{\mathrm{val}}$ as the total valence electron density n_{val}, the analog of Eq. (13) is then obtained by a quite similar procedure. In the metal, however, we take additional advantage of the fact that both δn_{val} and the overlap of neighboring core densities are small. This allows us to approximate the full exchange-correlation potential as

$$\mu_{xc}(n) = \mu_{xc}(n_{\mathrm{unif}}) + \frac{d\mu_{xc}(n_{\mathrm{unif}})}{dn}\delta n_{\mathrm{val}} + \sum_i \left[\mu_{xc}(n_{\mathrm{unif}} + n^i_{\mathrm{core}}) - \mu_{xc}(n_{\mathrm{unif}})\right] , \tag{21}$$

with $n^i_{\mathrm{core}} \equiv n_{\mathrm{core}}(\vec{r} - \vec{R}_i)$. In addition, the sum over occupied valence states in the metal (excluding any d-state contribution already in E_{core}) has the form

$$\sum_{\alpha = \mathrm{val}} E_\alpha = T(n_{\mathrm{unif}}) + \int n_{\mathrm{unif}} \left(\int \frac{e^2 n_{\mathrm{unif}}}{|\vec{r} - \vec{r}\,'|} d\vec{r}\,' + \mu_{xc}(n_{\mathrm{unif}}) + \sum_i v_{\mathrm{ion}}(\vec{r} - \vec{R}_i) \right) d\vec{r} + \sum_{\alpha = \mathrm{val}} \delta E_\alpha , \tag{22}$$

where $v_{\mathrm{ion}}(\vec{r})$ is given by Eq. (14) with $n_{\mathrm{val}} = n_{\mathrm{unif}}$. Finally, the small quantities δn_{val} and $\sum_{\alpha = \mathrm{val}} \delta E_\alpha$ can be developed as systematic expansions in two effectively weak potentials: a pseudopotential W_0 and a d-state hybridization potential Δ.

The net result for the valence binding energy can be expressed as

$$E^{\mathrm{metal}}_{\mathrm{bind}} = E_{\mathrm{fe}} + E_{\mathrm{vol}} + E_{\mathrm{struc}} , \tag{23}$$

where E_{fe} is the free-electron binding energy associated with n_{unif},

$$E_{\mathrm{fe}} = \tfrac{3}{5} Z \epsilon_F + Z \epsilon_{xc}(n_{\mathrm{unif}}) - \tfrac{3}{5}(Ze)^2/R_{\mathrm{WS}} , \tag{24}$$

with $\epsilon_F = \hbar^2 (3\pi^2 n_{\mathrm{unif}})^{2/3}/2m$ and $R_{\mathrm{WS}} = (3\Omega_0/4\pi)^{1/3}$; and E_{vol} and E_{struc} are the remaining volume-dependent and structure-dependent contributions, respectively, arising from finite W_0 and Δ. The quantity E_{vol} is inherently first order in W_0 and Δ^2, while E_{struc} is formally second order in these quantities. For the cases of simple metals and metals with empty or filled d bands, the former can be written

$$E_{\mathrm{vol}} = \frac{2\Omega_0}{(2\pi)^3} \left(\int_{k<k_F} \langle \vec{k} | w^{\mathrm{pa}}_0 | \vec{k} \rangle \, d\vec{k} \mp \int_{k \gtrless k_F} \sum_d \frac{\langle \vec{k} | \Delta_{\mathrm{pa}} | \phi_d \rangle \langle \phi_d | \Delta_{\mathrm{pa}} | \vec{k} \rangle}{\epsilon_{\vec{k}} - E^{\mathrm{pa}}_d} \, d\vec{k} \right) + \cdots \tag{25}$$

in a plane-wave $|\vec{k}\rangle$, localized d-state $|\phi_d\rangle$ representation, where w^{pa}_0 and Δ_{pa} are the appropriate lowest-order contributions to W_0 and Δ, respectively, and the dots represent second-order terms. The hybridization term in Eq. (25), of course, is present only for d-band metals, with the upper signs appropriate to filled d bands (e.g., in the noble metals) and the lower signs to empty d bands (e.g., in the heavy alkaline-earth metals). The second-order terms in E_{vol} and E_{struc} arise both from the second-order components of W_0 and Δ^2 and the lowest-order components of W_0^2 and Δ^4 terms. All of these contributions can be obtained systematically without further approximation and the full expressions are given in Ref. 11. The results are too complex to warrant reproducing here, but for divalent and polyvalent metals they must normally be retained in an accurate calculation of $E^{\mathrm{metal}}_{\mathrm{bind}}$. Physically, the first-order terms reflect the average shift in the actual valence-band energies relative to their zero-order values, while the second-order terms encompass detailed band-structure and self-consistent-screening effects.

