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Core overlap interactions in metals*†

Roy Benedek
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

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Short-range interatomic forces associated with the overlap of closed core shells in both simple and noble metals have been investigated by means of the Heitler-London approach. The required overlap integrals were evaluated numerically; core orbitals were represented by neutral-atom Hartree-Fock wave functions. The calculated overlap interactions were found to vary exponentially with separation, as expected. For most simple metals, the overlap interaction is small compared with the screened-Coulomb interaction, until separations considerably smaller than the nearest-neighbor spacing are reached. In noble metals, on the other hand, the overlap and screened-Coulomb potentials are comparable at the nearest-neighbor position. Some general features of overlap potentials are discussed. The construction of a composite interatomic potential by interpolation between low- and high-energy theories is investigated.

I. INTRODUCTION

The interatomic forces in simple metals arise primarily from two separate effects: (a) a screened-Coulomb interaction that includes the Coulomb repulsion between bare ion cores as well as conduction-electron screening; and (b) a core-overlap interaction that accounts for the exchange forces which occur when wave functions of adjacent atomic cores overlap. It is assumed that one may distinguish clearly between core electrons and valence electrons. In simple metals, the valence electrons occupy nearly-free-electron-like bands, whereas the core-electron states are quite similar to those in isolated atoms.

Numerous calculations of screened-Coulomb interactions for simple metals exist in the literature. Most of these are based on the pseudopotential and pseudoatom models.[1] On the other hand, few calculations exist of the core-overlap potential in metals, although core-overlap interactions for rare gases and ionic crystals have been studied extensively. In the present work, the core-overlap interaction in simple metals is investigated by means of the Heitler-London (HL) method. Using the HL approach, one may calculate the interaction between a pair of closed-shell ions in a simple quantum-mechanical variational approximation. This interaction is expressed in terms of overlap integrals involving the core-electron wave functions. Employing neutral-atom Hartree-Fock wave functions, we have evaluated these integrals numerically for several metals.

It is of interest to compare the core-overlap interaction with the screened-Coulomb interaction in a metal. Not surprisingly, it is found that, for metals in which the outermost closed shell contains only *s* and *p* electrons, the core-overlap potential is negligible at normal lattice separations and begins to compete with the screened-Coulomb potential only at considerably shorter range. However, for several metals that contain *d* electrons in the outermost closed shell, overlap effects are quite important even at the nearest-neighbor spacing.

The interatomic potential has a strong bearing on many static and dynamical properties of metals. In particular, the interatomic potential at short range is important to the description of phenomena at high pressure, atomic collisions, and crystal defects. In the present paper, we will comment on some of the implications of the calculated potentials for lattice dynamics as well as for point defects and radiation damage. In the description of certain radiation-damage phenomena, the scattering cross sections that correspond to high-energy small-impact-parameter collisions are required. However, the theoretical techniques mentioned thus far, i.e., the HL method and pseudopotential theory, apply only to interaction energies $\lesssim 1$ eV. An alternative approach, in which the energy is characterized as a functional of the total electron density, has been employed over a much wider energy range.[2] The Thomas-Fermi and Thomas-Fermi-Dirac methods, for example, fall within this category. Recently, Hartree-Fock atomic wave functions, rather than statistical charge densities, have been employed in density-functional calculations of interatomic interactions.[3,4] The density-functional methods entail considerably less computational effort than the fully quantum-mechanical approaches. Comparison will be made between the HL calculations of the present work and density-functional calculations of core-overlap interactions.

In Sec. II, the formulation of the HL method and its application to the calculation of core-overlap interactions in metals are discussed. A review is given of the use of pseudopotentials in the calculation of screened-Coulomb interactions. The results of calculations of core-overlap potentials are presented and discussed in Sec. III. The s-p electron core metals and d-electron core metals are considered separately. In Sec. IV, an additional discussion is given of some of the approximations inherent in the HL approach. In Sec. V, the construction of a composite interatomic potential by interpolation between low- and high-energy theories is considered.

II. FORMULATION

The application of the HL method to calculate the closed-shell repulsion between a pair of Ne atoms was carried out by Bleick and Mayer.[5] The somewhat simpler problem of the interaction between two He atoms has also been treated in the HL framework.[6] The basic ingredients of HL may be summarized as follows: (a) expression of the wave function of a two-atom system as a Slater determinant of Hartree-Fock atomic core orbitals; (b) evaluation of the total energy as the expectation value of the Hamiltonian with respect to this wave function; and (c) neglect of all but direct and single exchange processes. Subtracting the energy corresponding to infinite separation of the atoms from the energy at separation R, one obtains[5] an expression for the overlap potential Φ_{ol} that has three types of contributions:

$$\Phi_{ol}(R)=E_C+E_{xc}+E_{xx} \ . \tag{1}$$

The first of these is the Coulomb interaction between the cores, which accounts for direct processes. The other two terms arise from the exchange of electrons between the two cores. E_{xc} may be interpreted[7] as the interaction between a positive "exchange charge" and the core charge and E_{xx} as the self-energy of this exchange charge, E_C, E_{xc}, and E_{xx} are defined[5] in terms of two-center overlap integrals.

In the case of He-He interactions, a useful approximation has been obtained[7]:

$$\begin{aligned} &E_C \simeq -2s^2e^2/R \ , \quad E_{xx} \simeq -4s^2e^2/R, \\ &E_{xc} \simeq 8s^2e^2/R \ , \end{aligned} \tag{2}$$

and therefore,

$$\Phi_{ol} \simeq 2s^2e^2/R \ , \tag{3}$$

where

$$s=\int d^3r\, \psi(\vec{r})\psi(\vec{r}-\vec{R})$$

is the overlap integral for the He 1s wave function, and e is the electronic charge. The quantity $4s^2$ is sometimes identified as the exchange charge[7] q_{ex}, and one may then write

$$\Phi_{ol} \simeq q_{ex}e^2/2R \ . \tag{4}$$

As we describe later, relations somewhat analogous to Eqs. (2) and (4) also apply to materials more complex than He.

