Quasiparticle Electronic Structure of Copper in the *GW* Approximation

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We show that the results of photoemission and inverse photoemission experiments on bulk copper can be quantitatively described within band-structure theory, with no evidence of effects beyond the single-quasiparticle approximation. The well-known discrepancies between the experimental band structure and the Kohn-Sham eigenvalues of density functional theory are almost completely corrected by self-energy effects. Exchange-correlation contributions to the self-energy arising from $3s$ and $3p$ core levels are shown to be crucial.

Experimental techniques for the determination of the electronic band structure of solids have made considerable progress in recent years [1]. From the theoretical point of view, state-of-the-art calculations within many-body perturbation theory allow us to obtain band energies in a rigorous way, i.e., as the poles of the one-particle Green's function G [2]. To obtain G, one needs the electron self-energy Σ, usually evaluated according to the so-called *GW* approximation, derived by Hedin in 1965 [3], which is based on an expansion in terms of the dynamically screened Coulomb interaction. However, due to the high complexity and large computational requirements of *ab initio* calculations of Σ, the experimental band structures are often compared with the results of (simpler) calculations performed within density functional theory (DFT) [4], in the local density approximation (LDA) [5] or in the generalized gradient approximation (GGA) [6]. The consequences of this approach (which can be set on a firm ground by considering the exchange-correlation potential of the LDA or GGA as an approximation to the self-energy operator) must, however, be considered with great care, particularly when the system under study differs from those—semiconductors and insulators—for which the approximation is usually made. A recent example is given by Ref. [1], where the measured Cu band structure is compared with state-of-the-art DFT-GGA results, finding discrepancies which are both large and dependent on the considered band and **k** point. As a consequence of this result, the authors of Ref. [1] state that it is intriguing to find such pronounced "deviations from the band theory," copper being much less correlated than metals with an open $3d$ shell (e.g., Ni).

In the present work, we demonstrate that copper does *not*, however, deviate from quasiparticle band theory. It deviates only from the simple "rigid shift" behavior of the self-energy commonly found in the case of semiconductors and insulators. For these, the application of the *GW* method to compute self-energy corrections on top of *ab initio* DFT results has become a quite well-established and standard technique, giving energy levels generally in good agreement with experiments, even for complicated

systems like reconstructed surfaces and clusters [2,7]. The gaps between empty and filled states generally increase by a substantial amount with respect to those obtained in the Kohn-Sham (KS) formulation of DFT, reaching agreement with experimental results. The KS-DFT underestimation of the experimental gap is generally found to be weakly dependent on the particular band or **k** point, although some semiconductor surface gaps show stronger quasiparticle (QP) corrections than bulk ones [8]. This is the basis for the introduction of the so-called "scissors operator," often invoked in order to correct the discrepancies by rigidly shifting upwards the DFT empty bands, hence avoiding explicit self-energy calculations. *A priori*, there is no reason why the "scissors" approach should also work for metals, where no gap exists between filled and empty states.

Unlike semiconductors, the case of metals has received limited attention so far. The bandwidth (i.e., the energy range of filled states) of simple metals has often been compared with that calculated for the homogeneous electron gas (jellium), finding discrepancies of a few tenths of eV [9]. On the other hand, the band structure of transition and noble metals cannot be approximated by that of jellium: valence electrons of d character play an important role both in the electronic structure and in the optical properties of these metals. Previous estimates of many-body corrections to the $3d$ Cu band structure, based on the self-energy of the homogeneous electron gas, yielded only partial agreement with the experimental data, suggesting that in the case of non–free-electron metals screening effects (accounted for by the dielectric function) should be included in a more realistic way [10]. This is precisely the aim of the present work, where a full, first-principles *GW* calculation of the QP band structure of bulk copper is performed. The resulting QP energies correct in a nontrivial way the DFT-LDA results, and are in remarkably good agreement with direct and inverse photoemission experiments.

