The electronic structure of palladium in the presence of many-body effects

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Abstract

Including on-site electronic interactions described by the multi-orbital Hubbard model we study the correlation effects in the electronic structure of bulk palladium. We use a combined density functional and dynamical mean field theory, LDA+DMFT, based on the fluctuation exchange approximation. The agreement between the experimentally determined and the theoretical lattice constant and bulk modulus is improved when correlation effects are included. It is found that correlations modify the Fermi surface around the neck at the \(L\)-point while the Fermi surface tube structures show little correlation effects. At the same time we discuss the possibility of satellite formation in the high energy binding region. Spectral functions obtained within the LDA+DMFT and \(GW\) methods are compared to discuss non-local correlation effects. For relatively weak interaction strength of the local Coulomb and exchange parameters spectra from LDA+DMFT shows no major difference in comparison to \(GW\).

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I. INTRODUCTION

Transition metals have their density of states characterized by a partially filled narrow $d$-band, superimposed on a broad free electron-like $sp$-band. The shape of the $d$-band especially in the $3d$ series is a consequence of the construction of the $d$-orbitals, as they overlap only to a limited extent with orbitals on neighboring atoms and consequently the hopping integrals between $d$-orbitals is small, as is the bandwidth. This points towards the importance of short range strong Coulomb repulsion for the $3d$ elements. An additional ingredient in the $3d$ series is the appearance of magnetism. In a partially filled shell of a free atom the exchange interaction between electrons favors the parallel alignment of electron spins (Hund’s rule). In solids electrons enter in extended states/orbitals so there is a competition between the kinetic energy of the electron which favors no spin alignment and the exchange interaction which favors spin alignment. If the band is narrow the energy gain from the exchange interaction may win and the spin alignment is favored. In that sense, the occurrence of magnetism in the $3d$ series is a consequence of the narrowness of the $3d$ band. A quantitative theory to explain the electronic structure and hence the physical properties of $3d$-elements has been consistently developed during the last decades in the form of the combined density functional theory (DFT) and dynamical mean field theory (DMFT) \[1-4\] which is generally referred to as the LDA+DMFT method \[4,5\] (LDA = local density approximation). In the LDA+DMFT scheme the LDA provides the \textit{ab initio} material dependent input (orbitals and hopping parameters), while the DMFT solves the many-body problem for the local interactions. Therefore the LDA+DMFT approach is able to compute, and even predict, properties of correlated materials. Theoretical results obtained with LDA+DMFT can be compared with experimental data obtained, for example, by photoemission spectroscopy (PES) \[6\]. In particular, this technique measures spectral functions, i.e., the imaginary part of the one-particle Green function, and thus determines correlation induced shifts of the spectral weight. Indeed, most experimental investigations on the electronic structure of the $3d$ metal Ni rely on PES \[7,8\]. Braun et al. \[9\] demonstrated the importance of local correlations in Ni by exploiting the magnetic circular dichroism in bulk sensitive soft X-ray PES measurements. One of the dominant correlation effects observed in the PES data for Ni is the satellite peak situated at 6 eV below the Fermi level \[10,11\]. This feature is not captured by LDA, but is well explained by LDA+DMFT \[12\]. LDA+DMFT also reproduces
the correct width of the occupied 3d bands and the exchange splitting [10, 12, 13].

As LDA+DMFT is very successful for 3d elements, this motivates us to investigate the applicability of LDA+DMFT to 4d transition metal elements. Transition metals from the 4d series have larger bandwidths compared to that of the 3d elements and correspondingly larger kinetic energies, which will favor an itinerant band-like picture over an atomic-like localized picture and somewhat weaker correlation effects. In our present study we focus on the 4d metal palladium. Despite being in the same group as Ni in the periodic table, the physical properties of Pd are very different, so a theoretical study including local and non-local correlation effects is particularly desirable. Due to its interest in fundamental condensed matter theory, and its industrial use as a catalyst and for hydrogen storage, the electronic structure of Pd has been widely studied over the years. As a late 4d transition metal element, Pd is not far from the ferromagnetic instability: it has a high density of states at the Fermi level and a large Stoner enhancement in the magnetic susceptibility [14]. On expansion of the lattice constant Pd turns ferromagnetic, as shown by DFT calculations [15]. Experimental studies involving PES have been used in the search for signatures of electronic correlations in Pd such as the existence of satellites in the spectral function [16, 17]. Liebsch [18, 19] investigated the satellite formation mechanism in detail using many-body methods, pointing out the importance of taking electron-hole and hole-hole scattering into account by ladder-like summations in the T-matrix formulation. Mårtensson and Johansson predicted a satellite in Pd [20], placing the satellite at 8 eV binding energy, in good agreement with later experimental findings (≈ 8.5 eV) by Chandesris et al. [16]. The method employed in Ref. [20] was semi-empirical, using thermodynamic input data. In this study we will discuss the satellite formation in Pd using ab initio self-consistent state-of-art calculations as well.

