Towards first-principles approaches to electronic excited states of materials

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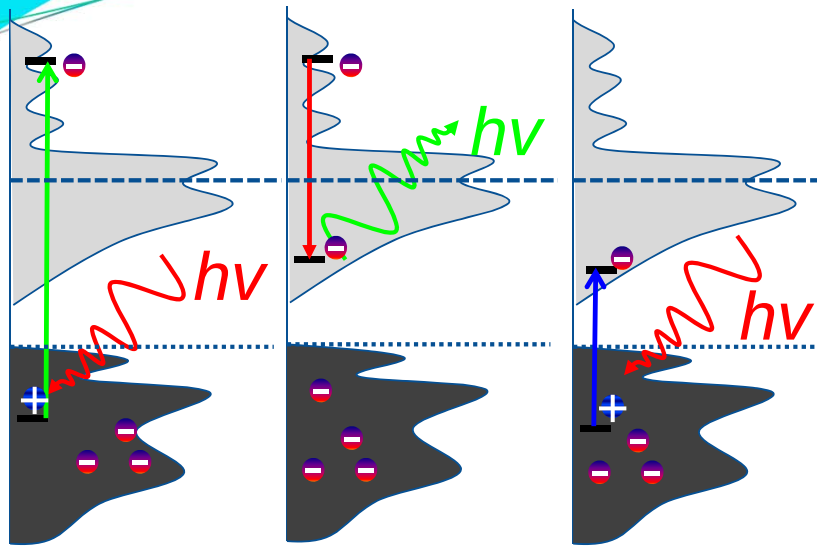
Outline

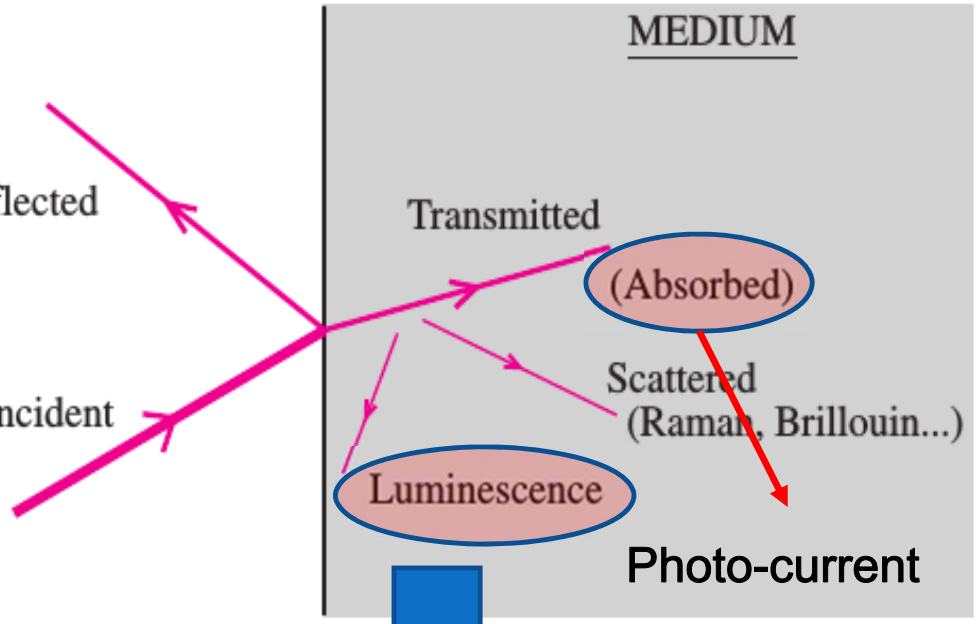
- Introduction: challenges for first-principles description of excited state properties of materials
- First-principles approaches to electronic band structures of materials
- First-principles approaches to optical absorption of solids
- First-principles approaches to self-trapped exciton (STE) luminescence in metal halides
- Concluding remarks

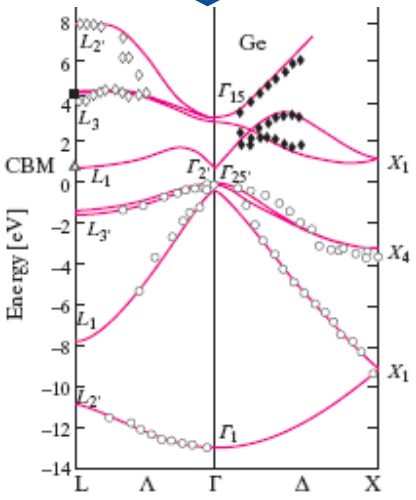
Introduction: challenges for first-principles description of excited state properties of materials

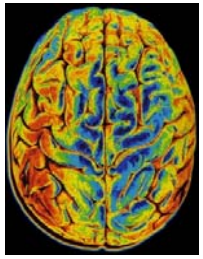
Electronic excitations



PES IPES optical abs.





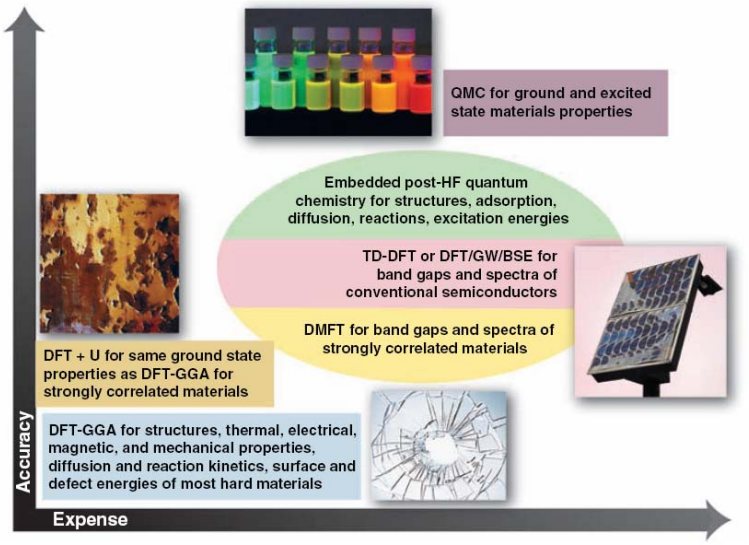


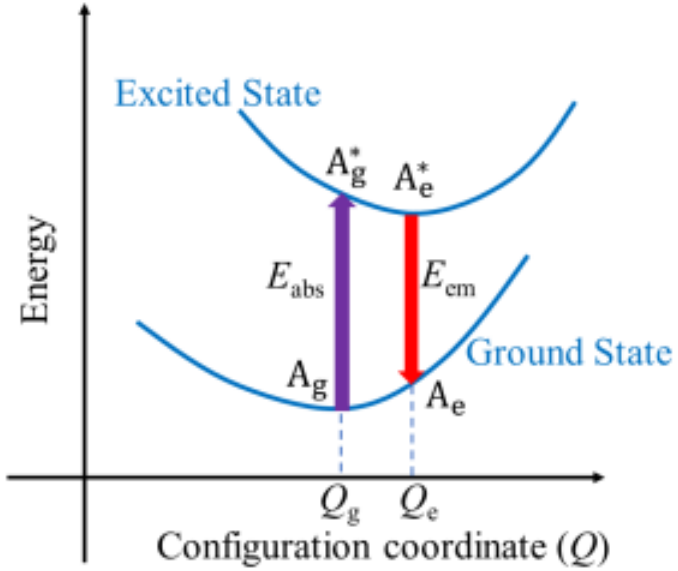
Yu and Cardona, Fundamentals of Semiconductors (2003).

Electronic structure theory for excited states

P.-F. Loos, A. Scemama, D. Jacquemin, *The Quest for Highly Accurate Excitation Energies: A Computational Perspective*, J. Phys. Chem. Lett. 11, 2374 (2020).

Excited states of materials: challenges for theory





E. A. Carter， Science（2008）

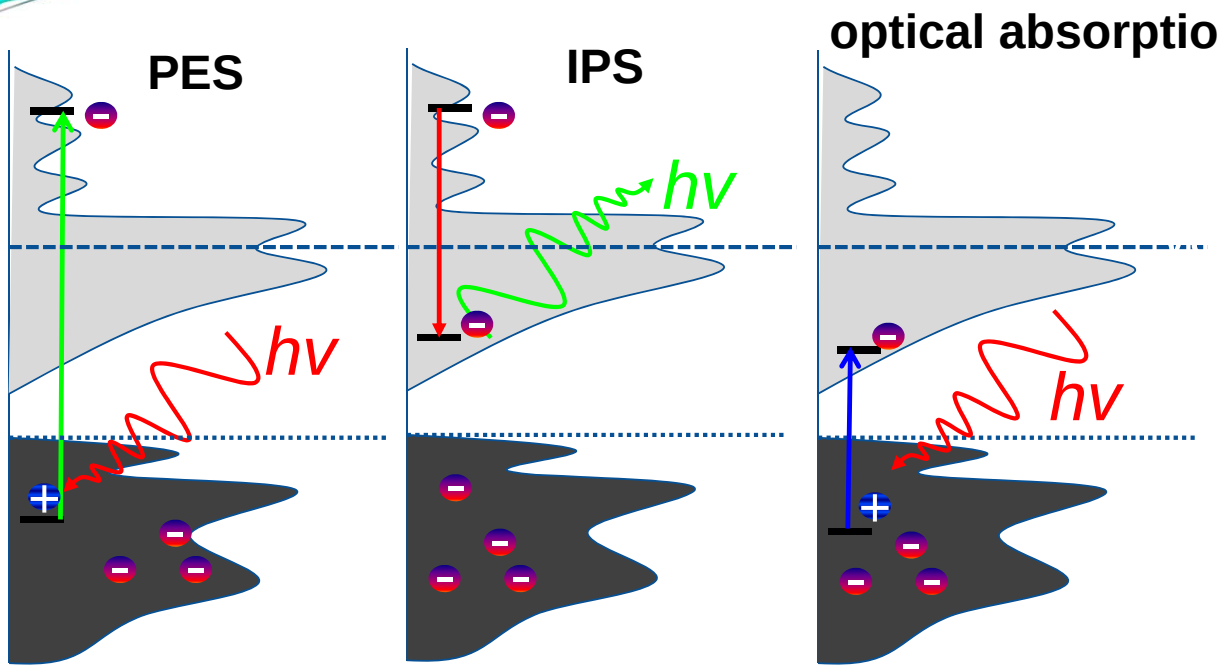
- Electronic band structure (***GW*** or hybrid functionals)
- Electronic excitations of materials (***GW*+BSE**, **TD-hybrids**, ……)
- Geometrical relaxation of excited states in extended systems (**OC-DFT** (ΔSDF),TD-hybrids, ……)
- Luminescent/photo-current efficiency: inter-state transitions (Fermi's Golden rule) , electron-vibration/phonon coupling, ……

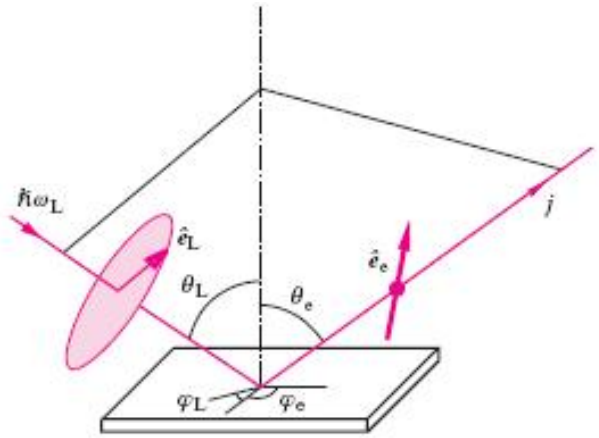
First-principles approaches to electronic band structures of materials

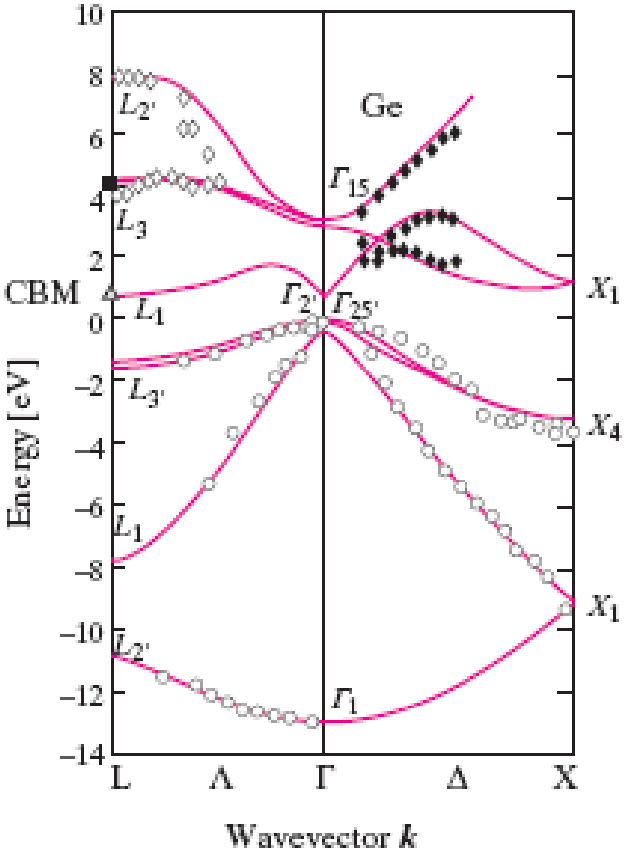
Recommended readings:

- L. Hedin and S. Lundqvist, *Effects of electron-electron and electron phonon interactions on the one-electron states of solids*, Solid State Physics, **23**, 1-181 (1970).
- D. Golze, M. Dvorak, and P. Rinke, *The GW Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy*, Front. Chem. **7**,1 (2019).
- H. Jiang, *The GW Method: Basic Principles, Latest Developments and Its Applications for d-and f-Electron Systems*, Acta Phys.-Chim. Sin. 26, 1017(2010).
- Hong Jiang, *Electronic band structure from first-principles Green's function approach: theory and implementations*, Frontiers of Chemistry in China,6,253-268(2011).

Electronic band structure: Experiment

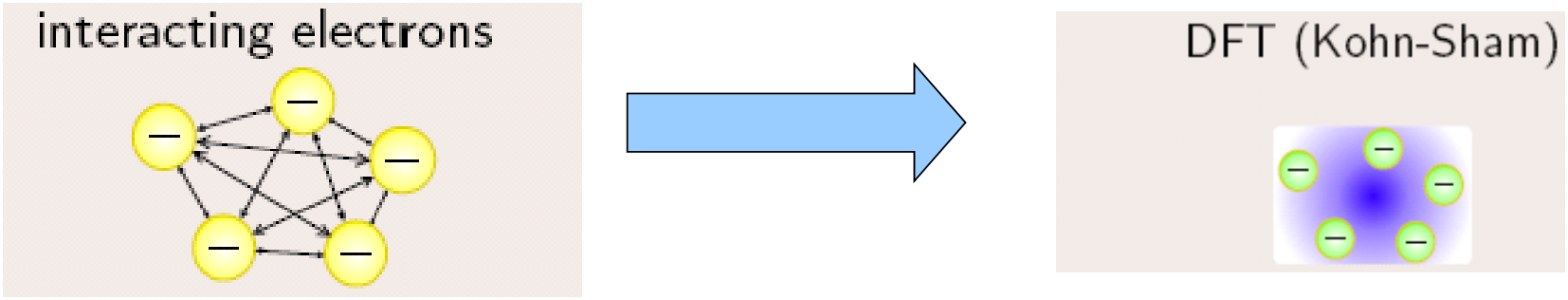




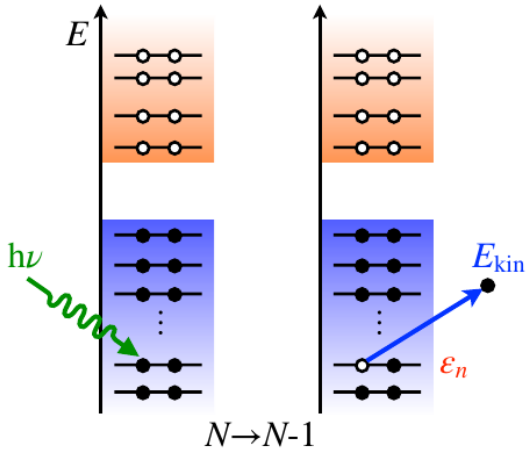


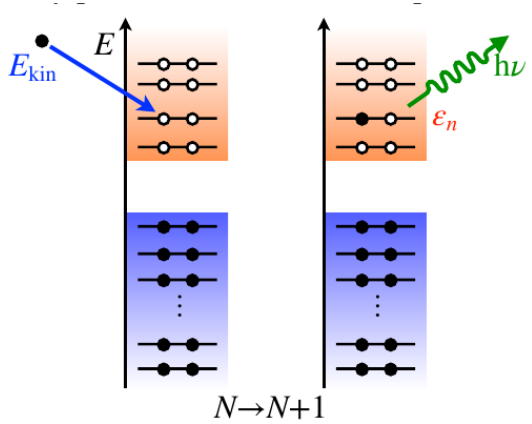
Yu and Cardona, Fundamentals of Semiconductors (2003)

Mean field approaches



$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

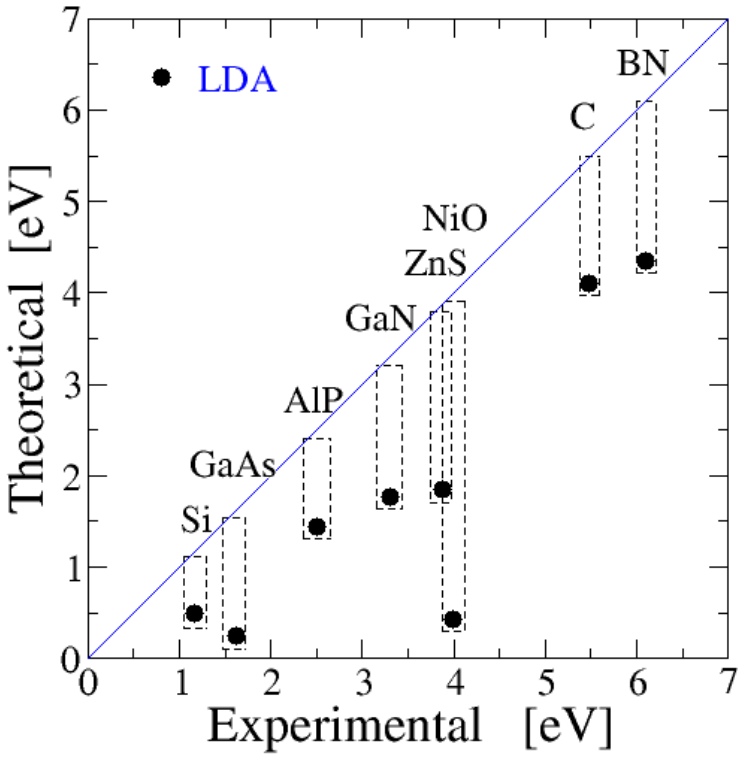


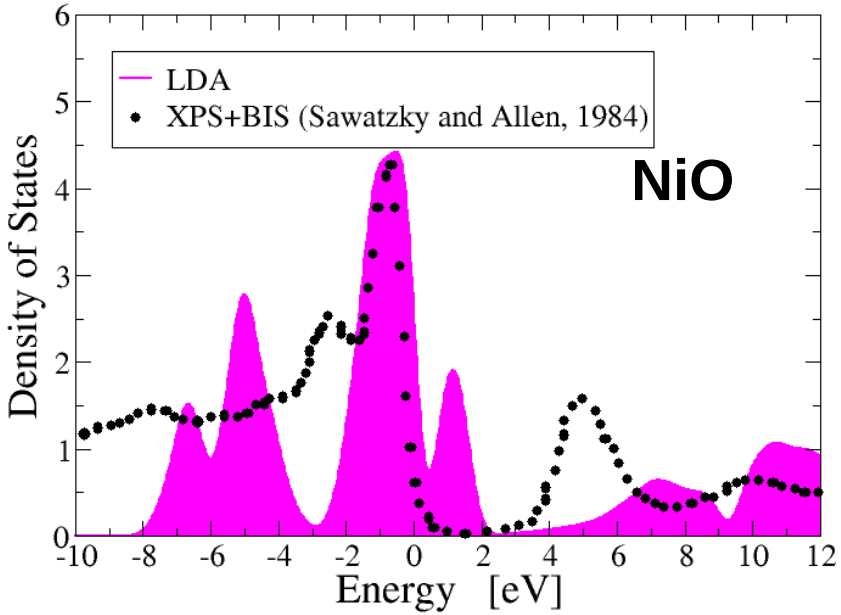


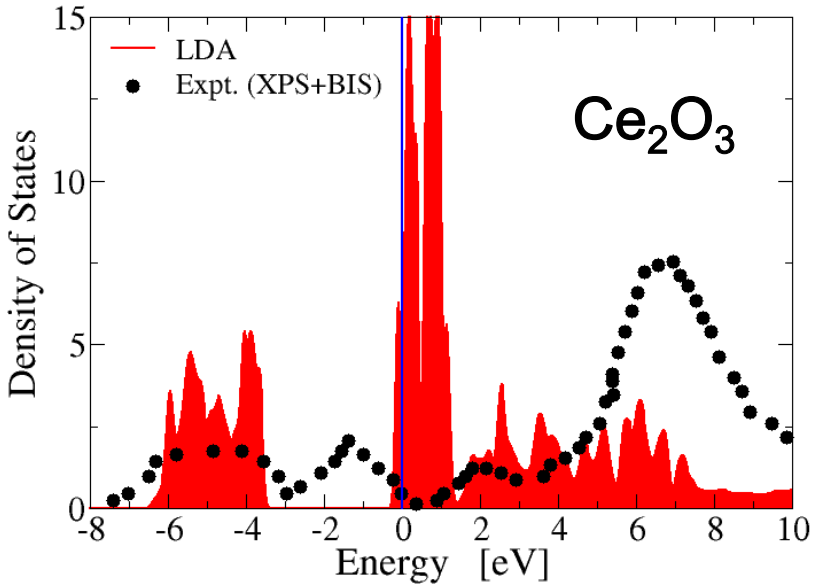
(Illustrations from G.-M. Rignanese's talk)

Remark: Kohn-Sham DFT is an in-principle exact many-body theory for the ground state total energy and electron density, but a mean-field approximation to electronic band structure.

The band gap problem



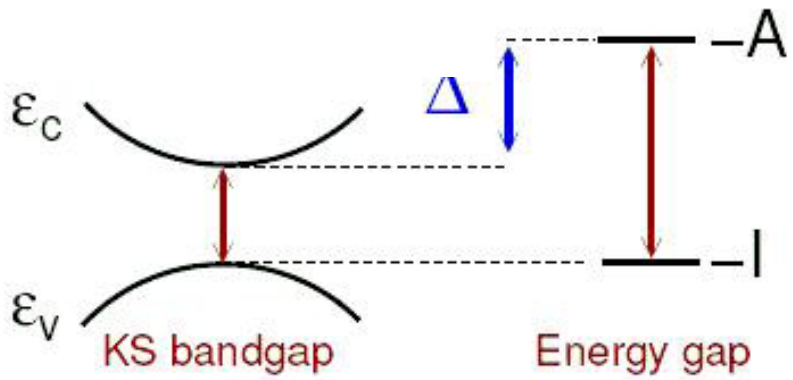




DFT band gap problem

$$\left[-\frac{\nabla^2}{2} + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm xc}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

$$\begin{aligned} E_{\rm gap} &= I - A \\ &\equiv [E(N-1) - E(N)] - [E(N) - E(N+1)] \\ &= [-\epsilon_N(N)] - [-\epsilon_{N+1}(N+1)] \\ &= [\epsilon_{N+1}(N) - \epsilon_N(N)] + [\epsilon_{N+1}(N+1) - \epsilon_{N+1}(N)] \\ &= \epsilon_{\rm gap}^{\rm KS} + \Delta_{\rm xc} \end{aligned}$$



- **KS HOMO-LUMO Gap ≠ $E_{\rm gap}$ even with exact $E_{\rm xc}$**
- But for all explicit density functionals, e.g. LDA/GGA, $\Delta_{\rm xc}$=0

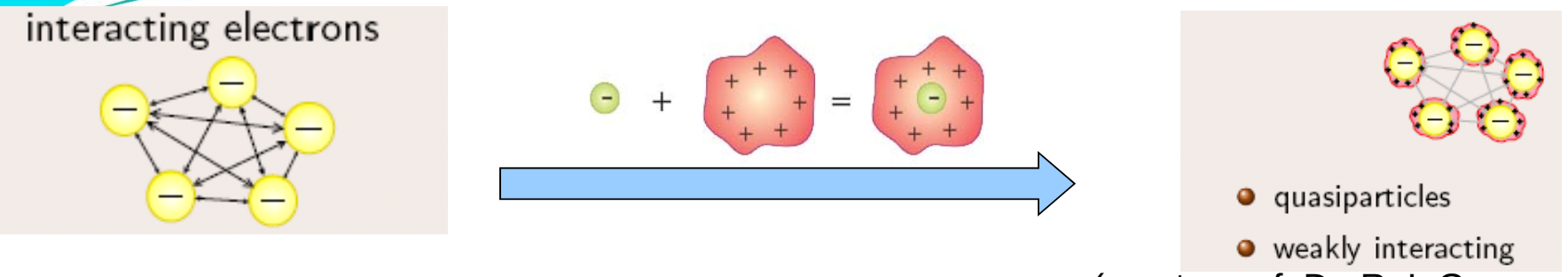
Perdew & Levy (1983); Sham & Schlueter (1983); Godby & Sham (1988)

State-of-the-art approaches to E_g of materials

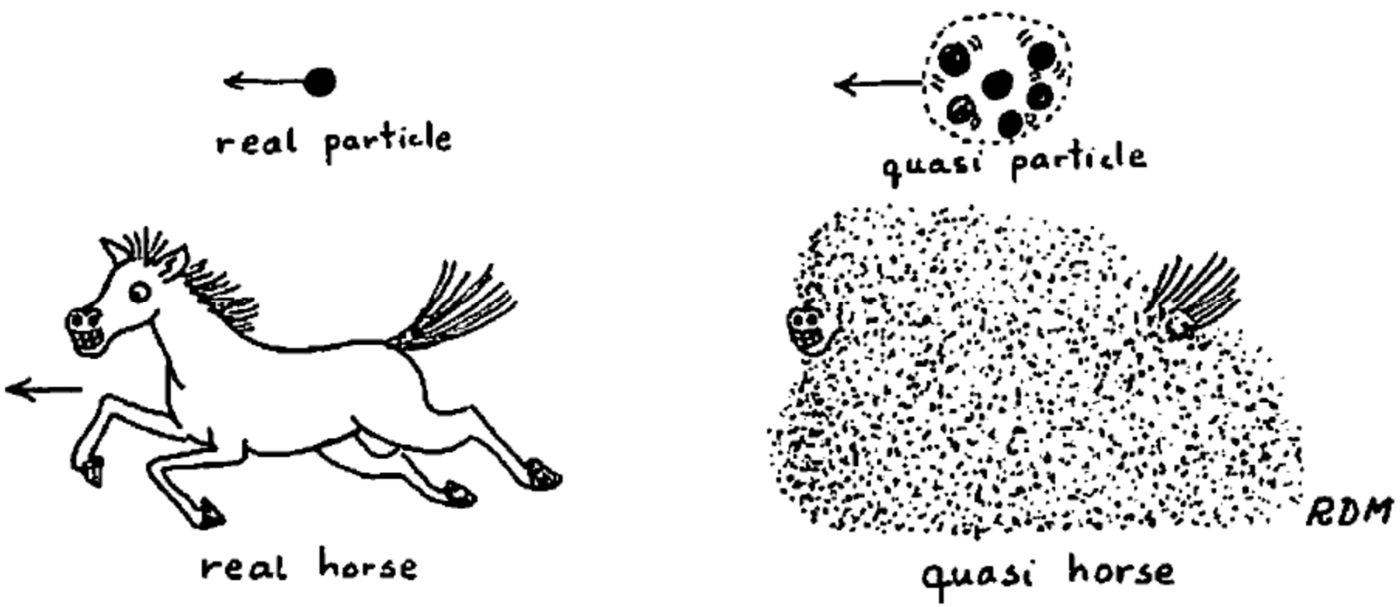
- **Band-gap tuned semi-local functional approaches**
  - modified Becke-Johnson potential (Tran (2009), Jiang (2013))
  - GLLB-SC (Gritsenko(1995), Kuisma(2010))
- **Hybrid functional approaches**
  - Hybrids with fixed parameters (PBE0, HSE, B3LYP)
  - **Hybrids with system-tuned parameters (Shimazaki(2009), Marques(2011), Skone (2014), Z.-H. Cui et al.(2018))**
- ***GW* approaches**
  - **G_0W_0 or GW_0@ LDA/GGA/DFT+U/hybrids (Jiang 2013, 2016, 2018)**
  - (Quasi-particle) self-consistent *GW* (Faleev (2005), Bruneval (2006),……)

蒋鸿，张旻烨，《中国科学:化学》50, 1344 (2020).
M.-Y. Zhang, …,H. Jiang, WIREs CMS, e1476(2020).

