A Multi-Scale Model for Optical Responses of Nano-Structures

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Outline

1. Light-Matter Interactions
2. Semiclassical Models
3. Linear Response Formulation
4. Numerical Examples
5. Conclusion
Light-Matter Interactions at *nano or atomic* scale: simultaneous determination of

\[
\begin{align*}
\{ & \text{Motion of matter.} \\
\{ & \text{Evolution of Electromagnetic (EM) field.}
\end{align*}
\]

- **Semiclassical Theories:**
  Quantum mechanical description of matter.
  But for EM field: use **classical treatments**.
  Compared to QED, lower computational burden.

Light: Evolution of the EM Field

Maxwell’s equations:

\[ \nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad \nabla \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c} \mathbf{J}, \]

\[ \nabla \cdot \mathbf{D} = 4\pi \rho, \quad \nabla \cdot \mathbf{B} = 0, \]

Continuity equation:

\[ \nabla \cdot \mathbf{J} = -\frac{\partial \rho}{\partial t} \]

Constitutive relations:

\[ \mathbf{D} = \varepsilon \mathbf{E}, \quad \mathbf{B} = \mu \mathbf{H}, \quad \mathbf{J} = \mathbf{j} + \sigma \mathbf{E}, \]

- \( c \): speed of light in vacuum.
- \( \varepsilon, \mu, \sigma \): permittivity, permeability, and conductivity, resp.
- \( \rho, \mathbf{j} \): charge density and impressed current density, resp.
In Vector and Scalar Potentials (under Coulomb gauge: $\nabla \cdot \mathbf{A} = 0$):

\[
\mathbf{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}, \\
\mathbf{B} = \nabla \times \mathbf{A}.
\]

Therefore, given input $\{\mathbf{j}, \rho\}$, the EM field given as (i.e., integral with scalar/dyadic Green’s functions),

\[
(\phi, \mathbf{A}) = \mathcal{M}[\mathbf{j}, \rho]. \tag{1}
\]
Matter: Motion of the Matter

Time-dependent Schrödinger eqn. in a given transverse EM field:

\[
\frac{i}{\hbar} \frac{\partial \psi(r_1, r_2, \ldots, r_N, t)}{\partial t} = H_M(t) \psi(r_1, r_2, \ldots, r_N, t).
\]

where the (nonrelativistic) Hamiltonian (Cho 2003):

\[
H_M \equiv \sum_l \frac{1}{2m_l} \left[ \mathbf{p}_l - \frac{e_l}{c} \mathbf{A}(r_l) \right]^2 + U \equiv H_0 + H_{int},
\]

- \(m_l, e_l, r_l, \mathbf{p}_l\): mass, charge, coordinate and conjugate momentum of the coordinate, resp. of \(l\)-th particle.
- Mutual Coulomb interaction: \(U = \frac{1}{2} \sum_{l \neq k} \frac{e_le_k}{|r_l - r_k|}\).
- Matter Hamiltonian: \(H_0 = \sum_l \frac{1}{2m_l} \mathbf{p}_l^2 + U\).
- Light-Matter Interaction:

\[
H_{int} = \sum_l \frac{1}{m_l} \left( -\frac{e_l}{c} \mathbf{A} \cdot \mathbf{p}_l + \frac{e_l^2}{2c^2} \mathbf{A}^2 \right).
\]
Motion of the Matter cont’ed

Ground state $\psi_0$: $H_0 \psi_0 = E \psi_0$. The matter state will experience time evolution after switching on radiation-matter interaction. Then, charge and current densities $(\rho(r, t), j(r, t))$ are given as expectation values,

$$
\rho(r, t) = \langle \psi | \hat{\rho} | \psi \rangle, \quad j(r, t) = \langle \psi | \hat{j} | \psi \rangle,
$$

with,

$$
\hat{\rho} = \sum_l e_l \delta(r - r_l),
\hat{j} = \sum_l \frac{e_l}{2m_l} \left[ p_l \delta(r - r_l) + \delta(r - r_l) p_l \right] - \sum_l \frac{e_l^2}{m_l c} A(r_l, t).
$$

Therefore, given input $\{ A, \phi \}$, the current and charge densities are given as

$$
(j, \rho) = \mathcal{H}[\phi, A]. \quad (2)
$$
The current and charge densities \((j, \rho)\) and the EM field \((\phi, A)\) must be determined self-consistently, through the coupled system, **Maxwell + Schrödinger**

\[
\begin{align*}
\text{By Maxwell’s eqn.:} & \quad (\phi, A) = M[j, \rho]. \\
\text{By Schrödinger eqn.:} & \quad (j, \rho) = H[\phi, A].
\end{align*}
\]

