First-Principles Interatomic Potentials in Transition Metals

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The first *ab initio* theory of structure-independent interatomic potentials in d-electron transition metals has been developed from a multi-ion expansion of the total energy within the density-functional formalism. Explicit results for the volume term and two-ion and three-ion potentials entering this expansion have been obtained and successfully tested for $3d$-series metals.

Over the past ten years, there has been a great deal of progress in the understanding of the energetics of d-electron transition metals from first principles, especially within the theoretical framework of the Kohn-Sham density-functional formalism.[1] With nonperturbative band-structure techniques, it has been possible to investigate basic properties of $3d$ and $4d$ elements such as cohesion,[2] structural phase stability,[3] and high-symmetry phonons[4] with only the atomic number and atomic mass as input. Heretofore, however, there has been lacking a corresponding first-principles theory

of rigorously transferable interatomic forces and potentials in transition metals capable of dealing with the full spectrum of structural, thermal, and mechanical properties of both the solid and the liquid state, as has been possible for nontransition metals with use of pseudopotential perturbation techniques.[5,6] In this Letter, I wish to present the first such theory.

We consider a homogeneous, elemental metal with a well-defined atomic volume Ω and seek to develop the total energy of the system as a multi-ion expansion in terms of the individual ion coordinates $\mathbf{R}_i$:

$$E_{\text{tot}}(\mathbf{R}_1, \ldots, \mathbf{R}_N) = E_0(\Omega) + \tfrac{1}{2} {\sum_{i,j}}' v_2(R_{ij}) + \tfrac{1}{6} {\sum_{i,j,k}}' v_3(R_{ij}, R_{jk}, R_{ki}) + \ldots \tag{1}$$

Here E_0 is a volume term and v_2, v_3, etc. are two-ion, three-ion, etc., interatomic potentials which are implicitly volume dependent, but explicitly *structure independent*, that is, they depend only on relative ion separations $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$, etc., and are thus completely *transferable* at fixed volume. In contrast, approaches which arbitrarily force the total energy into pair-potential form (i.e., $E_0 = v_3 = 0$, etc.) by inverting band calculations of E_{tot} as a function of volume produce inherently structure-dependent potentials lacking such transferability.[7]

The starting point for this theory is the usual Kohn-Sham self-consistent-field equations within the local-density approximation to exchange and correlation.[1,6] Working in a basis of plane waves $|\mathbf{k}\rangle$ and localized, atomiclike d states $|\phi_d\rangle$, we describe the transition-metal valence s and p bands by a free-electron energy ϵ_k and pseudopotential matrix elements $\langle \mathbf{k}'|w|\mathbf{k}\rangle$, the d bands by a mean energy E_d and near-neighbor overlaps $S_{dd'}(R_{ij}) = \langle \phi_d^i|\phi_{d'}^j\rangle$ and $\Delta_{dd'}(R_{ij}) = \langle \phi_d^i|\Delta|\phi_{d'}^j\rangle$, and the hybridization between them by the couplings $\langle \mathbf{k}|\phi_d\rangle$ and $\langle \mathbf{k}|\Delta|\phi_d\rangle$. Here $\Delta = \delta V - \langle \phi_d|\delta V|\phi_d\rangle$, with $\delta V = H_0 - H$ and $H_0|\phi_d\rangle = E_d|\phi_d\rangle$, where H is the metal Hamiltonian and H_0 is an appropriate reference Hamiltonian[6] which defines $|\phi_d\rangle$. The key feature of this representation is that w and Δ are both effectively weak potentials, corresponding in the electronic structure to small sp band gaps and narrow d bands, so that while the *intra-atomic* d-state scattering

is strong, all *interatomic* matrix elements are small, and an expansion like (1) is meaningful.

