Band structure of gold from many-body perturbation theory

T. Rangel,1,2,* D. Kecik,3,4 P. E. Trevisanutto,1,5,6 G.-M. Rignanese,1,2 H. Van Swygenhoven,3,4 and V. Olevano1,6
1European Theoretical Spectroscopy Facility (ETSF)
2Institute of Condensed Matter and Nanosciences (IMCN), Université Catholique de Louvain, Chemin des Étoiles 8 bte L7.03.01, B-1348 Louvain-la-Neuve, Belgium
3Paul Scherrer Institut, Materials Science and Simulation, NUM/ASQ, CH-5232 Villigen, Switzerland
4Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Materials (IMX), CH-1015 Lausanne, Switzerland
5National Nanotechnology Laboratory (NNL), Istituto Nanoscienze-CNR, Lecce, Italy
6Institut Néel, CNRS and UJF, Grenoble, France

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The theoretical determination of the band structure of gold has been an open issue for more than four decades. Early works from the 70s1–3 focused on relativistic effects which are responsible for its yellow color. Thereafter, the band structure calculated by Christensen and Seraphin1 has been used as a reference to interpret photoemission experiments. More recently, a few discussions on this topic appeared in the literature. The cohesive energy in noble metals was shown to contain large terms arising from dispersion forces, such as van der Waals interactions,4 pointing to the importance of many-body correlations for closed shell d electrons. Newer experimental5 and theoretical works confirmed previous findings.2 The gold band structure, calculated by density functional theory (DFT) within the local density approximation (LDA) or the generalized gradient approximation (GGA), presents an underestimation of the 5d–6s interband gap (see Fig. 1) by ~1.0 eV with respect to the available experimental data. Similar discrepancies were encountered for other noble metals. To solve these disagreements, quasiparticle (QP) corrections to the DFT eigenvalues have been applied with great success. For other noble metals. To solve these disagreements, quasiparticle (QP) corrections to the DFT eigenvalues have been applied with great success.

Hybrid functionals have also been proposed into the framework of an unrestricted DFT to solve the typical band gap underestimation of the LDA and GGA approximations. In these functionals, a fixed amount of Hartree-Fock exact nonlocal exchange is incorporated into the classical DFT local Kohn-Sham exchange-correlation potential. Among these, the one proposed by Heyd, Scuseria, and Ernzerhof14–16 (HSE) has been widely used lately. Hybrid functionals have proven to perform well for improving several properties of solids.14,17

1. INTRODUCTION

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In this paper, the band structure of gold is calculated within ab initio many-body perturbation theory (MBPT) in order to elucidate the role of correlations and to provide a more reliable theoretical band structure to interpret the experimental findings. Standard G0W0 corrections shift the unoccupied bands up by at most 0.2 eV and the first sp-character occupied band down, while leaving the 5d occupied bands unmodified. Self-consistency on the wave functions by the QSGW scheme lowers the 5d bands by 0.4 eV, reducing the discrepancy with the experimental measurements. Inclusion of sp semiconductor states is confirmed to be crucial for GW calculations in d-electron systems, as previously found.7,8 In contrast, here the plasmon-pole model (PPM) is found to be overall valid. The importance of relativistic effects in gold is also confirmed.6

The remaining disagreement with the experiments might be explained by the lack of relativistic many-body terms18–20 beyond the single-particle ones taken into account here.

Finally, we calculate the HSE hybrid functional band structure of gold and compare it to the QSGW results. Around the Fermi energy, HSE (and PBE) bands present a difference of ~0.3 eV from the corresponding QSGW ones. High-energy unoccupied HSE bands present a large discrepancy, by more than 6 eV, with respect to the experimental data and the GW results.

The article is organized as follows. In Sec. II, the theoretical background is given. The technical details of the calculations are shown in Sec. III. In Sec. IV, the band structure calculated
within the $G_0W_0$ approach is analyzed. The role of semicore orbitals and the validity of the PPM are discussed here. In Sec. V, the band structure calculated within the QSGW method is presented. Spin-orbit corrections are discussed in Sec. VI. In Sec. VII we discuss the weight of all our approximations with respect to the residual discrepancies with the experiment. An analysis of the HSE results is presented in Sec. VIII. Finally, in Sec. IX, the conclusions of this work are drawn. In addition, convergence issues are discussed in the Supplemental Material.

