Theoretical Methods for Dynamics of Correlated Electrons, Ions and Photons

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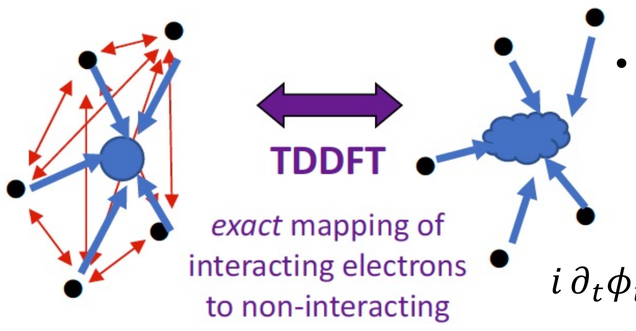
Electron Dynamics via TDDFT

Time-dependent density functional theory (TDDFT) is the most widely used method to get electronic excitations and dynamics in molecules and solids.



Our work:

- Build improved approximations for the exchange-correlation potential (v_{XC}), especially for cases where the usual approximations fail.

$$i\,\partial_t \phi_i(\mathbf{r},t) = (-\nabla^2/2 + v_s(\mathbf{r},t))\phi_i(\mathbf{r},t)$$

$$v_s[n;\Phi_0](\mathbf{r}t) = v_{ext}(\mathbf{r}t) + \int d^3r' \frac{n(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{XC}[n;\Psi_0,\Phi_0](\mathbf{r}t)$$

In particular:

Dependence of v_{XC} on the density $n(\mathbf{r},t)$ at earlier times and the initial states. → **Memory is missing from the usual approximations**

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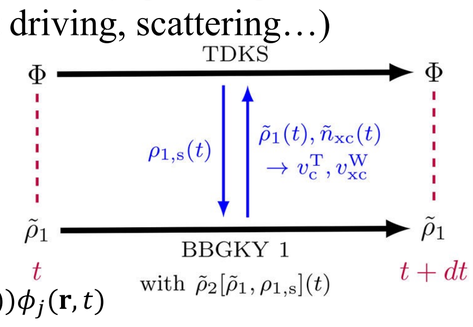
Inaccurate dynamics (e.g.: charge-transfer, resonant driving, scattering…)

Our **density-matrix coupled approach** has memory, and satisfies exact conditions important for time-dynamics:



Propagate side-by-side

$$i\,\partial_t \phi_j(\mathbf{r},t) = (-\nabla^2/2 + v_{ext}(\mathbf{r},t) + v_H(\mathbf{r},t) + v_{XC}(\mathbf{r},t))\phi_j(\mathbf{r},t)$$

$$\nabla\cdot(n\nabla v_{xc}) = \nabla\cdot\Big[\underbrace{\tfrac{1}{4}(\nabla'-\nabla)(\nabla^2-\nabla'^2)(\rho_1(\mathbf{r}',\mathbf{r},t)-(\rho_{1,s}(\mathbf{r}',\mathbf{r},t))|_{r'=r}}_{v_c^T} + \underbrace{n(\mathbf{r},t)\int n_{XC}(\mathbf{r}',\mathbf{r},t)\nabla w(|r'-r|)dr'}_{v_{xc}^W}\Big]$$

$\tilde{n}_{xc}$

approximation here

$$i\frac{\partial\tilde{\rho}_1}{\partial t} = [-\nabla^2/2 + v_{ext}, \tilde{\rho}_1](\mathbf{r},\mathbf{r}',t) + \int d^3\bar{r}(w(\mathbf{r},\bar{\mathbf{r}}) - w(\mathbf{r}',\bar{\mathbf{r}}))\tilde{\rho}_2[\tilde{\rho}_1,\rho_{1,s}](\mathbf{r},\bar{\mathbf{r}};\mathbf{r}',\bar{\mathbf{r}})$$

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Coupled Electron-Ion Dynamics via EF

- Dynamics of molecules **beyond the Born-Oppenheimer approximation** is increasingly relevant in many areas, e.g. photo-induced processes, solar-cell design, biomolecular mechanism modeling.
- The **Exact Factorization (EF)** approach allows to understand how quantum subsystems' dynamics influence each other, and to **develop mixed quantum-classical methods**.

$$\hat{H} = \hat{H}_{BO} + V^e_{ext}(\underline{r},t) + \hat{T}_n(\underline{R}) + V^n_{ext}(\underline{R},t) \qquad \hat{H}\Psi(\underline{r},\underline{R},t) = i\,\partial_t\Psi(\underline{r},\underline{R},t)$$

