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Quasiparticle and electron-hole excitations in solids: theory and computation
(Part 1)

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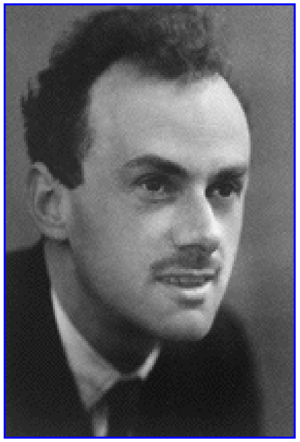
Outline

- Quasiparticle concept, quasiparticle band structure and band gap
- Quasiparticle equation, self-energy, and the GW approximation
- First-principles GW method
- Success and challenges of the GW method

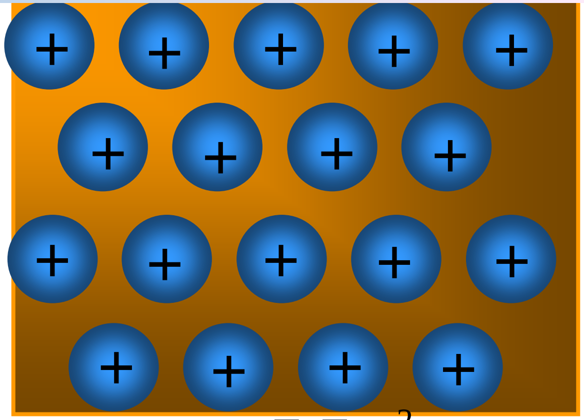
Materials properties from first-principles - A Hard Problem



"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus **completely known**, and the **difficulty** is only that the exact application of these laws leads to equations **much too complicated** to be soluble.”

- **Paul Dirac (1929)**

The many-body problem



- The Hamiltonian of a solid (any solids) is “trivial”

$$H = T^{e} + T^{ion} + V^{ee} + V^{e-ion} + V^{ion-ion}$$

$$T^{e} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^{2} \qquad T^{ion} = \sum_{i=1}^{M} -\frac{\hbar^2}{2M_j}\nabla_j^{2}$$

$$V^{ee} = \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} \qquad V^{e-ion} = -\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} \qquad V^{ion-ion} = \frac{1}{2}\sum_{i\neq j}\frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|}$$

- But solving the Schrodinger equation for a solid is hopelessly difficult

$$H\Psi(\{\vec{r}_i\},\{R_j\}) = E\Psi(\{\vec{r}_i\},\{R_j\})$$

Electron coordinates

Ion coordinates

- The use of the Born-Oppenheimer approximation decouples the motion of electrons from that of atoms, but we still have a many-electron problem

Materials properties from first-principles: Difficulties and efforts

$$H\psi = [\sum_{i=1}^{N}(-\frac{1}{2}\nabla_i^2 - \sum_{j=1}^{M}\frac{Z_j}{|\vec{r}_i - \vec{R}_j|}) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|}]\psi = E\psi$$

$$\psi = \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

$$E = <\psi | H | \psi>$$


Scanned at the American

- Early efforts:

- Hartree approximation: $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \approx \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\cdots\varphi_N(\vec{r}_N)$

- Hartree-Fock: $\psi(x_1, x_2, \ldots, x_N) \approx \det|\varphi_1(x_1)\,\varphi_2(x_2)\cdots\ \varphi_N(x_N)|$

$$[-\frac{1}{2}\nabla^2 + V^{e-ion} + V^H(\vec{r})]\varphi_i(\vec{r}) + \int V^X(\vec{r}, \vec{r}\,')\varphi_i(\vec{r}\,')d\vec{r}\,' = \varepsilon_i\varphi_i(\vec{r})$$

- Slater: Replaces the nonlocal exchange with a local potential

$$[-\frac{1}{2}\nabla^2 + V^{e-ion}(\vec{r}) + V^H(\vec{r}) + V^{ex}(\vec{r})]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

All these efforts relay on the wave functions.

Density functional theory (DFT)

$$E =< \Psi(\vec{r}_1, \vec{r}_1, \cdots \vec{r}_N) \,|\, H \,|\, \Psi(\vec{r}_1, \vec{r}_1, \cdots \vec{r}_N) >$$

X

$$\rho(\vec{r}) = N \int |\psi(\vec{r}, \vec{r}_2,, \cdots, \vec{r}_N)|^2 \, d\vec{r}_2 \cdots d\vec{r}_N$$

- In a paper published in 1964, Hohenberg and Kohn proved that the energy of a many-electron system is a universal functional of its charge density

$$E = E[\rho]$$

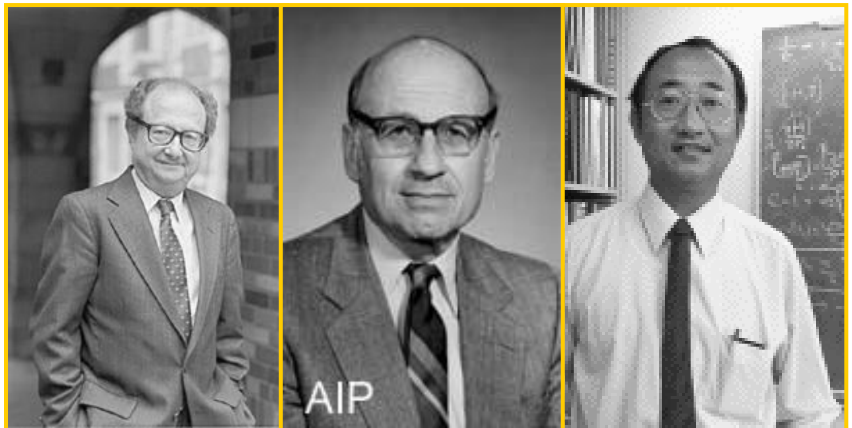
- In particular, the ground state energy of a many-electron system can be expressed as a universal functional of its ground state charge density

$$E_0 = E[\rho_0] \qquad \text{(Ground state energy)}$$

- The proof of this highly nontrivial fundamental theorem turns out to be surprisingly simple.

Density Functional Theory:
Electron Density as a Fundamental Variable

- In fact, the concept of “density functional” can be traced back to 1920’s.
  - In the Thomas-Fermi method, the electron density plays a central role.
- The Slater Xa potential can be regarded as an early version of LDA.
- DFT: Hohenberg and Kohn, 1964
  - The local electronic charge density can serve as a fundamental variable for solving many-body problems.
- Local density approximation (LDA): Kohn and Sham, 1965
  - Makes DFT useful and has been applied to various systems with great success.



The DFT band gap problem

- The success of the DFT-LDA is rather unexpected

> ***"we do not expect an accurate description of the chemical bonding" (within the LDA).*** **- Kohn and Sham, 1965**

- The "failure" of DFT-LDA: the DFT bandgap "problem"

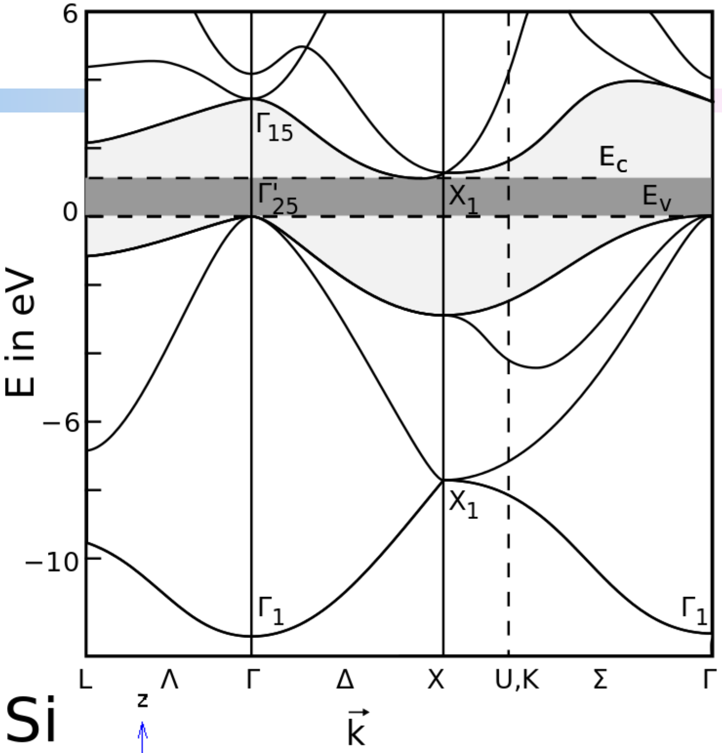
	LDA(eV)	*Exp (eV)*
diamond	3.9	5.48
Silicon	0.52	1.17
Germanium	~0	0.74
LiC	6.0	9.4

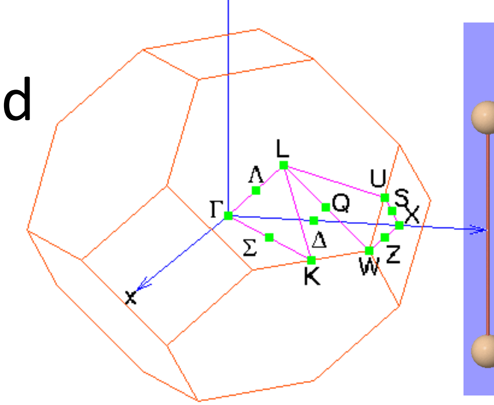
- The occupied band width of Na is significantly overestimated
  - 3.2 eV (LDA) vs 2.5 eV (exp)

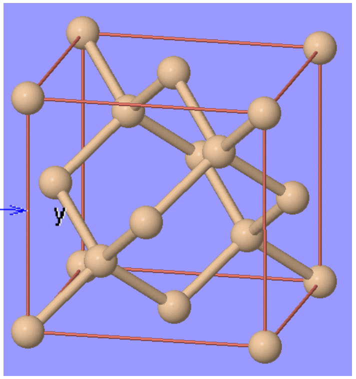
KS orbital energies are fictitious parameters; they cannot be interpreted as the quasiparticle energies.

