Green's function theory for solid state electronic band structure

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Outline

- Introduction: what is Green's functions for?
- Green's function for single-electron Schrödinger Equations
- Green's function for many-body systems: general formalism
- G*W* approximation and implementation
- Applications of the *GW* approach: examples

Further Readings

The GW approach

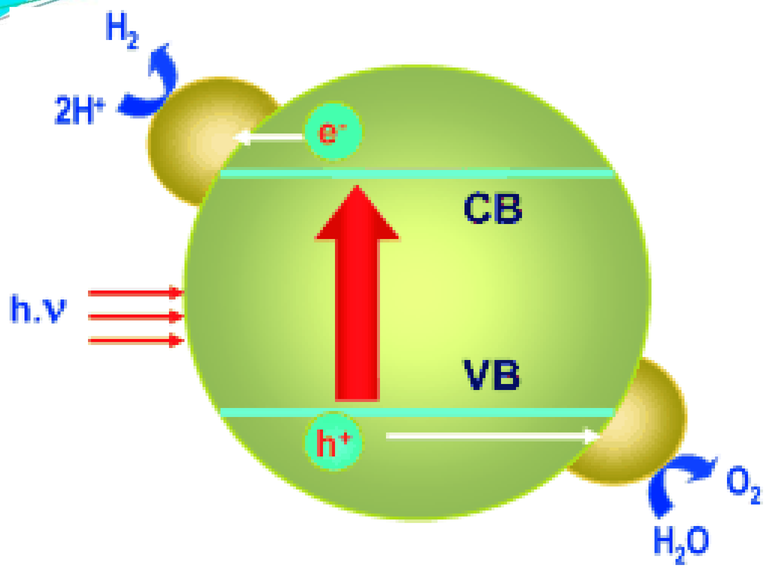
- G. Onida, L. Reining and A. Rubio, *Rev. Mod. Phys*. **74**, 601 (2002).
- W. G . Aulbur, L. Jonsson, J. Wilken, *Solid State Phys*., **54**, 1 (2000).
- F. Aryasetiawan and O. Gunnarsson, *Rep. Prog. Phys*. **61**, 237 (1998)
- L. Hedin and S. Lundqvist, *Solid State Phys*. **23**, 1-181 (1970).

Many-body theory in general

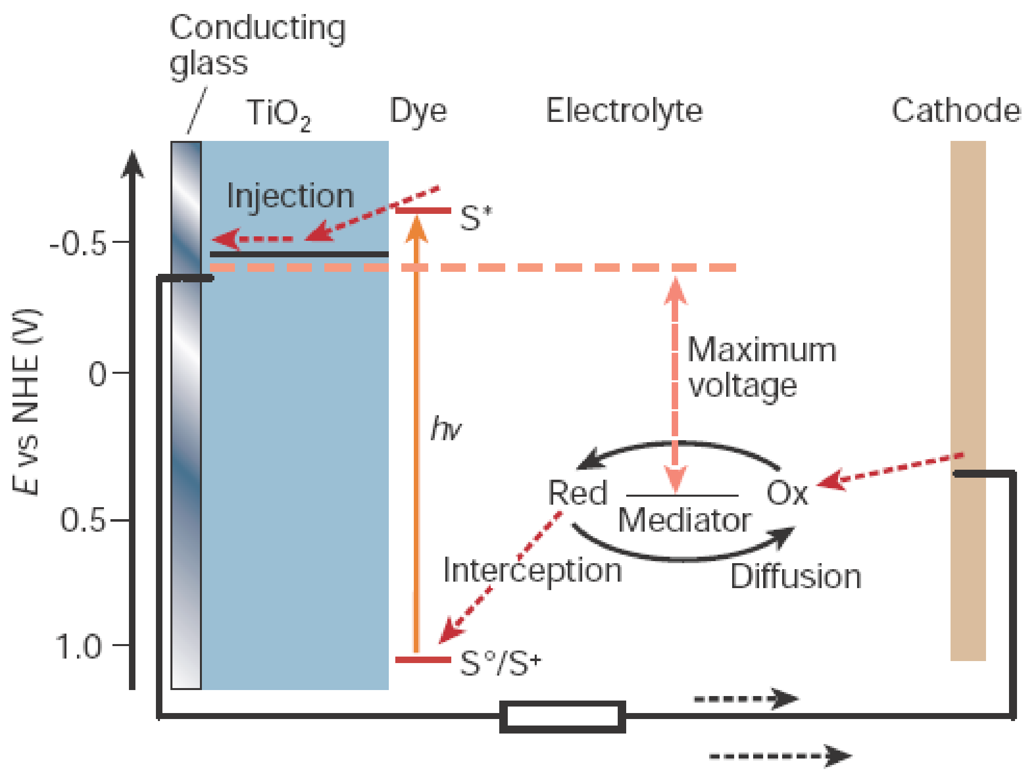
- J. C. Inkson, *Many-Body Theory of Solids: An Introduction* (Plenum Press, 1984).
- A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover, 2003).
- E. K. U. Gross, E. Runge, O. Heinonen, *Many-Particle Theory*, (IOP Publishing, 1991).
- R. D. Mattuck, *A guide to Feynman diagrams in the many-body problem*, (McGrow Hill, 1976).
- E. N. Economou, *Green's functions in Quantum Physics* (3rd ed., Springer, 2006).

Introduction: What are Green’s functions for?

Why are electronic band structure important?