II. THEORETICAL BACKGROUND

In MBPT, the electronic structure is obtained by solving the quasiparticle (QP) equation:

$$
\left( -\frac{1}{2} \nabla^2 + V^{\text{ext}}(r) + v^{H}(r) \right) \psi_{nk}^{\text{QP}}(r) + \int d^3r' \Sigma\left( \mathbf{r}, \mathbf{r}', \omega \right) \psi_{nk}^{\text{QP}}(r') = \epsilon_{nk}^{\text{QP}} \psi_{nk}^{\text{QP}}(r),
$$

where $V^{\text{ext}}(r)$ is the external potential, $v^{H}(r)$ is the classical repulsion Hartree term, and $\Sigma\left( \mathbf{r}, \mathbf{r}', \omega \right)$ is the self-energy, a non-Hermitian, nonlocal, and energy-dependent operator. The exact self-energy can be written as $\Sigma = GW\Gamma$, an expression containing the single-particle Green’s function $G$, the dynamically screened Coulomb potential $W$, and the vertex function $\Gamma$. Hedin\textsuperscript{22} provided a scheme based on a closed set of five Schwinger-Dyson integro-differential equations for $G$, $W$, $\Gamma$, $\Sigma$ and the polarizability $P$ to be solved iteratively up to the self-consistent solution for $G$ and $\Sigma$. Since the application of this scheme to real systems is usually computationally unfeasible, further approximations are required. Setting $\Gamma = \delta$, the self-energy operator becomes

$$
\Sigma\left( \mathbf{r}, \mathbf{r}', \omega \right) = \frac{i}{2\pi} \int d\omega' e^{i\omega'\eta} G\left( \mathbf{r}, \mathbf{r}', \omega + \omega' \right) W\left( \mathbf{r}, \mathbf{r}', \omega \right),
$$

where $\eta$ is an infinitesimal positive number. Due to its form, this is called the GW approximation. Starting from an initial approximation $G_0$ for the Green’s function (for example, the one constructed from DFT orbitals), one can iterate the equations up to self-consistency. Alternatively, one can stop at the first iteration obtaining the so-called $G_0W_0$ approximation.

In practice, it is very efficient to get QP energies using perturbation theory with respect to the DFT electronic structure, i.e., treating as perturbation the difference between the self-energy operator and the DFT exchange-correlation potential, $\Sigma - v_{xc}$. The DFT eigenvalues $\epsilon_{nk}^{\text{DFT}}$ and eigenstates $\psi_{nk}^{\text{DFT}}$ are used as a zeroth-order approximation for their quasiparticle counterparts. Thus, the QP energy $\epsilon_{nk}^{\text{QP}}$ is calculated by adding to $\epsilon_{nk}^{\text{DFT}}$ the first-order perturbation correction:

$$
\epsilon_{nk}^{\text{QP}} = \epsilon_{nk}^{\text{DFT}} + Z_n \left[ \psi_{nk}^{\text{DFT}} \right] \Sigma\left( \omega = \epsilon_{nk}^{\text{DFT}} - v_{xc} \right) \psi_{nk}^{\text{DFT}},
$$

with $Z$ the quasiparticle renormalization factor,

$$
Z = \left[ 1 - \left| \psi_{nk}^{\text{DFT}} \right| \frac{\partial \Sigma(\omega)}{\partial \omega} |_{\omega = \epsilon_{nk}^{\text{DFT}}} \left| \psi_{nk}^{\text{DFT}} \right| \right]^{-1},
$$

which accounts for the fact that, in Eq. (1), $\Sigma(\omega)$ should be calculated at the $\epsilon_{nk}^{\text{QP}}$. This procedure has been found to produce band structures in agreement with the experiment, provided that the DFT states are not too far from the QP states. Otherwise, a self-consistent approach on the eigenvalues and eigenstates may be necessary.

In the so-called QSGW calculations,\textsuperscript{12,13} the self-energy is constrained to be Hermitian and static, so that it can be diagonalized to update not only the energies but also the wave functions. Several successive iterations are needed to achieve the desired accuracy. At the end, the self-energy does not depend anymore on the DFT starting point.

