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Calculation of the exciton spectrum of $YBa_2Cu_3O_7$ using the intermediate exciton theory

Dietmar Wechsler and Janos Ladik
Chair for Theoretical Chemistry, Friedrich-Alexander-University, Erlangen-Nürnberg, Egerlandstrasse 3, D-91058 Erlangen, Germany

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Starting from the correlation corrected (quasiparticle) band structures of the CuO_2 plane and the CuO chain (always including the apical oxygen atom) of $YBa_2Cu_3O_7$ we have calculated the exciton spectra of both systems. For this the intermediate exciton theory was applied in its first-principles form. This leads to a Green's-matrix equation for the determination of the $E_{\mathbf{q}}$ exciton energies. We have applied in the denominator of the Green's-matrix quasiparticle one-electron energies instead of the Hartree-Fock ones. In this way we have found very good agreement with experiment for the calculated exciton energies of the CuO_2 plane (theoretical values 4.4–5.7 eV, experimental values 4.5–5.5 eV). Further there is a reflexion spectrum peak of $YBa_2Cu_3O_{6.9}$ at 8.0 eV which agrees well with our results obtained for the exciton energies of the chain. [S0163-1829(97)06945-2]

I. INTRODUCTION

In a previous paper[1] we computed the Hartree-Fock (HF) band structures of the CuO_2 plane and Cu-O chain in $YBa_2Cu_3O_7$. In both calculations the apical O atom in the BaO plane was included and the two subunits of the ''123'' were treated in a mutually consistent way (the charges obtained from the plane calculation were used as an input in the chain calculation and vice versa, until mutual consistency was reached). The calculated subunits were imbedded in a three-dimensional (3D) infinite Madelung potential, in which the charges of the Cu and O atoms were changed at each iteration step together with their charges in the directly calculated subunits [self-consistent-field Madelung potential[2]]. For the infinite 3D summation of the charges in the Madelung potential, Ewald's method[3] was used. Finally applying the inverse Dyson equation in its diagonal approximation[4] and using for the self-energy the Møller-Plesset[5] many-body perturbation theory in second order, the HF band structures were corrected for correlation[6,7] (for further details, see Ref. 1).

The obtained correlation corrected band structures agree quite well with the photoelectron spectra[8–10] and with the bands in the valence region above -8 eV calculated with local-density-functional methods.[11–16] It should be pointed out, however, that the local-density-approximation calculations have not provided any further Cu-3d bands below -8 eV. On the other hand, resonant photoemission measurements have found a Cu-3d satellite around -9.4 eV,[17] which agrees well with the four very narrow bands in our correlation corrected band structure for the CuO_2 plane (see Fig. 6 in Ref. 1). The other experimentally found satellite[17] of -12 eV agrees also well with our narrow 3d bands in the band structure of the CuO chain (see Fig. 7 of Ref. 1).

The purpose of the present paper is to report first-principles intermediate exciton calculations for excitations from the above-mentioned four narrow Cu-3d bands to the unfilled regions of the conduction band of the plane and the chain, respectively.

II. METHOD

The intermediate exciton theory was introduced in a simple form by Takeuti[18] and was put for infinite chains into a first-principles form by Suhai.[19] Since he wanted to apply it first of all for quasi-1D systems, he formulated his theory in terms of well localized Wannier functions.[20] This has proven to be advantageous in the calculation of the occurring two-electron integrals. Since, however, we were interested first of all in calculations for 2D systems, and in this case for the Wannier functions we could not localize well, we had to use the formalism in reciprocal ($\mathbf{k}$) space.

Without repeating the full derivation of Ref. 19 in $\mathbf{k}$ space we can write for the excitonic wave function

$$\psi_{\mathbf{q}}=\sum_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}_1-\mathbf{k}_2,\mathbf{q}}\Omega_{\mathbf{k}_1,\mathbf{k}_2}a^\dagger_{\mathbf{k}_1,C}b^\dagger_{\mathbf{k}_2,3d}|\phi_0\rangle. \tag{1}$$

Here the operator $a^\dagger_{\mathbf{k}_1,C}$ creates an electron in the unoccupied part of the partially filled conduction band with the quasimomentum $\mathbf{k}_1$, $b^\dagger_{\mathbf{k}_2,3d}$ is a hole in one of the low-lying d bands with quasimomentum $\mathbf{k}_2$, and $\mathbf{q}$ is the quasimomentum of the exciton. The Kronecker δ expresses the momentum conservation and $|\phi_0\rangle$ is the ground state of the system (including correlation).