A necessary condition for the validity of the HL approach is that the overlap parameter[5] $\mathcal{S}$ (equal to one-half the exchange charge) be small relative to unity. In the range of separations in which this requirement is satisfied, one may in practice restrict attention to overlap integrals that involve only outer shell electrons. This greatly reduces the required computational labor.

The above discussion refers to a two-atom system. Unfortunately, the HL approach is not directly generalizable to many atom systems. When clusters of many atoms are considered, $\mathcal{S}$ becomes large, and multiple exchange processes become important.[8] We do not deal with these difficulties in the present work, restricting our consideration here to two-body interactions. Three- and four-body forces associated with core overlap have been treated in a perturbation theory framework by Lombardi and Jansen.[9]

The HL approach may be adapted to metals in the following manner. The total potential is written

$$\Phi=\Phi_{sC}+\Phi_{ol} \ , \tag{5}$$

where Φ_{sC}, the screened-Coulomb interaction, comprises the bare interaction $Z_v^2e^2/R$ between ions of valence Z_v as well as the conduction-electron screening. Accordingly, the overlap potential is redefined as

$$\Phi_{ol}=E_{Cr}+E_{xc}+E_{xx} \ , \tag{6}$$

where the "residual" Coulomb interaction, given by

$$E_{Cr}=E_C-Z_v^2e^2/R \ ,$$

would vanish the absence of core overlap.

The overlap potential for two metallic ions, defined in Eq. (6), thus may be calculated exactly analogously to the overlap potential for two rare gas atoms, given in Eq. (1). It is important to recognize, however, that the problem of the overlap interaction between two ions in free space is not identical to that in a metallic environment. In a metal, the valence electrons screen each ion; this screening is manifested directly in Φ_{sC} and also indirectly in Φ_{ol}. As a consequence of screening, the core wave functions in a metal are nearly identical to those in a free atom. On the other hand, when two ions are brought close to each other in free space, the cores are polarized, and consequently a distortion of the core wave functions (relative to free-atom wave functions) occurs. Now, the HL approach, which does not allow for wave-function distortion, would be inappropriate for calculating the interaction between ions in free space; however, it should be reasonably valid for treating interactions in metals, at least when the separation is not too small. At quite small separations, of course, core–wave-function distortion does occur as the interpenetration of the cores becomes greater and the conduction-electron screening becomes less effective.

Wave-function–distortion effects are included in the molecular-orbital self-consistent-field method,[10] which goes beyond the HL approximation. Although the molecular-orbital self-consistent-field method is superior to the HL method for calculating intramolecular interactions, the latter would seem more appropriate for dealing with the overlap interaction of ions in a metal in the range of separations in which screening is effective.

Another source of interatomic interaction, which is not taken into account in Eq. (5), is the van der Waals or dispersion force. Normally, this is assumed to be negligible for simple metals, although little discussion of this point exists in the literature. Recently, the van der Waals interaction in noble metals has been calculated,[11] with screening effects included.

Equations (5) and (6) provide the basis for our investigation of interatomic forces in the low-energy ($\Phi \lesssim 1$ eV) regime. We have evaluated the overlap integrals entering Eq. (6) numerically for a number of metals, employing neutral atom nonrelativistic Hartree-Fock wave functions calculated by Mann.[12] The difficult two-electron overlap integrals occurring in E_{xx} were calculated by means of the spherical harmonic expansion procedure developed by Kunimune.[13] A detailed description of the entire calculational procedure will appear in a separate report.

For all materials studied in this work, the calculated overlap potentials are well approximated by the exponential Born-Mayer[14] form

$$\Phi_{01} = A e^{-R/\rho} , \tag{7}$$

where A and ρ are constants characteristic of the particular atomic cores being considered. The results of least-squares fits of A and ρ to Φ_{01} for several metals are given in Table I.

As mentioned earlier, the screened-Coulomb potential Φ_{sc} has been studied by means of pseudopotential techniques.[1] In general, the interaction is expressed in terms of the Fourier transform of the normalized energy wave-number characteristic $F_N(q)$,

$$\Phi_{sC}(R) = \frac{2Z^{*2}e^2}{\pi} \int_0^\infty [1 - F_N(q)]\, j_0(qR)\, dq , \tag{8}$$

where Z^* is the effective charge (slightly larger than the valence Z_v), and $j_0(x)$ is the zero-order spherical Bessel function $\sin x/x$. Unfortunately, the energy wave-number characteristic $F_N(q)$ is not uniquely defined for a given material; it varies with specific assumptions of the pseudopotential model. For a linearly screened local pseudopotential, one obtains[1]

$$F_N(q) = \left(\frac{4\pi Z e^2}{\Omega q^2}\right)^{-2} [w_b(q)]^2 \left(\frac{\epsilon_H(q) - 1}{\epsilon(q)}\right),$$

where Ω is the atomic volume, $w_b(q)$ is the form factor for the bare ionic pseudopotential, $\epsilon_H(q)$ is the Hartree dielectric function, and

$$\epsilon(q) = 1 + [\epsilon_H(q) - 1][1 - G(q)] ,$$

with $G(q)$ a correction for exchange and correlation. An important feature of the pseudopotential model is that the pair interaction Φ_{sC} is meaningful only in considering rearrangements of atoms at constant total volume. If the over-all volume is changed, volume-dependent contributions to the energy must be taken into account.[1] Experience has shown that $\Phi_{sC}(R)$ is quite sensitive to the exact form of $F_N(q)$, which depends on factors such as (a) whether the chosen pseudopotential is local or nonlocal[15,16]; (b) the choice of $G(q)$, which corrects the dielectric function for exchange and correlation[17]; (c) the treatment of conduction-electron–core-electron exchange[17b]; (d) the treatment of the orthogonalization hole[18]; (e) effective-mass corrections[19]; and (f) nonlinear corrections to the conduction-electron screening of the ions.[20] The sensitivity of Φ_{sC} to the above-mentioned factors increases with the valence. For

TABLE I. Born-Mayer parameters fitted by least squares to calculated overlap potentials for the materials discussed. The final column refers to the range over which the fit was performed.