Among transition metals, full quasiparticle calculations have been carried out so far only for Ni [11], while we are not aware of similar calculations for noble metals. In the case of Ni, *GW* yields a good description of photoemission

data, except for the 6 eV satellite, which is due to strong short-range correlations within the partially filled d shell. For copper, we expect band theory to work better than for transition metals, since d shells are completely filled. From the computational point of view, the very presence of strongly localized d bands makes the *ab initio* calculations based on plane wave (PW) and norm-conserving pseudopotentials (NCPP) for noble metals much heavier than those for semiconductors.

Let us first recall the relations between Kohn-Sham eigenvalues, the poles of the one-particle Green's function G, and experimental band energies measured in photoemission (PE) or inverse photoemission (IPE). In DFT, KS eigenvalues cannot be identified with electron addition or removal energies, since there is no equivalent of Koopman's theorem. Instead, the experimental band structure should be compared with the poles of the Green's function $G(\mathbf{r}, \mathbf{r}'; \omega)$. The latter are determined by an equation of the form

$$\left[-\frac{\hbar^2}{2m}\triangle_\mathbf{r} + V_{\text{external}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) \right]\psi_{n\mathbf{k}}(\mathbf{r}, \omega) + \int d\mathbf{r}' \, \Sigma(\mathbf{r}, \mathbf{r}'; \omega)\psi_{n\mathbf{k}}(\mathbf{r}', \omega) = E_{n\mathbf{k}}(\omega)\psi_{n\mathbf{k}}(\mathbf{r}, \omega), \qquad (1)$$

containing the nonlocal, non-Hermitian and frequency dependent self-energy operator Σ. The poles of G are the QP energies $\epsilon_{n\mathbf{k}}^{\text{QP}}$, the solutions of $\epsilon_{n\mathbf{k}}^{\text{QP}} = E_{n\mathbf{k}}(\epsilon_{n\mathbf{k}}^{\text{QP}})$. Following Ref. [12], we separate the static, bare-exchange part $\Sigma_x(\mathbf{r}, \mathbf{r}')$ from $\Sigma_c(\mathbf{r}, \mathbf{r}'; \omega)$, the energy-dependent correlation contribution. Equation (1) is formally similar to Kohn-Sham equations which are solved in the determination of the ground-state properties, where the local and energy independent exchange-correlation (xc) potential $V_{\text{xc}}(\mathbf{r})$ has been substituted by Σ. Hence, KS eigenvalues can be considered as a zeroth-order approximation to the true QP energies, if the xc potential of the DFT is seen as an approximation to the true self-energy operator Σ. This suggests the possibility to look for a first-order, perturbative solution of Eq. (1) with respect to $(\Sigma - V_{\text{xc-LDA}})$, where $V_{\text{xc-LDA}}$ is the xc potential of the LDA. We have checked that in bulk copper the off-diagonal elements of $(\Sigma - V_{\text{xc-LDA}})$ are 2 orders of magnitude smaller than the diagonal ones. To determinate the QP energies $\epsilon_{nk}^{\text{QP}}$ starting from the DFT-LDA values we have used an iterative procedure [13].

Our band structure calculation hence starts with a DFT-LDA calculation of the ground-state properties, performed using norm-conserving pseudopotentials (PPs) and a plane wave basis. The use of soft (Martins-Troullier [14]) PPs allows us to work at full convergence with a reasonable kinetic energy cutoff (60 Ry if the $3s$ and $3p$ atomic states are frozen into the core; 160 Ry when they are explicitly included in the valence). Details can be found in Ref. [15], where the nontrivial discrepancies between the LDA Kohn-Sham eigenvalues and the experimental band structure have also been made evident. In

particular, we find substantial differences with respect to the experiment for both the d bands width (3.70 instead of 3.17 eV) and position (more than 0.5 eV upshifted in the DFT), in agreement with previous calculations [1,16].

