The effective-energy technique: GW calculations without summing over empty states

Arjan Berger

Laboratoire des Solides Irradiés
Ecole Polytechnique, Palaiseau, France
European Theoretical Spectroscopy Facility (ETSF)

ABINIT Workshop, 12 April 2011, Han-sur-Lesse

Outline

- Introduction to GW
- Problem: Summation over empty states (screening + self-energy).
- EET: Use one effective energy for all empty states.
- Results: GW, BSE and TDDFT
- Conclusions and Outlook

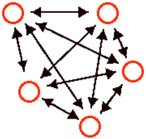
GW

Many-body perturbation theory:

Many-body effects contained in self-energy Σ.

Expansion in v_c:

$$\Sigma^{HF} = v_H + iGv_c$$



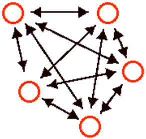
GW

Many-body perturbation theory:

Many-body effects contained in self-energy Σ.

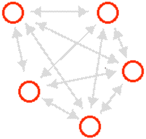
Expansion in v_c:

$$\Sigma^{HF} = v_H + iGv_c$$



Expansion in $W = \epsilon^{-1} v_c$:

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



Many-electron systems: electrons are screened by their Coulomb holes.

GW in practice: G^0W^0

Similarity of GW and Kohn-Sham Hamiltonians:

$$\hat{H}^{GW} = -\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + \Sigma_{xc}^{GW}(\mathbf{r}, \mathbf{r}', \omega)$$
$$\hat{H}^{KS} = -\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

GW in practice: G^0W^0

Similarity of GW and Kohn-Sham Hamiltonians:

$$\hat{H}^{GW} = -\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + \Sigma_{xc}^{GW}(\mathbf{r}, \mathbf{r}', \omega)$$
$$\hat{H}^{KS} = -\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

First-order perturbation theory:

$$\epsilon_n^{GW} = \epsilon_n^{KS} + \langle n|\Sigma_{xc}^{GW}(\epsilon_n^{GW}) - v_{xc}|n\rangle$$

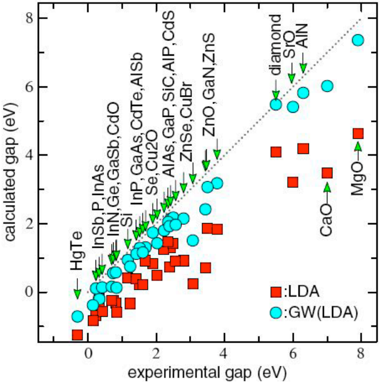
Taylor expansion around ϵ_n^{KS} up to first order:

$$\epsilon_n^{GW} = \epsilon_n^{KS} + Z\langle n|\Sigma_{xc}^{GW}(\epsilon_n^{KS}) - v_{xc}|n\rangle \qquad Z = \frac{1}{1 - \left.\frac{\partial\langle n|\Sigma_{xc}^{GW}(\omega)|n\rangle}{\partial\omega}\right|_{\omega=\epsilon_n^{KS}}}$$

We need (diagonal) matrix elements of the self-energy

G^0W^0 results

G^0W^0: Accurate quasi-particle energies of solids



$$\Sigma_{xc} = iG^0W^0$$
$$W^0 = \epsilon_{RPA}^{-1} v_c$$
$$\epsilon_{RPA} = 1 - v_c\chi^0$$

M. van Schilfgaarde, T. Kotani, and S. Faleev, PRL 96, 226402 (2006).

- G^0W^0 is computationally demanding.
- Large number of empty states in SOS expressions for Σ_{xc} and χ^0.