Materials	A (eV)	ρ (Å)	Range (Å)
Ne	6300	0.206	1.58–2.12
Na	22 200	0.168	1.32–2.12
Mg	52 500	0.140	1.32–2.12
Al	115 000	0.118	1.32–1.85
Cu	3390	0.246	2.15–2.55
Ag	9120	0.260	2.48–2.88
Au	9160	0.276	2.48–2.88
Zn	5130	0.221	2.26–2.66
Ga	18 500	0.181	2.04–2.44
K	41 100	0.231	2.12–2.91
Rb	52 200	0.258	2.38–3.18
Cd	27 400	0.229	2.07–2.97
Pb	213 000	0.191	1.99–2.39

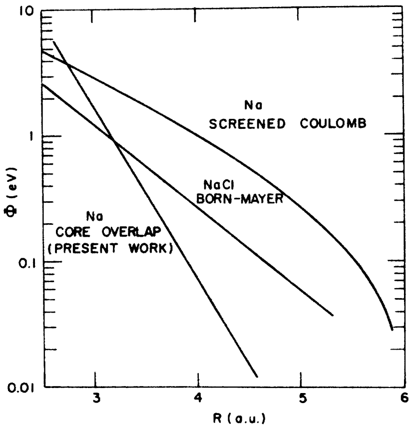

FIG. 1. Core-overlap and screened-Coulomb potentials for Na and empirical Born-Mayer potential for NaCl.

alkali metals, virtually all calculations give rise to a screened-Coulomb interaction that has a minimum and is negative in the vicinity of the nearest-neighbor position. In the case of Al, on the other hand, some calculations show such a minimum near the first-neighbor position, whereas others exhibit no minimum in this range.[15,17a] This sensitivity occurs because the value of Φ_{sC} is a small difference between large numbers; its magnitude is generally of the order of or less than 1% of the bare Coulomb interaction until quite small separations are reached. The extent of the cancellation is enhanced with increasing valence.

In the present work, we are interested in comparing Φ_{sC} with Φ_{01} to ascertain in what range of R they become competitive and to assess their relative importance. Because of uncertainties in the calculations of both quantities, one should perhaps not regard either as being known to much better than a factor of 2. Despite this reservation, we shall see that a number of meaningful, and in some cases quantitative, comparisons can be made.

III. RESULTS

When discussing the core-overlap potential Φ_{01}, it is useful to distinguish between metals that contain only s and p electrons (referred to as s-p core metals) and those containing d electrons (referred to as d-core metals) in their outermost closed shells. The former will be considered first.

A. *s-p* core metals

In this section we compare calculated core-overlap and screened-Coulomb potentials for some s-p core metals and discuss their relationship to to certain properties. Various general aspects of the overlap potential and its calculation are also discussed.

Figure 1 shows the overlap potential calculated for Na. For comparison, an empirically determined Born-Mayer potential for NaCl,[21] and a screened-Coulomb potential[22] Φ_{sC} for Na, based on the optimized model pseudopotential of Shaw,[23] are also shown. In early calculations[24a] of the phonon spectrum of Na, the overlap contribution was estimated from the Born-Mayer interaction of NaCl; at that time no calculation of Φ_{01} appropriate to Na metal was available.[24a] It was later pointed out by Vosko[25] that, because of the large atomic radius of the Cl^- ion, such a procedure grossly overestimates the effect of overlap. Assuming the NaCl Born-Mayer interaction were appropriate, one would obtain a roughly 10% contribution to the nearest-neighbor Born–von Kármán force constants of Na due to overlap.[24a] However, on the basis of the present overlap interaction for Na metal, one calculates overlap contributions about two orders of magnitude smaller. Therefore, if overlap is neglected in calculating the Na force constants, the error incurred is < 1%, which substantiates Vosko's remarks.[25]

Referring to Fig. 1, one also notes that the screened-Coulomb interaction Φ_{sC} dominates the overlap interaction Φ_{01} for separations greater than about half the nearest-neighbor spacing (7.01 a.u.). This is plausible in view of the small empirical ionic radius of Na,[26] $R_i = 1.85$. The crossover between Φ_{sC} and Φ_{01} occurs roughly at $2R_i$.

Interatomic potentials for Al are illustrated in Fig. 2. Values for Φ_{sC} were again taken from Ref.

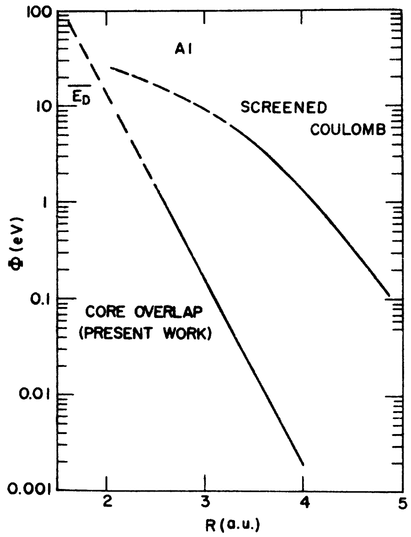

FIG. 2. Core-overlap and screened-Coulomb potentials for Al.

22. Because of its large nuclear charge, this metal has an even smaller core than Na. Therefore, core-overlap effects are insignificant until rather high energies are reached. Even a self-interstitial atom, which probes the interatomic potential at separations considerably smaller than the nearest-neighbor spacing (5.4 a.u.), is governed almost entirely by Φ_{sC}. Recent work[27] has shown that self-interstitials in Al occur in the [100] split dumbbell configuration, and the separation of the split pair is ~4.5 a.u. One observes in Fig. 2 that Φ_{01} is still quite small at this separation. Extrapolating the curves to higher energies (cf. the dashed lines in the figure), one would predict that Φ_{01} becomes competitive with Φ_{sC} at energies of the order of the displacement threshold,[28] $E_d = 16$ eV.

Recently, Friedli and Ashcroft[29] have calculated the lattice parameter as a function of pressure up to 3 Mbar for Al. At 3 Mbar they obtain a nearest-neighbor spacing of 4.2 a.u. Even at this pressure the overlap interaction is quite small.