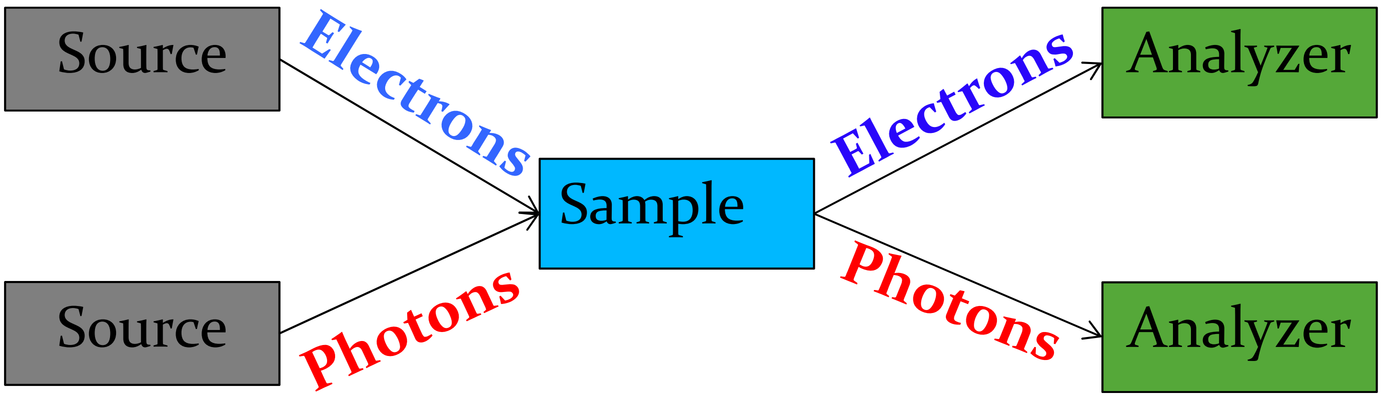


R. M. Navarro Yerga et al. (2009)



Graetzel, Nature (2001)

Electron excitations: experimental measurements



photon → 0: absorption, reflection

photon → photon : Raman scattering, Compton scattering, XES

photon → electron : PES (XPS, UPS)

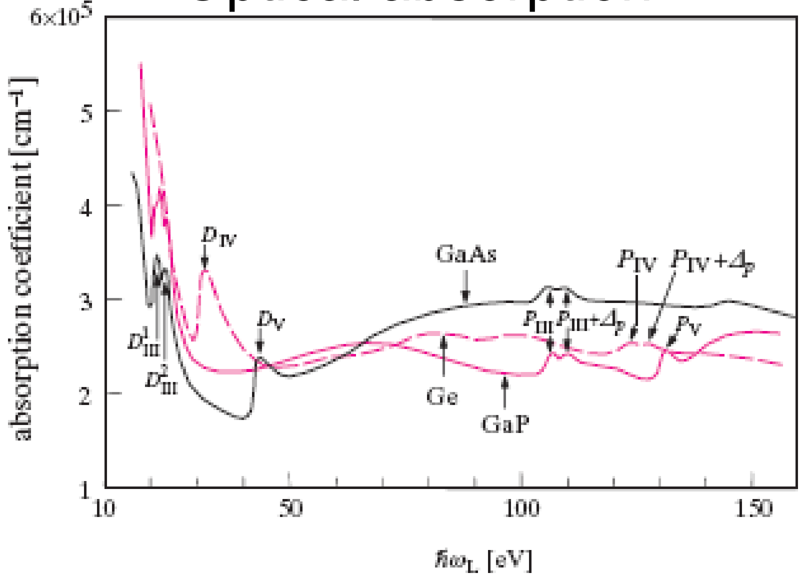
electron → electron: electron energy loss spectroscopy

electron → photon: inverse PES (BIS)

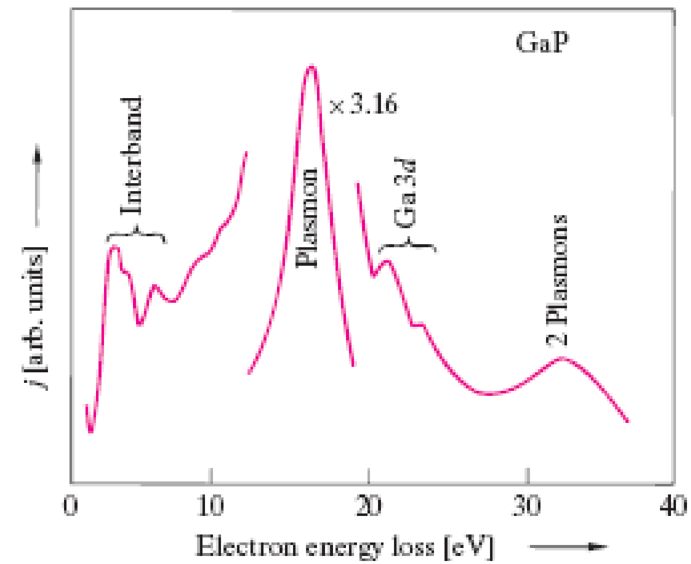
[Yu&Cardona] Yu and Cardona, Fundamentals of Semiconductors(3rd), Springer (2003)