Σ^{GW} matrix elements

Standard calculation: Sum-over-states (SOS)

$$\langle n|\Sigma_x(\omega)|n\rangle = -\sum_{\mathbf{q},\mathbf{G}}\sum_{v}^{occ}\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}$$

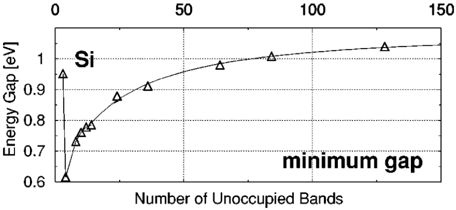
$$\langle n|\Sigma_c^{GW}(\omega)|n\rangle = \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_{j}W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\sum_{v}^{occ}\frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega+\omega_j-\epsilon_v}$$
$$+\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_{j}W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\sum_{c}^{empty}\frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c}$$

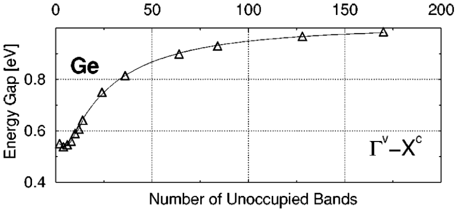
Σ^{GW} matrix elements

Standard calculation: Sum-over-states (SOS)

$$\langle n|\Sigma_x(\omega)|n\rangle = -\sum_{\mathbf{q},\mathbf{G}}\sum_{v}^{occ}\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}$$

$$\langle n|\Sigma_c^{GW}(\omega)|n\rangle = \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_{j} W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\sum_{v}^{occ}\frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega+\omega_j-\epsilon_v}$$
$$+\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_{j} W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\sum_{c}^{empty}\frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c}$$



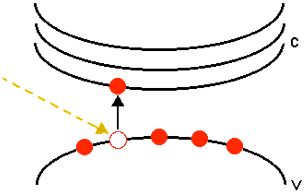


M. Tiago et al., PRB 69, 125212 (2004)

The Polarizability

Standard calculation of χ^0: SOS

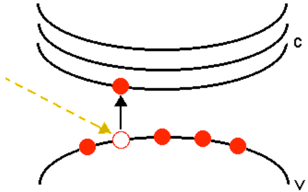
$$\chi^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_v^{occ} \sum_c^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$



The Polarizability

Standard calculation of χ^0: SOS

$$\chi^0_{\mathbf{GG}'}(\mathbf{q},\omega) = \sum_v^{occ} \sum_c^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$



Advantages:

- Systematic and controllable
- Easy to implement

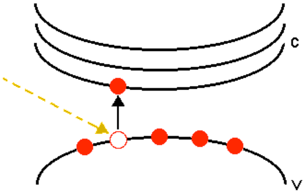
Disadvantages:

- Huge summation over empty states
- Slow (scaling=$N_c N_v N_{\mathbf{G}}^2$)

The Polarizability

Standard calculation of χ^0: SOS

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \sum_v^{occ} \sum_c^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$



Advantages:

- Systematic and controllable
- Easy to implement

Disadvantages:

- Huge summation over empty states
- Slow (scaling=$N_c N_v N_{\mathbf{G}}^2$)

Aim:
- Keep advantages of SOS
- Get rid of disadvantages: occupied states only

Getting rid of the empty states

Other approaches with less or no empty states:

COHSEX:	L. Hedin, PR A796 (1965)
Extrapolar method:	F. Bruneval and X. Gonze, PRB 78, 085125 (2008)
Sternheimer equation:	L. Reining *et al.*, PRB 56, R4302 (1997) P. Umari *et al.*, PRB 81 115104 (2010) F. Giustino *et al.*, PRB 81 115105 (2010)
Improved COHSEX:	W. Kang and M. Hybertsen, PRB 82, 195108 (2010)

Getting rid of the empty states

Other approaches with less or no empty states:

COHSEX:	L. Hedin, PR A796 (1965)
Extrapolar method:	F. Bruneval and X. Gonze, PRB 78, 085125 (2008)
Sternheimer equation:	L. Reining *et al.*, PRB 56, R4302 (1997) P. Umari *et al.*, PRB 81 115104 (2010) F. Giustino *et al.*, PRB 81 115105 (2010)
Improved COHSEX:	W. Kang and M. Hybertsen, PRB 82, 195108 (2010)

This talk: a simple and general method to get rid of all empty states.

