

SCIENTIFIC REPORTS



OPEN

Quasiparticle self-consistent *GW* study of cuprates: electronic structure, model parameters, and the two-band theory for T_c

Received: 19 January 2015

Accepted: 11 June 2015

Published: 24 July 2015

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Despite decades of progress, an understanding of unconventional superconductivity still remains elusive. An important open question is about the material dependence of the superconducting properties. Using the quasiparticle self-consistent *GW* method, we re-examine the electronic structure of copper oxide high- T_c materials. We show that QSGW captures several important features, distinctive from the conventional LDA results. The energy level splitting between $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ is significantly enlarged and the van Hove singularity point is lowered. The calculated results compare better than LDA with recent experimental results from resonant inelastic xray scattering and angle resolved photoemission experiments. This agreement with the experiments supports the previously suggested two-band theory for the material dependence of the superconducting transition temperature, T_c .

After the seminal work of finding high temperature superconductivity in a ceramic copper oxide material¹, efforts to understand the cuprate have long been a central part of modern condensed matter physics. Although many intriguing aspects of its electronic behaviors have been unveiled and great progress has been made, an understanding of its superconducting mechanism, the novel interplay between competing phases, and its relationship to other correlated phenomena is still far from clear^{2–12}. One simple, well-defined but still open question is what determines the superconducting transition temperature (T_c), or its material dependency. For example, the T_c of the single layer cuprates can be different by a factor of two; ~ 40 K for La_2CuO_4 and ~ 90 K for $\text{HgBa}_2\text{CuO}_4$. On the one hand, it may be too early to ask this question, while the superconducting mechanism itself still remains elusive. On the other, however, figuring out the detailed features behind the material dependency can provide the crucial hint for further understanding of superconductivity and other related properties. In fact, many directly or indirectly related theoretical studies have been performed on this issue^{13–25}.

In this regard, a notable suggestion has recently been made^{26–29}. According to this theory, the T_c of the single-layer cuprate can be described with a two-orbital model that considers both the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ Wannier orbitals, and the energy level offset between the two orbitals, ΔE , plays a key role in determining T_c . Whereas the larger value of this energy separation produces the higher T_c (e.g., the case of $\text{HgBa}_2\text{CuO}_4$) due to the better one band feature achieved, the smaller value results in the lower T_c (e.g., the case of La_2CuO_4) in spite of the better nested Fermi surface. The calculated Eliashberg parameter (λ) based on the many-body calculation using the fluctuating exchange (FLEX) approximation^{30,31}

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clearly exhibits a linear dependence on ΔE while the other parameters are shown to be less important. Further, this theory can be extended to the bilayer case²⁹, which explains the correlation between the Fermi surface shape and T_c ²⁴.

A possible experimental test to verify this two-band theory is to examine the correlation between T_c and ΔE , the Fermi surface shape, or the partial density of states of the $d_{3z^2-r^2}$ orbital, which can be measured by recent techniques such as resonant inelastic x-ray scattering (RIXS), and (angle resolved) photoemission spectroscopy (ARPES). However, while the theoretical ΔE or the Fermi surface shape was obtained from the LDA and used as the “inputs” for the many-body FLEX calculation in Refs 26–29, the experimentally determined ΔE and the Fermi surface shape should be regarded as the “outputs” or “results” after the consideration of the many-body correlation effects beyond LDA/GGA. In fact, while a RIXS study reports that T_c is higher for larger ΔE ³², the actual experimental value of ΔE is larger than the theoretical evaluation, presumably due to this “input vs. output” problem. One possible way to resolve this problem, at least partially, is to re-evaluate ΔE as an output of the FLEX calculation. However, this approach would suffer from various ambiguities regarding the Hubbard interaction strength and the definition of the renormalized ΔE . It is problematic since a quantitative comparison is required in between the theory and experiment, while only the qualitative comparison was made regarding T_c in Refs 26–29.

In the present paper, we use a first-principles approach, exploiting the quasiparticle self-consistent GW (QSGW) method. It enables us to take into account the correlation effects beyond LDA/GGA. In this way, we can obtain a well-defined renormalized ΔE without introducing adjustable parameters.

In Ref. 17, a quantum chemical approach was adopted to evaluate the energy level offset between $\text{Cu-}d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, where the correlation effects were taken into account within a cluster-based configuration-interaction-type calculation. A good agreement with the RIXS experiment was found by assuming the energy difference of ferromagnetically and antiferromagnetically ordered states to be $2J$, where J is the antiferromagnetic coupling constant. Our approach is fairly different and is along the line of the first-principles band calculation as in Refs 26–29. In the sense mentioned above, the calculated ΔE can be compared to the experiments, while it should not be regarded as an input parameter for the many-body calculation, because doing so would result in a partial double counting of the correlation effects. Still, the present approach can also provide a first-step hint toward obtaining a better “non-interacting” Hamiltonian that can be used as an input for the many-body calculation of superconductivity. In fact, it is known that the non-interacting Hamiltonian obtained from LDA has a problem when used as an input for the FLEX calculation, and the LDA/GGA estimation of ΔE for La_2CuO_4 is too small to account for the maximum T_c of 40 K in the La_2CuO_4 ³³. In this context, it is worth pointing out that the GW method has been successfully applied to the many of strongly correlated materials in combination with, for example, dynamical mean field theory (DMFT)^{34–37}.

