

Downfolding electron-phonon Hamiltonians from *ab initio* calculations: Application to K_3 picene

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We propose an electron-phonon parametrization which is constructed to reproduce target geometry and harmonic frequencies taken from first principles calculations or experiment. With respect to standard electron-phonon models, it adds a “double-counting” correction, which takes into account the lattice deformation as the system is dressed by low-energy electron-phonon processes. We show the importance of this correction by studying potassium-doped picene (K_3 picene), recently claimed to be a superconductor with a T_c of up to 18 K. The Hamiltonian parameters are derived from *ab initio* density functional theory, and the lattice model is solved by dynamical mean-field theory. Our calculations include the effects of electron-electron interactions and local electron-phonon couplings. Even with the inclusion of a strongly coupled molecular phonon, the Hubbard repulsion prevails and the system is an insulator with a small Mott gap of ≈ 0.2 eV.

I. INTRODUCTION

In recent years, a significant effort has been made to derive low-energy Hamiltonians from *ab initio* electronic structure calculations in order to model the effect of strong electron correlations in a predictive fashion [1,2]. Despite remarkable progress in the field, little attention has been paid on how to include lattice vibrations coupled to electrons in those Hamiltonians, with coupling strengths taken from experiments or from first principles. The major difficulty is to correctly estimate the “bare” couplings, i.e., the ones undressed from electron-electron (EE) or electron-phonon (EP) scattering processes explicitly treated in the low-energy manifold [3,4], and to avoid “double counting (DC),” i.e., summing up effects already treated in the model Hamiltonians.

Dealing with both EE and EP interactions is particularly important in molecular crystals, which are characterized by a tight competition between interactions. Phonons are thought to drive superconductivity close to the Mott regime, with unconventional features [5,6]. Superconductivity has indeed been found in the fullerenes [7], and later in the family of so-called aromatic superconductors, such as picene (K_3 picene) [8], coronene [9], and 1,2:8,9-dibenzopentacene [10], with T_c up to 33 K by intercalation with alkali atoms. These compounds are appealing from the viewpoint of potential applications, but their physics is poorly understood. Indeed, the metallicity and superconductivity are highly debated [11–16]. One difficulty is to intercalate large enough crystals, and some experimental groups have found an insulating behavior of K_3 picene at low temperature [16,17].

A common theoretical framework to study these systems is based on the Hubbard-Holstein Hamiltonian, where the electrons experience local interactions and are coupled to local vibrations. We use a generalized Holstein model where the local molecular mode does not simply couple with the charge density, and off-diagonal couplings in the orbital basis are included. We show that a proper derivation of the EP matrix elements must include a DC correction to

counteract the effect of the lattice relaxation already included in the low-energy Hamiltonian. We provide a prescription to compute the EP-DC correction from experimental or *ab initio* estimates of the geometry and phonon frequencies. We demonstrate the importance of this term by constructing a low-energy Hamiltonian for K_3 picene with intramolecular Hubbard interactions and EP couplings derived from density functional theory (DFT) calculations. Despite the strength of the EP coupling, the Coulomb repulsion prevails and the system is an insulator with a small gap of 0.2 eV.

The paper is organized as follows. Section II is devoted to explaining the origin of the electron-phonon double-counting problem and the way to correct it. In Sec. III we apply our theory to K_3 picene, by deriving an appropriate low-energy model from *ab initio* DFT calculations (Sec. III A), solving it by dynamical mean-field theory (Sec. III B), and showing the results (Sec. III C). Finally, the main conclusions are drawn in Sec. IV.

II. THEORY

In this section we analyze the minimal electron-phonon model that one should consider and show how the bare parameters of this model have to be chosen in order to reproduce the measured or computed relaxed geometry and screened phonon frequencies of a real system.

