Downfolding electron-phonon Hamiltonians from ab-initio calculations: application to K_3Picene

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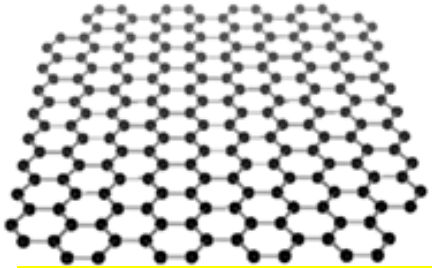
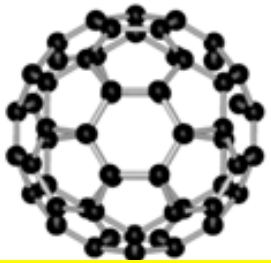
Superconductivity in carbon based materials

Intercalation chemistry for graphite, C_{60}, ….

graphite



C_{60}



Intercalation of alkali atoms to make the system superconductor

- KC_8 : $T_c = 0.14$ K
- CaC_6 : $T_c = 11.5$ K
- $RbCs_2C_{60}$: $T_c = 33$ K
- Cs_3C_{60} (7 kbar) : $T_c = 35$ - 38 K

Physics takes place at states above the HOMO level (HOMO-LUMO gap usually large)

General properties of molecular crystals

- Small bandwidth → large U/t → strong electron-electron correlation
- Large electron-phonon coupling (phonon mode activation under electron doping, Jahn-Teller effect for high symmetry molecules)
- Competition (or cooperation!) between strong electron-electron and electron-phonon couplings

Model these systems is challenging! The "usual" framework is the Hubbard-Holstein Hamiltonian

$$H = \sum_{ij}\sum_{\alpha\beta} t_{ij}^{\alpha\beta} c_{i\alpha}^{\dagger} c_{j\beta} + \sum_{\alpha\beta} U^{\alpha\beta}\hat{n}_{\alpha}\hat{n}_{\beta} + \sum_{i\alpha\beta}(a_i + a_i^{\dagger}) g^{\alpha\beta} c_{i\alpha}^{\dagger} c_{i\beta} + \omega \sum_{i} a_i^{\dagger} a_i$$

We would like to have model parameters from ab-initio calculations

"Downfolding" model parameters from ab-initio

Keep in the model only electrons above HOMO

→**Tracing-out high energy degrees of freedom**:

- high-energy screening processes must be included in the low-energy model in an effective way
- parameters renormalized by electron-electron interaction:

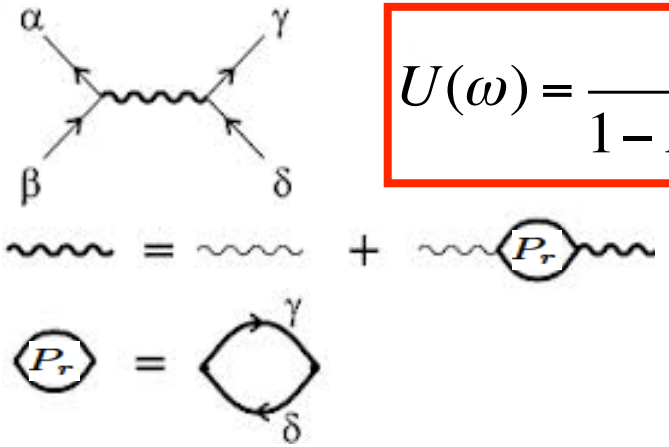
Partially screened U by constrained RPA

Aryasetiawan et al. PRB **70**, 195104 (2004)

Miyake et al. PRB **61**, 7172 (2000)

Miyake et al. PRB **80**, 155134 (2009)

Casula et al. PRL **109**, 126408 (2012)



$$U(\omega) = \frac{v}{1 - P_r(\omega)v}$$

Partially screened g and ω by constrained density functional perturbation theory (DFPT)

Nomura et al. PRL **112**, 027002 (2014)

How to get electron-phonon parameters?

- Usually geometry, ω, and g computed from DFT and DFPT in the relaxed system including the low-energy manifold

  → fully screened couplings!!!