Getting rid of the empty states

Other approaches with less or no empty states:

COHSEX:	L. Hedin, PR A796 (1965)
Extrapolar method:	F. Bruneval and X. Gonze, PRB 78, 085125 (2008)
Sternheimer equation:	L. Reining *et al.*, PRB 56, R4302 (1997) P. Umari *et al.*, PRB 81 115104 (2010) F. Giustino *et al.*, PRB 81 115105 (2010)
Improved COHSEX:	W. Kang and M. Hybertsen, PRB 82, 195108 (2010)

This talk: a simple and general method to get rid of all empty states.

Extrapolar method: Reducing the number of empty states

Standard approach:

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \sum_{c=N_v+1}^{N} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} + \sum_{c=N+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c}$$

Extrapolar method: Reducing the number of empty states

Standard approach:

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \sum_{c=N_v+1}^{N} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} + \sum_{c=N+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c}$$

Extrapolar method [F. Bruneval and X. Gonze, PRB 78, 085125 (2008)]:

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \sum_{c=N_v+1}^{M} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} + \sum_{c=M+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\bar{\epsilon}}$$

Closure relation: $\sum_{c=M+1}^{\infty} |c\rangle\langle c| = 1 - \sum_{i=1}^{M} |i\rangle\langle i|$

Reduction of number of empty states: $M < N$

Extrapolar method: Reducing the number of empty states

Standard approach:

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \sum_{c=N_v+1}^{N} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} + \sum_{c=N+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c}$$

Extrapolar method [F. Bruneval and X. Gonze, PRB 78, 085125 (2008)]:

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \sum_{c=N_v+1}^{M} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} + \sum_{c=M+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\bar{\epsilon}}$$

Closure relation: $\sum_{c=M+1}^{\infty} |c\rangle\langle c| = 1 - \sum_{i=1}^{M} |i\rangle\langle i|$

Reduction of number of empty states: $M < N$

Effective Energy Technique: Generalization of $\bar{\epsilon} \longrightarrow M = N_v$

EET: Σ_{GW} with sum over occupied states only

There exists an effective energy $\delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)$ such that

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \left(\sum_{c=N_v+1}^{\infty} |c\rangle\langle c|\right) e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta_{nj}(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)}$$

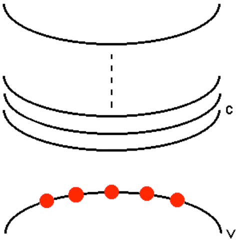
Closure relation: $\sum_{c=N_v+1}^{\infty} |c\rangle\langle c| = 1 - \sum_{v}^{occ} |v\rangle\langle v|$

EET: Σ_{GW} with sum over occupied states only

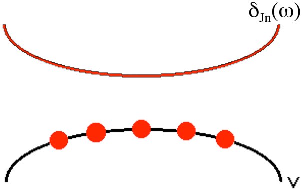
There exists an effective energy $\delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)$ such that

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\left(\sum_{c=N_v+1}^{\infty}|c\rangle\langle c|\right)e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)}$$

Closure relation: $\sum_{c=N_v+1}^{\infty}|c\rangle\langle c| = 1-\sum_{v}^{occ}|v\rangle\langle v|$



$\Longrightarrow$



EET: Effective Energy Technique

AB, L. Reining, F. Sottile, Phys. Rev. B 82, 041103(R) (2010)

Getting δ

Starting from the definition:

$$S \equiv \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\left(\sum_c^{empty}|c\rangle\langle c|\right)e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta}$$

Getting δ

Starting from the definition:

$$S \equiv \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \left(\sum_c^{empty}|c\rangle\langle c|\right) e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta}$$

Rearranging:

$$\delta = \epsilon_n + \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle(\epsilon_c - \epsilon_n)}{\omega - \omega_j - \epsilon_c} / S$$

