The one-particle Green's function and the GW approximation

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TDDFT school - Benasque 2012

European Theoretical Spectroscopy Facility

nano-bio spectroscopy group

Outline

References

- L. Hedin
  Phys. Rev. **139**, A796 (1965).
- L. Hedin and S. Lunqdvist
  Solid State Physics **23** (Academic, New York, 1969).
- G. Strinati
  Rivista del Nuovo Cimento **11**, (12)1 (1988).
- F. Aryasetiawan and O. Gunnarsson
  Rep. Prog. Phys. **61**, 237 (1998).
- Giovanni Onida, Lucia Reining, and Angel Rubio
  Rev. Mod. Phys. **74**, 601 (2002).
- Fabien Bruneval
  PhD thesis, Ecole Polytechnique (2005)
  `http://theory.polytechnique.fr/people/bruneval/bruneval_these.pdf`

Outline

What is “one electron” ?

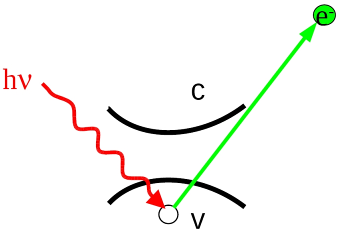
What is “one electron” ?

(in a many-electron system, e.g. a solid)

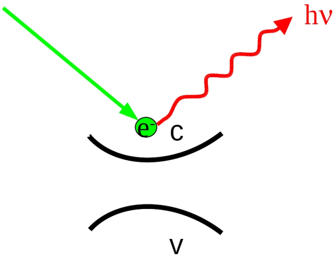
Operational definition: How to measure “one electron”?

Photoemission

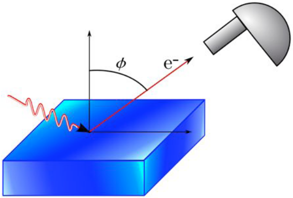
Direct Photoemission



Inverse Photoemission



Direct Photoemission

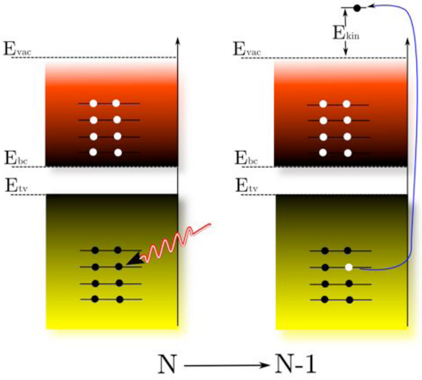


photon in - electron out

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

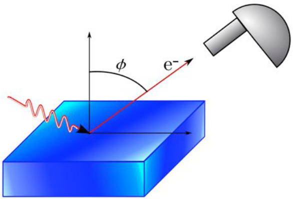
$$\epsilon_i = E(N) - E(N-1, i) = E_{kin} - h\nu$$

...plus momentum conservation ⇒ ARPES



occupied states

Direct Photoemission



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

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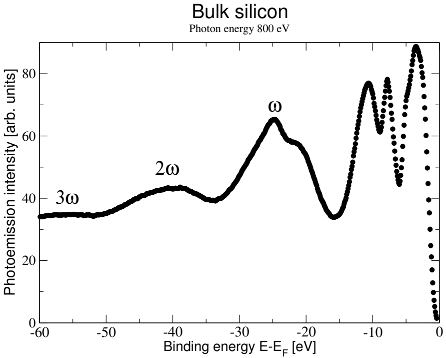
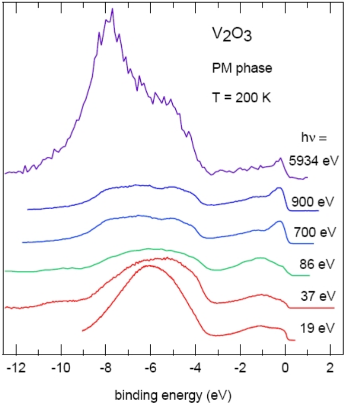


M. Guzzo *et al.*, PRL 107 (2011).

Photoemission



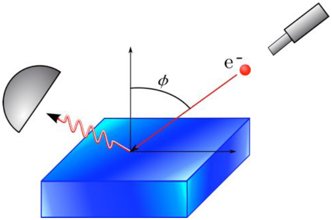
E. Papalazarou *et al.*, PRB 80 (2009)

Not discussed here:

- matrix elements - cross sections (dependence on photon energy / photon polarization)
- sudden approximation vs. interaction photoelectron - system
- surface sensitivity
- ...

S. Hüfner, *Photoelectron spectroscopy* (1995)

Inverse Photoemission

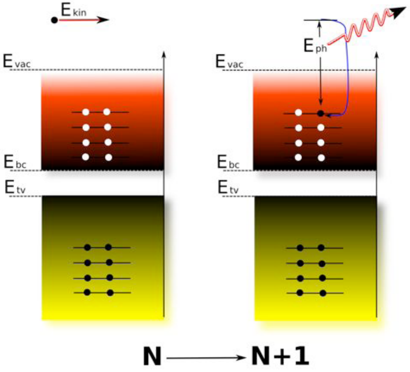


electron in - photon out

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

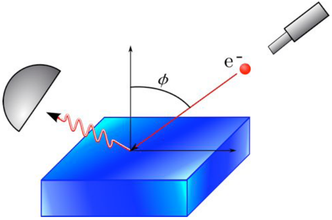
$$\epsilon_i = E(N+1, i) - E(N) = E_{kin} - h\nu$$

aka Bremsstrahlung
isochromat spectroscopy (BIS)

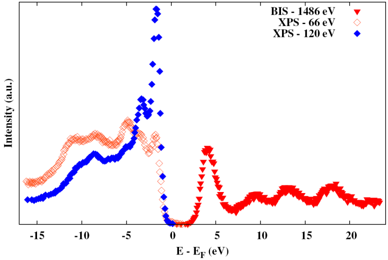


empty states

Inverse Photoemission

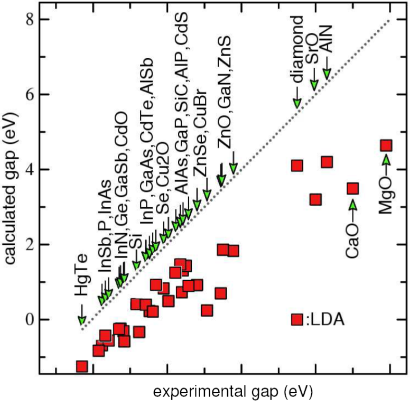


electron in - photon out



Nickel oxide
Sawatzky and Allen PRL 53 (1984)

Why do we have to study more than DFT?



adapted from M. van Schilfgaarde *et al.*, PRL **96** (2006)

Why do we have to study more than DFT?

What is “one electron” in DFT?

DFT is a “many-body theory of a collective variable”:
the density $\rho(r)$

Can we measure a Kohn-Sham electron?

Outline

One-particle Green's function

What is the one-particle Green's function $G(1,2) = G(\mathbf{x_1}, \mathbf{x_2}, t_1 - t_2)$?

One-particle Green's function

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The one-particle Green's function G

1. Propagation of one additional particle in the system

$$iG(\mathbf{x_1}, \mathbf{x_2}, t_1 - t_2) = \langle N | T \left[\psi(\mathbf{x_1}, t_1) \psi^\dagger(\mathbf{x_2}, t_2) \right] | N \rangle$$

How to calculate G?

One-particle Green's function

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   How to calculate G?

2. Resolvent of $H(\omega) = H_0 + \Sigma(\omega) = h_0 + V_H + \Sigma(\omega)$:

$$G^{-1}(\omega) = (\omega - H_0 - \Sigma(\omega)) = (G_0^{-1}(\omega) - \Sigma(\omega))$$

   What is $H(\omega)$? What is $\Sigma(\omega)$?