Complementary information can be obtained from the analysis of the Fermi surface (FS). Features of the Fermi surface can be experimentally probed by photoemission spectroscopy and de Haas-van Alphen (dHvA) measurements. The so called Kohn anomalies [21] may appear in the phonon dispersion relations of metals, arising from virtual scattering of conduction electrons from state \( \mathbf{k} \) to \( \mathbf{k}' \) connected by nesting vectors \( \mathbf{q} \), making the determination of possible FS nesting of interest. The appearance of a Kohn anomaly in Pd is still debated [22, 23].

Palladium is perhaps the best studied high-susceptibility paramagnet and played an important role in elucidating several aspects of the theory of spin fluctuations. Among the
elements, Pd is traditionally taken as the best candidate for observing spin fluctuations because of its high electronic density of states and large Stoner enhancement in the magnetic susceptibility. Specific heat experiments showed a reduction in the electronic specific heat coefficient of 7% in a magnetic field of about 10 T suggesting that strong spin fluctuations appear in Pd. The reduction of spin-fluctuation contributions to the electronic specific heat at high magnetic fields is well established theoretically by several works: Doniach and Engelsberg, Berk and Schrieffer, Béal-Monod and co-authors, and many others. In their classical works, the Crabtree group experimentally investigated the evidence of spin fluctuations in Pd by measuring the cyclotron effective masses and the amplitude of the dHvA effect as a function of the magnetic field. These typical measurements provide in principle information about spin-fluctuation contributions to the conduction electron properties. While the former allows one to obtain information about the density of states at the Fermi level, which determines the electronic specific heat, the latter measures the difference in volume between the spin up and spin-down Fermi surfaces, which determines the magnetization. The absence of significant field dependence of the cyclotron effective mass and the spin splitting factor implies that the spin-fluctuation contributions to the electronic specific heat and static spin susceptibility $\chi = M/H$ are not appreciably affected by applied fields up to $\sim 13$ T. This is consistent with the theoretical estimations made by Brinkmann and Engelsberg and Hertel et al. that magnetic fields much larger than 13 T are required to suppress the spin fluctuations in Pd. The magnetic properties and dynamical fluctuations in Pd were discussed recently by Larson et al. Highly accurate LDA calculations were performed to estimate the parameters entering in Moriya’s spin-fluctuation theory, in particular the Landau functional for Pd was used to connect critical fluctuations beyond the local density approximation with the band structure. It was pointed out that the key parameter for the non-trivial properties of Pd is the mean-square amplitude of the spin fluctuations, which is a non-local quantity determined by the momentum dependent spin susceptibility in a large part of the Brillouin zone, and therefore non-locality is expected to play a significant role in the physical properties. It is one of the aims of this work to identify local and non-local correlation effects on the spectral function by comparing results obtained via LDA+DMFT and $GW$ methods.

The results presented here include the electronic structure, the Fermi surface and nesting vectors of Pd, and the satellite formation in the high binding energy region of the density of
states. Most of our results have been obtained within the full potential linearized muffin-tin orbitals (FPLMTO) method implemented within the RSPt code \[36\], which has previously proven to be able to accurately determine ground state quantities within LDA+DMFT for 3d transition metals \[37, 38\]. Self-consistent quasiparticle \(GW\) calculations have also been performed \[39, 40\], which allows us to discuss the effect of non-local electronic correlations in Pd. The paper is organized as follows: Section \(\text{I}\) is an introduction. In Section \(\text{II}\) we present computational methods and details of the calculations. Section \(\text{III A}\) presents total energy data, from which we extract the optimal \(U\) and \(J\) values, to match the experimental and the calculated equilibrium lattice parameters. We also present results concerning the onset of ferromagnetic long range order upon lattice expansion. In Section \(\text{III C}\) the calculated spectral function of palladium is shown, and the relation to the photoemission satellite is discussed in detail. The effect of non-local correlations is discussed in Section \(\text{III D}\).

II. COMPUTATIONAL METHODS AND DETAILS

A. The LDA+DMFT method

Correlation effects in the valence Pd 4\(d\) orbitals were included via an on-site electron-electron interaction in the form \(\frac{1}{2} \sum_{i \{m, \sigma\}} U_{mm'm' m''m''} c_{im\sigma}^\dagger c_{im'\sigma'}^\dagger c_{im''\sigma} c_{im''\sigma'}\). Here, \(c_{im\sigma}/c_{im\sigma}^\dagger\) annihilates/creates an electron with spin \(\sigma\) on the orbital \(m\) at the lattice site \(i\). The Coulomb matrix elements \(U_{mm'm'm''}\) are expressed in the usual way \[41\] in terms of Slater integrals. Since specific correlation effects are already included in the local spin-density approximation (LDA), so-called “double counted” terms must be subtracted. To take this into account, we employed the interpolation double counting scheme \[42\]. For the impurity solver a fluctuation exchange (FLEX) \[43\] type of approximation was used for the multiorbital case \[44–46\]. In contrast to the original formulation of FLEX \[43\], the spin-polarized \(T\)-matrix FLEX (SPTFLEX), used for the present calculations treats the particle-particle and the particle-hole channel differently \[44–46\]. While the particle-particle processes are important for the renormalization of the effective interaction, the particle-hole channel describes the interaction of electrons with the spin-fluctuations, which represents one of the most relevant correlation effects in Pd. In addition the advantage of such a computational scheme is that the Coulomb matrix elements can be considered in a full spin and orbital
rotationally invariant form, for realistic materials.

