Local density theory of metallic cohesion*

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We present the results of extensive numerical experiments designed to test the ability of the local-density theory of electronic exchange and correlation to describe binding in both simple and transition metals. Predicted nuclear separations, cohesive energies, and bulk moduli for 26 third- and fourth-row metals exhibit remarkable agreement with experiment. The only input to these calculations is the atomic number.

Owing to its simplicity and universal applicability, the local-density approximation[1,2] to the density-functional theory[3] of electronic exchange and correlation is being applied widely in diverse problems of electronic structure. The theory requires the repeated solution of systems of partial differential equations, a very difficult subproblem unless the system in question possesses great symmetry. As a result, the content of the theory has been accurately exhibited only for a few atoms,[4] very small molecules,[5] and a few isolated solids.[6] The motivation for the present work is that, while chemical trends with atomic number are often even more important than results for specific systems, no quantitative study of how well local-density theory describes such trends has previously been made. Here, we compare with experiment the equilibrium nuclear separations, the cohesive energies and the bulk moduli implied by the theory for the metals in the third and fourth rows of the Periodic Table. The varying degree of agreement we obtain conveys, better than any other way we are aware of, the confidence we should place in local-density theory as we proceed to applications to more complex systems.

As atoms condense to form a solid or liquid several effects occur.[7] The discrete levels of the atom (i) broaden into bands, (ii) shift in energy, (iii) interact (hybridize), and as a result (iv) change their occupation. Finally, (v) the less restricted electronic motion in the condensed phase changes the way in which the motion of the different electrons is correlated. Most previous studies of metallic binding focus on the subset of these effects which appears to dominate the trend with atomic number in a particular group of metals. Thus, for example, several calculations[8] have shown that the kinetic energy saved by the partial occupation of the broadened d level [effect (i)] is primarily responsible for the large and roughly parabolic (in atomic number) cohesive energy in the transition series.[8] Similarly, in the alkalis effects (ii)–(iv) are not important and

the quantum-defect method[9] together with an electron-gas screening theory provides an accurate semiempirical description of the binding. Pseudopotential methods permit the extension of this type of analysis to the polyvalent simple metals.[10] Such calculations, by dealing with these effects separately,[7] provide valuable insight into their relative importance.

Our work provides a different kind of information. We have treated effects (i)–(iv) collectively. But, by means of elaborate numerical calculations, we have treated these effects essentially without approximation.[11] The comparison of our results with experiment, therefore, focuses on our treatment of exchange and correlation [effect (v)]. For the latter we have used the local-density theory of Kohn and Sham[1] and Hedin and Lundqvist[2] for all the electrons—core, valence, s, d, atomic, and metallic.[12] (For the magnetic atoms we used the local-spin-density formalism of von Barth and Hedin[13].) This treatment has the advantage over alternatives such as Hartree-Fock and its renormalized-atom modification,[14] of being applicable in a calculationally straightforward way to the vast majority of atomic, molecular, and condensed systems. Our systematic application of local-density theory to the third- and fourth-row metals exhibits the important trends both within and between the rows. (Similar calculations for isolated materials using both local density theory[6] and the $X\alpha$ formalism[15-18] have been reported.) Furthermore, since we compute both exclusively solid properties (nuclear separation and bulk modulus) and the cohesive energy, which compares the solid with the atom, we can shed light on the relative accuracy of the theory in the two cases.

