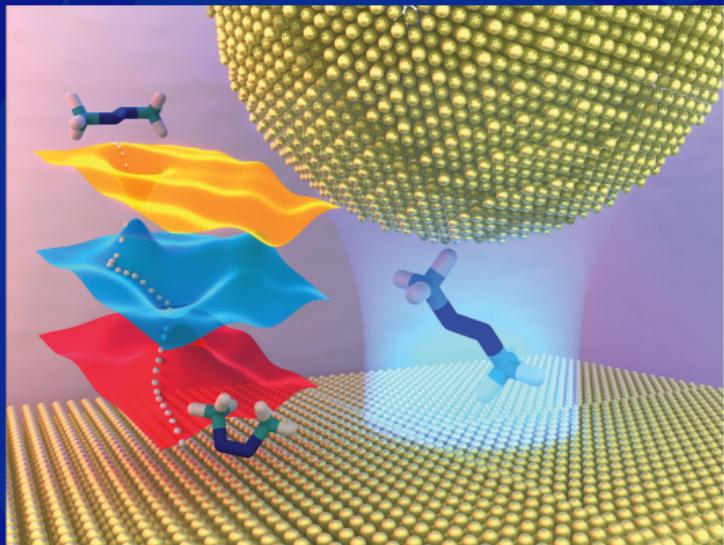


Light-Matter Hybridization and Entanglement from the First Principles

Yu Zhang

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Outline

Motivation

Variational Quantum Electrodynamics (QED) Hartree-Fock theory

Squeezing ansatz and light-matter entanglement

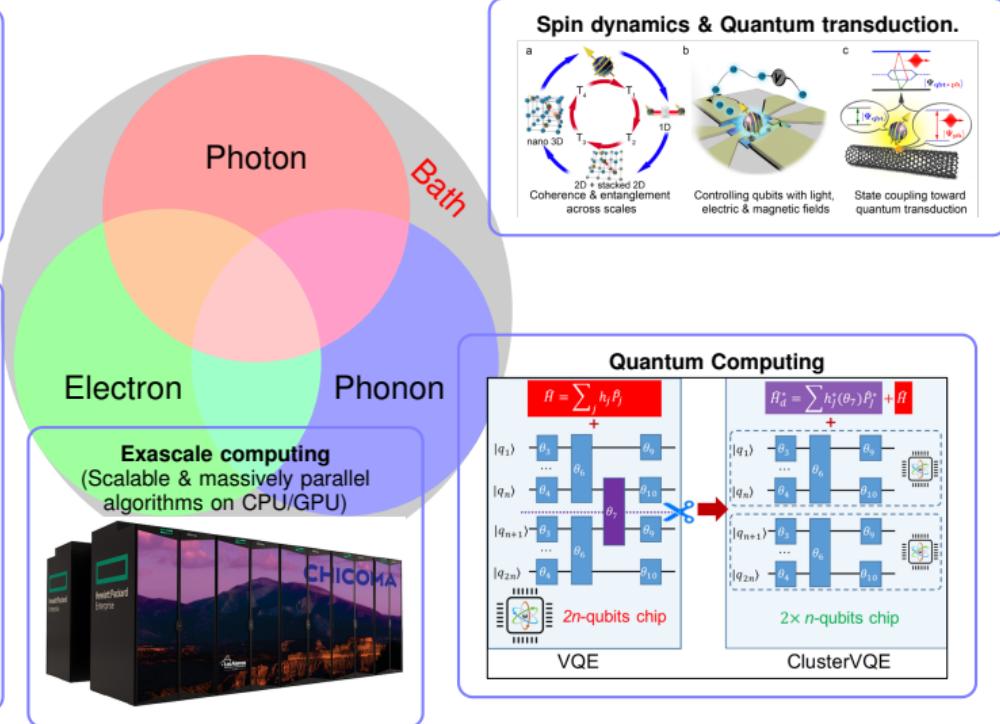
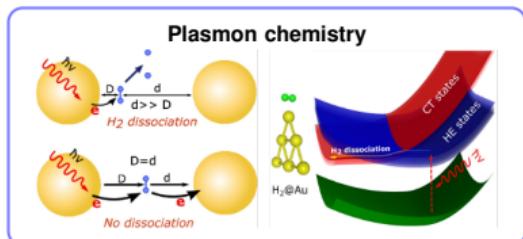
Quantum Monte Carlo methods for polariton chemistry

First-principles argumented methods toward collective coupling regime

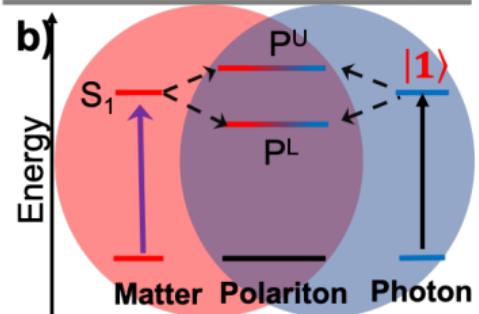
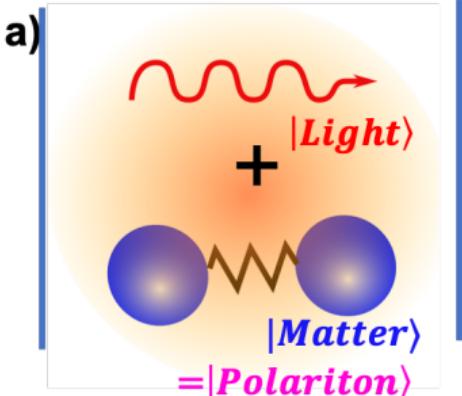


Light-Matter interactions

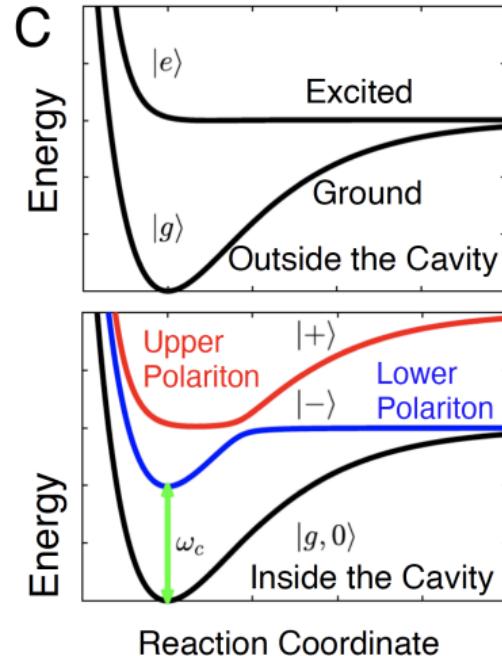
Understand and control the emergent matter behaviors that emerge from complex correlations of atomic, electronic, and photonic constituents



Polariton & polariton physics/chemistry



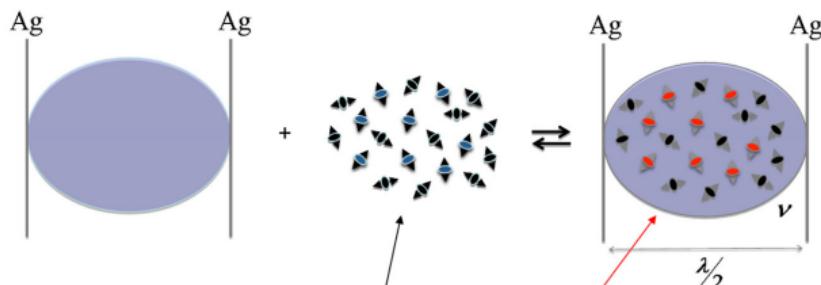
Polariton is a hybrid light-matter state.



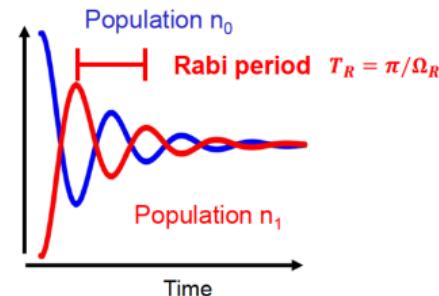
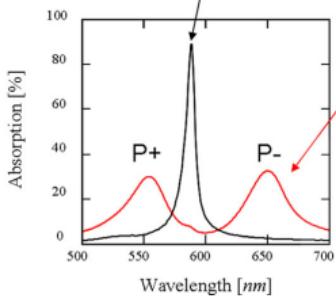
Molecular properties become tunable via the formation of polariton.

How strong is the “strong coupling”

a Cavity mode



b

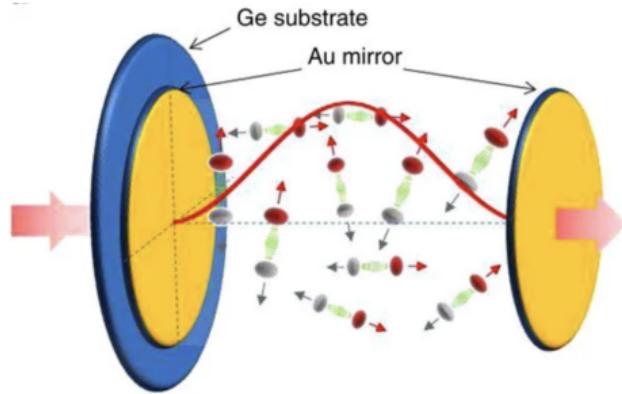


- Coupling should be strong enough to compete with or overcome each individual's dissipation or dephasing (line-width).
- The coupling strength can be characterized by the energy difference (Rabi splitting) between upper and lower polariton states.

