THE KAVLI INSTITUTE FOR THEORETICAL PHYSICS

REALISTIC THEORIES OF CORRELATED ELECTRON MATERIALS

All-electron GWA based on the PAW method:

Application to insulating materials

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Plan

I. The Projector Augmented Wave (PAW) method

- Description of the basis set
- Comparison with the FPLMTO optical spectra
- The band gap problem

II. Implementation of the GW-PAW approximation

- The quasiparticle (QP) equation
- The self-energy within the GW approximation

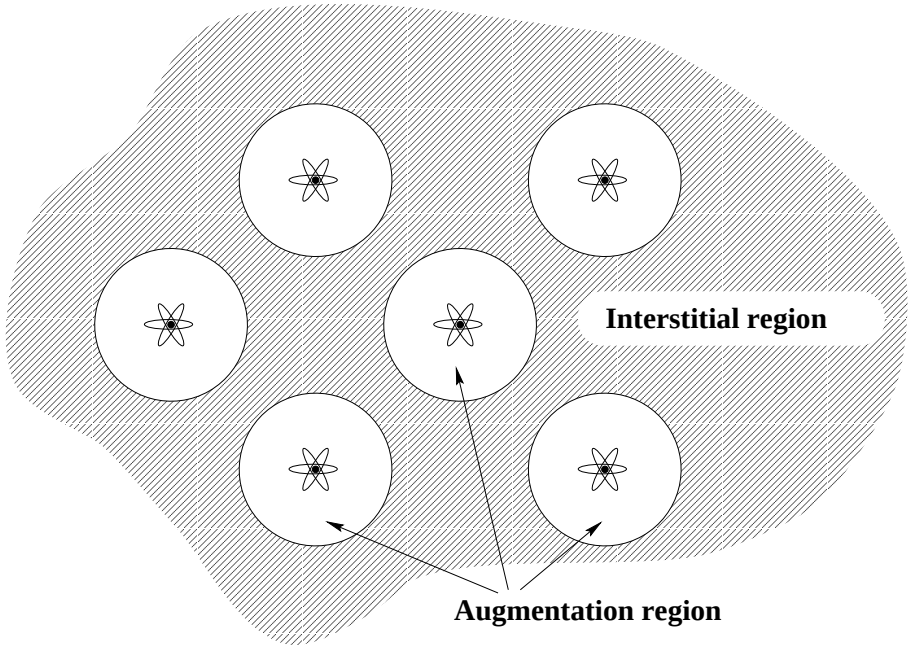
III. Applications

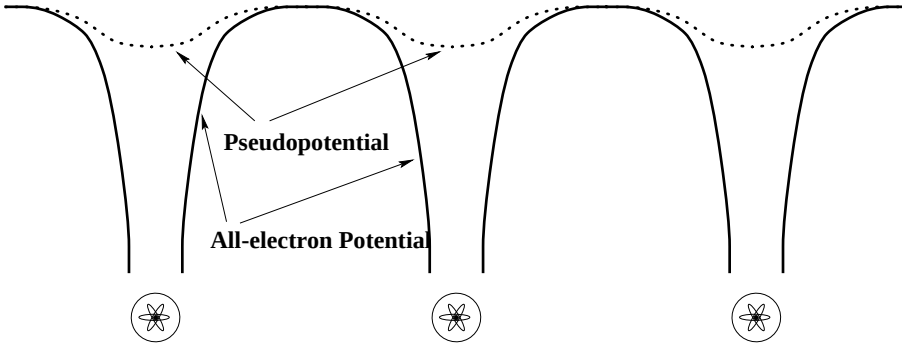
- QP energies of semiconductors and insulators
- Effects of correlation on optical spectra

The PAW method

The Projector augmented-wave (PAW) method was introduced by Blöchl, 1994.

- **Space representation**

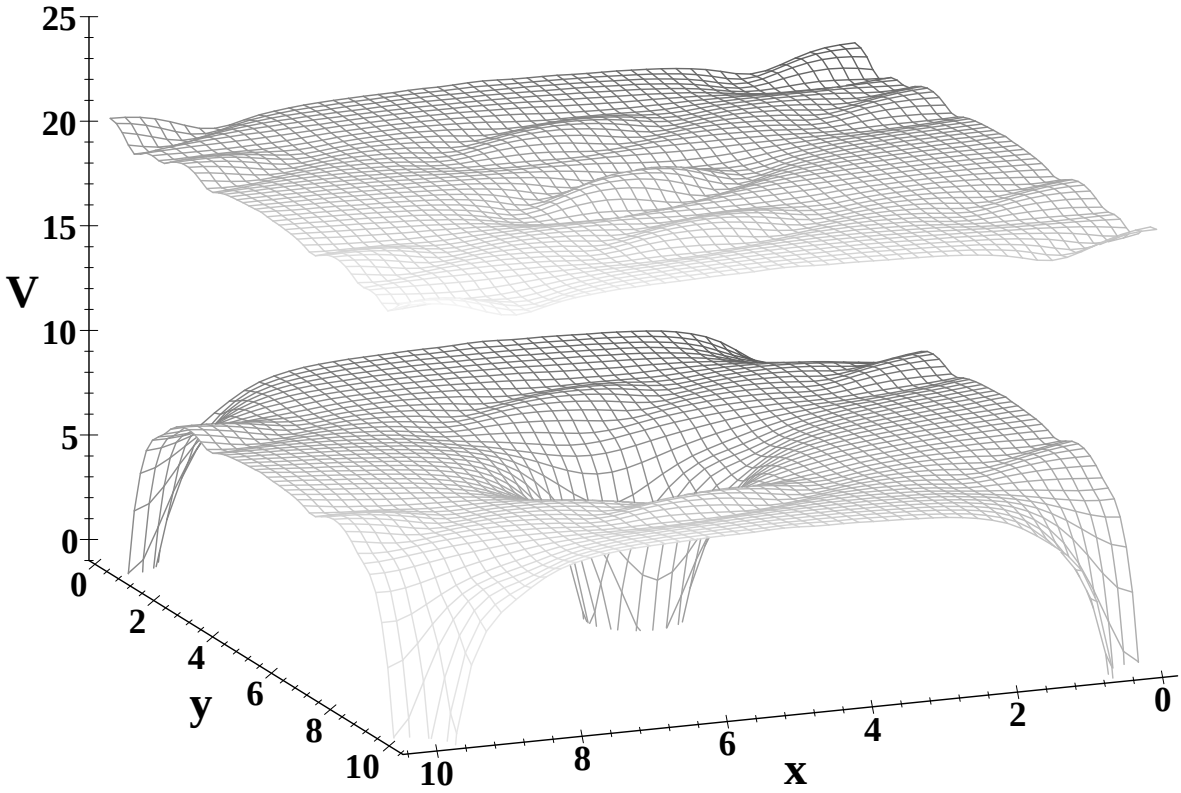




Idea :

$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi_{\text{aug}}\rangle - |\tilde{\Psi}_{\text{aug}}\rangle$$

The PAW method continued ...



LDA potential and $\tilde{v}_{eff}$ of Si on the (001) plan

The PAW method continued ...

1. Pseudopotential $\tilde{v}$: $|\tilde{\Psi}\rangle = \sum_{\mathrm{G}} a_{\mathrm{G}} \; |G\rangle$ (planes waves)
2. Atomic potential v^{at} : $|\Psi_{\mathrm{aug}}\rangle = \sum_i c_i |\phi_i\rangle$ (partial waves)
3. Atomic Pseudopotential $\tilde{v}^{\mathrm{at}}$: $|\tilde{\Psi}_{\mathrm{aug}}\rangle = \sum_i c_i |\tilde{\phi}_i\rangle$ (partial pseudo-waves)

Crystal wave function :

$$|\Psi\rangle \stackrel{\mathrm{def}}{=} |\tilde{\Psi}\rangle + \sum_i c_i |\phi_i\rangle - \sum_i c_i |\tilde{\phi}_i\rangle,$$

where the c_i are to be determined.
Conditions to be satisfied:

- $\mathrm{r} \in \Omega^{\mathrm{int}}$: $\Psi(\mathrm{r}) = \tilde{\Psi}(\mathrm{r})$ (true by construction)
- $\mathrm{r} \in \Omega^{\mathrm{aug}}$: $\Psi(\mathrm{r}) = \sum_i c_i \phi_i(\mathrm{r})$ (desired equality)

Condition satisfied if: $\tilde{\Psi}(\mathrm{r}) \stackrel{!}{=} \sum_i c_i \tilde{\phi}_i(\mathrm{r}) \quad (\mathrm{r} \in \Omega^{\mathrm{aug}})$
The projectors $|\tilde{p}_i\rangle$ are defined as:

$$\begin{aligned} \langle \mathrm{r} \in \Omega^{\mathrm{int}} | \tilde{p}_i \rangle &= 0 \qquad \forall\, i \\ \langle \tilde{p}_j | \tilde{\phi}_i \rangle &= \delta_{ij} \qquad \forall\, i, j \end{aligned}$$

$$\Longrightarrow \quad \langle \mathrm{r} | \tilde{\phi}_i \rangle = \langle \mathrm{r} | \phi_i \rangle \qquad \text{if } \mathrm{r} \in \Omega^{\mathrm{int}}.$$

The PAW method continued ...