Let us start from the tight-binding Hamiltonian H_{tb} , which gives the low-energy band structure:

$$H_{\text{tb}} = \sum_{\alpha\beta\sigma ij} t_{ij}^{\alpha\beta} c_{\alpha\sigma i}^\dagger c_{\beta\sigma j} - \mu \sum_{\alpha\sigma i} n_{\alpha\sigma i}, \quad (1)$$

where $c_{\alpha\sigma i}^\dagger$ ($c_{\alpha\sigma i}$) creates (annihilates) an electron on the lattice site i with spin σ in the orbital α , and $n_{\alpha\sigma i} = c_{\alpha\sigma i}^\dagger c_{\alpha\sigma i}$. The model in Eq. (1) is usually derived from a DFT electronic structure computed for the lattice geometry *relaxed* at a given chemical potential μ . Equation (1) includes both intermolecular (or intersite) and intramolecular (or intrasite) hoppings.

Thus, the orbitals α generate the *low-energy* manifold of the crystal.

To distinguish between the screening effects due to EE and EP interactions, let us keep the system noninteracting in the electron-electron part for the moment, while adding the electron-phonon couplings to the model in Eq. (1). In the first step, let us consider classical phonons. We parametrize the EP coupling in the system as a single-mode Holstein phonon of frequency ω_{bare} , locally coupled to the electronic manifold of Eq. (1) via matrix elements $\delta V_{\alpha\beta}$ [18]:

$$H_{\text{el-ph}} = H_{\text{tb}} + \sum_{\alpha\beta\sigma i} r_i \delta V_{\alpha\beta} c_{\alpha\sigma i}^\dagger c_{\beta\sigma i} + \frac{\omega_{\text{bare}}^2}{2} \sum_i (r_i - r^0)^2, \quad (2)$$

with r_i classical phonon displacements and r^0 a shift which sets the structural minimum. This is the most general way of writing a translationally invariant Hamiltonian with local harmonic oscillators locally coupled to the electrons. In previous formulations, r^0 has usually been neglected. Below, we show that its value is in general nonzero and gives rise to nontrivial effects.

As for the H_{tb} part, the $\delta V_{\alpha\beta}$ EP couplings for the noninteracting model in Eq. (2) can be estimated by *ab initio* density functional perturbation theory (DFPT) calculations on the relaxed and filled system. The bare phonon propagator with frequency ω_{bare} will then be screened by the EP interactions, resulting in a dressed propagator of frequency ω_{dressed} . This will result also in a modified quadratic potential, subsequently yielding a modification of the geometry due to the explicit inclusion of the EP couplings in the low-energy manifold.

In our procedure the ω_{bare} and r^0 bare parameters are chosen in such a way that the model solution at the given filling yields the equilibrium geometry ($r_i = 0$) and the phonon frequency (ω_{dressed}) of the physical system at the same filling. In other words,

$$\left. \frac{\partial \langle H_{\text{el-ph}} \rangle}{\partial r_i} \right|_{r_i=0} = 0, \quad \left. \frac{\partial^2 \langle H_{\text{el-ph}} \rangle}{\partial r_i^2} \right|_{r_i=0} = \omega_{\text{dressed}}^2, \quad (3)$$

i.e., the force vanishes at the equilibrium position and the harmonic contribution to the ion displacement is ω_{dressed} . The two independent model parameters r^0 and ω_{bare} are then univocally determined by solving the above set of equations.

By quantizing the phonon in Eq. (2) we obtain

$$H_{\text{el-ph}} = H_{\text{tb}} + \sum_{\alpha\beta\sigma i} \sqrt{2} x_i^0 g_{\alpha\beta}^{\text{bare}} c_{\alpha\sigma i}^\dagger c_{\beta\sigma i} + \sum_{\alpha\beta\sigma i} (a_i + a_i^\dagger) g_{\alpha\beta}^{\text{bare}} c_{\alpha\sigma i}^\dagger c_{\beta\sigma i} + \omega_{\text{bare}} \sum_i a_i^\dagger a_i, \quad (4)$$