The integration of Eq. (2) requires in principle the evaluation of $W(\omega)$ over a large number of frequencies. By modeling $W(\omega)$ with a single pole in the plasmon-pole model (PPM),\textsuperscript{24,25} it is possible to integrate Eq. (2) analytically. In the case of $d$ electrons, the applicability of this technique has been questioned.\textsuperscript{7} More accurate integration methods, such as the contour deformation (CD) approach, are frequently used. In this technique, the real axis integration path of Eq. (2) is modified as to run along the imaginary axis, picking up contributions coming from the poles of the Green’s function included in the deformed contour.\textsuperscript{29–31}

In principle, to fully take into account single-particle relativistic effects, one should solve the Dirac equation and work with Dirac spinors. Alternatively, one can use a nonrelativistic limit of the Dirac equation projected onto a Pauli two-component spinor formalism. This adds the fine-structure terms to the Hamiltonian. In the standard limit approach, there are three such terms: the $p^4$ relativistic correction to the velocity, the Darwin term, and the spin-orbit (SO) coupling. The scalar-relativistic approach includes only the first two terms and drops the SO coupling term. In some cases, the resulting equation already accounts for most of the Dirac physics. If needed, the SO coupling effects can be introduced on top of the scalar-relativistic approach, using the procedure detailed in Sec. VI. However, in the most severe cases, the SO coupling effects should be introduced from the beginning in a fully spinorial formalism.\textsuperscript{32,33} So far, this formalism has only been applied to the band structure of Hg chemical compounds,\textsuperscript{20} finding SO coupling corrections to the eigenvalues of $\sim$0.1 eV. This calculation was carried on only up to the first iteration of Hedin’s equations, i.e., at the $G_0W_0$
level. Going further in the direction of self-consistency and including relativistic corrections has not yet been tried on any real system.

In the case of gold, most of the relativistic effects in the band structure come from the scalar-relativistic terms.4,5 The SO coupling term mainly accounts for band splittings; hence, it introduces shape modifications mostly on the 5d bands.4,5

III. TECHNICAL DETAILS

All calculations are performed using the primitive unit cell of gold (FCC lattice). Note that in principle van der Waals interactions are important to determine the atomic distance in noble metals.4 To avoid this difficulty the experimental lattice constant (7.71 bohrs34) is used.35 The GW calculations are done using the ABINIT code,36 while the HSE ones are carried out with the VASP code.37 Scalar relativistic effects have been included everywhere.

In the GW calculations, the starting point wave functions and energies are obtained from a DFT calculation in which the XC energy is approximated by the GGA PBE functional.38 Scalar-relativistic norm-conserving pseudopotentials.39,40 are used to account for core-valence interactions.41 In order to elucidate the role of semicore states, two pseudopotentials are considered. The first one contains 11 valence electrons (5d10, 6s1), while the second contains 19 electrons (5s2, 5p6, 5d10, 6s1). The wave functions are expanded on plane-wave basis sets, up to a cutoff energy of 30 Ha when the semicore states are not included, and 50 Ha when they are. The Brillouin zone (BZ) is sampled using a shifted grid of 10 × 10 × 10 k points following the Monkhorst-Pack (MP) scheme.42 A total of 110 (100 empty) bands are used to compute the dielectric matrix and the self-energy. The dielectric matrix is computed for 145 k points in the irreducible BZ, truncating an energy cutoff of 4.0 Ha (corresponding to 59 plane waves). The Godby-Needs PPM is used here because it has demonstrated the best agreement with the methods which take fully into account the frequency dependence of the dielectric matrix.43,44 In the CD method, a total of 6 and 20 frequencies are used along the imaginary and real axis, respectively. All QSGW calculations are performed within the CD method. A total of 40 bands are considered when diagonalizing the self-energy.

In the calculations with the hybrid XC functional, only 11 valence electrons are treated explicitly by the projector augmented wave (PAW) method. The plane-wave cutoff energy for the wave functions is chosen to be 13 Ha. HF-type calculations are performed with the HSE06 functional,14 starting from previously converged DFT wave functions and energies. These calculations are considerably more costly than standard DFT ones. Hence, we could only afford to sample the BZ using a 20 × 20 × 20 unshifted Γ level grid of k points.

