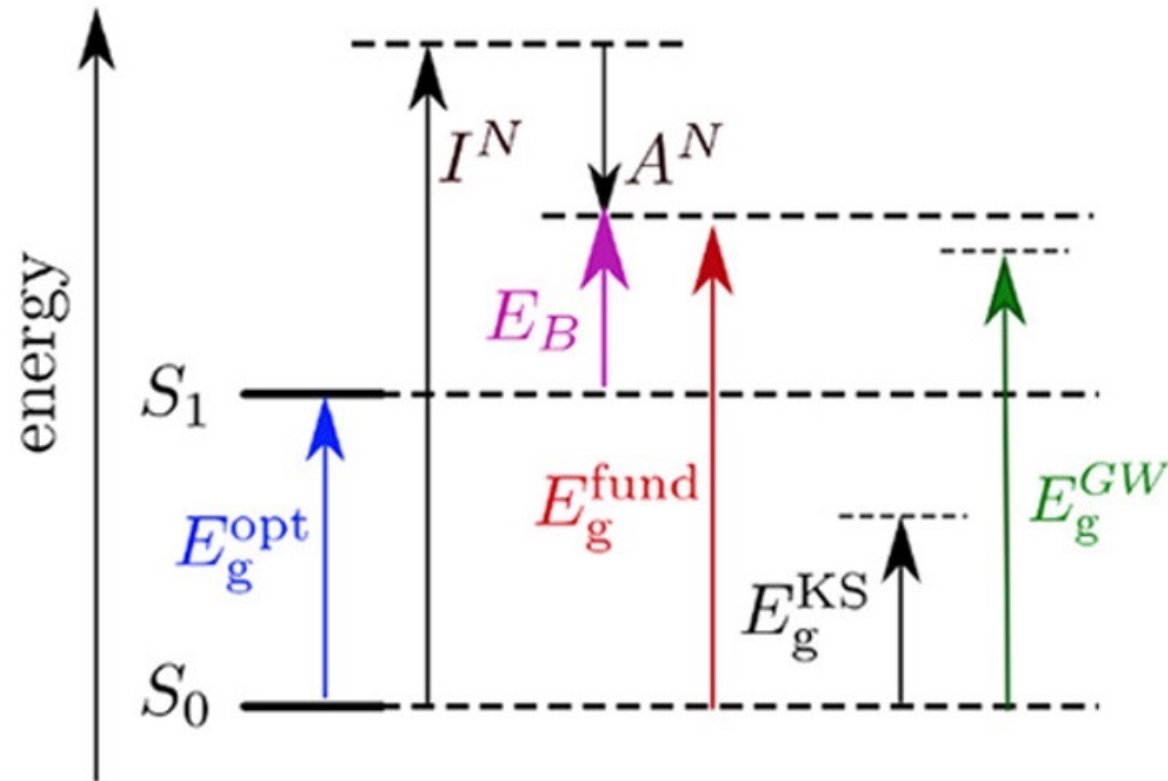


Wei Li

Calculating exciton - method

Görlitz // 26 Feb 2024

Kohn-Sham, quasiparticle, and optical gap



- photoemission
- transport
- optical absorption
- photoluminescence

Ground-state calculation: exciton g-factor

- Zeeman splitting

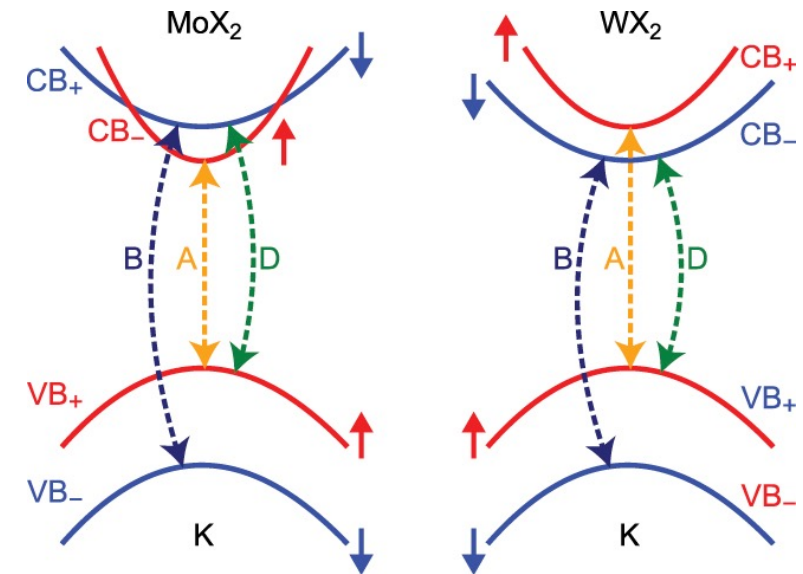