- We need to undress the DFT phonon propagator from low-energy electron-phonon processes to get the "bare" (partially screened) quantities of the model!

Incorrect vs correct phonon frequency and geometry

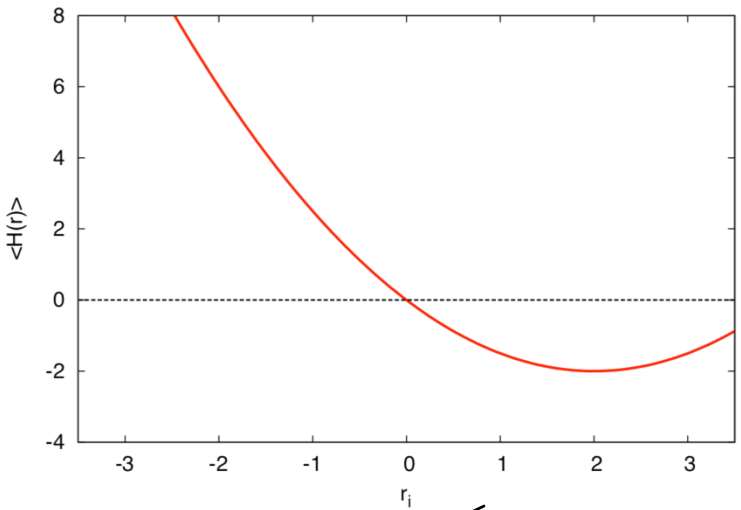
Take for the moment a classical phonon model

Find the energy minimum of $E = E(r) = \langle H(r) \rangle$

r_i : phonon displacement → geometry relaxation

Curvature around minimum → "dressed" frequency

$$H = \sum_{ij\sigma} t_{ij\sigma} c^{\dagger}_{i\sigma} c_{i\sigma} + \sum_{i\sigma} r_i \delta V c^{\dagger}_{i\sigma} c_{i\sigma} + \frac{{\omega_{\mathrm{DFT}}}^2}{2} \sum_i r_i^2$$



$$\omega_{\mathrm{dressed}} < \omega_{\mathrm{DFT}}$$

$$r_i \neq 0$$

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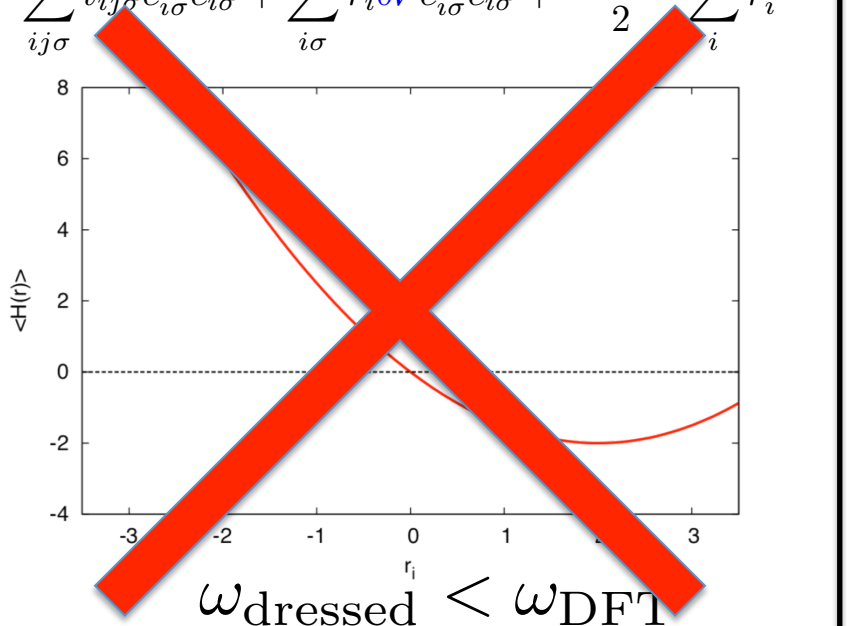