The ϵ_i are eigenvalues of $\hat{H}$ with eigenstates $|i\rangle$

Getting δ

Starting from the definition:

$$S \equiv \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \epsilon_c} = \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\left(\sum_c^{empty}|c\rangle\langle c|\right)e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle}{\omega - \omega_j - \delta}$$

Rearranging:

$$\delta = \epsilon_n + \sum_{c}^{empty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\rangle(\epsilon_c - \epsilon_n)}{\omega - \omega_j - \epsilon_c}/S$$

The ϵ_i are eigenvalues of $\hat{H}$ with eigenstates $|i\rangle$

$$\delta = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \sum_{c} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}[i\nabla]|n\rangle \cdot (\mathbf{q}+\mathbf{G})}{[\omega - \omega_j - \epsilon_c]}/S$$

A hierarchy of approximations for δ_{nj}

This scheme leads to simple approximations for $\delta_{nj}(\omega)$ ($\mathbf{G} = \mathbf{G}'$):

$$\delta_n^{(0)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2}$$

$$\delta_n^{(1)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}$$

$$\delta_{nj}^{(2)}(\omega) = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}} \frac{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}\right]}{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{jj}}{f_n^{\rho j}}\right]}$$

A hierarchy of approximations for δ_{nj}

This scheme leads to simple approximations for $\delta_{nj}(\omega)$ ($\mathbf{G} = \mathbf{G}'$):

$$\delta_n^{(0)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2}$$

$$\delta_n^{(1)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}$$

$$\delta_{nj}^{(2)}(\omega) = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}} \frac{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}\right]}{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{jj}}{f_n^{\rho j}}\right]}$$

-The $f_n^{\rho\rho}, f_n^{\rho j}, f_n^{jj}, \cdots$ are simple with sums over occupied states only.

$$f_n^{\rho j} = \left[\langle n|i\nabla|n\rangle - \sum_v^{occ} \langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}[i\nabla]|n\rangle\right] \cdot (\mathbf{q}+\mathbf{G})$$

-From $\delta_n^{(1)}$ onwards exact for the homogeneous electron gas.

-$\delta_{nj}^{(2)}(\omega)$ simple but nontrivial due to frequency dependence.

AB, L. Reining, F. Sottile, Phys. Rev. B 82, 041103(R) (2010)

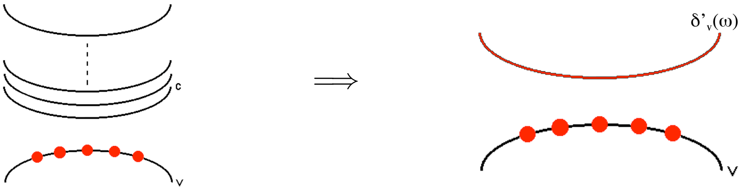
The Polarizability

We can apply a similar approach to the polarizability

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \sum_v^{occ} \sum_c^{empty} \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{i(\mathbf{q}+\mathbf{G'})\cdot\mathbf{r'}}|v\rangle}{\omega - (\epsilon_c - \epsilon_v) + i\eta} + A.R.$$

This can be rewritten as:

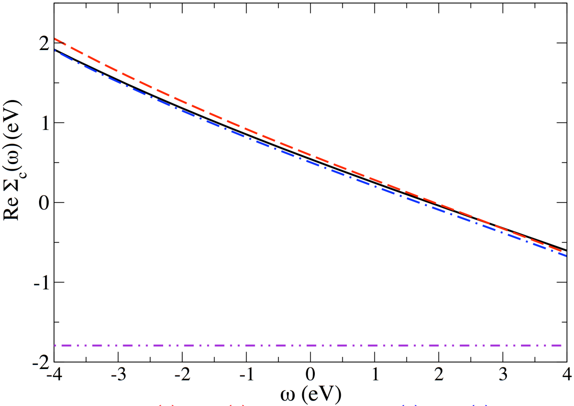
$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \sum_v \frac{\langle v|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \left(\sum_c^{empty} |c\rangle\langle c|\right) e^{i(\mathbf{q}+\mathbf{G'})\cdot\mathbf{r'}}|v\rangle}{\omega - (\delta'_v(\mathbf{q},\mathbf{G},\mathbf{G'},\omega) - \epsilon_v) + i\eta} + A.R.$$



Scaling: N_{at}^4 + small prefactor (gain of N_c/N_v) or $N_{at}^3 \log N_{at}$ + larger prefactor.