Results and Discussion

To our knowledge, there is no previous QSGW study for the cuprate band structure although it has been discussed conceptually³⁸. Here we first examine the electronic structure and the two-band theory for the material-dependent T_c of a single layer cuprate. While the QSGW calculation produces notable differences in the band structure and Fermi surface from LDA, the two-band explanation for T_c still remains valid. QSGW results of model parameters are presented and compared to the RIXS data as well as the LDA calculations. It clearly shows that the parameters produced by QSGW are in better agreement with the experiment. Finally, we investigate the epitaxially strained La_2CuO_4 whose noticeable T_c increase has been previously reported. Two-band theory also works well for this situation.

Electronic structure and the T_c of single layer compounds. Figure 1(a,b) show the band dispersion and projected density of states (PDOS) of La_2CuO_4 calculated by LDA and QSGW, respectively. The LDA result is in good agreement with the previous calculation (see, for example, Ref. 26 and 27). In the QSGW, several important differences are noted. First, the band width of both e_g orbitals are significantly reduced, by about 1.30 and 0.65 eV for $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, respectively, indicating that the band width overestimation (or effective mass underestimation) problem of LDA is somehow overcome by the QSGW procedure. Another key difference is that the separation between the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ bands becomes larger in QSGW, as seen in Fig. 1(b). The $d_{x^2-y^2}$ energy level, $E_{x^2-y^2}$, is shifted from -0.14 (LDA) to -0.03 (QSGW) while $E_{3z^2-r^2}$ is from -0.98 (LDA) to -1.68 (QSGW) (indicated by the arrows in Fig. 1; see also Table 1). It is a factor of two difference in ΔE_{e_g} ; 0.84 eV in LDA and 1.66 in QSGW. The correct estimation of this quantity is important especially in the two-band theory for T_c ^{26–29}. The large value of ΔE_{e_g} is indeed consistent with the RIXS data as will be discussed further below.

The same features are also found in $\text{HgBa}_2\text{CuO}_4$, as presented in Fig. 1(c,d). The $d_{x^2-y^2}$ band width is reduced by ~ 0.75 eV in QSGW compared to LDA and its center position of PDOS moves slightly upward by 0.15 eV. While the $d_{3z^2-r^2}$ dispersion in this material is already quite small due to the thicker blocking layer, its band width in QSGW is further reduced. ΔE_{e_g} is 2.25 in QSGW, again noticeably larger than the LDA value of 1.67 eV (see Table 1).

