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# Application of a screened self-interaction correction to transition metals: Copper and zinc

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A simplified form of the self-interaction correction (SIC) to the local-density approximation has recently been derived by Perdew and Norman and applied successfully to calculations on atoms and insulators. This success has led us to consider other solid systems. As is well known, at the end of the transition-metal series the *d* bands are too high and too disperse relative to experiment in the local-density approximation. This is therefore a prime testing ground for the effects of the self-interaction correction which should lower and narrow such bands. In this paper the above method is applied self-consistently to copper and zinc. Reasonable *d*-band dispersions are obtained but the *d* bands themselves are too low relative to experiment, which would indicate a relaxation shift of some sort. Indeed, the relaxation shift is due to metallic screening. Crudely incorporating this effect into a band model, we obtain reasonable *d*-band positions in both copper and zinc and correct a large part of the local-density error. Justifications for applying the SIC to transition metals with filled *d* bands are also given. Finally, core-level shifts due to SIC and metallic screening are discussed.

## I. INTRODUCTION

When one makes the local approximation to the exchange-correlation energy, a spurious self-interaction is introduced. One of the methods for subtracting this out has been discussed extensively by Perdew and Zunger,[1] and Perdew's form for the self-interaction correction (SIC) is the foundation for the work below. The problem is that the SIC terms are orbital dependent and break the symmetry of the system. Therefore, when extending to an infinite solid, these terms are zero in a Bloch representation as can easily be verified. But if one transforms to a Wannier representation, these terms are no longer nonzero (fortunately, these terms are positive for the electron gas[2]). This dramatically emphasizes the point that the SIC terms are not invariant under unitary transformations of the states. In fact, one of the methods of applying SIC to solids, that of Heaton, Harrison, and Lin,[3] involves solving the self-consistent equations in Bloch form but evaluating the SIC terms in Wannier form. We instead looked for an approximation to the SIC which would be invariant under a larger class of unitary transformations and that might, thus, be applied to a normal band code employing Bloch states.

In Ref. (4) such a form, the simplified SIC (SSIC), was derived:

$$\Delta V^{\mathrm{SIC}}(r)=0.104\hat{u}\cdot\frac{\vec{\nabla}\rho(r,\epsilon)}{\rho(r,\epsilon)} \tag{1}$$

in hartree where $\hat{u}$ is a unit vector in the direction of the gradient of the total electron density and $\rho(r,\epsilon)$ is the local density of states. It was applied successfully in a perturbative fashion to atoms resulting in electron-removal energies that were as good as their SIC counterparts when compared to experimental data.[4] As can be seen, this form is invariant under scale transformations (i.e., it is size consistent). This led to the hope that such a correction could be applied to solids. Unfortunately, a form using $\rho(r,\epsilon)$ would be difficult to implement self-consistently in solids. For this reason we replaced $\rho(r,\epsilon)$ by $\rho_v(r)$, the valence density, and analyzed the valence-band states and the band gap in Ne and NaCl (Ref. 5) (of course, the conduction states were given zero SIC since they are unoccupied in the ground state). Applied perturbatively, we found band gaps that were close to the experimental results and thus were a large improvement over their local-density counterparts, which severely underestimated the gaps. The valence-band dispersion was not changed very much. This in fact was the same trend found by Heaton, Harrison, and Lin[3] using a completely different implementation of the SIC, which is encouraging. Self-consistency had little effect, acting to improve the results. When we used $\rho_{nk}$, the Bloch density for band index *n* and wave vector *k*, in place of $\rho_v(r)$ (perturbatively), considerable harm was done to the valence band. This indicates that the energy smearing done by replacing $\rho(r,\epsilon)$ by $\rho_v(r)$ is a correct course of action. In fact, our correction using $\rho_v(r)$ should decrease as the band dispersion increases, thus taking into account the decrease in SIC as the states become more delocalized.

The question probably in the reader's mind now is why nonzero SIC should be allowed in solids. The author's own view of this matter will be a major foundation for applying SIC to metals. The experimental data in which we are interested in comparing is based on photoemission. During the photoemission process, a hole is left in the band. This hole effectively breaks the symmetry of the crystal. As long as the hole has a certain degree of localization, nonzero SIC terms will be present. Given the success of applying our SSIC to insulators, and with the above thoughts in mind, we turn now to applying it to transition metals.