G^0W^0 Self-energy: Silicon

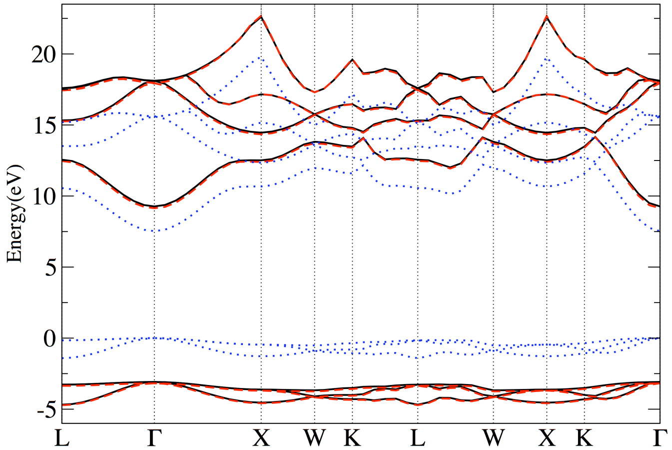
The real part of $\langle n|\Sigma_c(\omega)|n\rangle$ at Γ calculated for the highest occupied band around $\epsilon_n^{LDA} = 0$ using a plasmon-pole model for ϵ^{-1}.



Black: SOS; Red: EET:$\delta'^{(2)} + \delta^{(2)}$; Blue: EET:$\delta'^{(4)} + \delta^{(4)}$; Violet: COHSEX

AB, L. Reining, F. Sottile, Phys. Rev. B 82, 041103(R) (2010)

Band Structure of Solid Argon: G^0W^0



Black: SOS; Red: EET; Blue: LDA

AB, L. Reining, F. Sottile, Phys. Rev. B 82, 041103(R) (2010)

Band gaps

$G^0 W^0$ band gaps:

	LDA	$G^0 W^0$ (SOS)	$G^0 W^0$ (EET)	Experiment
Silicon (E_g)	0.52	1.20	1.19	1.17
Silicon ($\Gamma^v - \Gamma^c$)	2.56	3.23	3.22	3.40
Solid Argon (E_g)	7.53	12.4	12.3	14.2
Argon atom (HOMO-LUMO)	9.81	14.6	14.5	
SnO_2	0.91	2.88	2.94	3.6

Band gaps

G^0W^0 band gaps:

	LDA	G^0W^0 (SOS)	G^0W^0 (EET)	Experiment
Silicon (E_g)	0.52	1.20	1.19	1.17
Silicon ($\Gamma^v - \Gamma^c$)	2.56	3.23	3.22	3.40
Solid Argon (E_g)	7.53	12.4	12.3	14.2
Argon atom (HOMO-LUMO)	9.81	14.6	14.5	
SnO_2	0.91	2.88	2.94	3.6

- Good agreement between SOS approach and EET.
- G^0W^0 band gaps not always in agreement with experiment.

We have to include self-consistency

Self-consistent COHSEX + G^0W^0 + EET

The COHSEX self-energy is static:

$$\langle n|\Sigma_c^{COHSEX}|n\rangle = 2\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_j W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\sum_v^{occ}\frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega_j}$$
$$-\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_j W^j_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\frac{\langle n|e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}|n\rangle}{\omega_j}$$

Self-consistent COHSEX + G^0W^0 + EET

The COHSEX self-energy is static:

$$\langle n|\Sigma_c^{COHSEX}|n\rangle = 2\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_j W^j_{\mathbf{GG}'}(\mathbf{q})\sum_v^{occ}\frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\rangle\langle v|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega_j}$$