The system can be solved iteratively until self-consistent convergence to determine the motion of the matter and the evolution of the EM field.
Self-Consistent Determination: High Complexity

**Difficulty**: Need $N$-body wavefunction to compute current and charge densities, i.e.,

$$\psi(r_1, \ldots, r_N, t) \Rightarrow (j(r, t), \rho(r, t)).$$

$N$-body system $\Rightarrow 3N$ spatial variables.
Solving multi-component $N$-body Schrödinger equations $\Rightarrow$ too expensive!

**Note**: Only $(j(r, t), \rho(r, t))$ are needed in Maxwell’s equations. They have only 3 spatial variables!
Therefore: focus on computing $(j(r, t), \rho(r, t))$. 
Ehrenfest Molecular Dynamics

Denote $\tilde{\mathbf{r}} = (r_1, \ldots, r_{N_e})$, $\tilde{\mathbf{R}} = (R_1, \ldots, R_{N_n})$ as coordinates of electrons and nuclei, resp..

Separation of electrons and nuclei (with Born-Oppenheimer approximation): the electronic wavefunction $\psi$ for electrons,

$$\imath \hbar \frac{\partial \psi(\tilde{\mathbf{r}}, t)}{\partial t} = \left( \sum_{l=1}^{N_e} \frac{1}{2m_e} \left( \mathbf{p}_{r_l} - \frac{e_l}{c} \mathbf{A}(\mathbf{r}_l) \right)^2 + \langle W_{ee} + W_{nn} + W_{en} \rangle_{\tilde{\mathbf{R}}} \right) \psi(\tilde{\mathbf{r}}, t),$$

and the nuclear wavefunction $\mathbb{E}$ for nuclei,

$$\imath \hbar \frac{\partial \mathbb{E}(\tilde{\mathbf{R}}, t)}{\partial t} = \left( \sum_{k=1}^{N_n} \frac{1}{2M_k} \left( \mathbf{p}_{R_k} - \frac{Z_k}{c} \mathbf{A}(\mathbf{R}_k) \right)^2 + \langle H_e \rangle_{\tilde{\mathbf{r}}} \right) \mathbb{E}(\tilde{\mathbf{R}}, t),$$

(Marx and Hutter 2009, Ullrich 2012, etc.)
Ehrenfest Molecular Dynamics cont’ed

Where

\[
H_e = \sum_{l=1}^{N_e} \frac{1}{2m_e} \left( \mathbf{p}_{r_l} - \frac{e_l}{c} \mathbf{A}(\mathbf{r}_l) \right)^2 + W_{ee} + W_{nn} + W_{en},
\]

\[
W_{ee} = \frac{1}{2} \sum_{j \neq k}^{N_e} \frac{e_j e_k}{|\mathbf{r}_j - \mathbf{r}_k|},
\]

\[
W_{nn} = \frac{1}{2} \sum_{j \neq k}^{N_n} \frac{Z_j Z_k}{|\mathbf{R}_j - \mathbf{R}_k|},
\]

\[
W_{en} = \sum_{j=1}^{N_e} \sum_{k=1}^{N_n} \frac{e_j Z_k}{|\mathbf{r}_j - \mathbf{R}_k|},
\]
Electrons: Motion of Electrons

The electronic wavefunction $\psi(\tilde{r}, t)$

$$\hat{\hbar} \frac{\partial \psi}{\partial t} = \left( \sum_{l=1}^{N_e} \frac{1}{2m_e} \left( \frac{p_{r_l} - e_l}{c} \mathbf{A}(\mathbf{r}_l) \right)^2 + \langle W_{ee} + W_{nn} + W_{en} \rangle \tilde{\mathbf{R}} \right) \psi,$$

The electronic charge and current densities:

$$\rho_e(\mathbf{r}, t) = \langle \psi | \hat{\rho} | \psi \rangle, \quad j_e(\mathbf{r}, t) = \langle \psi | \hat{\mathbf{j}} | \psi \rangle,$$

The difficulty is still the $N_e$-body wavefunction (Schrödinger equation) involved in the computation of charge and current densities.
Hohenberg-Kohn (HK) theorems and time-dependent analogue:
The density and/or current density determine uniquely the external potentials and therefore all physical observables.