Quasi-particle theory



(courtesy of Dr. R. I. Gomez-Abal）



$$\left[-\frac{\nabla^2}{2} + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r}) + \int d^3\mathbf{r}'\Sigma_{\rm xc}(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})$$

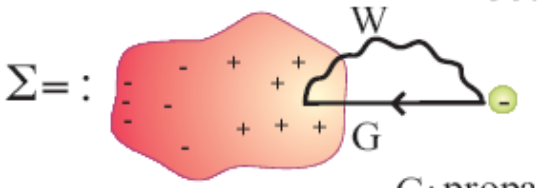
Mattuck, A Guide to Feynman Diagrams in the Many-Body Problem(McGrow-Hill,1976).

Hedin's equations and *GW* Approximation

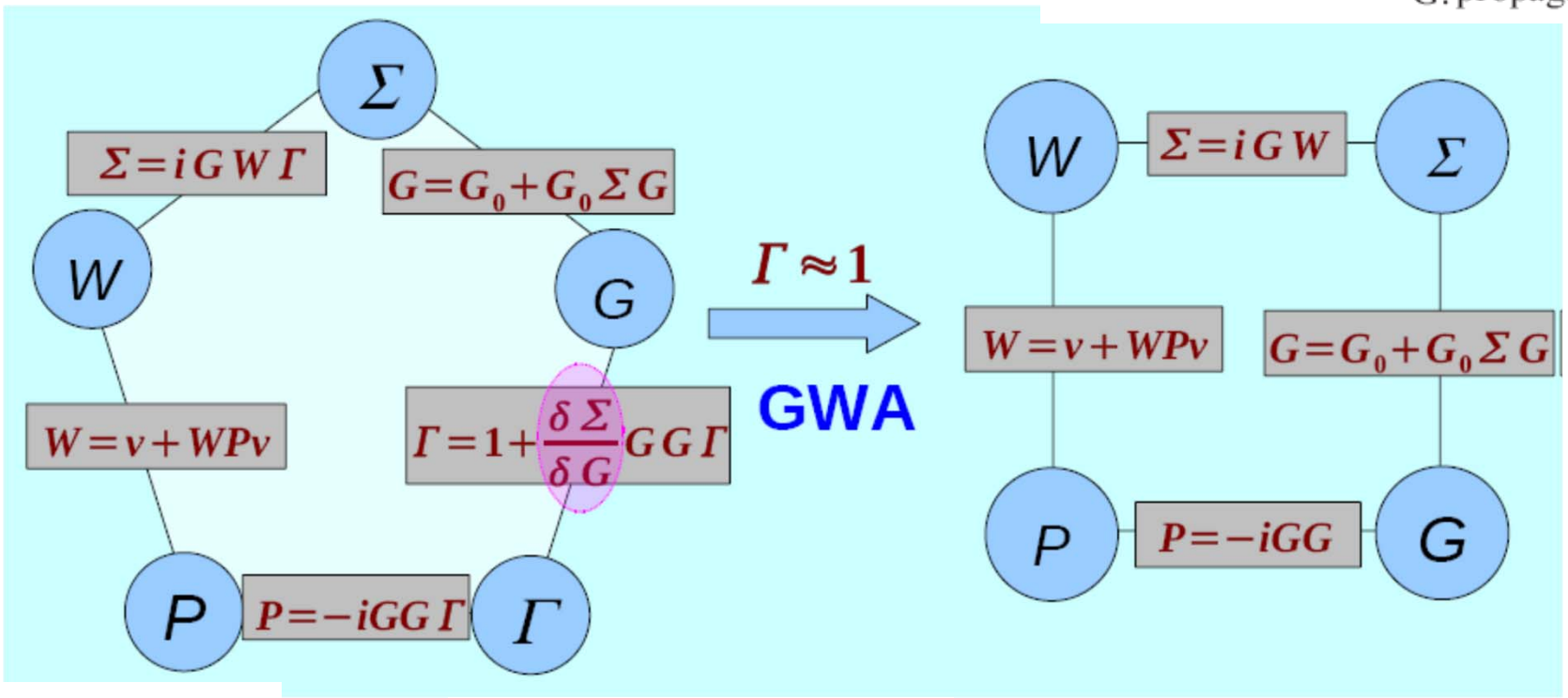
$$W(1,2) \equiv \int d(3)\varepsilon^{-1}(1,3)v(3,2)$$

$$\varepsilon^{-1}(1,2) \equiv \frac{\delta V(1)}{\delta \phi(2)} \qquad V(1) \equiv V_H(1) + \phi(1)$$

W: screened Coulomb



G: propagator



$$P(1,2) \equiv \frac{\delta \rho(1)}{\delta V(2)} \qquad \Gamma(1,2,3) \equiv -\frac{\delta G^{-1}(1,2)}{\delta V(3)}$$

"best *G* best *W*" : G_0W_0 and GW_0@DFA

$$\left[-\frac{\nabla^2}{2}+V_{\rm ext}(\mathbf{r})+V_{\rm H}(\mathbf{r})+V_{\rm xc}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r})=\epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

$$G_0(\mathbf{x},\mathbf{x}';\omega)=\sum_n\frac{\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')}{\omega-\epsilon_n}$$

$$W_0(\mathbf{x},\mathbf{x}';\omega)=\int d\mathbf{x}''\varepsilon^{-1}(\mathbf{x},\mathbf{x}'';\omega)v(\mathbf{r}''-\mathbf{r}')$$

$$\varepsilon(\mathbf{x},\mathbf{x}';\omega)=1-\int d\mathbf{x}''v(\mathbf{r},\mathbf{r}'')P_0(\mathbf{x}'',\mathbf{x}';\omega)$$

$$P_0(\mathbf{x},\mathbf{x}';\omega)=-\frac{i}{2\pi}\int G_0(\mathbf{x},\mathbf{x}';\omega+\omega')G_0(\mathbf{x}',\mathbf{x};\omega')d\omega'$$

$$\Sigma_{\rm xc}(\mathbf{r},\mathbf{r}';\omega)=\frac{i}{2\pi}\int G_0(\mathbf{r},\mathbf{r}';\omega'+\omega)W_0(\mathbf{r}',\mathbf{r};\omega')e^{i\eta\omega'}d\omega'$$

$$\begin{aligned}\mathcal{E}_n&=\epsilon_n+Z_n(\epsilon_n)\Re\langle\psi_n|\Sigma(\epsilon_n)-V_{\rm xc}|\psi_n\rangle\\&\equiv\epsilon_n+Z_n(\epsilon_n)\delta\Sigma_n(\epsilon_n)\end{aligned}$$

$$Z_n(E)=\left[1-\left(\frac{\partial}{\partial\omega}\langle\psi_n|\Sigma(\omega)|\psi_n\rangle\right)_{\omega=E}\right]^{-1}$$

GW_0@DFA

Hybertsen and Louie(1985); Godby, Schlüter and Sham (1986)

$$\Sigma_{\rm xc}(\mathbf{r},\mathbf{r}';\omega)=\frac{i}{2\pi}\int G(\mathbf{r},\mathbf{r}';\omega'+\omega)W_0(\mathbf{r}',\mathbf{r};\omega')e^{i\eta\omega'}d\omega'$$

$$G(\mathbf{r},\mathbf{r}';\omega)=\sum_n\frac{\psi_n(\mathbf{r})\psi_n(\mathbf{r}')}{\omega-\mathcal{E}_n}$$

Implementation of *GW*: main ingredients

Polarization function

$$P_0(\mathbf{x},\mathbf{x}';\omega) = -\frac{i}{2\pi}\int G_0(\mathbf{x},\mathbf{x}';\omega+\omega')G_0(\mathbf{x}',\mathbf{x};\omega')d\omega'$$

$$= \sum_{n,m} f_n(1-f_m)\psi_n(\mathbf{x})\psi_m^*(\mathbf{x})\psi_n^*(\mathbf{x}')\psi_m(\mathbf{x}')\left\{\frac{1}{\omega-\varepsilon_m+\varepsilon_n+i\eta}-\frac{1}{\omega+\varepsilon_m-\varepsilon_n-i\eta}\right\}$$

$$\equiv \sum_{n,m} F_{nm}(\omega)\Phi_{nm}(\mathbf{x})\Phi_{nm}^*(\mathbf{x}')$$

$$W_0(\mathbf{x},\mathbf{x}';\omega) = \int d\mathbf{x}''\varepsilon^{-1}(\mathbf{x},\mathbf{x}'';\omega)v(\mathbf{r}''-\mathbf{r}')$$

$$\varepsilon(\mathbf{x},\mathbf{x}';\omega) = 1-\int d\mathbf{x}''v(\mathbf{r},\mathbf{r}'')P_0(\mathbf{x}'',\mathbf{x}';\omega)$$

Self-energy

$$\langle\psi_m|\Sigma_{\mathrm{xc}}(\omega)|\psi_n\rangle = \sum_k \frac{i}{2\pi}\int d\omega' \frac{\langle\psi_m\psi_k|W_0(\omega)|\psi_k\psi_n\rangle}{\omega'+\omega-\tilde{\varepsilon}_k}$$

$$\tilde{\varepsilon}_k = \varepsilon_k + i\eta\,\mathrm{sgn}(\mu-\varepsilon_k)$$

$$\langle\psi_i\psi_j|W_0(\omega)|\psi_k\psi_l\rangle = \int\int \psi_i^*(\mathbf{r}')\psi_j^*(\mathbf{r}')W_0(\mathbf{r},\mathbf{r}';\omega)\psi_k(\mathbf{r})\psi_l(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

Key ingredients:

- How to expand the products of two orbitals ➔ the product basis
- How to treat frequency dependency

Matrix representation

$$\psi_{n\mathbf{k}}(\mathbf{r})\,\psi^{*}_{m\mathbf{k}-\mathbf{q}}(\mathbf{r}) = \sum_{i} M^{i}_{nm}(\mathbf{k},\mathbf{q})\,\chi^{\mathbf{q}}_{i}(\mathbf{r})$$

Product basis/density fitting/ Resolution of identity

$$O(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{q}}^{\mathrm{BZ}} \sum_{i,j} O_{ij}(\mathbf{q})\,\chi^{\mathbf{q}}_{i}(\mathbf{r})\left[\chi^{\mathbf{q}}_{j}(\mathbf{r}')\right]^{*}$$

$$\boldsymbol{O} = \boldsymbol{v},\ \boldsymbol{P},\ \boldsymbol{\varepsilon},\ \boldsymbol{W}^{c}\ (\equiv \boldsymbol{W} - \boldsymbol{v})$$

$$\Sigma^{\mathrm{X}}_{n\mathbf{k}} = -\frac{1}{N_c} \sum_{\mathbf{q}}^{BZ} \sum_{i,j} v_{ij}(\mathbf{q}) \sum_{m}^{\mathrm{occ}} \left[M^{i}_{nm}(\mathbf{k},\mathbf{q})\right]^{*} M^{j}_{nm}(\mathbf{k},\mathbf{q})$$

$$X_{nm}(\mathbf{k},\mathbf{q};\omega')$$

$$\Sigma^{\mathrm{c}}_{n\mathbf{k}}(\omega) = \frac{1}{N_c} \sum_{\mathbf{q}}^{\mathrm{BZ}} \sum_{m} \sum_{i,j} \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' \frac{\left[M^{i}_{nm}(\mathbf{k},\mathbf{q})\right]^{*} W^{\mathrm{c}}_{ij}(\mathbf{q},\omega') M^{j}_{nm}(\mathbf{k},\mathbf{q})}{\omega + \omega' - \tilde{\varepsilon}_{m\mathbf{k}-\mathbf{q}}}$$

Implementation: the product basis (1)

◆ Planewaves

$$\chi_i^{\mathbf{q}}(\mathbf{r}) \rightarrow \chi_{\mathbf{G}}^{\mathbf{q}}(\mathbf{r}) \equiv \frac{1}{\sqrt{V}} \exp\left[i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}\right]$$

$$\psi_{n\mathbf{k}} = \sum_{\mathbf{G}} C_{n\mathbf{k};\mathbf{G}} \chi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) \qquad M_{nm}^{\mathbf{G}}(\mathbf{k},\mathbf{q}) = V^{-1/2} \sum_{\mathbf{G}'} C_{n\mathbf{k};\mathbf{G}'} C_{m\mathbf{k}-\mathbf{q};\mathbf{G}'-\mathbf{G}}^{*}$$

$$v_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \frac{1}{|\mathbf{q}+\mathbf{G}|}\delta_{\mathbf{G},\mathbf{G}'}. \qquad \varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}'} - \frac{4\pi}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|} P_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega).$$

Codes: abinit, yambo, BerkeleyGW, SaX, vasp

◆ Atomic-like orbitals

$$\chi_{\alpha}^{\mathbf{q}}(\mathbf{r}) = \frac{1}{N_c^{1/2}} \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{t}_{\alpha})} \phi_{\alpha}(\mathbf{r}-\mathbf{R}-\mathbf{t}_{\alpha})$$

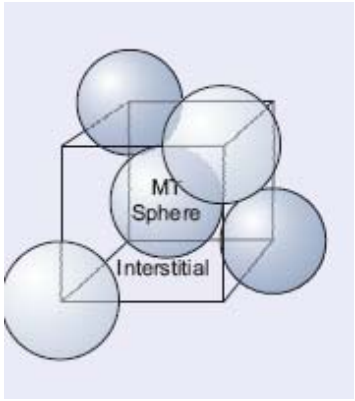
$$X(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{q}} \sum_{\alpha,\beta} \chi_{\alpha}^{\mathbf{q}}(\mathbf{r}) \left\langle \mathbf{X} \right\rangle_{\alpha\beta}(\mathbf{q}) \chi_{\beta}^{\mathbf{q}*}(\mathbf{r}). \qquad \left\langle \mathbf{X} \right\rangle(\mathbf{q}) = \mathbf{S}^{-1}(\mathbf{q}) \left[\mathbf{X} \right](\mathbf{q}) \mathbf{S}_{\mathbf{q}}^{-1}(\mathbf{q})$$

$$S_{\alpha\beta}(\mathbf{q}) \equiv \int_V d\mathbf{r} \left[\chi_{\alpha}^{\mathbf{q}}(\mathbf{r}) \right]^{*} \chi_{\beta}^{\mathbf{q}}(\mathbf{r}). \qquad \left[\mathbf{X} \right]_{\alpha\beta}(\mathbf{q}) \equiv \int_V d\mathbf{r} \int_V d\mathbf{r}' \chi_{\alpha}^{*}(\mathbf{r}) X(\mathbf{r},\mathbf{r}') \chi_{\beta}^{\mathbf{q}}(\mathbf{r}').$$

Codes: FHI-aims, FIESTA

Implementation: the product basis (2)

◆ Mixed basis



(L)APW+lo(+LO) basis

$$\phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{\zeta lm} A_{\alpha\zeta lm}(\mathbf{k}+\mathbf{G}) u_{\alpha\zeta l}(r^{\alpha}) Y_{lm}(\hat{r}^{\alpha}) & r^{\alpha} < R_{\mathrm{MT}}^{\alpha} \\ \dfrac{\theta_{\mathbf{G}}^{\mathrm{LO}}}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & \mathbf{r} \in I. \end{cases}$$

$$\{u_{\alpha\zeta l}(r) u_{\alpha\zeta' l'}(r)\} \xrightarrow[|l-l'|\le L\le l+l']{l,l' \le l_{\max}^{\mathrm{MB}}} \{v_{NL}(r)\}$$

$$\chi_i^{\mathbf{q}}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{R}\alpha} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{r}_{\alpha})} v_{NL}(r^{\alpha}) Y_{LM}(\hat{\mathbf{r}}^{\alpha}), & \mathbf{r} \in \text{MT spheres} \\ \dfrac{1}{\sqrt{V}} \sum_{|\mathbf{G}|<G_{\max}^{\mathrm{MB}}} S_{i,\mathbf{G}} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}, & \mathbf{r} \in \text{Interstitial} \end{cases}$$

Codes: GAP, SPEX, EXCITING

Implementation: frequency dependence

- Static approximations
  - Coulomb hole-screened exchange (COHSEX)

$$\mathrm{Re}\Sigma(\mathbf{r},\mathbf{r}';\omega) = -\sum_{n\mathbf{k}}^{occ}\psi_{n\mathbf{k}}(\mathbf{r})\psi^{*}_{n\mathbf{k}'}(\mathbf{r}')\Re W(\mathbf{r}',\mathbf{r};\omega-\varepsilon_{n\mathbf{k}}) - \sum_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})\psi^{*}_{n\mathbf{k}}(\mathbf{r}')\frac{1}{\pi}\mathcal{P}\int_0^{\infty}d\omega'\frac{\Im W_c(\mathbf{r}',\mathbf{r};\omega')}{\omega-\varepsilon_{n\mathbf{k}}-\omega'}$$

$$\approx -\sum_{n\mathbf{k}}^{occ}\psi_{n\mathbf{k}}(\mathbf{r})\psi^{*}_{n\mathbf{k}'}(\mathbf{r}')\Re W(\mathbf{r}',\mathbf{r};0) + \frac{1}{2}\delta(\mathbf{r}'-\mathbf{r})W_c(\mathbf{r},\mathbf{r}';0)$$

$$\equiv \Sigma^{\mathrm{SEX}}(\mathbf{r},\mathbf{r}') + \Sigma^{\mathrm{COH}}(\mathbf{r},\mathbf{r}')$$

- Generalized plasmon pole (GPP) model
- Full frequency treatment
  - Imaginary frequency + analytic continuation
  - real frequency Hilbert transform
  - Contour deformation

H. Jiang, *Front. Chem. China* 6(4): 253–268 (2011)

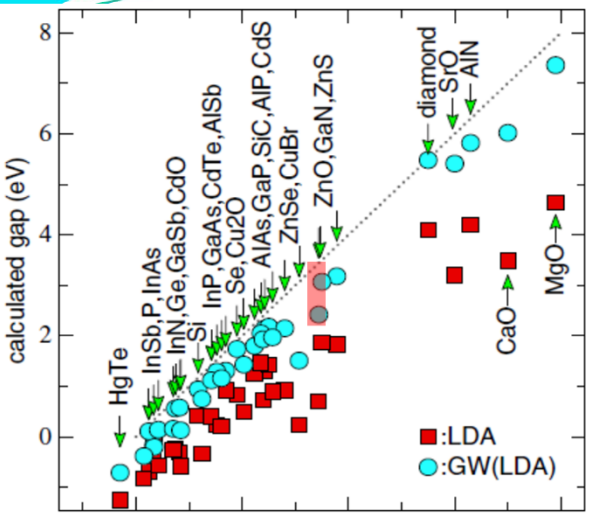
Main technical parameters in *GW* implementation

- Parameters for KS DFT:
  - Core-valence interactions:

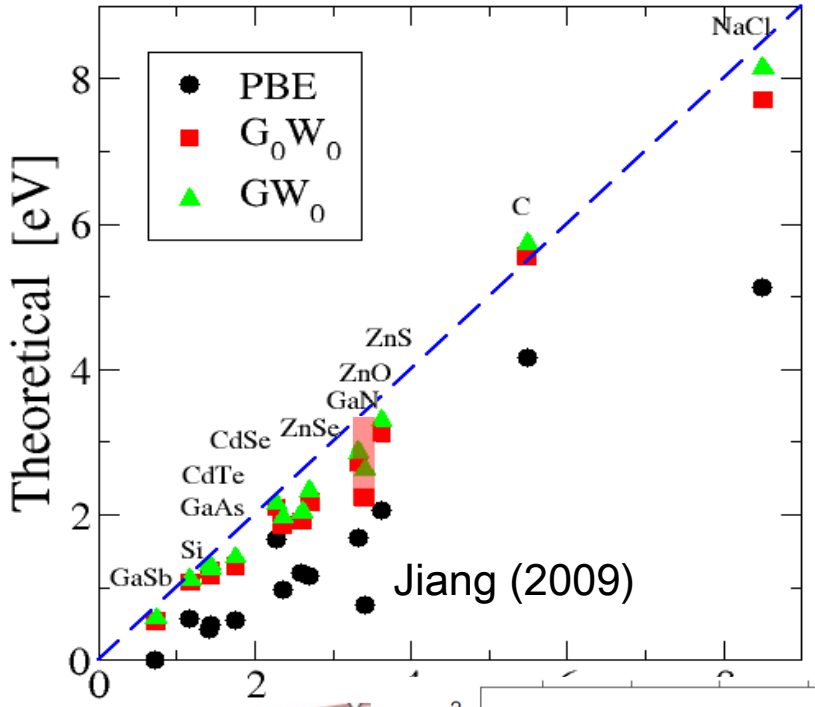
    pseudopotentials/PAW/LAPW?
  - basis for Kohn-Sham orbitals
- Quality of product basis
- Accuracy and completeness of unoccupied states considered (P & Σ_c)
- The k/q integration in the Brillouin zone
- The frequency treatment and related parameters

H. Jiang, *Front. Chem. China* 6(4): 253–268 (2011)

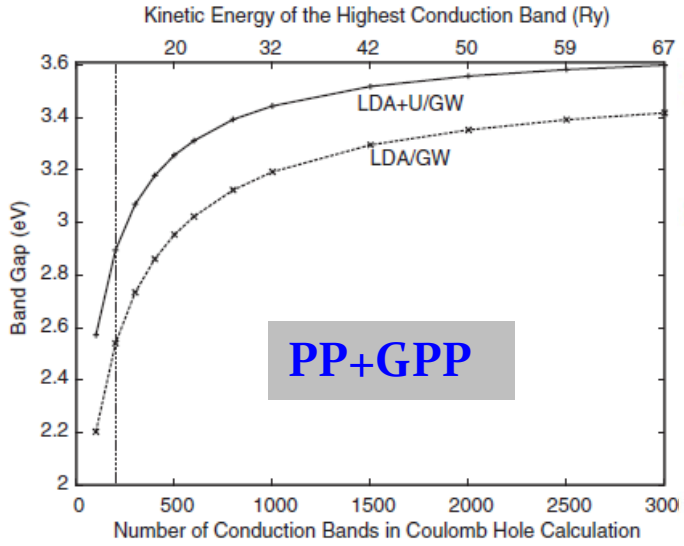
GW: "the ZnO puzzle"



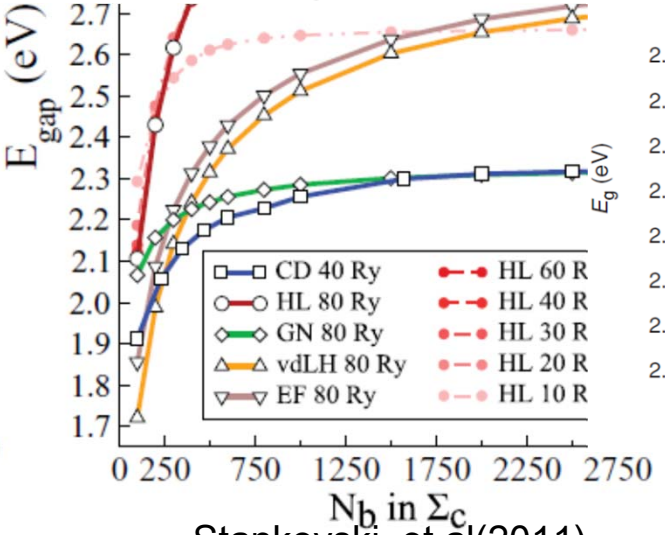
M. van Schilfgaarde et al. (2006)



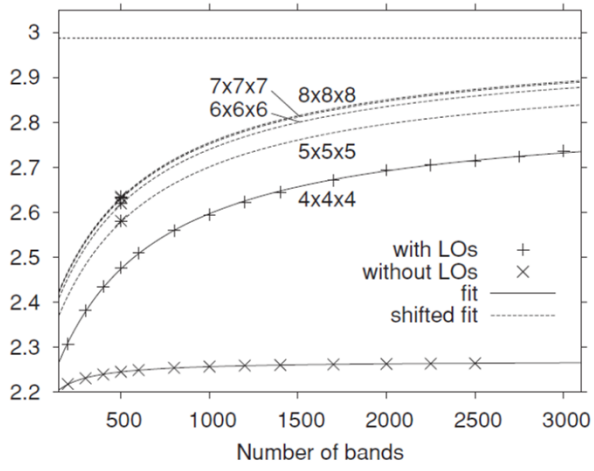
Jiang (2009)



Shih, et al (2010).