But what is the (quasiparticle) band gap

- Take, for example, a band structure of Si (often calculated using DFT methods)
- We can "calculate" the direct gap at Γ, indirect minimum gap, etc, by taking the energy difference between valence and conduction states
- What about experiment? How do we measure the "band gap", or more general, how do we measure the band structure of a solid?
- What are quasiparticles?







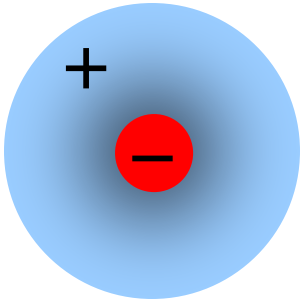
Quasiparticles

- In an interacting system (e.g., electrons in a solid), what is the meaning of one-particle states?
- Consider an electron moving in a solid: Electron will considerably distort the charge distribution of its surrounding as it moves.

  (1) Pauli exclusion principle (exchange hole, or fermi hole)

  (2) Coulomb repulsion (Coulomb hole, or correlation hole)

  (3) Electron will also cause distortions of ions (lattice)
- All these effects (interactions) introduce a positive charge cloud (or depletion of negative charge), i.e, a hole, around an electron



Quasiparticles and the self-energy

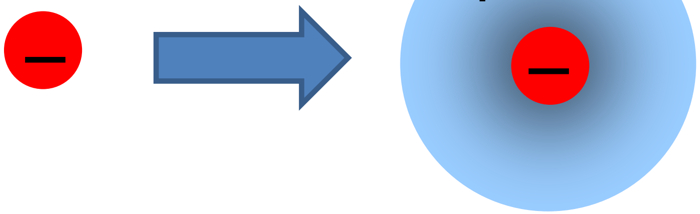
- We are not dealing with just a bare electron but an electron dressed with a positive polarization cloud

Quasiparticle:

electron + polarization cloud

QP energy:

non-interacting + self-energy



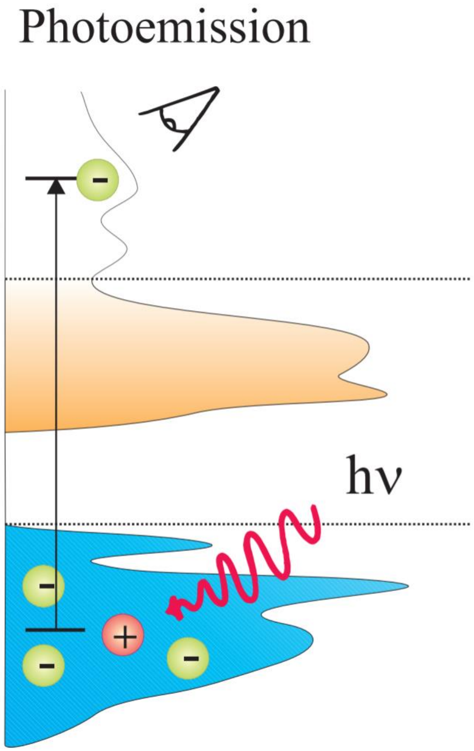
- The quasiparticles energy now has both real and imaginary parts:

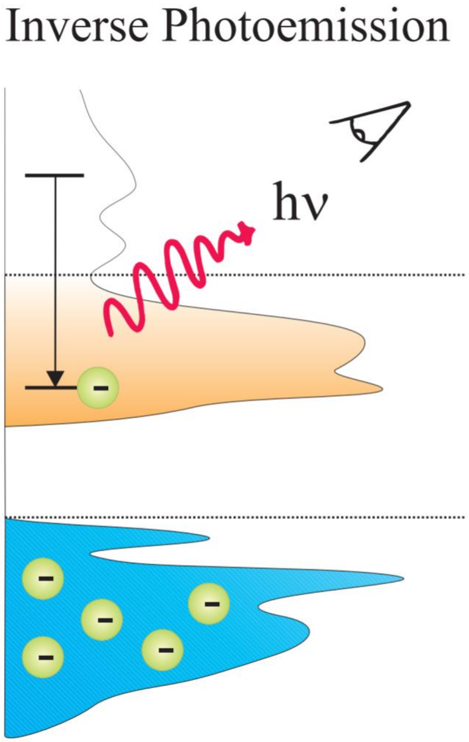
$$\begin{cases} \varepsilon_{n\vec{k}} = \varepsilon^{0}_{n\vec{k}} + \Sigma_{n\vec{k}} \\ \Sigma_{n\vec{k}} = \Delta\varepsilon_{n\vec{k}} + i\Gamma_{n\vec{k}} \end{cases}$$

- How do we measure these quasiparticle states?
- How do we calculate this self-energy

Measuring the (quasiparticle)band structures

- How do we measure “band structures”?





Occupied (valence) states

N to N-1 particles

Unoccupied (conduction) states

N to N+1 particles

What is the (qusiparticle) band gap?

- Quasiparticle energy of occupied state s: $\varepsilon_s = E_0(N) - E_s(N-1)$
- Quasiparticle energy of unoccupied state s: $\varepsilon_s = E_s(N+1) - E_0(N)$

$$\boxed{E_0(N): \text{Ground state energy of the N-electron system}}$$

- (minimum) Quasiparticle band gap

$$\begin{aligned} E_g &= [E_0(N+1) - E_0(N)] - [E_0(N) - E_0(N-1)] \\ &= E_0(N+1) + E_0(N-1) - 2E_0(N) \end{aligned}$$

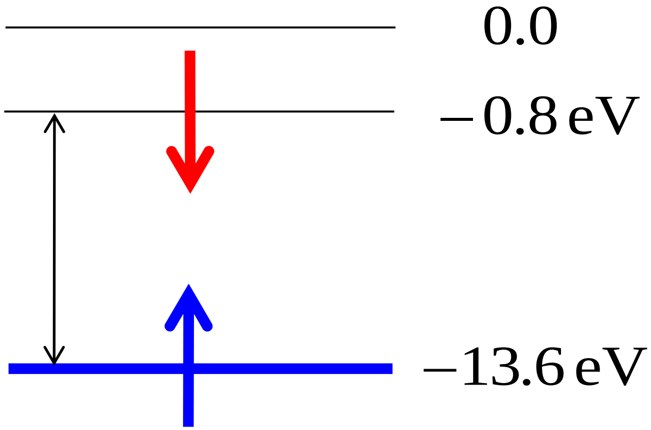
- The quasiparticle gap is actually related to the total energies of three different systems with N, N-1, and N+1 particles!
- Clearly, one cannot use the Kohn-Sham DFT eigen values to calculate the quasiparticle band gap (or more general, the quasiparticle band structure)

Quasiparticle gap of a hydrogen atom

$$
\begin{aligned}
E_g &= [E_0(N+1) - E_0(N)] - [E_0(N) - E_0(N-1)] \\
&= E_0(N+1) + E_0(N-1) - 2E_0(N) \\
&= [E_0(N+1) - E_0(N)] - [E_0(N) - E_0(N-1)] \\
&= IP - EA
\end{aligned}
$$

- For a hydrogen atom:

$$
\begin{aligned}
E_g &= IP - EA \\
&= 13.6 - 0.8 \\
&= 12.8\,\text{eV}
\end{aligned}
$$



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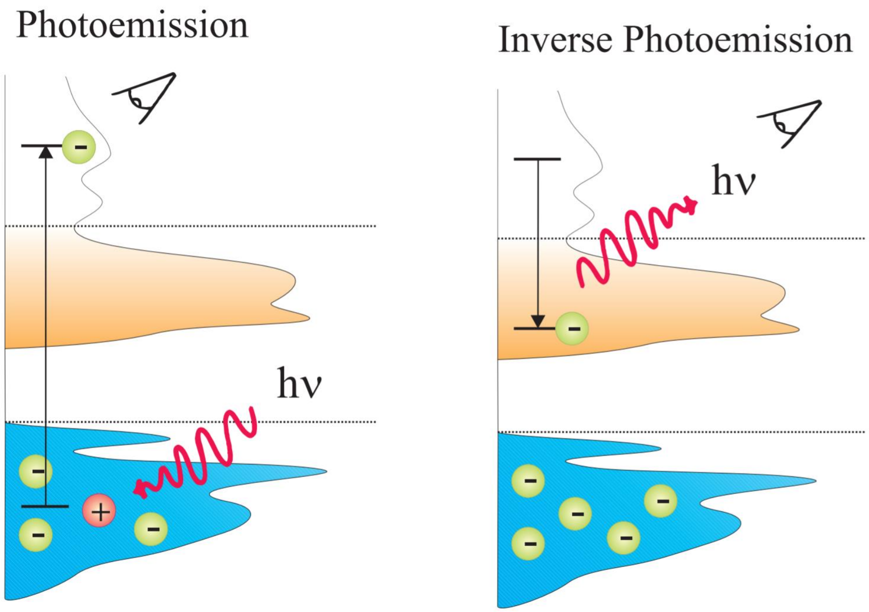
Green function

- Green function (GF) contains spectral information on single-particle excitations changing the number of particles by one:

$$G(\vec{r},\vec{r}',\omega)=\sum_{k}\frac{g_{\vec{k}}(\vec{r})g^{*}_{\vec{k}}(\vec{r}')}{\omega-(E^{N+1}_{\vec{k}}-E^{N}_{0})+i\delta}+\sum_{k}\frac{f_{\vec{k}}(\vec{r})f^{*}_{\vec{k}}(\vec{r}')}{\omega(E^{N-1}_{\vec{k}}-E^{N}_{0})-i\delta}$$

With quasiparticle amplitudes:

$$\begin{cases} g_{\vec{k}}(\vec{r}) = <\Psi^{N}_{0}\,|\hat{\psi}(\vec{r})|\,\Psi^{N+1}_{\vec{k}}> \\ f_{\vec{k}}(\vec{r}) = <\Psi^{N-1}_{\vec{k}}\,|\hat{\psi}(\vec{r})|\,\Psi^{N}_{0}> \end{cases}$$