The c_i coefficients are then given by:

$$\langle \tilde{p}_j | \tilde{\Psi} \rangle \;=\; \sum_i c_i \langle \tilde{p}_j | \tilde{\phi}_i \rangle \quad = \quad c_j$$

The crystal wave function becomes:

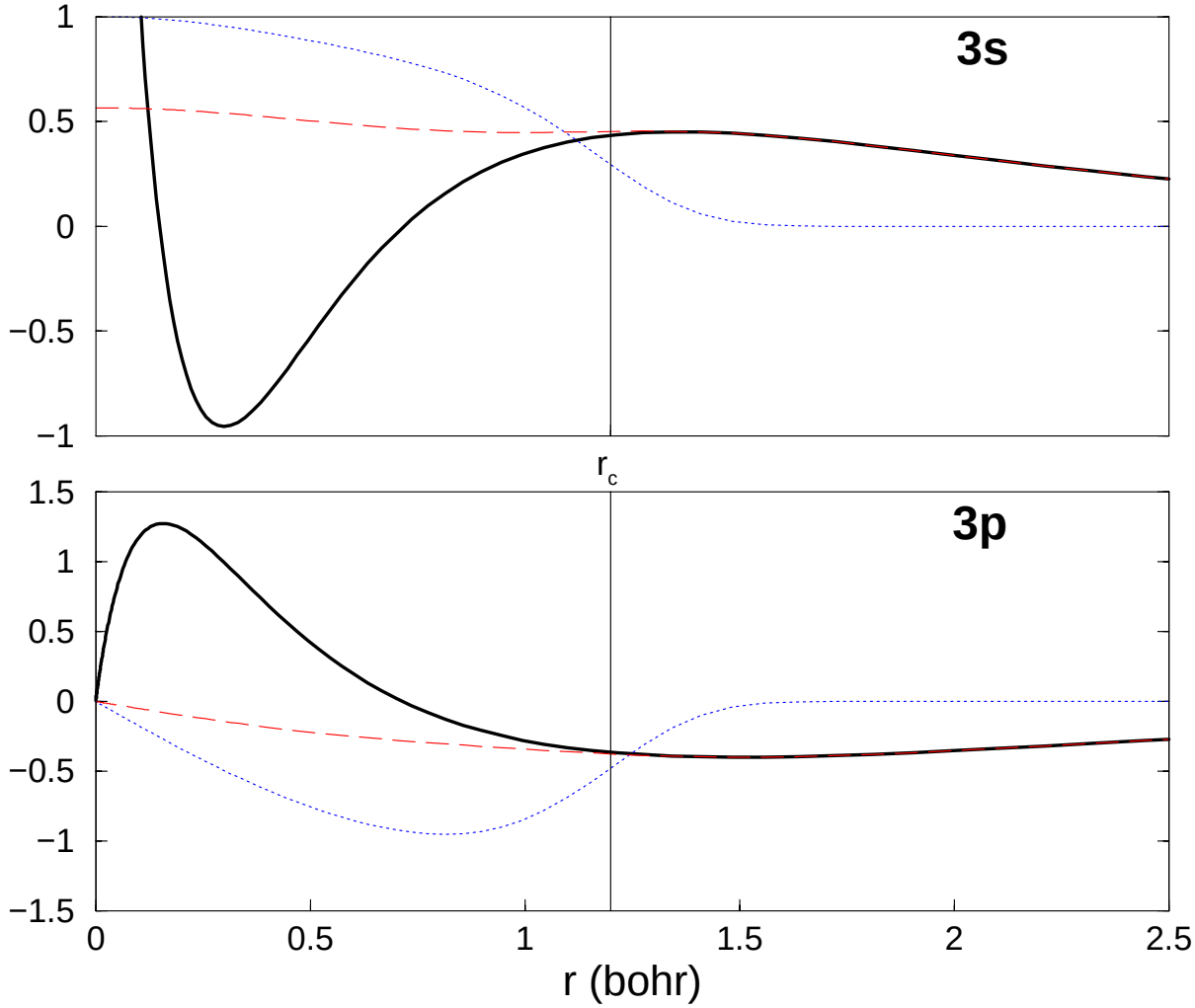
$$\begin{aligned} |\Psi\rangle \;&=\; |\tilde{\Psi}\rangle + \sum_i \langle \tilde{p}_i | \tilde{\Psi} \rangle \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \\ &= \left[\mathbb{1} + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i | \right] |\tilde{\Psi}\rangle \quad = \quad \mathcal{T} |\tilde{\Psi}\rangle \end{aligned}$$

The transformation operator $\mathcal{T}$ is defined as:

$$\mathcal{T} = \;\mathbb{1} + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i |$$

Illustration of the PAW Augmentation

Example: $3s$, and $3p$ partial, pseudo-partial waves, and projectors of Si.



Expectation value of a local operator

Expectation value of a local one-particle operator

$$\langle \boldsymbol{A} \rangle \;=\; \sum_{\boldsymbol{n}} \langle \tilde{\boldsymbol{\Psi}}_{\boldsymbol{n}} | \boldsymbol{A} | \tilde{\boldsymbol{\Psi}}_{\boldsymbol{n}} \rangle + \sum_{\boldsymbol{i},\boldsymbol{j}} \boldsymbol{D}_{\boldsymbol{i},\boldsymbol{j}} \langle \boldsymbol{\phi}_{\boldsymbol{i}} | \boldsymbol{A} | \boldsymbol{\phi}_{\boldsymbol{j}} \rangle - \sum_{\boldsymbol{i},\boldsymbol{j}} \boldsymbol{D}_{\boldsymbol{i},\boldsymbol{j}} \langle \tilde{\boldsymbol{\phi}}_{\boldsymbol{i}} | \boldsymbol{A} | \tilde{\boldsymbol{\phi}}_{\boldsymbol{j}} \rangle + \sum_{\boldsymbol{n}} \langle \boldsymbol{\Psi}^{\boldsymbol{c}}_{\boldsymbol{n}} | \boldsymbol{A} | \boldsymbol{\Psi}^{\boldsymbol{c}}_{\boldsymbol{n}} \rangle$$

with a one-center density matrix

$$\boldsymbol{D}_{\boldsymbol{i},\boldsymbol{j}} \;=\; \sum_{\boldsymbol{n}} \langle \tilde{\boldsymbol{p}}_{\boldsymbol{i}} | \tilde{\boldsymbol{\Psi}}_{\boldsymbol{n}} \rangle \langle \tilde{\boldsymbol{\Psi}}_{\boldsymbol{n}} | \tilde{\boldsymbol{p}}_{\boldsymbol{j}} \rangle$$

and the core state contribution $|\boldsymbol{\Psi}^{\boldsymbol{c}}_{\boldsymbol{n}}\rangle$.

Example: Electronic Density

Electronic density $n(r)$ is composed of a plane wave part $\tilde{n}(r)$ and two one-center components $n^1(r)$ and $\tilde{n}^1(r)$

$$
\begin{aligned}
n(r) &= \tilde{n}(r) + n^1(r) - \tilde{n}^1(r) \\
&= \sum_n f_n \tilde{\Psi}^*_n(r)\tilde{\Psi}_n(r) + \tilde{n}^c \\
&+ \sum_{i,j} \phi^*_i(r) D_{i,j} \phi_j(r) + n^c \\
&- \sum_{i,j} \tilde{\phi}^*_i(r) D_{i,j} \tilde{\phi}_j(r) - \tilde{n}^c \\
D_{i,j} &= \sum_n \langle \tilde{p}_i | \tilde{\Psi}_n \rangle f_n \langle \tilde{\Psi} | \tilde{p}_j \rangle
\end{aligned}
$$

where:

$$f_n = \text{occupation number (i.e. 0 or 1)}$$

The electronic density (like the wave function) is divided into:

- **A plane-wave part**
- **Two partial expansions per atom in radial functions times spherical harmonics**

PAW total energy

$$E([\tilde{\Psi}_n], R_i) = \tilde{E} + E^1 - \tilde{E}^1$$

Plane-wave part

$$\begin{aligned}\tilde{E} &= \sum_n f_n \langle \tilde{\Psi}_n| -\frac{1}{2}\nabla^2 |\tilde{\Psi}_n\rangle \\ &+ \frac{1}{2}\int d^3r \int d^3r' \frac{(\tilde{n}(r)+\hat{n}(r))(\tilde{n}(r')+\hat{n}(r'))}{|r-r'|} \\ &+ \int d^3r \tilde{n}(r)\epsilon_{xc}(r,[\tilde{n}]) + \int d^3r \bar{v}(r)\tilde{n}(r)\end{aligned}$$

One-center expansion of the plane-wave part

$$\begin{aligned}\tilde{E}^1 &= \sum_n D_{i,j} \langle \tilde{\phi}_i| -\frac{1}{2}\nabla^2 |\tilde{\phi}_j\rangle \\ &+ \frac{1}{2}\int d^3r \int d^3r' \frac{(\tilde{n}^1(r)+\hat{n}(r))(\tilde{n}^1(r')+\hat{n}(r'))}{|r-r'|} \\ &+ \int d^3r \tilde{n}^1(r)\epsilon_{xc}(r,[\tilde{n}^1]) + \int d^3r \bar{v}(r)\tilde{n}^1(r)\end{aligned}$$

One-center expansion of the true density

$$\begin{aligned}E^1 &= \sum_n D_{i,j} \langle \phi_i| -\frac{1}{2}\nabla^2 |\phi_j\rangle \\ &+ \frac{1}{2}\int d^3r \int d^3r' \frac{(n^1(r)+Z(r))(n^1(r')+Z(r'))}{|r-r'|} \\ &+ \int d^3r n^1(r)\epsilon_{xc}(r,[n^1])\end{aligned}$$

The compensation charge density $\hat{n}$ is such that $(n^1 + n^Z) - (\tilde{n}^1 + \hat{n})$ has vanishing electrostatic multipole moments $\longrightarrow$ it does not interact with the charge outside Ω^{aug}.