One-particle Green's function

The one-particle Green's function G

Definition and meaning of G:

$$iG(\mathbf{x_1}, t_1; \mathbf{x_2}, t_2) = \langle N| T\left[\psi(\mathbf{x_1}, t_1)\psi^\dagger(\mathbf{x_2}, t_2)\right] |N\rangle$$

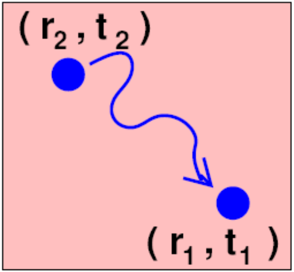
for $\quad t_1 > t_2 \Rightarrow iG(\mathbf{x_1}, t_1; \mathbf{x_2}, t_2) = \langle N|\psi(\mathbf{x_1}, t_1)\psi^\dagger(\mathbf{x_2}, t_2)|N\rangle$

for $\quad t_1 < t_2 \Rightarrow iG(\mathbf{x_1}, t_1; \mathbf{x_2}, t_2) = -\langle N|\psi^\dagger(\mathbf{x_2}, t_2)\psi(\mathbf{x_1}, t_1)|N\rangle$

One-particle Green's function

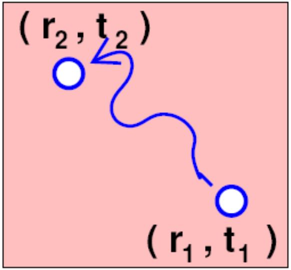
$t_1 > t_2$

$\langle N|\psi(\mathbf{x_1}, t_1)\psi^\dagger(\mathbf{x_2}, t_2)|N\rangle$



$t_1 < t_2$

$-\langle N|\psi^\dagger(\mathbf{x_2}, t_2)\psi(\mathbf{x_1}, t_1)|N\rangle$



One-particle Green's function

What is G ?

Definition and meaning of G:

$$G(\mathbf{x_1},\mathbf{x_2},t_1-t_2) = -i < N|T\left[\psi(\mathbf{x_1},t_1)\psi^\dagger(\mathbf{x_2},t_2)\right]|N>$$

Insert a complete set of $N+1$ or $N-1$-particle states and Fourier transform. This yields:

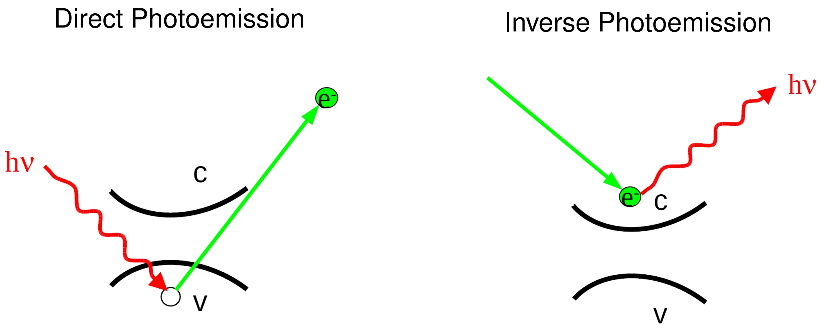
$$G(\mathbf{x_1},\mathbf{x_2},\omega) = \sum_j \frac{f_j(\mathbf{x_1})f_j^*(\mathbf{x_2})}{\omega - \varepsilon_j + i\eta sgn(\varepsilon_j - \mu)}.$$

where:

$$\varepsilon_j = \begin{array}{ll} E(N+1,j) - E(N), & \varepsilon_j > \mu \\ E(N) - E(N-1,j), & \varepsilon_j < \mu \end{array}$$

$$f_j(\mathbf{x_1}) = \begin{array}{ll} \langle N|\psi(\mathbf{x_1})|N+1,j\rangle, & \varepsilon_j > \mu \\ \langle N-1,j|\psi(\mathbf{x_1})|N\rangle, & \varepsilon_j < \mu \end{array}$$

Photoemission



One-particle excitations → poles of one-particle Green's function G

One-particle Green's function

One-particle Green's function

From one-particle G we can obtain:

- one-particle excitation spectra
- ground-state expectation value of any one-particle operator: e.g. density ρ or density matrix γ: $\rho(\mathbf{r}, t) = -iG(\mathbf{r}, \mathbf{r}, t, t^+) \qquad \gamma(\mathbf{r}, \mathbf{r}', t) = -iG(\mathbf{r}, \mathbf{r}', t, t^+)$
- ground-state total energy (e.g. Galitskii-Migdal)

One-particle Green's function

Spectral function

A useful definition: the spectral function

$$A(\mathbf{x},\mathbf{x}';\omega) = \frac{1}{\pi} \mid \mathrm{Im} G(\mathbf{x},\mathbf{x}';\omega) \mid = \sum_j f_j(\mathbf{x}) f_j^*(\mathbf{x}')\delta(\omega - \varepsilon_j).$$

One-particle Green's function

Spectral function

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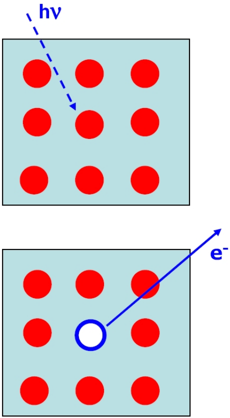
Non-interacting system:

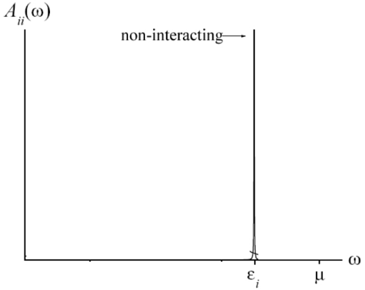
- $|N\rangle$ = Slater determinant
- Lehmann amplitudes = eigenfunctions of the one-particle Hamiltonian
- spectral function = sum of delta peaks at one-particle energies ϵ_j

