

^(a)Permanent address: Universidad Simon Bolivar, Department of Physics, Apartado 80659, Caracas, Venezuela.

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Cohesive Energies of Simple Metals as Determined from Atomic Kinetic Energies

James R. Chelikowsky

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

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We propose that the cohesive energies of simple metals can be accurately predicted solely from atomic kinetic energy terms. In this fashion, we are able to determine the cohesive energy of twenty simple metals to an accuracy better than 15%. Moreover, we are able to quantify orbital contributions to cohesion.

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One of the outstanding problems in local density theory is the role that inhomogeneous or gradient kinetic energy terms play in the cohesion of condensed matter. In a fundamental theorem on local energy density functionals, Teller¹ has asserted that density expressions without inhomogeneous corrections will lead to an unbound solution for an arbitrary diatomic molecule. Teller's theorem has been extended² to include systems comprised of an arbitrary number of atoms. Hence, it must apply to solids. Naturally, such a theorem is a devastating indictment of Thomas-Fermi models of cohesion as it declares that "Thomas-Fermi" matter will not exist in a bound state. Significantly, Teller's theorem does *not* apply to a local density description of condensed matter provided gradient kinetic energy terms are included. Both from a formal point of view³ and from a computational point of view⁴ it has been demonstrated that reasonable, i.e., bound solutions can be obtained with inhomogeneous

terms in the kinetic energy functional. Here we extend Teller's theorem by stating that cohesion in the specific case of simple metals arises entirely from the inhomogeneous kinetic energy expressions. We concentrate on simple metals because they appear to represent the family of solids best described by the Thomas-Fermi model.

We start by writing the total "homogeneous" energy, E_h , of an arbitrary system as $E_h[n] = T_h[n] + V[n]$, where T_h represents the homogeneous kinetic energy term (Thomas-Fermi term), V represents the total potential energy contribution including exchange and correlation, and n is the ground-state charge-density configuration.⁵ With this notation, Teller's theorem may be expressed as $E_{\text{coh}} = E_h[n_a] - E_h[n_m] \leq 0$, where n_a is the atomic charge density and n_m is the metallic charge density. Actually, we know that $E_h[n_m] = E_h[n_a]$ is always possible as we may separate the "metal" into atoms which are infinitely far apart. In practice, we find that $E_h[n_m]$

departs only weakly from $E_h[n_a]$ when we use the metallic density appropriate for a realistic density for the atom and the metal.⁴

If we include an inhomogeneous kinetic energy term,⁵ $T_i[n]$, in our energy functional then the total energy may be written as

$$E_i[n] = T_h[n] + T_i[n] + V[n] \quad (1)$$

and the cohesive energy of the system as

$$\begin{aligned} E_{\text{coh}} &= E_i[n_a] - E_i[n_m] \\ &= T_i[n_a] - T_i[n_m] + (E_h[n_a] - E_h[n_m]). \end{aligned} \quad (2)$$

The crux of our argument resides within Eq. (2). Suppose that even in the presence of inhomogeneous terms, Teller's theorem still applies. By direct computation for simple metals,⁴ we find the theorem does apply quite accurately and in the limit of vanishingly small gradient terms we know it must hold. If we assume $E_h[n_a] \approx E_h[n_m]$, then we find

$$E_{\text{coh}} \cong T_i[n_a] - T_i[n_m]. \quad (3)$$

Unfortunately, Eq. (3), while possibly intriguing and certainly simple, is not an obvious reduction of the cohesion problem. First, we must know the correct metallic ground state before we can apply (3) and second, we must know the precise form of the inhomogeneous correction. For simple metals, the former requirement is not difficult to satisfy. Physically, we know that the core regions are not strongly involved in chemical bonding. We divide up the inhomogeneous terms to the kinetic energy into core, T_i^c , and valence, T_i^v , contributions:

$$\begin{aligned} E_{\text{coh}} & \\ & \cong (T_i^v[n_a] - T_i^v[n_m]) + (T_i^c[n_a] - T_i^c[n_m]). \end{aligned} \quad (4)$$