In all cases, the band structures are interpolated using maximally localized Wannier functions (MLWFs) with the Wannier90 code as explained in Refs. 47 and 48. The Fermi level is obtained by integrating the density of states (DOS), calculated with an interpolated grid of 30 × 30 × 30 k points using MLWFs and a low Gaussian smearing of 0.005 Ha. It was verified that the Fermi levels obtained with a grid of 30 × 30 × 30 and 60 × 60 × 60 interpolated k points were equal within 0.01 eV. A full study of the convergence with respect to all parameters of the calculation is provided in the Supplemental Material.21

IV. THE GwW0 BAND STRUCTURE OF GOLD

In this section, we investigate the QP band structure of gold within the GwW0 approach, trying to clarify the influence of two commonly used approximations. First, the effect of freezing semicore orbitals in the pseudopotential is discussed. Second, the validity of the PPM is analyzed more thoroughly.

In Fig. 2, the band structure of gold calculated within GwW0 is reported using two different pseudopotentials. In the first one [solid orange (light grey) lines, labeled “w/o SC”], the 5s and 5p semicore orbitals are considered to be frozen in the core (leading to a total of 11 valence electrons). In the second one [dotted brown (medium grey) lines, labeled “with SC”], 19 electrons are treated as valence states. While within DFT the resulting band structures are on top of each other (the curves are not shown here for sake of clarity), the difference becomes important at the GW level. Indeed, when the semicore electrons are excluded (“w/o SC”), the 5d bands are shifted up while the 6p bands are shifted down in a nonhomogeneous way. This leads to a reduction of the 5d-6s interband gap. This effect is alarming in the neighborhood of the X point, where the lowest empty band is shifted by −1.7 eV while the topmost 5d band is shifted by +1.1 eV, thus leading to an inversion in the band ordering. This unphysical shifting of bands is solved by including the exchange contributions from the 5d to the 5s and 5p semicore orbitals (“with SC”). Although 5s and 5p states are separated in energy by more than 50 eV from the 5d ones, their spatial overlap with the 5d is important. Hence, they play an important role at the GW level and cannot be neglected.4,5 In the remainder of the paper all the GW calculations are performed treating explicitly these electrons as valence states.

FIG. 2. (Color online) Effect of the semicore orbitals on the band structure of gold calculated within GwW0 using a plasmon-pole model. The results obtained when the semicore states are not considered as valence electrons (w/o SC) are represented by solid orange (light grey) lines, while those calculated with the semicore states treated as valence electrons (with SC) are shown as dotted brown (medium grey) lines. The zero of energy has been set at the Fermi level. The corresponding Brillouin zone is shown on top. All the calculations in this paper are performed at least at the scalar-relativistic level.
PPMs are believed not to work satisfactorily in the presence of \( d \) electrons just below the Fermi level. Indeed, this may induce strong transitions in \( \Delta_{\text{GH}}(q, \omega) \). As a result, this function cannot always be approximated by a single-pole function at small values of \( G \) and \( G' \).\(^7\) Figure 3 shows the band structure of gold calculated within \( G_0W_0 \) using either a PPM [dotted brown (medium grey) lines] or the more accurate CD method [solid green (light grey) lines]. For bands located in the energy window going from the Fermi level to \( 5 \) eV below, both methods give similar results (within a maximum difference of 0.1 eV). Below this window, the use of the PPM tends to shift the bands down compared to CD, with a discrepancy of 0.1 eV. This PPM inaccuracy on the lowest band is also reported. It is found to be in agreement with previous calculations.\(^6\) The \( G_0W_0 \) band structure [solid green (light grey) lines] is almost on top of the DFT-PBE one, but the first unoccupied band is shifted up nonhomogeneously by up to \( 0.2 \) eV and the first occupied band is shifted down by \( \sim 0.4 \) eV at \( \Gamma \). These bands present a predominant \( sp \) character. The \( G_0W_0 \) corrections are, anyway, not modifying the 5\( d \) manifold of bands: Their shape, position, and bandwidths are the same as in the DFT-PBE case. As a consequence, the \( G_0W_0 \) 5\( d \)-6\( p \) interband gap does not change compared to the DFT-PBE value, which is smaller than the experimental evidence.

V. SELF-CONSISTENCY EFFECTS WITHIN THE QSGW APPROXIMATION

Figure 4 shows the band structure for different approaches: DFT-PBE [solid blue (black) lines], \( G_0W_0 \) [solid green (light grey) lines], and QSGW [dotted pink (grey) lines]. The transition energies at high-symmetry \( k \) points can also be read in Table I.

