Molecular Excited States and Time-Dependent Density Functional Theory

Yuan Jiao

School of Advanced Interdisciplinary Sciences,SAIS
University of Chinese Academy of Sciences

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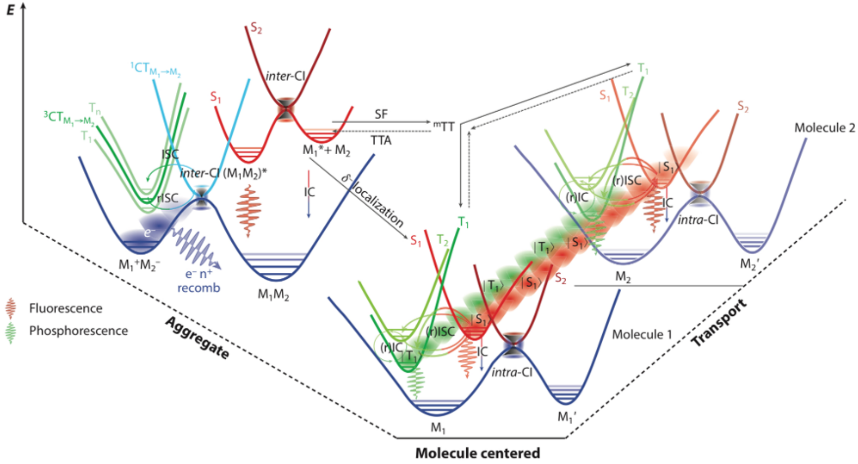
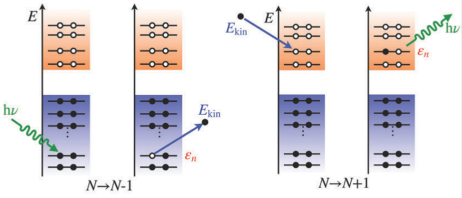
Contents

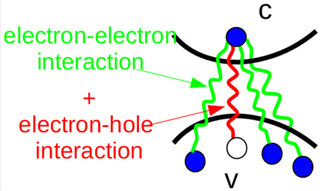
Contents

Molecular Excited States

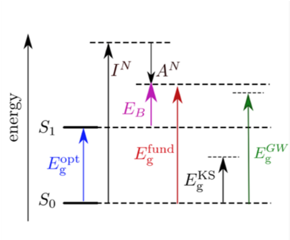


Absorption, Emission and Photoemission Process





- **Absorption**: Ground state to excited state
- **Emission**: Excited state to ground state
- **Photoemission**: Ground state to ionized state



Line spectra has two basic properties:

- **Location**: The location of the absorption peak-excitation ω_i
- **Intensity**: The height of the absorption peak-oscillator strength f_I

If we have the excited state wavefunction Ψ_I, the oscillator strength is defined as:

$$f_I = \frac{2}{3}\omega_I \sum_{n=x,y,z} |\langle \Psi_0 | \hat{r}_n | \Psi_I \rangle|^2$$

Where the Ψ_0 is the ground state wavefunction, and Ψ_I is the excited state wavefunction. We could also get the absorption spectra from the dynaimic polarizability $\alpha_{ij}(\omega)$:

$$\sigma(\omega) = -\frac{4\pi\omega}{3c}\Im(\alpha_{ii}(\omega))$$

Contents

Hohenberg-Kohn Theorem:

- HK I: The ground state or electron’s density is only depended on external potential.
- HK II: For a given external potential, the energy functional is the global minimum value varying every density. And this density could be considered as the ground state electron’s density.

Based on HK I ansatz, the many-electron Schrödinger equation is written in ν-representation as:

$$(\hat{T} + \hat{V}_{ee} + \hat{\nu})\Psi_0[\nu] = E_0[\nu]\Psi_0[\nu]$$

Based on HK II ansatz, the many-electron Schrödinger equation could be considered as a minimum problem of energy functional.

$$E_0[\nu] = \min_{\rho(\mathbf{r})\to N}\{F[\rho(\mathbf{r})] + \int d\mathbf{r}\nu(\mathbf{r})\rho(\mathbf{r})\}$$

The Runge-Gross theorem establishes the foundation of time-dependent density functional theory (TDDFT) by proving a one-to-one correspondence between the time-dependent electron density $\rho(\mathbf{r},t)$ and the external potential $v_{ext}(\mathbf{r},t)$, for a given initial state.

