Recent Advances in Periodic Bethe-Salpeter equation (BSE) Calculations with Numeric Atom-Centered Orbitals

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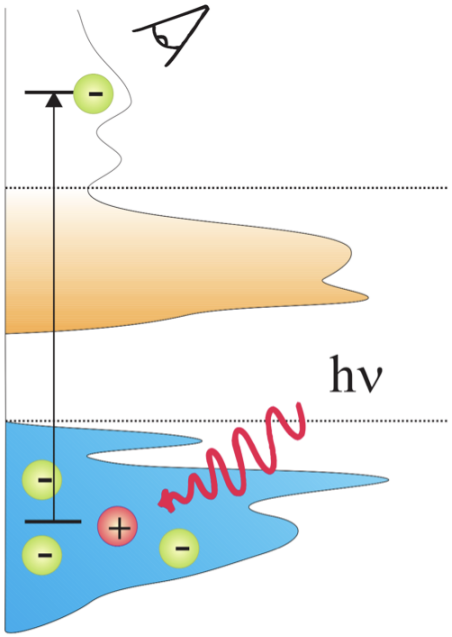
FHI-aims D&U Meeting 2026

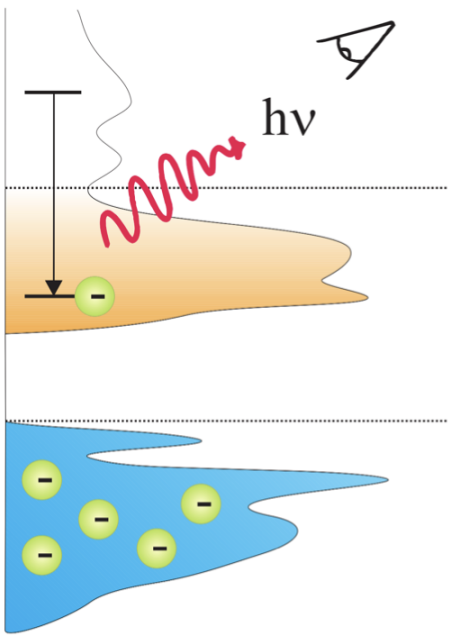
GW and Bethe-Salpeter Equation (BSE) method

