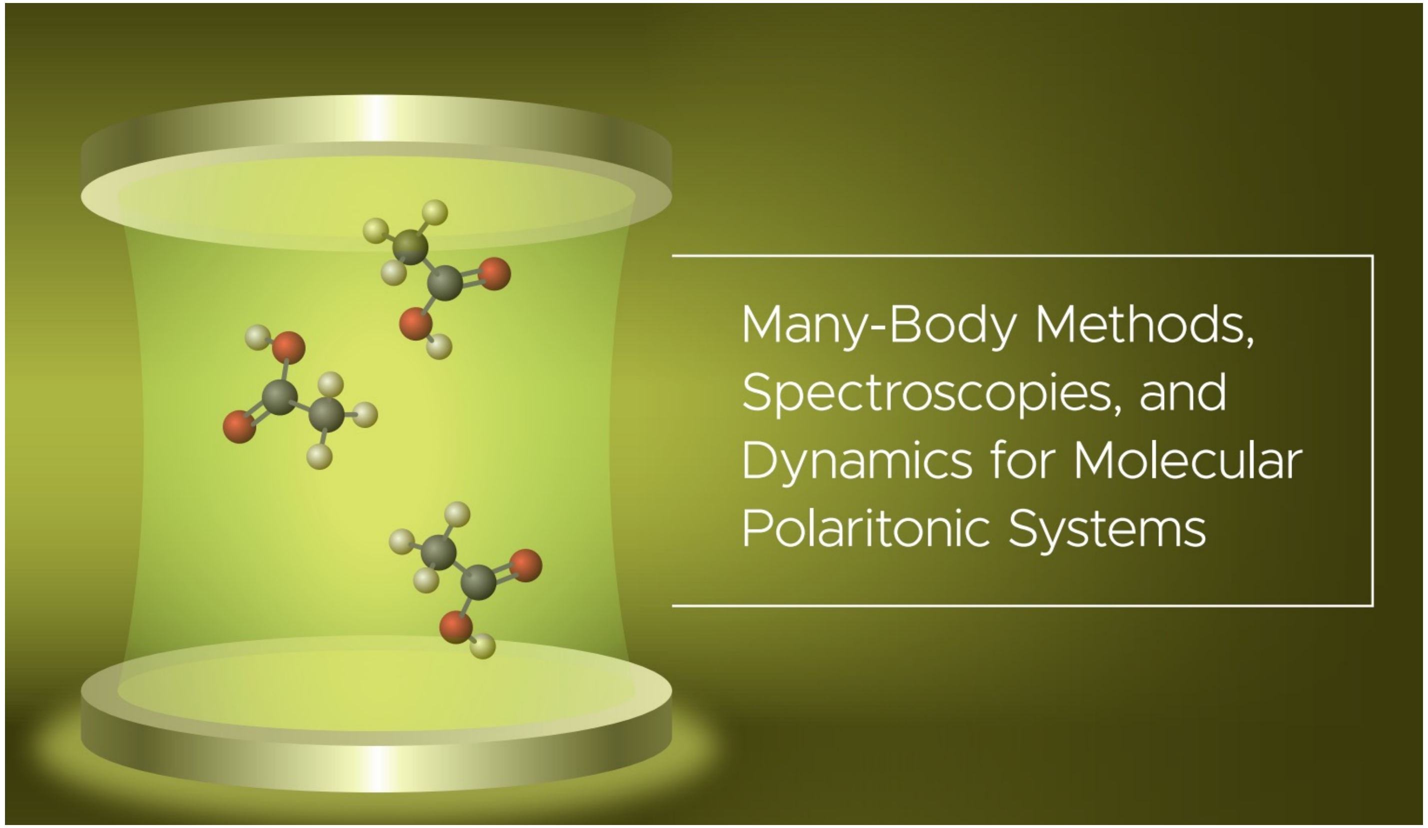
Jay Foley, Associate Professor
UNC Charlotte Department of Chemistry
https://foleylab.github.io/

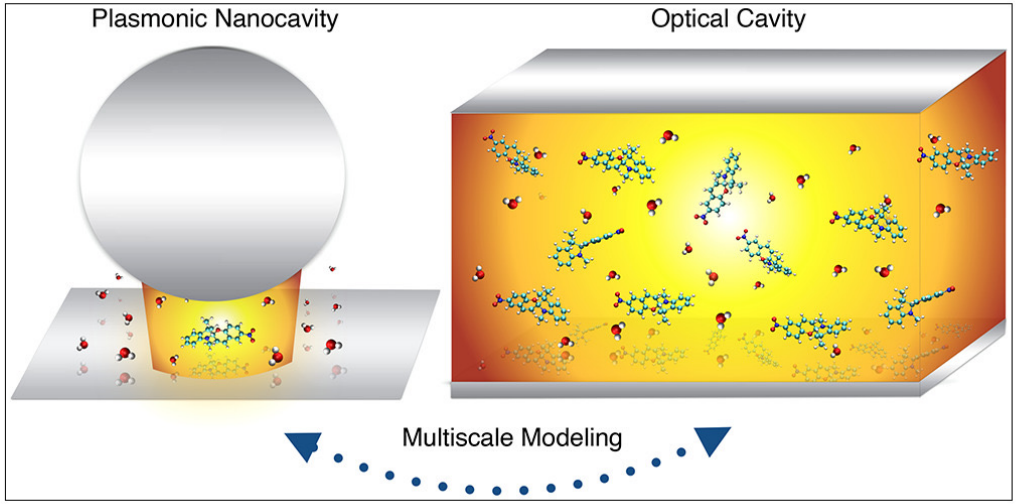


Ingredients of polaritonic chemistry

Strong interaction between light and molecular excitations

$\hbar g > \hbar\gamma \rightarrow$ Strong Coupling

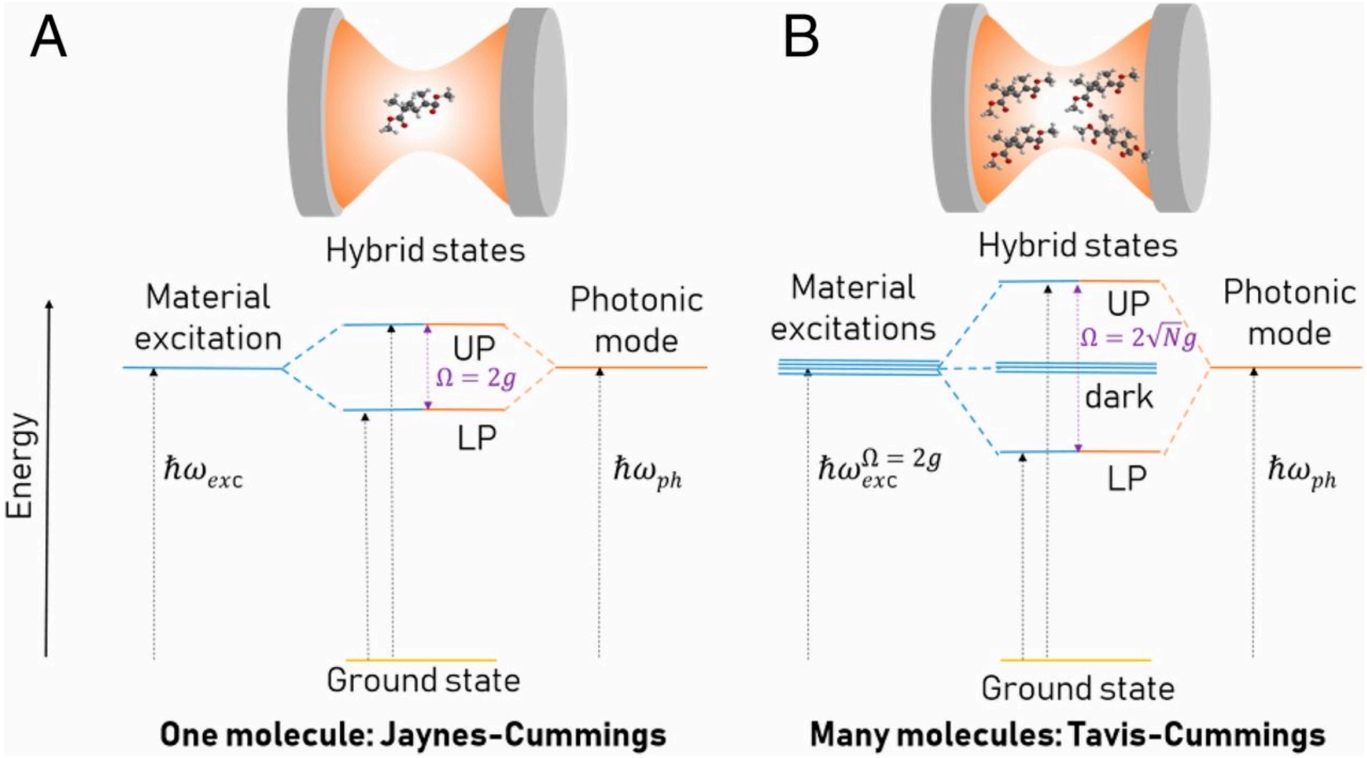
Interaction compared to energy dissipation



