

# Modification of excitation and charge transfer in cavity quantum-electrodynamical chemistry

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## Introduction

Quantum electrodynamic (QED) 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]

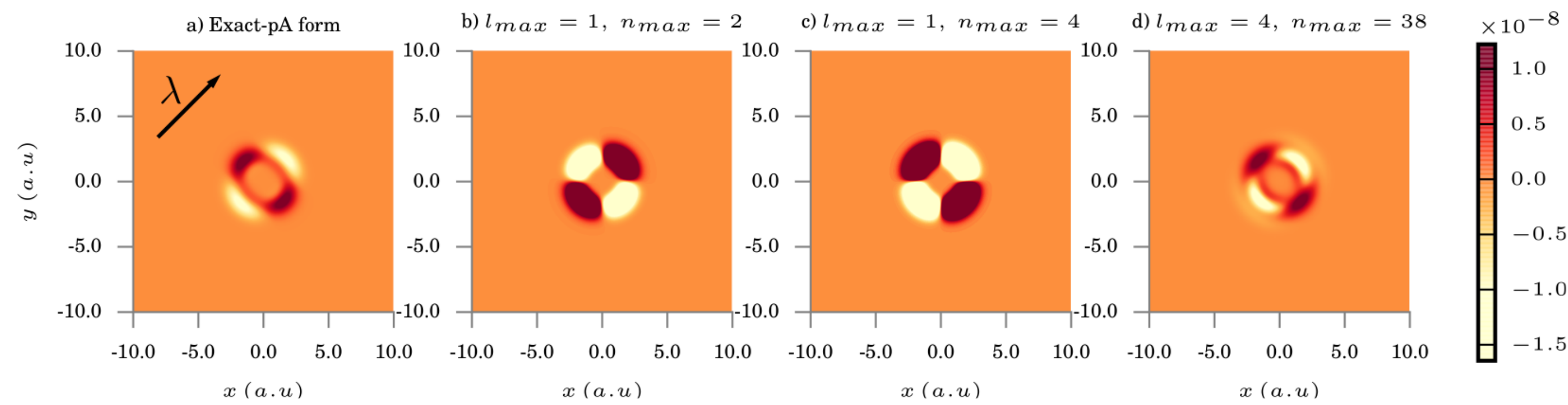


Figure 1: Photonic influence on the ground-state density for weak coupling  $\lambda = 0.005$ . The 2-level approximation (b), including counter-rotating terms, completely fails. More details and examples are discussed in [1]

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]

## Real-space model

$$\hat{H}(t) = -\sum_{n=1}^2 \frac{\hbar^2}{2m_e} \nabla_{x_n}^2 + \hbar\omega \hat{a}^\dagger \hat{a} + \frac{1}{2} (\lambda(t) \hat{X})^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{n,j=1}^2 \frac{Z_j}{\sqrt{(\hat{x}_n - R_j)^2 + 1}} + \frac{\xi(t)}{4\pi\epsilon_0} \frac{e^2}{\sqrt{(\hat{x}_1 - \hat{x}_2)^2 + 1}} - \sqrt{\frac{\hbar\omega}{2}} \lambda(t) \hat{X} (\hat{a}^\dagger + \hat{a})$$

