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First-principles treatment of Mott insulators: linearized QSGW+DMFT approach

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The theoretical understanding of emergent phenomena in quantum materials is one of the greatest challenges in condensed matter physics. In contrast to simple materials such as noble metals and semiconductors, macroscopic properties of quantum materials cannot be predicted by the properties of individual electrons. One of the examples of scientific importance is strongly correlated electron system. Neither localized nor itinerant behaviors of electrons in partially filled 3d, 4f, and 5f orbitals give rise to rich physics such as Mott insulators, high-temperature superconductors, and superior thermoelectricity, but hinder quantitative understanding of low-lying excitation spectrum. Here we present a new first-principles approach to strongly correlated solids. It is based on a combination of the quasiparticle self-consistent GW approximation and the dynamical mean-field theory. The sole input in this method is the projector to the set of correlated orbitals for which all local Feynman graphs are being evaluated. For that purpose, we choose very localized quasiautomatic orbitals spanning large energy window, which contains most strongly hybridized bands, as well as upper and lower Hubbard bands. The self-consistency is carried out on the Matsubara axis. This method enables the first-principles study of Mott insulators in both their paramagnetic and antiferromagnetic phases. We illustrate the method on the archetypical charge transfer correlated insulators La_2CuO_4 and NiO , and obtain spectral properties and magnetic moments in good agreement with experiments.

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INTRODUCTION

The first-principles description of strongly correlated materials is currently regarded as one of the greatest challenges in condensed matter physics. The interplay between correlated electrons in open *d*- or *f*- shell and itinerant band states gives rise to rich physics that makes these materials attractive for a wide range of applications such as oxide electronics, high-temperature superconductors, and spintronic devices. Various theoretical approaches are currently being pursued.¹ One of the most successful approaches is the dynamical mean-field theory (DMFT).² In combination with density functional theory,^{3,4} it has described many features of strongly correlated materials successfully and highlighted the surprising accuracy of treating correlations local to a small subset of orbitals exactly, while treating the remainder of the problem in a static mean-field manner.⁵

The numerous successes of DMFT in different classes of correlated materials revived the interest in the long-sought goal of achieving a diagrammatically controlled approach to the quantum many-body problem of solids, starting from the Green's function G and the screened Coulomb interactions W .^{6,7} The lowest order diagram in perturbation theory in this functional gives rise to the GW approximation,⁸ whereas the local approximation applied to the most correlated orbitals gives rise to an extended DMFT approach to the electronic structure problem.⁷ The addition of the GW and DMFT graphs was proposed and implemented in model Hamiltonian studies⁹ and in realistic electronic structure.^{10,11} There is now intense activity in this area with many recent publications^{12–15} triggered by advances in the quality of the impurity solvers,^{16,17} insights into

the analytic form of the high-frequency behavior of the self-energy,¹⁸ and improved electronic structure codes.

Several conceptual issues remain to be clarified before the long-sought goal of a robust electronic structure method for solids is attained. The first issue is the choice of local orbitals on which to perform the DMFT method (summation of all local Feynman graphs). The second issue is the level of self-consistency that should be used in the calculation of various parts of the diagrams included in the treatment (free or bare Green's function G_0 versus self-consistent interacting Green's functions G). These central issues are addressed in this letter.

The self-consistency issue appears already at the lowest order, namely the GW level and it has been debated over time. The corresponding issue in GW+DMFT is expected to be at least as important, but has not been explored, except for model Hamiltonians.^{19,20} At the GW level, it is now well established that Hedin's fully self-consistent formulation,⁸ while producing good total energies in solids,²¹ atoms, and molecules,^{22,23} does not produce a good approximation to the spectra of even three-dimensional electron gas and aluminum in comparison with non-self-consistent GW results.^{21,24} Instead, using a free (quasiparticle (QP)) Green's function in the evaluation of the polarization graph of the GW method gives much better results for spectral functions. This is the basis of the one-shot QP GW, starting from local density approximation (LDA)²⁵ or from others.²⁶ Unfortunately, the answer depends on the starting point. A solution for this problem is to impose a self-consistency equation to determine G_0 . This method, called the QP self-consistent GW (QSGW),²⁷ is very successful reproducing the spectra of many systems.²⁷ How to combine it with DMFT is an important open challenge.^{28,29}

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Previous GW+DMFT studies typically used a G_0 , which depends on the LDA starting point, and projectors spanning a relatively small energy window.^{12–15} In this work, we propose a different approach to the level of self-consistency and the choice of the DMFT orbital. We do a self-consistent QSGW calculation and then calculate local self-energy using DMFT with static U_d and J_H without feedback to non-local self-energy within GW. For the DMFT step, we choose a very localized orbital spanning large energy window, which contains most strongly hybridized bands, as well as upper and lower Hubbard bands.

