

Local-density approximation: Cohesion in the transition metals and $s \rightarrow d$ promotion in the transition-metal atoms

R. E. Watson, G. W. Fernando, M. Weinert, Y. J. Wang, and J. W. Davenport

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

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Systematics in cohesive energies (H_{coh}) and d -non- d atomic promotion energies have been examined for the transition elements treated within the local-density approximation (LDA). Cohesive energies involve the energy of the solid as compared with that of a reference state in the free atom; going from one atomic configuration to another (e.g., $d^{n-2}s^2 \rightarrow d^{n-1}s$) for that reference state involves a promotion energy. Errors in the LDA's ability to calculate promotion energies are then translated into changes in calculated H_{coh} . Employing the local-spin-density approximation (LSDA), scalar-relativistic values of the promotion energies have been obtained for atomic states of maximum spin multiplicity of the neutral atoms in the $3d$, $4d$, and $5d$ rows for those configurations for which experimental spectral data are available for comparison. The intent is that by scanning all three rows and those cases for which there are experimental data that those factors contributing to the LDA's shortcomings in describing electron-electron interactions in the transition elements may become better defined. Previously, other workers have obtained $d^{n-2}s^2 \rightarrow d^{n-1}s$ promotion energies for the $3d$ row, indicating that the LDA (or LSDA) significantly overestimates the stability of d valence electrons as compared with the non- d . The more extensive results obtained here indicate that, while often significant, $s \rightarrow d$ promotion energy errors are sometimes essentially zero valued. This variation in $s \rightarrow d$ promotion energy behavior has implications for what might be presumed to be the shortcomings of the LDA as applied to atoms and, in turn, to solids. Given the promotion energies, the consequences of choosing different reference states in estimates of H_{coh} for the $4d$ and $5d$ rows are explored and an envelope of H_{coh} values defined. No matter what the choice of reference state, the LDA significantly overestimates H_{coh} in the middle of the transition-element rows, a result consistent with previous estimates. This error becomes small upon going to the noble metals and, as has not been generally recognized, is essentially zero valued for the beginning members of each row. These matters are discussed.

I. INTRODUCTION

It is now commonplace to calculate the total energy of the system in the course of an electronic-band-structure calculation for a solid. Such calculations usually employ the local-density approximation (LDA) when constructing the potentials. Given total energies, it is possible to calculate the heats of formation of compounds and the cohesive energies of the elemental solids and, from these, infer the relative stabilities of competing phases. In the case of the heats of formation it is often possible to obtain heats which agree¹ with experiment to within the experimental uncertainties, particularly if the atomic packings in the compound and the elemental solids are similar. The situation is less satisfactory for the cohesive energy where the energy of a solid is being compared with that of a free atom, i.e.,

$$H_{\text{coh}} = E_{\text{sol}} - E_{\text{at}}. \quad (1)$$

Apparently local-density theory tends to do a better job for the solid than the free atom, resulting in H_{coh} which are too large. One purpose of the present paper is to consider how E_{at} is chosen and the consequence of that choice on the estimates of H_{coh} . Often one does LDA calculations for the atom in different atomic

configurations, e.g., $d^{n-2}s^2$ and $d^{n-1}s$ for a transition metal, and takes the lowest-energy value among these to be the "ground state" of the atom, hence E_{at} . Usually this is done with the local-spin-density approximation (LSDA) version of the theory where a spin-polarized calculation is done for the atomic configuration in its highest possible spin multiplicity. With few exceptions the resulting atomic energy is appropriate to an *average* over some set of multiplet levels and is *not* the energy of the lowest lying multiplet level alone. It is this lowest lying level with respect to which an experimental H_{coh} is measured. Another choice for the atomic energy would be to correct the calculated LSDA atomic energy for the promotion from the atomic zero to this average over states of highest spin so that the calculated cohesive energy becomes

$$H_{\text{coh}} = E_{\text{sol}} - (E_{\text{at}} - \Delta_p). \quad (2)$$

The promotion correction Δ_p can be obtained from experimental atomic spectral data.² The result of the two choices on the calculated H_{coh} for the $4d$ transition metals can be seen in Fig. 1. Here Eq. (2) was evaluated for the atoms in the highest spin multiplicities of the $4d^{n-1}5s$ configurations and compared with the uncorrected Eq. (1) LSD result for the atoms. Both sets of