QP energies are then computed by evaluating Σ as GW [3], so that the dynamically screened potential $W(\omega)$ [convolution of the inverse dielectric function $\epsilon^{-1}(\omega)$ with the bare Coulomb potential] is needed. Most GW calculations on semiconductor systems use a plasmon-pole approximation (PPA) for $W(\omega)$ [17], based on the observation that the Fourier components $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}; \omega)$ of the inverse dielectric function are generally peaked functions of ω, and can be approximated by a single pole. Since the evaluation of Σ_c involves an integration over the energy, the fine details of the ω dependence are not critical, and the PPA turns out to work reasonably well for most applications. However, in the case of Cu the use of a PPA becomes more critical. The presence of flat d bands 2 eV below the Fermi level implies the presence of strong transitions in $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}; \omega)$ spread over a large energy range. For small values of $\mathbf{G}$ and $\mathbf{G}'$, the behavior of $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}; \omega)$ is often very different from that of a single-pole function, leading to instabilities when determining the plasmon-pole parameters. Hence, we have found it more convenient to avoid the PPA. Instead, we explicitly compute $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}; \omega)$ over a grid of about 200 frequencies from zero to $\sim$130 eV, and perform the energy integral numerically. Another characteristic of metallic systems which leads to additional difficulties in practical GW calculations is the discontinuity of the band occupation crossing the Fermi surface. The problem already shows up in the evaluation of the bare-exchange matrix elements, which read

$$\langle \Sigma_x^{n\mathbf{k}} \rangle \equiv \langle n\mathbf{k}|\Sigma_x(\mathbf{r}, \mathbf{r}')|n\mathbf{k}\rangle = -\sum_{n_1} \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G}} 4\pi \left| \frac{\langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n_1\mathbf{k} - \mathbf{q}\rangle}{|\mathbf{q} + \mathbf{G}|} \right|^2 f_{n_1(\mathbf{k}-\mathbf{q})} . \qquad (2)$$

Here $0 \leq f_{n_\mathbf{k}} \leq 2$ is the occupation of band n at point $\mathbf{k}$, and its discontinuity at the Fermi surface slows down the convergency of any numerical evaluation of Eq. (2) on a finite $\mathbf{q}$ mesh, no matter how $\langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n_1\mathbf{k} - \mathbf{q}\rangle$ is smooth. To overcome this difficulty, we have first computed the integral of the term $f_{n_1(\mathbf{k}-\mathbf{q})}/|\mathbf{q} + \mathbf{G}|^2$ over small regular volumes centered around each $\mathbf{q}$ point used to

evaluate Eq. (2), and then used these values in the finite $\mathbf{q}$ sum. A similar approach has been used in Ref. [8]. This procedure yields results for $\langle \Sigma_x^{n\mathbf{k}} - V_{\text{xc-LDA}}^{n\mathbf{k}} \rangle$ computed with 19 $\mathbf{q}$ points in the IBZ converged within 0.1 eV, while barely evaluating Eq. (2) over the same set of $\mathbf{q}$ points yields an error of about 1.5 eV.

Normally (e.g., in *GW* calculations for semiconductors), the calculation of *G* and *W* to correct the DFT valence band structure can be performed by including only valence states, and fully neglecting the core states which have been frozen in the pseudopotential approach. In copper, however, when Σ is computed neglecting the $3s$ and $3p$ atomic core states (which in the solid create two flat bands, at about 112 and 70 eV, respectively, below the Fermi level), the resulting QP corrections on the *d* bands are clearly unphysical: *GW* corrections move the highest occupied *d* bands above the DFT-LDA Fermi level. On the other hand, the situation for s/p states (e.g., for the state $L_{2'}$) is much more reasonable, with correlation and exchange parts of the self-energy which cancel largely each other (as in the case of semiconductors), and negative QP corrections of order of the eV.