In the LDA+DMFT context, the choice of very localized orbitals has provided a great deal of universality, as the interactions do not vary much among compounds of the same family. This has been demonstrated in the studies of iron pnictides³⁰ and transition metal oxides.³¹ This choice results in a second advantage as we will show below, namely the frequency dependence of the interaction matrix can be safely ignored. Having chosen the correlated orbitals, all the other parameters are self-consistently determined. This is the first *ab initio* QP self-consistent GW+DMFT implementation and the first study on a paramagnetic (PM) Mott insulator within the GW+DMFT method.

RESULTS

Figure 2a shows the frequency dependence of real and imaginary parts of U_d of La_2CuO_4 shown in Figure 1. It is calculated on an imaginary frequency axis and analytically continued by a maximum entropy method.³² We also plot the fully screened Coulomb interaction W_d for comparison. Static U_d is 12.0 eV and U_d remains almost constant up to 10 eV. In contrast, in W_d , there are several peaks due to low-energy collective excitations below 10 eV. At very high energy, U_d approaches the bare coulomb interaction of 28 eV. Static value of U_{pd} is 2.0 eV, much smaller than U_d ; hence, we do not discuss its treatment further (The renormalization of U_d by the nonlocal Coulomb interaction can be understood by using the definition of Hubbard U by C Herring. According to Herring,³³ the Hubbard U can be obtained from the reaction of $2(d^{n_d} p^{n_p}) \rightarrow d^{n_d+1} p^{n_p-1} + d^{n_d-1} p^{n_p+1}$ between Cu- d and O- p orbitals, where n_d and n_p are the number of electrons in Cu- d and O- p orbitals, respectively. The energy cost

for the reaction is approximately $U_d - 2U_{pd} + U_p$ and this should be the sum of the renormalized U_d and renormalized U_p . In the simplest case, where we have one electron in p and d orbitals, renormalized U of Cu- d orbitals is $U_d - U_{pd}$ from the reaction of $d^1 p^1 \rightarrow d^2 p^0$. The renormalized U_d is derived more rigorously by Schüler *et al.*³⁴). Calculated J_H is 1.4 eV and has negligible frequency dependence. By contrast, conventional constrained random phase approximation, in which 10 bands of mostly Cu-3d character are excluded from screening, results in static $U_d = 7.6$ eV, which is too small to open the Mott gap, and which is also inconsistent with photoemission experiments on CuO charge transfer insulators.³⁵

We introduced a complementary method to compute the static U_d . The key idea is to first calculate the excitation spectra of La_2CuO_4 within Matsubara QSGW (MQSGW)+DMFT using local GW (with a static U_d) as the impurity solver and then determine U_d , by finding the value that best matches the full spin-polarized MQSGW spectra. The procedure starts from the non-spin-polarized MQSGW band structure without magnetic long-range order. We then allow spontaneous magnetic long-range order by embedding a polarized impurity self-energy for the Cu-3d electrons computed in a local GW approximation. We find that indeed magnetic ordering associated with Cu-3d is captured by spin-polarized local MQSGW using a static value of U_d and J_H , and spectral properties such as energy gap are very similar in value to the full spin-polarized MQSGW spectra. In Figure 2b, we allowed U_d to vary between 8 and 13 eV (at fixed $J_H = 1.4$ eV) and we plot the size of the indirect gap. The gap size of this method matches