- **Core statement**: $\rho(\mathbf{r},t) \leftrightarrow v_{ext}(\mathbf{r},t)$
- **Condition**: Initial state must be non-degenerate
- **Significance**: Time-dependent generalization of the Hohenberg-Kohn theorem

$$\rho(\mathbf{r},t) \leftrightarrow \Psi(\mathbf{r},t) \leftrightarrow v_{ext}(\mathbf{r},t)$$

Time-Dependent Kohn-Sham Equation from Action Integral

For a many-electron system, the time-dependent Schrödinger equation can be written as:

$$i\partial_t \Psi(\mathbf{r}, t) = \hat{H}\Psi(\mathbf{r}, t)$$

The details of Hamiltonian of Schrödinger equation is:

$$\hat{H} = \hat{T}(\mathbf{r}) + \hat{V}_{e-e}(\mathbf{r}) + \hat{V}_{n-e}(\mathbf{r}) + \hat{V}_{ext}(\mathbf{r}, t)$$

The action integral is defined as:

$$A = \int_{t_0}^{t_1} dt \, \langle\Psi| \, i\partial_t - \hat{H}(r, t) \, |\Psi\rangle$$

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Time-Dependent Kohn-Sham Equation from Action Integral

Just like ground state Kohn-Sham equation, the action integral of Kohn-Sham system is:

$$A_S[\rho] = B_S[\rho] - \int_{t_0}^{t_1} dt \int d^3r \rho_S(\mathbf{r}, t) v_S(\mathbf{r}, t)$$

The action integral B could be rewritten as:

$$B_s[\rho] = \int_{t_0}^{t_1} dt \sum_i \langle\phi_i[\rho]|\, i\partial_t - \hat{T}(\mathbf{r})\, |\phi_i[\rho]\rangle + \int_{t_0}^{t_1} dt \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|r - r'|}$$

The stationary condition of action integral gives:

$$\frac{\delta A_S[\rho]}{\delta\rho} = \frac{\delta B_S[\rho]}{\delta\rho} - v_S(\mathbf{r}, t) = 0$$

Time-Dependent Kohn-Sham Equation from Action Integral

So, the action integral could be rewritten as:

$$A[\rho] = B_S[\rho] - \int_{t_0}^{t_1} dt \int d^3\mathbf{r}\rho(\mathbf{r},t)v_{ext}(\mathbf{r},t)$$

$$-\int_{t_0}^{t_1} dt \int d^3\mathbf{r}d^3\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|r-r'|} - A_{xc}[\rho]$$

and the action integral of exchange-correlation is defined as:

$$A_{xc}[\rho] = B_S[\rho] - B[\rho]$$

$$B[\rho] = \int_{t_0}^{t_1} dt \, \langle\Psi[\rho]|\, i\partial_t - \hat{T}(\mathbf{r}) - \hat{V}_{e-e}(\mathbf{r})\, |\Psi[\rho]\rangle$$

Time-Dependent Kohn-Sham Equation from Action Integral

with adiabatic approximation of exchange-correlation functional:

$$E_{xc}[\rho] = \frac{\delta A_{xc}[\rho]}{\delta \rho}|_{\rho(t)=\rho(0)}$$

the effective potential is defined as:

$$v_s(\mathbf{r}, t) = v_{ext} + \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho]$$

Time-dependent Kohn-Sham equation:

$$i\partial_t \phi_i = [-\frac{1}{2}\nabla^2 + v_{ext} + \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho]]\phi_i$$

Contents

Assumptions of Time-Dependent Density Functional Theory

In most of the TDDFT calculations of molecular systems, we have some basic assumptions:

- **Adiabatic approximation**: The exchange-correlation potential at any time depends only on the instantaneous electron density, neglecting memory effects.
- **Spin-restriction**: The spin-up and spin-down electron densities are assumed to be equal, simplifying the treatment of spin effects.
- **No fractional occupation**: Electrons are assumed to occupy orbitals in integer numbers, avoiding complications from partial occupancies.
- **Non-periodic systems**: The systems under study are considered to be non-periodic, which simplifies the boundary conditions and computational methods used.