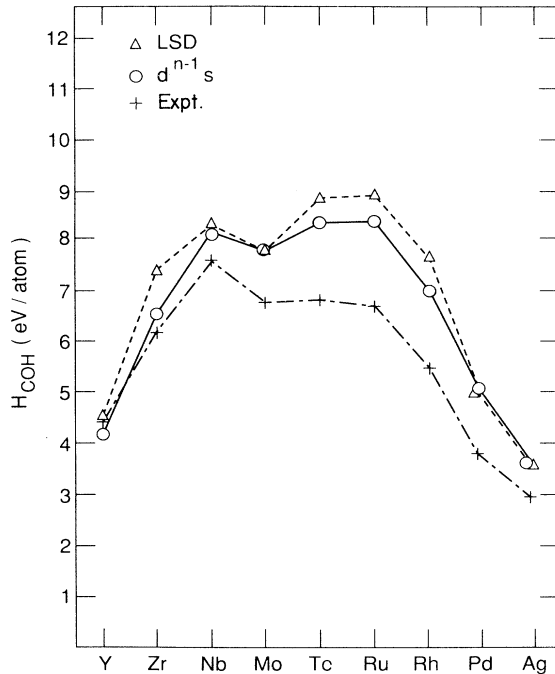


FIG. 1. The cohesive energies of the 4d transition metals with their observed structures and lattice constants as obtained: (i) with the LSDA approximation for the atoms (i.e., ignoring multiplet promotion energies in the free atom, and (ii) where the $d^{n-1}s$ LSDA free atom has been used in Eq. (2).

calculations lie markedly higher than experiment, particularly for the metals Tc and Ru, which have just over half-filled bands. Similar results have been reported previously³ for the 5d transition-metal row. The question arises of what are the consequences of employing an atomic configuration, other than the $d^{n-1}s$, in Eq. (2).

Granted the prescription that we have chosen to employ when evaluating Eq. (2), going to other atomic configurations when evaluating $(E_{at} - \Delta_p)$ is equivalent to calculating the valence $s \rightarrow d$ electron promotion energy in the free atom, such as

$$\Delta E_{sd} = E[d^{n-1}s] - E[d^{n-2}s^2] \quad (3)$$

for promoting an atom from the $d^{n-2}s^2$ to the $d^{n-1}s$ configuration. This may be compared with the equivalent experimental quantity to obtain the error

$$\delta(\Delta E_{sd}) = [\Delta E_{sd}]_{\text{obs}} - [\Delta E_{sd}]_{\text{calc}} \quad (4)$$

which is just equal to the change in the calculated cohesive energy on going from one atomic configuration to the other. Several years ago Gunnarsson and Jones obtained⁴ nonrelativistic LSDA promotion energies for p -shell atoms and the $3d^{n-2}4s^2 \rightarrow 3d^{n-1}4s$ promotion energies for the 3d transition-metal atoms. Comparing these with experiment, they identified energy changes associated with changes in wave-function nodality as those most prone to error in the local-density description of exchange; for the transition elements, this involves the

difference in exchange contribution from the outer core, as sampled by valence d versus valence s and p electrons. If these matters could be disentangled, they might offer a simple semiempirical modification of local-density potentials to account for this. As Gunnarsson and Jones emphasized, this will not be easy to do. The results of scalar-relativistic calculations will be reported here for various promotion energies in the 3d, 4d, and 5d rows. The cases chosen are based on the availability of spectroscopic data. If the promotion energy errors depend primarily on the above-mentioned error in outer core-valence shell exchange, one would expect similar, though not identical $\delta(\Delta E)$ for the $d^{n-2}s^2 \rightarrow d^{n-1}s$ and $d^{n-1}s \rightarrow d^n$ promotions since both involve similar $s \rightarrow d$ transitions. This is not the case. The situation appears rather more complicated.

The two major thrusts of this paper will be first to explore trends in LDA's predictions of atomic promotion energies, extending these to all three transition-metal rows and to all $s \rightarrow d$ and $p \rightarrow d$ promotions for which there is experimental data available for comparison. The pattern in the $\delta(\Delta E)$'s does suggest that the factor dominating in these errors is the inadequacy of the LDA in treating valence electron-valence electron interactions. Second, there will be the first scan of cohesive energies, based on full potential scalar-relativistic calculations, across the 4d and 5d rows. Emphasis will be placed on inspecting what effect the choice of the atomic reference state has on the predictions.

Some features of both the metallic and the free atom calculations will be described in Sec. II. The band calculations employ the linearized augmented Slater-type orbital (LASTO) method⁵ which has a basis set. The effect of basis set size and of going from muffin-tin to "full" (i.e., shape-independent) potentials on the total energies of the 4d metals will be reviewed. The effects show small differences to what has been reported previously for the 5d row. Cohesion in the 4d elements is being considered here so as to avoid the complications associated with the magnetism of the 3d row and because the spectroscopic data necessary for evaluating Eq. (4) is measurably better for the 4d than the 5d row. Promotion energies will be inspected in Sec. III and their consequences for estimates of 4d cohesion in Sec. IV.