Fregoni, Garcia-Vidal, Feist,
ACS Photonics 2022, 9, 4, 1096–1107

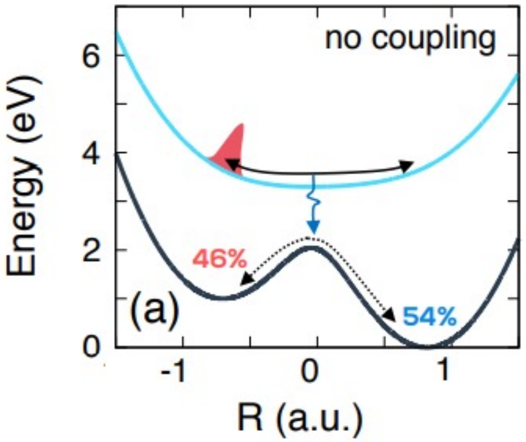
$\hbar g > \hbar\omega \rightarrow$ Ultra-strong Coupling

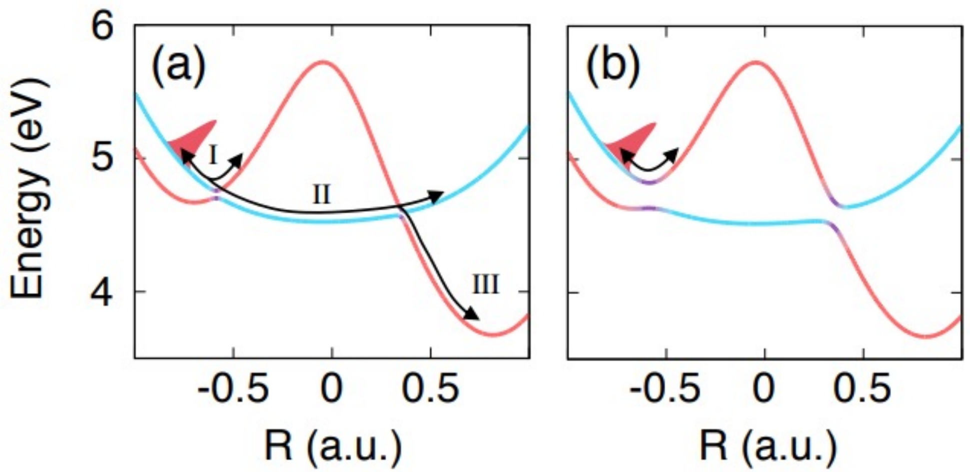
Interaction compared to excitation energies

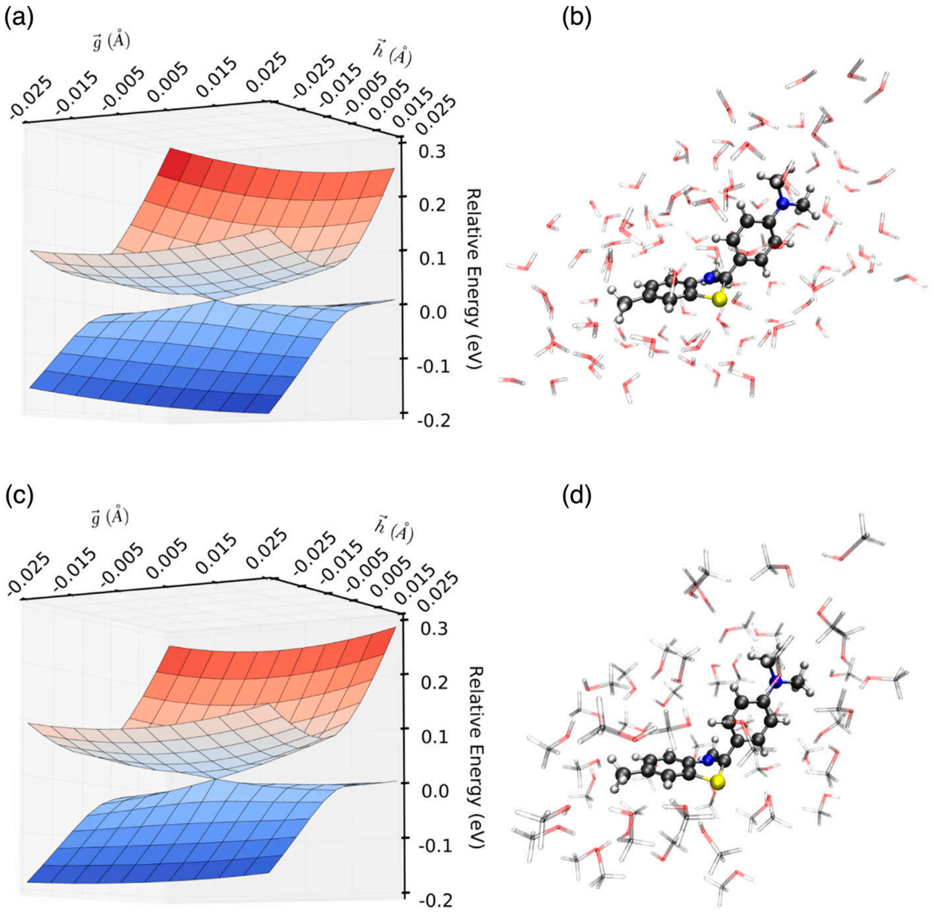


Yuen-Zhou and Menon, PNAS 2019, 116, 5214-5216

Quantum chemistry for polaritonic surfaces and couplings





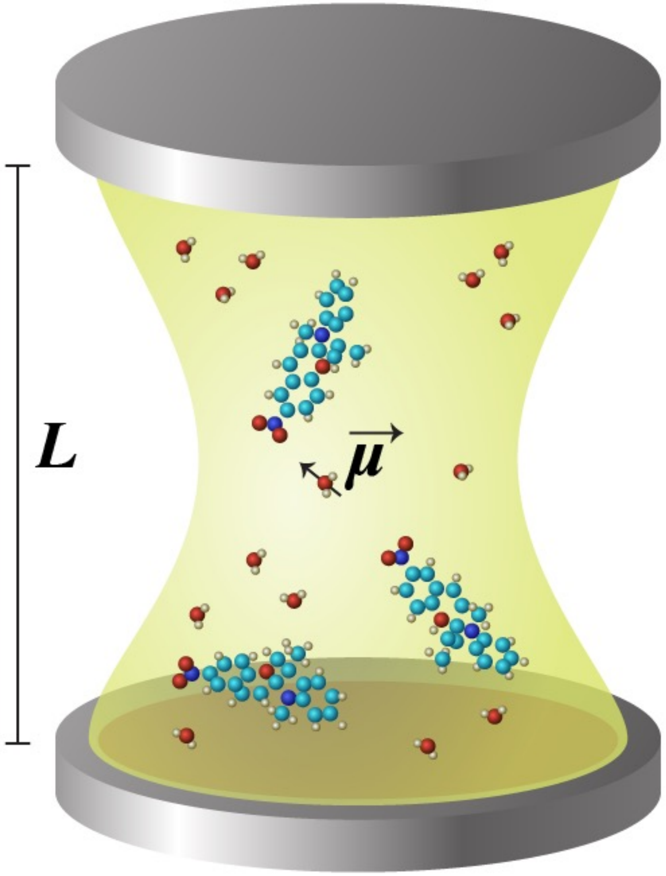


J. Chem. Phys.. 2017;147(9) doi:10.1063/1.5000476

Mandal and Huo, *J. Phys. Chem. Lett.*, **10**, 5519-5529 (2019)

