

January 01, 2005

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Recommended Citation

Barbiellini, B. and Bansil, A., "A spin-polarized scheme for obtaining quasi-particle energies within the density functional theory" (2005). *Physics Faculty Publications*. Paper 12. <http://hdl.handle.net/2047/d20000365>

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A spin-polarized scheme for obtaining quasi-particle energies within the density functional theory

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We discuss an efficient scheme for obtaining spin-polarized quasi-particle excitation energies within the general framework of the density functional theory (DFT). Our approach is to correct the DFT eigenvalues via the electrostatic energy of a majority or minority spin electron resulting from its interaction with the associated exchange and correlation holes by using appropriate spin-resolved pair correlation functions. A version of the method for treating systems with localized orbitals, including the case of partially filled metallic bands, is considered. Illustrative results on Cu are presented.

I. INTRODUCTION

As spectroscopic data using a variety of experimental techniques is becoming available at an ever increasing pace, there is great need to develop efficient methods for calculating electronic excitation energies in wide classes of materials. The GW approximation (GWA) has been the traditional route for addressing this problem¹. The GWA however is computationally quite intensive, which makes the routine application of the GWA in electronic structure computations difficult and for this reason GWA results have to date been limited largely to relatively simple systems.

With this motivation, in a previous study², we have attempted to develop a simplified scheme for obtaining quasi-particle energies by correcting the eigenvalues ϵ_n given by the density functional theory (DFT)³ with a state-dependent correction Δ_n associated with the self-energy Σ_{xc} of the exchange-correlation hole surrounding each electron. The results are similar to those obtained within other extensions of the DFT^{4,5,6,7,8,9,10}, which have been shown to describe the energy gaps in semiconductors with an accuracy comparable to that of the GWA. The purpose of the present work is to generalize the unpolarized case considered in Ref. 2 to include spin-polarization effects. We also address the treatment of self-interaction corrections in systems with localized d and f orbitals and suggest a scheme for handling metallic systems with partially filled bands of d or f character.

This article is organized as follows. The introduction is followed in Section II by a brief explanation of the relevant pair-correlation functions and their role in evaluating self-energies. The spin-resolution of the exchange and correlation energies is developed in Section III. A somewhat more general formulation of our scheme is taken up in Section IV which also presents illustrative results in Cu. Finally, Section V makes a few concluding remarks.

II. ROLE OF PAIR-CORRELATION FUNCTIONS

We consider the elements

$$\pi(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_3 \dots d\mathbf{r}_N, \quad (1)$$

of the two-particle density matrix, where N is the total number of electrons and Ψ is the ground state wavefunction of the many body electronic system. The pair correlation function $g(\mathbf{r}_1, \mathbf{r}_2)$ is then defined via the relation

$$\begin{aligned} \pi(\mathbf{r}_1, \mathbf{r}_2) &= n(\mathbf{r}_1)n(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2) \\ &= n(\mathbf{r}_1)n(\mathbf{r}_2)(1 + C(\mathbf{r}_1, \mathbf{r}_2)), \end{aligned} \quad (2)$$

where $n(\mathbf{r})$ denotes the electron density and the correlation factor $C(\mathbf{r}_1, \mathbf{r}_2)$ is defined by the second equality. For an uncorrelated system $g(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 1$, or equivalently, $C(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 0$.

Two effects must now be considered, namely, exchange and correlation. The antisymmetry of the many electron wavefunction Ψ prevents electrons of the same spin to come too close to one another and creates an 'exchange hole' around each electron. The associated exchange energy is:

$$E_x = \int d\mathbf{r} n(\mathbf{r})\epsilon_x(\mathbf{r}), \quad (3)$$

where

$$\epsilon_x(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \frac{n(\mathbf{r}')C_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (4)$$

is the exchange energy per particle and C_x is the exchange contribution to the pair correlation $C(\mathbf{r}, \mathbf{r}')$ of Eq. 2. The factor of 1/2 accounts for double counting of the electron-electron interaction. Thus, the exchange energy per particle $\epsilon_x(\mathbf{r})$ can readily be interpreted as the Coulomb interaction of an electron at \mathbf{r} with its exchange hole. For the homogeneous electron gas (HEG) of density n , C_x and ϵ_x have well-known analytical expressions $C_x^{HEG}(n)$ and $\epsilon_x^{HEG}(n)$ and, in particular, the familiar Hartree-Fock-Slater (HFS) potential is given by¹¹

