Many Body Pertubation Theory

GW approximation
RPA energies

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Outline

I. Introduction: going beyond DFT

II. Introducing the Green's function

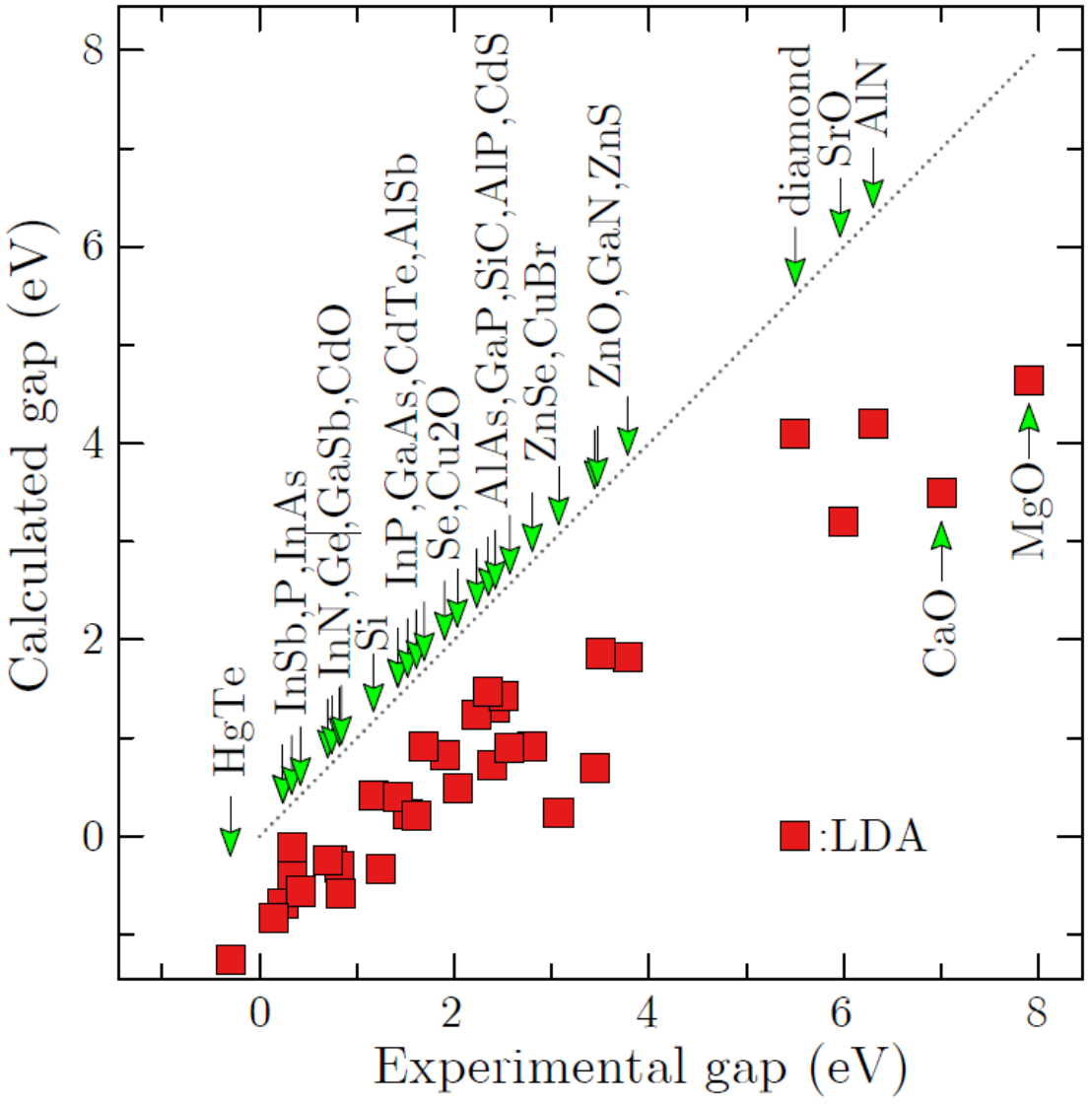
III. Exact Hedin's equations and the *GW* approximation

IV. Calculating the *GW* self-energy in practice

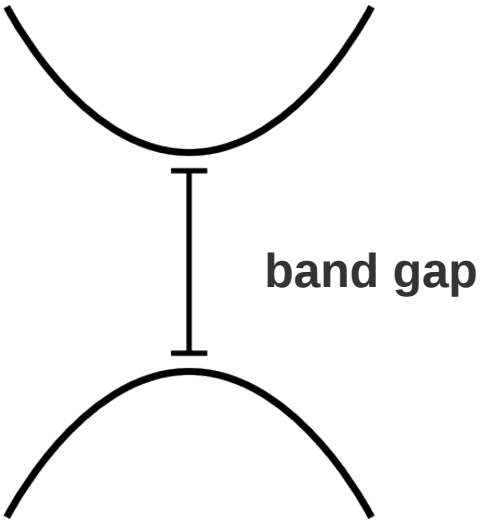
V. RPA total energies

VI. Some applications

Standard DFT has unfortunately some shortcomings



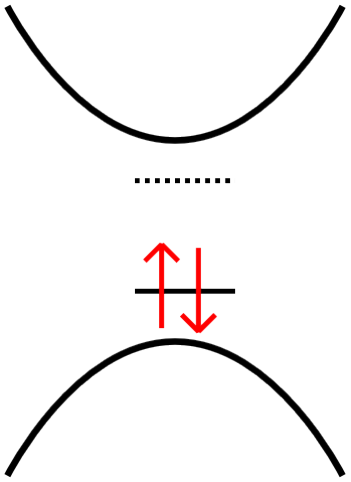
after van Schilfgaarde *et al* PRL **96** 226402 (2008)



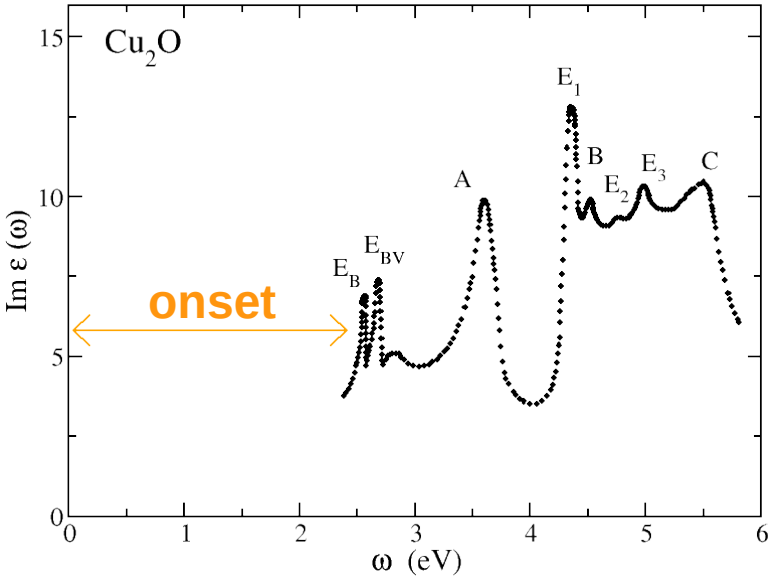
Band gap problem!

A pervasive problem

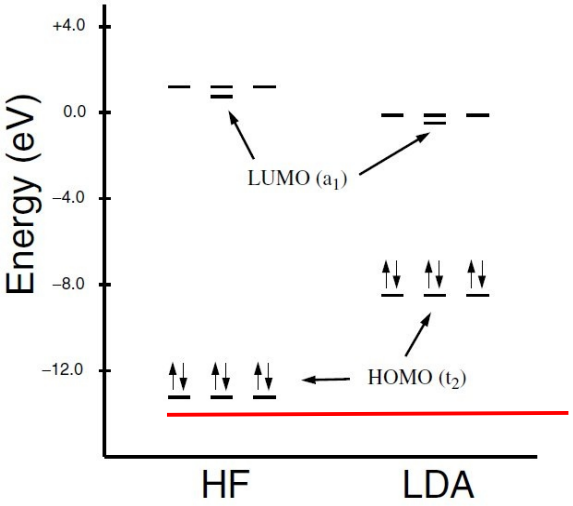
Defect formation energy,
dopant solubility



Optical absorption



Photoemission



Exp.

FIG. 1. Single-particle Hartree-Fock and local density approximation eigenvalue spectra (eV) for the SiH_4 molecule.

Gap re-normalization by a (metallic) substrate

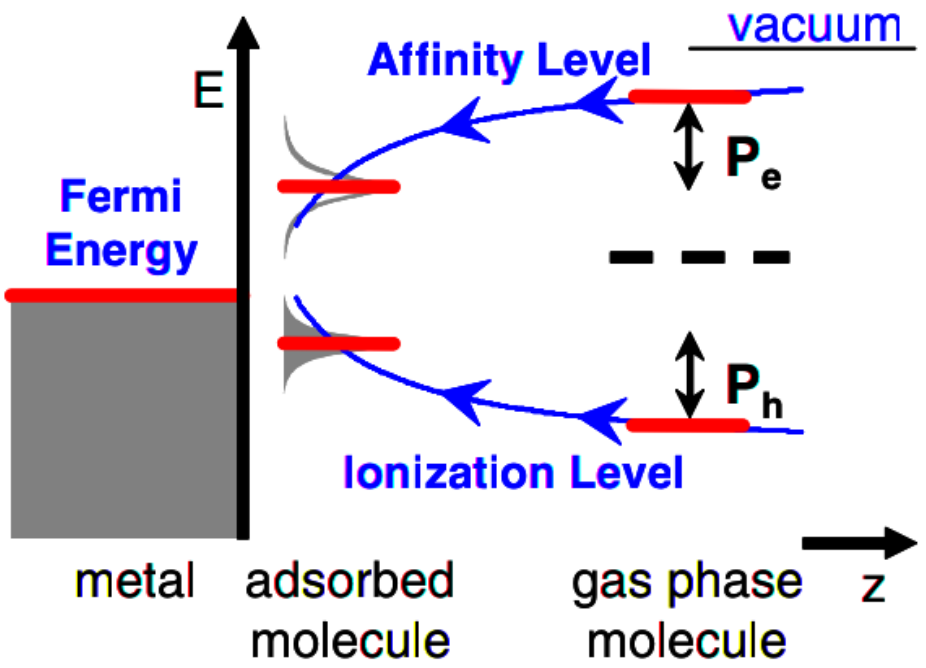


FIG. 1 (color online). Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface.

Benzene deposited on copper, gold, graphite

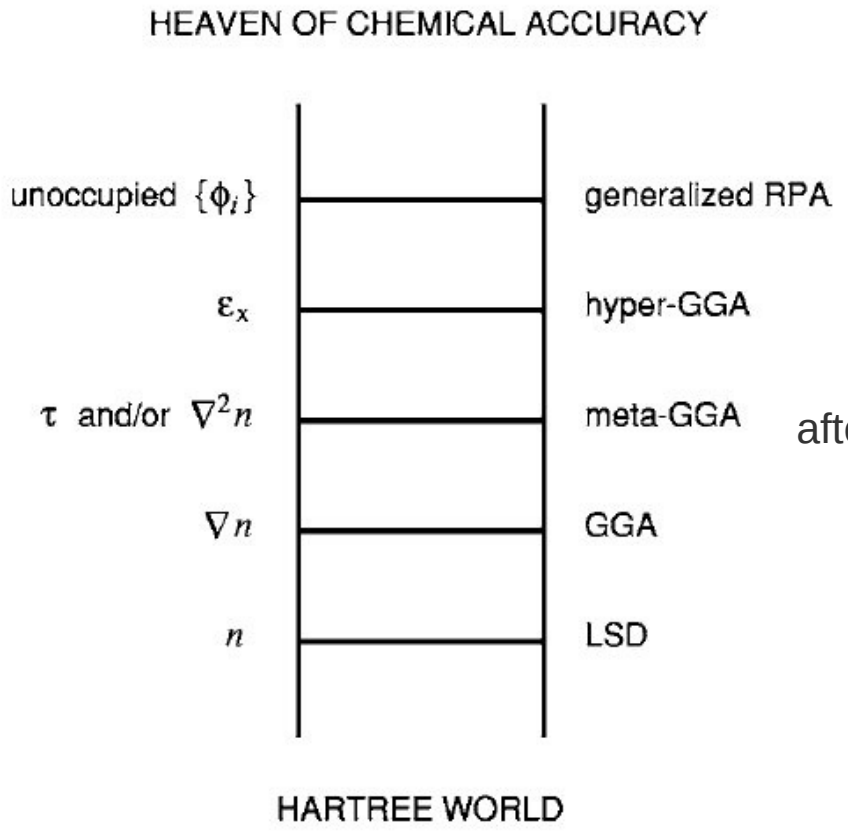
Neaton, Hybertsen, Louie PRL (2006)

How do go beyond within the DFT framework?

Not easy to find improvement within DFT framework

There is no such thing as a perturbative expansion

Perdew's Jacob's ladder does not help for the band gap



after J. Perdew JCP (2005).

FIG. 1. Jacob's ladder of density functional approximations to the exchange-correlation energy.

Need to change the overall framework!

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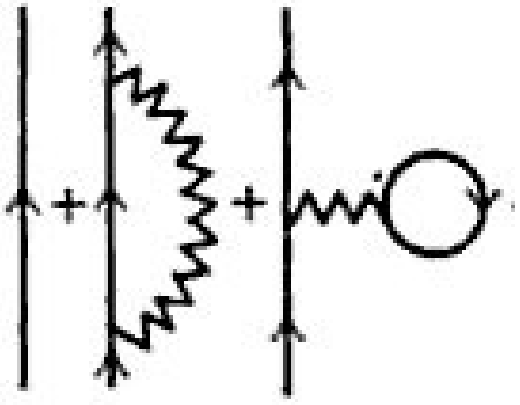
Many-body perturbation theory

Historically older than the DFT (from the 40-50's)!
Big names: Feynman, Schwinger, Hubbard, Hedin, Lundqvist

Green's functions
= propagator

$$G(\boldsymbol{r}t, \boldsymbol{r}'t') \approx$$



The Green's function

Exact ground state wavefunction: $|N,0\rangle$

Creation, annihilation operator: $\Psi^\dagger(\boldsymbol{r}\,t),\ \Psi(\boldsymbol{r}\,t)$

1. $\Psi^\dagger(\boldsymbol{r}\,t)|N,0\rangle$ is a (N+1) electron wavefunction not necessarily in the ground state

2. $\Psi^\dagger(\boldsymbol{r}'\,t')|N,0\rangle$ is another (N+1) electron wavefunction

Let's compare the two of them!

Green's function definition

$$\underbrace{\langle N,0|\Psi(\boldsymbol{r}\,t)}_{1}\underbrace{\Psi^{\dagger}(\boldsymbol{r}'\,t')|N,0\rangle}_{2}$$

$$=iG^{e}(\boldsymbol{r}\,t,\boldsymbol{r}'\,t') \quad \text{for} \quad t>t'$$

Mesures how an extra electron propagates from (*r't'*) to (*rt*).

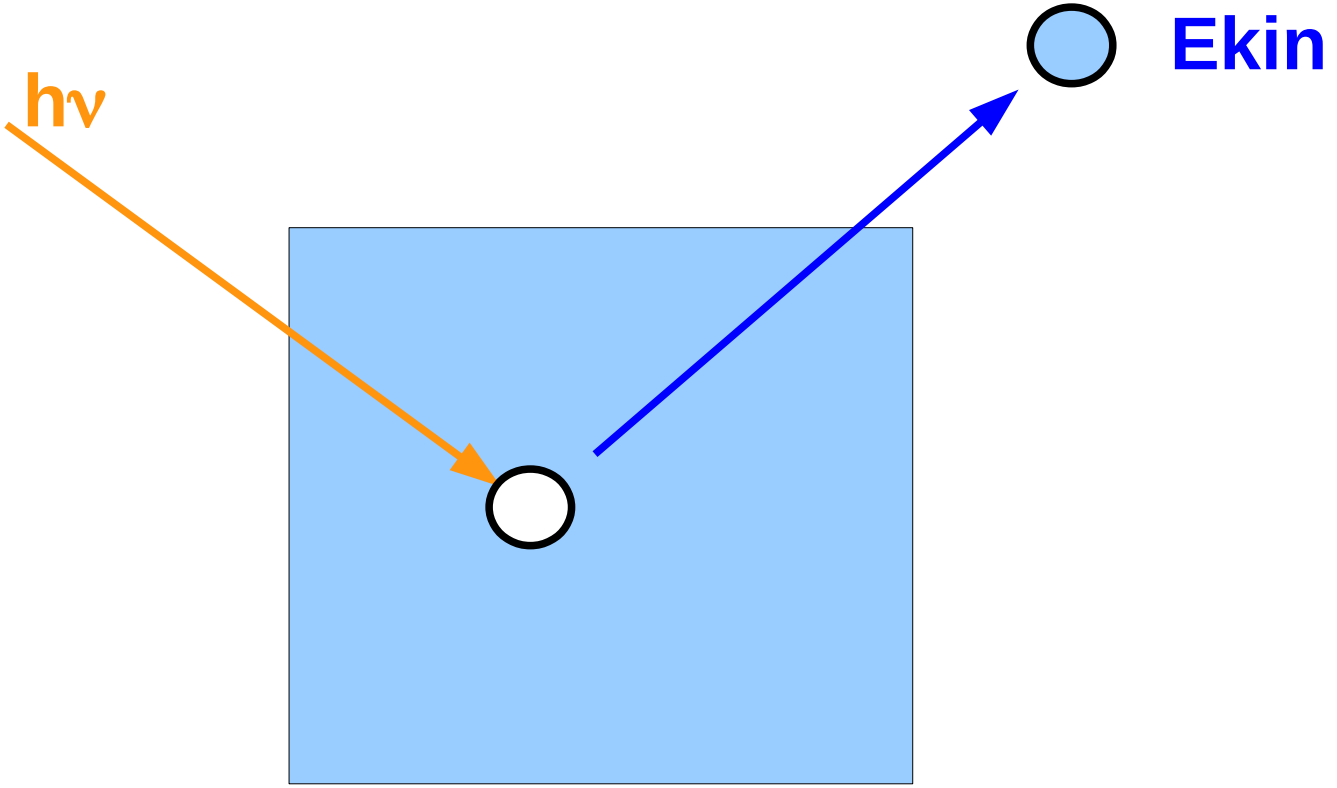
Green's function definition

$$\underbrace{\langle N,0|\Psi^{\dagger}(\boldsymbol{r}'t')}_{2}\underbrace{\Psi(\boldsymbol{r}t)|N,0\rangle}_{1}$$

$$= i G^{h}(\boldsymbol{r}'t',\boldsymbol{r}t) \quad \text{for} \quad t' > t$$

Mesures how a missing electron (= a hole) propagates from (*rt*) to (*r't'*).