Green function

- The poles of the GF give the corresponding excitation energies.
- The spectral function

$$A(\vec{r},\vec{r}\,',\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,G(\vec{r},\vec{r}\,',\omega)$$

$$= \sum_{k} g_{\vec{k}}(\vec{r})g^{*}_{\vec{k}}(\vec{r}\,')\delta(\omega - E^{N+1}_{\vec{k}} + E^{N}_{0}) + f_{\vec{k}}(\vec{r})f^{*}_{\vec{k}}(\vec{r}\,')\delta(\omega - E^{N}_{0} + E^{N-1}_{\vec{k}})$$

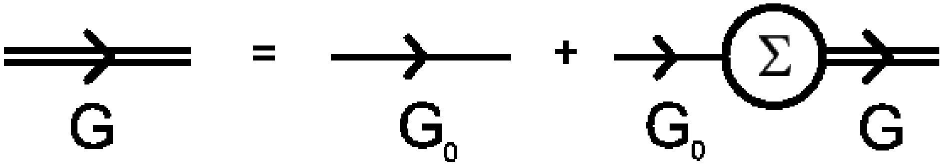
gives the quasiparticle density of states (DOS)

- For non-interacting systems (like KS systems), the spectral function is just the DOS calculated from the KS eigen states.

$$A(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,G_0(\omega)$$

Dyson equation and self-energy

- The Dyson equation: Relation between the bare and dressed propagators and the self-energy



$$G = G_0 + G_0 \Sigma G$$

- G_0 is just the propagator of the non-interacting particle

$$(\omega - H_0) G_0(\vec{r}, \vec{r}', \omega) = \delta(\vec{r} - \vec{r}')$$

- And G is call full propagator

$$(\omega - H) G(\vec{r}, \vec{r}', \omega) = \delta(\vec{r} - \vec{r}')$$

$$(\omega - H_0 - \Sigma) G(\vec{r}, \vec{r}', \omega) = \delta(\vec{r} - \vec{r}')$$

Quasiparticle equation

- Another form of Dyson equation: Quasiparticle equation

$$H^0\psi_{nk}^{Qp}(\vec{r})+\int\Sigma(\vec{r},\vec{r}'',E_{nk}^{QP})\psi_{nk}^{Qp}(\vec{r}'')d\vec{r}''=E_{nk}^{QP}\psi_{nk}^{Qp}(\vec{r})$$

$$H^0=T+V^H+V^{ext}:\ \text{One electron Hamiltonian}$$

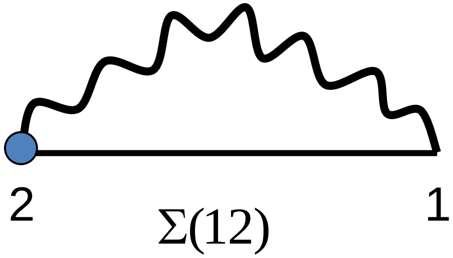
- The self-energy contains all effects of e-e interactions
- Compare with the Kohn-Sham equation

$$[H+V_{xc}(\vec{r})]\psi_{nk}^{KS}(\vec{r})=E_{nk}^{KS}\psi_{nk}^{KS}(\vec{r})$$

- One of the difficulties of quasiparticle calculations is that the self-energy is nonlocal, non-Hermitian, and energy dependent.
- Approximation to the self-energy:
  - The Hartree-Fock approximation: $\Sigma^{HF}(\vec{r},\vec{r}')=V^{ex}(\vec{r},\vec{r}')$
  - The LDA approximation: $\Sigma^{LDA}(\vec{r},\vec{r}')=V^{xc}(\vec{r})\delta(\vec{r},\vec{r}')$

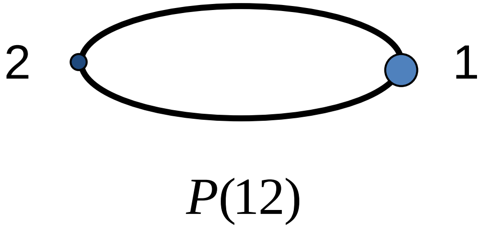
The Hedin equations for the self-energy

- Hedin's equations for the self-energy



Self-energy $$\Sigma(12) = i\int W(1^{+}3)G(14)\Gamma(42;3)d(34)$$

Screened Coul. $$W(12) = \int v(13)\varepsilon^{-1}(32)d(3)$$



Polarizability $$P(12) = -i\int G(23)G(42)\Gamma(34;1)d(34)$$

Vertex function $$\Gamma(12;3) = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(67;3)d(4567)$$

- Has to be solve iteratively (self-consistently)

- Extremely difficult!

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

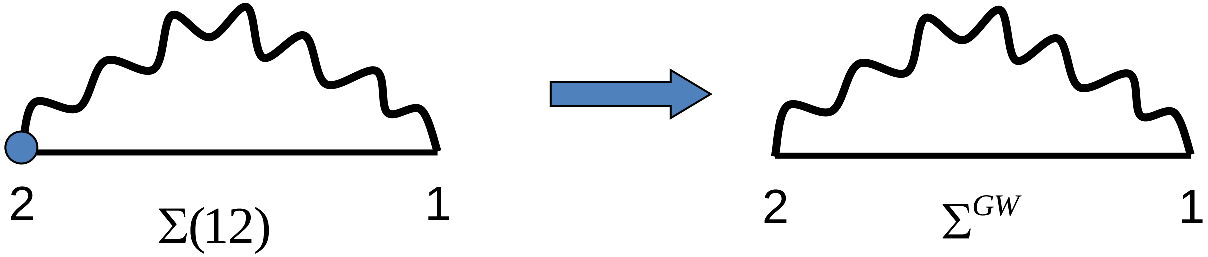
The GW approximation

- The GW approximation:

$$\Sigma(12) = i\int W(1^{+}3)G(14)\Gamma(42;3)d(34)$$

$$\Gamma(12;3) = \delta(12)\delta(13) + \int \xcancel{\frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(67;3)d(4567)}$$

$$\Gamma(12;3) = \delta(12)\delta(13) \Rightarrow \Sigma(12) = iW(1^{+}2)G(12)$$

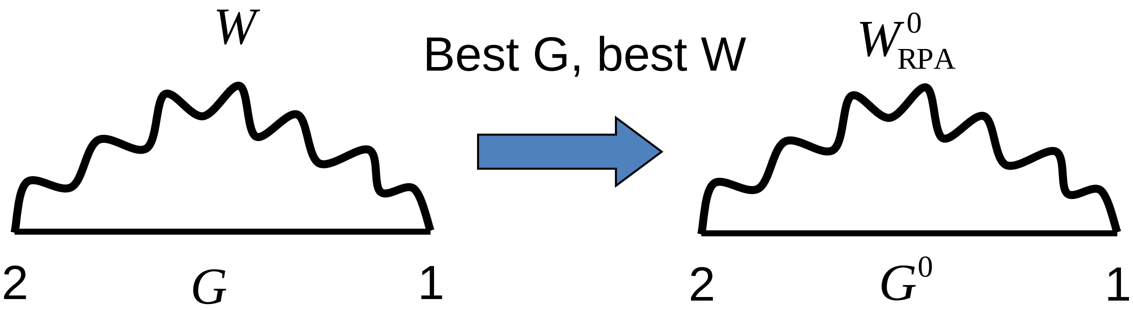


The G^0W^0 approximation

- Still, G is the fully-interacting one-body Green function; one still has to solve the following equations self-consistently (and it turns out to be a bad idea to do so):

$$H^0(r)\psi^{Qp}_{nk}(r)+\int\Sigma(r,r',E^{QP}_{nk})\psi^{Qp}_{nk}(r')dr'=E^{QP}_{nk}\psi^{Qp}_{nk}(r)$$

- The G^0W^0 approximation



$$\begin{cases} \Sigma = iG^0W^0_{RPA} \\ W^0_{\mathrm{RPA}} = \varepsilon^{-1}_{\mathrm{RPA}}v \\ \varepsilon^{-1}_{\mathrm{RPA}} = [1-vP^0]^{-1} \\ v:\text{bare Coulomb potential} \end{cases}$$

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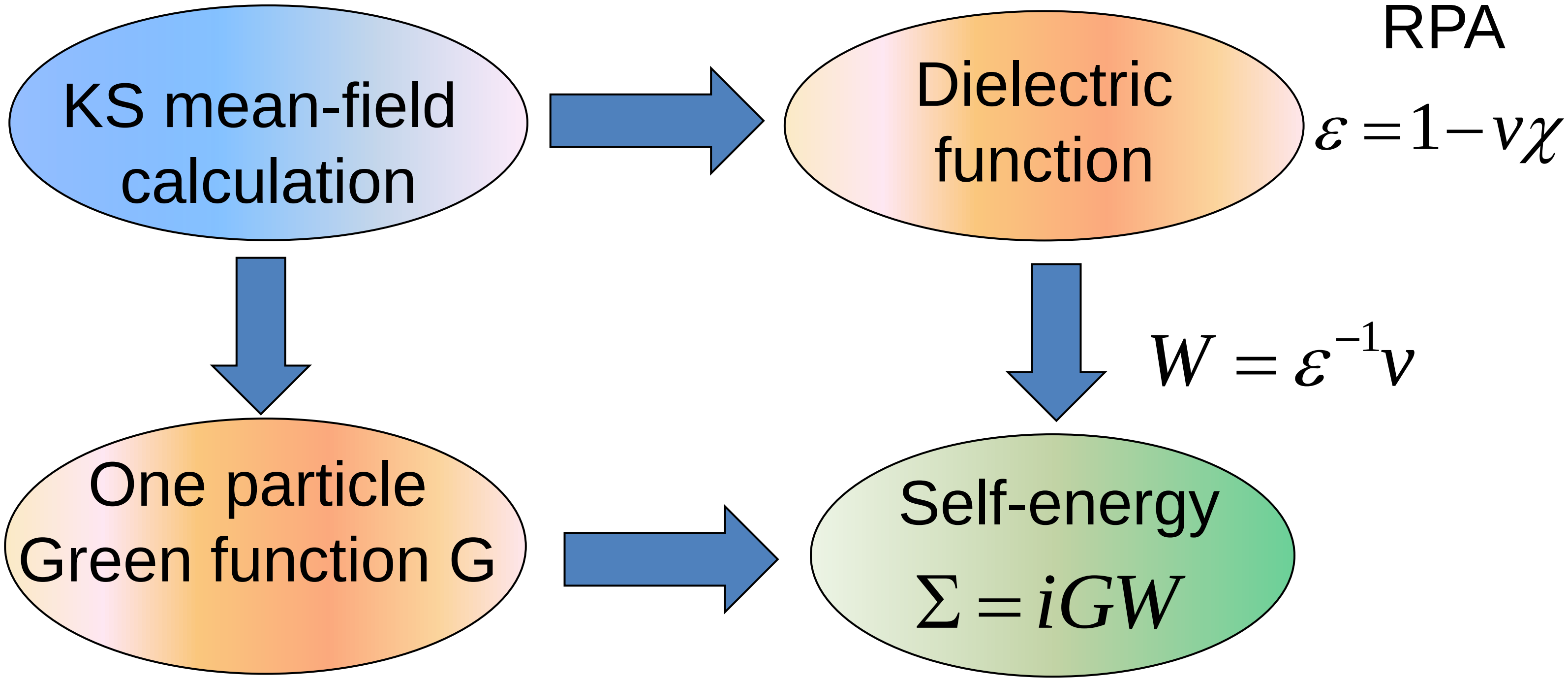
First-principles GW method