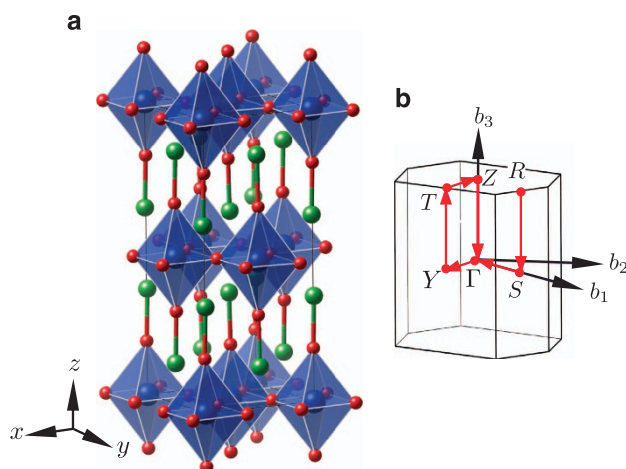


Figure 1. Atomic structure and first Brillouin zone of La_2CuO_4 . **(a)** Atomic structure of La_2CuO_4 in the single face-centered orthorhombic phase. Lanthanum atoms are represented by green spheres, copper atoms by blue spheres in the blue octahedrons, and oxygen atoms by red spheres. The structure is characterized by an alternating rotation of successive CuO_6 octahedra along the x direction. **(b)** First Brillouin zone of single face-centered orthorhombic phase. Red lines show the path along which electronic band structures are plotted in Figures 2c and 3.

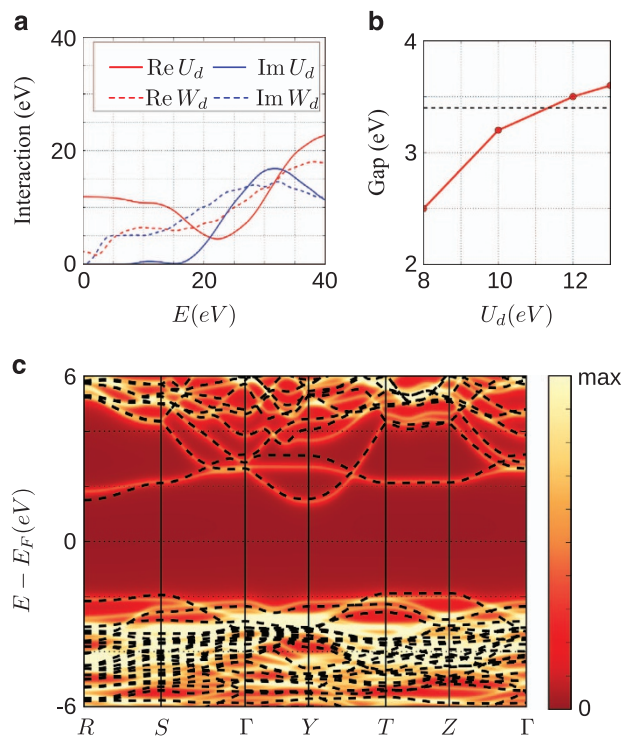


Figure 2. Hubbard U associated with Cu-3d orbitals in La_2CuO_4 . **(a)** Frequency dependence of W_d (dashed lines) and U_d (full lines) of La_2CuO_4 with a χ_{QP}^{low} defined in the energy window $E_F \pm 10$ eV. Real and imaginary parts of the parameter are marked by red and blue colors, respectively. **(b)** Bandgap dependence on U_d , in La_2CuO_4 , evaluated with impurity self-energy within spin-polarized GW approximation with $J_H = 1.4$ eV. The black dashed line represents bandgap within spin-polarized Matsubara QP self-consistent GW (MQSGW). **(c)** Spectral function of La_2CuO_4 with $U_d = 12$ eV and $J_H = 1.4$ eV. The black dashed-lines show band structures within spin-polarized MQSGW.

the gap of spin-polarized MQSGW when $U_d \approx 12$ eV. If this choice of U_d and J_H is correct, the resulting spectra must be similar to the prediction of spin-polarized MQSGW method. We show this comparison in Figure 2c to confirm a good match. In addition, the relative position of the Cu- d band (the lowest energy conduction band at S) to the La- d band (the lowest energy conduction band at Y) is also well matched, justifying the approximation of $\hat{\Sigma}^{DC}(i\omega_n) \simeq \hat{\Sigma}^{DC}(i\omega_n = 0)$. $\Sigma^{DC}(i\omega_n = 0)$ for Cu- $d_{x^2-y^2}$ orbital differs from nominal double counting energy³⁶ by only 1%, highlighting again the advantages of using a broad window and narrow orbitals.