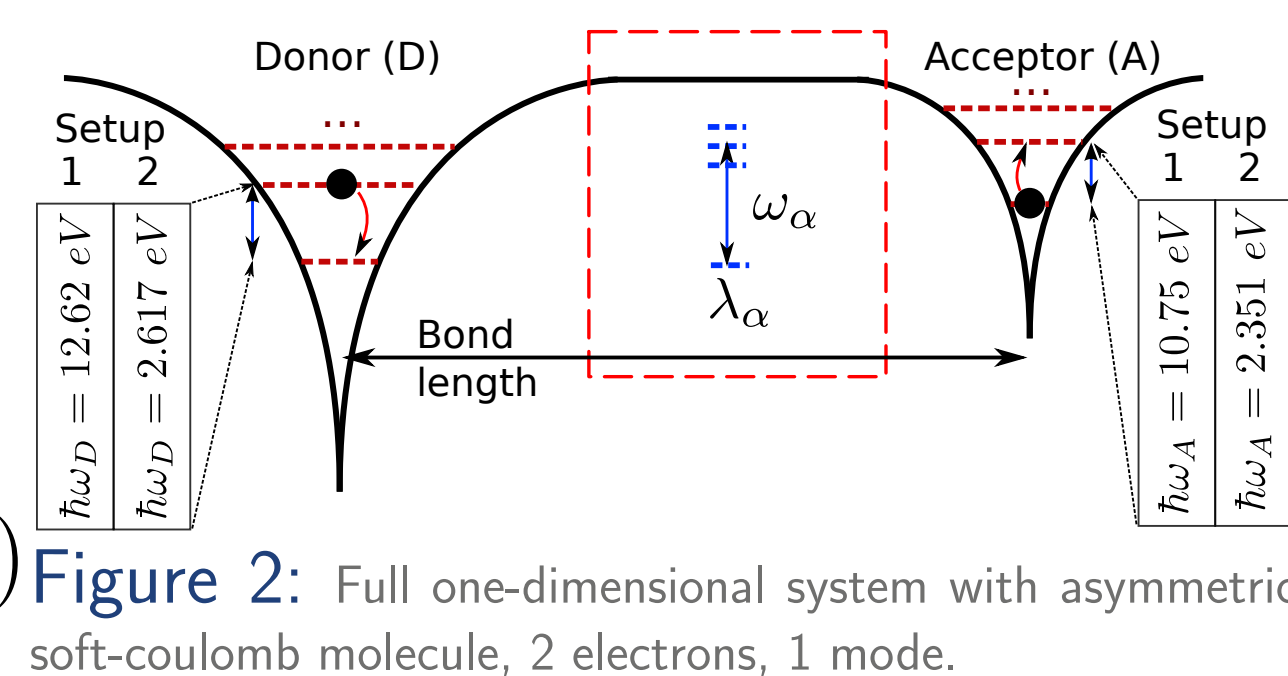


Figure 2: Full one-dimensional system with asymmetric soft-coulomb molecule, 2 electrons, 1 mode.

## Molecular correlation under cavity influence

e-p reduced density matrix with natural occupation  $n_k$

$$\rho_{ep}(x_1 q, x'_1 q') = \int dx_2 \Psi(x_1, x_2, q) \Psi^*(x'_1, x_2, q') = \sum_k n_k \psi_k(x_1 q) \psi_k^*(x'_1 q')$$

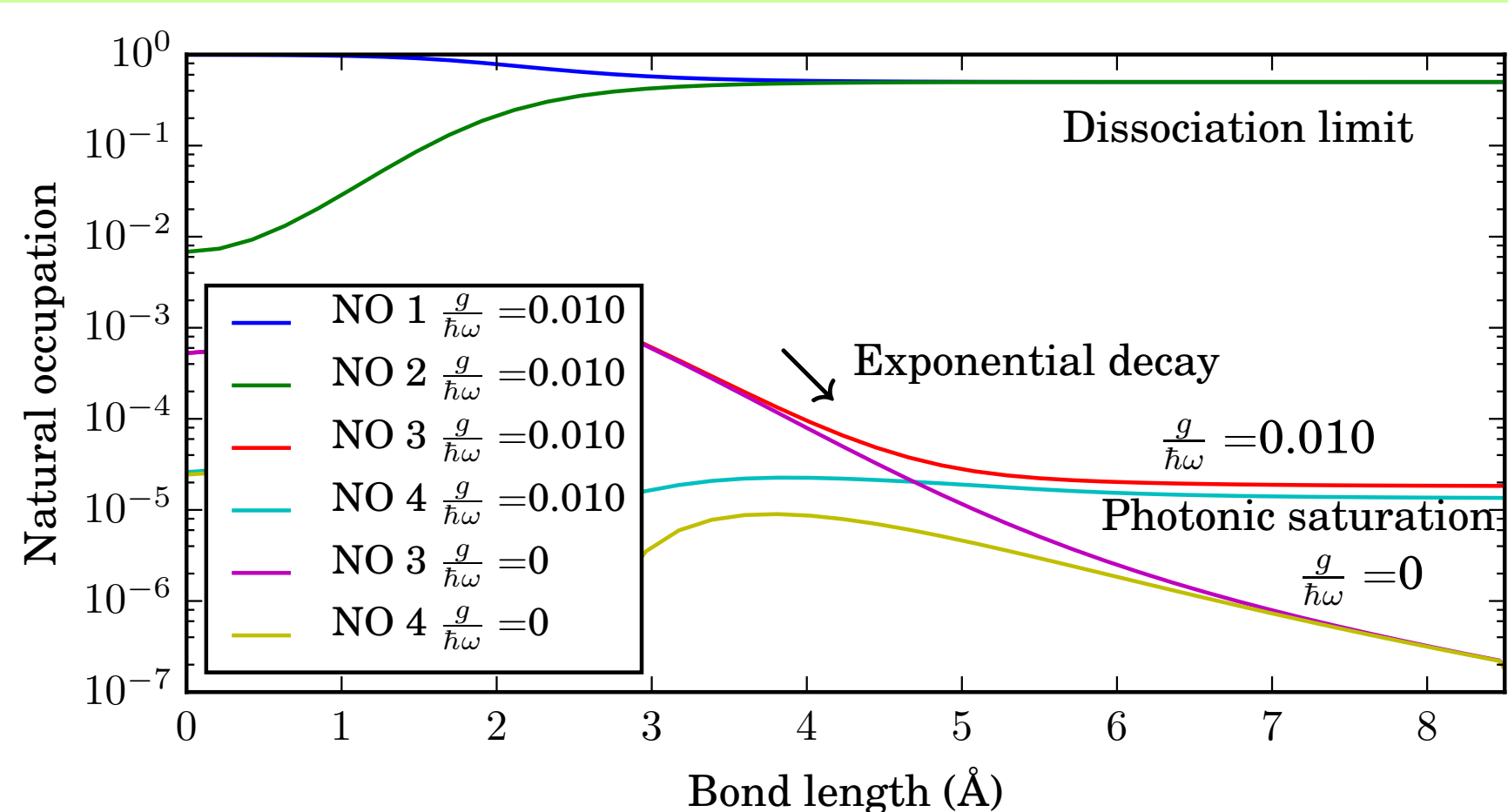


Figure 3: Natural occupations of  $\rho(x_1 q, x'_1 q')$  with and without photonic coupling for frequency  $\hbar\omega = 12.62$  eV, setup1.

