Electronic Excitations and Spectroscopy: Theory and Codes

Introduction
to the
GW approximation

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Outline

Outline

Band structure from one particle approximations

Any one-particle Hamiltonian: $h(\mathbf{r})$
$\rightarrow$ diagonalization
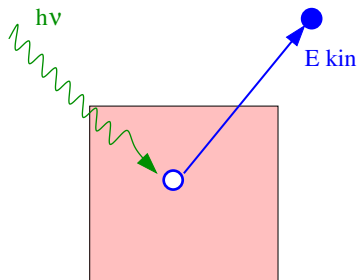$h(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$
and ϵ_i is called the band structure.

HOWEVER, in reality,

$$\mathcal{H}(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_i -\frac{\nabla_i{}^2}{2} + \sum_i V_{\text{nuclei}}(\mathbf{r}_i) + \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$\rightarrow$ ionization or affinity energy

Photoemission spectroscopy

Energy conservation:

- Before the experiment
  $h\nu + E_{N,0}$
- After the experiment
  $E_{kin} + E_{N-1,i}$

$h\nu - E_{kin} = E_{N-1,i} - E_{N,0} \hat{=} -\epsilon_i$
$\rightarrow$ ionization energy or binding energy or **valence band structure**

Wavefunctions methods

Hartree-Fock method: variationally best Slater determinant

$$\Phi_{N,0}(\mathbf{r}_1,...,\mathbf{r}_N) \propto \begin{vmatrix} \phi_1(\mathbf{r}_1) & \ldots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \ldots & \phi_N(\mathbf{r}_2) \\ \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \ldots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

made of N one-particle wavefunctions ϕ_i.

$$\mathcal{L} = \langle \Phi | \mathcal{H} | \Phi \rangle - \sum_i \epsilon_i^{\mathsf{HF}} \int d\mathbf{r} |\phi_i(\mathbf{r})|^2$$

$$\Rightarrow h^{\mathsf{HF}} \phi_i = \epsilon_i^{\mathsf{HF}} \phi_i$$

ϵ_i^{HF} obtained as N Lagrange multipliers

Hartree-Fock method

Valence Photoemission:

$$\Phi_{N-1,i}(\mathbf{r}_1,...,\mathbf{r}_{N-1}) \propto$$

$$\begin{vmatrix} \phi_1(\mathbf{r}_1) & \dots & \phi_{i-1}(\mathbf{r}_1) & \phi_{i+1}(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \dots & \phi_{i-1}(\mathbf{r}_2) & \phi_{i+1}(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_2) \\ \vdots & & \vdots & & & \\ \phi_1(\mathbf{r}_{N-1}) & \dots & \phi_{i-1}(\mathbf{r}_{N-1}) & \phi_{i+1}(\mathbf{r}_{N-1}) & \dots & \phi_N(\mathbf{r}_{N-1}) \end{vmatrix}$$
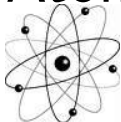
Koopmans theorem:

$$\epsilon_i = \langle N, 0 | \mathcal{H} | N, 0 \rangle - \langle N-1, i | \mathcal{H} | N-1, i \rangle$$
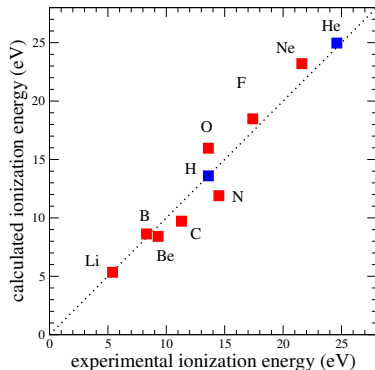
The eigenvalues ϵ_i do have a physical meaning
Approximation: **No relaxation** of the other orbitals
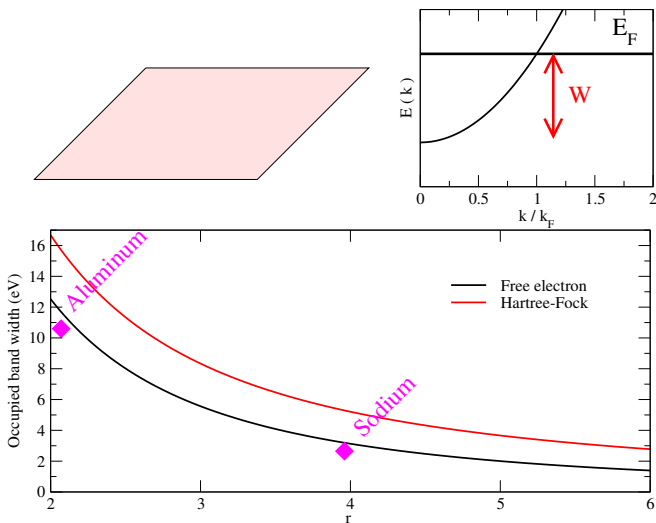
Hartree-Fock results

