Fast Algorithms for Estimating Optical Absorption Spectrum

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Outline

• Absorption spectrum estimation via linear response time-dependent density functional theory (LR-TDDFT)
• Model order reduction techniques for approximating absorption spectrum
• Solving linear response eigenvalue problems
• Computational examples
Excited States of Molecules and Optical Absorption Spectroscopy
Application

Quantum Many-body Problem

- \( H\Psi(r_1, r_2, \ldots, r_{n_e}) = \Psi(r_1, r_2, \ldots, r_{n_e})E \)
  \[
  H = -\sum_{i}^{n_e} \nabla_i^2 + \sum_{i}^{n_e} v_n(r_i) + \frac{1}{2}\sum_{i\neq j} \frac{1}{|r_i - r_j|} \]
- Ground state \( E_0 \) vs excited states \( E_1, E_2 \ldots \)
- \( |\Psi_j|^2 \) gives the probability density of find electron \( i \) at \( r_i \)
- Electron density \( \rho(r_1) = \int dr_2 \cdots dr_{n_e} |\Psi(r_1, r_2, \ldots, r_{n_e})|^2 \) (contains all information such as chemical bonding, energy etc.)
- Excitation energy \( E_1 - E_0, E_2 - E_1, \ldots \)

Computationally challenging!
Density Functional Theory (DFT) 
(turn many-body into single-particle)

- Ground-state observable as a functional of $\rho(r), r \in \mathbb{R}^3$ (Hohenberg-Kohn Theorem)
- The independent particle picture (interaction through a mean-contributed by all electrons)
- Kohn-Sham DFT at ground state
  \[ H\psi_j(r) = \varepsilon_j \psi_j(r) \]
  \[ H(\rho) = H_0 + V_{Hxc}(\rho), \rho = \sum_{j=1}^{n_e} |\psi_j|^2 \]
- Estimate excitation energy from occupied $\varepsilon_j$ and unoccupied $\varepsilon_\alpha$:
  \[ \Delta\varepsilon_{ja} = \varepsilon_\alpha - \varepsilon_j \]
Time-dependent DFT

- Observables determined by time-dependent charge density $\rho(r, t)$ (Runge-Gross Theorem)

- $H(t)\psi_i(r, t) = i \frac{\partial}{\partial t} \psi_i(r, t)$, where $H = H_0 + V_{Hxc}(\rho(r, t))$, $\rho(r, t) = \sum_{j=1}^{ne} |\psi_i(r, t)|^2$

- $\psi_i(r, 0) = \psi_i^{KS}(r)$, $\rho(r, 0) = \rho^{KS}(r)$

- Excite the system with an electric field $E(r, t) = -k_0 x \delta(t)$ (instantaneous Hamiltonian perturbation)

- Absorption spectrum: measure the change in $\rho$ or dynamical polarizability in frequency domain

$$\alpha_x(\omega) = -\int dr \ x \Delta \rho(r, \omega), \hspace{1cm} \Delta \rho(r, t) = \rho(r, t) - \rho^{KS}(r)$$

Must use small time steps
Linear Response TDDFT

- Hamiltonian perturbation
  \[ H(t) = H_{KS} + \delta \nu_{ext}(t) \]
- Charge density perturbative series (in orders of \( \delta \nu_{ext}(t) \))
  \[ \rho(r, t) = \rho_{KS}(r) + \Delta \rho^{(1)}(r, t) + \Delta \rho^{(2)}(r, t) + \cdots \]
- Linear response
  \[ \Delta \rho^{(1)}(r, \omega) = \chi(\omega) \delta \nu_{ext}(\omega) \]
- Resonance at the poles of the polarizability \( \chi(\omega) \)
  \[ \chi(r, r'; \omega) = \sum_j \frac{s_j(r)s_j(r')}{\omega - \lambda_j + i\eta} \]
- Spectral function and dynamic polarizability
  \[ \lim_{\eta \to 0^+} -\text{Im} \chi = \sum_j s_j(r)s_j(r')\delta(\omega - \lambda_j) \quad \alpha_{xx}(\omega) = -\langle x | \text{Im} \chi | x \rangle \]
Linear perturbation for linear problem

• $H$ is perturbed by an external potential $\Delta \nu$
  \[ H \rightarrow H + \Delta \nu \]