Time-Propagation Approach

The time-dependent Kohn-Sham equation is:

$$i\partial_t \phi_k(\mathbf{r}, t) = \hat{H}_{KS}(\mathbf{r}, t)\phi_k(\mathbf{r}, t)$$

with a simple external potential:

$$\nu_{ext}(\mathbf{r}, t) = -e\mathbf{r} \cdot \mathbf{E}_0 \delta(t) = -e\mathbf{r} \cdot \mathbf{E}_0 \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} d\omega$$

So, the ground state orbitals can be simply replaced by a time-evolution operator:

$$\phi_k(\mathbf{r}, t = 0^+) = exp(ie\mathbf{r} \cdot \mathbf{E}_0)\phi_k(\mathbf{r}, t = 0^-)$$

and the time-dependent dipole moment is defined as:

$$\mu(t) = -e \int \rho(\mathbf{r}, t)\mathbf{r} d^3\mathbf{r}$$

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The we could calculate the dynamic polarizability with Fourier transform of time-dependent dipole moment:

$$\alpha_{ij}(\omega) = \frac{1}{E_{0j}} \int_0^\infty exp(-i\omega t)[\mu_i(t) - \mu_i(0)]dt$$

Finally, the absorption spectrum comes from the diagonal elements of dynamic polarizability:

$$Absorption \;\; Spectrum \rightarrow \alpha_{ii}(\omega)$$

Make a series expension of the time-dependent Kohn-Sham orbitals with a small perturbation parameter λ:

$$\phi_i(\mathbf{r}, t) = \phi_i^{(0)}(\mathbf{r}, t) + \lambda \phi_i^{(1)}(\mathbf{r}, t) + \lambda^2 \phi_i^{(2)}(\mathbf{r}, t) + \dots$$

with a external perturbation potential:

$$\hat{H}_{KS}(\mathbf{r}, t) = \hat{H}_{KS}^{(0)}(\mathbf{r}) + \lambda v_{ext}^{(1)}(\mathbf{r}, t) + \lambda \hat{H}_{KS}^{(1)}(\mathbf{r}, t) + \lambda^2 v_{ext}^{(2)}(\mathbf{r}, t) + \lambda^2 \hat{H}_{KS}^{(2)}(\mathbf{r}, t) + \dots$$

and the density with different order of perturbation parameter λ:

$$\rho(\mathbf{r}, t) = \sum_i f_i |\phi_i|^2 = \rho^{(0)}(\mathbf{r}, t) + \lambda \rho^{(1)}(\mathbf{r}, t) + \lambda^2 \rho^{(2)}(\mathbf{r}, t) + \dots$$

in detail:

$$\rho^{(0)}(\mathbf{r},t) = \sum_i n_i |\phi_i^{(1)}|^2$$

$$\rho^{(1)}(\mathbf{r},t) = \sum_i n_i |[\phi_i^{(0)}]^* [\phi_i^{(1)}] + [\phi_i^{(1)}]^* [\phi_i^{(0)}]|$$

The first-order response Hamiltonian is defined as:

$$\hat{H}_{KS}^{(1)}(\mathbf{r},t) = \int d^3\mathbf{r}' \frac{\rho^{(1)}(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + \int d^3\mathbf{r}' f_{xc}^{(0)}(\mathbf{r},t;\mathbf{r}',t')\rho^{(1)}(\mathbf{r}',t')$$

and the TDKS equation is:

$$i\partial_t \phi_i^{(1)}(\mathbf{r},t) = \hat{H}_{KS}^{(0)}(\mathbf{r})\phi_i^{(1)}(\mathbf{r},t) + [v_{ext}^{(1)}(\mathbf{r},t) + \hat{H}_{KS}^{(1)}(\mathbf{r},t)]\phi_i^{(0)}(\mathbf{r},t)$$

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Consider a periodic perturbation with single frequency ω for most of the cases:

$$v_{ext}^{(1)}(\mathbf{r},t) = v_{ext}^{+\omega}(\mathbf{r})e^{i\omega t} + h.c.$$