Pauli-Fierz Hamiltonian

$$\lambda = \sqrt{\frac{\hbar}{\epsilon_0 L^3}}\hat{\mathbf{e}}$$



$$\hat{H} = \boxed{\hat{H}_{\mathrm{e}}} + \boxed{\omega_{\mathrm{cav}}\hat{b}^{\dagger}\hat{b}} - \boxed{\sqrt{\frac{\omega_{\mathrm{cav}}}{2}}(\lambda\cdot\hat{\mu})(\hat{b}^{\dagger}+\hat{b})} + \boxed{\frac{1}{2}(\lambda\cdot\hat{\mu})^2}$$

ab initio molecular Hamiltonian

Photonic Hamiltonian

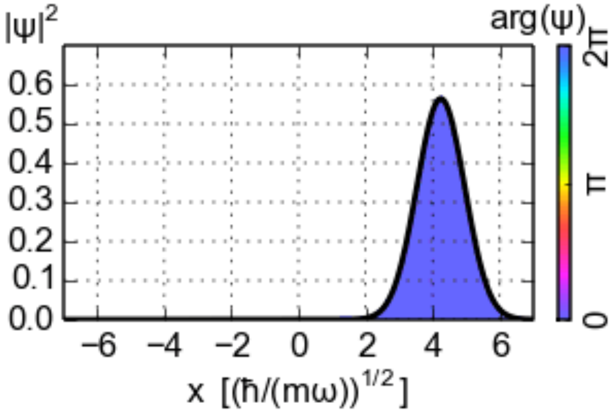
Bilinear molecule-photon coupling

Quadradic dipole self energy

Coherent state transformation

$$|0^{\mathrm{p}}\rangle = \sum_n (\hat{b}^\dagger)^n |0\rangle c_n = \hat{U}_{\mathrm{CS}}^\dagger |0\rangle$$

Coherent state



"It's just a state that, no matter what happens in life, can't be annihilated"

"It's just a state that, no matter what happens in life, never spreads"

$$\langle \Phi^{\mathrm{e}}_{SD} 0^{\mathrm{p}} | \hat{H} | 0^{\mathrm{p}} \Phi^{\mathrm{e}}_{SD} \rangle = \langle \Phi^{\mathrm{e}}_{SD} | \langle 0 | \hat{U}_{\mathrm{CS}} \hat{H} \hat{U}^\dagger_{\mathrm{CS}} | 0 \rangle | \Phi^{\mathrm{e}}_{SD} \rangle$$

$$\hat{U}_{\mathrm{CS}} = \exp\left(z(\hat{b}^\dagger - \hat{b}) \right) \qquad z = \frac{-\lambda \cdot \langle \hat{\mu} \rangle}{\sqrt{2\omega_{\mathrm{cav}}}}$$

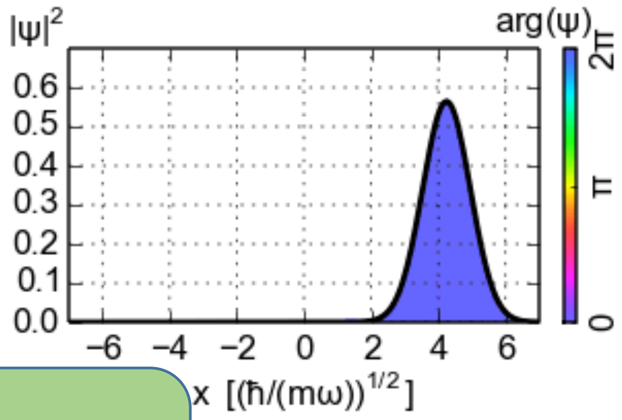
Koch and co-workers, PRX **10**, 041043 (2020)

Foley, McTague, DePrince, *Chem Phys Rev*, **4**, 041301 (2023)

Coherent state transformation and solution to QED-HF

$$|0^{\mathrm{p}}\rangle = \sum_n (\hat{b}^\dagger)^n |0\rangle c_n = \hat{U}_{\mathrm{CS}}^\dagger |0\rangle$$

Coherent state



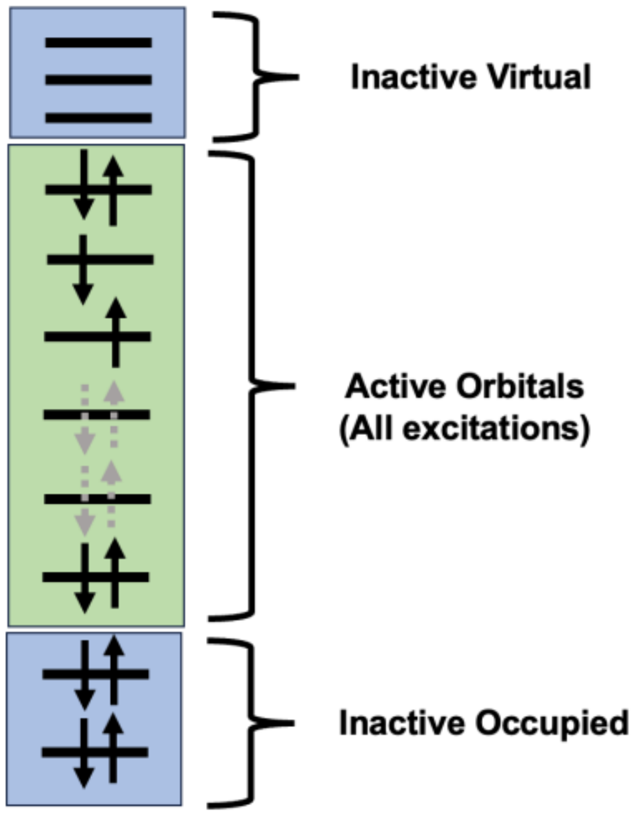
$$\langle \Phi^{\mathrm{e}}_{SD} 0^{\mathrm{p}} | \hat{H} | 0^{\mathrm{p}} \Phi^{\mathrm{e}}_{SD} \rangle = \langle \Phi^{\mathrm{e}}_{SD} | \langle 0 | \underbrace{\hat{U}_{\mathrm{CS}} \hat{H} \hat{U}_{\mathrm{CS}}^\dagger}_{} | 0 \rangle | \Phi^{\mathrm{e}}_{SD} \rangle$$

$$\hat{H}_{CS} = \hat{H}_e + \omega_{\mathrm{cav}} \hat{b}^\dagger \hat{b} - \sqrt{\frac{\omega_{\mathrm{cav}}}{2}} [\lambda \cdot (\hat{\mu} - \langle \hat{\mu} \rangle)](\hat{b}^\dagger + \hat{b}) + \frac{1}{2} [\lambda \cdot (\hat{\mu} - \langle \hat{\mu} \rangle)]^2$$

QED-CI for multiple polaritonic states

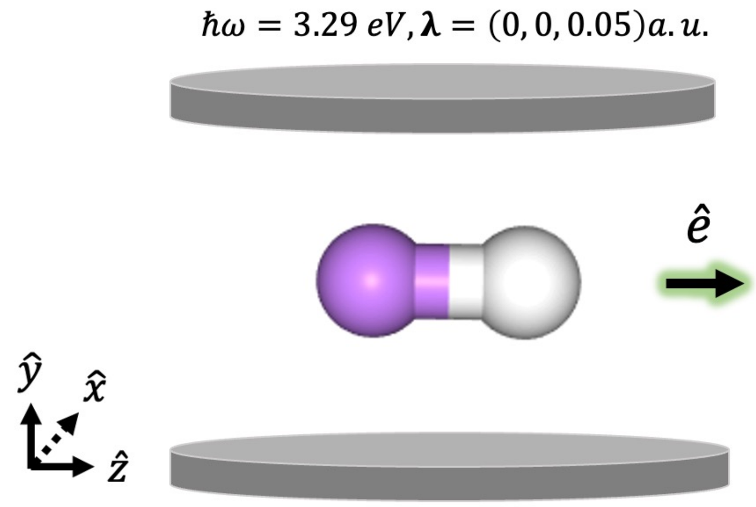
$$|\Psi\rangle = \sum_n \sum_I C_{I,n} |\Phi_I^{\mathrm{e}}\rangle |n^{\mathrm{p}}\rangle$$