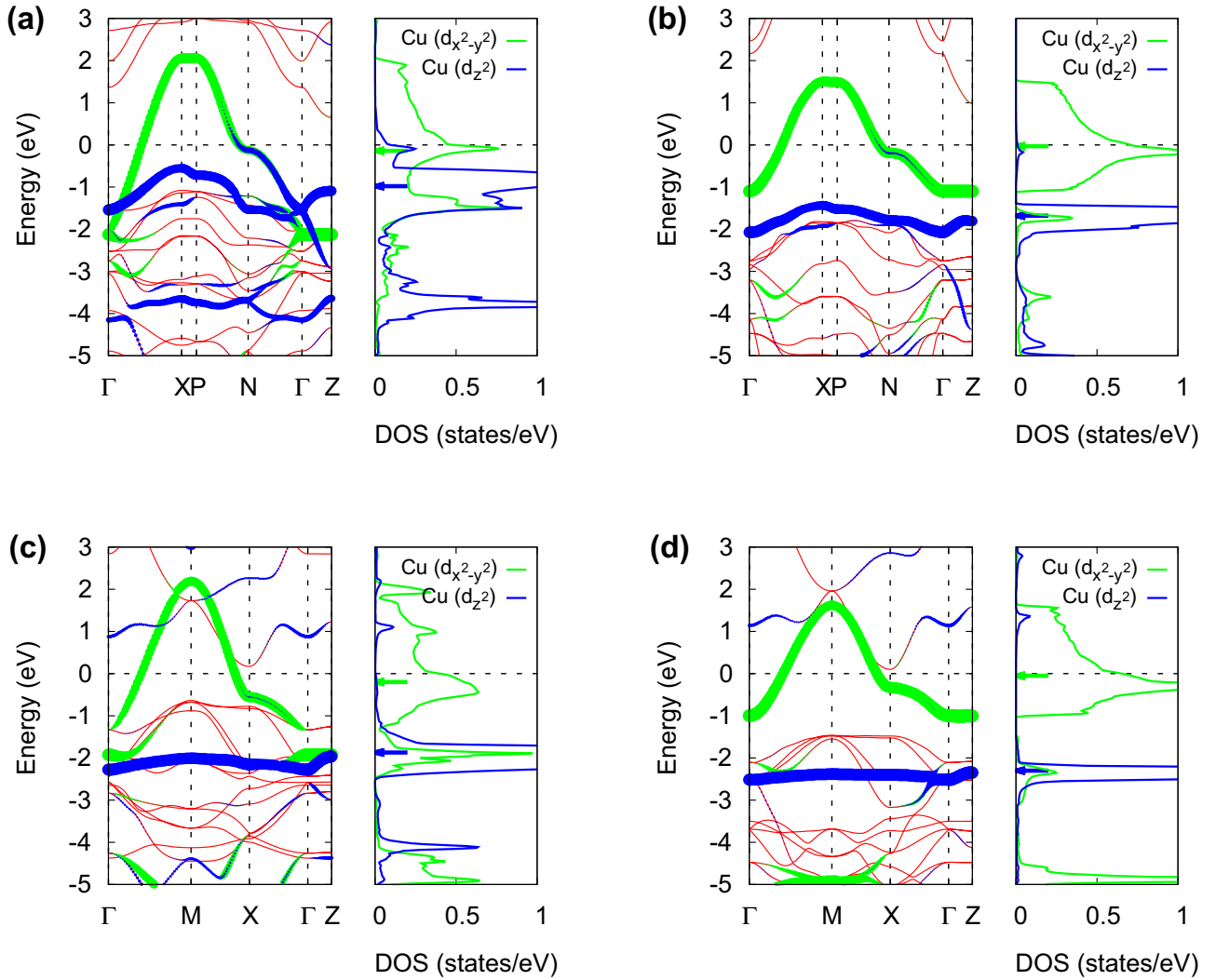


Figure 1. The band dispersion and PDOS of La_2CuO_4 (a,b) and $\text{HgBa}_2\text{CuO}_4$ (c,d) calculated by (a,c) LDA and (b,d) QSGW. The green and blue colors refer to the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ characters while the size of the colored dots represents their weight. The same color scheme was used for PDOS. Other bands than the two e_g states are represented by red color. The center of mass position of PDOS is marked by an arrow. Fermi energy is set to be 0.

In QSGW, the ΔE_{e_g} of both La_2CuO_4 and $\text{HgBa}_2\text{CuO}_4$ is enhanced compared to LDA/GGA. How does this affect the theoretical estimation of T_c ? First, it should be noted that these parameters cannot be directly adopted as the inputs for the FLEX calculation. This is because, in principle, the QSGW self energy should be partially subtracted before we put it into any of many-body calculations. While there is no well-defined prescription yet for this kind of ‘double-counting’ problem³⁹, the “best” ΔE_{e_g} that should be adopted in the FLEX evaluation of T_c may be lying somewhere in between the QSGW and LDA/GGA values. This can provide better quantitative agreement with the experiment, especially in La_2CuO_4 , for which the LDA/GGA value of ΔE_{e_g} is found to be too small to account for $T_c = 40$ K.

Oxygen states are also affected. Compared to LDA results, the O-2p levels obtained by QSGW are significantly lowered in energy, as indicated in Fig. 2. As summarized in Table 1, the center position of in-plane oxygen PDOS is located at -4.44 (-3.55) eV in LDA and at -5.06 (-4.05) eV in QSGW for La_2CuO_4 ($\text{HgBa}_2\text{CuO}_4$). The same feature is found for the apical O- p_z PDOS. As a result, the energy difference, $\Delta E_p = E_{\text{apical}} - E_{\text{inplane}}$, is changed from 1.68 (1.00) in LDA to 0.55 (-0.86) in QSGW for the case of La_2CuO_4 ($\text{HgBa}_2\text{CuO}_4$), see Table 1. The correct estimation of ΔE_p is also important for understanding T_c since it is an underlying quantity to determine ΔE_{e_g} ($\approx \Delta E \approx \Delta E_d + \Delta E_p$) in combination with other parameters. Note that our ΔE_{e_g} is different from ΔE_d and ΔE in Ref. 26–29 where $\Delta E \approx \Delta E_d + \Delta E_p$, $\Delta E_d = E_{x^2-y^2} - E_{3z^2-r^2}$, $\Delta E_p = E_{\text{apical}}^{\text{O}} - E_{\text{inplane}}^{\text{O}}$, and all of the parameters are calculated from the maximally localized Wannier orbital analysis. The ΔE contains the contribution from