Ionization energy

Atoms

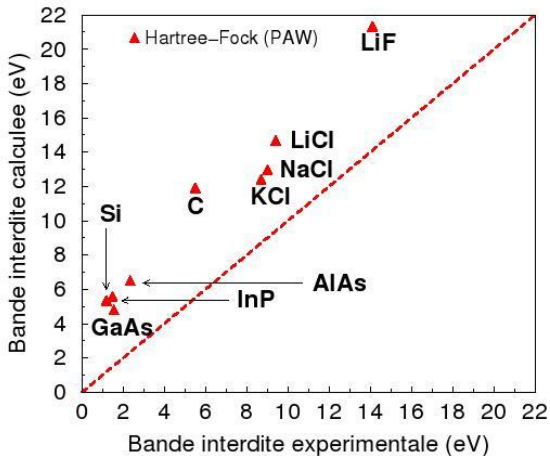calculated as the energy of the HOMO with gaussian 03

Hartree-Fock results

Homogeneous electron gas (=jellium) with constant density ρ_0

Hartree-Fock results

Band gap of semiconductors and insulators

courtesy of Brice Arnaud, Université de Rennes, France

Density Functional Theory
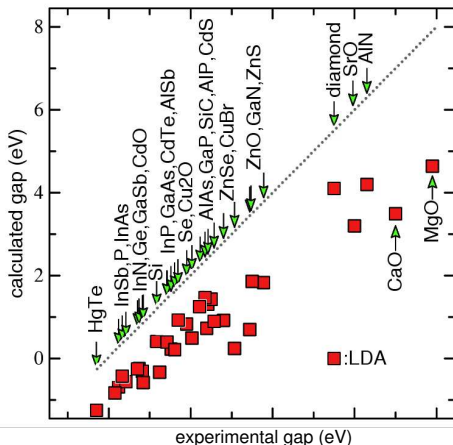
DFT well assessed for the structure of solids

BUT

$$\mathcal{L} = \langle \Phi | \mathcal{H}^{\mathsf{KS}} | \Phi \rangle - \sum_i \epsilon_i^{\mathsf{KS}} \int d\mathbf{r} |\phi_i^{\mathsf{KS}}(\mathbf{r})|^2$$

$$\Rightarrow h^{\mathsf{KS}}(\mathbf{r}) \phi_i^{\mathsf{KS}}(\mathbf{r}) = \epsilon_i^{\mathsf{KS}} \phi_i^{\mathsf{KS}}(\mathbf{r})$$

ϵ_i^{KS} obtained as N Lagrange multipliers

Kohn-Sham energies **cannot** be interpreted as removal/addition energies

Kohn-Sham

Band gaps of semiconductors and insulators

adapted from M. van Schilfgaarde *et al.*, PRL **96** 226402 (2006)
$\rightarrow$ underestimated

The solution?

Need for a tool that gives the **correct** band structure ϵ_i
i.e. the **correct** differences $E_{N,0} - E_{N\pm1,i}$

$\Rightarrow$ Green's functions

Outline

Green's functions: from HF to *GW*

- Review the many-body equations with a functional approach (Hedin 1965)
- Convince you that *GW* is a natural extension beyond HF

use of zero temperature Green's function formalism:

$$
\begin{aligned}
iG(1,2) &= \langle N,0|T\left[\Psi_H(1)\Psi_H^\dagger(2)\right]|N,0\rangle \\
&= \begin{cases}
\langle N,0|\Psi_H(1)\Psi_H^\dagger(2)|N,0\rangle & \text{if } t_1 > t_2 \\
-\langle N,0|\Psi_H^\dagger(2)\Psi_H(1)|N,0\rangle & \text{if } t_1 < t_2
\end{cases}.
\end{aligned}
$$

