Coupling electrons, vibrations and photons in molecular quantum chemistry

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We derive an electron–vibration model Hamiltonian in a quantum chemical framework and explore the extent to which such a Hamiltonian can capture key effects of nonadiabatic dynamics. The model Hamiltonian is a simple two-body operator, and we make preliminary steps at applying standard quantum chemical methods to evaluate its properties, including mean-field theory, linear response, and a primitive correlated model. The Hamiltonian can be compared to standard vibronic Hamiltonians, but it is constructed without reference to potential energy surfaces through direct differentiation of the one- and two-electron integrals at a single reference geometry. The nature of the model Hamiltonian in the harmonic and linear-coupling regime is investigated for pyrazine, where a simple time-dependent calculation including electron–vibration correlation is demonstrated to exhibit the well-studied population transfer between the S_2 and S_1 excited states.

We then extend the computational framework to describe polaritons, which treats photons and electrons on the same footing using coupled-cluster theory. As a proof of concept, we study the coupling between the first electronically excited state of carbon monoxide and an optical cavity. We focus, in particular, on how the interaction with the photonic mode changes the vibrational spectroscopic signature of the electronic state, and how this is affected when tuning the cavity frequency and the light-matter coupling strength. For this purpose, we consider different methodologies and investigate the validity of the Born-Oppenheimer approximation in such situations.

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