where now $g_{\alpha\beta}^{\text{bare}} = \delta V_{\alpha\beta} / \sqrt{2\omega_{\text{bare}}}$, $x_i = \sqrt{\omega_{\text{bare}}}(r_i - r^0) = \langle a_i + a_i^\dagger \rangle / \sqrt{2}$ is the dimensionless displacement, and $x^0 = \sqrt{\omega_{\text{bare}}} r^0$. Note that in this ‘‘standard’’ way of writing the quantum EP model, there is an implicit dependence of the $g_{\alpha\beta}^{\text{bare}}$ couplings to the bare phonon frequency ω_{bare} . In Eq. (4), the $\sum_{\alpha\beta\sigma i} \sqrt{2} x_i^0 g_{\alpha\beta}^{\text{bare}} c_{\alpha\sigma i}^\dagger c_{\beta\sigma i}$ term appears as a correction to the usual EP Hamiltonian. A closer inspection reveals that this term yields a band deformation related to the modified geometry before filling the low-energy bands. This correction

is necessary as the tight-binding model is defined at the given filling, while the bare quantities are computed by undressing the system from the low-energy electrons. The geometry deformation due to the change in filling is a genuine manifestation of the electron-phonon coupling. Analogously, the renormalization of the phonon frequency from ω_{bare} to ω_{dressed} is due to the EP interaction acting on the low-energy manifold.

Note that the spirit of including the EP-DC correction provided by x^0 is the same as for the DC correction of the electronic part, necessary whenever an EE interaction is explicitly added to Eq. (1). Usually, we require the EE-DC correction to provide the original DFT band structure when the many-body system is solved at the mean-field level. Analogously, if we take the bare $\delta V_{\alpha\beta}$ as the *variation* of the interaction due to the phonon displacement, we adjust the EP-DC term such that the mean-field solution of the model corresponds to the *ab initio* band structure, geometry, and phonon frequency. This gives a prescription on how to evaluate the EP term. Once $\delta V_{\alpha\beta}$ is computed from *ab initio* calculations, ω_{bare} and x^0 are set by solving Eqs. (3) self-consistently at the mean-field level. Importantly, the above procedure can be implemented also in the presence of EE interactions. We now apply our theory to K_3 picene and show the importance of including the EP-DC term to avoid a significant overestimate of the effects of EP coupling.

III. APPLICATION TO K_3 PICENE

A. Model

To study and reproduce the properties of K_3 picene, we choose the following low-energy Hamiltonian:

$$H = H_{\text{el-ph}} + \epsilon_{\text{EE-DC}} \sum_{\alpha\sigma i} n_{\alpha\sigma i} + U \sum_{\alpha\sigma i} n_{\alpha\sigma i} n_{\alpha-\sigma i} + U' \sum_{\substack{\alpha\beta\sigma i \\ \alpha \neq \beta}} n_{\alpha\sigma i} n_{\beta-\sigma i} + (U' - J) \sum_{\substack{\alpha\beta\sigma i \\ \alpha \neq \beta}} n_{\alpha\sigma i} n_{\beta\sigma i}, \quad (5)$$

where we add the EE part to $H_{\text{el-ph}}$ in Eq. (4), parametrized through U , U' , and J Hubbard and Hund parameters. In this case, the EE-DC correction $\epsilon_{\text{EE-DC}}$ is just a redefinition of the chemical potential shift μ .

1. Electron-electron interactions

The parameters in Eq. (5) are obtained by *ab initio* DFT calculations within the local density approximation (LDA) carried out with the QUANTUM ESPRESSO [19] package. The unit cell has been taken from powder diffraction data [8], and the molecular coordinates have been relaxed by energy minimization [12]. The hoppings $t_{ij}^{\alpha\beta}$ of the tight-binding model are derived from the Wannier construction [20], in order to reproduce the LDA low-energy bands $\epsilon_{m\sigma}(\mathbf{k})$. The maximally localized Wannier functions (MLWFs) are built by choosing an energy window which includes bands originating from the three lowest unoccupied molecular orbitals (LUMO, LUMO + 1 and LUMO + 2) of the neutral molecule [21]. The localized orbital set of Eq. (5) is defined by a rotation of the

MLWF basis such that the local $H_{\text{tb}} = -t_{ii}^{\alpha\beta}$ is *diagonal*. This corresponds to working with molecular orbitals (MOs) which are close to the MOs of an isolated molecule, as explained in Ref. [22].