The notation pa in w^{pa}_0, Δ_{pa}, and E^{pa}_d denotes "pseudoatom" and refers to the zero-order pseudoatom construction[11,18] used to define and calculate these quantities. The pseudoatom itself represents a zero-order estimate of the actual electron density and potential associated with a single Wigner-Seitz cell of the metal:

$$n_{\mathrm{pa}}(\vec{r}) = n_{\mathrm{unif}} + n_{\mathrm{core}}(\vec{r}) \tag{26}$$

and

$$v_{\mathrm{pa}}(\vec{r}) = v_{\mathrm{unif}}(\vec{r}) + v_{\mathrm{ion}}(\vec{r}) , \tag{27}$$

where v_{unif} is the Coulomb potential arising from that portion of n_{unif} contained within the sphere $r<R_{\text{WS}}$. The pseudopotential matrix element entering Eq. (25) is given by

$$\langle\vec{k}|w_0^{\text{pa}}|\vec{k}\rangle = \langle\vec{k}|v_{\text{pa}}|\vec{k}\rangle + \sum_{\alpha=c,d}(\epsilon_{\vec{k}} - E_\alpha^{\text{pa}})\langle\vec{k}|\phi_\alpha\rangle\langle\phi_\alpha|\vec{k}\rangle + \sum_d(\langle\vec{k}|\Delta_{\text{pa}}|\phi_d\rangle\langle\phi_d|\vec{k}\rangle + \text{c.c.}), \tag{28}$$

where $\epsilon_{\vec{k}} = \hbar^2 k^2/2m$,

$$E_\alpha^{\text{pa}} = \langle\phi_\alpha| -(\hbar^2/2m)\nabla^2 + v_{\text{pa}}|\phi_\alpha\rangle, \tag{29}$$

and the localized inner-core and d states, ϕ_c and ϕ_d, are those which make up the core density:

$$n_{\text{core}}(\vec{r}) = \sum_{\alpha=c,d}\phi_\alpha^*(\vec{r})\,\phi_\alpha(\vec{r}), \tag{30}$$

with only occupied states, of course, included in the latter sum. The expectation value E_d^{pa} represents a first approximation to the mean position of the d bands in the metal. The hybridization potential Δ_{pa}, on the other hand, arises from the fact that ϕ_d is not an exact eigenstate of $-(\hbar^2/2m)\nabla^2 + v_{\text{pa}}$. The extra localization potential v_{loc} needed to make it an eigenstate precisely defines Δ_{pa}:

$$\Delta_{\text{pa}} = v_{\text{loc}} - \langle\phi_d|v_{\text{loc}}|\phi_d\rangle. \tag{31}$$

In practice it is v_{loc} that is fixed,[19] and both ϕ_d and Δ_{pa} are self-consistently determined in terms of the choice made.[11,18]

The zero-order pseudoatom may be contrasted with the renormalized atom of Watson *et al.*[5] In the latter, the electron density within the Wigner-Seitz sphere is derived entirely from the free atom by renormalizing each orbital to unity within the Wigner-Seitz sphere and setting its value to zero outside the sphere. This renormalization has little effect on the tightly bound core electrons, but a large effect on the loosely bound valence electrons, with typically one electron's worth of charge being transferred from outside to inside the Wigner-Seitz sphere by renormalization.[5] Of course, the renormalized valence electron density will not be uniform, but its spatial variation outside the core is usually not rapid. In the case of copper, in fact, Gelatt *et al.*[3] found the Coulomb potential associated with this density rather close to v_{unif}. As far as the cohesive energy of d-band metals is concerned, probably a more significant difference between the zero-order pseudoatom and the renormalized atom concerns the treatment of exchange and correlation. Unlike the local exchange-correlation potential entering v_{pa}, the renormalized-atom method employs a nonlocal Hartree-Fock-like exchange operator which attaches a full self-Coulomb hole to the Wigner-Seitz cell. It is argued[5] that the latter is more appropriate for the d electrons of transition metals for which the method is primarily intended. Of interest in this paper is the overlapping case of the noble metals where the choice has a large effect on the hybridization contribution to E_{coh}, as discussed in Sec. III.