Effective Hamiltonian

The total energy E is stationary / variational parameters ($\tilde{\Psi}_{n\mathrm{k}}$), with the condition insuring the total number N of electrons

$$\sum_{m,\mathrm{k}} f_{m,\mathrm{k}} \langle \Psi_{m\mathrm{k}} | \Psi_{m\mathrm{k}} \rangle - N = 0.$$

The effective eigenvalue problem is then deduced from

$$\frac{\delta}{\delta \langle \tilde{\Psi}_{n\mathrm{k}}|} \left[E - \epsilon_{n\mathrm{k}} \left(\sum_{m,\mathrm{k}} f_{m,\mathrm{k}} \langle \tilde{\Psi}_{m\mathrm{k}} | \tilde{O} | \tilde{\Psi}_{m\mathrm{k}} \rangle - N \right) \right] = 0,$$

where $\epsilon_{n\mathrm{k}}$ are Lagrange parameters. The variational calculus leads to the effective Schrödinger equation

$$\tilde{H} | \tilde{\Psi}_{n\mathrm{k}} \rangle = \epsilon_{n\mathrm{k}} \tilde{O} | \tilde{\Psi}_{n\mathrm{k}} \rangle,$$

where the effective Hamiltonian is given by

$$\tilde{H} = -\frac{\nabla^2}{2} + \tilde{v}_{eff}(\mathrm{r}) + \sum_{\tau,i,j} |\tilde{p}_i^\tau \rangle \Gamma_{ij}^\tau \langle \tilde{p}_j^\tau|,$$

The local term $\tilde{v}_{eff}$ is given by

$$\tilde{v}_{eff}(\mathrm{r}) = \int d\mathrm{r}' \frac{\tilde{n}(\mathrm{r}') + \hat{n}'(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|} + \hat{v}(\mathrm{r}) + v_{xc}[\tilde{n}(\mathrm{r})]$$

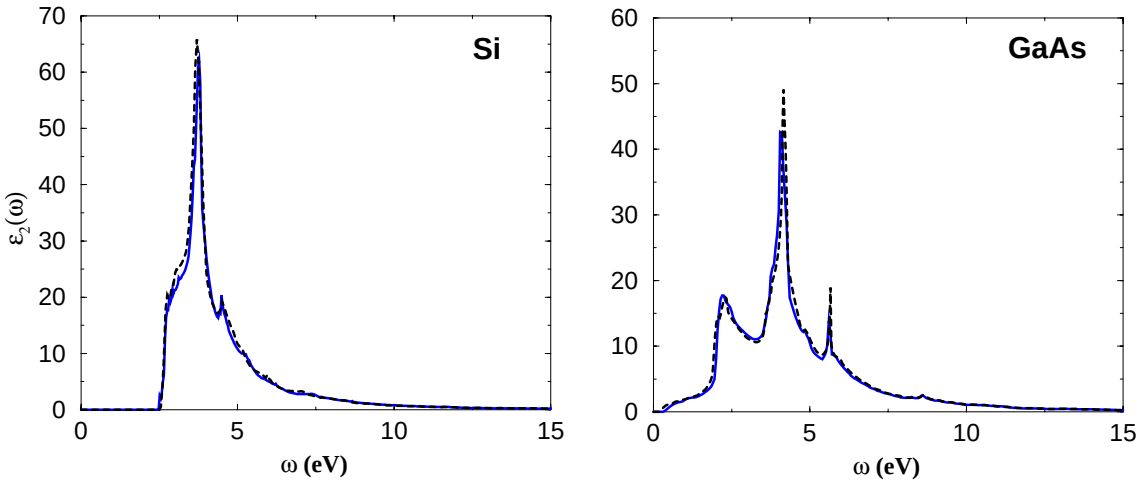
and the non local term is defined by the matrix elements $\Gamma_{ij}^\tau = H_{ij}^\tau - \tilde{H}_{ij}^\tau$, where

$$H_{ij}^\tau = \langle \phi_i^\tau | \frac{-\nabla^2}{2} + v_H[n_\tau + n_\tau^Z] + v_0^\tau(\mathrm{r}) + v_{xc}[n_\tau(\mathrm{r})] | \phi_j^\tau \rangle$$

and

$$\tilde{H}_{ij}^\tau = \langle \tilde{\phi}_i^\tau | \frac{-\nabla^2}{2} + v_H[\tilde{n}_\tau + \hat{n}_\tau] + v_0^\tau(\mathrm{r}) + v_{xc}[\tilde{n}_\tau(\mathrm{r})] | \tilde{\phi}_j^\tau \rangle$$

Dielectric function of Si and GaAs



The PAW (solid line) and the FPLMTO (dashed line) calculations are in good agreement. The local-field and the excitonic effects are not included in both calculations.

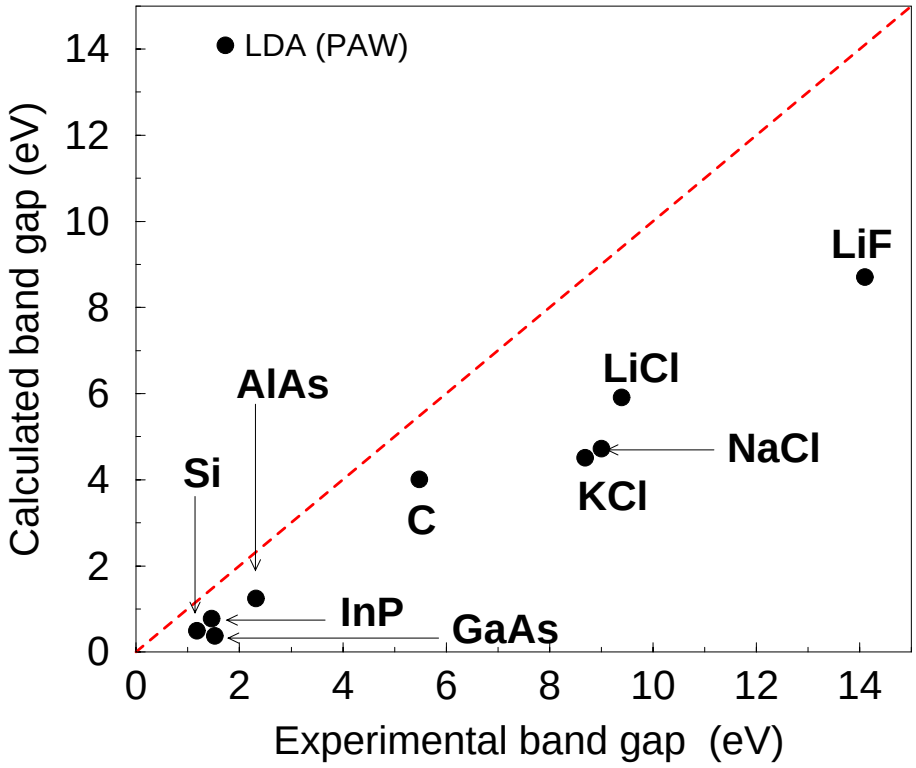
The DFT band-gap problem

- **Kohn-Sham Equation**

$$[h_0(\mathrm{r}) + V_{xc}(\mathrm{r})]\,\Psi_{n\mathrm{k}}(\mathrm{r}) = \epsilon_{n\mathrm{k}}\Psi_{n\mathrm{k}}(\mathrm{r})$$

$$\text{où } h_0(\mathrm{r}) = -\frac{\nabla^2}{2} + V_{ext}(\mathrm{r}) + V_H(\mathrm{r})$$

- **LDA band gaps**



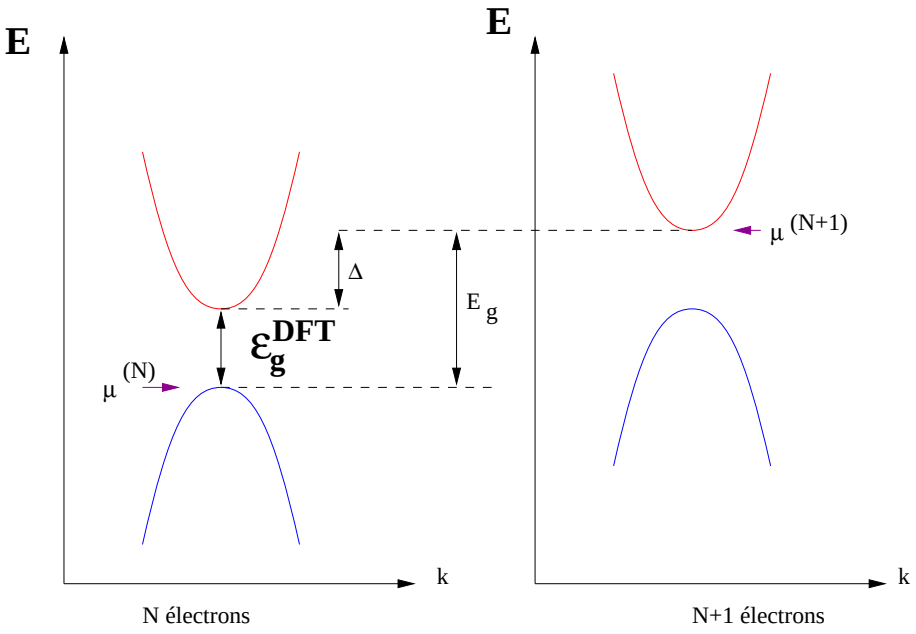
The DFT band-gap problem continued ...