Related to photoemission spectroscopy

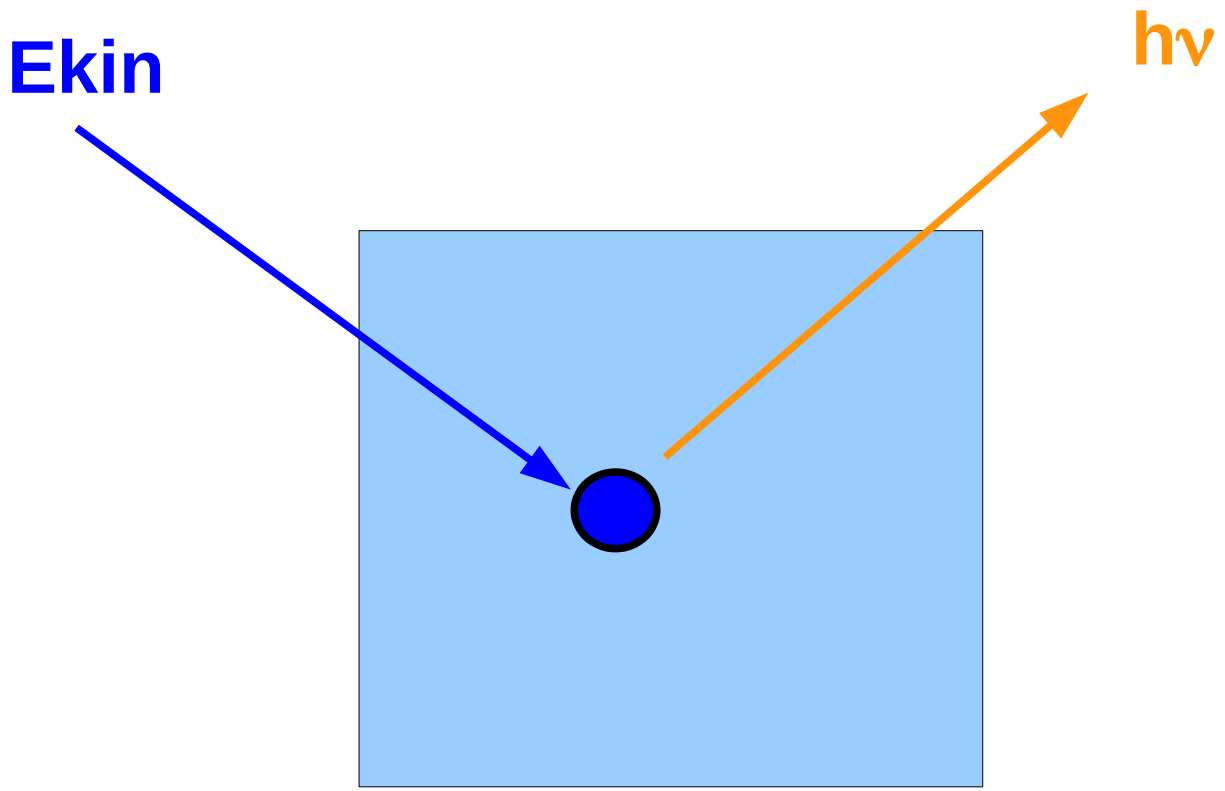


Energy conservation: before after

$$h\nu + E(N,0) = E_{kin} + E(N-1,i)$$

Quasiparticle energy: $$\epsilon_i = E(N,0) - E(N-1,i) = E_{kin} - h\nu$$

And inverse photoemission spectroscopy



Energy conservation: before after

$$E_{kin} + E(N,0) = h\nu + E(N+1,i)$$

Quasiparticle energy: $$\epsilon_i = E(N+1,i) - E(N,0) = E_{kin} - h\nu$$

Other properties of the Green's function

Get the electron density:

$$\rho(\boldsymbol{r}) = -i\,G(\boldsymbol{r}\,t^{-},\boldsymbol{r},t)$$

Galitskii-Migdal formula for the total energy:

$$E_{total} = \frac{1}{\pi}\int_{-\infty}^{\mu} d\,\omega\,\mathrm{Tr}\left[\left(\omega - h_0\right)\mathrm{Im}\,G\left(\omega\right)\right]$$

Expectation value of any 1 particle operator (local or non-local)

$$\langle O \rangle = \lim_{t \to t'} Tr\left[O\,G\right]$$

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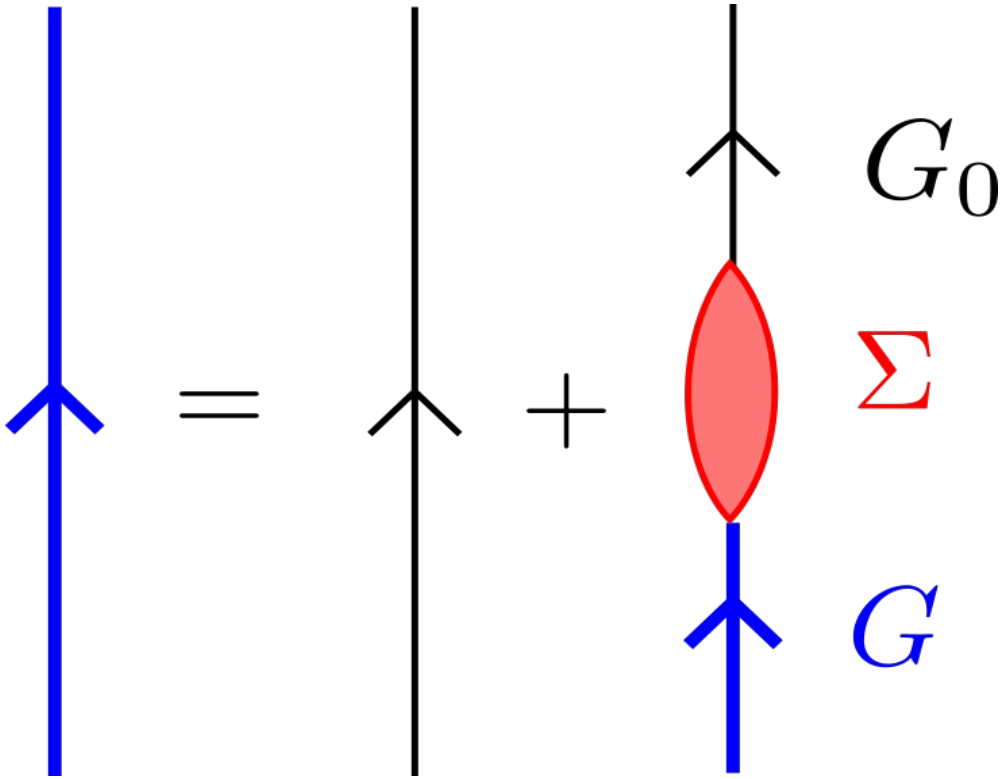
Dyson equation for the exact Green's function

Imagine there exists an operator that generates the exact *G*



$$G(1,2) = G_0(1,2) + \int d(34) G_0(1,3) \Sigma(3,4) G(4,2)$$

This operator is the famous “self-energy”:

- non-local in space
- time-dependent
- non-Hermitian

Everything else now deals with finding expressions for the self-energy!

Hedin's coupled equations

6 coupled equations: $1=(\boldsymbol{r}_1 t_1 \sigma_1)$ $2=(\boldsymbol{r}_2 t_2 \sigma_2)$

$$G(1,2)=G_0(1,2)+\int d34\, G_0(1,3)\Sigma(3,4)G(4,2)$$ **Dyson equation**

$$\Sigma(1,2)=i\int d34\, G(1,3)W(1,4)\Gamma(4,2,3)$$ **self-energy**

$$\Gamma(1,2,3)=\delta(1,2)\delta(1,3)+\int d4567\frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(5,7)\Gamma(6,7,3)$$ **vertex**

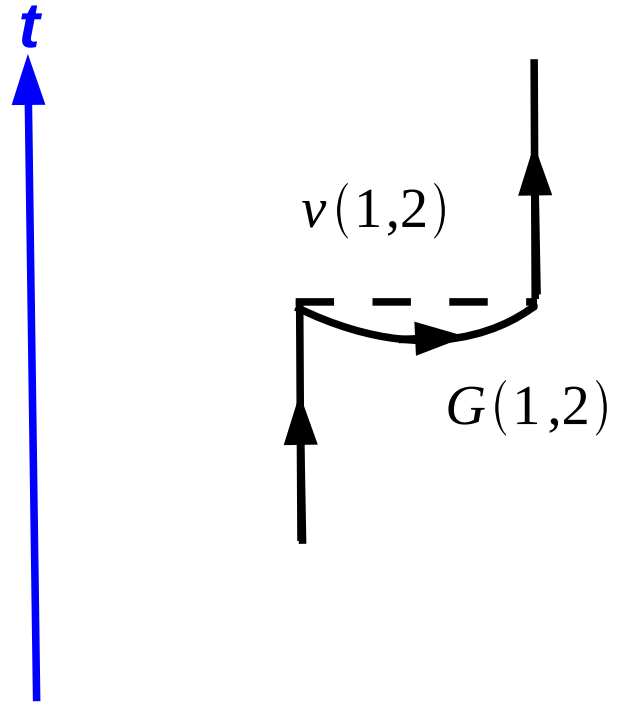
$$\chi_0(1,2)=-i\int d34\, G(1,3)G(4,1)\Gamma(3,4,2)$$ **polarizability**

$$\varepsilon(1,2)=\delta(1,2)-\int d3\, v(1,3)\chi_0(3,2)$$ **dielectric matrix**

$$W(1,2)=\int d3\, \varepsilon^{-1}(1,3)v(3,2)$$ **screened Coulomb interaction**

Simplest approximation

$$\Sigma(1,2) = iG(1,2)v(1^+,2)$$ ⟹ Fock exchange



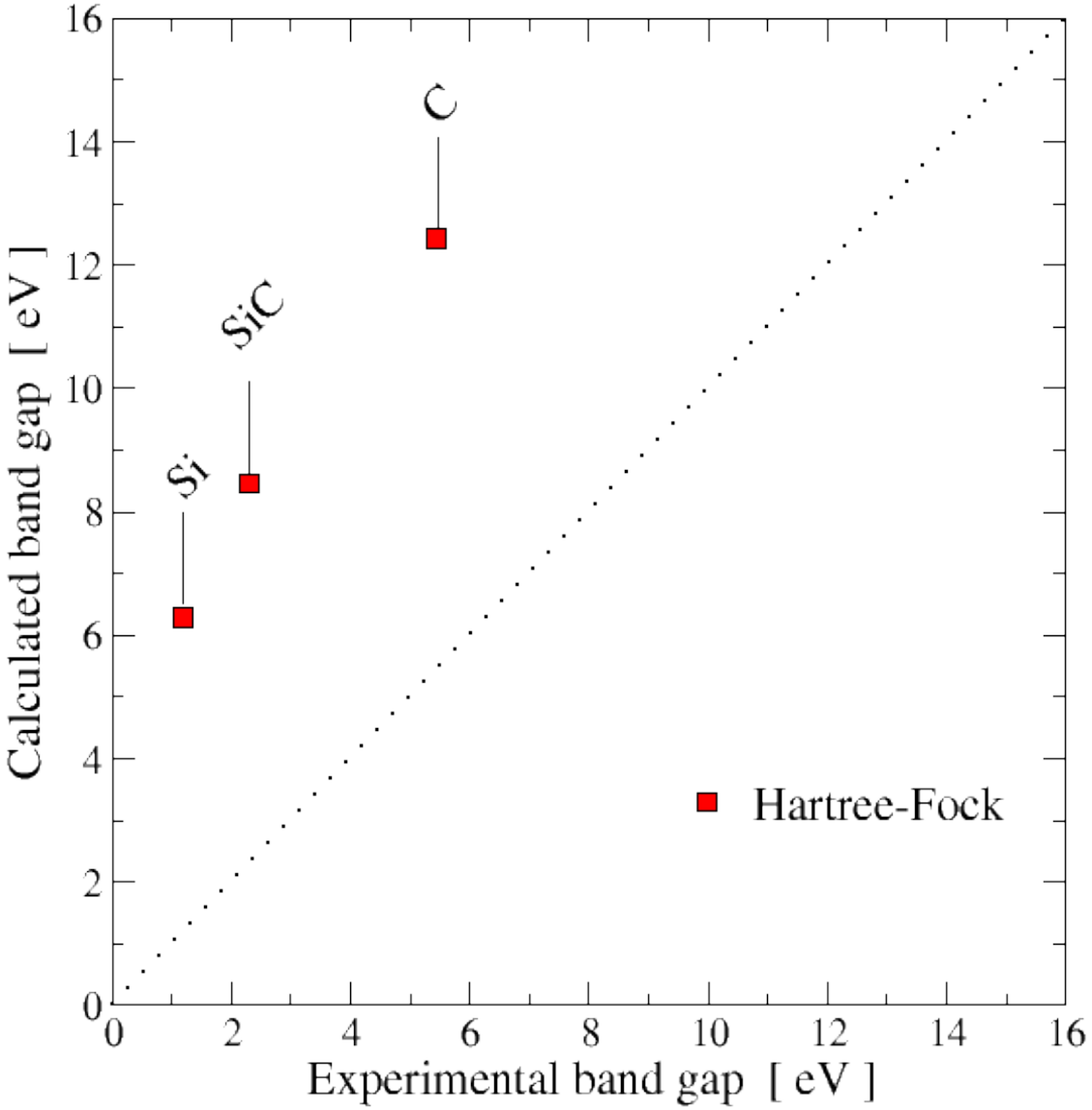
Dyson equation:

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

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

Not enough: Hartree-Fock is known to perform poorly for solids

Hartree-Fock approximation for band gaps



Hedin's coupled equations

6 coupled equations:

$$G(1,2) = G_0(1,2) + \int d34\, G_0(1,3)\,\Sigma(3,4)\,G(4,2)$$ **Dyson equation**

$$\Sigma(1,2) = i\int d34\, G(1,3)\,W(1,4)\,\Gamma(4,2,3)$$ **self-energy**

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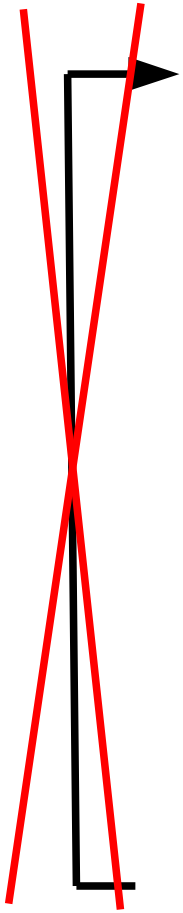
$$\chi_0(1,2) = -i\int d34\, G(1,3)\,G(4,1)\,\Gamma(3,4,2)$$

$$\varepsilon(1,2) = \delta(1,2) - \int d3\, v(1,3)\,\chi_0(3,2)$$

$$W(1,2) = \int d3\, \varepsilon^{-1}(1,3)\,v(3,2)$$ **screened Coulomb interaction**

Hedin's coupled equations

6 coupled equations:



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Hedin's coupled equations

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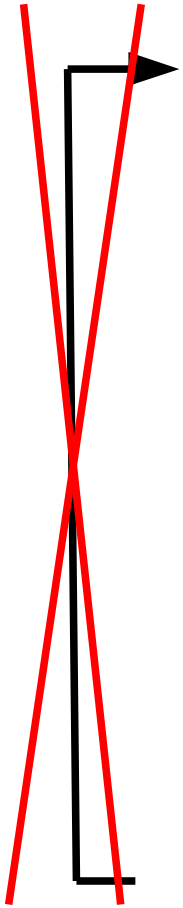

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$$\chi_0(1,2) = -i \int d34\, G(1,2)\,G(2,1)\,\Gamma(3,4,2)$$

$$\varepsilon(1,2) = \delta(1,2) - \int d3\, v(1,3)\,\chi_0(3,2)$$

$$W(1,2) = \int d3\, \varepsilon^{-1}(1,3)\,v(3,2)$$ **screened Coulomb interaction**