General case: overlap of many contributions

Hartree-Fock

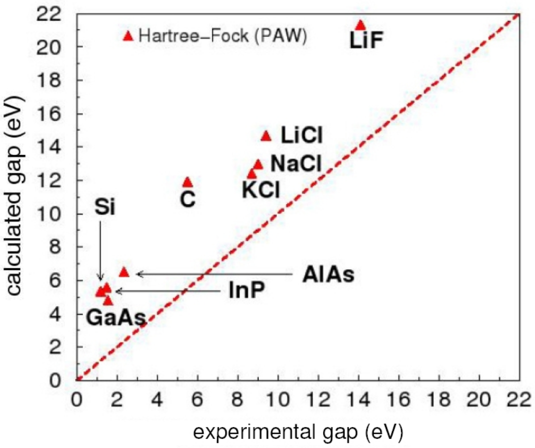


Independent particles:
no relaxation

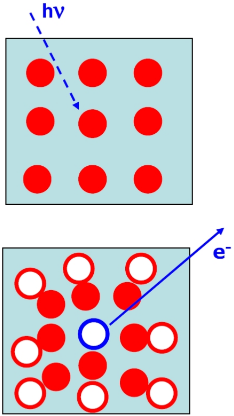


Hartree-Fock: Koopmans' theorem

Hartree-Fock

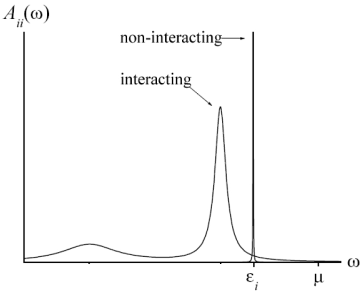


Screening: quasiparticles



Additional charge

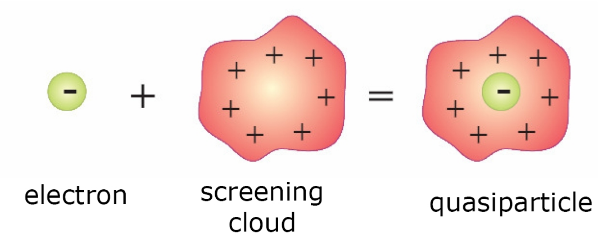
Relaxation – Screening - Correlation



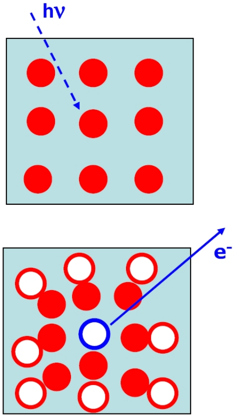
Quasiparticles

Screening: quasiparticles

Quasiparticle

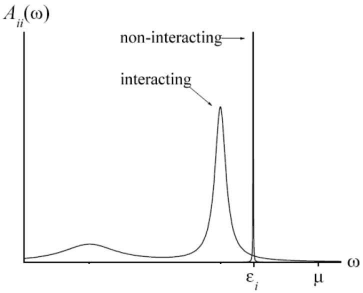


Screening: satellites



Additional charge

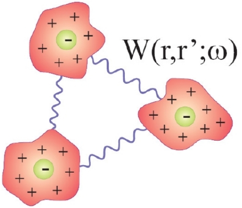
Relaxation – Screening - Correlation



Quasiparticles

Screened Coulomb interaction *W*

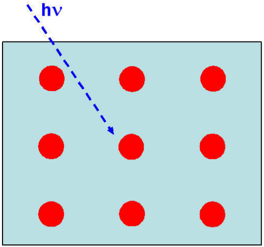
Screened potential W

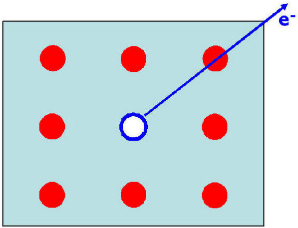


W = screened potential:
weaker than bare Coulomb interaction

$$W(r,r',\omega) = \int dr'' \frac{\varepsilon^{-1}(r,r'',\omega)}{|r''-r'|}$$

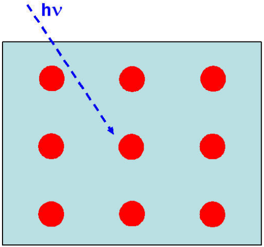
GW approximation

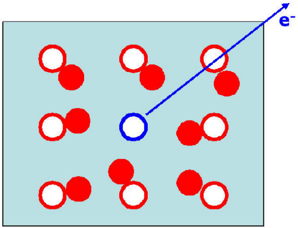




additional charge →

GW approximation





additional charge → reaction: polarization, screening

GW approximation

1. polarization made of noninteracting electron-hole pairs (RPA)
2. classical (Hartree) interaction between additional charge and polarization charge

Outline

Hedin's equations

Goal: calculate G

- an exact closed set of 5 equations in 5 unknown variables: G, Σ, W, P, Γ
- approximations: Hartree-Fock and GW
- beyond GW

One-particle Green's function

Straightforward?

$$G(\mathbf{x},t;\mathbf{x}',t') = -i < N|T\left[\psi(\mathbf{x},t)\psi^{\dagger}(\mathbf{x}',t')\right]|N >$$

One-particle Green's function

Straightforward?

$$G(\mathbf{x}, t; \mathbf{x}', t') = -i < N| T \left[\psi(\mathbf{x}, t)\psi^{\dagger}(\mathbf{x}', t')\right] |N >$$

$|N>$ = ??? Interacting ground state!

One-particle Green's function

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$|N>$ = ??? Interacting ground state!

Perturbation Theory?

Time-independent perturbation theories: messy.
Textbooks: adiabatically switched on interaction, Gell-Mann-Low theorem, Wick's theorem, expansion (diagrams). Lots of diagrams.....

Functional approach to the MB problem

Equation of motion

To determine the 1-particle Green's function:

$$\left[i\frac{\partial}{\partial t_1} - h_0(1)\right]G(1,2) = \delta(1,2) - i\int d3 v(1,3)G_2(1,3,2,3^+)$$

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.

Functional approach to the MB problem

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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, hierarchy of equations

$$\begin{array}{ccc} G_1(1,2) & \leftarrow & G_2(1,2;3,4) \\ G_2(1,2;3,4) & \leftarrow & G_3(1,2,3;4,5,6) \\ \vdots & \vdots & \vdots \end{array}$$

Self-energy

Perturbation theory starts from what is known to evaluate what is not known, hoping that the difference is small...
Let's say that we know $G_0(\omega)$ that corresponds to the Hamiltonian $H_0 = h_0 + V_H$
Everything that is unknown is put in

$$\Sigma(\omega) = G_0^{-1}(\omega) - G^{-1}(\omega)$$

This is the definition of the self-energy

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Everything that is unknown is put in

$$\Sigma(\omega) = G_0^{-1}(\omega) - G^{-1}(\omega)$$

This is the definition of the self-energy

Thus

$$[\omega - h_0 - V_H]G(\omega) - \int \Sigma(\omega)G(\omega) = 1$$

to be compared with:

$$[\omega - h_0]G(\omega) + i\int vG_2(\omega) = 1$$

One-particle Green's function

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

$$\frac{\delta G(1,2)}{\delta U(3)} = -G_2(1,3;2,3) + G(1,2)G(3,3)$$

One-particle Green's function

Trick due to Schwinger (1951):
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$$\frac{\delta G(1,2)}{\delta U(3)} = -G_2(1,3;2,3) + G(1,2)G(3,3)$$

Thus

$$[\omega - h_0 - U - V_H]G(\omega) - \int \Sigma(\omega)G(\omega) = 1$$

to be compared with:

$$[\omega - h_0 - U - V_H]G(\omega) - i\int v\frac{\delta G(\omega)}{\delta U} = 1$$

Vertex function

Screening = inverse of dielectric function

$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta U} = \frac{\delta(U + V_H)}{\delta U} = (1 - vP)^{-1}$$

Self-energy

$$\Sigma = -ivG\frac{\delta G^{-1}}{\delta U}$$

Vertex function

Screening = inverse of dielectric function

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Self-energy

$$\Sigma = -ivG\frac{\delta G^{-1}}{\delta U} = -ivG\frac{\delta G^{-1}}{\delta V_{tot}}\epsilon^{-1}$$

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Self-energy

$$\Sigma = -ivG\frac{\delta G^{-1}}{\delta U} = -ivG\frac{\delta G^{-1}}{\delta V_{tot}}\epsilon^{-1}$$

Vertex function

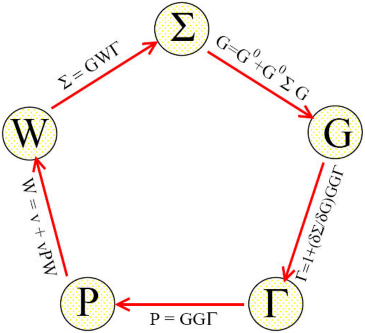
$$\Gamma = -\frac{\delta G^{-1}}{\delta V_{tot}} = 1 + \frac{\delta \Sigma}{\delta V_{tot}}$$

Hedin's equation

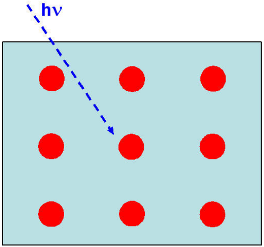
Hedin's equations

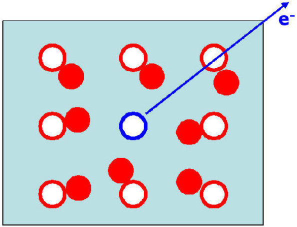
$$\Sigma = iGW\Gamma$$
$$G = G_0 + G_0 \Sigma G$$
$$\Gamma = 1 + \frac{\delta \Sigma}{\delta G} GG\Gamma$$
$$P = -iGG\Gamma$$
$$W = v + vPW$$

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



GW approximation





additional charge → reaction: polarization, screening

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Hedin's equation and GW

GW approximation

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$$G = G_0 + G_0 \Sigma G$$
$$\Gamma = 1$$
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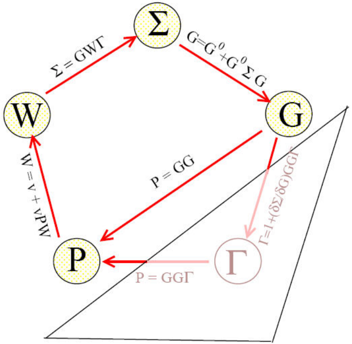

Hedin's equation and GW

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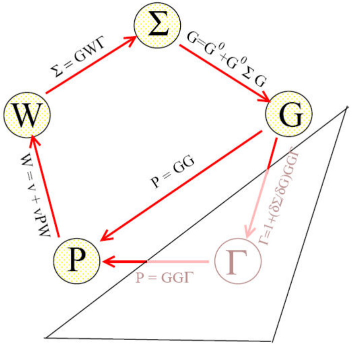