II. THE CALCULATIONS

The LASTO method employs a basis set of Slater-type orbitals in the interstitial region of the solid, augmenting these with explicit solutions of the wave equation inside atomic spheres. The full potential version of this scheme has been described recently.⁶ The calculations employ the local-density potential and treat the atomic core fully relativistically while treating the valence bands scalar relativistically, that is, spin-orbit coupling is omitted. Calculations were done for the observed crystal structures, using the observed, rather than variationally determined lattice volumes. Employing the observed volumes is unimportant to the total energies to the number of digits of importance here. It has been standard to use single s -like, p -like, and d -like Slater-type orbitals (STO) per

atom in the interstitial, where the screening constants of the STO have been optimized in calculations for the elemental metals. The resulting matrices, which are to be diagonalized, then have the structure of a LCAO scheme and the resulting wave functions are amenable to orbital population estimates of charge transfer of the type utilized by chemists. Such a single STO scheme has less variational freedom than that of the linearized augmented-plane-wave (LAPW) method. LASTO calculations, using a doubled STO basis of two s -like, two p -like, two d -like, plus an f -like orbital analogous to the "polarization" term of higher l employed in molecular calculations, yield essentially identical total energies for transition metals as do LAPW ones. The consequences of going from the single to the double basis sets for the elemental $4d$ metals may be seen in Fig. 2. The zero of the plot corresponds to the metals' total energies obtained with double basis sets and full potentials and the open circles indicate the energy loss on employing the single basis plus the full potentials. The consequence of keeping the single basis and going to muffin-tin potentials is indicated by the squares. Similar total-energy shifts, roughly one-third larger in magnitude, have been seen previously³ for the $5d$ transition-metal row. The effects of employing both the full potential and the larger basis set are of numerical significance to estimates of the cohesive energies which are 3–8 eV/atom. Employing the full potential introduces the more important correction to the total energy. When comparing the energies of two solids, the effects of basis set and the type of potential can be measurably less. For example, the calculated energy differences of the elemental metals in the fcc, bcc, and hcp structures are little affected³ by either choice of potential or size of basis set. This is because all three structures are similarly packed and gain similarly, in total energy, on going to the more rigorous treatment.

A version of the spin-polarized LSD scheme for atoms

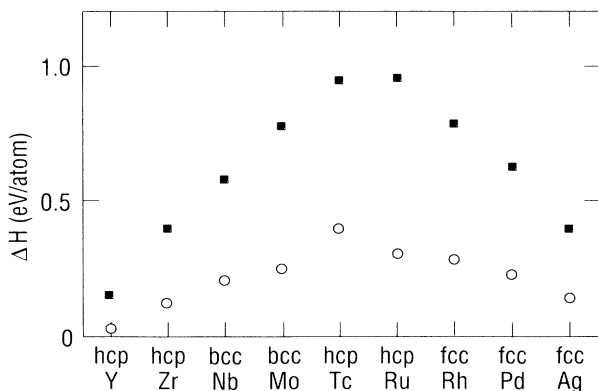


FIG. 2. Differences in the calculated crystal total energies for the elemental $4d$ metals. The zero, with respect to which the other energies are measured, is the total energy of calculations employing full potentials and the double Slater-type orbital basis set. The open circles are the energies of the full potential single STO calculations while the squares are the result of employing muffin-tin potentials and the single STO.

has been devised⁷ where the valence electrons are treated scalar relativistically (and for the atomic core electrons fully relativistically). By treating the valence electrons (and core) the same, as far as relativistic effects go, in the atom and in the metal, allows their total energies to be compared. Also, such a scalar-relativistic description of the valence electron is suitable when comparing with an average over all the observed multiplet levels of some spin multiplicity. This computational scheme has already been used⁷ in consideration of the $d^{n-2}s^2 \rightarrow d^{n-1}s$ promotion. Here it will be used for others as well.

III. PROMOTION ENERGIES AND PROMOTION ENERGY ERRORS

We are concerned⁸ with those multiplet levels having the maximum spin multiplicity for some atomic configuration. In the $3d$ and $4d$ rows there is reasonably complete experimental data for such levels in the $d^{n-2}s^2$, $d^{n-2}sp$, $d^{n-1}s$, $d^{n-2}p$, and d^n configurations. This allows us consideration of three $s \rightarrow d$ promotions, namely,

$$\begin{aligned} d^{n-2}s^2 &\rightarrow d^{n-1}s, \\ d^{n-1}s &\rightarrow d^n, \\ d^{n-2}sp &\rightarrow d^{n-1}p, \end{aligned}$$