$$v_S(\mathbf{r}) = 2\epsilon_x^{HEG}(n(\mathbf{r})). \quad (5)$$

Here the factor of 2 arises from the fact that variations with respect to a trial wavefunction of the form of a Slater determinant yield a potential term in one-particle equations which is twice as large as the corresponding energy term ϵ_x . The DFT within the local density approximation (LDA) provides a remarkably similar scheme in which the electron density $n(\mathbf{r})$ is treated as the variational parameter¹². The exchange hole is still described by the pair correlation function between like spin electrons, but the exchange potential

$$v_x(\mathbf{r}) = \frac{\delta E_x}{\delta n(\mathbf{r})} \quad (6)$$

differs from the HFS potential by a factor of 2/3.

Coulomb repulsion between electrons is an additional effect responsible for electron motions to become correlated. As a result, there also appears a 'correlation hole' around each electron, which is dominated by electrons of opposite spin, since the like spin electrons are already excluded via the exchange hole. The correlation hole is generally less deep compared to the exchange hole, especially at high electron densities. Note that the exchange hole goes to zero at the origin and excludes a total of one electron worth of charge in order to correct for self-interaction terms. In contrast, the correlation hole integrates to zero and involves only a redistribution of charge¹³.

A number of intuitive schemes for treating the exchange and correlation holes have been proposed, where the pair correlation functions are determined from a Schrodinger equation for an electron pair with appropriate boundary conditions.^{14,15,16,17,18} Such models are useful for generalizing the LDA by improving the description of exchange and correlation in inhomogeneous systems. Note, however, that in going beyond the LDA, a distinction should be made between theories which attempt to find better energy functionals but still lie within the framework of the DFT, and those theories which focus on the self-energy Σ_{xc} in order to obtain better quasi-particle energies. The present scheme belongs to the latter category where the excitation energies are given by

$$E_n = \epsilon_n + \Delta_n. \quad (7)$$

Here ϵ_n is the eigenvalue corresponding to the Kohn-Sham orbital ψ_n , and Δ_n is a state-dependent correction associated with the self-energy Σ_{xc} . By using a particular ansatz for Σ_{xc} , we have previously proposed²

$$\Delta_n = \int d^3\mathbf{r} (2\epsilon_{xc}(\mathbf{r}) - v_{xc}(\mathbf{r})) |\psi_n(\mathbf{r})|^2, \quad (8)$$

where

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}, \quad (9)$$

is the Kohn-Sham potential and

$$E_{xc} = \int d\mathbf{r} n(\mathbf{r})\epsilon_{xc}(\mathbf{r}) \quad (10)$$

is the exchange-correlation energy. The exchange-correlation energy per particle ϵ_{xc} can be expressed in terms of the pair correlation functions as

$$\epsilon_{xc}(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \int_0^1 d\lambda \frac{n(\mathbf{r}')C_\lambda(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (11)$$

where λ is the coupling constant from the Hellmann-Feynman theorem. Within the LDA, $\epsilon_{xc}(\mathbf{r})$ is a well-known function of the local density $n(\mathbf{r})$ obtained from homogeneous electron gas results³.

III. SPIN RESOLVED QUASI-PARTICLE CORRECTION

In the spin resolved case, the prescription for the correction to the excitation energy given by Eq. 8 becomes

$$\Delta_n^\sigma = \int d^3\mathbf{r} (2\epsilon_{xc}^\sigma(\mathbf{r}) - v_{xc}^\sigma(\mathbf{r})) |\psi_n^\sigma(\mathbf{r})|^2, \quad (12)$$

where

$$v_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n^\sigma(\mathbf{r})}, \quad (13)$$

is the spin-dependent DFT potential and n_σ the spin-resolved electron density. As in Eq. 11 above, the exchange-correlation energy per particle $\epsilon_{xc}^\sigma(\mathbf{r})$ is given by the Coulomb interaction of an electron of spin σ at \mathbf{r} with its exchange-correlation hole:

$$\epsilon_{xc}^\sigma(\mathbf{r}) = \frac{1}{2} \sum_{\sigma'} \int d\mathbf{r}' \int_0^1 d\lambda \frac{n_{\sigma'}(\mathbf{r}')C_\lambda^{\sigma, \sigma'}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (14)$$

in terms of the spin-resolved correlation functions $C_\lambda^{\sigma, \sigma'}(\mathbf{r}, \mathbf{r}')$. It is convenient to split $\epsilon_{xc}^\sigma(\mathbf{r})$ as

$$\epsilon_{xc}^\sigma(\mathbf{r}) = \epsilon_x^\sigma(\mathbf{r}) + \epsilon_c^\sigma(\mathbf{r}), \quad (15)$$

where ϵ_x^σ and ϵ_c^σ give the exchange and correlation components of $\epsilon_{xc}^\sigma(\mathbf{r})$, respectively. The spin-resolution of ϵ_x^σ is straightforward because the exchange hole only involves like spin electrons. On the other hand, the spin-resolution of ϵ_c^σ is more subtle since here both like and unlike spin electrons contribute. The energy per particle for the spin polarized HEG depends only on the density parameter r_s and the local spin polarization

$$\zeta = (n_\uparrow - n_\downarrow)/n. \quad (16)$$

In this connection, the spin-resolution of the correlation energy presented recently by Gori-Giorgi and Perdew¹⁹ for the HEG may usefully be employed. Ref. 19 defines spin resolved correlation energies

$$\epsilon_c^{\sigma\sigma'}(r_s, \zeta) = 2\pi \frac{n_\sigma}{n} \int_0^\infty n_{\sigma'} \bar{C}_c^{\sigma, \sigma'}(r_s, \zeta, u) u du, \quad (17)$$

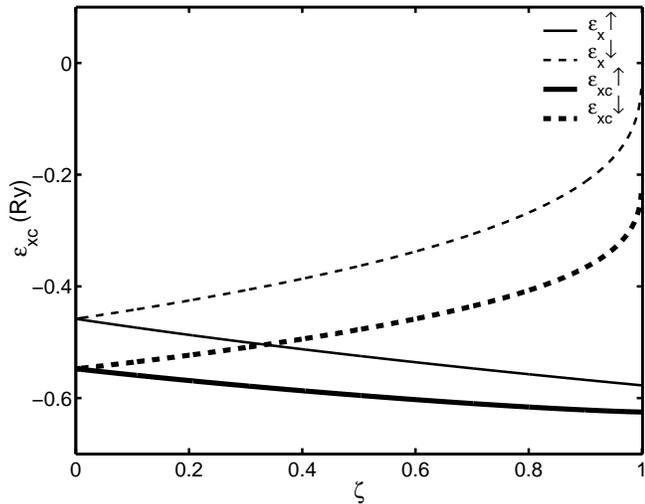


FIG. 1: Characteristic behavior of the spin-resolved exchange-correlation energies ϵ_{xc}^{\uparrow} and $\epsilon_{xc}^{\downarrow}$ and the corresponding spin only contributions ϵ_x^{\uparrow} and ϵ_x^{\downarrow} as a function of the spin polarization ζ for $r_s = 2$ in a HEG based on Eqs. 15-18. See legend for the meaning of various line types.

by using correlation holes $n_{\sigma'} \bar{C}_c^{\sigma, \sigma'}(r_s, \zeta, |\mathbf{r} - \mathbf{r}'|)$, where the pair correlation function $\bar{C}_c^{\sigma, \sigma}$ has been averaged over the coupling strength λ . Here we have made the dependence of various quantities on r_s and ζ explicit. Thus the interaction energy ϵ_c^σ of an electron of spin σ with its correlation hole can be resolved as

$$\epsilon_c^\sigma = \frac{n}{n_\sigma} \left(\epsilon_c^{\sigma, \sigma} + \frac{1}{2} \epsilon_c^{\sigma, -\sigma} \right), \quad (18)$$

Parameterized expressions for $\epsilon_c^{\sigma, \sigma}$ and $\epsilon_c^{\sigma, -\sigma}$ based on the HEG are given in Ref. 19.