Here comes the *GW* approximation

$$\Sigma(1,2) = iG(1,2)W(1,2)$$ *GW* approximation

$$\chi_0(1,2) = -iG(1,2)G(2,1)$$ RPA approximation

$$\varepsilon(1,2) = \delta(1,2) - \int d3\, v(1,3)\chi_0(3,2)$$

$$W(1,2) = \int d3\, \varepsilon^{-1}(1,3)v(3,2)$$

Let us play with diagrams

$$\chi_0(1,2) = -i\,G(1,2)G(2,1)$$

$$\Sigma(1,2) = i\,G(1,2)W(1,2)$$

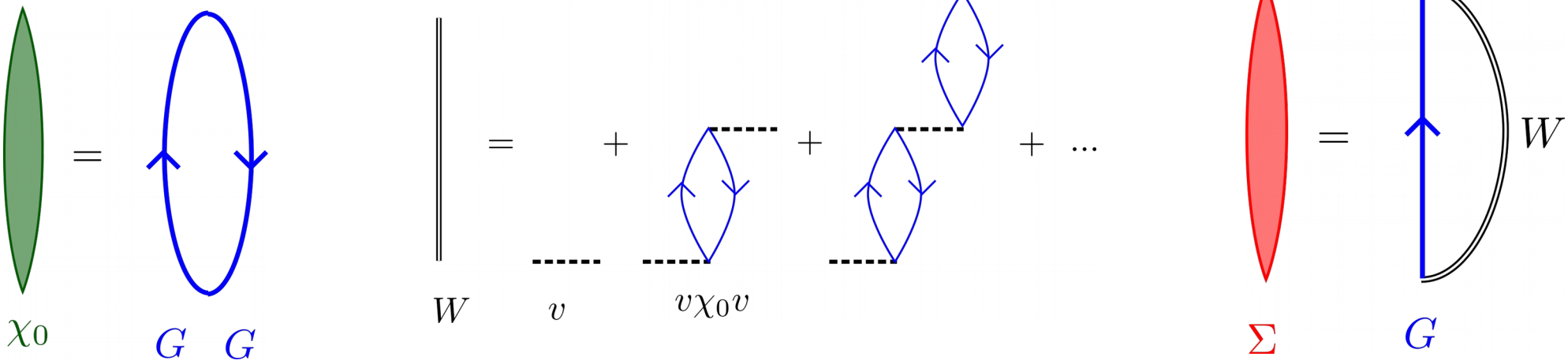
$$\varepsilon(1,2) = \delta(1,2) - \int d3\, v(1,3)\chi_0(3,2)$$

$$W(1,2) = \int d3\, \varepsilon^{-1}(1,3)\, v(3,2)$$

$$W = v + v\chi_0 W$$

$$= v + v\chi_0 v + v\chi_0 v\chi_0 v + \ldots$$

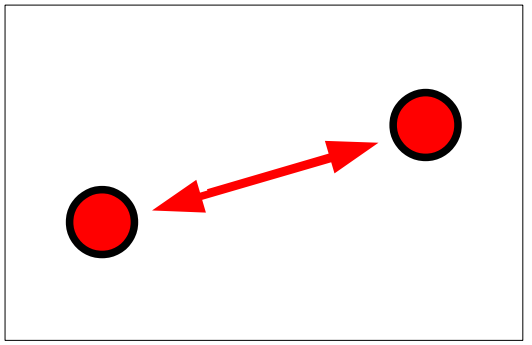
Infinite summation over bubble (or ring) diagrams



What is W?

Interaction between electrons in vacuum:

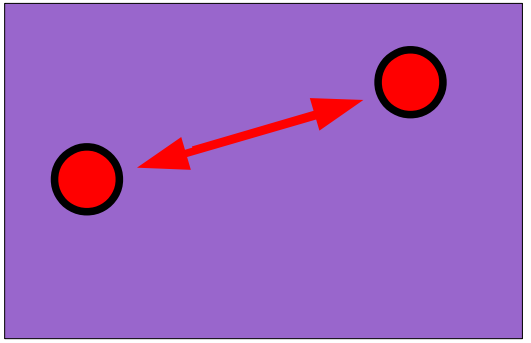
$$v(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$$



Interaction between electrons in a homogeneous polarizable medium:

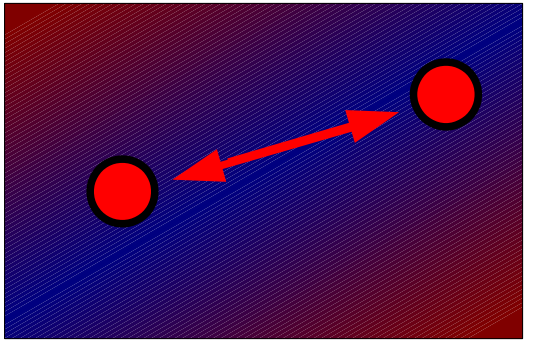
$$W(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{4\pi\varepsilon_0\varepsilon_r}\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Dielectric constant of the medium



Dynamically screened interaction between electrons in a general medium:

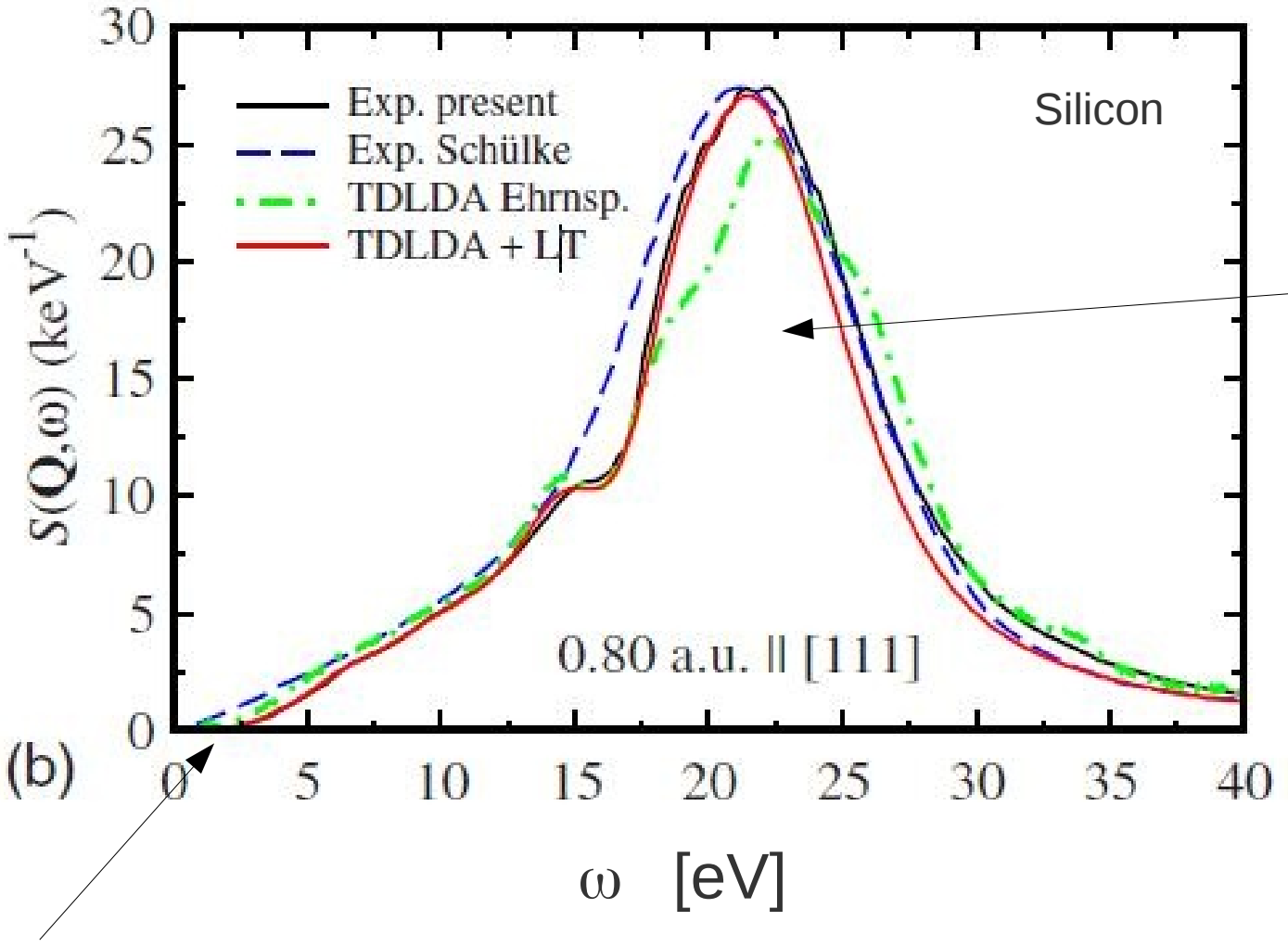
$$W(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{e^2}{4\pi\varepsilon_0}\int d\,r''\,\frac{\varepsilon^{-1}(\boldsymbol{r},\boldsymbol{r}'',\omega)}{|\boldsymbol{r}''-\boldsymbol{r}'|}$$



W is frequency dependent

W can measured directly by Inelastic X-ray Scattering

$$W(\boldsymbol{q}=0.80\,\text{a.u}\,,\omega)$$



Plasmon frequency

Zero below the band gap

H-C Weissker et al. PRB (2010)

GW viewed as a “super” Hartree-Fock

Hartree-Fock Approximation

$$\Sigma_x(\boldsymbol{r}_1,\boldsymbol{r}_2)=$$

$$\frac{i}{2\pi}\int_{-\infty}^{\mu} d\,\omega' G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega')v(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

= bare exchange

GW Approximation

$$\Sigma_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)=$$

$$\frac{i}{2\pi}\int d\,\omega' G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega+\omega')W(\boldsymbol{r}_2,\boldsymbol{r}_1,\omega')$$

$\Sigma_x(\boldsymbol{r}_1,\boldsymbol{r}_2)$

Bare exchange

$\Sigma_c(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)$

+ correlation

Non Hermitian dynamic

***GW* is nothing else but a “screened” version of Hartree-Fock.**

Summary: DFT vs *GW*

Electronic density

$$\rho(\boldsymbol{r})$$

Local and static

Green's function

$$G(\boldsymbol{r}t,\boldsymbol{r}'t')$$

Non-local, dynamic
Depends onto empty states

exchange-correlation potential

$$v_{xc}(\boldsymbol{r})$$

exchange-correlation operator = self-energy

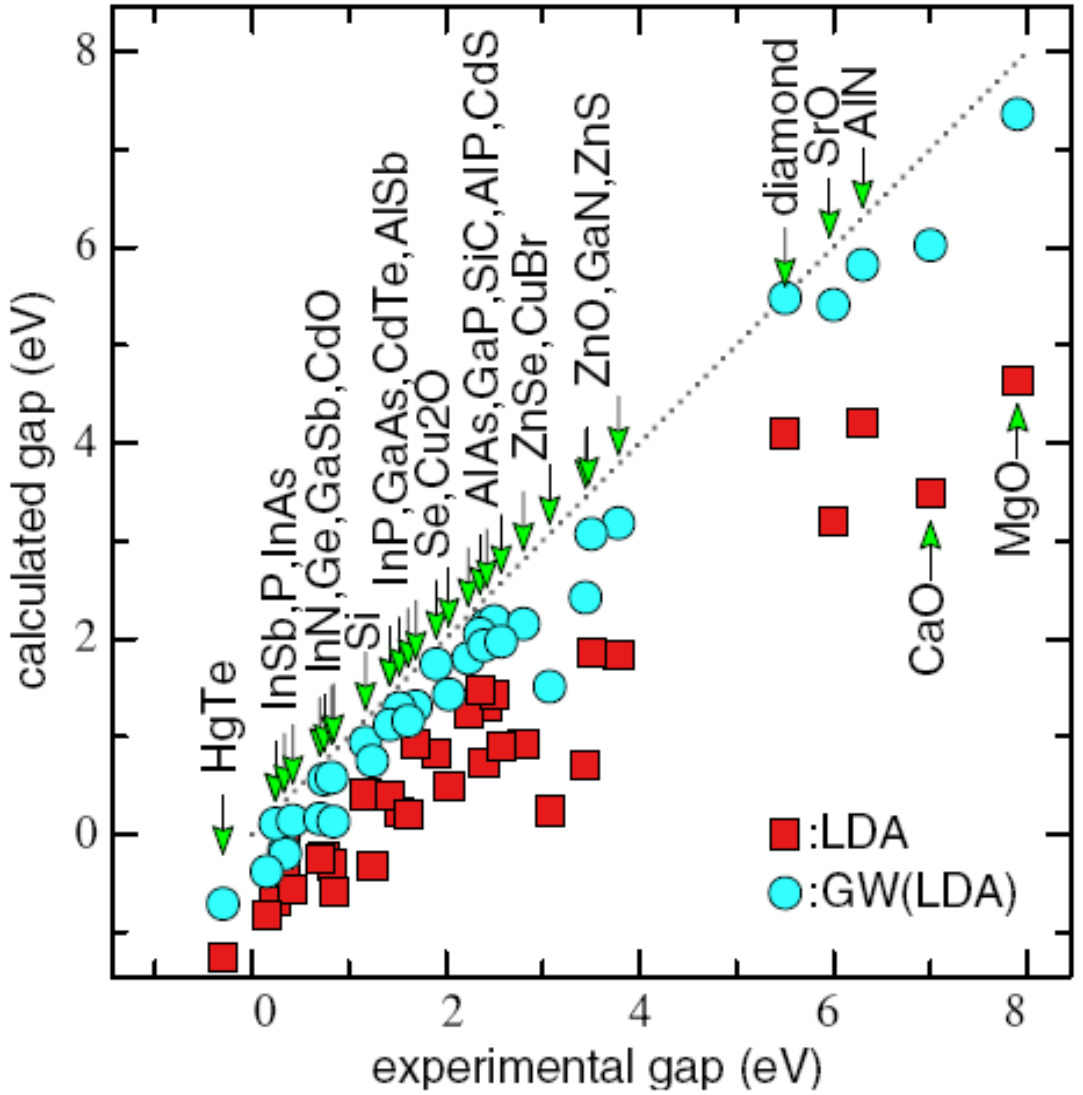
$$\Sigma_{xc}(\boldsymbol{r}t,\boldsymbol{r}'t')$$

Approximations: LDA, GGA, hybrids

GW approximation

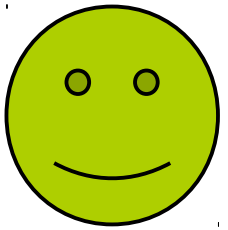
$$\Sigma_{GW}(\boldsymbol{r}t,\boldsymbol{r}'t')=iG(\boldsymbol{r}t,\boldsymbol{r}',t')W(\boldsymbol{r}t,\boldsymbol{r}'t')$$

GW approximation gets good band gap



after van Schilfgaarde *et al* PRL **96** 226402 (2008)

No more a band gap problem !



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Historical recap of *GW* calculations

- 1965: Hedin's calculations for the homogeneous electron gas
  Phys Rev **2201 citations**

- 1967: Lundqvist's calculations for the homogeneous electron gas
  Physik der Kondensierte Materie **299 citations**

- 1982: Strinati, Mattausch, Hanke for real semiconductors but based on tight-binding
  PRB **154 citations**

- 1985: Hybertsen, Louie for real semiconductors with ab initio LDA
  PRL **711 citations** & PRB **1737 citations**

- 1986: Godby, Sham, Schlüter for real semiconductors to get accurate local potential
  PRL **544 citations** & PRB **803 citations**

- ~2001: First publicly available *GW* code in ABINIT

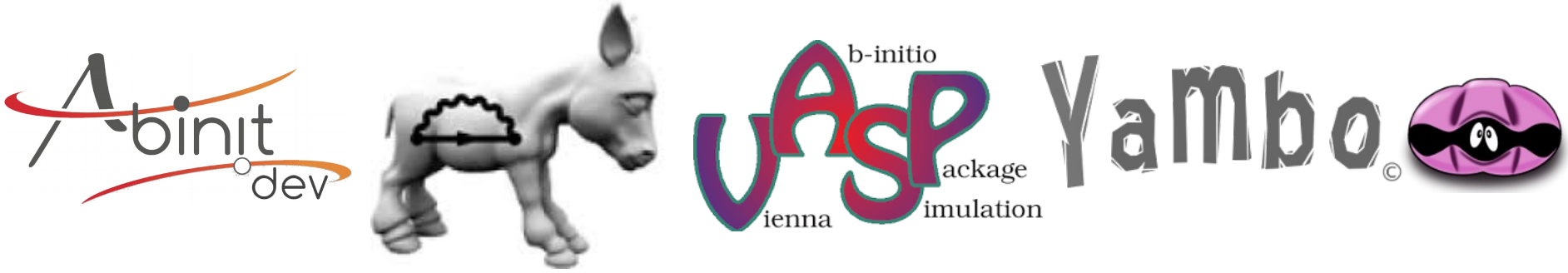
- 2003: Arnaud, Alouani for extension to Projector Augmented Wave
  PRB **102 citations**

- 2006: Shishkin, Kresse for extension to Projector Augmented Wave (again)
  PRB **256 citations**

GW approximation in practice

- For periodic solids: Abinit, BerkeleyGW, VASP, Yambo

based on plane-waves (with pseudo or PAW)