Density/Current Density ⇔ External Potential ⇔ Wavefunction

Kohn-Sham (KS) system:
The density and/or current density of the interacting system can be calculated as the density and/or current density of an auxiliary non-interacting system.

(Hohenberg and Kohn 1964, Kohn and Sham 1965, Runge and Gross 1984, Ghosh and Dhara 1988, etc.)
Density Functional Theory (DFT)

Time-independent Schrödinger equation:

\[ H_0 \psi_0(r_1, \ldots, r_{N_e}) = E \psi_0(r_1, \ldots, r_{N_e}). \]

Time-independent Kohn-Sham system (single-particle):

\[ H^{KS}_0 \psi_l(r) = \epsilon_l \psi_l(r), \quad l = 1, 2, \ldots, N_e. \]

\[ H^{KS}_0 = \frac{1}{2} \mathbf{p}^2 + v(r) + v_H(r) + v_{xc}(r). \]

Density:

\[ \rho_e(r) = \sum_l f_l |\psi_l(r)|^2, \]

with \( f_l \) the occupation number.

\( v \): external potential; \( v_H \): Hartree potential;
\( v_{xc} \): scalar exchange-correlation potential.
Time-Dependent Current Density Functional Theory (TDCDFT)

Time-dependent Schrödinger equation:
\[ i \frac{\partial \psi(r_1, \ldots, r_{N_e}, t)}{\partial t} = H_M \psi(r_1, \ldots, r_{N_e}, t). \]

Time-dependent Kohn-Sham system (single-particle):
\[ i \frac{\partial \psi_l(r, t)}{\partial t} = H_{KS}^M(t) \psi_l(r, t), \quad l = 1, \ldots, N_e. \]
\[ H_{KS}^M(t) = \frac{1}{2} \left[ p + \frac{1}{c} A(r, t) + A_{xc}(r, t) \right]^2 + v(r, t) + v_H(r, t) + v_{xc}(r, t). \]

\( v \): external potential; \( v_H \): Hartree potential;
\( v_{xc} \): scalar exchange-correlation potential.
\( A_{xc} \): vector exchange-correlation potential.
Density and Current density are computed as:

\[ \rho_e(r, t) = \sum_l f_l |\psi_l(r, t)|^2; \]

\[ \mathbf{j}_e(r, t) = -\frac{\hbar}{2} \sum_l f_l [\psi_l^* \nabla \psi_l - \psi_l \nabla \psi_l^*] + \frac{\rho}{c} (\mathbf{A} + \mathbf{A}_{xc}). \]

**Complexity:** \(3N_e\) spatial variables \(\Rightarrow\) 3 spatial variables.
Exchange-Correlation Potentials

Local Density Approximation (LDA):
Exchange-correlation energy functional:

\[ E_{xc}^{LDA}[\rho] = \int \rho(r) \epsilon_{xc}^{hom.}(\rho(r)) \, d\mathbf{r}, \]

\[ \epsilon_{xc}^{hom.}(\rho(r)) = \epsilon_x(\rho) + \epsilon_c(\rho). \]

\[ \epsilon_x(\rho) = -\frac{3}{4} \left( \frac{3\rho}{\pi} \right)^{1/3} ; \epsilon_c(\rho) \text{ is fitted into analytical functions.} \]

Then

\[ v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[\rho]}{\delta \rho}. \]

Adiabatic Local Density Approximation (ALDA): extension of LDA.

\[ v_{xc}^{ALDA}(\mathbf{r}, t) = \frac{\delta E_{xc}^{LDA}[\rho]}{\delta \rho} \bigg|_{\rho=\rho(t)}. \]
The Vignale-Kohn (VK) functional is derived and has the following expression in frequency domain,

$$\nu \omega A_{xc,l}(\mathbf{r}, \omega) = \partial_l v_{xc}^{ALDA} - \frac{1}{\rho_0(\mathbf{r})} \sum_j \partial_j \sigma_{xc,l,j}(\mathbf{r}, \omega), \text{ for } l = 1, 2, 3.$$ 

$\sigma_{xc}$ is of the form of a viscoelastic stress tensor.

