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MAX-PLANCK-GESELLSCHAFT

Large-Scale TDDFT for Finite and Periodic Systems: The new TDDFT in FHI-aims

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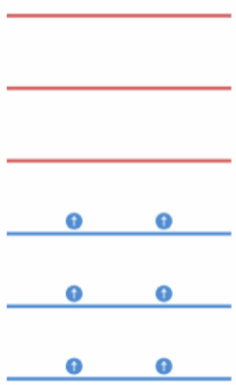
Overview

TDDFT in FHIaims

Theory and Implementation	The current TDDFT	The new TDDFT
Performance	Accuracy	Features

Time-dependent density functional theory (TDDFT)

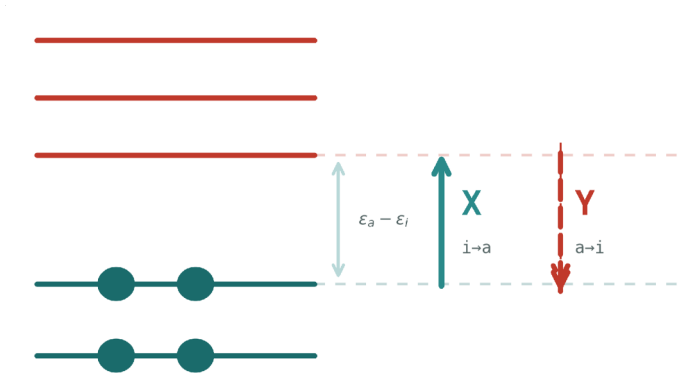
Excited state properties



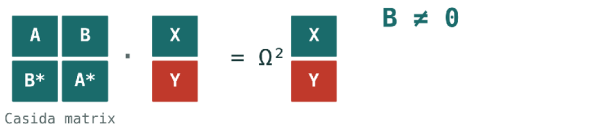
TDDFT is about figuring out **how the density reacts to a time-dependent response**

Full TDDFT

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Omega^2 \begin{pmatrix} X \\ Y \end{pmatrix}$$



$$B_{ia,jb} = (ia|bj) + \int\int \phi_i(\mathbf{r})\,\phi_a(\mathbf{r})\,f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')\,\phi_b(\mathbf{r}')\,\phi_j(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$



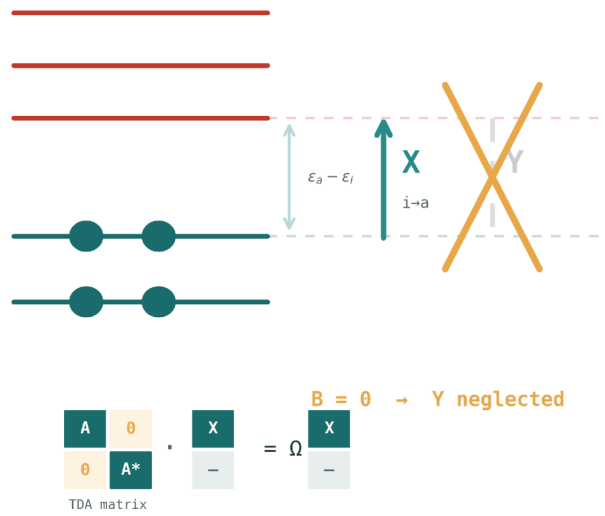
$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) + \int\int \phi_i(\mathbf{r})\,\phi_a(\mathbf{r})\,f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')\,\phi_j(\mathbf{r}')\,\phi_b(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$

A matrix
bare KS gap — zeroth order excitation energy
Coulomb: electron-hole attraction
XC kernel: dynamic screening
Mixes single-particle transitions
dressed particle-hole Hamiltonian

B matrix
excitation (j→b)
B = 0 → TDA; valid when |B| << |A|
B important: conical intersections

Tamm – Dankoff – Approximation (TDA)

$$A\,X = \Omega\,X$$



TDA
standard Hermitian eigenvalue problem
B matrix elements are small |B|/|A| ~ 0.01-0.1
TDA error smaller than XC functional error
Triplet instability: full matrix can become indefinite → imaginary excitation energies
Slightly blue-shifted excitation energies (~0.1-0.2 eV)

Old implementation

TDHF/RPA

TDDFT/TDA

LDA

No hybrid DFT
TDHF only serial

RI-V

No PBC

Dense solver

Restricted KS

New implementation

TDA

LDA/GGA
(extendable to meta GGA)