The band gap $\mathrm{E_g}$ is defined as the difference between the ionization energy and the electron affinity

$$\mathrm{E_g} = \left[E^{(N-1)} - E^{(N)}\right] - \left[E^{(N)} - E^{(N+1)}\right] = I - A$$

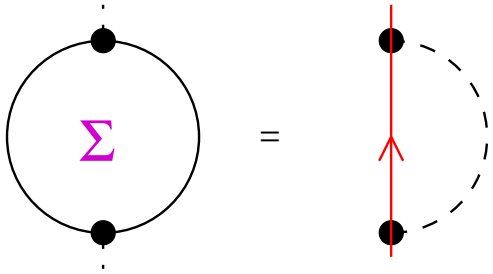
where $E^{(N\pm1)}$ represents the energy of the fundamental state of a system of $N \pm 1$ electrons.
It was shown by Schlüter and Sham (PRL, 83) that the *DFT band gap* $\epsilon_{\mathrm{g}}^{\mathrm{DFT}}$ *is not equal to the quasiparticle gap* E_{g}

$$\Delta = \mathrm{E_g} - \epsilon_{\mathrm{g}}^{\mathrm{DFT}} = \mathrm{E_g} - \left[E^{(N)}_{N+1,\mathrm{DFT}} - E^{(N)}_{N,\mathrm{DFT}}\right]$$
$$= V_{XC}^{(N+1)}(\mathrm{r}) - V_{XC}^{(N)}(\mathrm{r})$$

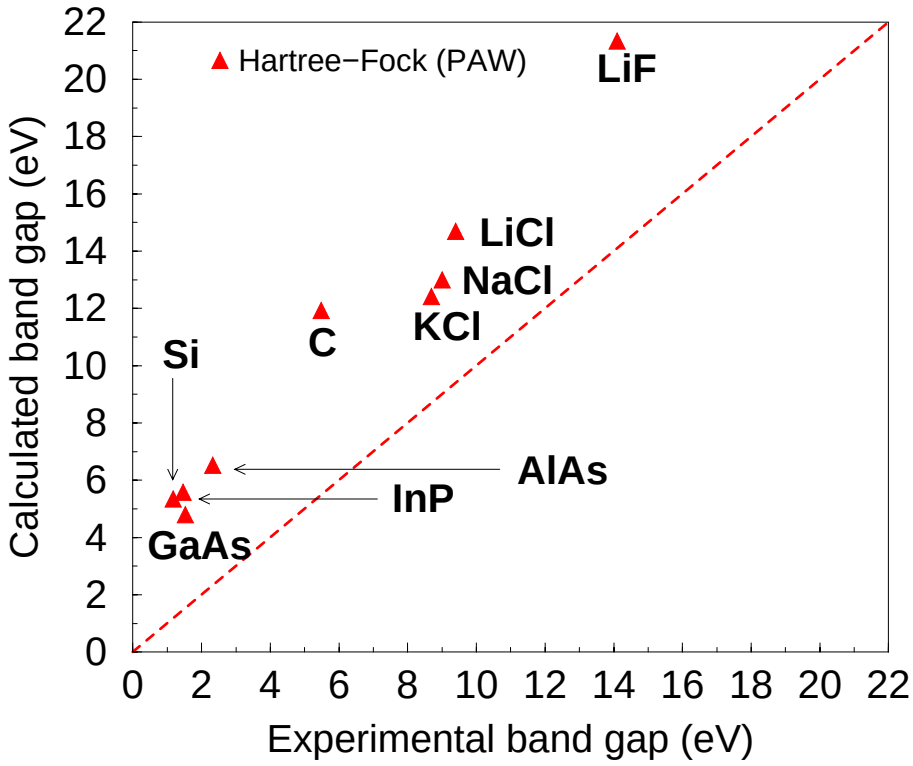


Hartree-Fock approximation

- **Self-energy Σ**



- **Hartree-Fock band gaps**



The GWA (Hedin, 1965)

- **Kohn-Sham equation**

$$[h_0(\mathrm{r}) + V_{xc}(\mathrm{r})]\,\Psi_{n\mathrm{k}}(\mathrm{r}) = \epsilon_{n\mathrm{k}}\Psi_{n\mathrm{k}}(\mathrm{r})$$

- **Quasiparticle equation**

$$h_0(\mathrm{r})\Psi^{qp}_{n\mathrm{k}}(\mathrm{r}) + \int d^3\mathrm{r}'\Sigma(\mathrm{r},\mathrm{r}',\epsilon^{qp}_{n\mathrm{k}})\Psi^{qp}_{n\mathrm{k}}(\mathrm{r}') = \epsilon^{qp}_{n\mathrm{k}}\Psi^{qp}_{n\mathrm{k}}(\mathrm{r})$$

- **Self-energy Σ**

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

where the dynamical screened interaction W is defined by

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

v represents the bare coulomb interaction and ϵ^{-1} the inverse of the dielectric function.
Any two point function $f(\mathrm{r},\mathrm{r}')$ such as $f(\mathrm{r}+\mathrm{R},\mathrm{r}'+\mathrm{R}) = f(\mathrm{r},\mathrm{r}')$ has the following Fourier transform

$$f(\mathrm{r},\mathrm{r}',\omega) = \frac{1}{\Omega}\sum_{\mathrm{q},\mathrm{G},\mathrm{G}'} e^{i(\mathrm{q}+\mathrm{G})\mathrm{r}} f_{\mathrm{G}\mathrm{G}'}(\mathrm{q},\omega)e^{-i(\mathrm{q}+\mathrm{G}')\mathrm{r}'}$$

$\mathrm{q}\in$ BZ, G a reciprocal vector, and Ω the crystal volume. The Fourier transform of the screened interaction W can be written as

$$W_{\mathrm{G},\mathrm{G}'}(\mathrm{q},\omega) = 4\pi\frac{1}{|\mathrm{q}+\mathrm{G}|}\epsilon^{-1}_{\mathrm{G},\mathrm{G}'}(\mathrm{q},\omega)\frac{1}{|\mathrm{q}+\mathrm{G}'|}$$

The Green function G is computed within the LDA

$$G(\mathrm{r},\mathrm{r}',\omega) = \lim_{\delta\to 0^+}\sum_{n\mathrm{k}}\frac{\Psi_{n\mathrm{k}}(\mathrm{r})\Psi^*_{n\mathrm{k}}(\mathrm{r}')}{\omega-\epsilon_{n\mathrm{k}}+i\delta\mathrm{sgn}(\epsilon_{n\mathrm{k}}-\mu)}$$

The GWA continued ...

The self-energy can be written as

$$\langle \Psi_{m\mathrm{k}} | \Sigma(\omega) | \Psi_{l\mathrm{k}} \rangle = \frac{1}{\Omega} \sum_{\mathrm{q}} \sum_{\mathrm{GG'}} \sum_{n} M^{nl}_{\mathrm{G'}}(\mathrm{k},\mathrm{q}) B^{n}_{\mathrm{GG'}}(\mathrm{k},\mathrm{q}) \left[M^{nm}_{\mathrm{G}}(\mathrm{k},\mathrm{q}) \right]^{*},$$

where

$$B^{n}_{\mathrm{GG'}}(\mathrm{k},\mathrm{q}) = \frac{i}{2\pi} \int d\omega' e^{i\delta\omega'} \frac{W_{\mathrm{GG'}}(q,\omega')}{\omega + \omega' - \epsilon_{n\mathrm{k}-\mathrm{q}} + i\delta \mathrm{sgn}(\epsilon_{n\mathrm{k}-\mathrm{q}} - \mu)},$$

and the matrix elements $M^{nm}_{\mathrm{G}}(\mathrm{k},\mathrm{q})$ are given by

$$M^{nm}_{\mathrm{G}}(\mathrm{k},\mathrm{q}) = \langle \Psi_{n\mathrm{k}-\mathrm{q}} | e^{-i(\mathrm{q}+\mathrm{G})\mathrm{r}} | \Psi_{m\mathrm{k}} \rangle$$

The self-energy can be decomposed into two terms which are integrated on the complex plan.
The first term is called the Hartree-Fock term and is given by

$$\langle \Psi_{m\mathrm{k}} | \Sigma^{hf} | \Psi_{l\mathrm{k}} \rangle = -\frac{4\pi}{\Omega} \sum_{n}^{occ} \sum_{\mathrm{q}} \sum_{\mathrm{G}} \frac{M^{nl}_{\mathrm{G}}(\mathrm{k},\mathrm{q}) \left[M^{nm}_{\mathrm{G}}(\mathrm{k},\mathrm{q}) \right]^{*}}{|\mathrm{q}+\mathrm{G}|^2}.$$

The second term is called the correlation term and is given by

$$\langle \Psi_{m\mathrm{k}} | \Sigma^{C}(\omega) | \Psi_{l\mathrm{k}} \rangle = \frac{1}{\Omega} \sum_{\mathrm{q}} \sum_{\mathrm{GG'}} \sum_{n} M^{nl}_{\mathrm{G'}}(\mathrm{k},\mathrm{q}) \left[M^{nm}_{\mathrm{G}}(\mathrm{k},\mathrm{q}) \right]^{*} C^{\mathrm{k},\mathrm{q},n}_{\mathrm{GG'}}(\omega),$$

where

$$C^{\mathrm{k},\mathrm{q},n}_{\mathrm{GG'}}(\omega) = \frac{i}{2\pi} \int d\omega' \frac{W^{C}_{\mathrm{GG'}}(q,\omega')}{\omega + \omega' - \epsilon_{n\mathrm{k}-\mathrm{q}} + i\delta \mathrm{sgn}(\epsilon_{n\mathrm{k}-\mathrm{q}} - \mu)},$$

and where W^{C} is given by

$$W^{C}_{\mathrm{GG'}}(q,\omega') = W_{\mathrm{GG'}}(q,\omega') - v_{\mathrm{GG'}}$$

GWA continued ...

- Solution of the QP equation

$$\Psi^{qp}_{m\mathrm{k}}(\mathrm{r}) = \sum_n \alpha_{mn}(\mathrm{k})\Psi_{n\mathrm{k}}(\mathrm{r})$$

In practice, $\alpha_{mn} \simeq \delta_{mn}$ (Hybertsen-Louie, 1986). Then the QP energies are provided by

$$\epsilon^{qp}_{m\mathrm{k}} = \epsilon_{m\mathrm{k}} + \langle\Psi_{m\mathrm{k}}|\Sigma(\epsilon^{qp}_{m\mathrm{k}})|\Psi_{m\mathrm{k}}\rangle - \langle\Psi_{m\mathrm{k}}|V_{xc}[n_v(\mathrm{r})]|\Psi_{m\mathrm{k}}\rangle$$

assuming that $V_{xc}^{core-val} \simeq V_{xc}[n_v + n_c] - V_{xc}[n_v]$

- Practical scheme

$$\epsilon^{qp}_{m\mathrm{k}} - \epsilon_{m\mathrm{k}} = Z_{m\mathrm{k}} \times \begin{cases} \langle\Psi_{m\mathrm{k}}|\Sigma(\mathrm{r},\mathrm{r}',\epsilon_{m\mathrm{k}})|\Psi_{m\mathrm{k}}\rangle \\ -\langle\Psi_{m\mathrm{k}}|V_{xc}(\mathrm{r})|\Psi_{m\mathrm{k}}\rangle \end{cases}$$

where the renormalization factor $Z_{n\mathrm{k}}$ is defined by

$$Z_{n\mathrm{k}} = [1 - \langle\Psi_{n\mathrm{k}}|\frac{\partial}{\partial\omega}\Sigma(\mathrm{r},\mathrm{r}',\epsilon_{n\mathrm{k}})|\Psi_{n\mathrm{k}}\rangle]^{-1}$$

Since $\frac{\partial}{\partial\omega}\Sigma < 0$, the renormalization factor should be between 0 and 1.