## Excitation transfer

Initial-state  $\hat{S}^- \psi_D^1(r_1) \otimes \psi_A^0(r_2) \otimes \mathbb{1}_p$ , quench  $\hat{H}(t) = \hat{H}_0 + \theta(t^+) [\hat{H}_{ee} + \hat{H}_p + \hat{H}_{ep}]$ . Calculate n'th order probability of transferring excitation from D to A

$$e_n(t) = |\langle \hat{S}^- \psi_D^0(r_1) \otimes \psi_A^n(r_2) \otimes \mathbb{1}_p | \Psi(t) \rangle|^2.$$

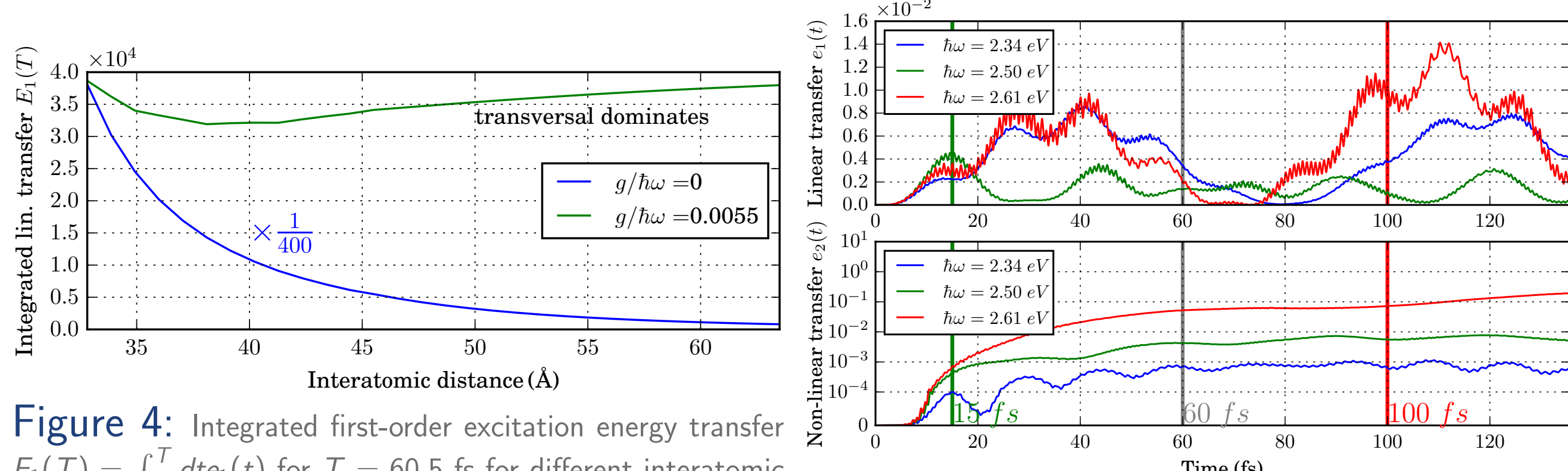


Figure 4: Integrated first-order excitation energy transfer  $E_1(T) = \int_0^T dt e_1(t)$  for  $T = 60.5$  fs for different interatomic distances. The Coulombic case (blue) decays as expected and is multiplied by a factor of 400 here to present the otherwise vanishingly small purely longitudinal transfer. Setup2