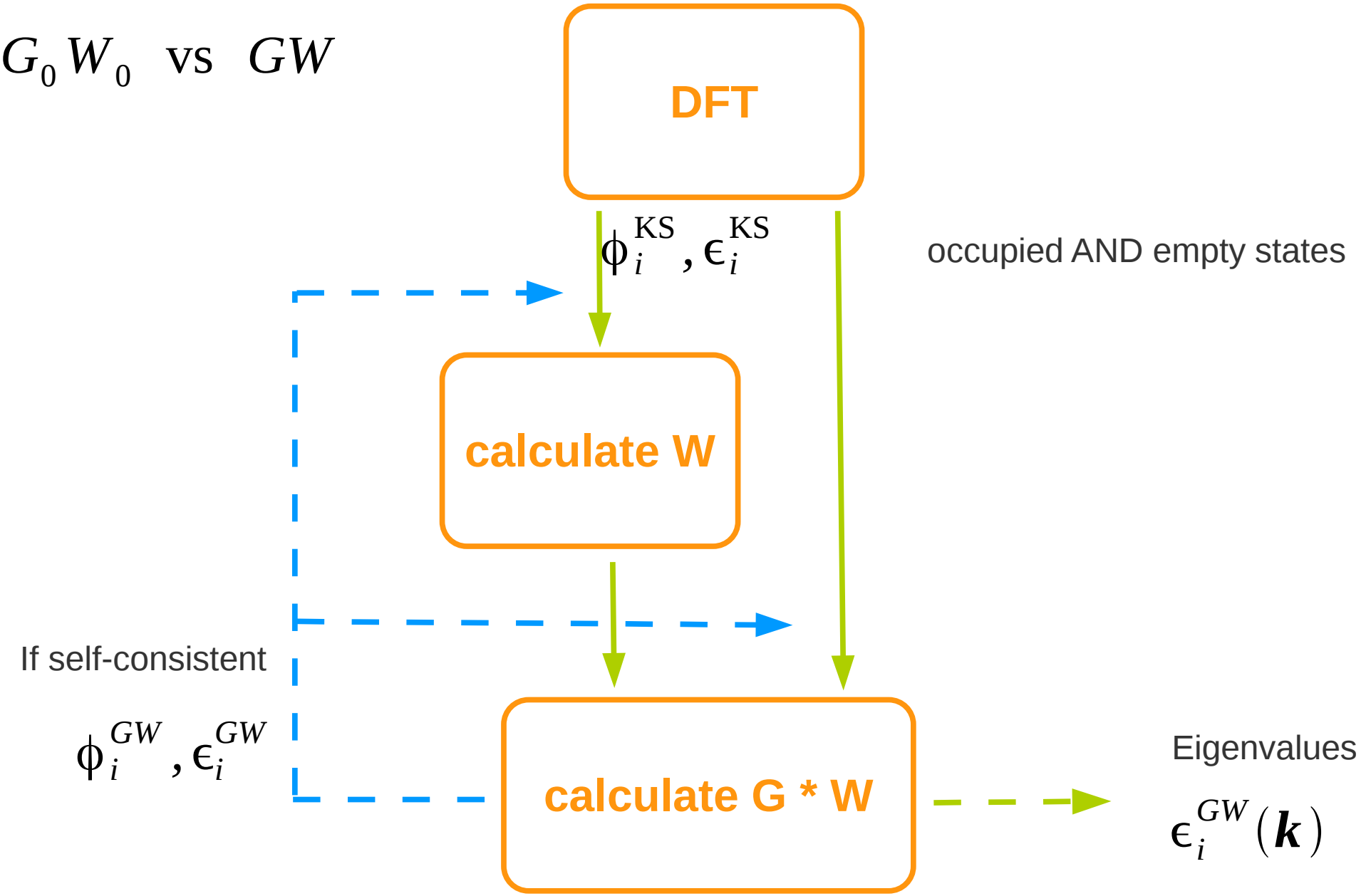


- For finite systems: MolGW, Fiesta, FHI-AIMS

based on localized orbitals (gaussians or slater or other)

Work flow of a typical *GW* calculation

G_0W_0 vs GW



How to get *G*?

From Kohn-Sham DFT

Remember

$$\left[\omega - h_{\mathrm{KS}}\right] G_{\mathrm{KS}} = 1$$

which means

$$G^{KS}(\boldsymbol{r_1}, \boldsymbol{r_2}, \omega) = \sum_i \frac{\phi_i^{\mathrm{KS}}(\boldsymbol{r_1})\,\phi_i^{\mathrm{KS}*}(\boldsymbol{r_2})}{\omega - \epsilon_i^{\mathrm{KS}} \pm i\,\eta}$$

This expression will be used to get W and Σ

How to get *W*?

From the RPA equation

$$\chi_0(1,2) = -iG(1,2)G(2,1)$$

which translates into

$$\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = \sum_{\substack{i\,\mathrm{occ}\\ j\,\mathrm{virt}}} \phi_i(\boldsymbol{r}_1)\phi_i^*(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}_2)\phi_j^*(\boldsymbol{r}_1) \times \left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\eta} - \frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\eta}\right]$$

This is the Alder-Wiser formula or the SOS formula

It involves empty states!

Then $\chi_0(1,2)$  $W(1,2)$

W in plane-waves

Non-interacting susceptibility

$$\chi_0(\boldsymbol{r_1},\boldsymbol{r_2},\omega)=\sum_{\substack{i\,\mathrm{occ}\\ j\,\mathrm{virt}}}\phi_i(\boldsymbol{r_1})\phi_i^*(\boldsymbol{r_2})\phi_j(\boldsymbol{r_2})\phi_j^*(\boldsymbol{r_1})\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\eta}\right]$$

Double Fourier transform into reciprocal space:

$$\chi_0(\boldsymbol{q}+\boldsymbol{G_1},\boldsymbol{q}+\boldsymbol{G_2},\omega)\;=\;\int d\boldsymbol{r_1}d\boldsymbol{r_2}e^{-i(\boldsymbol{q}+\boldsymbol{G_1}).\boldsymbol{r_1}}\chi_0(\boldsymbol{r_1},\boldsymbol{r_2},\omega)e^{i(\boldsymbol{q}+\boldsymbol{G_2}).\boldsymbol{r_2}}\;=\;\chi_{0\boldsymbol{G_1}\boldsymbol{G_2}}(\boldsymbol{q},\omega)$$

One needs to calculate the “matrix elements”:

$$M_{ji}(\boldsymbol{q}+\boldsymbol{G})=\int d\boldsymbol{r_1}\phi_i(\boldsymbol{r_1})\phi_j^*(\boldsymbol{r_1})e^{-i(\boldsymbol{q}+\boldsymbol{G}).\boldsymbol{r_1}}$$

Then the dielectric matrix is inverted

$$\varepsilon_{\boldsymbol{G_1}\boldsymbol{G_2}}(\boldsymbol{q},\omega)\;=\;\delta_{\boldsymbol{G_1}\boldsymbol{G_2}}-v_{\boldsymbol{G_1}}(\boldsymbol{q})\chi_{0\,\boldsymbol{G_1}\boldsymbol{G_2}}(\boldsymbol{q},\omega)$$

to calculate *W*

$$W_{\boldsymbol{G_1}\boldsymbol{G_2}}(\boldsymbol{q},\omega)=\varepsilon^{-1}_{\boldsymbol{G_1}\boldsymbol{G_2}}(\boldsymbol{q},\omega)v_{\boldsymbol{G_2}}(\boldsymbol{q})$$

Self energy evaluation in *GW*

Correlation part of the GW self energy requires a convolution in frequency:

$$\Sigma_c(\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega' G(\omega+\omega') W_p(\omega')$$

$$G(\omega) = \sum_i \frac{\phi_i(\boldsymbol{r})\phi_i^*(\boldsymbol{r}')}{\omega - \epsilon_i \pm i\eta}$$

?

How to deal with the frequency dependence in W?

How do we perform the convolution?
How do we treat the frequency dependence in *W*?

Plasmon-Pole Models in *GW*

Correlation part of the GW self energy requires a convolution in frequency:

$$\Sigma_c(\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\,\omega' G(\omega+\omega') W_p(\omega')$$

Generalized Plasmon-Pole Model:

$$\varepsilon^{-1}(\omega') - 1 = \frac{\Omega^2}{2\tilde{\omega}}\left[\frac{1}{\omega' - \tilde{\omega} + i\eta} - \frac{1}{\omega' + \tilde{\omega} - i\eta}\right]$$

Amplitude of the pole

Position of the pole

small real number

2 parameters need two constraints:

- Hybertsen-Louie (HL): $\varepsilon^{-1}(0)$ and f sum rule $\int_0^{+\infty} \omega\, \mathrm{Im}\,\varepsilon^{-1}(\omega) = -\frac{\pi}{2}\omega_p^2$
- Godby-Needs (GN): $\varepsilon^{-1}(0)$ and $\varepsilon^{-1}(i\omega)$

GW obtained as a first-order perturbation

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

$$G_{\mathrm{KS}} = G_0 + G_0 v_{xc} G_{\mathrm{KS}}$$

$$\Rightarrow \quad G^{-1} = G_{\mathrm{KS}}^{-1} - (\Sigma - v_{xc})$$

Approximation : $\phi_i^{GW} \approx \phi_i^{\mathrm{KS}}$

$$G^{-1} = \sum_i |\phi_i\rangle (\omega - \epsilon_i^{GW}) \langle \phi_i|$$

$$G_{\mathrm{KS}}^{-1} = \sum_i |\phi_i\rangle (\omega - \epsilon_i^{\mathrm{KS}}) \langle \phi_i|$$

$$\Rightarrow \quad \epsilon_i^{GW} = \epsilon_i^{\mathrm{KS}} + \left\langle \phi_i \middle| \Sigma(\epsilon_i^{GW}) - v_{xc} \middle| \phi_i \right\rangle$$

Linearization of the energy dependance

$$\epsilon_i^{GW} - \epsilon_i^{KS} = \left\langle \phi_i^{KS} \middle| \left[\Sigma\left(\epsilon_i^{GW}\right) - v_{xc} \right] \middle| \phi_i^{KS} \right\rangle$$

Not yet known

Taylor expansion:

$$\Sigma\left(\epsilon_i^{GW}\right) = \Sigma\left(\epsilon_i^{KS}\right) + \left(\epsilon_i^{GW} - \epsilon_i^{KS}\right) \frac{\partial \Sigma}{\partial \epsilon} + \ldots$$

Final result:

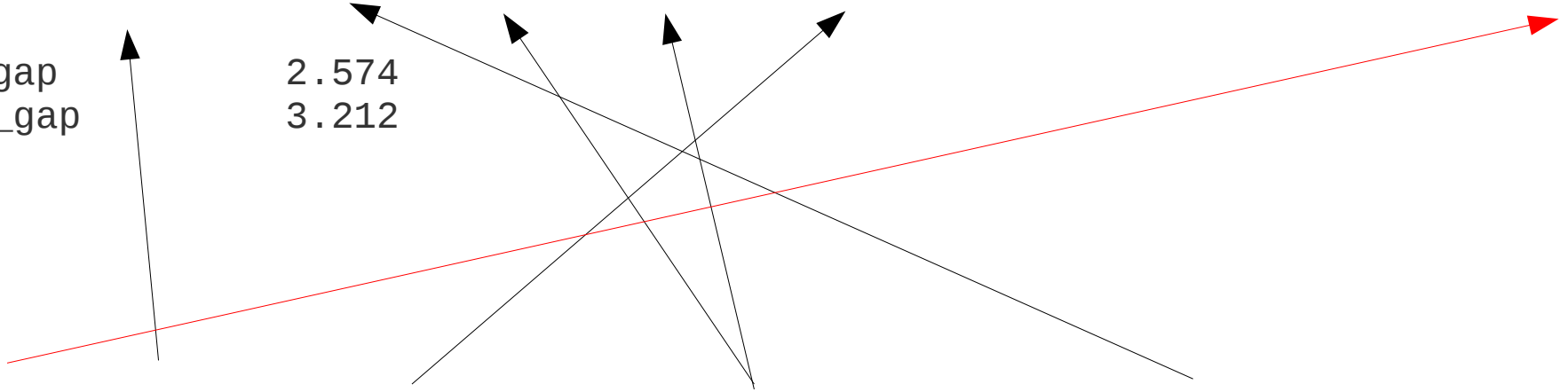
$$\epsilon_i^{GW} = \epsilon_i^{KS} + Z_i \left\langle \phi_i^{KS} \middle| \left[\Sigma\left(\epsilon_i^{KS}\right) - v_{xc} \right] \middle| \phi_i^{KS} \right\rangle$$

where $$Z_i = 1 \Big/ \left(1 - \left\langle i \middle| \frac{\partial \Sigma}{\partial \epsilon} \middle| i \right\rangle \right)$$

Quasiparticle equation

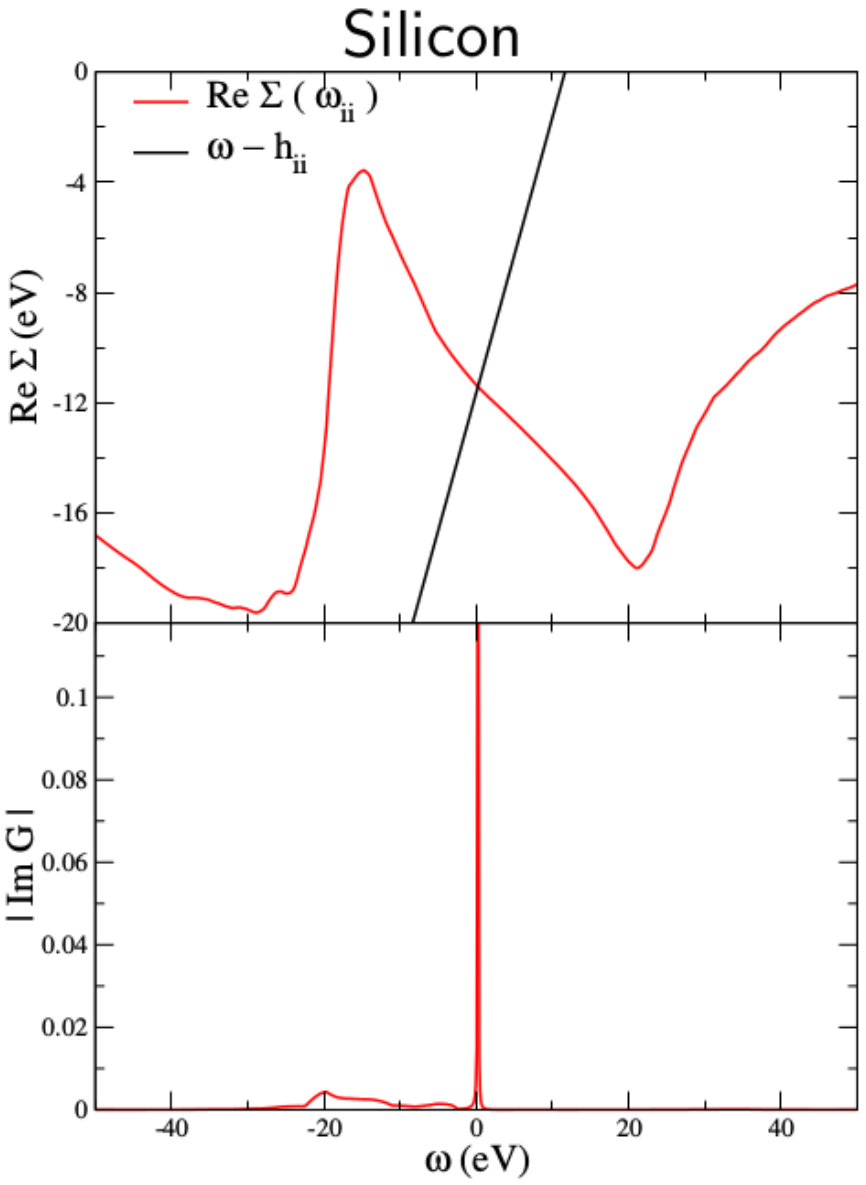
A typical ABINIT ouptput for Silicon at Gamma point