Nuclei: Motion of Nuclei

The nuclear wavefunction $\Psi(\tilde{R}, t)$,

$$\imath\hbar \frac{\partial \Psi}{\partial t} = \left( \sum_{k=1}^{N_n} \frac{1}{2M_k} \left( p_{R_k} - \frac{Z_k}{c} A(R_k) \right)^2 + \langle H_e \rangle_{\tilde{r}} \right) \Psi.$$  

Assume semiclassical-limit (mean-field) approximation:

$$\Psi(\tilde{R}, t) \approx a(\tilde{R}, t) e^{iS(\tilde{R}, t)/\hbar}, \text{ as } \hbar \rightarrow 0,$$

where $a$ is the amplitude and $S$ is the phase. Substitution implies Hamilton-Jacobi equation for the phase $S(\tilde{R}, t)$,

$$\frac{\partial S}{\partial t} + \sum_{k=1}^{N_n} \frac{1}{2M_k} |\nabla_{R_k} S|^2 + \sum_{k=1}^{N_n} \frac{1}{2M_k} \left( -\frac{2Z_k}{c} A(R_k) \cdot \nabla_{R_k} S + \frac{Z_k^2}{c^2} A^2(R_k) \right)$$

$$+ \langle H_e \rangle_{\tilde{r}} = 0.$$
Motion of Nuclei cont’ed

Denoting \( \mathbf{P}_k = \nabla_{\mathbf{R}_k} S \), we have the Hamilton’s ODEs

\[
\begin{align*}
\frac{d\mathbf{R}_k}{dt} &= \frac{\mathbf{P}_k}{M_k} - \frac{Z_k}{M_k c} \mathbf{A}, \\
\frac{d\mathbf{P}_k}{dt} &= \frac{Z_k}{M_k c} \nabla_{\mathbf{R}_k} \mathbf{A}(\mathbf{R}_k) \cdot \mathbf{P}_k - \frac{Z_k^2}{M_k c^2} \mathbf{A} \cdot \nabla_{\mathbf{R}_k} \mathbf{A} - \nabla_{\mathbf{R}_k} \langle H_e \rangle \tilde{\mathbf{r}}.
\end{align*}
\]

By taking the time derivative of first equation and using the second equation, we have the Hamilton’s equations,

\[
M_k \frac{d^2 \mathbf{R}_k}{dt^2} = -\frac{Z_k}{c} \left( \frac{\partial \mathbf{A}}{\partial t} \right) - \left( \nabla_{\mathbf{R}_k} W_{nn} + \nabla_{\mathbf{R}_k} \int d\mathbf{r} \rho_e(\mathbf{r}, t) W_{en} \right),
\]

for \( k = 1, \ldots, N_n \), with \( \rho_e \) the electron density.
Motion of Nuclei cont’ed

Then the nuclear charge and current densities are given as,

\[ \rho_n(R) = \sum_{k=1}^{N_n} Z_k \delta(R - R_k), \quad j_n(R) = \sum_{k=1}^{N_n} Z_k v_k \delta(R - R_k), \]

with

\[ v_k = \frac{dR_k}{dt}. \]
A simpler semiclassical model is derived,

\[
\text{Maxwell} + \text{Schrödinger} \nonumber
\]

\[
\downarrow
\]

\[
\text{Maxwell} + \text{Ehrenfest Molecular Dynamics} \nonumber
\]

\[
\downarrow
\]

\[
\text{Maxwell} + \text{TDCDFT for Electrons} + \text{Hamilton’s Eqn’s for Nuclei} \nonumber
\]
A Semiclassical Model: A Coupled System

The semiclassical model $\Rightarrow$ the coupled system,

- $(\phi, A) = \mathcal{M}[j, \rho]$. By Maxwell's equations of EM field.

- $(j_e, \rho_e) = \mathcal{H}[\phi, A]$. By TDCDFT for electrons.

- $(j_n, \rho_n) = \mathcal{N}[\phi, A, j_e, \rho_e]$. By Hamilton's Eqn's for nuclei.

with

$$j = j_e + j_n, \quad \rho = \rho_e + \rho_n.$$

This coupled system can be solved iteratively until self-consistent convergence. Note: the system is 3-D.
Linear Response Theory