At the end of the transition-metal series, the local-density approximation (LDA) yields *d* bands which are too high and too disperse relative to experimental photoemission data, in particular for Pd and Pt,[6] for Cu, Ag, and Au,[7] and for Zn.[8] The interesting case of Ni will be touched on briefly in the discussion section. The local-density error increases as the $d$ states drop in energy, in particular the $d$-band position error is 0.5 eV in Cu and over 2 eV in Zn. This has been attributed to self-energy effects. But recently a Kohn-Sham self-energy treatment in the slowly varying density approximation was applied to copper by Sachetti.[9] Although he found out about the correct mass enhancement at the Fermi surface, there was little change in the band eigenvalues. We therefore apply our version of SIC to copper and zinc with the hope of describing the large excitation and relaxation effects that occur when $d$ electrons are ejected out of filled $d$ bands.

## II. CALCULATIONAL PROCEDURE

The code employed is a linear augmented-plane-wave (LAPW) package[10] kindly provided by Koelling. Although the potential is made spherical inside the muffin tins, it is allowed to be of general shape in the interstitial region (the warped muffin-tin approximation[11]). This should be a pretty good approximation in the cases of copper and zinc (for a discussion of the small non-muffin-tin terms in copper, see Ref. 7). The Bloch equations are solved in the semirelativistic approximation[12] with the neglect of spin orbit. The correlation piece of the local exchange-correlation functional is taken to be that of von Barth and Hedin.[13] The lattice constant used for copper was 6.8309 a.u. As the code is designed for cubic systems, we approximated zinc by using an fcc lattice with a lattice constant of 7.25 a.u. which was the technique used by Moruzzi *et al.*[14] As zinc is actually an hcp lattice, we will carefully keep this in mind. The number of plane-wave basis functions at $\Gamma$ was 59 in both cases corresponding to $RK=8$, where $K$ is the length of the greatest reciprocal-lattice vector and $R$ is the muffin-tin radius. The Brillouin zone was approximated by an 89-point mesh. All calculations were performed self-consistently to a moderately good degree of convergence with the charge density being constructed with the use of a tetrahedron scheme. The SSIC was applied to the valence states only, but in Sec. III D results with core SSIC in copper are presented.

## III. RESULTS

### A. Copper

In Table I we report calculations in the LDA as well as those with the addition of our correction both in a perturbative and self-consistent fashion. By a perturbative approach we mean the addition of $\langle \psi_{nk} | \Delta V^{\text{SIC}} | \psi_{nk} \rangle$ to $\epsilon_{nk}$ where $\psi_{nk}$ and $\epsilon_{nk}$ are the LDA Bloch functions and eigenvalues, respectively. First, we note good agreement of our LDA work with that of Ref. 7 except that our Fermi energy appears to be about 5 mRy too high. This is due to the more careful evaluation of the Fermi energy in the case of Ref. 7 (our Fermi energy was found using a tetrahedron package based on our 89-point mesh). This point is further elaborated in Ref. 17. Thus the rest of the numbers reported are for a Fermi energy that has been adjusted 0.06 eV downward as was done in Ref. 17. We carefully remind the reader of this. Note that the LDA yields $d$ bands which are 0.5 eV too high and about 0.3 eV too disperse at the edge of the Brillouin zone.

An analysis of the SSIC perturbative results indicates a huge displacement of the $d$ band by about 2.4 eV downward from the LDA results, about a 50% narrowing of the $d$ band, and an overall narrowing of the valence band. Obviously, a perturbative treatment will not suffice here. The next column in the table indicates the same results but with the SSIC term reduced by a factor of 5, resulting in good agreement with experiment. This indicates that some effect is canceling a large part of the SIC. That be-

TABLE I. SSIC valence eigenvalues in copper (eV). Pert denotes perturbative, SC denotes self-consistent, and $E_F$ denotes the Fermi energy.

