The *GW* method and the *GW* implementation in FHI-aims

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Workshop on advanced electronic-structure methods and artificial intelligence for materials

November 5-8, 2025, Shanghai University

Contents

- Basics of the *GW* method
- The *GW* implementation in FHI-aims
- Bethe Salpeter Equation (BSE)

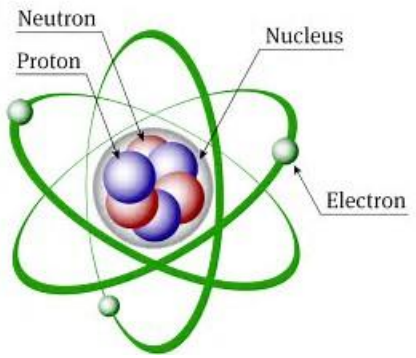
The quantum many-body Hamiltonian behind (condensed matter) physics, chemistry and materials science

$$\hat{H} = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

Electronic part

$$-\sum_{\alpha=1}^{N_{nul}} \frac{\nabla_\alpha^2}{2M_\alpha} + \frac{1}{2}\sum_{\alpha\neq\beta}^{N_{nul}} \frac{Z_\alpha Z_\beta e^2}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|}$$

Nuclear part



$$-\sum_{i=1}^{N_e}\sum_{\alpha=1}^{N_{nul}} \frac{Z_\alpha e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|}$$

Electron-nuclei interaction

Many-body Schrodinger Eq.: $\hat{H}\Psi_{\boldsymbol{k}}(\{\boldsymbol{r}_i\},\{\boldsymbol{R}_\alpha\}) = E_k\Psi_k(\{\boldsymbol{r}_i\},\{\boldsymbol{R}_\alpha\})$

Ground state and excited states of many-body systems

Under the Born-Oppenheimer approximation

$$\hat{H}^e[\boldsymbol{R}] = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_i^{N_e} V^{ext}_{\{\boldsymbol{R}_\alpha, Z_\alpha\}}(\boldsymbol{r}_i) + E_{NN}$$

$$\hat{H}^e[\boldsymbol{R}]\Phi_s(\{\boldsymbol{r}_i\}) = U_s[\boldsymbol{R}]\Phi_s[\boldsymbol{R}](\{\boldsymbol{r}_i\})$$

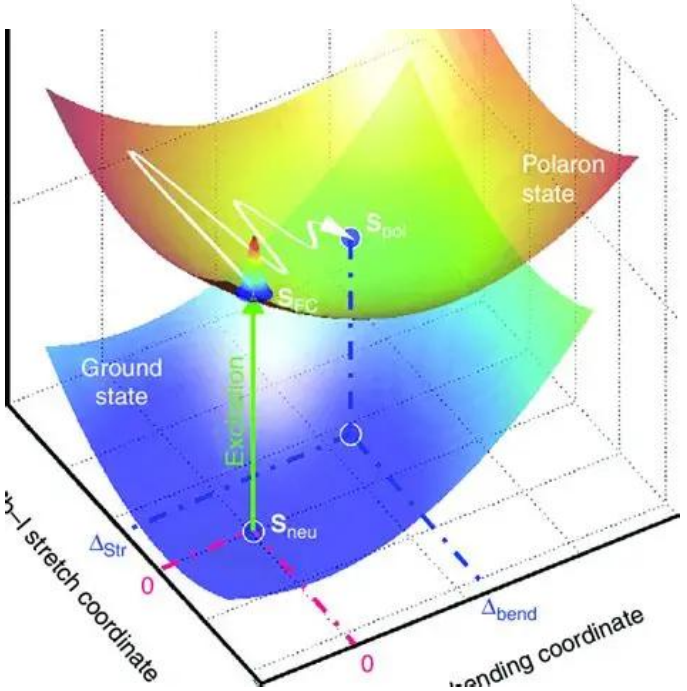
$U_s[\boldsymbol{R}]$: potential energy surface (PES)

$s = 0$: Ground state

=> Structure, cohesive energies, phonon spectra, magnetic ordering, …

$s \geq 1$: Excited states

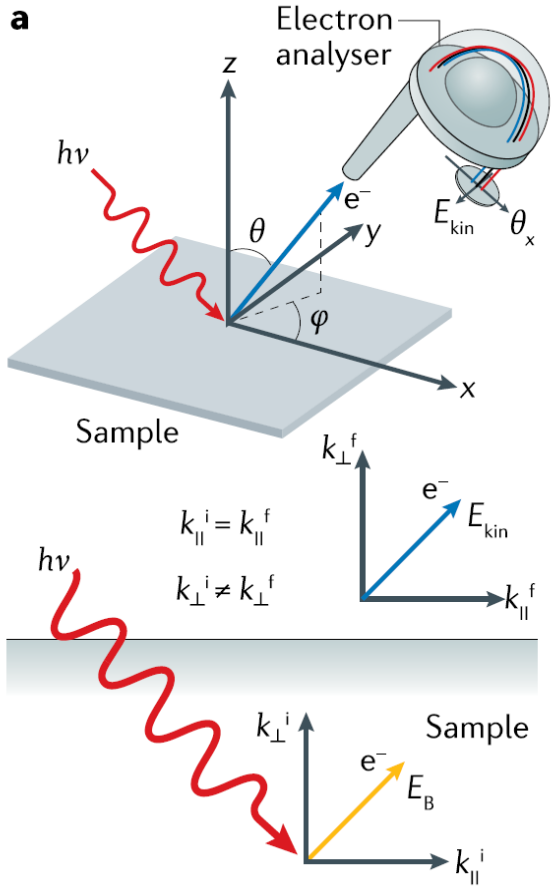
=> Specific heat, photoemission spectra, optical adsorption spectra, energy gaps, transport properties, thermodynamic phase transitions, …

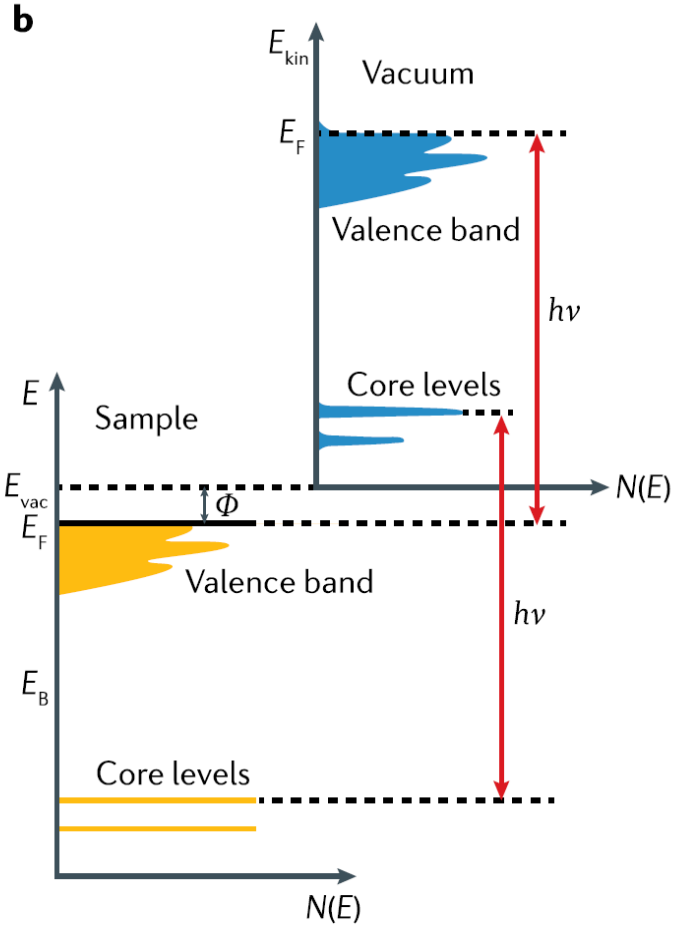


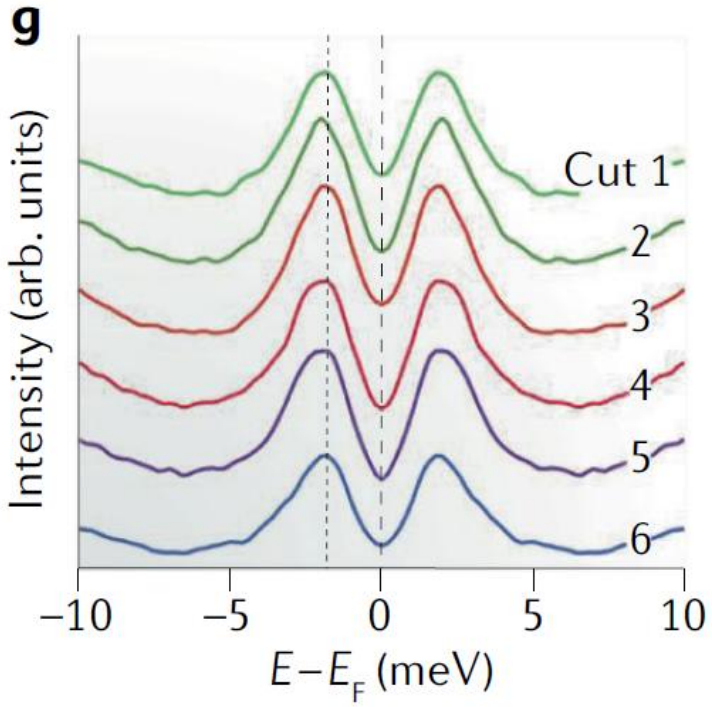
The system is often under excited states under experimental conditions!