We now assert $T_i^c[n_a] \cong T_i^c[n_m]$ and $T_i^v[n_m] \ll T_i^v[n_a]$. $T_i^c[n_a] \cong T_i^c[n_m]$ since we do not expect the core regions to be altered in passing from the atom to the metal. The inequality $T_i^v[n_m] \ll T_i^v[n_a]$ has long been established for simple metals by Wigner and Seitz.⁷ Via this line of reasoning, we have arrived at the result $E_{\text{coh}} \cong T_i^v[n_a]$. However, unless we know the form of the inhomogeneous kinetic energy term we still have not arrived at an operationally useful expression. We avoid this problem by noting that the inhomogeneous term can be defined formally as the difference between the quantum mechanical, T_q , and Thomas-Fermi kinetic energy, T_h , terms. Thus we may write

$$E_{\text{coh}} \cong T_q^v[n_a] - T_h^v[n_a], \quad (5)$$

where in atomic units

$$\begin{aligned} T_q^v &= -\frac{1}{2} \sum_j \int_{R_c}^{\infty} \psi_j^* \nabla^2 \psi_j d\tau, \\ T_h^v &= \frac{3}{10} (3\pi^2)^{2/3} \int_{R_c}^{\infty} (\sum_i |\psi_i|^2)^{5/3} d\tau, \end{aligned}$$

and ψ_j is the atomic valence wave function.⁸ The sums are over the occupied states. R_c is the core radius. Obviously the choice of R_c is somewhat arbitrary. However, we can provide a prescription for its definition. We choose R_c to be the position of the wave-function maximum outside the outermost node of the most loosely bound valence level. For a different choice of R_c we expect a correlation of E_{coh} with $T_q^v - T_h^v$; however, the equality of Eq. (5) need not hold.

Before examining the accuracy of the cohesive energy expression, we should discuss the physical meaning of Eq. (5) and the validity of some of our approximations. In essence, we assert that the cohesive energy of simple metals is related directly to the deviation of the atomic quantum mechanical kinetic energy, in the wave-function tail region, from the atomic Thomas-Fermi kinetic energy. This assertion follows from Teller's theorem.¹ If both the atom and the metal were true Thomas-Fermi systems, then according to Teller's theorem no cohesion would occur. If the simple metallic state, as we argue, is to a first approximation a Thomas-Fermi system, then the deviation of the quantum mechanical kinetic energy from the Thomas-Fermi kinetic energy in the atomic state is a measure of the cohesive energy of the bulk metal. If we examine an archetypical simple metal such as sodium, we find that the charge density is nearly constant over ~90% of the Wigner-Seitz cell.⁷ In addition, the metallic density does not significantly deviate from the atomic density inside the core region (the core-region-valence-region separation occurring at the atomic wave-function maximum). The central point is that a simple metal such as sodium exists with respect to its valence properties as a "true" Thomas-Fermi system; i.e., inhomogeneous kinetic energy terms are negligible.

In Fig. 1 we illustrate the calculated cohesive energy for twenty simple metals. Despite some obvious simplifications which we have employed to arrive at Eq. (5), the overall correlation is striking. Our accuracy is better than 15%; the best *ab initio* calculations for simple metals are accurate to about 10%.¹⁰ We note that certain tetravalent elements, e.g., Ge, Sn, and Pb, probably should not be included in our discussion.

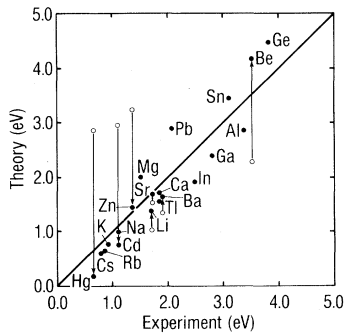


FIG. 1. Experimental cohesive energies (Ref. 9) compared with the theoretically predicted values. The theoretical values have been determined from a "kinetic energy" rule, Eq. (5). In certain cases, nonlocal or orbital contributions to cohesion are important, e.g., Zn, Cd, and Hg. For these cases, we have corrected the cohesive energies using Eq. (6) as outlined in the text. The open circles indicate the predicted cohesive energies with no corrections; the solid circles indicate the cohesive energies with the nonlocal corrections.

One might wonder why Ge works at all and, in particular, why it is predicted to have a *higher* cohesive energy than experiment. We might expect that, if Eq. (5) really works, it should contain only metallic contributions and it should omit covalent forces which would add to the cohesion of Ge. We believe the answer to the Ge problem resides in our definition of the core region. From previous work⁴ we know that the deviation of metallic densities from atomic densities for polyvalent metals, as contrasted with monovalent metals, is pushed out toward the cell boundary. For our purposes we have arbitrarily fixed the core region at the wave-function maximum. To do otherwise we would not be able to establish an unequivocal verification of Eq. (5). In any event, we feel that our core region is too small for Ge and this accounts for its fortuitous placement.