So, the general solution of first-order TDKS equation is:

$$\phi_i(\mathbf{r},t) = e^{-i\varepsilon_i^{(0)}t-\lambda i\Delta\varepsilon_i^{(1)}t}\{\phi_i^{(0)}(\mathbf{r})+$$

$$\lambda[\phi_i^{(1),+\omega}(\mathbf{r})e^{i\omega t} + \phi_i^{(1),-\omega}(\mathbf{r})e^{-i\omega t}]\} + O(\lambda^2)$$

Where the $\phi_i^{(1),+\omega}(\mathbf{r})$ and $\phi_i^{(1),-\omega}(\mathbf{r})$ are the first-order response orbitals with frequency of $+\omega$ and $-\omega$. And the $\Delta\varepsilon_i^{(1)}$ is the level shift of first-order response Hamiltonian.

$$\Delta\varepsilon_i^{(1)} = \int dt\,\langle\phi_i^{(0)}(\mathbf{r})|\,[v_{ext}^{(1)}(\mathbf{r},t) + \hat{H}_{KS}^{(1)}(\mathbf{r},t)]\,|\phi_i^{(0)}(\mathbf{r})\rangle$$

Sternheimer Approach

So, the first-order density is:

$$\rho^{(1)}(\mathbf{r},t) = \sum_i n_i |[\phi_i^{(0)}]^*[\phi_i^{+\omega,(1)}] + [\phi_i^{-\omega,(1)}]^*[\phi_i^{(0)}]| e^{-i\omega t} + cc.$$

After some algebra, we could get the Sternheimer equation:

$$i\partial_t e^{-i\varepsilon_i^{(0)}t-\lambda i\Delta\varepsilon_i^{(1)}t}\{\phi_i^{(0)}(\mathbf{r}) + \lambda[\phi_i^{(1),+\omega}(\mathbf{r})e^{i\omega t} + \phi_i^{(1),-\omega}(\mathbf{r})e^{-i\omega t}]\}$$

$$= \hat{H}_{KS}^{(0)}(\mathbf{r})e^{-i\varepsilon_i^{(0)}t-\lambda i\Delta\varepsilon_i^{(1)}t}\{\phi_i^{(0)}(\mathbf{r}) + \lambda[\phi_i^{(1),+\omega}(\mathbf{r})e^{i\omega t} + \phi_i^{(1),-\omega}(\mathbf{r})e^{-i\omega t}]\}$$

$$+\lambda\{[\int d^3 f_{Hxc}\rho^{(1)}(\mathbf{r}'.t) + v_{ext}^{(1)}(\mathbf{r},t)]\phi_i^{(0)}(\mathbf{r})\}e^{-i\varepsilon_i^{(0)}t-\lambda i\Delta\varepsilon_i^{(1)}t}$$

Now we devide the equation into two parts with frequency of $+\omega$ and $-\omega$ for resonant and anti-resonant solution. So we could rewrite the Sternheimer equation in a compact form:

$$\{\hat{H}_{KS}^{(0)}(\mathbf{r}) - \varepsilon_i^{(0)} + \omega + i\eta\}\phi_i^{(1),+\omega}(\mathbf{r}) =$$

$$-\{[\int d^3 f_{Hxc}\rho^{+\omega,(1)}(\mathbf{r}'.t) + v_{ext}^{+\omega}(\mathbf{r})]\}\phi_i^{(0)}(\mathbf{r})$$

$$\{\hat{H}_{KS}^{(0)}(\mathbf{r}) - \varepsilon_i^{(0)} - \omega + i\eta\}\phi_i^{(1),-\omega}(\mathbf{r}) =$$

$$-\{[\int d^3 f_{Hxc}\rho^{-\omega,(1)}(\mathbf{r}'.t) + v_{ext}^{-\omega}(\mathbf{r})]\}\phi_i^{(0)}(\mathbf{r})$$

with a decay factor η of external perturbation in $e^{-\eta t}$.