The quantities needed to obtain E_{tot}, namely, the total electron density $n(\mathbf{r})$ and sum of one-electron energies E_{one}, are formally accessible through coupled Green's-function equations in a $|\mathbf{k}\rangle$, $|\phi_d\rangle$ representation.[8] The present approach then represents the partially-filled-d-band limit of the generalized pseudopotential theory (GPT), which I have previously developed for empty- and filled-d-band metals.[6] In the present case, $n(\mathbf{r})$ consists of a uniform density Z/Ω, where Z is an effective sp valence, inner-core and d-state electron densities for each ion n_{ic} and n_d, respectively, and a small oscillatory density δn_{val}. The valence Z and the number of d electrons per atom, $Z_d = \int n_d(\mathbf{r})d^3r$, are self-consistently linked by the equations $Z + Z_d = \text{const}$, $Z_d = (10/\pi)\delta_2(\epsilon_F)$, and $\epsilon_F = (\hbar^2/2m)(3\pi^2 Z/\Omega)^{2/3}$, where the $l = 2$ phase shift is $\delta_2(E) = -\text{Im}\{\ln[E_d - E + \Gamma_{dd}(E)]\}$, with $\Gamma_{dd}(E)$ the d-state self-energy.[8] Keeping only the one-ion, linear-response contribution to δn_{val} leads to a good description of the electron density with an appropriate choice[9] of $|\phi_d\rangle$. For example, in agreement with muffin-tin band theory,[2,3] I find $Z \approx 1.5$ across the entire $3d$ series from Ca to Cu, with both the trend and magnitude of $n(\mathbf{r})$ well reproduced.

The quantity E_{one} is obtained in the desired form through a simultaneous expansion in w and the relative d-state coupling strength

$$t_{dd'}(R_{ij}, E) = \frac{(E_d - E)S_{dd'}(R_{ij}) - \Delta_{dd'}(R_{ij}) + \Gamma_{dd'}(R_{ij}, E)}{(E_d - E) + \Gamma_{dd}(E)}, \tag{2}$$

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where $\Gamma_{dd'}(R_{ij},E)$ is a long-range hybridization interaction between sites i and j which reduces to $\Gamma_{dd}(E)$ for $R_{ij} = 0$, so that $t_{dd}(0,E) = 1$. In addition, $|t_{dd'}| < 1$ for all R_{ij} of interest and $t_{dd'} \to 0$ as $R_{ij} \to \infty$. The calculation of the d-state contribution to E_{one} proceeds by our considering the limit of large R_{ij}, expanding all quantities in powers of $t_{dd'}$, and then collecting terms with a common structural dependence and resumming them to continue the result analytically to arbitrary R_{ij}. The two-ion d-state component of E_{one} is thereby found to be

$$(2/\pi)\text{Im}\int_0^{\epsilon_F} \ln(1 - T_{ij}T_{ji})\,dE; \tag{3}$$

the three-ion component is

$$(2/\pi)\text{Im}\int_0^{\epsilon_F} \{\ln[1 - (T_{ij}T_{ji} + T_{jk}T_{kj} + T_{ki}T_{ik}) + T_{ij}T_{jk}T_{ki} + T_{ik}T_{kj}T_{ji}]$$
$$- \ln(1 - T_{ij}T_{ji}) - \ln(1 - T_{jk}T_{kj}) - \ln(1 - T_{ki}T_{ik})\}\,dE; \tag{4}$$

and four-ion and higher components are given similarly. In Eqs. (3) and (4), T_{ij} is the 5×5 matrix with elements $t_{dd'}$ coupling sites i and j, and the trace of all matrix products is understood. Combining these results with remaining pseudopotential, electrostatic, and exchange-correlation contributions then yields the desired expansion (1).

The behavior of the resulting two-ion potentials v_2 across the $3d$ series is illustrated in Fig. 1(a). At the beginning of the series (Ca), the d-state contribution (3) is weakly attractive, yielding a potential qualitatively similar to that for a simple metal. As one moves to the right in the series, Eq. (3) becomes increasingly attractive, representing the bonding nature of partially filled d bands. This results in a deep first minimum in v_2, the depth of which becomes maximized near the center of the series (V, Cr) and then recedes as one moves further to the right. At the end of the series (Cu), Eq. (3) actually becomes positive, representing the extra kinetic energy of nearly full, overlapping d shells, and a repulsive potential results. The corresponding three-ion potential v_3 is dominated by d-electron contributions and is everywhere approximated by Eq. (4) alone. In Ca and Cu we find v_3 to be negligible, but in V and Cr, v_3 is significantly repulsive for near-neighbor interactions, with a strong angular dependence, as shown in Fig. 1(b) for V. Both v_2 and v_3 possess long-range hybridization tails, which require special treatment in real-space calculations. Physically, I expect these tails to be damped by the higher multi-ion interactions because of the nonspherical nature of transition-metal Fermi surfaces, but considerable further study of this question is needed. For the present, I have developed effective practical schemes to deal with this complication.[10]