Hybrid DFT
fully parallel

RI-LVL

NTOs

PBC

Iterative solver

RKS/UKS

The “new” TDDFT

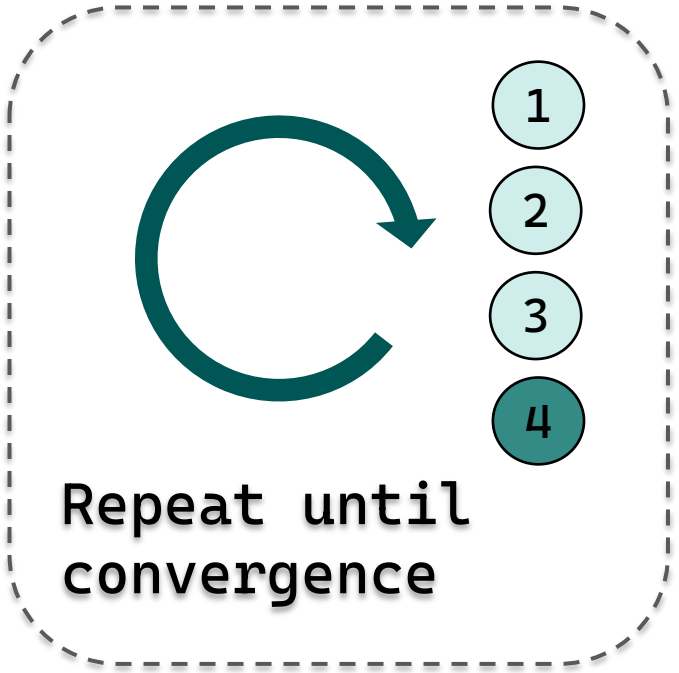
0 Trial Vector v_{ia}

1 First order Density $P_{\mu\nu} = \sum_{ia} c_\mu^i v_{ia} c_\nu^a$

2 Coulomb HFX $G_{\mu\nu}[P] = \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\lambda\sigma) - \alpha(\mu\lambda|\nu\sigma)]$

3 Fock Matrix $F_{\mu\nu} = G_{\mu\nu}[P] + F^{\mathrm{xc}\mu\nu}[P]$

4 Vector $\widetilde{v_{ia}} = (\epsilon_a - \epsilon_i)v_{ia} + [\mathbf{C_o^T F C_v}]_{ia}$



The “new” TDDFT

`Coulomb HFX` $G_{\mu\nu}[P] = \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\lambda\sigma) - \alpha(\mu\lambda|\nu\sigma)]$

`Coulomb` $\sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\lambda\sigma)]$

`Exchange` $-\alpha \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\lambda|\nu\sigma)]$

Fock routines calculate **Coulomb** and can now handle **non-symmetric density matrices**

RI-LVL

`Coulomb` is pure local quantity

`Exchange` is the bottleneck and **P** is non-symmetric

The “new” TDDFT

$$
\begin{aligned}
{}^1\widetilde{F}^{XC}_{\mu\nu} \mathrel{+}= & \; w_q \left[\frac{\delta^2 f}{\delta \rho_\alpha^2}\right]_q + \left[\frac{\delta^2 f}{\delta \rho_\alpha \delta \rho_\beta}\right]_q g^q \phi^q_\mu \phi^q_\nu \\
& + w_q \left(2\left[\frac{\delta f}{\delta \gamma_{\alpha\alpha}}\right]_q + \left[\frac{\delta f}{\delta \gamma_{\alpha\beta}}\right]_q \right) \mathbf{h}^q \cdot \nabla(\phi^q_\mu \phi^q_\nu) \\
& + w_q \left(\left[\frac{\delta^2 f}{\delta \rho_\alpha \delta \gamma_{\alpha\alpha}}\right]_q + \left[\frac{\delta^2 f}{\delta \rho_\alpha \delta \gamma_{\beta\beta}}\right]_q + \left[\frac{\delta^2 f}{\delta \rho_\alpha \delta \gamma_{\alpha\beta}}\right]_q \right) \left[(\nabla \rho^q \cdot \mathbf{h}^q)\phi_\mu \phi_\nu + g^q (\nabla \rho^q \cdot \nabla(\phi^q_\mu \phi^q_\nu)) \right] \\
& + w_q \left(\left[\frac{\delta^2 f}{\delta \gamma^2_{\alpha\alpha}}\right]_q + \frac{1}{2}\left[\frac{\delta^2 f}{\delta \gamma^2_{\alpha\beta}}\right]_q + 2\left[\frac{\delta^2 f}{\delta \gamma_{\alpha\alpha}\delta \gamma_{\alpha\beta}}\right]_q + \left[\frac{\delta^2 f}{\delta \gamma_{\alpha\alpha}\delta \gamma_{\beta\beta}}\right]_q \right) |\nabla \rho^q|^2 \, \mathbf{h}^q \cdot \nabla(\phi^q_\mu \phi^q_\nu)
\end{aligned}
$$