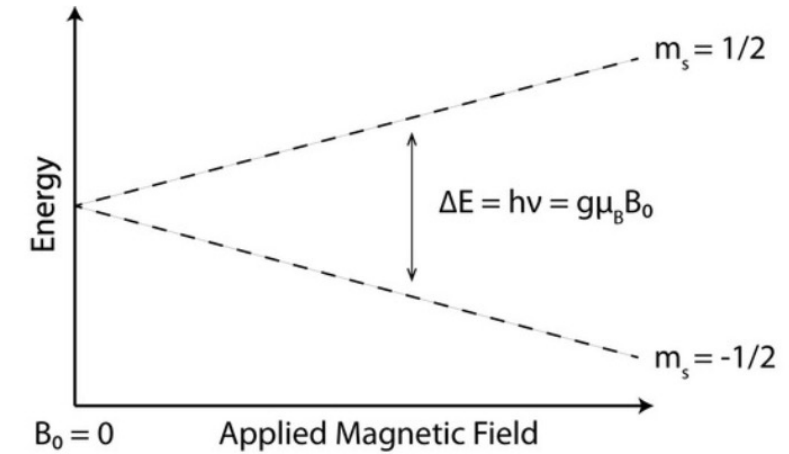
$$\Delta_n(\mathbf{k}) = V_n(+\mathbf{k}) - V_n(-\mathbf{k}) = 2\mu_B B [g_0 s + L_n(\mathbf{k})]$$

- electron g-factor

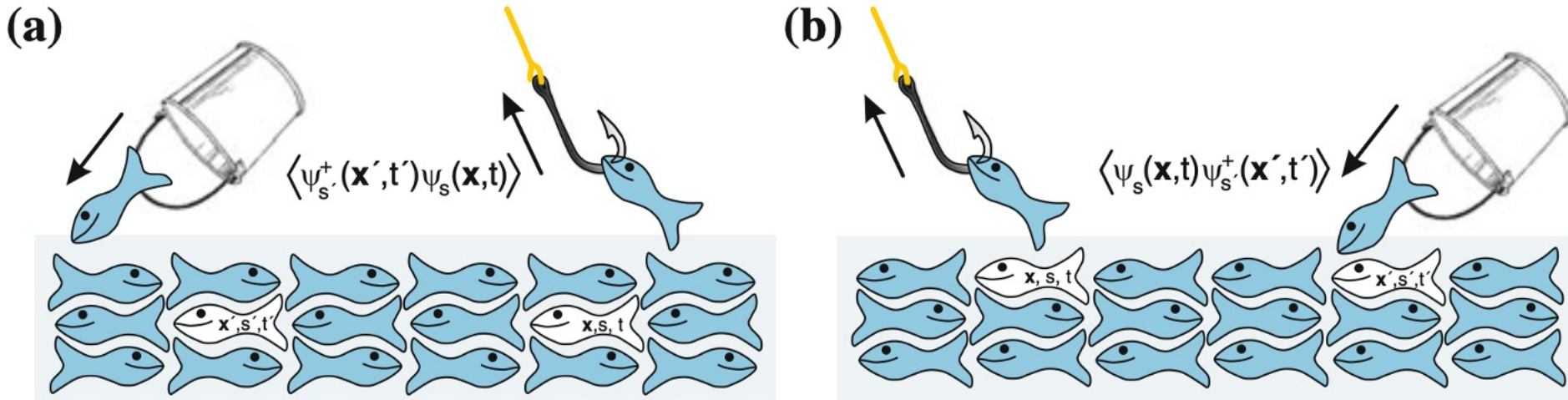
$$g_n(\mathbf{k}) = \frac{\Delta_n(\mathbf{k})}{\mu_B B} = 2g_0 s + 2L_n(\mathbf{k})$$