From Eq. (1) taking into account the expressions in $\mathbf{k}$ space of the electronic Hamiltonian $\hat{H}_e$, the hole one $\hat{H}_h$, and the electron-hole interaction operator $\hat{H}_{e-h}$, the Hamiltonian $\hat{H}$ will be

$$\hat{H}=\hat{H}_e+\hat{H}_h+\hat{H}_{e-h} \tag{2}$$

(in complete analogy to Suhai's formulation working in direct space[19] because of the application of the Wannier functions). From $\hat{H}$ one can derive the equation

$$\psi_{\mathbf{q}}=[E_{\mathbf{q}}-(\hat{H}_e+\hat{H}_h)]^{-1}\hat{H}_{e,h}\psi_{\mathbf{q}}. \tag{3}$$

Substituting Eq. (1) into Eq. (3) one obtains for the coefficients $\Omega_{\mathbf{k}_1,\mathbf{k}_2}$ the equation

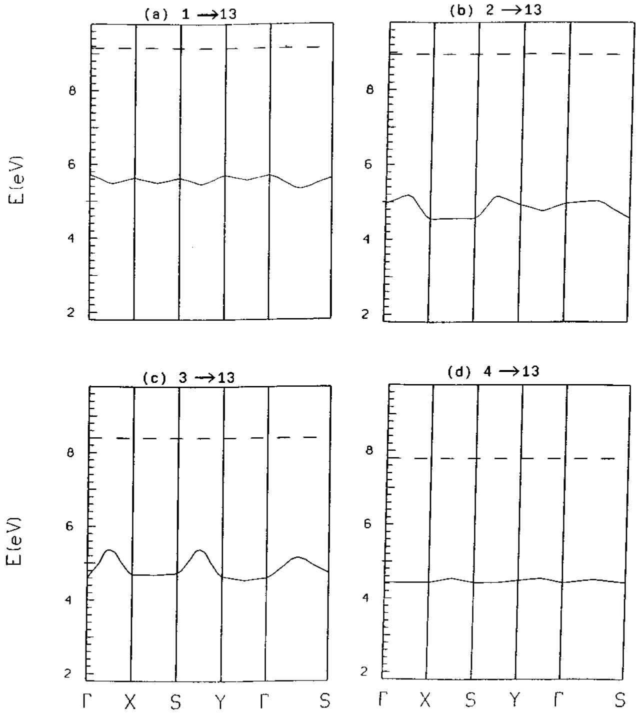

FIG. 1. The exciton energies $E_{\mathbf{q}}$ (full curves —) as a function $\mathbf{q}$ in the case of the CuO_2 plane for excitations from the four low-lying narrow $3d$ bands. The broken line --- indicates the minimal quasiparticle energy difference between the concerning $3d$ band and the Fermi level E_F [all bands, the four $3d$'s, and the conduction band (No. 13), are counted from the bottom of Fig. 6 in Ref. 1].

$$\Omega_{\mathbf{k}_1,\mathbf{k}_2}=\delta_{\mathbf{k}_1-\mathbf{k}_2,\mathbf{q}}\,\frac{1}{E_{\mathbf{q}}-\varepsilon^{\mathrm{QP}}_{\mathbf{k}_1,C}+\varepsilon^{\mathrm{QP}}_{\mathbf{k}_2,3d}}\times\left[-\sum_{\mathbf{k}_1',\mathbf{k}_2'}\delta_{\mathbf{k}_1'-\mathbf{k}_2',\mathbf{q}}\Omega_{\mathbf{k}_1',\mathbf{k}_2'}\left\{W\left(\begin{smallmatrix}\mathbf{k}_1 & \mathbf{k}_2'\\ C & 3d\end{smallmatrix}\middle|\begin{smallmatrix}\mathbf{k}_2 & \mathbf{k}_1'\\ 3d & C\end{smallmatrix}\right)-\text{exch.}\right\}\right].\tag{4}$$

Equation (4) can be put, using the relations $i\equiv(\mathbf{k}_1,\mathbf{k}_2)$, $j\equiv(\mathbf{k}_1',\mathbf{k}_2')$, in the matrix form

$$\mathbf{\Omega}=\mathbf{G}\cdot\mathbf{V}\cdot\mathbf{\Omega},$$

$$(\Omega_i=\Omega_{\mathbf{k}_1,\mathbf{k}_2}).\tag{5}$$

Here

$$G_{ij}=\begin{cases}\dfrac{1}{E_{\mathbf{q}}-\varepsilon^{\mathrm{QP}}_{\mathbf{k}_1,C}+\varepsilon^{\mathrm{QP}}_{\mathbf{k}_2,3d}} & \text{for } i=j,\\ 0, \text{ otherwise,}\end{cases}\tag{6}$$

and

$$V_{ij}=-\left[W\left(\begin{smallmatrix}\mathbf{k}_1 & \mathbf{k}_2'\\ C & 3d\end{smallmatrix}\middle|\begin{smallmatrix}\mathbf{k}_2 & \mathbf{k}_1'\\ 3d & C\end{smallmatrix}\right)-\text{exch.}\right].\tag{7}$$

The integrals

$$W\left(\begin{smallmatrix}\mathbf{k}_1 & \mathbf{k}_2'\\ C & 3d\end{smallmatrix}\middle|\begin{smallmatrix}\mathbf{k}_2 & \mathbf{k}_1'\\ 3d & C\end{smallmatrix}\right)=\langle\phi^{\mathbf{k}_1}_{C}(\mathbf{r}_1)\phi^{\mathbf{k}_2'}_{3d}(\mathbf{r}_2)|r_{12}^{-1}|\phi^{\mathbf{k}_2}_{3d}(\mathbf{r}_2)\phi^{\mathbf{k}_1'}_{C}(\mathbf{r}_1)\rangle\tag{8}$$