Removal of the double counting

- **LDA decoupling:** $V_{xc}^{core-val} \simeq V_{xc}[n_v + n_c] - V_{xc}[n_v]$

$$\epsilon_{mk}^{qp,1} = \begin{cases} \epsilon_{mk} + \langle \Psi_{mk} | \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_{mk}^{qp,1}) | \Psi_{mk} \rangle \\ - \langle \Psi_{mk} | V_{xc}[n_v(\mathbf{r})] | \Psi_{mk} \rangle \end{cases}$$

- **Hartree-Fock decoupling:** $V_{xc}^{core-val} \simeq V_X^c$

$$\epsilon_{mk}^{qp,2} = \begin{cases} \epsilon_{mk} + \langle \Psi_{mk} | \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_{mk}^{qp,2}) | \Psi_{mk} \rangle \\ - \langle \Psi_{mk} | V_{xc}[n_v(\mathbf{r}) + n_c(\mathbf{r})] | \Psi_{mk} \rangle + \langle \Psi_{mk} | V_X^c(\mathbf{r}, \mathbf{r}') | \Psi_{mk} \rangle \end{cases}$$

- **Results for silicon**

	$V_{xc}[n_v + n_c] - V_X^c$	$V_{xc}[n_v]$	$\epsilon^{qp,2}$	$\epsilon^{qp,1}$
$\Gamma_{25'v}$	-11.60	-11.45	0.0	0.0
Γ_{15c}	-10.34	-10.19	3.15	3.15
X_{4v}	-10.85	-10.74	-3.05	-3.01
X_{1c}	-9.25	-9.15	1.10	1.15
$L_{3'v}$	-11.33	-11.20	-1.28	-1.26
L_{1c}	-10.39	-10.28	2.12	2.16

Comparison with plasmon-pole model

- **Homogeneous electron gas**

$$\epsilon^{-1}(q,\omega) = 1 + A_q \left(\frac{1}{\omega - (\omega_q - i\delta)} - \frac{1}{\omega + (\omega_q - i\delta)} \right)$$

- **Calculation of parameters A_q and ω_q**

(1) Static limit of $\epsilon^{-1}(q,\omega)$

(2) Johnson sum rule

$$\int_0^\infty d\omega \; \omega \; \mathrm{Im}\left[\epsilon^{-1}(q,\omega)\right] = -\frac{\pi}{2}\omega_p^2$$

- **Results for silicon**

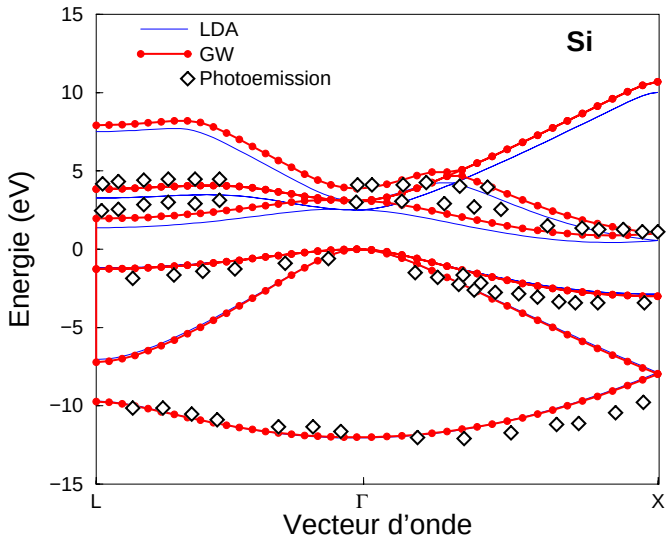
	LDA	GW	GW with Plasmon-pole model	
			Von der Linden et Horsch	Engel-Farid
$\Gamma_{25'v}$	0.00	0.00	0.00	0.00
Γ_{15c}	2.54	3.09	3.09	3.13
X_{4v}	-2.85	-2.90	-3.01	-2.97
X_{1c}	0.61	1.01	1.09	1.17
$L_{3'v}$	-1.19	-1.16	-1.28	-1.27
L_{1c}	1.44	2.05	2.09	2.12

Direct integration versus Padé

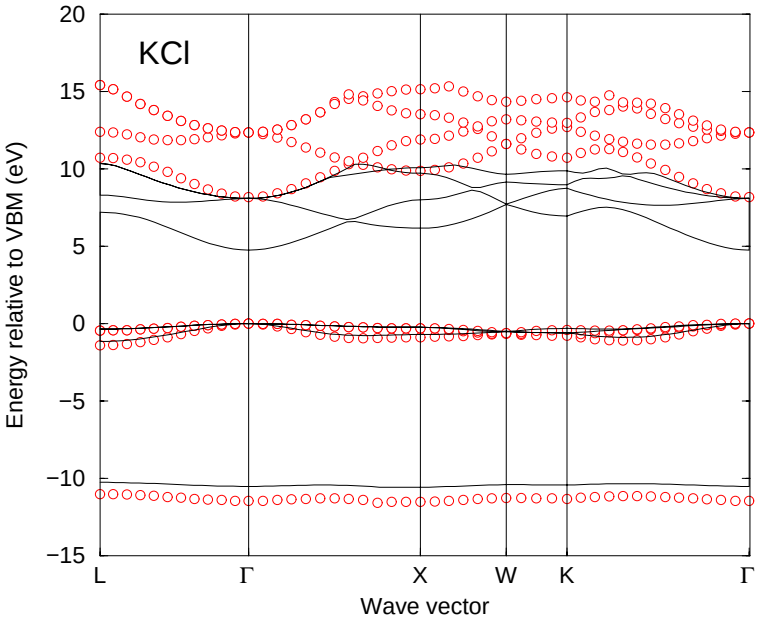
	Contour integral	Analytical continuation
$\mathbf{\Gamma_{1v}}$	-11.85	-11.87
$\mathbf{\Gamma_{25'v}}$	0.00	0.00
$\mathbf{\Gamma_{15c}}$	3.09	3.09
$\mathbf{\Gamma_{2'c}}$	4.05	4.06
$\mathbf{X_{1v}}$	-7.74	-7.68
$\mathbf{X_{4v}}$	-2.90	-2.91
$\mathbf{X_{1c}}$	1.01	1.03
$\mathbf{X_{4c}}$	10.64	10.59
$\mathbf{L_{2'v}}$	-9.57	-9.50
$\mathbf{L_{1v}}$	-6.97	-6.90
$\mathbf{L_{3'v}}$	-1.16	-1.17
$\mathbf{L_{1c}}$	2.05	2.03
$\mathbf{L_{3c}}$	3.83	3.83
$\boldsymbol{E_g}$	0.92	0.90

Calculated quasiparticle energies of silicon using two different integration schemes. The results are in good agreement.