Green's functions: from HF to *GW*

$t_1 > t_2$

$\langle N, 0 | \Psi_H(1) \Psi_H^\dagger(2) | N, 0 \rangle$

$\Psi_H^\dagger(2) | N, 0 \rangle$
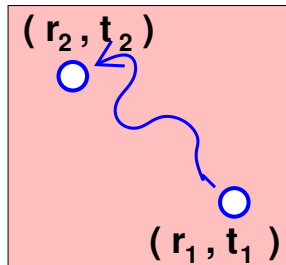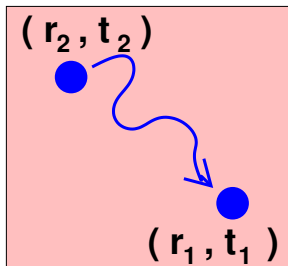
$\Psi_H^\dagger(1) | N, 0 \rangle$

$t_1 < t_2$

$\langle N, 0 | \Psi_H^\dagger(2) \Psi_H(1) | N, 0 \rangle$

$\Psi_H(2) | N, 0 \rangle$

$\Psi_H(1) | N, 0 \rangle$

Functional approach to the MB problem

To determine the 1-particle Green's function

$$[i\frac{\partial}{\partial t} - h_0]G + i \int vG_2 = 1$$

where $h_0 = -\frac{1}{2}\nabla^2 + v_{ext}$ is the independent particle Hamiltonian.

The 2-particle Green's function describes the motion of 2 particles.
Unfortunately, a whole hierarchy of equations:

$$G_1(1,2) \quad \leftarrow \quad G_2(1,2;3,4)$$
$$G_2(1,2;3,4) \quad \leftarrow \quad G_3(1,2,3;4,5,6)$$
$$\vdots \qquad \vdots \qquad \qquad \vdots$$

Self-energy

Perturbation theory starts from what is known to evaluate what is not known, hoping that the difference is small...

Let's say we know G_0 that corresponds to the Hamiltonian h_0

Everything that is unknown is put in

$$\Sigma = G_0^{-1} - G^{-1}$$

This is the definition of the self-energy

Thus,

$$[i\frac{\partial}{\partial t} - h_0]G - \int \Sigma G = 1$$

to be compared with

$$[i\frac{\partial}{\partial t} - h_0]G + i\int vG_2 = 1$$

Functional derivation of the MB problem

Trick due to Schwinger (1951):
introduce a small external potential $U(3)$, that will be made equal to zero at the end, and calculate the variations of G_1 with respect to U

Self-energy

$$\Sigma(1,2) = -i \int d3d4 v(1^+,3) G(1,4) \frac{\delta G^{-1}(4,2)}{\delta U(3)}$$

Vertex function

$$\Gamma(1,2;3) = -\frac{\delta G^{-1}(1,2)}{\delta U(3)}$$

Dyson equation

$$G^{-1}(1,2) = G_0^{-1}(1,2) - U(1)\delta(1,2) - \Sigma(1,2)$$

Functional definition of the self-energy

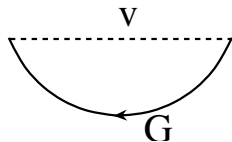> ### Exact equations
>
> $$G^{-1} = G_0^{-1} - \Sigma$$
>
> $$\Sigma = iGv\Gamma$$
>
> $$\Gamma = 1 + \left[-iv + \frac{\delta\Sigma}{\delta G} \right] GG\Gamma$$

$$\Gamma^{(0)} = 1$$

$$\Sigma^{(1)} = iGv = \Sigma_x$$

$\rightarrow$ **Hartree Fock** approximation

Functional definition of the self-energy

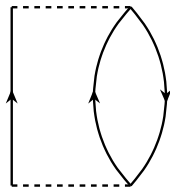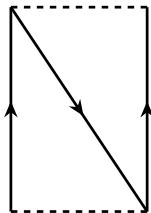### Exact equations

$$G^{-1} = G_0^{-1} - \Sigma$$

$$\Sigma = iGv\Gamma$$

$$\Gamma = 1 + \left[-iv + \frac{\delta\Sigma}{\delta G} \right] GG\Gamma$$

$$\Sigma^{(1)} = iGv$$

$$\Gamma^{(1)} = 1 + ivGGv + ivGvG$$

$$\Sigma^{(2)} = \Sigma_x - GvGGv - GvGvG$$

$\rightarrow$ 2nd order in v

New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

LARS HEDIN†

Argonne National Laboratory, Argonne, Illinois

(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main interest to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(\mathbf{k})$ and quasiparticle interactions $f(\mathbf{k},\mathbf{k}')$. The very first approximation gives a good value for the magnitude of $E(\mathbf{k})$. To estimate the derivative of $E(\mathbf{k})$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for f. Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