Casida Approach

The electron-hole basis is defined as:

$$\phi_i^{(1)} = \sum_a c_{ai} \phi_a^{(0)}(\mathbf{r})$$

Then, rewrite the first-order Sternheimer :

$$\sum_{aj} (-\omega + \varepsilon_j^{(0)}) \delta_{ab} \delta_{ij} e^{-i\omega t} c_{aj}^{+\omega} + \sum_{aj} (\omega + \varepsilon_i^{(0)}) \delta_{ab} \delta_{ij} e^{i\omega t} c_{aj}^{-\omega}$$

$$= \sum_{aj} \varepsilon_a^{(0)} \delta_{ab} \delta_{ij} c_{aj}^{+\omega}(t) + \sum_{aj} \varepsilon_a^{(0)} \delta_{ab} \delta_{ij} c_{aj}^{-\omega}(t)$$

$$+ \langle \phi_b^{(0)} | f_{Hxc}[\rho^{(0)}] \rho^{(1)} + v_{ext}^{(1)}(\mathbf{r}, t) | \phi_i^{(0)} \rangle$$

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Casida Approach

The Hartree-exchange-correlation kernel:

$$\langle \phi_b^{(0)} | f_{Hxc}[\rho^{(0)}]\rho^{(1)}(\mathbf{r},t) | \phi_i^{(0)} \rangle = \int d^3\mathbf{r} \int d^3\mathbf{r}' [\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r},\mathbf{r}')]$$

$$\sum_{aj} n_j \{ \{ \phi_j^{*(0)}(\mathbf{r}') c_{aj}^{+\omega} \phi_a^{(0)}(\mathbf{r}') + [c_{aj}^{-\omega}]^* \phi_{*a}^{(0)}(\mathbf{r}') \phi_j^{(0)}(\mathbf{r}') \} e^{-i\omega t} +$$

$$\{ \phi_j^{*(0)}(\mathbf{r}') c_{aj}^{-\omega} \phi_a^{(0)}(\mathbf{r}') + [c_{aj}^{+\omega}]^* \phi_a^{*(0)}(\mathbf{r}') \phi_j^{(0)}(\mathbf{r}') \} \} \phi_b^{*(0)}(\mathbf{r}) \phi_i^{(0)}(\mathbf{r})$$

More clearly

$$\langle \phi_b^{(0)} | f_{Hxc}[\rho^{(0)}]\rho^{(1)}(\mathbf{r},t) | \phi_i^{(0)} \rangle = \sum_{aj} n_j \{ K_{bi,aj} \{ c_{aj}^{+\omega} e^{-i\omega t} + c_{aj}^{-\omega} e^{i\omega t} \}$$
$$+ K_{bi,ja} \{ c_{aj}^{+\omega} e^{i\omega t} + c_{aj}^{-\omega} e^{-i\omega t} \} \}$$

Casida Approach

with the coupling matrix:

$$K_{bi,aj} = \int d^3\mathbf{r} \int d^3\mathbf{r}' \phi_a^{*(0)}(\mathbf{r}')\phi_j^{(0)}(\mathbf{r}')[f_{Hxc}(\mathbf{r},\mathbf{r}')]\phi_b^{*(0)}(\mathbf{r})\phi_i^{(0)}(\mathbf{r}) \rightarrow K$$

$$K_{bi,ja} = \int d^3\mathbf{r} \int d^3\mathbf{r}' \phi_j^{*(0)}(\mathbf{r}')\phi_a^{(0)}(\mathbf{r}')[f_{Hxc}(\mathbf{r},\mathbf{r}')]\phi_b^{*(0)}(\mathbf{r})\phi_i^{(0)}(\mathbf{r}) \rightarrow K'$$

$$\begin{bmatrix} \Delta E + \omega I & 0 & -\eta & 0 \\ 0 & \Delta E - \omega I & 0 & -\eta \\ \eta & 0 & \Delta E + \omega I & 0 \\ 0 & \eta & 0 & \Delta E - \omega I \end{bmatrix} \begin{bmatrix} Re[C^{+\omega}] \\ Re[C^{-\omega}] \\ Im[C^{+\omega}] \\ Im[C^{-\omega}] \end{bmatrix}$$

$$= -\begin{bmatrix} K & K' & 0 & 0 \\ K' & K & 0 & 0 \\ 0 & 0 & K & -K' \\ 0 & 0 & -K' & K \end{bmatrix} N \begin{bmatrix} Re[C^{+\omega}] \\ Re[C^{-\omega}] \\ Im[C^{+\omega}] \\ Im[C^{-\omega}] \end{bmatrix} - N^{\frac{1}{2}} \begin{bmatrix} Re[V^{+\omega}] \\ Re[V^{-\omega}] \\ Im[V^{+\omega}] \\ Im[V^{-\omega}] \end{bmatrix}$$

where $\Delta E_{bi,b'i'} = [\varepsilon_b^{(0)} - \varepsilon_i^{(0)}]\delta_{bb',ii'}$ and $N_{bi,b'i'} = \delta_{bb',ii'} n_{i'}$