GW and Hartree-Fock

Hartree-Fock

$$\Sigma(12) = iG(12)v(1^+2)$$

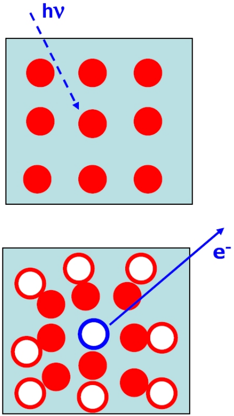
- v infinite range in space
- v is static
- Σ is nonlocal, hermitian, static

GW

$$\Sigma(12) = iG(12)W(1^+2)$$

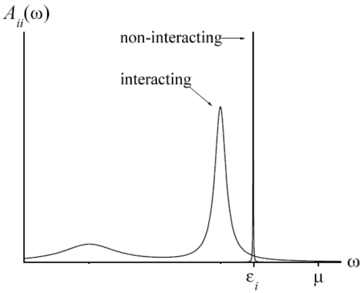
- W is short ranged
- W is dynamical
- Σ is nonlocal, complex, dynamical

GW and Hartree-Fock



Additional charge

Relaxation – Screening - Correlation



Quasiparticles

Outline

Dyson equation

$$[\omega - H_0(\mathbf{r}_1)]\, G(\mathbf{r}_1, \mathbf{r}_2, \omega) - \int d\mathbf{r}_3 \Sigma(\mathbf{r}_1, \mathbf{r}_3, \omega) G(\mathbf{r}_3, \mathbf{r}_2, \omega) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$$

Biorthonormal representation: analytic continuation of G

$$G(\mathbf{r}_1, \mathbf{r}_2, z) = \sum_\lambda \frac{\Phi_\lambda(\mathbf{r}_1, z)\tilde{\Phi}_\lambda(\mathbf{r}_2, z)}{z - E_\lambda(z)}$$

$$H_0(\mathbf{r}_1)\Phi_\lambda(\mathbf{r}_1, z) + \int d\mathbf{r}_2 \Sigma(\mathbf{r}_1, \mathbf{r}_2, z)\Phi_\lambda(\mathbf{r}_2, z) = E_\lambda(z)\Phi_\lambda(\mathbf{r}_1, z)$$

$$H_0(\mathbf{r}_1)\tilde{\Phi}_\lambda(\mathbf{r}_1, z) + \int d\mathbf{r}_2 \tilde{\Phi}_\lambda(\mathbf{r}_2, z)\Sigma(\mathbf{r}_2, \mathbf{r}_1, z) = E_\lambda(z)\tilde{\Phi}_\lambda(\mathbf{r}_1, z)$$

$$\int d\mathbf{r}\; \tilde{\Phi}_\lambda(\mathbf{r}, z)\Phi_{\lambda'}(\mathbf{r}, z) = \delta_{\lambda\lambda'}$$

Dyson equation

Quasiparticles = complex poles of G

$$E_i - E_\lambda(E_i) = 0 \qquad \Rightarrow \qquad E_i = E_\lambda(E_i)$$

$$\phi_i(\mathbf{r}) = \Phi_\lambda(\mathbf{r}, E_i)$$

Biorthonormal representation: analytic continuation of G

$$G(\mathbf{r}_1, \mathbf{r}_2, z) = \sum_\lambda \frac{\Phi_\lambda(\mathbf{r}_1, z)\tilde{\Phi}_\lambda(\mathbf{r}_2, z)}{z - E_\lambda(z)}$$

$$H_0(\mathbf{r}_1)\Phi_\lambda(\mathbf{r}_1, z) + \int d\mathbf{r}_2 \Sigma(\mathbf{r}_1, \mathbf{r}_2, z)\Phi_\lambda(\mathbf{r}_2, z) = E_\lambda(z)\Phi_\lambda(\mathbf{r}_1, z)$$

$$H_0(\mathbf{r}_1)\tilde{\Phi}_\lambda(\mathbf{r}_1, z) + \int d\mathbf{r}_2 \tilde{\Phi}_\lambda(\mathbf{r}_2, z)\Sigma(\mathbf{r}_2, \mathbf{r}_1, z) = E_\lambda(z)\tilde{\Phi}_\lambda(\mathbf{r}_1, z)$$

$$\int d\mathbf{r}\ \tilde{\Phi}_\lambda(\mathbf{r}, z)\Phi_{\lambda'}(\mathbf{r}, z) = \delta_{\lambda\lambda'}$$

G_0W_0: QP corrections

Standard perturbative G_0W_0

$$
\begin{aligned}
H_0(\mathbf{r})\varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(r) &= \epsilon_i \varphi_i(\mathbf{r}) \\
H_0(\mathbf{r})\phi_i(\mathbf{r}) + \int d\mathbf{r}' \; \Sigma(\mathbf{r},\mathbf{r}',\omega = E_i) \; \phi_i(\mathbf{r}') &= E_i \, \phi_i(\mathbf{r})
\end{aligned}
$$

First-order perturbative corrections with $\Sigma = iGW$:

$$
E_i - \epsilon_i = \langle \varphi_i | \Sigma(E_i) - V_{xc} | \varphi_i \rangle
$$

G_0W_0: QP corrections

Standard perturbative G_0W_0

$$H_0(\mathbf{r})\varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(r) = \epsilon_i\varphi_i(\mathbf{r})$$

$$H_0(\mathbf{r})\phi_i(\mathbf{r}) + \int d\mathbf{r}'\ \Sigma(\mathbf{r},\mathbf{r}',\omega = E_i)\ \phi_i(\mathbf{r}') = E_i\,\phi_i(\mathbf{r})$$

First-order perturbative corrections with $\Sigma = iGW$:

$$E_i - \epsilon_i = \langle\varphi_i|\Sigma(E_i) - V_{xc}|\varphi_i\rangle$$

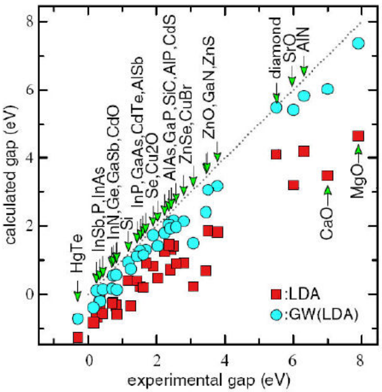
$$\Sigma(E_i) = \Sigma(\epsilon_i) + (E_i - \epsilon_i)\partial_\omega\Sigma(\omega)|_{\epsilon_i}$$

$$E_i = \epsilon_i + Z_i\langle\varphi_i|\Sigma(\epsilon_i) - V_{xc}|\varphi_i\rangle$$

$$Z_i = (1 - \langle\varphi_i|\partial_\omega\Sigma(\omega)|_{\epsilon_i}|\varphi_i\rangle)^{-1}$$

Hybersten and Louie, PRB **34** (1986);
Godby, Schlüter and Sham, PRB **37** (1988)

G_0W_0: QP results



M. van Schilfgaarde *et al.*, PRL **96** (2006)

G_0W_0 results

Great improvement over LDA.