Perturbed quantities (in frequency domain $\omega$):

\[
\delta A(r, \omega) = -\frac{1}{c} \int G(r - r') \delta j(r') dr',
\]

\[
\delta \phi(r, \omega) = -\int G(r - r') \delta \rho(r') dr',
\]

\[
\delta j_e(r, \omega) = \int \left( \chi_{jj}(r, r', \omega) - \chi_{jj}(r, r', 0) \right) \cdot \delta A_{KS}(r', \omega) dr'
+ \int \chi_{j\rho}(r, r', \omega) \delta v_{KS}(r', \omega) dr',
\]

\[
\delta \rho_e(r, \omega) = \int \chi_{\rho j}(r, r', \omega) \cdot \delta A_{KS}(r', \omega) dr'
+ \int \chi_{\rho\rho}(r, r', \omega) \delta v_{KS}(r', \omega) dr',
\]
\[ \delta R_k = Z_k \left( -\frac{\iota \omega}{c} A_0(R^0_k) \right) - \nabla_{R_k} W_{nn}(R^0) - \int dr (\rho^0_e \nabla_{R_k} W_{en}(R^0)) \\
+ Z_k \left( -\frac{\iota \omega}{c} \delta A(R^0_k) \right) - \int dr \delta \rho_e \nabla_{R_k} W_{en}(R^0) \]

\[ \frac{Z_k \frac{i \omega}{c} \nabla_{R_k} A_0(R^0_k) - \omega^2 M_k}{Z_k \frac{i \omega}{c} \nabla_{R_k} A_0(R^0_k) - \omega^2 M_k} \]

\[ \delta j_n(r, \omega) = \sum_{k=1}^{N_n} Z_k \iota \omega \delta R_k \delta(R - R^0_k), \]

\[ \delta \rho_n(r, \omega) = -\sum_{k=1}^{N_n} Z_k \nabla_R \delta(R - R^0_k) \cdot \delta R_k. \]

Linear Response Theory cont’ed

\( G (\mathbf{G}) \): appropriate scalar (tensorial) Green’s function;
\( \chi \): linear response functions:

\[
\chi_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i,a} f_i \left( \frac{\psi_i(\mathbf{r}) \alpha \psi_a(\mathbf{r}) \psi_a(\mathbf{r}') \beta \psi_i(\mathbf{r}')} { (\epsilon_i - \epsilon_a) + \omega } \right) \\
+ f_i \left( \frac{\psi_i(\mathbf{r}) \alpha \psi_a(\mathbf{r}) \psi_a(\mathbf{r}') \beta \psi_i(\mathbf{r}')} { (\epsilon_i - \epsilon_a) - \omega } \right); \\
\]

(\( \psi_i, \epsilon_i \)): occupied ground-state KS orbitals;
(\( \psi_a, \epsilon_a \)): unoccupied ground-state KS orbitals.
\( \alpha, \beta \): density operator \( \rho = 1 \) and/or paramagnetic current density operator \( \mathbf{j}_p = -i (\mathbf{p} - \mathbf{p}^\dagger) / 2 \).
Kohn-Sham (KS) potentials:

\[ \delta v_{KS}(\mathbf{r}, \omega) = \delta v_H(\mathbf{r}, \omega) + \delta v_{xc}(\mathbf{r}, \omega); \]
\[ \delta A_{KS}(\mathbf{r}, \omega) = \frac{1}{c}(A_0(\mathbf{r}, \omega) + \delta A(\mathbf{r}, \omega)) + \delta A_{xc}(\mathbf{r}, \omega). \]

Hartree potentials:

\[ \delta v_H(\mathbf{r}, \omega) = \int \frac{\delta \rho_e(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \]

Exchange-correlation potentials:

\[ \delta v_{xc}(\mathbf{r}, \omega) = \int f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \delta \rho_e(\mathbf{r}', \omega) d\mathbf{r}' ; \]
\[ \delta A_{xc}(\mathbf{r}, \omega) = \int f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \delta \mathbf{j}_e(\mathbf{r}', \omega) d\mathbf{r}', \]

with \( f_{xc} \) and \( f_{xc} \) being the scalar and tensor xc-kernels respectively.
Define P-matrix:

\[ P_{lm} = \frac{-\omega}{\epsilon_m - \epsilon_l} \int d\mathbf{r} \psi_l(\mathbf{r}) j_p \psi_m(\mathbf{r}) \delta A_{KS} + \int d\mathbf{r} \psi_l(\mathbf{r}) \psi_m(\mathbf{r}) \delta v_{KS} \]

\[ \epsilon_m - \epsilon_l + \omega \]

and \( P_{lm} = P_{ml} - P_{lm} \), the above perturbed quantities can be rewritten as,

\[ \delta j_e(\mathbf{r}, \omega) = \sum_{ia} f_i \frac{-\omega}{\epsilon_i - \epsilon_a} \psi_i(\mathbf{r}) j_p \psi_a(\mathbf{r}) P_{ai}(\omega), \]

\[ \delta \rho_e(\mathbf{r}, \omega) = \sum_{ia} f_i \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) P_{ai}(\omega), \]