Electron excitations: examples

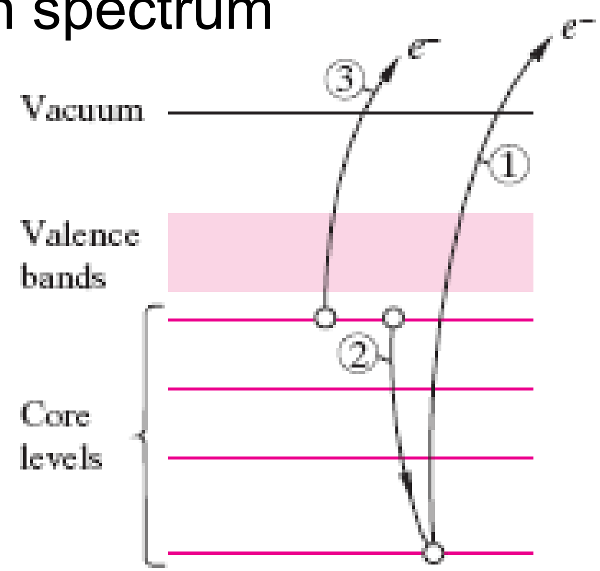
Optical absorption



Electron energy loss spectrum

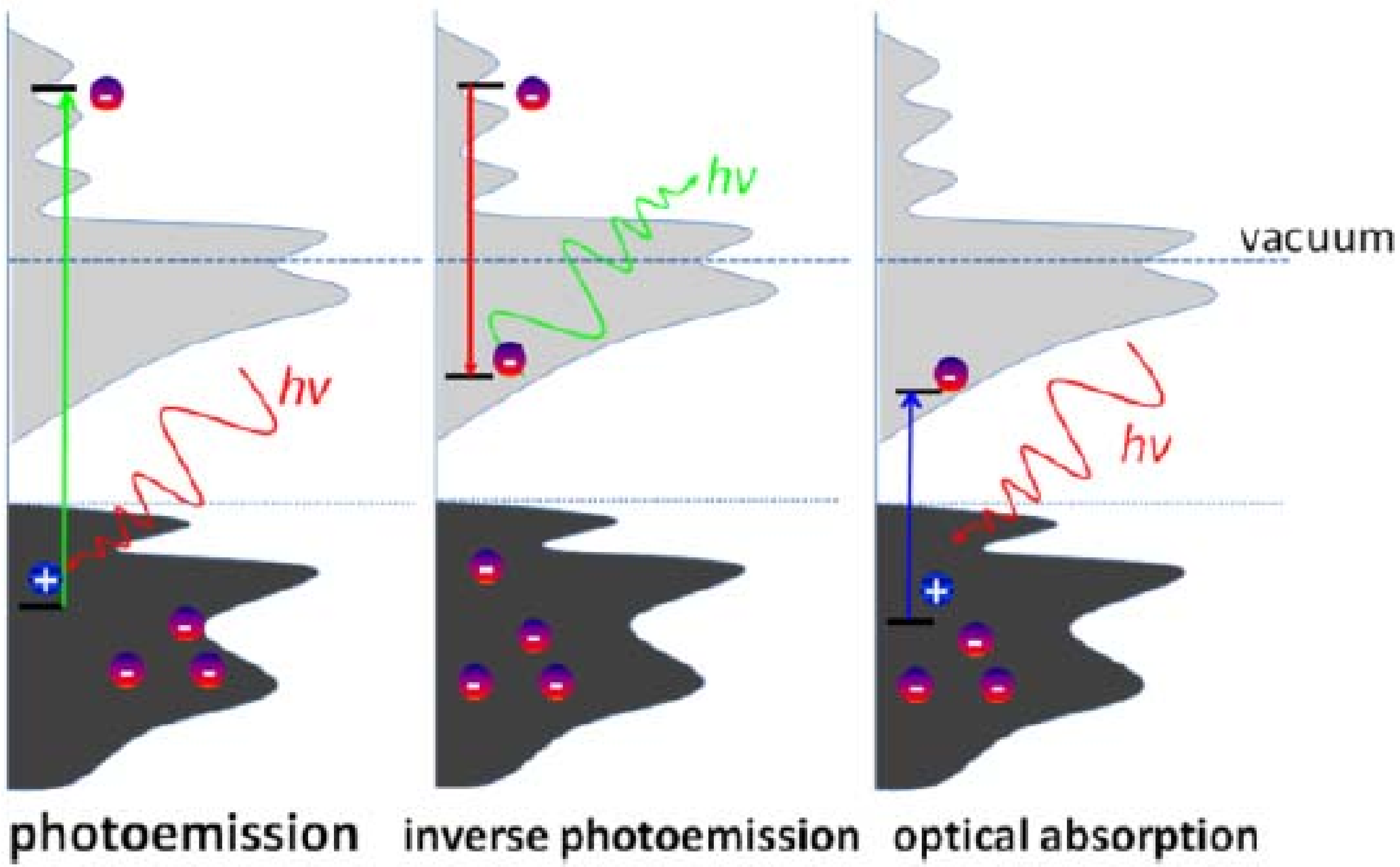


Auger electron spectrum



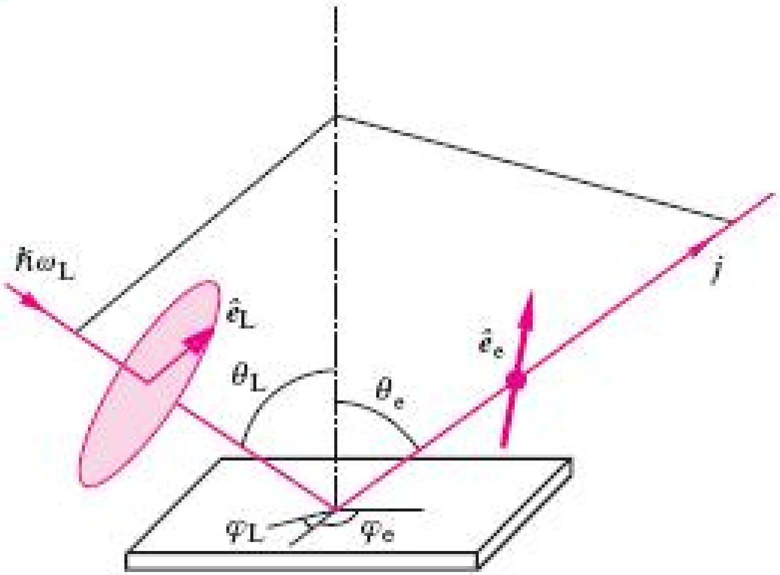
[Yu&Cardona]