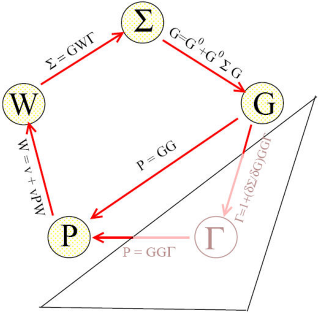
Drawback: dependency on the starting point

G_0W_0 results

- OK for *sp* electron systems
- questionable for *df* electron systems (and whenever LDA is bad)

Beyond G_0W_0: fully self-consistent GW

$$G = G_0 + G_0 \, \Sigma[G] \, G$$



Self-consistent GW

- bad for spectral properties in solids
- OK for atoms, small molecules
- necessary for total energy (conserving approximation)

Beyond G_0W_0: alternative starting points

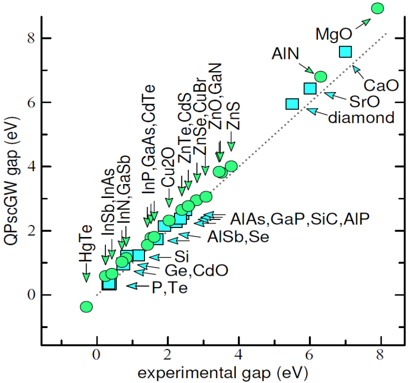
Looking for a better starting point

- Kohn-Sham with other functionals (EXX, LDA+U) - e.g. Rinke 2005, Jiang 2009
- hybrid functionals (HSE06) - e.g. Fuchs 2006
- effective quasiparticle Hamiltonians
  - QPscGW scheme - Faleev 2004
  - Hedin's COHSEX approximation - Bruneval 2005
  - Löwdin procedure - Sakuma 2009

Beyond G_0W_0: QPscGW scheme

Only retain hermitian part of GW Σ and iterate QP:

$$\langle \phi_i|\Sigma|\phi_j\rangle = \frac{1}{2}\mathrm{Re}[\langle \phi_i|\Sigma(E_i)|\phi_j\rangle + \langle \phi_i|\Sigma(E_j)|\phi_j\rangle]$$



S. V. Faleev, M. van Schilfgaarde, and T. Kotani, PRL 93 (2004)

M. van Schilfgaarde *et al.*, PRL 96 (2006)

Beyond G_0W_0: COHSEX approximation

GW self-energy

$\Sigma = \Sigma_1 + \Sigma_2$ (from poles of G or $W_p = W - v$):

$$\Sigma_1(\mathbf{r}_1, \mathbf{r}_2, \omega) = -\sum_i \theta(\mu - E_i)\phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)W(\mathbf{r}_1, \mathbf{r}_2, \omega - E_i)$$

$$\Sigma_2(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2) \int_0^\infty d\omega' \frac{D(\mathbf{r}_1, \mathbf{r}_2, \omega')}{\omega - E_i - \omega'}$$

with

$$D(\mathbf{r}_1, \mathbf{r}_2, \omega) = -\frac{1}{\pi}\mathrm{Im}W_p(\mathbf{r}_1, \mathbf{r}_2, \omega)\mathrm{sgn}(\omega)$$

COHSEX approximation

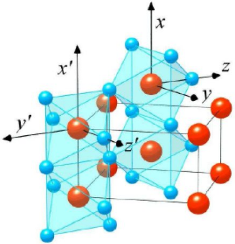
Set $\omega - E_i = 0$:

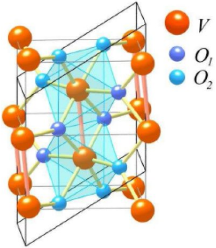
$$\Sigma_{SEX}(\mathbf{r}_1, \mathbf{r}_2) = -\sum_i \theta(\mu - E_i)\phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)W(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)$$

$$\Sigma_{COH}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\delta(\mathbf{r}_1 - \mathbf{r}_2)W_p(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)$$

Beyond G_0W_0: VO_2

VO_2: double phase transition





T_c = 340 K
(Morin '59)

for $T > T_c$

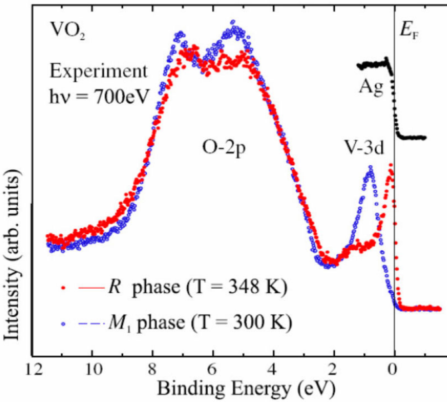
Rutile + Metal

for $T < T_c$

Monoclinic + Insulator

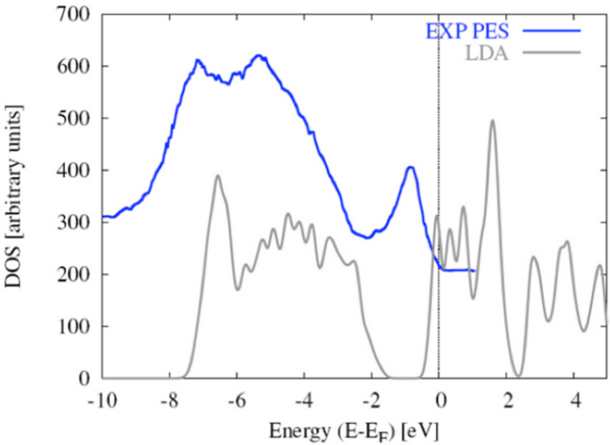
Beyond G_0W_0: VO_2

Photoemission data

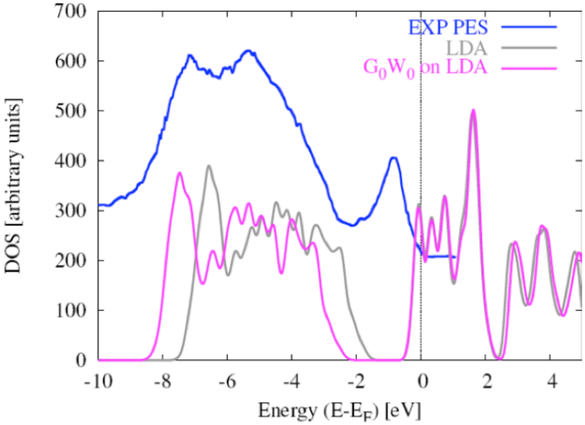


from Koethe *et al.*, PRL **97** (2006)

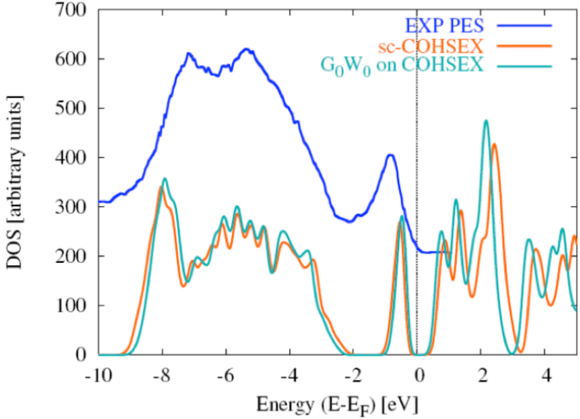
Beyond G_0W_0: insulating VO_2



Beyond G_0W_0: insulating VO_2

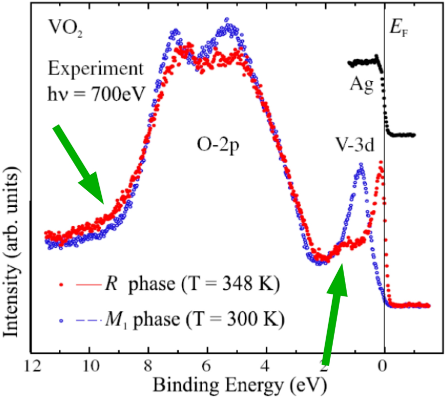


Beyond G_0W_0: insulating VO_2



Beyond QP: VO_2

Photoemission data

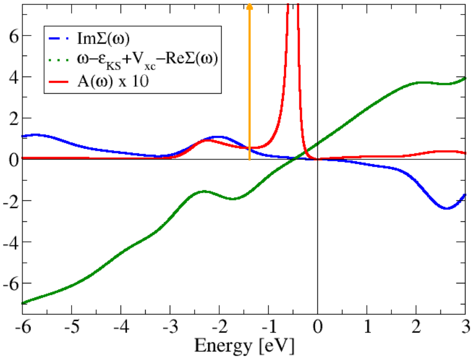


from Koethe *et al.*, PRL **97** (2006)

Beyond QP: spectral function

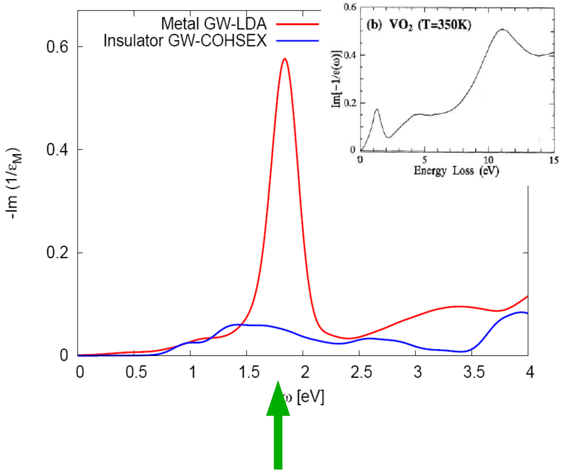
$$A_i(\omega) = \frac{1}{\pi}|\mathrm{Im}G_i(\omega)|$$