Need for screening

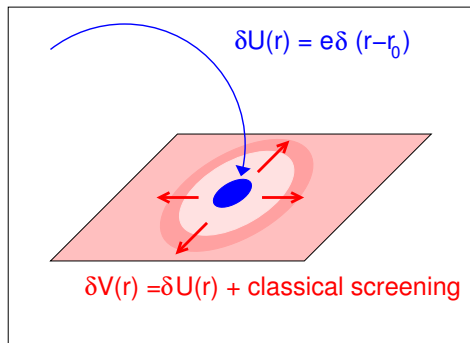$$A[U] = G[U] \text{ or } \Gamma[U] \text{ or } \Sigma[U]$$

variations of some operator with respect to a local bare perturbation: $\frac{\delta A}{\delta U}$
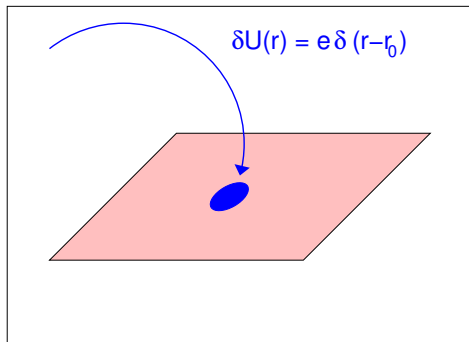
Need for screening

Purely classical interaction

$$\delta V(1) = \delta U(1) + \int d2 \, v(1,2) \delta \rho(2)$$

the variations of the charge density $\delta \rho$ tends to oppose to the perturbation.

Need for screening

We'd better work with $G[V]$, $\Sigma[V]$, $\Gamma[V]$, etc.
than with $G[U]$, $\Sigma[U]$, $\Gamma[U]$, etc.

$$
\begin{aligned}
\Gamma(1,2;3) &= -\frac{\delta G^{-1}(1,2)}{\delta U(3)} \\
&= -\int d4 \frac{\delta G^{-1}(1,2)}{\delta V(4)} \frac{\delta V(4)}{\delta U(3)} \\
&= -\int d4 \frac{\delta G^{-1}(1,2)}{\delta V(4)} \varepsilon^{-1}(4,3)
\end{aligned}
$$

where ε is the dielectric function of the medium.

Towards Hedin's equations

$$\Sigma = iG v \varepsilon^{-1} \tilde{\Gamma}$$

irreducible vertex

$$
\begin{aligned}
\tilde{\Gamma} &= -\frac{\delta G^{-1}}{\delta V} \\
&= 1 + \frac{\delta \Sigma}{\delta G} G G \tilde{\Gamma}
\end{aligned}
$$

screened Coulomb interaction

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

dielectric function

$$\epsilon = 1 - v \tilde{\chi}$$

irreducible polarizability

$$\tilde{\chi} = \frac{\delta \rho}{\delta V} = -iG G \tilde{\Gamma}$$

Hedin's equations

$$
\begin{aligned}
\Sigma &= iGW\tilde{\Gamma} \\
\tilde{\Gamma} &= 1 + \frac{\delta\Sigma}{\delta G}GG\tilde{\Gamma} \\
W &= \epsilon^{-1}v \\
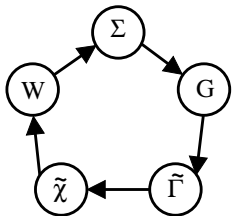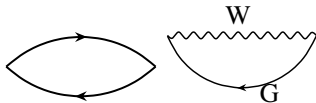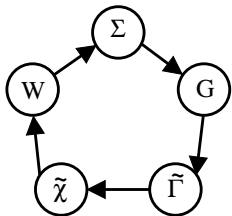\epsilon &= 1 - v\tilde{\chi} \\
\tilde{\chi} &= -iGG\tilde{\Gamma} \\
G^{-1} &= G_0^{-1} - \Sigma
\end{aligned}
$$

$$\Sigma^{(0)} = 0$$

$$\Gamma^{(1)} = 1$$

$$\tilde{\chi}^{(1)} = -iGG = \chi_{\mathrm{RPA}}$$

$$\Sigma^{(1)} = iGW$$

Hedin's wheel

Hedin's equations

$$
\begin{aligned}
\Sigma &= iGW\tilde{\Gamma} \\
\tilde{\Gamma} &= 1 + \frac{\delta\Sigma}{\delta G}GG\tilde{\Gamma} \\
W &= \epsilon^{-1}v \\
\epsilon &= 1 - v\tilde{\chi} \\
\tilde{\chi} &= -iGG\tilde{\Gamma} \\
G^{-1} &= G_0^{-1} - \Sigma
\end{aligned}
$$