Eigensolver

SLEPc/PETSc

01 – Ritz extraction

$$V^T A V\,\mathbf{s} = \theta\,\mathbf{s}, \qquad \mathbf{u} = V\mathbf{s}$$

02 – Residual

$$\mathbf{r} = (A - \theta I)\,\mathbf{u}$$

03 – Diagonal preconditioner

$$t_i = \frac{-r_i}{D_{ii} - \theta}, \qquad D = \mathrm{diag}(A)$$

04 – Orthogonalisation

$$\mathbf{t} \leftarrow \mathbf{t} - V\left(V^T\mathbf{t}\right), \qquad \mathbf{t} \leftarrow \mathbf{t} \,/\, \|\mathbf{t}\|$$

05 – Subspace expansion

$$\mathcal{V} \leftarrow \mathcal{V} + \mathrm{span}\{\mathbf{t}\}$$

repeat until $\|\mathbf{r}\| < \varepsilon$

Screening in exact exchange part **breaks linearity**

Heuristic adjustment of screening (`crit_val`)

```
Eigval.      : 1.0E-05
eV
crit_val     : 1.0E-07
```

```
Settings for
ground state !
```

Eigenvalues converge faster than eigenvectors

Accuracy, Performance and some Features

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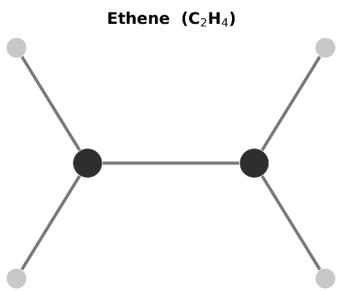
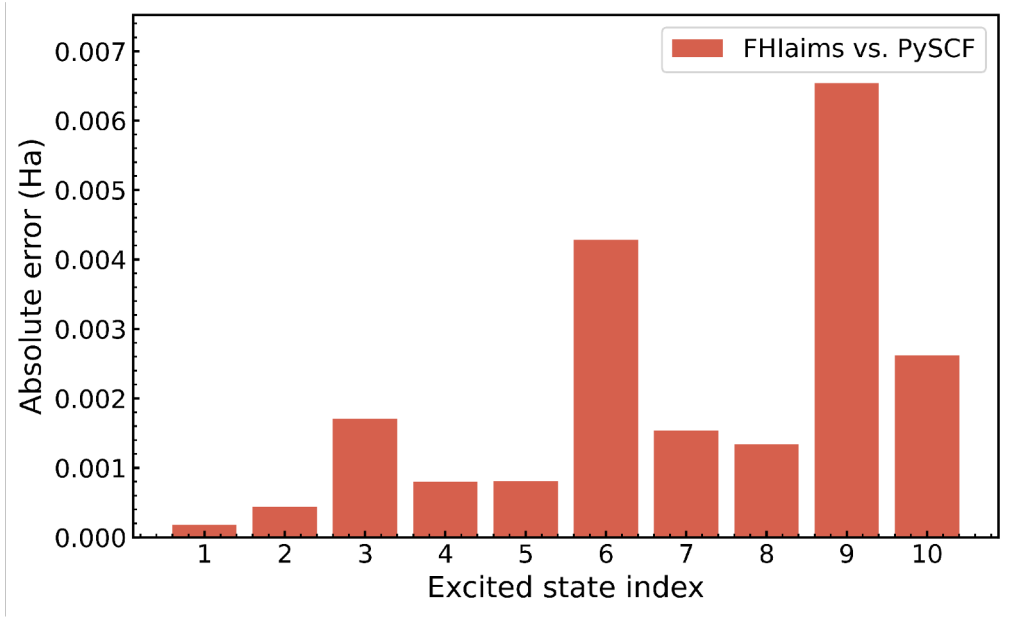
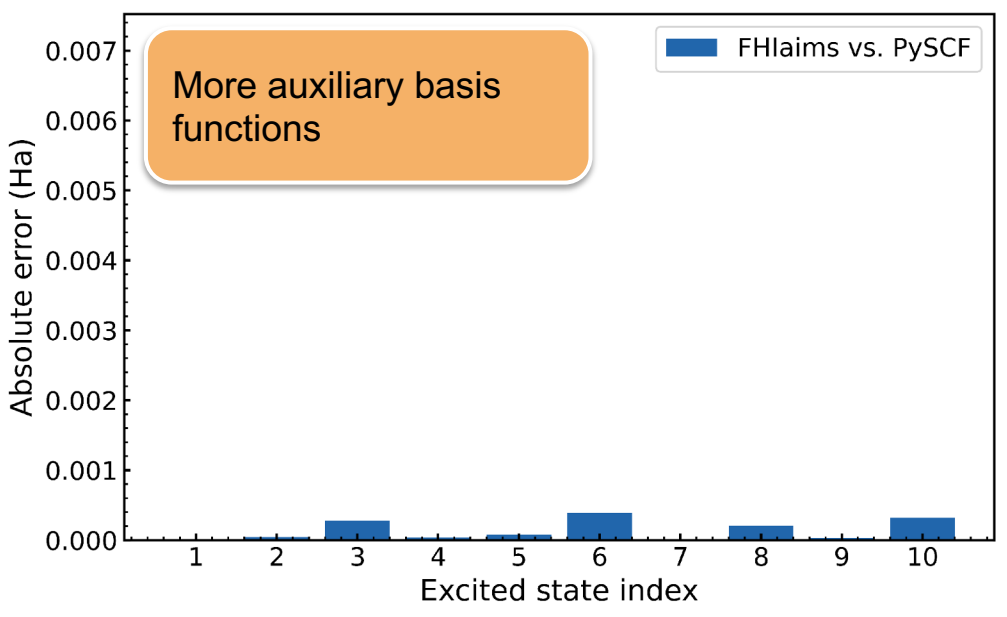
RI-LVL