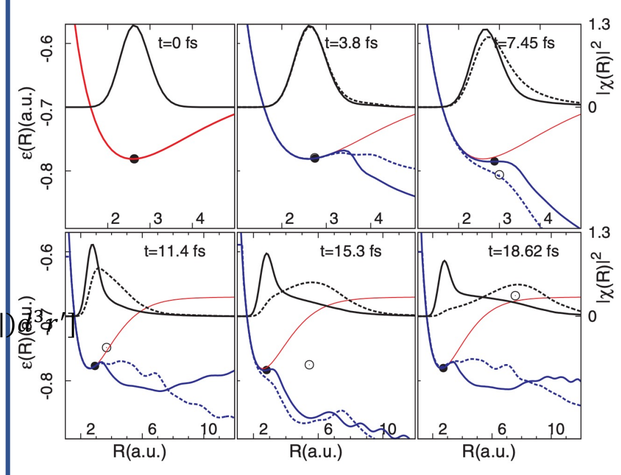
$$\hat{H}_{BO} = \hat{T}_e(\underline{r}) + W_{ee}(\underline{r}) + V_{en}(\underline{r},\underline{R}) + W_{ee}(\underline{R})$$

EF

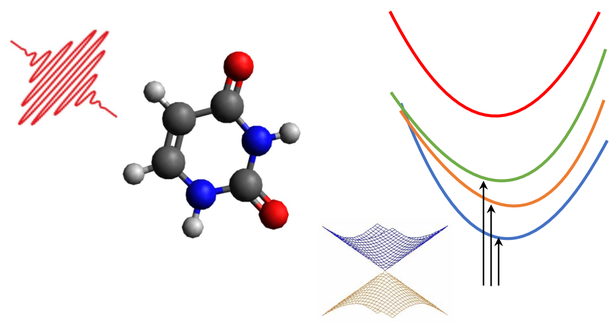
$$\Psi(\underline{r},\underline{R},t) = \Phi_{\underline{R}}(\underline{r},t)\chi(\underline{R},t) \quad \text{where} \quad \int d\underline{r}|\Phi_{\underline{R}}(\underline{r},t)|^2 = 1$$

- The exact equations for χ and Φ_R contain potentials that **exactly capture the electron-nuclear correlation**. They give rise to rigorous mixed quantum-classical methods, including surface-hopping approaches with first-principles decoherence corrections.

Exact potential driving electron in laser driven molecular dissociation



- Coupled-trajectory approach based on the exact electron-nuclear correlation from the EF to describe quantum (de)-coherence in large molecules



Dynamics of excited uracil cation: quantum (de)-coherence can be treated correctly at the same computational cost as the original SH dynamics.

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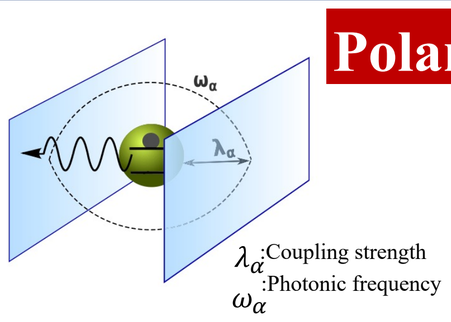
Polaritonic Chemistry



Molecule in a nanoscale cavity greatly enhances the light-matter coupling strength

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Hybrid light-matter states (*polariton*)
Quantized nature of light becomes important

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Manipulate light and matter properties (recent experimental advances in cavity QED)

Our work:

Exact factorization and trajectory methods to gain insight and model the new phenomena

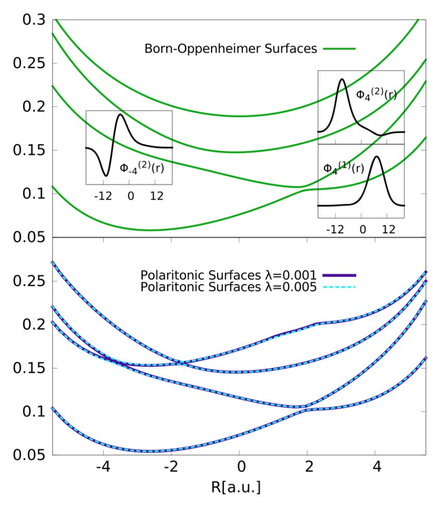
$$\Psi(\underline{r},\underline{R},\underline{q},t) = \chi(\underline{q},t)\Phi_{\underline{q}}(\underline{r},\underline{R},t) = \chi(\underline{R},t)\Phi_{\underline{R}}(\underline{r},\underline{q},t) = \chi(\underline{r},t)\Phi_{\underline{r}}(\underline{q},\underline{R},t)$$