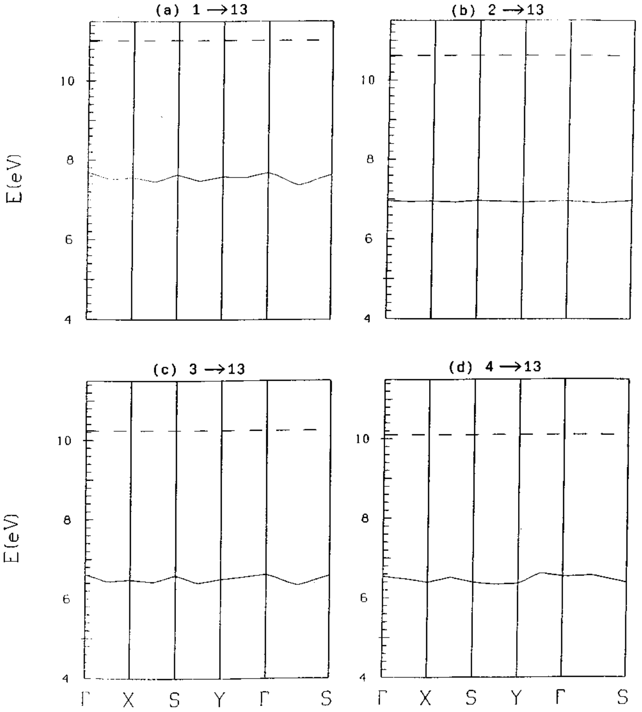

FIG. 2. The same as in Fig. 1, but in the case of the CuO chain.

are the usual two-electron integrals between HF crystal orbitals, which were already applied in our previous paper[1] for the calculation of the correlation corrected band structures [for their accelerated calculation see the remarks after Eq. (9) of Ref. 1]. It is important to mention that according to our previous experience[21] in Eq. (6) not the HF one-electron energies, but the correlation corrected quasiparticle one-electron energies have to be substituted to obtain good agreement with experiment. The condition of the nontrivial solution of the system of equations (5) is

$$|\mathbf{GV}-\mathbf{1}|=0.\tag{9}$$

The solution of Eq. (9) provides then the exciton energies $E_{\mathbf{q}}$. For this purpose we have looked after the sign change of the determinant between each energy difference $\varepsilon^{\mathrm{QP}}_{\mathbf{k}_1,C}-\varepsilon^{\mathrm{QP}}_{\mathbf{k}_2,3d}$. The corresponding energy region was scanned with a grid of $\Delta E\leqslant 10^{-3}$ eV. In this way taking into account $\mathbf{k}_1-\mathbf{k}_2=\mathbf{q}$ differences we have obtained the exciton energies $E_{\mathbf{q}}$ (measured from the correlated ground state) for the different excitations.

III. RESULTS AND THEIR DISCUSSION

Figure 1 shows the $E_{\mathbf{q}}$ values for excitations from one of the four $3d$ bands to the unfilled parts of the conduction band in the case of the CuO_2 plane as a function of $\mathbf{q}$. One can see that the exciton energies $E_{\mathbf{q}}$ lie between 4.4 and 5.7 eV. These values are by 3.4–4.4 eV smaller than the $\varepsilon^{\mathrm{QP}}_{\mathbf{k}_1,C}-\varepsilon^{\mathrm{QP}}_{\mathbf{k}_2,3d}$ quasiparticle one-electron energy differences (exciton binding energies).

In the case of the chain as one can see from Fig. 2 the $E_{\mathbf{q}}$ values lie higher between 6.4 and 7.7 eV, which are by

$\sim$3.5 eV smaller than the corresponding quasiparticle energy differences. If one compares the calculated exciton energies $E_{\mathbf{q}}$ in the case of CuO_2 with the experimental exciton spectrum of 123,[22] one finds that the theoretical values of 4.4–5.7 eV agree quite well with the absorption peak 4.5–5.5 eV (Ref. 22) (which they classify as a charge-transfer transition). Since this peak is quite high it has to do with a dipole-allowed transition. This should be also the case, because the transitions occur between Cu-3d bands and a conduction band which consists mainly of Cu-4p and C-2p orbitals. One should mention that the reflexion spectrum of 123 shows also a strong peak at 5.7 eV.[23]

Another reflexion spectrum measurement of $YBa_2Cu_3O_{6.9}$ shows one maximum at 5.0 eV and another one (with an onset at 7 eV) at 8.0 eV.[24] The first value falls into the calculated exciton energy region of the plane (4.4–5.7 eV), the second one agrees reasonably well with our CuO chain results (6.4–7.7 eV). We intend to apply these results for the calculation of the main characteristics of the superconducting state of 123.

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