We have seen that for Na and Al the overlap interaction is considerably smaller than the screened-Coulomb interaction at the nearest-neighbor separation. This is generally true for simple metals. It is, therefore, somewhat difficult to find a direct experimental test of the calculated overlap interactions. Overlap interactions are, however, more accessible in the case of ionic crystals such as the alkali halides. Gilbert[30] has postulated certain combining rules that would allow one to extract Born-Mayer parameters for the individual ions from empirical data on ionic crystals. He tested these rules for a set of alkali halides that consist of combinations of five alkali and four halide ions for which accurate spectroscopic data were available. Consistent "soft-sphere radii" and "softnesses" were found for the nine ions in question. It is interesting to compare Gilbert's Born-Mayer parameters with HL calculations of alkali-metal interactions. In Table II such a comparison is made for Na, K, and Rb. As one may observe, the agreement is excellent in the case of Na, although somewhat less satisfactory for K and Rb.

TABLE II. Born-Mayer parameters calculated in the present work are compared with those obtained by Gilbert from an application of combining rules to alkali halides.

	A (10^4 eV) Present work	A (10^4 eV) Gilbert	ρ (Å) Present work	ρ (Å) Gilbert
Na	2.22	1.86	0.168	0.158
K	4.11	1.92	0.231	0.211
Rb	5.22	2.52	0.258	0.229

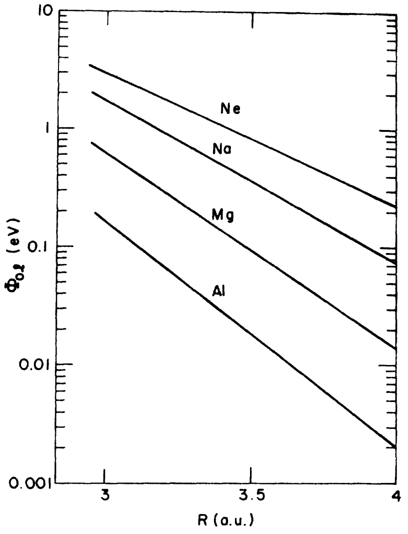

FIG. 3. Core-overlap potentials for third period elements Ne through Al.

In the remainder of this section some general features of the calculated overlap potentials are discussed.

In Fig. 3 overlap interactions for the elements Ne through Al are plotted. As the nuclear charge increases with a given row of the Periodic Table, the core size decreases and hence the overlap potential decreases. The slope $1/\rho$ of a given exponential potential [cf. Eq. (7)] may be referred to as its "hardness." The hardness is seen in Fig. 3 to increase with atomic number. This behavior is readily understood in terms of the core-electron properties. The wavefunction of a core electron may be roughly represented as $\psi \sim \exp(-2\sqrt{\mathcal{E}}\, r)$ at large r,[31] where $\mathcal{E}$ is the binding energy. The overlap integrals for such wavefunctions vary exponentially with $\sqrt{\mathcal{E}}$ and therefore $\rho \sim 1/\sqrt{\mathcal{E}}$. The extent to which this simple scaling relation is obeyed may be seen in Fig. 4, where $\rho\sqrt{\mathcal{E}}$ is plotted for the elements Ne through Al and Cu through Ga. The binding energies were taken from the calculations of Mann.[12] One observes that the plotted quantity is roughly constant.

According to Eq. (2), E_C, E_{xc}, and E_{xx} are mutually proportional in the case of He-He interactions. In view of the exponential behavior of the overlap integral s, it follows that one obtains essentially straight parallel lines when these quantities are plotted as functions of R on a semilog scale. This proportionality was also found to be obeyed for the third period elements studied in the present work. Figure 5 illustrates the results for Al. One observes that the curves for E_{Cr}, E_{xc}, and E_{xx} are nearly parallel, but the relative mag-

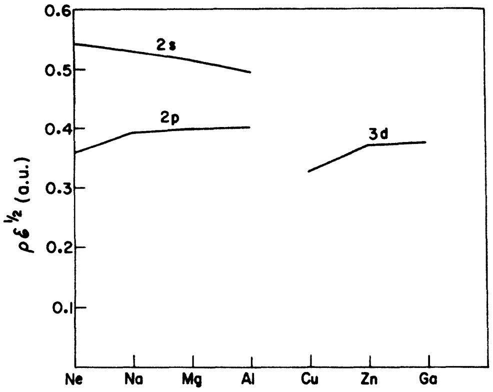

FIG. 4. The product of the softness ρ and the square root of the binding energy $\mathcal{E}$ of outermost closed-shell electrons. The latter is taken from the atomic HF calculations of Mann.

nitudes are somewhat different than for He. The ratios E_{xx}/E_{xc} and E_{Cr}/E_{xc} for a given material depend particularly on the nuclear charge Z, as is shown in Fig. 6. As Z becomes larger, the relative magnitude of E_{xc} increases.

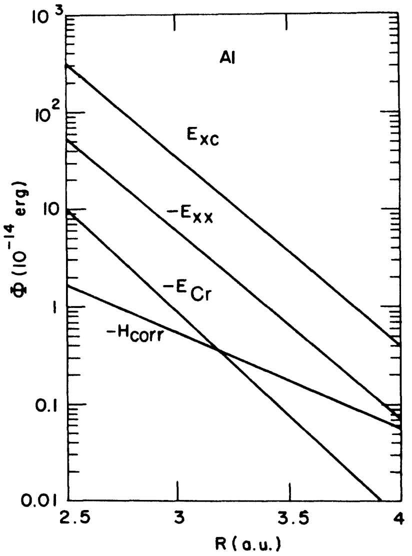

FIG. 5. Individual terms contributing to core-overlap potential in the HL formulation; H_{corr} is an estimate of the contribution of core-core correlation to the potential (see Sec. IV).