| | LDA | | SSIC | | | |
|---|---|---|---|---|---|---|
| | Ref. 7 | Present[a] | Pert | Pert[b] | SC | Expt.[c] |
| $d$ widths: | | | | | | |
| $E_{\Gamma_{12}}-E_{\Gamma'_{25}}$ | 0.82 | 0.80 | 0.58 | 0.76 | 0.74 | 0.80 |
| $E_{X_5}-E_{X_1}$ | 3.43 | 3.43 | 1.89 | 3.12 | 2.91 | 3.15 |
| $E_{L_3}-E_{L_1}$ | 3.43 | 3.43 | 1.62 | 3.07 | 2.80 | |
| $d$ positions: | | | | | | |
| $E_F-E_{\Gamma_{12}}$ | 2.34 | 2.40,2.34 | 4.56 | 2.78 | 3.67 | 2.85 |
| $E_F-E_{X_5}$ | 1.58 | 1.64,1.58 | 3.93 | 2.05 | 2.93 | 2.05 |
| $E_F-E_{L_3}$ | 1.76 | 1.80,1.74 | 4.07 | 2.21 | 3.09 | 2.25 |
| $s$-$p$ bottom: | | | | | | |
| $E_F-E_{\Gamma_1}$ | | 9.47,9.41 | 7.29 | 8.99 | 8.80 | 8.60[d] |

[a] Numbers after the commas are adjusted by 0.06 eV to agree with column 1 for reasons discussed in the text. All other results, including those in Tables II and IV, have been similarly adjusted.

[b] The perturbative SSIC was reduced by a factor of 5.

[c] Reference 15.

[d] Reference 16.

lief is reinforced when the calculation is performed self-consistently. The position of the *d* band has now been displaced by about 1.3 eV downward (still too low), but the band dispersion is now close to the experimental results. This is a good sign for a relaxation shift of some sort.

### B. Screened copper

The relaxation shift is due to metallic screening. When a hole is created in the *d* band, the screening charge from outside the unit cell enters to neutralize the positive charge. In a metal such as copper with a filled *d* band, the screening charge will be primarily *s*-*p* in character and should result in very efficient screening with a large shift in the *d*-hole self-energy as a consequence. This point is extensively discussed by Egelhoff.[18] With an analysis of experimental data, he concludes that the *d* holes are screened as effectively as the core holes by the *s*-*p* screening charge. Although the *d* hole is mobile, the *s*-*p* screening charge is more mobile and thus the *d* hole can be considered localized with respect to the screening charge. Not only would this allow a nonzero SIC for this case, but this points to the relaxation shift mentioned. The screening charge has not been taken into account in our functional. To properly do the screening would require a cluster calculation that would defeat our purpose of simplicity. Instead, we make use of the fact that the screening charge is highly localized in the unit cell[19] and we thus approximate the screened hole by a screened hole in every unit cell. This is a technique similar to that used by researchers doing transition-state calculations in insulators and semiconductors.[20] Thus we remain in the band model and have simplified things considerably. Since the SIC eigenvalues should approximate the physical removal energies,[1] we simply self-consistently run a screened cell calculation (i.e., we screen *first)* and *then* use the SIC eigenvalues to yield the energy for creating a hole. To screen, we place an extra electron in the unit cell. Of course, the unit cell is never physically charged, but the program compensates for this when the Ewald technique is applied by using a uniform positive charge density to neutralize the extra negative charge.[11] This is the second approximation. It should be a better approximation than equating the screened hole to the next element in the Periodic Table, which has been previously used to analyze the relaxation effects.[21]

In Table II we report the screened results. As a preliminary test, we simply allowed the Fermi energy to float from 11 electrons per cell to 12 electrons per cell. At the end of the run when the density was converged, we found the *d*-band position with respect to a Fermi energy for 11 electrons per cell. The results are amazingly good. Although the *d*-band position still overshoots, the error is about 50% of the local-density error (the LDA undershoots this of course). The band dispersion, which was overestimated by about 0.3 eV at the edge of the Brillouin zone in the LDA, is now very close to the experimental numbers. [The next column in the table shows the addition of the Langreth-Mehl (LM) gradient correction[22] which slightly improves the *d*-band position. Previous applications of LM to LDA calculations in Cu and V are extensively discussed in Ref. 17.] Given this success, we handled the screening more carefully by searching for the lowest unoccupied state on our 89-point mesh and occupying it by an entire electron. The state had an angular momentum decomposition inside the muffin-tin sphere of 20% *s*, 27% *p*, and 37% *d*. This time, although the band dispersion was too large by 0.15 eV, the band position fell on top of the experimental numbers. Given the crudeness of the method for handling the screening, the agreement with experiment can be considered rather fortuitous. But the indication is that the real physical effects have been isolated correctly. To test further, we move on to zinc.