B. The self-consistent quasiparticle $GW$ method

In recent years, first-principle calculations involving the $GW$ approximation \cite{35} are becoming more popular. In particular self-consistent $GW$ formulations are promising because they can more accurately calculate quantities like band gaps compared to “one-shot” $GW$ approaches \cite{40}. In such methods the first step is to compute the band structure of the solid, usually within DFT-LDA. Using the random phase approximation (RPA), the density response function is then calculated and used to evaluate the dielectric function and the screened Coulomb interaction $W$. The matrix elements of the self-energy are added as corrections to the LDA eigenvalues, and the effective potential is self-consistently updated. In spite of the simplified formalism of calculation, compared to that of the full $GW$ scheme, a good agreement with experiment for several materials has been obtained \cite{40}. In this study we employed the quasiparticle self-consistent $GW$ (QSGW) method \cite{39, 40}. Our main object of interest is the self-energy corrected eigenvalue for band $n$ and Bloch vector $k$,

$$E_{kn} = \epsilon_{kn} + Z_{kn}\Delta\Sigma_{kn} \quad (1)$$

where the operator $\Delta\Sigma_{kn} = \langle \Psi_{kn} | \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_{kn}) - V_{xc}(\mathbf{r}) | \Psi_{kn} \rangle$. The self-energy is given in terms of the Green’s function and the screened Coulomb interaction $W$: $\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \omega - \omega') W'(\mathbf{r}, \mathbf{r}', \omega') e^{-\delta\omega'}$. From the slope of the real part one can get the renormalization factor

$$Z_{kn} = \left[ 1 - \frac{\partial Re\Sigma_{kn}(\omega)}{\partial\omega} \right]^{-1}. \quad (2)$$

In a direct comparison with the LDA+DMFT results, $GW$ calculations reveal if significant non-local correlation effects occur in Pd.

C. Technical details

The LDA+DMFT calculations were done using the full-potential FPLMTO code RSPt \cite{36} as a base for the underlying density functional theory calculations. The RSPt calculations were based on the local-density approximation with the parametrization of Perdew and Wang \cite{47} for the exchange-correlation functional. Three kinetic energy tails were used,
with corresponding energies 0.3, -2.3 and -1.5 Ry. Palladium is a face-centered cubic metal, and the \( k \)-mesh we used had the size \( 16 \times 16 \times 16 \) for the equations of state, \( 24 \times 24 \times 24 \) for the other calculations, and Fermi-Dirac smearing with \( T = 400 \) K (the same temperature as was used for the imaginary frequency Matsubara mesh). The muffin-tin radius was set to 2.45 Bohr atomic units (a.u.), and was kept constant throughout for all unit cell volumes. For the charge density and potential angular decomposition inside the muffin-tin spheres, a maximum angular momentum \( l_{\text{max}} = 8 \) was set. The calculations included spin-orbit coupling and scalar-relativistic terms within the muffin-tin spheres, unless otherwise noted. The SPTFLEX impurity solver was implemented in the Matsubara domain, and we used 2048 imaginary frequencies and an electronic temperature 400 K. The analytic continuations of the self-energy from imaginary frequencies to the real energy axis in the complex plane were performed by Padé approximants [48].

The QSGW scheme used in this study is implemented into the LMSuite package [39, 40], which is based on the full-potential linear muffin-tin orbitals code by M. Methfessel et al. [49]. The muffin-tin radius was chosen to be 2.63 a.u, and the integration of the Brillouin zone (BZ) was mapped with \( 24 \times 24 \times 24 \) \( k \)-points. For the GW calculation, we reduced the \( k \)-points to \( 6 \times 6 \times 6 \) [40]. A double-\( \kappa \) basis set with \( l_{\text{max}} = 4 \) was used, including the semicore 4\( p \) states with local orbitals. This basis set allows for an accurate description of the high-lying conduction band states. Spin-orbit coupling was included within the muffin-tin spheres.

We point out that both the RSPt and the QSGW methods are employing the full-potential linearized muffin-tin orbital basis set, but using different implementations. As can be seen in Section III.D, this causes no major differences between the RSPt and the QSGW LDA level results.