When recalculating the QP wave functions within the QSGW approach, the 5\( d \) bands are shifted with respect to DFT-PBE by \( \sim 0.4 \) eV. This is the major difference with respect to one-shot \( G_0W_0 \). In addition, the first unoccupied bands are further shifted, achieving \( +0.3 \) eV from DFT-PBE. As a consequence, the interband gap between the 5\( d \) and the unoccupied bands is opened by 0.4 to 0.8 eV with respect to the DFT-PBE energies. For instance, the transition energies \( X_5 \rightarrow X_4 \) and \( L_3 \rightarrow L_1 \) are opened by 0.45 and 0.75 eV, respectively. This points out the significance of correcting the DFT-PBE wave functions in order to obtain a more accurate band structure.

To understand the effect of quasiparticle self-consistency, the QP and DFT-PBE wave functions are compared in Fig. 5. It is found that QSGW introduces a mixing of DFT-PBE states which corresponds to rotations and small relocalizations of the wave functions. These changes depend on the \( k \) point \( k \) and the band index \( n \).

In Fig. 5(a), we plot the square of overlap between the QP and DFT-PBE wave functions at \( k \) points \( L \) and \( A \), the latter being a random low-symmetry \( k \) point with reduced coordinates (0.5, 0.3, 0.1). This is a direct indication of the band mixing resulting from the QSGW procedure. The square modulus of the QP and DFT-PBE wave functions, \( |\psi_{nk}^{\text{QP}}|^2 \) and

| Transition Energies of Gold (in eV) Calculated within Scalar-Relativistic DFT-PBE, \( G_0W_0 \), and QSGW. |
|---|---|---|
| \( \Gamma_1 \rightarrow \Gamma_{25'} \) | 5.2 | 5.6 | 5.0 |
| \( \Gamma_{25'} \rightarrow \Gamma_{12} \) | 1.5 | 1.5 | 1.5 |
| \( X_4 \rightarrow X_2 \) | 4.8 | 4.8 | 4.7 |
| \( X_4 \rightarrow X_1 \) | 2.6 | 2.3 | 3.1 |
| \( X_4 \rightarrow X_4 \) | 4.8 | 5.4 | 5.2 |
| \( L_1 \rightarrow L_{3'} \) | 2.8 | 2.9 | 2.8 |
| \( L_1 \rightarrow L_{2'} \) | 1.0 | 0.4 | 1.2 |
| \( L_2 \rightarrow L_1 \) | 4.0 | 4.8 | 4.6 |
FIG. 5. (Color online) Illustration of the DFT band mixing at the QSGW level. Panel (a) represents the square of the overlap between the QP and DFT-PBE wave functions at the L (left) and A (right) \( k \) points. The A point is a random low-symmetry \( k \) point with reduced coordinates (0.5, 0.3, 0.1). The square modulus of the QP and DFT-PBE wave functions, \(|\psi_{nQ}^2|\) and \(|\psi_{nDFT}^2|\), for band index \( n = 4 \) at \( k \) point L are shown in panels (b) and (c), respectively. Panel (d) shows the difference \(|\psi_{nQ}^2| - |\psi_{nDFT}^2|\) for band index \( n = 6 \) at \( k \) point A. Gold atoms in the FCC lattice are represented by yellow (light grey) spheres. In panels (b)–(d), the isosurfaces correspond to +1 \( \rho \) in red (grey) and −1 \( \rho \) in blue (black). 

VI. SPIN-ORBIT COUPLING EFFECTS

In order to fully take into account relativistic effects at least at the single-particle level, in principle one should solve the Dirac equation and work with Dirac spinors. Alternatively, one can continue to work with Pauli spinors by choosing an appropriate nonrelativistic limit of the Dirac equation which adds some relativistic corrections to the Schrödinger equation Hamiltonian. In the scalar-relativistic (SR) approximation, one solves a Schrödinger equation including the relativistic correction to the velocity by the mass and the Darwin terms. These terms may cause important band shifts and they should already capture most of the relativistic effect.\(^52\)–\(^54\) In addition, one can include the spin-orbit (SO) coupling term which may cause important band splitting and changes to the band shape. Hereafter, this procedure is referred to as SR + SO.