The experimental spectroscopy measurement

Angle-Resolved Photoemission Spectroscopy (ARPES) ⟶ $A(\boldsymbol{k}, \omega)$







$$E_{kin}(\boldsymbol{k}) = h\nu - \Phi - E_B(\boldsymbol{k})$$

*Cartoon from B. Lv, T. Qian, and H. Ding, Nat. Rev. Phys. **1**, 609 (2019)*

Definition of the Green function

- Density: $n_\sigma(\boldsymbol{r}) = \langle \Psi_0 | \hat{\psi}^\dagger(x)\hat{\psi}(x) | \Psi_0 \rangle$

  $x = (\boldsymbol{r}, \sigma)$

- Density matrix: $\rho_{\sigma\sigma'}(\boldsymbol{r}, \boldsymbol{r}') = \langle \Psi_0 | \hat{\psi}^\dagger(x')\hat{\psi}(x) | \Psi_0 \rangle$

- Time-ordered single-particle Green function:

Time-ordered operator

Time-dependent field operator:

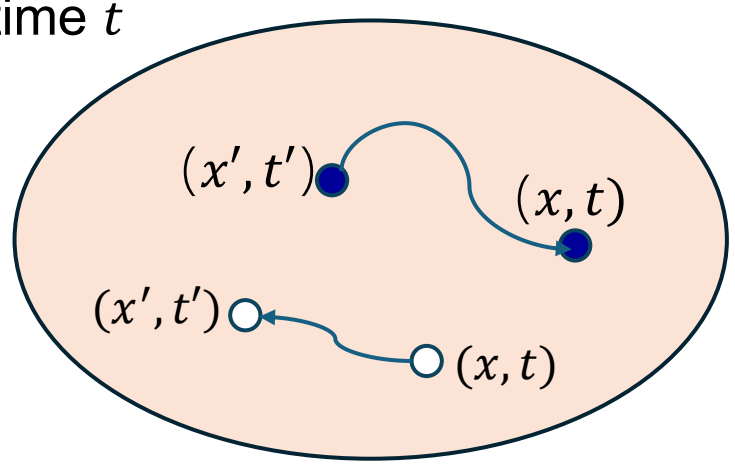
$$\hat{\psi}^\dagger(x,t) = e^{i\hat{H}t}\hat{\psi}^\dagger(x)e^{-i\hat{H}t}$$

$$G(x,t;x',t') = -i\langle \Psi_0 \mid T\hat{\psi}(x,t)\hat{\psi}^\dagger(x',t') \mid \Psi_0 \rangle$$

Many-body ground state

$$T\hat{\psi}(x,t)\hat{\psi}^\dagger(x',t') = \begin{cases} \hat{\psi}(x,t)\hat{\psi}^\dagger(x',t'), & t > t' \\ -\hat{\psi}^\dagger(x',t')\hat{\psi}(x,t), & t < t' \end{cases}$$

Annihilating a particle at spatial point x at time t



Properties of one-particle Green function

- Green function is a useful quantity; many physical observables of a system can be directly obtained if the Green function is known.

One-particle Green function →

1. the expectation value of any single-particle operator within the ground state

   e.g., density $n(\boldsymbol{r})$, density matrix $\rho(\boldsymbol{r},\boldsymbol{r}')$, kinetic energy $\tau(\boldsymbol{r})$

2. the ground-state energy

   $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$

3. the excitation spectrum of the system

   $\epsilon_s = E_s(N \pm 1) - E_0(N)$ (This is what the photoemission experiments measure!)

- Many-body theories can be most conveniently expressed in terms of the Green function

Hedin's equation

$1 = (x_1, t_1) = (\boldsymbol{r}_1, \sigma_1, t_1)$

$$P(1,2) = -i \int G(1,3)G(4,1)\Gamma(3,4,2)d3d4$$ (Polarization function)

$$W(1,2) = v(1,2) + \int v(1,3)P(3,4)W(4,2)d3d4$$ (Screened Coulomb interaction)

$$\Sigma(1,2) = i \int G(1,3)W(4,1)\Gamma(3,4,2)d3d4$$ (Self-energy)

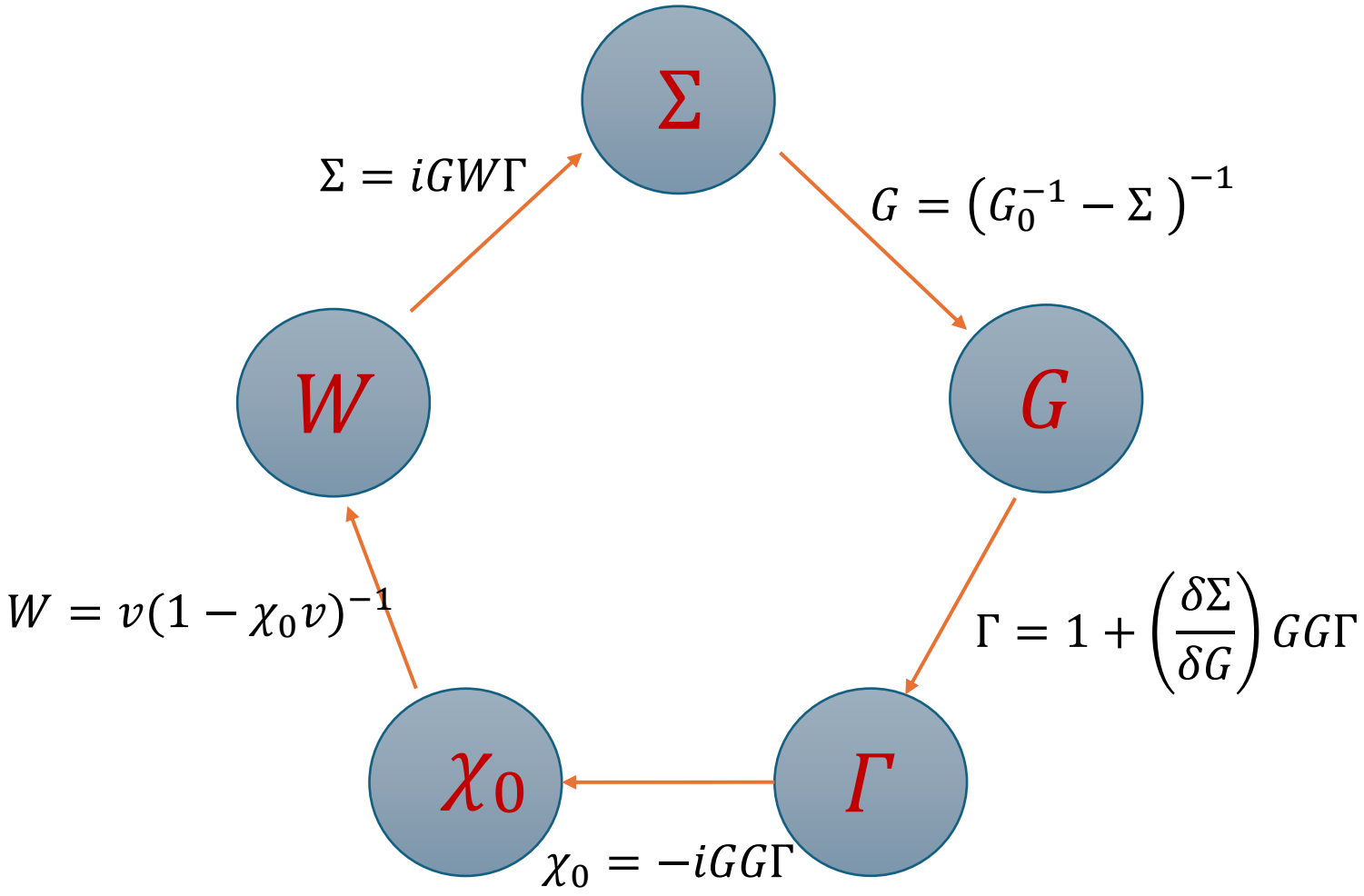
$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\,\Gamma(6,7,3)d4d5d6d7$$ (Vertex function)