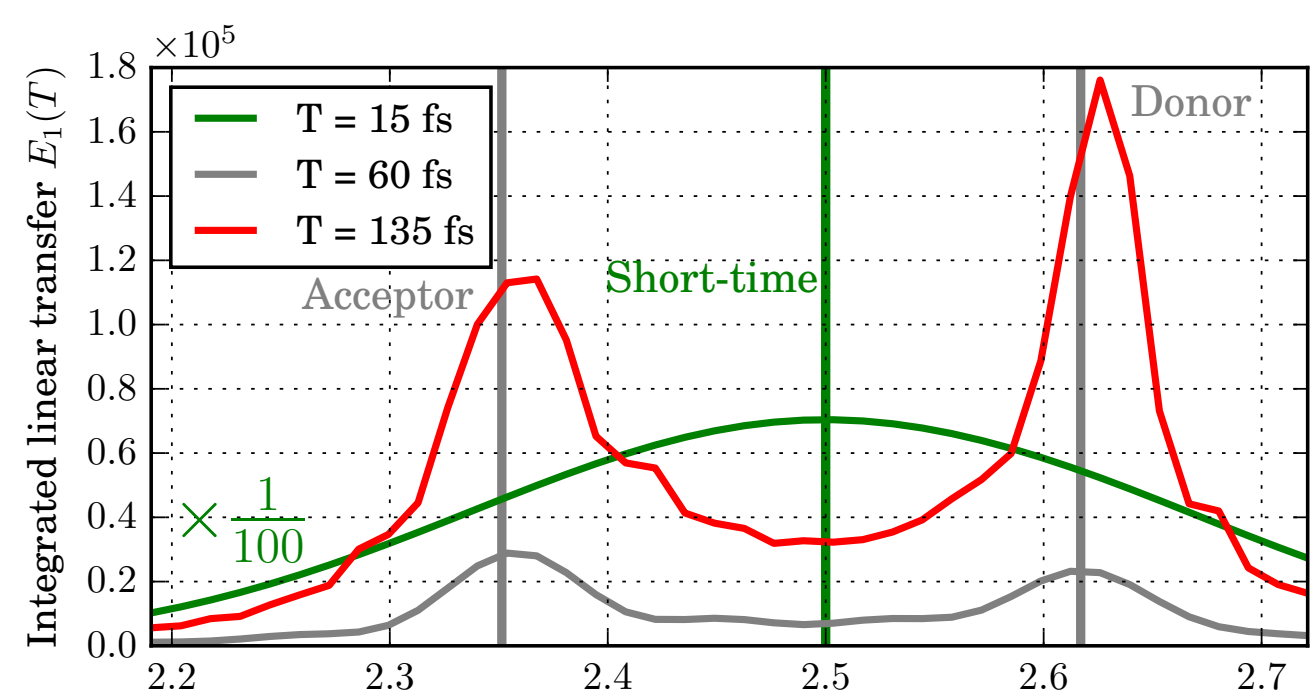


Figure 6:  $E_1(T)$  with interatomic distance 42.3 Å and weak coupling (for the reference frequency  $\omega_{ref} = 2.340$  eV we have  $g/\omega_{ref} = 0.0058$ ) for different frequencies and three different integration times  $T = \{15, 60, 135\}$  fs. Setup2