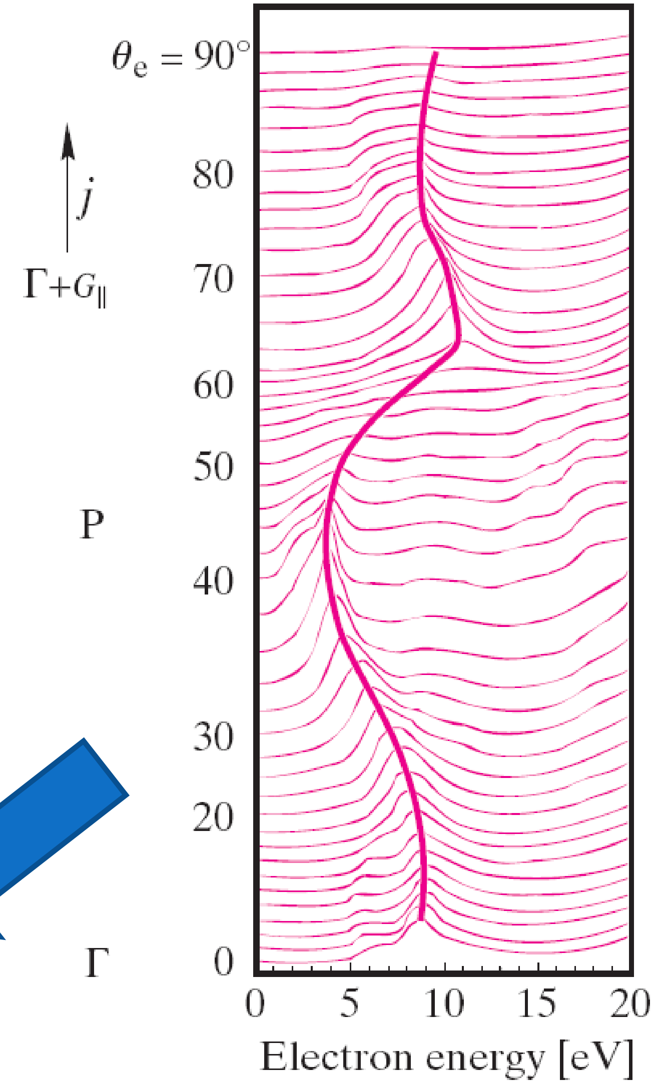
Photoelectron spectroscopy and optical absorption

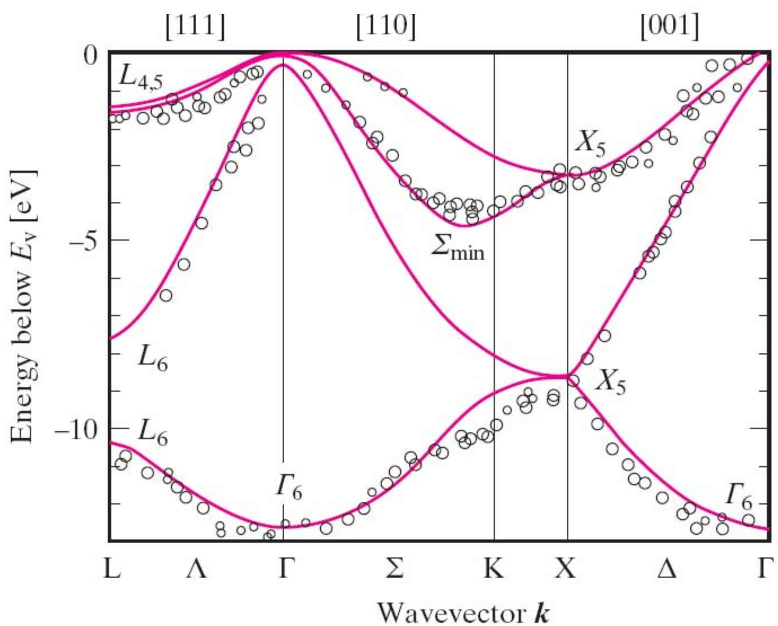


[Jiang12]

Electronic band structure of semiconductors

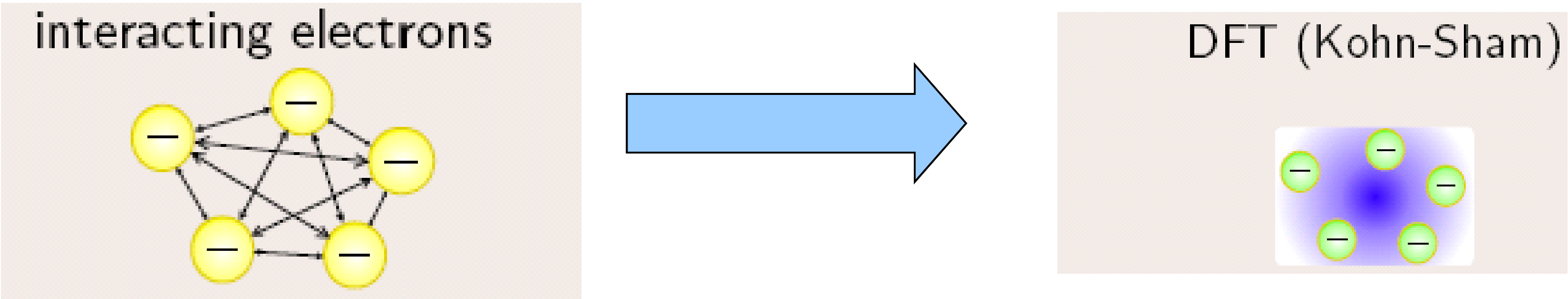




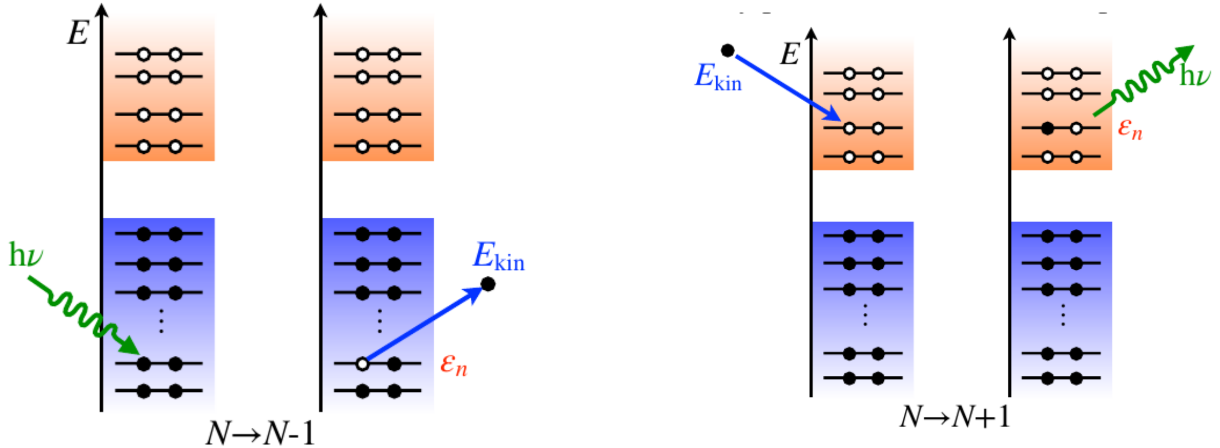


[YuBook]