Figs. 1 and 2 present illustrative results concerning the r_s and ζ dependencies of the exchange and correlation energies in the HEG. Fig. 1 shows the behavior of ϵ_{xc}^σ as a function of ζ for $r_s = 2$. The correlation contribution ϵ_c^σ here has been obtained from Eq. 18. The spin-splitting of ϵ_{xc}^σ is seen from Fig. 1 to increase steadily with ζ . The exchange contribution at a given density depends linearly on $(1 \pm \zeta)^{1/3}$ so that when ζ is small ϵ_x^σ displays a linear behavior with ζ . Notably, ϵ_x^σ for minority spin electrons is seen in Fig. 1 (thin dashed line) to vanish in the ferromagnetic limit ($\zeta = 1$) reflecting the fact that a minority spin electron has no other electrons to exchange with in this case. In contrast, the correlation energy per particle of the minority spin electrons does not vanish in the limit $\zeta = 1$ due to the contribution of opposite spin electrons in Eq. 18. The effect of correlations is to reduce the ζ dependency of ϵ_x^σ . As a result, in the linear region, the slopes of ϵ_{xc}^σ curves are seen to be smaller and magnetic splittings are significantly reduced.

In order to further highlight the role of correlations, we show ϵ_c^\uparrow (upper surface) and ϵ_c^\downarrow (lower surface) as a function of the parameters ζ and r_s in Fig. 2. It is

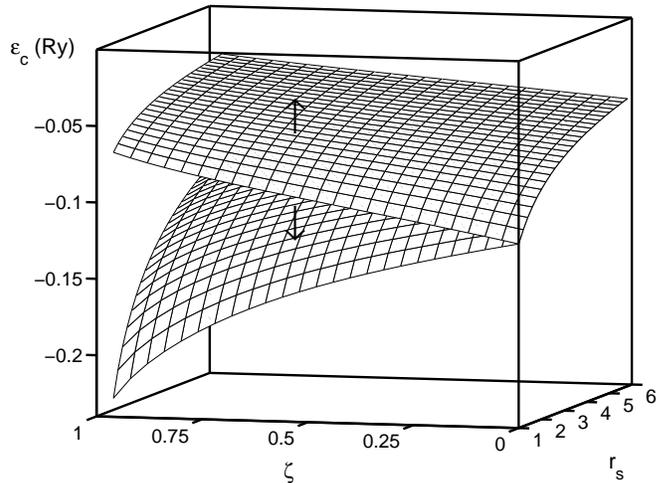


FIG. 2: Spin-resolved correlation energies $\epsilon_c^\sigma(r_s, \zeta)$ (see Eq. 18) in a HEG are shown in surface plots as a function of the spin polarization ζ and the density parameter r_s . Upper and lower surfaces refer to the majority (\uparrow) and minority (\downarrow) spins, respectively.

clear immediately that correlations yield a less attractive hole for the majority spins compared to that for the minority spins. The reason is that correlation effects are dominated by the contribution of opposite spin electrons which are not prevented by the Pauli principle to come close to each other. The splitting of the two surfaces increases with increasing spin polarization ζ but decreases with increasing r_s . At $\zeta = 0$ the two surfaces collapse on to the well known paramagnetic curve, which scales as¹³

$$\epsilon_c = -\frac{0.127}{\sqrt{r_s}} \text{ Ry} \quad (19)$$

for typical metallic densities ($r_s = 1 - 6$).

IV. A MORE GENERAL FORMULATION

This section presents a framework for generalizing Eq. 7. This formulation also allows us to connect our approach to some related methods in the literature. In the interest of notational simplicity, we will omit from hereon the obvious spin dependencies and the associated spin-indices.