In Fig. 6 we show the comparison between the band plot of a DFT-PBE calculation which only includes the SR terms in the Kohn-Sham Hamiltonian with that of a fully relativistic \((SR + SO)\) DFT-PBE calculation, which also includes the SO coupling. In the case of gold, most of the relativistic effects in the band structure come from the scalar-relativistic terms.\(^1\)\(^,\)\(^6\) The SO coupling term mainly accounts for band splittings, as shown in Fig. 6. To illustrate the effect of the SO coupling on the wave functions, the overlap between the SR and SR + SO DFT-PBE wave functions is calculated at the \( \Gamma \) point, as shown in Fig. 7. The overlap is close to 1 for the occupied bands 1, 5, and 6, meaning that these bands are almost unaffected by the SO coupling term. However, the \( d \) bands 2, 3, and 4 are strongly changed by the SO coupling term. The \( \Gamma_{2S} \) state found in the scalar-relativistic calculation is split into the \( \Gamma_{7} \) and \( \Gamma_{8} \) states, once the SO coupling term is taken into account. Similar effects are observed in other \( k \) points as explained in Ref. 6.

Within MBPT, relativistic fine-structure effects should in principle be calculated within a fully spinorial GW

FIG. 6. (Color online) DFT-PBE band structure of gold calculated within the scalar-relativistic (SR) approximation [solid blue (black) lines] and including also the spin-orbit coupling (SR + SO) [dotted red (grey) lines]. The zero of energy is set at the Fermi level.
Nevertheless, the occupied L bands are listed in Table II.

In this work, we add SO effects perturbatively on top of the QSGW and HSE band structures by the following procedure:

1. We evaluate the SO corrections to DFT-PBE eigenvalues by a fully spinorial Kohn-Sham calculation.
2. We compute \( \Sigma^{SO}_{nk} = \epsilon_{nk}^{SR+SO} - \epsilon_{nk}^{SR} \), the difference between the SR and SR + SO DFT-PBE eigenvalues at a given \( k \) point and band index \( n \).
3. We add \( \Sigma^{SO}_{nk} \) to the corresponding QP (HSE) eigenvalue.

Figure 8 shows the PBE + SO [dotted red (grey) lines], QSGW + SO [solid black lines], and HSE + SO [dashed green (light grey) lines] band structures including SO coupling effects. The experimental band structure along the \( L \rightarrow \Gamma \) path taken from Ref. 5 is also shown. The experimental and theoretical eigenvalues are listed in Table II.

The error due to the use of QSGW instead of a full GW self-consistency is currently unknown. However, the use of a different self-consistent scheme, namely SC-COHSEX \( + G_0 W_0 \), seems to provide results in agreement with QSGW. Of course, one cannot exclude that both schemes at the same time provide deviations from full self-consistent GW larger than 0.1 eV.

Other possible sources of these discrepancies might be vertex corrections beyond GW. Here we checked the local vertex correction and a nonlocal vertex correction to \( W \) only. These account for small corrections of no more than 0.1 eV, as explained in Ref. 57.

Intraband \( q \rightarrow 0 \) Drude peak contributions to the polarizability, which were neglected in our calculations, may lead to a spurious gap at the Fermi level in simple (alkali) metals. However, no spurious gaps were observed here. In fact, the neglect of the Drude peak in slightly more complex metals, such as aluminium, does not lead to significant errors.

The relativistic corrections taken into account here, as well as in Ref. 20, are only at the single-particle level. At present, the effect of many-body relativistic terms, such as the Breit interaction or the spin-of-one-electron orbit-of-the-second, etc., is unknown. In systems like gold, where relativistic effects are important, these terms might explain the remaining discrepancies.

VII. RESIDUAL DISCREPANCIES

The inclusion into the QP band structure of spin-orbit effects by the present perturbative treatment might be considered as the source of the residual nonnegligible discrepancies. However, a more correct treatment within GW of such effects, as in Ref. 20, was found to affect the result by not more than 0.1 eV.