P-matrix Formulation cont’ed

\[ \delta A(r, \omega) = \sum_{ia} f_i \frac{\omega}{c(\epsilon_i - \epsilon_a)} \int G(r - r') \psi_i(r') j_p \psi_a(r') dr' P_{ai}(\omega) \]

\[ - \frac{1}{c} \int G(r, r') \delta j_n dr', \]

\[ \delta \phi(r, \omega) = \sum_{ia} f_i \int G(r - r') \psi_i(r') \psi_a(r') dr' P_{ai}(\omega) + \int G(r, r') \delta \rho_n dr'. \]

From the classical MD equation for nuclei, assume we can solve to obtain:

\[ \delta R_k = \sum_{ia} C_{ia}^R P_{ia} + D_R^R, \]

with appropriate coefficients \( C_R^k \) and \( D_R^k \).
Then, we have

\[
\delta \rho_n = - \sum_{ia} \sum_{k=1}^{N_n} Z_k \nabla_R \delta(R - R_k^0) \cdot C_{ia}^{R_k} P_{ia} - \sum_{k=1}^{N_n} Z_k \nabla_R \delta(R - R_k^0) \cdot D^{R_k},
\]

\[
\delta j_n = \sum_{ia} \sum_{k=1}^{N_n} Z_k \omega \delta(R - R_k^0) C_{ia}^{R_k} P_{ia} + \sum_{k=1}^{N_n} Z_k \omega \delta(R - R_k^0) D^{R_k}.
\]
Therefore, all the terms can be written as spectral expansions w.r.t. the P-matrix (w.l.o.g.):

\[
\delta A = \sum_{ia} C^A_{ia} \mathcal{P}_{ia} + D^A, \quad \delta \phi = \sum_{ia} C^\phi_{ia} \mathcal{P}_{ia} + D^\phi,
\]

\[
\delta j_e = \sum_{ia} C^j_{ia} \mathcal{P}_{ia}, \quad \delta \rho_e = \sum_{ia} C^\rho_{ia} \mathcal{P}_{ia},
\]

\[
\delta j_n = \sum_{ia} C^j_{ia} \mathcal{P}_{ia} + D^j, \quad \delta \rho_n = \sum_{ia} C^\rho_{ia} \mathcal{P}_{ia} + D^\rho,
\]

\[
\delta W_{en} = \sum_{ia} C^{W}_{ia} \mathcal{P}_{ia} + D^{W},
\]

where the coefficients $C$’s and $D$’s can be derived from previous equations.
Then we can derive,

$$ (\epsilon_a - \epsilon_i + \omega) P_{ai} = \frac{-\omega}{\epsilon_a - \epsilon_i} \int \psi_i(\mathbf{r}) j_p \psi_a(\mathbf{r}) A_0 \frac{\mathbf{r}}{c} d\mathbf{r} $$

$$ + \frac{-\omega}{\epsilon_a - \epsilon_i} \int \psi_i(\mathbf{r}) j_p \psi_a(\mathbf{r}) D^A d\mathbf{r} + \int \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) D^{Wen} d\mathbf{r} $$

$$ + \sum_{jb} \frac{-\omega}{\epsilon_a - \epsilon_i} \int \psi_i(\mathbf{r}) j_p \psi_a(\mathbf{r}) C_{jb}^A d\mathbf{r} P_{jb} $$

$$ + \sum_{jb} \frac{-\omega}{\epsilon_a - \epsilon_i} \int \int \psi_i(\mathbf{r}) j_p \psi_a(\mathbf{r}) f_{xc}(\mathbf{r}, \mathbf{r}', \omega) C_{jb}^{je} d\mathbf{r}' d\mathbf{r} P_{jb} $$

$$ + \sum_{jb} \int \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) C_{jb}^{Wen} d\mathbf{r} P_{jb} $$

$$ + \sum_{jb} \int \int \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega) C_{jb}^{pe} d\mathbf{r}' d\mathbf{r} P_{jb}. $$
and,

\[(\epsilon_i - \epsilon_a + \omega) P_{ia} = \frac{-\omega}{\epsilon_i - \epsilon_a} \int \psi_a(r) j_p \psi_i(r) \frac{A_0}{c} \, dr + \frac{-\omega}{\epsilon_i - \epsilon_a} \int \psi_a(r) j_p \psi_i(r) D^A \, dr + \int \psi_a(r) \psi_i(r) D^{Wen} \, dr\]