TABLE II. Screened SSIC valence eigenvalues in copper (eV). SC denotes self-consistent screened SSIC and LDS denotes screened calculation with no SSIC.

| | LDS[a] | SC[a] | SC[b] | SC[c] | Expt.[d] |
|---|---|---|---|---|---|
| *d* widths: | | | | | |
| $E_{\Gamma_{12}}-E_{\Gamma'_{25}}$ | 0.88 | 0.78 | 0.78 | 0.80 | 0.80 |
| $E_{X_5}-E_{X_1}$ | 3.92 | 3.17 | 3.21 | 3.32 | 3.15 |
| $E_{L_3}-E_{L_1}$ | 3.99 | 3.07 | 3.10 | 3.25 | |
| *d* positions: | | | | | |
| $E_F-E_{\Gamma_{12}}$ | 1.89 | 3.12 | 3.03 | 2.88 | 2.85 |
| $E_F-E_{X_5}$ | 1.07 | 2.37 | 2.27 | 2.09 | 2.05 |
| $E_F-E_{L_3}$ | 1.26 | 2.54 | 2.44 | 2.26 | 2.25 |
| *s*-*p* bottom: | | | | | |
| $E_F-E_{\Gamma_1}$ | 10.13 | 9.04 | 9.07 | 9.22 | 8.60[e] |

[a] This screened calculation was performed using a Fermi energy for 12 electrons per cell although $E_F$ is the Fermi energy for 11 electrons per cell (see text).

[b] Langreth-Mehl gradient correction added to calculation in previous column.

[c] Screening state $n=6, k=(\frac{3}{2},\frac{1}{2},0)$ occupied.

[d] Reference 15.

[e] Reference 16.

TABLE III. Screened SSIC valence eigenvalues in fcc zinc (eV). SC denotes self-consistent screened SSIC results.

| | LDA | | SSIC | | | |
|---|---|---|---|---|---|---|
| | Ref. 14 | Present | Pert[a] | SC[b] | SC[c] | Expt.[d] |
| $d$ widths: | | | | | | |
| $E_{\Gamma_{12}}-E_{\Gamma'_{25}}$ [e] | 0.41 | 0.42 | 0.27 | 0.35 | 0.35 | |
| | | (0.60,0.34) | | (0.53,0.27) | (0.53,0.28) | (0.53,0.28) |
| $E_{X_5}-E_{X_1}$ | 1.63 | 1.63 | 0.68 | 1.24 | 1.24 | |
| $E_{L_3}-E_{L_1}$ | 1.51 | 1.57 | 0.43 | 1.09 | 1.10 | 1.02 |
| $d$ positions: | | | | | | |
| $E_F-E_{\Gamma_{12}}$ [e] | 7.81 | 7.66 | 15.63 | 10.19 | 10.18 | 9.77 |
| | | (7.60) | | (10.13) | (10.12) | |
| $E_F-E_{X_5}$ | 7.40 | 7.24 | 15.32 | 9.82 | 9.80 | |
| $E_F-E_{L_3}$ | 7.48 | 7.33 | 15.39 | 9.90 | 9.88 | 9.60 |
| $s$-$p$ bottom: | | | | | | |
| $E_F-E_{\Gamma_1}$ | 10.87 | 11.02 | 11.02 | 10.83 | 10.80 | |
| $s$-$p$ states: | | | | | | |
| $E_F-E_{L_1}$ ($s$) | 1.20 | 1.37 | 1.37 | 1.87 | 1.90 | 2.9 |
| $E_F-E_{L'_2}$ ($p$) | 3.33 | 3.25 | 3.25 | 2.76 | 2.66 | 3.9 |

[a] Only the $d$ states have been shifted by SSIC (perturbative SSIC, unscreened). All other states, including $E_F$, have their LDA values.