The local EE interaction in Eq. (5) is justified by the molecular nature of the crystal, with the on-site repulsion larger than any other energy scale. The values of the full local interaction matrix have been computed in Ref. [23] by the constrained-random-phase approximation (cRPA) method in the two-orbital MLWF basis. We obtain the corresponding interaction in the MO basis by rotation, which gives $U = 0.68$ eV, $U' = 0.63$ eV, and $J = 0.10$ eV. We extend these values to the three-MO model of Eq. (5), by assuming that they are insensitive to the MO type, and by neglecting descreening due to the LUMO+2 channel. However, this is a minor effect compared to the large screening coming from the full frequency dependence of $U(\omega)$, which goes up to 4.4 eV in the unscreened ($\omega \rightarrow \infty$) limit (U_{bare}). In Ref. [2], it was proven that the correct low-energy model which includes the high-energy screening processes is the Hamiltonian with the $U(\omega = 0)$ static interaction and the bandwidth t renormalized by the factor $Z_B = \exp(1/\pi \int_0^\infty d\omega \text{Im}U(\omega)/\omega^2)$. We estimate Z_B from the experimental loss function ($\text{Im}[-1/\epsilon(\omega)]$) of K₃ picene, which has been measured up to 40 eV by electron energy-loss spectroscopy [24]. By neglecting the crystal momentum dependence of the full dielectric function, we can obtain an estimate of the imaginary part of the retarded U as $\text{Im}U(\omega) \approx U_{\text{bare}} \text{Im}[-1/\epsilon(\omega)]$. Using a low-energy cutoff corresponding to the MOs included in the model, all hoppings in Eq. (5) are renormalized by $Z_B = 0.76$.

2. Electron-phonon interactions

To make the many-body calculations feasible, we parametrize the phonon branches $\omega_{\mathbf{q}\nu}$ (\mathbf{q} is the phonon momentum and ν is the phonon mode) by a single monochromatic local phonon. The presence of the explicit EE interaction in the Hamiltonian of Eq. (5) implies that the phonon propagator of the model has to be descreened not only by the EP interactions, as treated in Sec. II, but also by the EE interactions. Therefore, δV has to be replaced by δV^{bare} . Indeed, the g matrix is now screened by both EE and EP processes within the low-energy manifold. To undress the system from EE screening involving LUMO+ n states and obtain the *bare* EP couplings, one can adopt a method recently proposed in Ref. [4], which is based on the same cRPA theory used to screen the Hubbard and Hund parameters, described in the section above. Here, we take another route, and perform an LDA DFPT calculation [19,25] of a neutral isolated molecule taken in the same geometry as the one stabilized by the crystal, assuming $\delta V_{\alpha\beta}^{\text{bare}} \approx \delta V_{\alpha\beta}^{\text{mol}}$. In the neutral molecule we naturally disregard the dopant electrons. The system is an insulator, with a large highest occupied molecular orbital (HOMO)-LUMO gap. Therefore, the $\delta V_{\alpha\beta}^{\text{mol}}$ couplings are not affected by the metallic screening coming from the low-energy bands, generated by the LUMO+ n states. The EP couplings calculated in this way are thus local and “bare.”