\[+ \sum_{jb} \frac{-\omega}{\epsilon_i - \epsilon_a} \int \psi_a(r) j_p \psi_i(r) C^A_{jb} \, dr \, P_{jb}\]

\[+ \sum_{jb} \frac{-\omega}{\epsilon_i - \epsilon_a} \int \int \psi_a(r) j_p \psi_i(r) f_{xc}(r, r', \omega) C^e_{jb} \, dr' \, dr \, P_{jb}\]

\[+ \sum_{jb} \int \psi_a(r) \psi_i(r) C^{Wen}_{jb} \, dr \, P_{jb}\]

\[+ \sum_{jb} \int \int \psi_a(r) \psi_i(r) f_{Hxc}(r, r', \omega) C^{pe}_{jb} \, dr' \, dr \, P_{jb}.\]
Let us denote:

\[ F_{ia} \equiv \frac{-\omega}{\epsilon_a - \epsilon_i} \int \psi_i(r) j_p \psi_a(r) \frac{A_0}{c} dr + \frac{-\omega}{\epsilon_a - \epsilon_i} \int \psi_i(r) j_p \psi_a(r) D^A dr + \int \psi_i(r) \psi_a(r) D^{W_{en}} dr'. \]

\[ M_{ia,jb} \equiv \frac{-\omega}{\epsilon_a - \epsilon_i} \int \psi_i(r) j_p \psi_a(r) C^A_{jb} dr. \]

\[ K_{ia,jb} \equiv \frac{-\omega}{\epsilon_a - \epsilon_i} \int \int \psi_i(r) j_p \psi_a(r) f_{xc}(r, r', \omega) C^i_{jb} dr' dr + \int \psi_i(r) \psi_a(r) C^{W_{en}}_{jb} dr + \int \int \psi_i(r) \psi_a(r) f_{H} f_{xc}(r, r', \omega) C^\rho_{jb} dr' dr. \]

\[ \Rightarrow \begin{cases} (\epsilon_a - \epsilon_i + \omega) P_{ai} = F_{ia} + \sum_{jb} (M_{ia,jb} + K_{ia,jb}) P_{jb}, \\ (\epsilon_i - \epsilon_a + \omega) P_{ia} = F_{ai} + \sum_{jb} (M_{ai,jb} + K_{ai,jb}) P_{jb}. \end{cases} \]
A Linear System on $\mathcal{P}$

By simple subtraction and addition, we have a linear system on $\mathcal{P}_{ia}$,

$$(S - \omega^2 I)\mathcal{P} = F,$$  \hspace{1cm} (3)

with

$$S_{ia,jb} = (\epsilon_a - \epsilon_i)^2 \delta_{ij} \delta_{ab} - 2(\epsilon_a - \epsilon_i)(M_{ia,jb} + K_{ia,jb}),$$

and $F_{ia} = 2(\epsilon_a - \epsilon_i)F_{ia}$.

From the system, we can study

1. Given incident light $A_0$ with frequency $\omega$, solve the system $\Rightarrow$ self-consistent determination of the interactions.

2. Determination of the resonant eigenmodes $\omega \Leftrightarrow$ 
   $$\det(S - \omega^2 I) = 0.$$
About the linear system:

- The system is multiscale in nature: a multiscale scheme needs to be designed and applied.
- $S$ is of size $(\text{occ} \cdot \text{unocc}) \times (\text{occ} \cdot \text{unocc})$. $\text{occ, unocc}$: # of occupied and unoccupied KS orbitals.
- $S$ is nonlinear in $\omega$. Explicit form is difficult to use. Fortunately, matrix-vector product can be evaluated, which is good enough for Krylov subspace methods.
A Multiscale Scheme

A multi-scale scheme has the following steps: at iteration $m$,

1. **Micro solver**: Linear response of TDCDFT with $(\delta \phi^m, \delta A^m)$ and $\delta \tilde{R}^m((\delta j^m_n, \delta \rho^m_n))$ to obtain $(\delta j_{e}^{m+1}, \delta \rho_{e}^{m+1})$; and Classical MD with $(\delta \phi^m, \delta A^m)$ and $(\delta j_{e}^{m}, \delta \rho_{e}^{m})$ to obtain $\delta \tilde{R}^{m+1}((\delta j_{n}^{m+1}, \delta \rho_{n}^{m+1}))$. Microscale on a smaller domain.