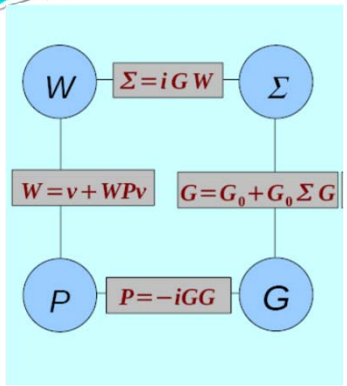


Stankovski, et al(2011).



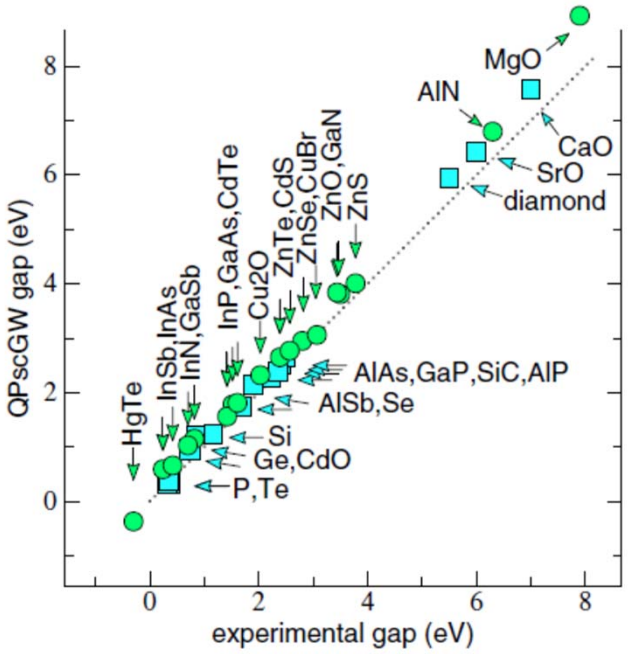
Friedrich et al (2011)

(Quasi-particle) self-consistent *GW* (QSGW)

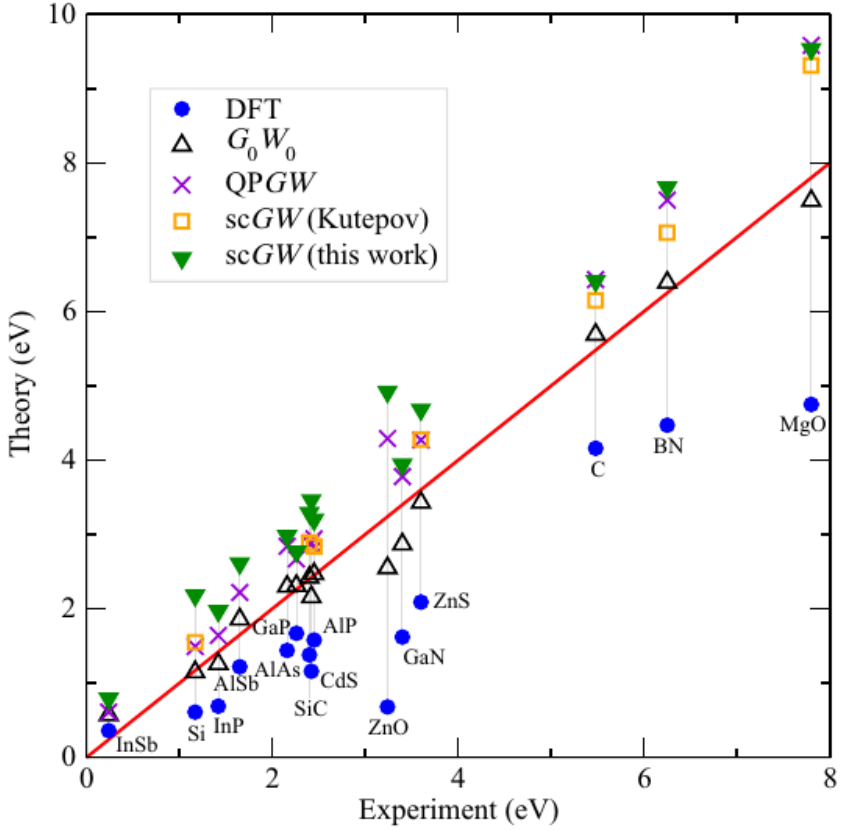


$$\left[-\frac{1}{2}\nabla^2+\boldsymbol{V}_{\text{ext}}(\mathbf{r})+\boldsymbol{V}_{\text{H}}(\mathbf{r})\right]\Psi_n(\mathbf{r})+\int d\mathbf{r}'\Sigma_{\text{xc}}(\mathbf{r},\mathbf{r}';\boldsymbol{E}_n)\Psi_n(\mathbf{r})=\boldsymbol{E}_n\Psi_n(\mathbf{r})$$

$$\hat{H}(\mathcal{E}_n) \;\rightleftharpoons\; \hat{H}_s \qquad \hat{H}_s \rightarrow \overline{H}^{(i)}_{\mu\nu} \equiv \langle\psi_\mu|\,\hat{H}_0\,|\psi_\nu\rangle + \frac{1}{2}\left[\overline{\Sigma}_{\mu\nu}(\epsilon_\mu)+\overline{\Sigma}_{\mu\nu}(\epsilon_\nu)\right]$$



M. van Schilfgaarde et al. PRL 96, 226402 (2006)

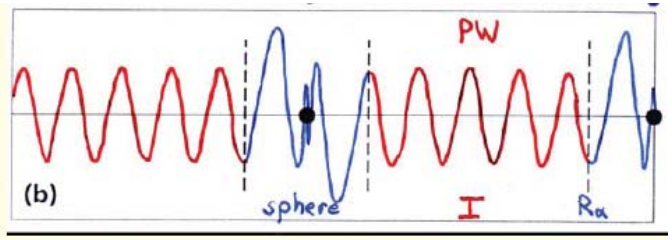


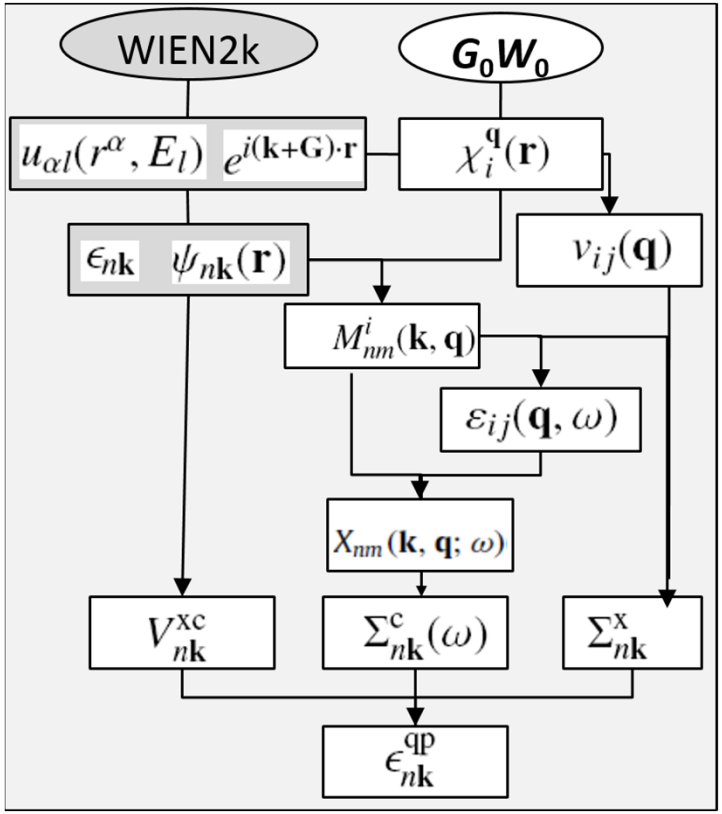
Grumet, et al. Phys. Rev. B 98, 155143 (2018)

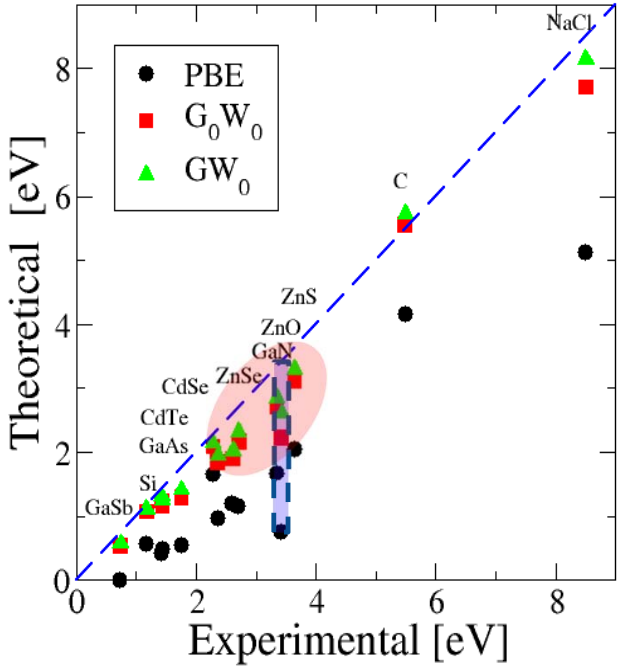
Implementation: *GW* with Augmented Planewaves

GAP (*GW* with Augmented Planewaves)

- Based on LAPW (no pseudopotentials !)
- Interfaced with WIEN2k (P. Blaha et al. (2001))



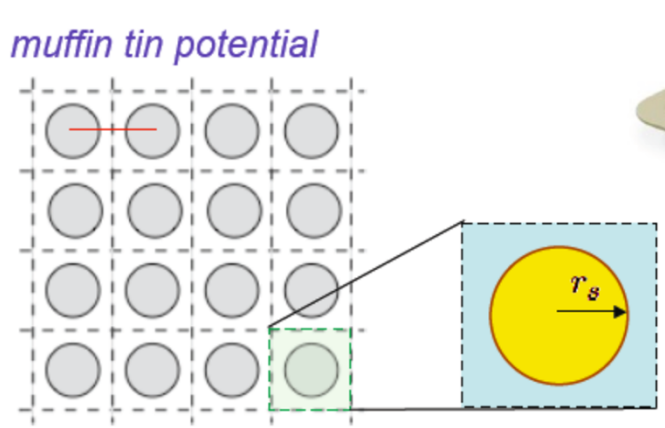




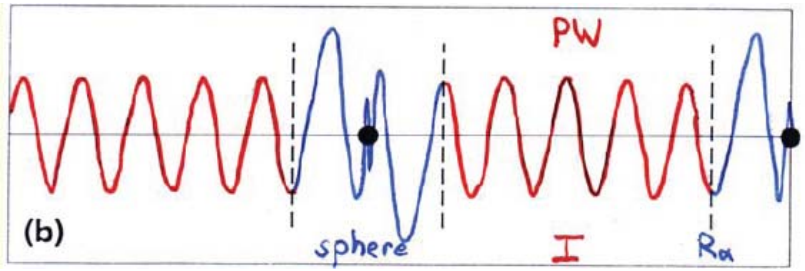
H. Jiang, *Acta Phys.-Chim. Sin.*,**26**, 1017(2010).

H. Jiang, R. I. Gomez-Abal, **X. Li**, ..., M. Scheffler, *Computer Phys. Commun.*, **184**, 348 (2013).

LAPW + LO basis



Wigner Seitz cell



Linearized Augmented Plane Waves (LAPW)

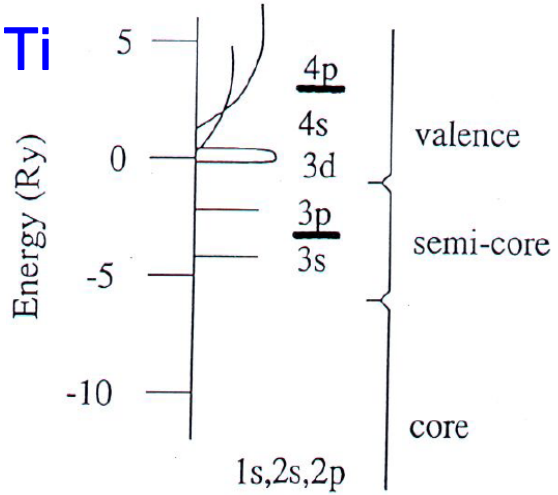
$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \begin{cases} \Omega^{-1/2} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & (\mathbf{r}\in I) \\ \sum_{l=0}^{l_{\max}} \sum_{m} [A_{lm}^{\alpha}(\mathbf{k}+\mathbf{G}) u_l(r^{\alpha};E_l) + B_{lm}^{\alpha}(\mathbf{k}+\mathbf{G}) \dot{u}_l(r^{\alpha};E_l)] Y_{lm}(\hat{\mathbf{r}}^{\alpha}) & (\mathbf{r}\in S_{\alpha}) \end{cases}$$

O. K. Anderson, Phys. Rev. B 12, 3060 (1975).

Local Orbital (LO)

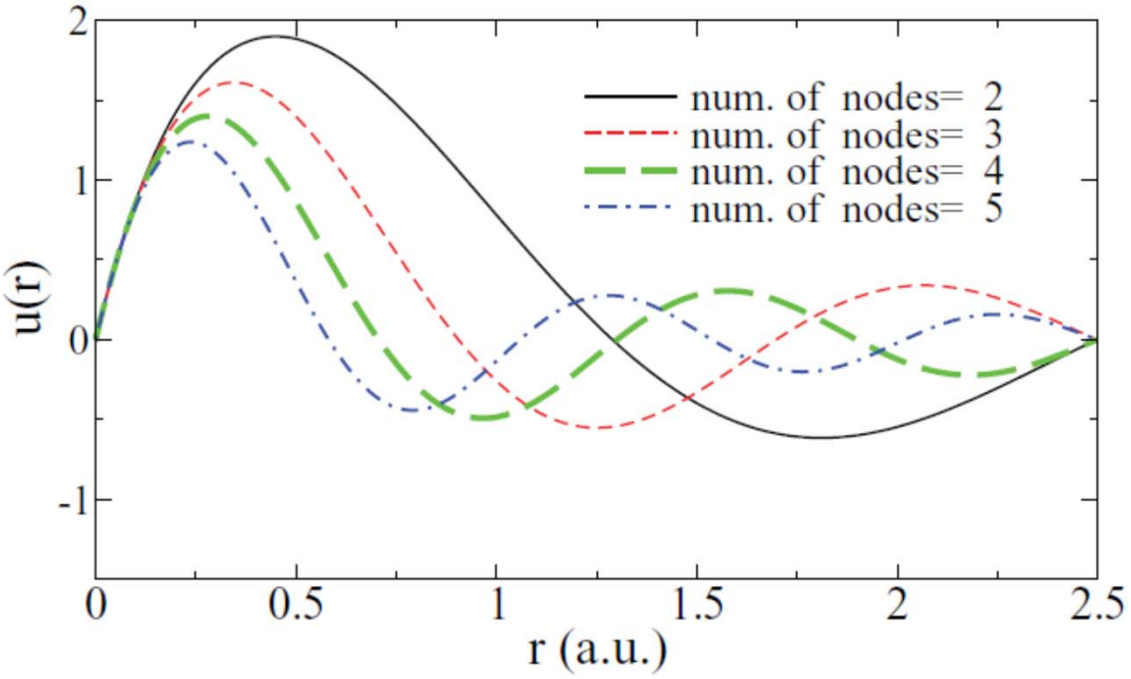
$$\phi_{\mathrm{LO}}(\mathbf{r}) = \begin{cases} 0 & (\mathbf{r}\in I) \\ [A_{lm}^{\alpha} u_l(r^{\alpha};E_l) + B_{lm}^{\alpha} \dot{u}_l(r^{\alpha};E_l) + C_{lm}^{\alpha} u_l(r^{\alpha};E_l^{(2)})] Y_{lm}(\hat{\mathbf{r}}^{\alpha}) & (\mathbf{r}\in S_{\alpha}) \end{cases}$$

D. Singh, Phys. Rev. B, 43, 6388 (1991)



LAPW with high-energy LOs (LAPW+HLOs)

$$\phi_{\mathrm{LO}}(\mathbf{r}) = \begin{cases} 0 & (\mathbf{r} \in I) \\ [A_{lm}^{\alpha} u_l(r^{\alpha}; E_l) + B_{lm}^{\alpha} \dot{u}_l(r^{\alpha}; E_l) + C_{lm}^{\alpha} u_l(r^{\alpha}; E_l^{(2)})] Y_{lm}(\hat{\mathbf{r}}^{\alpha}) & (\mathbf{r} \in S_{\alpha}) \end{cases}$$



R. Laskowski & P. Blaha, Phys. Rev. B, 85, 035132 (2012)

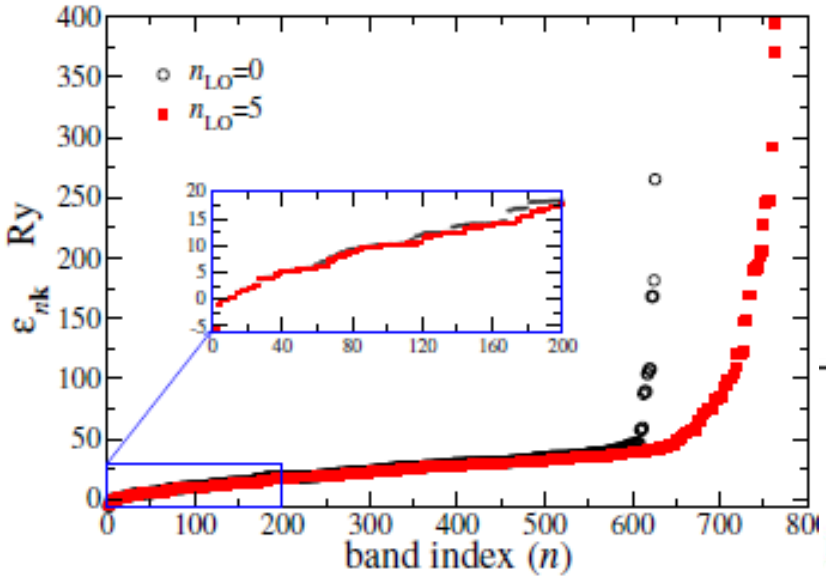
the default:

$$l_{\max}^{(\mathrm{LO})} = \min\left(3, l_{\max}^{(\mathrm{v})} + 1\right)$$

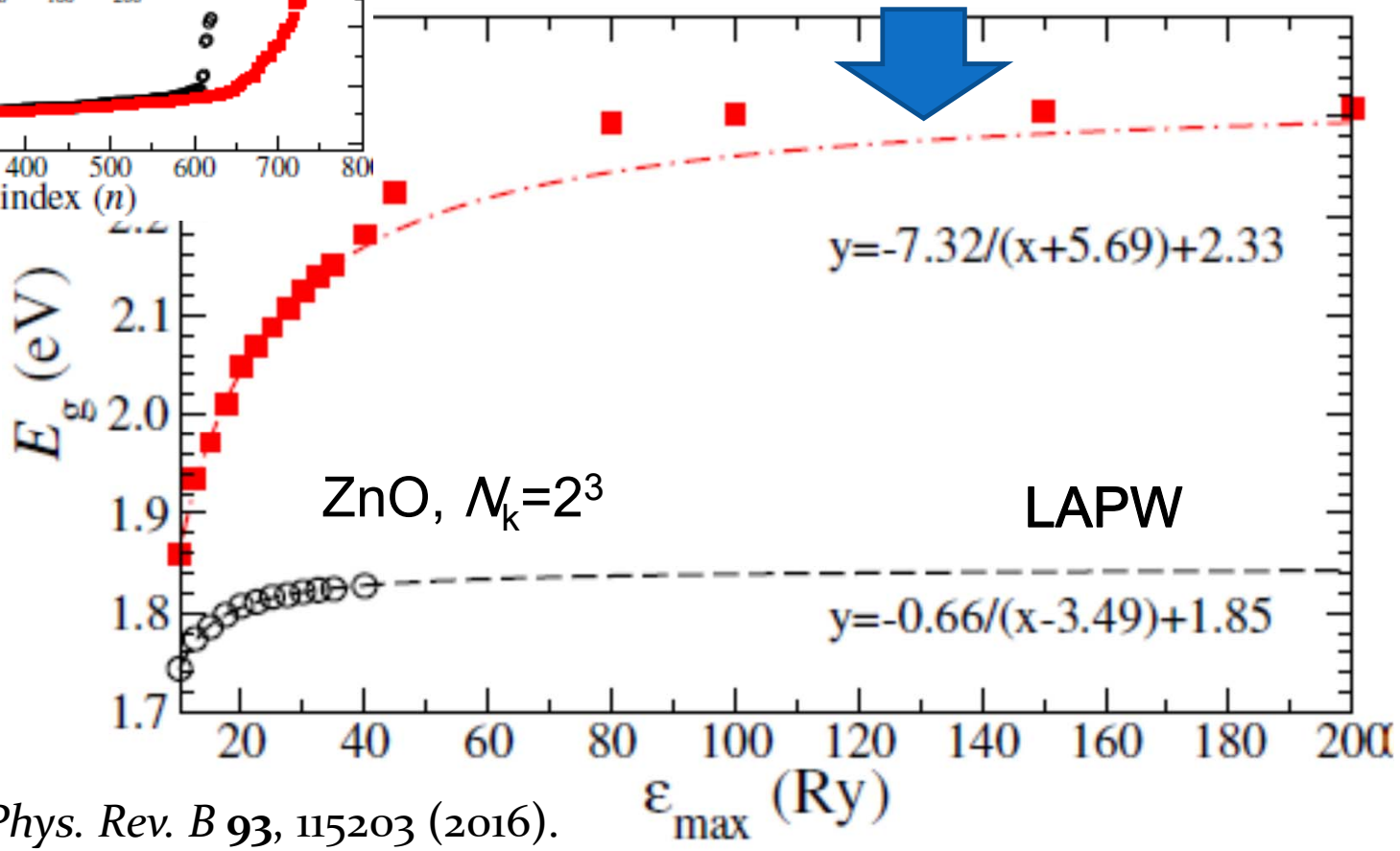
n_{LO} : additional number of radial nodes in highest-energy LO

$l_{\max}^{(\mathrm{LO})}$: maximal l of the angular channels with HLOs

Numerically accurate *GW* with LAPW+HLOs

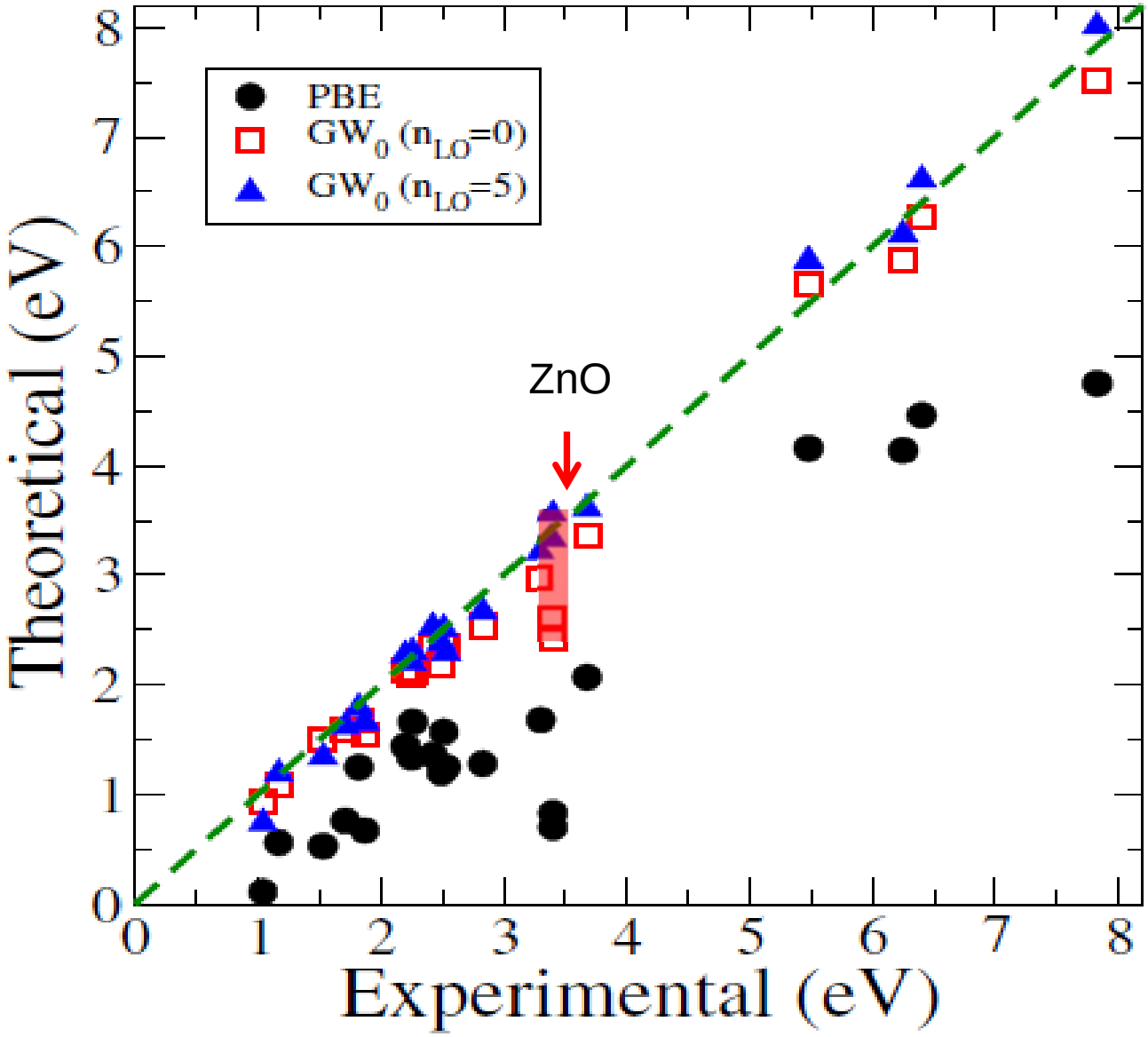


LAPW+HLOs



H. Jiang*, P. Blaha, *Phys. Rev. B* **93**, 115203 (2016).

Numerically accurate *GW* with LAPW+HLOs



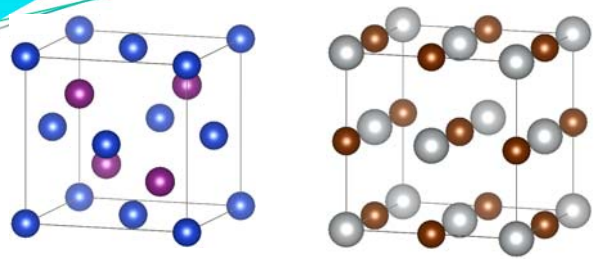
H. Jiang*, P. Blaha, *Phys. Rev. B* **93**, 115203 (2016).