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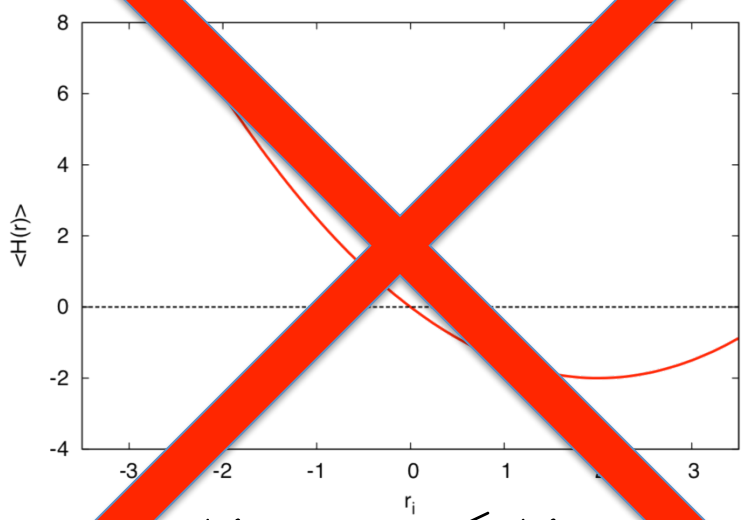

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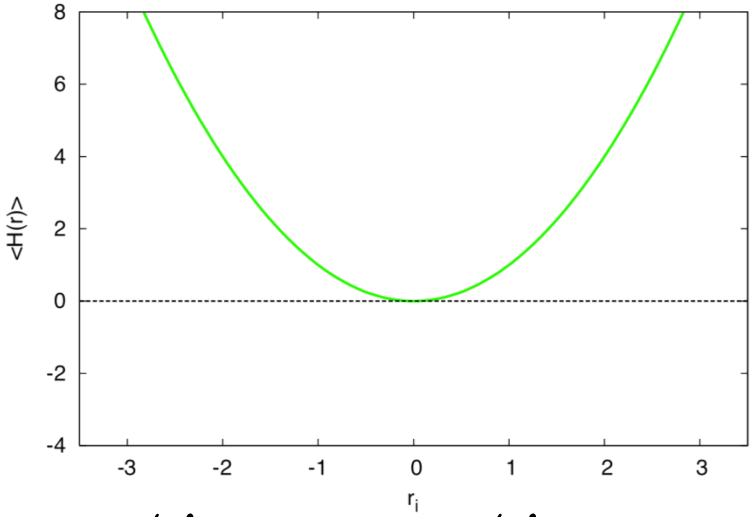
$$r_i \neq 0$$

$$H = \sum_{ij\sigma} t_{ij\sigma} c^\dagger_{i\sigma} c_{i\sigma} + \sum_{i\sigma} r_i \delta V c^\dagger_{i\sigma} c_{i\sigma} + \frac{{\omega_{\mathrm{bare}}}^2}{2} \sum_i (r_i - r_0)^2$$



$$\omega_{\mathrm{dressed}} = \omega_{\mathrm{DFT}}$$

$$r_i = 0$$

Fixing the model parameters

$$H = \sum_{ij\sigma} t_{ij\sigma} c^{\dagger}_{i\sigma} c_{i\sigma} + \sum_{i\sigma} r_i \delta V\, c^{\dagger}_{i\sigma} c_{i\sigma} + \frac{\omega_{\mathrm{bare}}{}^2}{2} \sum_i (r_i - r_0)^2$$

ω_{bare} and r_0 such that the following Eqs are both satisfied

$$\left. \frac{\partial \langle H_{\text{el-ph}} \rangle}{\partial r_i} \right|_{r_i = 0} = 0$$

Relaxed geometry equal to ab-initio equilibrium geometry

$$\left. \frac{\partial^2 \langle H_{\text{el-ph}} \rangle}{\partial r_i^2} \right|_{r_i = 0} = \omega^2_{\text{dressed}}$$