Metallic VO_2:
top valence at Γ

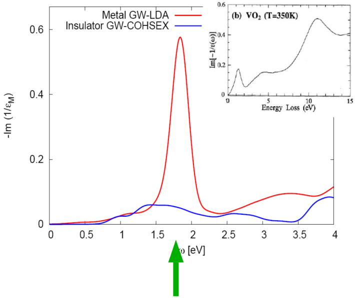


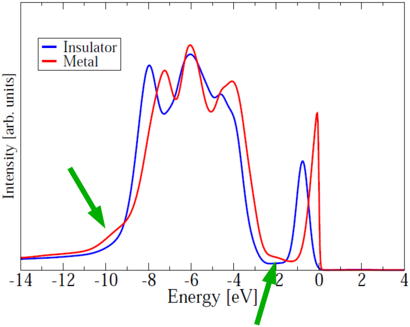
$$A_i(\omega) = \frac{1}{\pi}\frac{|\mathrm{Im}\Sigma_i(\omega)|}{[\omega - \epsilon_i - (\mathrm{Re}\Sigma_i(\omega) - V_i^{xc})]^2 + [\mathrm{Im}\Sigma_i(\omega)]^2}$$

Loss function

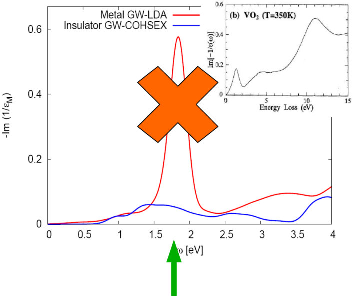


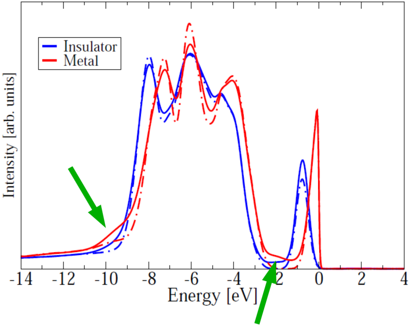
Beyond QP: spectral function





Beyond QP: spectral function





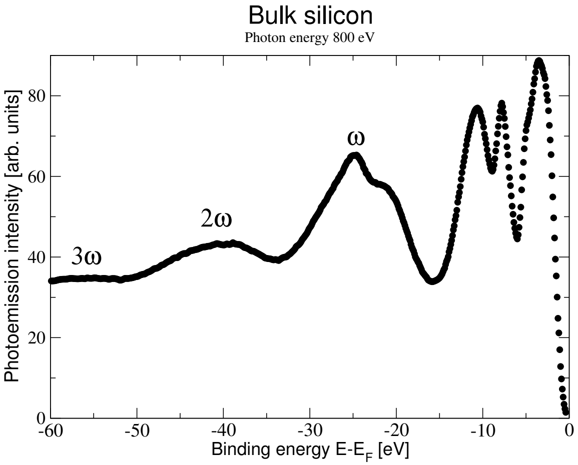
Outline

Beyond GW: vertex corrections

Beyond GW

- multiple plasmon satellites: cumulant expansion
- self-screening
- atomic limit
- additional interactions: T matrix

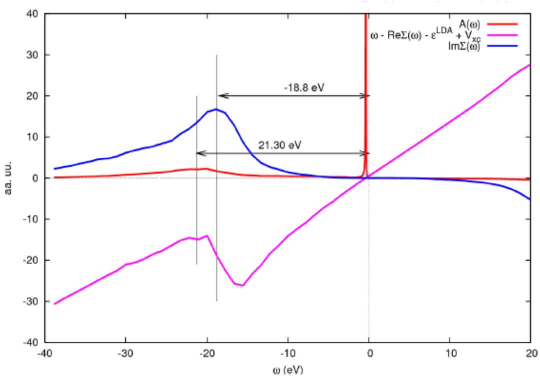
Multiple satellites in silicon: PES



M. Guzzo *et al.*, PRL 107 (2011).

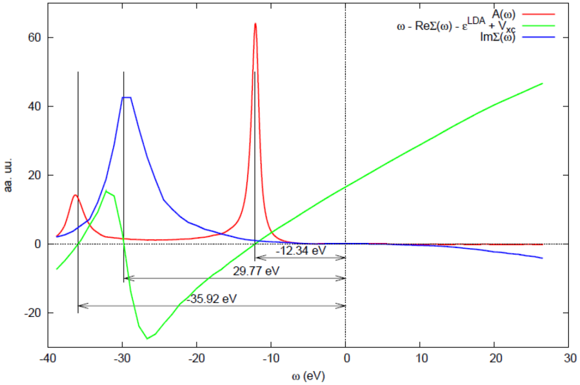
Multiple satellites in silicon: GW

GW spectral function: top valence at Γ
A very weak plasmon satellite



Multiple satellites in silicon: GW

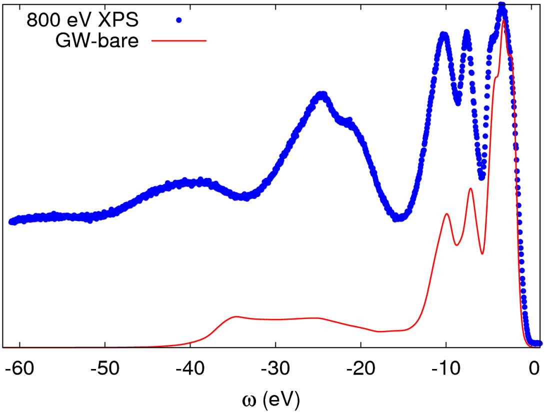
GW spectral function: bottom valence at Γ
A plasmaron satellite



B. I. Lundqvist, Phys. Kondens. Mater. 6 (1967)

Multiple satellites in silicon: GW

GW spectral function



Decoupling approximation: exponential solution

Equation of motion of G :

$$G = \tilde{G}_0 + \tilde{G}_0 V_H G + \tilde{G}_0 U G + i\tilde{G}_0 v \frac{\delta G}{\delta U} \quad \text{with} \quad \tilde{G}_0 = (\omega - h_0)^{-1}$$

1. Linearize: $V_H = V_H^0 + v\chi U + ...$

$$G = G_0 + G_0 \bar{U} G + iG_0 W \frac{\delta G}{\delta \bar{U}} \quad \text{with} \quad \bar{U} = \epsilon^{-1} U, G_0 = (\omega - h_0 - V_H^0)^{-1}$$

Decoupling approximation: exponential solution

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2. Optimize QP such that G and G_{QP} are diagonal in the basis $|k\rangle$:

$$\text{holes:} \quad G_k^{QP}(\tau) = i\theta(-\tau) e^{-i\epsilon_k^{QP}\tau}$$

$$\forall k : G = G^{QP} + G^{QP}(\bar{U} - \Delta^{QP})G + iG^{QP} W \frac{\delta G}{\delta \bar{U}}$$

Decoupling approximation: exponential solution

Equation of motion of G :

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1. Linearize: $V_H = V_H^0 + v\chi U + ...$

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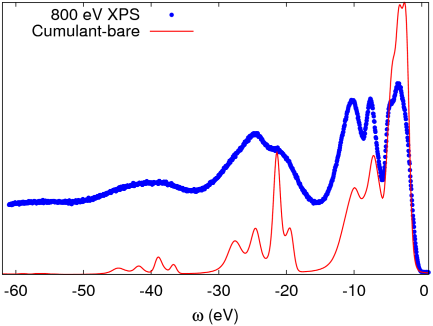
$$\forall k : G = G^{QP} + G^{QP}(\bar{U} - \Delta^{QP})G + iG^{QP} W \frac{\delta G}{\delta \bar{U}}$$