GW based on LAPW+HLOs vs PAW

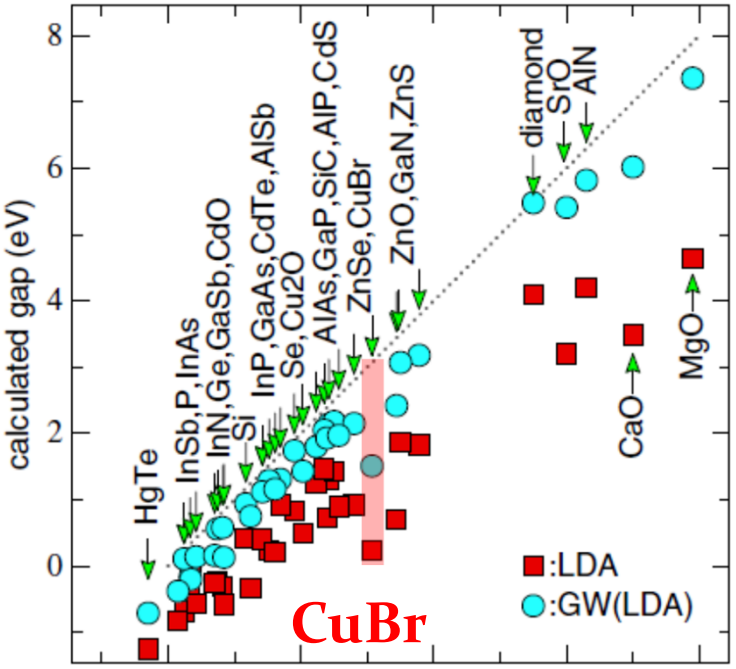
Systems	Expt.	PBE	G_0W_0	GW_0	G_0W_0	GW_0	δE_g	GW_0(NC-PAW)[a]
			$n_{LO}=0$		$n_{LO}=5$			
C	5.48	4.16	5.49	5.66	5.69	5.87	0.21	5.81
Si	1.17	0.56	1.03	1.09	1.12	1.19	0.10	1.21
SiC	2.42	1.36	2.23	2.36	2.38	2.53	0.17	2.60
BN	6.4	4.46	6.04	6.27	6.36	6.61	0.34	6.66
BP	2.4, 2.1	1.34	2.01	2.09	2.11	2.20	0.11	
wz-AlN	6.2-6.3	4.14	5.60	5.88	5.80	6.11	0.23	
AlP	2.51	1.57	2.25	2.36	2.37	2.51	0.15	2.62
AlAs	2.1	1.34(0.10)	1.94	2.03	2.06	2.17	0.14	2.35
AlSb	1.6	1.03(0.22)	1.40	1.45	1.50	1.57	0.12	1.76
GaN	3.30	1.68	2.78	2.96	3.00	3.21	0.25	3.48
GaP	2.26	1.66	2.05	2.12	2.21	2.30	0.18	2.40
GaAs	1.42	0.42(0.11)	1.31	1.39	1.15	1.23	-0.16	1.21
GaSb	0.81	-0.12(0.23)	0.64	0.71	0.47	0.51	-0.20	0.51
ZnO	3.4	0.70	2.05	2.41	2.78	3.32	0.91	
wz-ZnO	3.4	0.83	2.24	2.59	3.01	3.55	0.96	3.40
ZnS	3.68	2.07	3.15	3.35	3.35	3.61	0.26	3.72
ZnSe	2.7	1.15(0.13)	2.23	2.41	2.34	2.54	0.13	2.66
ZnTe	2.26	0.98(0.27)	1.95	2.08	1.89	2.02	-0.06	2.15
wz-CdS	2.49	1.20	2.02	2.18	2.19	2.38	0.20	
wz-CdSe	1.75	0.55(0.12)	1.29	1.42	1.39	1.54	0.12	1.60
CdTe	1.43	0.48(0.28)	1.20	1.30	1.23	1.34	0.04	1.44
LiF	14.20	9.28	12.36	13.98	14.27	15.13	1.15	
MgO	7.83	4.75	7.08	7.52	7.50	8.01	0.49	8.03
MAE		1.54	0.47	0.25	0.24	0.17		
MARE(%)		48	14	9	9	5		

[a] Y. Hinuma et al. Phys. Rev. B 90, 155405 (2014).

The “band gap problem” for CuX/AgX



Zinc-blende(ZB) ： CuX, AgI
Rock-salt (RS)： AgCl, AgBr

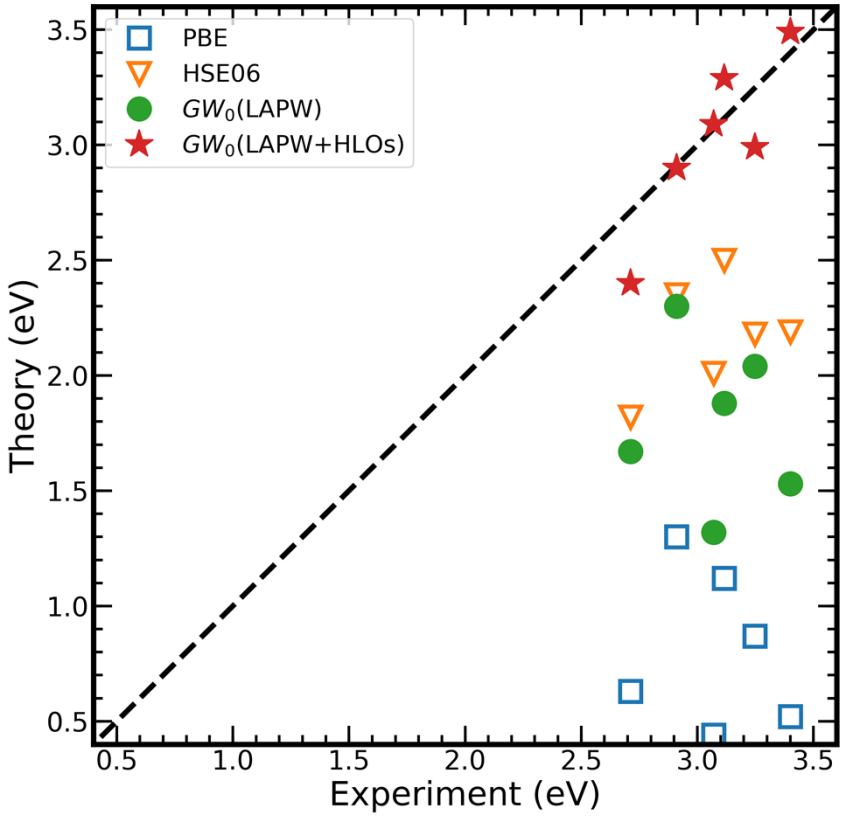


Fundamental band gap of CuBr

PBE	0.5~1 eV
G_0W_0@PBE(PP)[1]	0.64
G_0W_0@LDA(AE)[2]	1.5
G_0W_0@LDA(HL-PPM)[3]	2.38
G_0W_0@LDA+U(HL-PPM) [4]	3.08
QSGW [2]	2.9
Expt. [5]	3.07

[1] M. van Setten, *Phys. Rev. B* **96**, 155207(2017).
[2] M. van Schilfgaarde et al. *Phys. Rev. Lett.* **96**, 226402(2006);
[3] A. Pishtshev, et al *J. Chem. Phys.* **146**, 064706(2017);
[4] W. Gao et al. *Phys. Rev. B* **98**, 045108(2018).
[5] Goldmann, A. *Phys. Status Solidi B* **81**, 9(1977).

Band gaps of CuX&AgX by *GW* with LAPW+HLOs



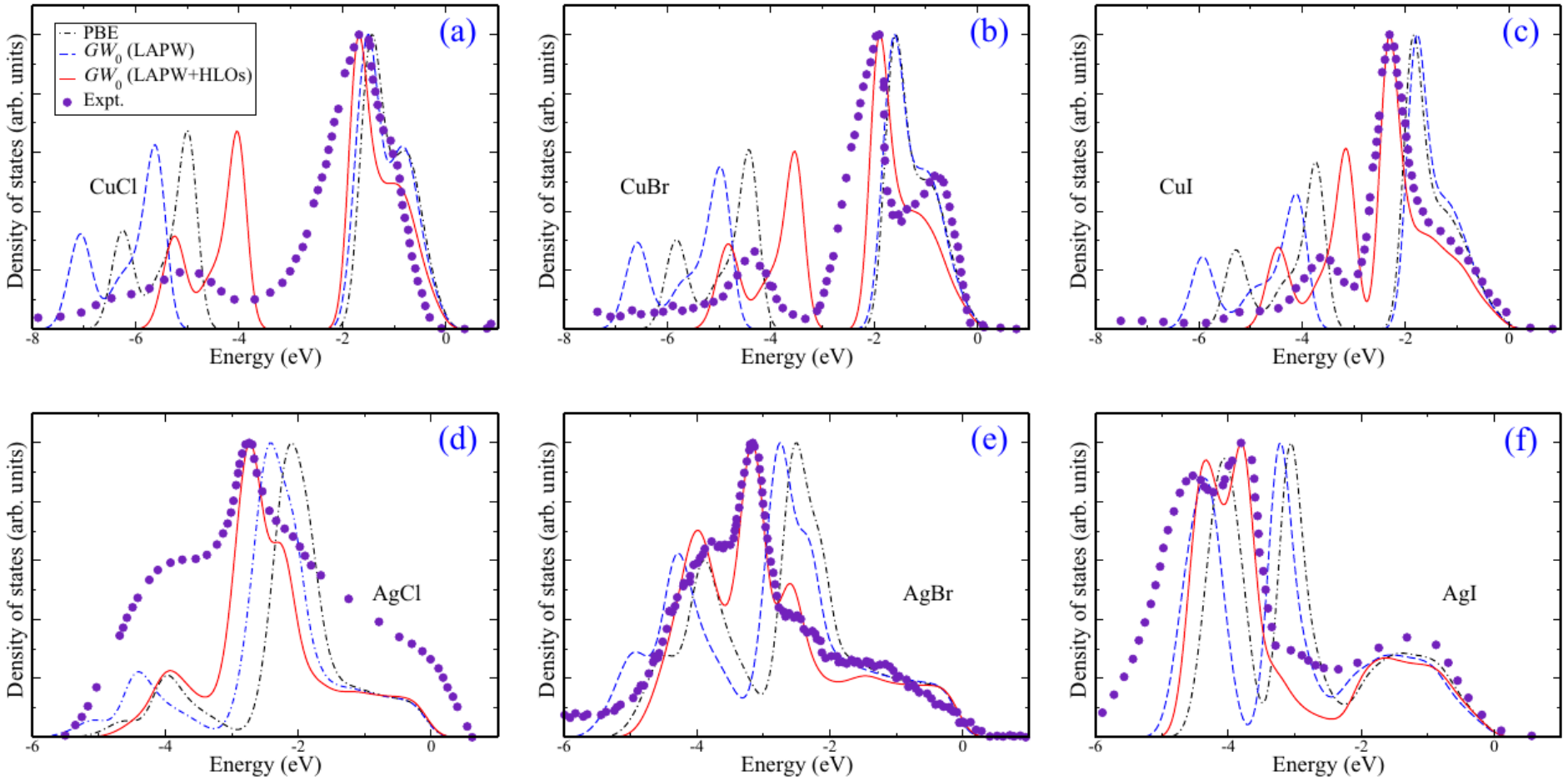
	MAE
PBE	2.36
HSE06	0.99
G_0W_0@PBE(LAPW)	1.55
G_0W_0@PBE(LAPW+HLOs)	**0.61**
GW_0@PBE(LAPW)	1.38
GW_0@PBE(LAPW+HLOs)	**0.18**

Including HLOs increases GW_0 gaps by about **1.2 eV** on average

➔ good agreement with experiment as for typical sp semiconductors

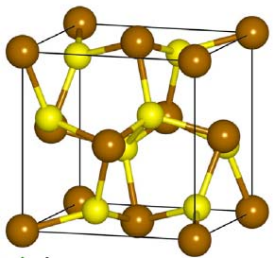
M.-Y. Zhang, H. Jiang*, *Phys. Rev. B.* **100**, 205123(2019)

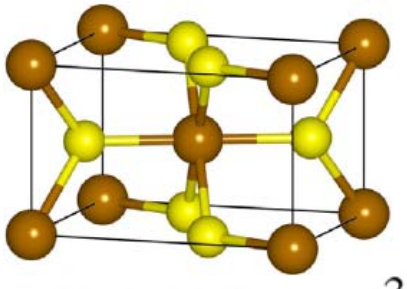
Band gaps of CuX&AgX



M.-Y. Zhang, H. Jiang*, *Phys. Rev. B.* **100**, 205123(2019)

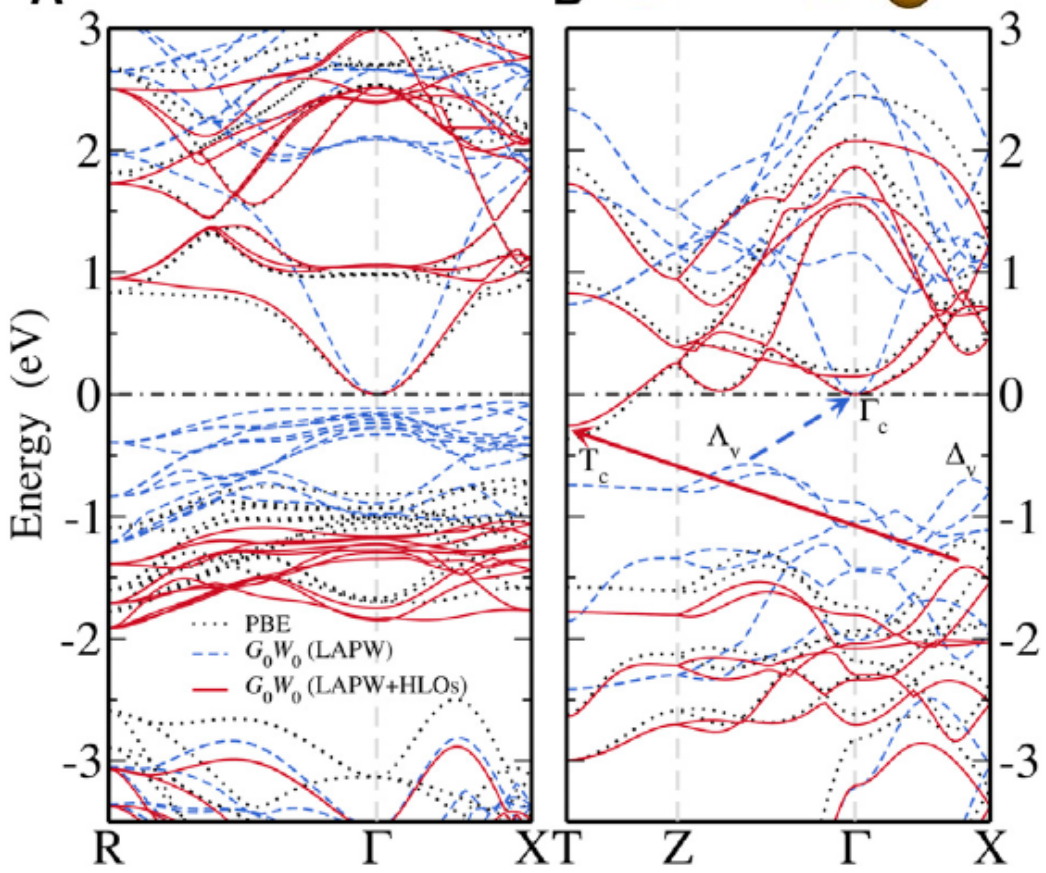
Band gap problem of FeS_2

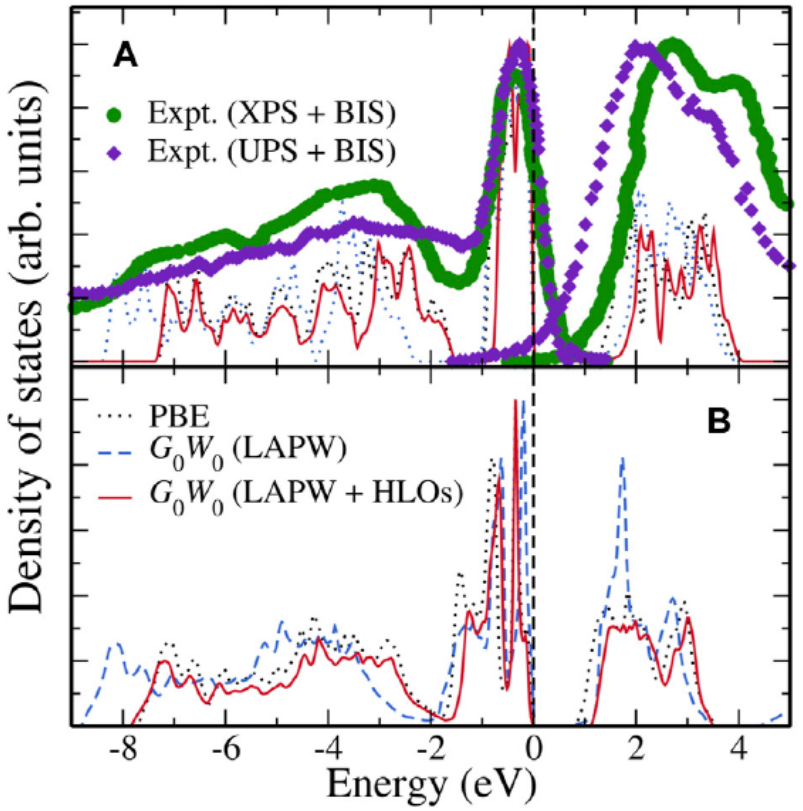




	$\Gamma \to \Gamma$	$X \to \Gamma$	$R \to \Gamma$
PBE	0.66	0.63	0.96
G_0W_0 (w Fe $3s$, $3p$ LOs)	0.28	0.31	0.59
G_0W_0 (o Fe $3s$, $3p$ LOs)	0.61	0.63	0.90

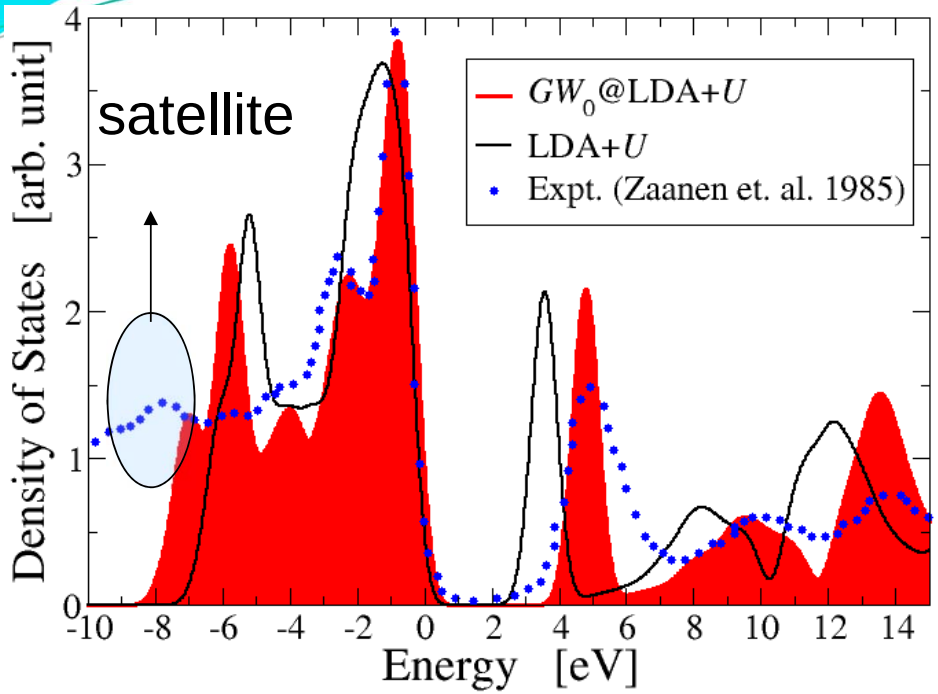
Schena et al. *PRB* **88**, 235203 (2013).

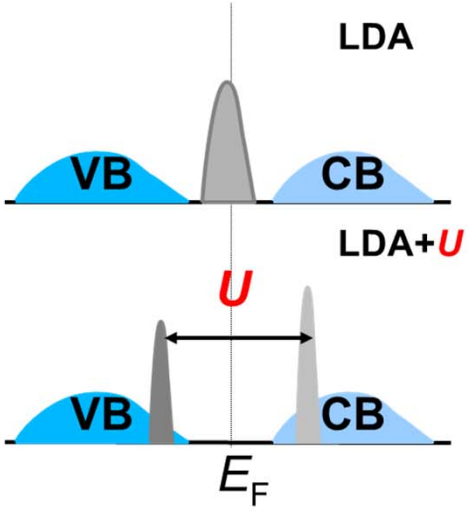


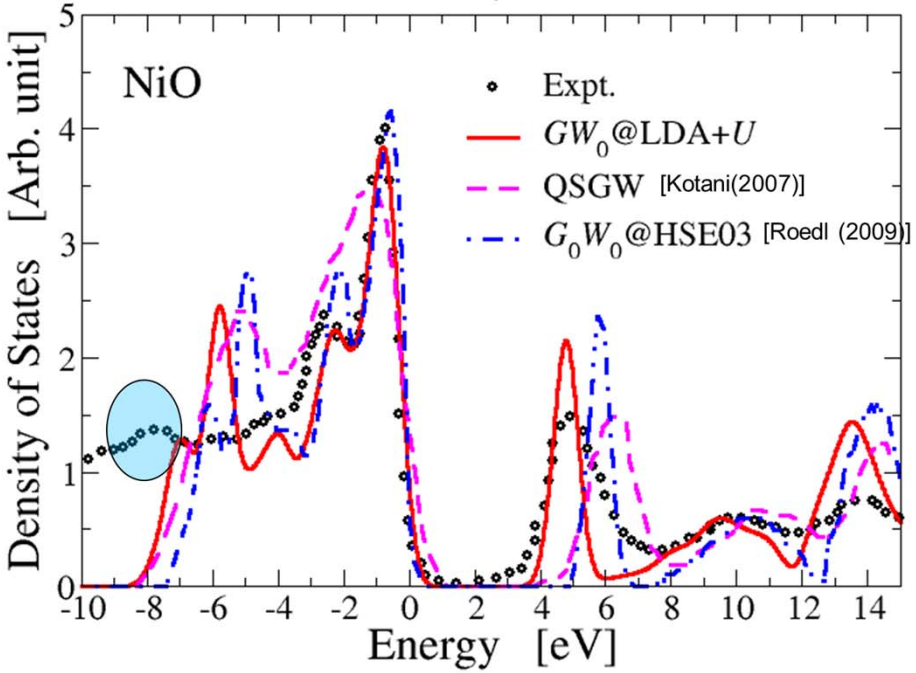


M.-Y. Zhang, H. Jiang*, *Front. Chem.* **9**, 747972 (2021).