We take the molecular phonon with the largest $|g^{\text{bare}}|$ as the representative of the total EP coupling. The molecular

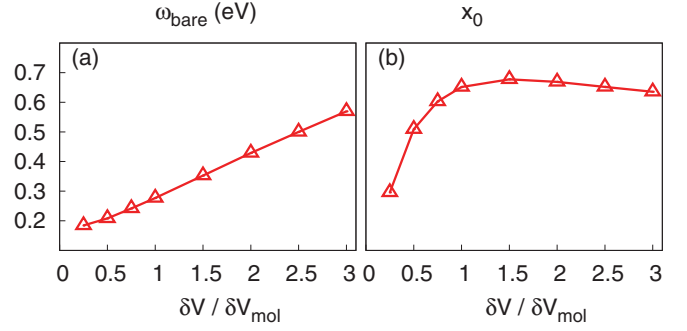


FIG. 1. (Color online) Mean-field solution of Eqs. (3) as a function of the deformation potential δV , taken with respect to the *ab initio* molecular value δV_{mol} . The geometry is constrained to the crystal relaxed DFT solution, and the dressed frequency is set to the crystal DFT $\omega_{\text{dressed}} = 0.173$ eV, yielding (a) ω_{bare} and (b) x^0 .

phonon frequency of the most coupled mode is 0.193 eV, and its corresponding phonon frequency in the crystal is $\omega_{\text{dressed}} = 0.173$ eV (from LDA-DFPT calculations of the crystal). By plugging ω_{dressed} , $\delta V_{\alpha\beta}^{\text{mol}}$ (from LDA-DFPT calculations of the molecule), and the crystal LDA bands H_{tb} in Eq. (2) and solving the related Eqs. (3) at the mean-field level, we get $\omega_{\text{bare}} = 0.277$ eV as a solution (see Fig. 1), and the corresponding $g_{\alpha\beta}^{\text{bare}}$ (in eV):

$$\begin{pmatrix} 0.066 & -0.010 & -0.002 \\ -0.010 & -0.038 & -0.051 \\ -0.002 & -0.051 & -0.018 \end{pmatrix}. \quad (6)$$

Note that g has sizable interorbital matrix elements, of the same magnitude as the diagonal ones. In the following, we study the dependence of the solution on the EP coupling strength by taking into account three sets of $g_{\alpha\beta}^{\text{bare}}$, corresponding to the DFPT value $\delta V_{\alpha\beta}^{\text{mol}}$, and to the larger values $2\delta V_{\alpha\beta}^{\text{mol}}$ and $3\delta V_{\alpha\beta}^{\text{mol}}$.

B. Methods

In order to solve the Hamiltonian in Eq. (5) with the above parameters, we use dynamical mean-field theory (DMFT) [26]. The DMFT equations are solved with an exact-diagonalization (ED) impurity solver [27], and some of the results are cross-checked using a continuous time quantum Monte Carlo (CTQMC) solver [28]. DMFT maps the Hubbard-Holstein lattice problem (5) onto an Anderson-Holstein impurity model (AHIM) [29] with a self-consistently defined bath. We solve this model by performing standard calculations with the number of bath levels set to 9, but we also benchmark our results against calculations with 12 bath levels.

The three-orbital impurity has a local noninteracting Hamiltonian with EP-DC correction, $h_{\alpha\beta} = (E^\alpha - \mu)\delta_{\alpha\beta} + \sqrt{2}x^0 g_{\alpha\beta}^{\text{bare}}$, hybridized through $V_{l\alpha}$ with N_{bath} bath levels of energy ϵ_l , and coupled to an on-site harmonic oscillator. $c_{\alpha\sigma}$ denotes the annihilation operator for the impurity level α with spin σ , $b_{l\sigma}$ the operator for the l th level in the bath, and a the

operator for a local phonon of frequency ω_{bare} :