Photoemission



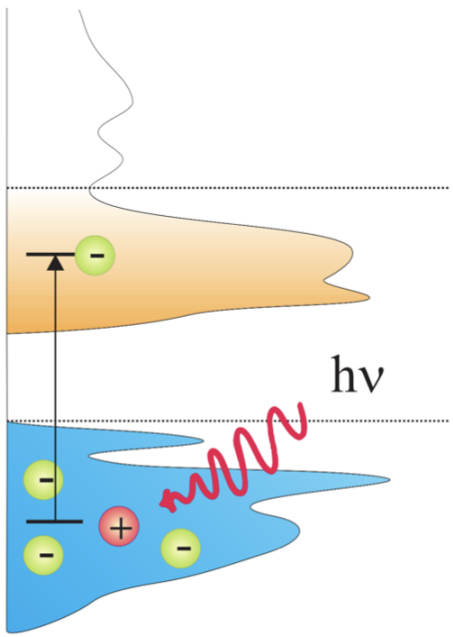
GW

Inverse photoemission



GW

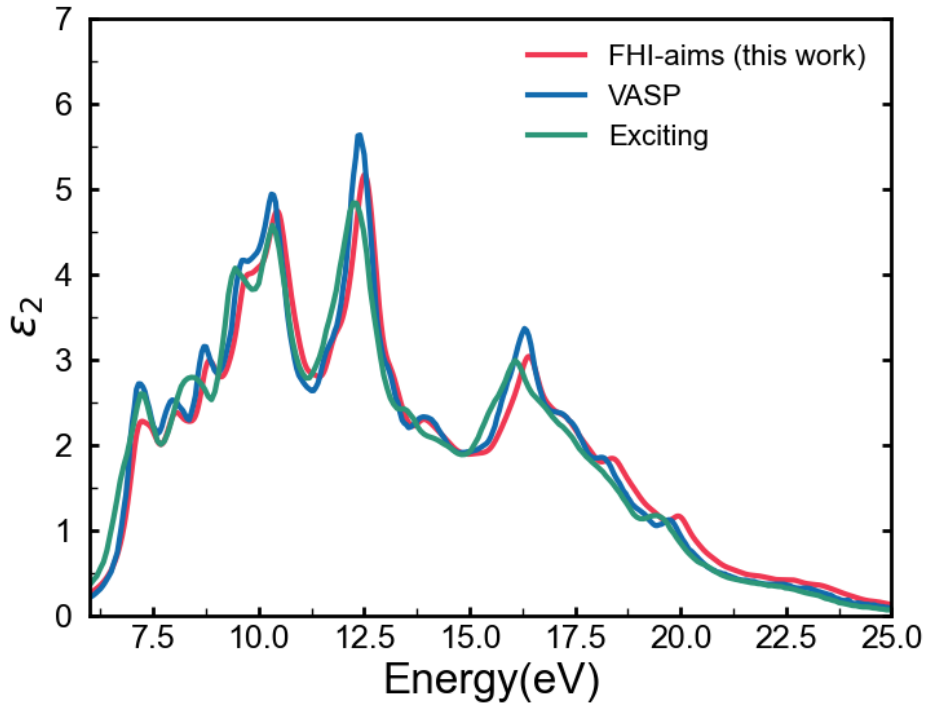
Absorption



BSE

Since last developer meeting in 2023

Absoroption Spectrum of MgO



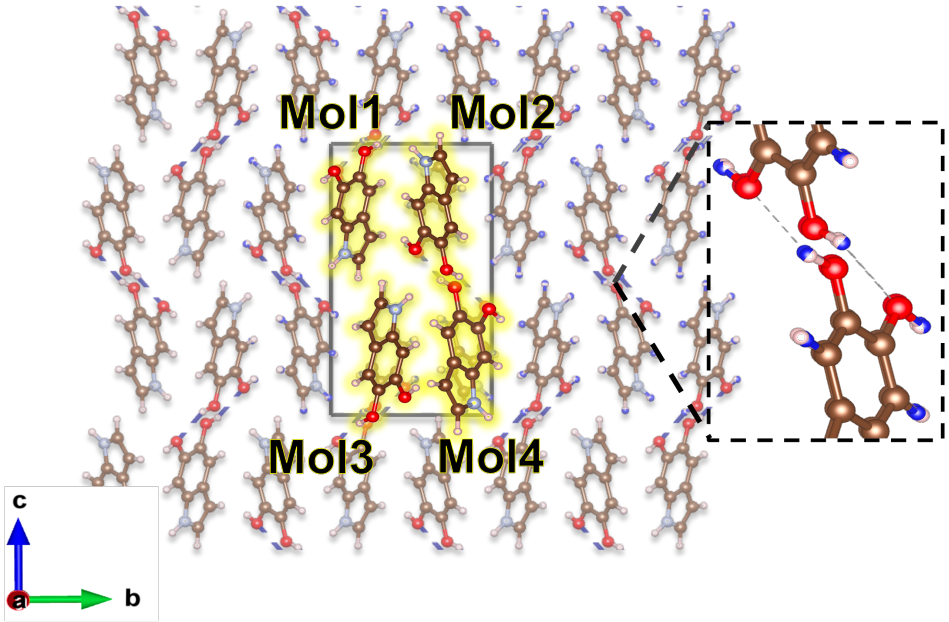
Zhou, R., Yao, Y., Blum, V., Ren, X., & Kanai, Y. (2024).
Journal of Chemical Theory and Computation, **21**(1), 291–306.

Hydrogen Bonding and Exciton Delocalization

Hydrogen bonds have been hypothesized to help delocalize excitons, contributing to the photofunction of eumelanin.

Chem. Sci., **2022**, 13, 2331-2338.

