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The Holstein–Hubbard Dimer of Variable Length as the Building Block of the CuO Plane: Electronic and Phononic Transitions

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A polaronic Hamiltonian is obtained for a dimer of length a, including an Einstein phonon of frequency Ω, a Holstein coupling g_0, and all the electronic one- and two-body terms consistent with a single orbital per site (the latter evaluated in terms of Wannier functions built from Gaussian atomic orbitals). Its ground state for given a, g_0, and Ω is identified by independent and simultaneous optimization of the electronic and phononic parameters. As a varies, we find discontinuous changes of both electronic and phononic states, with interesting physical implications.

KEY WORDS: Extended Hubbard Hamiltonian; Holstein dimer; polarons; superconductivity.

1. THE MODEL

For a dimer consisting of identical ions centered at $\mathbf{R}_1$ and $\mathbf{R}_2$ we consider the Hamiltonian $H \equiv H_{el} + H_{ph} + H_{ep}$ which, in standard notation [1], reads

$$\begin{aligned} H_{el} = {} & \varepsilon_0 \sum_\sigma (n_{1\sigma} + n_{2\sigma}) - \sum_\sigma [t - X(n_{1,-\sigma} + n_{2,-\sigma})] \\ & \times (a_{1\sigma}^\dagger a_{2\sigma} + \text{h.c.}) + U \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow} \\ & + V n_1 n_2 - 2J_z S_1^z S_2^z - J_{xy}(S_1^+ S_2^- + \text{h.c.}) \\ & + P(a_{1\uparrow}^\dagger a_{1\downarrow}^\dagger a_{2\downarrow} a_{2\uparrow} + \text{h.c.}) \end{aligned} \tag{1}$$

$$H_{ph} = \hbar\Omega \sum_{i=1,2} (b_i^\dagger b_i + \tfrac{1}{2}),$$

$$H_{ep} = g_0 \sum_{i\sigma} (n_{i\sigma} - \tfrac{1}{2})(b_i^\dagger - b_i) \tag{2}$$

The bare electronic interaction parameters ε_0, t, X, U, V, P ($J_z = J_{xy} = P$) were evaluated using normalized Gaussian "orbitals"

$$\phi_i(\mathbf{r}) = (2\Gamma^2/\pi)^{3/4} \exp[-\Gamma^2(\mathbf{r} - \mathbf{R}_i)^2] \qquad (i = 1, 2)$$

with overlap $S \equiv \langle \phi_1 | \phi_2 \rangle = \exp(-\Gamma^2 a^2/2)$, where $a = |\mathbf{R}_1 - \mathbf{R}_2|$ is the length of the dimer. Then, the two orthonormalized Wannier functions are

$$\Phi_{1(2)}(r) = A_{+(-)}(S)\phi_1(r) + A_{-(+)}(S)\phi_2(r)$$

with

$$A_\pm(S) = [(1+S)^{-1/2} \pm (1-S)^{-1/2}]/2$$

Following the procedure of [2] for the antiadiabatic limit, we obtain the effective polaronic Hamiltonian H_{pol} by first performing on H a displaced-oscillator transformation through the operator $e^R \equiv \exp[\delta\gamma_0 \sum_\sigma (n_{1\sigma} - n_{2\sigma})(d^\dagger - d)]$, where $d \equiv b_1 - b_2$ and $\gamma_0 \equiv g_0/\hbar\Omega$. Then we take the average of $e^R H e^{-R}$ over the squeezed phonon wavefunction: $|\Psi(\alpha)\rangle = \exp[-\alpha(d^\dagger d^\dagger - dd)]|\Psi(0)\rangle$, where $d|\Psi(0)\rangle = 0$. The result is a polaronic Hamiltonian $H_{pol} = H_{el}(\varepsilon_0^*, t^*, X^*, U^*, V^*, J_{xy}^*, J_z^*, P^*) + E_{ph}$,

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where

$$\begin{aligned} \varepsilon_0^* &= \varepsilon - \hbar\Omega\gamma_0^2\delta(2-\delta) \\ U^* &= U - 2\hbar\Omega\gamma_0^2\delta(2-\delta) \\ V^* &= V - \hbar\Omega\gamma_0^2[1-\delta(2-\delta)] \\ t^* &= \tau t, \qquad X^* = \tau X, \qquad P^* = \tau^4 P \\ E_{ph} &= \hbar\Omega[Sh^2(2\alpha)+\tfrac{1}{2}] \end{aligned} \tag{3}$$

with $\tau \equiv \exp[-2(\delta\gamma_0)^2 e^{-4\alpha}]$. The parameters J_z and J_{xy} remain unchanged. Details can be found in [1].