and two $p \rightarrow d$ promotions

$$d^{n-2}sp \rightarrow d^{n-1}s,$$

and

$$d^{n-1}p \rightarrow d^n.$$

In the $5d$ row the d^n configuration is high lying and there is reliably assigned data for this configuration for only one atom, hence the promotions associated with this configuration must be omitted from consideration for the $5d$ atoms. The upper panel of Fig. 3 shows the calculated and experimental $d^{n-2}s^2 \rightarrow d^{n-1}s$ promotion energies of the $4d$ row. The breaks in the curves are associated with a half-filling of the d shells. The fact that the calculated values lie below experiment implies that the calculations have overestimated the stability of the d versus the non- d levels. The bottom panels show the errors, $\delta(\Delta E)$, for the $d^{n-2}s^2 \rightarrow d^{n-1}s$ and $d^{n-1}s \rightarrow d^n$ promotions for the $3d$, $4d$, and $5d$ rows. The $\delta(\Delta E)$ increase on going from the $5d$ row to the $4d$ and, in turn to the $3d$. The $d^{n-1}s \rightarrow d^n$ values lie well below their $d^{n-2}s^2 \rightarrow d^{n-1}s$ counterparts and are almost zero valued for the $4d$ row, i.e., theory and experiment are in reasonable numerical agreement in this one case. There is a dip in the curves for Cr in the $d^{n-1}s \rightarrow d^n$ transition which occurs more weakly for Mo and also for Mn, Tc, and Re in the $d^{n-2}s^2 \rightarrow d^{n-1}s$ transition. This is associated with the half-filling of the d shell. Otherwise the curves are relatively smooth despite the fact that some of the high-spin multiplets of interest have other multiplets, which are close lying in energy and of the same symmetry, e.g., both the d^7s^2 and d^8s involve 4F and 4P levels. Some configuration mixing will arise in such circumstances and, if the levels are close enough in energy, the mixing

can be substantial. There is little or no visible effect of such mixing in the curves. The $3d d^{n-2}s^2 \rightarrow d^{n-1}s$ $\delta(\Delta E)$ are smaller than those of Gunnarsson and Jones for the heavier $3d$ elements. This is due to the inclusion here of relativistic effects which stabilize the valence s electrons relative to the d electrons.

Of course, the most important feature of Fig. 3 is the disparity in the $\delta(\Delta E)$ for the two different $s \rightarrow d$ promotions. These would be expected to be similar, though not qualitatively identical, if $\delta(\Delta E)$ arose primarily from a difference in error in the d - versus the s -electron sampling of exchange with the atomic core.

The spectral data, upon which the $\delta(\Delta E)$ are based, is less complete for the other promotions which are

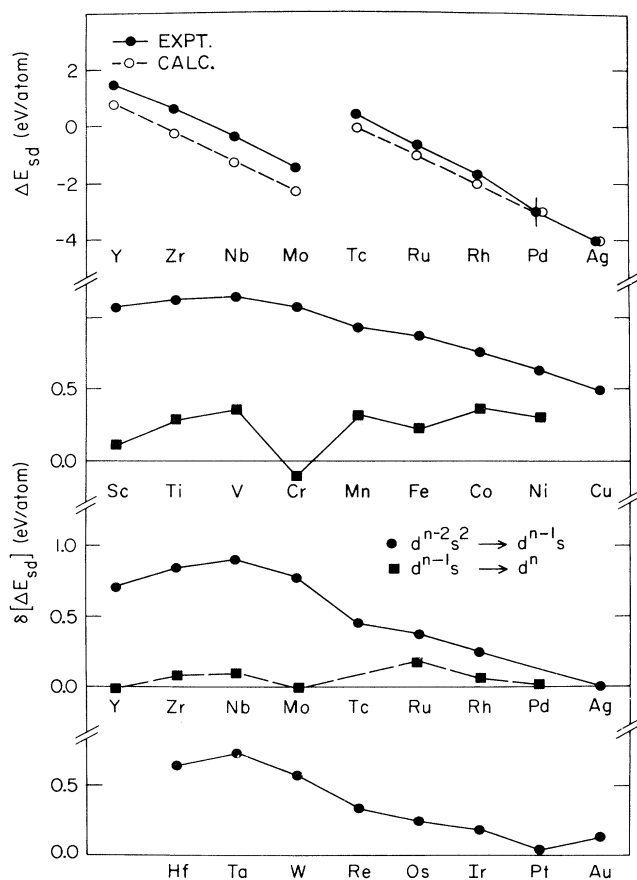


FIG. 3. The upper panel shows the experimental and calculated $d^{n-2}s^2 \rightarrow d^{n-1}s$ promotion energies for the $4d$ atoms in their highest spin multiplicities appropriate to the configuration in question (the vertical bar on the experimental value for Pd is the uncertainty due to incomplete experimental data). The bottom three panels show the errors in the calculated $s \rightarrow d$ promotion energies, $\delta(\Delta E)$, for $d^{n-2}s^2 \rightarrow d^{n-1}s$ and for $d^{n-1}s \rightarrow d^n$ for the $3d$, $4d$, and $5d$ atoms (in their highest spin multiplicity for the atomic configuration in question). Inadequate experimental data for the $5d$, $d^{n-1}s \rightarrow d^n$, and several other cases, lead to their omission from the figure. Positive $\delta(\Delta E)$ imply results where the d electrons are calculated to be more stable relative to the non- d valence electrons than is experimentally the case.