Energy curvature equal to ab-initio curvature

Quantizing the phonons

$$H_{\text{el-ph}} = H_{\text{tb}} + \sum_{\alpha\beta\sigma i} \sqrt{2} x^0 g^{\text{bare}}_{\alpha\beta} c^\dagger_{\alpha\sigma i} c_{\beta\sigma i}$$

$$+ \sum_{\alpha\beta\sigma i} (a_i + a_i^\dagger) g^{\text{bare}}_{\alpha\beta} c^\dagger_{\alpha\sigma i} c_{\beta\sigma i} + \omega_{\text{bare}} \sum_i a_i^\dagger a_i$$

where $g^{\text{bare}}_{\alpha\beta} = \delta V_{\alpha\beta} / \sqrt{2\omega_{\text{bare}}}$

$$x_i = \sqrt{\omega_{\text{bare}}} (r_i - r^0) = \langle a_i + a_i^\dagger \rangle / \sqrt{2}$$

$$x^0 = \sqrt{\omega_{\text{bare}}}\, r^0$$

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$$x^0 = \sqrt{\omega_{\text{bare}}}\, r^0$$

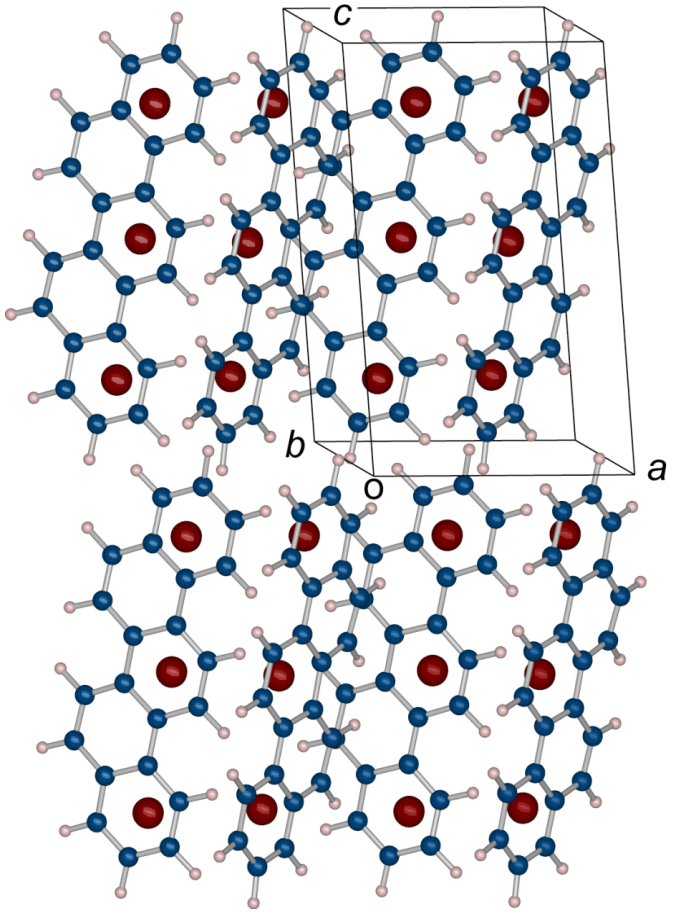
Electron-phonon double counting (EP-DC) correction:

it counteracts the band deformation due to low-energy geometry relaxation effects ALREADY included in the DFT solution of the filled system.

Application to K_3Picene

Mitsuhashi *et al.*, Nature, **464**, 76 (2010)