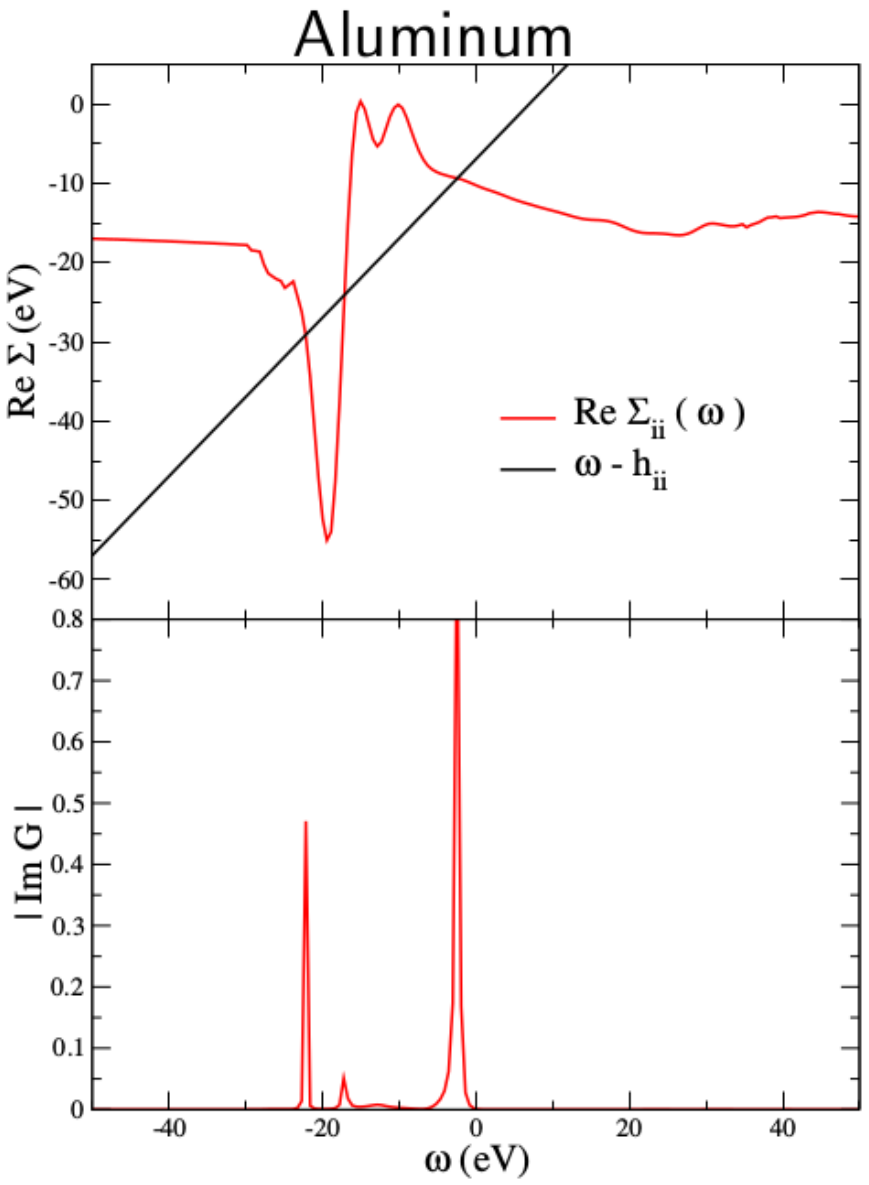
```
k =    0.000   0.000   0.000
Band      E0 <VxcLDA>   SigX SigC(E0)      Z dSigC/dE  Sig(E)    E-E0       E
   4   0.506 -11.291 -12.492   0.744   0.775  -0.291 -11.645  -0.354   0.152
   5   3.080 -10.095  -5.870  -3.859   0.775  -0.290  -9.812   0.283   3.363

E^0_gap         2.574
E^GW_gap        3.212
```



$$\epsilon_i^{GW} = \epsilon_i^{\mathrm{LDA}} + Z_i \left\langle \varphi_i^{\mathrm{LDA}} \middle| \left[\Sigma_{xc}\left(\epsilon_i^{\mathrm{LDA}}\right) - v_{xc}^{\mathrm{LDA}} \right] \middle| \varphi_i^{\mathrm{LDA}} \right\rangle$$

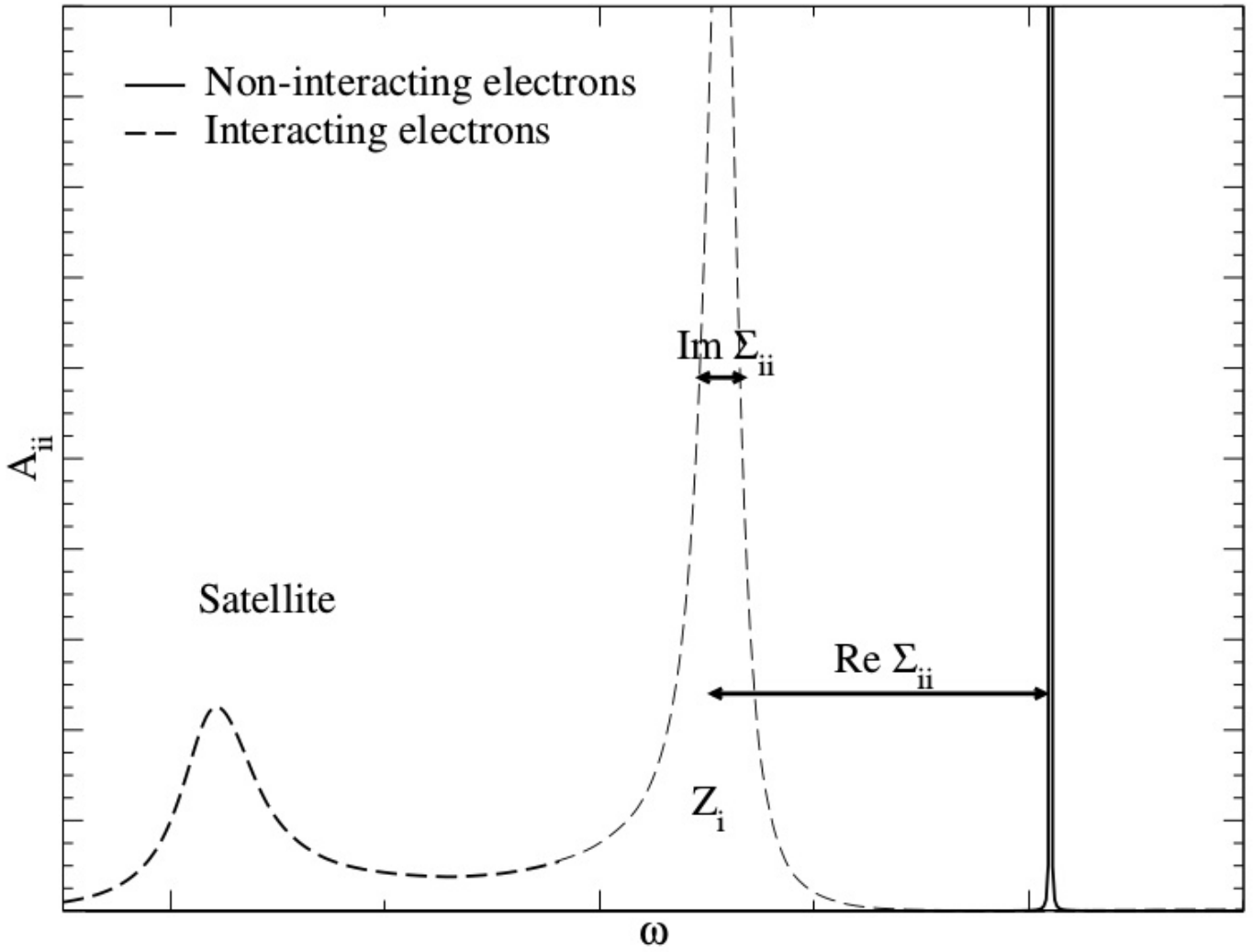
Full quasiparticle solution





Spectral function

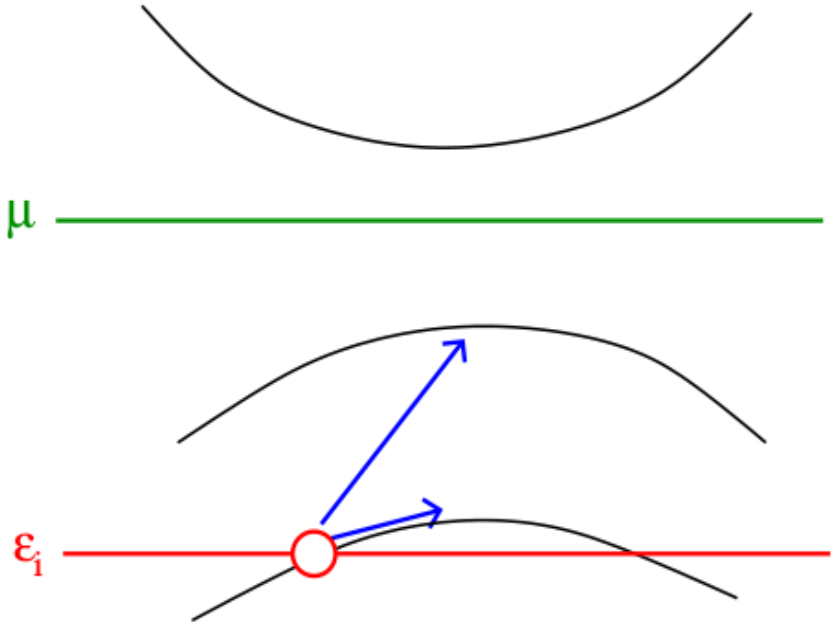
$$A(\omega) = |\mathrm{Im}\, G(\omega)| \;/\; \pi$$



Excitation lifetime

Hole self-energy:

$$\mathrm{Im}\{\langle i|\Sigma(\epsilon_i)|i\rangle\} = -\sum_{j\mathbf{q}\mathbf{G}\mathbf{G}'} M_{ij}(\mathbf{q}+\mathbf{G})M^*_{ij}(\mathbf{q}+\mathbf{G}') \times \mathrm{Im}(W-v)_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\epsilon_j-\epsilon_i) \times \theta(\mu-\epsilon_j)\theta(\epsilon_j-\epsilon_i)$$



Outline

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IV. Calculating the *GW* self-energy in practice

V. RPA total energies

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Several expressions for the energy

Galitskii-Migdal expression:

Tr stands for $\int d\omega \int d\boldsymbol{r}$

$$E_{\mathrm{GM}} = \frac{1}{2}\mathrm{Tr}\left[(\omega - h_0)G\right]$$

Klein (=Pines=Nozières=RPA) expression:

$$E_{\mathrm{K}}[G] = -\mathrm{Tr}\left[\ln\left(-G^{-1}\right)\right] - E_H - \mathrm{Tr}\left[\left(G_{\mathrm{KS}}^{-1} + v_{xc}\right)G - 1\right] + E_x + \Phi_{\mathrm{GW}}$$

$$\Rightarrow \quad E_{\mathrm{K}}[G_{\mathrm{KS}}] = T + E_{\mathrm{ext}} + E_H + E_x + \Phi_{\mathrm{GW}}$$

Luttinger-Ward expression:

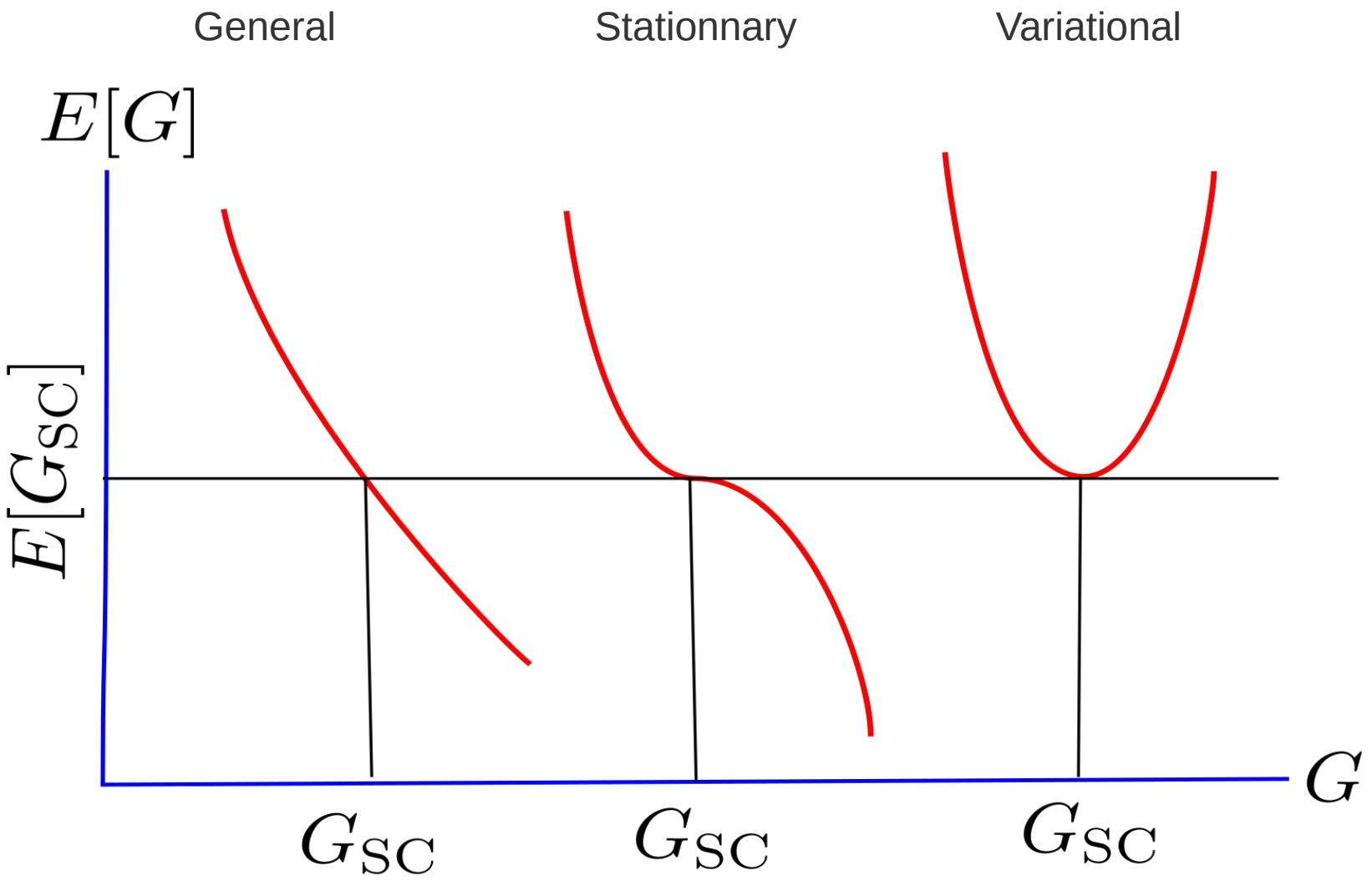
$$E_{\mathrm{LW}}[G] = -\mathrm{Tr}\left[\ln\left(h_0 + v_H + \Sigma(\omega) - \omega\right)\right] - E_H - \mathrm{Tr}\left[\Sigma G\right] + E_x + \Phi_c$$

$$\Rightarrow \quad E_{\mathrm{LW}}[G_{\mathrm{KS}}] = T + E_{\mathrm{ext}} + E_H + E_x + \Phi_{\mathrm{GW}} - \mathrm{Tr}\left[\ln\left(1 - \Sigma_c \widetilde{G}_{\mathrm{KS}}\right) + \Sigma_c \widetilde{G}_{\mathrm{KS}}\right] - \mathrm{Tr}\left[\Sigma_c\left(G_{\mathrm{KS}} - \widetilde{G}_{\mathrm{KS}}\right)\right]$$

Magic:

$$E_{\mathrm{GM}}[G_{\mathrm{SC}}] = E_{\mathrm{K}}[G_{\mathrm{SC}}] = E_{\mathrm{LW}}[G_{\mathrm{SC}}]$$

Energy functionals



What happens with an **approximate** Green's function *G?*

RPA functional = GW total energy

Self-energy:

$\Sigma_{GW} =$  $+ \dots$

Energy:

$\Phi_{GW} =$ $-\frac{1}{2}$  $-\frac{1}{4}$  $-\frac{1}{6}$  $+ \dots$

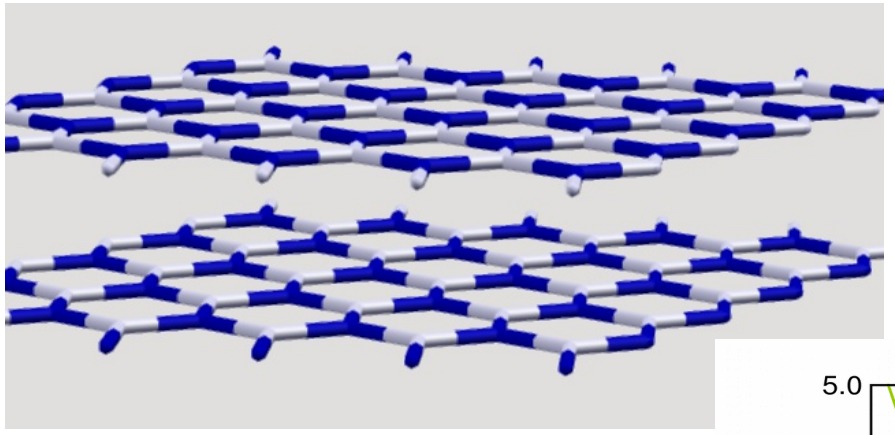
$$\Sigma_{GW}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{\delta \Phi_{GW}}{\delta G(\boldsymbol{r}',\boldsymbol{r},-\omega)}$$

analogous to DFT

$$v_{xc}(\boldsymbol{r}) = \frac{\delta E_{xc}}{\delta \rho(\boldsymbol{r})}$$

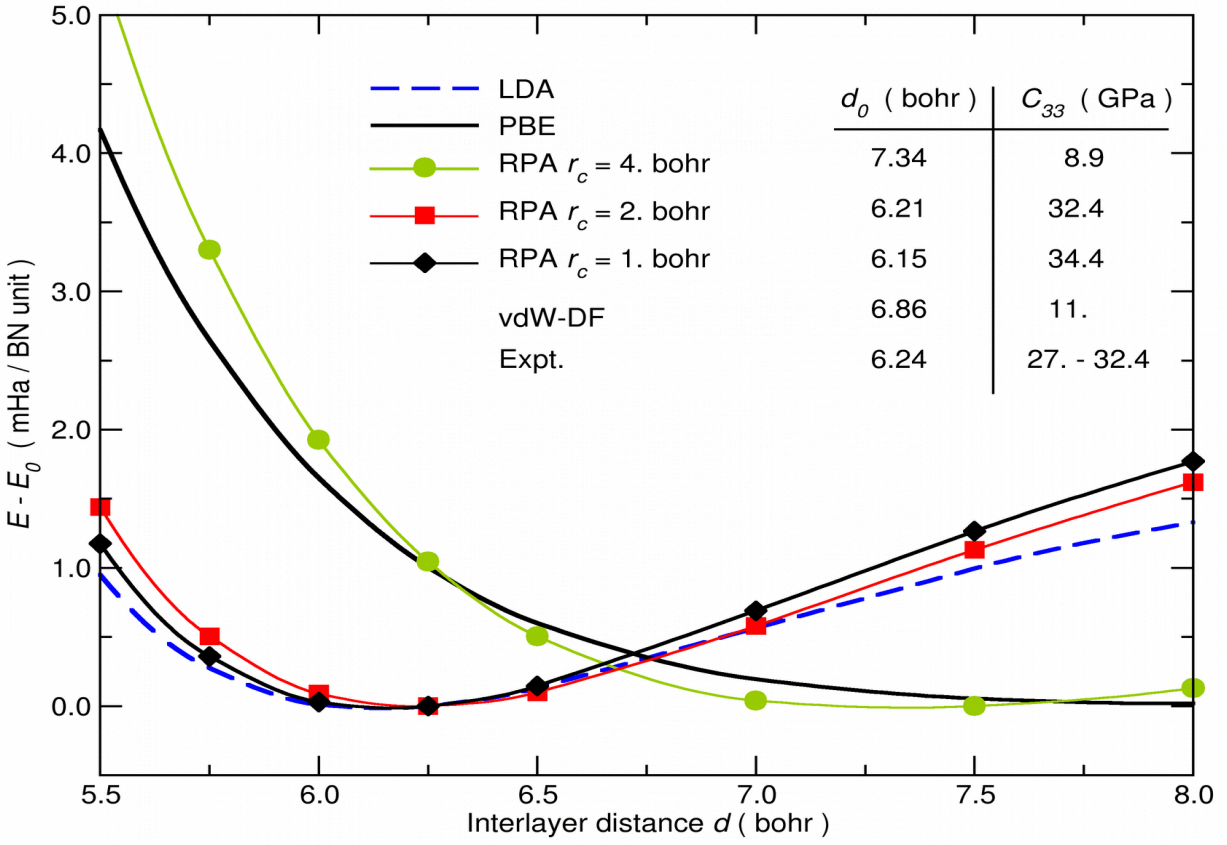
Calculation of Φ_{GW} is **very demanding**, even for unit cells.