We recall that the standard definition of the the self-energy operator Σ_{xc} is:

$$\Sigma_{xc} = G_0^{-1} - G^{-1}, \quad (20)$$

where G is the exact single-particle Green's function and G_0 is the reference Green's function obtained within the Hartree approximation. Thus Σ_{xc} in principle contains all quasiparticle effects beyond the Hartree approxima-

tion. We now write Σ_{xc} (suppressing spin-indices) as

$$\Sigma_{xc} = v_{xc} + \sum_n \Delta_n |\psi_n\rangle\langle\psi_n|, \quad (21)$$

where v_{xc} is the spin-dependent exchange-correlation potential associated with the spin-dependent Kohn-Sham orbitals ψ_n .²⁰ The state-dependent correction Δ_n is more general than the expression of Eq. 12 and it can be the basis for curing the unphysical interaction of an electron with itself which occurs in the DFT. In fact, the right side of Eq. 12 attempts to correct for such self-interactions by using the Coulomb potential of the exchange-correlation hole, but does so only approximately since it assumes every electron to possess the same pair-correlation function. In systems with localized orbitals, it makes sense to subtract out the self-interaction for each occupied orbital explicitly by using²¹

$$\Delta_n = \int d^3\mathbf{r} (-u_n(\mathbf{r}) - v_{xc}^n(\mathbf{r})) |\psi_n(\mathbf{r})|^2, \quad (22)$$

where $u_n(\mathbf{r})$ and $v_{xc}^n(\mathbf{r})$ are the electrostatic and the exchange-correlation potential, respectively, created by the charge density $|\psi_n(\mathbf{r})|^2$. The self-interaction correction (SIC) given by Eq. 22 has been proposed by Perdew and Zunger²² for atomic systems and possesses a straightforward spin-dependence. For atoms, SIC lowers the LDA eigenvalues and improves agreement with measurements¹. Note, however, that in extended systems SIC encounters conceptual problems due to the delocalized character of the Bloch functions.²³ In fact, the SIC correction turns to be zero for plane-waves. A route around this problem is to renormalize the wavefunction within the unit cell and perform the correction within the atomic spheres.²⁴

The so-called LDA+U can be considered a simplified version of the SIC where the correction Δ_n^σ acts only on localized d - or f -states, often splitting the metallic LDA bands into upper and lower Hubbard bands descriptive of Mott-Hubbard insulators^{25,26,27}. However, problems with both SIC and the LDA+U arise for systems with partially filled $3d$ shells which are metallic, as for example in the transition metals.^{1,27} In order to handle cases where a conduction band crosses the Fermi energy E_F , we observe first that here the DFT potential v_{xc} generally provides a reasonable approximation to the self-energy at the Fermi surface (FS)²⁸ and we may impose the condition

$$\Sigma_{xc}|_{FS} = v_{xc} \quad (23)$$

on the self-energy. We now write Δ_n as

$$\Delta_n = \bar{\Delta} + \Lambda_n, \quad (24)$$

where $\bar{\Delta}$ is defined to be the average correction on the FS and Λ_n is a state-dependent contribution. It is clear that the condition of Eq. 23 can be satisfied by setting

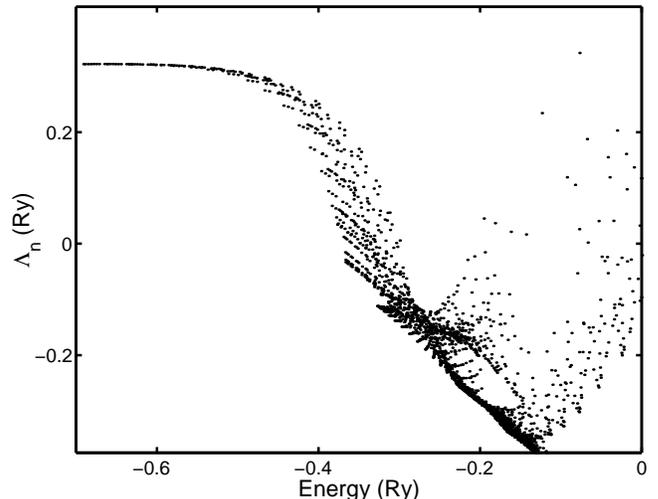


FIG. 3: State-dependent correction Λ_n based on Eqs. 24 and 22 in Cu as a function of energy with zero denoting the Fermi energy. Each dot gives the value of Λ_n for a particular state. Total number of states shown is 6×505 corresponding to 6 valence bands at each of the 505 k-points computed in the 1/48th irreducible portion of the Brillouin zone of Cu as discussed in the text.