Mean field approaches



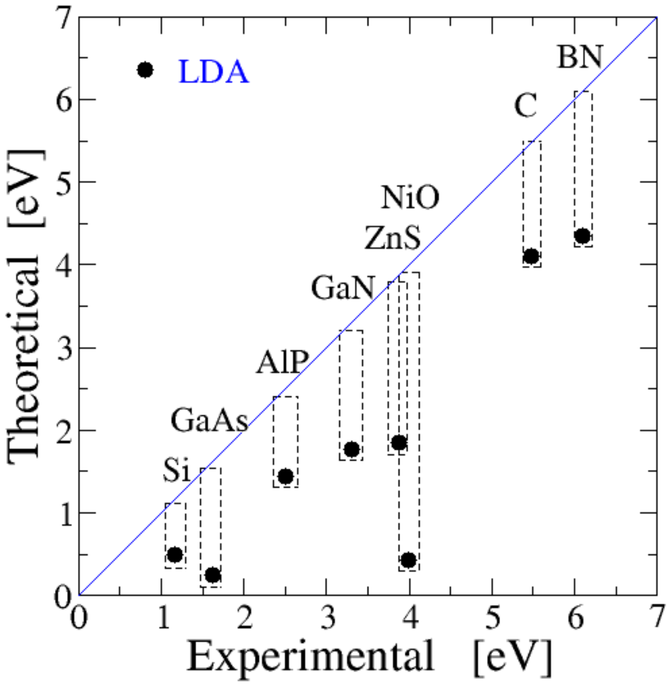
$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

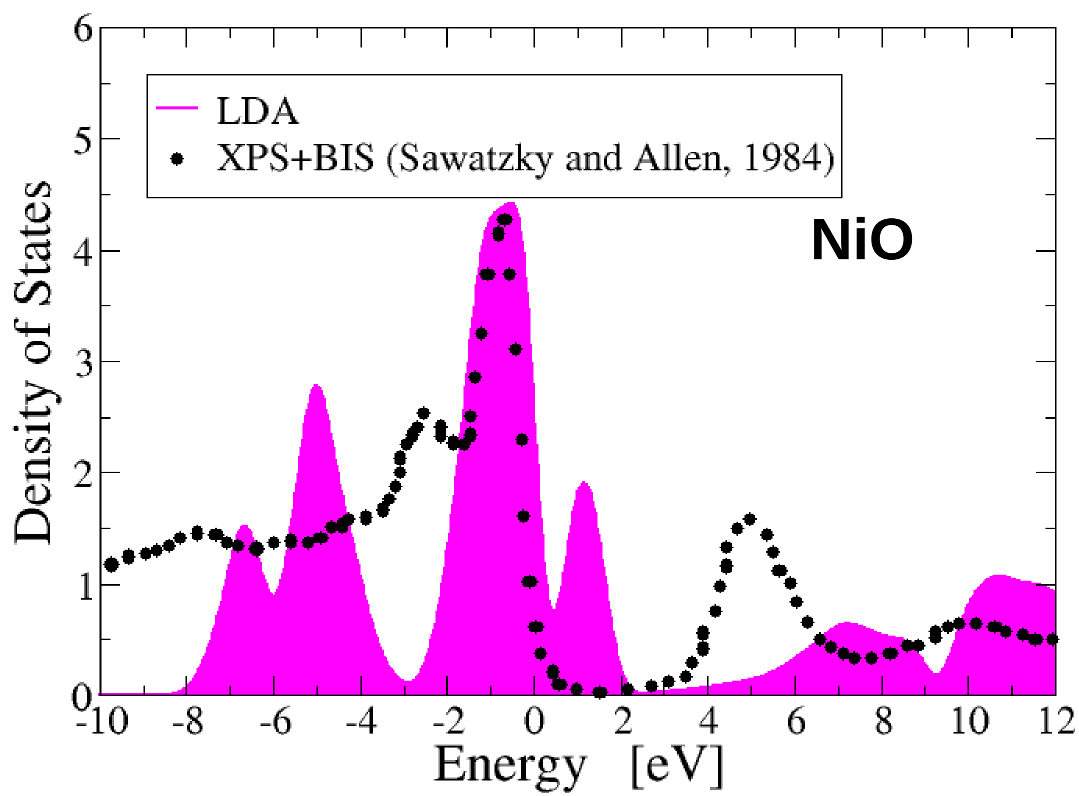


(Illustrations from G.-M. Rignanese's talk)

Remark: Kohn-Sham DFT is a many-body theory for the ground state total energy , but a mean-field approximation for single-electron excitation spectrum.