DHI crystal

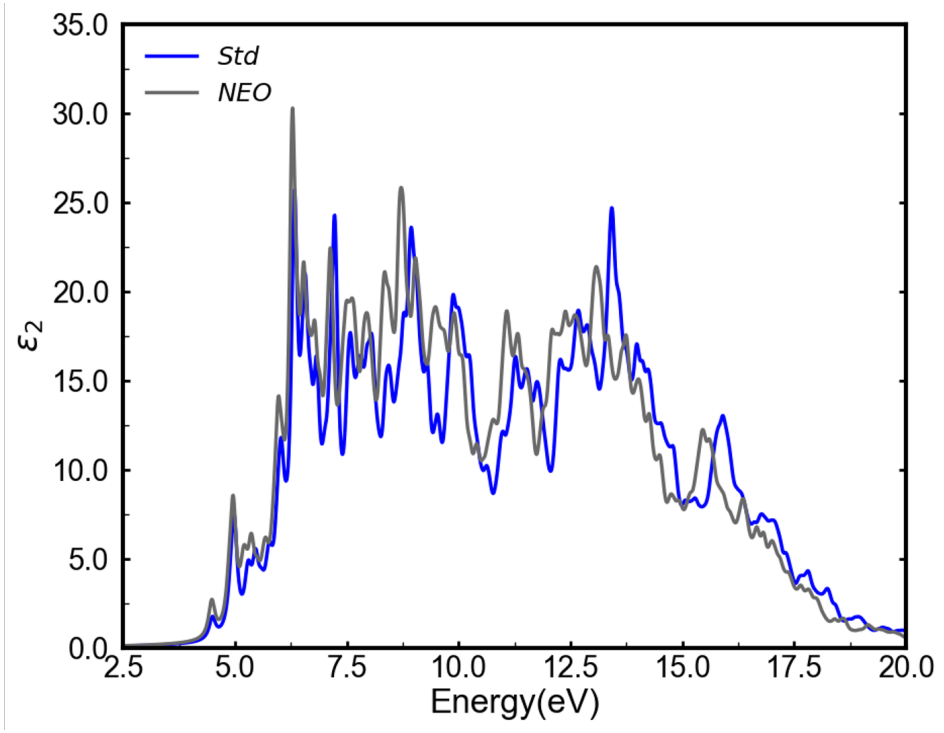


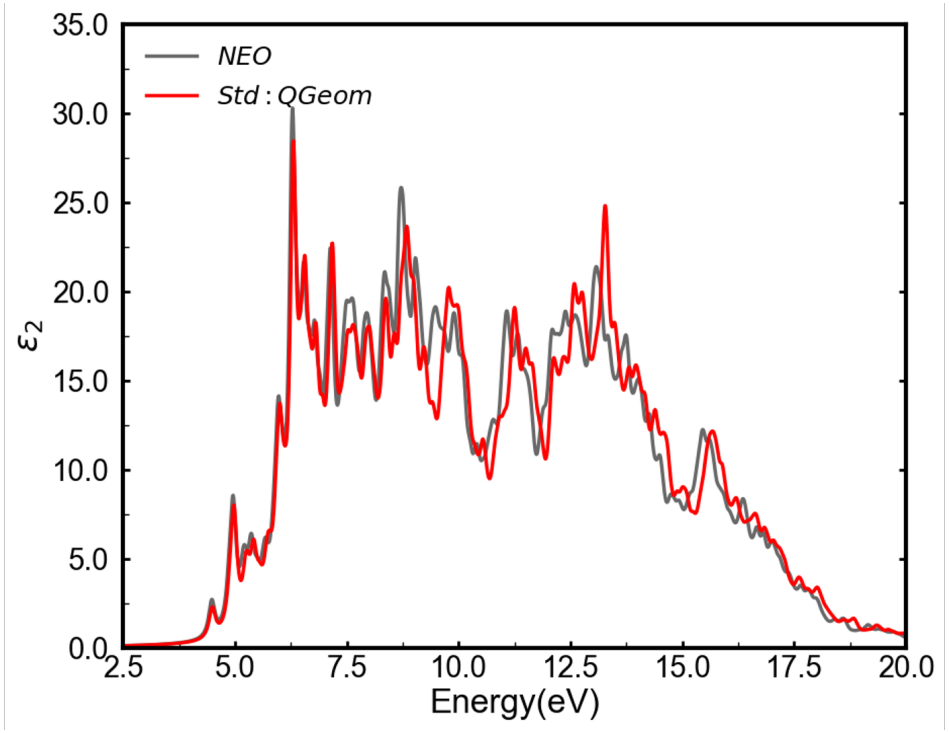
Methodology: BSE@G_0W_0@NEO-DFT

Note: NEO Method from Yosuke's talk.

Proton Quantum Effects in Hydrogen Bonds on Excitons

Legend: Std: DFT | **NEO**: NEO-DFT | **Std-Q-Geom**: DFT @ $\langle r_{H,NEO} \rangle$





The geometry effect is the dominant factor.

Bhattacharya, S., Xu, J., Zhou, R., & Kanai, Y., *J. Phys. Chem. Lett.* **2026**, 17, 5, 1419–1427.

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Static vs. Dynamical Exciton Effects

Standard Static Approximation:

- Assumes the screened Coulomb interaction is instantaneous.
- Works well when transition energies are much smaller than the plasma frequency.

$$W(\omega) \approx W(\omega = 0) \quad \Rightarrow \quad AX = E_S X \tag{1}$$

Dynamical BSE:

- Essential for systems with significant excitonic character and large exciton binding energies (e.g., organic solids, doped 2D materials).
- Requires solving a coupled, frequency-dependent eigenvalue problem (Exact Diagonalization):

$$A(\omega)X(\omega) = E_S(\omega)X(\omega) \quad \text{where} \quad E_S(\omega) = \hbar\omega \tag{2}$$

Approximations to Dynamical BSE

Perturbation Approach (Rohlfing & Louie):

- Treats the dynamical effect as a first-order perturbation to the static solutions.

$$E_{\Lambda}^{dyn} \approx E_{\Lambda}^{sta} + \langle A_{\Lambda} | \tilde{W}(E_{\Lambda}^{sta}) - W^{sta} | A_{\Lambda} \rangle \tag{3}$$

- Computationally faster for lowest states, but keeps wavefunctions unchanged.

Physical Review B, **2000**,*62(8), 4927.*

Effective Screening Approach (Bechstedt):

- Bypasses the frequency-dependent eigenvalue problem completely by using an effective static screening function based on exciton binding energy.

Bechstedt, F. (2016). Many-body approach to electronic excitations.