KS mean-field calculation

Dielectric function

RPA

$\varepsilon = 1 - v\chi$

$W = \varepsilon^{-1} v$

One particle Green function G

Self-energy

$\Sigma = iGW$

$$\Sigma = i\int \frac{dE'}{2\pi} e^{-i\delta E'} G(\mathbf{r}, \mathbf{r}'; E - E')\, W(\mathbf{r}, \mathbf{r}'; E')$$

Hybertsen and Louie, 1986

First-principles GW method

- Formally, the electron self-energy within the GW approximation can be written as

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

$$G(\vec{r},\vec{r}\,',\omega)=\sum_{n\vec{k}}\frac{\varphi_{n\vec{k}}(\vec{r})\varphi^{*}_{n\vec{k}}(\vec{r}\,')}{\omega-\varepsilon_{n\vec{k}}-i\delta_{n\vec{k}}} \quad (\delta_{n\vec{k}}=0^{+}\text{ if }\varepsilon_{n\vec{k}}<\mu;\delta_{n\vec{k}}=0^{-}\text{ if }\varepsilon_{n\vec{k}}>\mu)$$

- The screened Coulomb interaction in momentum space:

$$W(\vec{r},\vec{r}\,',\omega)=\sum_{\vec{q},\vec{G},\vec{G}'}e^{i(\vec{q}+\vec{G})\cdot\vec{r}}W_{\vec{G}\vec{G}'}(\vec{q},\omega)e^{-i(\vec{q}+\vec{G}')\cdot\vec{r}\,'}$$

$$W_{\vec{G}\vec{G}'}(\vec{q},\omega)=\varepsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q},\omega)v(\vec{q}+\vec{G}')$$

$$v(\vec{q})=\frac{4\pi}{q^{2}}\text{ is the Fourier transform of the Coulomb potential}$$

First-principles GW method

- A critical step in first-principles GW method is the calculation of the dielectric matrix, therefore the screened Coulomb interaction W

$$W_{\vec{G}\vec{G}'}(\vec{q},\omega) = \varepsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q},\omega) v(\vec{q}+\vec{G}')$$

- In the exercise, we will not calculate the full frequency-dependent dielectric matrix (or screened Coulomb interaction).
- Instead, we will use the so-called Hybertsen-Louie generalized plasmon pole (HL-GPP) model to extend the calculated static dielectric matrix to finite frequencies
- More details can be found in

PRB 34, 5390 (1986)
Compt. Phys. Commun. 183, 1269 (2012)

First-principles GW method

- The static dielectric function is related to the (irreducible) electron polarizability

$$\chi_{\vec{G}\vec{G}'}(\vec{q}) = \sum_{n,n',\vec{k}} M_{nn'}(\vec{k},\vec{q},\vec{G}) M^{*}_{nn'}(\vec{k},\vec{q},\vec{G}') \frac{f_{n',\vec{k}+\vec{q}} - f_{n,\vec{k}}}{\varepsilon_{n',\vec{k}+\vec{q}} - \varepsilon_{n,\vec{k}}}$$

via $\varepsilon_{\vec{G}\vec{G}'}(\vec{q}) = \delta_{\vec{G}\vec{G}'} - \dfrac{4\pi}{(\vec{q}+\vec{G})^2} \chi_{\vec{G}\vec{G}'}(\vec{q})$

where $M_{nn'}(\vec{k},\vec{q},\vec{G}) = < n,\vec{k} \,|\, e^{-i(\vec{q}+\vec{G})\cdot\vec{r}} \,|\, n',\vec{k}+\vec{q} >$

and $\varepsilon_{n,\vec{k}}$, and $f_{n,\vec{k}}$ are the KS eigenvalue and the Fermi occupation function of state $| n,\vec{k} >$

First-principles GW method

- We have now all ingredients to calculate the electron self-energy
- The quasiparticle energy of a given state:

$$E_{n\vec{k}}^{QP} = \varepsilon_{n\vec{k}}^{KS} + < n\vec{k} \,|\, \Sigma_{n\vec{k}}(\vec{r},\vec{r}\,',E_{n\vec{k}}^{QP}) \,|\, n\vec{k} > - < n\vec{k} \,|\, V_{xc}^{KS} \,|\, n\vec{k} >$$

- Still, the self-energy has to be calculated at the quasiparticle energy, which we do not know until we calculate the self-energy!

- If the self-energy $\Sigma_{n\vec{k}}(\omega) =< n\vec{k} \,|\, \Sigma_{n\vec{k}}(\vec{r},\vec{r}\,',\omega) \,|\, n\vec{k} >$ is a slow-varying function of ω, we can carry out a first-order expansion:

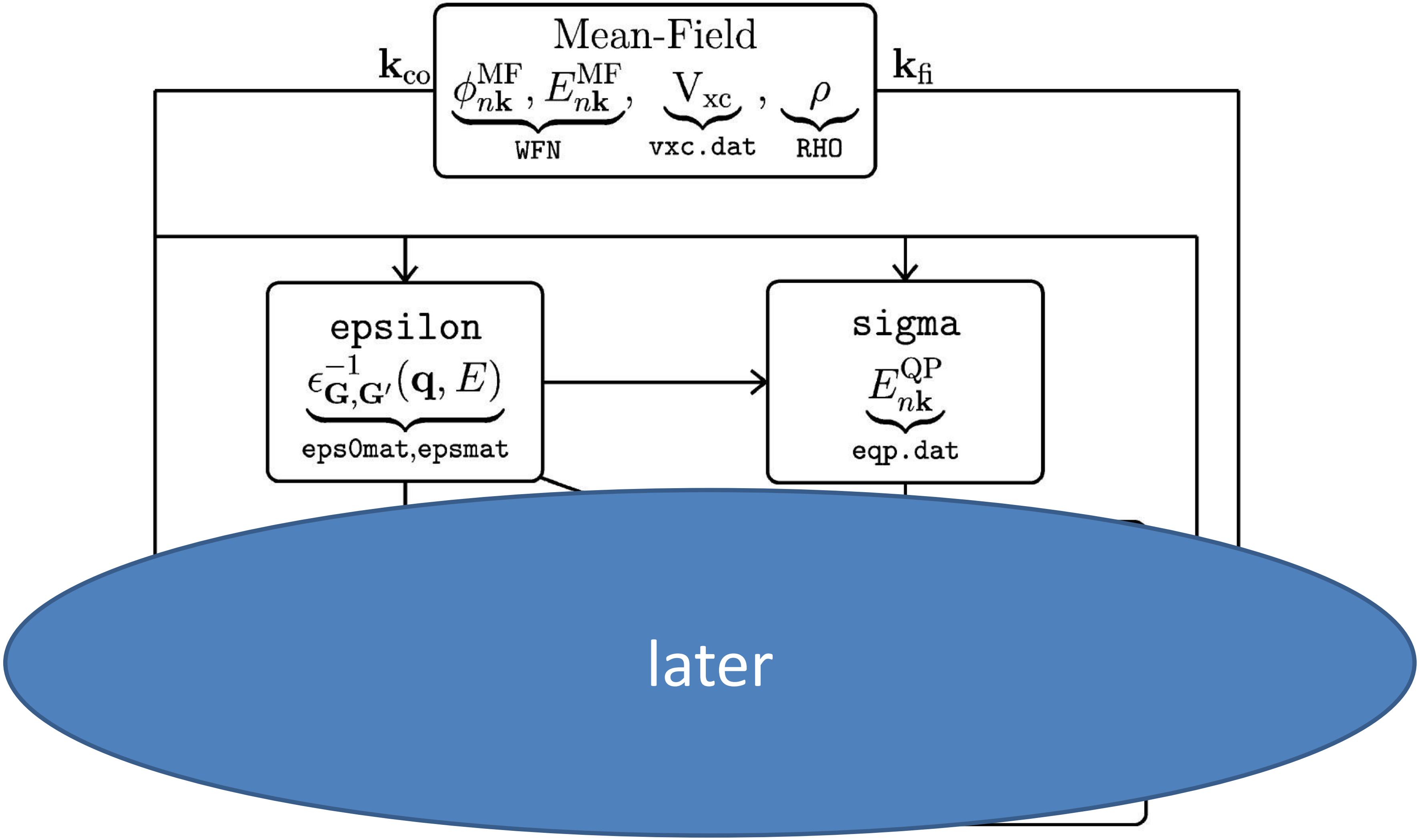
$$E_{n\vec{k}}^{QP} = E_{n\vec{k}}^{0} + Z_{nk} \cdot (E_{n\vec{k}}^{0} - \varepsilon_{n\vec{k}}^{KS})$$

where $E_{n\vec{k}}^{0} = \varepsilon_{n\vec{k}}^{KS} + < n\vec{k} \,|\, \Sigma_{n\vec{k}}(\vec{r},\vec{r}\,',\varepsilon_{n\vec{k}}^{KS}) \,|\, n\vec{k} > - < n\vec{k} \,|\, V_{xc}^{KS} \,|\, n\vec{k} >$

and

$Z_{nk} = \dfrac{d\Sigma_{n\vec{k}}(E)/dE}{1 - d\Sigma_{n\vec{k}}(E)/dE}$ is called quasiparticle renormalization factor