RI-LVL introduces errors for “diffuse” excitations



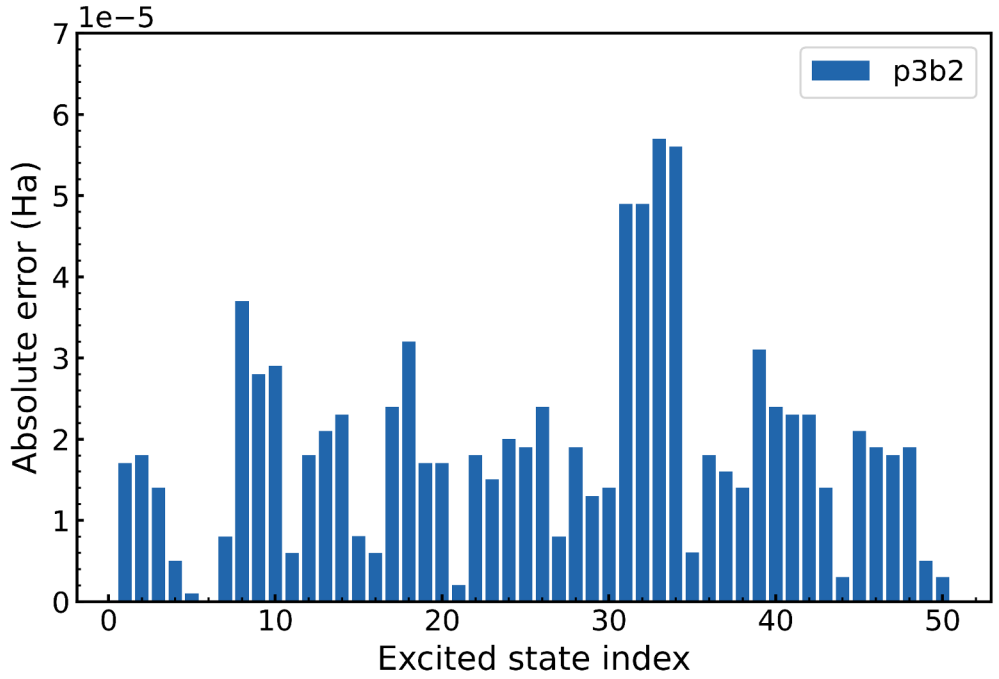


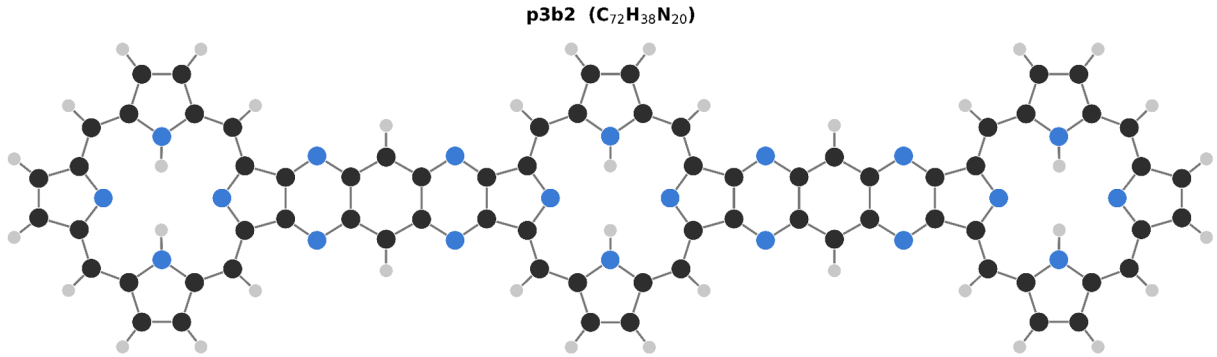


Rydberg-like states in **small molecules** need more auxiliary basis functions

RI-LVL

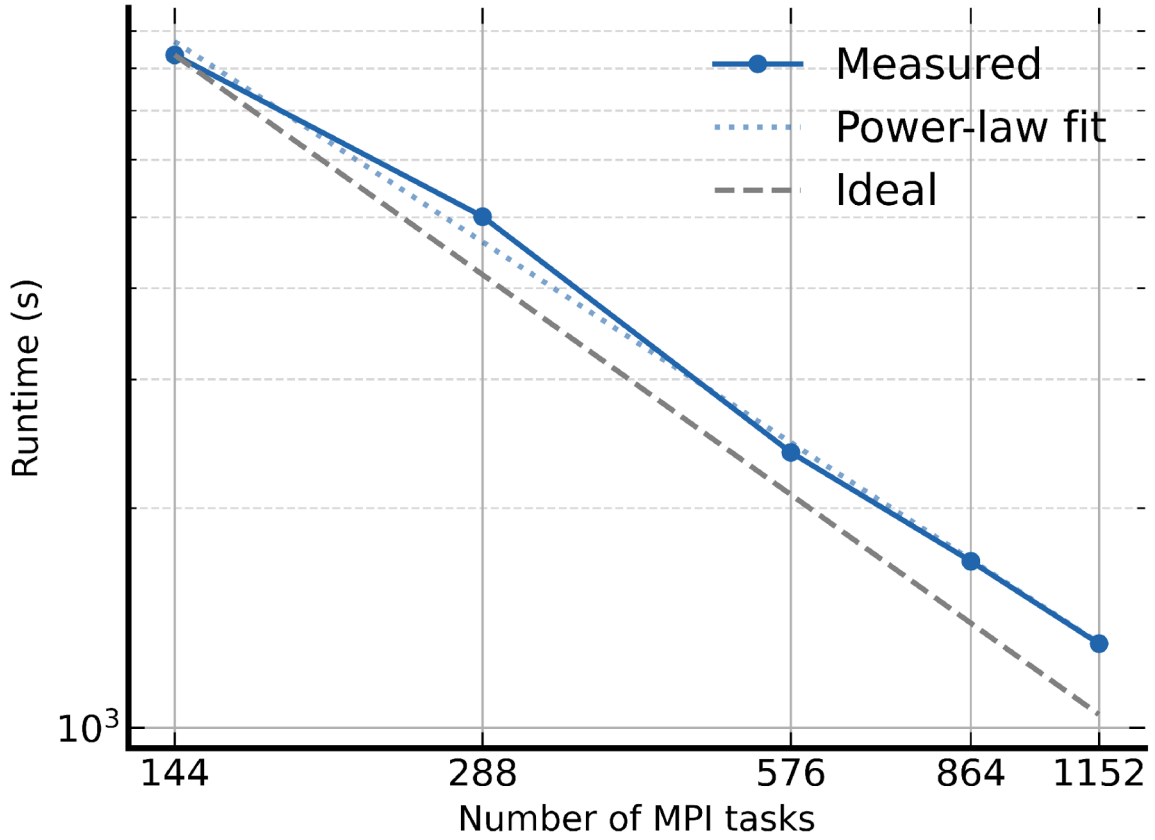
P3B2 – Dye molecule (130 atoms)