[b] Screening state $n=6$, $k=(2,\frac{1}{2},0)$ occupied.

[c] Screening state $n=7$, $k=(\frac{3}{2},\frac{5}{4},\frac{1}{4})$ occupied.

[d] Reference 8.

[e] The $\Gamma'_{25}$ state (fcc notation) is probably spin orbit split by 0.25 eV experimentally. This is verified by us by applying spin orbit perturbatively (Ref. 23) at $\Gamma$. The eigenvalues in parentheses are the spin-orbit results.

### C. Zinc

In Table III we list results for zinc. Our own LDA results are close to those of Moruzzi *et al.*,[14] who also performed a self-consistent fcc calculation, except that our $d$ band is 0.15 eV higher and the bottom of our valence band is 0.15 eV lower. Since our $d$-band position and the bottom of our valence band in copper were in close agreement with the results of Ref. 14, we can only speculate here on the discrepancy. One of the points is that the energy of the $d$ levels in zinc is probably fairly sensitive to the potential (or technique) employed given the greater localized character. Since the effects we are analyzing are rather large in zinc, we will not discuss this point further. The perturbative SSIC calculation was performed on the $d$ states only. The rest of the states and the Fermi energy were left at their LDA values. The result of this assumption of $d$-state localization is that the $d$ states fell below the $s$-$p$ band (15.3—16 eV below the Fermi energy). This interesting point will be further elaborated in the discussion section. We turn now to the screened calculations which were performed again by adding an electron to the lowest unoccupied state on the 89-point mesh. Unfortunately, there were two states that were energetically close to each other. When the first state was occupied, the other would drop below the first state on the next iteration and become occupied instead, etc. Thus we converged the calculation twice, once by forcing the occupation of the first state with $n=6$, $k=(2,\frac{1}{2},0)$, and angular momentum decomposition inside the muffin tin of 72% $p$, 4% $d$, and 2% $f$, and the next by forcing the other state to become occupied with $n=7$, $k=(\frac{3}{2},\frac{5}{4},\frac{1}{4})$, and a decomposition of 64% $p$, 8% $d$, and 1% $f$. As can be seen, there is not much difference between the two runs. What can be seen, though, is that the screened SSIC calculations, although they overshoot the $d$-band position, correct about 80—90 % of the local-density error. The local-density error in the band dispersion at $L$ is also corrected by about 85%. In Ref. 8 Himpsel *et al.* found that the $\Gamma'_{25}$ state (fcc notation) was split, which they speculated was due to spin-orbit effects. We verified this by applying the spin orbit perturbatively[23] at $\Gamma$. All calculations show the correct experimental splitting, although only the screened calculations gave the split levels' positions with respect to $\Gamma_{12}$ right.

Of course, certain factors must be taken into account. We are approximating an hcp lattice by that which is fcc. Correcting for this either improve these results or worsen them. Looking at the numbers for the hcp and fcc calculations listed in Ref. 8, the author doubts whether the effect of this would be greater than 0.2 eV, and it probably would be less. Also, note the difference in experimental data as discussed in Ref. 8. Ultraviolet photoemission spectroscopy (UPS) data tend to give higher $d$-band centroids than x-ray photoemission spectroscopy (XPS) data [$-9.5$ (Ref. 24) and $-10.08$ eV (Ref. 25), respectively].

The XPS data would be closer to our results. Finally, we listed eigenvalues for two non-*d* states, the $L_1$ state (a pure *s* state) and the $L_2'$ state (a *p* state with some *d* admixture). The reason is, to point out, in particular, that SSIC takes the $L_2'$ state energy away from experiment. This is to be expected since the occupation of a *p* screening state should shift the other *p* states upward in energy. Thus, the use of a SSIC for a *p* hole screened by a *p* state has violated some principles discussed previously, in particular that of locality of the hole with respect to the screening charge. We will return to this in the discussion section.