represented in Fig. 4. In the case of Ir and Pt some of the higher lying of the multiplet levels are not tabulated and averaging over those which are available causes the calculated values of $\delta(\Delta E)$ to be the upper bounds (hence the vertical arrows in the plot). (This, in turn, implies that the H_{coh} calculated for these configurations are also upper bounds.) The shortcomings in some of the data for Os, Co, and Ni are even worse and it is impossible to say whether the $\delta(\Delta E)$ are over or underestimated, hence the parentheses indicating uncertainties in the plotted points for these cases. Despite the uncertainties, some things can be said. The $s \rightarrow d$ ($d^{n-2}sp \rightarrow d^{n-1}p$) promotion error lies between the two $s \rightarrow d$ promotion energies errors already considered in Fig. 3 for the elements to the left-hand side of the plot while tending to coalesce with the $d^{n-1}s \rightarrow d^n$ to the right. The $p \rightarrow d$ promotion errors also lie between those values on the left but do not display the decrease seen for all the $s \rightarrow d$ errors for the Co, Ni, and Cu columns of the figure. The $d^{n-1}p \rightarrow d^n$ values tend to lie below the other $p \rightarrow d$ cases and similarly the $d^{n-1}s \rightarrow d^n$ generally lies below the other $s \rightarrow d$ ones. The factors controlling this disparate behavior remain to be disentangled.

IV. COHESION IN THE $4d$ ROW

The results of employing the d^n , $d^{n-1}s$, and $d^{n-2}s^2$ configurations as the reference states for the $4d$ elements

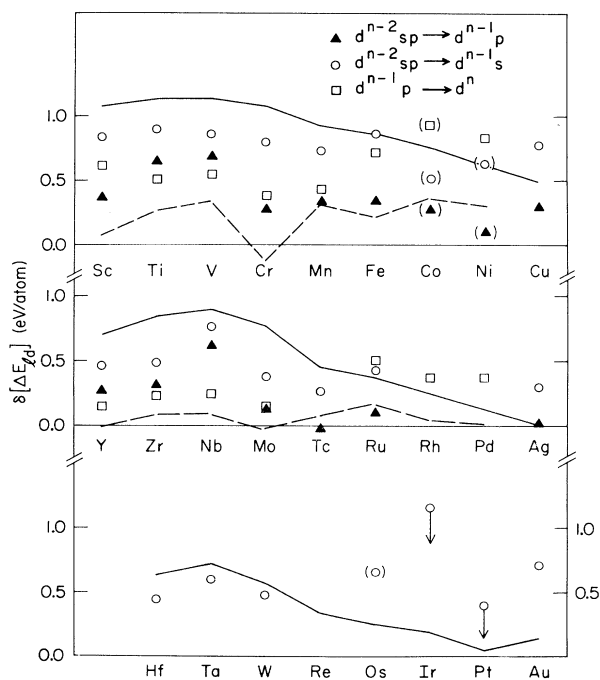


FIG. 4. $s \rightarrow d$ (the solid triangles) and $p \rightarrow d$ (open circles and squares) promotion energy errors, $\delta(\Delta E)$, for the $3d$, $4d$, and $5d$ atoms in the manner of Fig. 3. Lack of experimental data for higher lying multiplets causes the $\delta(\Delta E)$ for Ir and Pt to be upper bounds (hence the vertical arrows) while incomplete data for other cases, which are plotted in parentheses, causes their exact values to be somewhat uncertain. The plotted lines come from Fig. 3.

in Eq. (2) are summarized in Fig. 5. Similar results were obtained³ for the $d^{n-1}s$ and $d^{n-2}s^2$ for the $5d$ metals as seen in Fig. 6, except that the agreement between calculation and experiment was better for Pt and Au than it is here for Pd and Ag. The differences between the predictions employing the $d^{n-2}s^2$ and $d^{n-1}s$ configurations are substantial and, if the error is in the valence-core exchange, might suggest that going to the d^n values would produce a moderate improvement in the H_{coh} in the middle of the transition-metal row while leading to measurable underestimates of this quantity for the left-hand members of the row. This is not the case because of the near zero valued $\delta(\Delta E)$ for $d^{n-1}s \rightarrow d^n$. As can be seen in Fig. 7, going to the remaining configurations yields results which are bracketed by those obtained for the $d^{n-2}s^2$ and $d^{n-1}s$ —at least when employing the atomic levels of highest spin multiplicity as is done here. Inspection of Fig. 1 shows that the LSDA result, based on Eq. (1) also falls within this envelope. A similar envelope may be defined for the $5d$ elements except that, as seen in Fig. 6, its upper boundary appears to be defined by the $d^{n-2}sp$ configuration for many of the elements (but note there these H_{coh} are upper bounds on these values due to limitations in spectral data). There is modest accord between theory and experiment for the cohesive energies at either end of the transition-metal rows but there are overestimates, of the order of 2 eV/atom, for those metals having just over half-filled d bands.