The BerkeleyGW package (https://berkeleygw.org/)



Computer Physics Communications 183, 1269 (2012)

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Success of the GW method

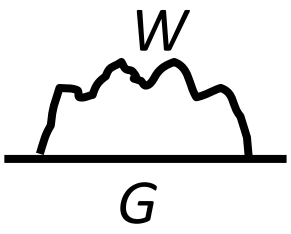
$$E^{QP}_{n\vec{k}} = \varepsilon^{KS}_{n\vec{k}} + < n\vec{k} \,|\, \Sigma - V_{xc} \,|\, n\vec{k} >$$

$$\Sigma^{GW} = iGW$$

G : electron Green function

W : screened Coulomb interaction

$$\Sigma^{GW} =$$



	LDA (eV)	*GWA$^{(a)}$ (eV)*	*Exp (eV)*
diamond	3.9	**5.6**	**5.48**
Silicon	0.52	**1.29**	**1.17**
Germanium	~0	**0.75**	**0.74**
LiC	6.0	**9.1**	**9.4**

Typical accuracy of ab initio G^0W^0 methods: ~ 0.1 – 0.2 eV

Hedin, 1965; Hybertsen and Louie, 1986

Not all materials are “GW friendly”

- The band gap of InN was found to be 0.7 ~ 0.8 eV in 2002! By experimentalists!!! Previously “accepted” value was 1.9 eV
  - What have theorists been doing???

- ZnO: LDA band gap: 0.7 eV
  - Earlier GW calculations by several groups: 1.5 ~ 2.5 eV
  - Experimental gap: ~ 3.6 eV

- CuCl: LDA band gap: 0.32 eV
  - “Straightforward” GW calculations give Eg < 2.0 eV
  - Experiment: 3.4 eV

- GWA does not work for these materials?

- The devil is in the detail: Convergence behavior of several truncation parameters has to be carefully examined!

The dielectric function

- The dielectric function: $\varepsilon = 1 - v\chi^0$

$$\chi^0_{\boxed{\mathbf{G},\mathbf{G}'}}(\mathbf{q},\omega) = \frac{1}{2}\boxed{\sum_{c,v,\mathbf{k}}} M_{vc}(\mathbf{k},\mathbf{q},\mathbf{G}) M^*_{vc}(\mathbf{k},\mathbf{q},\mathbf{G}')\times$$

$$\left(\frac{1}{E_{v\mathbf{k}+\mathbf{q}} - E_{c\mathbf{k}} - \omega + i\delta} + \frac{1}{E_{v\mathbf{k}+\mathbf{q}} - E_{c\mathbf{k}} + \omega + i\delta}\right)$$

- Two truncation parameters in practical calculations

  - Number of conduction bands (Nc) included in the summation
  - Kinetic energy cutoff (G_{cut}) for the dielectric matrix $\varepsilon_{GG'}(q,\omega)$

- In practical calculations, truncations are almost always applied
  - Nc number of conduction bands needed to converge the GW results scales with the system volume
  - Nc and anc G_{cut} are both highly materials dependent

The Coulomb-hole self-energy

- The self-energy is usually decomposed into two terms

$$\Sigma(r,r';E)=\Sigma_{\mathrm{SX}}(r,r';E)+\Sigma_{\mathrm{CH}}(r,r';E)$$

where $\Sigma_{\mathrm{SX}}:\text{screened exchange};\quad \Sigma_{\mathrm{CH}}:\text{Coulomb hole}$

$$<\Sigma_{\mathrm{CH}}>_{n\vec{k}}=\frac{1}{2}\boxed{\sum_{m}^{\text{all states}}}\sum_{\vec{q},\vec{G},\vec{G}'}[M_{\vec{G}}^{n,m}(\vec{k},\vec{q})]^{*}M_{\vec{G}'}^{n,m}(\vec{k},\vec{q})[\frac{\Omega_{\vec{G}\vec{G}'}^{2}(\vec{q})}{\tilde{\omega}_{\vec{G}\vec{G}'}(\vec{q})[E-\varepsilon_{m,\vec{k}-\vec{q}}-\tilde{\omega}_{\vec{G}\vec{G}'}(\vec{q})]}]v(\vec{q}+\vec{G}')$$

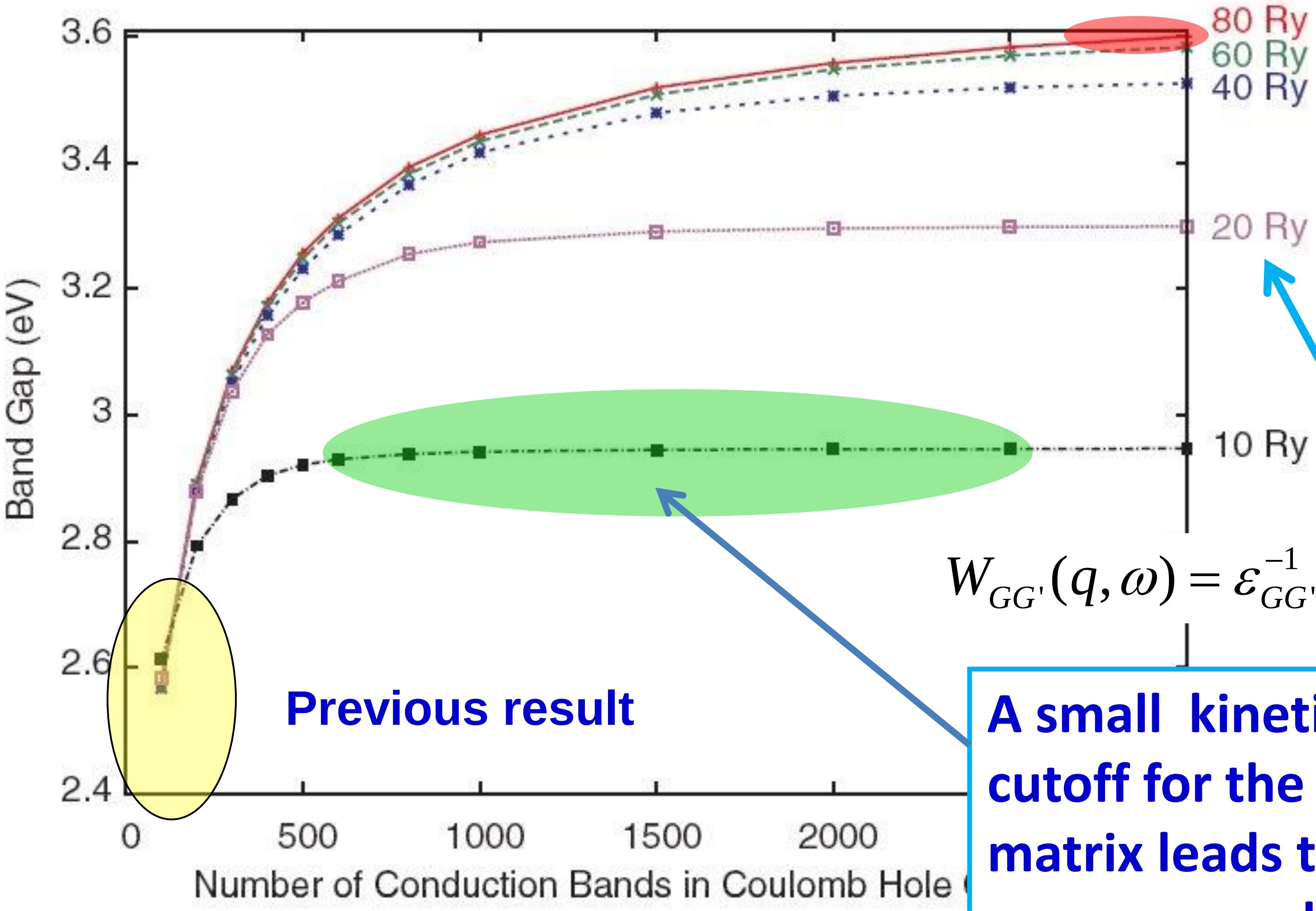
$$M_{\mathbf{G}}^{nm}(\mathbf{k},\mathbf{q})=\langle m\mathbf{k}-\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n\mathbf{k}\rangle$$

- The summation in principle should include ***all*** conduction bands

Convergence issues in GW calculations

- Two important cutoff parameters:
  - Band summation
  - Kinetic energy cutoff of the dielectric matrix $\begin{cases} \varepsilon_{GG'}(\vec{q}) \\ E_{cut} = |G_{cut}|^2 / 2 \end{cases}$
- The convergence issue in GW calculations is well recognized but often "ignored" (sometimes intentionally)
  - Hard to perform convergence tests for all GW calculations
  - For some materials (e.g., Si, Ge), GW results may converges quickly
  - For others (e.g. ZnO, MgO, CuCl), unconverged results may lead to false predictions and/or wrong interpretations