Ways of achieving strong couplings and corresponding modeling challenges

Coupling strength is $\propto \sqrt{N/V}$, N number of molecules, V cavity volume.

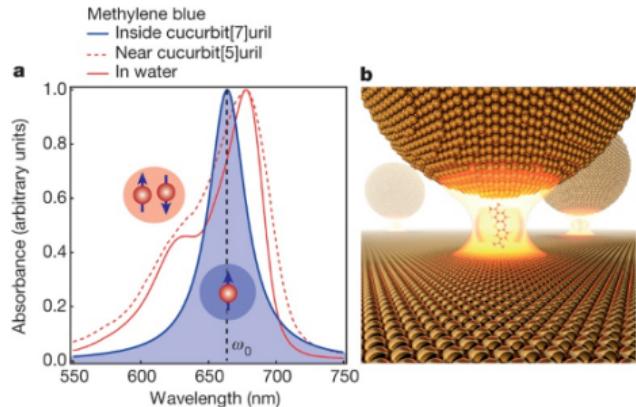
Photonic cavity – many molecules



Nat. Commun. 6, 5981 (2015)

- Pros: High quality (weak dissipation)
- Cons: large cavity volume ($\sim \lambda^3$ or $\sim um^3$), Many molecules (10^6 or more) are required.

Plasmonic cavity – Few molecules

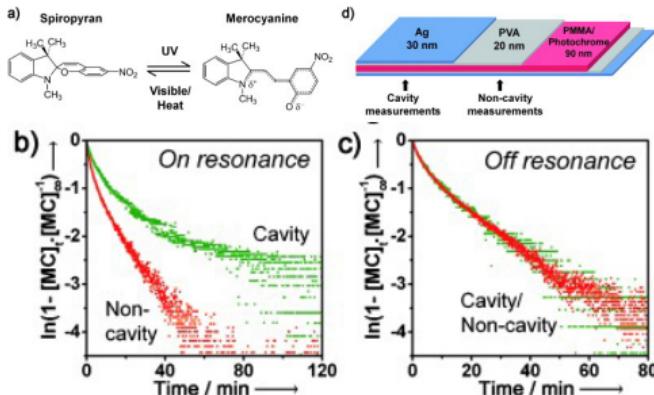


Nature 535, 127(2016).

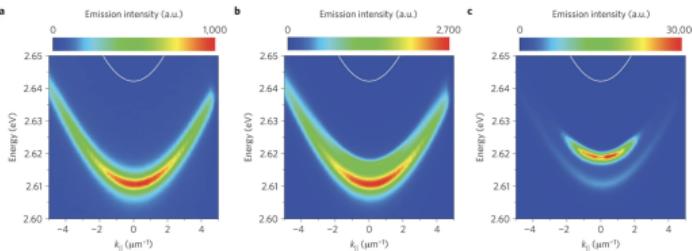
- Pros: Small mode volumes ($\sim nm^3$), stronger electric field.
- Cons: Lossy (strong dissipation)

Experimental demonstrations

Exciton-polariton

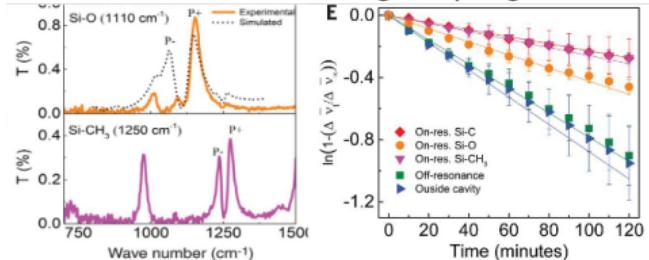


Angew. Chem., Int. Ed. 2012, 51, 1592 (2012)

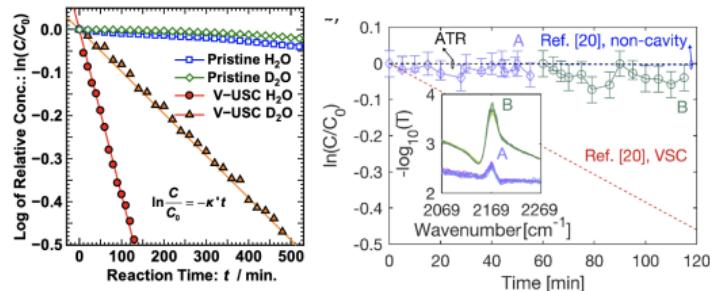


Nat. Mat. 13, 247 (2014)

Vibrational strong coupling



Science 363, 615 (2019)



chemRxiv:7234721 (2018); JCP 154, 191103 (2021);

Controversies in the field call for new atomistic methods to understand the underlying physics

Negligible Effect of Vibrational Polaritons on Chemical Reaction Rates via the Density of States Pathway

Igor Vurgaftman,* Blake S. Simpkins, Adam D. Dunkelberger, and Jeffrey C. Owrutsky



Cite This: *J. Phys. Chem. Lett.* 2020, 11, 3557–3562



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ABSTRACT: We show that the polariton density of states in planar optical cavities strongly coupled to vibrational excitations remains much lower than the density of vibrational states even at the frequency of the lower and upper polaritons under most practical circumstances. The polariton density of states is higher within a narrow window only when the inhomogeneous line width is at least an order of magnitude smaller than the Rabi splitting. Therefore, modification of reaction rates via the density-of-states pathway appears small or negligible for the scenarios reported in the literature. While the polariton density of states is bounded from above by the free-space optical density of states in dielectric cavities, it can be much higher for localized phonon polariton modes of nanoscale particles. We conclude that other potential explanations of the reported reactivity changes under vibrational strong coupling should be examined.

Cavity-enabled enhancement of ultrafast intramolecular vibrational redistribution over pseudorotation

Teng-Teng Chen^{1†}, Matthew Du^{1†}, Zimo Yang^{2†}, Joel Yuen-Zhou^{1*}, Wei Xiong^{1,2,3*}

Vibrational strong coupling (VSC) between molecular vibrations and microcavity photons yields a few polaritons (light-matter modes) and many dark modes (with negligible photonic character). Although VSC is reported to alter thermally activated chemical reactions, its mechanisms remain opaque. To elucidate this problem, we followed ultrafast dynamics of a simple unimolecular vibrational energy exchange in iron pentacarbonyl $[Fe(CO)_5]$ under VSC, which showed two competing channels: pseudorotation and intramolecular vibrational-energy redistribution (IVR). We found that under polariton excitation, energy exchange was overall accelerated, with IVR becoming faster and pseudorotation being slowed down. However, dark-mode excitation revealed unchanged dynamics compared with those outside of the cavity, with pseudorotation dominating. Thus, despite controversies around thermally activated VSC modified chemistry, our work shows that VSC can indeed alter chemistry through a nonequilibrium preparation of polaritons.

Liyang Chen, Ashley P. Fidler, Alexander M. McKillop, and Marissa L. Weichman*

Exploring the impact of vibrational cavity coupling strength on ultrafast CN + $c\text{-C}_6\text{H}_{12}$ reaction dynamics

Abstract: Molecular polaritons, hybrid light-matter states resulting from strong cavity coupling of optical transitions, may provide a new route to guide chemical reactions. However, demonstrations of cavity-modified reactivity in clean benchmark systems are still needed to clarify the mechanisms and scope of polariton chemistry. Here, we use transient absorption to observe the ultrafast dynamics of CN radicals interacting with a cyclohexane ($c\text{-C}_6\text{H}_{12}$) and chloroform (CHCl_3) solvent mixture under vibrational coupling of a C–H stretching mode of $c\text{-C}_6\text{H}_{12}$. By modulating the $c\text{-C}_6\text{H}_{12}\text{:CHCl}_3$ ratio, we explore how solvent complexation and hydrogen (H)-abstraction processes proceed under collective cavity coupling strengths ranging from 55–85 cm^{-1} . Reaction rates remain unchanged for all extracavity, on-resonance, and off-resonance cavity coupling conditions, regardless of coupling strength. These results suggest that insufficient vibrational cavity coupling strength may not be the determining factor for the negligible cavity effects observed previously in H-abstraction reactions of CN with CHCl_3 .

Reproducibility of cavity-enhanced chemical reaction rates in the vibrational strong coupling regime

Cite as: *J. Chem. Phys.* 154, 191103 (2021); doi: 10.1063/5.0046307

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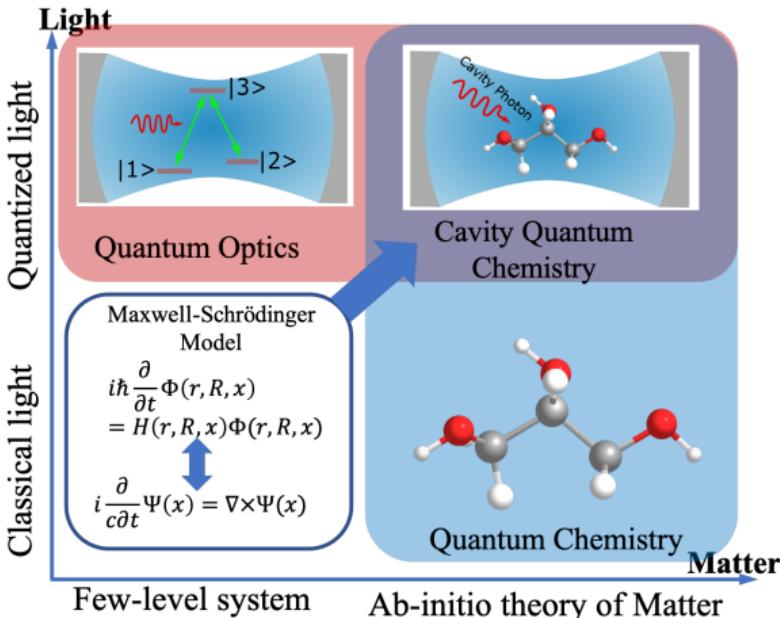


Mario V. Imperatore,¹ John B. Asbury,² and Noel C. Giebink^{1,3*}



Challenge of ab-initio modeling of polariton chemistry/physics

Light-Matter interaction is fundamentally a multiscale problem with multiple interactions across different time/length scales.