- exciton g-factor

$$g^{(cv)}(\mathbf{k}_c, \mathbf{k}_v) = g_c(\mathbf{k}_c) - g_v(\mathbf{k}_v)$$



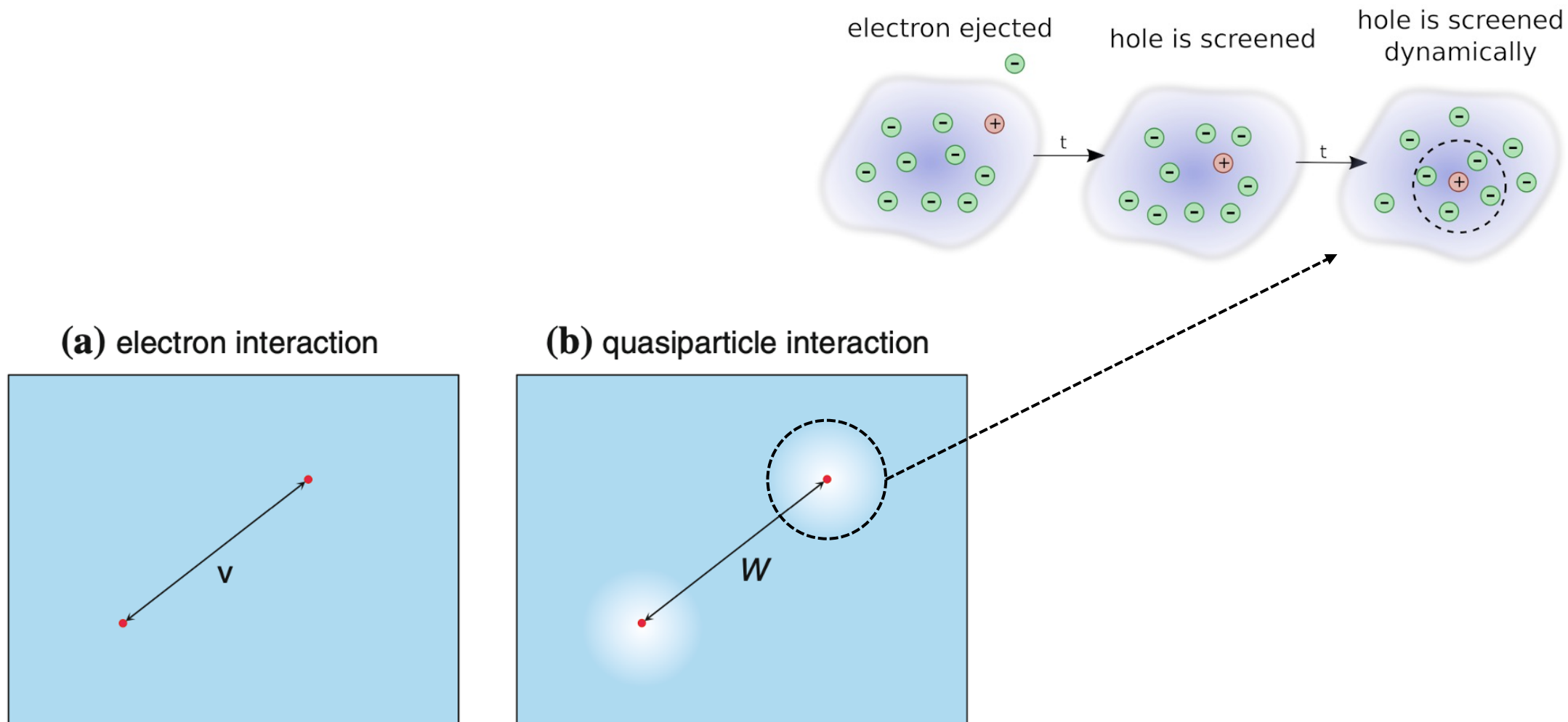
From electron and hole propagation to Green's function



