Real-space, real-time approach to quantum-electrodynamical time-dependent density functional theory

Justin Malave, Alexander Ahrens, Daniel Pitagora, Cody Covington, and Kalman Varga,
J. Chem. Phys. 157, 194106 (2022)

Presented by Justin Malave
Department of Physics and Astronomy

VANDERBILT
College of Arts *and* Science

The Research Problem

The theoretical and computational description of many-body electron systems in a cavity: Quantum emitter; cavity; strong coupling – energy exchange much larger than dissipation process

Many-body theories for cQED

- Coupled cluster QED (QED-CC)
- Stochastic variational method QED (QED-SVM)
- **QED density functional theory (QEDFT)**

The Research Problem

The theoretical and computational description of many-body electron systems in a cavity: Quantum emitter; cavity; strong coupling – energy exchange much larger than dissipation process

Many-body theories for cQED

- Coupled cluster QED (QED-CC)
- Stochastic variational method QED (QED-SVM)
- **QED density functional theory (QEDFT)**

From QED to Pauli-Fierz to QEDFT

QED equations of motion $\rightarrow$ Non-relativistic limit $\rightarrow$ Pauli-Fierz Hamiltonian $\rightarrow$ Second Quantize $\mathbf{A}$ $\rightarrow$ Dipole approximation $\rightarrow$ Density functionalize V

$$H = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{x})}_{\text{Matter Operators}} + \underbrace{\frac{1}{2}\left[p^2 + \omega^2\left(q - \frac{\boldsymbol{\lambda}}{\omega}\cdot\mathbf{D}\right)^2\right]}_{\text{Cavity Operators and Coupling Operators}}$$

Methods

Quantum Electrodynamical Density Functional Theory

The Hamiltonian: one photon mode only

Method 1: Dual propagation of coupled photon-matter equations

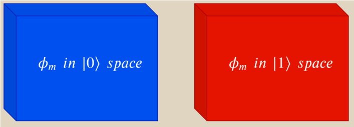
$$i\hbar\frac{\partial}{\partial t}\Phi = \left(\frac{\mathbf{p}^2}{2m} + V_{KS} + V_{PH}\right)\Phi \qquad \left(\frac{\partial^2}{\partial t^2} + \omega^2\right) q = \omega\boldsymbol{\lambda}\cdot\int d\mathbf{x}\, \mathbf{e}\mathbf{x}\, \rho(\mathbf{x})$$

Method 2: Tensor product approach

$$H\Phi_{mn} = -\frac{\hbar^2}{2m}\nabla^2\Phi_{mn} + V_{KS}\Phi_{mn}(\mathbf{x}) + \frac{1}{2}\left[p^2 + \omega^2\left(q - \frac{\boldsymbol{\lambda}}{\omega}\cdot\mathbf{D}\right)^2\right]\Phi_{mn}$$

$$\Phi_{mn} = \phi_{mn}(x)|n\rangle$$

- m: **index the electron orbitals**
- n: **index the photon space**



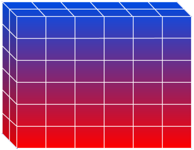
Methods

Real-space, real time

Real-space grid

A continuous coordinate space is replaced with a computationally amenable **discretized** grid. Parameters and observables are only defined at the grid points.

$\phi_m(x, y, z)$ *in* $|n\rangle$ *space*



$\phi_m(x_i, y_j, z_k)$ *in* $|n\rangle$ *space*

Time propagation: Taylor expansion approach

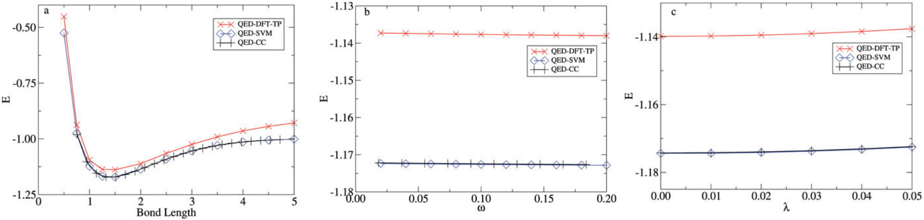
"Short time interval" time evolution operator is expanded to the fourth order, then applied at every time step δt. Good for when the Hamiltonian cannot be diagonalized.