GW_0@LDA+U for NiO



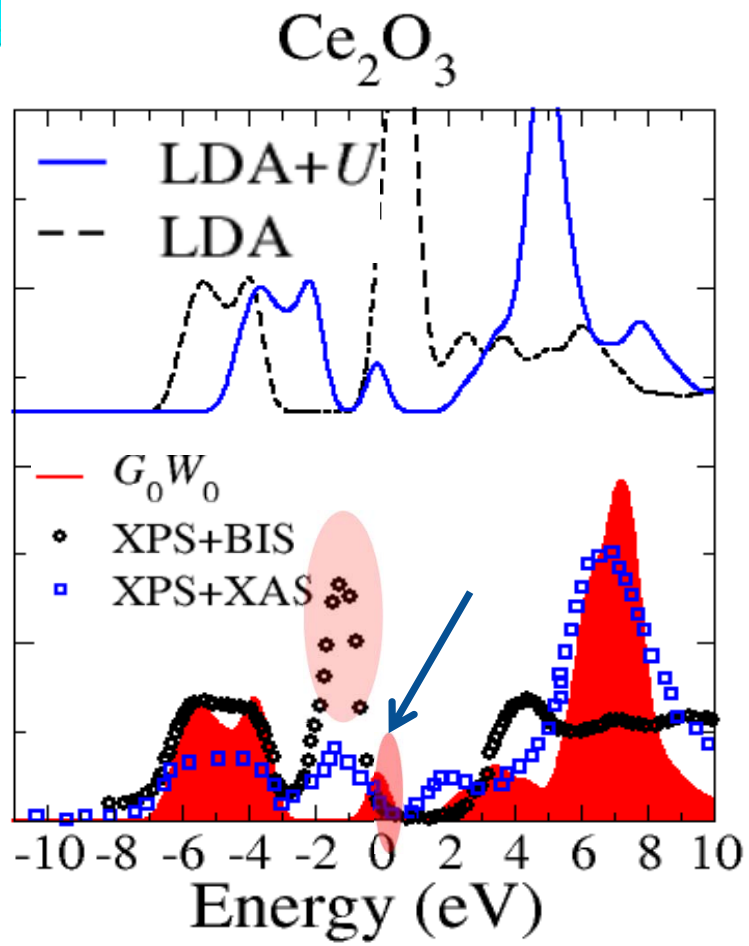


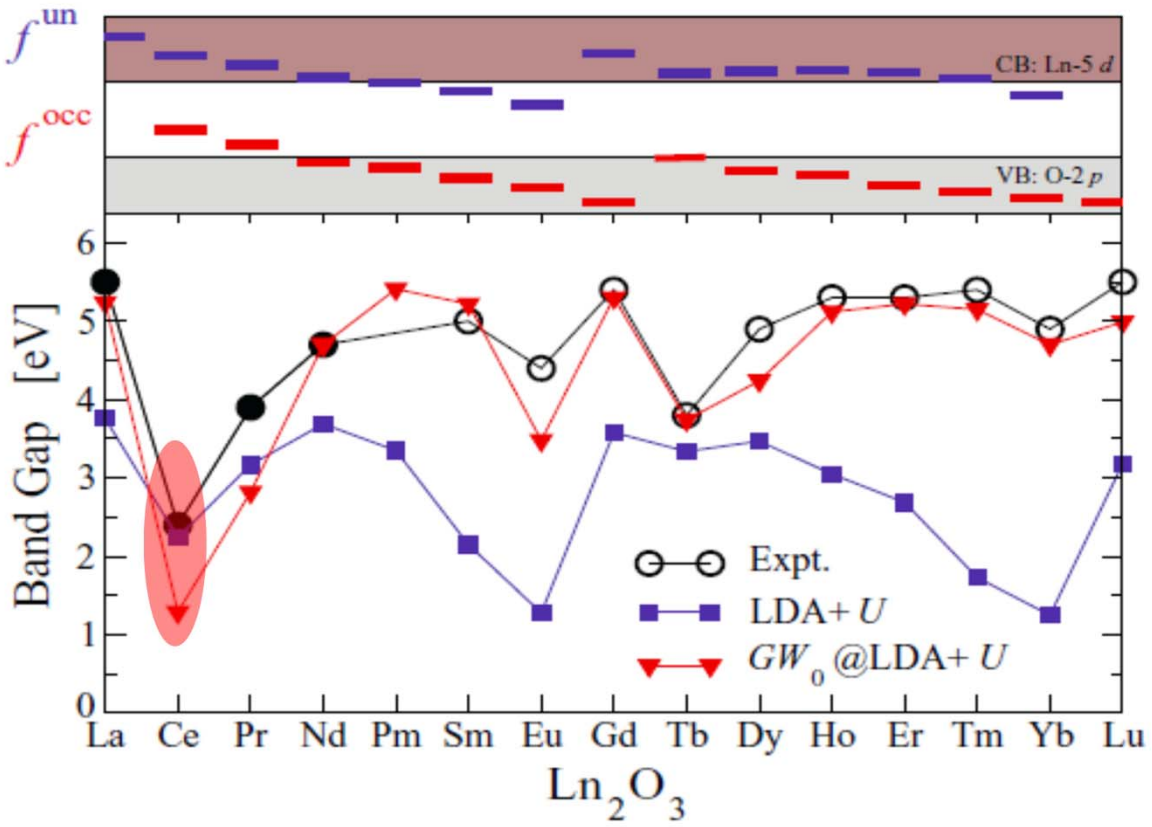


- Most features (band gap, peak positions) are well-reproduced
- *GW* has no satellite, but shows *d*-peak at slighter lower binding energy

H. Jiang et al, *Phys. Rev. B* **82**, 045108 (2010).

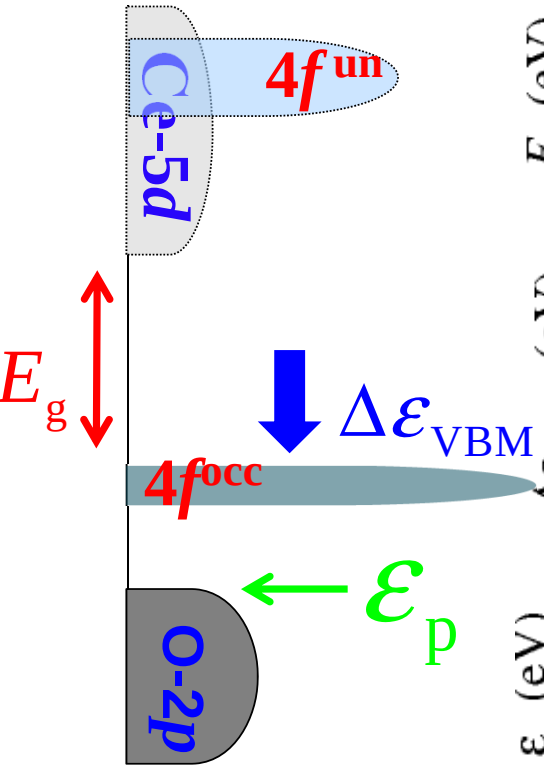
GW@LDA+*U*: Ln_2O_3 band gaps

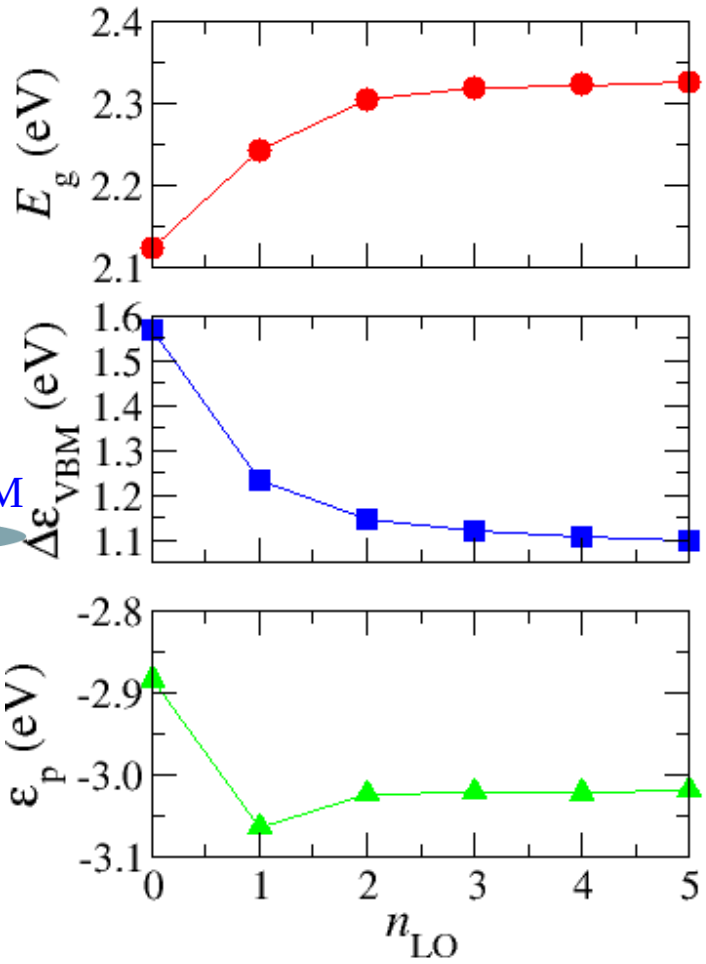


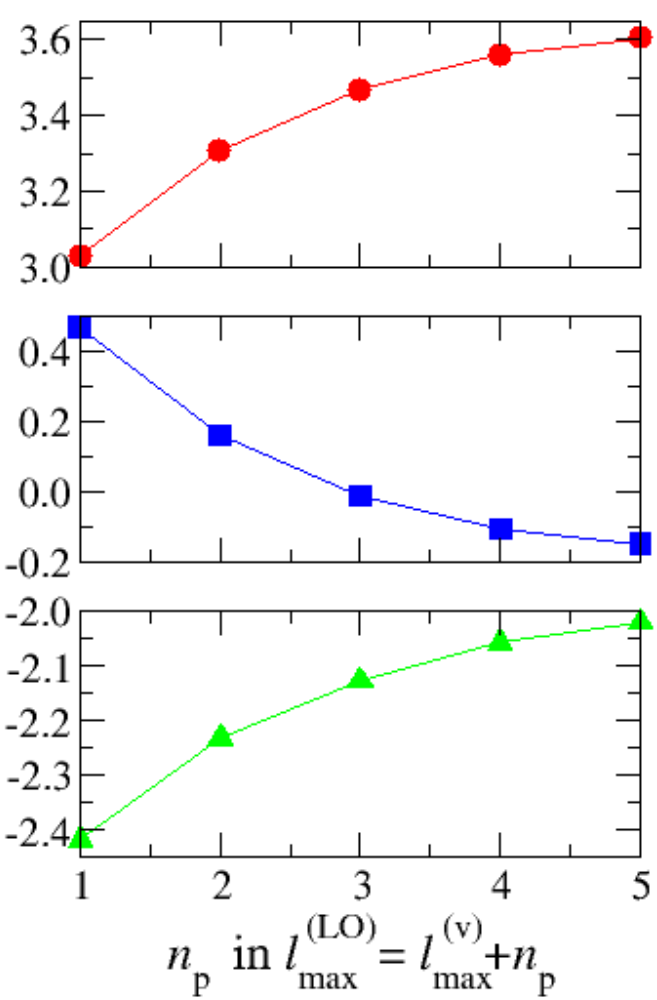


H. Jiang *et al*. *Phys. Rev. Lett.* **102**, 126403(2009); *Phys. Rev. B* **86**, 125115(2012).

Effects of HLOs: Ce_2O_3







G_0W_0@LDA+U (6.8 eV)

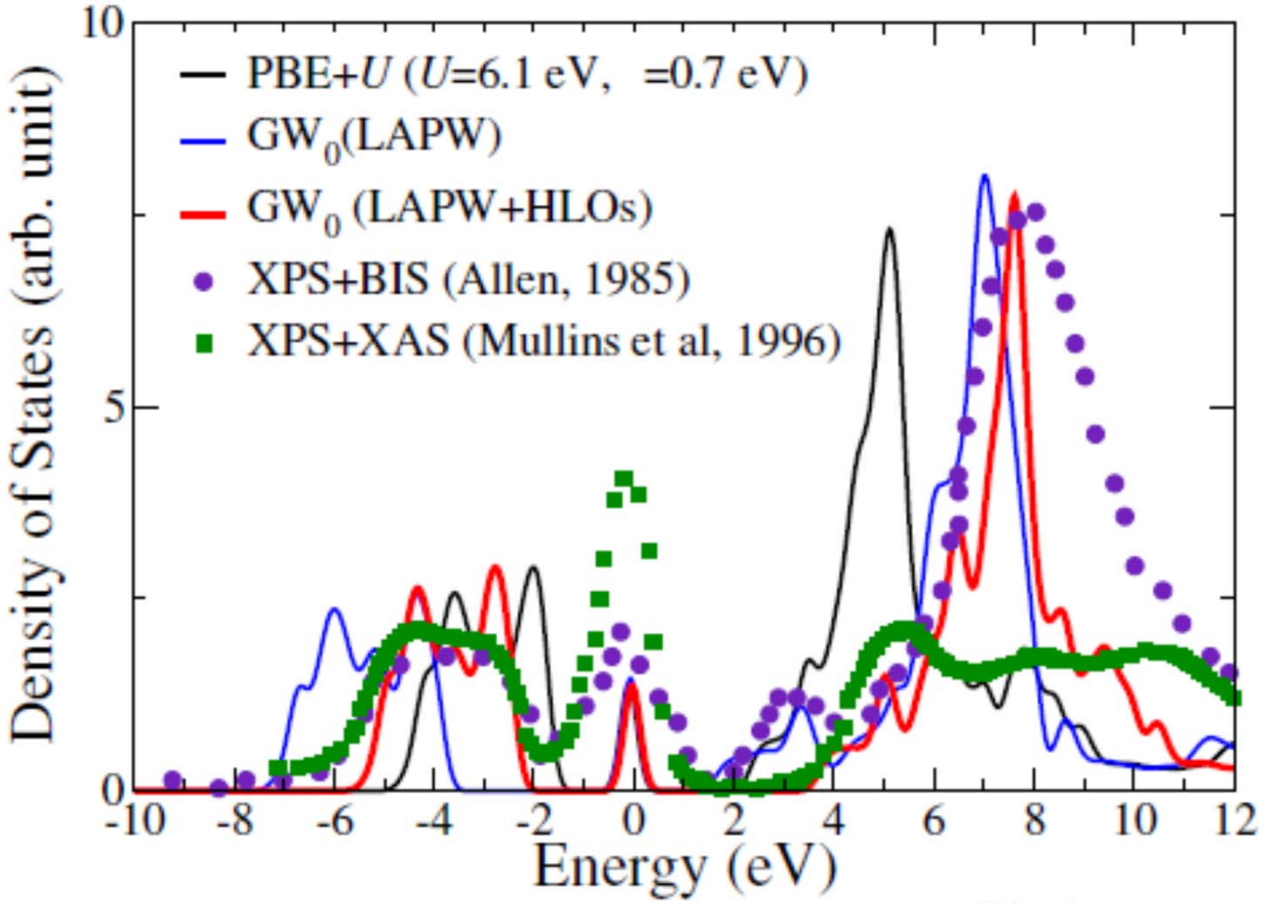
N_k=2x2x1

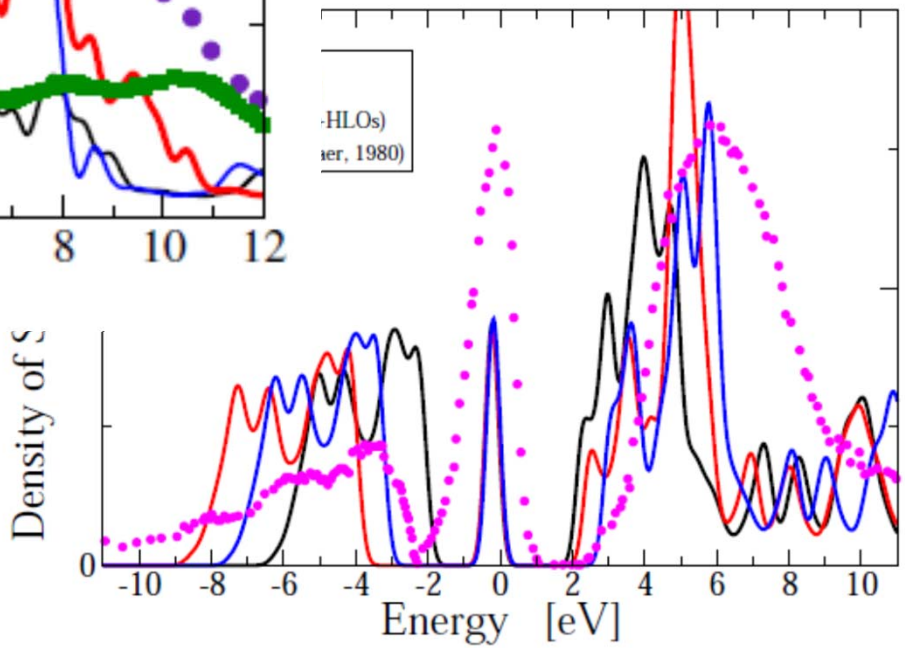
$l_{max}^{(LO)} = 3$

$n_{LO} = 5$

H. Jiang , *Phys. Rev. B* **97**, 245132(2018).

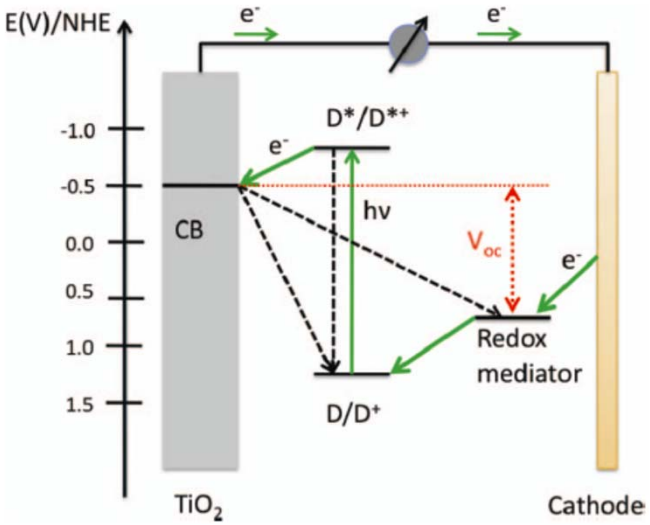
Effects of HLOs: Ce_2O_3 and UO_2

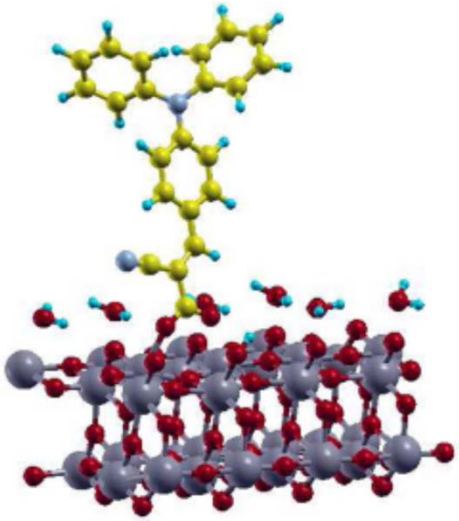


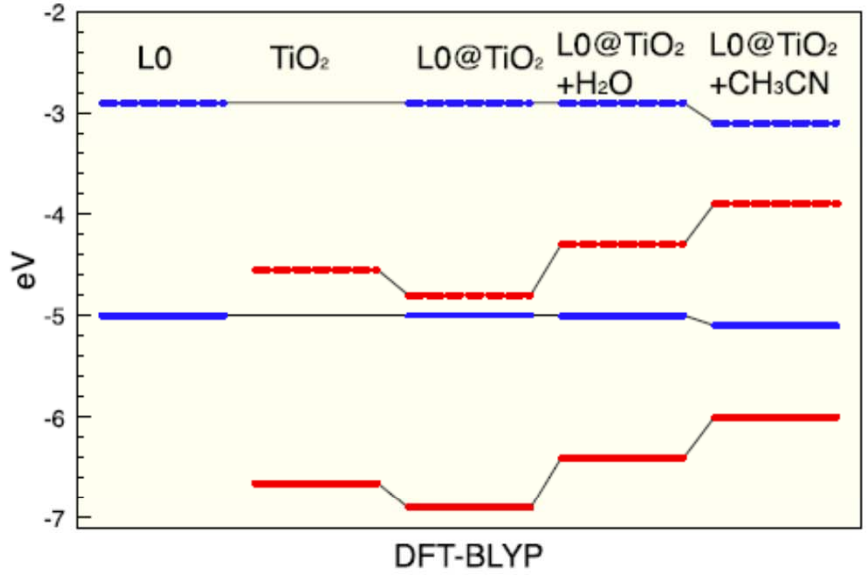


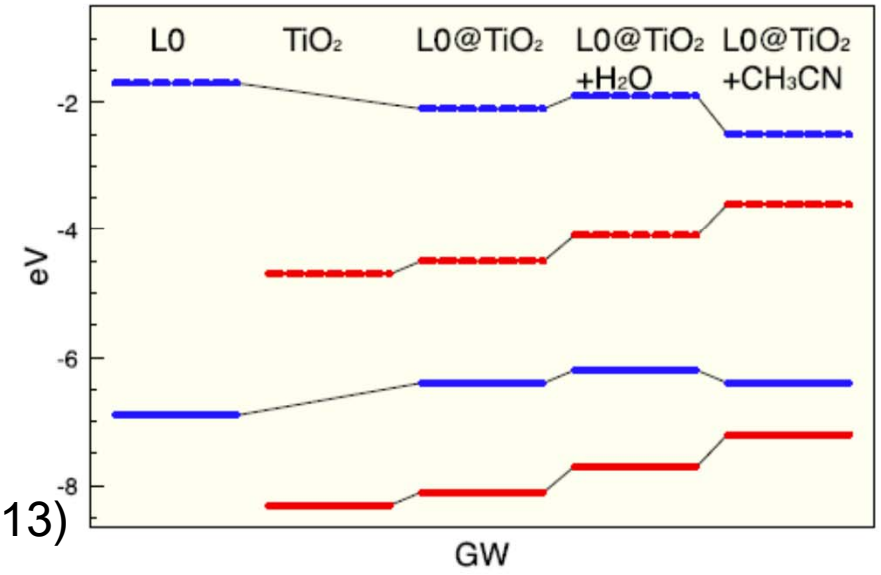
H. Jiang , *Phys. Rev. B* **97**, 245132(2018).

More complex systems: Level alignment in DSSCs



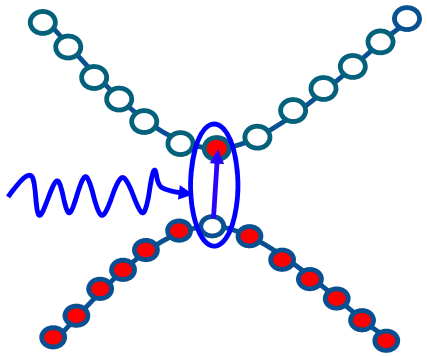






P. Umari et al. J. Chem. Phys. 139, 014709 (2013)
C. Verdi et al, Phys. Rev. B 90, 155410 (2014)

First-principles approaches to optical absorption of solids



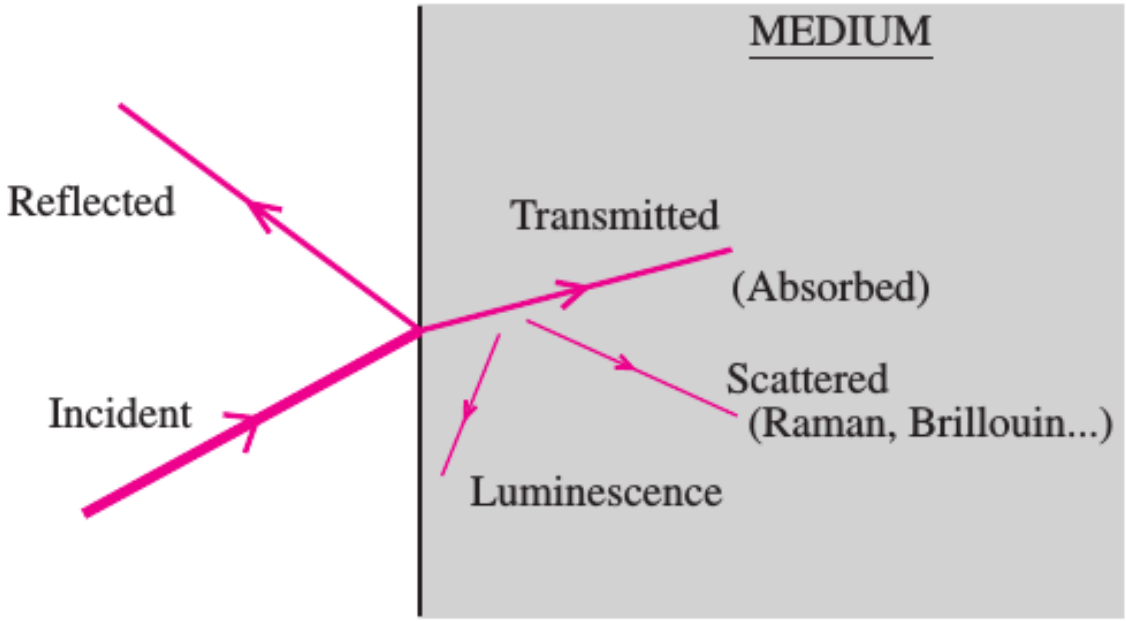
Recommended Readings:

- G. Onida, L. Reining, A. Rubio, *Electronic excitations: density-functional versus many-body Green's-function approaches*, Rev. Mod. Phys. **74**, 601 (2002).
- G. Strinati, *Application of the Green's Functions Method to the Study of the Optical Properties of Semiconductors*, Riv. Nuovo Cimento **11**, 1 (1988).