	$E_{d_{x^2-y^2}} - E_{\text{Fermi}}$ (eV)		$E_{d_{z^2}} - E_{\text{Fermi}}$ (eV)		$E_{O_{p_{x,y}}} - E_{\text{Fermi}}$ (eV)		$E_{O_{p_z}} - E_{\text{Fermi}}$ (eV)		
	LDA	QSGW	LDA	QSGW	LDA	QSGW	LDA	QSGW	
$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	-0.29	0.01	-1.23	-2.05	-4.67	-4.92	None	None	
La_2CuO_4	-0.14	-0.03	-0.98	-1.68	-4.44	-5.06	-2.76	-4.06	
$\text{HgBa}_2\text{CuO}_4$	-0.20	-0.05	-1.87	-2.30	-3.55	-4.05	-3.00	-4.91	
CaCuO_2	-0.30	-0.17	-2.34	-2.63	-3.67	-4.05	None	None	
	ΔE_{e_g} (4Ds + 5Dt) (eV)			3Ds - 5Dt (eV)			10Dq (eV)		
	LDA	QSGW	Exp (Ref. 32)	LDA	QSGW	Exp (Ref. 32)	LDA	QSGW	Exp (Ref. 32)
$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	0.94	2.05	1.97	0.22	0.21	0.33	0.81	1.82	1.50
La_2CuO_4	0.84	1.66	1.70	0.17	0.11	0.32	1.47	2.13	1.80
$\text{HgBa}_2\text{CuO}_4$	1.67	2.25	None	0.42	0.42	None	0.90	1.57	None
CaCuO_2	2.04	2.46	2.65	0.05	0.28	0.31	0.92	1.69	1.64

Table 1. The calculated parameters by LDA and QSGW. The $p_{x,y}$ is from the in-plane oxygen, and p_z from the out-of-plane. The definitions of parameters can be found in Fig. 4. The experimental values are taken from Ref. 32.

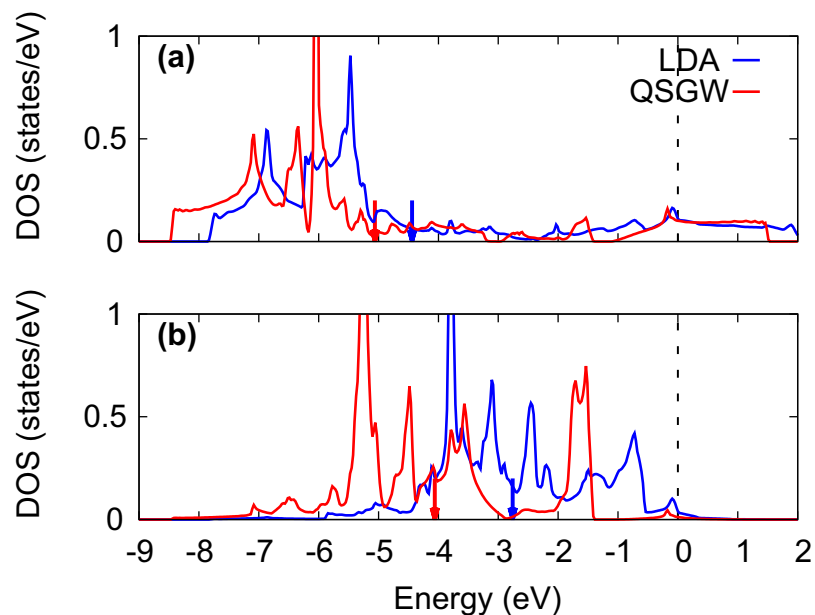


Figure 2. The calculated oxygen PDOS of La_2CuO_4 by LDA and QSGW. (a) In-plane oxygen $p_{x,y}^\sigma$ and (b) out-of-plane oxygen p_z^σ orbitals are plotted. The center of mass position of each PDOS is marked by an arrow. Fermi energy is set to be 0.

oxygen hybridization. We note, however, that our ΔE_{e_g} becomes effectively quite similar with ΔE in Ref. 26–29 since we set our $E_{\text{min,max}}$ to cover only the anti-bonding band complex. Actually one can make it almost equal, *i.e.*, $\Delta E_{e_g} \approx \Delta E$, by fine-tuning the $E_{\text{min,max}}$ range.

Some other changes produced by QSGW are also noted. The $d_{3z^2-y^2}$ components in the bands below -1.5 eV in Fig. 1(a) are reduced in QSGW, and the free-electron-like bands at Γ and Z points above the Fermi energy are shifted upward. As the position of the t_{2g} complex is lowered (red color), the $d_{x^2-y^2}$ band has almost no mixture with other bands below the Fermi energy. Higher-lying La-4f bands (not shown) move further upward as has been previously noted in the nickelate systems⁴⁰.

Fermi surface. The shape of the Fermi surface is important for understanding cuprate superconductivity. For example, its nesting is crucial for the spin fluctuation pairing. Also, a notable correlation

