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Downfolding electron-phonon Hamiltonians from ab-initio calculations: application to K_3 Picene

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We propose an electron-phonon parameterization which reliably reproduces the geometry and harmonic frequencies of a real system. 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.

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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 difficulties are 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, applying our theory to build a low-energy Hamiltonian for K_3 Picene with intramolecular Hubbard interactions and EP couplings whose amplitudes have been determined by density functional theory (DFT) calculations. We show that 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.

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

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

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 (system at rest).

In the first step, let us consider classical phonons. We are going to quantize them later. We parameterize 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 the $\delta V_{\alpha\beta}^{bare}$ [18] matrix elements:

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

with r_i classical phonon displacements and the shift corresponding to the structural minimum parametrized by r^0 , which is in general non-zero and gives rise to non-trivial effects, as we show below. The bare couplings are such 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:

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

which states that the force vanishes at the equilibrium position and the harmonic contribution to the ion displacement is given by ω_{dressed} .

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

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

where now $g_{\alpha\beta}^{\text{bare}} = \delta V_{\alpha\beta}^{\text{bare}} / \sqrt{2\omega_{\text{bare}}}$, $x_i = \sqrt{\omega_{\text{bare}}}(r_i - r^0) = \langle a_i + a_i^\dagger \rangle / \sqrt{2}$ is the dimensionless displacement, and $x^0 = \sqrt{\omega_{\text{bare}}} r^0$. In Eq. (4), the $\sum_{\alpha\beta\sigma i} \sqrt{2} x^0 g_{\alpha\beta}^{\text{bare}} c_{\alpha\sigma i}^\dagger c_{\beta\sigma i}$ 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. 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 in 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 $\delta V_{\alpha\beta}^{\text{bare}}$ is computed from ab-initio calculations, ω_{bare} and x^0 are set by solving Eqs. (3) self-consistently at the mean-field level. This is also doable in the presence of EE interactions. We now apply our theory to K₃picene and show the importance of including the EP-DC term to get meaningful results.

Model To study and reproduce the properties of K₃Picene, 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 the $H_{\text{el-ph}}$ in Eq. (4), parameterized 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 .

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 lattice unit cell has been taken from powder diffraction data [8], and the internal molecular coordinates 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 very close to the actual MOs of an isolated picene 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 (molecular) repulsion larger than the other energy scales of the system. According to constrained-random phase approximation (c-RPA) estimates [23], the nearest-neighbor repulsion is around 1/3 of the local U . The values of the full local interaction matrix have been computed in Ref. 23 by the c-RPA 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, $J=0.10$ 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 de-screening 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, we have 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 K₃Picene, 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 (much smaller than its energy dependence in a molecular crystal), we can obtain a rough 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 we obtain a renormalization $Z_B = 0.76$ for all the hoppings in Eq. (5).

To make the many-body calculations feasible, we parameterize the phonon branches $\omega_{\mathbf{q}\nu}$ (\mathbf{q} is the phonon momentum and ν is the phonon mode) by a single monochromatic local (molecular) phonon. We take the molecular phonon with the largest $|g^{\text{bare}}|$ as the representative of the total EP coupling. The g matrix is screened by both EE and EP processes within the low-energy manifold. To undress the system from screening involving LUMO+ n states and obtain the *bare* couplings, we perform a density functional perturbation theory (DFPT) calculation [19, 25] of a neutral isolated molecule, instead of

undressing g by c-RPA as recently suggested in Ref. 4. Therefore $\delta V_{\alpha\beta}^{\text{bare}} \approx \delta V_{\alpha\beta}^{\text{mol}}$, and the local bare matrix elements are the molecular ones. The molecular 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 DFPT calculations of the crystal). From $\delta V_{\alpha\beta}^{\text{mol}}$ computed by DFPT and from $\omega_{\text{bare}} = 0.277$ eV evaluated through Eqs. (3) (Fig. 1), we get $g_{\alpha\beta}^{\text{bare}}$ (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 inter-orbital matrix elements, of the same magnitude as the diagonal ones. In the following, we are going to study the dependence of the solution on the EP coupling strength by taking into account 3 sets of $g_{\alpha\beta}^{\text{bare}}$, based on $\delta V_{\alpha\beta}^{\text{mol}}$, $2 \delta V_{\alpha\beta}^{\text{mol}}$, and $3 \delta V_{\alpha\beta}^{\text{mol}}$.