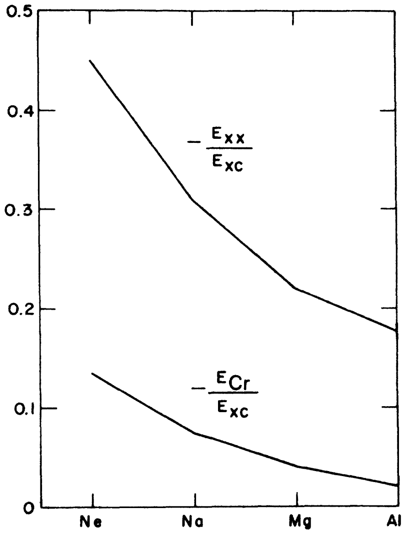

FIG. 6. The ratios E_{xx}/E_{xc} and E_{Cr}/E_{xc} obtained for elements Ne through Al. Averaged values were taken since these quantities vary slightly with the internuclear separation.

The proportionality of E_{Cr}, E_{xc}, and E_{xx} has a counterpart in the density-functional approach[2] mentioned earlier and we digress briefly to discuss this. In the density-functional approach, the total energy of a given system is written in the form

$$E = \int \mathcal{F}(n(\vec{r}))\, d^3r ,$$

where $\mathcal{F}$ is a functional of the total electron density $n(\vec{r})$. The form of this functional is determined from a consideration of the energetics of a free-electron gas.[2] If one considers a two-atom (a, b) system characterized by electron density $n_{ab}(\vec{r})$, then the pair interaction potential may be written

$$\Phi = \int \mathcal{F}[n_{ab}] - \mathcal{F}[n_a] - \mathcal{F}[n_b]\, d^3r , \tag{9}$$

where $n_a(\vec{r})$ and $n_b(\vec{r})$ are, respectively, the electron densities associated with isolated atoms a and b. Now, $\mathcal{F}$ is commonly divided into four parts: $\mathcal{F} = \mathcal{F}_k + \mathcal{F}_{ex} + \mathcal{F}_{Coul} + \mathcal{F}_{corr}$, corresponding to kinetic, exchange, Coulomb, and correlation energies, respectively. Substituting this relation into Eq. (9), one may decompose the pair interaction in a similar manner

$$\Phi = H_k + H_{ex} + H_{Coul} + H_{corr} . \tag{10}$$

It is interesting to compare Eq. (10) with Eq. (1). Roughly speaking, E_c corresponds to H_{Coul}, E_{xc} to H_k, and E_{xx} to H_{ex}. (H_{corr} has no counterpart in the HL approach.) When a detailed numerical comparison is made, based, for example, on the results for Ar-Ar interactions presented by Gordon and Kim,[4] one finds that H_k and H_{ex} are somewhat smaller in absolute magnitude than E_{xc} and E_{xx}, respectively. (E_C and H_{Coul} are formally identical.) The slopes of the logarithm of $E_{xc}(R)$, $E_{xx}(R)$, and $H_k(R)$ are rather similar, whereas that of $H_{ex}(R)$ is somewhat smaller. The over-all core-overlap interaction Φ_{01} for the alkali metals and for Ne specified in Table I may be compared with results given for these materials by Gordon and Kim.[3,4]

The density-functional results are uniformly smaller than the HL values; for Ne the difference is only (10–20)%, but for K, for example, the results differ by roughly a factor of 4. Gordon and Kim employed different wave functions from those used in the present work, but this would not account for such a large discrepancy. At present there is no clear cut criterion to establish which approach, HL or the density-functional method, gives better results for core-overlap interactions in metals.

We return now to our discussion of the HL calculations. The terms E_{xx} and E_{xc} constitute the largest contributions to Φ_{01}, E_{Cr} being somewhat smaller. E_{xx} and E_{xc} may be thought of as arising from exchange charge interactions, as discussed in Sec. II. It is somewhat appealing, therefore, to attempt to express the overlap interaction approximately in terms of a pointlike exchange charge.[7,32] This charge is located between the atoms and is of magnitude

$$q_{\mathrm{ex}} = 4 \sum_{\alpha,\beta} |s_{\alpha\beta}|^2 ,$$

where

$$s_{\alpha\beta} = \int d^3r\, \psi_\alpha(\vec{r})\psi_\beta(\vec{r}-\vec{R}) .$$

α refers to a core orbital on atom a and β refers to a core orbital on atom b. In an attempt to generalize Eqs. (2) and (3), Dick and Overhauser[7] suggested the form

$$\Phi_{01} = \gamma q_{\mathrm{ex}} e^2/R , \tag{11}$$

where γ is a constant for each pair of atoms considered; in the case of He-He interactions, $\gamma = \frac{1}{2}$. Fitting Eq. (11) to the exponential Born-Mayer form, Eq. (4), for several metals, we obtain softness parameters ρ rather close to those corresponding to the full HL calculation (given in Table I). Unfortunately, at present no reliable prescription exists for determining the constant γ, other than performing the full HL calculation according to Eq. (3).

B. *d* core metals

For metals with d electrons in their outermost closed shells, the atomic cores are relatively larger, and core-overlap effects are more pronounced than in the simple metals. For example, core-overlap effects constitute the major contribution to the shear elastic constants of Cu,[33] whereas they contribute negligibly to the elastic constants of metals we have been considering. In d core metals, however, a complicating feature exists that is not present in the simple metals, namely, the hybridization of the d electrons and the valence electrons. Because of hybridization, some question exists as to the applicability of the methods described in Sec. II. It was assumed there that core and valence electrons were clearly distinguishable or, in the framework of band theory, they are separated by a large energy gap and the core electrons occupy essentially flat bands. In the noble metals, on the other hand, the d-electron bands overlap and mix with the valence band. We now argue that this does not necessarily invalidate the model described in Sec. II. Because of symmetry considerations, only one of the five d bands in Cu hybridizes appreciably.[34] The others are relatively flat. Therefore, in calculating properties, such as Φ_{01}, which average over all the d electrons, the neglect of hybridization is probably a reasonable approximation. On the other hand, hybridization definitely has an appreciable effect on Φ_{sC}. This occurs because of the delicate balance between the bare Coulomb interaction and the valence electron screening, which was discussed in Sec. II; even a small modification in the screening can produce a large relative change in Φ_{sC}.