$$\begin{aligned}
 H_{\text{AHIM}} = & \sum_{\alpha\beta\sigma} h_{\alpha\beta} c_{\alpha\sigma}^\dagger c_{\beta\sigma} + U \sum_{\alpha\sigma} n_{\alpha\sigma} n_{\alpha-\sigma} \\
 & + U' \sum_{\substack{\alpha\beta\sigma \\ \alpha \neq \beta}} n_{\alpha\sigma} n_{\beta-\sigma} + (U' - J) \sum_{\substack{\alpha\beta\sigma \\ \alpha \neq \beta}} n_{\alpha\sigma} n_{\beta\sigma} \\
 & + \sum_{l\sigma} \epsilon_l b_{l\sigma}^\dagger b_{l\sigma} + \sum_{l\alpha\sigma} V_{l\alpha} (c_{\alpha\sigma}^\dagger b_{l\sigma} + \text{H.c.}) \\
 & + \sum_{\alpha\beta\sigma} g_{\alpha\beta} c_{\alpha\sigma}^\dagger c_{\beta\sigma} (a^\dagger + a) + \omega_{\text{bare}} a^\dagger a. \quad (7)
 \end{aligned}$$

Then the dynamical Weiss field which describes the hybridization with the bath is $\mathcal{G}_{0\alpha\beta}^{-1}$, which can be defined as

$$\mathcal{G}_{0\alpha\beta}^{-1}(i\omega_n) = i\omega_n - h_{\alpha\beta} - \sum_{l=1}^{N_{\text{bath}}} \frac{V_{l\alpha}^* V_{l\beta}}{i\omega_n - \epsilon_l}. \quad (8)$$

Note that the Weiss field Eq. (8) has off-diagonal components in the orbital basis. Correspondingly, we have to compute all the elements of the impurity Green's function matrix $G_{\alpha\beta}$, and the self-energy $\Sigma_{\alpha\beta}$ will also have off-diagonal components. The local lattice Green's function is $G_{\text{loc}}^{\alpha\beta}(i\omega_n) = 1/N_k \sum_k (i\omega_n + \mu - H_{\alpha\beta}^{\text{DFT}}(k) - \Sigma_{\alpha\beta})^{-1}$, where the sum runs over the Brillouin zone and $H_{\alpha\beta}^{\text{DFT}}(k)$ is the Fourier transform of the DFT-LDA noninteracting Hamiltonian including the EP-DC correction ($H_{\text{tb}} + \sum_{\alpha\beta\sigma i} \sqrt{2} x^0 g_{\alpha\beta}^{\text{bare}} c_{\alpha\sigma i}^\dagger c_{\beta\sigma i}$).

By equating $G_{\alpha\beta}$ to $G_{\text{loc}}^{\alpha\beta}$ we can obtain a new Weiss field which is then fitted to Eq. (8) and determines the new set of parameters $V_{l\alpha}$ and ϵ_l . The above procedure is iterated until convergence is reached.

Since nondiagonal EP terms cannot be treated with the Monte Carlo technique of Ref. [30], we restrict the CTQMC calculations to the model without EP coupling. In the MO basis it turns out that the sign problem is negligible, even though the off-diagonal hybridizations are relatively large.

C. Results

By taking the electronic part of our Hamiltonian (5) only, we find K_3 picene to be a Mott insulator: the LUMO (LUMO+2) orbital is completely filled (empty) while the orbital LUMO+1 is half-filled and has well-pronounced Hubbard bands hybridized with the LUMO and LUMO+2 orbitals (see Fig. 2). This insulating state is consistent with

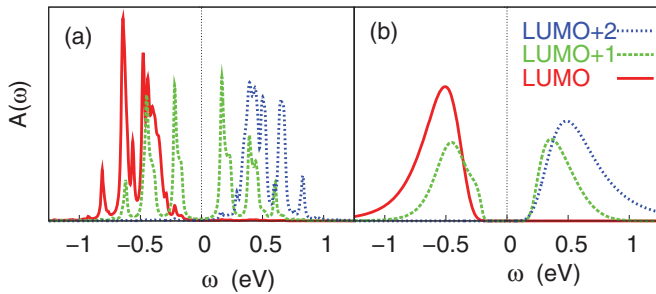


FIG. 2. (Color online) Paramagnetic spectral functions obtained by (a) ED and (b) CTQMC without phonons at $T = 0$ eV (ED) and 0.01 eV (CTQMC).