2. RESULTS

We evaluated [1] the eigenstates and eigenvalues of H_{el}, obtaining a singlet bonding state

$$|Sb\rangle = \frac{1}{\sqrt{2}}[\sin\theta(a_{1\downarrow}^\dagger a_{1\uparrow}^\dagger + a_{2\downarrow}^\dagger a_{2\uparrow}^\dagger) - \cos\theta(a_{1\downarrow}^\dagger a_{2\uparrow}^\dagger + a_{2\downarrow}^\dagger a_{1\uparrow}^\dagger)]|0\rangle$$

and its antibonding counterpart

$$|Sa\rangle = \frac{1}{\sqrt{2}}[\cos\theta(a_{1\downarrow}^\dagger a_{1\uparrow}^\dagger + a_{2\downarrow}^\dagger a_{2\uparrow}^\dagger) + \sin\theta(a_{1\downarrow}^\dagger a_{2\uparrow}^\dagger + a_{2\downarrow}^\dagger a_{1\uparrow}^\dagger)]|0\rangle$$

a charge transfer state

$$|CT\rangle = \frac{1}{\sqrt{2}}[a_{1\downarrow}^\dagger a_{1\uparrow}^\dagger + a_{2\downarrow}^\dagger a_{2\uparrow}^\dagger]|0\rangle$$

and a triplet state, whose components labeled by $S_1^z + S_2^z$ are

$$|T, 1(-1)\rangle = a_{1\uparrow(\downarrow)}^\dagger a_{2\uparrow(\downarrow)}^\dagger|0\rangle$$

and

$$|T, 0\rangle = \frac{1}{\sqrt{2}}[a_{2\downarrow}^\dagger a_{1\uparrow}^\dagger - a_{1\downarrow}^\dagger a_{2\uparrow}^\dagger]|0\rangle$$

By defining $E_U \equiv 2\varepsilon_0 + U + P$, $E_V \equiv 2\varepsilon_0 + V + J_{xy}$, $G \equiv \sqrt{(E_U - E_V)^2 + 16(t-X)^2}$ and $\tan(\theta) \equiv -4(t-X)/(E_U - E_V + G)$ the eigenvalues read: $E_{Sb} = \frac{1}{2}(E_U + E_V - G)$; $E_{Sa} = \frac{1}{2}(E_U + E_V + G)$; $E_{CT} = 2\varepsilon_0 + U - P$; $E_{T,\pm1} = 2\varepsilon_0 + V - J_z$ and $E_{T,0} = 2\varepsilon_0 + V - J_{xy}$. The corresponding energies for H_{pol} are obtained from the values above by replacing the bare interactions with the effective ones. Choosing $\hbar\Omega = 0.1$ eV, and a dimer-length range $0.5 \le a \le 3.0$ Å, the ground state of H_{pol} for several g_0 values was identified by independent and simultaneous optimization of the parameters defining the orbital shape (Γ), the displaced-oscillator transformation (δ), and the squeezing-effect strength ($e^{-4\alpha}$). Figure 1 shows (bottom panel) that, if g_0 is sizable, as a varies, the equilibrium Γ has sharp transitions between two asymptotic curves, shown by the continuous and dashed lines, respectively corresponding to low and high g_0 values. Also the optimal δ (middle panel) and α (top panel) depend on the electronic state, so that discontinuous transitions between different phononic regimes are correspondingly obtained. Level crossings are found, corresponding to the transitions of the parameters in Fig. 1. The delocalized singlet bonding state $|Sb\rangle$ is stable at low a for all values of g_0. At $a = a_c$ it transforms into either a triplet $|T\rangle$ or a charge-transfer state $|CT\rangle$, both of localized character. The cases shown in Fig. 1 correspond to a single $|Sb\rangle \to |T\rangle$ transition ($g_0 = 0.32$ eV), to a single $|Sb\rangle \to |CT\rangle$ transition ($g_0 = 0.47$ eV), and to a double $|Sb\rangle \to |CT\rangle \to |T\rangle$ transition ($g_0 = 0.45$ eV). Through Γ, also the equilibrium shape of the wavefunctions depends significantly on the phononic parameters as well as on the type of ground state, so that the effective