$$G(1,2) = G_0(1,2) + \int G_0(1,3)\Sigma(3,4)G(4,2)d3d4$$

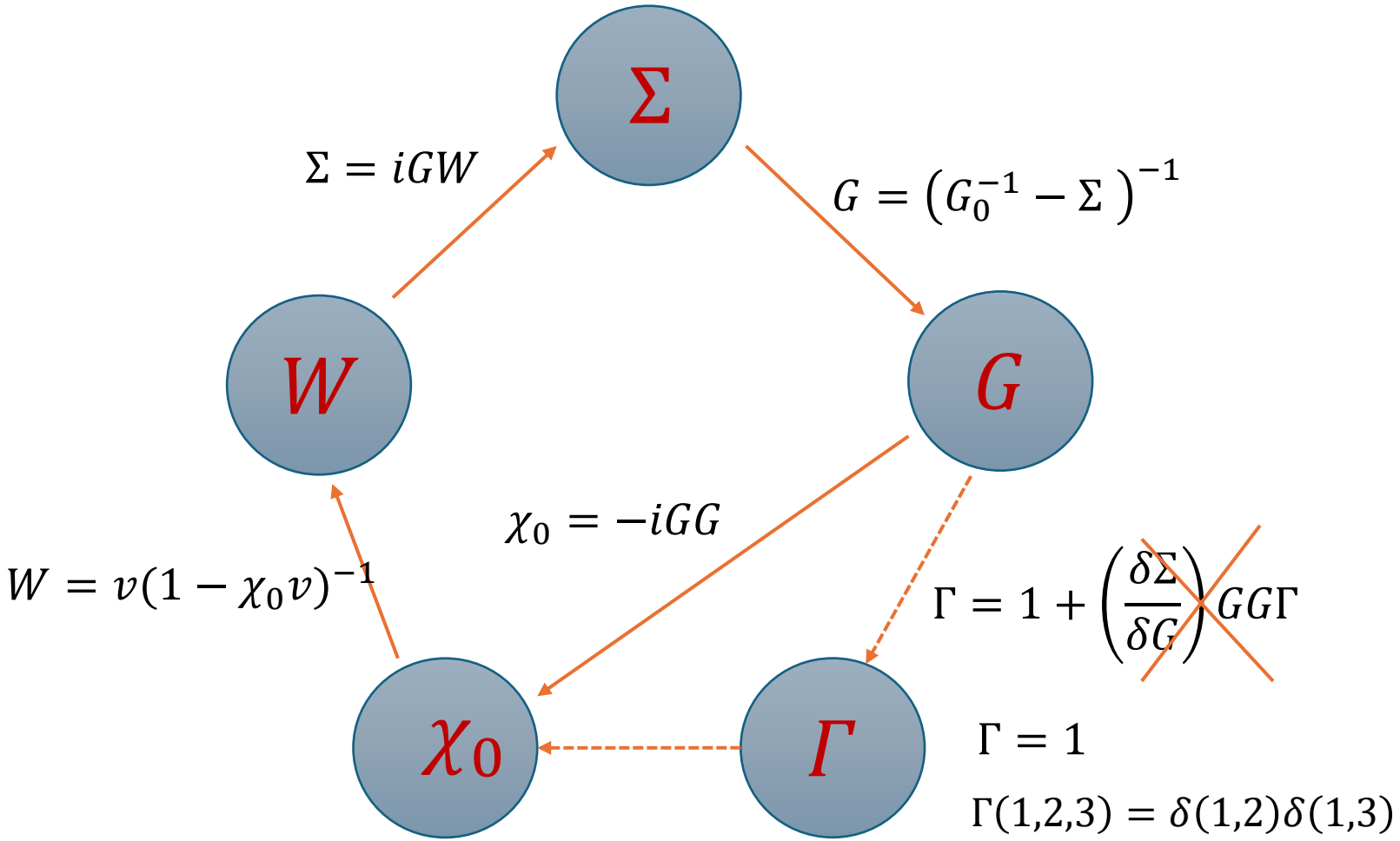
Reformulation of the many-electron Schrödinger's equation using five quantities, χ_0, W, Σ, Γ, G

L. Hedin, Phys. Rev. **139**, A796 (1965)

Pictorial illustration of Hedin's equation



GW approximation from Hedin's equation



The *GW* equations

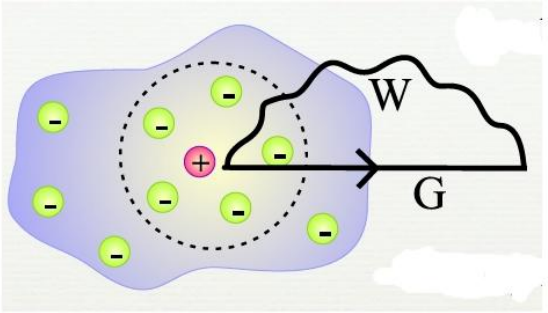
$$\Sigma^{GW}(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int d\,\omega' G(\mathbf{r},\mathbf{r}';\omega-\omega')W(\mathbf{r},\mathbf{r}';\omega')e^{i\omega' 0^+}$$

$$W(\mathbf{r},\mathbf{r}';\omega) = \int d\,\mathbf{r}''\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)v(\mathbf{r}''-\mathbf{r}')$$

$$\epsilon(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}') - \int d\,\mathbf{r}''\chi_0(\mathbf{r},\mathbf{r}'';\omega)v(\mathbf{r}''-\mathbf{r}')$$

$$\chi_0(\mathbf{r},\mathbf{r}';\omega) = -\frac{i}{2\pi}\int d\,\omega' G(\mathbf{r},\mathbf{r}';\omega-\omega')G(\mathbf{r},\mathbf{r}';\omega')$$

$$G(\boldsymbol{r},\boldsymbol{r}';\omega) = G_0(\boldsymbol{r},\boldsymbol{r}';\omega) + \int dr_1\, dr_2 G_0(\boldsymbol{r},\boldsymbol{r}_1;\omega)\Sigma\big(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega\big)G(\boldsymbol{r}_2,\boldsymbol{r}';\omega)$$

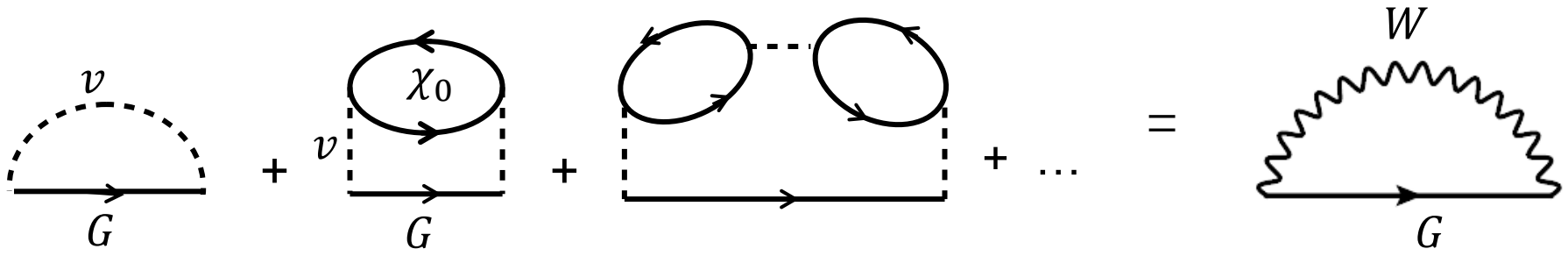


Under certain discretization (basis representation), these integral equations will become matrix equations.

Diagrammatic illustration of the *GW* approximation

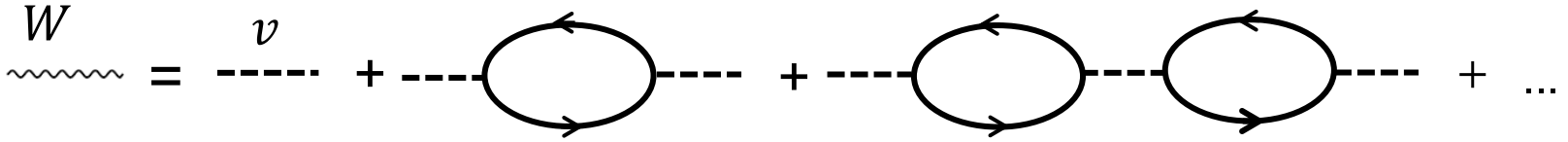
The essence of the *GW* approximation is a special choice of Feynman diagrams for the self-energy

$$\Sigma^{GW}[G] = \Sigma_{\mathrm{x}}^{\mathrm{exact}} + \Sigma_c^{GW} =$$



The screened Coulomb interaction

$$\chi_0 = -iGG$$



$$W = v + v\chi_0 v + v\chi_0 v\chi_0 v + \cdots = \frac{v}{1 - \chi_0 v} = \varepsilon^{-1} v$$