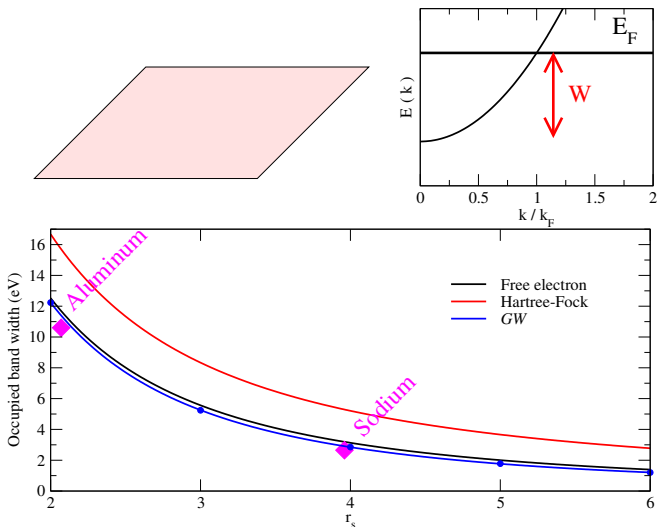$$\Sigma^{(0)} = 0$$

$$\Gamma^{(1)} = 1$$

$$\tilde{\chi}^{(1)} = -iGG = \chi_{\mathrm{RPA}}$$

$$\Sigma^{(1)} = iGW$$

Hedin's wheel

GW for the jellium

Homogeneous electron gas with constant density ρ_0

From the Coulomb interaction to the screened Coulomb interaction

Hartree-Fock self-energy

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

GW self-energy

$$\Sigma(1,2) = iG(1,2)W(1^+,2)$$

The only difference is in the *v* or *W*

What is different in v and in W

- W is shorter ranged than v
  with a crude model for W in metal:

$$W(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^{-\lambda_{TF} \cdot |\mathbf{r}_1 - \mathbf{r}_2|}}{|\mathbf{r}_1 - \mathbf{r}_2|}$$
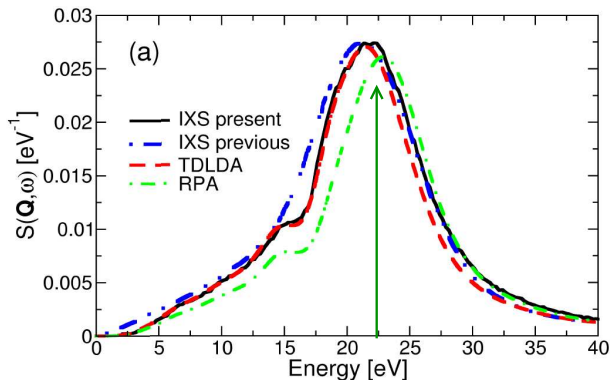
- v is static, whereas W is dynamic

$$v(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = \delta(t_1 - t_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$W(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2)$$

How does *W* look like?

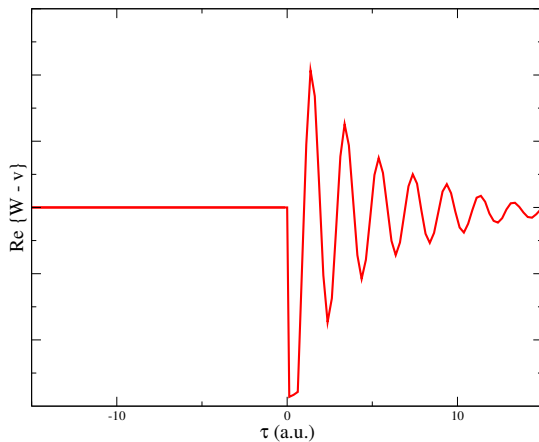*W* in frequency domain can be calculated and also measured!

Silicon

It can be measured by EELS, IXSS.
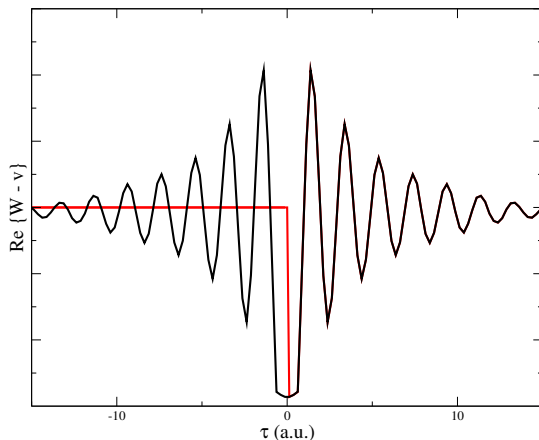
How does W look like?