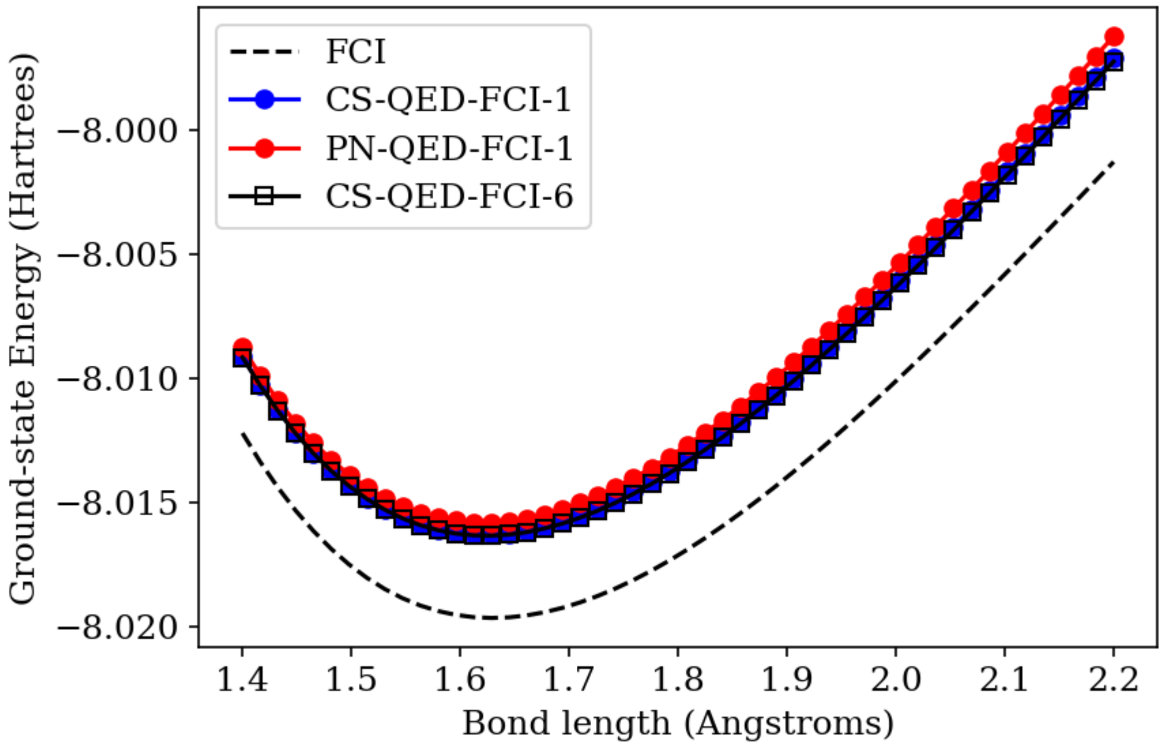
$$\mathbf{H} = \begin{bmatrix} \mathbf{A}+\boldsymbol{\Delta} & \mathbf{G} & 0 & \dots & 0 & 0 \\ \mathbf{G} & \mathbf{A}+\boldsymbol{\Delta}+\boldsymbol{\Omega} & \sqrt{2}\mathbf{G} & \dots & 0 & 0 \\ 0 & \sqrt{2}\mathbf{G} & \mathbf{A}+\boldsymbol{\Delta}+2\boldsymbol{\Omega} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & \mathbf{A}+\boldsymbol{\Delta}+(N^{\mathrm{p}}-1)\boldsymbol{\Omega} & \sqrt{N^{\mathrm{p}}}\mathbf{G} \\ 0 & 0 & 0 & \dots & \sqrt{N^{\mathrm{p}}}\mathbf{G} & \mathbf{A}+\boldsymbol{\Delta}+N^{\mathrm{p}}\boldsymbol{\Omega} \end{bmatrix}$$