III. RESULTS AND DISCUSSION

A. Equation of state

We begin our study by showing that our LDA+DMFT method can accurately determine the equilibrium lattice constant and bulk modulus, two important ground state properties. The Coulomb and exchange parameters \( U \) and \( J \) that are to be used in the DMFT calcula-
TABLE I: Experimental lattice constants $a$ (and equivalent unit cell volume) of palladium from various sources, as function of temperature.

| $T$ [K] | $a$ [Å] | $a$ [a.u.] | Volume [a.u.$^3$] | Reference |
|---------|---------|------------|-------------------|-----------|
| 853     | 3.9184  | 7.4047     | 101.50            | Ref. 50   |
| 673     | 3.9088  | 7.3866     | 100.76            | Ref. 50   |
| 297     | 3.9049  | 7.3792     | 100.45            | Ref. 51   |
| 296     | 3.8904  | 7.3518     | 99.34             | Ref. 50   |
| 296     | 3.8902  | 7.3514     | 99.32             | Ref. 50   |
| 120     | 3.8830  | 7.3378     | 98.77             | Ref. 50   |
| 23      | 3.8907  | 7.3524     | 99.36             | Ref. 51   |
| 0$^a$   | 3.881   | 7.334      | 98.62             | Ref. 52   |
| 0$^b$   | 3.877   | 7.326      | 98.32             | Ref. 52   |

$^a$Estimated from room temperature using linear thermal expansion coefficient, see Ref. 52.

$^b$Corrected for zero-point anharmonic expansion, see Ref. 52.

TABLE II: Equilibrium volumes $V_0$ and bulk modulii $B_0$ extracted from equation of state fitting function (Birch-Murnaghan), for different sets of $U$ and $J$ parameters. The experimental volume 99.3 a.u.$^3$ is taken from the room-temperature data of Ref. 50, which differs from the $T = 0$ K data by < 1%. The experimental bulk modulus is 189 GPa [53].

| $U$ [eV] | $J$ [eV] | $V_0$ [a.u.$^3$] | $B_0$ [GPa] |
|----------|----------|------------------|-------------|
| 0        | 0        | 95.94            | 226.6       |
| 1.0      | 0.3      | 99.02            | 190.6       |
|          | 0.4      | 98.92            | 192.2       |
|          | 0.6      | 99.03            | 192.2       |
|          | 0.8      | 99.05            | 193.2       |
| 1.1      | 0.3      | 99.92            | 181.7       |
| 1.3      | 0.4      | 101.74           | 167.7       |
|          | 0.6      | 101.42           | 171.9       |
|          | 0.8      | 101.31           | 174.7       |
FIG. 1: (Color online) Equation of state curves. Top: Effect of increasing $U$. LDA (red) compared to $U = 1.0$ eV, $J = 0.3$ eV (green); $U = 1.1$ eV, $J = 0.3$ eV (turquoise); $U = 1.3$ eV, $J = 0.4$ eV (blue). Bottom: Effect of altering $J$ while keeping $U$ fixed, for $U = 1.0$ eV (dashed line) and $U = 1.3$ eV (solid line).
tions are considered as adjustable parameters in this study, but can in principle be calculated within a first-principles framework [54]. In this section we have decided to adjust the \( U \) and \( J \) values until the calculated equation of state (EOS) energy-volume curve reproduces the experimental lattice constant (see Table I for a collection of experimental lattice constants from the literature).

In Figure 1 (top) EOS curves for different values of \( U \) and \( J \) are presented. The experimental volume has been marked out. The equilibrium volume \( V_0 \) and bulk modulus \( B_0 \) for each of the curves can be seen in Table III. It is seen (Figure 1 top) that \( U = J = 0 \) eV (red curve), i.e. the LDA, underestimates the volume, which is commonly known. The generalized gradient approximation (GGA) to the exchange-correlation potential, as pointed out for Pd in Ref. 55, overestimates the lattice constant, and leads to a ferromagnetic ground state and is therefore unsuitable. As the value of \( U \) is increased, the computed lattice constant is increased towards the experimental value. For \( U = 1.0 \) eV the calculated \( V_0 \) and \( B_0 \) for different exchange parameters \( J \) are given in Table III and the values are closer to experiment than the LDA value. The effect on the EOS by varying the exchange parameter \( J \) can be seen in Figure 1 (bottom, dashed lines). The equilibrium volumes are tabulated in Table III and give a standard deviation of 0.05 a.u.\(^3\), which is of the same order as the scattering in the data for room temperature (See \( T = 296 \) K in Table I). At \( U = 1.1 \) eV and \( J = 0.3 \) eV, \( V_0 \) is overestimated compared to the experimental value and \( B_0 \) is underestimated. Increasing \( U \) to 1.3 eV leads to an even larger \( V_0 \) and smaller \( B_0 \). Varying \( J \) at this value of \( U \) gives a standard deviation of 0.18 a.u.\(^3\), which is an order of magnitude larger then the standard deviation at \( U = 1.0 \) eV. The effect of exchange \( J \) on the volume is larger for \( U = 1.3 \) eV than for \( U = 1.0 \) eV, but it is still below the effect of the experimentally observed thermal expansion (see Table I). The increase of \( J \) (for a fixed \( U = 1.3 \) eV) decreases the equilibrium volume, which is opposite to the trend given by increasing \( U \). However, this is a small effect and not relevant to this study.