In real time:

Macroscopic response to $U(1) = e\delta(\mathbf{r}_1)\delta(t_1)$

How does *W* look like?

In real time:

Macroscopic response to $U(1) = e\delta(\mathbf{r}_1)\delta(t_1)$

From Hartree-Fock to *GW*

The only difference is in the *v* or *W*

Coulomb interaction

$$v(1,2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\delta(t_1 - t_2)$$

Screened Coulomb interaction

$$W(1,2) = \int d\mathbf{r}_3 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|}\epsilon^{-1}(\mathbf{r}_3, \mathbf{r}_2, t_1 - t_2)$$

GW self-energy

Hartree-Fock self-energy

$$\Sigma_x(\cancel{\omega}) = iGv$$

$$\begin{aligned}
\Sigma_{GW}(\omega) &= iGW \\
&= iGv + iG[W - v] \\
&= \Sigma_x + \Sigma_c(\omega)
\end{aligned}$$

non local
hermitian, static

non local
non hermitian, dynamic

$\rightarrow$ Deep consequences for the spectral function $A(\omega) = |\text{Im}\{\text{Tr}G(\omega)\}|$

Spectral function

The spectral functions can be calculated

$$
\begin{aligned}
\langle i|A(\omega)|i\rangle &= |\mathrm{Im}\langle i|G(\omega)|i\rangle| \\
&= \left| \frac{1}{\omega - h_{\mathrm{hartree}ii} - \Sigma_{ii}(\omega)} \right| \\
&= \frac{|\mathrm{Im}\Sigma_{ii}(\omega)|}{[\omega - h_{\mathrm{hartree}ii} - \mathrm{Re}\Sigma_{ii}(\omega)]^2 + [\mathrm{Im}\Sigma_{ii}(\omega)]^2}
\end{aligned}
$$
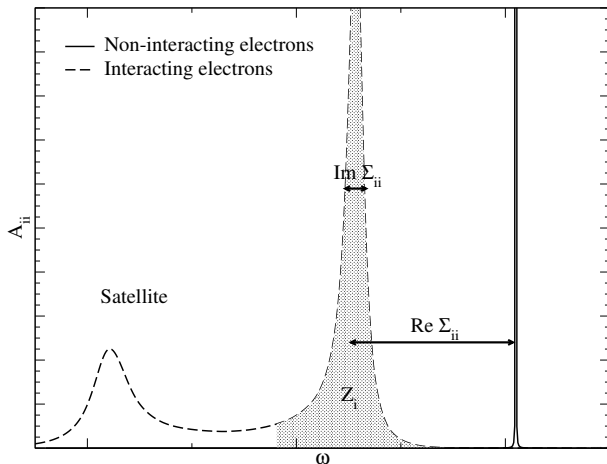
where $G_{ii}^{-1} = G_{0ii}^{-1} - \Sigma_{ii}$
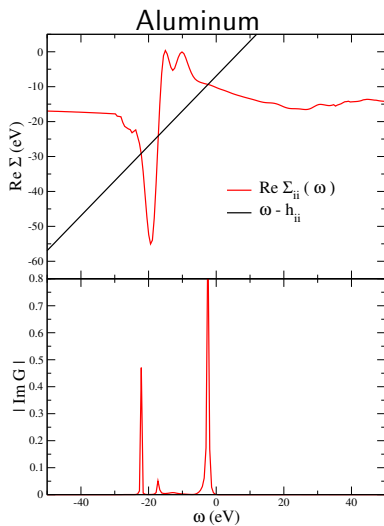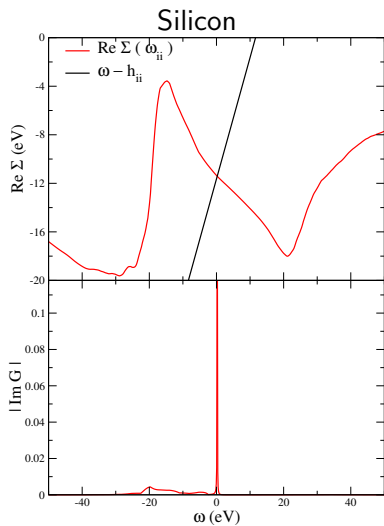Lorentizian shape:
Centered on the *GW* QP energy.
Width $\mathrm{Im}\Sigma$