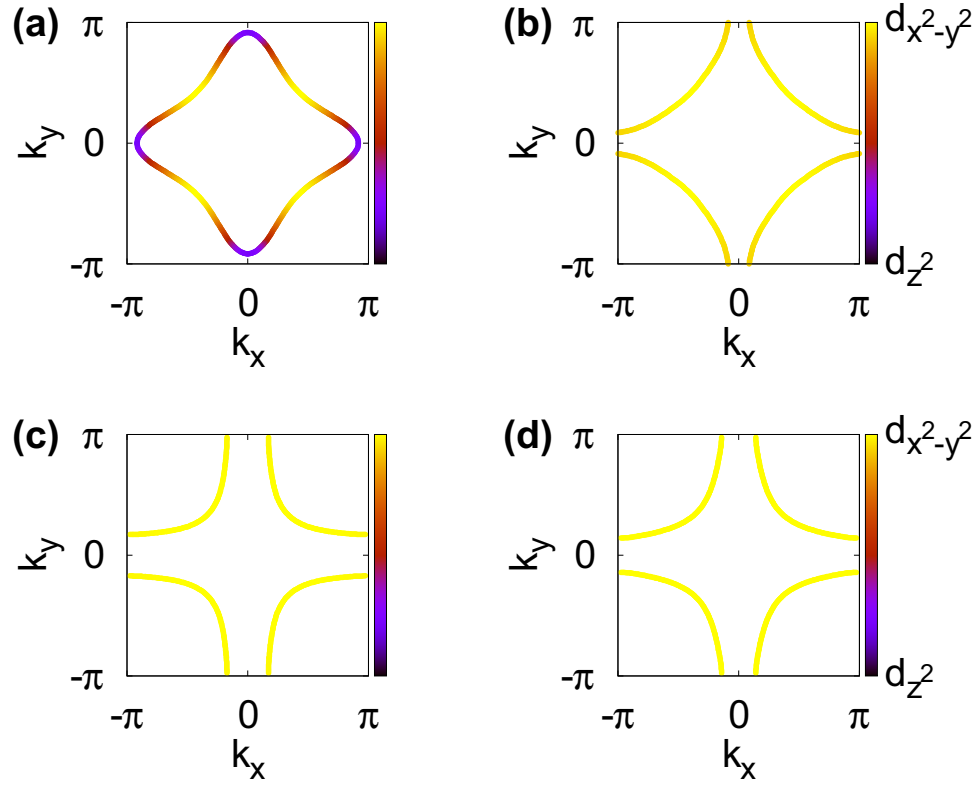


Figure 3. The orbital-resolved Fermi surfaces ($k_z=0$ plane) at the reduced e_g band filling by 0.15 (hole doping): (a) La_2CuO_4 (LDA), (b) La_2CuO_4 (QSGW), (c) $\text{HgBa}_2\text{CuO}_4$ (LDA), and (d) $\text{HgBa}_2\text{CuO}_4$ (QSGW). The color represents the amount of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ character.

between the experimentally observed T_c at the optimal doping (T_c^{max}) and the Fermi surface warping has been identified by Pavarini *et al.*²⁴. Here we discuss the Fermi surface calculated by QSGW in comparison to the LDA result and experiment.

The calculated Fermi surfaces are presented in Fig. 3; LDA ((a, c)) and QSGW ((b, d)). The hole doping is simulated by the rigid band shift method so that the electron occupation in e_g orbitals is reduced by $0.15e$ per unit cell. Notable features are found in the QSGW Fermi surface for La_2CuO_4 . Contrary to the LDA result of Fig. 3(a), Fig. 3(b) has the pocket centered at (π, π) point as in $\text{HgBa}_2\text{CuO}_4$ Fermi surface (see Fig. 3(c,d)). This feature is in good agreement with ARPES data⁴¹ which also reports the pocket centered at (π, π) point. Further, the $d_{3z^2-r^2}$ -orbital character (dark purple) is significantly reduced and the $d_{x^2-y^2}$ character (bright yellow) is dominant in the QSGW result, which is distinctive from the LDA in which the significant amount of $d_{3z^2-r^2}$ components are observed near $(\pi, 0)$ and $(0, \pi)$.

In the case of $\text{HgBa}_2\text{CuO}_4$, the difference between LDA and QSGW is less pronounced, see Fig. 3(c,d). While the QSGW Fermi surface is slightly more rounded, the overall shape is not much different. Since the $d_{x^2-y^2}$ orbital character is dominant and $d_{3z^2-r^2}$ band is well separated from Fermi level already in LDA due to the thicker blocking layers enhancing two-dimensional feature, the LDA result is quite similar to QSGW.

Comparison with RIXS. We now turn to the comparison with the RIXS data. Recently, Sala *et al.*³² successfully extracted the important model parameters for several different cuprate materials based on RIXS spectra. In this subsection, we examine the material dependent parameters by QSGW and compare them to the experimental values. With Ref. 32 as our main reference, we include two more compounds, namely, $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and CaCuO_2 . Although $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is also one of the single-layer cuprates, it has $\text{Cl}-\text{Cu}-\text{Cl}$ bonding (instead of $\text{O}-\text{Cu}-\text{O}$) along c -axis and therefore the naive comparison of parameters such as ΔE_{e_g} and ΔE_p in the line of T_c discussion may be misleading. This material is excluded in Ref. 26–29 because of the same reason.