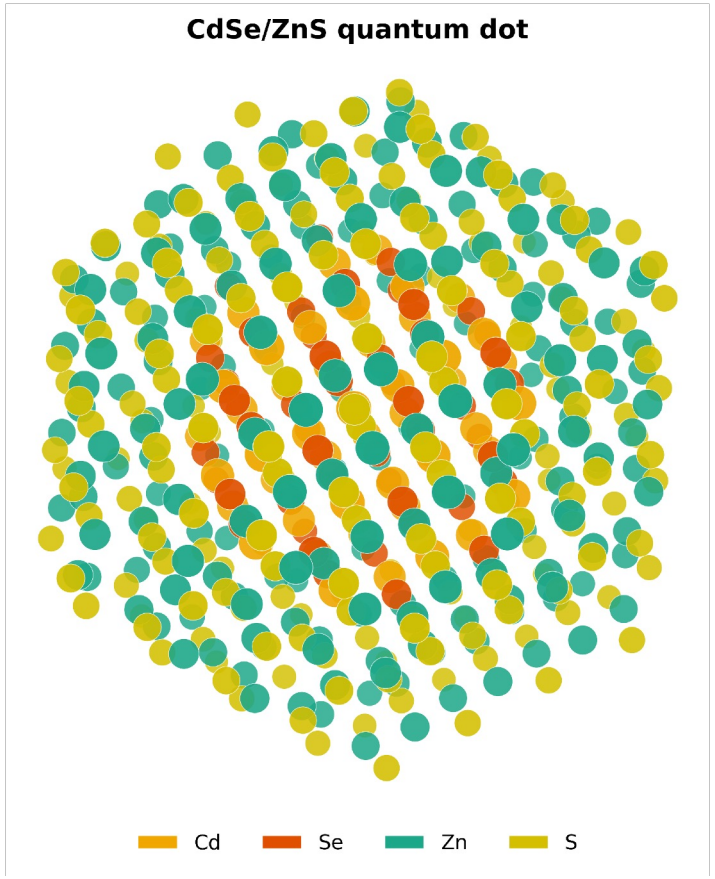




For valence excitation “standard” RI-LVL is sufficient.