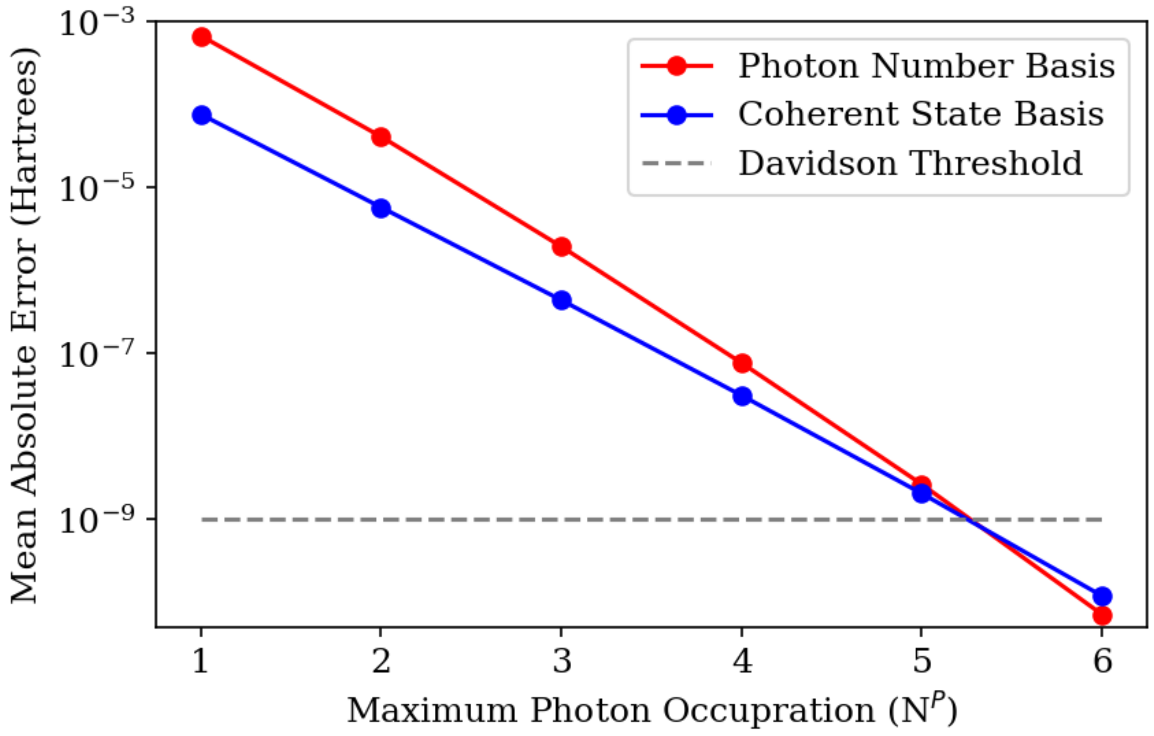


The CI space can be FCI, truncated CI, or CASCI

QED-FCI in Coherent State vs Photon Number State – LiH/6-311G

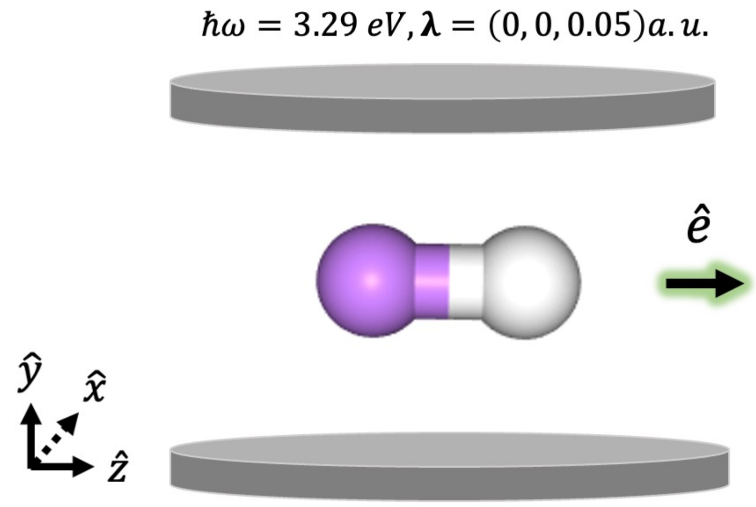


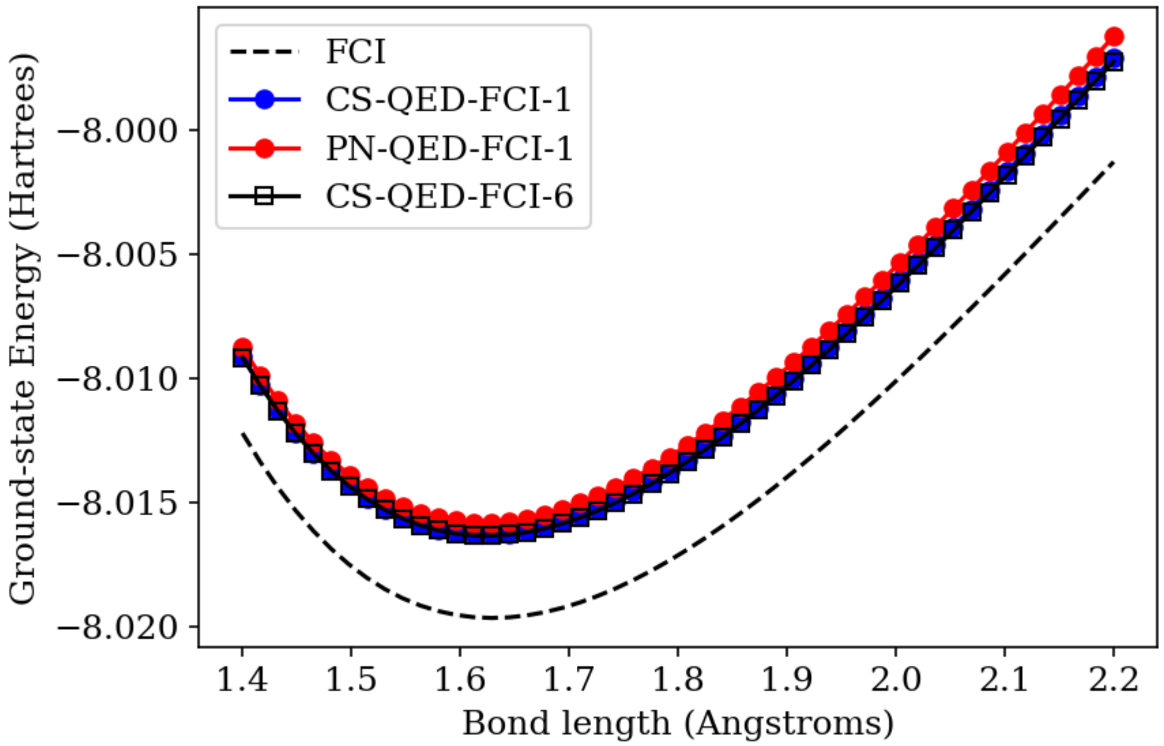


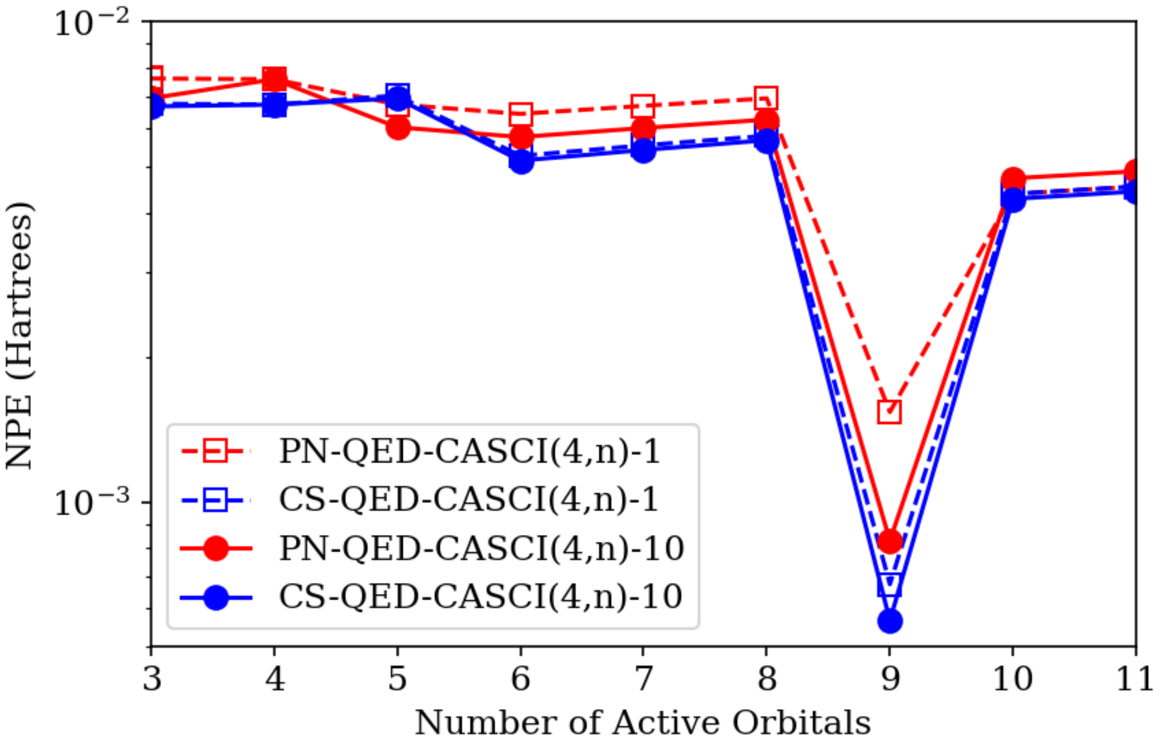


Vu, Mejia-Rodriguez, Bauman, Panyala, Mutlu, Govind, Foley, *Under Revision at JCTC*, Chemrxiv: 10.26434/chemrxiv-2023-kbhcv

QED-FCI in Coherent State vs Photon Number State – LiH/6-311G







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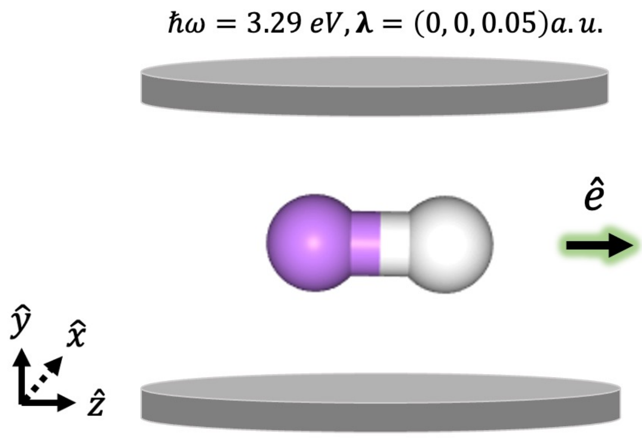
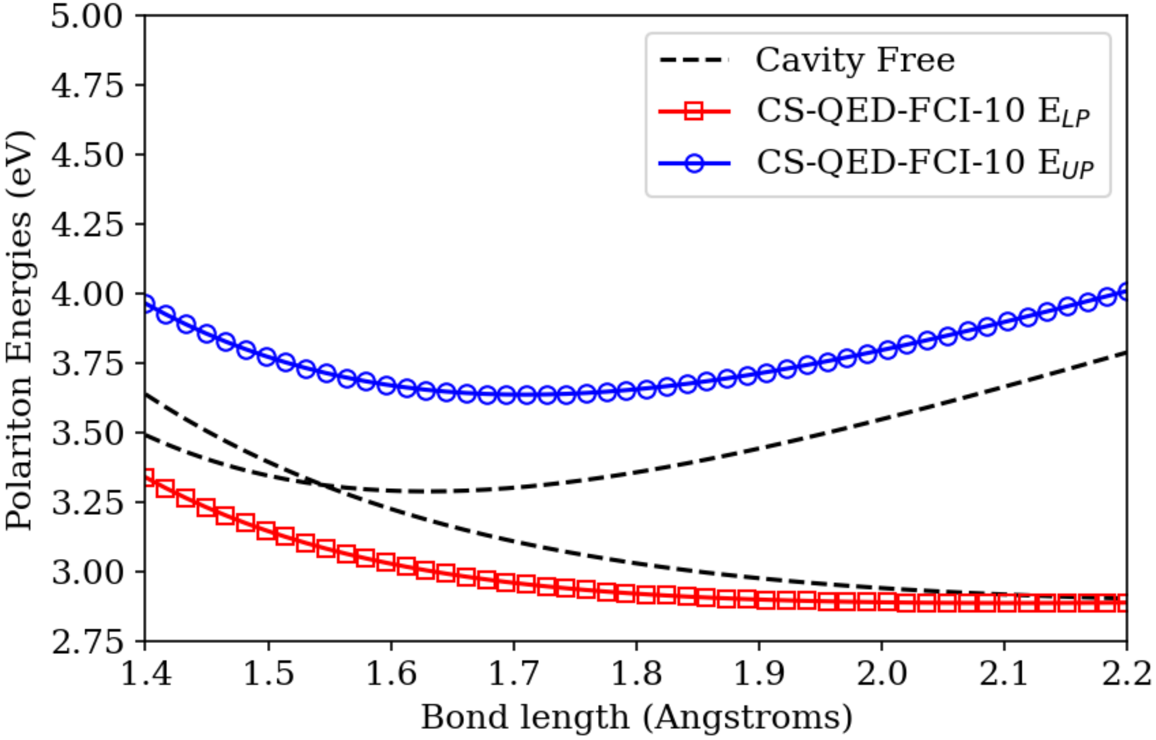
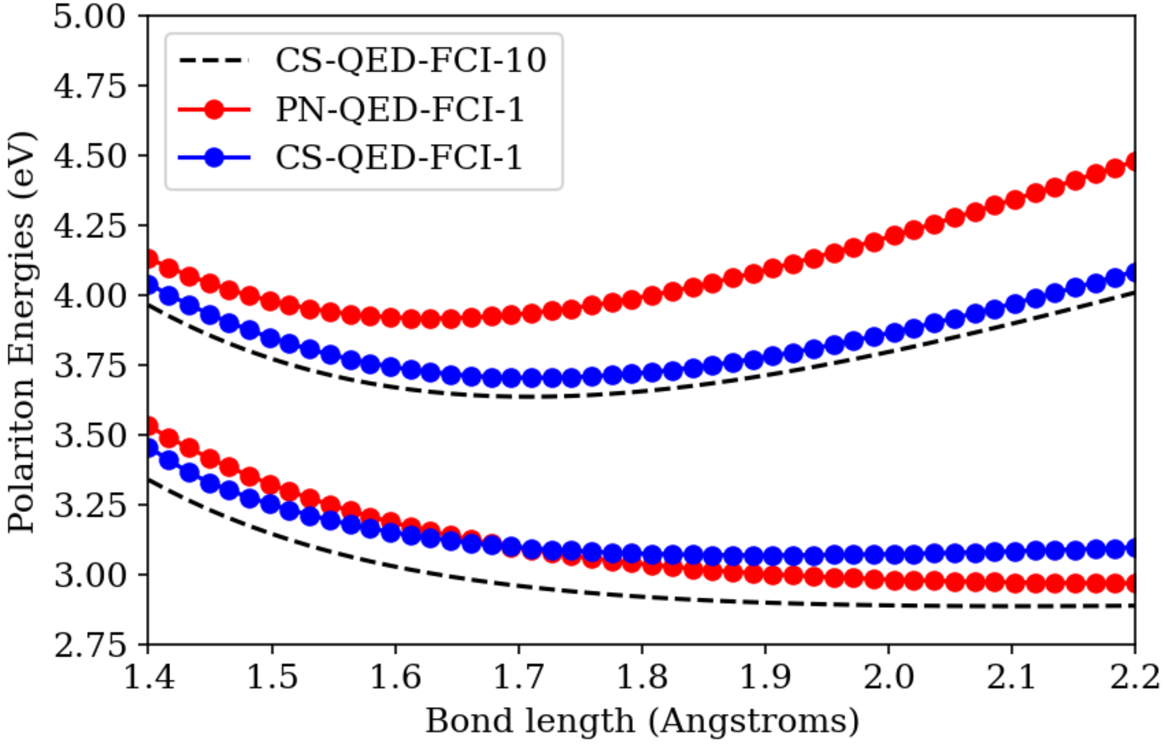
QED-FCI in Coherent State vs Photon Number State