Our results are summarized in Table 1, Figs 4 and 5. The values of $10Dq$, defined as the difference between two energy levels of $d_{x^2-y^2}$ and d_{xy} (see Fig. 4(a)), are larger in the QSGW calculation by ~62–125% than the LDA values. While LDA underestimates $10Dq$ compared to the experiment, QSGW

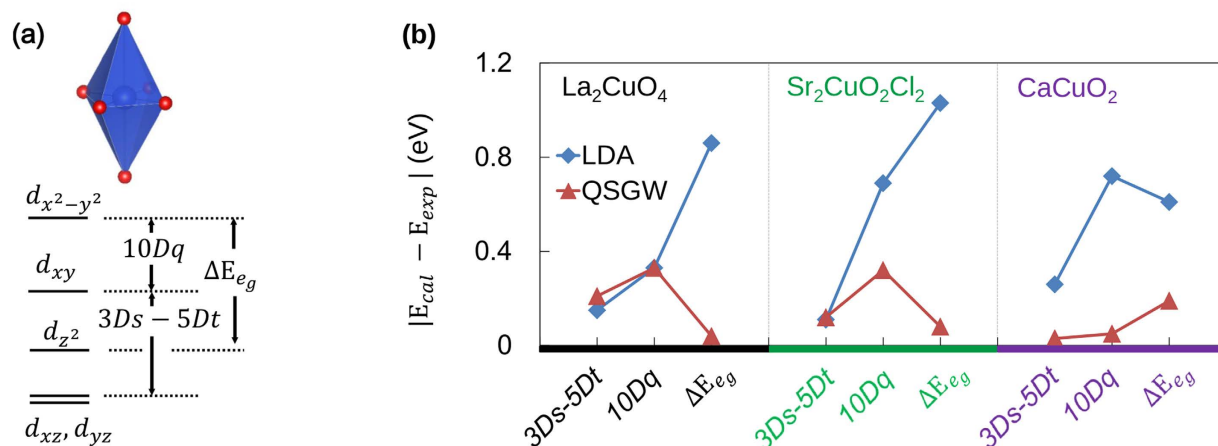


Figure 4. (a) The three model parameters for the comparison to Ref. 32. Note that ΔE_{e_g} is denoted by $4Ds + 5Dt$ in Ref. 32. (b) The difference of the calculated model parameters (E_{cal}) from the experiments (E_{exp}).

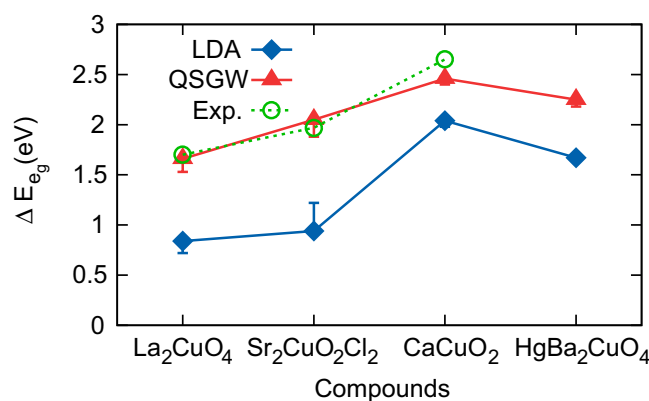


Figure 5. The values of ΔE_{e_g} (or $4Ds + 5Dt$ in the notation of Ref. 32) estimated by LDA (blue squares), QSGW (red triangles), and RIXS data (green circles).

slightly overestimates, which is related to the tendency that $\text{Cu-}t_{2g}$ bands are pushed down relative to e_g , as was also observed in the previous QSGW calculations for other transition-metal oxides^{40,42,43}. It is important to note that overall the QSGW result is in better agreement with experiment, as clearly seen in Fig. 4(b).

As noted in the above, according to the two-band theory by Sakakibara *et al.*^{26,27}, the important parameter that governs T_c is ΔE_{e_g} (or $4Ds + 5Dt$ in Ref. 32). Figures 4(b) and 5 clearly show that the calculated values of ΔE_{e_g} by QSGW are in excellent agreement with those from RIXS spectra; the difference is 2–8%. The LDA values are noticeably smaller than the experiments although the difference gets reduced in the higher T_c materials, CaCuO_2 and $\text{HgBa}_2\text{CuO}_4$ (see Fig. 5). This can be taken as a strong support for the two-band theory in the sense that the LDA value of ΔE_{e_g} as an input for FLEX provides qualitative information of material dependence, while the ΔE_{e_g} by QSGW already contains the correlation effect beyond LDA, being consistent with RIXS.

Another parameter deduced from RIXS in Ref. 32 is $3Ds - 5Dt$, the energy level difference between d_{xy} and $d_{yz, zx}$. In this case, the LDA results are not much different from QSGW and experiment (see Fig. 4(b)).

