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Electronic and Phononic States of the Holstein–Hubbard Dimer of Variable Length: A Variational Approach

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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). In the quarter- and half-filled orbital cases, the possible ground states for varying a, at given g_0 and Ω, are identified by independent and simultaneous optimization of the electronic and phononic parameters.

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

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

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

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

$$H_{\rm ep} = g_0 \sum_{i\sigma} (n_{i\sigma} - \tfrac{1}{2})(b_i^\dagger + b_i) \tag{3}$$

The bare electronic interaction parameters $\varepsilon_0, t, X, U, V, P$ $(J_z = J_{xy} = P)$ were evaluated using two orthonormalized Wannier functions built from normalized Gaussian "orbitals"

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

We obtain the effective polaronic Hamiltonian $H_{\rm pol}$ by performing on H a displaced-oscillator transformation (allowing the characteristic parameter to take, in principle, any value in the range 0, 1) followed by taking the average of $e^R H e^{-R}$ over a squeezed phonon wavefunction. Full details of the procedure can be found in Ref. 1. The resulting polaronic Hamiltonian $H_{\rm pol} = H_{\rm el}(\varepsilon_0^*, t^*, X^*, U^*, V^*, J_{xy}^*, J_z^*, P^*)$ can be exactly diagonalized for any filling. The ground state of $H_{\rm pol}$ for several values of g_0 was identified by searching the minimum of the total, i.e., electronic plus phononic, energy upon independent and simultaneous optimization of the parameters that define the shape of the orbitals (Γ), the displaced-oscillator strength, and the squeezing-effect strength. Space limitations allows for only a very sketchy summary of the results for $N = 1$ (quarter filled case) and $N = 2$ (half filled case). For a full discussion, the reader is referred to Ref. 1.

For $N = 1$, the polaron undergoes localization for a larger than a critical value a_c, depending on g_0. On approaching the transition, one sees a competition between the counteracting affects of displacement, reducing the itineracy, and squeezing, which tries to preserve the electronic energy $\approx t^*$, up to the point where the increase in phononic energy due to

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squeezing is too large with respect to t^*, and the system suddenly localizes, with maximum displacement and negligible squeezing. Differently from the phononic parameters, the shape parameter Γ is scarcely affected by the localization. The transition can also be driven by increasing g_0 at fixed a. Then, for small a the localization happens discontinuously above a critical value of g_0. However, if a is such that the *bare* hopping amplitude t is by itself small, the loss in electronic energy when t^* vanishes is not very important, and the localization transition happens continuously.

The half-filled case presents a more complex behavior than the quarter-filled one, due to the electron–electron interactions that become effective in this case. The physics of the system is dominated by a singlet bonding state $|Sb\rangle$, which is always the lowest-lying energy level. Below a threshold value for g_0 (which, if $\hbar\Omega = 0.1$ eV, is ≈ 0.45 eV), on increasing a, $|Sb\rangle$ becomes degenerate with a triplet state, $|T\rangle$. Above the threshold, $|Sb\rangle$ becomes degenerate with a charge-transfer state $|CT\rangle$. The same happens if g_0 is increased at given a. All the $|Sb\rangle \rightarrow |CT\rangle$ transitions are discontinuous. These degeneracies just mean that these states are no longer appropriate to describe the system, which has become a pair of isolated atoms. Indeed, one can say that, for g_0 below the threshold, the system evolves continuously from an extended singlet state to a localized antiferromagnetic state with one electron per site. Conversely, for g_0 increasing above the threshold at fixed a an on-site bipolaron is formed, and eventually localizes in one of the sites, leaving the other one empty. In the $|Sb\rangle$ state, there is almost no displacement, but strong squeezing. In this case, the electrons are insensitive to the phonons, even if g_0 is far from negligible. In $|CT\rangle$, the displacement is maximal, and the squeezing very small.

Due to the values of the shape parameter Γ, as well as of displacement and squeezing, being very different in $|Sb\rangle$ compared with $|CT\rangle$, the effective interactions are strongly renormalized when the ground state changes. For instance, at the $|Sb\rangle \rightarrow |CT\rangle$ transition, U^* decreases sharply, even if it remains positive, while V^* increases remarkably, favoring the double occupancy. For a narrow range of values of g_0, just above the threshold, as a is increased at given g_0, we find a sequence of two discontinuous transitions: from delocalized $|Sb\rangle$ to $|CT\rangle$ to localized $|Sb\rangle$. To complete the picture, it is important to mention that, bordering the localization transition, for small a and g_0 above threshold, there is a region where $|Sb\rangle$ is the ground state, but U^* and V^* suffer, respectively, a significant reduction and an increase, while the effective hopping is only slightly reduced. As a consequence, the charge mobility remains finite, even if charge-transfer fluctuations build up, and the intersite spin (or magnetic) correlations are still important. We would like to stress that the existence of this region of the parameters space for our system depends strongly on the squeezing of the phonon states. Indeed, the squeezing effect counteracts a large oscillator displacement present there, and succeeds in preserving a rather itinerant character even in the presence of both appreciable charge transfer and magnetic correlations. We have checked that, if squeezing is forcibly blocked, that region disappears.

In summary, our study puts into evidence that the variation of the dimer length and/or the strength of the electron–phonon coupling yield, in different ground states, a strong renormalization of the interaction constants and also of the width of the Wannier functions describing the local orbitals, which establishes a link between the electronic interactions and the phonons at a deeper level than predicted by the standard polaron approach. The squeezing of the phonon states appears to be particularly relevant, triggering sharp changes in the state of the system as the dimer length is varied at fixed electron–phonon coupling and frequency.

The experimental interest of those results is that situations where the interatomic distances can be varied, even by a small amount, either uniformly by an external pressure, or inhomogeneously by dimerization in a chain compound, can lead to important changes in the system's behavior. In connection to the HTSC materials, our most significant finding is that there is a region in the parameter space where the kinetic energy, the charge transfer and the magnetic correlations are simultaneously large, while the phonon state is strongly squeezed. This result suggests that it is perhaps not necessary to set a sharp alternative between either magnetic or charge instabilities.

REFERENCE

1. M. Acquarone, J. R. Iglesias, M. A. Gusmão, C. Noce, and A. Romano, *Phys. Rev. B* **58**, 7626 (1998).