It must also be stressed that the renormalized atom and the zero-order pseudoatom are utilized to somewhat different ends in practice. The former purports to adequately approximate the actual electron density in the metal, such that the potential, valence band structure, and sum of one-electron valence energies may be directly calculated from it. But the renormalized-atom itself is not self-consistent and the actual Hartree-Fock energy gained in renormalization does *not* approximate the cohesive energy, as has been emphasized by Wood *et al.*[20] for the alkali metals. The success of the method is thus dependent upon the insensitivity of the computed band structure to errors in the assumed electron density and potential. The zero-order pseudoatom, on the other hand, acts only to define first-order expansion parameters and any errors in n_{pa} are, in effect, self-consistently corrected in the determination of the metal binding energy.

The zero-order pseudoatom technique was used in Ref. 11 to obtain $E_{\text{bind}}^{\text{metal}}$ and its three components defined in Eq. (23) for 19 of the metals under consideration here. These calculations employed the same form of $\epsilon_{xc}(n)$ used in the free-atom calculations discussed above and by Janak and co-workers[7,8] in their local-density studies. Values of E_{fe}, E_{vol}, E_{struc}, and $E_{\text{bind}}^{\text{metal}}$ are listed in Table VI of Ref. 11 and have been used unaltered in the cohesive energy analysis presented below. Added to these results for the present study have been corresponding first-order calculations on copper, silver, and gold.[19,21]

III. COHESIVE ENERGY

To obtain the cohesive energy one must now relate $E_{\text{bind}}^{\text{metal}}$ to the total free energy of the metal, $F_{\text{tot}}^{\text{metal}}$. For a metal with N identical atoms at zero temperature and pressure, this relationship is simply

$$F_{\text{tot}}^{\text{metal}} = N(E_{\text{bind}}^{\text{metal}} + E_{\text{core}} + E_{\text{ph}}^0), \tag{32}$$

where E_{ph}^0 is the familiar zero-point vibrational energy

$$E_{\text{ph}}^0 = \frac{1}{2N}\sum_{\vec{q}} h\omega_{\vec{q}}. \tag{33}$$

The phonon frequencies $\omega_{\vec{q}}$ may be obtained entirely within the framework of the generalized pseudopotential theory from a knowledge of the structure-dependent energy $E_{\rm struc}$.[11,18] In practice, of course, $E_{\rm ph}^0$ is at most a small fraction of the cohesive energy. We retain this contribution here only for completeness and because it was also included in the previous local-density studies[7,8] (although in an empirical fashion through the measured Debye temperature).

The next step is to equate the free-atom and metal core energies. In doing this we note from Eq. (8) that $E_{\rm core}$ depends only on the core electron density and hence on the localized inner-core and d orbitals. In practice the inner-core states obtained from the zero-order pseudoatom are virtually identical with those of the free atom. The precise shape of the d states, on the other hand, is controlled by the localization potential. It is possible to choose $v_{\rm loc}$ such that ϕ_d is exactly a free-atom d state, but this is neither necessary nor an optimum procedure in practice.[11,18] For empty-d-band metals, of course, ϕ_d is unfilled and makes no contribution to either the core density or energy. In filled-d-band metals, on the other hand, the practical requirement is only that $\phi_d(\vec{r})$ for $r<R_{\rm WS}$ closely approximate the free-atom wave function and this condition is fulfilled for the d states used in the present work.[19]

More generally, e.g., in most transition metals, one must also account for any change in d-state occupation between the free atom and the metal before cancelling core energies. This requires first promoting the free-atom electrons to an excited-state configuration corresponding to the valence assumed in the metal. The energy needed to accomplish this promotion, $E_{\rm pro}$, must then be subtracted from $E_{\rm coh}$.