From Hartree-Fock to *GW*

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

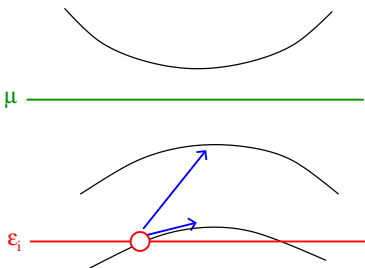# Solution of the quasiparticle equation

Lifetime and *GW* self-energy

Hole self-energy:

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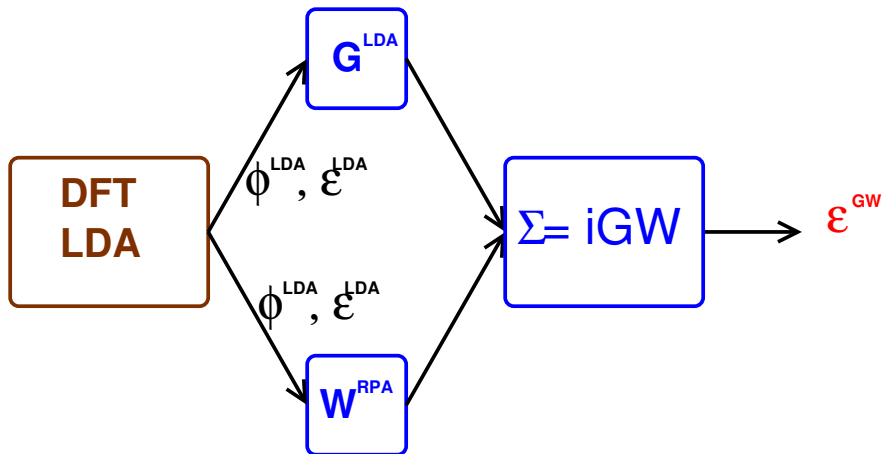$$\times \theta(\mu-\epsilon_j)\theta(\epsilon_j-\epsilon_i)$$

Outline

Schematic GW calculation

Recipe by Hybertsen and Louie, PRL **55** 1418 (1985) called "$G_0 W_0$" or "best G best W"

GW for realistic materials

Assumption

$$\phi_i^{GW} \approx \phi_i^{KS}$$

Quasiparticle equations

$$h_0(\mathbf{r}_1)\phi_i^{GW}(\mathbf{r}_1) + \int d\mathbf{r}_2 \Sigma(\mathbf{r}_1, \mathbf{r}_2, \epsilon_i^{GW})\phi_i^{GW}(\mathbf{r}_2) = \epsilon_i^{GW}\phi_i^{GW}(\mathbf{r}_1)$$

Kohn-Sham equations

$$h_0(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) + v_{xc}(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) = \epsilon_i^{KS}\phi_i^{KS}(\mathbf{r}_1)$$

Differences

$$\langle \phi_i^{KS}|\Sigma(\epsilon_i^{GW}) - v_{xc}|\phi_i^{KS}\rangle = \epsilon_i^{GW} - \epsilon_i^{KS}$$

GW for realistic materials

Assumption

$$\phi_i^{GW} \approx \phi_i^{KS}$$

Quasiparticle equations

$$h_0(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) + \int d\mathbf{r}_2 \Sigma(\mathbf{r}_1, \mathbf{r}_2, \epsilon_i^{GW})\phi_i^{KS}(\mathbf{r}_2) = \epsilon_i^{GW}\phi_i^{KS}(\mathbf{r}_1)$$

Kohn-Sham equations

$$h_0(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) + v_{xc}(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) = \epsilon_i^{KS}\phi_i^{KS}(\mathbf{r}_1)$$

Differences

$$\langle\phi_i^{KS}|\Sigma(\epsilon_i^{GW}) - v_{xc}|\phi_i^{KS}\rangle = \epsilon_i^{GW} - \epsilon_i^{KS}$$

GW for realistic materials

Assumption

$$\phi_i^{GW} \approx \phi_i^{KS}$$

Quasiparticle equations

$$h_0(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) + \int d\mathbf{r}_2 \Sigma(\mathbf{r}_1, \mathbf{r}_2, \epsilon_i^{GW})\phi_i^{KS}(\mathbf{r}_2) = \epsilon_i^{GW}\phi_i^{KS}(\mathbf{r}_1)$$