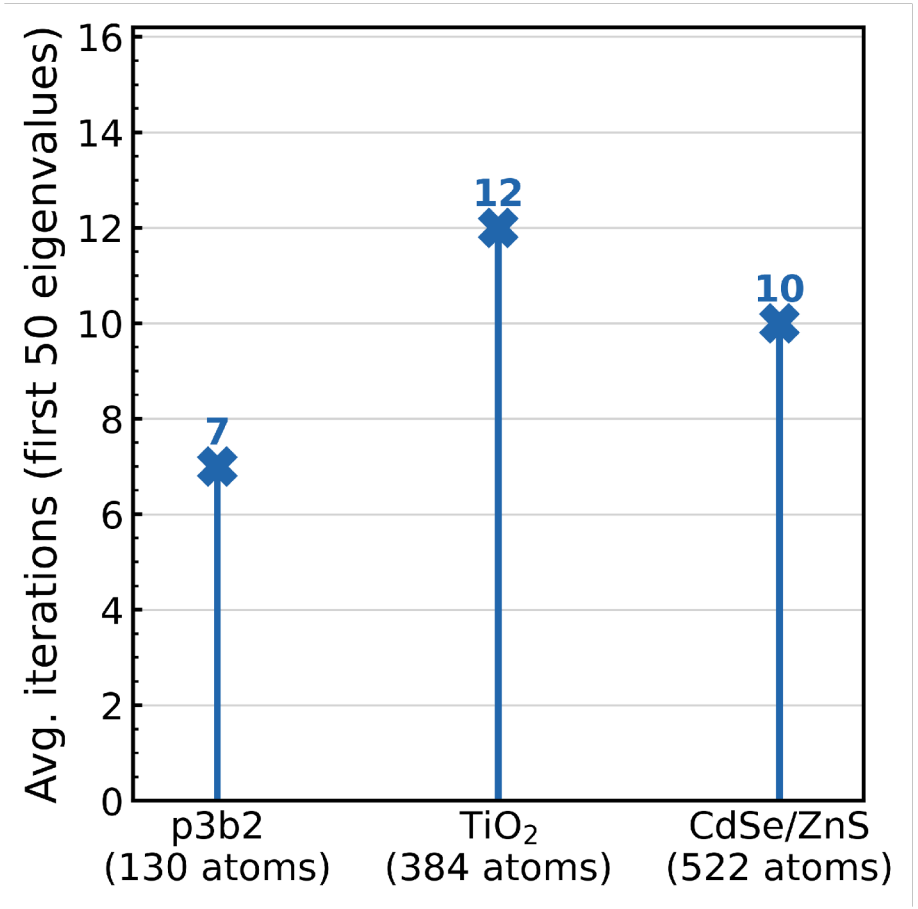
Strong Scaling

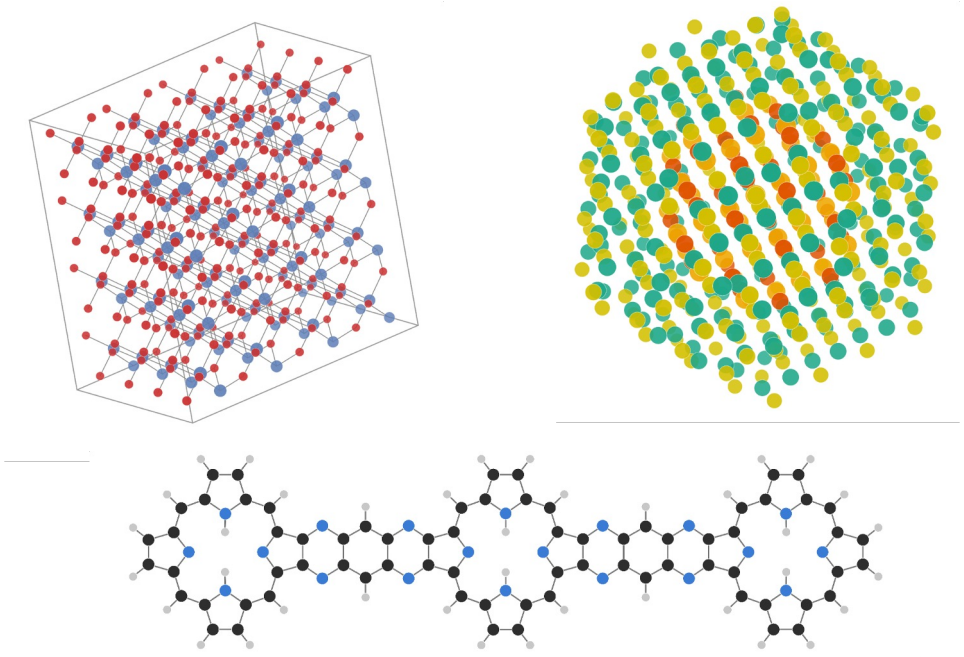





```
c = 0.92
```

Iterative eigensolver