Based on the results presented in this Section, \( U = 1.0 \) eV and \( J = 0.3 \) eV can be taken as reasonable choices in order to be able to reproduce the lattice constant and bulk modulus within our LDA+DMFT method.
FIG. 2: (Color online) Magnetic moment calculated as a function of volume, within the LDA (red circles) and within LDA+DMFT (green circles) for $U = 1.0$ eV and $J = 1.3$ eV. Relativistic effects were treated using the scalar relativistic approximation.

B. Ferromagnetic instability

It is known that palladium is on the verge of ferromagnetism, having a large density of states at the Fermi level $D(E_F)$ leading to a large static susceptibility. An early theory that tried to explain the magnetic transition in itinerant electron systems was the Stoner model. According to this model, a magnetic state is favored over a non-magnetic state when the criterion $D(E_F)I \geq 1$ is fulfilled, where $I$ is the Stoner parameter [56]. This criterion points to the possibility of inducing magnetic order by increasing $D(E_F)$. In some cases, this can be achieved by reducing the effective dimensionality of the system. To create magnetic order attempts have been made to lower the dimensionality of Pd systems, e.g. by creating nanoparticles/wires [57,59] or thin films [60]. There also exists density functional theory studies that indicate that bulk palladium turns ferromagnetic as the volume is expanded [15,61,63].

In Figure 2, the magnetic moment in units of $\mu_B$ is plotted as a function of lattice constant.
For the LDA within the scalar-relativistic approximation (red curve) a magnetic onset is brought about at a lattice constant of 7.65 a.u. This is \( \sim 4\% \) larger than the experimental lattice constant, which is in accordance with previous studies, where the magnetic onset varies between a 1%-6% increase of the lattice constant. Hong and Lee [63] points out that this variance could be due to the sensitivity of \( D(E_F) \) on the \( \mathbf{k} \)-point mesh, and shows that \( D(E_F) \) is difficult to fully converge even at dense mesh sizes. Note that the curve reaches a maximum (\( \sim 0.4 \mu_B \)) and then decreases toward zero magnetic moment at large lattice constants. A full charge transfer to the \( d \)-states has then been accomplished, leading to fully occupied \( d \)-states with no net magnetic moment [15].

We next calculated the magnetic moment as a function of increasing lattice constant within the LDA+DMFT scheme, using the scalar-relativistic approximation, and setting \( U = 1.0 \) eV and \( J = 0.3 \) eV (Figure 2, green curve). The magnetic transition is pushed further upwards in volume, compared to the scalar-relativistic LDA curve (red), giving a transition first into a “low-moment” and then into a “high-moment” state. We also note that the LDA+DMFT curve more or less coincide with the LDA curve at larger lattice constants. The system is then close to having a fully occupied \( d \)-band, where correlation should have negligible effect.

DMFT is able to capture some dynamical spin fluctuation effects, and this could explain the suppression of the magnetic moment at those intermediate volumes where the LDA still gives noticeable moments.

C. Density of states and Fermi surface

1. Spectral functions and the formation of satellite structure

Density of states (DOS) at the experimental lattice constant is presented in Figure 3. Including electronic correlations, for increased values of the local Coulomb parameter \( U \) in the higher binding energy region a satellite structure develops. We tuned \( J \) for fixed \( U \) and saw no significant change in DOS (not shown). Hence, the satellite position is mostly insensitive to the value of the exchange parameter \( J \).

The quasiparticle weights \( Z = (1 - \partial Re[\Sigma(E)]/\partial E|_{E_F})^{-1} \) for the different \( U \) are reported in Figure 3, being in the range \( Z = 0.975 - 0.916 \) for \( U = 1 - 4 \) eV. These correspond to
FIG. 3: (Color online) Total density of states as a function of the Coulomb interaction $U$. Note that the peak closest to the Fermi level (marked by A) is pinned and that the lowest lying peak (C) decreases in intensity while a satellite structure is formed for high binding energies (see inset). Corresponding quasiparticle weights $Z = (1 - \partial R\text{e}[\Sigma(E)]/\partial E|_{E_F})^{-1}$ in the upper left corner.