Kohn-Sham equations

$$h_0(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) + v_{xc}(\mathbf{r}_1)\phi_i^{KS}(\mathbf{r}_1) = \epsilon_i^{KS}\phi_i^{KS}(\mathbf{r}_1)$$

Differences

$$\langle \phi_i^{KS} | \Sigma(\epsilon_i^{GW}) - v_{xc} | \phi_i^{KS} \rangle = \epsilon_i^{GW} - \epsilon_i^{KS}$$

$G_0 W_0$ calculation

To calculate the *GW* self-energy:

$$\Sigma(1, 2) = iG(1, 2)W(1^+, 2)$$

which is Fourier transformed into frequencies

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

We need the following ingredients:

- The KS Green's function: $G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \frac{\phi_i^{KS}(\mathbf{r}_1)\phi_i^{KS*}(\mathbf{r}_2)}{\omega - \epsilon_i^{KS} \pm i\eta}$
- The RPA dielectric matrix: $\varepsilon_{\mathbf{GG'}}^{RPA \; -1}(\mathbf{q}, \omega)$

G_0W_0 calculation

To calculate the *GW* self-energy:
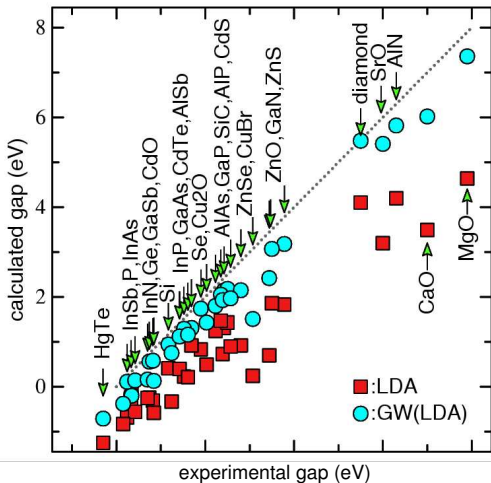
$$\Sigma(1,2) = iG(1,2)W(1^+,2)$$

which is Fourier transformed into frequencies

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

We need the following ingredients:

- The KS Green's function: $G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \frac{\phi_i^{\text{KS}}(\mathbf{r}_1)\phi_i^{\text{KS}*}(\mathbf{r}_2)}{\omega - \epsilon_i^{\text{KS}} \pm i\eta}$
- The RPA dielectric matrix: $\varepsilon_{\mathbf{GG'}}^{\text{RPA}\,-1}(\mathbf{q}, \omega)$
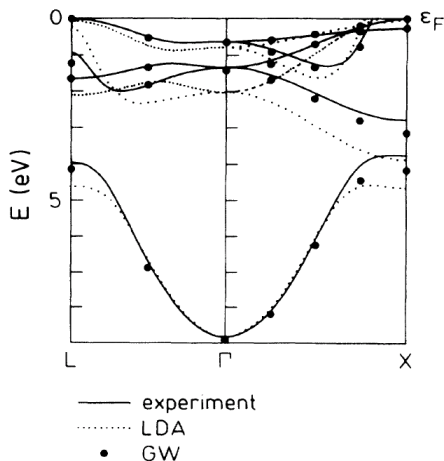
Band gaps of semiconductors

from M. van Schilfgaarde *et al.*, PRL **96** 226402 (2006).
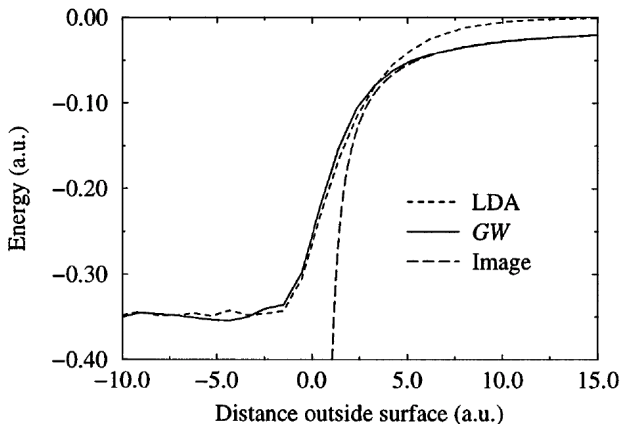
Result for a complex metal

Nickel

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

Surfaces

Al(111): potential

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

References

- 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).
- www.abinit.org
- theory.polytechnique.fr/people/bruneval/