Optical processes

R: coefficient of reflection (reflectivity)

$n \equiv \frac{c}{v}$: refractive index

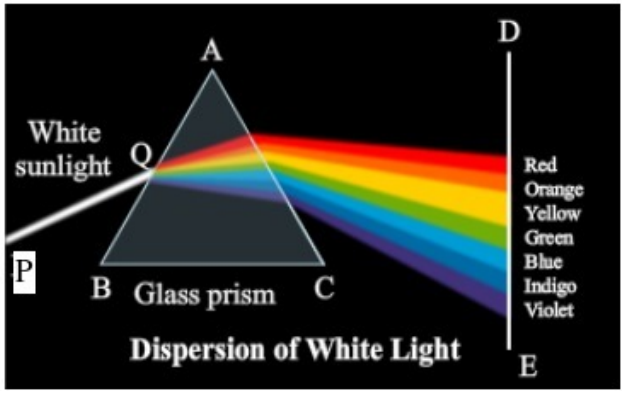


Absorption coefficient α

$$I(z) = I_0 e^{-\alpha z}$$

Dispersion:

$$n = n(\omega)$$



Optical absorption: the dielectric constant

Complex refractive index $\tilde{n} = n + \mathrm{i}\kappa$

Electromagnetic wave in a medium

$$E(z,t) = E_0\, \mathrm{e}^{i(kz-\omega t)}$$

in a medium

$$k = \frac{\omega}{v} = \frac{\tilde{n}\omega}{c} = \frac{(n+i\kappa)\omega}{c}$$

$$E(z,t) = E_0\, \mathrm{e}^{\mathrm{i}(nz/c-\omega t)}\, \mathrm{e}^{-\frac{\kappa\omega}{c}z}$$

$$I \propto \left|E(z,t)\right|^2 \Rightarrow I = I_0\, \mathrm{e}^{-\frac{2\kappa\omega}{c}z} \quad \Rightarrow \quad \alpha(\omega) = \frac{2\omega\kappa}{c}$$

$$\tilde{n} = \sqrt{\varepsilon_{\mathrm{M}}} = \sqrt{\varepsilon_1 + \mathrm{i}\varepsilon_2}$$

$$n = \frac{1}{\sqrt{2}}\left(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\right)^{1/2}$$

$$\kappa = \frac{1}{\sqrt{2}}\left(-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}\right)^{1/2}$$

$\kappa \ll n$

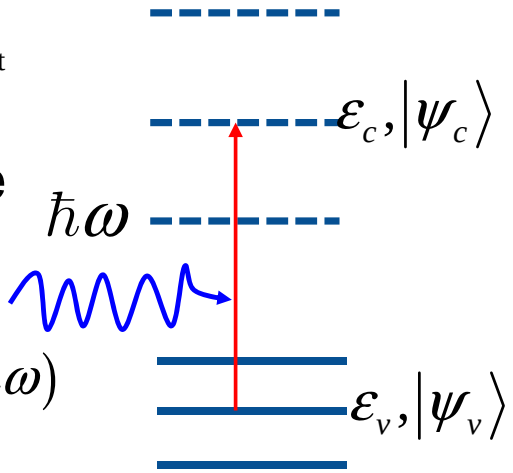
$$\alpha(\omega) \simeq \frac{\omega\varepsilon_2(\omega)}{nc} = \frac{\omega}{nc}\,\mathrm{Im}\,\varepsilon_{\mathrm{M}}(\omega)$$

Optical absorption: independent particle appr. (IPA)

$$\hat{H} = \frac{1}{2m_e}\left[\hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}(\mathbf{r},t)\right]^2 + V(\mathbf{r}) \equiv \hat{H}_0 + \hat{H}_{\text{int}}$$

$$\hat{H}_{\text{int}}(t) = \frac{eA_0}{m_e c} e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}\mathbf{e}\cdot\hat{\mathbf{p}} + c.c.$$

Fermi's golden rule

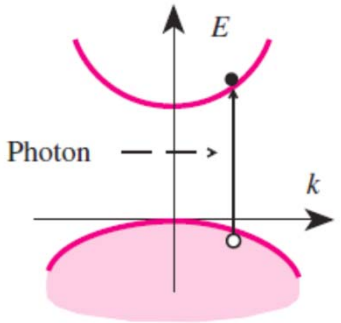


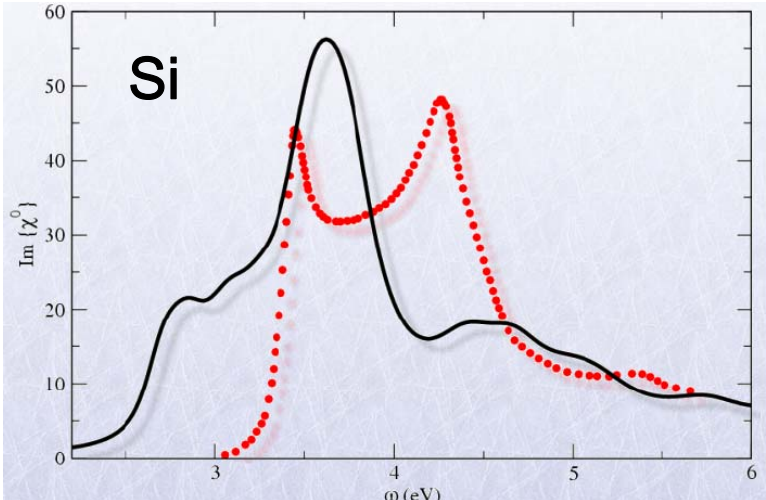
$$P_{i\to f}(\mathbf{q},\omega) = \frac{2\pi}{\hbar}\left(\frac{eA_0}{m_e\hbar}\right)^2 \left|\left\langle\psi_c^{(0)}\left|e^{i\mathbf{q}\cdot\mathbf{r}}\mathbf{e}\cdot\hat{\mathbf{p}}\right|\psi_v^{(0)}\right\rangle\right|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega)$$

$$\varepsilon_2(\mathbf{q},\omega) = \frac{8\pi^2 e^2}{m_e{}^2\omega^2}\frac{1}{V}\sum_{v,c,\mathbf{k}}\left|\left\langle\psi_{c\mathbf{k}+\mathbf{q}}^{(0)}\left|e^{i\mathbf{q}\cdot\mathbf{r}}\mathbf{e}\cdot\hat{\mathbf{p}}\right|\psi_{v\mathbf{k}}^{(0)}\right\rangle\right|^2 \delta(\varepsilon_{c\mathbf{k}+\mathbf{q}} - \varepsilon_{v\mathbf{k}} - \hbar\omega)$$

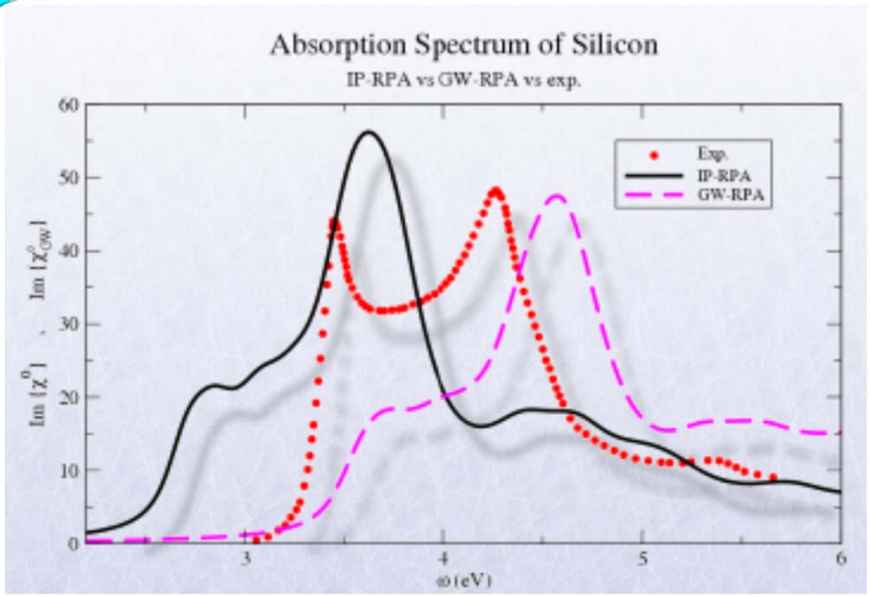
For optical absorption around visible light regime: **q≈0.**

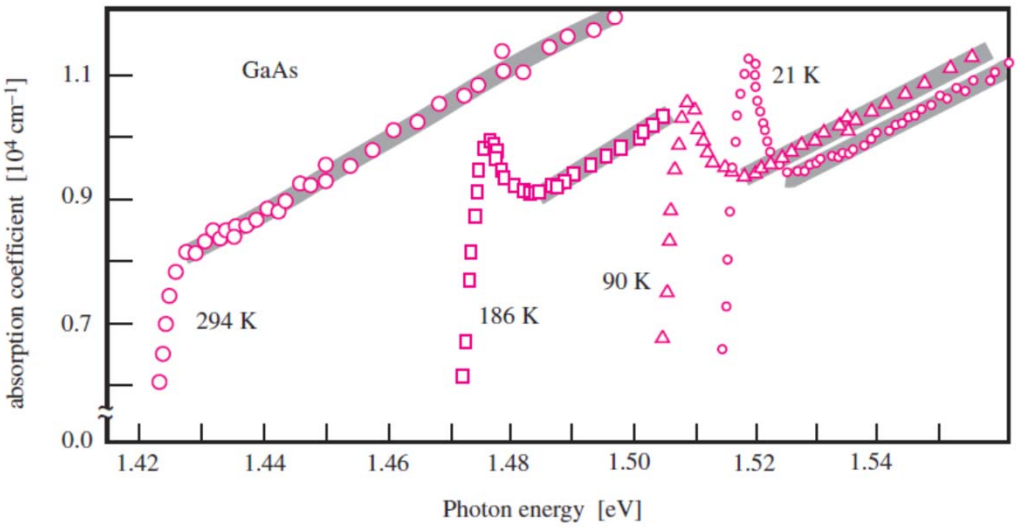
➔ Dipole approx.



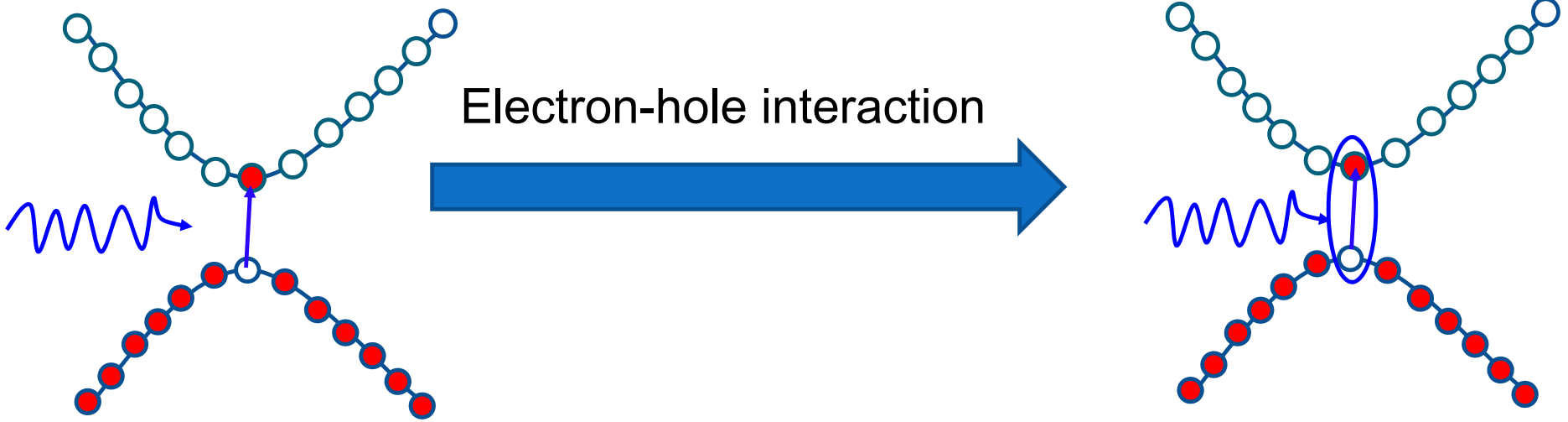


What is missing?





(from F. Sottile's talk)



Microscopic description of optical absorption

reducible polarizability $\chi(1,2) = \dfrac{\delta\rho(1)}{\delta V_{\text{ext}}(2)}$

$1 \equiv (\mathbf{r}_1, s_1, t_1) \equiv (\mathbf{x}_1, t_1)$

irreducible polarizability $P(1,2) = \dfrac{\delta\rho(1)}{\delta V(2)}$

Inverse dielectric function

$$V(1) = V_{\text{ext}}(1) + V_{\text{H}}(1) = V_{\text{ext}}(1) + \int \frac{\rho(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}(2)$$

$$\varepsilon^{-1}(1,2) = \frac{\delta V(1)}{\delta V_{\text{ext}}(2)} = \delta(1,2) + \int d(3) \frac{\delta V_{\text{H}}(1)}{\delta\rho(3)} \frac{\delta\rho(3)}{\delta V_{\text{ext}}(2)}$$

$$= \delta(1,2) + \int d(3) v(1,3) \chi(3,2)$$

On the other hand

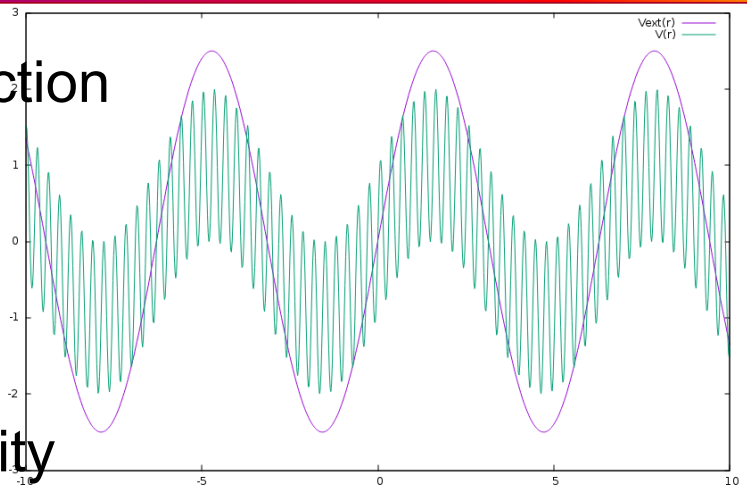
$$\chi(1,2) = \int d(3) \frac{\delta\rho(1)}{\delta V(3)} \frac{\delta V(3)}{\delta V_{\text{ext}}(2)} = \int d(3) P(1,3) \varepsilon^{-1}(3,2)$$

dielectric function

$$\varepsilon(1,2) = \delta(1,2) - \int d(3) v(1,3) P(3,2)$$

Macroscopic dielectric constant and local field effect

Optical radiation field: a spatially smooth function



$$V_{\text{ext}}(\mathbf{r};\omega) = V_{\text{ext};0}(\mathbf{q};\omega)\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$V(\mathbf{r};\omega) = \sum_{\mathbf{G}} V_{\mathbf{G}}(\mathbf{q},\mathbf{G};\omega)\, e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}$$

Macroscopic averaging of microscopic quantity

$$\bar{V}(\mathbf{r};\omega) = V_{\mathbf{G}=0}(\mathbf{q};\omega)\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$V_{\mathbf{G}}(\mathbf{q};\omega) = \sum_{\mathbf{G}'} \varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q};\omega) V_{\text{ext};\mathbf{G}'}(\mathbf{q};\omega) = \varepsilon^{-1}_{\mathbf{G},0}(\mathbf{q};\omega) V_{\text{ext};0}(\mathbf{q};\omega)$$

Macroscopic dielectric function

$$\varepsilon_{\text{M}}(\mathbf{q},\omega) = \frac{V_{\text{ext};\mathbf{G}=0}(\mathbf{q};\omega)}{V_{\mathbf{G}=0}(\mathbf{q};\omega)} = \frac{1}{\varepsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}$$

Neglecting local field effect (LFE) ⇒ $\varepsilon_{\text{M}}(\mathbf{q},\omega) \simeq \varepsilon_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)$

Adler, Phys. Rev. **126**, 413 (1962); N. Wiser, Phys. Rev. **129**, 62 (1963).

Theoretical approaches to optical absorption

- Independent particle approximation (IPA)

$$\varepsilon_{\mathrm{M}}(\mathbf{q},\omega) \simeq 1 - v_{\mathbf{G}=0}(\mathbf{q}) P_{0;\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega) \qquad P_0(\mathbf{x},\mathbf{x}';\omega) = \sum_{i,j} \left(f_i - f_j \right) \frac{\psi_i(\mathbf{x})\psi_j^*(\mathbf{x})\psi_j(\mathbf{x}')\psi_i^*(\mathbf{x}')}{\omega - \left(\varepsilon_j - \varepsilon_i \right) + i\eta}$$

- Random phase approximation (RPA i.e. IPA with LFE)

$$\varepsilon(1,2) = \delta(1,2) - \int d(3) v(1,3) P_0(3,2) \qquad \varepsilon_{\mathrm{M}}(\mathbf{q},\omega) = \frac{1}{\varepsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}$$

- Linear-Response Time-dependent DFT (LR-TDDFT)

$$\chi(1,2) = \chi_{\mathrm{KS}}(1,2) + \int d(\mathbf{34}) \chi_{\mathrm{KS}}(1,3) \left[v(3,4) + f_{\mathrm{xc}}(3,4) \right] \chi(4,2)$$

$$\varepsilon^{-1}(1,2) = \delta(1,2) + \int d(3) v(1,3) \chi(3,2)$$

$$\chi_{\mathrm{KS}}(1,2) \equiv \frac{\delta\rho(1)}{\delta V_{\mathrm{KS}}(2)} \sim P_0(1,2)$$

$$\varepsilon_{\mathrm{M}}(\mathbf{q},\omega) = \frac{1}{\varepsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}$$

- Bethe-Salpeter equation (BSE)

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

Optical absorption: LR-TDDFT

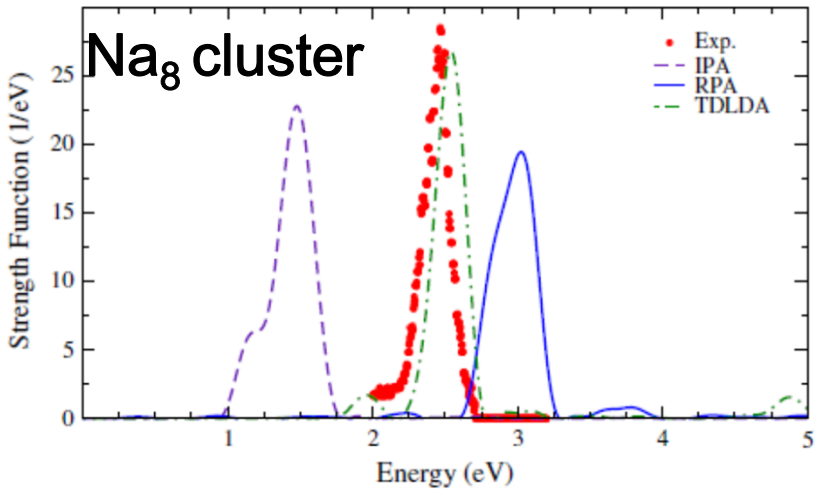
$$\chi(\mathbf{x},\mathbf{x}';\omega) \equiv \chi_{\mathrm{KS}}(\mathbf{x},\mathbf{x}';\omega) + \int d\mathbf{x}''\, d\mathbf{x}'''\, \chi_{\mathrm{KS}}(\mathbf{x},\mathbf{x}'';\omega)\left[\frac{1}{|\mathbf{r}''-\mathbf{r}'''|} + f_{\mathrm{xc}}(\mathbf{x}'',\mathbf{x}''';\omega)\right]\chi(\mathbf{x}''',\mathbf{x}';\omega)$$

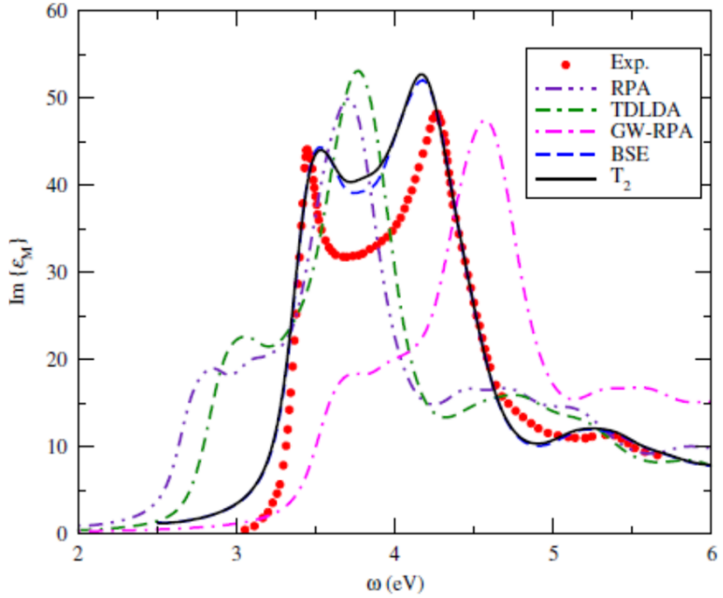
$$\sum_{v'c'}\left[(\varepsilon_c - \varepsilon_v)\,\delta_{vc.v'c'} + K_{vc,v'c'}\right]A_{v'c',s} = \Omega_s A_{vc,s}$$

$$K_{vc,v'c'} \equiv \int d\mathbf{x}\int d\mathbf{x}'\, X^*_{vc}(\mathbf{x})\, f_{\mathbf{Hxc}}(\mathbf{x},\mathbf{x}';\Omega) X_{v'c'}(\mathbf{x}')$$

$$= \int d\mathbf{x}\int d\mathbf{x}'\, X^*_{vc}(\mathbf{x}) v(\mathbf{r},\mathbf{r}') X_{v'c'}(\mathbf{x}') + \int d\mathbf{x}\int d\mathbf{x}'\, X^*_{vc}(\mathbf{x})\, f_{\mathrm{xc}}(\mathbf{x},\mathbf{x}';\Omega) X_{v'c'}(\mathbf{x}')$$

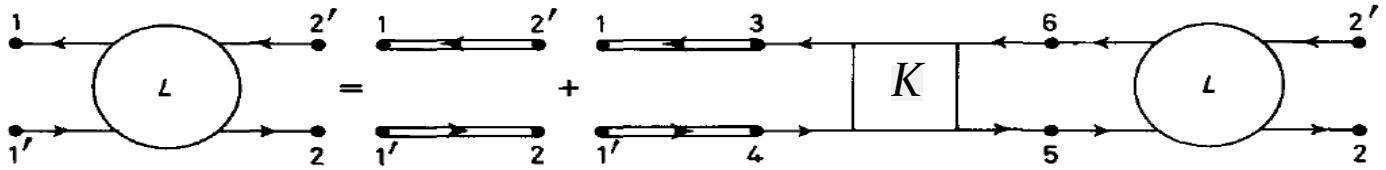
$$= K^{\mathrm{x}}_{vc,v'c'} + K^{f_{\mathrm{xc}}}_{vc,v'c'} \qquad X_{vc}(\mathbf{x}) \equiv \psi_c(\mathbf{x})\psi^*_v(\mathbf{x})$$





M. E. Casida, in *Density Functional Methods, Part I (*ed. DP Chong), p. 155. World Sci. (1995); M. A. L. Marques, E. K. U. Gross, in A Primer in Density Functional Theory (2003). S. Botti et al. Rep. Prog. Phys. 70,357(2007).

Optical absorption: GW+BSE



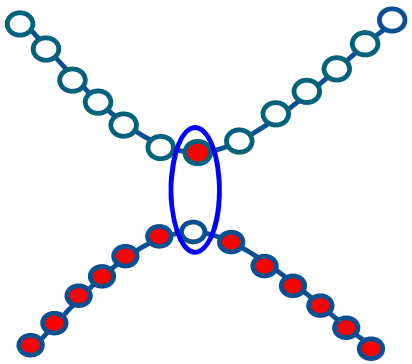
$$L(1,2;1',2') = L_0(1,2;1',2') + \int \mathrm{d}(3456) L_0(1,4;1',3) K(3,5;4,6) L(6,2;5,2')$$

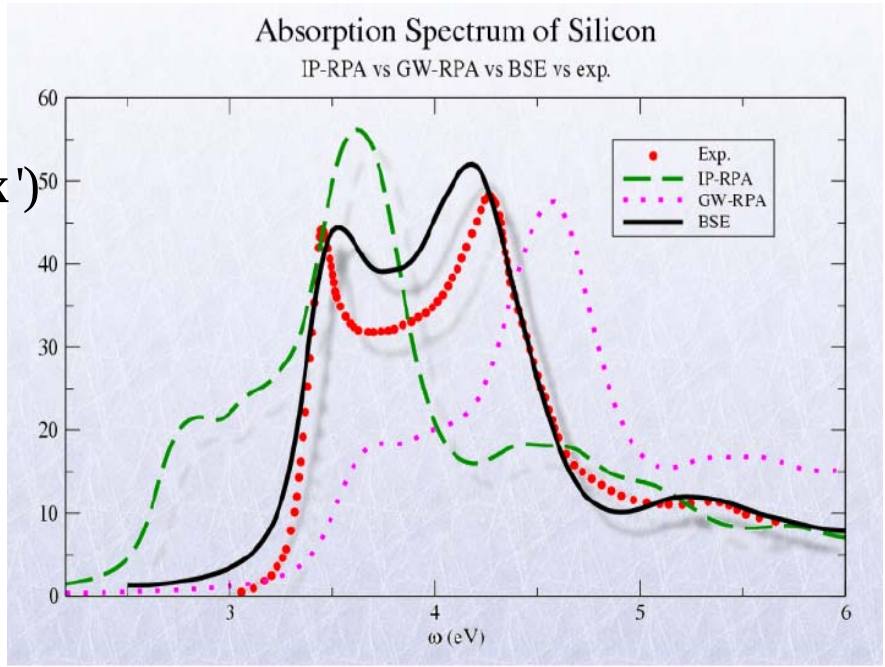
$$\sum_{v'c'} \left[\left(E_c - E_v \right) \delta_{vc.v'c'} + K_{vc,v'c'} \left(\Omega_s \right) \right] A_{v'c',s} = \Omega_s A_{vc,s} \quad \text{(Tamm-Dancoff Approx.)}$$

$$K^{\mathrm{x}}_{vc,v'c'} = \int d\mathbf{x} d\mathbf{x}' \, X^*_{vc}(\mathbf{x},\mathbf{x}) v(\mathbf{r},\mathbf{r}') X_{v'c'}(\mathbf{x}',\mathbf{x}')$$

$$K^{\mathrm{d}}_{vc,v'c'} = -\int d\mathbf{x} d\mathbf{x}' \, X^*_{vc}(\mathbf{x},\mathbf{x}') W(\mathbf{r},\mathbf{r}';\omega=0) X_{v'c'}(\mathbf{x},\mathbf{x}')$$

$$X_{vc}\left(\mathbf{x}_1,\mathbf{x}_1'\right) \equiv \psi_c\left(\mathbf{x}_1\right) \psi_v^*\left(\mathbf{x}_1'\right)$$





Albrecht et al., *Phys. Rev. Lett.* 80, 4510 (1998).
M. Rohlfing, S. Louie, *Phys. Rev. B* 62, 4927 (2000).