QP band structures

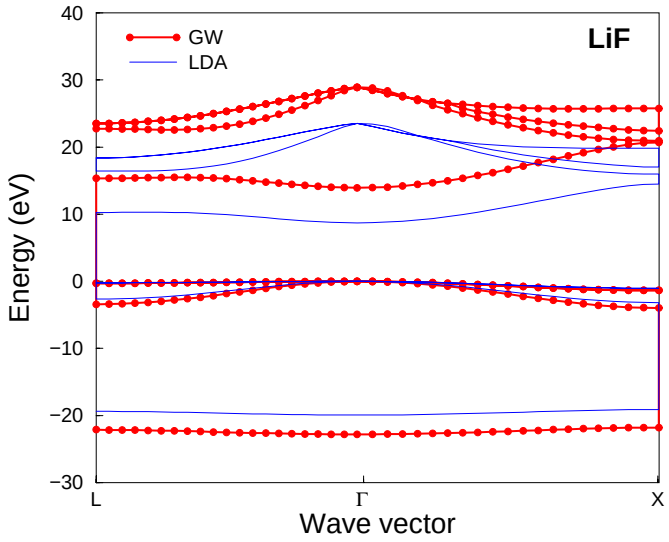


Band gap: LDA 0.5 eV; GW 1.12 eV; Expt. 1.17 eV



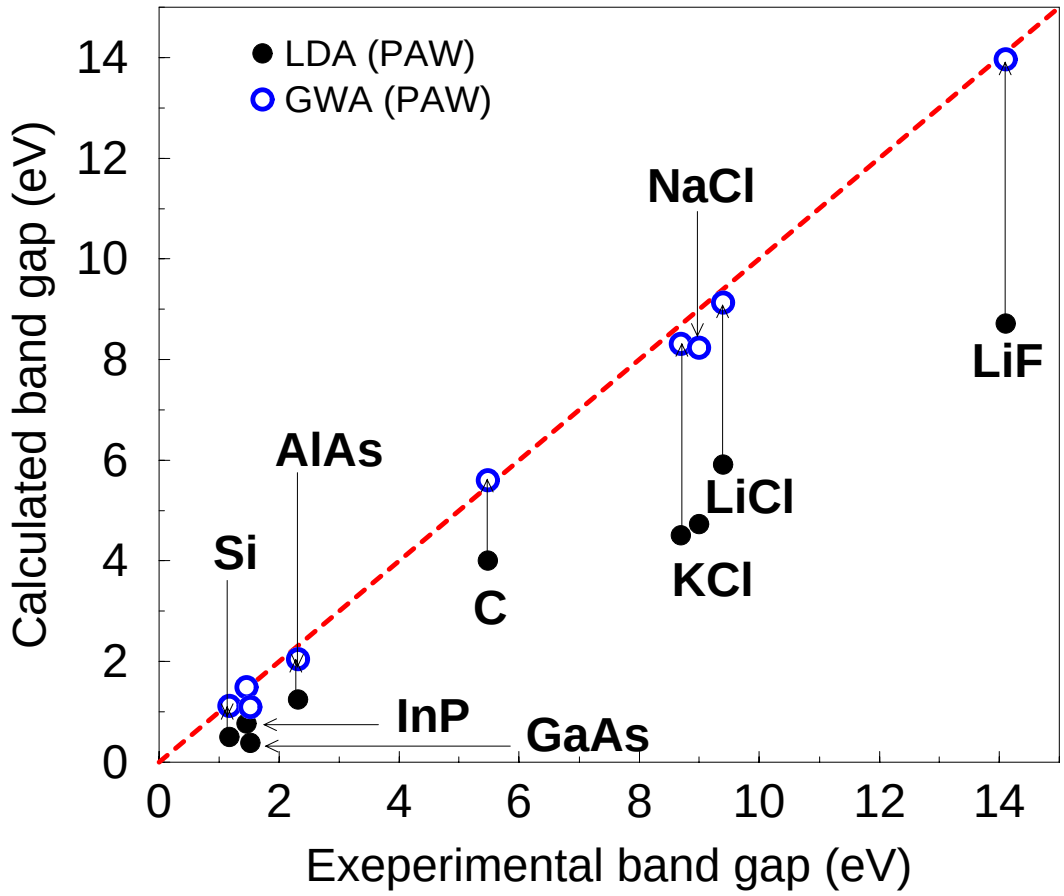
Band gap: LDA 4.75 eV; GW 8.24 eV; Expt. 8.69 eV

Electronic structure of LiF

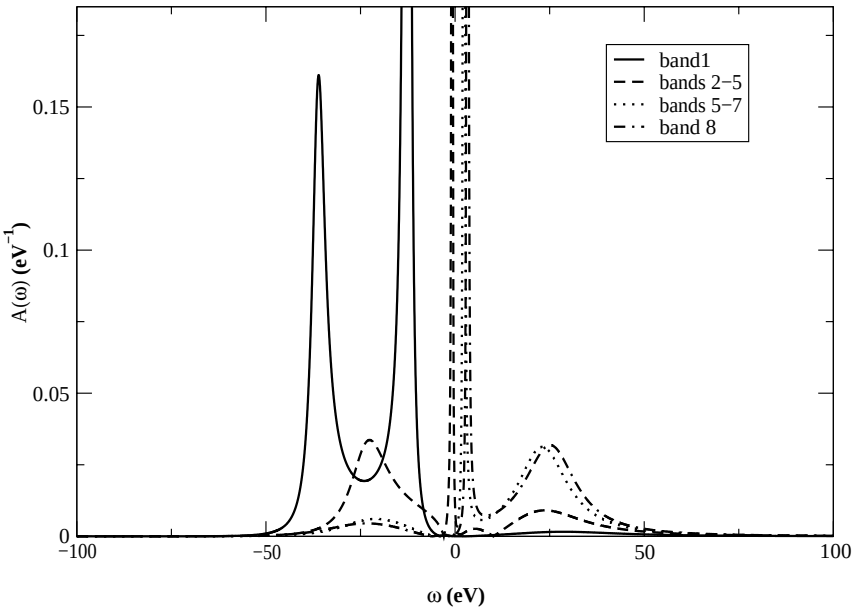


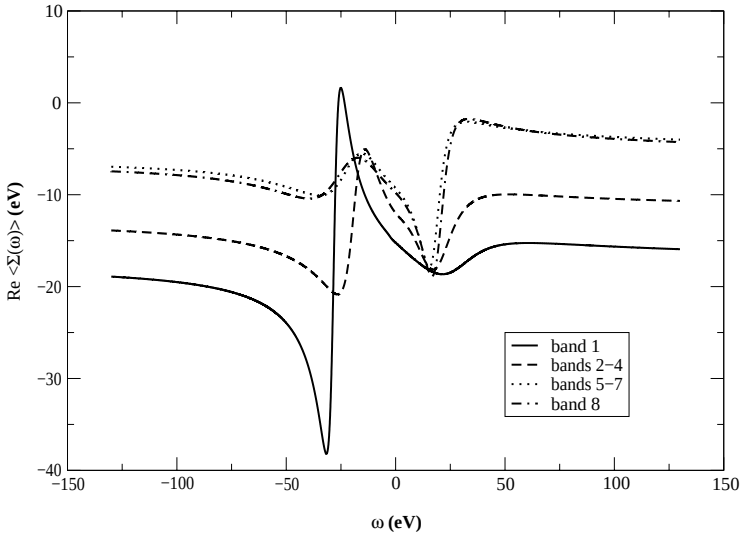
Band gap: LDA 8.71 eV; GW 13.97 eV; Expt. 14.1 eV
Band width F 2p: LDA 3.17 eV; GW 3.76 eV; Expt. 3.5 eV

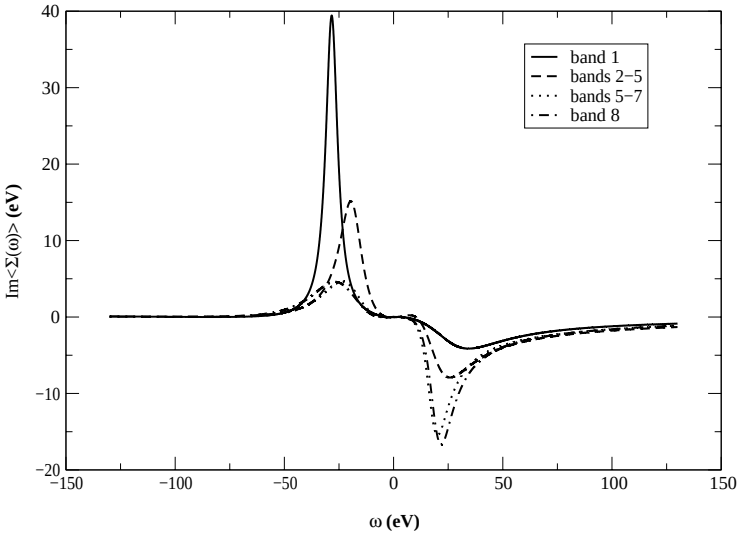
GW band gaps


LDA (PAW)
GWA (PAW)
Calculated band gap (eV)
Exeperimental band gap (eV)
0
2
4
6
8
10
12
14
NaCl
LiF
AlAs
LiCl
Si
KCl
C
InP
GaAs