For all simple, alkaline-earth and noble metals, no promotion is required and the cohesive energy is just

$$E_{\rm coh} = E_{\rm bind}^{\rm atom} - E_{\rm bind}^{\rm metal} - E_{\rm ph}^0 . \qquad (34)$$

Using our calculated values of $E_{\rm bind}^{\rm atom}$ from Table I and the values of $E_{\rm bind}^{\rm metal}$ and $E_{\rm ph}^0$ from Refs. 11 and 21, we have evaluated Eq. (34) for all 22 nontransition metals. In Table II we compare our values of $E_{\rm coh}$ for representative metals with those obtained by Janak *et al.*[7] by direct total-energy subtraction in the limit of no free-atom spin polarization. Except for the anomalous case of beryllium, the agreement is within about 10%, with our values of $E_{\rm coh}$ systematically lower than the total-energy-subtraction ones. Table II also indicates the quantitative effect of spin-polarization in the odd-Z elements.

The relatively small cohesive energy we calculate in beryllium seems to be closely correlated with our neglect of higher-order contributions to $E_{\rm bind}^{\rm metal}$. Very approximate calculations on simple metals[22] show that the third-order energy is always negative and hence lowers $E_{\rm bind}^{\rm metal}$ and raises $E_{\rm coh}$, in accord with the requirements of Table II. The unique situation in beryllium presumably comes about because of the large pseudopotential and the corresponding slow convergence of $E_{\rm bind}^{\rm metal}$ in this metal. In this regard, we find the net second-order contribution to $E_{\rm bind}^{\rm metal}$ in beryllium to be 1.70 eV (or 59% of $E_{\rm coh}$) and an order of magnitude larger than that of any other divalent or monovalent metal.

The importance of Eq. (34) for $E_{\rm coh}$ is that it may be readily analyzed using the results of Sec. II. If one regards the Wigner-Seitz formula, Eq. (1), as the benchmark of our understanding of cohesion in nontransition metals, then it is natural to separate $E_{\rm coh}$ into a sum of four components:

$$E_{\rm coh} = \Delta E_{\rm fe} + \Delta E_{sp} + \Delta E_{sd} + \Delta E_{\rm ph}^0 , \qquad (35)$$

where (i) $\Delta E_{\rm fe}$ is the free-electron-band formation

TABLE II. Cohesive energy of representative metals in the Kohn–Sham local–density formalism, as calculated from the simplified theory developed in the text and from direct total–energy subtraction. All values are in eV.

Calculation	Present work	Total-energy subtraction[a]		Experiment[b]
Free-atom spin polarization	No	No	Yes	
Li	1.76	2.01	1.64	1.63
Na	1.34	1.43	1.10	1.11
K	1.07	1.13	0.90	0.93
Be	2.89	4.00	4.00	3.32
Mg	1.57	1.64	1.64	1.51
Ca	2.01	2.23	2.23	1.84
Cu	4.22	4.45	4.20	3.49
Al	3.62	4.02	3.83	3.39

[a] Reference 7.

[b] Reference 23.

energy:

$$\Delta E_{\mathrm{fe}} = E_{\mathrm{bind}}^{\mathrm{atom}} - E_{\mathrm{fe}} - Z\langle 0|w_0^{\mathrm{pa}}|0\rangle$$
$$= E_{\mathrm{bind}}^{\mathrm{atom}} - Z(E_\Gamma + \tfrac{3}{5}\epsilon_F)\,, \tag{36}$$

with

$$E_\Gamma = \langle 0|w_0^{\mathrm{pa}}|0\rangle - \tfrac{3}{5}Ze^2/R_{\mathrm{WS}} + \epsilon_{xc}(n_{\mathrm{unif}}) \tag{37}$$

and $|0\rangle \equiv |\vec{\mathrm{k}} = 0\rangle$; (ii) ΔE_{sp} is the *sp* band-structure energy obtained by formally setting $\Delta = 0$ for filled *d* bands and $\phi_d = 0$ for empty *d* bands in $E_{\mathrm{bind}}^{\mathrm{metal}}$:

$$\Delta E_{sp} = \frac{2\Omega_0}{(2\pi)^3}\int_{k<k_F}\sum_{\alpha=c,d}\left[-E_\alpha^{\mathrm{pa}}|\langle 0|\phi_\alpha\rangle|^2 - (\epsilon_{\vec{\mathrm{k}}} - E_\alpha^{\mathrm{pa}})\,|\langle\vec{\mathrm{k}}|\phi_\alpha\rangle|^2\right]d\vec{\mathrm{k}} + \cdots\,, \tag{38}$$

using Eqs. (25) and (28), noting that $\langle\vec{\mathrm{k}}|v_{\mathrm{pa}}|\vec{\mathrm{k}}\rangle$ is independent of $\vec{\mathrm{k}}$, and where the sum over α includes only occupied states; (iii) ΔE_{sd} is the remaining *sd* hybridization energy in $E_{\mathrm{bind}}^{\mathrm{metal}}$:

$$\Delta E_{sd} = \frac{2\Omega_0}{(2\pi)^3}\Bigg(\int_{k\gtrless k_F}\sum_d \frac{|\langle\vec{\mathrm{k}}|\Delta_{\mathrm{pa}}|\phi_d\rangle|^2}{|\epsilon_{\vec{\mathrm{k}}} - E_d^{\mathrm{pa}}|}\,d\vec{\mathrm{k}}$$
$$- \int_{k<k_F}\sum_d\left[2|\langle\vec{\mathrm{k}}|\Delta_{\mathrm{pa}}|\phi_d\rangle\langle\phi_d|\vec{\mathrm{k}}\rangle| + \Theta(E_d^{\mathrm{pa}} - \epsilon_F)(\epsilon_{\vec{\mathrm{k}}} - E_d^{\mathrm{pa}})\,|\langle\vec{\mathrm{k}}|\phi_d\rangle|^2\right]d\vec{\mathrm{k}}\Bigg) + \cdots\,, \tag{39}$$

again using Eqs. (25) and (28) and noting that $\epsilon_F - E_d^{\mathrm{pa}}$ is positive (negative) for filled (empty) *d* bands; and (iv) ΔE_{ph}^0 is the zero-point vibrational contribution

$$\Delta E_{\mathrm{ph}}^0 = -E_{\mathrm{ph}}^0\,. \tag{40}$$

The second form of Eq. (36) is, of course, a simple generalization of the Wigner-Seitz formula with E_Γ being identified as the binding energy of an electron at the bottom of the valence band in the metal.

We have listed in Table III E_{coh} and its four components, together with the experimentally observed cohesive energy,[23] for each of the 22 metals considered here. Note first that the overall agreement with experiment for E_{coh} is within 20% for nonrelativistic metals ($Z_a \leqslant 56$) and still within 33% for the relativistic metals. Equally important is the fact that all trends with both atomic number and valence are given correctly, apart from the minor exception of the ordering of E_{coh} in strontium and barium. The next point to notice is that, outside of the alkali metals, neither the quantitative agreement with experiment nor even the qualitative trends with Z_a and Z in E_{coh} can be explained by free-electron-band formation alone. Although ΔE_{fe} gives positive cohesion in all cases except beryllium, it tends to increase with Z_a in a given column in contrast to the behavior of E_{coh}. The *sp* band-structure energy ΔE_{sp} is responsible for correctly reversing the trend and its variation for a fixed valence is easily understood from the first-order terms in Eq. (38). Because the matrix element $\langle 0|\phi_\alpha\rangle$ is nonzero only for *s* states, each *s* core state contributes positively while all *p*, *d*, and *f* core states contribute negatively to ΔE_{sp}. The ratio of non-*s* to *s* core states goes from zero in the second period (lithium and beryllium) to a value greater than one in the sixth period, so that ΔE_{sp} tends to decrease as one moves down a given column. Physically, this behavior may be interpreted as the effect of energy-level repulsion in the solid: Core levels push valence levels of the same symmetry to higher energy.