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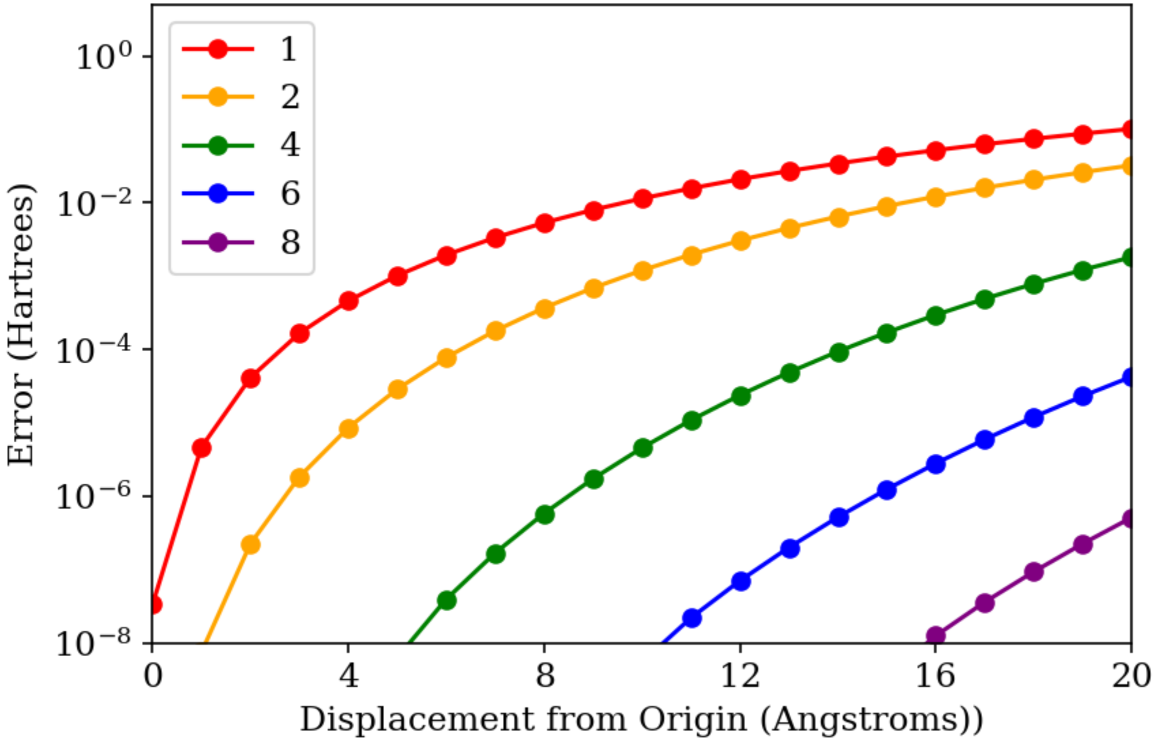
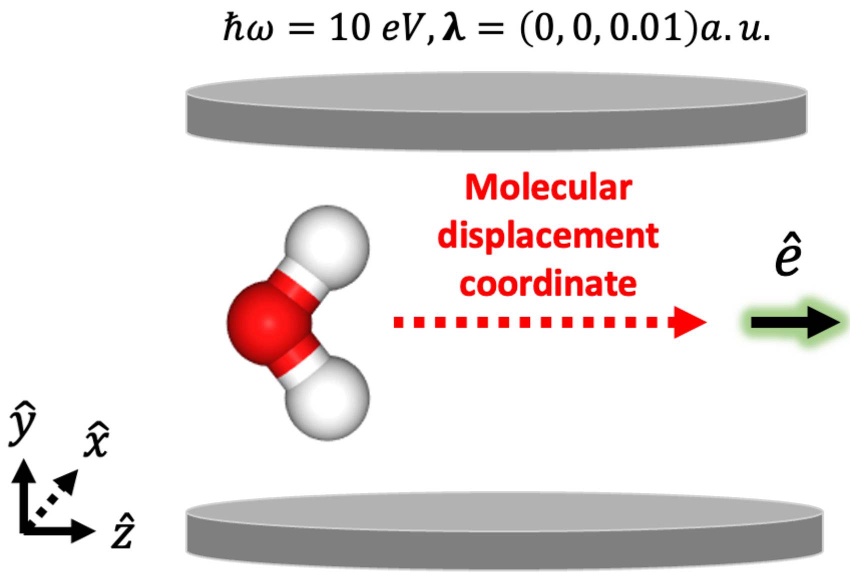
QED-FCI in Coherent State vs Photon Number State





