Holstein–Peierls Hamiltonian

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_\alpha g_{ij\alpha} \left(b_\alpha^\dagger + b_\alpha \right) c_i^\dagger c_j$$

here c_i – quasiparticles (excitons, holes etc.) described by coarse-grained Hamiltonian, b_α – normal modes or phonons,

$$H_{ij}^{1p} = \delta_{ij}\varepsilon_i + (1 - \delta_{ij}) V_{ij},$$

ε_i – onsite energy, V_{ij} – transfer integral, $g_{ij\alpha}$ – electron-phonon coupling (local for $i = j$, nonlocal otherwise)

Approximations:

- mean field approximation for electrons (one may add interaction terms)
- harmonic approximation for atomic motion (essential for quantum modes)
- linear electron-phonon coupling

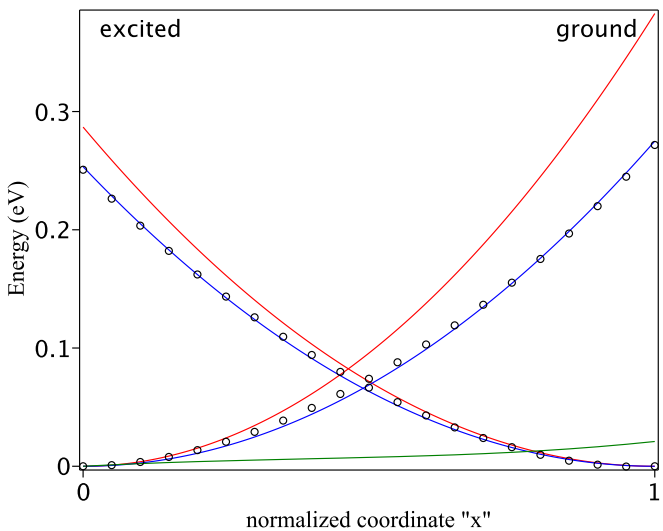
Calculating vibronic couplings

1. Local couplings (Holstein model):

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{i\alpha} \hbar\omega_\alpha g_{i\alpha} \left(b_\alpha^\dagger + b_\alpha \right) n_i$$

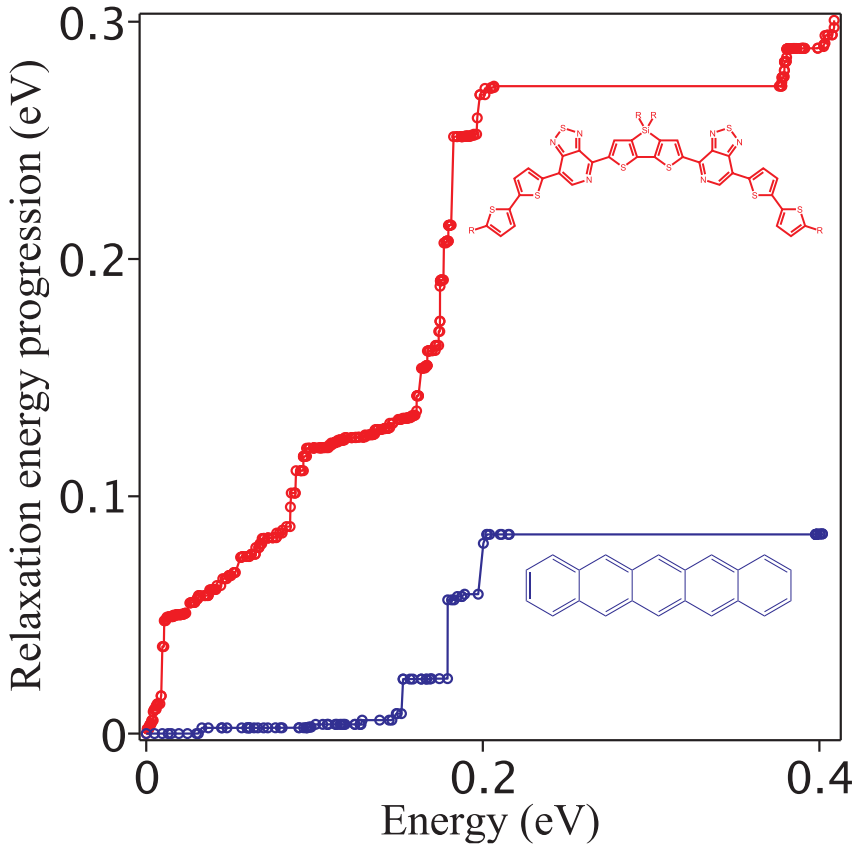
and $g_{i\alpha} g_{j\alpha} = 0$ for $i \neq j$