the average shift $\bar{\Delta}$ to zero and requiring that Δ_n goes to zero at the E_F , which leads us to suggest the form

$$\Lambda'_n = \Lambda_n \frac{\varepsilon_n - E_F}{E_B - E_F}, \quad (25)$$

in metallic systems. Here E_B denotes the bottom of the conduction band. The linear interpolation given by Eq. 25 is equivalent to a band renormalization near the Fermi level given by

$$\tilde{\xi}_n = (1 + \lambda_n)\xi_n, \quad (26)$$

where

$$\lambda_n = \frac{\Lambda_n}{E_B - E_F} \quad (27)$$

and $\xi_n = (\varepsilon_n - E_F)$. Such a renormalization due to self-energy effects is often invoked phenomenologically within the framework of Fermi liquid theories.²⁹

Fig. 3 shows illustrative results in Cu where the electronic structure involves states of a mixed $s-p$ and d character. For this purpose, the standard LDA-based energy bands and Bloch wavefunctions were computed for the 6 valence bands of fcc Cu on a uniform 505 k-point mesh in the irreducible 1/48th of the Brillouin zone. The correction Δ_n of Eqs. 22 and 24 was then computed for each of the 505×6 states³⁰. The resulting values of Λ_n after the average $\bar{\Delta}$ is subtracted are shown in the 'dot-plot' of Fig. 3. Λ_n is seen to be positive and fairly constant at low band energies (-0.7 to -0.5 Ry), where the states mainly possess s character. At intermediate energies (-0.4 to -0.2 Ry), where the d admixture increases,

Λ_n decreases rapidly as self-interaction effects become stronger. Closer to the Fermi energy (-0.1 to 0.0 Ry), the $s - p$ character increases once again and this is reflected in the upturn in Λ_n values seen in Fig. 3. Using $E_F - E_B = 0.691$ Ry, we find that near the FS, typical λ_n values are $\approx 10\%$, which is consistent with the value of the renormalization parameter $\lambda \approx 8\%$ adduced from fitting experimental photoemission results^{23,29,31}.

In ferromagnetic metals such as Fe and Ni the present scheme leaves the band structure at the Fermi energy and hence the majority and minority spin FS's and the corresponding spin magnetic moments unchanged due to the constraint of Eq. 23. However, energy bands away from the Fermi level are modified. In particular, the top-most occupied d states in $3d$ and $4d$ transition metals, which are more localized within the atomic sphere than the d states toward the bottom of the band, will experience larger corrections (lowering). As a result, d -band widths would become narrower giving trends consistent with photoemission experiments³².

V. SUMMARY AND CONCLUSIONS

We discuss how DFT eigenvalues can be corrected via a spin-dependent self-energy Σ_{xc}^σ to obtain improved quasi-particle energies. For this purpose, Σ_{xc}^σ is evaluated as the Coulomb energy associated with the exchange and correlation holes surrounding each electron in terms of the appropriate spin-resolved pair correlation functions

for the homogeneous electron gas. The approach is similar to that followed in our earlier treatment of the unpolarized case², and should yield quasi-particle energies with an accuracy comparable to that of the more demanding GWA. Notably, our scheme does not involve the limitations of the standard implementations of the GWA in which the screened interaction W is assumed to be spin-independent. We also show how our scheme can be viewed in a somewhat more general context, so that quasi-particle energies can be corrected on a state-by-state basis for self-interaction terms in the DFT along the lines of the familiar SIC scheme²². The question of applying self-interaction correction to a metallic band is considered and an interpolation formula to handle such a case is suggested. Finally, illustrative results in Cu are presented and the computed renormalization of the DFT eigenvalues of the conduction band in Cu is found to be in reasonable accord with the corresponding experimental results.

Acknowledgments

We acknowledge Paola Gori-Giorgi, Hsin Lin and Robert Markiewicz for useful discussions. This work is supported by the US Department of Energy contract DE-AC03-76SF00098 and benefited from the allocation of supercomputer time at NERSC and Northeastern University's Advanced Scientific Computation Center (ASCC).

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