Cavity

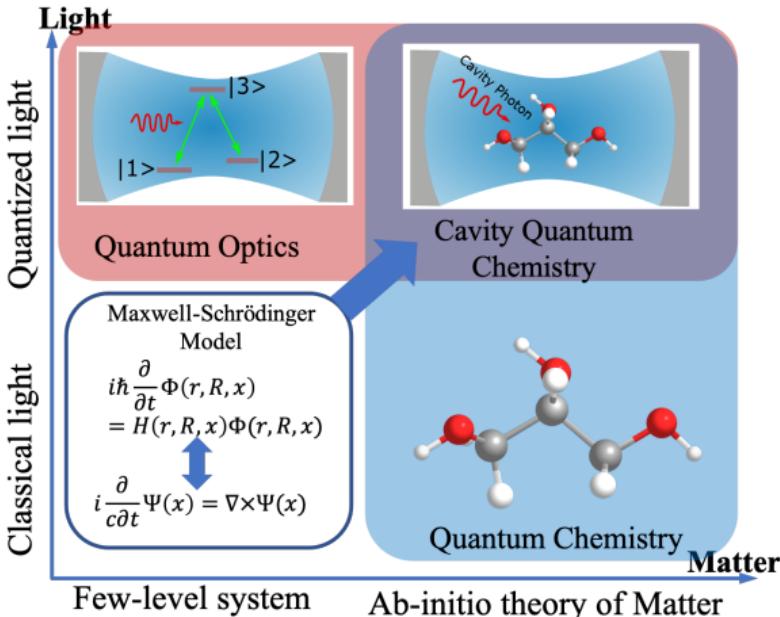
- Realistic cavity property needs to be solved from Maxwell's equations
- Heterogenous field in nanoplasmonic cavities
- Multimode cavity

Molecule:

- Realistic molecule/materials with (strong) correlations (HF, Post-HF)
- Interplay between electronic, photonic, and nuclear DOFs.
- Many molecules and disorders
- Solvent effects

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- Interplay between electronic, photonic, and nuclear DOFs.
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Dynamical interactions among electrons, nuclei, and photons across different time/length scales

Our developments

- Various QEDHF methods
- Quantum Monte-Carlo: Diffusion QMC
- Machine learning approach
- Auxiliary-Field Quantum Monte-Carlo
- QED-Coupled Cluster theories: “Linear-scaling” QED-CC
- Gutzwiller wavefunction method
- Multiscale (Coupled Maxwell-Schrödinger) solvers



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Introduction to the Hamiltonian

The nonrelativistic Pauli-Fierz Hamiltonian for molecular QED in the dipole approximation:

$$\begin{aligned}\hat{H}_{\text{PF}} = & \hat{H}_e + \sum_{\alpha} \left[\omega_{\alpha} (\hat{a}_{\alpha}^{\dagger} \hat{a}_{\alpha} + \frac{1}{2}) \right. \\ & \left. + \sqrt{\frac{\omega_{\alpha}}{2}} \boldsymbol{\lambda}_{\alpha} \cdot \hat{\mathbf{D}} (\hat{a}_{\alpha}^{\dagger} + \hat{a}_{\alpha}) + \frac{1}{2} (\boldsymbol{\lambda}_{\alpha} \cdot \hat{\mathbf{D}})^2 \right].\end{aligned}$$

- \hat{H}_e : electronic Hamiltonian
 $\hat{H}_e = \sum_{\mu\nu} h_{\mu\nu} \hat{c}_{\mu}^{\dagger} \hat{c}_{\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} I_{\mu\nu\lambda\sigma} \hat{c}_{\mu}^{\dagger} \hat{c}_{\lambda}^{\dagger} \hat{c}_{\sigma} \hat{c}_{\nu}.$
- $\sqrt{\frac{\omega_{\alpha}}{2}} \boldsymbol{\lambda}_{\alpha} \cdot \hat{\mathbf{D}} (\hat{a}_{\alpha}^{\dagger} + \hat{a}_{\alpha})$: bilinear coupling term
- $(\boldsymbol{\lambda} \cdot \hat{\mathbf{D}})^2$: Dipole self-energy (DSE)

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- $(\boldsymbol{\lambda} \cdot \hat{\mathbf{D}})^2$: Dipole self-energy (DSE)

Compared to bare electronic Hamiltonian, QED Hamiltonian includes a) electron-electron, b) electron-photon, and c) photon-mediated electron-electron correlations.

Introduction to QEDHF theory

QEDHF ansatz: decompose the wavefunction as a single tensor product of electronic Hartree-Fock reference and Photonic Fock states,

$$|\Psi\rangle = |\text{HF}\rangle \otimes |0_p\rangle ,$$

i.e., single determinant for both electronic and photonic DOFs.

Then QEDHF energy is

$$E_{\text{QEDHF}} = \langle \text{HF} | \hat{H}_e | \text{HF} \rangle + \frac{1}{2} \sum_{\alpha} \langle (\boldsymbol{\lambda}_{\alpha} \cdot \hat{\mathbf{D}})^2 \rangle .$$

The corresponding Fock matrix can be obtained

via $F_{\mu\nu} = \frac{\partial E}{\partial \rho_{\mu\nu}}$.



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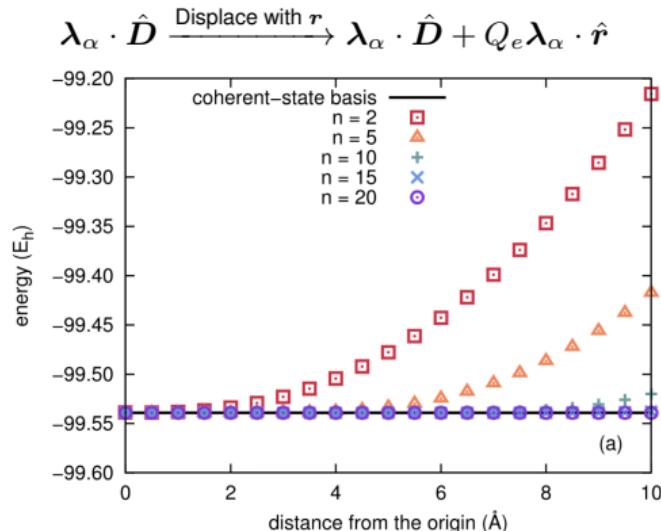
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Chem. Phys. Rev. 4, 041301 (2023)

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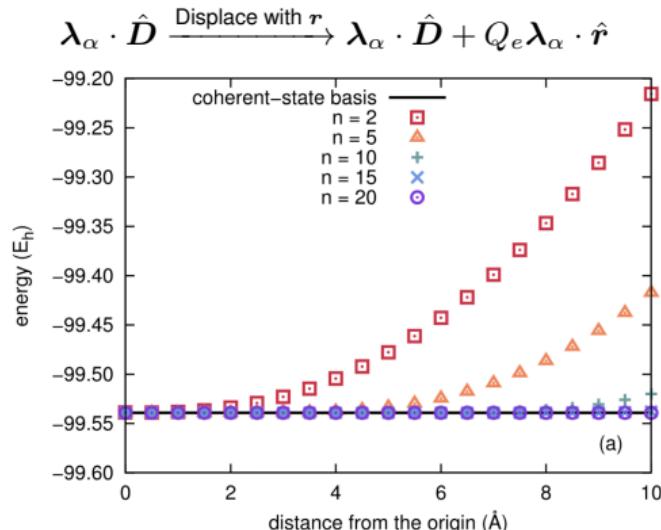
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In principle, QEDHF works for strong coupling, but in practice, QEDHF (in the absence of an infinite basis set) is more like a weak coupling theory.

QEDHF with coherent state

The origin-dependence problem in QEDHF can be mitigated with coherent state (CS) ansatz:

$$|\Psi\rangle = |\text{HF}\rangle \otimes |z_\alpha\rangle$$

where $z = -\frac{\lambda \cdot D}{\sqrt{2\omega}}$ is determined by the coupling strength.

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Coherent state:

$$|z_\alpha\rangle \equiv e^{z_\alpha \hat{a}_\alpha^\dagger - z_\alpha^* \hat{a}_\alpha} |0\rangle \equiv \hat{U}(z_\alpha) |0_p\rangle$$

i.e., it's linear combination of Fock state:

$$|z_\alpha\rangle = e^{-\frac{|z_\alpha|^2}{2}} \sum_{n=0}^{\infty} \frac{z_\alpha^n}{\sqrt{n!}} |n_\alpha\rangle$$

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But the MOs are still origin-dependent since z factor is not a orbital-dependent displacement (example will shown later).