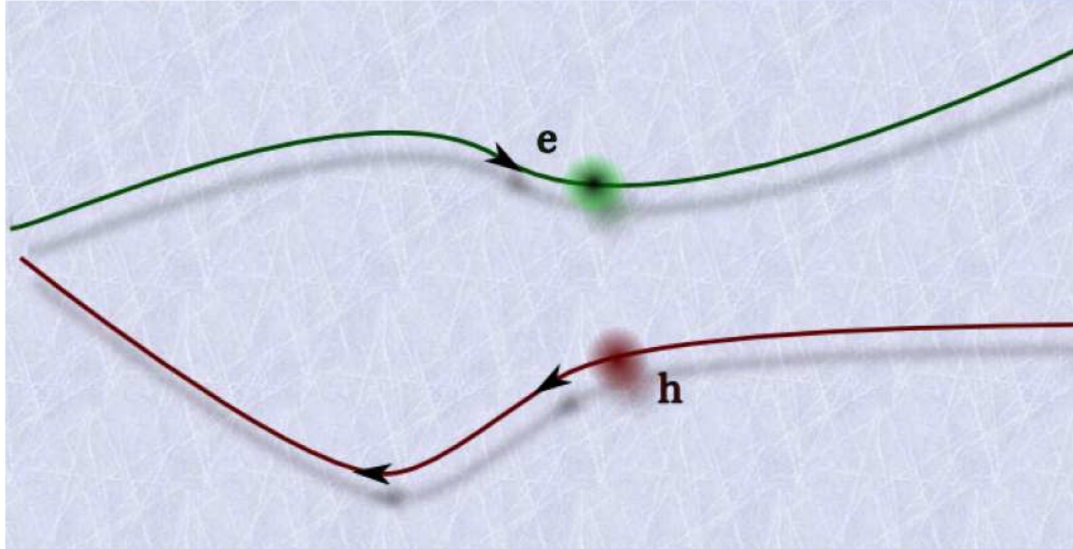
- single-particle Green's function

$$G(\mathbf{r}, \sigma, t, \mathbf{r}', \sigma', t') = -i \langle N | \hat{T} \{ \hat{\psi}(\mathbf{r}, \sigma, t) \hat{\psi}^\dagger(\mathbf{r}', \sigma', t') \} | N \rangle$$