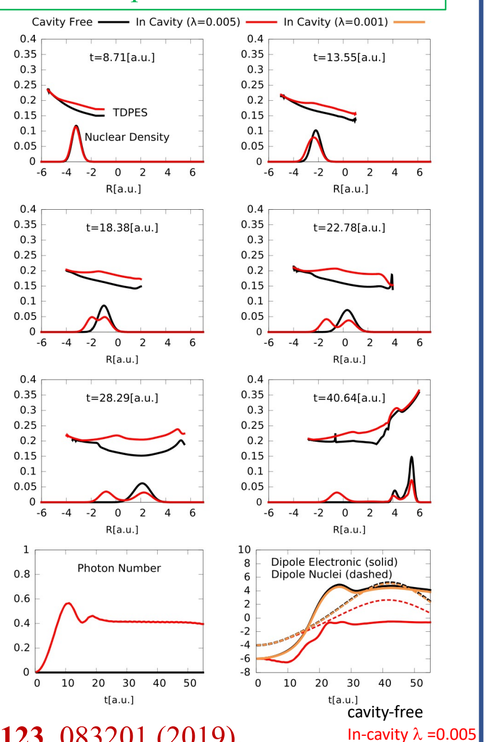
- TDSE for the photons
- corrections to the quadratic form due to matter-photon coupling

- TDSE for the nuclei
- Exact potential driving the nuclei coupled to electrons and photons

- EF gives cavity-modified time-dependent potential energy surfaces for proton-coupled electron transfer that directly indicate suppression:

Ehrenfest trajectories for photons' displacement field coordinates work well.





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Electronic Embedding via EF (EVEF)

Systems containing *strong correlation* require us to go beyond usual density-functional methods. We are developing a new, practical, first-principles **quantum electronic embedding based on exact factorization (EF) in Fock Space**:

For $H\Psi = E\Psi$, factorize

$$\Psi(n_1,n_2,..n_k,n_{k+1},..n_M) = \chi(\underline{n})\Phi_{\underline{n}}(\underline{m})$$

$\underline{\tilde{n}}$ $\underline{\tilde{m}}$

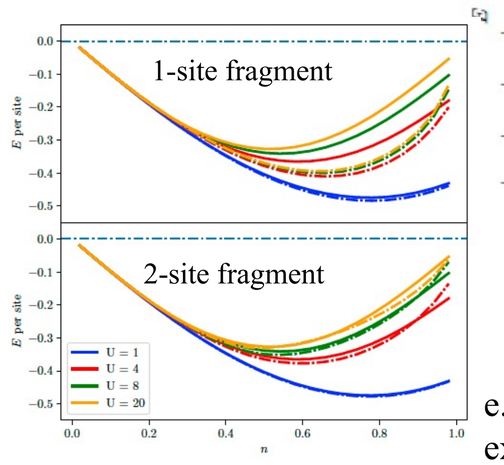
Site-occupations for chosen fragment, e.g. those with strongly-correlated orbitals

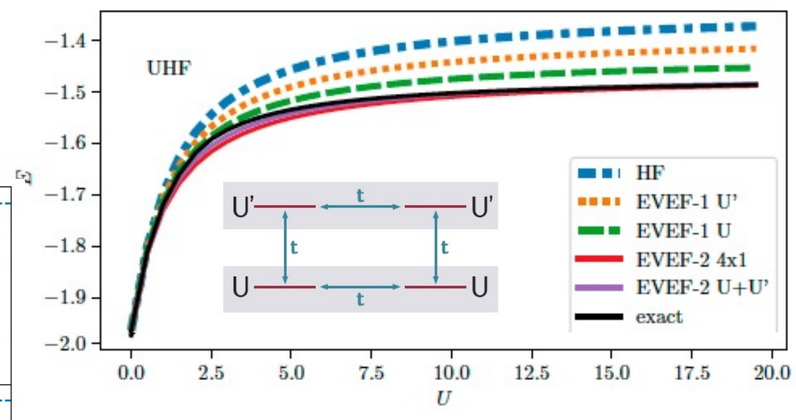
$$\sum_{\underline{m}}\Phi^*_{\underline{n}}(\underline{m})\Phi_{\underline{n}}(\underline{m}) = 1$$

Embedding Hamiltonian: $h_{\underline{n};\underline{n}'} \equiv \sum_{\underline{m}',\underline{m}} \Phi^*_{\underline{n}}(\underline{m})H_{\underline{n},\underline{m};\underline{n}',\underline{m}'}\Phi_{\underline{n}'}(\underline{m}')$

Use mean-field method→Ψ→extract $\Phi_{\underline{n}}$ and embedding h →solve $h\chi = E\chi$ for fragment χ with high-level method→accurate energy E

e.g. Hubbard tetramer: two sites with fixed interaction $U' = 0.1$ and two sites with variable U





- **EVEF captures full range of weak to strong correlation well.**

e.g. 100-site uniform Hubbard ring, EVEF (dash-dot), exact (solid)

L. Lacombe and N. T. Maitra, Phys. Rev. Lett. **124**, 206401 (2020)

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