Comparison may be made with other cohesive energy estimates. The classic calculations⁹ of the IBM group

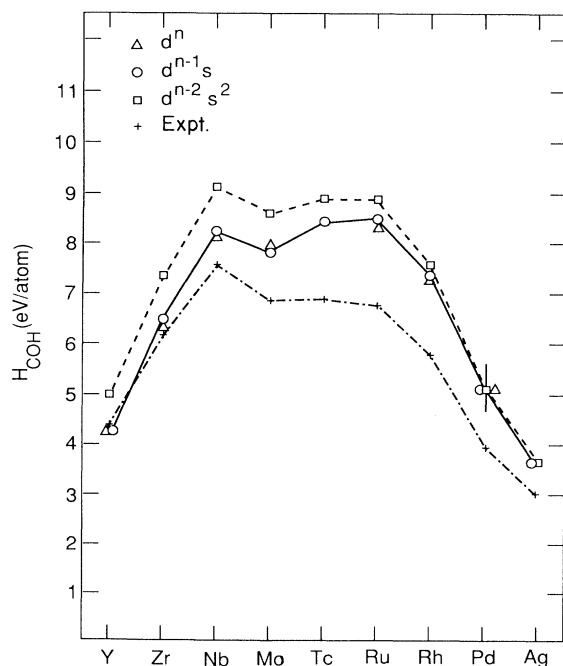


FIG. 5. The cohesive energies of the $4d$ transition metals employing the $d^{n-2}s^2$, $d^{n-1}s$, and d^n atomic configurations as reference states to which the promotion energy correction of Eq. (2) has been applied.

yield $4d$ metal H_{coh} , that are in better numerical accord with experiment than those seen there. This is because those calculations were nonrelativistic muffin-tin potential calculations and both the inclusion of relativistic effects¹⁰ and making no shape approximations to the potential (see Fig. 2) increase E_{tot} and hence H_{coh} . Thus the better agreement obtained in those earlier calculations arises from the omission of these terms. Other full potential, relativistic calculations¹¹ are in accord with the envelopes obtained here.

V. DISCUSSION

The impact of the local-density approximation on predicting transition-metal cohesion and on estimating atomic $s \rightarrow d$ promotion energies has been considered here. The calculations for the metals were done within the LDA, while those for the atoms involved LSDA treatments of the atoms in the highest possible spin multiplicity allowed for some given configuration. Dealing with the highest spin multiplets⁸ has accounted for the spin part of the Hund's rule splittings to the extent allowed within the local-density theory, and hence one is

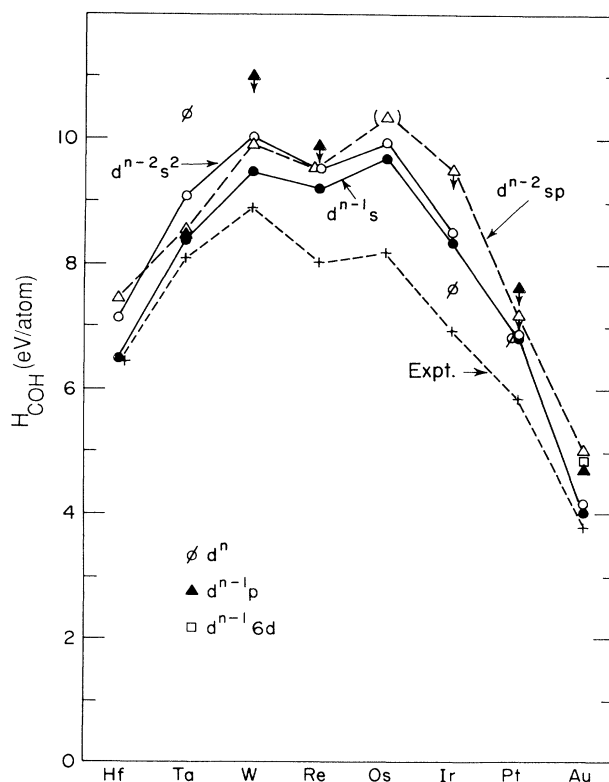


FIG. 6. The cohesive energies of the $5d$ transition metals (after Ref. 3) employing Eq. (2) and various atomic configurations (in the highest spin multiplicities). Cases where, due to incomplete spectral data, the estimates are upper bounds are indicated by vertical arrows. The d^n results for Ta and Ir lie out of line which is likely due to errors in the assignments of the experimental spectral data.