### D. Core SSIC in copper

Previously, we have ignored SIC effects in the core, although the core is not frozen in our calculations. As the core levels in these metals are energetically deep (about 4 Ry from the valence-band bottom to the 3*p* levels), the effect of SIC in the core on the valence band itself will be small. For the case of copper, though, we decided to calculate the core SSIC perturbatively as described in Sec. III A using the orbital density for each level to calculate the eigenvalue shift. The numbers reported in Table IV are for the LDA core eigenvalues and the LDA and screened LDA values with perturbative core SSIC added. The reason we used the local-density runs is that we assume the holes are now created in the core states and, therefore, the valence states should be well given by their LDA values. Also tabulated are the experimental results of Sevier.[26] As can be seen, the SSIC results are much better than their LDA counterparts, the screened SSIC results being an improvement over the unscreened results. The overshoot of the SSIC numbers compared to experiment is probably due to the perturbative nature of the calculation. Finally, we wish to point out the difference between the screened and unscreened results, which can be attributed to a relaxation shift due to screening. The $n=1$ and 2 core levels are shifted 1.3—1.6 eV upward due to screening, and the $n=3$ levels by 0.7 eV. Note that the valence 3*d* levels were also shifted up by about 0.6 eV.

## IV. DISCUSSION

At the end of the transition-metal series, the LDA *d* bands are too high and disperse relative to experimental photoemission data. This has been attributed to self-energy effects. Extensive applications of the self-energy have been done in the particular case of nickel (see Ref. 27, and references therein), mainly by using approximations based on self-energy corrections to Hartree-Fock theory. Recently, a Kohn-Sham self-energy correction in the slowly varying density approximation was applied by Sachetti to copper.[9] The top of the *d* band at *X* dropped by only 0.05 eV and the band at *X* *widened* by 0.14 eV. This casts doubts on the validity of this approximate self-energy away from the Fermi energy (note, he did get the correct mass enhancement at the Fermi surface). In this paper we have attempted to obtain an approximate self-energy from another viewpoint, that of subtracting the spurious self-interaction from the LDA potential. The advantage here is that the self-interaction effects were isolated from the relaxation effects due to "extra-atomic screening" (we might note that SIC apparently takes into account intra-atomic relaxation effects[1]). This is similar in spirit to work done by Zunger on 3*d* excitations in GaAs clusters.[28] Of course, there are other advantages. One is that of staying in a band model. The other advantage is quite significant. Since the SIC eigenvalues should approximate the physical removal energies,[1] we are able to screen in a general fashion and find all the hole creation energies in *one* calculation. Of course, given the approximations involved in performing the screened calculation, these numbers are subject to change, but we feel not by much. It may be stated, though, that finding extra-atomic relaxation shifts for the valence states from an atomic model will probably not work, at least in copper, since the Fermi energy itself is highly sensitive where the *d* states are placed, and the energy shift needed is small from an atomic viewpoint. The author has performed various atomic runs on copper using self-consistent SIC in the formalism of Ref. 1. He has found that the difference in ionization energies for removing a *d* electron from a copper atom with and without an extra *s* electron (i.e., $s^2$ and $s^1$) is an extremely large 8.03 eV. Even if one looks at the 3*d* eigenvalue difference between the $d^{10}s^1$ and $d^{10}s^2$ configurations, one still gets 6.61 eV.

TABLE IV. Core eigenvalues, $-\epsilon$, in copper (eV) with respect to the Fermi energy. LDS denotes local-density screened calculation.

| | LDA | LDA[a] | LDS[a,b] | Expt.[c] |
|---|---|---|---|---|
| 1*s* | 8828.8 | 8993.6 | 8991.3 | 8980.5 |
| 2*s* | 1058.2 | 1094.1 | 1092.6 | 1098.6 |
| $2p^{1/2}$ | 927.9 | 963.6 | 962.1 | 952.6 |
| $2p^{3/2}$ | 907.5 | 942.4 | 940.8 | 932.8 |
| 3*s* | 111.88 | 123.24 | 122.53 | 122.45 |
| $3p^{1/2}$ | 71.46 | 82.08 | 81.39 | 77.23 |
| $3p^{3/2}$ | 68.85 | 79.27 | 78.60 | 75.07 |

[a] Core SSIC added perturbatively.

[b] Calculation performed as in a of Table II.

[c] Reference 26.