Quasiparticle Gap of ZnO (LDA+U/GW)



experiment

Previous result

$$\varepsilon_{GG'}(\vec{q})$$

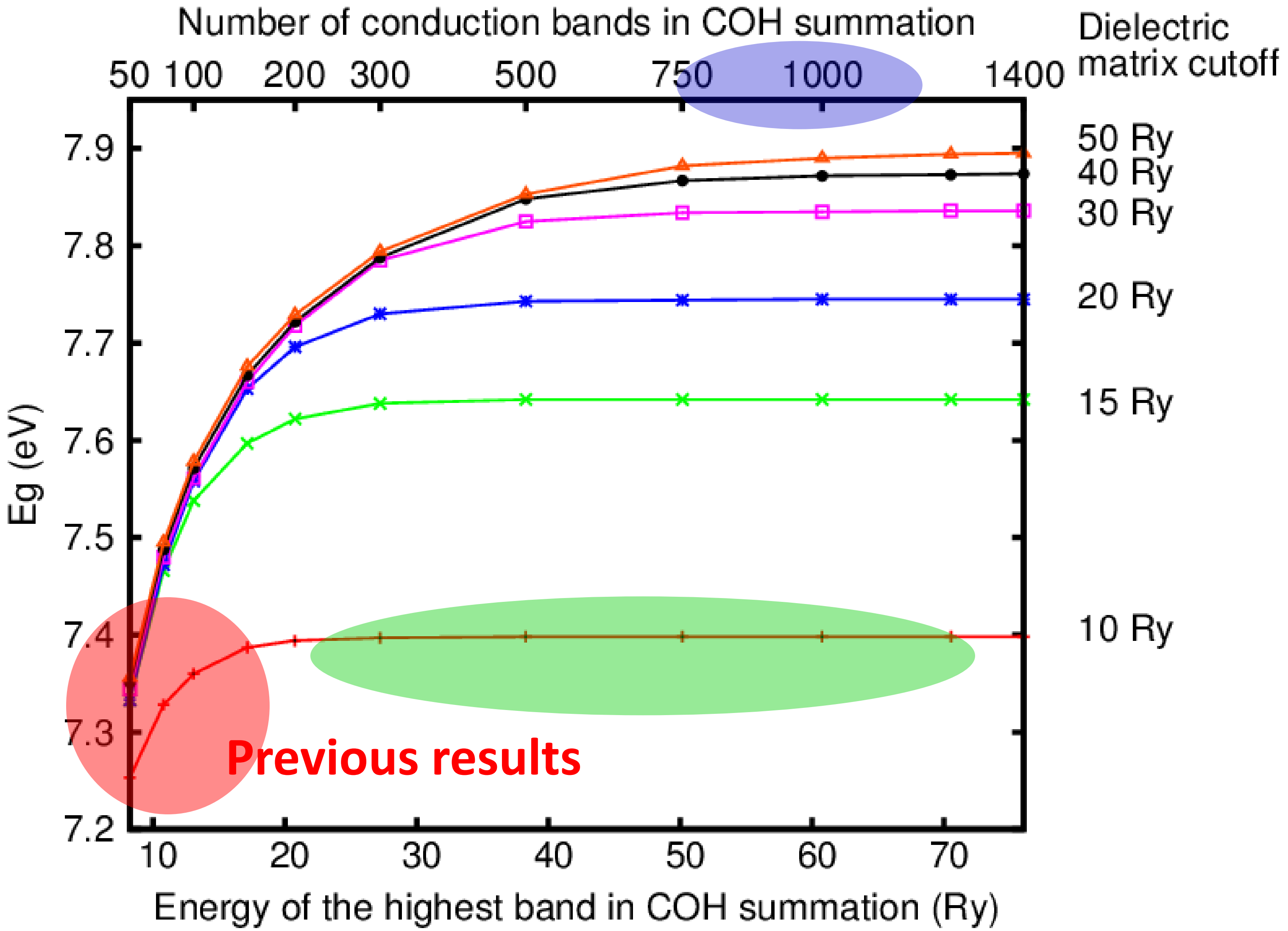
$$E_{cut} = |G_{\max}|^2 / 2$$

$$W_{GG'}(q,\omega) = \varepsilon^{-1}_{GG'}(q,\omega) v(q+G')$$

A small kinetic energy cutoff for the dielectric matrix leads to a false convergence behavior

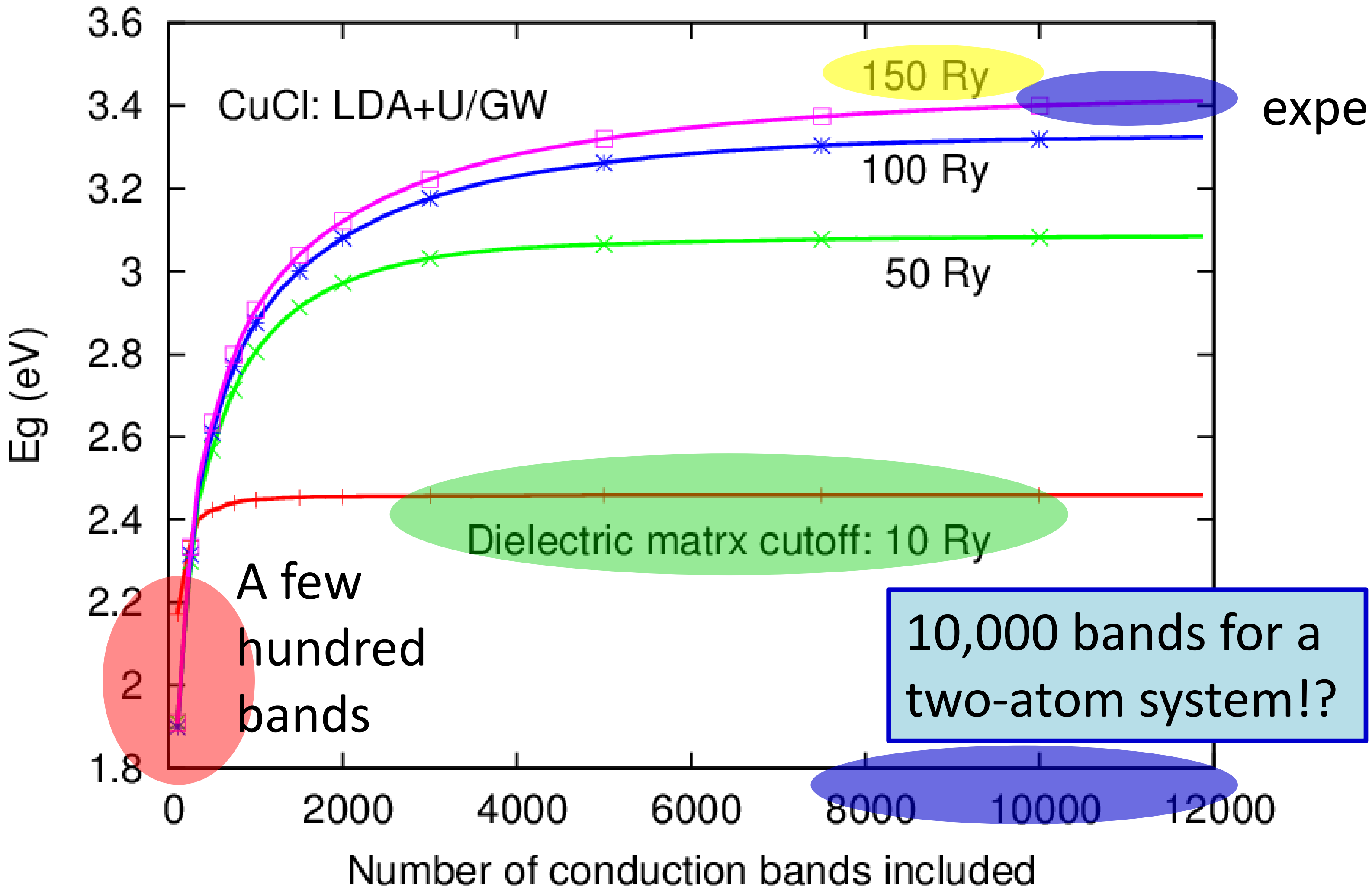
PRL 105, 146401 (2010)

Quasiparticle gap of MgO



Scientific Reports **6**, 36849 (2016).

Quasiparticle gap of CuCl



experiment

A few hundred bands

10,000 bands for a two-atom system!?

PRB **98**, 045108 (2018)

Systems with d-states

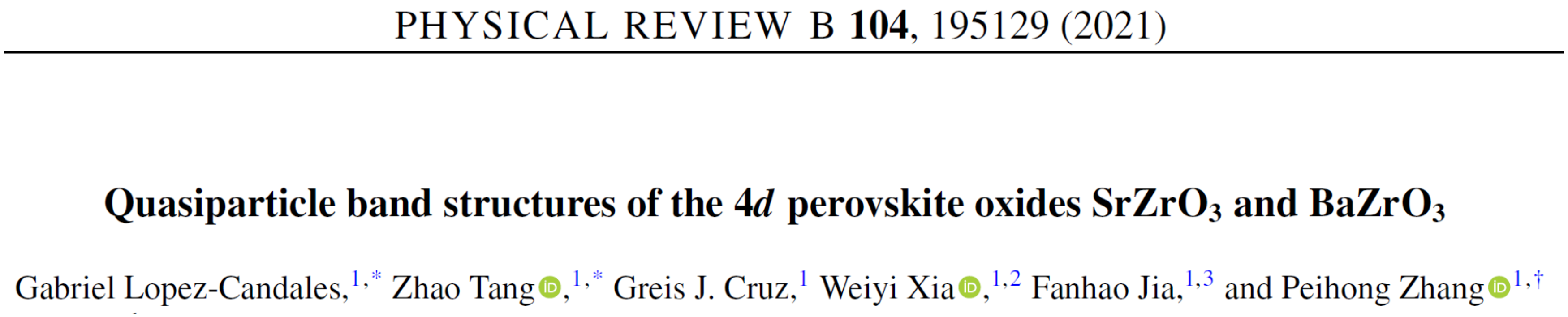
- GW calculations for systems involving localized d states and oxides are particular challenging due to the computational costs (high cutoffs and large number of bands), the slow convergence, and the poor DFT description of the correlated d electrons
- Fortunately, with our newly developed accelerated methods (more later) and the development of combined DFT+U and GW, we are now able to accurate predict the quasiparticle properties of oxides (ZnO discussed earlier, SrTiO3, BaTiO3, SrZrO3, etc)