$$e^{-iH\delta t} \approx \sum_{j=0}^{4} \frac{(-i\delta t)^j}{j!} H^j \qquad \Phi_m(\mathbf{x}, t+\delta t) = e^{-iH\delta t}\Phi_m(\mathbf{x}, t)$$

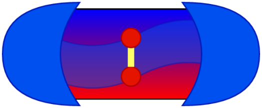
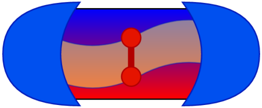
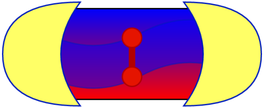
If the total time T equals $N\delta t$, then

$$\Big[\underbrace{e^{-iH\delta t}}_{\text{first application}} \times \underbrace{e^{-iH\delta t}}_{\text{second application}} \times \ldots \times \underbrace{e^{-iH\delta t}}_{\text{Nth application}}\Big]\Phi_m(\mathbf{x}, 0) = (e^{-iH\delta t})^N \Phi_m(\mathbf{x}, 0) = \Phi_m(\mathbf{x}, T)$$

Ground state energy dependencies

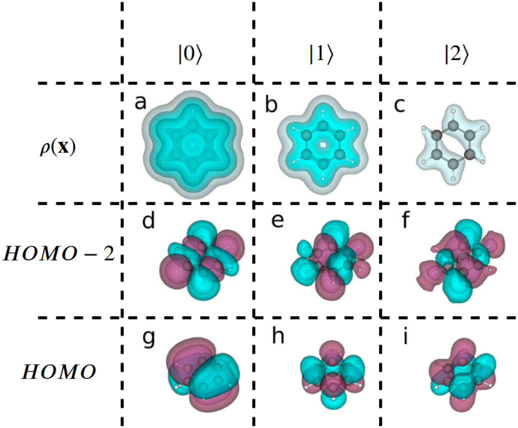


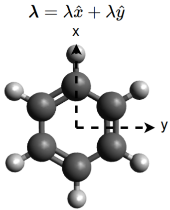
H_2 energy dependence on bond length, frequency, and coupling strength calculated using different approaches

(a)  (b)  (c) 

The yellow element is what is being changed

Electron densities

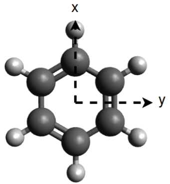




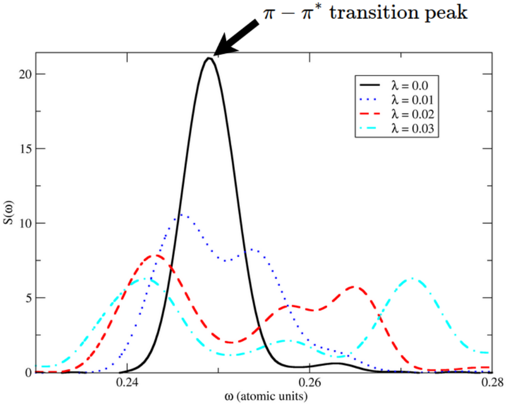
(Above) Coupling dir. (Left) Density, HOMO, and HOMO-2 isosurfaces for benzene coupled to a cavity. For the HOMO images, cyan and purple are, respectively, positively and negatively valued.

Rabi Splitting for benzene

$\boldsymbol{\lambda} = \lambda\hat{x}$

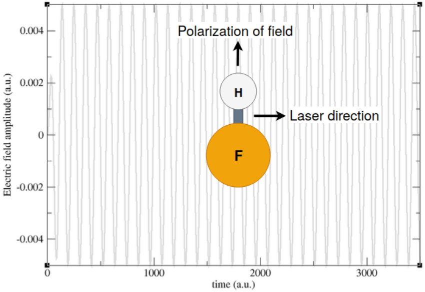


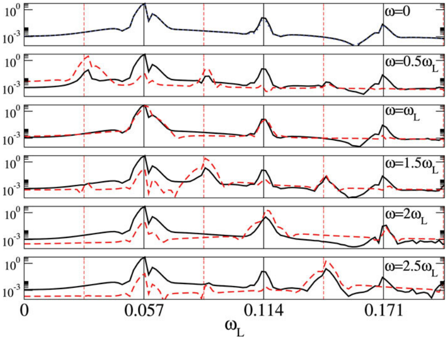
Coupling direction



Rabi splitting in cavity coupled benzene at difference cavity coupling strengths

High harmonic generation in HF





(Left) HF in 800 nm, continuous laser field. Coupling is parallel to the bond vector.
(Right) High harmonic generation spectra of HF at different photon frequencies