RPA can describe van der Waals bonds



Interlayer distance

Hexagonal boron nitride

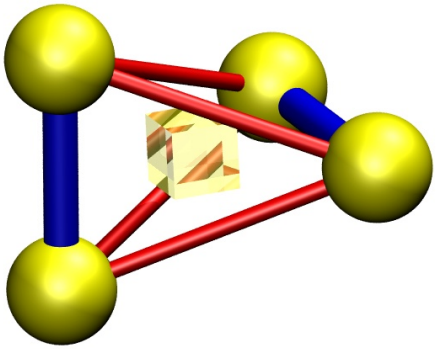


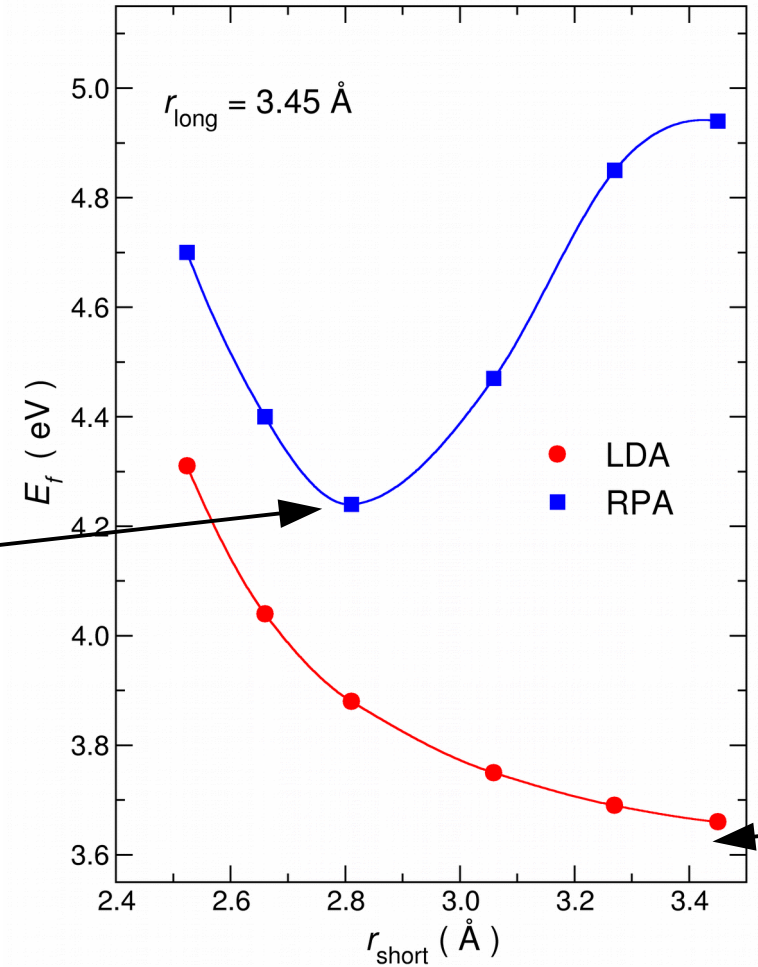
Jahn-Teller distortion of the vacancy

V_{Si} 64 atoms

Neutral charge state

	LDA	PBE	HSE06	RPA
Ef (eV)	3.66	3.71	4.56	4.24





0.7 eV difference

Jahn-Teller distortion

Tetrahedric symmetry conserved

F. Bruneval, PRL (2012)

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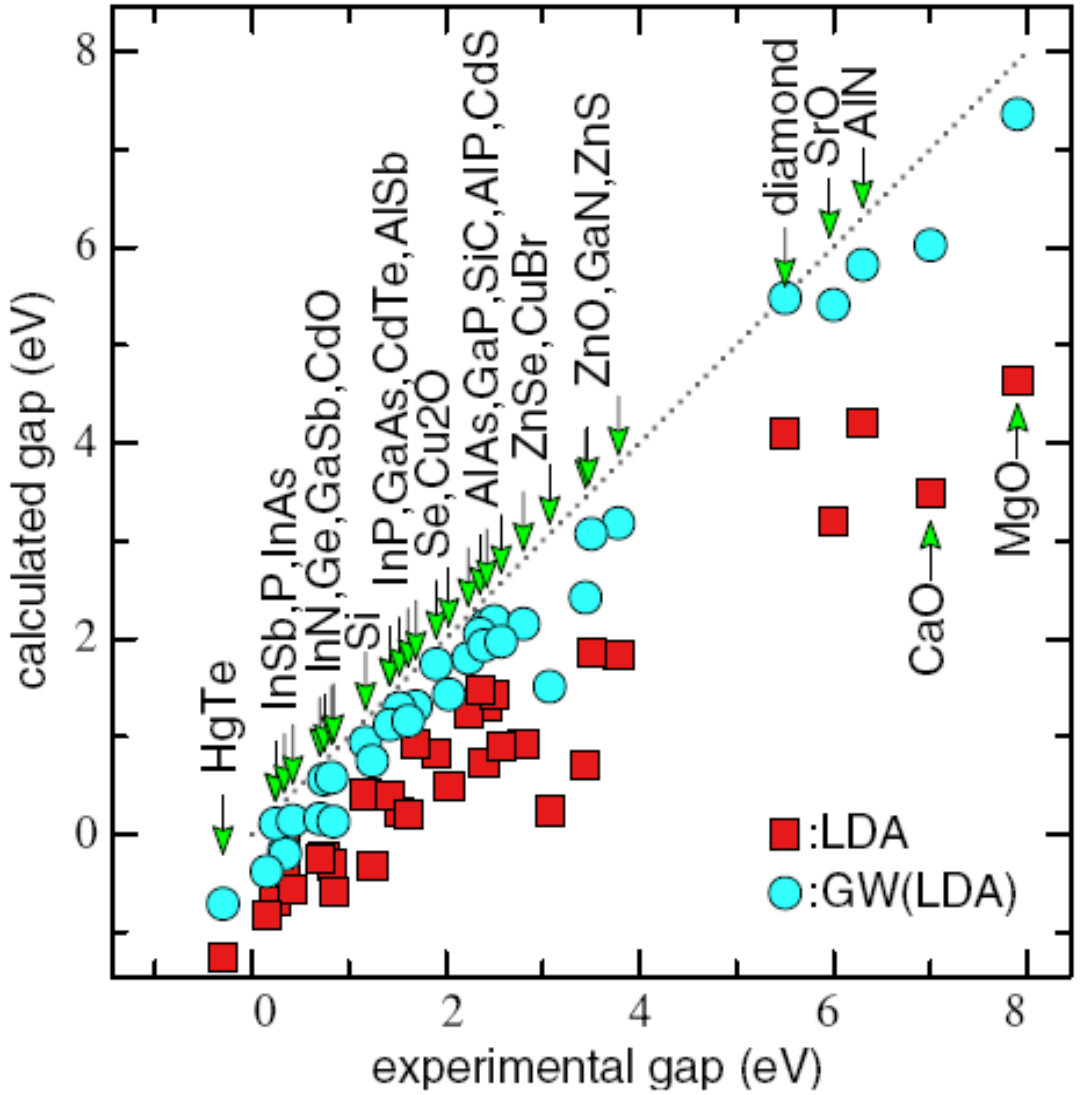
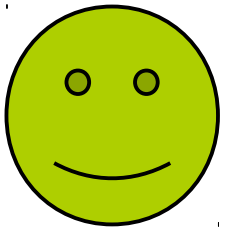
GW approximation gets good band gap



van Schilfgaarde *et al* PRL **96** 226402 (2008)

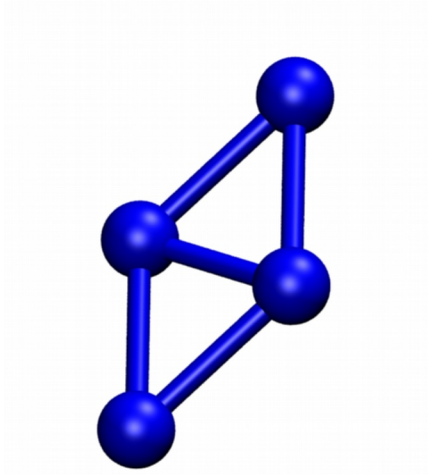
No more a band gap problem !



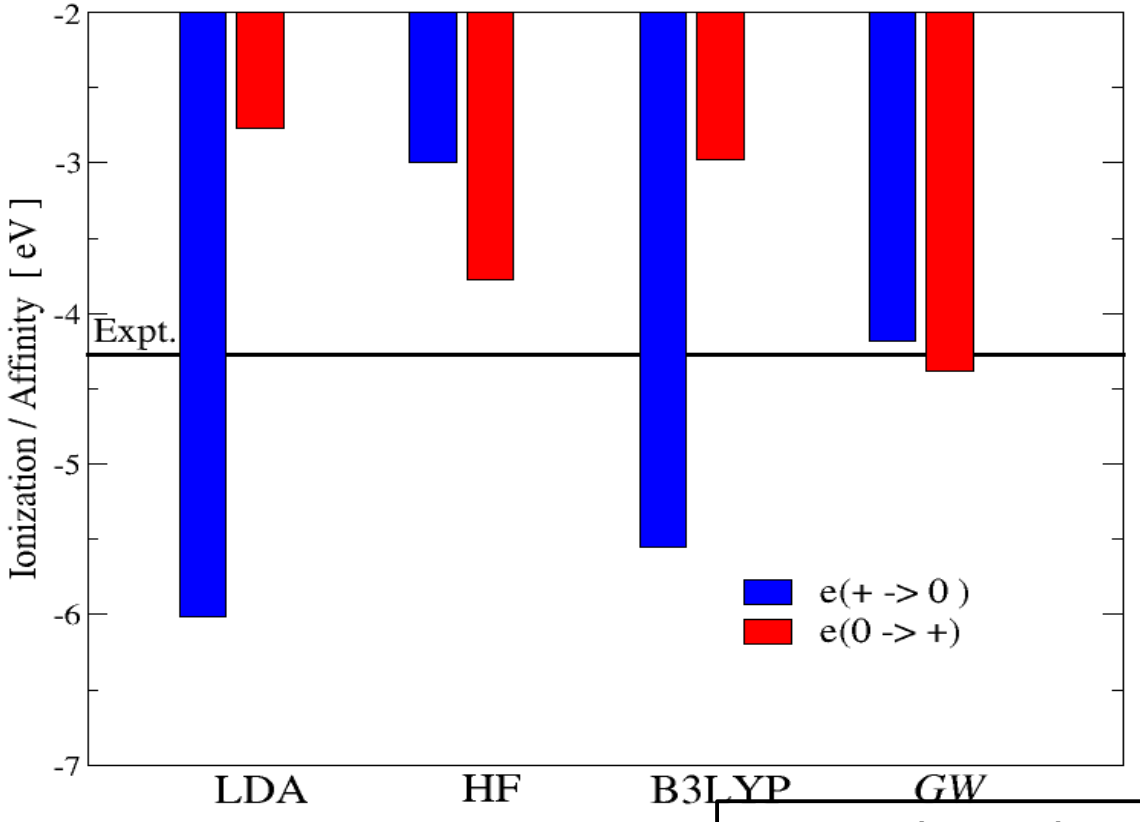
Clusters de sodium

$$Na_4^+ + e^- \Leftrightarrow Na_4$$

$$E_0(Na_4) - E_0(Na_4^+) = \begin{cases} \epsilon(\mathbf{HOMO}, \mathbf{Na_4}) \\ \epsilon(\mathbf{LUMO}, \mathbf{Na_4^+}) \end{cases}$$



Na_4^+/Na_4



Bruneval PRL (2009)

What is the best starting point for G_0W_0?

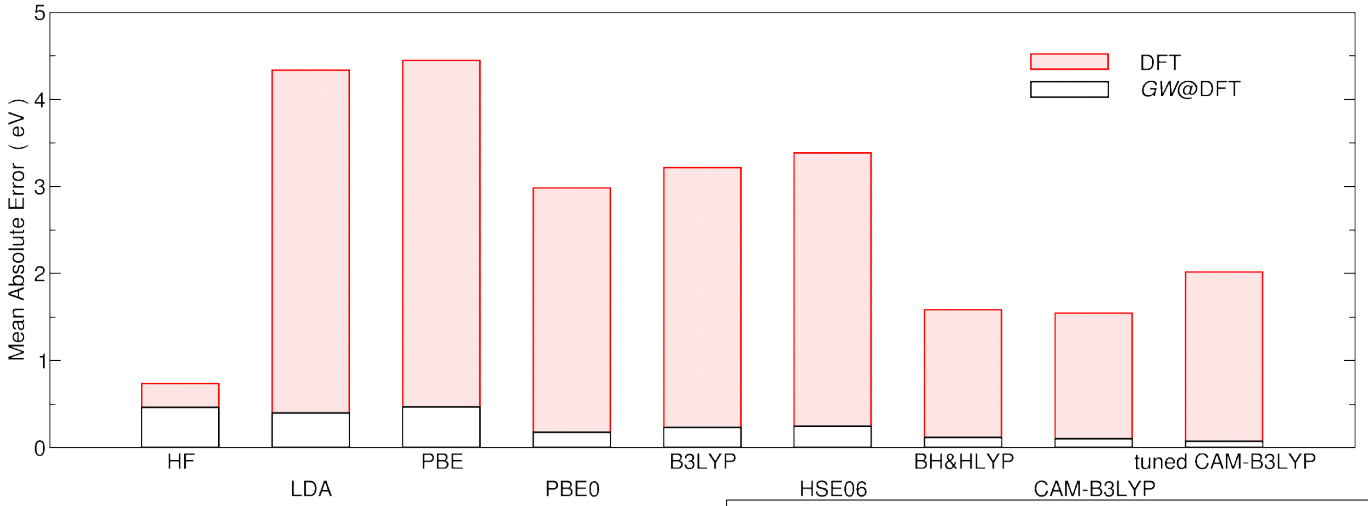
Ionization of small molecules

Journal of Chemical Theory and Computation — Article

Table 1. G_0W_0 HOMO Energy of the 34 Molecules Employing Different Starting Points with the cc-pVQZ Basis Set[a]