Effective Screening Approach

Effective Screened Coulomb Interaction:

$$\langle v\mathbf{k}v'\mathbf{k}'|\hat{W}^{\text{eff}}|c\mathbf{k}c'\mathbf{k}'\rangle = \frac{1}{\Omega}\sum_{\mathbf{q}}\sum_{\mathbf{G},\mathbf{G}'} v\left(\sqrt{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}\right) B_{c\mathbf{k}}^{c'\mathbf{k}'}(\mathbf{q}+\mathbf{G}) B_{v\mathbf{k}}^{v'\mathbf{k}'*}(\mathbf{q}+\mathbf{G}') \times \left\{\delta_{\mathbf{G}\mathbf{G}'} + \int_0^\infty \frac{d\hbar\omega'}{\pi} \text{Im}\varepsilon^{-1}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega') \frac{2}{\hbar\omega' + E_b}\right\} \delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'} \tag{4}$$

With Plasmon-Pole Model & Diagonal Approximation:

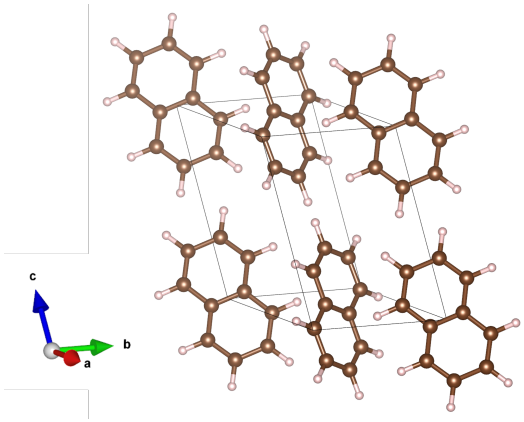
$$\langle v\mathbf{k}v'\mathbf{k}'|\hat{W}^{\text{eff}}|c\mathbf{k}c'\mathbf{k}'\rangle = \frac{1}{\Omega}\sum_{\mathbf{q}}\sum_{\mathbf{G}} v(|\mathbf{q}+\mathbf{G}|) B_{c\mathbf{k}}^{c'\mathbf{k}'}(\mathbf{q}+\mathbf{G}) B_{v\mathbf{k}}^{v'\mathbf{k}'*}(\mathbf{q}+\mathbf{G}) \times \left\{1 - \frac{\hbar\omega_p}{2}\left[1-\epsilon^{-1}(\omega=0)\right]^{1/2}\left[\frac{2}{\hbar\omega_p(1-\epsilon^{-1}(\omega=0))^{-1/2}+E_b}\right]\right\}\delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'} \tag{5}$$

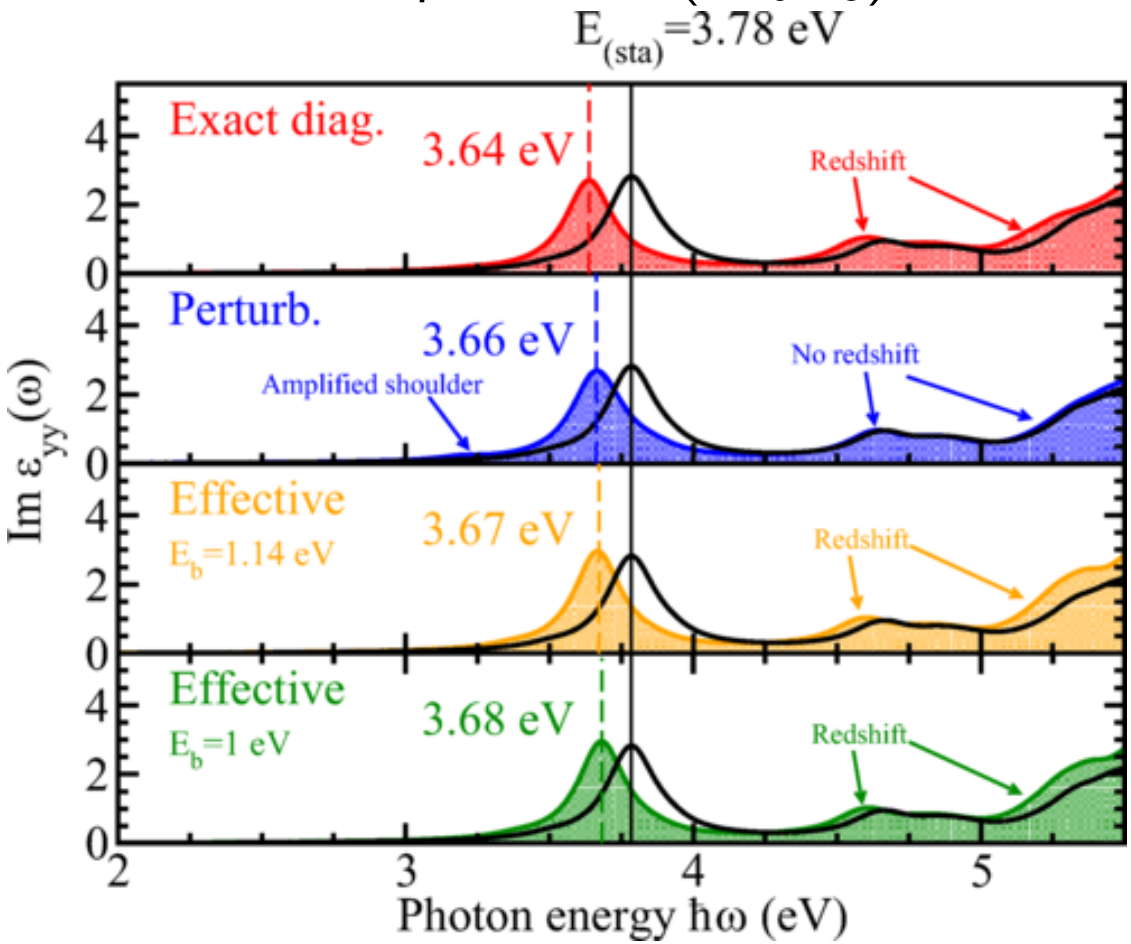
First implemented in VASP within Plane Wave (PW) basis.