The band gap problem

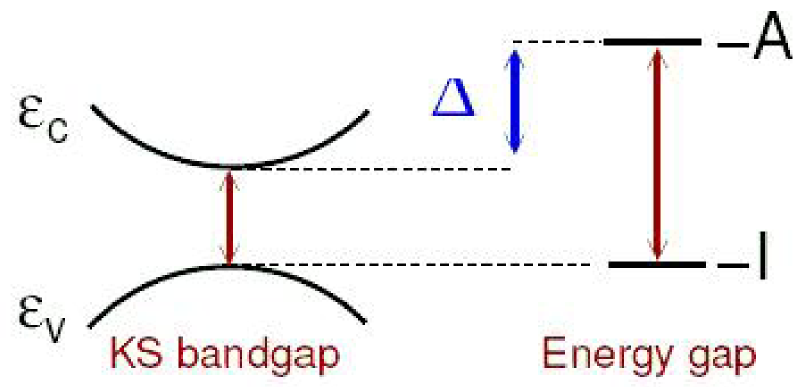




The origin of the DFT band gap problem

$$\left[-\frac{\nabla^2}{2}+V_{\text{ext}}(\mathbf{r})+V_{\text{H}}(\mathbf{r})+V_{\text{xc}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r})=\epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

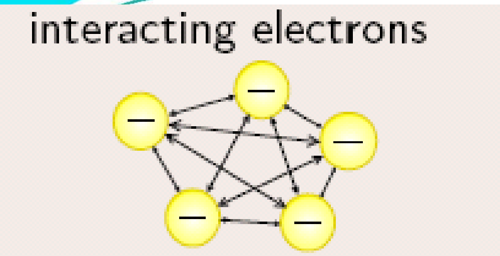
$$\begin{aligned}E_{\text{gap}} &= I - A\\ &\equiv [E(N-1)-E(N)]-[E(N)-E(N+1)]\\ &= [-\epsilon_N(N)]-[-\epsilon_{N+1}(N+1)]\\ &= [\epsilon_{N+1}(N)-\epsilon_N(N)]+[\epsilon_{N+1}(N+1)-\epsilon_{N+1}(N)]\\ &= \epsilon_{\text{gap}}^{\text{KS}}+\Delta_{\text{xc}}\end{aligned}$$

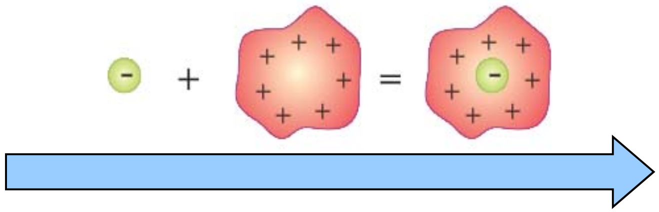


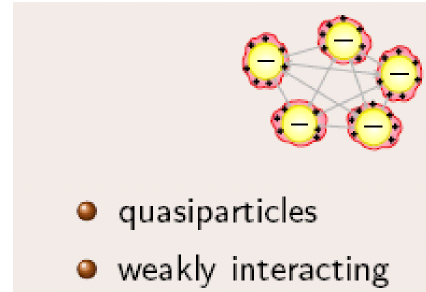
- **KS HOMO-LUMO Gap ≠ E_{gap} even with exact E_{xc}**
- But for all explicit density functionals, e.g. LDA/GGA, $\Delta_{\text{xc}}=0$

Perdew & Levy (1983); Sham & Schlueter (1983); Godby & Sham (1988)