Figure 7 shows the separate contributions to the interatomic potential of Cu in the vicinity of the nearest-neighbor site. The overlap potential Φ_{01} was calculated on the basis of Eq. (6). The $3d$ electrons were treated as tightly bound core states. The screened-Coulomb interaction Φ_{sC} was calculated from the energy wave-number characteristic $F_N(q)$ obtained by Moriarty.[35] The work of Moriarty, based on a generalized pseudopotential developed by Harrison[36] represents the most ambitious attempt to include hybridization

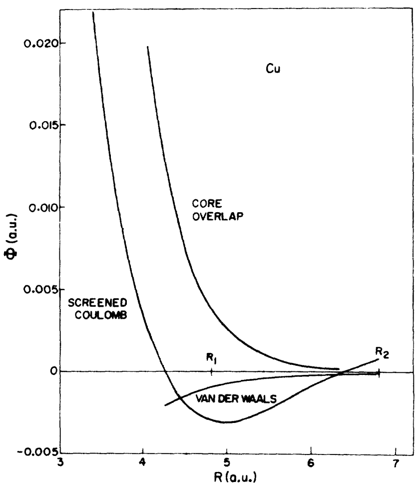

FIG. 7. Contributions to the interatomic potential of Cu associated with the core-overlap, screened-Coulomb, and van der Waals interactions, respectively.

TABLE III. Born–von Kármán force constants for the two nearest neighbors in Cu. The first two rows give the contributions associated with the core-overlap and the screened-Coulomb interactions, respectively. The sum of these terms appears in the third row. The bottom row is taken from Ref. 38.[a]

	$l = \langle 110 \rangle$			$l = \langle 200 \rangle$	
Category	ϕ_{xx}	ϕ_{zz}	ϕ_{xy}	ϕ_{xx}	ϕ_{yy}
Overlap	1.22	−0.24	1.46	0.04	0.00
Screened Coulomb	0.82	−0.05	0.87	−0.37	0.03
Total	2.04	−0.29	2.33	−0.33	0.03
Experiment	1.314	−0.123	1.498	0.006	−0.011

[a] Units: 10^4 dyn/cm.

in a calculation of the total energy of a *d*-electron metal.[37] The van der Waals interactions Φ_{vdW} was taken from the work of Rehr *et al.*[11] One observes in the figure that the overlap potential becomes dominant at separations just below the nearest-neighbor spacing. The van der Waals interaction is small but not entirely negligible.

It is interesting to compare the Born–von Kármán force constants predicted from these potentials with those obtained by fitting to observed phonon spectra. Such a comparison is made in Table III for the first two nearest neighbors. The fitted force constants are taken from the work of Svensson *et al.*[38] The results shown in the table indicate that the overlap and the screened-Coulomb interactions make contributions of roughly the same magnitude to the nearest-neighbor force constants. The sum of these contributions is somewhat higher than the experimentally determined force constants.

Force constants calculated for Ag and Au are compared with fitted force constants in Tables IV and V, respectively. The discrepancy between theory and experiment is somewhat larger for these metals than for Cu. Two factors that may contribute to this are: (i) the use of nonrelativistic wavefunctions in the calculations of Φ_{01}; and (ii) the neglect of many-body (i.e., nonpairwise) forces. For heavy metals, relativistic effects on the outer-shell wave functions may be significant and will tend to reduce Φ_{01}. Analysis of the phonon spectra of Au has shown[39] that a pairwise central force (axially symmetric model) is not capable of giving a good fit to the data. This is in contrast to the situation for Cu and Ag, the phonon spectra of which can be fit reasonably well under the assumption of axial symmetry.

TABLE IV. Born–von Kármán force constants for the two nearest neighbors in Ag. The first two rows give the contributions associated with the core-overlap and the screened-Coulomb interactions, respectively. The sum of these terms appears in the third row.[a] The bottom row is taken from W. A. Kamitakahara and B. N. Brockhouse [Phys. Lett. 29, A639 (1969)].

	$l = \langle 110 \rangle$			$l = \langle 200 \rangle$	
Category	ϕ_{xx}	ϕ_{zz}	ϕ_{xy}	ϕ_{xx}	ϕ_{yy}
Overlap	1.54	−0.31	1.84	0.03	0.00
Screened Coulomb	0.75	−0.03	0.78	−0.31	0.03
Total	2.29	−0.34	2.62	−0.28	0.03
Experiment	1.071	−0.175	1.232	0.006	−0.023

[a] Units: 10^4 dyn/cm.

TABLE V. Born–von Kármán force constants for the two nearest neighbors in Au. The first two rows give the contributions associated with the core-overlap and the screened-Coulomb interactions, respectively. The sum of these terms appears in the third row. The bottom row is taken from Ref. 39.[a]

	$l = \langle 110 \rangle$			$l = \langle 200 \rangle$	
Category	ϕ_{xx}	ϕ_{zz}	ϕ_{xy}	ϕ_{xx}	ϕ_{yy}
Overlap	2.58	−0.55	3.13	0.08	−0.01
Screened Coulomb	1.00	−0.08	1.08	−0.41	0.04
Total	3.58	−0.63	4.21	−0.33	0.03
Experiment	1.643	−0.654	1.993	0.404	−0.127

[a] Units: 10^4 dyn/cm.

It is interesting to compare the overlap potential for noble metals calculated in the present work with semiempirically fitted Born-Mayer potentials. The latter have been determined by fitting the parameters A and ρ to various experimental data. [Actually it is more common to specify $A' = A \exp(-R_1/\rho)$, where R_1 is the nearest neighbor separation, than A.] In Table VI we list Born-Mayer parameters for Cu obtained by a number of authors.[40] The large diversity of values is a consequence of the fact that different properties were selected to be fit and of the differing assumptions adopted regarding the valence-electron contribution to those properties. In general, hybridization is not taken into account. It may be noted that the softness ρ obtained in the present calculation is somewhat larger than that of any of the semiempirical potentials. It is possible that, in neglecting hybridization, the semiempirical fits have systematically underestimated electronic effects and overestimated overlap effects.