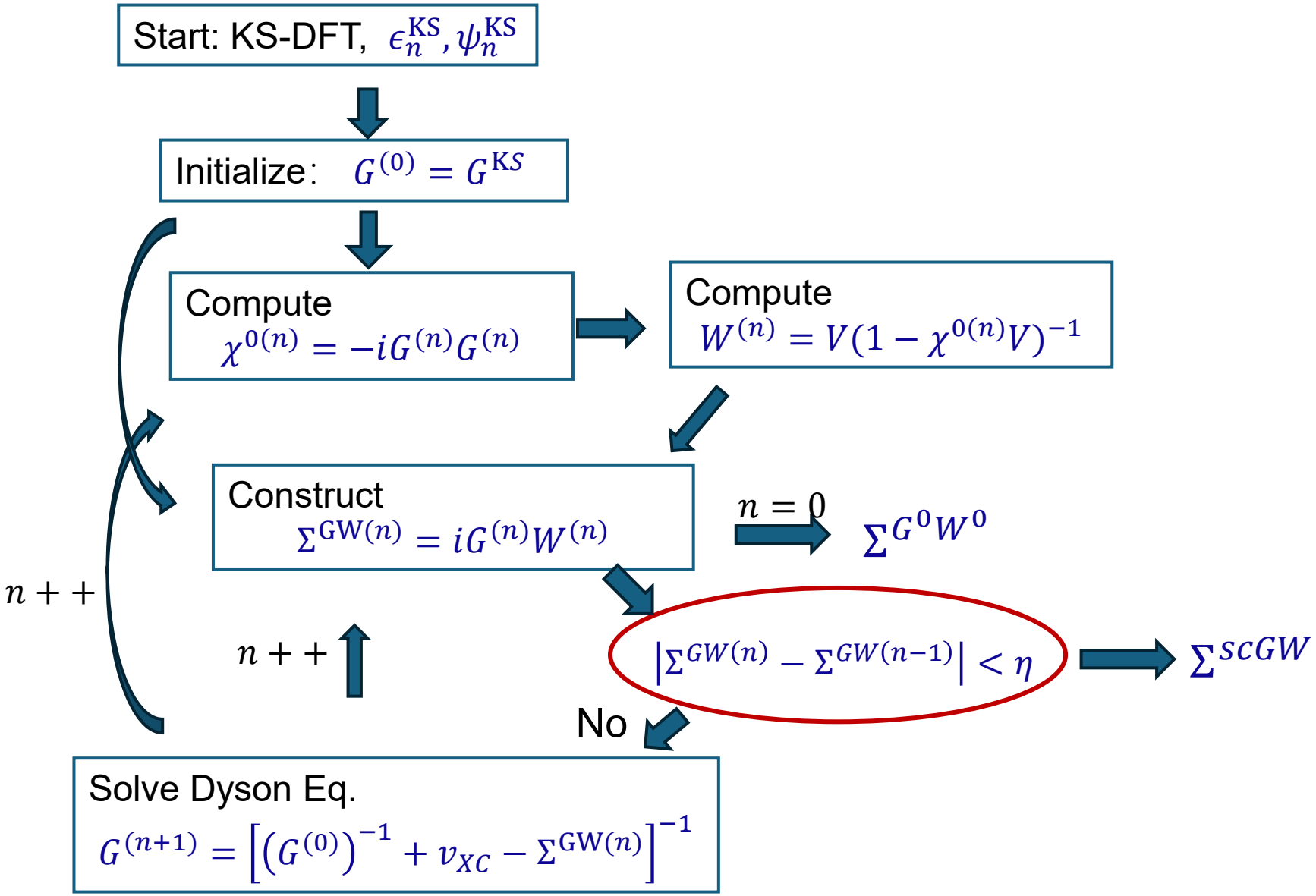
(RPA approximation)

ε: the dielectric function

Current status of the *GW* method

- Various flavors of *GW* schemes :
  - G^0W^0
  - Eigenvalue-only self-consistent *GW* (ev-*GW*)
  - Partial self-consistent, e.g., GW^0
  - Quasiparticle self-consistent *GW* (QP*GW*)
  - Fully self-consistent *GW* (sc*GW*)
  - Best *G*, best *W*
- Applications:
  - State of the art for band structure calculations in semi-conductors in last 30 years.
  - Increasingly more important in surface/interface calculations and molecular spectroscopy

Workflow of the *GW* method



Outcome of the *GW* calculations

- G^0W^0 calculations

  => Quasiparticle energy (QP) levels

KS states

$$E_{n\mathbf{k}}^{\mathrm{QP}} = \epsilon_{n\mathbf{k}}^{\mathrm{KS}} + \mathrm{Re}\,\langle n\boldsymbol{k} \mid \Sigma^{G^0W^0}(E_{n\mathbf{k}}^{\mathrm{QP}}) - V_{xc}^{\mathrm{KS}} \mid n\boldsymbol{k}\rangle$$

1. Determine $\Sigma^{G^0W^0}(E_{n\mathbf{k}}^{\mathrm{QP}})$ on the real frequency axis
2. Solve the above QP equation iteratively (or linearizing it)

KS energy levels $\epsilon_{n\mathbf{k}}^{\mathrm{KS}}$ => QP energy levels => G^0W^0 band structure

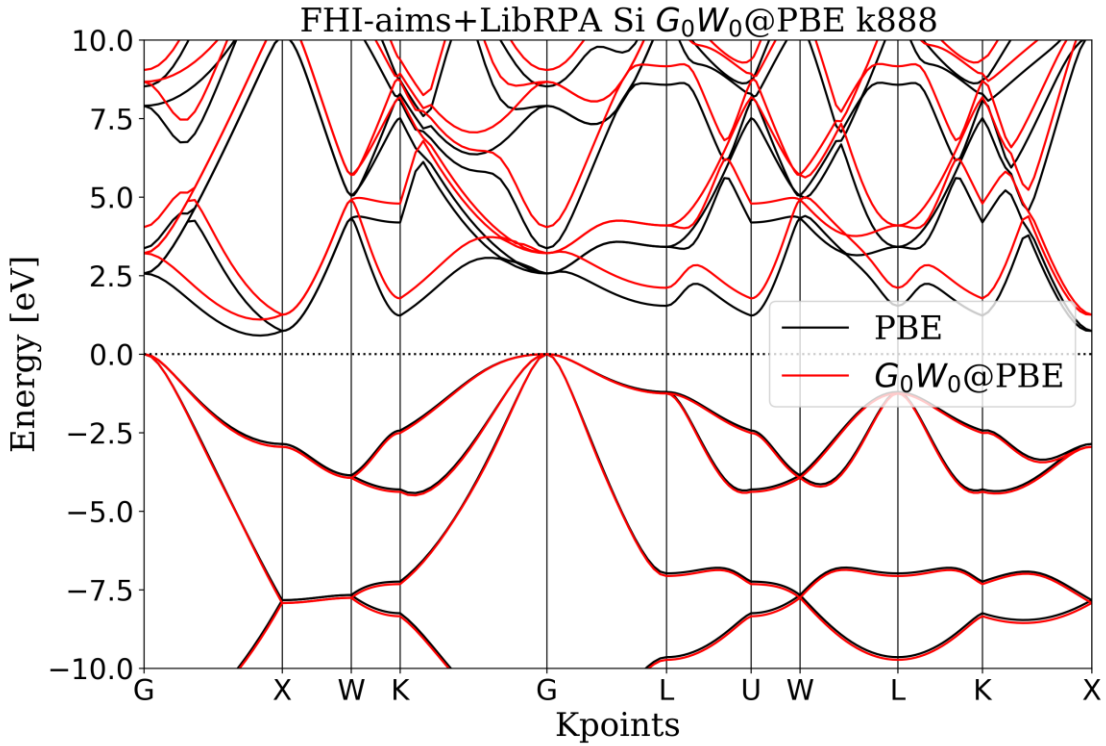
- Self-consistent GW calculations

  Self-consistent Green function $G(\boldsymbol{k},\omega)$ =>

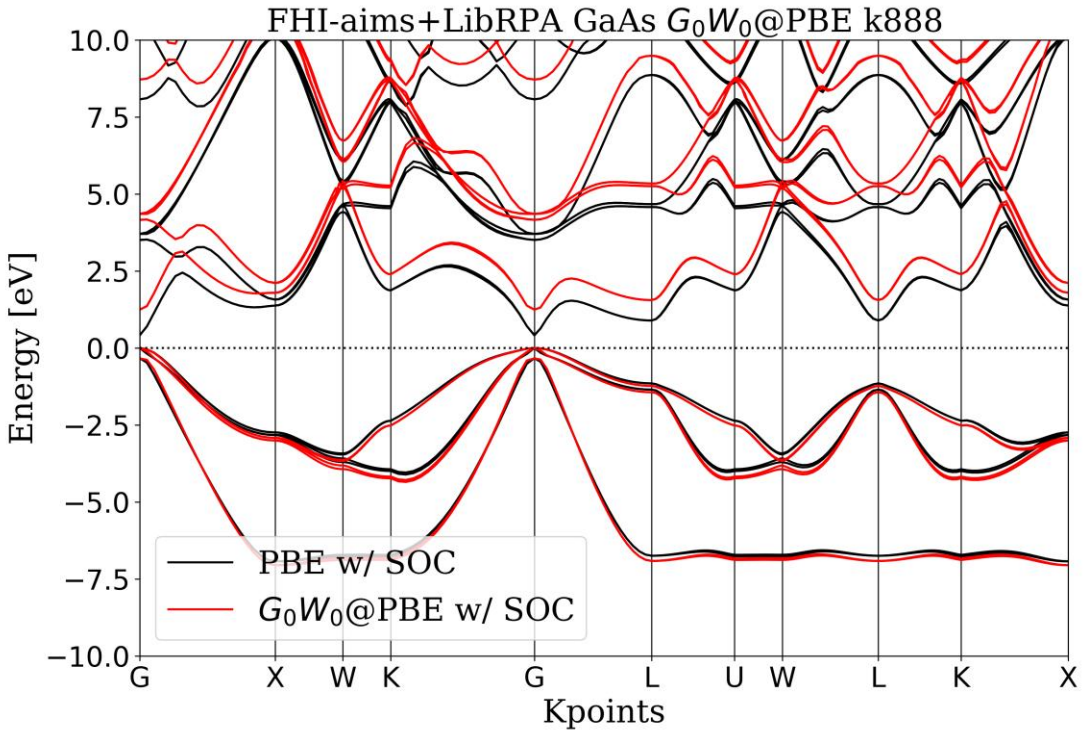
  - Energy spectrum $A(\boldsymbol{k},\omega) = -\frac{1}{\pi}\mathrm{Im}G(\boldsymbol{k},\omega)$
  - Electron density, total energy
  - QP wavefunctions