TABLE I. MO occupations from the ED/DMFT solution of Eq. (5). Results are reported for a system with and without EP-DC terms, for different EP couplings. The purely electronic case ($\delta V = 0$) is also shown. The rightmost column is the most populated phonon level, $N_{\text{ph}}^{\text{max}}$.

	LUMO	LUMO + 1	LUMO + 2	$N_{\text{ph}}^{\text{max}}$
$\delta V = 0$	1.00	0.50	0.00	
Without EP-DC correction ($\omega_{\text{bare}} = 0.193$ eV, $x^0 = 0$)				
$\delta V = \delta V_{\text{mol}}$	1.00	0.45	0.05	1
$\delta V = 2\delta V_{\text{mol}}$	1.00	0.29	0.21	3
$\delta V = 3\delta V_{\text{mol}}$	1.00	0.25	0.25	9
With EP-DC correction (ω_{bare} and x^0 from Fig. 1)				
$\delta V = \delta V_{\text{mol}}$	0.99	0.50	0.01	0
$\delta V = 2\delta V_{\text{mol}}$	0.98	0.50	0.02	0
$\delta V = 3\delta V_{\text{mol}}$	0.94	0.53	0.03	0

the result of previous DMFT calculations (in which a much larger U was used) [16]. However, in our case the Mott gap is significantly smaller (gap half-width of ≈ 0.2 eV) and the system is quite close to the Mott transition. The results obtained using the ED and CTQMC solvers are consistent, confirming the reliability of both approaches and the limited impact of the ED truncation.

The discrepancy between the Mott-insulating behavior of K_3 picene found here and the recent reports of superconducting signatures may suggest an important role of EP interactions in stabilizing the superconducting phase. We thus add in our ED/DMFT scheme the Holstein-type $g_{\alpha\beta}$ terms. We first discuss the results without EP-DC correction. In this case the effect of the EP interaction on the electronic structure is remarkable. Table I lists the MO occupations found in the ED/DMFT solution of Eq. (5) with EP coupling strengths of different magnitude. The coupling with phonons moves the LUMO+1 orbital away from half filling, and induces a strong hybridization between the LUMO+1 and LUMO+2 orbitals.

For $\delta V = 3\delta V_{\text{mol}}$ both LUMO+1 and LUMO+2 are 1/4 filled, and the system is at the edge of an insulator-to-metal transition driven by the EP coupling (although still on the insulating side). To understand the origin of this effect, we analyze the phonon population distribution. For this large value of the coupling, it features a broad maximum centered around nine excited phonons, a Frank-Condon behavior related to a finite molecular deformation. The system geometry changes as the EP coupling increases, by pulling the minimum away from the original center of the phonon oscillators. This is clear from the last column of Table I, where the phonon peak shifts to higher levels as the coupling gets stronger. The phonon displacement has several consequences: it mixes the unperturbed MO's states already at the molecular on-site level and shifts the bands leading to a more asymmetric structure and to the observed occupations [see Fig. 3(a)]. These effects are mainly a consequence of the off-diagonal EP couplings which transfer electrons between orbitals. These terms are resilient to the Hubbard interaction as opposed to the density terms which are quenched by strong correlations [31,32].