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. In order to solve this impurity problem using the Lanczos method we have to truncate the Hilbert space by limiting the number of bath levels N_{bath} (here 9) and the maximum number of excited phonons (here we use 20). We have therefore a three-orbital impurity whose local non-interacting Hamiltonian contains the EP-DC correction $h_{\alpha\beta} = (E^\alpha - \mu)\delta_{\alpha\beta} + \sqrt{2}x^0 g_{\alpha\beta}^{\text{bare}}$. The impurity is hybridized with N_{bath} bath levels with 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_0 :

$$\begin{aligned} H_{\text{AHIM}} = & \sum_{\alpha\beta\sigma} h_{\alpha\beta} c_{\alpha\sigma}^\dagger c_{\beta\sigma} + U \sum_{\alpha\sigma} n_{\alpha\sigma} n_{\alpha-\sigma} \\ & + U' \sum_{\substack{\alpha\beta\sigma \\ \alpha \neq \beta}} n_{\alpha\sigma} n_{\beta-\sigma} + (U' - J) \sum_{\substack{\alpha\beta\sigma \\ \alpha \neq \beta}} n_{\alpha\sigma} n_{\beta\sigma} \\ & + \sum_{l\sigma} \epsilon_l b_{l\sigma}^\dagger b_{l\sigma} + \sum_{l\alpha\sigma} V_{l\alpha} (c_{\alpha\sigma}^\dagger b_{l\sigma} + h.c.) \\ & + \sum_{\alpha\beta\sigma} g_{\alpha\beta} c_{\alpha\sigma}^\dagger c_{\beta\sigma} (a^\dagger + a) + \omega_0 a^\dagger a. \end{aligned} \quad (7)$$

Then the dynamical Weiss field $\mathcal{G}_{\alpha\beta}^{-1}$ can be defined as

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

Note that the bath function in Eq. (8) has off-diagonal components. Correspondingly, we have to compute all elements

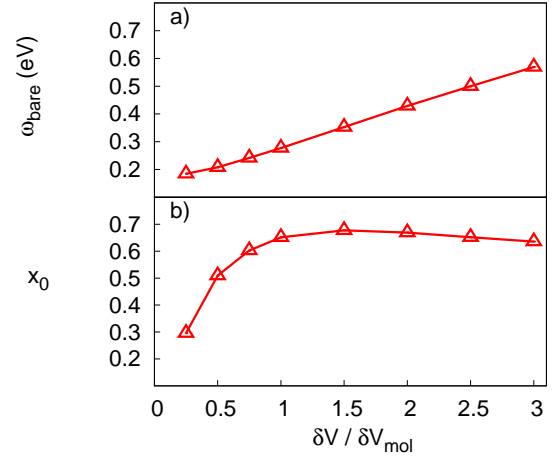


FIG. 1: Mean-field solution of Eqs. (3) as a function of the deformation potential δV , taken with respect to the ab-initio molecular value δV_{mol} . The geometry is constrained to the crystal relaxed DFT solution $x_{\text{min}} = 0$, and the dressed frequency is set to the crystal ab-initio DFT value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

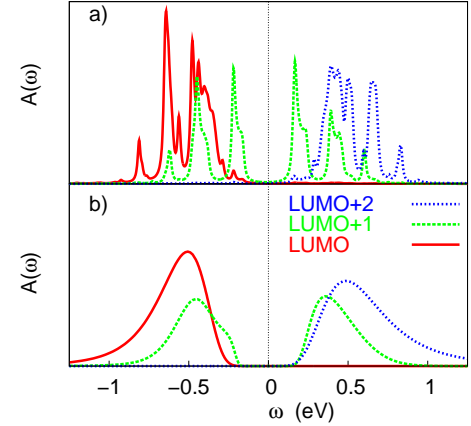


FIG. 2: (Color online) Paramagnetic spectral functions obtained by ED (a) and CTQMC (b) considering c-RPA EE interactions and a bandwidth reduction Z_B at $T = 0$ K (ED) and $\beta = 1/(k_B T) = 100$ eV $^{-1}$ (CTQMC).