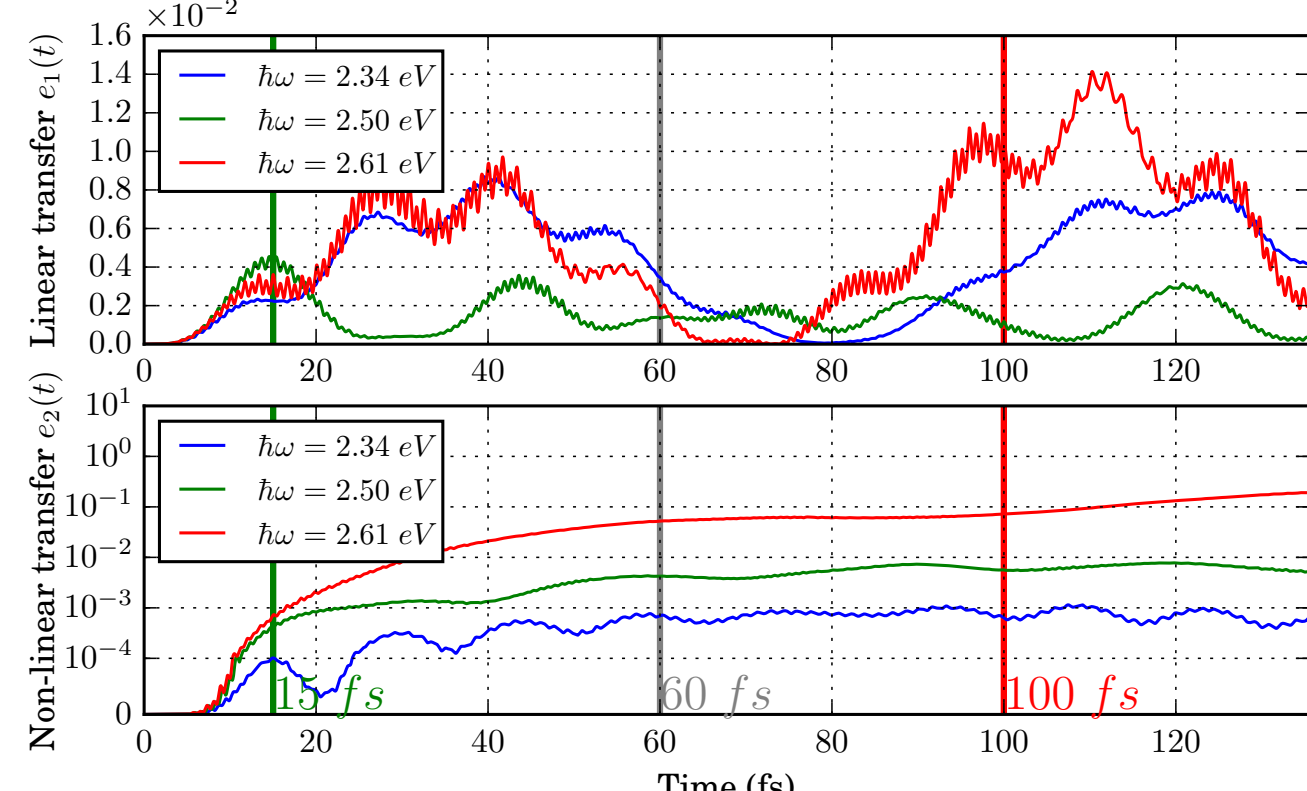


Figure 5: First-order (Upper) and second-order (Lower) excitation energy transfer for weak coupling (for the reference frequency  $\omega_{ref} = 2.340$  eV, this is  $g/\omega_{ref} = 0.0058$ ) with interatomic distance 42.3 Å. Setup2

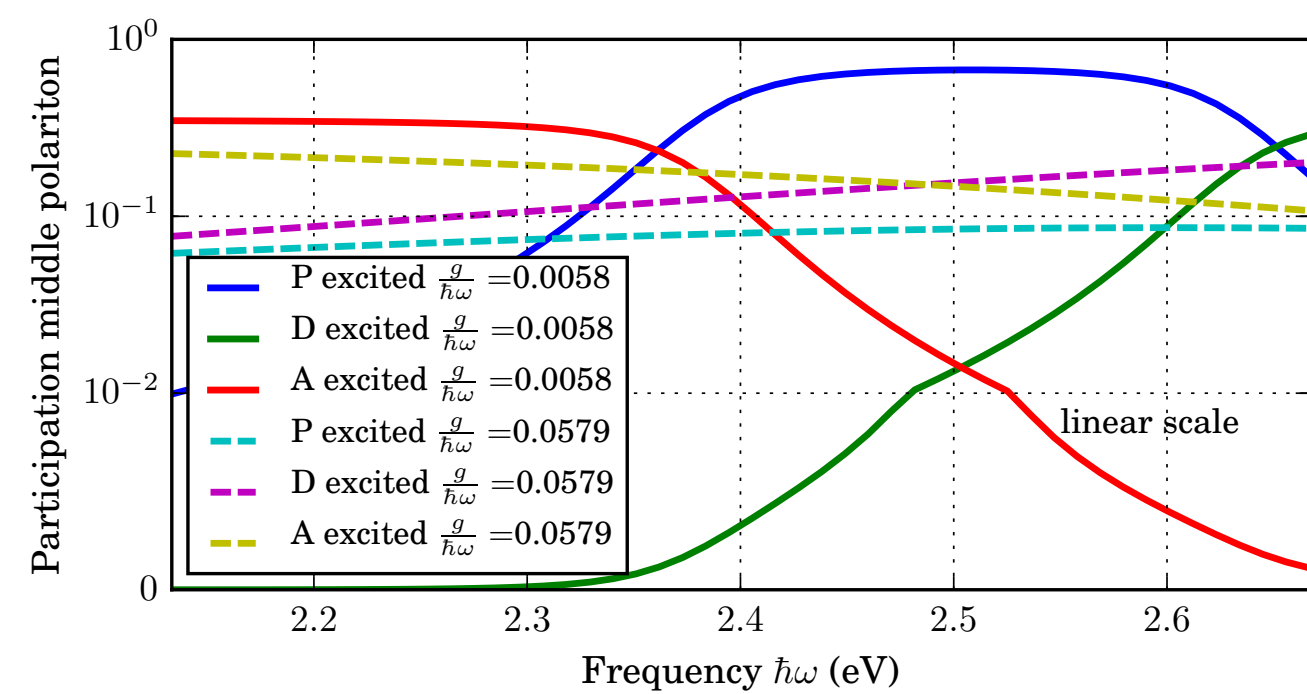


Figure 7: Hopfield coefficients for the middle polariton with interatomic distance 21.2 Å for different frequencies. The coupling is given with respect to the reference frequency  $\omega_{ref} = 2.340$  eV. For  $\omega = 2.50$  eV, we observe equal weights of D and A. In line with [3]. Setup2

## Charge transfer

Linear perturbation of charge-transfer state (singlet, large occupation on D) with  $\hat{H}(t) = \hat{H} + \hat{r} E_0 \delta(t^+)$ .