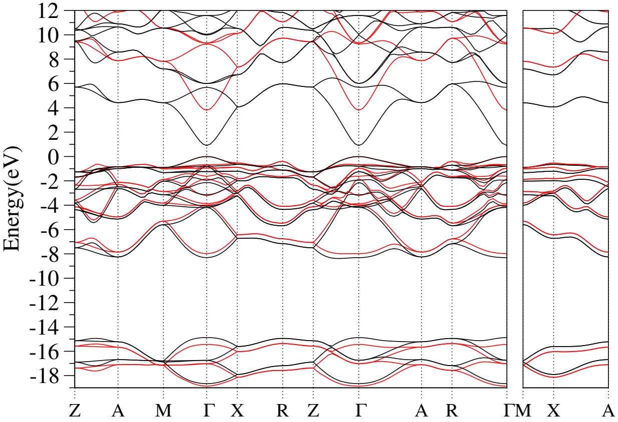
$$-\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\sum_j W^j_{\mathbf{GG}'}(\mathbf{q})\frac{\langle n|e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}|n\rangle}{\omega_j}$$

GW = scCOHSEX + G^0W^0 (Bruneval *et al.* PRB 74, 045102 (2006))

	LDA	GW(EET)	Experiment
SnO_2 (E_g)	0.91	3.8	3.6

AB, L. Reining, F. Sottile, Phys. Rev. B 82, 041103(R) (2010)

SnO_2: Band structure

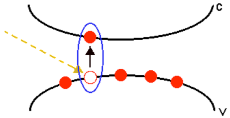


Black: LDA; Red: $GW(EET)$

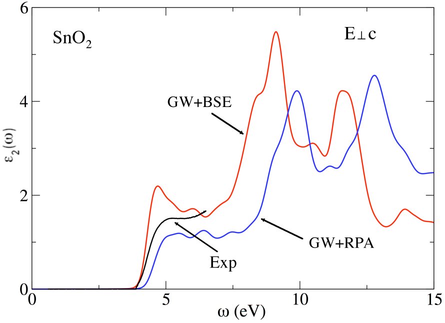
Optical absorption: EET for BSE

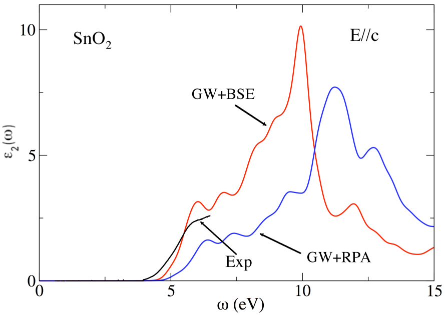
The Bethe-Salpeter equation:

$$^{(4)}\chi = {}^{(4)}\chi_0 + {}^{(4)}\chi_0 ({}^{(4)}v_c + {}^{(4)}W)^{(4)}\chi$$



Optics: Many, many k-points required; very tough to calculate W.

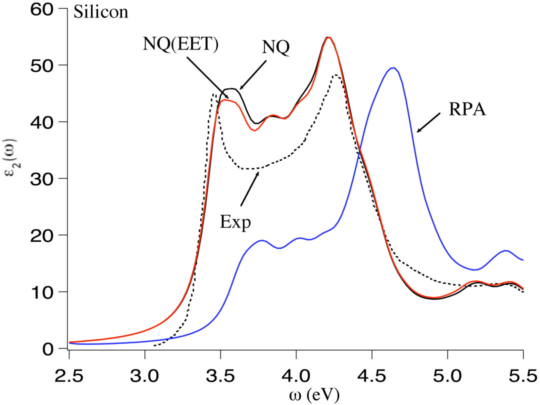




Optical absorpton: EET for TDDFT kernel

The NanoQuanta (NQ) TDDFT kernel (Sottile *et al*, PRL, 91, 056402(2003)):

$$\chi = \chi_0 + \chi_0(v_c + f_{xc})\chi$$
$$f_{xc}^{NQ} = \chi_0^{-1(3)}\chi^0 W^{(3)}\chi^0\chi_0^{-1}$$



NQ(EET): explicit functional of Kohn-Sham density matrix $\rho_{KS}(\mathbf{r}, \mathbf{r}')$.