The $V_{b'i'}^{+\omega}$ and $V_{b'i'}^{-\omega}$ is the external perturbation matrix element in electron-hole basis:

$$V_{b'i'}^{+\omega} = \langle \phi_{b'}^{(0)} | \, v_{ext}^{+\omega}(\mathbf{r}) \, | \phi_{i'}^{(0)} \rangle$$
$$V_{b'i'}^{-\omega} = \langle \phi_{b'}^{(0)} | \, v_{ext}^{-\omega}(\mathbf{r}) \, | \phi_{i'}^{(0)} \rangle$$

Now, we rewrite the above equation in a linear form:

$$\left[\begin{bmatrix} -\Delta E - \mathbf{K} & -\mathbf{K}' & -\eta & 0 \\ \mathbf{K}' & \Delta E + \mathbf{K} & 0 & -\eta \\ \eta & 0 & -\Delta E - \mathbf{K} & \mathbf{K}' \\ 0 & \eta & -\mathbf{K}' & \Delta E + \mathbf{K} \end{bmatrix} - \omega I\right] \begin{bmatrix} Re[B^{+\omega}] \\ Re[B^{-\omega}] \\ Im[B^{+\omega}] \\ Im[B^{-\omega}] \end{bmatrix} = -N \begin{bmatrix} -Re[V^{+\omega}] \\ Re[V^{-\omega}] \\ -Im[V^{+\omega}] \\ Im[V^{-\omega}] \end{bmatrix}$$

Where the $B_{bi}^{+\omega} = N^{\frac{1}{2}} c_{bi}^{+\omega}$ and $\mathbf{K} = N^{\frac{1}{2}} K N^{\frac{1}{2}}$.

Casida Approach

When the response process of electron cloud is much faster than the decay process, decay factor η is 0.

$$\left[\begin{bmatrix} -\Delta E - \mathbf{K} & -\mathbf{K}' \\ \mathbf{K}' & \Delta E + \mathbf{K} \end{bmatrix} - \omega I\right] \begin{bmatrix} Re[B^{+\omega}] \\ Re[B^{-\omega}] \end{bmatrix} = -N \begin{bmatrix} -Re[V^{+\omega}] \\ Re[V^{-\omega}] \end{bmatrix}$$

When only considering the eigen-excitation which means the $V \longrightarrow 0$, we could get a more simplified Sternheimer equation called Casida equation:

$$\left[\begin{bmatrix} -\Delta E - \mathbf{K} & -\mathbf{K}' \\ \mathbf{K}' & \Delta E + \mathbf{K} \end{bmatrix} - \omega I\right] \begin{bmatrix} Re[B^{+\omega}] \\ Re[B^{-\omega}] \end{bmatrix} = 0$$

Casida Approach

We rewrite the Casida equation in a more familiar form:

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

with the matrix elements:

$$A_{bi,aj} = \delta_{ij}\delta_{ab}(\epsilon_j - \epsilon_b) + \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r})\phi_b(\mathbf{r})[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}]\phi_a^*(\mathbf{r}')\phi_j(\mathbf{r}')$$

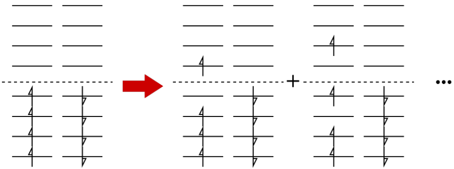
$$B_{bi,aj} = \int d\mathbf{r} \int d\mathbf{r}' \phi_i^*(\mathbf{r})\phi_b(\mathbf{r})[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}]\phi_j^*(\mathbf{r}')\phi_a(\mathbf{r}')$$