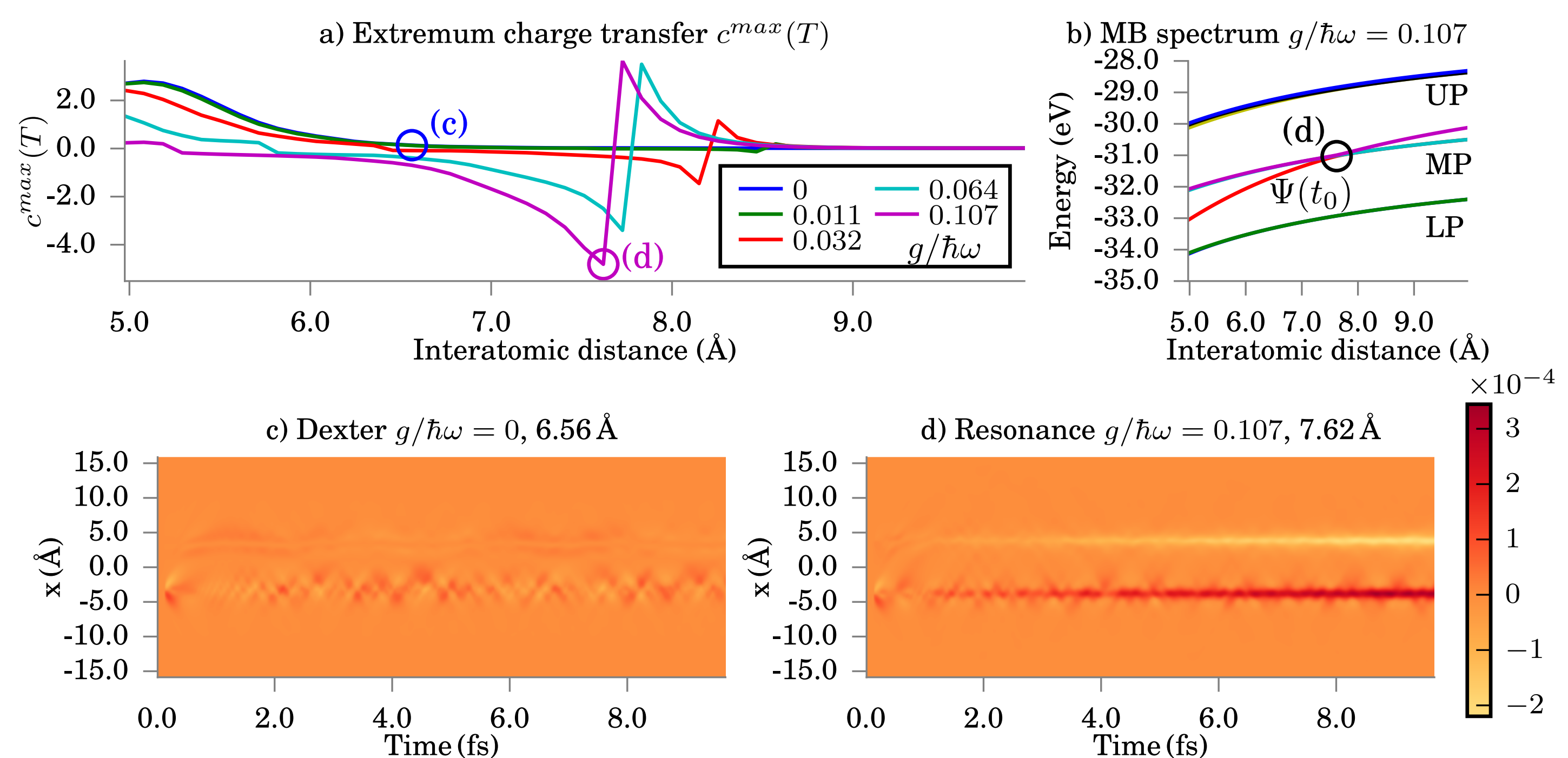


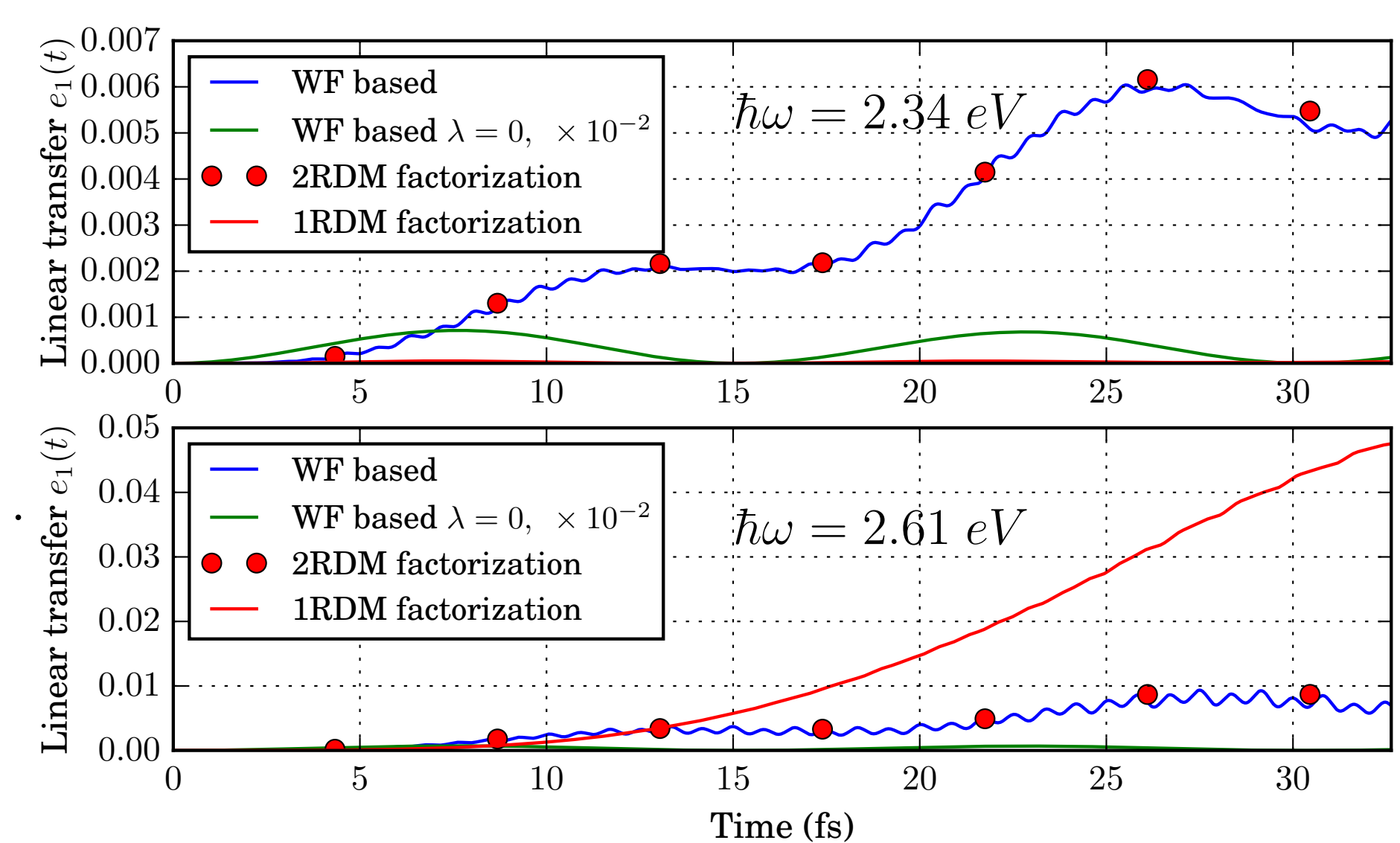
Figure 8: (A) Integrated charge transfer ( $\xi = 1$ ,  $\omega = 11.97$  eV). New (inverse) maxima of charge transfer arise, and they are connected to avoided crossings of the initial many-body eigenstate with polariton many-body (MB) eigenstates in (B). (C,D) density-difference  $n(x, t) - n(x, 0)$  for the indicated interatomic distances. Setup1