The effect of epitaxial strain. An interesting aspect found in the T_c trend of the cuprates is its significant enhancement in the thin film form. Locquet *et al.* reported⁴⁴ that T_c can be controlled by epitaxial strain by about factor of two⁴⁵. The underdoped La_2CuO_4 with its bulk T_c of 25 K exhibits a higher and lower T_c of ~49 K and 10 K when it is grown on SrLaAlO_4 (SLAO) and SrTiO_3 (STO) substrates,

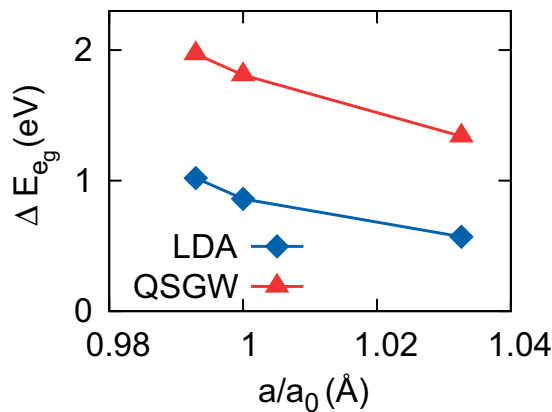


Figure 6. The calculated ΔE_g as a function of epitaxial strain. The $a_0 = 3.782 \text{ \AA}$ is the experimental value for bulk La_2CuO_4 . The compressive and tensile strain are simulated with $a = 3.755$ and 3.905 \AA considering the substrate of SrLaAlO_4 and SrTiO_3 , respectively⁴⁴.

respectively⁴⁴. It is therefore important to check whether the two-band theory is also consistent with this observation.

In order to simulate the tensile and compressive strain produced by STO and SLAO, we first optimized the c lattice parameter with two different in-plane lattice constants, $a^{\text{STO}} = 3.905$ and $a^{\text{SLAO}} = 3.755 \text{ \AA}$, for La_2CuO_4 , which originally has $a_0 = 3.782 \text{ \AA}$ and $c_0 = 13.25 \text{ \AA}$. As expected, the optimized out-of-plane parameters get smaller and larger under the tensile and compressive strain, respectively; $c_{\text{STO}}^{\text{opt}} = 12.96$ and $c_{\text{SLAO}}^{\text{opt}} = 13.36 \text{ \AA}$. As a result, the ratio between the out-of-plane and in-plane Cu—O distance, $r = d_{\text{apical}}/d_{\text{inplane}}$, is found to be 1.32, 1.28, and 1.24, for a^{SLAO} , a_0 and a^{STO} , respectively.

The calculated values of ΔE_g are plotted in Fig. 6. Both LDA and QSGW predict that ΔE_g gets enhanced and reduced under compressive and tensile strain, respectively, which is consistent with the experimental observation⁴⁴. The reduction of ΔE_g at $a = a_{\text{STO}}$ is about 0.16 eV in both LDA and QSGW, and the enhancement at $a = a_{\text{SLAO}}$ is 0.29 (LDA) and 0.47 eV (QSGW).

Summary and Conclusion

Using the QSGW method, we re-examined the electronic structure of copper oxide high temperature superconducting materials. Several important features were found to have been captured by the GW procedure, such as effective mass enhancement. The shape and orbital character of the Fermi surface were also notably changed, especially for the case of La_2CuO_4 , and they are in good agreement with the ARPES data⁴¹. Important model parameters including the key quantity for the two-band theory of T_c , ΔE_g , were examined, and the QSGW results were in excellent agreement with RIXS data.

The present study shows that the first-principles band calculation can quantitatively reproduce the experimental observation by taking into account the correlation effects beyond LDA. We emphasize that it is not inconsistent with the previous study by Sakakibara *et al.* which takes the LDA result as an input for the many-body calculation of superconductivity. While the QSGW result cannot be used as a direct input for the FLEX-type calculation because of the partial double-counting of the many-body correlation, the “best” non-interacting Hamiltonian, that can serve as an input, may lie somewhere in between the LDA and QSGW. Obtaining a well-defined non-interacting Hamiltonian is, therefore, an important future direction for the first-principles-based description of high-temperature superconductivity, and it may quantitatively resolve the problem of low T_c in La_2CuO_4 produced by the LDA input³³.

Methods

Quasiparticle self-consistent GW. The QSGW^{42,43,46} calculates H_0 (non-interacting Hamiltonian describing quasiparticles or band structures) and W (dynamically-screened Coulomb interactions between the quasiparticles within the random phase approximation) in a self-consistent manner. While the ‘one-shot’ GW is a perturbative calculation starting from a given H_0 (usually from LDA/GGA), QSGW is a self-consistent perturbation method that can determine the one-body Hamiltonian within itself. The GW approximation gives the one-particle effective Hamiltonian whose energy dependence comes from the self-energy term $\Sigma(\omega)$ (here we omit index of space and spin for simplicity), and in QSGW, the static one-particle potential V^{xc} is generated as

$$V^{\text{xc}} = \frac{1}{2} \sum_{ij} |\psi_i\rangle \left\{ \text{Re}[\Sigma(\varepsilon_i)]_{ij} + \text{Re}[\Sigma(\varepsilon_j)]_{ij} \right\} \langle \psi_j|, \quad (1)$$

where ε_i and $|\psi_i\rangle$ refer to the eigenvalues and eigenfunctions of H_0 , respectively, and $\text{Re}[\Sigma(\varepsilon)]$ is the Hermitian part of the self-energy^{42,43,46}. With this V^{xc} , one can define a new static one-body Hamiltonian H_0 , and continue to apply GW approximation until converged. In principle, the final result of QSGW does not depend on the initial conditions. Previous QSGW studies, ranging from semiconductors^{42,43} to the various 3d transition metal oxides^{42,43,47} and 4f-electron systems⁴⁸, have demonstrated its capability in the description of weakly and strongly correlated electron materials.