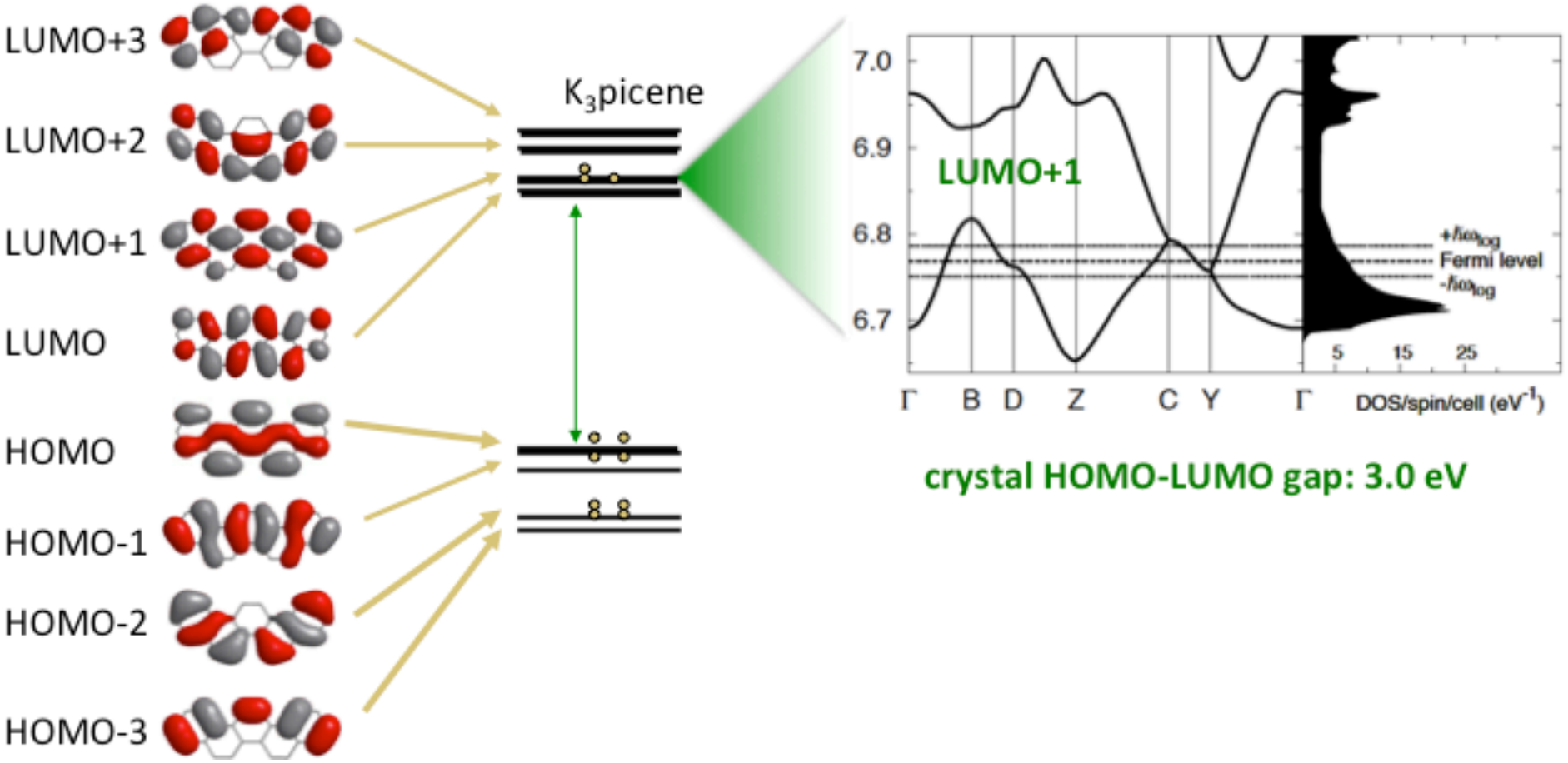
picene



K intercalated crystal

K_3Picene – Electronic Structure

molecule ➔ crystal



crystal HOMO-LUMO gap: 3.0 eV

Including strong correlation

Downfolding to **3-band Hubbard Hamiltonian**
written in the Wannier molecular orbital basis (LUMO, LUMO+1, LUMO+2)