Finally, the relative importance of the *sd* hybridization energy in *d*-band metals can be seen from Table III. Note that ΔE_{sd} is negligible in the heavy alkali metals but contributes 30%–55% of E_{coh} in the heavy alkaline earths and 45%–60% of E_{coh} in the noble metals, before falling off and becoming slightly negative in the group IIB elements. This behavior can be readily explained in terms of Eq. (39). When the *d* bands are in close proximity to the Fermi level, as in the heavy alkaline-earth and noble metals, the first, and inherently positive, term in ΔE_{sd} is dominant. But the position of the *d* bands falls rapidly in energy as one moves to the right from the noble metals and already in the group-IIB metals the second, negative term in Eq. (39) wins out. At the same time, the magnitude of the hybridization matrix element $\langle\vec{\mathrm{k}}|\Delta_{\mathrm{pa}}|\phi_d\rangle$ decreases rapidly, so that ΔE_{sd} in the group-IIIA and -IVA metals, which was explicitly set to zero in the present calculations, indeed becomes negligible.

It is of interest to compare our results with those of obtained by Gelatt *et al.*[3] from the re-

TABLE III. Cohesive energy $E_{\rm coh}$ and its free-electron ($\Delta E_{\rm fe}$), *sp* band-structure (ΔE_{sp}), *sd* hybridization (ΔE_{sd}), and zero-point-vibrational ($\Delta E^{0}_{\rm ph}$) contributions, as described in the text, for 22 metals, in eV.

Metal	$\Delta E_{\rm fe}$	ΔE_{sp}	ΔE_{sd}	$\Delta E^{0}_{\rm ph}$	$E_{\rm coh}$	$E^{\rm expt\ a}_{\rm coh}$
Li	1.23	0.57	0.0	−0.04	1.76	1.63
Na	1.39	−0.03	0.0	−0.02	1.34	1.11
K	1.21	−0.16	0.03	−0.01	1.07	0.93
Rb	1.16	−0.22	0.03	−0.01	0.95	0.85
Cs	1.09	−0.27	0.05	−0.00	0.87	0.80
Be	−0.86	3.87	0.0	−0.12	2.89	3.32
Mg	1.35	0.24	0.0	−0.03	1.57	1.51
Ca	1.78	−0.39	0.65	−0.02	2.01	1.84
Sr	1.87	−0.71	0.53	−0.01	1.69	1.72
Ba	2.01	−1.28	0.88	−0.01	1.60	1.90
Cu	1.82	−0.08	2.48	−0.03	4.22	3.49
Ag	1.93	−0.28	1.34	−0.02	2.99	2.95
Au	1.89	−0.40	2.12	−0.01	3.61	3.81
Zn	1.19	0.23	−0.04	−0.02	1.36	1.35
Cd	1.68	−0.24	−0.24	−0.01	1.18	1.16
Hg	1.83	−0.48	−0.47	−0.01	0.89	0.67
Al	2.36	1.31	0.0	−0.04	3.62	3.39
Ga	1.71	1.07	0.0	−0.01	2.77	2.81
In	2.97	−0.30	0.0	−0.01	2.67	2.52
Ti	3.37	−0.97	0.0	−0.01	2.39	1.88
Sn	1.25	1.50	0.0	−0.01	2.74	3.14 [b]
Pb	2.06	0.49	0.0	−0.01	2.55	2.03

[a] Reference 23.

[b] α−Sn, the semiconducting form.

normalized-atom method in the overlapping cases of potassium, copper, and silver. To make this comparison, we identify their conduction-band contribution to $E_{\rm coh}$ as the sum of our free-electron-band formation and *sp* band-structure energies:

$$\Delta E_{\rm cond} = \Delta E_{\rm fe} + \Delta E_{sp} . \qquad (41)$$

Our values of $\Delta E_{\rm cond}$ and ΔE_{sd} are listed together with the renormalized-atom values in Table IV. As expected, there is basic agreement in the case of potassium, where the renormalized-atom method reduces to a Wigner-Seitz calculation with $E_{\rm coh}$ given by Eq. (1). In copper and silver, on the other hand, our values of $\Delta E_{\rm cond}$ and ΔE_{sd} are all 0.4–1.0 eV higher in energy than the renormalized-atom estimates. This is in spite of the fact that our present noble-metal results do not include second- and higher-order contributions, which are expected to be positive.[21] As can be seen from Table II, only about 0.25 eV of the discrepancies in $\Delta E_{\rm cond}$ can be attributed to our neglect of spin polarization. The differences in ΔE_{sd}, on the other hand, seem closely correlated with the respective treatments of exchange and correlation in the two methods. The local-density exchange-correlation potential is effectively weak in comparison to the $l=2$ component of a Hartree-Fock-type potential, so that the *d* bands are wider and sit higher in the free-electron valence bands with the former. In this regard, it has been established[24] in copper that the local-density theory overestimates the size of the Fermi surface necks by about 20%. This clearly results from an excess of *sd* hybridization at the Fermi level and suggests that our value of $\Delta E_{sd} = 2.48$ eV is similarly too large. In-