- **Computational Advantage:** Dynamical screening is effectively represented in term of three terms: plasma frequency (ω_p), static dielectric function ($\epsilon(\omega=0)$), and exciton binding energy (E_b).

Advantage of Effective Screening Approach

Organic Crystal Monoclinic Naphthalene ($C_{10}H_8$)





Zhang, X., Leveillee, J. A., Schleife, A. (2023).
Physical Review B, 107(23), 235205.

Numerical Atom-Centered Orbital (NAO) Implementation

Utilizes Localized Resolution-of-Identity (LRI) to express operators in auxiliary basis functions (ABFs).

- Spectral Decomposition of Static Inverse Dielectric Matrix:

$$\epsilon^{-1}_{\mu\nu}(\mathbf{q},\omega=0)=\sum_{\lambda}X_{\mu\lambda}(\mathbf{q})\widetilde{\epsilon}^{-1}_{\lambda}(\mathbf{q},\omega=0)X^{*}_{\nu\lambda}(\mathbf{q}) \tag{6}$$

- Nonlinear Transformation to Effective Dielectric Eigenvalues:

$$(\widetilde{\epsilon}^{-1}_{\mathrm{eff}})_{\lambda}(\mathbf{q})=1-\frac{\hbar\omega_p[1-\widetilde{\epsilon}^{-1}_{\lambda}(\mathbf{q},\omega=0)]}{\hbar\omega_p+E_b[1-\widetilde{\epsilon}^{-1}_{\lambda}(\mathbf{q},\omega=0)]^{\frac{1}{2}}} \tag{7}$$

- Transformation Back to Auxiliary Basis:

$$[\epsilon^{-1}_{\mathrm{eff}}(\mathbf{q})]_{\alpha\beta}=\sum_{\lambda}X_{\alpha\lambda}(\mathbf{q})(\widetilde{\epsilon}^{-1}_{\mathrm{eff}})_{\lambda}(\mathbf{q})X^{*}_{\beta\lambda}(\mathbf{q}) \tag{8}$$

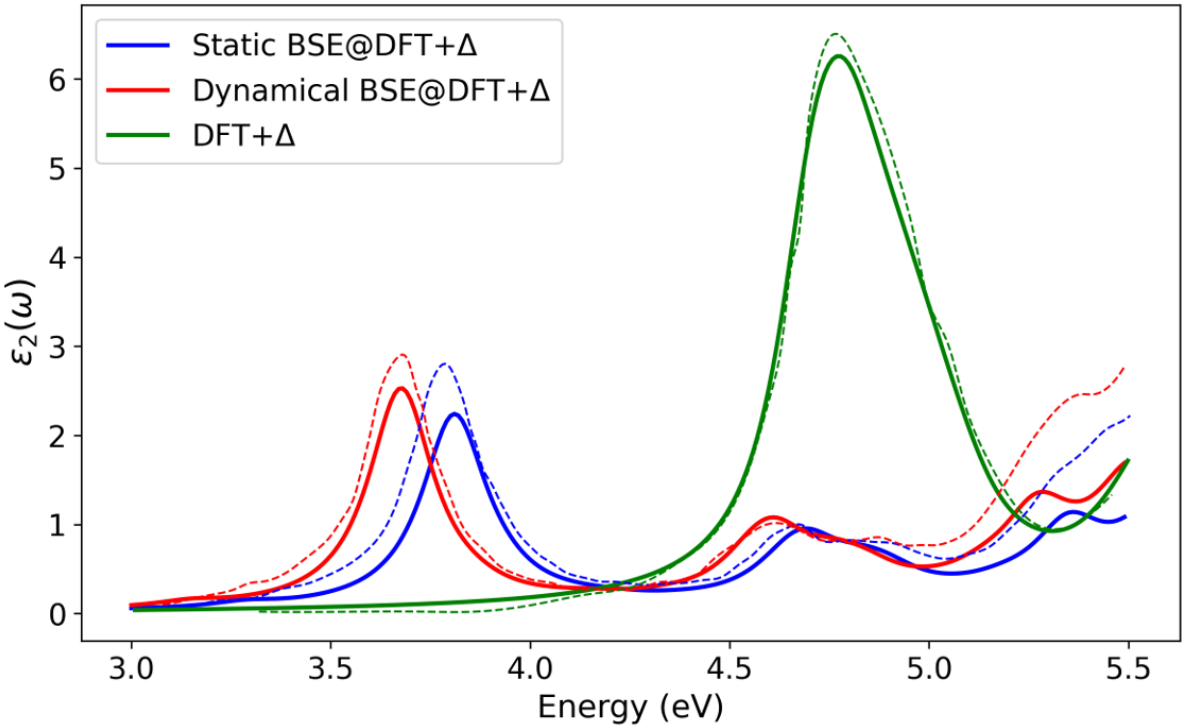
- Effective Screened Coulomb Interaction in ABFs:

$$W^{\mathrm{eff}}_{\mu\nu}(\mathbf{q})=\sum_{\alpha\beta}V^{\frac{1}{2}}_{\mu\alpha}(\mathbf{q})[\epsilon^{-1}_{\mathrm{eff}}(\mathbf{q})]_{\alpha\beta}V^{\frac{1}{2}}_{\beta\nu}(\mathbf{q}) \tag{9}$$

Together with Songrui Liu, Jianhang Xu and Yosuke Kanai.
arXiv:2606.08350

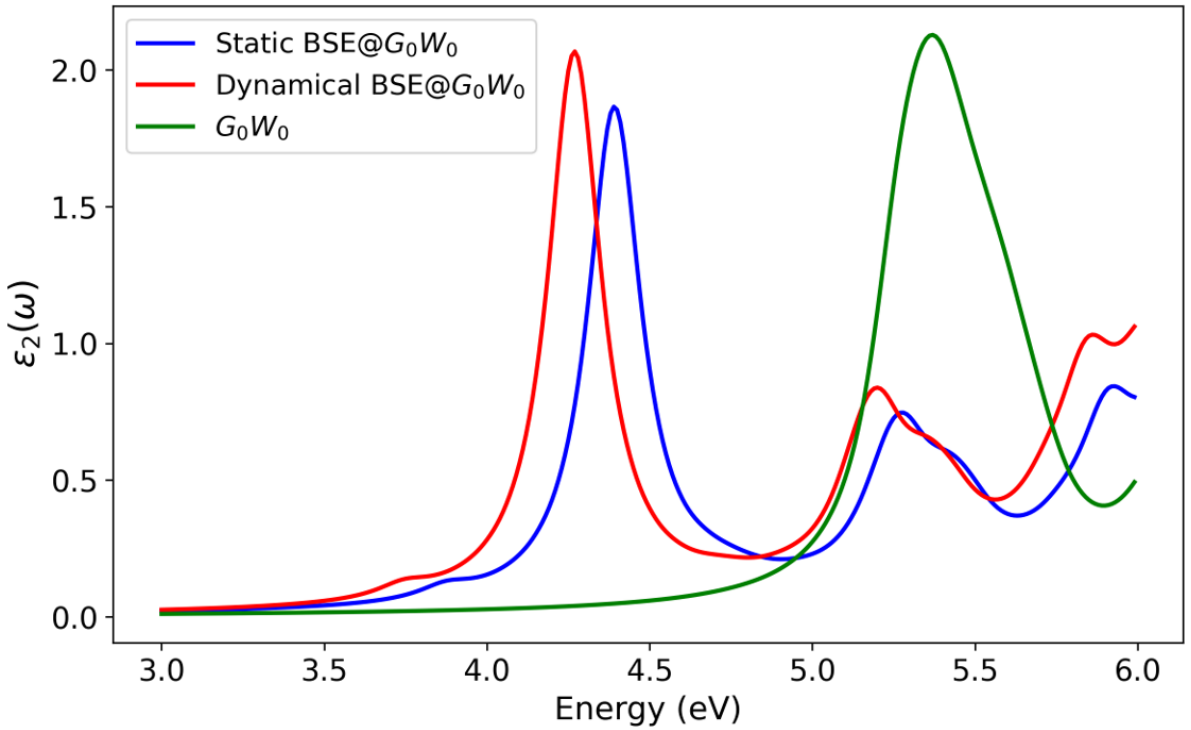
Validation Example: Monoclinic Naphthalene ($C_{10}H_8$)

- **Method:** BSE@DFT+Δ with scissored conduction band Kohn-Sham eigenvalues (shifted by 1.55 eV).
- Naphthalene exhibits strong excitonic effects with $E_b \approx 1.0$ eV.