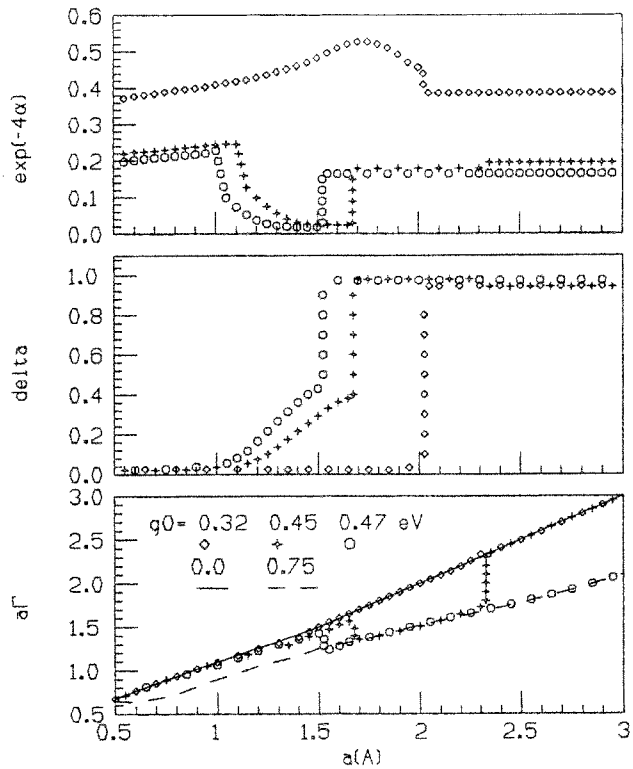

Fig. 1. The parameters $a\Gamma$ (bottom panel), δ (middle panel), and $\exp(-4\alpha)$ (top panel) vs. dimer length a in Å, for some values of g_0 in eV.

Table I. The Correlation Functions $F^{Z}_{|i\rangle} \equiv \langle i|\langle \Psi_{SQ}|e^{R} Z\, e^{-R}|\Psi_{SQ}\rangle|i\rangle$ for Several Operators Z (First Column) in the Eigenstates $|i\rangle$

Z	$\|Sb\rangle$	$\|T,\pm1\rangle$	$\|T,0\rangle$	$\|CT\rangle$
$n_j d_k^{\dagger} d_k$ $(j\neq k=1,2)$	$Sh^2(2\alpha)/4+\gamma_0^2-\gamma_0^2\delta(2-\delta)\sin^2\theta$	$Sh^2(2\alpha)/4+\gamma_0^2$	$Sh^2(2\alpha)/4+\gamma_0^2$	$Sh^2(2\alpha)/4+\gamma_0^2(1-\delta)^2$
$n_1 n_2/4$	$\cos^2\theta/4$	1/4	1/4	0
$S_1^z S_2^z$	$-\cos^2\theta/4$	1/4	$-\cos^2\theta/4$	0
$a_{2\downarrow}a_{1\uparrow}a_{2\uparrow}^{\dagger}a_{1\downarrow}^{\dagger}$	$\cos^2\theta/2$	0	1/2	0
$a_{2\downarrow}a_{2\uparrow}^{\dagger}a_{1\uparrow}^{\dagger}a_{1\downarrow}$	$\tau^4\sin^2\theta/2$	0	0	$-\tau^4/2$

electronic interactions are appreciably phonon-renormalized as a varies, particularly on passing to a different ground state. To explain the physical implications, we have evaluated some correlation functions (CF). The CF related to a generic operator Z in one of the eigenstates $|i\rangle$ of the effective Hamiltonian is defined as $F^{Z}_{|i\rangle} \equiv \langle i|\langle \Psi_{SQ}|e^{R} Z\, e^{-R}|\Psi_{SQ}\rangle|i\rangle$. The results are shown in Table I. Further comments can be found in [3,4]. As in [2], we also define the charge transfer as

$$F^{ct}_{|i\rangle} \equiv \frac{\langle i|\langle \Psi_{SQ}|e^{R}(n_1-n_2)(d^{\dagger}+d)\, e^{-R}|\Psi_{SQ}\rangle|i\rangle}{\sqrt{\langle i|\langle \Psi_{SQ}|e^{R}(d^{\dagger}+d)^2 e^{-R}|\Psi_{SQ}\rangle|i\rangle}} \tag{4}$$