I have tested the functionals E_0, v_2, and v_3 in calculations of cohesion, structural phase stability, and phonons across the $3d$ series in the nonmagnetic limit. The cohesive energy E_{coh} obtained at the pair-potential level, by omission of v_3, is plotted in Fig. 2(a) and compared against muffin-tin band-theory results.[2] The trends are given correctly, as are the magnitudes except near the left center of the series (Ti, V, and Cr), where E_{coh} is overestimated. This picture is confirmed
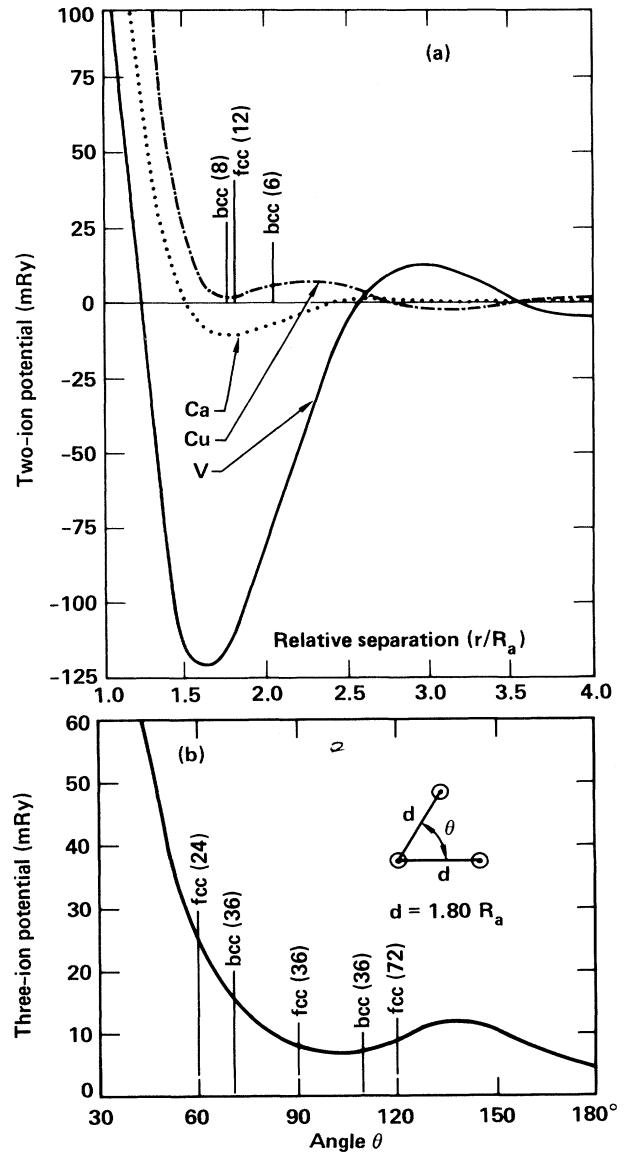