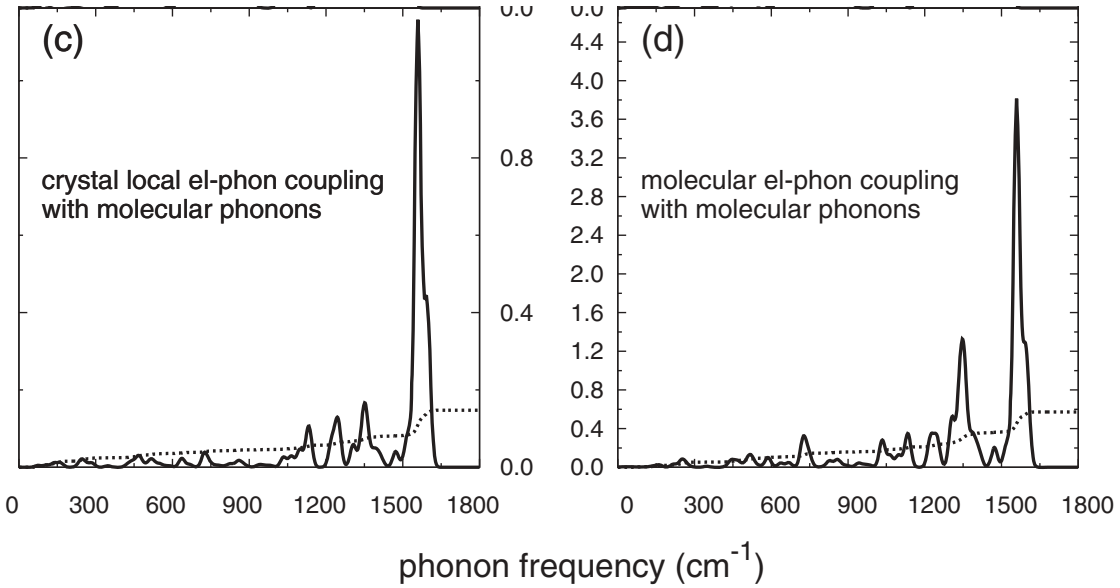
$$H = -\sum_{ml\sigma ij} t_{ij}^{ml} c_{m\sigma i}^{\dagger} c_{l\sigma j} + U \sum_{m\sigma i} n_{m\sigma i} n_{m-\sigma i}$$
$$+ U' \sum_{\substack{ml\sigma i \\ m\neq l}} n_{m\sigma i} n_{l-\sigma i} + (U' - J) \sum_{\substack{ml\sigma i \\ m\neq l}} n_{m\sigma i} n_{l\sigma i}$$

U=0.68 eV U'=0.63 eV J=0.10 eV
derived by c-RPA with basis rotation from maximally localized Wannier functions (Nomura, Nakamura, Arita, PRB **85**, 155452 (2012))