TABLE IV. Present theory vs the renormalized-atom method (RA) for the cohesive energy $E_{\rm coh}$ and its conduction-band ($\Delta E_{\rm cond}$), *sd* hybridization (ΔE_{sd}), and zero-point-vibrational ($\Delta E^{0}_{\rm ph}$) components in the three metals where the existing calculations overlap. All values are in eV; the RA and experimental results are from Refs. 3 and 23, respectively.

	$\Delta E_{\rm cond}$	ΔE_{sd}	$\Delta E^{0}_{\rm ph}$	$E_{\rm coh}$
K:				
Present	1.05	0.03	−0.01	1.07
RA	0.90	•••	•••	0.90
Experiment	•••	•••	•••	0.93
Cu:				
Present	1.74	2.48	−0.03	4.22
RA	0.8	1.9	•••	2.7
Experiment	•••	•••	•••	3.49
Ag:				
Present	1.65	1.34	−0.01	2.99
RA	1.1	0.3	•••	1.4
Experiment	•••	•••	•••	2.95

terestingly, the observed cohesive energy of 3.5 eV in copper may be obtained by reducing our ΔE_{sd} by 20% and subtracting the 0.25-eV spin-polarization energy from ΔE_{cond}. In silver, on the other hand, the local-density theory appears to be rather accurate. Here the renormalized-atom potential puts the d bands too low in energy,[3] resulting in a very small calculated hybridization contribution to E_{coh}. In this case our value of ΔE_{sd} seems the more reasonable of the two.

It is also of interest to contrast the values of ΔE_{sd} in Table IV with other previous calculations of this quantity. The original renormalized-atom studies of the cohesive energy by Watson and Ehrenreich[2] used independent band-structure estimates of 2.25 eV in copper and 2.0 eV in silver, which are in line with the above conclusions. Other early work,[25,26] however, suggested that the hybridization contribution to E_{coh} was essentially negligible in copper and negative in silver. Both of these conclusions were implied, in fact, in our own initial application of the generalized pseudopotential theory to the noble metals.[25] Fortunately, the apparent contradiction with the present work is mostly a matter of the definition of ΔE_{sd}. In our original calculational technique, setting $\Delta = 0$ had the here unwanted effect of shifting the free-electron bands down in energy with respect to the core and d levels. The result of this was to attach a substantially different meaning to the hybridization contribution to $E_{\text{bind}}^{\text{metal}}$ and E_{coh} than given in Eq. (39).

The other report of a negligible value of ΔE_{sd} in copper was due to Deegan.[26] Using a simplified resonance form of the transition-metal band-structure equations,[27] he derived the approximate limiting formula

$$\Delta E_{sd} = -(5/\pi) W_d \ln |(\epsilon_F - E_d)/E_d| , \qquad (42)$$

where E_d and W_d are the position and width of the d resonance of a single-site potential in the metal. From this result Deegan estimated $\Delta E_{sd} = 0.13$ eV in copper, which is about a factor of 20 smaller than we have obtained here. In this case, the discrepancy arises from the heretofore unnoticed fact that Eq. (42) is very inaccurate in both the alkaline-earth and noble metals. As we had pointed out previously,[10] the formula itself can be obtained from the generalized pseudopotential theory using certain simplifying approximations. The quantitative inadequacy of these approximations can best be appreciated by returning to the common origin of both Eq. (42) and the first-order components of Eq. (39) in terms of the full-d-state self-energy $\Gamma_{dd}(E)$,[10]

$$\begin{aligned}\Delta E_{sd} &= \frac{1}{\pi} \operatorname{Im} \sum_d \lim_{\epsilon \to 0} \int_0^{\epsilon_F} \frac{\Gamma_{dd}(E)}{E + i\epsilon - E_d} dE \\ &= \frac{1}{\pi} \sum_d \mathrm{P} \int_0^{\epsilon_F} \frac{\operatorname{Im}\Gamma_{dd}(E)}{E - E_d} dE \\ &\quad - \sum_d \operatorname{Re}\Gamma_{dd}(E_d)\,\Theta(\epsilon_F - E_d) , \end{aligned} \qquad (43)$$