Introduction to sc-QEDHF theory (Polariton (Lang-Firsov) transformation)

In the infinite coupling limite, i.e., $\hat{H}_{ep} + \hat{H}_p \gg \hat{H}_e$, the eigenstates of the PF Hamiltonian is

$$|\Psi^\infty\rangle = e^{-\sum_\alpha \frac{\lambda_\alpha}{\sqrt{2\omega_\alpha}} \mathbf{e}_\alpha \cdot \hat{\mathbf{D}}(\hat{a}_\alpha - \hat{a}_\alpha^\dagger)} |\text{HF}, 0\rangle \equiv \hat{U}_\lambda |\text{HF}, 0\rangle.$$



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Polariton (Lang-Firsov) transformation

$$\hat{H}_{PF} |\Psi\rangle = E |\Psi\rangle \longrightarrow (\hat{U}_\lambda^\dagger \hat{H}_{PF} \hat{U}_\lambda) |\text{HF}, 0\rangle = E |\text{HF}, 0\rangle$$



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Electronic/photonic operators are displaced under the transformation:

$$\hat{U}_\lambda^\dagger \hat{c}_\nu \hat{U}_\lambda = \sum_\nu \hat{c}_\nu X_{\mu\nu},$$

$$\hat{U}_\lambda^\dagger \hat{a}_\alpha \hat{U}_\lambda = \hat{a}_\alpha - \frac{\lambda_\alpha}{\sqrt{2\omega_\alpha}} \mathbf{e}_\alpha \cdot \hat{\mathbf{D}},$$

where

$$X_{\mu\nu} = \exp \left[-\sum_\alpha \frac{\lambda_\alpha}{\sqrt{2\omega_\alpha}} \mathbf{e}_\alpha \cdot \hat{\mathbf{D}}(\hat{a}_\alpha^\dagger - \hat{a}_\alpha) \right] |_{\mu\nu}.$$

Before transformation

$$\hat{H}_{PF} = \hat{H}_e + \sum_\alpha \left[\omega_\alpha (\hat{a}_\alpha^\dagger \hat{a}_\alpha + \frac{1}{2}) + \sqrt{\frac{\omega_\alpha}{2}} \boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{D}} (\hat{a}_\alpha^\dagger + \hat{a}_\alpha) + \frac{1}{2} (\boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{D}})^2 \right].$$

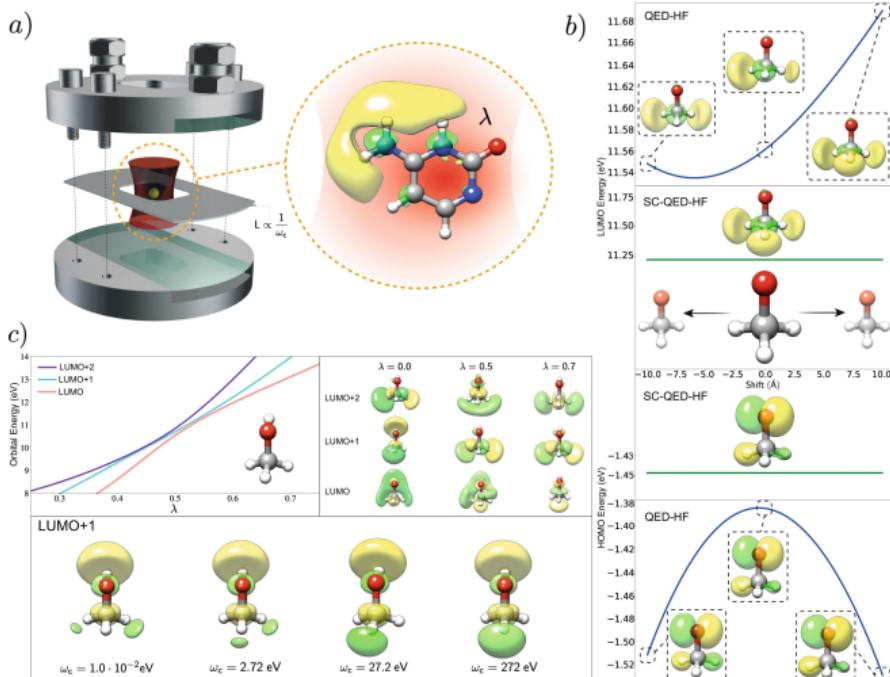
After transformation

$$\tilde{H} = \hat{U}_\lambda^\dagger \hat{H}_e \hat{U}_\lambda + \sum_\alpha \left[\omega_\alpha (\hat{a}_\alpha^\dagger \hat{a}_\alpha + \frac{1}{2}) + \sqrt{\frac{\omega_\alpha}{2}} \boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{D}} (\hat{a}_\alpha^\dagger + \hat{a}_\alpha) + \frac{1}{2} (\boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{D}})^2 \right].$$

Nat. Commun. 13, 1368 (2022).



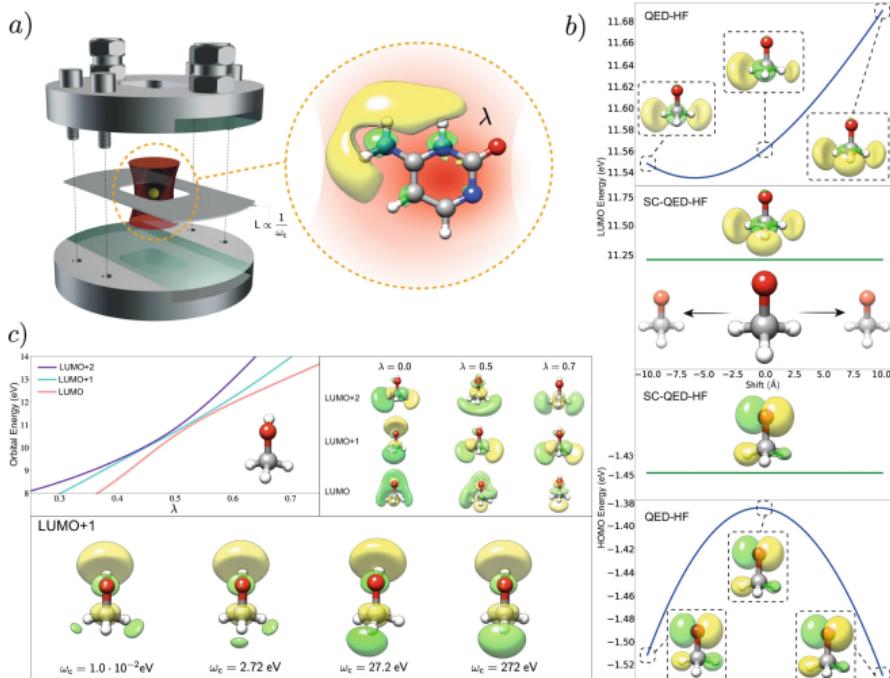
Example of SC-QEDHF method



SC-QEDHF solves the origin-invariance problem in energy and molecular orbitals.

Nat. Commun. 13, 1368 (2022).

Example of SC-QEDHF method



SC-QEDHF solves the origin-invariance problem in energy and molecular orbitals.

But SC-QEDHF only works for (ultra)strong coupling regimes. *Nat. Commun. 13, 1368 (2022).*

Variational transformation for arbitrary coupling strengths

Comparison between polariton transformation and its variational counterpart: $\tilde{H} \equiv \hat{U}^\dagger H_{PF} U$.

Polariton transformation

$$\hat{U}(\lambda) = \exp \left[- \sum_{\alpha} \frac{\lambda_{\alpha}}{\sqrt{2\omega_{\alpha}}} \mathbf{e}_{\alpha} \cdot \mathbf{D} (\hat{a}_{\alpha} - \hat{a}_{\alpha}^{\dagger}) \right]$$

$$\begin{aligned} \tilde{H}_e &= \sum_{\mu\nu} h_{\mu\nu} c_{\mu}^{\dagger} X_{\mu}^{\dagger} c_{\nu} X_{\nu} \\ &+ \sum_{\mu\nu\lambda\sigma} I_{\mu\nu\lambda\sigma} c_{\mu}^{\dagger} X_{\mu}^{\dagger} c_{\nu}^{\dagger} X_{\nu}^{\dagger} c_{\lambda} X_{\nu} c_{\sigma} X_{\nu} \end{aligned}$$

$$\tilde{H}_{ph} = 0$$

where

$$X_{\mu\nu} = \exp \left[- \sum_{\alpha} \frac{\lambda_{\alpha}}{\sqrt{2\omega_{\alpha}}} d^{\alpha} (\hat{a}_{\alpha}^{\dagger} - \hat{a}_{\alpha}) \right] |_{\mu\nu}.$$

- $f_{\alpha} = \lambda_{\alpha}$ leads to polariton transformation
- $f_{\alpha} = 0$ corresponds to no transformation.