G^0W^0 band structures

Si

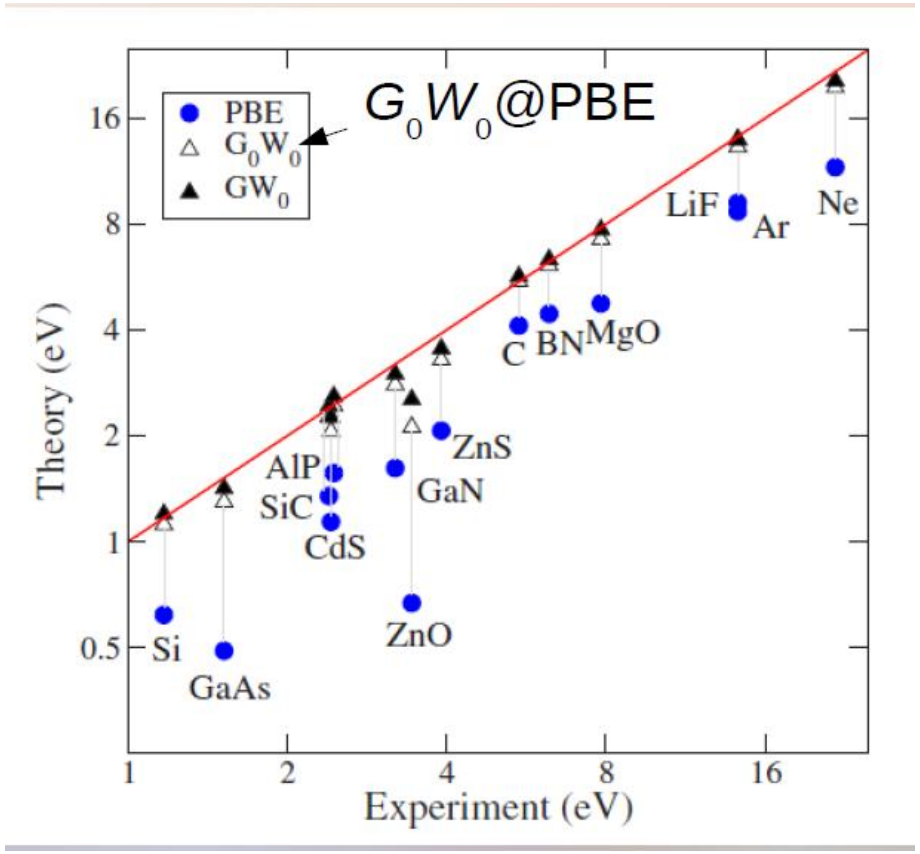


GaAs (with spin-orbit coupling)

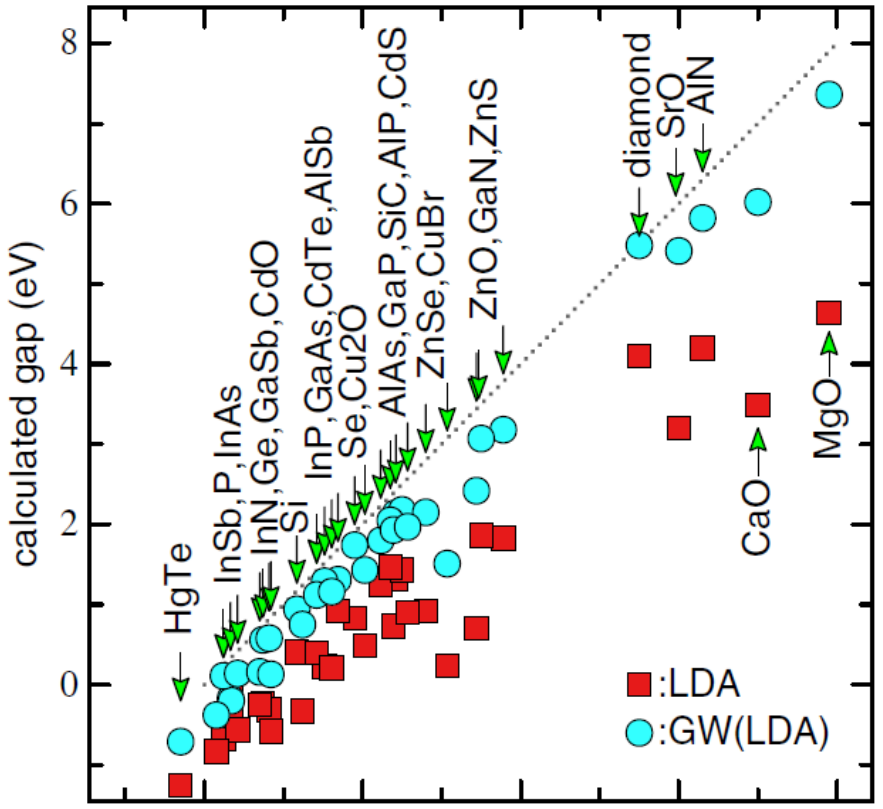


Calculated by Huanjing Gong using “FHI+aims + LibRPA”

GW band gaps



M. Shinskin and G. Kresse, PRB 75, 235102 (2007)



*van Schilfgaarde, Faleev, and Kotani, PRL **96**, 226402 (2006).*

- DFT(LDA/GGA): underestimates the band gaps by 30-40% ;
- GW: in agreement with experimental gaps within 5-10% .

Contents

- Basics of the *GW* method
- The *GW* implementation in FHI-aims
- Bethe Salpeter Equation (BSE)

Implementation of the *GW* equations

- What basis functions to use to represent the real-space dependence of one- and two-particle quantities?
  - Green function & self-energy (one-particle quantities)

$$G(\boldsymbol{r},\boldsymbol{r}';\omega)=\sum_{ij}\varphi_i(\boldsymbol{r})G_{ij}(\omega)\varphi_j(\boldsymbol{r}')\,;\quad \Sigma(\boldsymbol{r},\boldsymbol{r}';\omega)=\sum_{ij}\varphi_i(\boldsymbol{r})\Sigma_{ij}(\omega)\varphi_j(\boldsymbol{r}')$$

  - Response function & screened Coulomb interaction (two-particle quantities)

$$\chi^0(\boldsymbol{r},\boldsymbol{r}';\omega)=\sum_{ij}P_\mu(\boldsymbol{r})\chi^0_{\mu\nu}(\omega)P_\nu(\boldsymbol{r}')\,;\quad W(\boldsymbol{r},\boldsymbol{r}';\omega)=\sum_{ij}P_\mu(\boldsymbol{r})\,W_{\mu\nu}(\omega)P_\nu(\boldsymbol{r}')$$

- How to treat the frequency dependence of dynamic quantities?
  - Plasmon-pole approximation
  - Full real-frequency treatment
  - Imaginary time/frequency plus analytical continuation
  - Imaginary frequency plus contour deformation
  - …

Implementation of the *GW* equations

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Basis set choices of different softwares

Numerical framework	One-electron orbital basis functions $\{\varphi_i(\boldsymbol{r})\}$	Auxiliary basis functions $\{P_\mu(\boldsymbol{r})\}$	Representative codes
Pseudopotentials, PAW	Plane waves	Plane waves	VASP, QE, Abinit
Augmented basis LAPW	LAPW	Mixed product basis	Wien2k, Exciting, Fleur-SPEX
Local atomic orbitals (NAOs, GTOs, STOs)	Gaussian-type orbitals	Atom-centered auxiliary basis functions	Turbomole, PySCF
	Slater-type orbitals		ADF
	Numerical atomic orbitals		FHI-aims, ABACUS

Basic features of the *GW* implementation in FHI-aims

- Using numeric atom-centered orbitals (NAO) to expand the Kohn-Sham (KS) wave function and the Green function & self-energy

$$\varphi_i(\boldsymbol{r}) = \varphi_{a,\kappa,l,m}(\boldsymbol{r}) = u_{a,k,l}(r)Y_{lm}(\hat{\boldsymbol{r}}), i = 1, \cdots, N_b$$

G, Σ: $N_b \times N_b$ matrices

$$\psi(\boldsymbol{r}) = \sum_i c_i \varphi_i(\boldsymbol{r}); \quad G(\boldsymbol{r}, \boldsymbol{r}'; \mathrm{i}\omega) = \sum_{ij} \varphi_i(\boldsymbol{r}) G_{ij}(i\omega) \varphi_j(\boldsymbol{r}')$$

- Using atom-centered auxiliary basis functions (ABFs) to expand the response function, dielectric function and screened Coulomb interaction

$$P_\mu(\boldsymbol{r}) = P_{a\kappa lm}(\boldsymbol{r}) = \xi_{a\kappa l}(r)Y_{lm}(\theta, \varphi), i = 1, \cdots, N_{\mathrm{ABF}}$$

χ^0, ε, W: $N_{\mathrm{ABF}} \times N_{\mathrm{ABF}}$ matrices

$$\varphi_i(\boldsymbol{r})\varphi_j(\boldsymbol{r}) = \sum_\mu C_{ij}^\mu P_\mu(\boldsymbol{r}); \quad W(\boldsymbol{r}, \boldsymbol{r}'; i\omega) = \sum_{\mu\nu} P_\mu(\boldsymbol{r}) W_{\mu\nu}(i\omega) P_\nu(\boldsymbol{r})$$