Systems with d-states

PHYSICAL REVIEW B **103**, 035128 (2021)

Quasiparticle band structure of $SrTiO_3$ and $BaTiO_3$: A combined LDA + U and G^0W^0 approach

Gabriel Lopez-Candales,[1] Zhao Tang,[1] Weiyi Xia,[1] Fanhao Jia,[1,2] and Peihong Zhang[1,*]

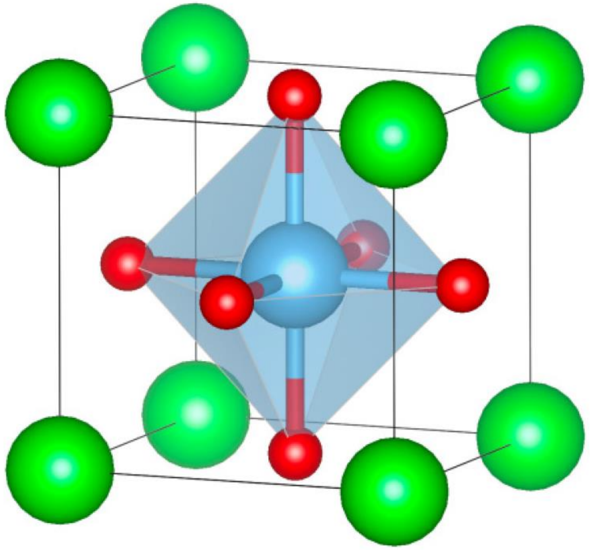


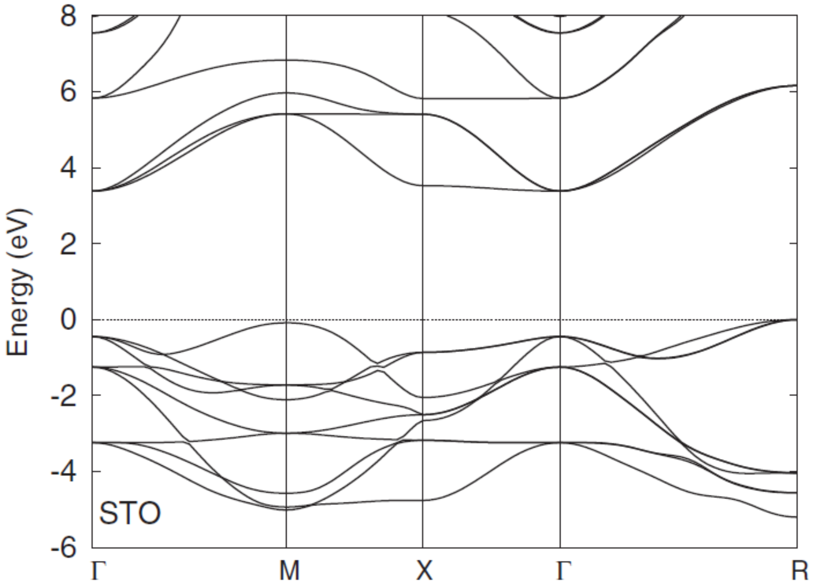
PHYSICAL REVIEW B **104**, 195129 (2021)

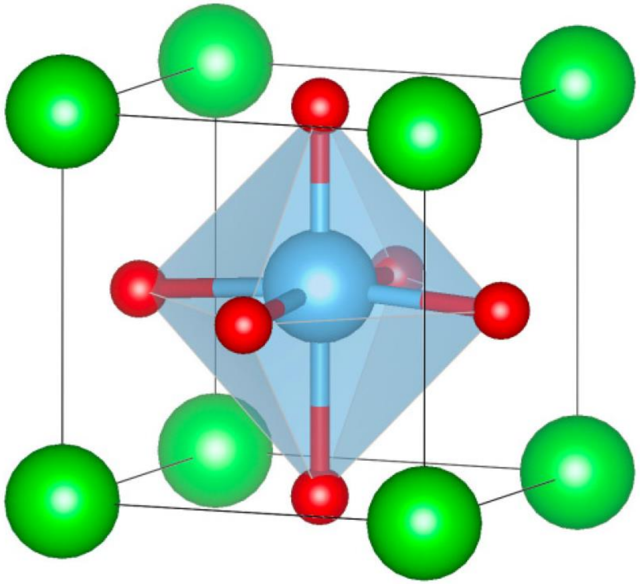
Quasiparticle band structures of the 4*d* perovskite oxides $SrZrO_3$ and $BaZrO_3$

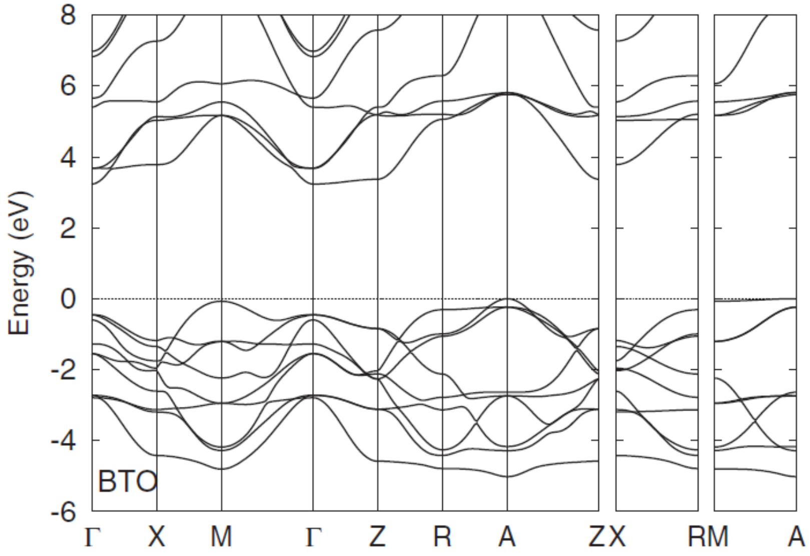
Gabriel Lopez-Candales,[1,*] Zhao Tang,[1,*] Greis J. Cruz,[1] Weiyi Xia,[1,2] Fanhao Jia,[1,3] and Peihong Zhang[1,†]

Quasiparticle band structures of STO and BTO









Systems with d-states

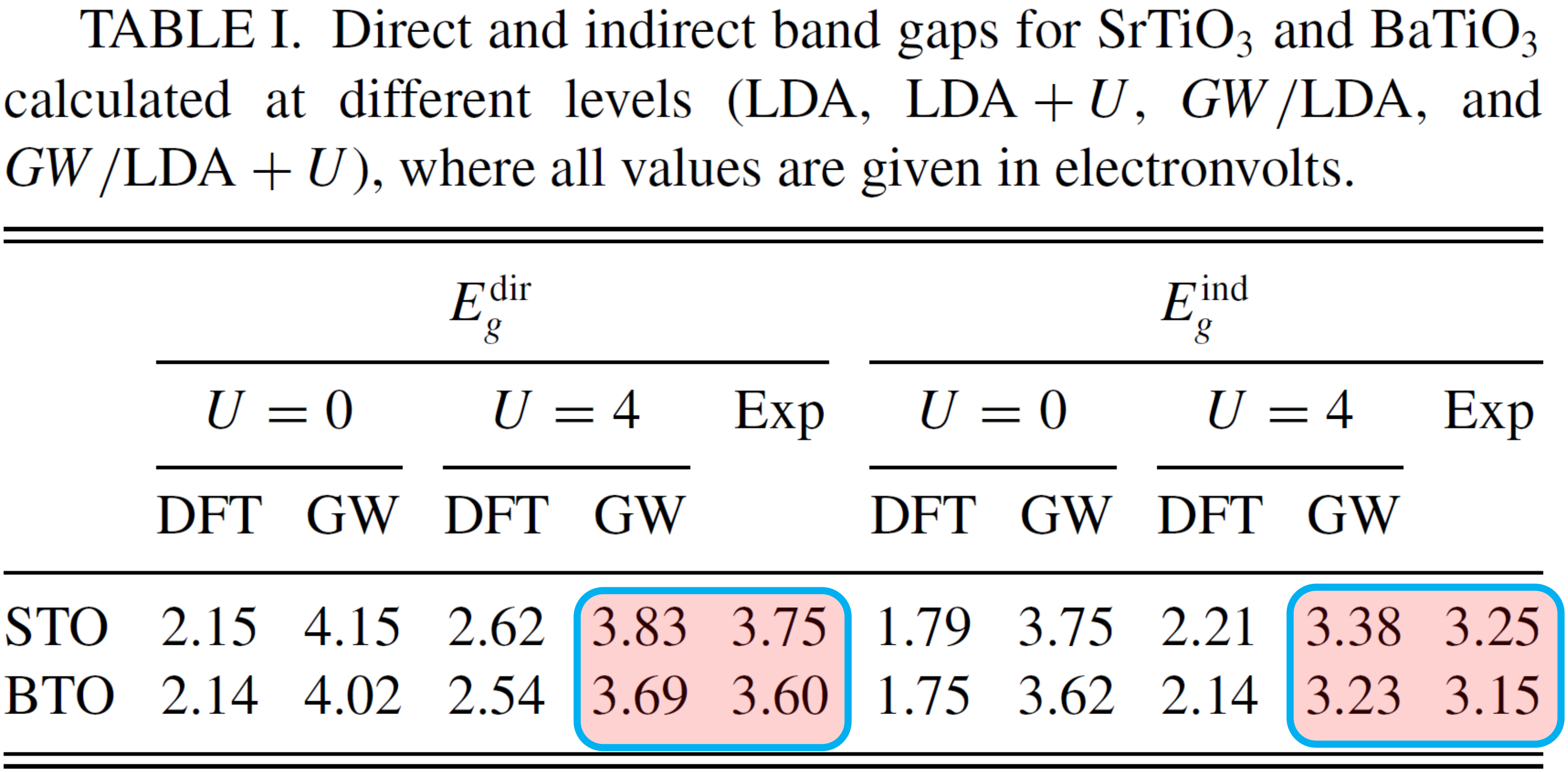
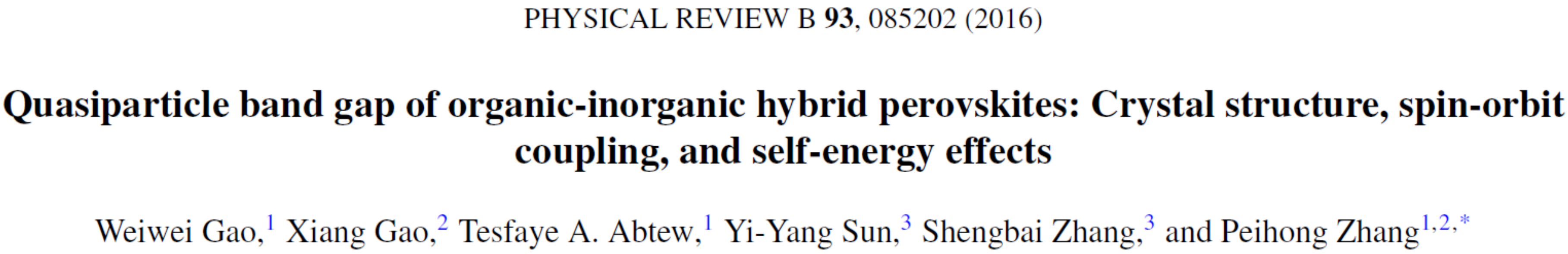