	GW@										
starting point	HF	LDA	PBE	PBE0	B3LYP	HSE06	BH&HLYP	CAM-B3LYP	tuned CAM-B3LYP	CCSD(T)	exp
LiH	−8.20	−7.24	−7.07	−7.66	−7.53	−7.47	−7.91	−8.03	−8.07	−7.94	
Li_2	−5.36	−5.13	−5.12	−5.29	−5.23	−5.19	−5.30	−5.32	−5.38	−5.17	
LiF	−11.62	−10.61	−10.37	−10.93	−10.82	−10.89	−11.29	−11.49	−11.45	−11.51	
Na_2	−4.98	−4.91	−4.89	−4.97	−4.96	−4.91	−4.97	−4.98	−5.01	−4.82	
NaCl	−9.36	−8.56	−8.43	−8.82	−8.77	−8.70	−9.06	−9.15	−9.22	−9.13	−9.80
CO	−14.97	−13.63	−13.55	−14.00	−13.92	−13.92	−14.36	−14.26	−14.11	−14.05	
CO_2	−14.38	−13.45	−13.32	−13.68	−13.57	−13.59	−13.91	−13.91	−13.82	−13.78	
CS	−13.08	−10.97	−10.93	−11.43	−11.31	−11.33	−11.79	−11.69	−11.55	−11.45	
C_2H_2	−11.65	−11.10	−11.08	−11.27	−11.23	−11.21	−11.40	−11.41	−11.41	−11.42	−11.49
C_2H_4	−10.85	−10.39	−10.37	−10.53	−10.52	−10.48	−10.65	−10.67	−10.66	−10.69	−10.68
CH_4	−14.86	−14.07	−14.03	−14.30	−14.27	−14.23	−14.52	−14.53	−14.48	−14.40	−14.40[44]
CH_3Cl	−11.74	−11.02	−10.98	−11.21	−11.18	−11.15	−11.41	−11.43	−11.41	−11.41	−11.29
CH_3OH	−11.69	−10.70	−10.64	−10.97	−10.89	−10.88	−11.20	−11.22	−11.17	−11.08	−10.96
CH_3SH	−9.81	−9.18	−9.17	−9.36	−9.35	−9.30	−9.53	−9.55	−9.53	−9.49	

Hybrids perform better, preferably with a large content of EXX ~ 50 %

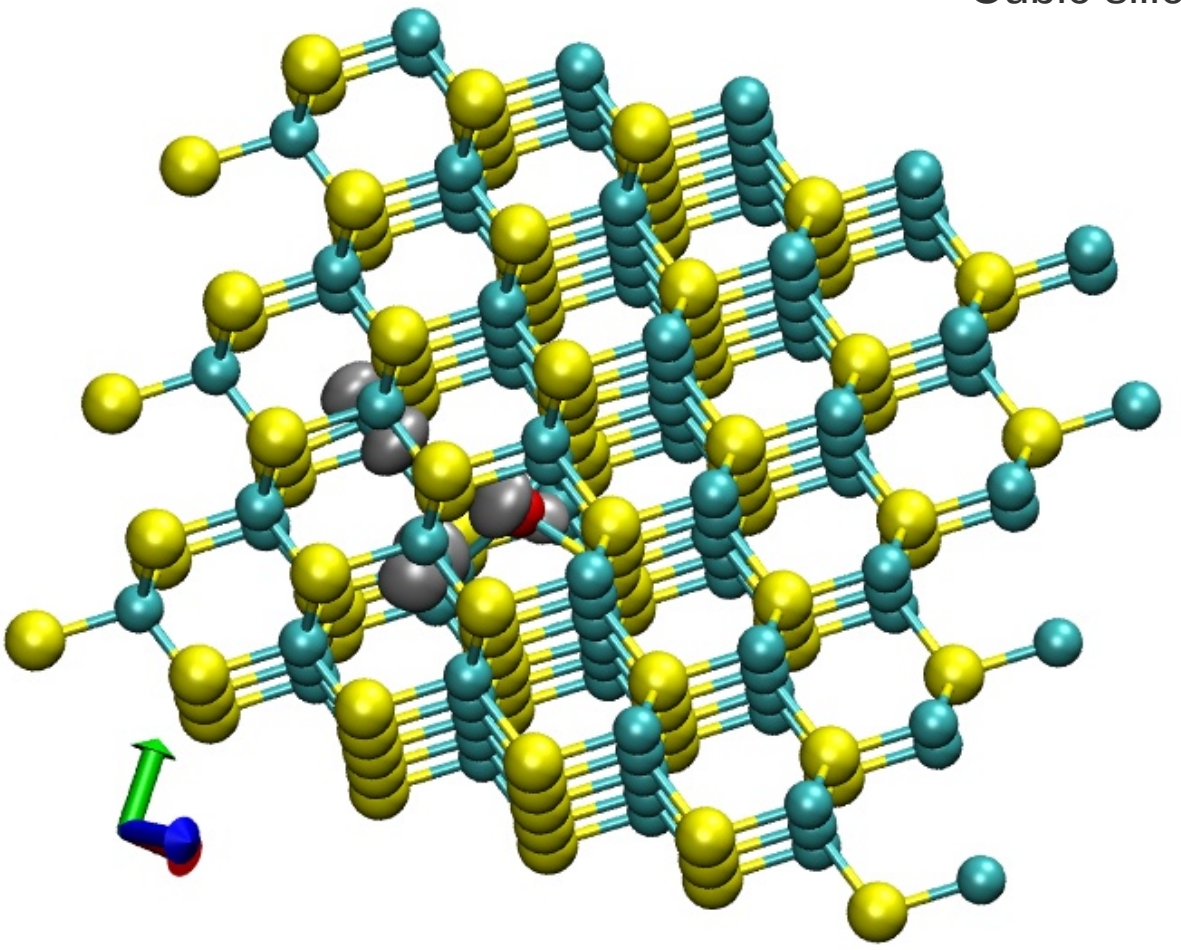


F. Bruneval & MAL Marques, JCTC (2013)

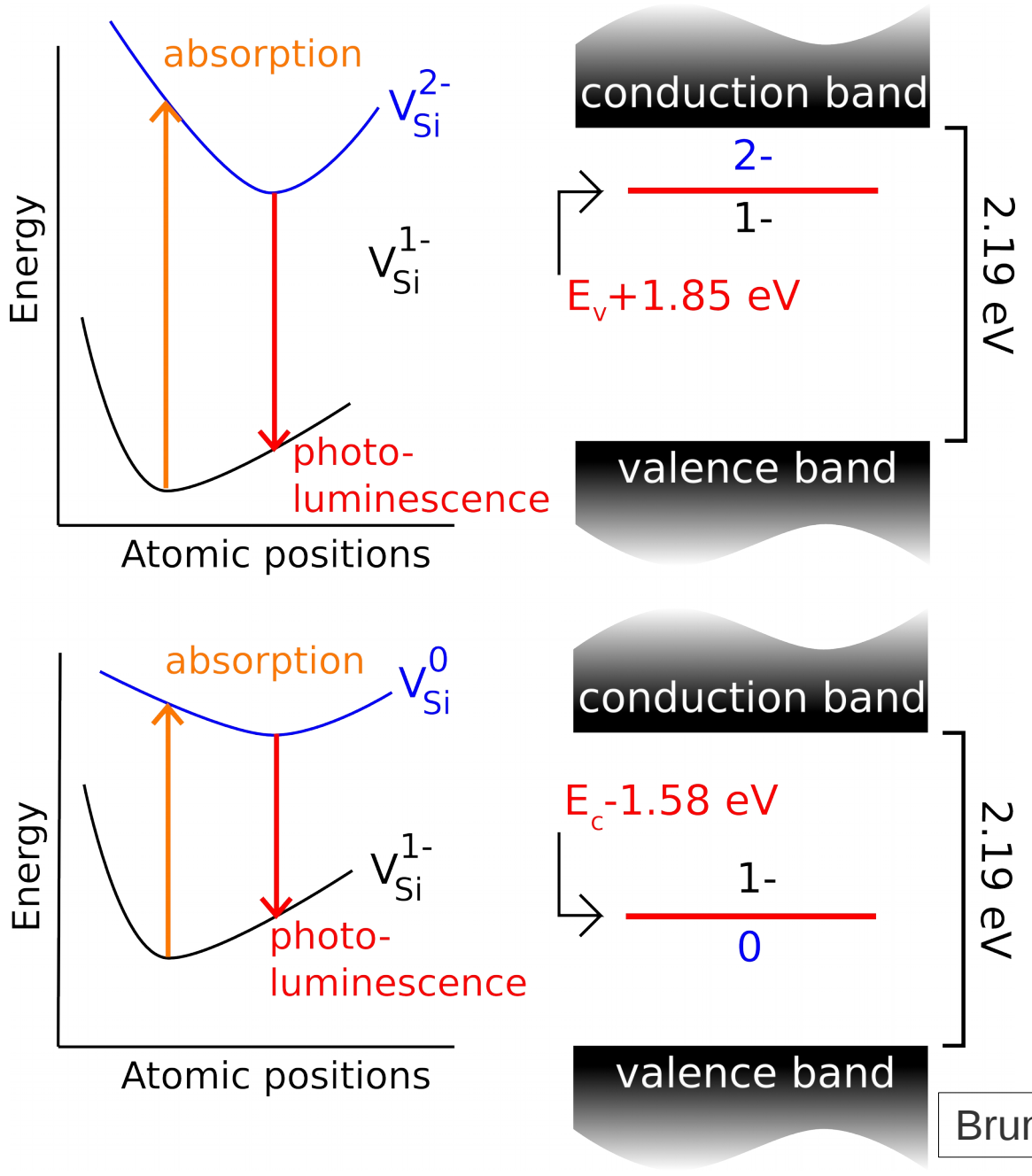
Defect calculation within GW approximation

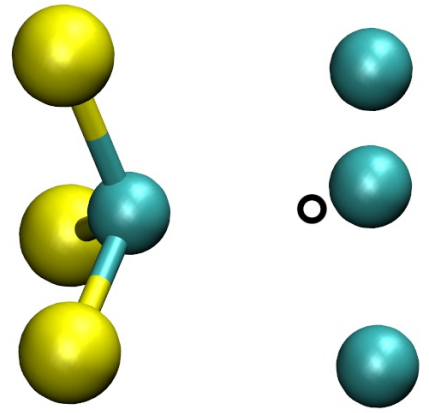
Up to 215 atoms

Cubic silicon carbide



Photoluminescence of V_{Si}

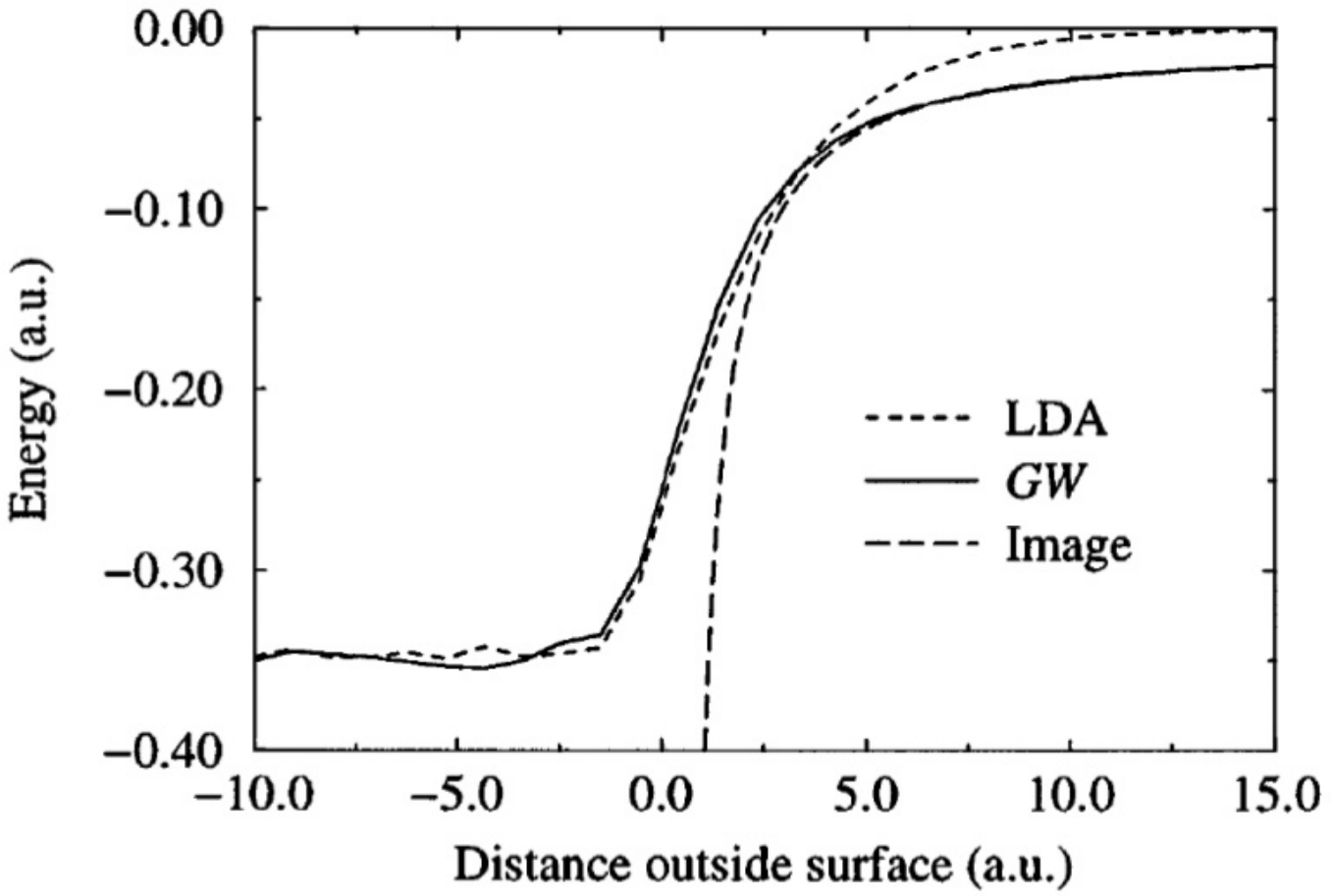




Bruneval and Roma PRB (2011)

Correct long-range potential

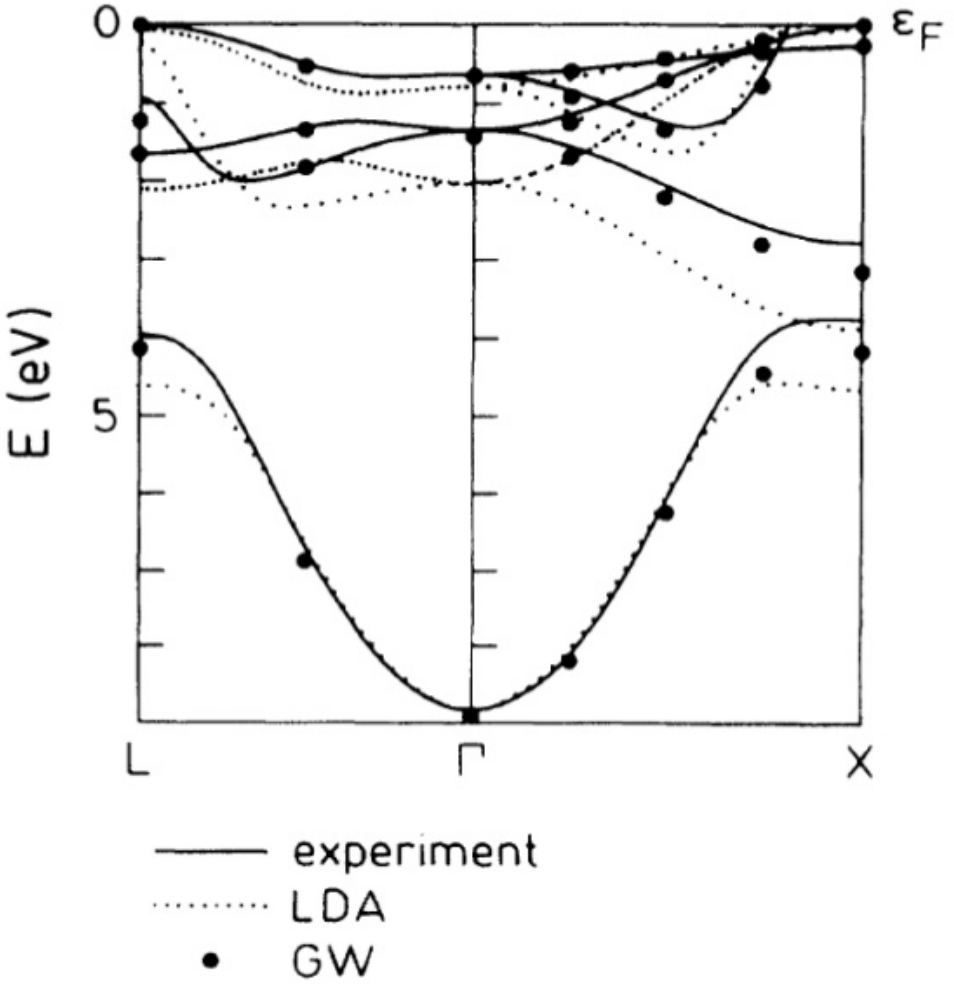
Al(111): potential



from I.D. White *et al*, PRL **80**, 4265 (1998).