Variational polariton transformation

$$\hat{U}(f) = \exp \left[- \sum_{\alpha} \frac{f_{\alpha}}{\sqrt{2\omega_{\alpha}}} \mathbf{e}_{\alpha} \cdot \hat{D} (\hat{a}_{\alpha} - \hat{a}_{\alpha}^{\dagger}) \right]$$

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$$\begin{aligned} \tilde{H}_{ph} &= \sum_{\alpha} \sqrt{\frac{\omega_{\alpha}}{2}} (\Delta \lambda_{\alpha}) \mathbf{e}_{\alpha} \cdot \mathbf{D} (\hat{a}_{\alpha}^{\dagger} + \hat{a}_{\alpha}) \\ &+ \frac{(\Delta \lambda_{\alpha})^2}{2} (\mathbf{e}_{\alpha} \cdot \mathbf{D})^2. \end{aligned}$$

where

$$X_{\mu\nu} = \exp \left[- \sum_{\alpha} \frac{f_{\alpha}}{\sqrt{2\omega_{\alpha}}} \mathbf{e}_{\alpha} \cdot \mathbf{D} (\hat{a}_{\alpha}^{\dagger} - \hat{a}_{\alpha}) \right] |_{\mu\nu}.$$

Variational transformation based self-consistent QEDHF method (VT-QEDHF)

VT-QEDHF ansatz:

$$|\Psi\rangle = \exp \left[- \sum_{\alpha} \frac{f_{\alpha}}{\sqrt{2\omega_{\alpha}}} \mathbf{e}_{\alpha} \cdot \hat{\mathbf{D}} (\hat{a}_{\alpha} - \hat{a}_{\alpha}^{\dagger}) \right] |HF\rangle \otimes |0_p\rangle,$$

VT-QEDHF energy in dipole basis (Eigenstate of $\mathbf{e}_{\alpha} \cdot \hat{\mathbf{D}}$):

$$\begin{aligned} E[\rho, \{f_{\alpha}\}] &= \sum_{pq} \tilde{h}_{pq} \rho_{pq} G_{pq} + \frac{1}{2} \sum_{pqrs} \tilde{I}_{pqrs} \left(\rho_{pq} \rho_{rs} - \frac{1}{2} \rho_{ps} \rho_{rq} \right) G_{pqrs} \\ &\quad + \sum_{\alpha} \frac{(\Delta\lambda_{\alpha})^2}{2} \langle HF | \langle 0 | (\mathbf{e}_{\alpha} \cdot \hat{\mathbf{D}})^2 | HF \rangle | 0 \rangle. \end{aligned}$$

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VT-QEDHF energy in dipole basis (Eigenstate of $\mathbf{e}_{\alpha} \cdot \hat{\mathbf{D}}$):

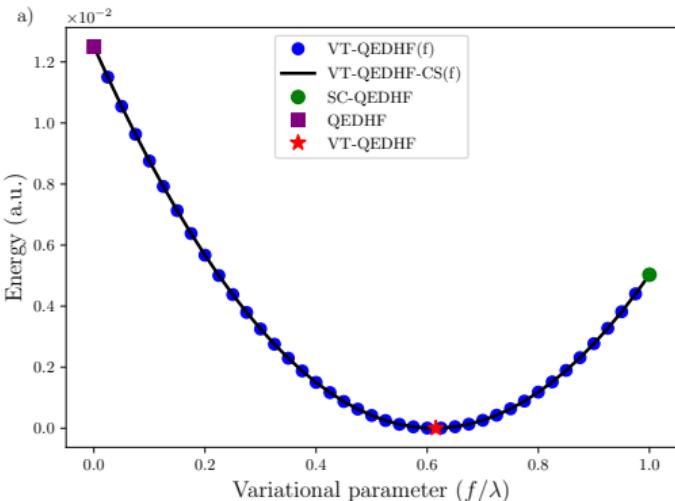
$$\begin{aligned} E[\rho, \{f_{\alpha}\}] &= \sum_{pq} \tilde{h}_{pq} \rho_{pq} G_{pq} + \frac{1}{2} \sum_{pqrs} \tilde{I}_{pqrs} \left(\rho_{pq} \rho_{rs} - \frac{1}{2} \rho_{ps} \rho_{rq} \right) G_{pqrs} \\ &\quad + \sum_{\alpha} \frac{(\Delta\lambda_{\alpha})^2}{2} \langle HF | \langle 0 | (\mathbf{e}_{\alpha} \cdot \hat{\mathbf{D}})^2 | HF \rangle | 0 \rangle. \end{aligned}$$

- The formula is similar to the conventional QEDHF, but lifted all the drawbacks.
- One-body and two-body integrals are dressed by the coupling with f as the indicator of the formation of polariton.
- $G_{pq} = \langle X_p^{\dagger} X_q \rangle$ and $G_{pqrs} = \langle X_p^{\dagger} X_q^{\dagger} X_r X_s \rangle$ are the Franck-Condon factors
- $E_{\text{VT-QEDT}} = \min_{\rho, \{f_{\alpha}\}} E(\rho, \{f_{\alpha}\}) | \int \rho(r) dr = N, 0 \leq f_{\alpha} \leq \lambda_{\alpha} \rangle$.

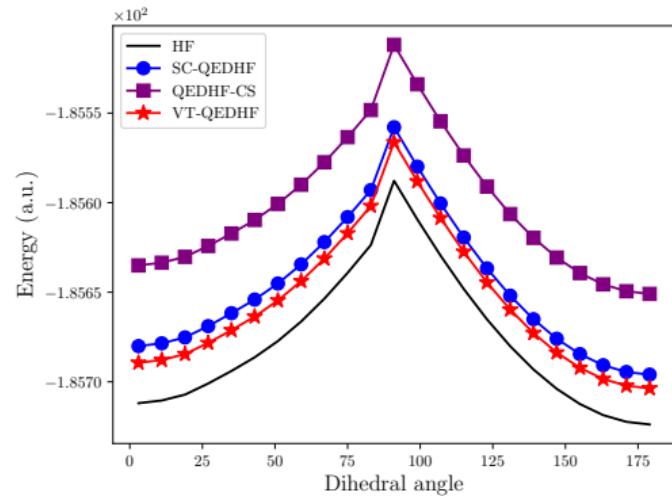
X. Li; Y. Zhang; arXiv:2310.18228;



Examples



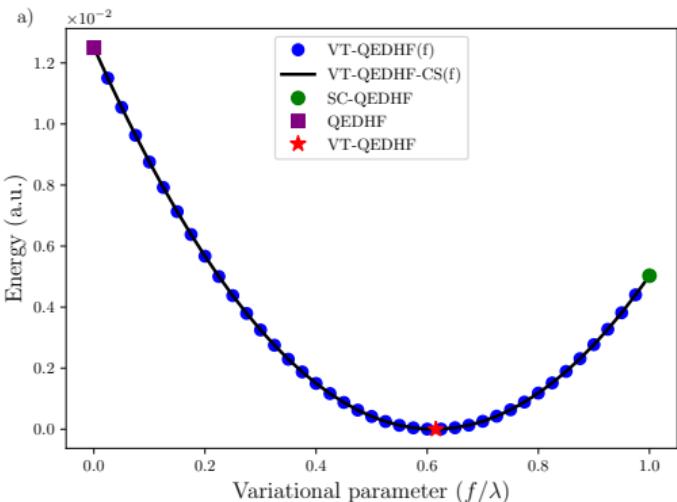
VT-QEDHF connects to QED-HF and SC-QEDHF methods at the two limits.



Ground state potential energy surface of the $C_2N_2H_6$ isomer.



Examples

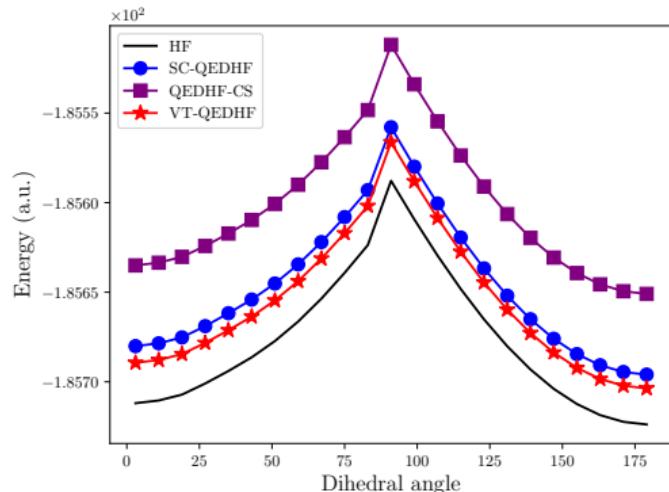


VT-QEDHF connects to QED-HF and SC-QEDHF methods at the two limits.

Due to the more flexibility in the variational optimization:

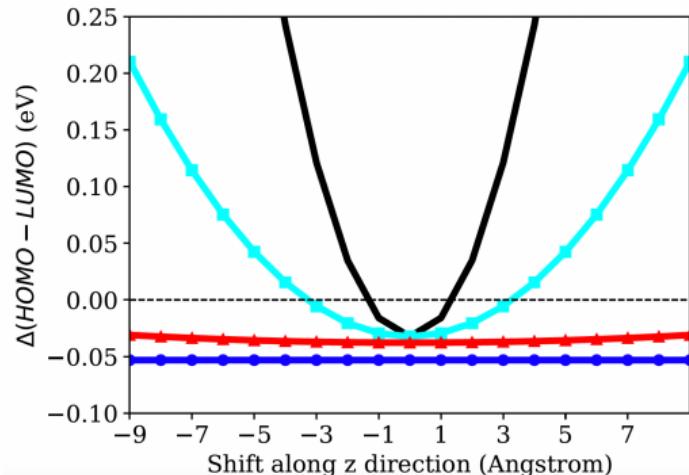
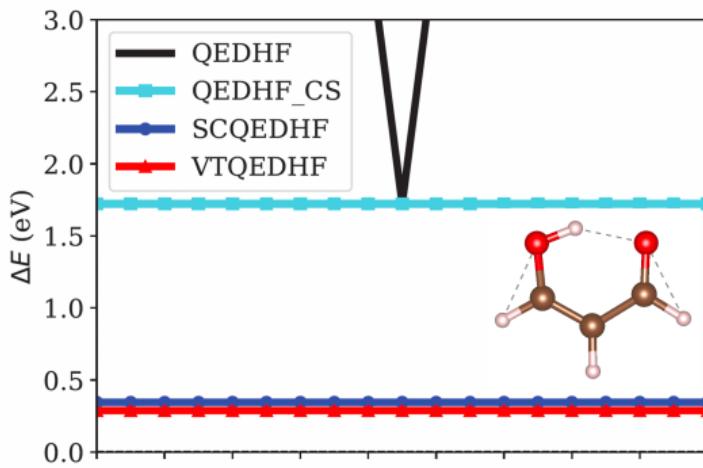
$$E_{\text{VT-QEDHF}}(f) \leq E_{\text{VT-QEDHF}}(f = \lambda) = E_{\text{SC-QEDHF}} \leq E_{\text{QEDHF}}$$