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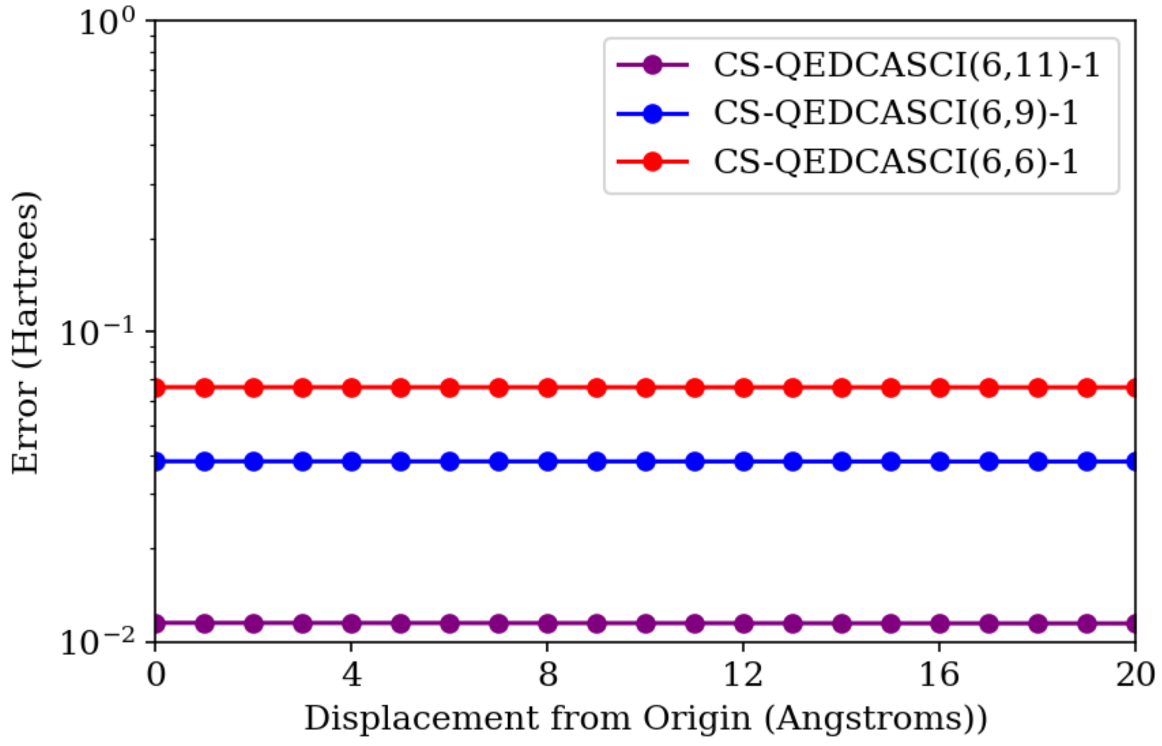
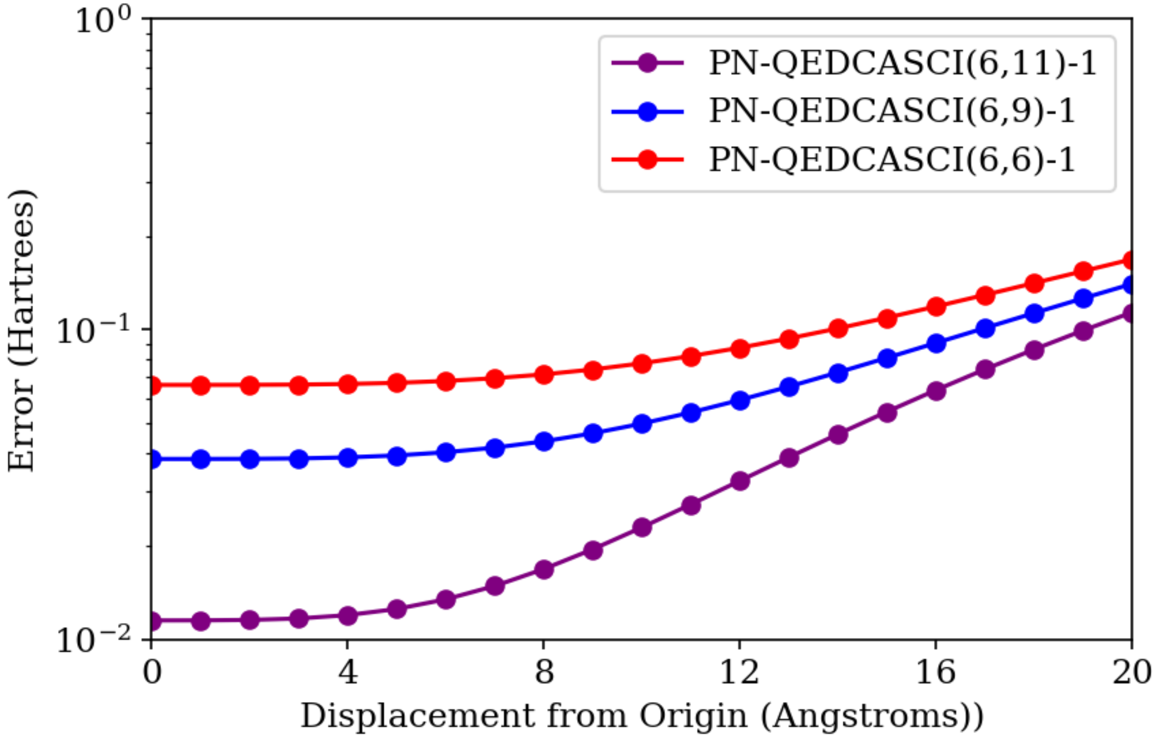
QED-CASCI in Coherent State vs Photon Number State





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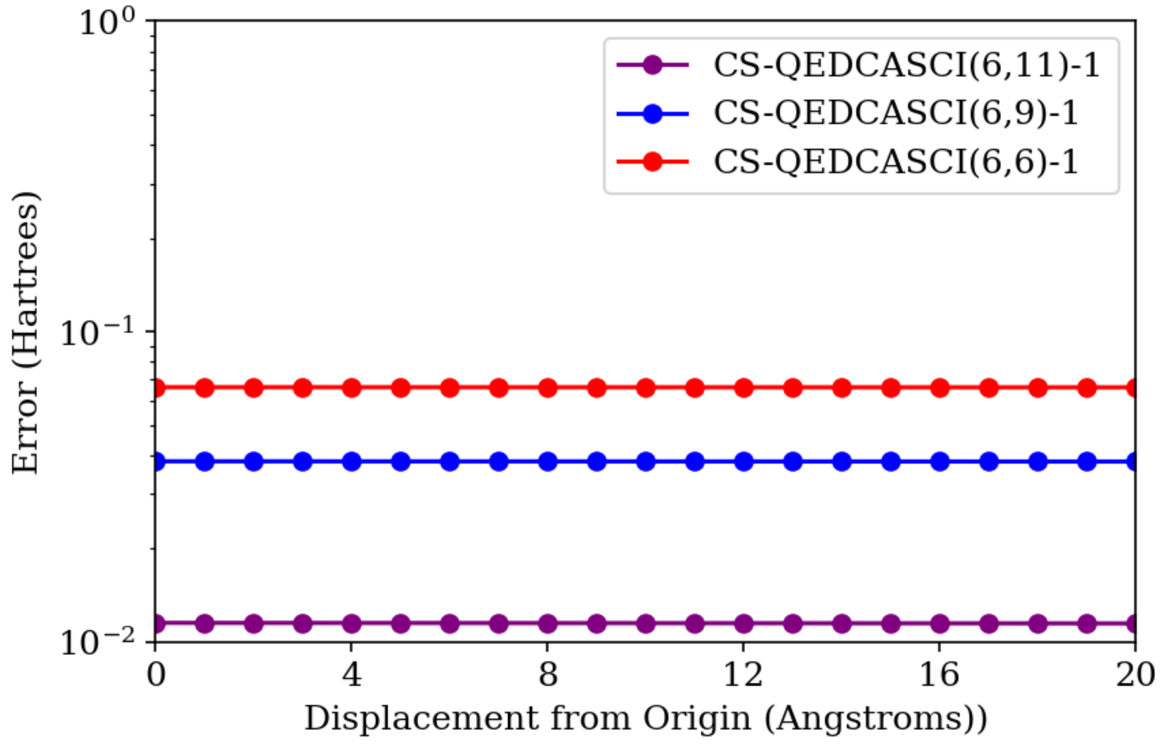
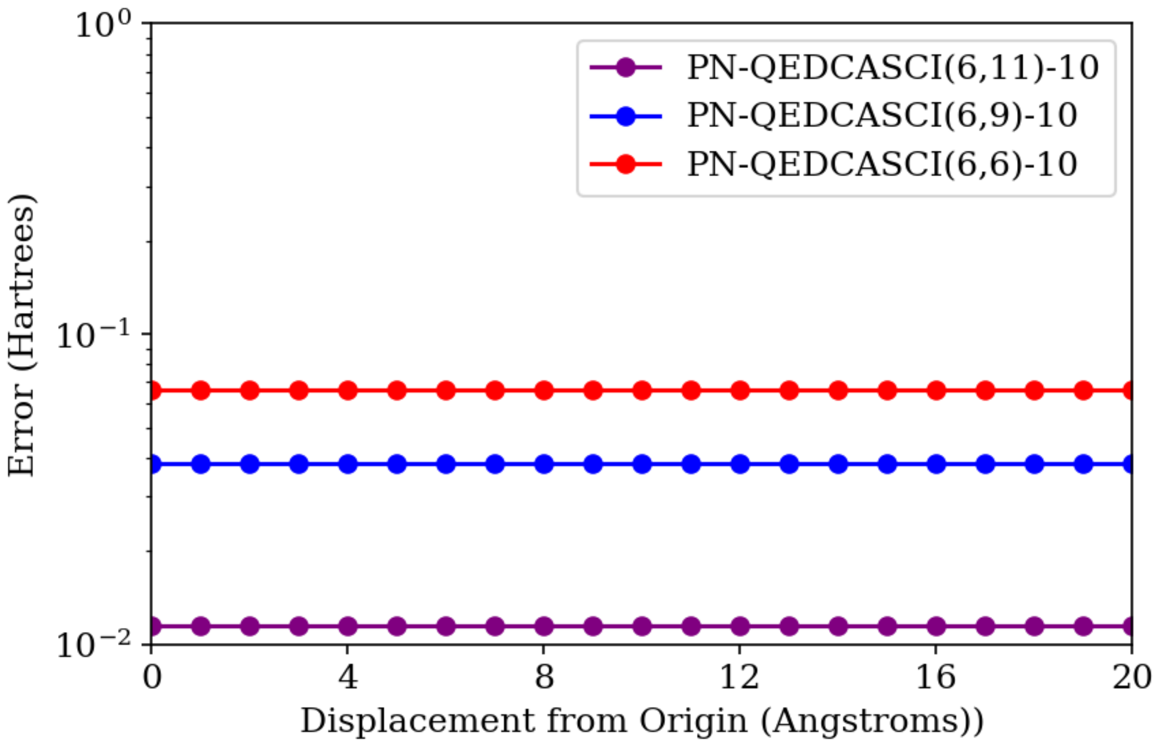
QED-FCI in Coherent State vs Photon Number State