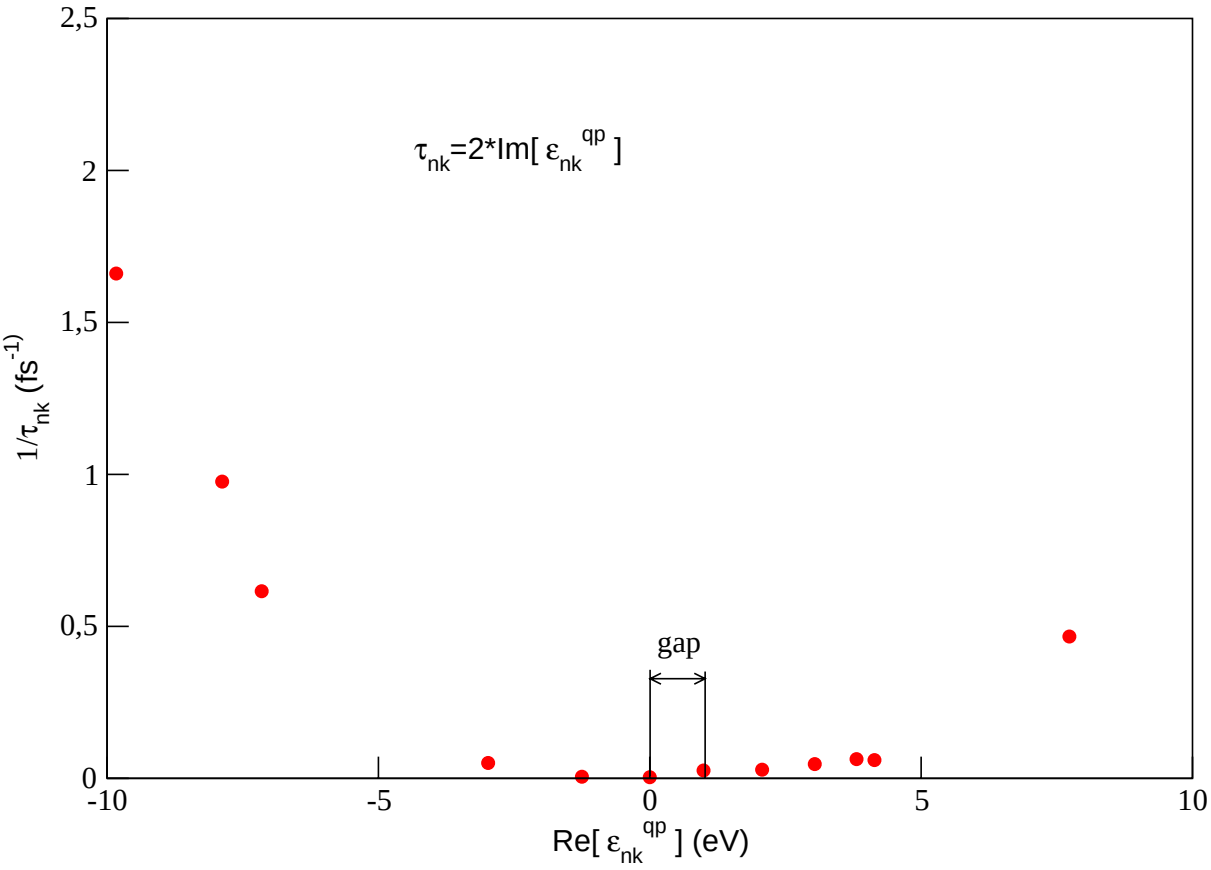
Spectral function of silicon at Γ







Life time of the QP of Si at Γ

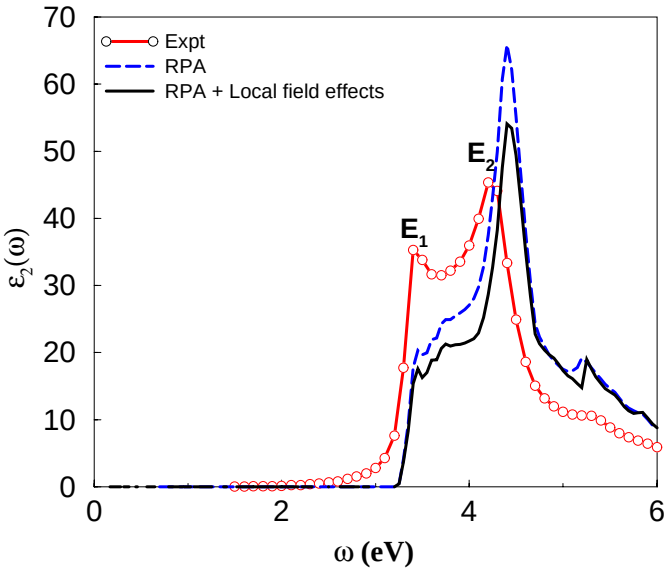


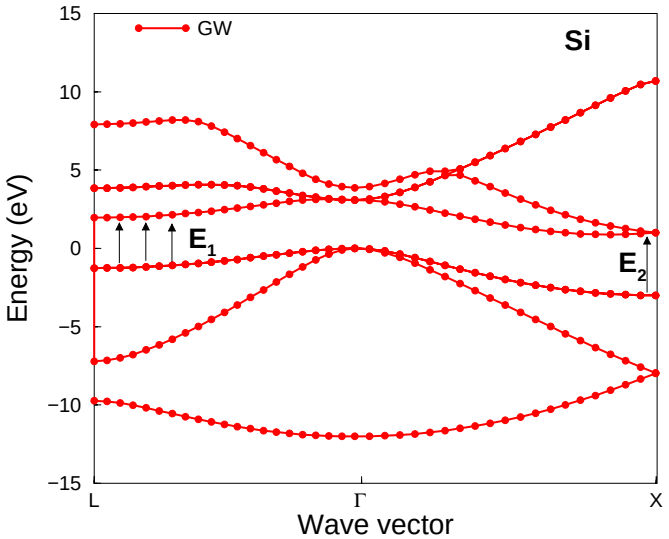
Optical properties within RPA

- **RPA formulation**

$$\epsilon(\omega) = \lim_{q\to 0} \epsilon_{0,0}(q,\omega) - \lim_{q\to 0} \sum_{G,G'\neq 0} \epsilon_{0,G}(q,\omega)\epsilon^{-1}_{G,G'}(q,\omega)\epsilon_{G',0}(q,\omega)$$

- **RPA dielectric function of Silicon**

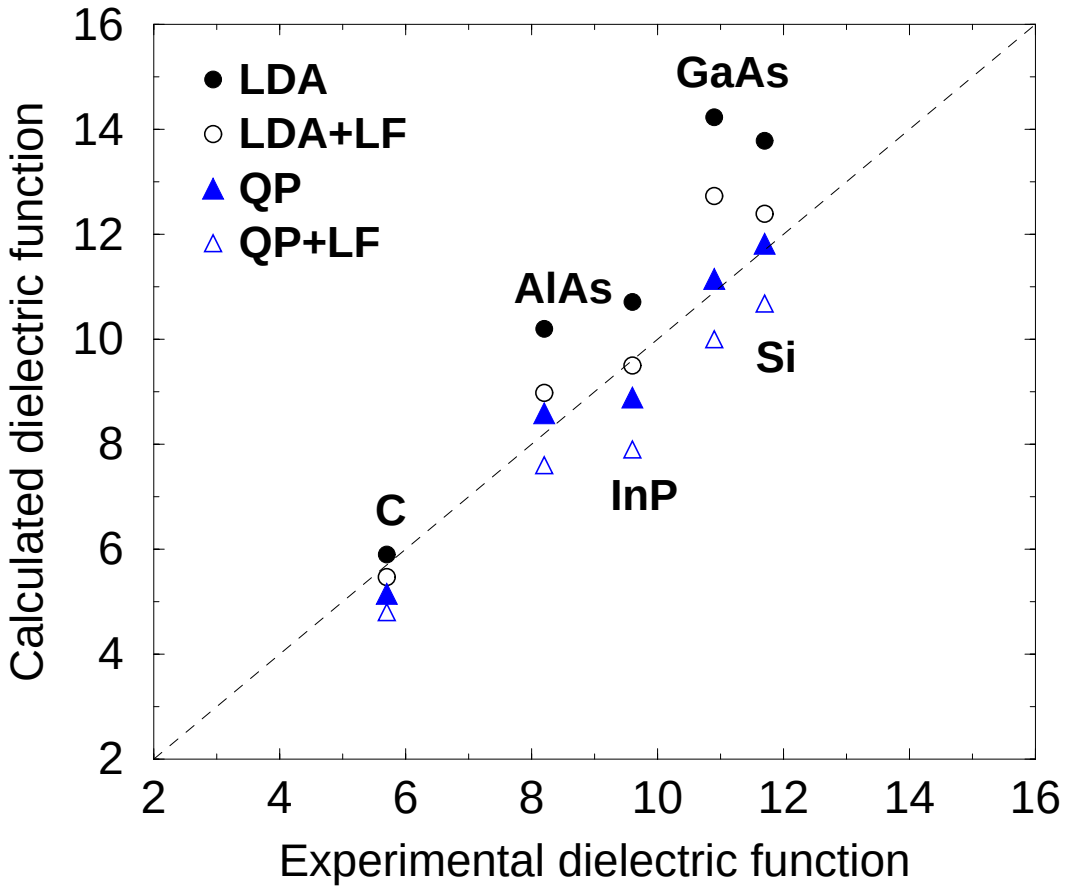




Static dielectric function

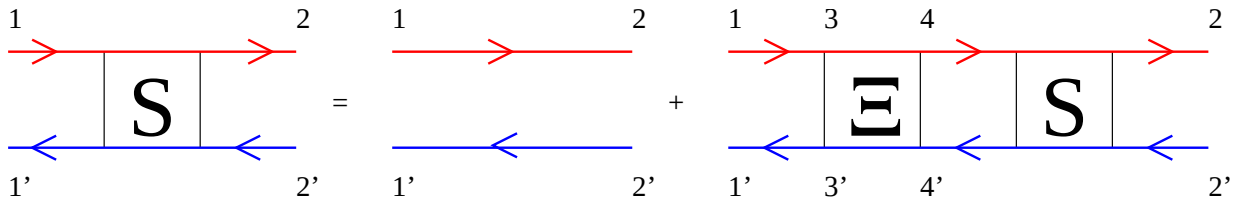
The static dielectric function is obtained using the KK relations

$$\epsilon_\infty = 1 + \lim_{q\to 0} \frac{2}{\pi} P \int_0^\infty d\omega' \frac{\epsilon_2(q,\omega')}{\omega'}$$



Excitonic effects (Hanke-Sham, 1975)

- Bethe-Salpeter equation
- Expression for the Kernel

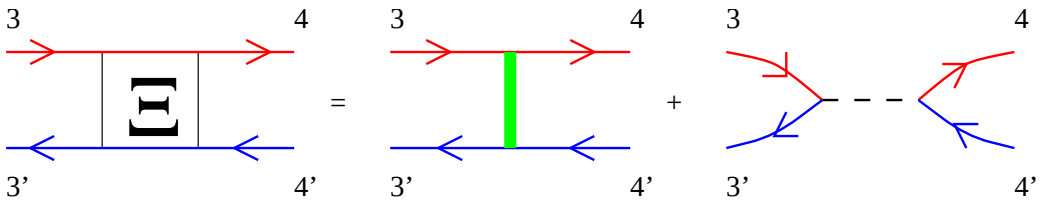


$$S = S^0 + S^0 \, \Xi \, S$$

Ξ

$$\Xi(3,3',4,4') = i\delta(3,4)\delta(3',4')W(3,3') - i\delta(3,3')\delta(4,4')v(3,4)$$

- Reformulation of the Bethe-Salpeter equation



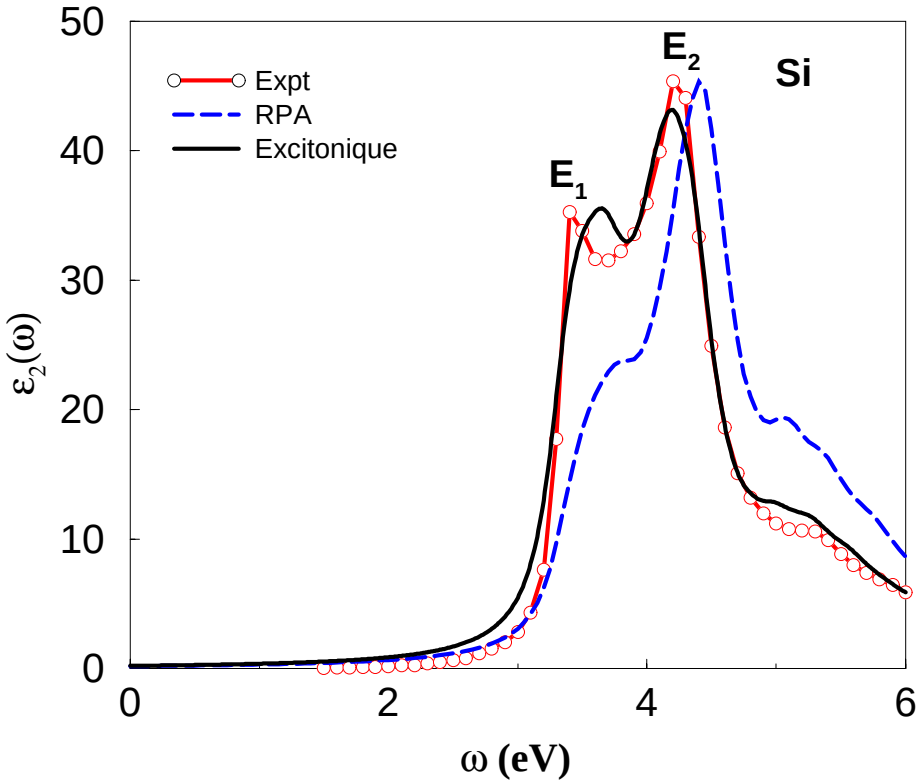
$$(\epsilon^{qp}_{ck} - \epsilon^{qp}_{vk})\, A^{\lambda}_{vck} + \sum_{v',c',k'} \langle vck|\Xi|v'c'k'\rangle\, A^{\lambda}_{v'c'k'} = E_{\lambda} A^{\lambda}_{vck}$$