X. Li; Y. Zhang; arXiv:2310.18228;



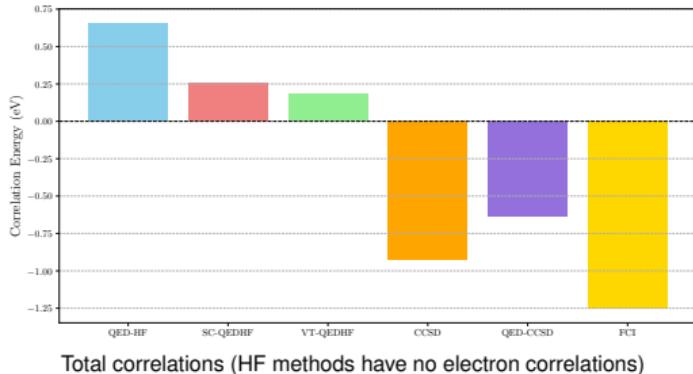
Ground state potential energy surface of the $\text{C}_2\text{N}_2\text{H}_6$ isomer.

Translational invariance of VT-QEDHF methods



VT-QEDHF method conserves origin-independence in both energy and HOMO-LUMO gaps.

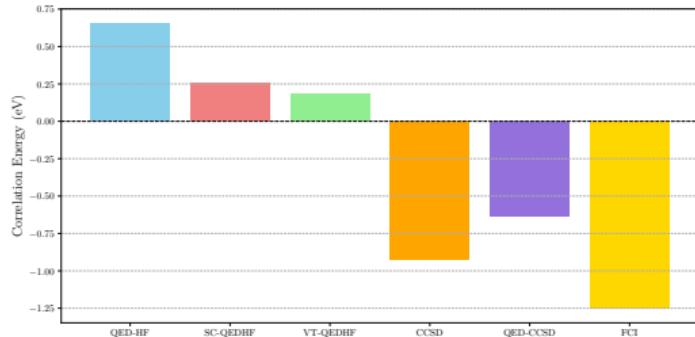
Why mean-field method (or bosonic ansatz) matters?



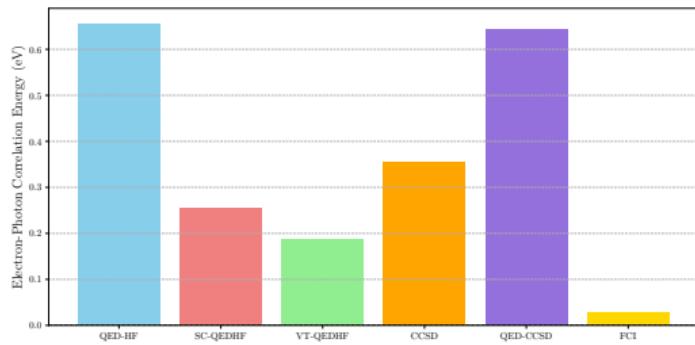
In preparation.



Why mean-field method (or bosonic ansatz) matters?



Total correlations (HF methods have no electron correlations)

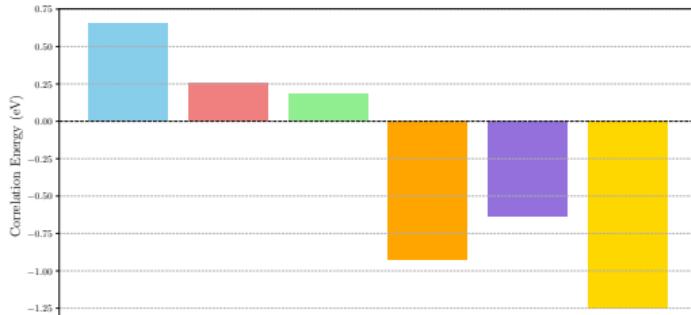


After extracting electron correlations

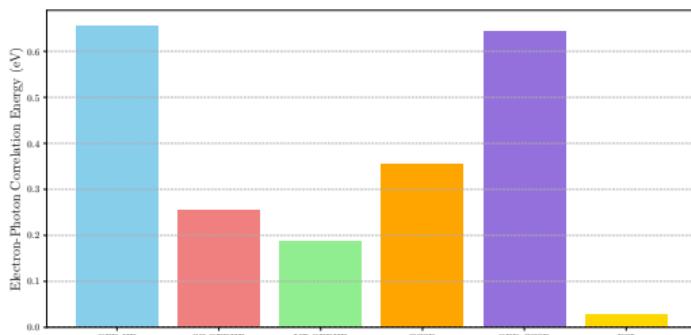
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Why mean-field method (or bosonic ansatz) matters?



Total correlations (HF methods have no electron correlations)



After extracting electron correlations

- Like the conventional HF method, QEHF cannot capture the electron-electron correlation
- Trivial QEDHF overestimates the cavity effect.
- QED-CCSD (with trivial Fock states) does not improve too much on the electron-photon correlation
- But, better photon ansatz can significantly improve the description of electron-photon interactions.

In preparation.



Can we further improve the QEDHF method?

Squeeze operator and uncertainty principle

Uncertainty principle (or Heisenberg's indeterminacy principle): $\Delta x \Delta p > \frac{\hbar}{2}$.

Squeeze operator

$$\hat{S}(F) = \exp \left[\frac{1}{2} (F^* \hat{b}^\dagger - F \hat{a}^{\dagger 2}) \right]$$

can generate squeezed state from the vacuum

$$|F\rangle = \hat{S}(F) |0\rangle$$

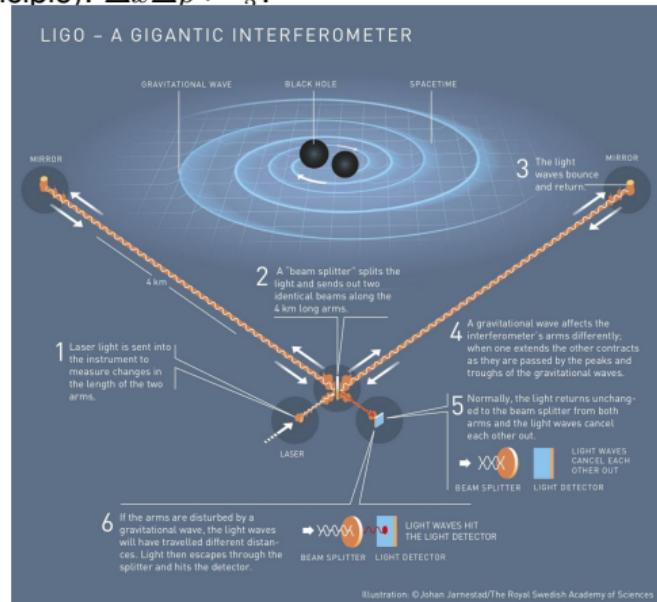
For a quantum harmonic oscillator with frequency ω ,

$$\hat{x} = \sqrt{\frac{2\hbar}{m\omega}} (\hat{a} + \hat{a}^\dagger)$$

The uncertainties of \hat{x} and \hat{p} become,

$$(\Delta x)^2 = \frac{\hbar}{2m\omega} e^{-2F}$$

$$(\Delta p)^2 = \frac{m\hbar\omega}{2} e^{2F}$$



LIGO (Laser Interferometer Gravitational Wave Observatory, Nobel prize in 2017) uses squeezed states to improve the measurement precision.

QEDHF with Variational squeeze ansatz

The ansatz is $|\Psi\rangle = \hat{U}(f)\hat{S}(F)|\text{HF}\rangle \otimes |0_p\rangle$



QEDHF with Variational squeeze ansatz

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The PF Hamiltonian after the transformation becomes,

$$\begin{aligned}\hat{\mathcal{H}}_{CS} = & \hat{\mathcal{H}}_e[\hat{\mathcal{X}}(f_\alpha, F)] + \sum_\alpha e^{-r} \sqrt{\frac{\omega_\alpha}{2}} (\Delta\lambda_\alpha) \mathbf{e}_\alpha \cdot \mathbf{D} (\hat{b}_\alpha^\dagger + \hat{b}_\alpha) \\ & + \frac{(\Delta\lambda_\alpha)^2}{2} (\mathbf{e}_\alpha \cdot \mathbf{D})^2 + \hat{\mathcal{H}}_{ph}.\end{aligned}$$

The dressed photonic Hamiltonian $\hat{\mathcal{H}}_{ph}$ is

$$\hat{\mathcal{H}}_{ph} = \omega_\alpha \left[\cosh(2r)(\hat{b}_\alpha^\dagger \hat{b}_\alpha + \frac{1}{2}) - \sinh(2r)(\hat{b}_\alpha^2 + \hat{b}_\alpha^{\dagger 2}) \right].$$

$\hat{\mathcal{X}}_{ij}$ is

$$\hat{\mathcal{X}}(f, F) = \hat{S}^\dagger(r) \left[e^{-\frac{f_\alpha \boldsymbol{\lambda} \cdot \mathbf{D}}{\sqrt{2\omega}} (\hat{b}_\alpha^\dagger - \hat{b}_\alpha)} \right] \hat{S}(r) = \exp \left[-\frac{f_\alpha \boldsymbol{\lambda} \cdot \mathbf{D}}{\sqrt{2\omega}} (\hat{b}_\alpha^\dagger - \hat{b}_\alpha) e^{r\alpha} \right].$$