We mentioned previously that the neglect of hybridization may be a questionable feature of the present calculations of overlap potentials for noble metals. For the multivalent metals to the right of the noble metals in the Periodic Table,

TABLE VI. Born-Mayer parameters for Cu obtained by semiempirical fitting procedures. $R_1 = 2.55$ Å is nearest-neighbor spacing.

$A\exp(-R_1/\rho)$ (eV)	ρ (Å)	Authors
0.032	0.150	Huntington and Seitz
0.051	0.200	Dienes
0.053	0.183	Huntington
0.038	0.148	
0.073	0.201	Hiki, Thomas, and Granato
0.096	0.186	Collins
0.139	0.219	Jaswal and Girifalco
0.096	0.191	
0.051	0.196	Gibson *et al.*
0.017	0.106	Sinha
0.045	0.196	Thompson
0.045	0.159	Daniels and Smith
0.063	0.171	Thomas
0.011	0.095	Mann and Seeger
0.041	0.154	
0.077	0.188	
0.075	0.203	
0.091	0.211	
0.108	0.217	
0.075	0.175	
0.078	0.193	
0.129	0.234	
0.044	0.167	
0.016	0.105	
0.046	0.155	
0.082	0.186	
0.120	0.221	Toya
0.185	0.222	White
0.181	0.241	Duvall and Koehler
0.107	0.246	Present work

hybridization is less significant. In the case of Zn, for example, the 3*d* bands lie about 0.5 Ry below the valence bands and are quite narrow.[41] Pseudopotential calculations of the phonon spectra for this metal were found[42] to be insensitive to hybridization. We believe that the neglect of hybridization in calculating the overlap potential is well justified for Zn.

Overlap and screened-Coulomb[22] potentials for Zn are plotted in Fig. 8. As expected, the importance of overlap for this metal is somewhat less than for Cu. Nevertheless, overlap should be taken into account, for example, in *ab initio* calculations of elastic constants and phonon spectra for Zn. It has been customary to neglect the overlap interaction in such calculations,[43] however.

Figure 9 exhibits the overlap interactions of Cu, Zn, and Ga. This figure illustrates trends similar to those shown in Fig. 3; with an increase in valence the hardness increases and the net overlap interaction decreases.

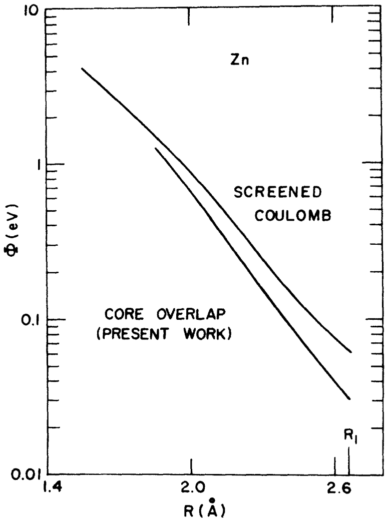

FIG. 8. Core-overlap and screened-Coulomb (Ref. 21) potentials for Zn. The nearest-neighbor spacing, $R_1 = 2.66$ Å, is indicated.

IV. APPROXIMATIONS

We now discuss two of the approximations inherent in the HL approach, namely the neglect of (a) core-core correlation and (b) wave-function distortion. Correlation refers to effects that go beyond an exact Hartree-Fock calculation. (The HL method may be viewed as an approximation to Hartree-Fock.) A rough calculation of the correlation energy may be performed via the density-functional approach. When Wigner's interpolation function[44]

$$\mathcal{F}_{\rm corr} = -\frac{0.88n(r)}{0.62[n(r)]^{-1/3}+7.8}\ \mathrm{Ry}$$

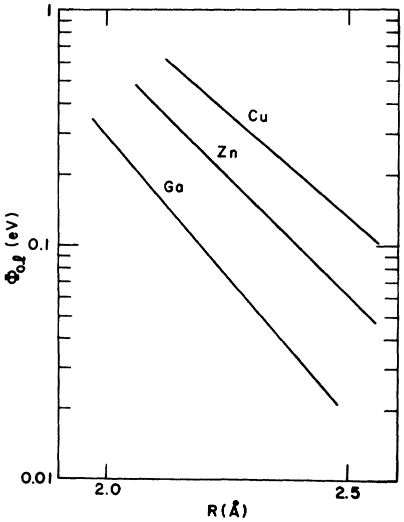

FIG. 9. Core-overlap potentials for Cu, Zn, and Ga.

is substituted into Eq. (9), the correlation contribution to the pair interaction is estimated. The curve labeled $H_{\rm corr}$ in Fig. 5 shows the result for Al. This quantity varies more slowly with R than the other contributions to the potential. It is relatively unimportant until large separations are reached.· At large separations the over-all potential is dominated by Φ_{sc} in any case. These features were found to apply to all materials treated in the present work. Therefore the neglect of correlation seems well justified.

Wave-function distortion refers to the fact that core wave functions are somewhat different in a metallic environment than in isolated atoms. (Recall that neutral atom wave functions were used in the present calculations.) This difference arises from hybridization, crystal-field effects, and because the valence electron density in the core region is less in a solid metal than in an isolated atom. To obtain some idea of the sensitivity of the overlap integrals to this effect, separate calculations were performed for Ag, based on neutral atom[12] and on $\rm Ag^+$ wave functions.[45] The overlap potential Φ_{01} calculated for ions was ~30% smaller than that for neutral atoms, owing to the slightly more compact cores of the ions. We believe that neutral atom wave functions rather than ionic wave functions are a better representation of the core states in a metal. However, since Φ_{01} is extremely sensitive to the assumed wave functions, the wave-function distortion effect is possibly one of the main sources of error in the present approach.

V. CONSTRUCTION OF COMPOSITE INTERATOMIC POTENTIAL BY INTERPOLATION

The validity of the methods described for calculating overlap and screened-Coulomb interactions is restricted to energies $\lesssim 1$ eV. On the other hand, at considerably higher energies at which core overlap is quite extensive, density-functional methods should be accurate. The possibility of constructing a "complete" interatomic potential by interpolating between the high- and the low-energy theories is suggested. Such a potential would be useful, for example, in the study of radiation-damage phenomena that occur in the range 1–100 eV.