- Perform frequency integration along the imaginary axis, and then obtain the self-energy at the real frequency by analytical continuation (AC) or contour deformation (CD)

$$\Sigma_{ij}(i\omega) \xrightarrow[\text{rotation}]{} \Sigma_{nn}(i\omega) \xrightarrow[\text{AC/CD}]{} \Sigma_{nn}(\omega) \longrightarrow \text{QPE } E_n$$

Basis representation of χ^0

$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = 2\sum_{m,n}\frac{(f_m - f_n)\psi_m{}^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n{}^*(\mathbf{r}')\psi_m(\mathbf{r}')}{\varepsilon_m - \varepsilon_n - i\omega}$$

$$= \sum_{\mu,\nu} P_\mu(\mathbf{r})\chi^0_{\mu\nu}(i\omega)P_\nu(\mathbf{r}')$$

Density fitting (resolution of identity)

$$\psi^*_m(\mathbf{r})\psi_n(\mathbf{r}) = \sum_\mu C^\mu_{mn} P_\mu(\mathbf{r})$$

Fermi occupation factor

C^μ_{mn}: RI expansion coefficients

Then $\chi^0_{\mu\nu}(i\omega) = 2\sum_{m,n}\frac{(f_m - f_n)C^\mu_{mn}C^\nu_{mn}}{\varepsilon_m - \varepsilon_n - i\omega}$

Computational expression for G_0W_0

$$\chi^0(\mathbf{r},\mathbf{r}',i\omega) = \sum_{\mu,\nu} P_\mu(\mathbf{r})\chi^0_{\mu\nu}(i\omega)\,P_\nu(\mathbf{r}')$$

$$\chi^0_{\mu\nu}(i\omega) = 2\sum_{m,n}\frac{(f_m - f_n)C^\mu_{mn}C^\nu_{mn}}{\varepsilon_m - \varepsilon_n - i\omega} \qquad V_{\mu\nu} = \int d^3r\, d^3r' \frac{P_\mu(\mathbf{r})P_\nu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Define $\Pi_{\mu\nu} = [V^{\frac{1}{2}}\chi^0 V^{\frac{1}{2}}]_{\mu\nu}$

$$W_{\mu\nu}(i\omega) = \left[V^{1/2}[1-\Pi(i\omega)]^{-1}V^{1/2}\right]_{\mu\nu}$$

The key is to compute C^μ_{mn}

Computational Expression for G^0W^0

The screened Coulomb interaction:

$$W_{\mu\nu}(i\omega) = \left[V^{1/2}[1-\Pi(i\omega)]^{-1}V^{1/2}\right]_{\mu\nu}$$

The G_0W_0 self-energy:

$$\Sigma_n^{G^0W^0}(i\omega) = -\frac{1}{2\pi}\sum_m\sum_{\mu,\nu}\int_{-\infty}^{\infty} d\omega' \frac{1}{i\omega - i\omega' + \mu - \varepsilon_m} C_{mn}^{\mu} W_{\mu\nu}(i\omega') C_{mn}^{\nu}$$

G_0 W_0

Analytical Continuation:

$$\Sigma_n^{G^0W^0}(i\omega) \rightarrow \Sigma_n^{G^0W^0}(\omega)$$

Quasiparticle energy:

$$E_n = \varepsilon_n + \Sigma_n^{G^0W^0}(E_n) - \langle \psi_n | v_{xc}^{DFT} | \psi_n \rangle$$

Ren, Rinke, Blum, Wieferink, Tkatchenko, Sanfilippo, Reuter, and Scheffler, New J. Phys. 14, 053020 (2012)

Accuracy of FHI-aims *GW* calculations for atoms

Atoms	GW@PBE (B-spline)	GW@PBE (FHI-AIMS, tier 4 + a5Z)	Difference (Ry)
H	0.917	0.920	0.003
He	1.722	1.734	0.012
Li	0.405	0.417	0.012
Be	0.657	0.664	0.007
N	0.997	0.997	0.000
Ne	1.514	1.510	-0.004
Na	0.383	0.401	0.018
Mg	0.552	0.567	0.015
P	0.743	0.743	0.000
Ar	1.132	1.118	-0.014
MAE	-	-	0.009

FHI-aims calculations: X. Ren et al., New J. Phys. 14, 053020 (2012)

B-spline calculation: S. Vacondio,D. Varsano,A. Ruini,A. Ferretti, *Numerically Precise Benchmark of Many-Body Self-Energies on Spherical Atoms*, *J. Chem. Theory Comput.* **18**, 3703–3717 (2022)

GW: from molecular systems to periodic systems

Noninteracting response function:

$$\chi^0_{\mu\nu}\ (\boldsymbol{q}, i\omega)\ = 2\sum_{m,n,\boldsymbol{k}} \frac{(f_{m,\boldsymbol{k}+\boldsymbol{q}} - f_{n,\boldsymbol{k}})C^{\mu,\boldsymbol{q}}_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{k}}C^{*\nu,\boldsymbol{q}}_{m,\boldsymbol{k}+\boldsymbol{q};n,\boldsymbol{k}}}{\varepsilon_{m,\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{n,\boldsymbol{k}} - i\omega}$$

Screened Coulomb interaction:

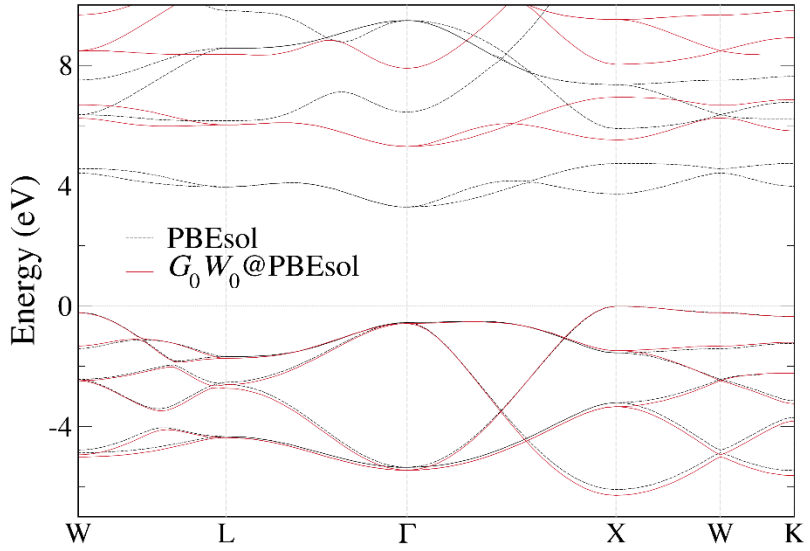
$$W_{\mu\nu}(\boldsymbol{q}, i\omega) = [V(\boldsymbol{q})(1 - \chi^0(\boldsymbol{q}, i\omega)V(\boldsymbol{q}))^{-1}]_{\mu\nu}$$

The G_0W_0 self-energy

$$\Sigma_n^{G_0W_0}(\mathbf{k}, i\omega) = -\frac{1}{2\pi}\sum_m \sum_{\boldsymbol{q}\in 1.\mathrm{BZ}} \sum_{\mu,\nu} \int_{-\infty}^{\infty} d\omega' \frac{1}{i\omega - i\omega' + \mu - \varepsilon_{m,\boldsymbol{k}-\boldsymbol{q}}} \times C^{\mu,\boldsymbol{q}}_{n,\boldsymbol{k};m,\boldsymbol{k}-\boldsymbol{q}} W_{\mu\nu}(\boldsymbol{q}, i\omega') C^{*\nu,\boldsymbol{q}}_{n,\boldsymbol{k};\boldsymbol{m},\boldsymbol{k}-\boldsymbol{q}}$$

Quasi-particle band structures of ZrO_2

Band structure from FHI-aims



Common parameters
- k-grids 6x6x6
- analytic continuation using Padé
- Perturbative expansion of Σ in solving QPE

KS/GW band gaps from three different codes

- FHI-aims: all-electron NAO
- ABINIT: pseudopotential plane-wave
- Exciting: all-electron linearized augmented plane-wave