From quasiparticle to GW approximation

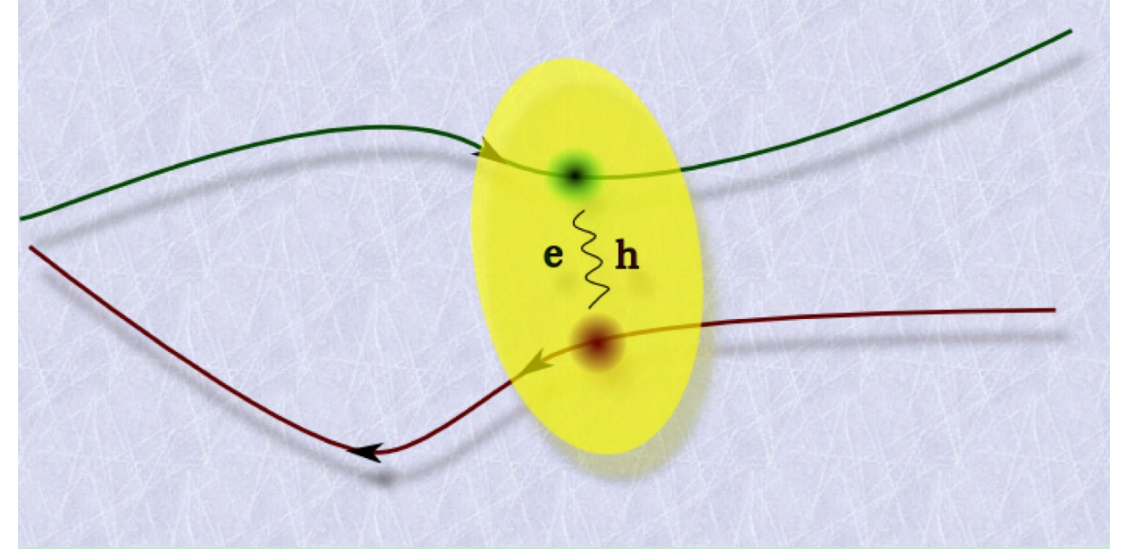


Two-particles Green's function



- independent-particle: RPA

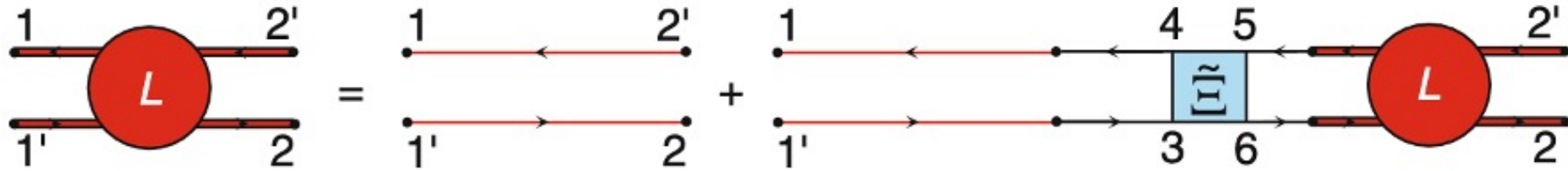
$$\chi(12) = iG(12)G(21)$$



- excitonic effects

$$L(1,2; 1',2') = \frac{\partial G(1,1')}{\partial U(2,2')}$$

From GW to Bethe-Salpeter Equation



- electron-hole correlation function

$$L(1,2; 1',2') = L_0(1,2; 1',2') + \int d(3456) L_0(1,4; 1',3) K(3,4; 5,6) L(6,2; 5,2')$$

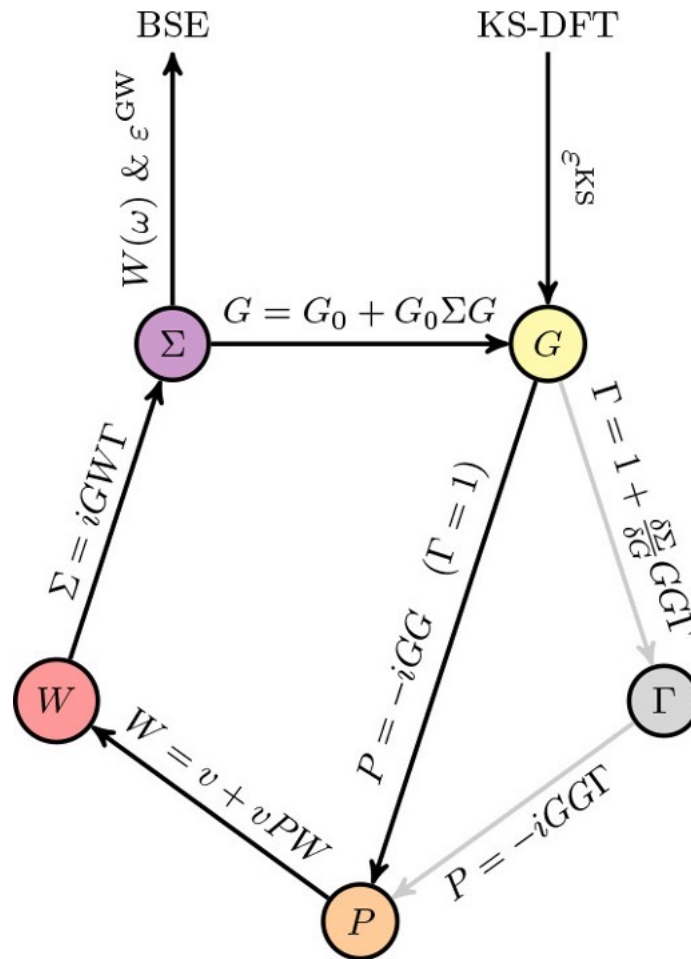
- BSE kernel

$$iK(3,4; 5,6) = v(3,6)\delta(3,4)\delta(5,6) + i \frac{\partial \Sigma_{xc}(3,4)}{\partial G(5,6)}$$

- Casida-like equations ($\omega \rightarrow 0$)

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^\dagger & -\mathbf{A}^\dagger \end{bmatrix} \begin{bmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{bmatrix} = \Omega_s \begin{bmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{bmatrix}$$

Procedure for BSE@GW



What can you calculate with GW?

- Ionization potentials (IPs) given by occupied MO energies
- Electron affinities (EAs) given by virtual MO energies
- Fundamental (HOMO-LUMO) gap

What can you calculate with BSE?