QEDHF with Variational squeeze ansatz

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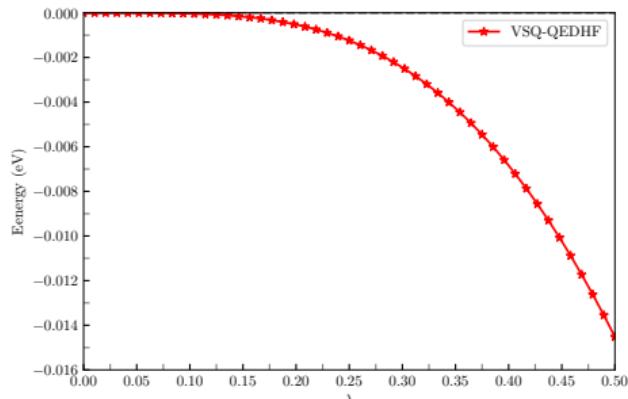
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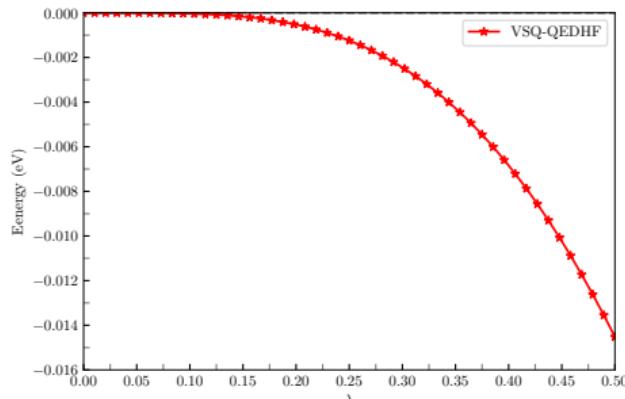
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Squeezing ansatz introduces the anharmonic effect (due to the electron motion) on the photon modes, further lowers down the energy, particularly in the strong coupling regime.

In preparation



Light-matter entanglement

Trial QEDHF has no entanglement with the decoupled ansatz: $|\Psi\rangle = |\text{HF}\rangle \otimes |0_p\rangle$

In preparation



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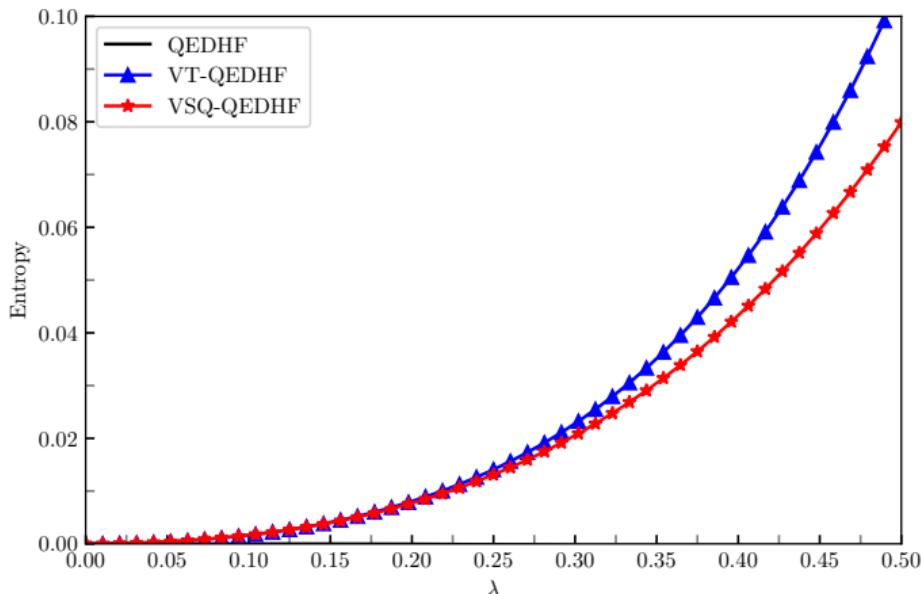
Oct 2nd, 2024 | 25

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Entanglement in VSQ formalism:

$$|\Psi\rangle = e^{-\frac{f\lambda \cdot D(\hat{b} - \hat{b}^\dagger)}{\sqrt{2\omega}}} |\text{HF}\rangle \otimes \hat{S}(F) |0_p\rangle = \sum C_i |i\rangle \otimes |\eta_i, F\rangle$$



In preparation



Outline

Motivation

Variational Quantum Electrodynamics (QED) Hartree-Fock theory

Squeezing ansatz and light-matter entanglement

Quantum Monte Carlo methods for polariton chemistry

First-principles argumented methods toward collective coupling regime



Quantum Monte Carlo method

Most ground-state QMC methods are based on the imaginary time evolution,

$$|\Psi_0\rangle \propto \lim_{\tau \rightarrow \infty} e^{-\tau \hat{H}} |\Psi_T\rangle.$$

that projects out the ground state $|\Psi_0\rangle$ of \hat{H} from any known trial state $|\Psi_T\rangle$ if $\langle\Psi_T|\Psi_0\rangle \neq 0$, which can be obtained iteratively by

$$|\Psi^{(n+1)}\rangle = e^{-\Delta\tau \hat{H}} |\Psi^{(n)}\rangle.$$

Thus, ground-state expectation $\langle\hat{O}\rangle$ of a physical observable \hat{O} is given by

$$\langle\hat{O}\rangle = \lim_{\tau \rightarrow \infty} \frac{\langle\Psi^{(n)}|\hat{O}|\Psi^{(n)}\rangle}{\langle\Psi^{(n)}|\Psi^{(n)}\rangle}$$

QMC methods carry out the iteration by Monte Carlo sampling.

Diffusion Quantum Monte-Carlo for polariton chemistry

The imaginary time Schrodinger equation,

$$\frac{\partial}{\partial \tau} \psi(\mathbf{r}, \tau) = \left(\frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}, \tau),$$

The above equation can be solved via the Green's function,

$$\psi(\mathbf{r}, \tau) = \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}', \tau) \psi(\mathbf{r}', 0),$$

$G(\mathbf{r}, \mathbf{r}', \tau)$ can be approximated by the Trotter-Suzuki splitting of the time-evolution operator,

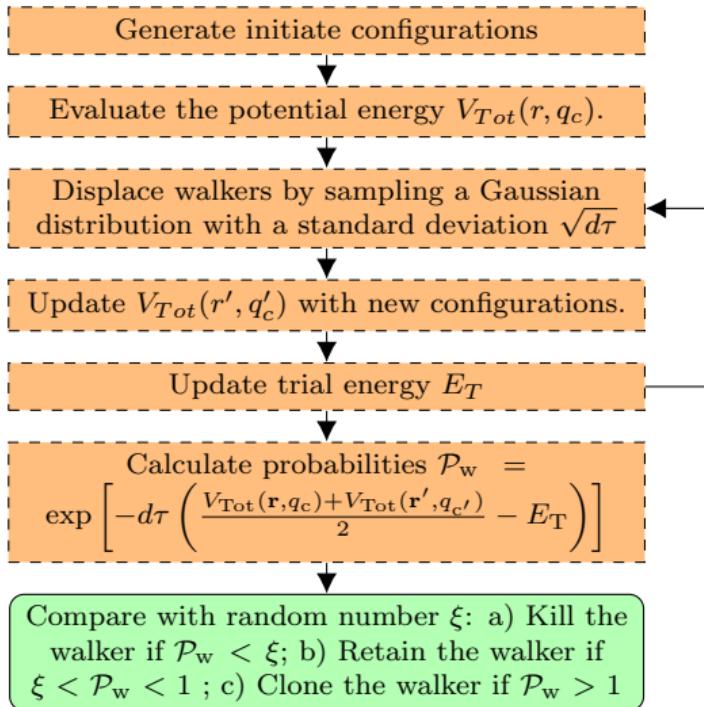
$$G(\mathbf{r}, \mathbf{r}', \tau) = \lim_{d\tau \rightarrow 0} \left[G_T(\mathbf{r}, \mathbf{r}', d\tau) G_{B/D}(\mathbf{r}, \mathbf{r}', d\tau) \right]^{N_s}.$$

where

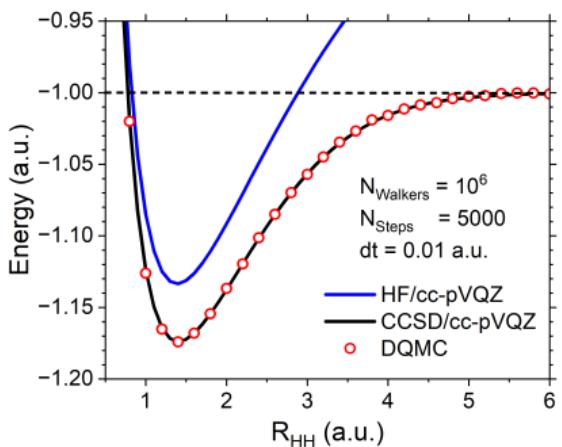
$$G_T(\mathbf{r}, \mathbf{r}', d\tau) = e^{-\frac{(\mathbf{r}-\mathbf{r}')^2}{2d\tau}}$$

$$G_{B/D}(\mathbf{r}, \mathbf{r}', d\tau) = e^{-d\tau \frac{V(\mathbf{r})+V(\mathbf{r}')}{2}}.$$

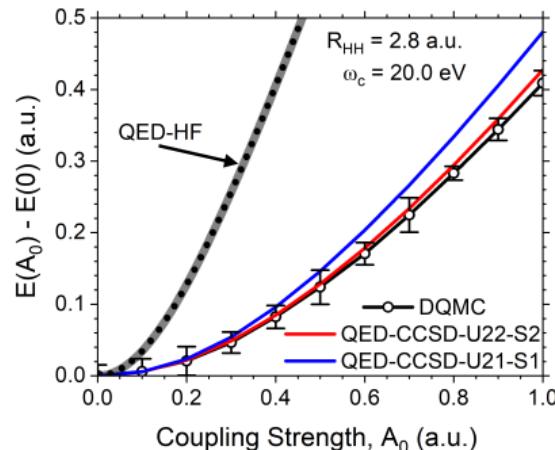
Phys. Rev. A. 109 , 032804 (2023).