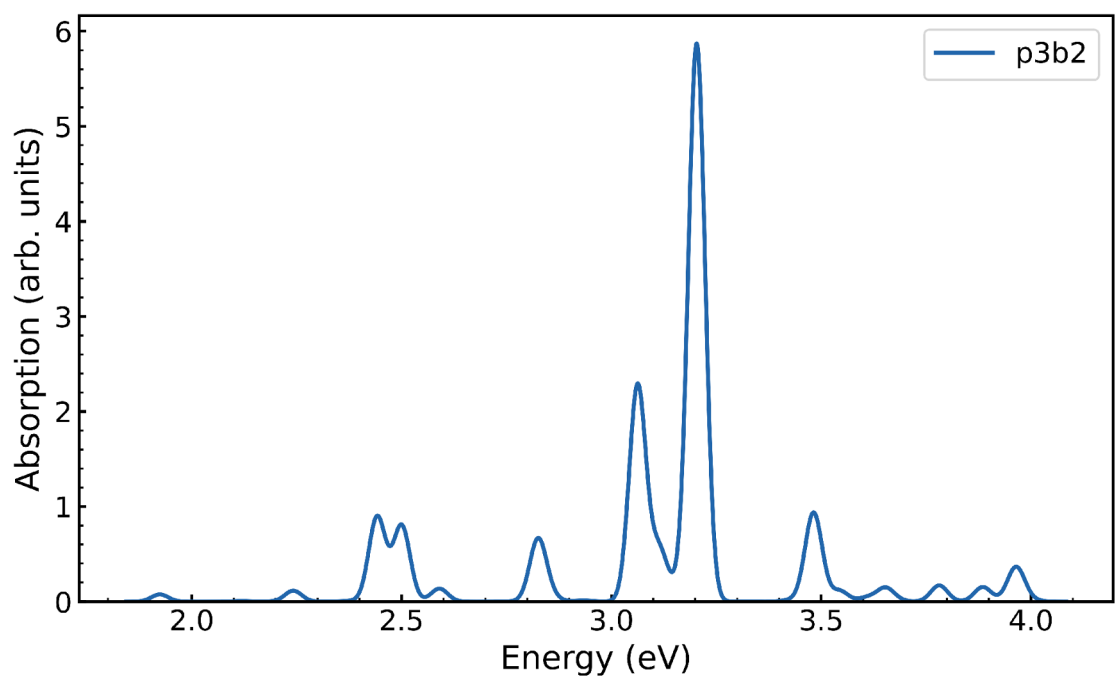


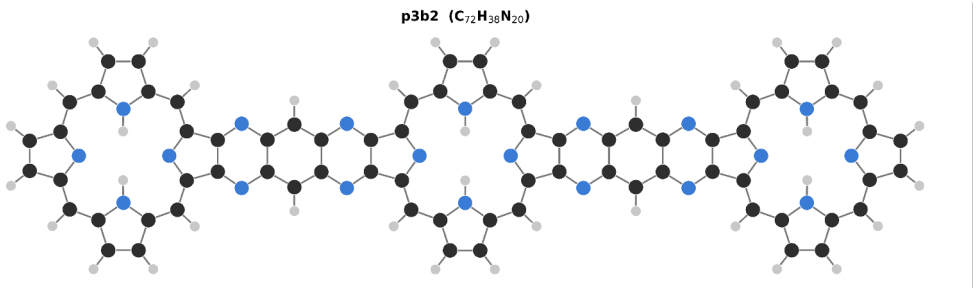


```
block size
default: 1
optimal: 1-3
```