Effective mass ratios $m^*/m_{LDA} = Z^{-1} = 1.03 - 1.09$, where $m_{LDA}$ is the LDA band mass. This should be compared with $m^*_{sp.heat}/m_{LDA} = 1.66$, where $m^*_{sp.heat}$ is estimated from electronic specific heat measurements and $m_{LDA}$ is taken from band structure calculations [64, 65], which is considerably larger than what we get in this study. It should be noted that the electron-phonon coupling $\lambda_{e-ph}$ is not included in our self-energy, and previous theoretical studies have shown this quantity to be on the order $\lambda_{e-ph} \sim 0.35 - 0.41$ [66, 67]. Recent angle-resolved PES (ARPES) by Hayashi et al. [65] estimated the electron-phonon coupling to be $\lambda_{e-ph} \sim 0.39$, and the electron-electron and electron-paramagnon coupling to be $\lambda_{e-e} + \lambda_{e-para} \sim 0.08$, leading to an effective mass $m_{ARPES}^*/m_{LDA} = 1 + \lambda_{tot} \sim 1.5$. Using Hayashi et al.’s [65] value for $\lambda_{e-ph}$ and our calculated self-energy gives the effective mass $m^*/m_{LDA} = 1.42 - 1.48$, for $U = 1 - 4$ eV, which is in good agreement with Hayashi
et al. [65], but still underestimating the data from specific heat measurements. It should be noted that our quasiparticle weights $Z$ are averaged over the BZ, while Ref. [65] investigated specific paths in the BZ, while also being a surface sensitive study. This comparison however shows that our results are of similar magnitude.

Just below the Fermi level a dominant peak with a relatively large value of the density of states is situated at $\sim -0.15$ eV (marked by A) for all investigated $U$ values. A second major peak (B) is situated in the middle of the valence band at $\sim -2.7$ eV at $U = 0$, and is shifted to $\sim -2.5$ eV as $U$ is increased. The third major peak (C) is at the bottom of the $d$-band at $\sim -4.7$ eV, and is shifted to $\sim -4.4$ eV as correlation is increased. The contributions of different bands to the peaks in the DOS can be inferred by studying the spectral function along high symmetry lines in the BZ, see Figure 4.

Concerning the high-energy binding region in the photoemission spectra, there exist discrepancies on the order of $\sim 0.5$ eV between experiment and band structure calculations, as pointed out by Kang et al. [68]. The LDA seems to overestimate the bandwidth of Pd compared to the measured PES bandwidth, and some experimental states are located closer to the Fermi level than the theoretical states [68–71]. It was proposed [68] that surface and correlation effects could modify the LDA band structure, explaining the discrepancies. It is not altogether clear how to separate these two effects from each other since both bulk and surface states will contribute to the PES, especially for low photon energies. Kang et al. [68] performed a combined PES and LDA level band structure calculation study for Pd, and their results indicated that surface effects could indeed explain the bandwidth narrowing. However, they also ruled out many-body correlation effects since they found no trace of a satellite in the PES. The missing satellite might be due to the neglect of the $4p - 4d$ photoabsorption threshold in Ref. [68], since the energy range of interest (around $\sim 55$ eV photon energy) does not seem to be investigated. The experimental photoemission studies in Refs. [16, 17] scan this range and do indeed find a satellite. The $4p - 4d$ photoabsorption process can be viewed as follows: A photon with energy at the $4p$ core level will excite a core electron to the Fermi level. As the $4p$ core hole is filled by a valence electron, the resulting valence hole will interact with the photoabsorbed electron and contribute to the satellite intensity. Note that the $4p - 4d$ photoabsorption will affect the satellite intensity, but not its position [72]. The satellite position will be determined by the valence hole spectral function, which we access in our calculations. We can not capture the contribution from the
core levels on the spectra, and hence the satellite intensity we obtain should not be directly compared with experiment. From comparison with Figure 3 and the experimental satellite position 8.5 eV [16], the $U$-value needed to reproduce the satellite position can be estimated to be between 2-3 eV. By including correlation we also get a shift of the B and C peaks to lower binding energy, in better agreement with experiment. The B peak position has been measured at $-2.55$ eV (Ref. 70), $-2.4$ eV (Ref. 17) and $-2.5$ eV (estimated from Ref. 68), which indicates that the LDA positions this peak at too high binding energy ($\sim -2.7$ eV

FIG. 4: (Color online) LDA orbital-resolved spectral functions along high symmetry lines in the BZ. Top: $e_g$-symmetry. Bottom: $t_{2g}$-symmetry.
in this study) and that including correlation will improve the peak position in comparison with experiment. We here mention that no attempt was made to model the surface states, instead only bulk calculations were performed. Note that matrix element effects were also not taken into account in this study.

As shown in Section III A a $U$-value above 1.0 eV would overestimate the equilibrium lattice constant. Hence, to capture the experimental spectra, a different $U$ is needed than the one that captures the experimental volume. That the $U$-value needed to reproduce spectral features might differ from the value that reproduce the ground-state properties has been observed also for Ni [37, 73], which makes it plausible that similar behavior is observed for Pd.