## Photon induced correlation

Calculate  $e_1(t)$  as before (Setup1) exact and compare to uncorrelated approximations along the line

$$\hat{\rho}(t) \approx \hat{\rho}_{ph}^{(1)}(t) \otimes \hat{\rho}_e^{(2)}(t) \text{ and } \approx \hat{\rho}_{ph}^{(1)}(t) \otimes \hat{\rho}_1^{(1)}(t) \otimes \hat{\rho}_2^{(1)}(t)$$

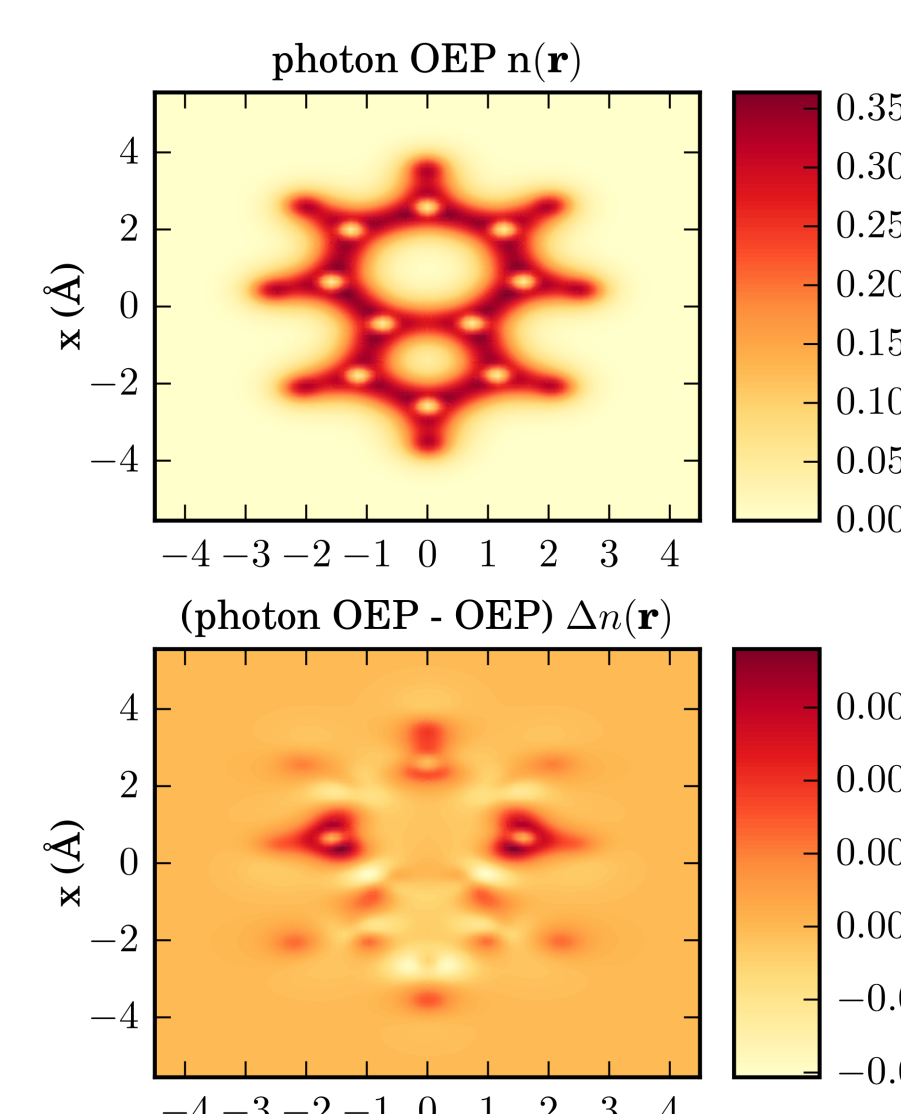
$$g/\omega_{ref} = 0.0058, \omega_{ref} = 2.340 \text{ eV}$$