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 $G_{\text{loc}}^{\alpha\beta}(i\omega_n) = \sum_k (i\omega_n + \mu - H_{\alpha\beta}^{\text{DFT}}(k) - \Sigma_{\alpha\beta})^{-1}$, where the sum runs over the Brillouin zone and $H_{\alpha\beta}^{\text{DFT}}(k)$ is the Fourier transform of the DFT-LDA non-interacting Hamiltonian. 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 non-diagonal 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.

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 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. We note that the results obtained using the ED and CTQMC solvers are consistent, so this finding is not affected by truncations in the ED treatment.

The discrepancy between the Mott insulating behavior of K_3 Picene found here and the recent reports of superconducting signatures suggests 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 and LUMO+2 orbitals, which increases as we increase the EP coupling.

For $\delta V = 3\delta V_{\text{mol}}$ both LUMO+1 and LUMO+2 are 1/4 filled, and the system is prone to metallicity (although still on the insulating side). To understand the origin of this effect, we analyze the phonon population distribution. It features a broad peak centered around the $n = 9$ phonon level, a Frank-Condon behavior related to the 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 Tab. I, where the phonon peak shifts to higher levels as the coupling gets stronger. This has several consequences: it mixes the unperturbed MO's states already at the molecular (on-site) level and drifts the bands leading to a more asymmetric structure and to the observed occupations (see Fig. 3(a)). These effects

TABLE I: MO occupations from the ED/DMFT solution of Eq. (5). Results are reported for a system with and without EP double-counting terms in the lower and upper panel, respectively, for different EP couplings. The purely electronic case ($\delta V = 0$) is also shown. The right 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

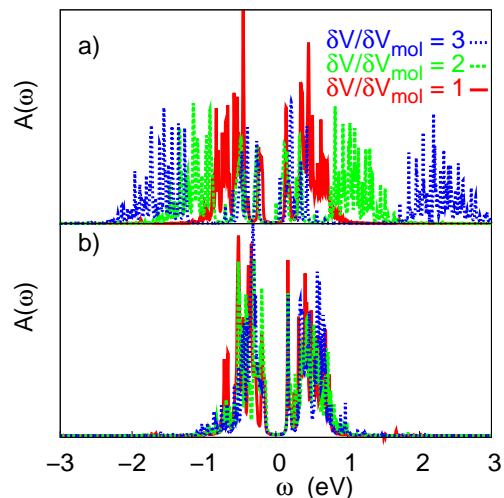


FIG. 3: (Color online) Panel (a): spectral functions obtained by ED/DMFT considering c-RPA electron interactions, a bandwidth reduction $Z_B = 0.76$ and Holstein-type couplings at $T = 0$ without EP-DC correction. Panel (b): same as panel (a), but with the EP-DC correction term included in the Hamiltonian.

are related to 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].

The result changes both qualitatively and quantitatively when the EP-DC correction is added. The deformation driven 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 (Tab. I), signaling that with the EP-DC correction the EE correlation alone is not able to deform the DFT geometry. The system remains a small gap insulator, as in the case without phonons.

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. 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 modify qualitatively the electronic structure when the EP-

DC correction is added. The results are qualitatively modified by the EP-DC correction, which calls for a critical re-analysis of the theoretical work done so far on EP models for molecular crystals, whenever the EP-DC correction has been disregarded. Our EP parameterization goes well beyond the specific case of K_3 Picene, and can be applied also to more general EP Hamiltonians.

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