Introduction to GW

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Outline

1. GW approximation
2. GW approximation in practice

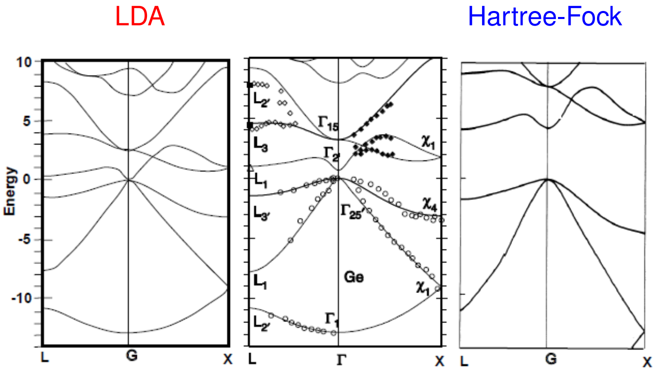
References

- L. Hedin
  Phys. Rev. **139**, A796 (1965).
- L. Hedin and S. Lundqvist
  Solid State Physics **23** (Academic, New York, 1969).
- G. Strinati
  Rivista del Nuovo Cimento **11**, (12)1 (1988).
- G. Onida, L. Reining, and A. Rubio
  Rev. Mod. Phys. **74**, 601 (2002).
- F. Bruneval
  PhD thesis, Ecole Polytechnique (2005)
  `https://etsf.polytechnique.fr/thesis`
- F. Bruneval and M. Gatti
  Topics in Current Chemistry **347**, 99 (2014).
- L. Reining
  WIREs Computational Molecular Science **8** (2017).

Outline

1. GW approximation
2. GW approximation in practice

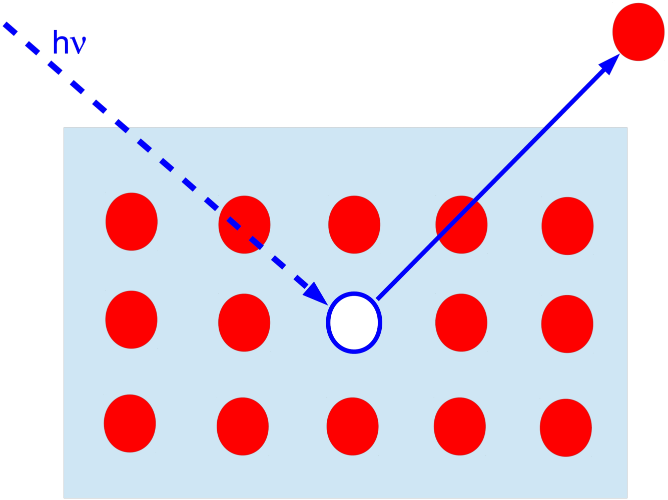
Why more than Hartree-Fock?



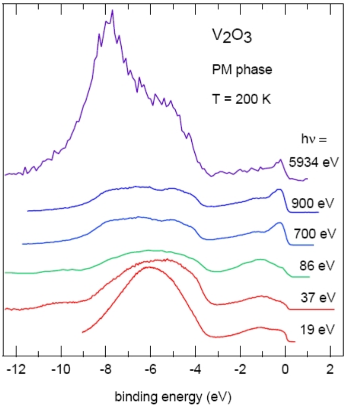
Germanium band structure

Exp. from PRB **32** (1985); PRB **47** (1993);
Hartree-Fock from PRB **35** (1987); GW from PRB **48** (1993)