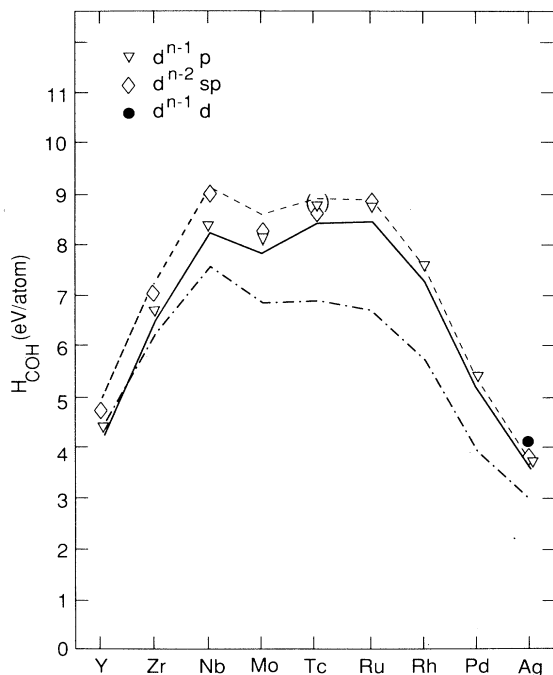


FIG. 7. Cohesive energies calculated with Eq. (2) for the 4d elements, the plotted points involving reference configurations having one valence electron which is other than 4d or 5s. The dot-dashed line is the experiment while the other lines come from Fig. 5.

dealing with the lowest lying set of the atomic levels within some configuration. The effect of going, instead, to the center of gravity of a configuration may, of course, be estimated. As in Eq. (4), it is convenient to define the difference between the LSDA-based spin-polarization energy and the experimental energy cost on going from the average of the high-spin multiplets to an average over all multiplets. Calculations show that the LDA overestimates this effect. (In this, the LDA would appear to be similar to the Hartree-Fock theory in its treatment of Hund's rule spin state splittings. Exchange is the origin of these splittings and correlation effects, omitted from the Hartree-Fock theory, act to stabilize the low-spin states relative to those of high spin, thus causing the theory to overestimate the splittings.) For Rb, the d^0s^1 alkali metal adjacent to the 4d elements, the LSDA spin-polarization energy is 0.23 eV. This increases to 0.8 eV for Y d^2s , ~ 1.3 eV for Mo, and then drops to 0.2 eV for Ag $d^{10}s$. Now for Rb and Ag the spin-polarized and the unpolarized results are for the *same* single multiplet level. The 0.2 eV discrepancy in energy arises, primarily, from a difference in treatment of the self-interaction: In the LDA as opposed to Hartree-Fock, the self-Coulomb interaction is only approximately cancelled by the exchange term for a given electron. The spin polarization in the LSDA in Ag and Rb acts mainly to improve the cancellation of the self-interaction of the single unpaired s electron. In a solid, the effect of the LSDA is not so clear since the basic assumption of an electron gas is better satisfied than is the case for an atom and there exists a

“quenching” of the spin in analogy to the quenching of orbital angular moments.

The comparison with the experimental atomic promotion energies shows that LSDA overestimates the stability of the transition-metal d electrons relative to the other valence electrons. It would be convenient if the atomic results provided insights for how to deal with the solids, in particular, if it offered a semiempirical scheme for “correcting” the local-density potentials for the s - d error. Gunnarsson and Jones emphasized⁴ that the issue is complex and this is borne out by Fig. 4. No simple trend appears in the promotion energy errors, e.g., the $d^{n-2}s^2 \rightarrow d^{n-1}s$ and the $d^{n-1}s \rightarrow d^n$, which can reasonably be expected to be quantitatively similar, are not. The two $p \rightarrow d$ promotion terms show greater similarities than do the $s \rightarrow d$. Figures 3 and 4 indicate that the errors in the calculated promotion energies are greatest in the 3d row and least in the 5d row, which is perhaps associated with the more compact character of the 3d orbitals.

Does local-density theory also overestimate the d stability in solids? One way to possibly answer this question is to experimentally measure the position of the d bands with respect to the s -like Γ_1 state and compare it with calculations. The bands of both Cu (Ref. 12) and Ni (Ref. 13) have been measured. For Ni, the Γ_1 state relative to the Fermi level (E_F) is in reasonable agreement with calculations,⁹ but the calculated d band is too wide and deep compared with experiment. The data for Ni apparently support the conclusion that the LDA overestimates the stability of the d configurations. On the other hand, the data⁹ for Cu is more difficult to interpret. The LDA Γ_1 state is 0.8 eV too low relative to the Fermi energy and the d bands are ~ 0.3 eV closer to E_F in the calculation, although the d band width is in excellent agreement with experiment. Thus at first glance Cu and Ni seem to go in opposite directions and no trend is apparent.