Solid line: Our NAO result.
Dashed line: Reference PW-PAW (VASP) result.

BSE@G_0W_0 QP Energy



- Dynamical screening redshifts excitonic peaks by $\sim$0.12 eV (4.39 eV $\rightarrow$ 4.27 eV), strengthening the electron-hole interaction.

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Computational Bottlenecks in BSE@G_0W_0

- Converging BSE optical spectra requires a significantly denser **k**-point grid compared to standard G_0W_0 calculations.
- This dense sampling introduces two major computational hurdles:
  1. Evaluating G_0W_0 quasiparticle (QP) energies on dense **k**-grids.
  2. Constructing and diagonalizing the massive BSE Hamiltonian.

BSE Hamiltonian Matrix Elements in the Auxiliary Basis:

$$\langle i\mathbf{k}a\mathbf{k}|\hat{V}|j\mathbf{k}'b\mathbf{k}'\rangle = \sum_{\mu\nu} \tilde{C}^{\mu*}_{i,a}(\mathbf{k},\mathbf{k}) V_{\mu\nu}(\mathbf{q}=0) \tilde{C}^{\nu}_{j,b}(\mathbf{k}',\mathbf{k}') \tag{10}$$

$$\langle i\mathbf{k}j\mathbf{k}'|\hat{W}|a\mathbf{k}b\mathbf{k}'\rangle = \sum_{\mu\nu} \tilde{C}^{\mu*}_{i,j}(\mathbf{k},\mathbf{k}') W_{\mu\nu}(\mathbf{q}=\mathbf{k}'-\mathbf{k}) \tilde{C}^{\nu}_{a,b}(\mathbf{k},\mathbf{k}') \tag{11}$$

- The number of BZ sampling grids (**q**) for ABFs is equal to the number of **k**-points. Explicitly evaluating the screened Coulomb interaction $W_{\mu\nu}(\mathbf{q}=\mathbf{k}'-\mathbf{k})$ across this massive dense grid dominates the computational cost.

Symmetry Adaptation

- **Core Idea:** Compute properties only within the Irreducible Brillouin Zone (IBZ) and use crystallographic space group operations ($\hat{S}$) to map to the full BZ.

1. **Transformation of Auxiliary Basis Functions (ABFs):**

$$\hat{S} P_{\nu}^{\mathbf{q}_{\mathrm{IBZ}}}(\mathbf{r}) = \sum_{\mu} \mathcal{D}_{\mu\nu}(\hat{S}, \mathbf{q}) P_{\mu}^{\mathbf{q}}(\mathbf{r}) \tag{12}$$

2. **The Transformation Matrix ($\mathcal{D}_{\mu\nu}$):**

$$\mathcal{D}_{\mu\nu}(\hat{S}, \mathbf{q}) = \underbrace{\delta_{I,\hat{S}(J)}}_{\text{Atom Permutation}} \delta_{ll'} \underbrace{\mathcal{R}^{l}_{mm'}(R)}_{\text{Wigner Rotation}} \underbrace{e^{-i\mathbf{q}\cdot\mathbf{R}_{\mathrm{shift}}}}_{\text{Bloch Phase}} \tag{13}$$

3. **Recovery of the Screened Coulomb Interaction:**

$$W_{\mu\nu}^{\mathrm{eff}}(\mathbf{q}) = \sum_{\alpha\beta} \mathcal{D}_{\mu\alpha}(\hat{S}, \mathbf{q}) W_{\alpha\beta}^{\mathrm{eff}}(\mathbf{q}_{\mathrm{IBZ}}) \mathcal{D}^{*}_{\nu\beta}(\hat{S}, \mathbf{q}) \tag{14}$$

First implemented by Yi Yao in Periodic G_0W_0.
arXiv:2606.08350

Computational Savings: IBZ vs. Full BZ

- By restricting explicit $W(\mathbf{q})$ calculations to the IBZ, we bypass redundant operations for symmetry-equivalent points.

System	**k-point Grid**	**IBZ Points**	**Full BZ Points**
Naphthalene	$5 \times 7 \times 5$	52	175
MgO	$8 \times 8 \times 8$	29	512
MgO	$15 \times 15 \times 15$	120	3375
Si	$16 \times 16 \times 16$	145	4096

A huge saving on the computational cost.