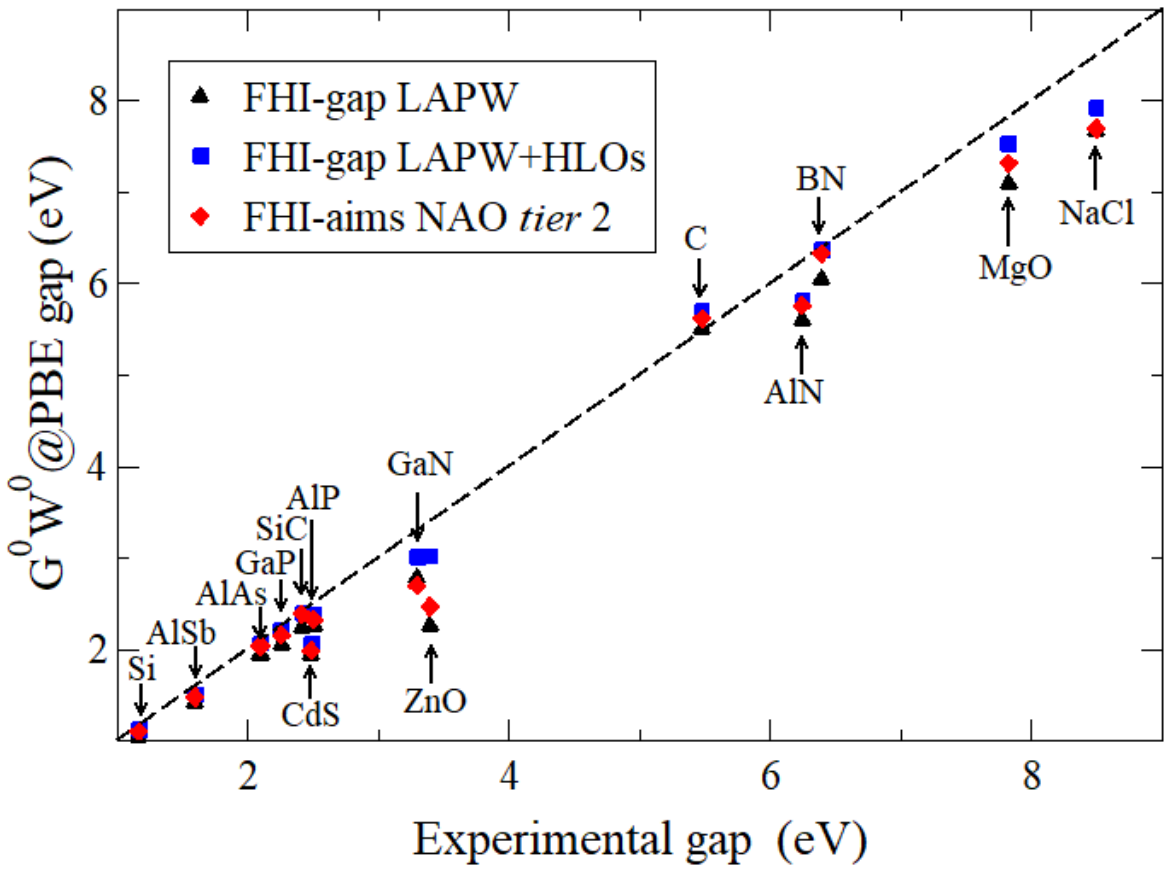
PBEsol	FHI-aims	ABINIT	Exciting
$X \rightarrow \Gamma$	3.303	3.320	3.321
$\Gamma \rightarrow \Gamma$	3.847	3.867	3.865
$X \rightarrow X$	3.725	3.750	3.748

G_0W_0@PBEsol	FHI-aims	ABINIT	Exciting
$X \rightarrow \Gamma$	5.361	5.300	5.319
$\Gamma \rightarrow \Gamma$	5.928	5.896	5.883
$X \rightarrow X$	5.608	5.587	5.573

M. Azizi et al, Comput. Mater. Sci. ***250****, 113655 (2025)*

Converging parameters to achieve at least 0.05 eV accuracy

Benchmark G_0W_0 calculations for semiconductors and insulators



First NAO-based periodic *GW* implementations

For half of the materials (11 of 21), the agreement is within 0.1 eV, with LAPW+HLO results

Ren, Merz, Jiang, Yao, Rampp, Lederer, Blum, Scheffler, Phys. Rev. Mater. ***5****, 013807 (2021).*

FHI-gap results:
Jiang & Blaha, Phys. Rev. B ***93*** *115203 (2016)*

Major FHI-aims *GW* capabilities

	Molecular geometry	Periodic system (finite k points)
GW flavors	G^0W^0, ev*GW*, evGW^0, scGW^0, sc*GW*	G^0W^0
Frequency integration	AC, CD, CD-WAC	AC
Relativistic treatment	scalar relativistic, SOC	scalar relativistic, SOC (via LibRPA)
Vertex correction	GW+SOSEX	No

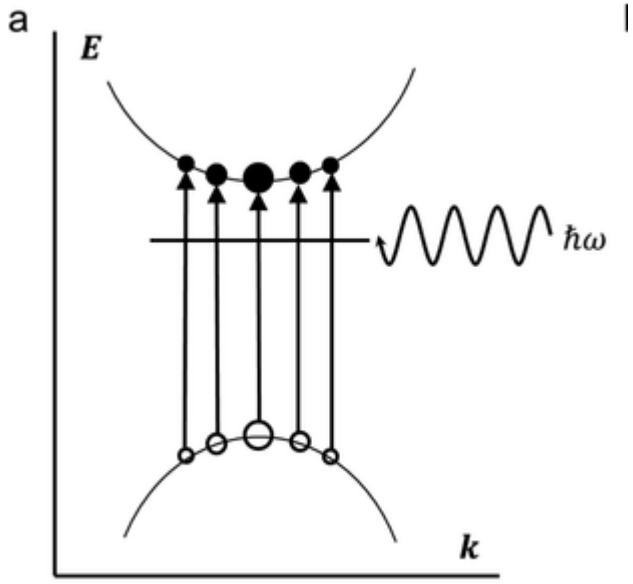
Further details can be found in Sec. 4.3 and 4.4 of the big FHI-aims paper

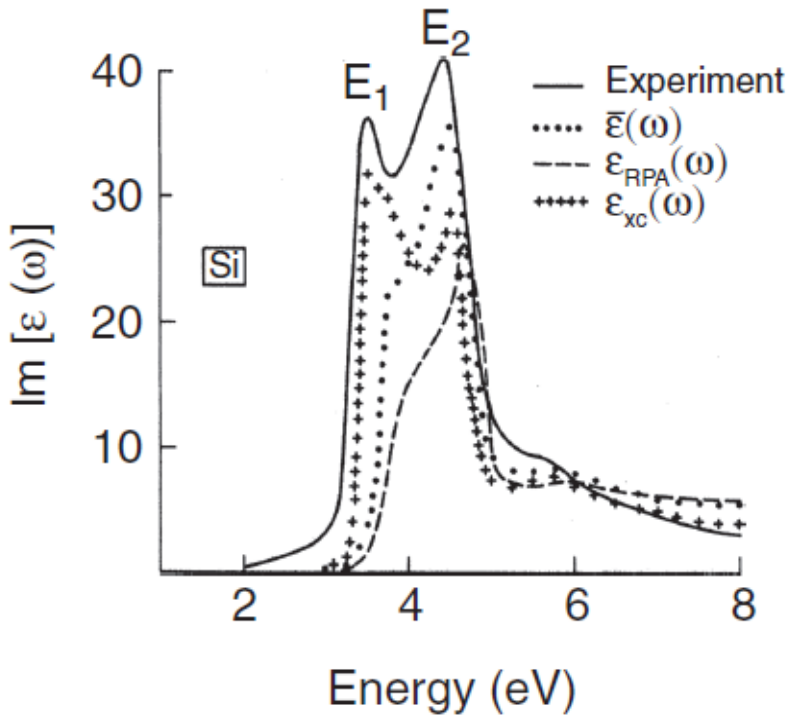
"Roadmap on Advancements of the FHI-aims Software Package", arXiv:2505.00125

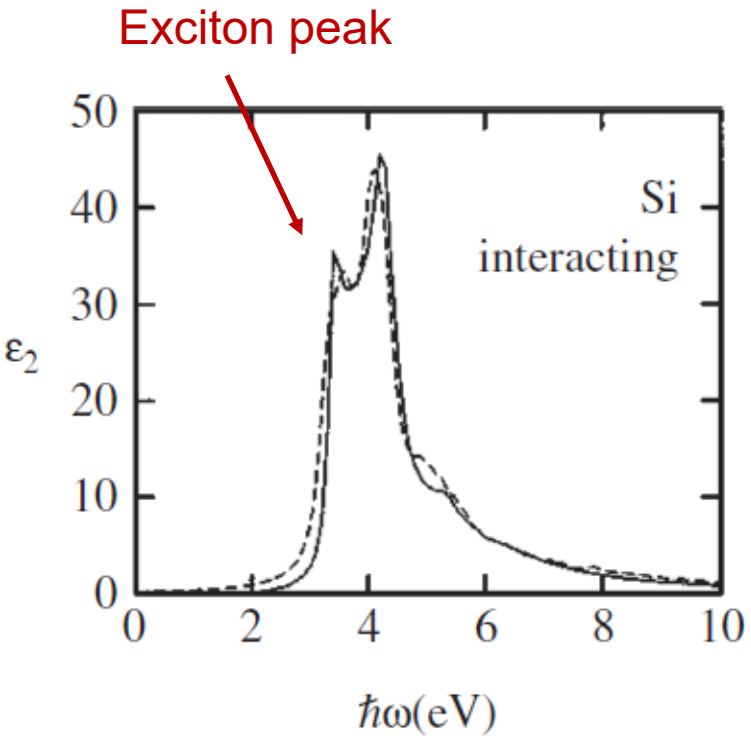
Contents

- Basics of the *GW* method
- The *GW* implementation in FHI-aims
- Bethe Salpeter Equation (BSE)

Optical adsorption spectrum







From Martin, Reining, and Ceperley, "Interacting Electron: Theory and Computational Approaches", Cambridge University Press, 2016

Equation of motion for the Green function

$G_1(1,2) \equiv G_1(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2)$

Equation of Motion

$$\left[i\frac{\partial}{\partial t_1} - \hat{h}(\mathbf{r}_1) - v_H(\mathbf{r}_1) \right] G_1(1,2) + \mathrm{i}\int d3v(1,3)\, G_2(1,3^+;2,3^{++}) = \delta(1,2)$$

$$G_2(1,2;1',2') \equiv (-i)^2 \langle N,0 | \hat{T}\{\hat{\psi}(\mathbf{r}_1,t_1)\hat{\psi}(\mathbf{r}_2,t_2)\hat{\psi}^\dagger(\mathbf{r}_2',t_2')\hat{\psi}^\dagger(\mathbf{r}_1',t_1')\} | N,0 \rangle$$