Photoemission



Photoemission: beware the reality

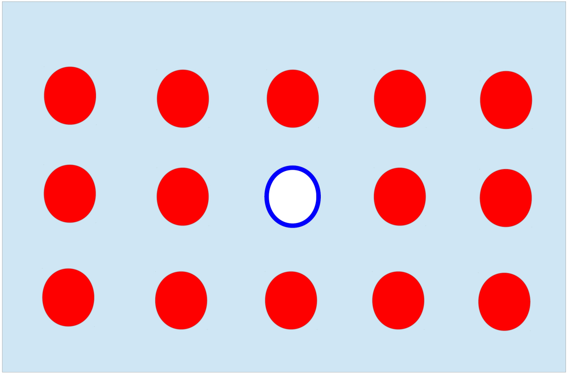


E. Papalazarou *et al.*, PRB 80 (2009)

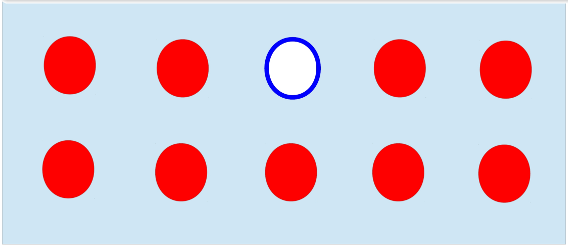
Not discussed in the following:

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

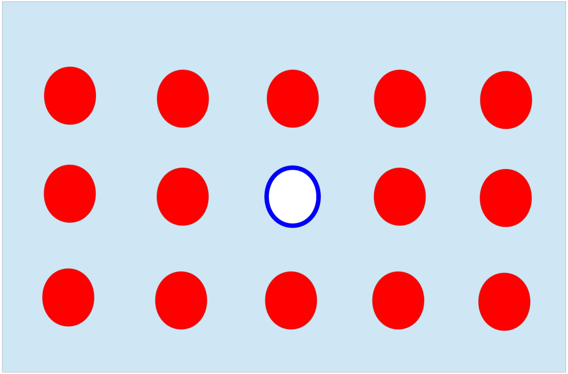
S. Hüfner, *Photoelectron spectroscopy* (1995)



What happens?



Non-interacting particles



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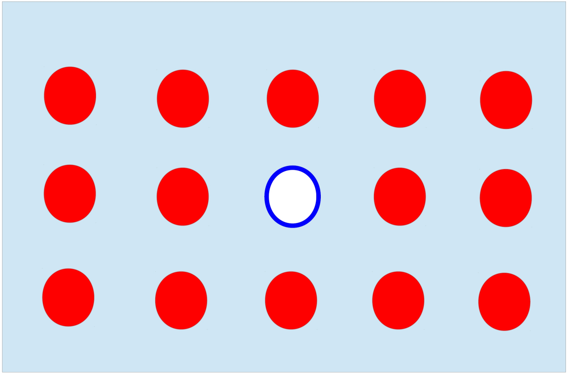
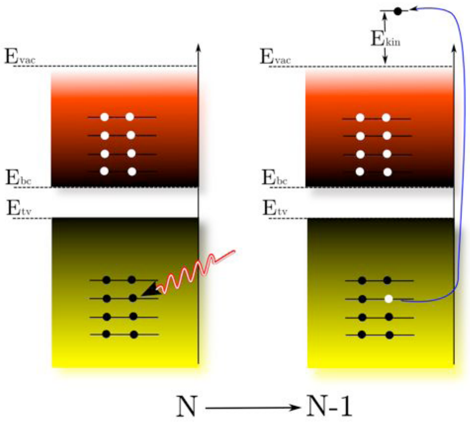
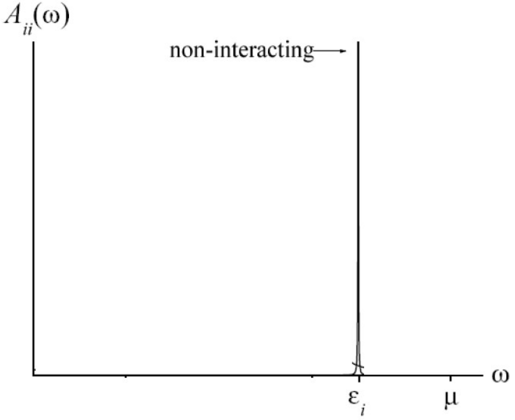