We now discuss the magnetic moment associated with Cu and the electronic excitation spectra of La_2CuO_4 by using MQSGW+DMFT (with $U_d = 12.0$ eV, $J_H = 1.4$ eV) in which the impurity is solved by the numerically exact continuous-time quantum Monte-Carlo^{16,17} and compare them with other methods. Local spin density approximation does not have a magnetic solution. In contrast, spin-polarized MQSGW, QSGW,²⁷ and MQSGW+DMFT predict $0.7 \mu_B$, $0.7 \mu_B$, and $0.8 \mu_B$, respectively. This is consistent with experimental measurements, although the later span quite large range $0.4 \sim 0.8 \mu_B$.³⁷⁻³⁹

In the low-energy spectrum of La_2CuO_4 , local spin density approximation does not have an insulating solution; there is a single non-magnetic solution with zero energy gap as shown in the bandstructure (Figure 3a) and total density of states (Figure 4a). The non-spin-polarized MQSGW also predicts metal as shown in Figure 4a, but the two bands of primarily Cu- $d_{x^2-y^2}$ character near the Fermi level are well-separated from the rest of the bands (dashed lines in Figure 3b). Spin-polarized MQSGW calculation (dashed lines in Figure 3c) yields qualitative different results from local spin density approximation and non-spin-polarized MQSGW calculation. The two Cu- $d_{x^2-y^2}$ bands are now well separated from each other with a bandgap of 3.4 eV. Spin-polarized QSGW²⁷ also yields insulating phase with a gap of 4.0 eV. In the experiment, the larger direct gap, as measured by optics, is ~ 2 eV.^{40,41}

We show that these deficiencies of LDA, QSGW and MQSGW in the low-energy spectra can be remedied by adding all local Feynman diagrams for the Cu- d orbitals using the DMFT. The LDA+DMFT calculation in Figure 4a, carried out by the all-electron LDA+DMFT method,^{31,36} predicts reasonable gap of 1.5 and 1.8 eV in PM and antiferromagnetic (AFM) phases, in good agreement with experiment and previous LDA+DMFT studies.^{31,42-45} Within MQSGW+DMFT, we find gaps of 1.5 and 1.6 eV in PM and AFM phases, respectively, as shown in Figure 4b. The excitation spectra of MQSGW+DMFT in PM and AFM phase as shown in Figure 3b,c are very similar, as both are insulating with well-separated

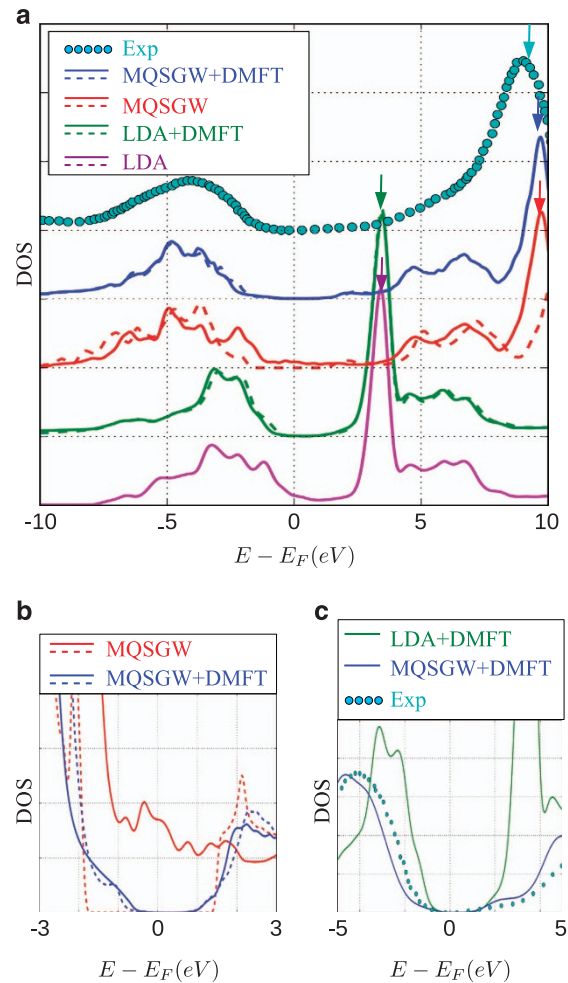


Figure 4. The density of states of La_2CuO_4 . (a) Total density of states of La_2CuO_4 from local density approximation (LDA) (magenta), LDA+dynamical mean-field theory (DMFT) (green), Matsubara QP self-consistent GW (MQSGW) (red), and MQSGW+DMFT (blue). Full lines and dashed lines represent quantities within non-spin-polarized and spin-polarized versions of each calculation, respectively. The cyan dotted line shows photoemission/inverse photoemission data.⁴⁶ The positions of La- f peaks are marked by arrows. (b) A zoom-in view in the low-energy region. (c) The overlap of total density of states of La_2CuO_4 within LDA+DMFT as well as MQSGW+DMFT and photoemission/inverse photoemission data.⁴⁶