where P denotes the principal value of the integral which follows. If one expands $\Gamma_{dd}(E)$ in terms of the hybridization potential Δ and E_d, the top line of Eq. (43) can be integrated exactly term by term. Equation (39), apart from the definitionally inserted step function $\Theta(E_d^{\text{pa}} - \epsilon_F)$, derives from making the lowest-order approximations $\Delta = \Delta_{\text{pa}}$ and $E_d = E_d^{\text{pa}}$ to the exact result. If, on the other hand, one neglects the energy dependence of $\Gamma_{dd}(E)$ by approximating

$$\operatorname{Im}\Gamma_{dd}(E) \sim \operatorname{Im}\Gamma_{dd}(E_d) = -\tfrac{1}{2} W_d , \qquad (44)$$

and for filled-d-band metals

$$\operatorname{Re}\Gamma_{dd}(E_d) \sim 0 , \qquad (45)$$

one obtains the Deegan formula from the second line of Eq. (43). Making the appropriate identifications[11,18]

$$E_d = E_d^{\text{pa}} \qquad (46)$$

and (in Rydberg atomic units)

$$W_d = 2\Omega_0 k_d \Delta_{\text{pa}}^2(k_d) , \qquad (47)$$

with

$$\langle \vec{\mathrm{k}}_d | \Delta_{\text{pa}} | \phi_d \rangle = -4\pi \Delta_{\text{pa}}(k_d) Y_{2m}(\vec{\mathrm{k}}_d) \qquad (48)$$

and $k_d = (E_d^{\text{pa}})^{1/2}$, we find that Eq. (42) underestimates ΔE_{sd} by 2.2 eV in copper and, at the same time, overestimates ΔE_{sd} by 4.0 eV in calcium. Thus in both the alkaline-earth and noble metals an order of magnitude error results from the approximations (44) and (45). Unfortunately, the predictions of Eq. (42) have often been sited as justification for neglecting sd hybridization in treating the cohesion of the noble metals.[28]

It is interesting to note, however, that the approximations (44) and (45) appear to fare better in pure transition metals. For partially filled d bands, E_d in the denominator of the top line of Eq. (43) must be replaced by $E_d + \Gamma_{dd}(E)$,[10] so that Eq. (42) is generalized to

$$\Delta E_{sd} = -\frac{5}{2\pi} W_d \ln \left| \frac{(\epsilon_F - E_d)^2 + (W_d/2)^2}{E_d^2 + (W_d/2)^2} \right| . \qquad (49)$$

Using the structure-independent resonance parameters of Pettifor[29] for iron ($E_d = 0.540$, $W_d = 0.088$, and $\epsilon_F - E_d = 0.121$ Ry), Eq. (49) gives $\Delta E_{sd} = 2.7$ eV. This compares favorably with the approximate 3.0-eV value obtained by Gelatt *et al.*[3] More generally, the prospects of extending the full theory of Secs. II and III to transition metals appear good, but this clearly would require a substantial developmental effort.

A more immediate possibility is a component-by-component analysis of related aspects of cohesion, such as the equilibrium atomic volume and the bulk modulus, for the 22 metals treated in Table III. Work of this kind has recently been carried out on copper and titanium by Gelatt *et al.*[3] and on the 4d transition metals by Pettifor.[4] The favorably experience of Janak and co-workers[7,8] in applying the local-density theory to all ground-state properties bodes well for a successful analysis with the present theory. Such a study could potentially be very informative in the d-band alkaline-earth and noble metals and also in the heavy metals, where the apparent weak volume dependence of the relativistic energy shifts could be more closely examined.

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$$\left(\sum_{\text{core, val}} \langle \psi_{\text{val}} | \psi_{\text{core}} \rangle = 0\right) \ll \left(\sum_{\text{val}} \langle \psi_{\text{val}} | \psi_{\text{val}} \rangle + \sum_{\text{core}} \langle \psi_{\text{core}} | \psi_{\text{core}} \rangle = Z_a \right).$$

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