Optical absorption: TD hybrid functional approach

Time-dependent generalized Kohn-Sham equations

$$\mathrm{i}\frac{\partial}{\partial t}\psi_i(\mathbf{x},t)=\left[-\frac{1}{2}\nabla^2+V_{\mathrm{ext}}(\mathbf{x},t)+V_{\mathrm{Hxc}}(\mathbf{x},t)+\hat{V}_{\mathrm{x}}^{\mathrm{NL}}(\mathbf{x},t)\right]\psi_i(\mathbf{x},t)$$

$$\hat{V}_{\mathrm{x}}^{\mathrm{NL}}(\mathbf{x},t)\psi_i(\mathbf{x},t)=-\sum_{j\in\mathrm{occ}}\int\psi_j^*(\mathbf{x}',t)\psi_i(\mathbf{x}',t)v_{\mathrm{sc}}^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')\psi_j(\mathbf{x},t)\,d\mathbf{x}'$$

Linear response theory

$$\sum_{v'c'}\left[(\varepsilon_c-\varepsilon_v)\delta_{vc.v'c'}+K_{vc,v'c'}\right]A_{v'c',s}=\Omega_s A_{vc,s}$$

$$K_{vc,v'c'}=K^{\mathrm{x}}_{vc,v'c'}+K^{f_{\mathrm{xc}}}_{vc,v'c'}+K^{\mathrm{NL}}_{vc,v'c'}$$

PBE0, B3LYP:

$$K^{\mathrm{NL}}_{vc,v'c'}=-\int d\mathbf{x}d\mathbf{x}'\,X^*_{vc}(\mathbf{x},\mathbf{x}')v_{\mathrm{sc}}^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')X_{v'c'}(\mathbf{x},\mathbf{x}')$$

$$v_{\mathrm{sc}}^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')=\frac{\alpha_{\mathrm{HF}}}{|\mathbf{r}-\mathbf{r}'|}$$

HSE06:

$$v_{\mathrm{sc}}^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')=\frac{\alpha_{\mathrm{HF}}\,\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

Screened exchange (SX)

$$v_{\mathrm{sc}}^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')=\frac{\exp(k_{\mathrm{TF}}|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

J. Paier et al. Phys. Rev. B 78, 121201(R) (2008).

BSE vs TDDFT vs TD hybrid

$$\sum_{v'c'}\left[(\varepsilon_c-\varepsilon_v)\delta_{vc.v'c'}+K_{vc,v'c'}\right]A_{v'c',s}=\Omega_s A_{vc,s}$$

- BSE:

$$K_{vc,v'c'}=K^{\mathrm{x}}_{vc,v'c'}+K^{\mathrm{d}}_{vc,v'c'}$$

$$K^{\mathrm{x}}_{vc,v'c'}=\int d\mathbf{x}d\mathbf{x}'\,X^{*}_{vc}(\mathbf{x},\mathbf{x})v(\mathbf{r},\mathbf{r}')X_{v'c'}(\mathbf{x}',\mathbf{x}')$$

$$K^{\mathrm{d}}_{vc,v'c'}=-\int d\mathbf{x}d\mathbf{x}'\,X^{*}_{vc}(\mathbf{x},\mathbf{x}')W(\mathbf{r},\mathbf{r}';\omega=0)X_{v'c'}(\mathbf{x},\mathbf{x}')$$

- TD DFT (based on local $V_{xc}(\mathbf{x})$)

$$K_{vc,v'c'}=K^{\mathrm{x}}_{vc,v'c'}+K^{f_{\mathrm{xc}}}_{vc,v'c'}$$

$$K^{f_{\mathrm{xc}}}_{vc,v'c'}=\int d\mathbf{x}\int d\mathbf{x}'\,X^{*}_{vc}(\mathbf{x})f_{\mathrm{xc}}(\mathbf{x},\mathbf{x}';\Omega)X_{v'c'}(\mathbf{x}')$$

$$W_{\mathbf{GG}'}(\mathbf{q};\omega)=\frac{4\pi\varepsilon^{-1}_{\mathbf{GG}'}}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}$$

model BSE

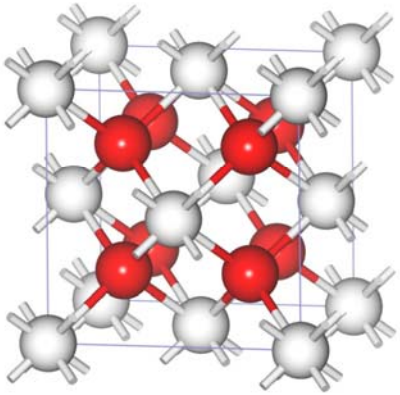
- TD-hybrid DFT:

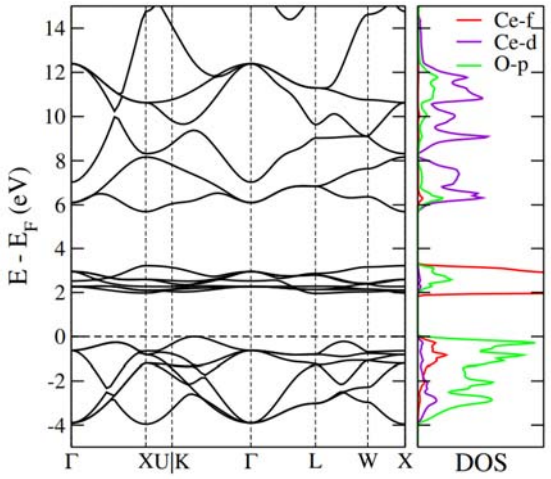
$$K_{vc,v'c'}=K^{\mathrm{x}}_{vc,v'c'}+K^{f_{\mathrm{xc}}}_{vc,v'c'}+K^{\mathrm{NL}}_{vc,v'c'}$$

$$K^{\mathrm{NL}}_{vc,v'c'}=-\int d\mathbf{x}d\mathbf{x}'\,X^{*}_{vc}(\mathbf{x},\mathbf{x}')v^{\mathrm{NL}}_{\mathrm{sc}}(\mathbf{r},\mathbf{r}')X_{v'c'}(\mathbf{x},\mathbf{x}')$$

J. Sun et al. Phys. Rev. Mater. 2, 013091 (2020).

CeO_2 optical absorption by GW-BSE and TDDFT

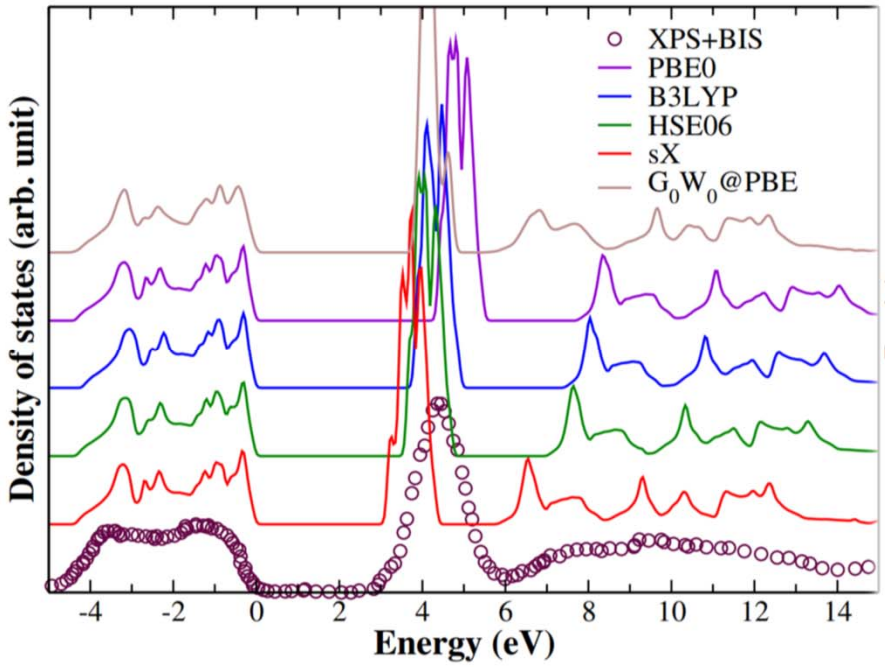


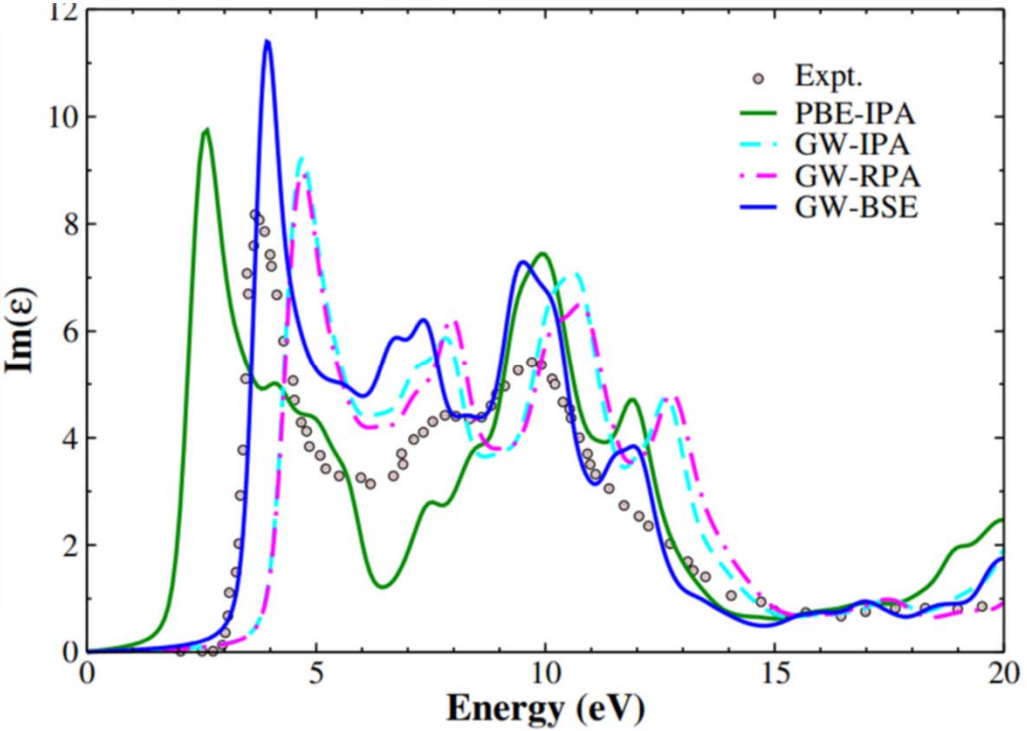


Ce-5d

Ce-4f

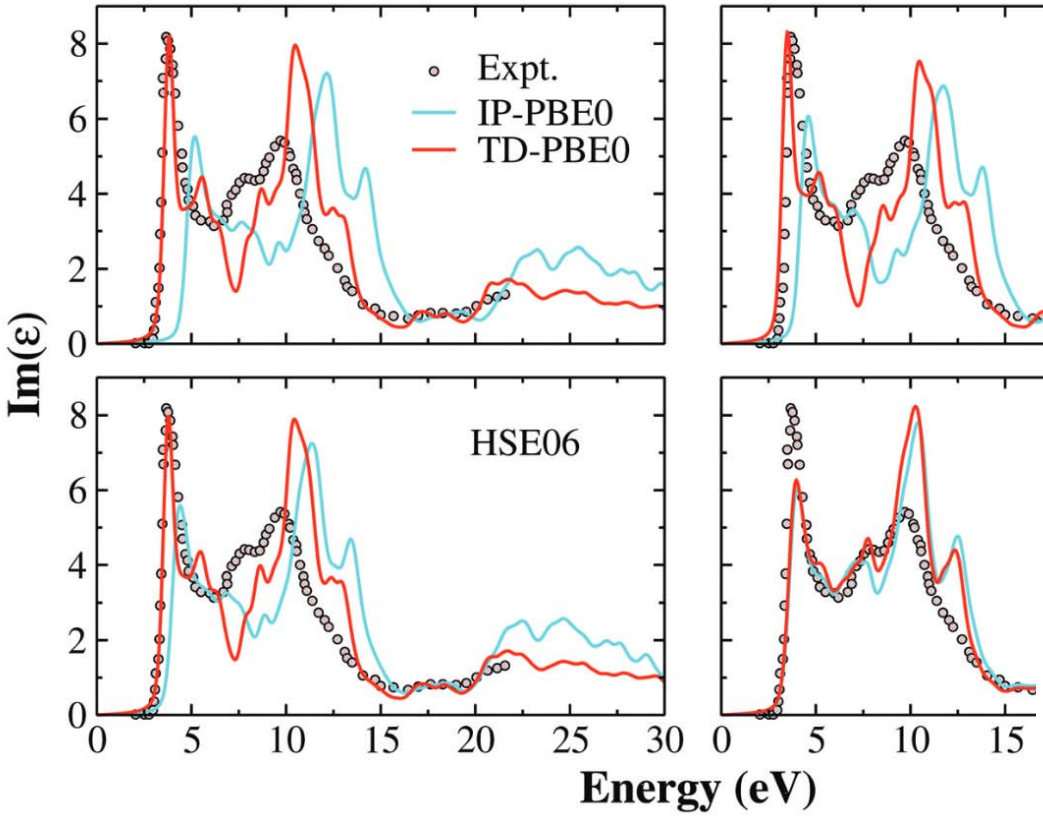
O-2p

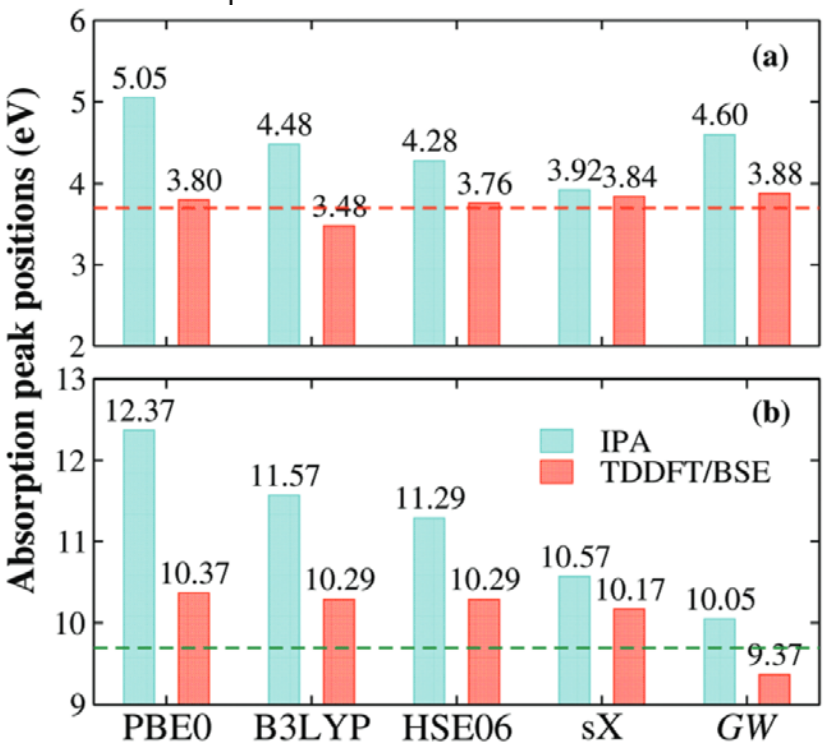




H.-Y. Sun, S.-X. Li, H. Jiang, Phys. Chem. Phys. Chem. **23**, 16296 (2021).

CeO_2 optical absorption by TD-hybrid DFT

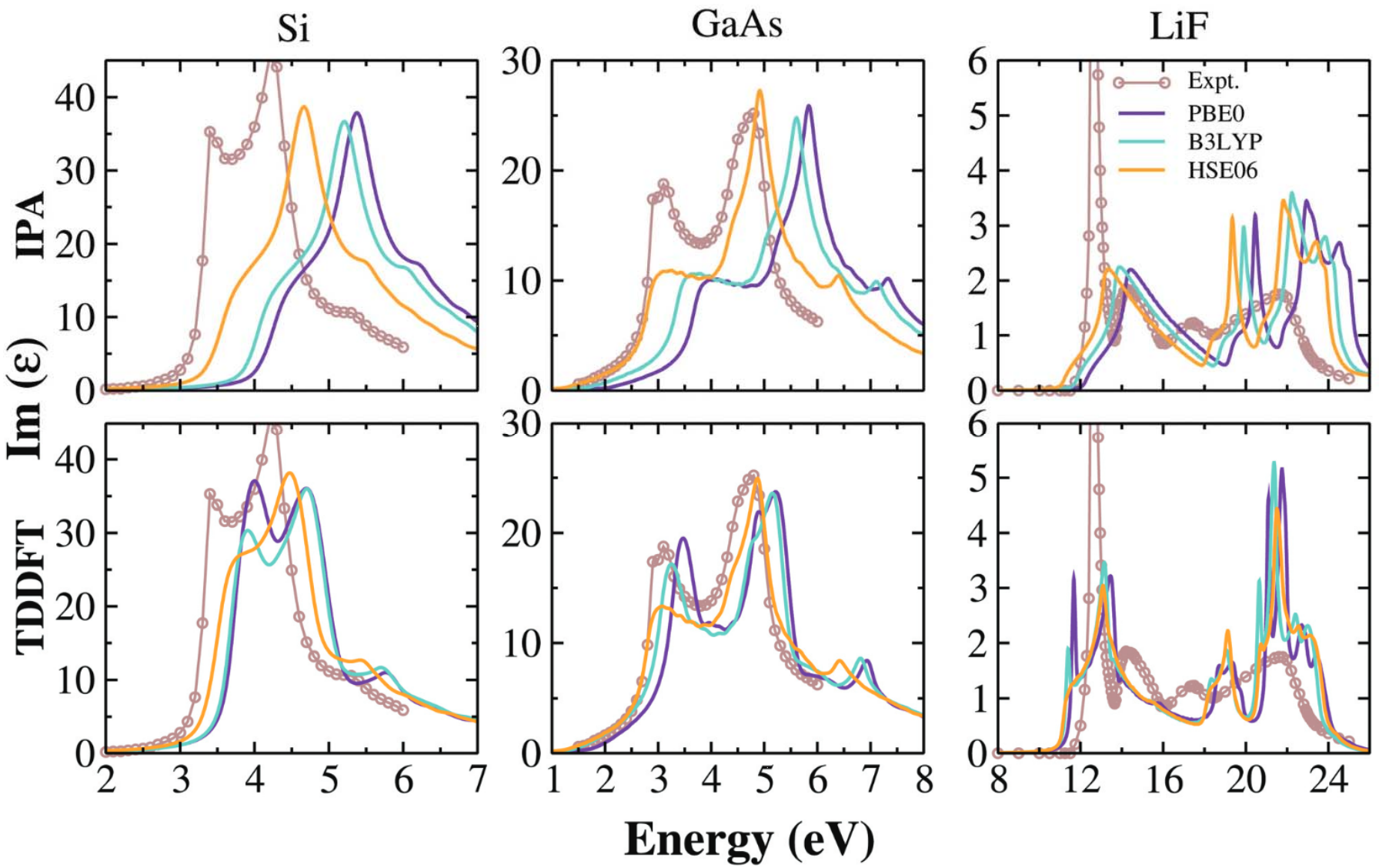




- IPA spectra reflecting band gaps
- Nearly identical TDDFT spectra
- Special behavior of sX

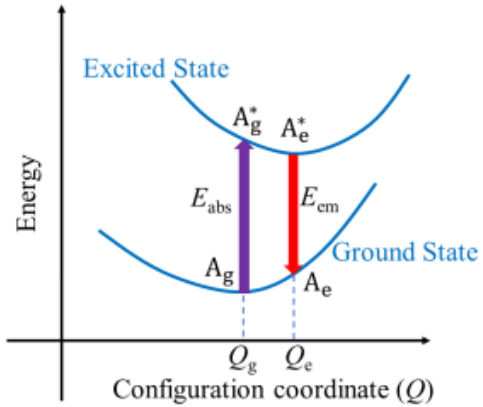
H.-Y. Sun, S.-X. Li, H. Jiang, Phys. Chem. Phys. Chem. **23**, 16296 (2021).

Universality of weak functional dependence



H.-Y. Sun, S.-X. Li, H. Jiang, Phys. Chem. Phys. Chem. **23**, 16296 (2021).

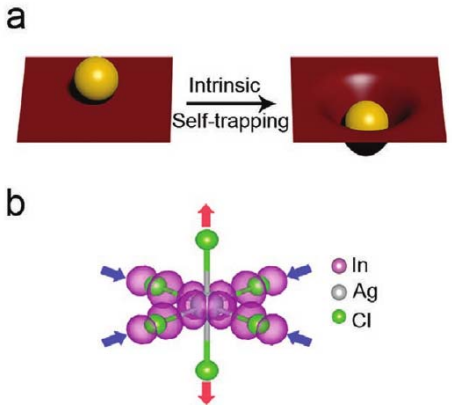
First-principles approaches to self-trapped exciton (STE) luminescence in metal halides

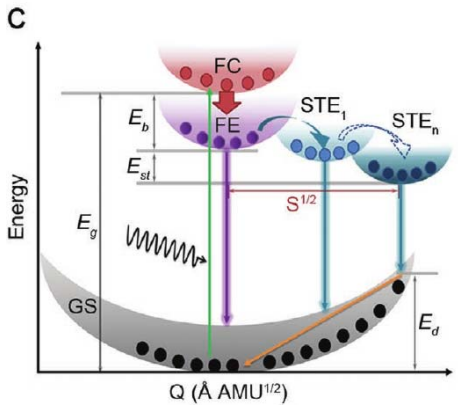


Recommended readings:

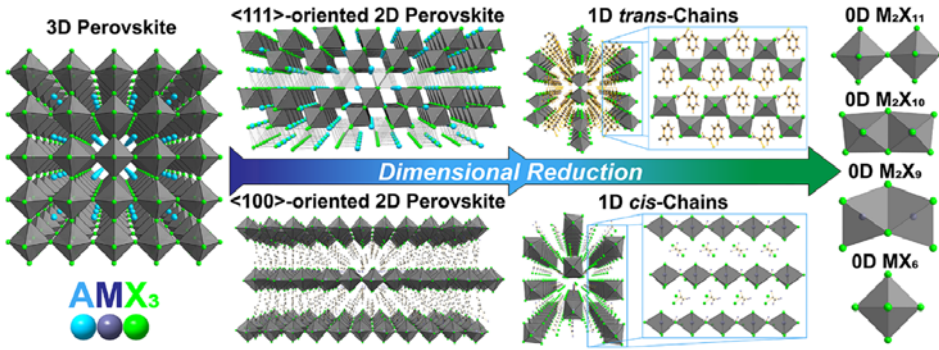
- H.-Y. Sun, L. Xiong and H. Jiang*, *Towards first-principles approaches for mechanistic study of self-trapped exciton luminescence*, *Chem. Phys. Rev.* 4, 031302 (2023).