TABLE I. Direct and indirect band gaps for $SrTiO_3$ and $BaTiO_3$ calculated at different levels (LDA, LDA + U, GW/LDA, and GW/LDA + U), where all values are given in electronvolts.

	$E_g^{\rm dir}$					$E_g^{\rm ind}$				
	$U = 0$		$U = 4$		Exp	$U = 0$		$U = 4$		Exp
	DFT	GW	DFT	GW		DFT	GW	DFT	GW	
STO	2.15	4.15	2.62	3.83	3.75	1.79	3.75	2.21	3.38	3.25
BTO	2.14	4.02	2.54	3.69	3.60	1.75	3.62	2.14	3.23	3.15

Hybrid organic-inorganic perovskites

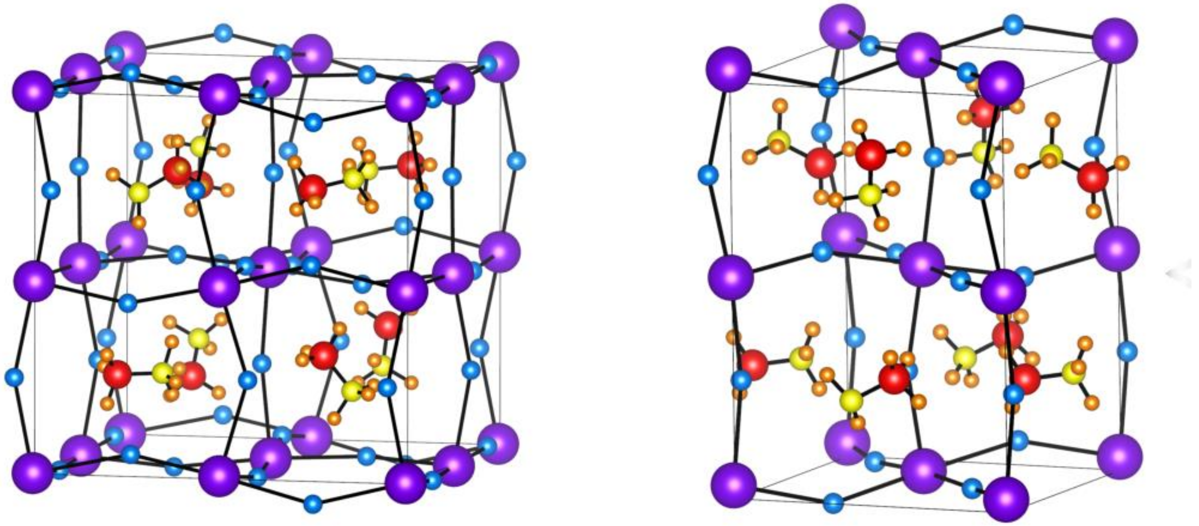


PHYSICAL REVIEW B **93**, 085202 (2016)

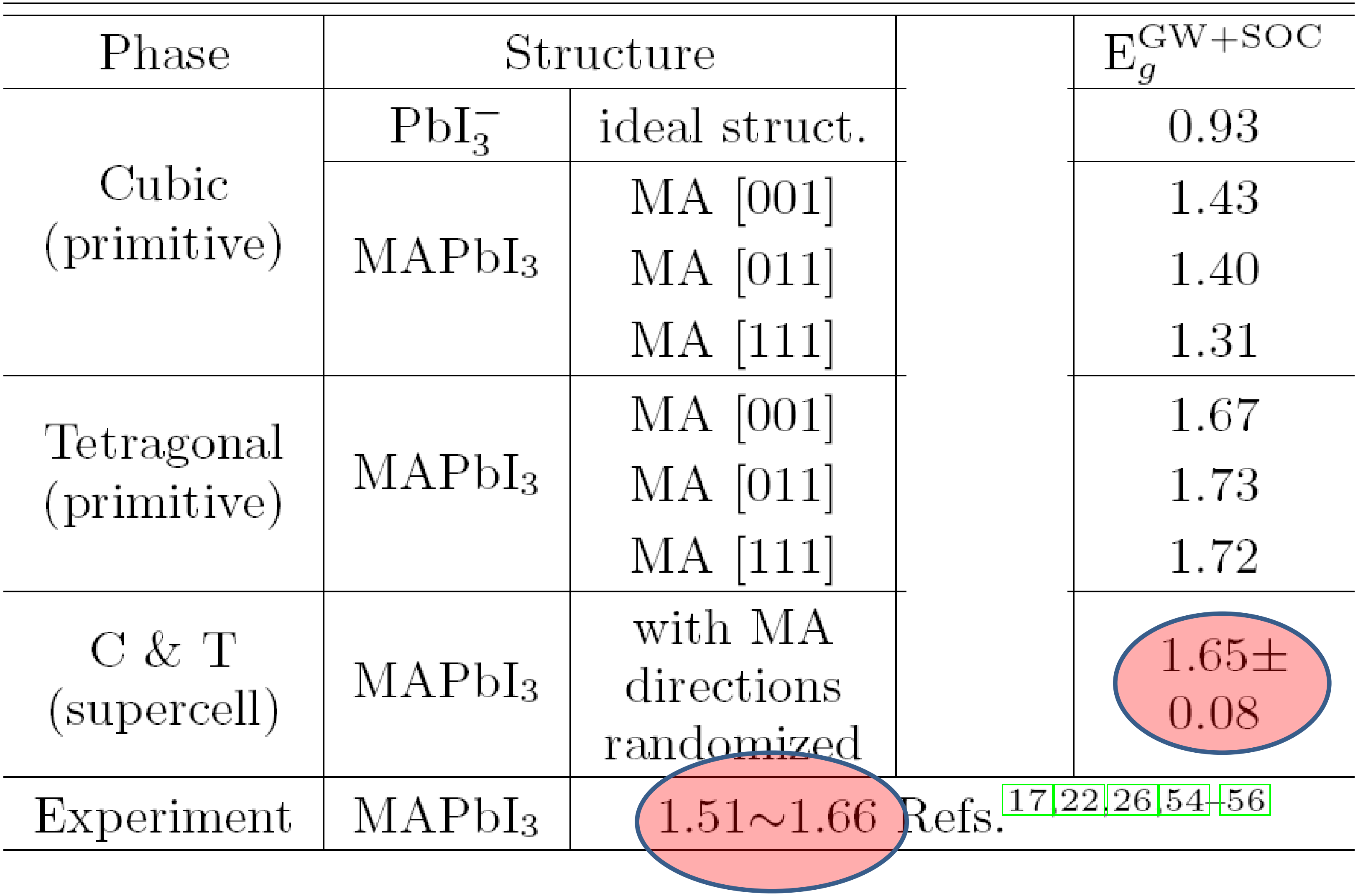
Quasiparticle band gap of organic-inorganic hybrid perovskites: Crystal structure, spin-orbit coupling, and self-energy effects

Weiwei Gao,[1] Xiang Gao,[2] Tesfaye A. Abtew,[1] Yi-Yang Sun,[3] Shengbai Zhang,[3] and Peihong Zhang[1,2,*]

- One of the difficulties of calculating the quasiparticle properties of hybrid perovskites is random orientations if the organic molecule and the structure distortions – need large unit cells and average over many distorted structures



Quasiparticle band gap of MAPbI3



Phase	Structure		E_g^{GW+SOC}
Cubic (primitive)	PbI_3^-	ideal struct.	0.93
	$MAPbI_3$	MA [001]	1.43
		MA [011]	1.40
		MA [111]	1.31
Tetragonal (primitive)	$MAPbI_3$	MA [001]	1.67
		MA [011]	1.73
		MA [111]	1.72
C & T (supercell)	$MAPbI_3$	with MA directions randomized	1.65± 0.08
Experiment	$MAPbI_3$	1.51∼1.66 Refs. [17,22,26,54–56]	

PRB **93**, 085202 (2016)

GW calculations for large systems? High-throughput GW calculations?

- (Forget about ZnO or CuCl) For a 2-atom MgO, we need about 1,000 conduction bands to converge the result

- Suppose we are interest in a system containing 200 atoms (e.g, a supercell containing a defect), we will need

$$\boxed{1000\times(200/2)=100{,}000\ \text{conduction bands}}$$

to achieve the same level of convergence

- Not only calculating the wave functions is hard (if possible), but storing these wave functions is extremely problematic, not to mention the subsequent GW calculations