The result changes both qualitatively and quantitatively when the EP-DC correction is added. The deformation driven

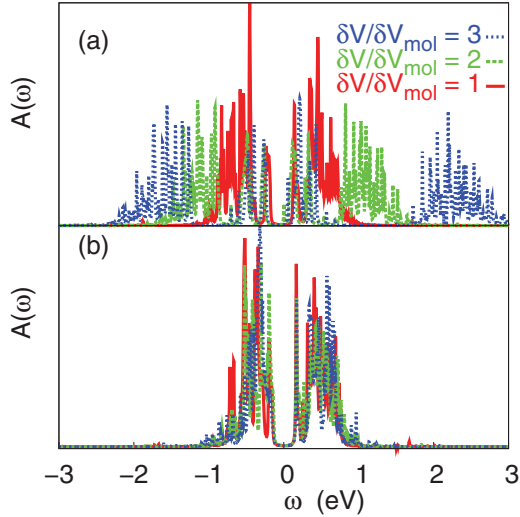


FIG. 3. (Color online) (a) $T = 0$ ED/DMFT spectral functions including both EE and EP interactions without EP-DC correction. (b) Same as (a), but with the EP-DC correction.

by the bare EP coupling is counterbalanced by the EP-DC correction, which constrains the model to have the correct *ab initio* DFT geometry when it is solved at the mean-field level. The ω_{bare} and x^0 fixed by that constraint are plotted in Fig. 1, as a function of δV . We find that ω_{bare} increases linearly with δV , while x^0 saturates after a first linear growth. The ED/DMFT spectrum of the model with EP-DC correction is shown in Fig. 3(b). The effect of phonons is much less dramatic. The spectrum and electron populations remain close to the results in the absence of EP coupling, while the phonon population stays peaked at the lowest phonon state (Table I), signaling that with the EP-DC correction the EE correlation alone is not able to deform the DFT geometry.

IV. CONCLUSIONS

In conclusion, we have shown the importance of including the EP double-counting correction to model the EP coupling from *ab initio* DFT results or experimental data. K_3 picene is an ideal test case for our theory, as in molecular crystals the bandwidth, the local EP coupling, and the local EE repulsions live on the same energy scale, and the properties result from a subtle competition between them. Therefore, theoretical predictions are extremely sensitive to the quality of the model.

Using the LDA + DMFT approach, we found that K_3 picene is a Mott insulator, but close to a metallic instability. The local Hubbard repulsion opens a small gap of ≈ 0.2 eV, while local Holstein phonons, whose coupling has been estimated from *ab initio* molecular calculations, do not affect the electronic structure when the EP-DC correction is added. The Mott state found by solving our model is not compatible with

a superconducting behavior, whereas it is in agreement with valence-band photoemission spectroscopy performed on picene multilayer samples and reported in Ref. [17], where a small gap has indeed been found. More work is necessary, both theoretical and experimental, to assess the conducting properties of K-doped picene, particularly in relation to the molecular arrangement of the crystal once the intercalation is performed. From the point of view of synthesizing a new superconducting material, the closeness of the Mott state to a metallic transition is a rather good sign. Indeed, our calculations, done on a more refined model than the one in Ref. [16], give a gap which is only half as wide, and show that a molecular deformation driven by a large EP coupling would be able to further reduce the gap. The closeness to a Mott transition, but on the metallic side, would favor the superconductivity by a phonon mechanism with coupling enhanced by correlations [6]. However, a better understanding of the experimental conditions is necessary, to make the intercalation effective in order to synthesize a clean conducting crystal, as already mentioned in the introduction.

The main result of our paper is very general, and goes well beyond the particular application to K_3 picene. We showed that a DC electron-phonon term is necessary to derive the proper couplings of an electron-phonon Hamiltonian from a system computed or measured at rest. Indeed, one must avoid double counting relaxation effects, in such a way that the relaxed geometry and measured phonon frequencies are obtained by the Hamiltonian solution, after *dressing* it by low-energy electron processes. The double-counting term presented in our paper corrects the Hamiltonian for these effects, by taking into account the modification of the phonon propagator due to electron-phonon low-energy interactions.

Our application to K_3 picene shows that this EP-DC correction can lead to sizable effects. Indeed, the results are qualitatively modified by the EP-DC correction, which calls for a critical reanalysis of the theoretical work done so far on EP models for molecular crystals. Finally, our EP parametrization is not restricted to the specific case of generalized Hubbard-Holstein models and can be applied also to more general EP Hamiltonians.

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