• Its eigenvalues and eigenfunctions will change also, i.e.
  \[ \psi_j \rightarrow \psi_j + \Delta \psi_j, \ \varepsilon_j \rightarrow \varepsilon_j + \Delta \varepsilon_j \]

• Change in $\rho = \sum_j |\psi_j|^2$, $\rho \rightarrow \rho + \Delta \rho$

• In general, linear perturbation analysis yields

$$\chi_0 = \sum_{j,a} \frac{\psi_j(r)\psi_a(r)\psi_j(r')\psi_a(r')}{\omega - (\varepsilon_j - \varepsilon_a) + i\eta} - \sum_{j,a} \frac{\psi_a(r)\psi_j(r)\psi_a(r')\psi_j(r')}{\omega + (\varepsilon_j - \varepsilon_a) + i\eta}$$

$$\Delta \rho = \chi_0 \Delta \nu,$$
Self-consistent perturbation

• When the Hamiltonian of the TDDFT Hamiltonian is perturbed by $\delta v_{\text{ext}}$ at $t=0$
• The changes in the wavefunction and charge density $\rho$ must be *self-consistent*
• The cumulative change in Hamiltonian

$$\Delta v = \delta v_{\text{ext}} + \Delta v_{Hxc}(\Delta \rho), \Delta v_{Hxc} = \int \frac{1}{|r-r'|} \Delta \rho(r') dr' + \int \frac{\delta v_{xc}}{\delta \rho} \Delta \rho(r') dr'$$

$$\Delta \rho = \chi_0 \Delta v$$
From $\chi_0$ to $\chi$

- Find $\chi$ such that $\Delta \rho \approx \chi \delta v_{\text{ext}}$
- Start from $\Delta \rho = \chi_0 \Delta v = \chi_0 (\delta v_{\text{ext}} + f_{\text{Hxc}} \Delta \rho)$, where $f_{\text{Hxc}} \equiv \frac{1}{|r-r'|} + \frac{\delta v_{\text{xc}}(\rho(r))}{\delta \rho(r')}$
- Rearrange terms
  \[(I - \chi_0 f_{\text{Hxc}}) \Delta \rho = \chi_0 \delta v_{\text{ext}}\]
- Therefore
  \[\chi(\omega) = (I - \chi_0(\omega) f_{\text{Hxc}})^{-1} \chi_0(\omega)\]
- We are interested in the poles of $\chi$
Simplification

\[ \chi_0 = \sum \frac{\psi_j(r)\psi_a(r)\psi_j(r')\psi_a(r')}{\omega-(\varepsilon_j-\varepsilon_a)+i\eta} - \sum \frac{\psi_a(r)\psi_j(r)\psi_a(r')\psi_j(r')}{\omega+(\varepsilon_j-\varepsilon_a)+i\eta} \]

- Define \( \Phi(r) = \{\psi_j(r)\psi_a(r) \ldots\} \), \( \hat{\Phi}(r) = \{\Phi(r) \Phi(r)\} \)

and \( D(\omega) = \begin{bmatrix} (\omega + i\eta)I - D_0 & 0 \\ 0 & -(\omega + i\eta)I - D_0 \end{bmatrix} \) with \( D_0 = \text{diag}\{\varepsilon_j - \varepsilon_a, \ldots\} \),

- Rewrite \( \chi_0 \) as \( \chi_0 = \hat{\Phi}D(\omega)^{-1}\hat{\Phi}^T \), where
Sherman-Morrison-Woodbury

- $\chi = (I - \chi_0 f_{Hxc})^{-1} \chi_0, \quad \chi_0 = \hat{\Phi} D(\omega)^{-1} \hat{\Phi}^T$
- $\chi = \left[ I + \hat{\Phi} (D - \hat{\Phi}^T f_{Hxc} \hat{\Phi})^{-1} \hat{\Phi}^T f_{Hxc} \right] \hat{\Phi} D^{-1} \hat{\Phi}^T$
- Define
  $$H = \begin{pmatrix} D_0 + \Phi^T f_{Hxc} \Phi & \Phi^T f_{Hxc} \Phi \\ \Phi^T f_{Hxc} \Phi & D_0 + \Phi^T f_{Hxc} \Phi \end{pmatrix}$$
- If follows that
  $$\chi(\omega) = \hat{\Phi} \left[ (\omega + i\eta)S - H \right]^{-1} \hat{\Phi}^T,$$
  where
  $$S = \begin{pmatrix} I & \\ -I & \end{pmatrix}$$
Casida Eigenvalue Problem