Features

Oscillator Strength (Transition Dipoles)

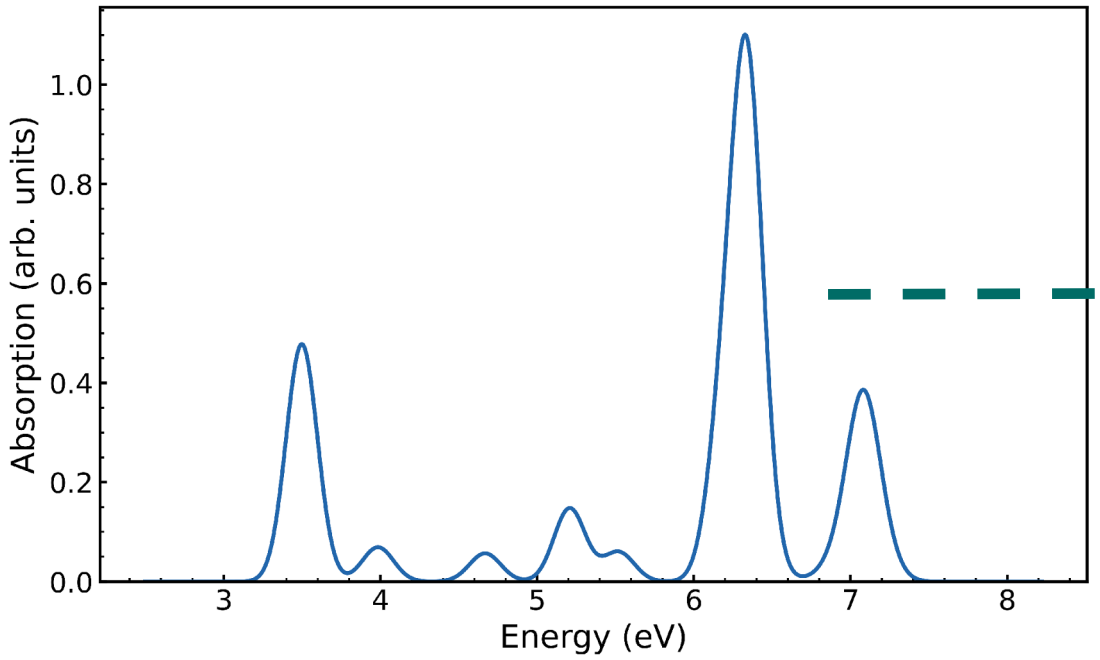


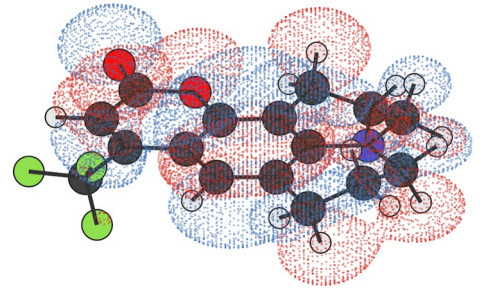


$$f_I = \frac{2}{3}\omega_I \sum_{\alpha\in\{x,y,z\}} \left(\sum_{ia} X_{ia}^I \langle \psi_i | \hat{r}_\alpha | \psi_a \rangle \right)^2$$

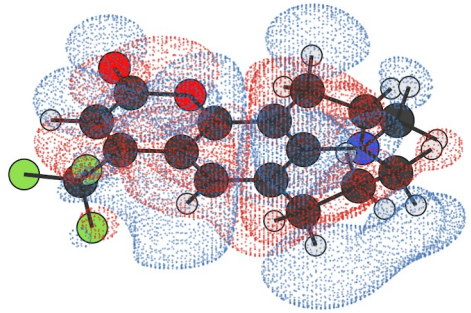
Features

`Natural transition orbitals (NTOs)`





hole



particle

$$\rho^{\mathrm{trans}}(\mathbf{r},\mathbf{r}') = \sum_k \lambda_k \, \phi_k^{\mathrm{hole}}(\mathbf{r}) \, \phi_k^{\mathrm{particle}}(\mathbf{r}')$$

Conclusion

TDA

LDA/GGA

Hybrid DFT

PBC

Iterative solver

length gauge

velocity gauge

RI-LVL

NTOs

RKS/UKS

Oscillator strengths

Outlook

k-points

f_{xc}

HFX

Next:

Coulomb

Full TDDFT/ Spin flip TDDFT

easy to implement
SLEPc/PETSc BSE solver
(2025)