Acknowledgements

PI: Kalman Varga
Collaborator: Cody Covington

Undergraduates: Alexander Ahrens, Daniel Pitagora

Vanderbilt Department of Physics and Astronomy Faculty and Staff

VANDERBILT
College of Arts *and* Science

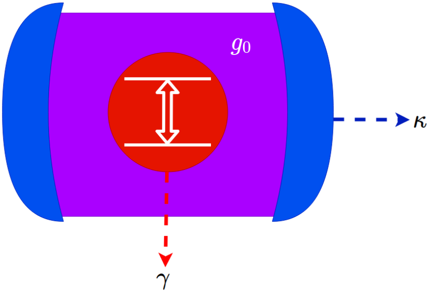
NSF

Thank You

The Optical Cavity

Essential cavity elements

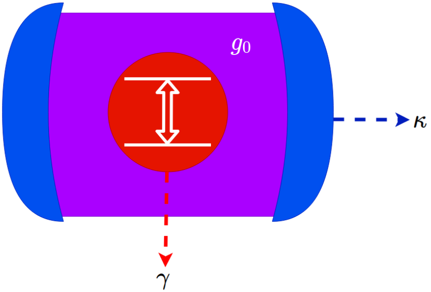
- Cavity
  - κ: Cavity decay mechanism
- Quantum emitter (two-level system)
  - λ: Emitter decay mechanism
- Photon-Emitter Coupling
  - g_0: the coupling parameter



The Optical Cavity

Essential cavity elements

- Cavity
  - κ: Cavity decay mechanism
- Quantum emitter (two-level system)
  - λ: Emitter decay mechanism
- Photon-Emitter Coupling
  - g_0: the coupling parameter



Strong light-matter coupling

When the energy exchange rate between emitter and cavity greatly exceeds decay and dissipation rates, the quantum nature of light becomes important

$$g_0 \gg (\lambda, \kappa) = \text{Strong Coupling Regime}$$

2012 Nobel Prize: **Serge Haroche**, David Wineland

Cavity Quantum Electrodynamics (cQED)

cQED Theory

The essential physics

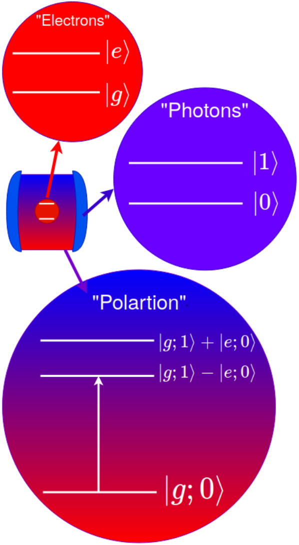
- Photon emission becomes reversible
- Uncoupled electron-photon degeneracy lifted
- Formation of light-matter hybrid states

Polariton state function

$$\Psi_1^{\pm} = \frac{1}{\sqrt{2}}(|g;1\rangle \mp |e;0\rangle)$$

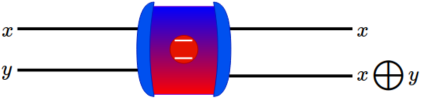
Polariton energy separation

$$E_1^{\pm} \propto g_0 \propto \frac{\textit{Quality factor}}{\textit{Volume}}$$

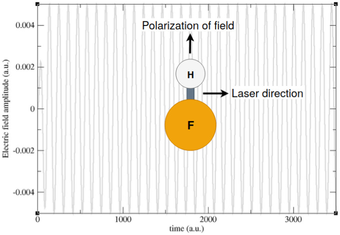


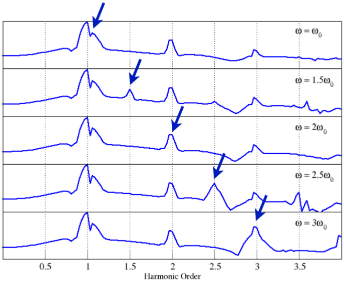
What are optical cavities good for?

- Quantum networks (nodes and repeaters): CNOT gates



- Impact on high harmonic generation





- Interesting physics!