**VIBRO-POLARITONS FROM FIRST PRINCIPLES VIA LINEAR RESPONSE**

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**Motivation**

Optical cavity experiments realize strong light-matter coupling resulting in hybrid polariton states with mixed electron, nuclear, and photon character. Possible to tune states to influence chemical reactions and other properties.

**QEDFT and CBOA**

Within quantum electrodynamical density functional theory (QEDFT) photons are quantized and coupled to matter degrees of freedom

\[ H = \hat{T} + \hat{V}_e + \hat{V}_{\text{bio}} + \hat{V}_{\text{bio-bio}} + \hat{V}_{\text{nuc-nuc}} + \hat{H}_{\text{ext}} \]

Within the dipole approximation:

\[ \hat{V}_{\text{bio}} = \sum \beta \sum \omega \hat{d}_{\beta \omega} - \frac{1}{2} \sum \omega \hat{d}_{\beta \omega}^2 \]

For vibrational coupling regime we employ the Cavity Born Oppenheimer approximation (CBOA), solving the electronic system at fixed nuclei and photon displacement field. Flick et al. PRL 121, 113002 (2018)

**Model**

The energy surface as a function of \( \mathbf{R} \) and \( \mathbf{q} \) can be written to harmonic order with nuclear coordinates rotated to a basis of uncoupled vibration modes with amplitudes \( N \)

\[
E(N, \mathbf{q}) = \sum_{\alpha, \beta} \frac{1}{2} (\omega_{\alpha} \delta_{\beta \beta} \Delta_{\alpha} + \sum_{\varepsilon \not= \alpha} (\varepsilon \hat{N}_{\varepsilon} \cdot \lambda_{\varepsilon} ) \frac{\partial (\mu \varepsilon)}{\partial N_{\varepsilon}} \) \sum_{\alpha} \Delta_{\alpha} + \sum_{\alpha \not= \beta} \frac{1}{2} (\omega_{\alpha} \delta_{\beta \beta} \Delta_{\alpha} + \sum_{\varepsilon \not= \alpha} (\varepsilon \hat{N}_{\varepsilon} \cdot \lambda_{\varepsilon} ) \frac{\partial (\mu \varepsilon)}{\partial N_{\varepsilon}} ) N_{\alpha} N_{\beta}
\]

\[
\Delta_{\alpha} = \frac{d }{d N_{\alpha}} \left( \frac{d }{d N_{\alpha}} (\hat{H} - \hat{V}_{\alpha}) \right) - \omega_{\alpha} \delta_{\beta \beta} \]

Parameters \( \Delta_{\alpha} \) and \( \omega_{\alpha} \) are all dependent on coupling strength \( \lambda \) through the \( \lambda \) dependence of the electronic state. At strong coupling the cavity impacts electronic states altering effective vibration and photon modes.

**Results**

**CO2**

- Rabi splitting in agreement with time dependent perturbation calculation
- Asymmetric splitting seen at larger coupling strengths
- Asymmetry related to the \( \lambda \) dependence of model parameters

**Multiple CO2**

- Linear response approach enables calculations on larger systems
- Collective polaritons + dark modes seen with multiple molecules
- Increasing number of molecules results in nearly identical Rabi splitting as increasing \( \lambda \) on a single molecule
- Model parameters for much larger number of molecules can be extracted from two molecule calculation

**Fe(CO)5**

- Fe(CO)5 coupled to 3 cavity mode harmonics
- Small \( \lambda \): central photon mode couples to doubly degenerate xy-modes and a z-mode resulting in upper, middle, and lower polaritons + one dark mode
- Very large \( \lambda \): lower polariton and lower photon mode hybridize resulting in mode with mixed photon character

**Outlook**

- Further study of collective vs local strong light-matter coupling
- Comparisons to experiments
- Implementation for periodic systems
- Use method as starting point for studying other effects:
  - anharmonicity, cavity induced symmetry breaking, and more