FIG. 1. (a) Radial dependence of v_2 for $3d$-series metals. (b) Angular dependence of v_3 for near-neighbor interactions in V. Here R_a is the atomic-sphere radius; the number and location of two-ion neighbors and three-ion triangles in fcc and bcc structures is indicated.
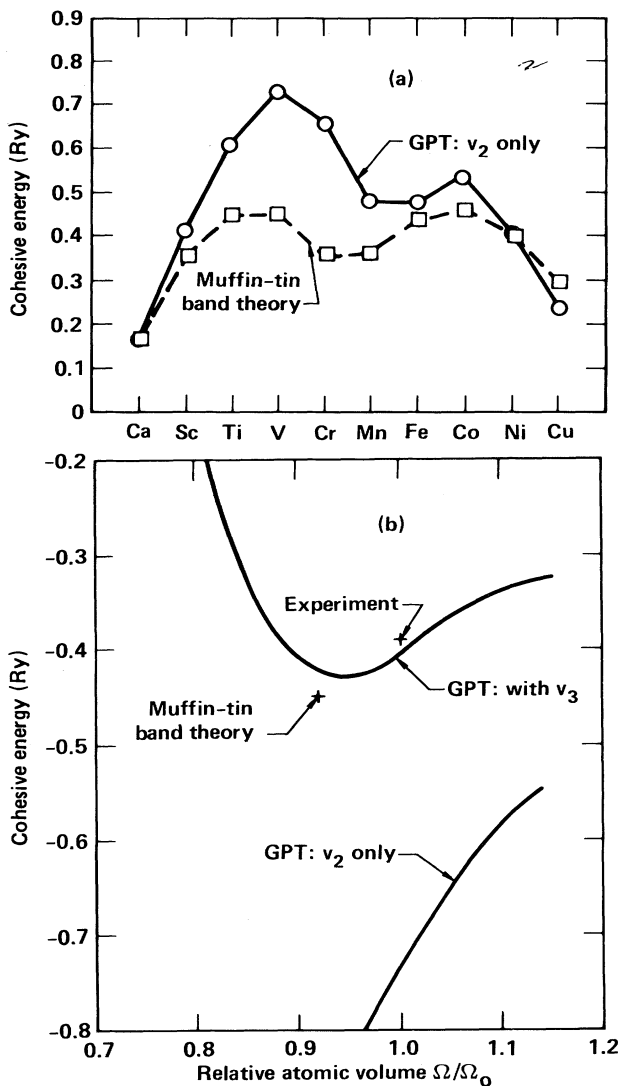
FIG. 2. Cohesive energy for $3d$-series metals. (a) Magnitude of GPT two-ion results compared with muffin-tin band theory (Ref. 2). (b) Volume dependence of $E_{\rm coh}$ for V with and without v_3.

FIG. 3. Calculated bcc-fcc energy difference across the $3d$ series from GPT two-ion potentials and from muffin-tin band theory (Ref. 3).

when the volume dependence of $E_{\rm coh}$ is studied. In Cu, for example, excellent results are obtained at the pair-potential level for both the equilibrium atomic volume Ω_0 and the bulk modulus. In V, on the other hand, $E_{\rm coh}$ continues to grow in magnitude as the volume is reduced, as shown in Fig. 2(b). In this case, however, the addition of the three-ion contribution is sufficient to reverse the trend and produce good values for both $E_{\rm coh}$ and Ω_0, as also shown in Fig. 2(b). The big impact of v_3 here comes not simply from its magnitude [which is actually much smaller than that of v_2 (see Fig. 1)] but from the fact that a large number of triangular interactions add constructively.
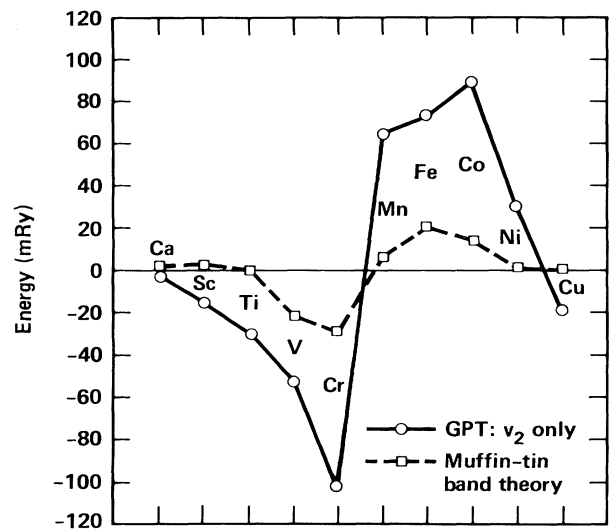
The dominant structural trend in transition metals is

the appearance of the bcc structure near the center of each series and close-packed structures on either side. This has long been recognized to be a density-of-states effect and is semiquantitatively accounted for in the most complete muffin-tin energy-band calculations.[3] Qualitatively at least, this trend is also predicted by the present pair potentials, as illustrated in Fig. 3, although the calculated energy differences are too large. In this case, however, the basic trend is established by near-neighbor interactions and most of the quantitative overestimate is an artifact of the long-range tails of v_2. Damping of these tails[10] brings the GPT energies much more in line with the band calculations, and, if one further adds three-ion contributions, leads to good results for both the bcc-fcc and hcp-fcc energy differences when compared with exper-

TABLE I. Structural energy differences for V and Cu in millirydbergs.