- The poles of $\chi(\omega) = \hat{\Phi}[(\omega + i\eta)S - H]^{-1} \hat{\Phi}^T$ are at the eigenvalues of the Casida Hamiltonian

$$H = \begin{pmatrix} A & B \\ B & A \end{pmatrix}, \quad S = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad \text{where}$$

$$A = D_0 + \Phi^T f_{Hxc} \Phi, \quad B = \Phi^T f_{Hxc} \Phi,$$

$$D_0 = \text{diag}\{\varepsilon_j - \varepsilon_a, \cdots\}$$
Absorption spectrum

- Dynamic polarizability $\alpha(\tilde{\omega})$, $\tilde{\omega} = \omega + i\eta$
  
  $\alpha(\tilde{\omega}) \equiv d^T G^{-1}(\tilde{\omega}) d$

  $$d = \begin{pmatrix} d_x & d_y & d_z \\ d_x & d_y & d_z \end{pmatrix}, \quad G(\tilde{\omega}) = H - \tilde{\omega} S,$$

  $$H = \begin{pmatrix} A & B \\ B & A \end{pmatrix}, \quad S = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad A = A^T, B = B^T$$

  $A, B \in \mathbb{R}^n$, $n \propto \text{(number of atoms)}^2$

- Absorption spectrum
  
  $\sigma(\omega) \propto -\text{Im}(\text{Tr}[\alpha(\tilde{\omega})])$
Computing $\sigma(\omega)$ via Diagonalization

- Eigendecomposition of $S^{-1}H = \begin{pmatrix} A & B \\ -B & -A \end{pmatrix} = \begin{pmatrix} U & V \\ V & U \end{pmatrix} \begin{pmatrix} \Lambda & \\ & -\Lambda \end{pmatrix} \begin{pmatrix} U & -V \\ -V & U \end{pmatrix}^T$

- $\sigma(\omega) = -\text{Im} \sum_{j=1}^{n} f_i^2 \left[ \frac{1}{\omega-\lambda_j+i\eta} - \frac{1}{\omega+\lambda_j+i\eta} \right]$

where $f_i = d^T(u_i + \nu_i)$

- $\lim_{\eta \to 0^+} \sigma(\omega) = \sum_{j=1}^{n} f_j^2 \left[ \delta(\omega - \lambda_j) + \delta(\omega + \lambda_j) \right]$
Approximating $\sigma(\omega)$ directly

- Choose a set of frequency samples $\omega_1$, $\omega_2$, ..., $\omega_k$, and evaluate $\alpha(\tilde{\omega}_i) \equiv d^T G^{-1}(\tilde{\omega}_i) d$, 
  $\tilde{\omega}_i = \omega_i + i\eta$
  by solving a number of linear systems
- May require many samples to resolve different peaks
Model Order Reduction (MOR)

- Construct a reduced order model from a subspace spanned by $V$:

$$
\hat{\sigma}(\omega) = -\text{Im} \left( \text{Tr} \left[ \hat{d}^T \hat{G}^{-1}(\hat{\omega}) \hat{d} \right] \right), \quad \text{where}
\hat{d} = V^T d, \quad \hat{G} = V^T HV - \hat{\omega} V^T SV
$$

- Diagonalize the projected pencil $(\hat{H}, \hat{S})$, where $\hat{H} = V^T HV$, $\hat{S} = V^T SV$

$$
\hat{\sigma}(\omega) = -\text{Im} \sum_{j=1}^{k} \hat{f}_j^2 \left[ \frac{1}{\omega - \theta_j + i\eta} - \frac{1}{\omega + \theta_j + i\eta} \right]
$$
Connection with Reduced order models for linear dynamical systems

• Laplace transform of a linear dynamical system

\[ \Sigma = \begin{cases} 
(H - \omega S)x(\omega) = b \\
y(\omega) = c^T x 
\end{cases} \]

• Transfer function:

\[ y(\omega) = c^T (H - \omega S)^{-1} b \]

• Reduce order model:

\[ \hat{\Sigma} = \begin{cases} 
(\hat{H} - \omega \hat{S})\hat{x}(\omega) = \hat{b} \\
\hat{y}(\omega) = \hat{c}^T \hat{x} \\
\hat{y}(\omega) = \hat{c}^T (\hat{H} - \omega \hat{S})^{-1} \hat{b} 
\end{cases} \]
Choice of the MOR Subspace