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Fourier Interpolation

- The computational cost for $W(\mathbf{k})$ (for all $\mathbf{k}$ grids) scales $O(N_{\mathbf{k}}^3)$.
- The NAO basis can be regarded as a "Wannier" basis.

$$W_{\mu\mathbf{0},\nu\mathbf{R}} = \sum_{\mathbf{k}} e^{-i\mathbf{k}_{\text{cor}}\cdot\mathbf{R}} W_{\mu\nu}(\mathbf{k}_{\text{cor}}) \tag{15}$$

$$W_{\mu\nu}(\mathbf{k}_{\text{fin}}) = \sum_{\mathbf{R}} e^{i\mathbf{k}_{\text{fin}}\cdot\mathbf{R}} W_{\mu\mathbf{0},\nu\mathbf{R}} \tag{16}$$

- Enables $\mathbf{k}$-point offset-shifted Brillouin Zone (BZ) sampling (no longer Γ-centered).

Implemented in ABACUS@libRPA by Ziqing Guan, Minye Zhang, and Xinguo Ren.

Symmetry-Averaged **k**-Point Offset

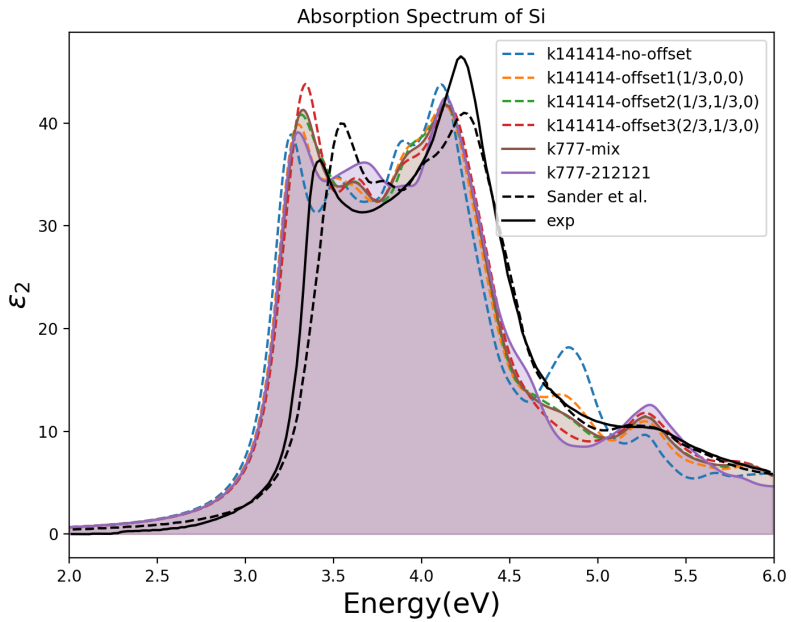
The macroscopic BSE absorption spectrum can be efficiently computed by symmetry-averaging over a reduced set of IBZ shifted BZ sampling.

$$\bar{\epsilon}_2(\omega) = \sum_{i \in \text{IBZ}} w_i \epsilon_2^{(i)}(\omega) \tag{17}$$

Physical Review B 92, 045209 (2015).

Irreducible k-points (Fractional)
for a Γ-Centered $3 \times 3 \times 3$ FCC Grid

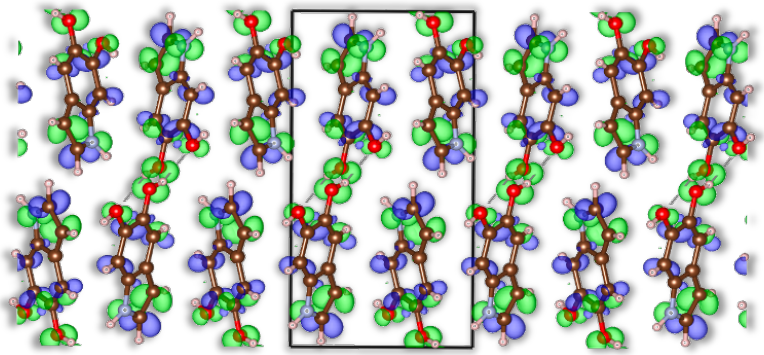
IBZ k-point	**Weight** (w_i)
$(0, 0, 0)$	$\frac{1}{27}$
$(\frac{1}{3}, 0, 0)$	$\frac{8}{27}$
$(\frac{1}{3}, \frac{1}{3}, 0)$	$\frac{6}{27}$
$(\frac{1}{3}, \frac{2}{3}, 0)$	$\frac{12}{27}$



To be submitted.

Visualize the Exciton

Cube Density Plot



Mulliken Population Analysis

Orbital	Hole Contrib.	Elec. Contrib.
s	0.003	**0.966**
p	**0.920**	0.034
d	0.002	0.001
f	0.076	0.000

An Python post-processing analysis package is coming soon!

Summary

- **Dynamical Screening in NAO Basis:** Implemented an efficient Effective Screening Approach for dynamical BSE within NAO framework.
- **Overcoming Computational Bottlenecks:** Accelerated periodic BSE calculations by applying IBZ symmetry adapted mapping to the screened Coulomb interaction $W(\mathbf{q})$.
- **Exciton Visualization & Analysis**

Thank you for your attention!