## First-principles tools

### Electron-Photon OEP

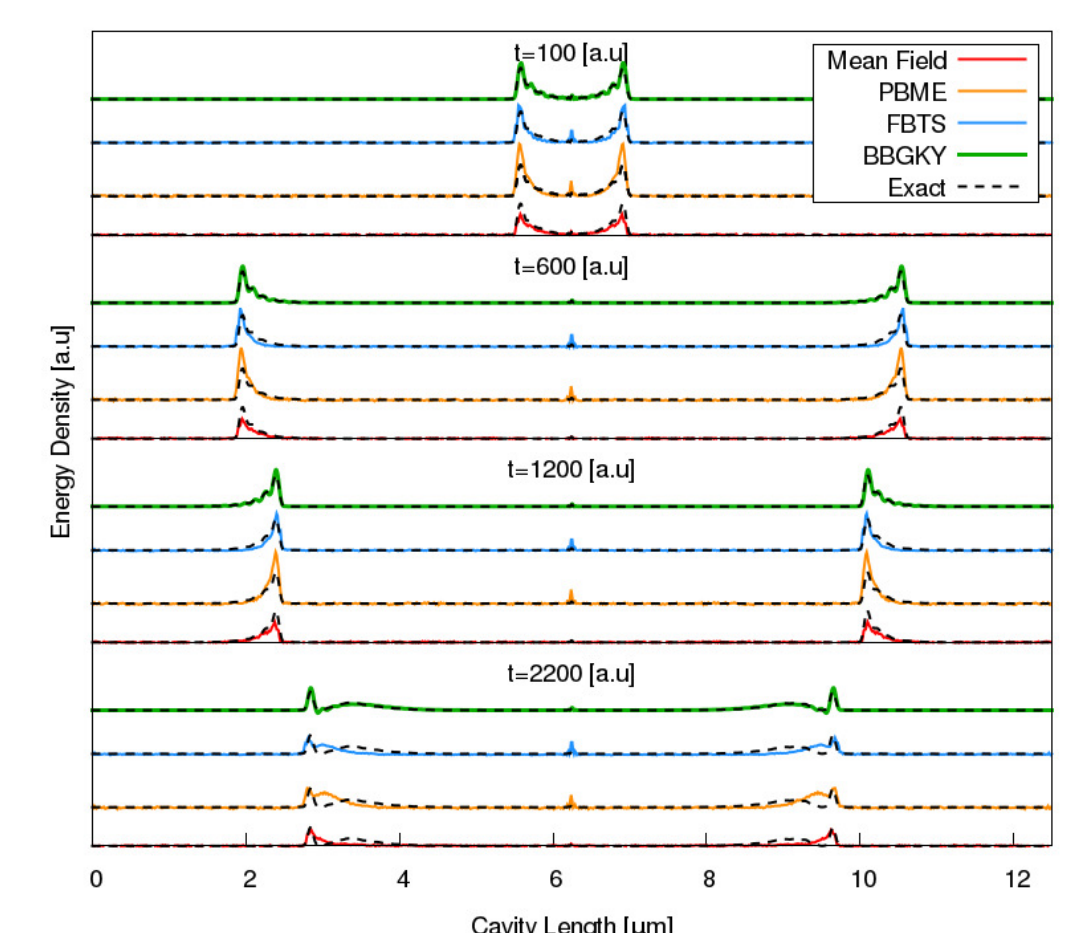
Connection of DFT and many-body perturbation theory opens a path for the development of accurate functionals. Its limitation is based on the order of perturbation diagram included.[4]



Also strongly correlated approaches  $\phi_s(rq, t)$  are possible. [7]

### 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]



## References

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