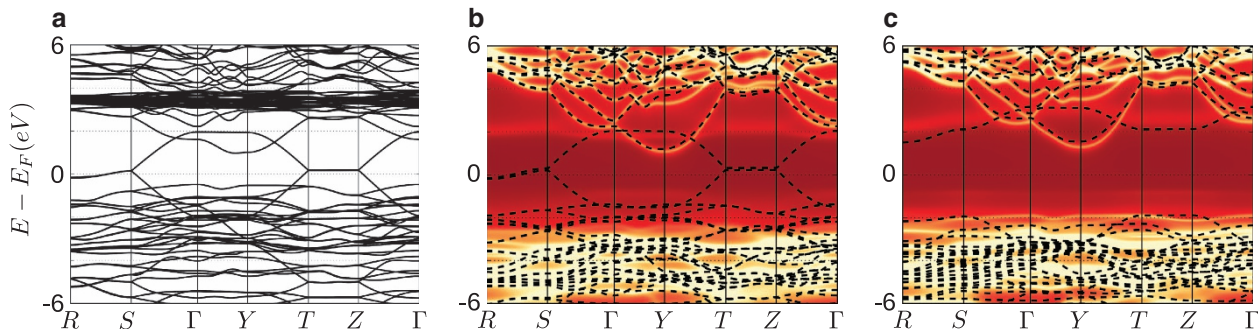


Figure 3. The low-energy spectral function of La_2CuO_4 . (a) Electronic bandstructures of La_2CuO_4 within local spin density approximation and spectral functions from (b) non-spin-polarized Matsubara QP self-consistent GW (MQSGW)+dynamical mean-field theory (DMFT) (c) and spin-polarized MQSGW+DMFT calculations along the path shown in Figure 1b. The dashed lines in b, c represent electronic band structures within non-spin-polarized MQSGW and spin-polarized MQSGW, respectively.

Cu- $d_{x^2-y^2}$ bands, which is now also substantially broadened due to large scattering rate in Hubbard-like bands. In addition, MQSGW+DMFT improves the line-shape of LDA+DMFT. Near the top of the valence bands with oxygen p character, the lineshape within LDA+DMFT is too sharp in comparison with the experiments as shown in Figure 4c. By treating oxygen p levels within GW, the lineshape becomes smoother and in a better agreement with experiments.

In the high-energy region of La_2CuO_4 , the most distinctive difference is the position of La- f peak. It appears at ~ 3 eV within LDA and LDA+DMFT, but at around ~ 9 eV in the inverse-photoemission spectra (cyan dotted line in Figure 4a).⁴⁶ By treating La- f within GW approximation, it appears at ~ 10 eV within MQSGW and MQSGW+DMFT. The underestimation of unoccupied La- f excitation energy is attributed to the local approximation to the electron self-energy within LDA. Within LDA, Hartree and exchange-correlation potential applied to La- f orbitals are orbital independent, as charge density is averaged over 14 different m channels.⁴⁷ In contrast, these potentials within MQSGW are orbital dependent and non-local. The effect of orbital-dependent potential can be tested within LDA+U approaches, as LDA+U adds orbital-dependent potential and subtracts orbital-independent potential explicitly.³ From LDA+U approaches, we can also understand MQSGW better, as LDA+U can be regarded as a local and static approximation to GW approximation.³ According to Czyzyk and Sawatzky⁴⁸, La- f peaks shift from E_F+3 eV to E_F+3 eV+ $U/2$ with $U=11$ eV for La- f .