It is interesting to discuss the satellite formation in Pd, in comparison with Ni. The effect of electron correlation on one-electron removal energies from a partially filled band is described in terms of interactions between three-body configurations, one hole plus one electron-hole pair giving rise to hole-hole and hole-electron scattering [18, 19]. The effectiveness of these scattering processes depends not only on the strength of the screened on-site electron-electron interaction, but also on the orbital occupations involved in the scattering process. In particular on the number of empty $d$-states necessary for the creation of three-particle configurations since no electron-hole pair can be added to a completely filled band: in the case of nickel where only the minority-spin band has a sizable number of empty states available the creation of a majority-spin hole will be followed by scattering processes involving only opposite spin electron-hole pairs. The interaction strength for this channel is of intensity proportional to $U$, while the creation of a minority-spin hole will involve a scattering of strength proportional to $U - J$ with parallel spin electron-hole pairs only. In Pd both spin channels are symmetric at the equilibrium lattice parameter and fewer empty $d$-states are present in comparison with Ni. Despite the reduced scattering events in generating electron-hole pairs the existence of the $T$-matrix is enough in generating a satellite structure, although the scattering event is not very effective, since the satellite is hardly discernible for valence state spectroscopy.
FIG. 5: (Color online) Fermi surfaces. Top, left: 3-dimensional Fermi surface in the first BZ, projected on the $k_x$-$k_y$ plane. Note the $X$ hole pockets centered at the square faces (hole side blue/electron side yellow), the $L$ hole pockets centered at the hexagonal faces (hole side red/electron side turquoise) and the tube hole structures intersecting at the $X$-points (hole side red/electron side turquoise). Also note that the $L$ pockets only exist if spin-orbit terms are included. A large electron surface sheet is centered around the $\Gamma$-point (purple). Top, right: Hole tube structure as seen in the extended zone scheme. Bottom, left: Cut at $k_z = 0$ within the LDA. Bottom, right: Cut at $k_z = 0$ within the LDA+DMFT, $U = 1.0$ eV and $J = 0.3$ eV. The 3-dimensional Fermi surface was created with the XCrysden software [74].
2. Fermi surface

Many calculations for the Fermi surface of Pd exist in the literature \cite{64, 75, 76}. We present a cut of the LDA Fermi surface in the $k_x - k_y$ plane (Figure 5 bottom left) together with a projection of the 3-dimensional FS sheets (Figure 5 top left). The Fermi surface geometry contains the closed electron surface around the $\Gamma$ point, and a set of hole ellipsoids at the $X$ points. Open hole surfaces consists of cylinders, extending in the [100] and [010] directions (i.e. along the $X - W - X$ paths) and intersecting in pairs at the symmetry points $X$, see top right of Figure 5. The open hole surfaces are particularly interesting as they are associated with the large effective masses and contribute substantially at the density of states near the Fermi level \cite{76}. The Kohn anomaly \cite{21} in the slope of the $[\xi \xi 0]$ transverse acoustic branch of the Pd phonon dispersion is attributed to Fermi surface nesting between these open hole cylinders (see Ref. 22 and references therein). Previous calculations also predicted the existence of small $L$-pockets, which were seen if spin-orbit coupling was taken into account \cite{64, 75}. These $L$-pockets were later confirmed by magnetoacoustic measurements \cite{77}.

The orbital character of the FS sheets can be determined by investigation of the orbital-resolved spectral function, see Figure 4. The tube structure (stemming mostly from the flat band between the $W$ and the $X$ symmetry points) has mostly $t_{2g}$ character, which was pointed out already by Kanamori \cite{78}. Switching on correlation through DMFT, the FS can be seen in Figure 5 (bottom right). No large difference between the Fermi surface within the LDA is seen, and no topological transition occurs. The Fermi surface nesting vector believed to be responsible for the Kohn anomaly seen in the phonon dispersion of Pd is estimated to be $\mathbf{q} = \frac{2\pi}{a}[0.30, 0.30, 0]$, in close agreement with previous studies \cite{22}.

We end this section by pointing out that the negligible change in diameter of the tube structure as correlation is increased is reassuring. This is so since the Kohn anomaly is well captured already at the level of the LDA \cite{22}, and a change in radius would change also the FS nesting, destroying the agreement with experiment.

D. Local and non-local correlation effects

In order to investigate the effect of non-local electron correlations on the electronic structure of Pd, calculations were also performed using the QSGW method. Band structure;
FIG. 6: (Color online) Blue color map corresponds to LDA+DMFT, $U = 1.0$ eV and $J = 0.3$ eV. Top left: Band structure along high symmetry directions in the BZ. Top right: QSGW and LDA+DMFT DOS. Bottom left: Fermi surface cut in $k_x - k_y$ plane. Bottom right: Fermi surface cut including $L$ point.

Spectral functions and Fermi surfaces were calculated using the experimental volume.