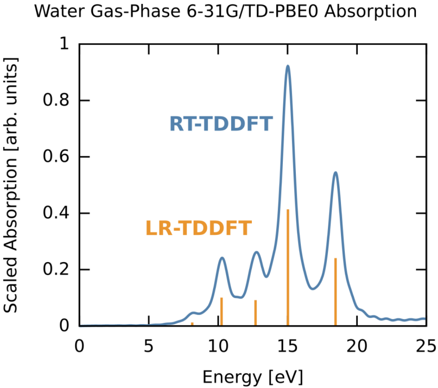
Excited wave function with CIS wave function form:

$$\Phi = \Psi_0 + \sum_{i,b} X_{ib}\Psi_i^b + Y_{ib}\Psi_b^i$$

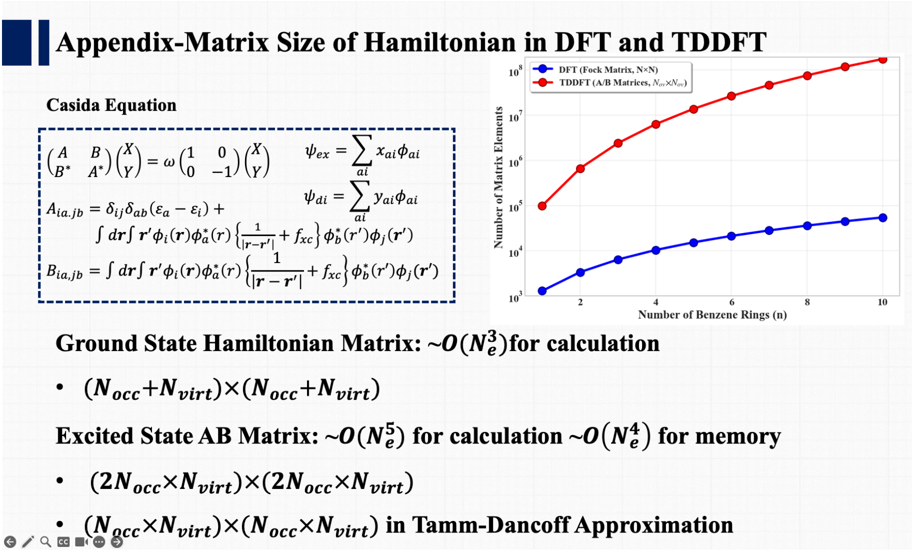
Overview of three Approaches

- Time-Propagation Approach
- Sternheimer Approach
- Casida Approach





Overview of three Approaches



Appendix-Matrix Size of Hamiltonian in DFT and TDDFT

Casida Equation

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} \qquad \psi_{ex} = \sum_{ai} x_{ai}\phi_{ai}$$

$$\psi_{di} = \sum_{ai} y_{ai}\phi_{ai}$$

$$A_{ia.jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + \int d\boldsymbol{r}\int \boldsymbol{r}'\phi_i(\boldsymbol{r})\phi_a^*(r)\left\{\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + f_{xc}\right\}\phi_b^*(r')\phi_j(\boldsymbol{r}')$$

$$B_{ia,jb} = \int d\boldsymbol{r}\int \boldsymbol{r}'\phi_i(\boldsymbol{r})\phi_a^*(r)\left\{\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + f_{xc}\right\}\phi_b^*(r')\phi_j(\boldsymbol{r}')$$

Ground State Hamiltonian Matrix: ~$O(N_e^3)$for calculation

- $(N_{occ}+N_{virt})\times(N_{occ}+N_{virt})$

Excited State AB Matrix: ~$O(N_e^5)$ for calculation ~$O(N_e^4)$ for memory

- $(2N_{occ}\times N_{virt})\times(2N_{occ}\times N_{virt})$
- $(N_{occ}\times N_{virt})\times(N_{occ}\times N_{virt})$ **in Tamm-Dancoff Approximation**

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Contents

Given the Casida matrix:

$$\mathcal{L} = \begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix}$$

and we want to solve

$$\mathcal{L}\Psi_k = \omega_k \Psi_k$$

where Ψ_k stacks (X_k, Y_k).
Assume we have a set of orthonormal subspace trial vectors:

$$\{\Psi_j\}_{j=1}^{m}, \quad \Psi_j = \begin{pmatrix} X_j \\ Y_j \end{pmatrix}$$

Construct matrix $W \in \mathbb{C}^{2N\times m}$, with columns Ψ_j.