Schwinger derivative

$$\Sigma(1,2) \equiv i\int d345v(1^+,3)\frac{\delta G_1(1,4)}{\delta U(3)} G_1^{-1}(4,2)$$

$$\frac{\delta G_1(1,2)}{\delta U(3,4)} = -G_2(1,4;2,3) + G_1(1,2)G_1(4,3)$$

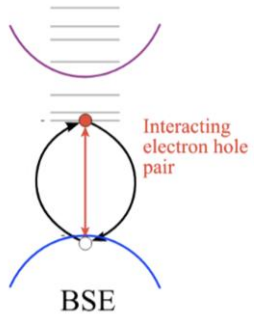
Two-particle Green function describes the two-particle excitation processes in the system (two-electron, two-hole, 1 electron+1 hole)

e.g. van Leeuwen, PRL, 76, 3610 (1996)

Bethe-Salpeter Equation (BSE)

Two-particle correlation function

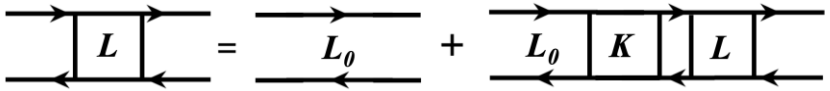
$$L(1,2;1',2') \equiv -G_2(1,2;1',2') + G_1(1,1')G_1(2,2')$$



Bethe-Salpeter equation (BSE)

Strinati, Phys. Rev. B, 29, 5718 (1984)
Rohlfing and Louie, Phys. Rev. B, 62, 4927 (2000)

$$L(1,2;1',2') = \underbrace{L_0(1,2;1',2')}_{G_1(1,2')G_1(2,1')} + \int d(3456)\underbrace{L_0(1,3;1',3)}_{G_1(1,3)G_1(4,1')} K(3,5;4,6)L(6,2;5,2')$$



$$K(3,5;4,6) = \frac{\delta[\Sigma(3,4) + v_H(3)\delta(3-4)]}{\delta G_1(6,5)}$$

$$\Sigma(3,4) \approx iG_1(3,4)W(3,4)$$

GW approximation

Lehman representation

$$L(1,2;1',2';\omega) = i\sum_S \left[\frac{\chi_S(\mathbf{r}_1,\mathbf{r}_1')\chi_S^*(\mathbf{r}_2',\mathbf{r}_2)}{\omega - \Omega_S} - \frac{\chi_S(\mathbf{r}_2,\mathbf{r}_2')\chi_S^*(\mathbf{r}_1',\mathbf{r}_1)}{\omega + \Omega_S}\right]$$

Excitation Energy

$$\chi_S(\mathbf{r},\mathbf{r}') = -\langle N,0|\hat{\psi}^\dagger(\mathbf{r}')\hat{\psi}(\mathbf{r})\,|N,S\rangle = \sum_i^{Occ.}\sum_a^{Unocc.} X_{ia}^S\psi_a^{KS}(\mathbf{r})\psi_i^{KS*}(\mathbf{r}') + Y_{ia}^S\psi_i^{KS}(\mathbf{r})\psi_a^{KS*}(\mathbf{r}')$$

BSE Calculation as an eigenvalue problem

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^S \\ \mathbf{Y}^S \end{pmatrix} = \Omega^S \begin{pmatrix} \mathbf{X}^S \\ \mathbf{Y}^S \end{pmatrix}$$

Excitation Energy

$$\mathrm{A}^S_{iajb} = \delta_{ij}\delta_{ab}(\varepsilon_a^{QP} - \varepsilon_i^{QP}) + \mathrm{K}^X_{iajb} + \mathrm{K}^d_{iajb}$$

GW QPE

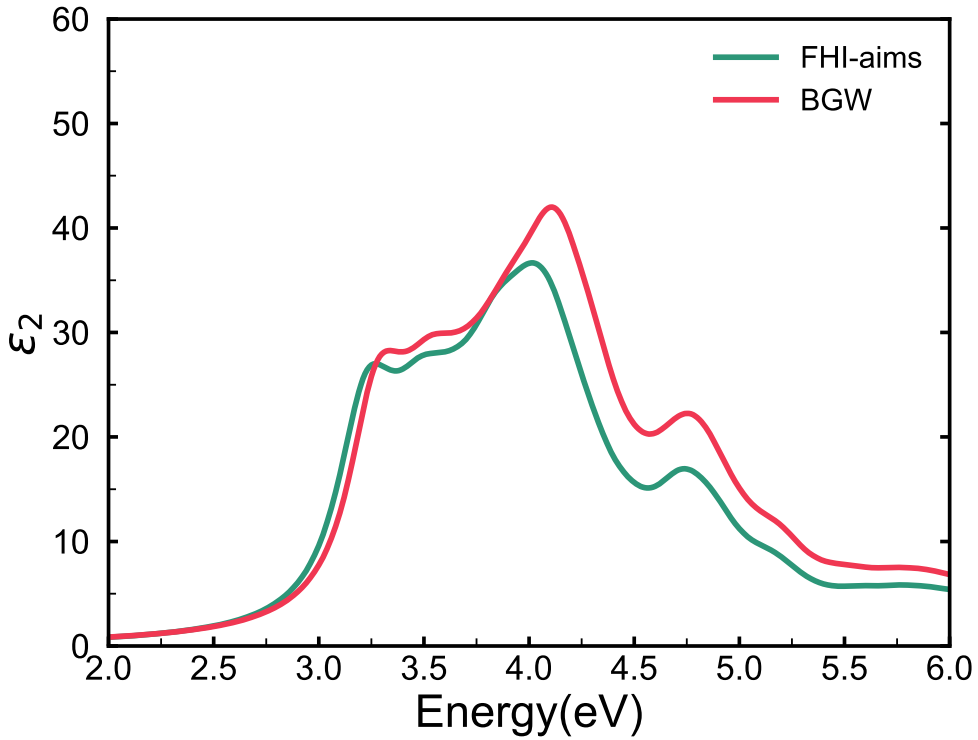
$$\mathrm{B}^S_{iajb} = \mathrm{K}^X_{iajb} + \mathrm{K}^d_{iajb}$$

$$\mathrm{K}^X_{iajb} = \iint d\mathbf{r}d\mathbf{r}'\psi_i^{KS}(\mathbf{r})\psi_a^{KS*}(\mathbf{r})\, v(\mathbf{r},\mathbf{r}')\psi_j^{KS}(\mathbf{r}')\psi_b^{KS*}(\mathbf{r}')$$

$$\mathrm{K}^d_{iajb} = -\iint d\mathbf{r}d\mathbf{r}'\psi_a^{KS*}(\mathbf{r})\psi_b^{KS}(\mathbf{r})W(\mathbf{r},\mathbf{r}',\omega=0)\psi_i^{KS}(\mathbf{r}')\psi_j^{KS*}(\mathbf{r}')$$

Screened Coulomb interaction from *GW*

BSE spectrum for Si: comparison to PW-PP results



$$\epsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_n |\mathbf{e} \cdot \langle 0| \hat{\mathbf{v}} |S_n\rangle|^2 \delta(\omega - \omega_n)$$

Implementation and calculation done by Ruiyi Zhou

R. Zhou, Y. Yao, V. Blum, X. Ren, and Y. Kanai, J. Chem. Theory Comput. ***21****, 291 (2024).*

Summary

- ***GW*** **and** ***GW*****+BSE are very useful tools for describing the excited state properties of molecules and materials from first principles**

- **FHI-aims have implemented a variety of favors of these approaches which are ready for use.**

Check it out at the Tutorial Session this afternoon!

Acknowledgement

Thank you!

4.2 All-Electron *GW* for Finite Systems

Volker Blum[1,2], *Fabio Caruso*[3,4,a], ***Dorothea Golze***[5], *Jannis Kockläuner*[5], *Moritz Leucke*[5], *Qinglong Liu*[5], *Ramón L. Panadés-Barrueta*[5], ***Xinguo Ren***[6,7,b], *Patrick Rinke*[8,9,10,11], *Yanyong Wang*[12], and *Tong Zhu*[13]

4.3 *GW* Calculations for Periodic Systems

Volker Blum[1,2], *Francisco A. Delesma*[3], *Uthpala Herath*[1], *Hermann Lederer*[4], *Florian Merz*[5], ***Xinguo Ren***[6,11,a], *Patrick Rinke*[7,8,9,10], *Matthias Scheffler*[11], *Yi Yao*[11,b], and *Min-Ye Zhang*[6,11]

4.4 Neutral Excited States: Casida Equation for Linear-Response Time-Dependent Density Functional Theory and Bethe-Salpeter Equation

Yosuke Kanai[1,2], *Ruiyi Zhou*[1], *Chi Liu*[3], *Jan Kloppenburg*[4], *Yi Yao*[1,5,a], *Dorothea Golze*[6], *Marc Dvorak*[7], *Patrick Rinke*[7,8,9,10], *Xinguo Ren*[11,12,b], and *Volker Blum*[3,5]