The case of Cu is not, however, quite so straightforward. Cu has a filled d band and its Fermi surface is determined by where the s -like band encloses one electron. Because the relative position of the s and d states affect the hybridization and dispersion of this band, a simple conclusion is difficult to draw. (The position of a filled band is not directly tied to the Fermi level and thus is fairly free to move.) It is conceivable that the calculated s - d separation is not so much a consequence of the relative s - d stability, but rather due to the requirement of a nearly free-electron-like Fermi surface. Related to this type of question are what experimental data best give insight into the relative stability. Measurements of Γ_1 versus d -band position suffer from the significantly different self-energy (lifetime) effects for these states because of their positions below E_F . Preferably, one would like to compare the relative energies of states that have approximately the same binding energies (and self-energies), but with different orbital character. One set of states that satisfy these basic requirements are the X_1 and X_3 levels: The X_3 state is pure d , while X_1 is an $sd_{3z^2-r^2}$ hybrid. In a tight-binding picture, the separation of these levels can be written in terms of the s - d separation and

various hopping-matrix elements. In the spirit of the promotion energy differences [as defined in Eq. (4)], we want a difference of separations between the theoretical and experimental s and d levels. Crudely, this can be done by comparing the separation between the X_1 and X_3 states, both theoretically and experimentally, with the larger separation corresponding to the more bound d state. Using the X_3 - X_1 separations and the tight-binding parameters fit from the experimental^{9,10} and theoretical¹¹ bands, the LDA d level is found to be more bound than the experimental one by ~ 0.1 eV for Cu and ~ 0.25 eV for Ni. The direction, and even the magnitude of these differences are not significantly affected for any reasonable changes of the tight-binding parameters, and thus the conclusions are more general than the tight-binding argument might suggest. Whether this simple correlation will hold up in the face of systematic experimental studies across the transition-metal rows is an important question and deserves further experimental investigation.

The present sampling of $4d$ and $5d$ transition-metal cohesive energies is more comprehensive than what has been available previously for rigorous relativistic band calculations employing full potentials. The results, providing the $d^{n-1}s$ configuration is used as the atomic reference, are in reasonable accord with experiment for the left-hand end of the transition-metal rows. The error is worst, of the order of 2 eV, for the metals Ru and Os which have just over half-filled d bands; finally, calculations approach experiment again for the noble metals. This trend correlates with the electron density in the interstitial region as manifested by the experimental bulk moduli, i.e., Ru and Os have the largest moduli and the largest interstitial densities. One may do other calculations employing the averages of configuration, as the reference atoms (rather than averages over states of maximum spin multiplicity as done here). Such calculations yield results which modify these observations slightly. With theory predicting these atomic levels to lie higher than experiment, the result is to increase the calculated H_{coh} by the amounts cited above in this section, i.e., roughly speaking, the solid $d^{n-1}s$ line of Fig. 5 for the heavier elements would rise slightly above the dashed

($d^{n-2}s^2$) curve. Then Tc (as best one can estimate⁸ for it) and Ru share in having the largest errors in H_{coh} in the $4d$ row, as do Re and Os in the $5d$ row. Whether or not the largeness of these errors is associated with these metals having the largest interstitial densities remains to be disentangled.

VI. CONCLUSION

Let us reiterate the two main thrusts of this paper. First, $s \rightarrow d$ and $p \rightarrow d$ promotion energy errors were scanned for all three transition-metal rows within the valence shells for which there is experimental data. The scan indicates that, as a rule, the LDA overestimates the relative stability of the valence d electrons, but this error strongly depends on whether or not there are non- d electrons in the final-state configuration. This observation strongly suggests that the error resides primarily in LDA's treatment of interactions between valence electrons. Further, LDA's errors appear largest for the more compact $3d$ atoms.

Second, the effect of choice of the reference level on calculated H_{coh} was scanned for the $4d$ and $5d$ transition elements. The different H_{coh} , obtained for a given element, lie with a well-defined band or "envelope." Contrary to the generally accepted wisdom that H_{coh} is always overestimated, good agreement was obtained for those metals with the most diffuse electron densities, namely, those at the beginning of the transition-metal rows. Significant disagreement is obtained in the middle of the rows and this is not remedied by the choice of the atomic reference state. The errors there are most likely due to the inability of the LDA to properly account for the change in valence electron-valence electron interactions on going from the free atom to the solid.

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because experimental values for the energetically low-lying high-spin terms are generally identified and listed (see Ref. 2), while those for low spin are often not observed (and, when seen and listed, can sometimes have their identification questioned). The problem is particularly severe in the middle of a transition-metal row. Among the $4d$ elements, Nb and Mo have eight and Tc seven low-spin multiplet levels which are not tabulated for their $d^{n-1}s$ configurations. For Nb and Tc this is about half of all the atom's levels. Crude estimates can be made for the positions of these missing levels with the resulting estimate of the energy of configuration's center of gravity having an uncertainty of several tenths of an eV.

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