Converging GW calculations with EET

Increase precision: Add a couple of empty states

$$\sum_{c=N_v+1}^{\infty} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} = \sum_{c=N_v+1}^{M} \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c\rangle\langle c|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\epsilon_c} + \frac{\langle n|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\left(\sum_{c=M+1}^{\infty}|c\rangle\langle c|\right)e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\rangle}{\omega-\omega_j-\delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)}$$

Effective energy $\delta_{nj}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)$ is automatically adjusted.

Current implementation: EET input variables

- gw_eet: Order of approximation (Default: no EET)
- gw_eet_nband: Number of bands in SOS (Default: only occupied)
- gw_eet_inclvkb: Include or not the commutator of Hamiltonian with nonlocal part of PP (Default: not)

$$\delta_n^{(0)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2}$$

$$\delta_n^{(1)} = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}$$

$$\delta_{nj}^{(2)}(\omega) = \epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}} \frac{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{\rho j}}{f_n^{\rho\rho}}\right]}{\omega - \omega_j - \left[\epsilon_n + \frac{|\mathbf{q}+\mathbf{G}|^2}{2} + \frac{f_n^{jj}}{f_n^{\rho j}}\right]}$$

Polarizability:

- nband: Number of bands in SOS for head and wings of $\chi^0_{\mathbf{GG}'}(\mathbf{q}=0,\omega)$

Conclusions and Outlook

- With the EET we can perform GW calculations with occupied states only.
- The approach is simple with immediate speed ups of at least an order of magnitude for any system size.
- The EET is general and can be applied to other methods (BSE,TDDFT) and other spectral representations.
- Potential future applications include:
  - Self-consistency beyond COHSEX: updating only occupied states.
  - optimized effective potentials.
  - PAW

Acknowledgments

Palaiseau

- Francesco Sottile
- Lucia Reining

Louvain-la-Neuve

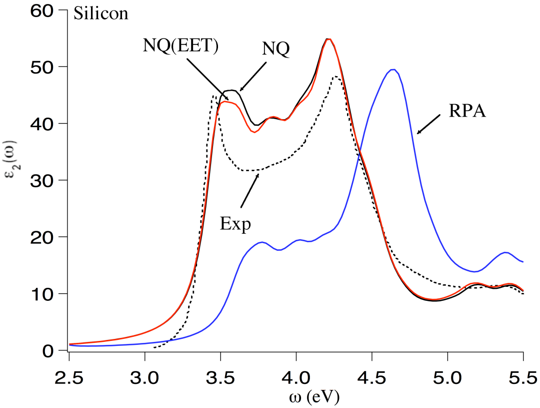
- Matteo Giantomassi
- Martin Stankovski
- Xavier Gonze

Optical absorpton: EET for TDDFT kernel

The NanoQuanta (NQ) TDDFT kernel (Sottile *et al*, PRL, 91, 056402(2003)):

$$\chi = \chi_0 + \chi_0(v_c + f_{xc})\chi$$

$$f_{xc}^{NQ} = \chi_0^{-1(3)}\chi^0 W^{(3)}\chi^0\chi_0^{-1}$$



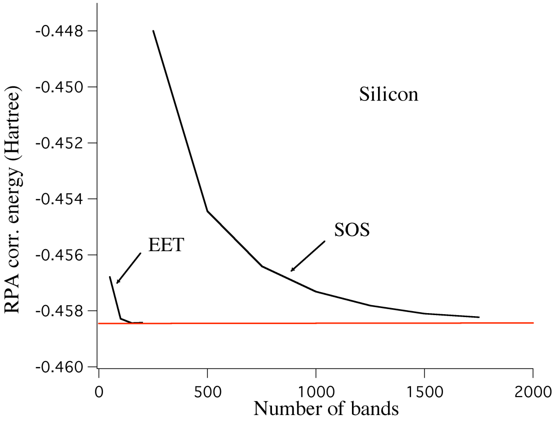
NQ(EET): explicit functional of Kohn-Sham density matrix $\rho_{KS}(\mathbf{r}, \mathbf{r}')$.