Quasi-particle theory

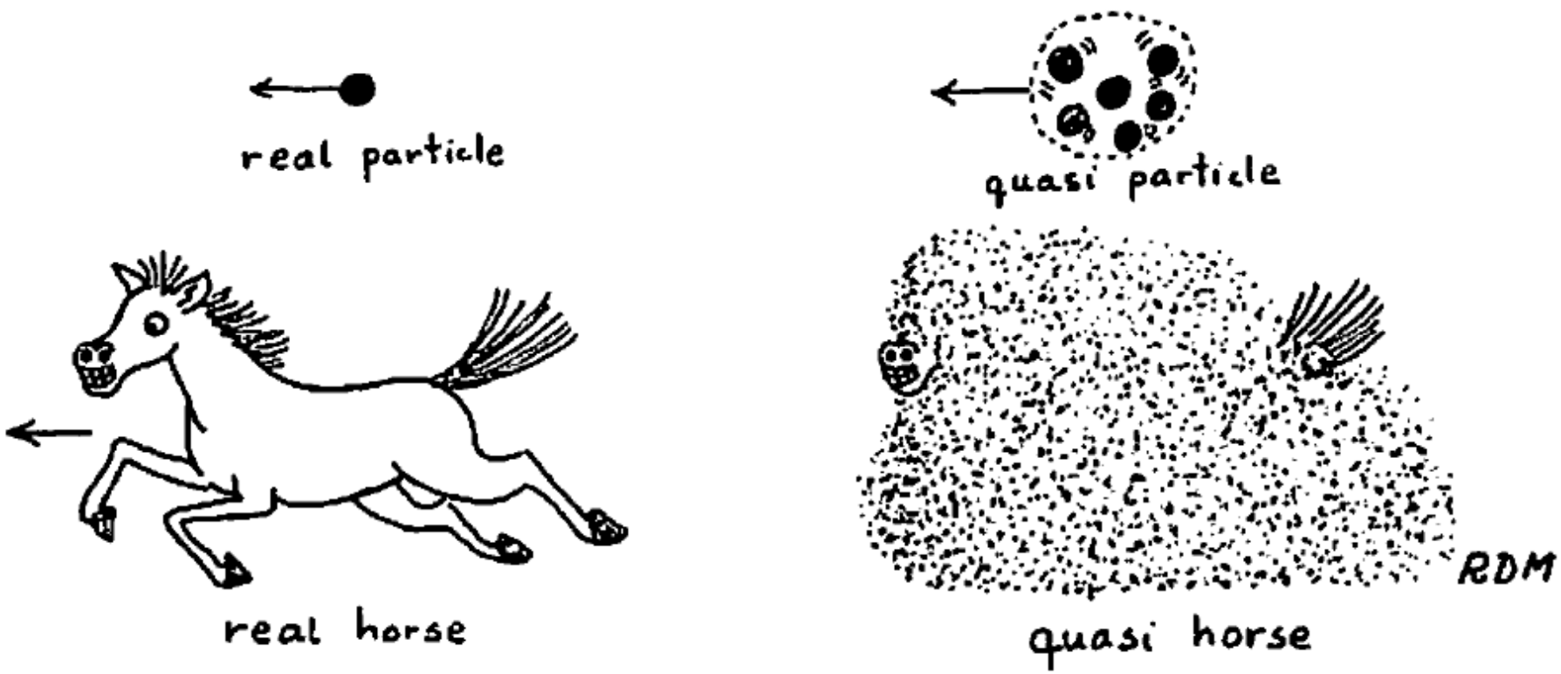






(courtesy of Dr. R. I. Gomez-Abal）

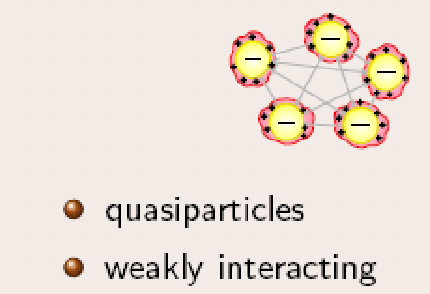
Concept of quasi-particles



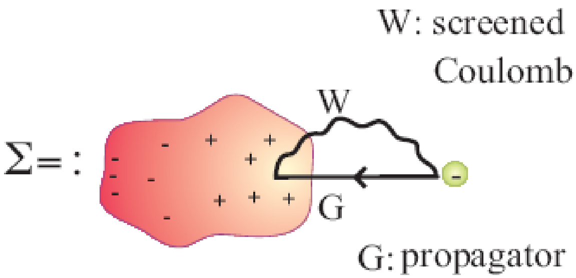
[Mattuck]

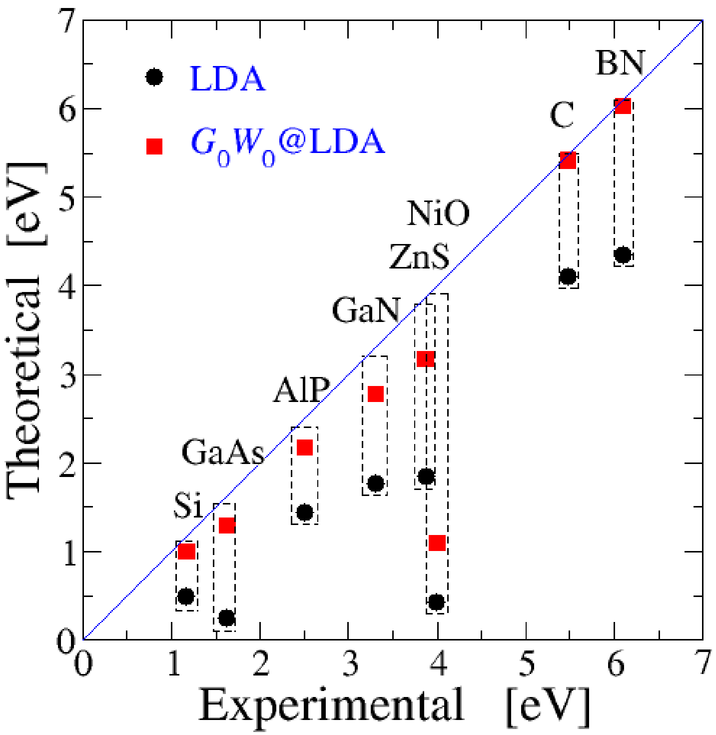
quasi-particle theory and *GW* approximation

Quasi-particle equation



$$\left[-\frac{\nabla^2}{2}+V_{\rm ext}(\mathbf{r})+V_{\rm H}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r})+\int d^3\mathbf{r}'\Sigma_{\rm xc}(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}')=E_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})$$





H. Jiang, Acta Phys.-Chim. Sin. 26, 1017(2010)

Green's functions for single-electron Schrödinger Equations

Green's function ⇔ Green function

Definition of Green's function (mathematically)

Consider a partial differential equation of the general form with a certain boundary condition

$$\left[z-\hat{H}(\mathbf{r})\right]\psi(\mathbf{r})=0$$

z : a complex number

$\hat{H}(\mathbf{r})$: a general Hermitian differential operator

Green's function $G(\mathbf{r},\mathbf{r}';z)$ is defined as the solution of the following equation with **the same boundary condition** for $\psi(\mathbf{r})$:

$$\left[z-\hat{H}(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}';z)=\delta(\mathbf{r}-\mathbf{r}')$$

Analytic properties of Green's function

$$\left[z - \hat{H}(\mathbf{r})\right] G(\mathbf{r},\mathbf{r}';z) = \delta(\mathbf{r}-\mathbf{r}')$$

$$\hat{H}(\mathbf{r})\phi_n(\mathbf{r}) = \varepsilon_n \phi_n(\mathbf{r}) \qquad \sum_n \phi_n(\mathbf{r})\phi_n^*(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$

$$G(\mathbf{r},\mathbf{r}';z) = \sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{z-\varepsilon_n} = \sum_n{}' \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{z-\varepsilon_n} + \int \frac{\phi_\varepsilon(\mathbf{r})\phi_\varepsilon^*(\mathbf{r}')}{z-\varepsilon} d\varepsilon$$

$G(\mathbf{r},\mathbf{r}';z)$ is analytic in the z-plane except at the eigenvalues of $\widehat{H}$

- $z = \varepsilon_n$ (discrete eigenvalues of $\widehat{H}$): simples poles
- $z = \varepsilon$ (**continuum** eigenvalues of $\widehat{H}$ and $\psi_\varepsilon(\mathbf{r})$ **extended** states): a branch cut

$$G^{\pm}(\mathbf{r},\mathbf{r}';\varepsilon) = G^{\pm}(\mathbf{r},\mathbf{r}';\varepsilon \pm i\eta), \qquad \eta = 0^+$$

- $z = \varepsilon$ (**continuum** eigenvalues of $\widehat{H}$ and $\psi_\varepsilon(\mathbf{r})$ **localized** states): a natural boundary