Exact solution:

$$G(t_1, t_2) = G^{QP}(t_1 - t_2)e^{i\Delta^{QP}(t_1 - t_2)} e^{i\int_{t_1}^{t_2} dt' \left[U(t') - \int_{t'}^{t_2} dt'' W(t', t'')\right]}$$

Multiple satellites in silicon: exponential solution

Plasmon-pole approximation to W: $W(\tau) = -i\lambda_k \left[\theta(\tau)e^{-i\tilde{\omega}_k\tau} + \theta(-\tau)e^{i\tilde{\omega}_k\tau}\right]$

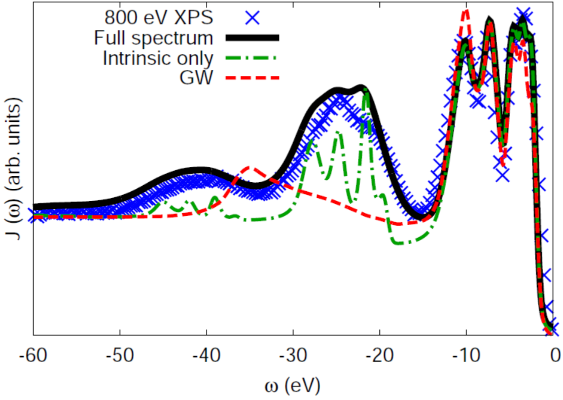


Exponential solution - cumulant expansion

$$A_k(\omega) = \frac{e^{-a_k}}{\pi} \sum_{n=0}^{\infty} \frac{a_k^n}{n!} \frac{\mathrm{Im}\epsilon_k^{QP}}{(\omega - \mathrm{Re}\epsilon_k^{QP} + n\tilde{\omega}_k)^2 + (\mathrm{Im}\epsilon_k^{QP})^2},$$

Multiple satellites in silicon: exponential solution

Plus contributions from:
extrinsic effects, interference effects, cross sections, background



M. Guzzo *et al.*, PRL 107 (2011)

The vertex and the self-energy

$$\Gamma(123) = -\frac{\delta G^{-1}(12)}{\delta V_{tot}(3)} = \delta(13)\delta(12) + \frac{\delta\Sigma(12)}{\delta V_{tot}(3)}$$

Hedin

$$\frac{\delta\Sigma}{\delta V_{tot}} = \frac{\delta\Sigma}{\delta G}\frac{\delta G}{\delta V_{tot}} = -\frac{\delta\Sigma}{\delta G}G\frac{\delta G^{-1}}{\delta V_{tot}}G$$

$$\Gamma(123) = \delta(12)\delta(13) + \frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(673)$$

The vertex and the self-energy

$$\Gamma(123) = -\frac{\delta G^{-1}(12)}{\delta V_{tot}(3)} = \delta(13)\delta(12) + \frac{\delta\Sigma(12)}{\delta V_{tot}(3)}$$

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$$\Gamma(123) = \delta(12)\delta(13) + \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)$$

Using density functional

$$\frac{\delta\Sigma}{\delta V_{tot}} = \frac{\delta\Sigma}{\delta\rho}\frac{\delta\rho}{\delta V_{tot}}$$

$$\Gamma(123) = \delta(12)\delta(13) + \frac{\delta\Sigma(12)}{\delta\rho(4)} P(43)$$

F. Bruneval, F. Sottile, V. Olevano, R. Del Sole, and L. Reining, PRL **94** (2005)

$$\Sigma(12) = iG(14)W(31)\Gamma(423)$$

$$\Gamma(123) = \delta(12)\delta(13) + \frac{\delta\Sigma(12)}{\delta\rho(4)}P(43)$$

The self-energy

Self-energy = exchange + induced Hartree + induced exchange-correlation

$$\Sigma(12) = iG(12)v(12) + iG(12)W_p(12) + iG(14)\frac{\delta\Sigma(42)}{\delta\rho(5)}\chi(53)v(31)$$

$$W_p(12) = W(12) - v(12) = v(13)\chi(34)v(42)$$

Beyond GW

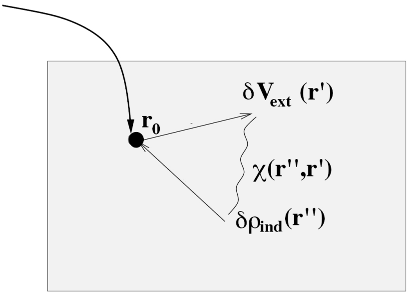
Screened potential

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

$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}}$$

$$\delta V_{tot} = \delta V_{ext} + \delta V_{ind}$$

$$\delta \rho_{ind} = \chi \delta V_{ext}$$



Beyond GW

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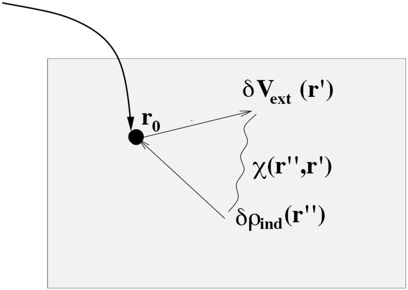


GW (RPA)

$$\chi = \frac{1}{1 - v\chi_0}\chi_0$$

test-charge $\delta V_{ind} = v \delta \rho_{ind}$

Beyond GW

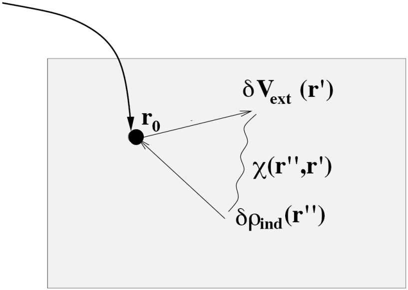
Screened potential

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

$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}}$$

$$\delta V_{tot} = \delta V_{ext} + \delta V_{ind}$$

$$\delta \rho_{ind} = \chi \delta V_{ext}$$



Beyond GW: better test-charge

$$\chi = \frac{1}{1 - (v + f_{xc})\chi_0} \chi_0$$

test-charge $\delta V_{ind} = v \delta \rho_{ind}$

Beyond GW

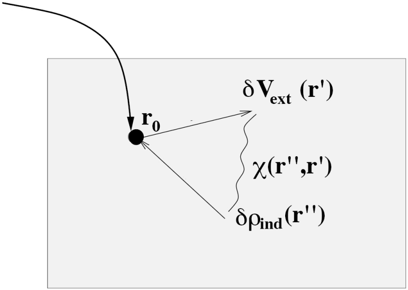
Screened potential

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

$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}}$$

$$\delta V_{tot} = \delta V_{ext} + \delta V_{ind}$$

$$\delta \rho_{ind} = \chi \delta V_{ext}$$



Beyond GW: test-electron

$$\chi = \frac{1}{1 - (v + f_{xc})\chi_0}\chi_0$$

test-electron $\qquad \delta V_{ind} = v \delta \rho_{ind} + f_{xc} \delta \rho_{ind}$

Self-screening

Particle in a box: add or remove

$$(-\nabla^2/2 + V_{box})\phi = \varepsilon\phi$$

$$\varepsilon = -(E_{N=0} - E_{N=1}) = E_{N=1} - E_{N=0}$$

Self-screening

Particle in a box: add or remove

$(-\nabla^2/2 + V_{box})\phi = \varepsilon\phi$

$\varepsilon = -(E_{N=0} - E_{N=1}) = E_{N=1} - E_{N=0}$

- Kohn-Sham

  $(-\nabla^2/2 + V_{box} + \rho v - \rho v)\phi = \varepsilon\phi$

Self-screening

Particle in a box: add or remove

$$(-\nabla^2/2 + V_{box})\phi = \varepsilon\phi$$

$$\varepsilon = -(E_{N=0} - E_{N=1}) = E_{N=1} - E_{N=0}$$

- Kohn-Sham

  $$(-\nabla^2/2 + V_{box} + \rho v - \rho v)\phi = \varepsilon\phi$$

- Hartree-Fock

  $$(-\nabla^2/2 + V_{box} + \rho v)\phi - \phi^*\phi v\phi = \varepsilon\phi$$

Self-screening

Particle in a box: add or remove

$$(-\nabla^2/2 + V_{box})\phi = \varepsilon\phi$$

$$\varepsilon = -(E_{N=0} - E_{N=1}) = E_{N=1} - E_{N=0}$$

- Kohn-Sham

  $$(-\nabla^2/2 + V_{box} + \rho v - \rho v)\phi = \varepsilon\phi$$

- Hartree-Fock

  $$(-\nabla^2/2 + V_{box} + \rho v)\phi - \phi^*\phi v\phi = \varepsilon\phi$$

- GW

  $$(-\nabla^2/2 + V_{box} + \rho v)\phi - \phi^*\phi v\phi + \Sigma_c\phi = \varepsilon\phi$$

  $W = v + W_p = v + v\chi^{RPA}v$ $\quad$ W_p should be zero!