- Get two relaxed geometries: for zero and one quasiparticle at site
- Project atomic displacement onto normal modes ξ_α, then $g_\alpha = -\frac{\xi_\alpha^{(0)}}{\sqrt{2}}$
- Rescale g and ω for weak anharmonic effects



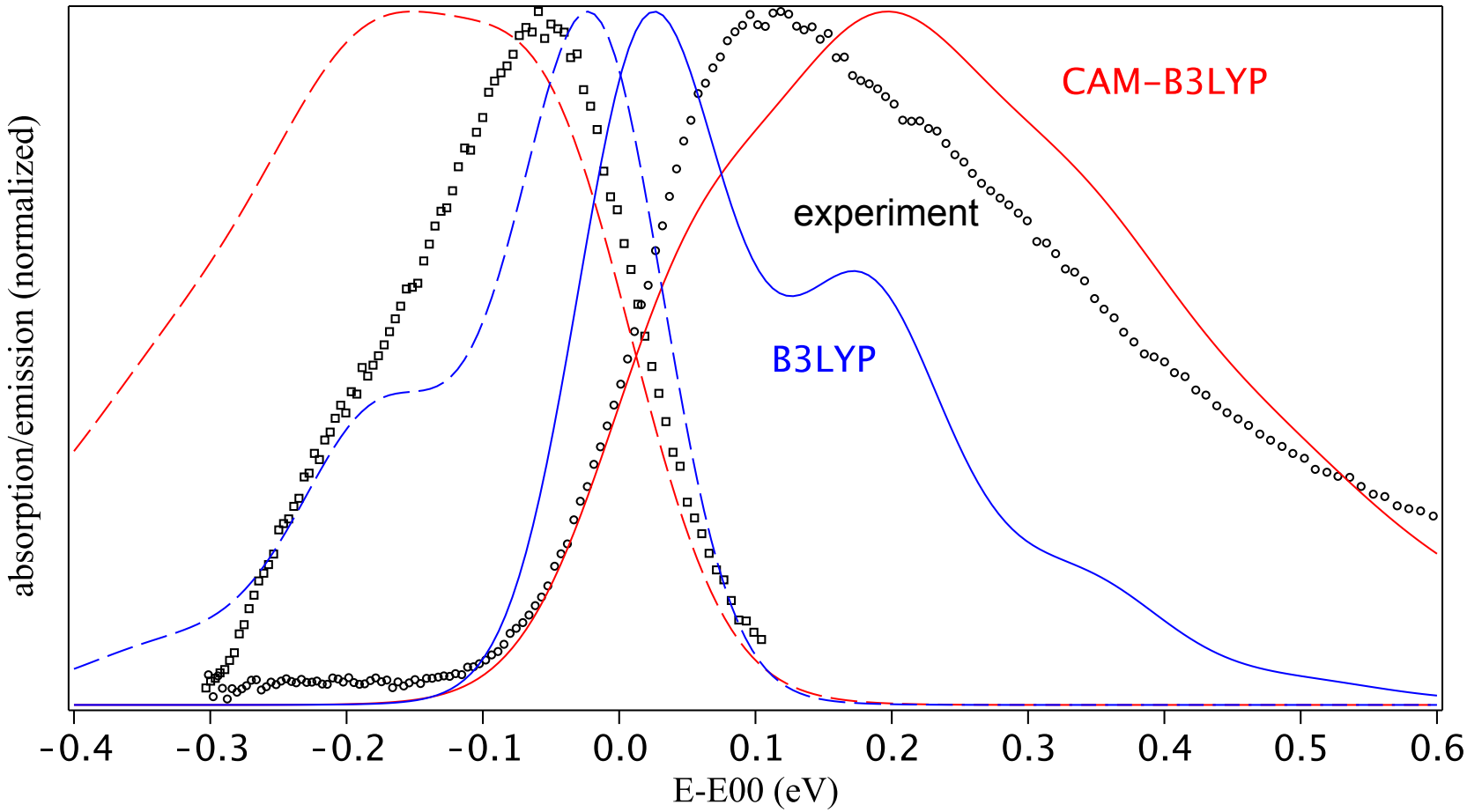
2. Nonlocal (intermolecular) couplings see [Phys Stat Sol B 248, 511], but is challenging computationally

Vibronic couplings: example



$$\lambda(E) = \sum_{\hbar\omega_\alpha < E} g_\alpha^2 \hbar\omega_\alpha$$

Vibronic couplings: choice of density functional is critical



B3LYP underestimates vibronic couplings for low-ω modes
CAM-B3LYP overestimates vib. couplings for high-ω modes