The solution of this puzzling situation is provided by the role of the above-mentioned $3s$ and $3p$ states, which, despite being well separated *in energy* from the $3d$ ones, have a large *spatial* overlap with the latter. As a consequence, non-negligible contributions to the self-energy are expected from the *exchange* contributions between $3d$ and $3s/3p$ states. These contributions can be included in our calculation in a straightforward way, by starting with a pseudopotential which puts the whole 3rd atomic shell into the valence (see Ref. [15]). Indicating with G_0^{core} the noninteracting Green's function containing also the $3s/3p$ levels, the self-energy computed as $G_0^{core}W$ will yield the desired dynamical exchange between $3d$ bands and core bands composed of a bare-exchange (static) contribution Σ_x^{core} plus a correlation part Σ_c^{core}. Naturally, a larger plane-wave cutoff (160 Ry) is needed for convergence. As a result, we find large bare-exchange contributions from core levels, leading to very different values of $\langle \Sigma_x^{n\mathbf{k}} - V_{xc\text{-LDA}}^{n\mathbf{k}} \rangle$ for s/p and *d* states, as illustrated in Fig. 1. The role of core levels in the calculation of the bare-exchange contributions (whose importance was already addressed for transition metals by Aryasetiawan and Gunnarsson [2], but estimated to be of the order of 1 eV) is hence crucial in the case of copper [18]. Moreover, their effect is unexpected on the basis of DFT-LDA calculations, where the band structure does not change appreciably even if the $3s/3p$ orbitals are fully included in the valence [15]. The effect of the core states is expected to be smaller on the correlation part of $\Sigma(\omega)$, since the screened and bare Coulomb interaction, whose difference is involved in Σ_c^{core}, are very similar to each other in the core region. As a result, Σ_c^{core} is small, of the order of 0.5 eV for *d* bands, and close to zero for s/p bands. The inclusion of the correlation part Σ_c^{core} does not change the widths of *d* bands, that remain in good agreement with the experimental results, but improves considerably their absolute positions [19].

In Table I we compare our calculations with selected experimental data reported in Ref. [16]. In Fig. 2 the full theoretical band structure is compared with experimental data: the agreement is remarkably good and the fact that
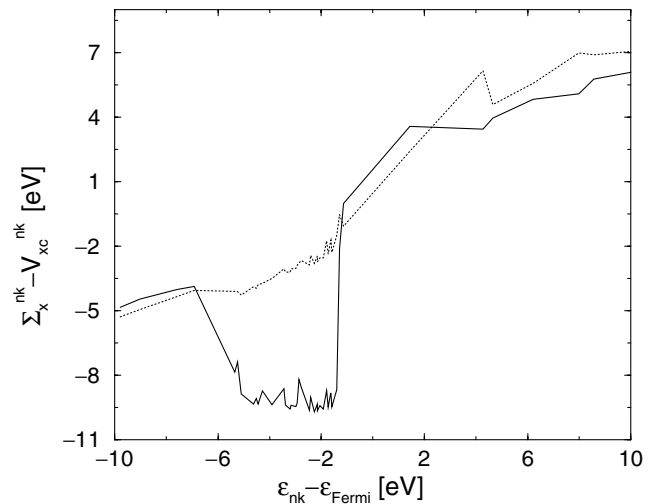
FIG. 1.   Values of $\langle \Sigma_x^{n\mathbf{k}} - V_{xc}^{n\mathbf{k}} \rangle$ for bulk copper, plotted as a function of the noninteracting energies $\epsilon_{n\mathbf{k}}$. The dotted line represents the results obtained without the contributions from the $3s$ and $3p$ core states.

the *GW* corrections cannot be reproduced by any rigid shift of the LDA bands clearly appears. For instance, at the *L* point the shifts change sign for different valence bands, with QP corrections ranging from -0.29 eV to -0.61 eV, to 0.57 eV for the three *d* bands. As a consequence, the L_1-$L_{2'}$ gap *decreases* after inclusion of self-energy corrections (see also Table I, last line), in contrast with the usual behavior occurring in semiconductors and insulators. The other gaps at *L* and *X*, instead, increase. All of them come to good agreement with experimental data. Unoccupied (conduction) bands at points *L*, *X*, and *K* are also obtained in very good agreement with the experimental data. These findings demonstrate that strong deviations from the single quasiparticle band theory do not

TABLE I.   Theoretical bandwidths and band energies (LDA values + *GW* corrections, in eV) for copper, at high-symmetry points. The striking agreement with the experimental results demonstrates that copper is very well described within a single-quasiparticle band theory, at the *GW* level. The values in the last column are averages over several experiments, as reported in Tables I and XIII of Ref. [16].