In Figure 6 (top left) the band structure is plotted along high symmetry lines within the Brillouin zone. The bands within the LDA from RSPt (green solid lines) and from QSGW (blue dashed lines) coincide well. Turning on correlation effects, the bands are modified compared to the LDA result. The QSGW (red dots) and the LDA+DMFT (blue energy scale) are seen to be nearly coinciding around the Fermi level, and differences are seen at higher energies. Around the Γ-point for energies between $-6$ eV and the Fermi level, the QSGW bands are shifted towards the Fermi level to a larger extent than the LDA+DMFT bands. For energies more negative than $-6$ eV, the lowest band is shifted
downwards in energy to a larger extent than the LDA+DMFT bands. The trends (shift upwards/downwards in energy) is however the same for both methods, indicating that the \( U \)-value used in LDA+DMFT (\( U = 1.0 \) eV) is too small to reproduce the correct quasiparticle eigenvalue position. This was also seen when comparing the LDA+DMFT spectral function with experiment in Section III C.

In Figure 6 (top right) the DOS calculated within the QSGW method is plotted (red line). The DOS corresponding to the initial starting LDA solution is plotted in blue. The effect of correlation is most easily seen by inspecting the three main peaks in the DOS. In Figure 6 (top right) we also show the LDA+DMFT \( k \)-integrated spectral function. The spectral functions within LDA+DMFT are calculated along a horizontal complex contour at a distance \( \delta \) from the real axis, giving a broadening to the DOS. We performed LDA density of states calculations within RSPt along the real axis as well, and found excellent agreement with the LDA from QSGW (not shown). As correlation is turned on, similar trends in the three main peaks can be seen for the QSGW metod as was seen within the LDA+DMFT method. One main difference is that LDA+DMFT can produce the high energy satellite, while QSGW can not. This can attributed to the \( T \)-matrix ladder diagrams which are present in the LDA+DMFT self-energy, but not in the QSGW self-energy. There exist extensions of the \( GW \) formalism that allow for \( T \)-matrix diagrams, see Refs. [79, 80].

In Figure 6 (bottom left) the calculated Fermi surface in a cut of the \( k_x - k_y \)-plane from both LDA+DMFT and QSGW can be seen. Both of the two methods changes the FS slightly. The topology of the sheets is unchanged, but the \( k \)-space volume enclosed by the sheets shows some effect of correlation. The largest changes can be seen in the tube structure running along the \( X - W - X \) symmetry directions. In the case of LDA+DMFT (blue intensity scale) the tube radius is slightly reduced, while for QSGW (green line) the radius is slightly increased. A different cut in the BZ, including the \( L \)-pocket, is shown in Figure 6 (bottom right). QSGW and LDA+DMFT display similar trends in the change of the FS, mainly the beginning of a “neck”-formation in the \( \Gamma - L \) direction and a decreasing of the \( L \)-pocket diameter. Note that within the LDA solution used as a starting point for the QSGW, the \( L \)-pocket and the “tongue” feature are connected along the \( X - L - X \) direction. We found that this was attributed to the use of the tetrahedron \( k \)-point integration method, which pushes the hole sheet slightly upwards in energy, creating the connection.

To conclude this section, we note that non-local effects captured by the QSGW method
on the spectral functions come close to our LDA+DMFT data.

IV. CONCLUSION

Electron correlation is commonly assumed to affect the electronic structure of the 3\textit{d} elements to a larger degree than in the 4\textit{d} elements due, in part, to the difference in \textit{d}-state bandwidth. By electronic structure calculations within a LDA+DMFT context, we could show that even though the LDA can provide a reasonable description of the electronic structure of Pd, correlation effects give important contributions to ground-state and spectral properties. We could improve the equilibrium lattice constant and bulk modulus from that of the LDA, and on expansion of the lattice constant Pd was shown to be ferromagnetic with a magnetic moment suppressed by spin fluctuations. The spectral function calculated with LDA+DMFT supported a formation of a satellite in the high-energy binding region, while at the same time improving the band positions in comparison with experiment. The spectral function and the Fermi surface showed no major difference between the LDA+DMFT and QSGW method, and in particular the nesting vector in the $[\xi\xi \zeta]$-direction was only slightly changed from its LDA value.

Within the presently investigated LDA+DMFT method spin fluctuation effects were shown to influence the magnetic transition volume, pushing it to higher values than within the LDA. These results could point to that spin fluctuations could be important also for the case of low dimensional systems like surfaces, nanoparticles and epitaxial thin films of Pd.

This study confirms the band narrowing and favors the satellite formation seen in experiment for Pd. Previously the difference between the PES and band structure calculations has been attributed to surface effects [68], but our results indicate that also correlation should be taken into account, as was pointed out earlier based on empirical arguments [17, 20]. The LDA+DMFT method should be able to probe the effect of correlation on the PES on an \textit{ab initio} level, and further studies in conjunction with bulk and surface sensitive PES should hopefully make it possible to disentangle surface and correlation effects from each other.

By performing \textit{GW} calculations with a \textbf{k}-dependent self-energy, we could investigate the effect of non-local correlations on the spectral properties of Pd. A closer inspection into momentum dependence of other properties could be interesting. Especially interesting would be to look into momentum dependent susceptibilities, which would be needed to correctly
address paramagnons, which were recently observed in Pd [81].

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