We also tested our proposed scheme with one more charge transfer insulator, NiO. Figure 5a shows the frequency dependence of U_d and W_d for the Ni-3d orbitals in the low-energy region. In contrast to W_d , U_d is almost constant up to 5 eV. Static U_d is 9.6 eV. In the high-energy limit, U_d and W_d approach the bare value of

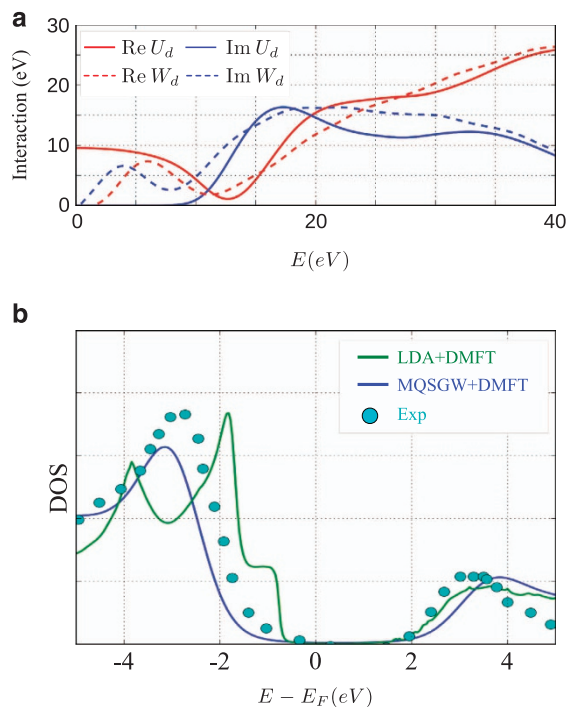


Figure 5. Hubbard U associated with Ni-3d orbitals in NiO (a) Frequency dependence of W_d (dashed lines) and U_d (full lines) of NiO, with a χ_{QP}^{low} defined in the energy window in E_F-11 eV to E_F+10 eV. Real and imaginary parts of the parameter are marked by red and blue colors, respectively. (b) Total density of states of NiO within LDA+dynamical mean-field theory (DMFT) (green) and Matsubara QP self-consistent GW (MQSGW)+DMFT (blue). The cyan dotted line shows photoemission/inverse photoemission data.⁴⁹

26.0 eV. Calculated J_H for the Ni-3d orbitals has negligible frequency dependence and static J_H is 1.4 eV. Figure 5b shows the total density of states of NiO within LDA+DMFT and MQSGW+DMFT in its PM phase. Photoemission/inverse photoemission data are also plotted for comparison.⁴⁹ The LDA+DMFT calculation is being carried out by the all-electron LDA+DMFT method³⁶ with $U_d=10$ eV, $J_H=0.9$ eV and nominal double-counting energy. In the PM phase, LDA+DMFT and MQSGW+DMFT predict insulator in an agreement with previous LDA+DMFT studies,^{50,51} but MQSGW+DMFT improves the lineshape of LDA+DMFT. Near the top of the valence bands, the lineshape within LDA+DMFT is too sharp in comparison with the experiments. By treating oxygen p levels within GW, the lineshape becomes smoother and in a better agreement with experiments. In the AFM phase, magnetic moment associated with Ni- d orbitals is $1.6 \mu_B$ within MQSGW+DMFT, in agreement with experimental value of $1.6-1.9 \mu_B$.^{50,52,53}

In summary, we introduced a new methodology within MQSGW+DMFT and tested it in the classic charge transfer insulator La_2CuO_4 and NiO. Our methodology predicts a Mott-insulating gap in the PM phase, thus overcoming the limitation of LDA and QSGW. It yields more precise peak positions of the La- f states in La_2CuO_4 and valence band lineshape, thus improving the results of LDA+DMFT. The method should be useful in understanding electronic excitation spectrum of other strongly correlated materials, in particular, those where precise position of both the itinerant and correlated states is important.

METHODS

Our approach is carried out entirely on the Matsubara axis, which requires a different approach to the QP self-consistency in GW,⁵⁴ called MQSGW, where the QP Hamiltonian is constructed by linearizing the self-energy and renormalization factor (MQSGW is a form of QP self-consistency that replaces $\tilde{\Sigma}(i\omega_n)$ with $\tilde{\Sigma}(0) + i\omega_n \tilde{\Sigma}'(0)$ on the Matsubara axis. It is similar to, but not identical with the form in reference 55 on the real frequency axis, which replaces $\langle i|\tilde{\Sigma}(\omega)|j\rangle$ with $Re(\langle i|\tilde{\Sigma}(\epsilon_i)|j\rangle + \langle j|\tilde{\Sigma}(\epsilon_j)|i\rangle)/2$, derived from a norm minimization principle. Here, ϵ_i and $|j\rangle$ are QP energy and wavefunction, respectively). Working on the Matsubara axis is numerically very stable, provide a natural interface with advanced DMFT solvers such as continuous-time quantum Monte-Carlo,^{16,17} and has very good scaling in system size as in the space-time method (see Supplementary Note on MQSGW calculations).