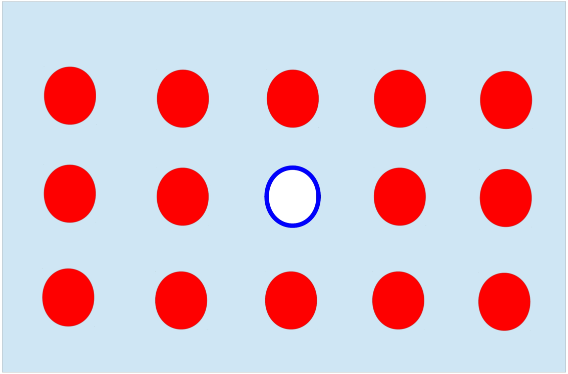


E_kin
E_vac
E_bc
E_tv
E_vac
E_bc
E_tv
N
N-1

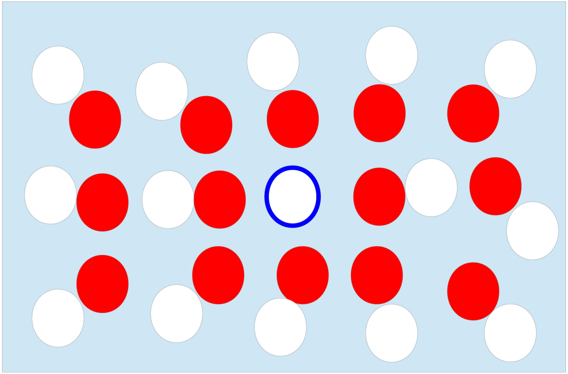


$A_{ii}(\omega)$
non-interacting
ω
ε_i
μ

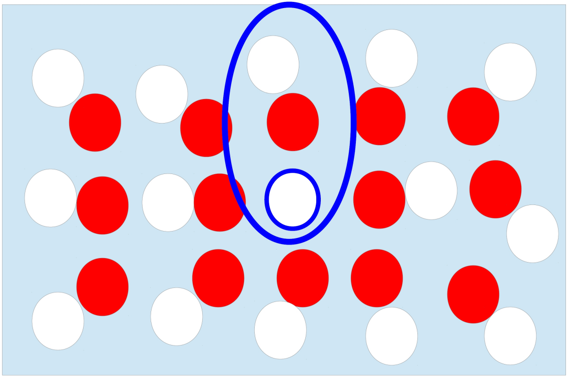
Interacting particles



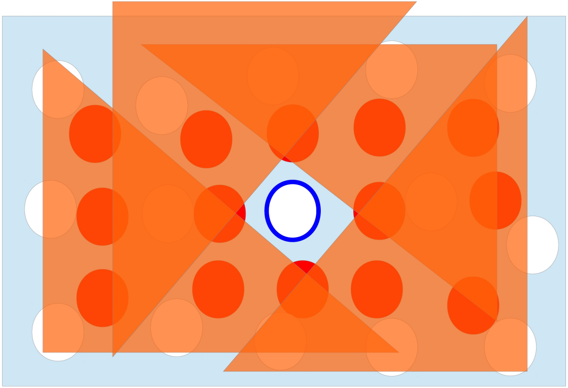
Interacting particles



Interacting particles



Interacting particles

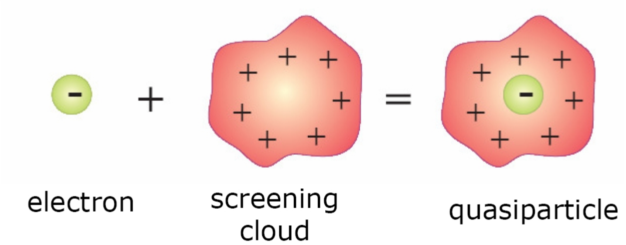


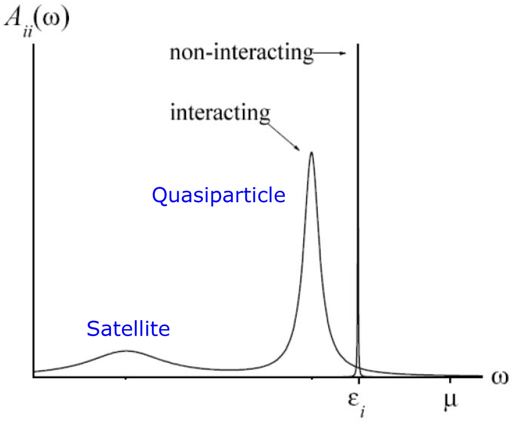
Interacting particles

Screening

$$W(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int d\mathbf{r}_3 \epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3, \omega) v(\mathbf{r}_3, \mathbf{r}_2)$$