As for the Fermi surface itself, by undertaking an excited-state calculation, we have destroyed the ground-state properties of the system. As a demonstration of this, the screened SSIC calculation in copper yielded a neck radius, $k_{\text{rad}}^{\text{neck}}/k_F^0$, of 0.100 where $k_F^0$ is the free-electron Fermi radius compared to an experimental number of 0.189 (Ref. 29) and our own LDA number of 0.199 [the inclusion of non-muffin-tin terms yields 0.192 (Ref. 7)]. Of course, this should be expected since we are mocking an excited state of the system. This would go a long way to explain why one cannot get both the Fermi surface and the *d*-band position correctly in copper using a local-density functional. LDA gives the correct Fermi surface and not the *d* bands. Screened SSIC gets the *d* bands but not the Fermi surface. This is correct since LDA is designed to get the ground-state properties and screened SSIC gets the excited-state properties.

From the above discussion, we can conclude that in copper the initial *d* states before photoemission are well described by the LDA. The final state after photoemission can be regarded as a screened hole propagating through the lattice (semilocalized). The case of zinc, though, is different. Ley *et al.*[30] estimated that in the initial state of zinc, the *d* states are localized about 15 eV below the Fermi energy and thus are below the *s*-*p* band. In the final state, the *d* holes move up into the *s*-*p* band due to relaxation, and the final state can be regarded as a semilocalized exciton—a screened hole propagating through the lattice. Our own results are a verification of this point. The unscreened SSIC results (assuming only *d* localization) yielded a narrow *d* band about 15.3—16.0 eV below the Fermi energy and, thus, below the *s*-*p* band. The screened results, which can be regarded as a realization of their semilocalized exciton, were in good agreement with their XPS data which indicated a *d* band at about 10.18 eV below the Fermi energy.

Before we mention other systems, two points must be brought up. First, the variation of the experimental data in zinc (XPS vs UPS) as discussed in Ref. 8 leads one to suspect a sensitivity of the *d* states to the way the excitation is performed, which would not be surprising given our results. Second, we are not really in a position to discuss the core-level shifts due to atom-metal differences. We do emphasize the large effect due to SSIC and the smaller relaxation effect from screening. An important point is that the relaxation shift for the 3*d* states was about the same as for the 3*s* and 3*p* states. This is a good indication, therefore, that the 3*d* holes indeed have a comparable localization with respect to the screening charge as the 3*s* and 3*p* core holes.

Can this method be applied to other systems? We believe it can within certain guidelines. With the inclusion of spin polarization, a calculation on nickel should prove interesting. We would propose using a separate SSIC valence correction for the spin-up and spin-down valence densities. As for the other transition metals (except Pd, Pt, Ag, and Au), the application of SSIC to these metals is on questionable grounds. One of the problems is that the *d* hole is not as localized given the partially filled character of the band and the large band dispersion. Another point is that the screening state and the hole state should be spatially similar in these systems, and thus the hole will not be localized with respect to the screening state. This would imply small SSIC and small relaxation effects which would tend to cancel each other. Since the LDA eigenvalues, e.g., vanadium,[17] are fairly close to the experimental photoemission data, this would seem to support this view. The author has also performed SSIC calculations on silicon in the warped muffin-tin approximation. Even though the large non-muffin-tin terms were neglected, he still got a band gap of 0.3 eV [compared to a full non-muffin-tin result of 0.5 eV (Ref. 31)]. The inclusion of SSIC, either perturbatively or self-consistently, yielded an increase in the gap by 1.5 eV which is far too great (experimentally, the gap is 1.1 eV). This indicates that screening effects must be taken into account here also. Performing the screening in a semiconductor in our model will be much more difficult since the screening in a semiconductor is not as efficient as in a metal, and thus localizing the effect to the unit cell may not be a sufficient approximation. Of course, the best way would be to incorporate the screening into the functional itself via a dielectric function. Wang and Pickett have done this for the self-energy in silicon in a density-functional approximation[32] and Hanke and others in a hybrid approach[33] with a fair amount of success. Lastly, we might mention that recently Tibbetts and Harmon have performed an LDA calculation on lutetium (which has a filled *f* band) which had a tendency to place the *f* levels too high.[34] They indicate that this may be a similar situation to that of copper and zinc.