• Preserve spectral properties of the full model within the frequency interval of interest
  - E.g., Krylov subspace
    \[ V = \text{orth} \left\{ \nu_0, S^{-1}H\nu_0, (S^{-1}H)^2\nu_0, \ldots \right\} \]
  - Provides a good approximation to the overall and both ends of spectrum of \((H, S)\)
  - Not sufficient for interior part of the spectrum

• Preserve additional (2 by 2 block) structure of the full model, and the pairing of the negative and positive eigenvalues
Structured Transformation

• Apply orthogonal $Q = \frac{1}{\sqrt{2}} \begin{pmatrix} I & -I \\ I & I \end{pmatrix}$ to $G(\tilde{\omega})$

$$Q^T G(\tilde{\omega}) Q = \begin{pmatrix} K & 0 \\ 0 & M \end{pmatrix} - \tilde{\omega} \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}$$

where $K = A - B$, $M = A + B$ are symmetric positive definite

• Rewrite $\alpha(\tilde{\omega})$ as

$$\alpha(\tilde{\omega}) = \tilde{d}^T \tilde{G}(\tilde{\omega})^{-1} \tilde{d}$$

where $\tilde{d} = (d_x, d_y, d_z)$, $\tilde{G}(\tilde{\omega}) = MK - \tilde{\omega}^2 I$
MOR by $K$-inner product Lanczos

- $MK$ is generally nonsymmetric, but it is self-adjoint with respect to $K$-inner product
  \[ \langle x, MKy \rangle_K = x^T KMKy = \langle MKx, y \rangle_K \]
- A reduced order model can be constructed from a $K$-orthonormal basis of the Krylov subspace
  \( \{d, MKd, (MK)^2d, \ldots \} \)
  \[ MKV_k = V_k T_k + f_k e_k^T, V_k^T K V_k = I_k, V_k^T K f_k = 0 \]
- \( \hat{\sigma}(\omega) = -\sum_{j=1}^{k} \tau_j^2 Im \left[ \frac{1}{\omega - \theta_j + i\eta} + \frac{1}{\omega + \theta_j + i\eta} \right] \), where
  \[ Ty_j = \theta_j y_j, \tau_j = e_{1}^T y_j \]
Numerical example

- P3B2 molecule
- Size of Kohn-Sham Hamiltonian
  $n = 1,364$
- $n_o = 305, n_v = 1,059$, dimension of the full $H$ is:
  $2n_on_v = 645,990$, with frozen core approximation dimension reduces to 451,134
- Reduced order (Lanczos steps)
  $k = 400$
- Compare with
  - Time domain simulation: $\Delta t = 0.0048$ fs, $T = 25$ fs (~5200 steps)
  - Davidson algorithm for computing the lowest 100 eigenpairs of the full model
RT-TDDFT took 15 hours
• Davidson for 100 eigenpairs (up to 4 eV) 4 hours
• Lanczos-TDDFT 2.5 hours

400 Lanczos steps
Rational Interpolating MOR

• Interior part of the absorption spectrum describes core excitation (by e.g., X-rays), difficult to estimate by Lanczos based MOR

• Construct a subspace of the form
  \[ V = \text{span}\{(H - \tau_1S)^{-1}d, (H - \tau_2S)^{-1}d, \ldots, (H - \tau_kS)^{-1}d\} \]
  where \(\tau_1, \tau_2, \ldots, \tau_k\) are carefully chosen interpolating frequencies, i.e.,
  \[ \alpha(\tau_j) = \hat{\alpha}(\tau_j) \]
Exploiting structure again

• Construct a subspace of the form
  \[ V = \text{span} \left\{ (MK - \tau_1^2 I)^{-1} d, (MK - \tau_2^2 I)^{-1} d, \ldots, (H - \tau_k^2 I)^{-1} d \right\} \]

• Make \( V \) \( K \)-orthonormal

• Projection: \( \hat{MK} = V^T KMKV \), \( \hat{d} = V^T K d \)

• Reduced order model:
  \[ \hat{\sigma}(\omega) = -\text{Im} \left( \text{Tr} \left[ \hat{d}^T (\hat{MK} - (\omega + i\eta)^2)^{-1} \hat{d} \right] \right) \]
### Numerical example