Challenges for theoretical study of STE emission





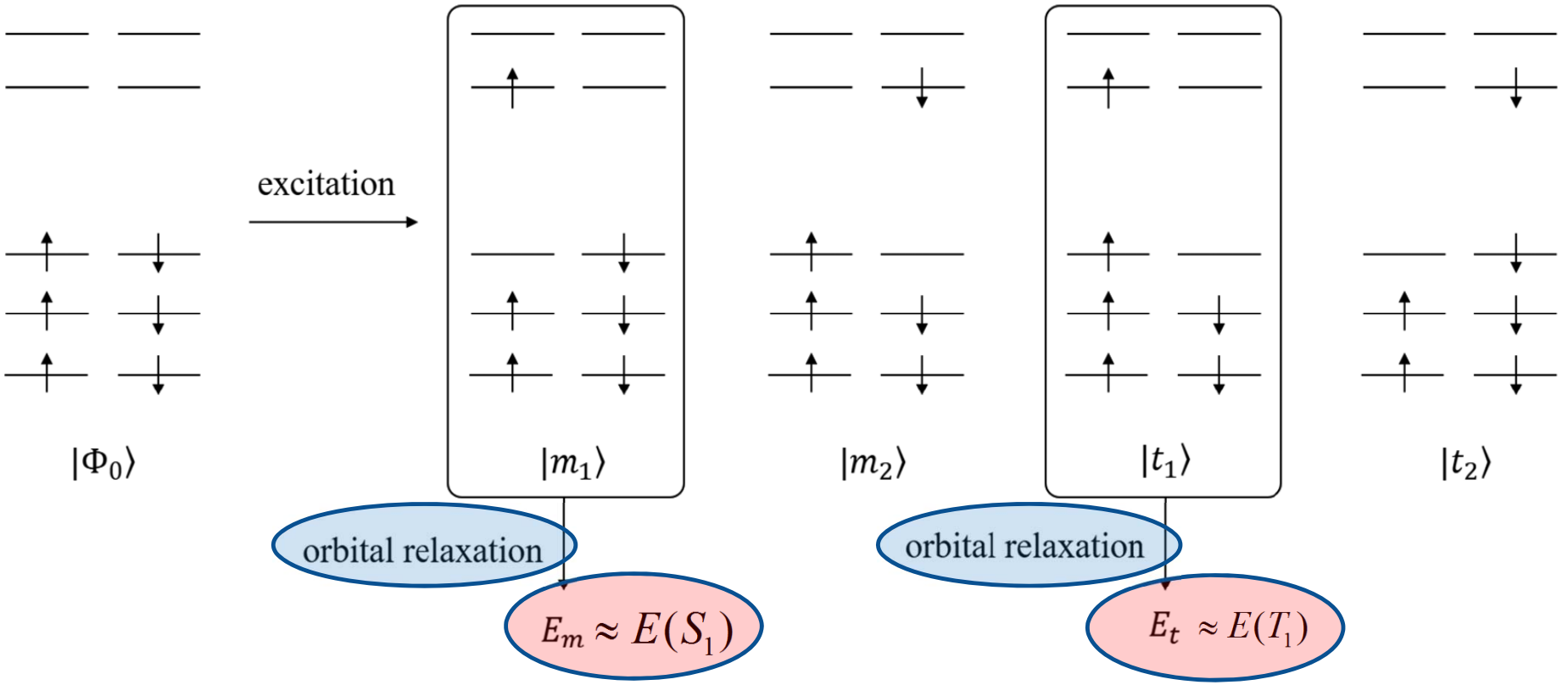
Guo et al. *Adv. Mater.* 2022, 2201008.



K. M. McCall et all, ACS Mater. Lett. 2, 1218 (2020).

- Electronic excitations (band gap, exciton) with **fixed structure** are difficult or expensive to calculate: (*GW*-BSE, TD-hybrid …)
- Few methods available for **geometry relaxation for excited states** of **extended** system
- Multiple **high-dimensional** excited state PES coupled with different electron-lattice couplings ➔ Highly complicated structure-property relationships

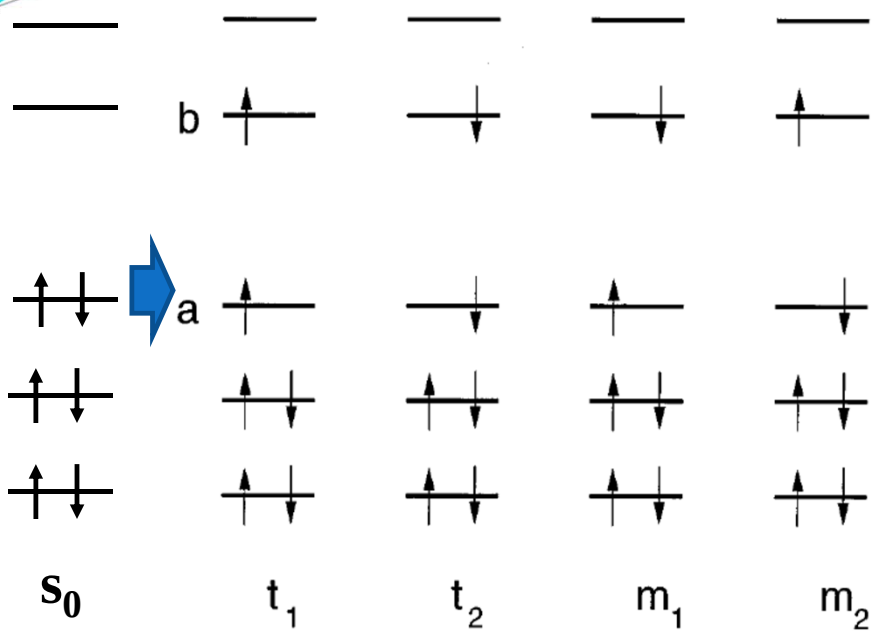
Occupancy-constrained DFT/ΔSCF



- SCF calculation with occupancies like $|m_1\rangle$ or $|t_1\rangle$ gives **approximate** singlet or triplet excited states.
- OC-DFT is also known as ΔSCF.

H.-Y. Sun, L. Xiong and H. Jiang*, *Chem. Phys. Rev.* 4, 031302 (2023).

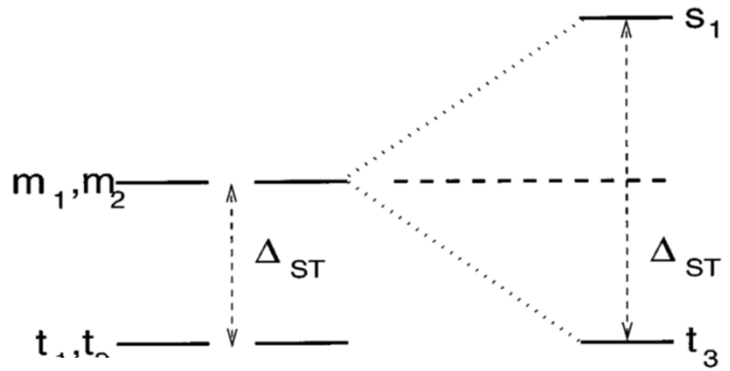
Restricted Open-Shell Kohn-Sham (ROKS)



$$t_1 = |1\bar{1}\cdots a\bar{b}\rangle \qquad m_1 = |1\bar{1}\cdots a\bar{b}\rangle$$

$$t_2 = |1\bar{1}\cdots \bar{a}\bar{b}\rangle \qquad m_2 = |1\bar{1}\cdots \bar{a}b\rangle$$

$$t_3 = \frac{1}{\sqrt{2}}(m_1 + m_2) \qquad s_1 = \frac{1}{\sqrt{2}}(m_1 - m_2)$$



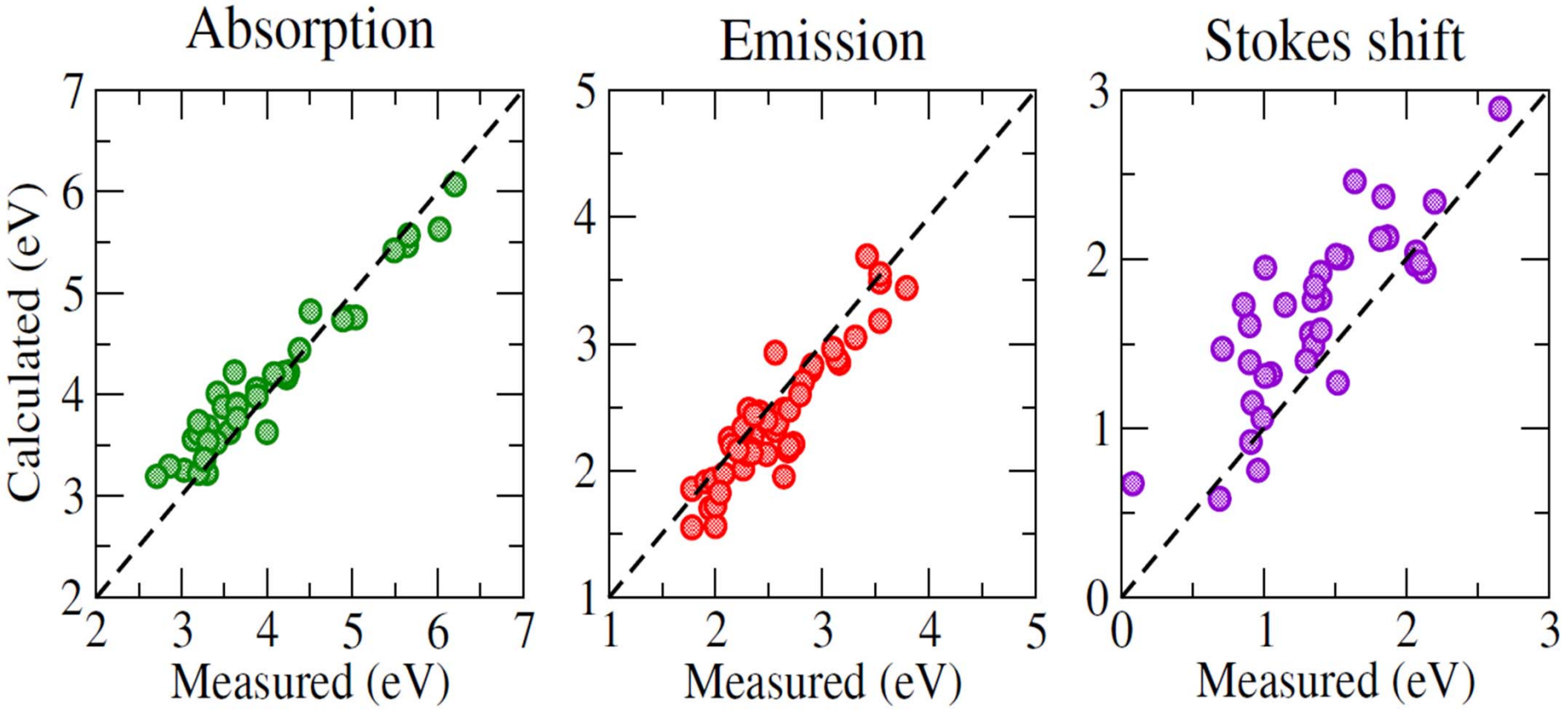
$$E(m_1) = \frac{1}{2}\langle s_1 + t_3|\hat{H}|s_1 + t_3\rangle = \frac{1}{2}\left[E(s_1) + E(t_3)\right]$$

$$E(s_1) = 2E(m_1) - E(t_1) = 2E(\Phi_m) - E(\Phi_t)$$

$$E(\mathrm{S}_1) = \min_{\{\psi_i\}}\left\{2E_m^{\mathrm{DFT}}\left[\{\psi_i\}\right] - E_t^{\mathrm{DFT}}\left[\{\psi_i\}\right]\right\}$$

I. Frank, J. Hutter, D. Marx, and M. Parrinello, J. Chem. Phys. 108, 4060 (1998).

Performances of OC-DFT/ROKS for STE materials



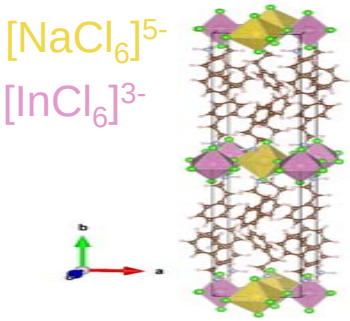
MAE = 0.23 eV

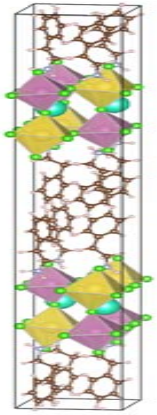
MAE = 0.21 eV

MAE = 0.36 eV

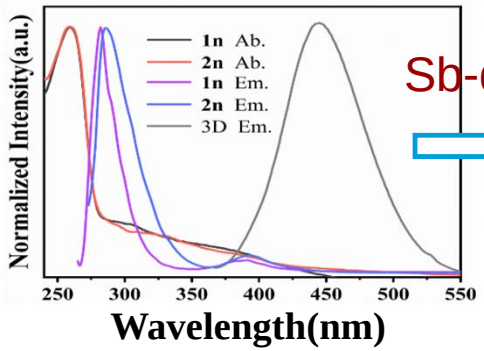
H.-Y. Sun, L. Xiong and H. Jiang*, *Chem. Phys. Rev.* 4, 031302 (2023).

Broad band emission of Sb-doped double perovskites



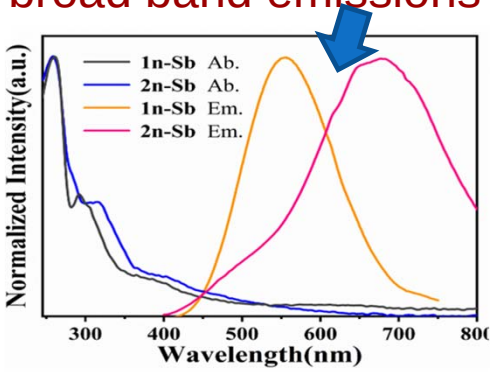


1n: $(PEA)_4NaInCl_8$
2n: $(PEA)_2CsNaInCl_7$

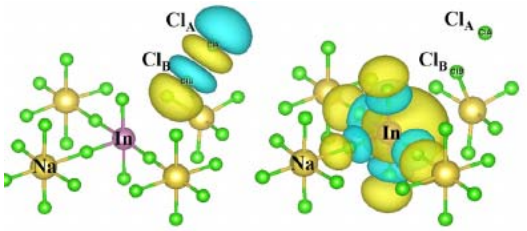


Sb-doping

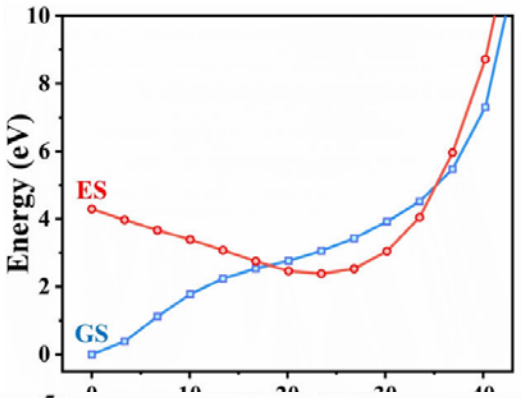
broad band emissions



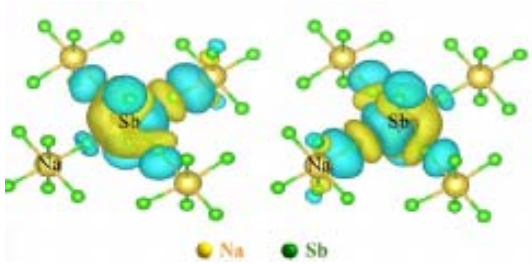
Without doping

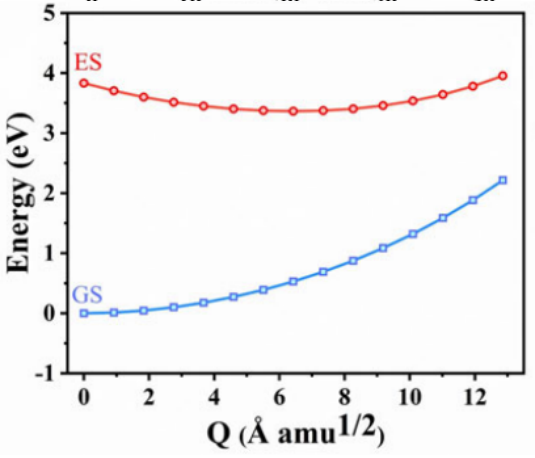


hole electron



With doping

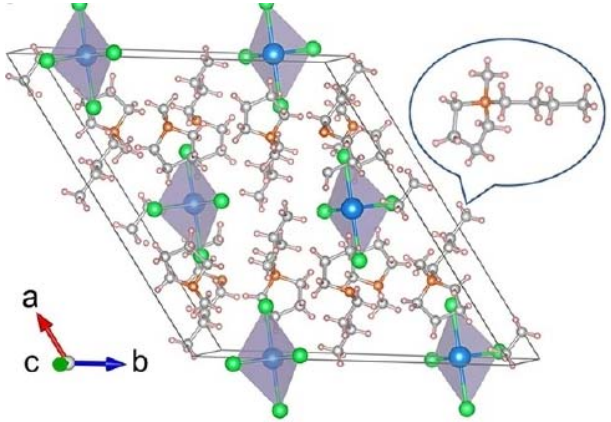


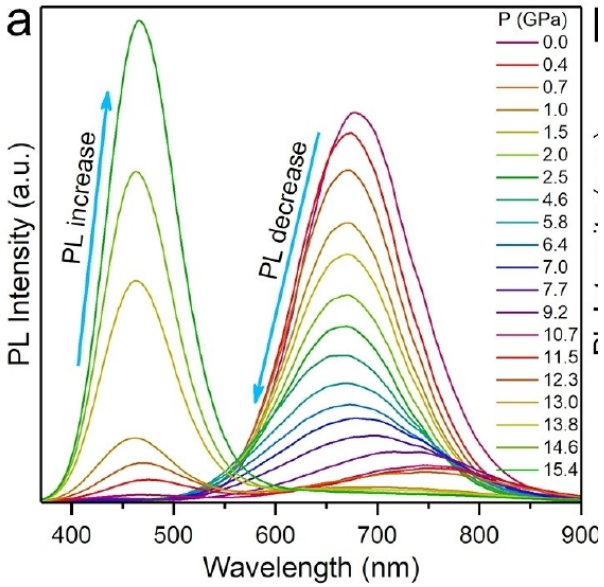


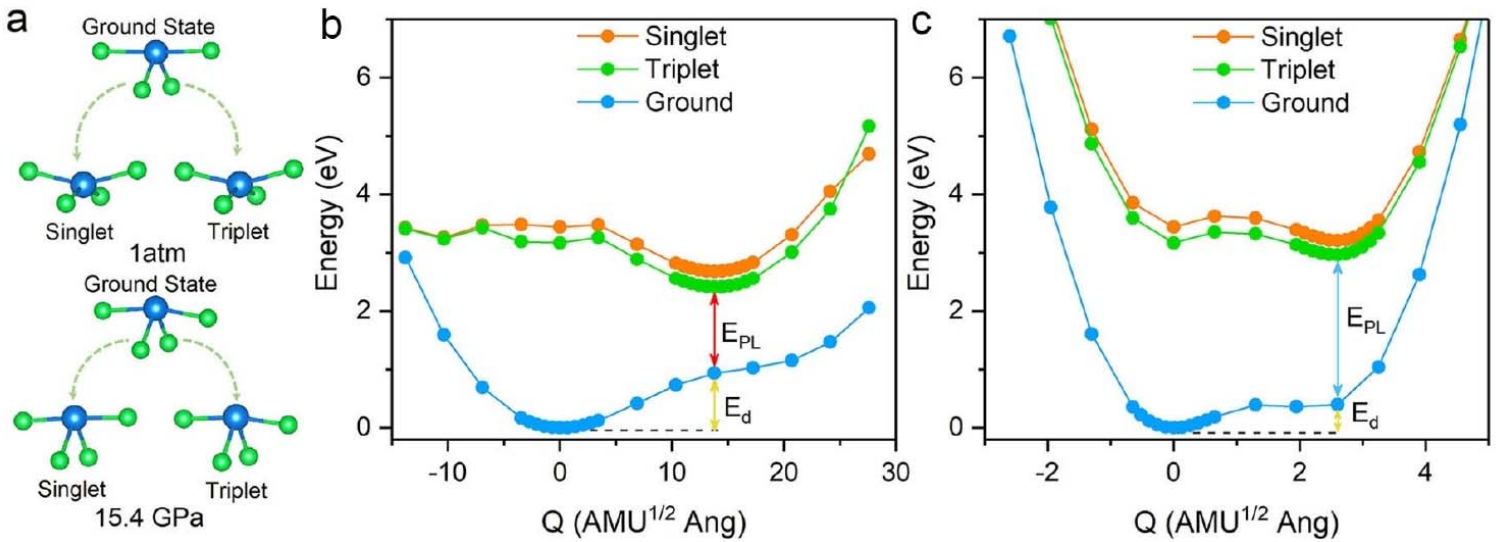
Zhang, Liu, Sun, …,**HJ***, J. Liu* and D. Xu*, ACIE, 60, 7587 (2021

Pressure tuning of lone-pair-driven luminescence in 0D tin halides

$(C_9NH_{20})_2SnBr_4$





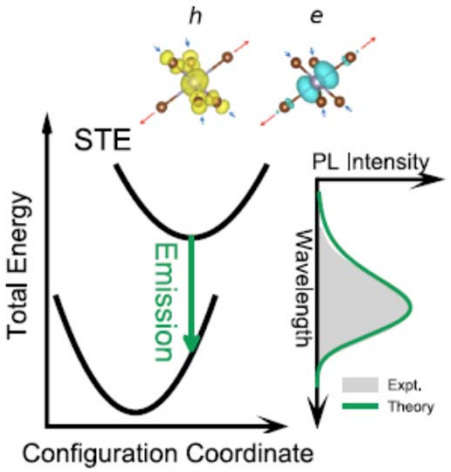


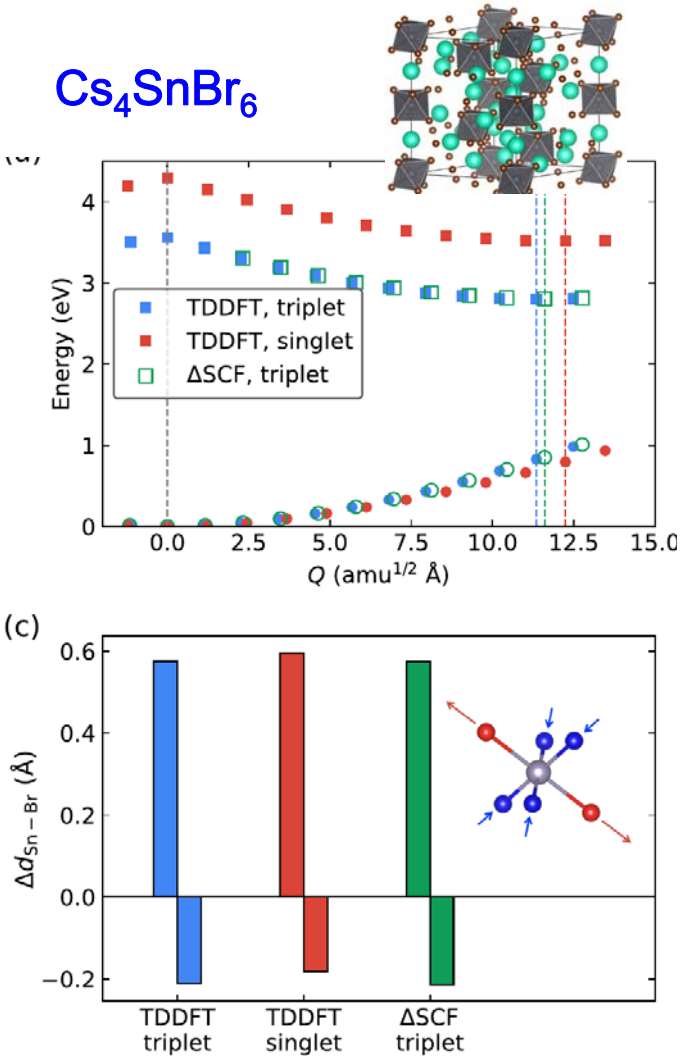
In collaboration with Prof. Kai Wang's group at Jilin Uni.

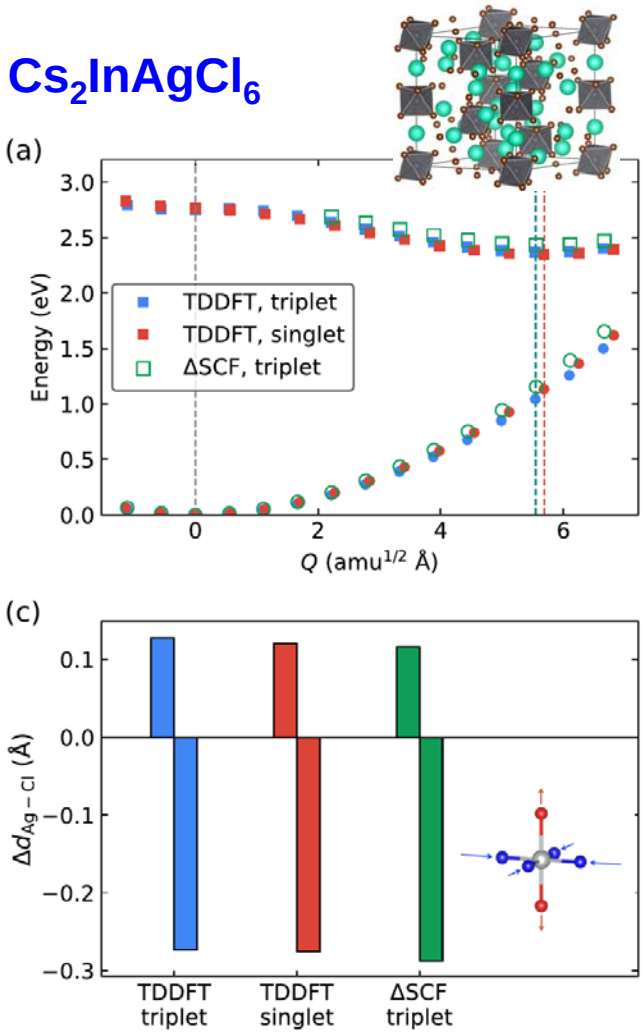
L. Zhang, S.Li, …, K. Wang*, H. Jiang*, L. Sui*, …,Bo Zou*, *ACIE* 62, e202311912 (2023).

Beyond OC-DFT: periodic TD hybrid-DFT

- Periodic TDDFT with dielectric-dependent hybrid functionals







Y. Jin, M. Rusishvili, M. Govoni, and G. Galli, *J. Phem. Chem. Lett.* 15, 3229 (2024).

Concluding remarks

- **Electronic excitations**, especially those of extended systems, are currently challenging frontiers of electronic structure theory.
- ***GW* method**: the state of the art for electronic band structure, but challenging to obtain numerically accurate results for some systems.
- ***GW*+BSE**: accurate for moderately correlated insulating systems, but computationally very expensive.
- **TD-hybrid:** capable to describe excitonic effects to some extent, an alternative to *GW*+BSE.
- Electronic excitations are always strongly coupled to nuclear dynamics

➔ Considerations of electron-phonon coupling are crucial

➔ Structural relaxation of electronic excited states, necessary for luminescence, even more challenging.