Computation details. We used our new implementation of QSGW⁴⁹ by adopting the ‘augmented plane wave (APW) + muffin-tin orbital (MTO)’, designated by ‘PMT’^{50,51}, for the one-body solver. The accuracy of this full potential PMT method is proven to be satisfactory in the supercell calculations of homo-nuclear dimers from H₂ through Kr₂ with the significantly low APW energy cutoff of ~4 Ry, by including localized MTOs⁵¹. A key feature of this scheme for QSGW is that the expansion of V^{xc} can be made with MTOs, not APWs, which enables us to make the real space representation of V^{xc} at any k point.

We performed the calculations with the experimental crystal structures^{52–55}, and used $10 \times 10 \times 10$, $12 \times 12 \times 12$, $12 \times 12 \times 8$, and $14 \times 14 \times 14$ k points for LDA calculations of Sr₂CuO₂Cl₂, La₂CuO₄, HgBa₂CuO₄, and CaCuO₂, respectively. As for QSGW calculations, in order to reduce the computation cost, the number of k points were reduced to be $5 \times 5 \times 5$, $7 \times 7 \times 7$, $8 \times 8 \times 4$, and $8 \times 8 \times 8$ for the first Brillouin zone of Sr₂CuO₂Cl₂, La₂CuO₄, HgBa₂CuO₄, and CaCuO₂, respectively. The MTO radii used in our calculations were as follows: (i) 1.58, 1.04, 0.89, and 1.38 Å for Sr, Cu, O, and Cl in Sr₂CuO₂Cl₂, (ii) 1.43, 0.97, and 0.86 Å for La, Cu, and O in La₂CuO₄, (iii) 1.10, 1.59, 1.05, and 0.83 Å for Hg, Ba, Cu, and O in HgBa₂CuO₄, and (iv) 1.54, 1.01, and 0.86 for Ca, Cu, and O in CaCuO₂.

Many of the key parameters in this study are defined in terms of the energy levels of each orbital, such as $E_{x^2-y^2}$ and $E_{3z^2-r^2}$. To quantify them we simply take the center of mass position of PDOS:

$$E_\alpha = \frac{\int_{E_{\min}}^{E_{\max}} E g_\alpha(E) dE}{\int_{E_{\min}}^{E_{\max}} g_\alpha(E) dE}, \quad (2)$$

where $g_\alpha(E)$ is PDOS for a given orbital α . An ambiguity is inevitably introduced in determining $E_{\min, \max}$, and we set the range to cover the whole antibonding band complex for Cu- e_g states. ($E_{\min}^{e_g}$, $E_{\max}^{e_g}$) for La₂CuO₄ is (−1.95 eV, 2.05 eV) in LDA and (−2.20, 1.55) in QSGW. For HgBa₂CuO₄, the band dispersion changes and the values of $E_{\min}^{e_g}$ and $E_{\max}^{e_g}$ are redefined accordingly: ($E_{\min}^{e_g}$, $E_{\max}^{e_g}$) = (−2.40, 2.50) in LDA and (−2.55, 1.65) in QSGW. If we choose two different ranges for two e_g orbitals to include only the main peak of each orbital PDOS, we can actually produce the better agreement with the numbers in the previous study by Sakakibara *et al.* where the levels are defined using maximally localized Wannier function method^{26,27}. Even if the ranges are set to cover the whole window of Cu- e_g bands including bonding parts, the trend reported in this work does not change. The same is true for O-2p and Cu- t_{2g} levels. In other words, none of the reasonably defined energy ranges change our conclusion, and the values are well compared with those reported in the previous study using a maximally localized Wannier function^{26,27}.

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Acknowledgments

We thank Ryotaro Arita for helpful comment and Prof. Hiroshi Katayama-Yoshida for hosting the helpful discussion. S.W.J. and M.J.H. were supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education(2014R1A1A2057202). The computing resource is supported by National Institute of Supercomputing and Networking/Korea Institute of Science and Technology Information with supercomputing resources including technical support (KSC-2014-C3-050) and by Computing System for Research in Kyushu University. T. K. was supported by the Advanced Low Carbon Technology Research and Development Program (ALCA), the “High-efficiency Energy Conversion by Spinodal Nano-decomposition” program of the Japan Science and Technology Agency (JST), and by the JSPS Core-to-Core Program (A) Advanced Research Networks (Computational Nano-materials Design on Green Energy).

Author Contributions

S.W.J., T.K. and H.K. performed the calculations. All authors contributed in analyzing the results and writing the paper.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Jang, S. W. *et al.* Quasiparticle self-consistent *GW* study of cuprates: electronic structure, model parameters, and the two-band theory for T_c . *Sci. Rep.* **5**, 12050; doi: 10.1038/srep12050 (2015).



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