- Macroscopic dielectric function

$$\epsilon^{(2)}(\omega) = \lim_{q\to 0} \frac{4\pi^2}{\Omega} \times \frac{1}{q^2} \times \sum_{\lambda} \left| \sum_{vck} \langle vk|e^{-iq.r}|ck\rangle\, A^{\lambda}_{vck} \right|^2 \delta(\omega - E_{\lambda})$$

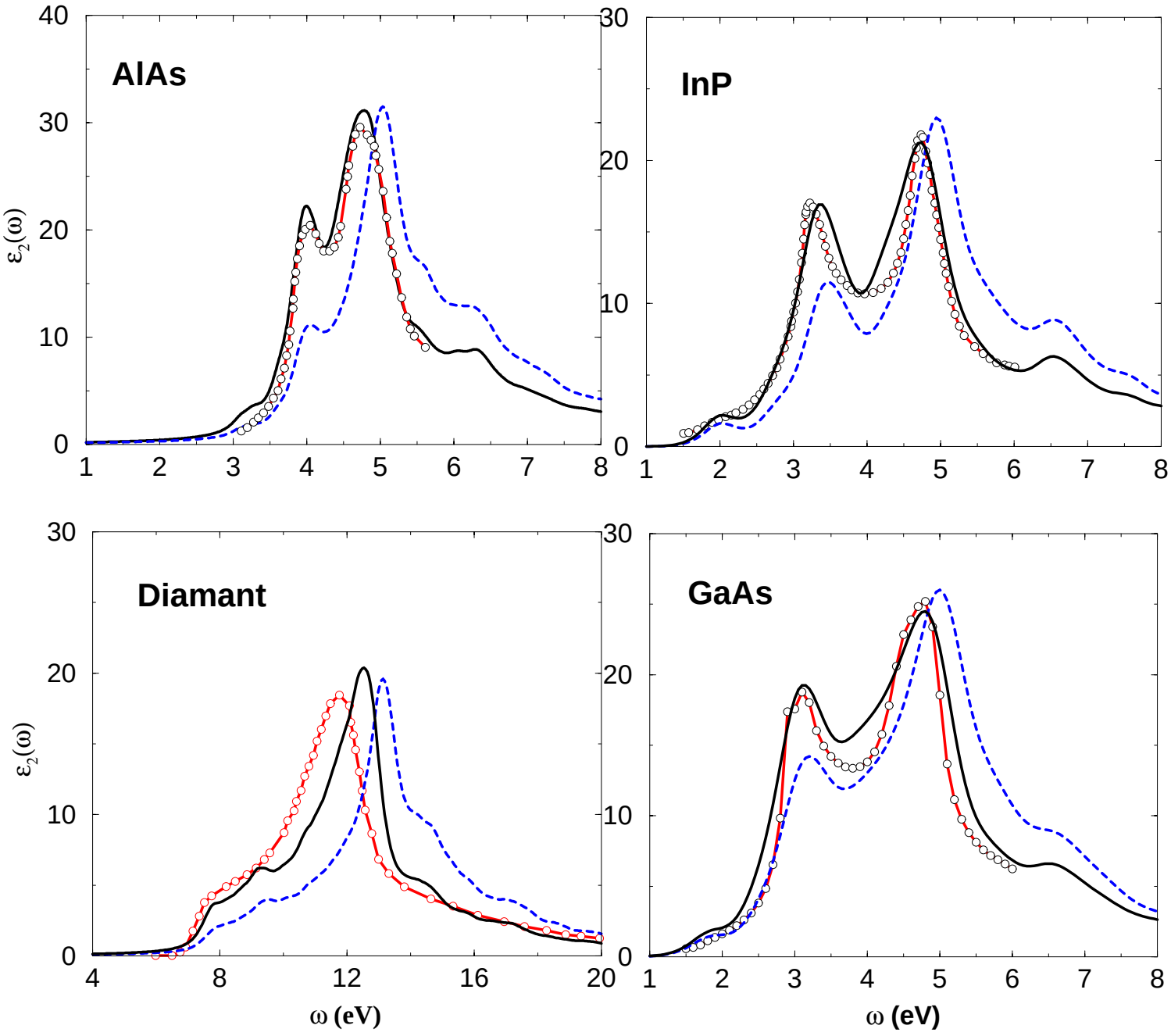
Excitonic effects (Hanke-Sham, 1975)

- Silicon



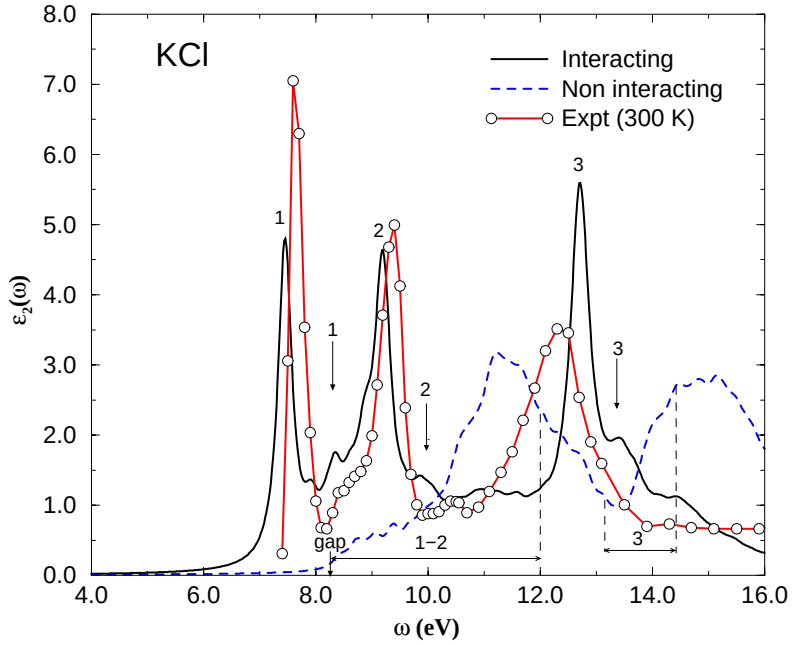
electron-hole attraction: $\frac{e^2}{\epsilon_\infty r}$ when $r \longrightarrow \infty$

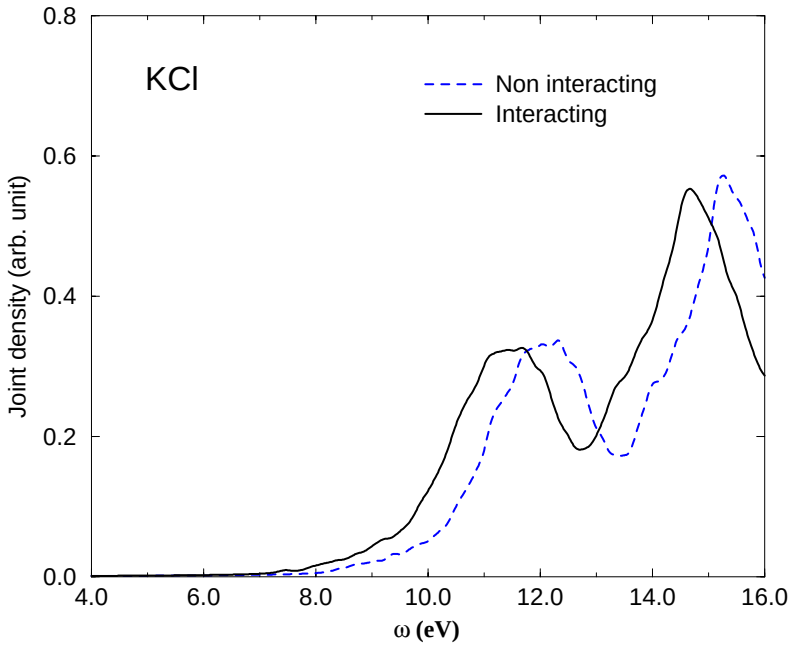
Semiconductors of type III-V and diamond



electron-hole attraction: $\frac{e^2}{\epsilon_\infty\, r}$ when $r \longrightarrow \infty$

Ionic insulators





	Band gap		Position of the first excitonic peak		
	GW	Expt.	Theory	Expt at 10 K	Expt at 300 K
KCl	8.24	8.69	7.44	7.79	7.6

Conclusion

Results

- GW-PAW $\Rightarrow \epsilon^{qp}_{n\mathbf{k}}$ in good agreement with experiment
- $\epsilon^{qp}_{n\mathbf{k}} \Rightarrow$ Calculation of the optical properties
- Excitonic effects crucial $\Rightarrow$ Bethe-Salpeter equation

Outlooks

- Extension to more complex systems
- Selfconsistent GW-DMFT
- Determination of XAS spectra