Introduction

Quantum electrodynamical calculations quickly run into the infamous exponential wall and as a consequence one is tempted to apply historic approximation strategies outside their regime of validity. [1]

We try to deliver new and complimentary inside by using a real-space formulation from first principles that keeps all the electronic degrees of freedom in the model explicit and simulates changes in the environment by an effective photon mode. We can easily connect to well-known quantum-chemical results such as Dexter charge- and Förster excitation-transfer reactions taking into account the often disregarded Coulomb and self-polarization interaction. In this work, we highlight that these processes as well as other chemical properties can be drastically altered by modifying the vacuum fluctuations of the electromagnetic field in a cavity. [2]

Figure 1: Photonic influence on the ground-state density for weak coupling \(\lambda = 0.0058\). The 2-level approximation [8], including counter-rotating terms, completely fails. More details and examples are discussed in [1].

Real-space model

\[
\hat{H}(t) = \sum_{\alpha} \frac{\hbar^2}{8\pi^2} \int \frac{d^2k}{(2\pi)^2} \bar{v}_{\alpha}(k) \left( \hat{q}(k) + \hat{q}(k) \right) + \frac{1}{2} \left( \hat{q}(k) + \hat{q}(k) \right) \left( \hat{q}(k) + \hat{q}(k) \right) \delta_k.
\]

Molecular correlation under cavity influence

\[
\rho(t) = \int \frac{d^2q}{(2\pi)^2} \left| \psi^\text{phys}(q, t) \right|^2 - \left| \psi(q, t) \right|^2.
\]

Excitation transfer

Initial-state \(S = \psi^\text{phys}(q, t) \otimes \psi(q, t) \otimes \rho(t)\), quench \(\hat{H}(t) = \hat{h}_t + \hat{h}_0 + \hat{\rho}_0\).

Calculate \(n\)th order probability of transferring excitation from D to A

\[
e_t(n) = \left| \left( \hat{S}^n \psi^\text{phys}(q, t) \otimes \psi(q, t) \otimes \rho(t) \right) / \right|^2.
\]

Charge transfer

Linear perturbation of charge-transfer state (singlet, large occupation on D) with \(\hat{H}(t) = \hat{H} + E\delta\psi(t)%3C;\%

\[
a)\text{Extremum charge transfer } \psi'(\cdot) \text{.} \quad \text{b) MB spectrum } \psi(\cdot) = \psi(\cdot) \text{.} \quad \text{c) Dexter g/} \bar{\hbar}\omega = 0.0058, 6.56 \text{ Å}
\]

Photon induced correlation

Calculate \(e_t(t)\) as before (Setup1) exact and compare to uncorrelated approximations along the line

\[
\bar{\rho}(t) = \left( \hat{\rho}_1(t) \otimes \hat{\rho}_0(t) \right) \text{ and } \bar{\rho}(t) = \left( \hat{\rho}_1(t) \otimes \hat{\rho}_0(t) \right).
\]

First-principles tools

Electron-Photon OEP

Connection of DFT and many-body perturbation theory opens a path for the development of accurate functionals. Its limitation is based on the order of perturbation diagram included [4].

Multi-trajectory and BBGKY

Ensemble approach, tricky to capture interferences, first-principles feasible [5]. Truncation of the BBGKY hierarchy to self-consistent second Born level gives excellent results. [6]. In progress

Also strongly correlated approaches \(\phi_t(q, r, t)\) are possible. [7]

References


Christian Schäfer, Michael Ruggenthaler, and Angel Rubio.

https://scholar.google.de/citations?user=1KCuZ08AAAJ

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