	Muffin-tin band theory[a]	GPT[b]	Experiment[c]
	bcc-fcc		
V	−20.6	−9.2	−6.9
Cu	1.1	3.6	4.8
	hcp-fcc		
V	+2.7	−1.3	−2.1
Cu	0.8	0.5	0.5

[a]Reference 3.
[b]Optimum representation, Refs. 9 and 10.
[c]Estimates of L. Kaufman and H. Bernstein, Computer Calculation of Phase Diagrams (Academic, New York, 1970).
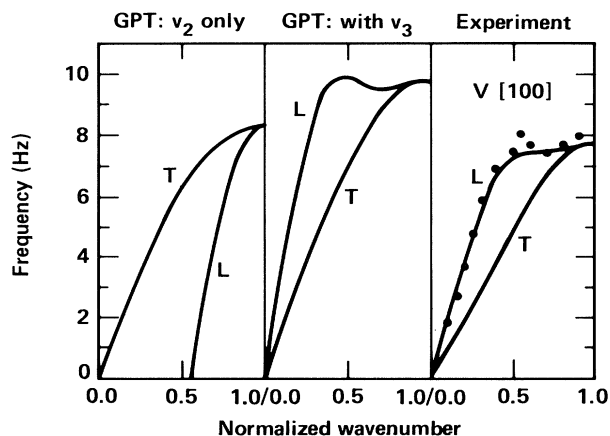
FIG. 4. Longitudinal (L) and transverse (T) [100] pho-nons in V. GPT results are for an optimum representation (Refs. 9 and 10). Experimental results are from Ref. 12 (points, data for L branch; solid lines, fit to the average of several sets of data).

iment, as demonstrated in Table I for V and Cu.

Perhaps the most demanding test of the present in-teratomic potentials comes in the calculation of the phonon spectrum. In the fcc metals Ca and Cu, indi-vidual phonons are calculated at the pair-potential lev-el to about 10% accuracy, but the real challenge comes for the bcc metals V and Cr. These latter metals (to-gether with their $4d$ counterparts Nb and Mo) are well known for anomalous phonon spectra, and semiempir-ical tight-binding calculations[11] in the $3d$ series suggest that these are driven by multi-ion interactions. Our results confirm this. At the pair-potential level, the magnitudes of zone-boundary phonons are given rath-er well, but the shapes of the branches show none of the observed anomalous behavior and furthermore display incorrect ordering and instabilities at small wave number, as shown in Fig. 4 for V. The inclusion of three-ion forces, however, immediately remedies this situation in V and Cr. This is particularly so for the longitudinal [100] branch, which is pushed well above the transverse branch by v_3, with a midzone peak, and for V, a dip towards the outer portion of the zone, in agreement with experiment as also illustrated in Fig. 4. Analysis of this behavior reveals that it is

dominated by the strong repulsive second-shell forces provided by v_3. The further inclusion of four-ion forces and calculations on the $4d$ series of metals are in progress. These results together with a full elaboration of the theory will be published at a later time.

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[9]The nominal choice of d state corresponds to the center of the d band (logarithmic derivative $D_2 = -3$) and is used here except where noted. This choice is optimum in Cu, but not in V where a slightly more bonding d state $(D_2 = -2)$ is needed.

[10]The hybridization tail of v_2 can be handled exactly in re-ciprocal space and this has been done in the results of Figs. 2 and 3. If real-space damping of the tails is used (Table I and Fig. 4), this is done by our multiplying v_2 by $\exp[-2\alpha(r-r_0)^2/r_0^2]$ for $r > r_0$, choosing r_0 beyond near-neighbor shells, and determining α so that the longitudinal [100] zone-boundary phonon is exactly preserved. For v_3 and a d state with $D_2 = -2$, $\Delta_{dd'} \gg \Gamma_{dd'}$ for near-neighbor interac-tions and one can drop the hybridization contribution.

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