Quasiparticle





$A_{ii}(\omega)$
non-interacting
interacting
Quasiparticle
Satellite
ω
ε_i
μ

GW approximation: summary

Screening

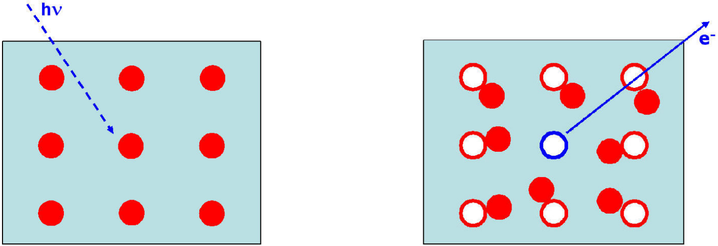
$$W = \epsilon^{-1} v$$

Equivalently (remember: $\epsilon^{-1} = 1 + v\chi$):

$$W = v + v\chi v$$

- W = bare Coloumb interaction v + interaction with polarization charge
- χ is calculated in RPA

GW approximation



additional charge $\rightarrow$ reaction: polarization, screening

GW approximation

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

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

Outline

1. GW approximation

2. GW approximation in practice

Hartree Fock: self-consistent vs. perturbative solution

Kohn-Sham vs. Hartree-Fock

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right] \varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(r) = \epsilon_i \varphi_i(\mathbf{r})$$

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' \; \Sigma_x(\mathbf{r}, \mathbf{r}') \; \phi_i(\mathbf{r}') = E_i \, \phi_i(\mathbf{r})$$

with: $\Sigma_x(\mathbf{r}, \mathbf{r}') = -\dfrac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = -\dfrac{\sum_i^{occ} \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$

Hartree Fock: self-consistent vs. perturbative solution

Kohn-Sham vs. Hartree-Fock

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right] \varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(r) = \epsilon_i \varphi_i(\mathbf{r})$$

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First-order perturbation theory

Hypothesis: $\phi_i(\mathbf{r}) \simeq \varphi_i(\mathbf{r})$

Hartree Fock: self-consistent vs. perturbative solution

Kohn-Sham vs. Hartree-Fock

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right] \varphi_i(\mathbf{r}) + V_{xc}(\mathbf{r})\varphi_i(r) = \epsilon_i \varphi_i(\mathbf{r})$$

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' \; \Sigma_x(\mathbf{r},\mathbf{r}') \; \phi_i(\mathbf{r}') = E_i \, \phi_i(\mathbf{r})$$

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$$\Sigma_x(\mathbf{r},\mathbf{r}') = -\frac{\gamma(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \simeq -\frac{\sum_i^{occ} \varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

First-order perturbative correction:

$$E_i \simeq \epsilon_i + \langle \varphi_i | \Sigma_x - V_{xc} | \varphi_i \rangle$$

Hartree Fock vs. GW: self-energy

Hartree-Fock

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

$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_i \frac{\phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)}{\omega - E_i}$$

$$\Sigma_x(\mathbf{r}_1, \mathbf{r}_2) = \frac{i}{2\pi}\int d\omega' e^{i\eta\omega'} G(\mathbf{r}_1, \mathbf{r}_2, \omega')v(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\gamma(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Σ_x is nonlocal, hermitian, static

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Σ_x is nonlocal, hermitian, static

GW

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

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

Σ is nonlocal, complex, dynamical (frequency dependent)

G ???

Hartree Fock vs. GW: Dyson equation

Hartree-Fock

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

GW

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

with $H_0(\mathbf{r}) = -\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})$

G_0W_0: Quasiparticle corrections

Standard perturbative G_0W_0

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

G_0W_0: Quasiparticle corrections

Standard perturbative G_0W_0

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

G_0W_0: Quasiparticle corrections

Standard perturbative G_0W_0

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

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G_0W_0: Quasiparticle corrections

Standard perturbative G_0W_0

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

Hypothesis: $\phi_i(\mathbf{r}) \simeq \varphi_i(\mathbf{r})$

First-order perturbative corrections with $\Sigma = iG_0W_0$:

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

G_0W_0: Quasiparticle corrections

Standard perturbative G_0W_0

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

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First-order perturbative corrections with $\Sigma = iG_0W_0$:

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

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

Quasiparticle energies

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

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

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