c-RPA static limit values + bandwidth renormalization due to dynamic U

DFPT estimates of local el-ph coupling

Crystal G^2 Molecular G^2

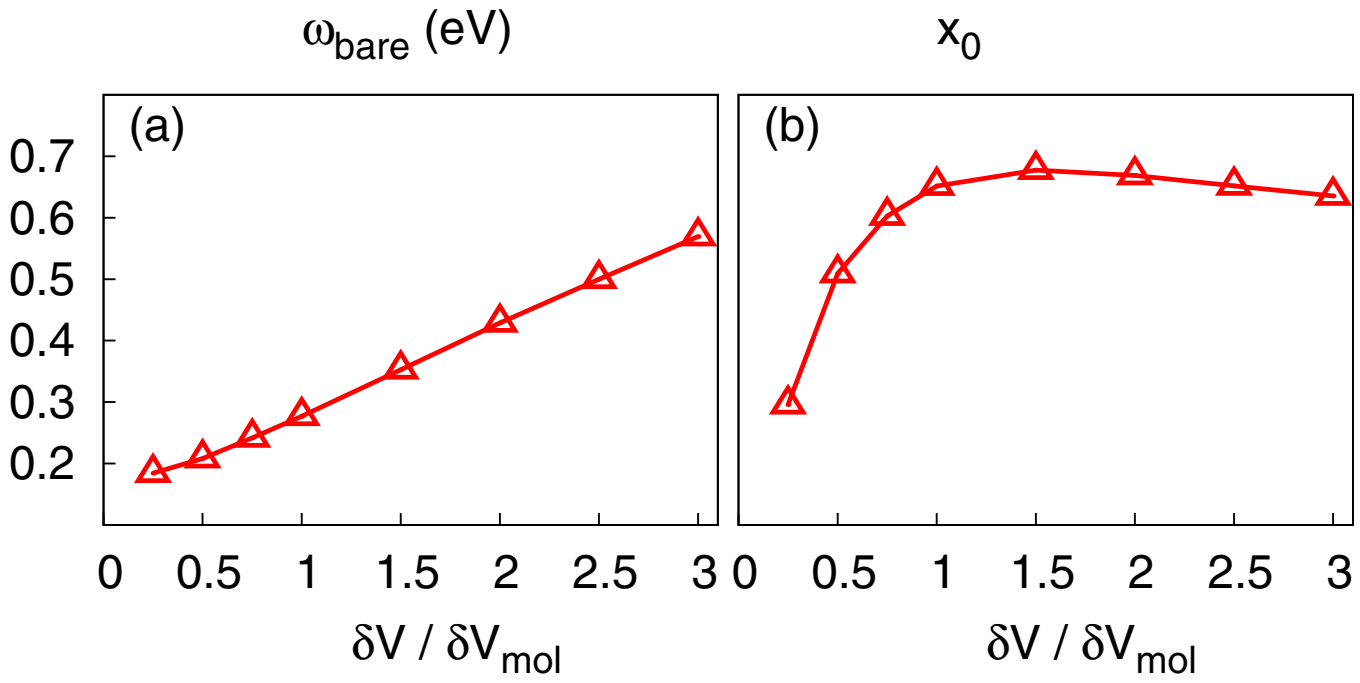


Phonon frequency of the largest coupling G: ω_{DFT} = 0.193 eV = 1556 cm^{-1}

$$g_{\alpha\beta}^{\text{bare}} = \begin{pmatrix} 0.066 & -0.010 & -0.002 \\ -0.010 & -0.038 & -0.051 \\ -0.002 & -0.051 & -0.018 \end{pmatrix}$$

Strong inter-orbital couplings!

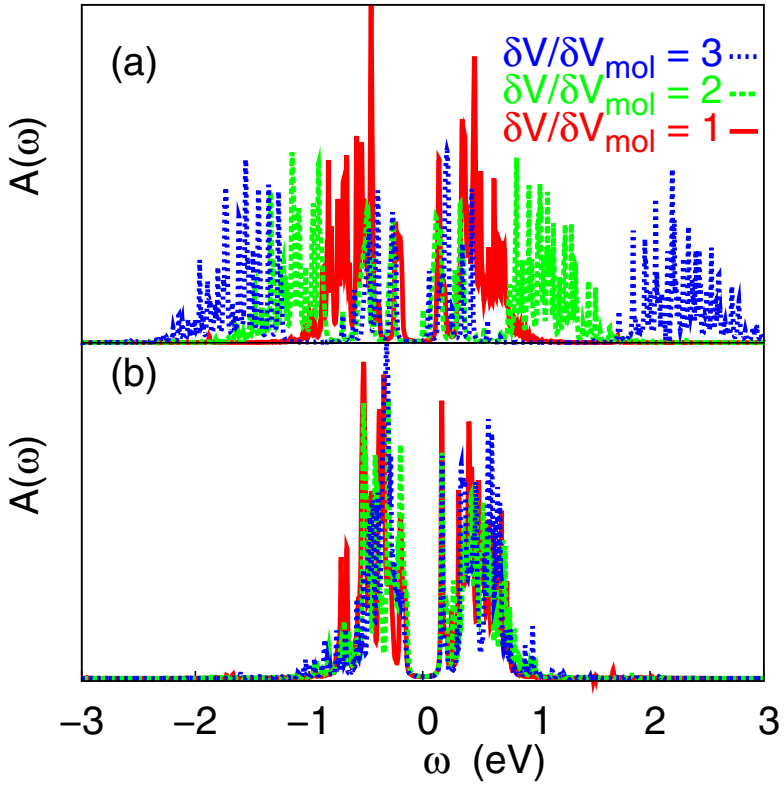
ω_{bare} and x_0 from our prescription



What is their impact on the final solution?

DMFT-ED spectral function

Solving the Hubbard-Holstein model by dynamical mean field theory (DMFT) with exact diagonalization (ED)
(Hilbert space of the quantum impurity problem includes also the Holstein phonon)



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

Conclusions

- Electron-phonon interaction acting on low-energy electrons has a strong effect on the renormalized parameters (geometry, phonon frequency, electron-phonon vertex)
- Results extremely sensitive to the electron-phonon double counting correction
- Effects of electron-phonon undressing largely unexplored in realistic electron-phonon models

Reference for this work

Giovannetti, Casula, Werner, Mauri, and Capone,
Physical Review B **90**, 115435 (2014)