VIII. THE HSE BAND STRUCTURE OF GOLD

Within HSE, the partially occupied bands close to the Fermi level are in good agreement with the QP and experimental energies. For instance, the position of \( L_0 \) is within 0.1 eV of...
TABLE II. Experimental and theoretical values (in eV) for the energy bands of gold at the high-symmetry points $\Gamma$ and L. The theoretical results include SO coupling corrections (see the text). Experimental errors are shown in parentheses (eV).

| Symmetry label | PBE + SO | QSGW + SO | HSE + SO | Expt. |
|---------------|---------|-----------|---------|-------|
| $\Gamma^+_6$ | (1)     | 10.19     | 10.39   | 10.30 |
| $\Gamma^+_8$ | (2.3)   | -5.67     | -6.02   | -6.31 |
| $\Gamma^+_7$ | (4)     | -4.46     | -4.85   | -4.82 |
| $\Gamma^+_1$ | (5.6)   | -3.37     | -3.67   | -4.00 |
| $\Gamma^+_1$ | (7)     | 15.76     | 15.36   | 23.27 |
| $\Gamma^+_6$ | (8)     | 18.08     | 17.97   | 24.38 |
| L$^+_5$      | (1)     | -7.74     | -8.01   | -8.15 |
| L$^+_4$      | (2)     | -5.79     | -6.16   | -6.40 |
| L$^+_3$      | (3)     | -4.61     | -4.97   | -5.36 |
| L$^+_2$      | (4)     | -2.61     | -2.95   | -3.25 |
| L$^+_1$      | (5)     | -1.90     | -2.24   | -2.60 |
| L$^+_6$      | (6)     | -1.37     | -1.63   | -1.12 |
| L$^+_5$      | (7)     | 2.93      | 3.19    | 3.29  |

The experimental data (see Table II). For this particular point, HSE presents a better agreement with the experimental data than QSGW does. The QP and HSE bands along the W to X and $\Gamma$ to L paths agree almost perfectly from $-1$ to $3$ eV [the Fermi level is at zero] (see Fig. 8). However, in this energy range, a disagreement of $\sim 0.4$ eV is found in the vicinity of the X point. Moreover, the HSE 5$d$ bands are $\sim 0.3$ eV below the QSGW results and the experimental data. This shows that HSE opens the interband gap between the unoccupied and the 5$d$ bands too much. For higher energy bands, the agreement is quite poor. For instance, the HSE eigenvalues at the $\Gamma^+_7$ and $\Gamma^+_6$ points are $\sim 6$ to $7$ eV above the GW and experimental data.

Our findings, and in contemporary those of other authors, show that the HSE functional does not systematically predict reliable band widths and gaps. In fact, the amount of exact exchange in the HSE functional is chosen so to provide good structural, thermochemical, and bonding properties of solids. For metals, our results, in agreement with Refs. 67 and 68, show that HSE overestimate transition energies. Moreover, the modification in the $d$ wave functions as provided by self-consistent GW are not catched by HSE, and the corresponding physics is not reproduced.

IX. CONCLUSIONS

In summary, we have studied the band structure of gold using MBPT with several flavors of the GW approximation and using the HSE hybrid functional. While the inclusion of semicore 5$s$ and 5$p$ states in the valence shell has negligible effects in DFT, it becomes crucial in GW, leading to a wrong inverse ordering of bands at the Fermi level when they are neglected. Within $G_0W_0$, the plasmon-pole model is found to be a good approximation for gold. The PPM provides the same results, within 0.1 eV, as the full contour-deformation integration method, except for the lowest bands where deviations can be up to 0.2 eV. With respect to DFT-PBE, the single-shot $G_0W_0$ shifts the empty bands up by $\sim 0.2$ eV and the lowest sp occupied band down by 0.4 eV, while leaving the 5$d$ occupied bands unchanged. Updating the DFT-PBE wave functions, as in the QSGW approach, is important to shift down by 0.4 eV the occupied 5$d$ bands, thus improving the agreement with the experiment. A residual discrepancy of up to 0.6 eV in the 5$d$-6$s$p interband gap is still present, probably due to relativistic effects beyond those included here, as well as the lack of a unified relativistic many-body approach. Finally, the position of the 5$d$ bands calculated within HSE ends up $\sim 0.3$ eV below the experimental data. HSE becomes more and more off for higher states, with an error of $\sim 6$ eV at 16 eV from the Fermi level.

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*tonatiuh.rangel@cea.fr; present address: CEA, DAM, DIF, F-91297 Arpajon, France.

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