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Project $\mathcal{L}$ into this subspace:

$$H_{\text{eff}} = W^{\dagger}\mathcal{L}W \in \mathbb{C}^{m\times m}$$

Solve the projected problem:

$$H_{\text{eff}}\mathbf{y}_i = \omega_i \mathbf{y}_i$$

Ritz vectors:

$$\Psi_i^{(\text{Ritz})} = W\mathbf{y}_i$$

Residuals:

$$\mathbf{r}_i = \mathcal{L}\Psi_i^{(\text{Ritz})} - \omega_i \Psi_i^{(\text{Ritz})}$$

If all $\|\mathbf{r}_i\|$ are below tolerance, the solution is found. Otherwise, use preconditioned residuals to further expand subspace W and repeat.

Numerical Method of TDDFT

If the residual is too large, expand the subspace as follows:

1. Compute the residual:

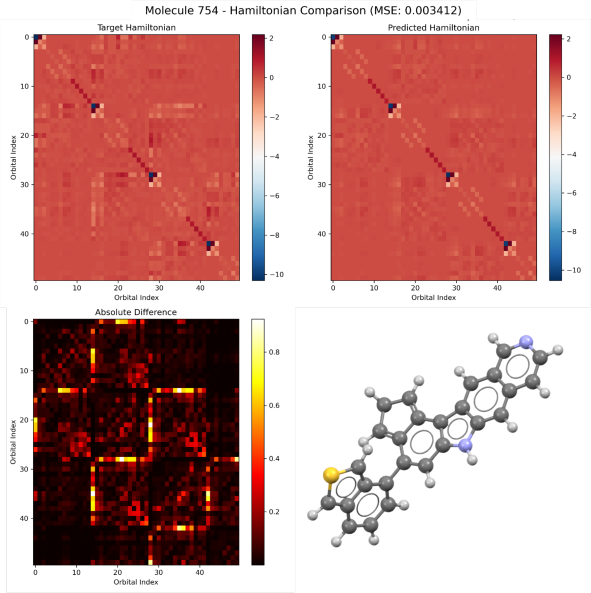
$$\mathbf{r}_i = \mathcal{L}\Psi_i^{(\text{Ritz})} - \omega_i \Psi_i^{(\text{Ritz})}$$

2. Apply a preconditioner:

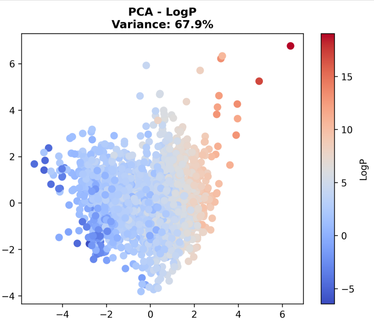
$$t_i \approx \frac{\mathbf{r}_i}{\operatorname{diag}(H_{\text{eff}}) - \omega_i}$$

3. Orthonormalize t_i against existing subspace vectors.
4. If t_i is not linearly dependent ($\|t_i\|$ big enough), add it to the subspace.
5. Repeat the Rayleigh-Ritz projection with the enlarged subspace.

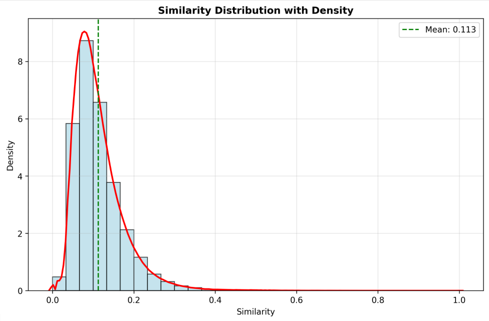
Some Results of DeepMolH



Some Results of DeepMolH



PCA - LogP
Variance: 67.9%



Similarity Distribution with Density

Some Results of DeepMolH

Ground-state DFT:

- Architecture of DeepMolH and implement it. MSE:4meV-2meV,MAE:40meV-20meV
- Architecture of DeepRSH and Dataset.→ Testing ! - PySCFAD
- DeepMolH-E3 !!! Equiformer_v2 with Equivariant Hamiltonian Generator