2. **Macro solver**: Maxwell’s equations with inputs $(\delta j^{m+1}_e, \delta \rho^{m+1}_e)$ to update $(\delta \phi^{m+1}, \delta A^{m+1})$; Macroscale on a larger domain.

3. Repeat until self-consistent convergence.

Linear interpolation is used for the communication between the numerical solutions of the micro and macro solvers.
Linear Solver and Eigensolver


1. Initialization: an initial guess of $\omega_0$.
2. With $\omega^m$, update $S(\omega^m)$.
3. With $S(\omega^m)$, update $\omega^{m+1}$.
4. Repeat until convergence.

The solvers are incorporated into the multiscale scheme.
Within the BiCGSTAB and Jacobi-Davidson algorithms:  
Macro solver: hybrid edge-nodal finite element method for Maxwell’s equations.  
Micro solver: TDCDFT and Hamilton’s Eqn’s.  
Meshes for macro and micro solvers:

**Figure**: Left: domain and mesh for Maxwell’s eqn; Right: a slice at $z = 0$.  
Example 1

Computed lowest eigenfrequency: 0.3452 (a.u.) with 4 occ, 8 unocc.

Computed linear response spectra:

Figure: For methane ($CH_4$): Response spectra (frequency in a.u.).
Example 2

Computed lowest eigenfrequency: 0.3053 (a.u.) with 4 occ, 8 unocc.

Computed linear response spectra:

Figure: For silane ($SiH_4$): Response spectra (frequency in a.u.).
Example 3

Computed lowest eigenfrequency: 0.142514180708 (a.u.) with 34 $occ$, 34 $unocc$.

Computed linear response spectra:

Figure: For $trans$-Azobenzene ($C_{12}H_{10}N_2$): Response spectra (frequency in a.u.).
Example 3 cont’ed

Computed lowest eigenfrequency: 0.142514180708 (a.u.) with 34 occ, 34 unocc.

Computed linear response spectra:

Figure: Left: dipole moment; Right: $|\delta \mathbf{R}|$. 
Example 3 cont’ed

With surface plasmon enhancement:

Figure: Gold nano particles and molecule
Example 3 cont’ed

With surface plasmon enhancement:

Figure: Plots of $|E|$ with $\omega = 0.15$ (a.u.). Radius of the nano particle is 10nm, and inter-distance of the nano particles is 2, 4, 6nm. The maximum magnitude is 6.352e0, 5.050e0, 4.434e0 corresponding to the inter-distances.
With surface plasmon enhancement:

**Figure:** Plots of $|E|$ with $\omega = 0.15$ (a.u.). Radius of the nano particle is 15, 20, 25 nm, and inter-distance of the nano particles is 2 nm. The maximum magnitude is $8.017e0, 1.048e1, 1.459e1$ corresponding to the inter-distances.
Example 3 cont’ed

With surface plasmon enhancement:

\[
\begin{align*}
|\mu| & \quad \text{Size of nano particles} = 10 \text{nm}, \text{inter-distance} = 10 \text{nm}; \\
& \quad \text{Angle between the polarization direction and the } x\text{-axis is } 0, \frac{\pi}{6}, \frac{\pi}{3}, \frac{\pi}{2}. \text{ Red: sphere; Black: no Gold particles}
\end{align*}
\]

**Figure**: Dipole moment $|\mu|$. Size of nano particles $= 10\text{nm}$, inter-distance $= 10\text{nm}$; Angle between the polarization direction and the $x$-axis is $0, \pi/6, \pi/3, \pi/2$. Red: sphere; Black: no Gold particles
Example 3 cont’ed

With surface plasmon enhancement:

![Graphs showing dipole moment |µ| as a function of frequency.](image)

**Figure:** Dipole moment |µ|. Size of nano particles = 20nm, inter-distance = 10nm; Angle between the polarization direction and the x-axis is $0, \pi/6, \pi/3, \pi/2$. Red: sphere; Black: no Gold particles
Conclusion

• Multiphysics modeling and multiscale computation of optical response of nanostructure with semiclassical theory.

• Semiclassical model: Maxwell + TDCDFT + Hamilton’s Eqn. Linear response formulation is derived.

• Multiscale Scheme: micro solver and macro solver. Self-consistent determination of the interactions, and computation of resonant eigenfrequencies.

• Future plans: more real problems; time-domain implementations.
Thank You

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