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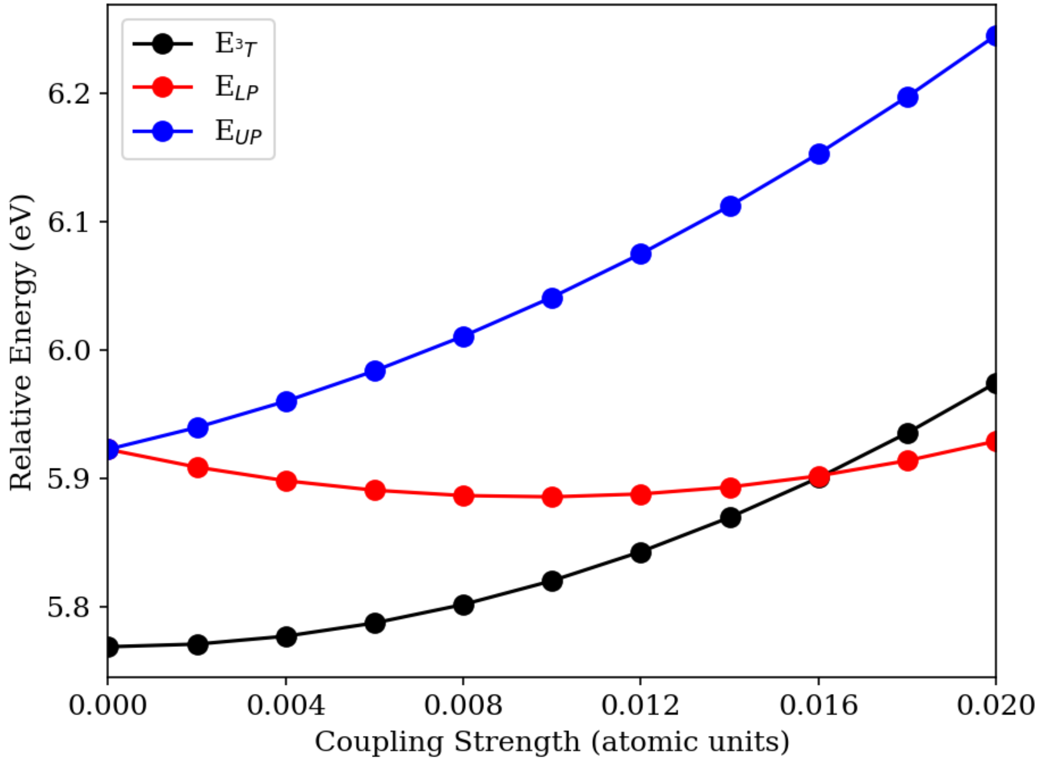
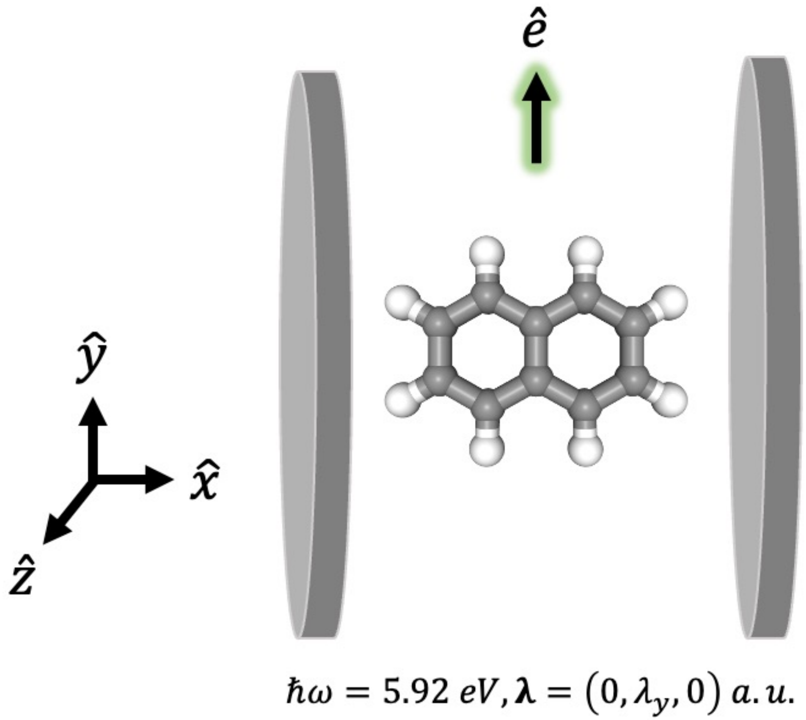
QED-FCI in Coherent-state vs Photon Number State basis





5 roots for a (12,12) active space with 100 photon states takes < 4 hours in our reference implementation!

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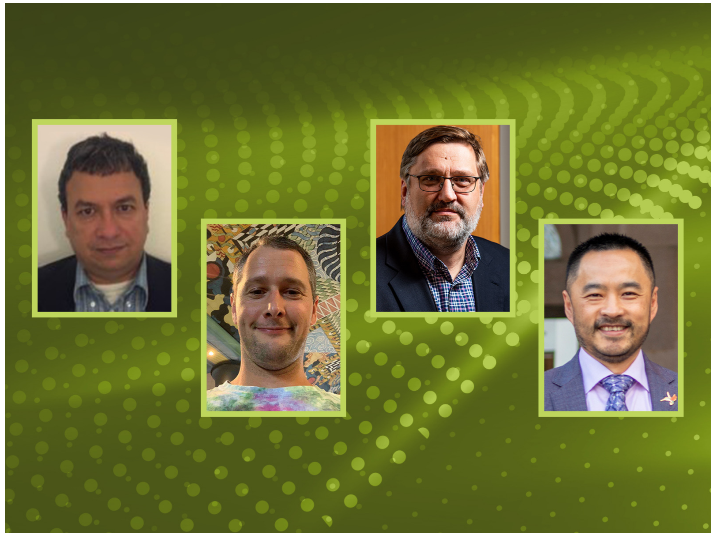
- Reference implementations for QED-HF, QED-CIS-1 available in Psi4Numpy repo; QED-CIS Prism, QED-CASCI, QED-FCI available in group repos
- Psi4Education Module -> MolSSI-MAPOL-Charlotte Workshop
- Tutorials for QED-HF and QED-CIS Prism available
- Production implementations in EXACHEM coming soon
- High-order response, (non)adiabatic forces from automatic differentiation within 3 years

Nam Vu, Peyton Roden, Lane Tolley, Jay, Ruby Manderna



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