Self-screening

Corrections to GW

- W test-charge
  use exact χ instead of $\chi^{RPA} \Rightarrow \chi = \chi_0$
  $\Rightarrow W_p = v\chi_0 v \neq 0$

Self-screening

Corrections to GW

- W test-charge
  use exact χ instead of $\chi^{RPA} \Rightarrow \chi = \chi_0$
  $\Rightarrow W_p = v\chi_0 v \neq 0$
- W test-electron
  local vertex: $W_p = (v + f_{xc})\chi_0 v = 0 \qquad (f_{xc} = -v)$

W. Nelson, P. Bokes, P. Rinke, and R. W. Godby, Phys. Rev. A 75 (2007)
P. Romaniello, S. Guyot, and L. Reining, JCP 131 (2009)
F. Aryasetiawan, R. Sakuma, and K. Karlsson, arXiv:1110.6765

Beyond GW: GWΓ

TDLDA f_{xc}

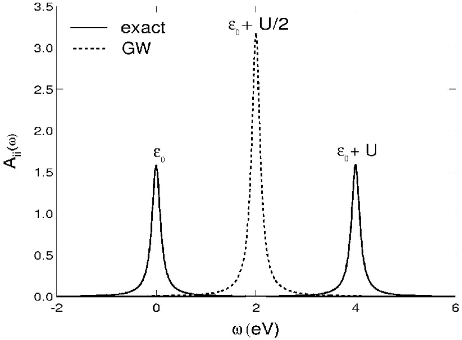
Quasiparticle corrections in bulk silicon

	GW RPA	GW K_{xc}	$GW\Gamma$
Direct gap at Γ	0.64	0.56	0.65
Direct gap at X	0.78	0.57	0.73
Direct gap at L	0.68	0.58	0.72
Valence bandwidth	-0.56	-1.01	-0.48
Minimum gap	0.63	0.59	0.66
Valence band maximum	-0.36	-0.44	0.01
Conduction band minimum	0.27	0.14	0.67

R. Del Sole, L. Reining, R. W. Godby, PRB **49** (1994).

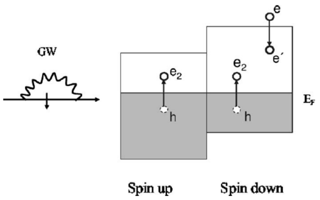
Atomic limit

One electron in two-site Hubbard model



P. Romaniello, S. Guyot, and L. Reining, JCP 131 (2009)

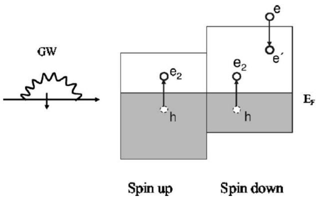
GW and T matrix



GW

- Add one primary electron e, spin $\downarrow$
- Disexcitation $(e, \downarrow) \rightarrow (e', \downarrow)$
- Creation of electron-hole pairs e_2-h in both spin channels.

GW and T matrix



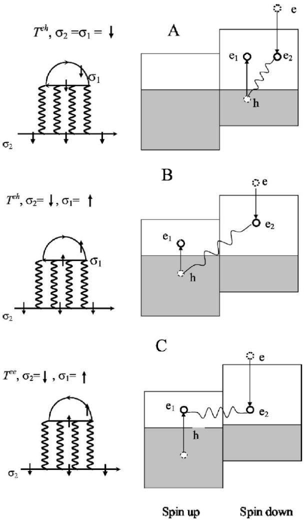
GW

- Add one primary electron e, spin $\downarrow$
- Disexcitation $(e,\downarrow) \rightarrow (e',\downarrow)$
- Creation of electron-hole pairs e_2-h in both spin channels.

Note

- primary electron: final spin = initial spin (no spin flips)
- no interaction between primary electron and secondary particles
- analogously for additional hole

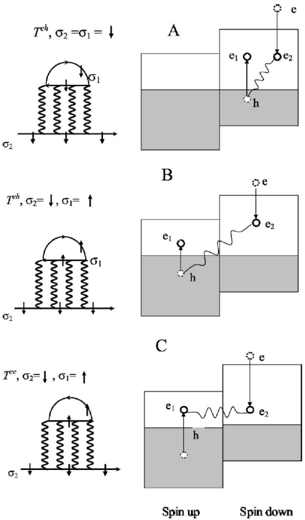
GW and T matrix



T matrix

- Add one primary electron e, spin $\downarrow$
- Disexcitation $(e, \downarrow) \rightarrow (e_2, \downarrow)$
- Creation of electron-hole pairs e_1-h in both spin channels
- Interaction between primary electron and hole of electron-hole pair (A,B)
- Interaction between primary electron and electron of electron-hole pair (C)

GW and T matrix



T matrix

- Add one primary electron e, spin $\downarrow$
- Disexcitation $(e, \downarrow) \rightarrow (e_2, \downarrow)$
- Creation of electron-hole pairs e_1-h in both spin channels
- Interaction between primary electron and hole of electron-hole pair (A,B)
- Interaction between primary electron and electron of electron-hole pair (C)

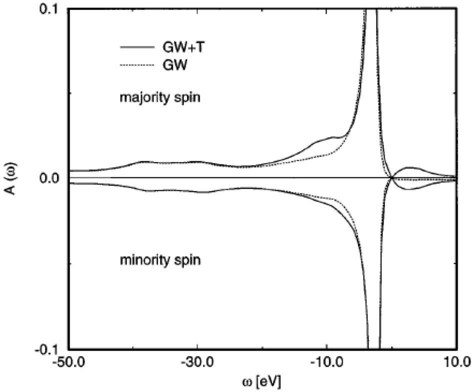
Note

- (B) spin flips: coupling with spin-waves, magnons, paramagnons
- analogously for additional hole

V. P. Zhukov, E. V. Chulkov, and P. M. Echenique, PRB 72 (2005)

T matrix

T matrix: hole-hole interaction
6 eV satellite in Nickel



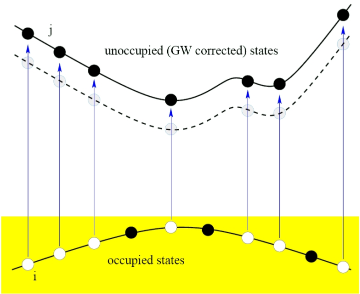
M. Springer, F. Aryasetiawan, and K. Karlsson, PRL 80 (1998)

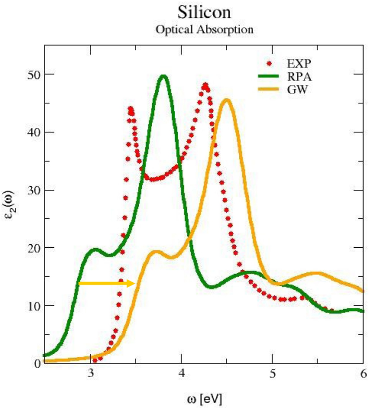
Outline

Independent (quasi)particles: GW

Independent transitions:

$$\epsilon_2(\omega) = \frac{8\pi^2}{\Omega\omega^2} \sum_{ij} |\langle \varphi_j | \mathbf{e}\cdot\mathbf{v} | \varphi_i \rangle|^2 \delta(E_j - E_i - \omega)$$





What is wrong?

What is missing?

What is wrong?

What is missing?

We need the BSE...

What is wrong?

What is missing?

We need the BSE... and Ilya.

MBPT & TDDFT

MBPT helps improving DFT & TDDFT

DFT & TDDFT help improving MBPT

Conclusion

(TD)DFT & MBPT...

try to learn both!

Many thanks!

Acknowledgements

- Fabien Bruneval
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