- Singlet and triplet optical excitations (vertical absorption energies)
- Oscillator strengths (absorption intensities)

Time dependent DFT (TDDFT)

$$\left[-\frac{\nabla^2}{2} + v_s[n](\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t) = i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) \longrightarrow \sum_j |\varphi_j(\mathbf{r}, t)|^2 = n(\mathbf{r}, t)$$

Density $n(\mathbf{r}', t')$ over all space and times $t' \leq t$ (initial value problem)

$n(\mathbf{r}, t')$

t_0 t_1 Time

Ψ_0, Φ_0 $v_s[n, \Psi_0, \Phi_0](\mathbf{r}, t)$

the Runge–Gross theorem: at any time, the density uniquely determines the external potential

Linear response in TDDFT (LR-TDDFT)

- Taylor expansion in powers of v_{ext}

$$n(\mathbf{r}, t) = n_0 + n_1(\mathbf{r}, t) + n_2(\mathbf{r}, t) + n_3(\mathbf{r}, t) + \dots$$

- The first-order (linear) density response

$$n_1(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', t') v_{ext}^1(\mathbf{r}' t')$$

density-density
response
function

- In Kohn-Sham system

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi_0(\mathbf{r}, \mathbf{r}', \omega) + \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_0(\mathbf{r}, \mathbf{r}_1, \omega) K(\mathbf{r}_1, \mathbf{r}_2, \omega) \chi(\mathbf{r}_2, \mathbf{r}', \omega)$$

$$K(\mathbf{r}_1, \mathbf{r}_2, \omega) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega)$$

Oscillators and excitation energy

- Casida equation

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^\dagger & -\mathbf{A}^\dagger \end{bmatrix} \begin{bmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{bmatrix} = \Omega_s \begin{bmatrix} \mathbf{X}_s \\ \mathbf{Y}_s \end{bmatrix}$$

$$A_{ij}^{ab}(\omega) = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 2(ia|f_H + f_{xc}[n_0](\omega)|jb), \quad B_{ij}^{ab}(\omega) = 2(ia|f_H + f_{xc}[n_0](\omega)|bj)$$

XC kernel

- Tamm Dancoff approximation

$$\mathbf{A}\mathbf{X}_s = \Omega_s\mathbf{X}_s$$

TDDFT vs BSE

TDDFT	Connection	BSE
One-point density $n(1)$	$n(1) = -iG(11^+)$	Two-point Green's function $G(12)$
Two-point susceptibility $\chi(12) = \frac{\delta n(1)}{\delta U(2)}$	$\chi(12) = -iL(12; 1^+2^+)$	Four-point susceptibility $L(12; 34) = \frac{\delta G(13)}{\delta U(42)}$
Two-point kernel $K(12) = v(12) + \frac{\delta v^{xc}(1)}{\delta n(2)}$		Four-point kernel $iK(1234) = v(13)\delta(12)\delta(34) - \frac{\delta^2 \Sigma_{xc}(12)}{\delta G(34)}$

- hybridizing TDDFT and BSE, see *J. Chem. Phys.* 2018, 149, 101101
- dynamical correction within BSE, see, for example, *J. Chem. Phys.* 2020, 153, 114120

Performance

- BSE@GW:
 - parameter-free and suitable Frenkel, Wannier and charge-transfer excitons.
 - bad performance for triplet instability
 - no excited-state PES
- TDDFT:
 - range-separated hybrids for triplet instability and charge-transfer complexes.
 - long-range kernels are better for molecules than for solids

Computational cost

- time for solving Casida/BSE equation: $O(N^4)$ with iterative solver (depends on codes)
- BSE@GW is much more expensive because of GW calculation

Codes

- TDDFT codes^[1]:
 - ELK, Firefly, GAMESS-US, Gaussian, Amsterdam Density Functional, deMon2k, CP2K, Dalton, NWChem, Octopus, pw-teleman library, PARSEC, Qbox/Qb@II, Q-Chem, Spartan, TeraChem, TURBOMOLE, YAMBO code, ORCA, Jaguar, GPAW, ONETEP, VASP, Quantum ESPRESSO
- BSE@GW codes^[1]:
 - Yambo - plane-wave pseudopotential
 - BerkeleyGW – plane-wave pseudopotential
 - ExC - plane-wave pseudopotential
 - Fiesta - Gaussian all-electron
 - Abinit - plane-wave pseudopotential
 - VASP - plane-wave pseudopotential

Backup: Ionization potential and Electron affinity

- $IP_S = -\epsilon_S = h\nu - E_{kin} - \Phi$
- $-EA_S = \epsilon_S = E_{kin} - h\nu + \Phi$
- ϵ_S : energy of the (bound) state
- ν : frequency of the incoming light
- E_{kin} : kinetic energy of the emitted electron
- Φ : work function of the material
- E_F : Fermi level
- E_{vac} : vacuum level

Backup: RPA