3d metal band structure

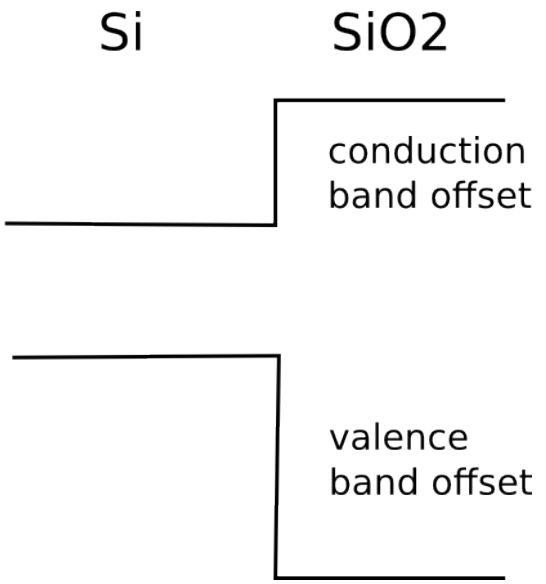
Nickel



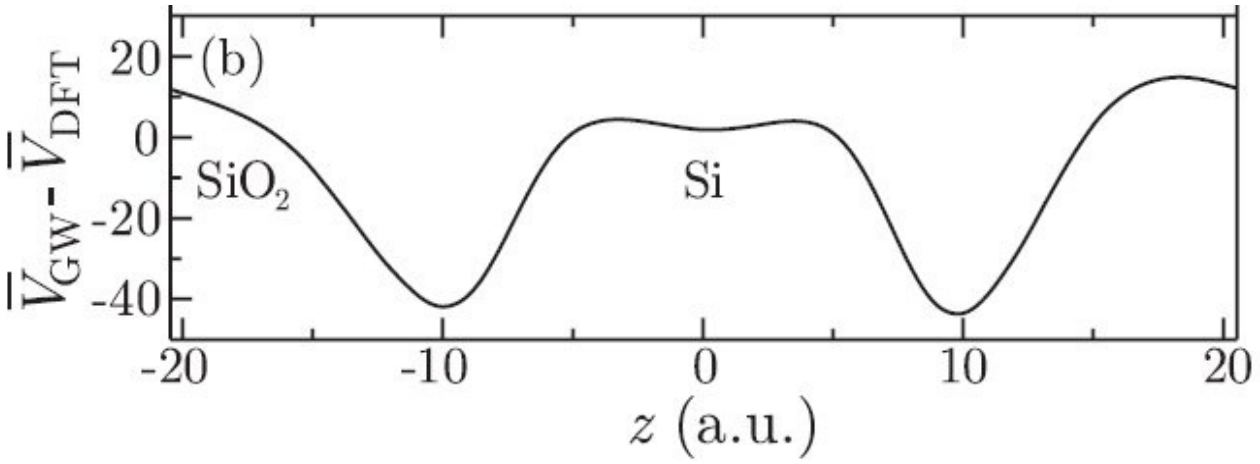
from F. Aryasetiawan, PRB **46** 13051 (1992).

Band Offset at the interface between two semiconductors

Very important for electronics!



Example: Si/SiO_2 interface for transistors



GW correction with respect to LDA

R. Shaltaf et al. PRL (2008).

Summary

- The *GW* approximation **solves the band gap problem!**
- The calculations are extremely heavy, so that we resort to many additional technical approximations: **method named G_0W_0**
- The complexity comes from
  - Dependence upon empty states
  - Non-local operators
  - Dynamic operators that requires freq. convolutions

Reviews - Links

Reviews:

• L. Hedin, Phys. Rev. **139** A796 (1965).
• L. Hedin and S. Lunqdvist, in Solid State Physics, Vol. **23** (Academic, New York, 1969), p. 1.
• F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61** 237 (1998).
• W.G. Aulbur, L. Jonsson, and J.W. Wilkins, Sol. State Phys. **54** 1 (2000).
• G. Strinati, Riv. Nuovo Cimento **11** 1 (1988).

• F. Bruneval and M. Gatti, “Quasiparticle Self-Consistent GW Method for the Spectral Properties of Complex Materials”, Top. Curr. Chem (2014) 347: 99–136

Codes:

• http://www.abinit.org

• http://www.berkeleygw.org/
• https://github.com/bruneval/molgw

Tutorials ABINIT:

```
~abinit/doc/tutorial/lesson_gw1.html
~abinit/doc/tutorial/lesson_gw2.html
```

Supplemental Information

Final expression for the Green's function

$$i G(\boldsymbol{r}t, \boldsymbol{r}'t') = \left\langle N,0 \middle| T\left[\Psi(\boldsymbol{r}t)\Psi^{\dagger}(\boldsymbol{r}'t')\right] \middle| N,0 \right\rangle$$

time-ordering operator

$$G(\boldsymbol{r}t, \boldsymbol{r}'t') = G^{e}(\boldsymbol{r}t, \boldsymbol{r}'t') - G^{h}(\boldsymbol{r}'t', \boldsymbol{r}t)$$

Compact expression that describes both the propagation of an extra electron and an extra hole

Lehman representation

$$iG(\boldsymbol{r},\boldsymbol{r}',t-t') = \langle N,0 | T\left[\Psi(\boldsymbol{r}t)\Psi^{+}(\boldsymbol{r}'t')\right] | N,0\rangle$$

Closure relation

$$\sum_{M,i} | M,i\rangle\langle M,i |$$

Lehman representation:

$$G(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{i} \frac{f_i(\boldsymbol{r})\, f_i^{*}(\boldsymbol{r}')}{\omega - \epsilon_i \pm i\eta}$$

where $\epsilon_i = \begin{cases} E(N+1,i) - E(N,0) \\ E(N,0) - E(N-1,i) \end{cases}$

Exact excitation energies!

Equation of motion of Green's functions: Dyson equation

Let us start with a non-interacting Green's function G_0 corresponding to a hamiltonian h_0

$$\int d\,\boldsymbol{r}_2 \delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\left[\omega-h_0(\boldsymbol{r}_2)\right]G_0(\boldsymbol{r}_2,\boldsymbol{r}_3,\omega)=\delta(\boldsymbol{r}_1-\boldsymbol{r}_3)$$

In short:

$$\left[\omega-h_0\right]G_0=1 \qquad \text{or} \qquad G_0^{-1}=\left[\omega-h_0\right]$$

Imagine h_0 is Hartree and h_{KS} is Kohn-Sham

$$\left[\omega-h_{\mathrm{KS}}\right]G_{\mathrm{KS}}=1$$

$$\hookrightarrow \left[\omega-h_0-v_{xc}\right]G_{\mathrm{KS}}=1$$

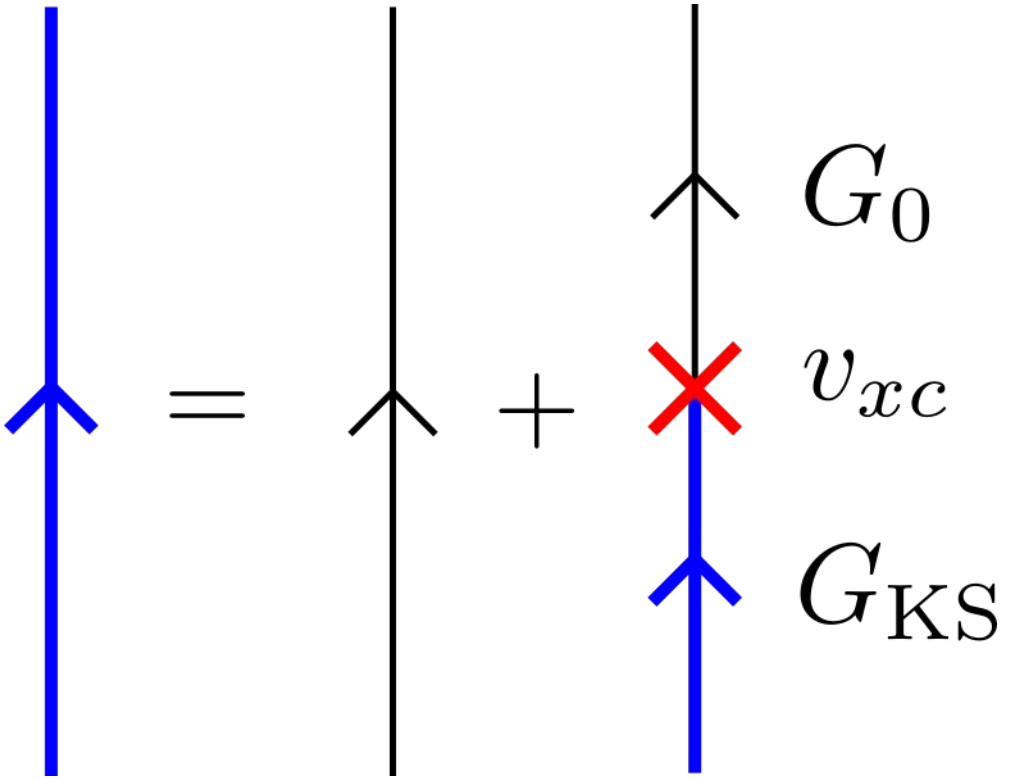
$$\hookrightarrow \left[G_0^{-1}-v_{xc}\right]G_{\mathrm{KS}}=1$$

$$\hookrightarrow G_{\mathrm{KS}}=G_0+G_0\,v_{xc}\,G_{\mathrm{KS}}$$

$$\hookrightarrow G_{\mathrm{KS}}=G_0 + G_0 v_{xc} G_0 + G_0 v_{xc} G_0 v_{xc} G_0 + \ldots$$

Exercice

A first contact with diagrams



$$G_{\mathrm{KS}}(1,2) = G_0(1,2) + \int d3\, G_0(1,3) v_{xc}(3) G_{\mathrm{KS}}(3,2)$$

Dyson equation connects the Green's functions arising from different approximations

What about the **exact Green's function?**

A hierarchy of equations of motion

In fact there is an exact expression for the self-energy as a function of the **two-particle Green's function**

$$\left[G_0^{-1} - \Sigma\right] G = 1$$

$$\left[G_0^{-1} - G_2\right] G = 1$$

$$G_2(1,2;3,4) = \langle N,0 | T[\Psi(1)\Psi(2)\Psi^+(3)\Psi^+(4)] | N,0 \rangle$$

And try to guess the equation of motion for the two-particle Green's function?

$$G_2 \quad \text{needs} \quad G_3$$

$$G_3 \quad \text{needs} \quad G_4$$

$$G_4 \quad \text{needs} \quad G_5$$

.....

An expression for the self-energy

Trick due to Schwinger (1951):

- Introduce a small external potential *U* (that will be made equal to zero at the end)
- Calculate the variations of *G* with respect to *U* $G_2(1,3;2,3)=\frac{\delta G(1,2)}{\delta U(3)}$

Obtain a perturbation theory with basic ingredients *G* and *v*
1st order is Hartree-Fock
2nd order is MP2

However MP2 diverges for metals!

Trick due to Hubbard+Hedin (late 1950's – early 1960's):

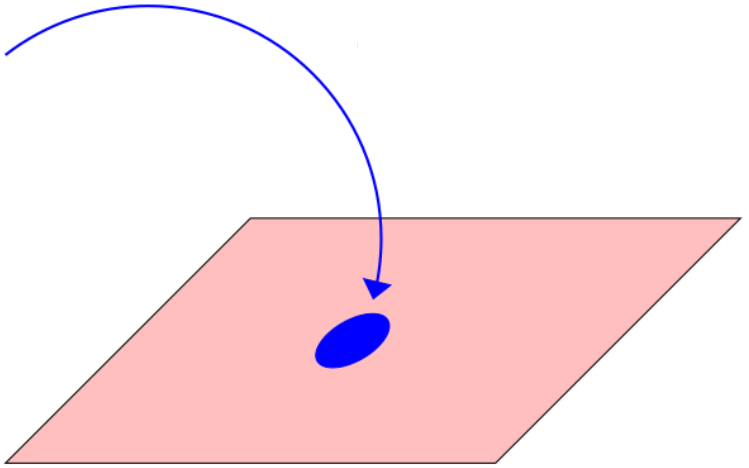
- Introduce the electrostatic response *V* to *U* $V(1)=U(1)-i\int d2\, v(1,2)\delta G(2,2)$
- Calculate the variations of *G* with respect to *V*

Obtain **a new renormalized perturbation theory** with basic ingredients *G* and *W*

1st order is *GW*

Shifting from *U* to *V*

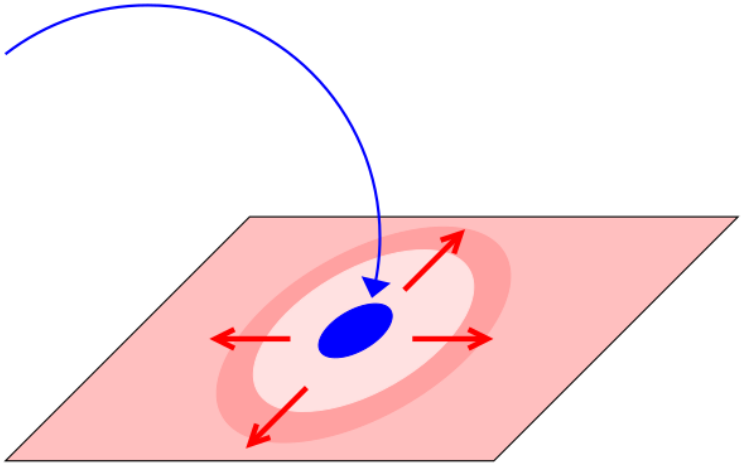
$$U(1) = \varepsilon\,\delta(\boldsymbol{r} - \boldsymbol{r_1})\,\delta(t - t_1)$$



Everything is functional of *U*

$$G[U]$$

$$U(1) = \varepsilon\,\delta(\boldsymbol{r} - \boldsymbol{r_1})\,\delta(t - t_1)$$



$$V(1) = U(1) + \int d\boldsymbol{r}\, v(r_1 - r)\,\delta\rho(\boldsymbol{r})$$

V also includes the electrostatic response

Everything is functional of *V*

$$G[V]$$

Exercise 1

Green's function in frequency domain

$$iG(\mathbf{r_1}t_1,\mathbf{r_2}t_2)=\theta(t_1-t_2)\sum_{i\,\mathrm{virt}}\phi_i(\mathbf{r_1})\phi_i^*(\mathbf{r_2})e^{-i\epsilon_i(t_1-t_2)} - \theta(t_2-t_1)\sum_{i\mathrm{occ}}\phi_i(\mathbf{r_2})\phi_i^*(\mathbf{r_1})e^{-i\epsilon_i(t_2-t_1)}$$

$$G(\mathbf{r_1},\mathbf{r_2},\omega)=\int d(t_1-t_2)e^{i\omega(t_1-t_2)}G(\mathbf{r_1}t_1,\mathbf{r_2}t_2)$$

$$G(\mathbf{r_1},\mathbf{r_2},\omega)=\sum_i \frac{\phi_i(\mathbf{r_1})\phi_i^*(\mathbf{r_2})}{\omega-\epsilon_i\pm i\eta}$$

Exercise 2:

Fock exchange from Green's functions

$$\Sigma_x(1,2) = iG(1,2)v(1^+,2) \quad \Longrightarrow \quad \Sigma_x(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = -\sum_{i\text{occ}} \frac{\phi_i(\boldsymbol{r}_1)\phi_i^*(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

Exercise 3: let's play with Dyson equations

1) The multiple faces of the Dyson equation

$$\left[\omega - h_{\mathrm{KS}}\right] G_{\mathrm{KS}} = 1$$

$$\left[\omega - h_0 - v_{xc}\right] G_{\mathrm{KS}} = 1$$

$$\left[G_0^{-1} - v_{xc}\right] G_{\mathrm{KS}} = 1$$

$$G_{\mathrm{KS}} = G_0 + G_0 v_{xc} G_{\mathrm{KS}}$$

$$G_{\mathrm{KS}} = G_0 + G_0 v_{xc} G_0 + G_0 v_{xc} G_0 v_{xc} G_0 + \ldots$$

$$G_{\mathrm{KS}}^{-1} = G_0^{-1} - v_{xc}$$

2) Combining the Dyson equations

$$\left.\begin{aligned} G^{-1} &= G_0^{-1} - \Sigma \\ G_{\mathrm{KS}}^{-1} &= G_0^{-1} - v_{xc} \end{aligned}\right\} \quad G^{-1} = G_{\mathrm{KS}}^{-1} - \left(\Sigma - v_{xc}\right)$$

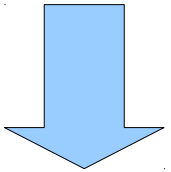
$$1 = \left[G_{\mathrm{KS}}^{-1} - \left(\Sigma - v_{xc}\right)\right] G$$

$$1 = \left[\omega - h_0 - \Sigma\right] G$$

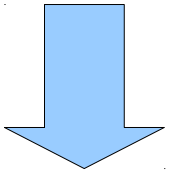
Exercise 4

Show the standard Adler-Wiser formula (1963):

$$\chi_0(1,2) = -i\,G(1,2)G(2,1)$$



$$\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = -\frac{i}{2\pi}\int d\omega' G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega+\omega')G(\boldsymbol{r}_2,\boldsymbol{r}_1,\omega')$$

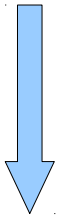


$$\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega) = \sum_{\substack{i\,\mathrm{occ}\\ j\,\mathrm{virt}}} \phi_i(\boldsymbol{r}_1)\phi_i^*(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}_2)\phi_j^*(\boldsymbol{r}_1) \times\left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)-i\eta}-\frac{1}{\omega-(\epsilon_i-\epsilon_j)+i\eta}\right]$$

Exercise 5

Show that the product in time becomes a convolution in frequency:

$$\Sigma(\boldsymbol{r}_1,\boldsymbol{r}_2,t_1-t_2)=iG(\boldsymbol{r}_1,\boldsymbol{r}_2,t_1-t_2)W(\boldsymbol{r}_2,\boldsymbol{r}_1,t_2-t_1)$$



$$G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)=\int d(t_1-t_2)e^{i\omega(t_1-t_2)}G(\boldsymbol{r}_1 t_1,\boldsymbol{r}_2 t_2)$$

$$G(\boldsymbol{r}_1,\boldsymbol{r}_2,t_1-t_2)=\frac{1}{2\pi}\int d\omega e^{-i\omega(t_1-t_2)}G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)$$

$$\Sigma(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)=\frac{i}{2\pi}\int d\omega' G(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega+\omega')W(\boldsymbol{r}_2,\boldsymbol{r}_1,\omega')$$