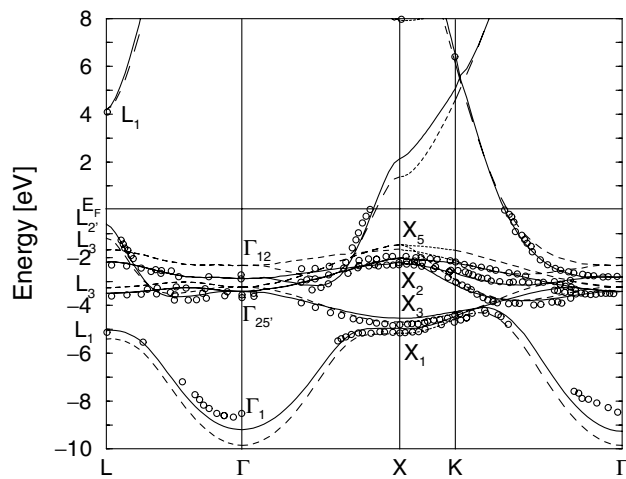|		DFT-LDA	*GW*	Experiment
Positions of *d* bands	Γ_{12}	-2.27	-2.81	-2.78
	X_5	-1.40	-2.04	-2.01
	L_3	-1.63	-2.24	-2.25
Widths of *d* bands	Γ_{12}-$\Gamma_{25'}$	0.91	0.60	0.81
	X_5-X_3	3.23	2.49	2.79
	X_5-X_1	3.70	2.90	3.17
	L_3-L_3	1.58	1.26	1.37
	L_3-L_1	3.72	2.83	2.91
Positions of s/p bands	Γ_1	-9.79	-9.24	-8.60
	$L_{2'}$	-1.12	-0.57	-0.85
L gap	L_1-$L_{2'}$	5.40	4.76	4.95

FIG. 2. Solid line: present *GW* results for the bulk copper band structure, compared with the DFT-LDA results (dashed line), and with the experimental data reported in Ref. [16] (circles).

occur in copper. QP band theory in the *GW* approximation, instead, remarkably deviates from the DFT-LDA + scissors-operator approach, due to the interplay of the different localization and correlation properties of *d* and *s/p* states.

In conclusion, we have carried out the first *ab initio* quasiparticle calculation for a noble metal, copper. In order to do that, we had to overcome several problems, namely, the large number of plane waves needed to describe *d* orbitals, the calculation of **k**-space sums close to the Fermi surface, and the inclusion of the exchange interaction between valence and core levels. The single-quasiparticle band structure computed within Hedin's *GW* approximation for the electron self-energy turns out to be in very good agreement with experiments. The *GW* method, originally devised to describe the *long-range* charge oscillations [20], is hence shown to yield a good description also of copper, a system characterized by localized orbitals and short-range correlation effects. The corrections to the LDA Kohn-Sham eigenvalues for the *d* bands are highly nontrivial, since even their *sign* turns out to be **k** point and band dependent, ruling out the validity of any scissors operator approximation. Furthermore, exchange effects between *d* electrons and 3*s*, 3*p* core states play a key role and cannot be neglected in the calculation of QP corrections. Finally, a full screening calculation of the self-energy has been carried out, avoiding the single-plasmon pole approximation. This allows a realistic treatment also of the imaginary part of the self-energy (and therefore the calculation of QP lifetimes), which will be studied in a forthcoming work.

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[19] Physically, Σ_c^{core} would also include *polarization* effects between core and conduction states, which would correspond, in our scheme, to including core states also in the calculation of $W(\omega)$. However, Fig. 1 shows that core levels have a strong interaction only with *d* orbitals, which are completely filled in copper. Hence $W(\omega)$ can involve only excitations from core levels to *s/p* conduction bands, leading to small contributions to Σ_c^{core}, which are here neglected.

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