To conclude, SIC effects are not always nonzero in solids and can be quite crucial, even in transition metals, for predicting excitation energies. Correcting for self-interaction should yield eigenvalues close to experimental removal energies as long as the appropriate physical effects, such as screening, are taken into account. The indication here is that the 3*d* holes in copper and zinc have a certain degree of localization with respect to the *s*-*p* screening charge in the final state. It must be remembered, though, that SIC cannot be blindly used in a solid without appreciation for its applicability to that particular system. As we saw, the initial states in copper and zinc are radically different, the first having delocalized *d* states and the latter having localized *d* states.

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[1] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
[2] M. R. Norman, Phys. Rev. B 28, 3585 (1983).
[3] R. A. Heaton, J. G. Harrison, and C. C. Lin, Solid State Commun. 41, 827 (1982); Phys. Rev. B 28, 5992 (1983).
[4] J. P. Perdew and M. R. Norman, Phys. Rev. B 26, 5445 (1982).
[5] M. R. Norman and J. P. Perdew, Phys. Rev. B 28, 2135 (1983).
[6] A. H. MacDonald, J. M. Daams, S. H. Vosko, and D. D. Koelling, Phys. Rev. B 23, 6377 (1981).
[7] A. H. MacDonald, J. M. Daams, S. H. Vosko, and D. D. Koelling, Phys. Rev. B 25, 713 (1982).

[8] F. J. Himpsel, D. E. Eastman, E. E. Koch, and A. R. Williams, Phys. Rev. B 22, 4604 (1980).

[9] F. Sachetti, J. Phys. F 12, 281 (1982).

[10] D. D. Koelling and G. O. Arbman, J. Phys. F 5, 2041 (1975); O. K. Andersen, Phys. Rev. B 12, 3060 (1975).

[11] For a discussion on the construction of the warping potential, see N. Elyashar and D. D. Koelling, Phys. Rev. B 13, 5362 (1976).

[12] B. N. Harmon and D. D. Koelling, J. Phys. C 7, L210 (1974).

[13] U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[14] V. L. Moruzzi, A. R. Williams, and J. F. Janak, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[15] J. A. Knapp, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B 19, 4952 (1979).

[16] P. Thiry, D. Chandesris, J. Lecante, C. Guillot, R. Pinchaux, and Y. Petroff, Phys. Rev. Lett. 43, 82 (1979).

[17] M. Norman and D. D. Koelling, Phys. Rev. B 28, 4357 (1983).

[18] W. F. Egelhoff, Jr. (unpublished).

[19] J. R. Smith, F. J. Arlinghaus, and J. G. Gay, Phys. Rev. B 26, 1071 (1982).

[20] S. B. Trickey, A. K. Ray, and J. P. Worth, Phys. Status Solidi B 106, 613 (1981).

[21] B. Johansson and N. Martensson, Phys. Rev. B 21, 4427 (1980).

[22] D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. 47, 446 (1981); Phys. Rev. B 28, 1809 (1983).

[23] A. H. MacDonald, W. E. Pickett, and D. D. Koelling, J. Phys. C 13, 2675 (1980).

[24] P. T. Poole, R. C. G. Leckey, J. G. Jenkin, and J. Liesegang, Phys. Rev. B 8, 1401 (1973).

[25] S. K. Wertheim, M. Campagna, and S. Hufner, Phys. Condens. Matter 18, 133 (1974).

[26] K. D. Sevier, At. Data Nucl. Data Tables 24, 323 (1979).

[27] L. Kleinman and K. Mednick, Phys. Rev. B 24, 6880 (1981).

[28] A. Zunger, Phys. Rev. Lett. 50, 1215 (1983).

[29] P. T. Coleridge and I. M. Templeton, J. Phys. F 2, 643 (1972).

[30] L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 8, 2392 (1973).

[31] D. R. Hamann, Phys. Rev. Lett. 42, 662 (1979).

[32] C. S. Wang and W. E. Pickett, Phys. Rev. Lett. 51, 597 (1983).

[33] G. Strianti, H. J. Mattausch, and W. Hanke, Phys. Rev. B 25, 2867 (1982); W. Hanke (unpublished).

[34] T. A. Tibbetts and B. N. Harmon, Solid State Commun. 44, 1409 (1982).