For DMFT, it is essential to obtain bandstructures in a fine enough crystal momentum (\mathbf{k}) mesh to attain desired frequency resolution of physical quantities. To achieve such momentum resolution, we use a Wannier-interpolated MQSGW bandstructure in a large energy window using maximally localized Wannier function⁵⁶ and then constructed local projector in a fine momentum mesh. In contrast to SrVO_3 ,¹²⁻¹⁵ where a set of t_{2g} states is reasonably well separated from the other bands, correlated 3d orbitals in La_2CuO_4 and NiO, and are strongly hybridized with other itinerant bands. In this case, it is necessary to construct local projectors from states in a wide-enough energy windows to make projectors localized near the correlated atoms. We constructed local projectors in the energy window $E_F \pm 10$ eV in which there are ~ 82 bands at each \mathbf{k} point, where E_F is the Fermi level for La_2CuO_4 . For NiO, we constructed local projectors in the energy window of E_F-11 eV to E_F+10 eV. Next, we confirmed that absolute value of its overlap to the muffin-tin orbital (of which radial function is determined to maximize electron occupation in it) is $>95\%$. Our choice of energy window is justified by the Cu-3d spectra being entirely contained in this window. Using constructed maximally localized Wannier function s_i , we defined our local projector $P_{i,n}(\mathbf{k}) = \sum_{\mathbf{r}} (W_{\mathbf{r}i}|\psi_{n\mathbf{k}}\rangle e^{-i\mathbf{k}\cdot\mathbf{r}}/\sqrt{N_{\mathbf{k}}}$, where $W_{\mathbf{r}i}(\mathbf{r})$ is the maximally localized Wannier function with an index i , $\psi_{n\mathbf{k}}(\mathbf{r})$ is the QP wavefunction with an index n , and $N_{\mathbf{k}}$ is the number of \mathbf{k} points in the first Brillouin zone.

Static U_d and J_H are evaluated by a modification of the constrained random phase approximation method,⁵⁷ which avoids screening by the strongly hybridized bands. This screening by hybridization is included in our large-energy window DMFT. For details, see Supplementary Note on U_d and J_H . We divide dynamic polarizability within MQSGW approximation χ_{QP} into two parts, $\chi_{QP} = \chi_{QP}^{low} + \chi_{QP}^{high}$. Here, χ_{QP}^{low} is defined by all transitions between the states in the energy window accounted for by the DMFT method ($E_F \pm 10$ eV for La_2CuO_4 and E_F-11 eV to E_F+10 eV for NiO).

Using χ_{QP}^{high} , we evaluate partially screened Coulomb interaction $U^{-1}(\mathbf{r}, \mathbf{r}', \mathbf{k}, i\omega_n) = V^{-1}(\mathbf{r}, \mathbf{r}', \mathbf{k}) - \chi_{QP}^{high}(\mathbf{r}, \mathbf{r}', \mathbf{k}, i\omega_n)$ and parametrize static U_d and J_H by Slater's integrals,^{58,59} where V is bare Coulomb interaction.

The Feynman graphs included in both MQSGW and DMFT (double counting) are the local Hartree and the local GW diagram. They are computed using the local projection of the MQSGW Green's function (\hat{G}_{QP}) $\hat{G}_{QP}^{loc}(i\omega_n) = \frac{1}{N_k} \sum_{\mathbf{k}} \hat{P}(\mathbf{k}) \hat{G}_{QP}(\mathbf{k}, i\omega_n) \hat{P}^\dagger(\mathbf{k})$ and the local Coulomb matrix constructed from Slater's integrals. For the details, see Supplementary Note on double counting energy.

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CONTRIBUTIONS

G.K. designed the framework of the code. S.C. developed the code, building on earlier developments of A.K and K. H. and performed the calculations. G.K., K.H. and S.C. analyzed the data with the help of A.K. and M.v.S. All authors provided comments on the paper.

COMPETING INTERESTS

The authors declare no conflict of interest.

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