One obvious deficiency of all discussions of cohesion in terms of atomic ground-state properties is the exclusion of orbital corrections in passing from the atom to the metal. Consider the atomic valence levels of Li and Na. The energy levels of the 2s and 3s orbitals for Li and Na, respectively, are within 0.005 Ry of one another and the charge densities of these orbitals are nearly identical. Yet Li has a cohesive energy which exceeds Na by 50%.⁹ To understand differences between Li and Na we must explore the excited-state atomic spectrum. Here Li and Na differ dramatically. Within the framework of pseudopotential theory, we expect a very attrac-

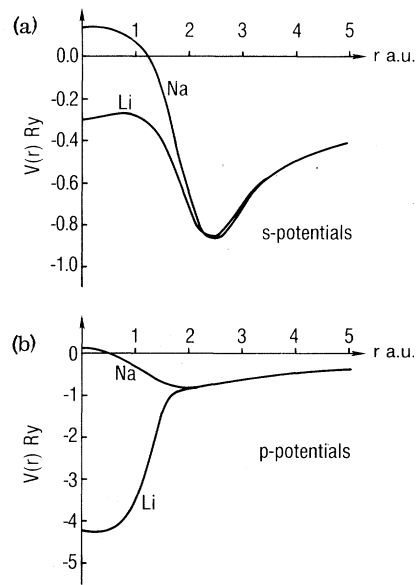


FIG. 2. Pseudopotentials for Li and Na: (a) *s* potentials and (b) *p* potentials. The Li *p* potential is dramatically different from the Na *p* potential. We attribute the strong differences in the ground-state properties of Li and Na to this fact. Note the change of scale from (a) to (b).

tive *p*-state potential for Li, but not for Na. One may attribute the differences between Na and Li to the lack of occupied *p* states in Li. Since *p* states in Li need not be orthogonal to core states, Li valence electrons in *p* states need not experience an effective repulsive potential from orthogonality requirements. The situation is indicated in Fig. 2. We display the *s* and *p* potentials for Li and Na.¹¹ While the *s* potentials differ only slightly in the core region, the *p* potential difference is dramatic.

In addition to *s-p* nonlocality in the first-row elements, we expect *s-d* nonlocality to become significant when *d* orbitals, either occupied or empty in the atomic state, reside close in energy to occupied atomic *s* states. Examples of this effect should be present in Ca and Zn. In Ca the empty 3*d* level lies very close to the occupied 4*s* state. When we pass from the atom to the metal we expect *s-d* mixing to occur and to contribute to cohesion. This effect is significant; Moriarty¹² has estimated it to be ~30% of the total cohesive energy.

In Fig. 1 we find evidence for the neglect of orbital contributions. For the *s-p* problem (Li and Be) we find that we underestimate cohesion using Eq. (5). Likewise for the heavy alkaline

earths, we predict a lower cohesive energy than observed. For the case of Zn, Cd, and Hg the effect is spectacular. We do not include the repulsive effect of the filled d shell in Eq. (5) and, as a consequence, results based only on Eq. (5) overestimate cohesive energies by nearly a fac-

$$\Delta E_{\text{NL}} = [6\pi(2l+1)/\Omega_a] \int_0^\infty dr r^2 \Delta V_{\text{NL}}(r) \{ [j_l(k_F r)]^2 - j_{l+1}(k_F r) j_{l-1}(k_F r) \}, \quad (6)$$

where Ω_a is the atomic volume, k_F is the free-electron Fermi wave vector, j_l is a spherical Bessel function,¹³ and $l=1$ ($l=2$) for an s - p (s - d) correction. ΔV_{NL} is the difference in the orbital components of the pseudopotential.¹¹ For example, in Zn we would take the difference between the $4d$ and $4s$ pseudopotentials to form ΔV_{NL} . In this fashion, we have examined eight simple metals in which s - p or s - d corrections may play a significant role (Li, Be, Ca, Sr, Ba, Zn, Cd, and Hg). In each case, we find improvement in our cohesive energy based on Eq. (5). This result tends to confirm the essence of Eq. (5) and the concept of orbital contributions to cohesion.

In summary, we note that Teller's theorem may have implications for cohesion which have not been fully explored. Here we have demonstrated that cohesion in simple metals can be understood through a "kinetic energy" rule, Eq. (5), which appears to follow directly from Teller's work. Moreover, discrepancies between the cohesive energies predicted from our rule and the observed cohesive energies can be attributed to orbital effects.

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In order to quantify approximately these orbital corrections, we have approached the problem by assuming free-electron wave functions for the metal. Using an appropriate pseudopotential¹¹ difference to determine the nonlocality we find that the energy correction is

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