$$f^{\rho j}(\mathbf{q}, \mathbf{G}, \mathbf{G}) = -\int d\mathbf{r}d\mathbf{r}' e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} \rho_{KS}(\mathbf{r}', \mathbf{r})\nabla' \rho_{KS}(\mathbf{r}, \mathbf{r}') \cdot (\mathbf{q} + \mathbf{G})$$

EET for RPA correlation energies

RPA correlation energy:

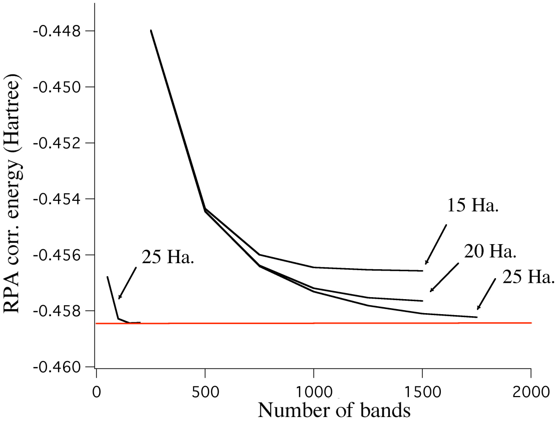
$$E_c = \int_0^\infty \frac{d\omega}{2\pi} Tr \left[\ln(1 - \chi^0(i\omega) v_c) + \chi^0(i\omega) v_c \right]$$



EET for RPA correlation energies

RPA correlation energy:

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} Tr\left[\ln(1-\chi^0(i\omega)v_c) + \chi^0(i\omega)v_c\right]$$



A Kohn-Sham density-matrix TDDFT kernel

$$f_{xc}^{NQ} = \chi_0^{-1} T \chi_0^{-1}$$

where $T = {}^{(3)}\chi^0 \tilde{W}^{(3)}\chi^0$ and $\tilde{W} = (1 - v_c\tilde{\chi}^0)^{-1} v_c$

$$\tilde{\chi}^0_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \int d\mathbf{r}d\mathbf{r}' e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} g_{\mathbf{G}}(\mathbf{q},\omega)|\rho_{KS}(\mathbf{r},\mathbf{r}')|^2$$

$$\begin{aligned}T_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = g_{\mathbf{G}}(\mathbf{q},\omega) g_{\mathbf{G}'}(\mathbf{q},\omega)\Bigg(\int d\mathbf{r} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \int d\mathbf{r}_1 \rho_{KS}(\mathbf{r},\mathbf{r}_1)\tilde{W}(\mathbf{r}_1,\mathbf{r})\rho_{KS}(\mathbf{r}_1,\mathbf{r}) - \\ \int d\mathbf{r}d\mathbf{r}' e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} \rho_{KS}(\mathbf{r}',\mathbf{r}) \int d\mathbf{r}_1 \rho_{KS}(\mathbf{r},\mathbf{r}_1) \\ \times \left[\tilde{W}(\mathbf{r}_1,\mathbf{r}) + \tilde{W}(\mathbf{r}_1,\mathbf{r}') - \int d\mathbf{r}_2 \rho_{KS}(\mathbf{r}_2,\mathbf{r})\tilde{W}(\mathbf{r}_1,\mathbf{r}_2)\rho_{KS}(\mathbf{r}',\mathbf{r}_2)\right] \rho_{KS}(\mathbf{r}_1,\mathbf{r}')\Bigg)\end{aligned}$$

where $g_{\mathbf{G}}(\mathbf{q},\omega) = 1/[\omega - |\mathbf{q}+\mathbf{G}|^2/2]$.