Our results consist of three aspects of the binding curve (the total energy of the solid, minus that of the atom, as a function of nuclear separation): the position and depth of the minimum and the curvature near the minimum. The top row of Fig. 1 shows the variation of the minimum position (equilibrium nuclear separation) with atomic number. Not only is the trend with atomic num-
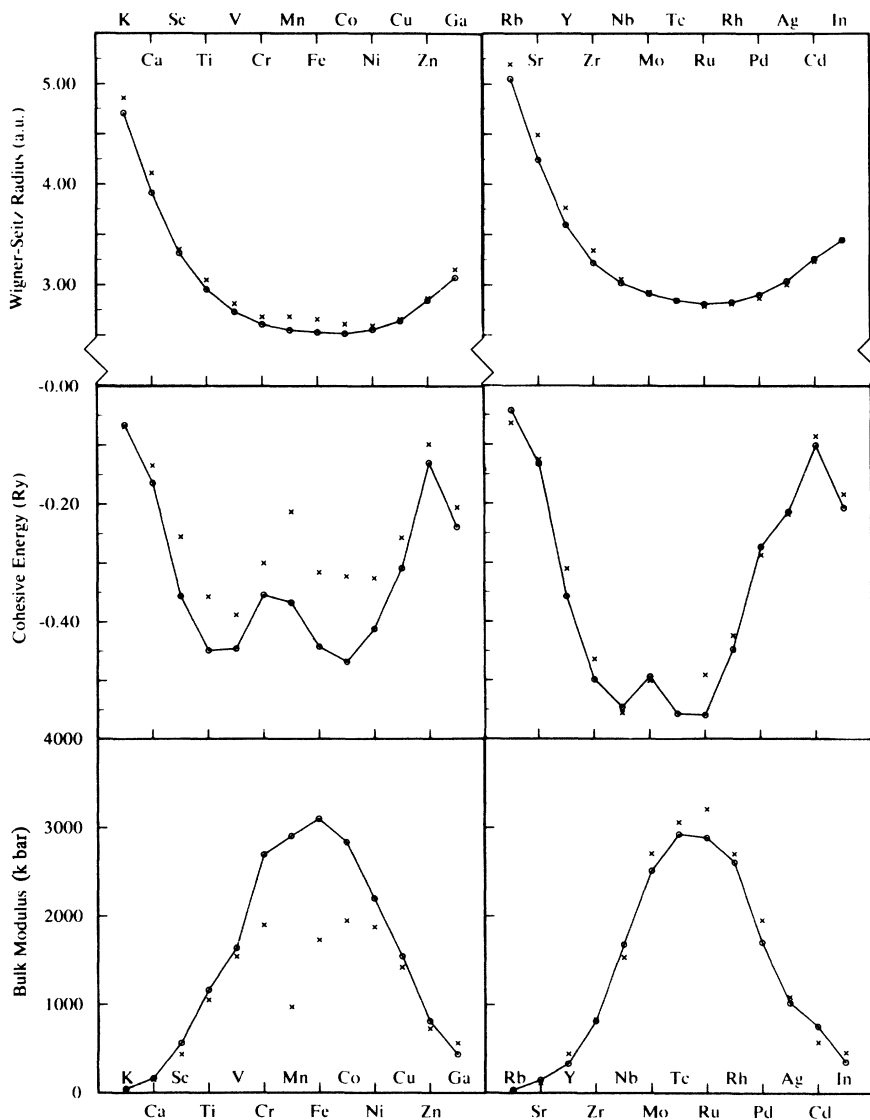
FIG. 1. Cohesive properties versus atomic number. Top row—equilibrium nuclear separation in terms of Wigner-Seitz radius. Middle row—cohesive energy in Ry per atom. Bottom row—bulk modulus in kilobars. The atomic number increases in steps of one from 19 to 31 in the left-hand column and from 37 to 49 in the right-hand column. Measured values (low temperature where available) are indicated by crosses (Ref. 19).

ber correctly described, but the absolute nuclear separations are predicted to within a few percent. The middle row of Fig. 1 compares the calculated depth of the minimum (cohesive energy) with measured values. The trend with atomic number is once again reproduced showing, in particular, the rapid increase in cohesion in both transition series as the bonding d states are occupied.

The fact that our atomic calculations allow for spin polarization[6,20] permits us to make two interesting inferences. First, it is the gain in atomic exchange energy resulting from the Hund's rule splitting of the d level which is responsible

for the loss in cohesion near the center of both transition series.[21] Second, because our atomic calculations assume the electron density to be spherically symmetric, they are particularly appropriate to atoms such as K and Mn, where individual members of the ground-state multiplet (the $M_s = \frac{5}{2}$ member of the ^6S multiplet in Mn, e.g.) can be described by a single product wave function corresponding to a spherically symmetric electron density.[22] The fact that the cohesive energy error for Mn is not smaller than those for Cr, Fe, Co, and Ni, where our calculations provide only an average over several multiplet energies, suggests,

therefore that these errors stem from correlations involving configuration changes (spin flip, e.g.) rather than the angular correlations responsible for multiplet structure. Note that the inclusion of spin polarization in the solid calculation would only lower the solid total energy, thereby increasing the discrepancies. The sharp increase in cohesion of Ga over Zn and In over Cd is also an atomic effect, stemming in this case from the required occupation of the relatively high lying $3p$ level in Ga ($4p$ in In).

The quantitative agreement between the measured and calculated cohesive energies should not be interpreted as the accuracy with which total energies, as opposed to total energy differences, can be calculated. We use the identical theory of exchange and correlation for both the atom and the solid thereby profiting from the cancellation of errors of several rydbergs.[6] (The fractional error is very small; the total energies for the elements considered here range from 1200 to 12 000 Ry.)

The bottom row of Fig. 1 compares the calculated curvature of the binding curve (bulk modulus) with measured values. With the exception of four $3d$ transition elements possessing strong magnetic effects, the agreement is truly remarkable. There is in fact considerable change (with nuclear separation) in the curvature of the binding curve for these elements; the curvature at the measured separation is much closer to the experimental value. Spin-polarized calculations for Fe and Ni (see Ref. 23) confirm the sensitivity of the nuclear separation and bulk modulus to magnetic ordering.

The principal implication of our work, particularly when taken together with similar calculations for small molecules[5] and rare-gas solids,[6,17] is that the local-density approximation to exchange and correlation effects accurately describes binding in a wide variety of systems, providing the required one-electron analysis is carefully done. This should prove to be of substantial practical importance in research areas, such as surface and molecular physics, where nuclear separations, bond energies, and vibrational frequencies are often difficult to determine.

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