- Water clusters with 5, 10, 15, 20, 25 water molecules
- Energy window \([540eV, 600eV]\)
- \(\eta = 1eV\)
- reduced order scale favorably

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Matrix size $n = 50,000$, # eigenvalues = 8,172
Performance and scaling

(a) Wall time

(b) Total number of GEMMs
Solving the Linear Response Eigenvalue Problem

• Formulation:

1. \[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix} = \begin{pmatrix}
U & V \\
V & U
\end{pmatrix} \begin{pmatrix}
\Lambda & 0 \\
0 & -\Lambda
\end{pmatrix} \begin{pmatrix}
U & -V \\
-V & U
\end{pmatrix}^T
\]

2. \[
\begin{pmatrix}
0 & K \\
M & 0
\end{pmatrix} \begin{pmatrix}
Y \\
X
\end{pmatrix} = \begin{pmatrix}
Y \\
X
\end{pmatrix} \Lambda
\]

3. \[MKX = X\Lambda^2, KMY = Y\Lambda^2\]

• Interested in positive eigenvalues close to zero (valence excitation) or interior eigenvalues (core excitation)

• Use the fact that \(MK\) is self-adjoint with respect to \(K\);

• No need to compute both \(X\) and \(Y\) together;

\[Y = KXX\Lambda^{-1}\]
Optimization Based Approach

- Formulation: \( \min_{X,\Lambda} \frac{1}{2} \text{trace} \langle X, M K X \rangle_K \)
- Projected gradient: \( R = M K X - X \Lambda^2 \)
- \( K \)-inner product Davidson:
  - Extract approximation from
    \( S^{(i)} \leftarrow \text{span}\{S^{(i-1)}, T^{-1} R^{(i)}\} \)
- \( K \)-inner product LOBPCG
  - Approximate from
    \( \text{span}\{X^{(i)}, T^{-1} R^{(i)}, X^{(i-1)}\} \)
Preconditioner $T$

- Choose $T = D_K D_M$
- Choose $T = D^2$, where $D = \text{diag}\{\varepsilon_j - \varepsilon_a, \ldots\}$
- Choose $T_i = D_K D_M - \theta_i^2$, i.e.
  $$T^{-1} R = (T_1^{-1} R e_1, T_2^{-1} R e_2, \ldots)$$

- Flops: one $K$ and $M$ multiplications per iteration
- Memory: $3n_e$
Existing Algorithms

• Davidson based on:

\[
\begin{pmatrix}
S \\
S
\end{pmatrix}^T \begin{pmatrix}
0 & K \\
M & 0
\end{pmatrix} \begin{pmatrix}
Y \\
X
\end{pmatrix} - \begin{pmatrix}
Y \\
X
\end{pmatrix} \Theta = 0
\]

\[
S = \text{orth}\{S, T_K^{-1}R_K, T_M^{-1}R_M\}, R_K = KSX - SY\Theta
\]

• Minimization of Thoulous functional

\[
\min_{X^TY=I} \frac{1}{2} \text{trace} \left( X^T KX + Y^T M Y \right)
\]

Need both \(X\) and \(Y\), twice the amount of work, twice the memory footprint compared to K-inner product based algorithms
Example

• HBDMI:
  – Basis set: 6-31G
  – $n_o = 57$, $n_v = 207$
  – 5 eigenpairs

• Indigo:
  – Basis set: cc-pVTZ
  – $n_o = 68$, $n_v = 252$
  – 5 eigenpairs
MATVEC counts
Conclusion

• Absorption spectrum is a useful tool for screening molecules and materials for desirable optical properties
• In the linear response TDDFT framework, absorption spectrum can be accurately approximated by model order reduction techniques
• Valence excitation can be accurately approximated by $K$-inner product Lanczos
• Core absorption can be approximated by rational interpolating reduced order models
• Eigenpairs of the linear response operator provide a more precise description of the excitation process (hard to measure in experiments).
  – K-LOBPCG or K-Davidson is more efficient for positive eigenvalues close to 0
  – Interior eigenvalues need a different solver
• Further improve:
  – low rank approximation of the kernel matrices $A$, $B$ to reduce the cost of matrix-vector (matrix) multiplication
  – Efficient solution of multiple related linear systems