Diffusion Monte-Carlo: examples



In the absence of electron-photon coupling, CCSD is exact for a two-electron system.



In the presence of electron-photon coupling, QED-CCSD underestimates the correlations

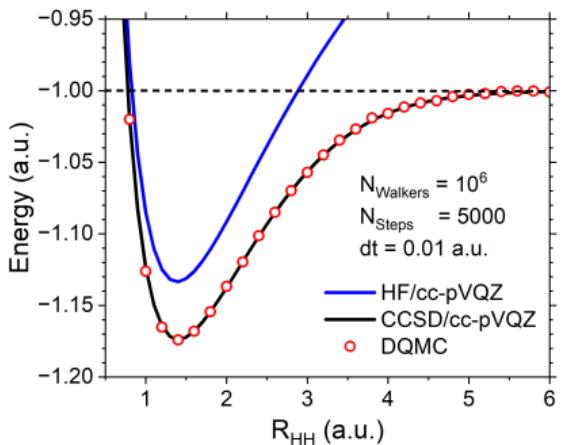
Our DQMC provides a promising route toward the direct and accurate simulation of simple systems.

BTW: QED-CCSD with VT-QEDHF reference leads to the “same results” as QMC.

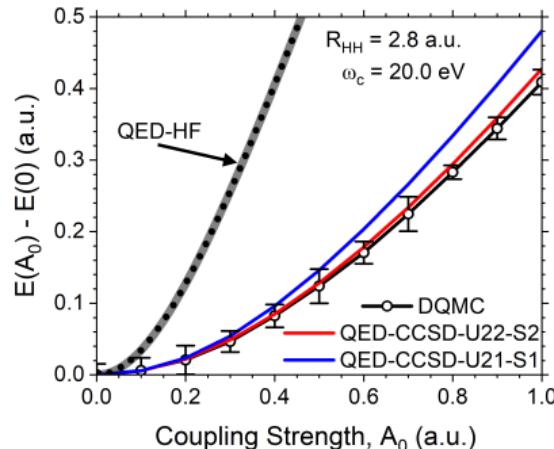
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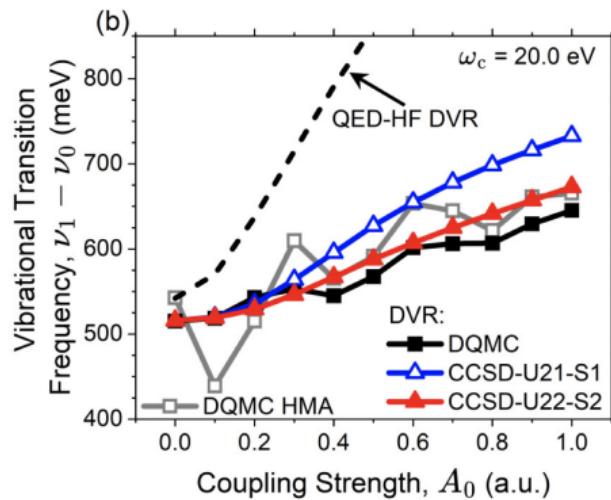
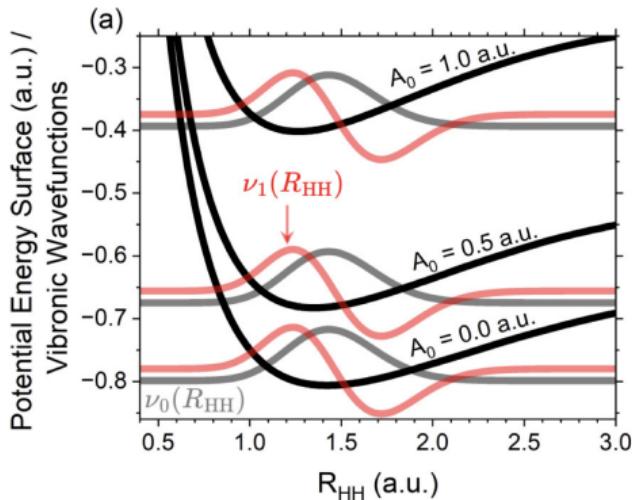
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Diffusion Monte-Carlo computation of vibronic transitions in the cavity



As in the case of the ground-state energy itself, with increasing coupling strength, the HF approach overestimates the cavity effects. The DQMC approach suggests the weakest effects

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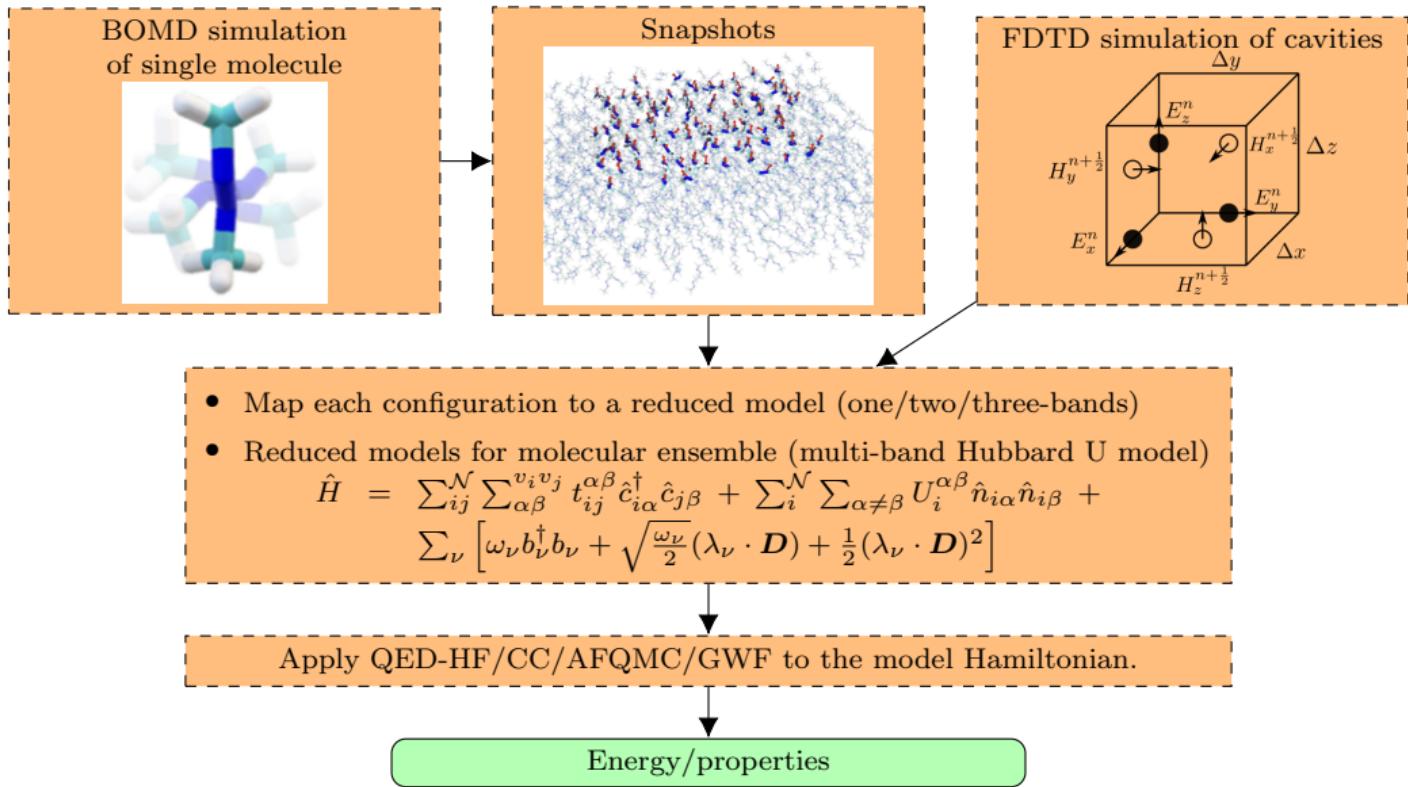
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Who cares about single-molecule in cavity?

First-principles augmented model Hamiltonian for many molecules



Acknowledgement

LANL collaborators

- **Braden Weight** (GRA, UR)
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- Anders Niklasson (T-1)
- Sergei Tretiak (T-1)
- Kipton Barros (T-1)
- Han Htoon (MPA-CINT)



External collaborators:

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- Thomas Frauenheim (Bremen)
- Hua Guo (UNM)
- Yihan Shao (OU)
- Pengfei Huo (UR)
- Garnet Chan (Caltech)
- Chih-Feng Wang (PNNL)

All the developed code is available (or to be available) on Github



OpenMS: Multiscale solvers for coupled Maxwell-Schrödinger equations in **Open** quantum environments.