A bit of algebra yields

$$F^{ct}_{|i\rangle} \equiv -4\sqrt{2}\delta\gamma_0 \frac{\sin^2\xi}{\sqrt{Sh^2(2\alpha)+1/2+8\delta^2\gamma_0^2\sin\xi}} \tag{5}$$

where $\xi=\theta, \pi/2, 0$ if $|i\rangle=|Sb\rangle, |CT\rangle, |T\rangle$ respectively. The results are visualized in Fig. 2. As can be checked from Table I, the plot of the spin CF ($Z=S_1^z S_2^z$) can be used to read also the values of both the intersite charge ($Z=n_1 n_2/4$) and bipolaron ($Z=a_{2\downarrow}a_{1\uparrow}a_{2\uparrow}^{\dagger}a_{1\downarrow}^{\dagger}$) CF's. Except for the on-site bipolaron CF ($Z=a_{2\downarrow}a_{2\uparrow}a_{1\uparrow}^{\dagger}a_{1\downarrow}^{\dagger}$), the other CF's are very sensitive to the type of ground state. Therefore the

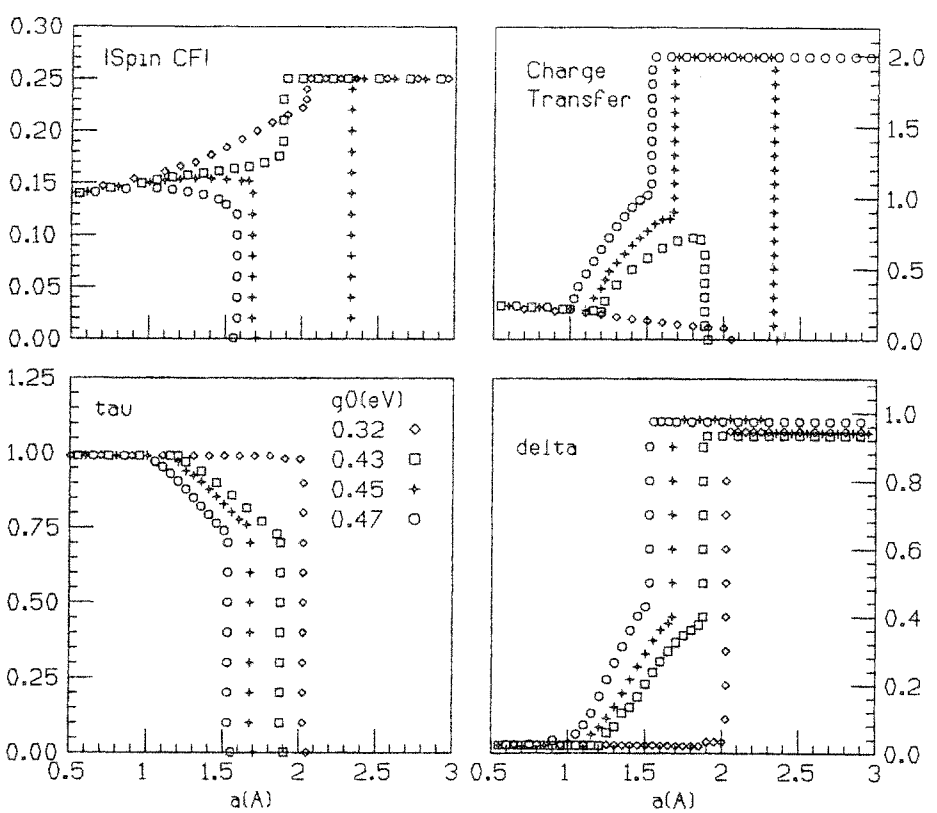

Fig. 2. Correlation functions and charge transfer vs. dimer length a in Å, for some values of g_0 in eV.

type of experimental response can change completely following a slight variation of either a [5] or g_0. Typical examples are the charge transfer and the electron–phonon CF for $1.5 \leq a \leq 2.0$ Å and $0.43 \leq g_0 \leq 0.47$ eV. Notice also that in the $|Sb\rangle$ state, for a close to a_c, both the charge transfer and the spin CF can simultaneously be rather large. If one thinks of the dimer as the building block of the CuO plane, this finding is interesting in relation not only to the arguments [6] requiring the normal state of HTSC's to be close to a charge or a magnetic instability, but also to the great sensitivity of HTSC's to pressure.

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