In Fig. 10, a composite interatomic potential for Zn is constructed by interpolation. The high-energy segment was calculated from the Thomas-Fermi formula obtained by Firsov[46]

$$\Phi = (Z^2e^2/R)\,\chi[(2Z^{1/2})^{2/3}R/C]\ ,$$

where χ is the Thomas-Fermi screening function, and $C = 0.468$ Å. The low-energy segment consists of the sum of the overlap and screened-Coulomb potentials shown in Fig. 8. The dashed line interpolates smoothly between these two segments. The entire curve has remarkably little structure, considering more than five decades of energy are spanned. For example, one might expect "bumps" to appear in the potential curves when discrete atomic shells of two overlapping atoms come into contact. Indeed such structure would be detected if the potential were capable of being measured on a very fine scale, but, for most purposes, it should be of minor importance.

It is interesting at this point to make reference to the studies of the anisotropy of the threshold energy for Frenkel-pair production in hexagonal metals by Maury and co-workers.[47] These authors have measured the resistivity increments due to defect production by electron irradiation in several crystallographic directions. They analyze their data in terms of a simple geometrical model of the displacement mechanism. They suggest three sets of Born-Mayer parameters for Zn that are more or less consistent with their results. These are shown in Fig. 11 along with a linear approximation to the composite Zn potential appearing in Fig. 10. According to a simple model,[47] the region of critical importance for threshold events in Zn lies roughly from 1.5 to 2 Å. In this region, the magnitude of the composite potential is fairly close to that of the empirical potentials. However, the hardness of the composite potential is approximately twice that of the others. This discrepancy appears large, but it may be partially due to the somewhat indirect nature of the analysis

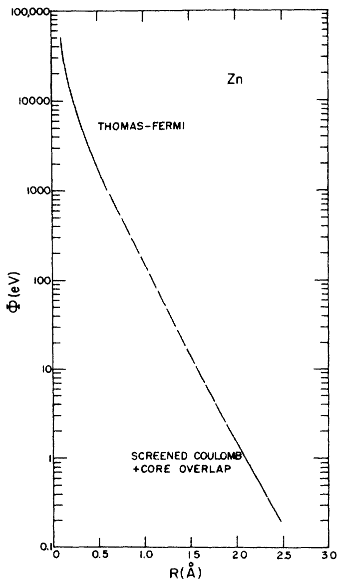

FIG. 10. Composite interatomic potential for Zn.

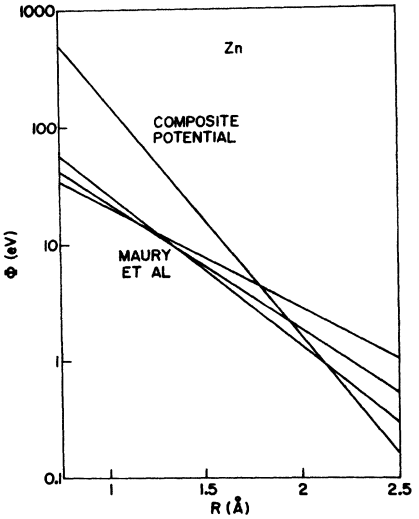

FIG. 11. Composite potential for Zn is compared with Born-Mayer potentials for this metal suggested in Ref. 47.

required to derive an interatomic potential from the experimental damage curves. Many assumptions are necessary to make this analysis tractable, and if some of these were altered, different potentials, perhaps closer to the present theory, might be obtained.

VI. SUMMARY

We have investigated core-overlap interactions in both simple and noble metals by means of a modification of the Heitler-London method. The calculated overlap potentials were found to follow closely the exponential form (7) proposed by Born and Mayer.[14] These overlap potentials were compared with screened-Coulomb potentials calculated by means of pseudopotential methods.

In metals that have only *s* and *p* electrons in their outer closed shells, the core-overlap interaction is typically small compared with the screened-Coulomb interaction at normal lattice separations. In the case of Al, for example, the core-overlap interaction becomes comparable to the screened-Coulomb interaction at $R \simeq 1$ Å (the nearest-neighbor spacing is 2.84 Å). For such metals, core overlap has a negligible effect on most properties. Core-overlap effects become significant only at energies of the order of the displacement damage threshold energy. An indirect check on the calculated core-overlap potentials for *s*-*p* core metals is given by means of a comparison with the semiempirical Born-Mayer parameters obtained by Gilbert[10] from an application of certain combining relations to alkali halide data. The agreement was found to be reasonable for the alkali metals Na, K, and Rb (cf. Table II).

The relationship between the HL and density functional approaches was explored. In general, the former seems to give somewhat larger core-overlap interactions.

For metals with *d* electrons in their outer core shells, core overlap is quite pronounced. In the noble metals and even in the divalent metals Zn, Cd, and Hg, overlap effects are significant to distances of the order of nearest-neighbor separation. Some doubt may exist, however, regarding the applicability of the Heitler-London method to the noble metals because of the effect of hybridization. Calculated Born–von Kármán force constants for the noble metals, including both screened-Coulomb and overlap interactions, are somewhat higher than those obtained from experiment, particularly in the cases of Ag and Au. The neglect of nonpairwise forces may be one source of this discrepancy. Semiempirical Born-Mayer potentials for Cu, which were derived with hybridization neglected, were found to be somewhat harder than the present calculated overlap potential.

The HL approach is restricted to relatively small overlaps and energies ($\Phi_{01} \lesssim 1$ eV). A more complete potential may be constructed by interpolation between high-energy (e.g., Thomas-Fermi) and low-energy theories. This procedure was illustrated for the case of Zn and a smooth potential covering the range 0.1–10^5 eV was obtained.

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†A preliminary account of this work is given in the Proceedings of the International Conference on Fundamental Aspects of Radiation Damage in Metals, held October 5–12, 1975, Gatlinburg, Tenn.

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