Green's function for perturbation theory

$$\left[z-\hat{H}(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}';z)=\delta(\mathbf{r}-\mathbf{r}')$$

$$\left[z-\hat{H}(\mathbf{r})\right]\psi(\mathbf{r})=f(\mathbf{r})$$

$$\psi(\mathbf{r})=\begin{cases}\int G(\mathbf{r},\mathbf{r}';z)f(\mathbf{r}')d\mathbf{r}', & (\mathrm{z}\neq\varepsilon_n,\varepsilon)\\ \int G^{\pm}(\mathbf{r},\mathbf{r}';\varepsilon)f(\mathbf{r}')d\mathbf{r}'+\phi_\varepsilon(\mathbf{r}) & (\mathrm{z}=\varepsilon)\end{cases}$$

$$\left[E-\hat{H}_0(\mathbf{r})\right]\psi_0(\mathbf{r};E)=0 \quad\Rightarrow\quad G_0^{\pm}(\mathbf{r},\mathbf{r}';E)$$

$$\left[E-\hat{H}_0(\mathbf{r})-V(\mathbf{r})\right]\psi(\mathbf{r};E)=0 \quad\Rightarrow\quad \left[E-\hat{H}_0(\mathbf{r})\right]\psi(\mathbf{r};E)=V(\mathbf{r})\psi(\mathbf{r};E)$$

$$\psi^{\pm}(\mathbf{r};E)=\psi_0(\mathbf{r};E)+\int G_0^{\pm}(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi^{\pm}(\mathbf{r}';E)d\mathbf{r}'$$

(Lippman-Schwinger equation)

Dyson's equation

In many cases, we are interested in the perturbation expansion of **Green's functions** instead of that of wave functions

$$\left[z-\hat{H}_0\right]G_0(z)=\hat{1}$$

$$\left[z-\hat{H}_0-\hat{V}\right]G(z)=\hat{1}$$

$$\hat{G}_0(z)=\left[z-\hat{H}_0\right]^{-1}\equiv\frac{1}{z-\hat{H}_0}$$

$$\hat{G}(z)=\left[z-\hat{H}_0-\hat{V}\right]^{-1}\equiv\frac{1}{z-\hat{H}_0-\hat{V}}$$

$$\hat{G}_0^{-1}(z)=z-\hat{H}_0$$

$$\hat{G}^{-1}(z)=z-\hat{H}_0-\hat{V}$$

$$\hat{G}^{-1}(z)=\hat{G}_0^{-1}(z)-\hat{V}$$

$$\hat{G}_0(z)\hat{G}^{-1}(z)\hat{G}(z)=\hat{G}_0(z)\left[\hat{G}_0^{-1}(z)-\hat{V}\right]\hat{G}(z)$$

$$\hat{G}(z)=\hat{G}_0(z)+\hat{G}_0(z)\hat{V}\hat{G}(z)$$

➔ a Dyson's equation

Time-dependent Green's function

Time-dependent Schrödinger equation

$$\left[i\frac{\partial}{\partial t}-\hat{H}(\mathbf{r})\right]\psi(\mathbf{r},t)=0$$

(all in atomic units!)

$$\left[i\frac{\partial}{\partial t}-\hat{H}(\mathbf{r})\right]G(\mathbf{r}t,\mathbf{r}'t')=\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

For $\hat{H}(\mathbf{r})$ independent of time, $G(\mathbf{r}t,\mathbf{r}'t')\equiv G(\mathbf{r},\mathbf{r}';t-t')$

Fourier transform $G(\mathbf{r},\mathbf{r}';t-t')=\frac{1}{2\pi}\int_{-\infty}^{+\infty}G(\mathbf{r},\mathbf{r}';\omega)e^{-i\omega(t-t')}d\omega$

$$\left[\omega-\hat{H}(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}';\omega)=\delta(\mathbf{r}-\mathbf{r}')$$

But: $\boldsymbol{G}(\mathbf{r},\mathbf{r}';\boldsymbol{\omega})$ is singular if $\boldsymbol{\omega}$ is equal to any eigenvalue of $\hat{\boldsymbol{H}}(\mathbf{r})$!

Retarded and advanced Green's function

$$\left[i\frac{\partial}{\partial t} - \hat{H}(\mathbf{r}) \right] G(\mathbf{r}t, \mathbf{r}'t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

Retarded Green's function

$$G^{\mathrm{R/A}}(\mathbf{r},\mathbf{r}';t-t') = \frac{1}{2\pi}\int_{-\infty}^{+\infty} G^{+/-}(\mathbf{r},\mathbf{r}';\omega) e^{-i\omega(t-t')} d\omega$$

$$\equiv \frac{1}{2\pi}\int_{-\infty}^{+\infty} G(\mathbf{r},\mathbf{r}';\omega \pm i\eta) e^{-i\omega(t-t')} d\omega$$

$$G(\mathbf{r},\mathbf{r}';z) = \sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{z-\varepsilon_n}$$

$$G^{\mathrm{R}}(\mathbf{r},\mathbf{r}';\tau) = -i\theta(\tau)\sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{z-\varepsilon_n} e^{-i\varepsilon_n \tau}, \qquad (\tau \equiv t-t')$$

$$G^{\mathrm{A}}(\mathbf{r},\mathbf{r}';\tau) = i\theta(-\tau)\sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{z-\varepsilon_n} e^{-i\varepsilon_n \tau}$$

The use of Green's function

- Eigenvalues from the poles of Green's functions

$$G(\mathbf{r},\mathbf{r}';z)=\sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{z-\varepsilon_n}$$

- Density matrix

$$G^{\mathrm{R/A}}(\mathbf{r},\mathbf{r}';\omega)=\sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{\omega-\varepsilon_n \pm i\eta}=\sum_n \phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')\left[\hat{\mathrm{P}}\frac{1}{\omega-\varepsilon_n}\mp i\pi\delta(\omega-\varepsilon_n)\right]$$

$$=\hat{\mathrm{P}}\sum_n \frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}')}{\omega-\varepsilon_n}\mp i\pi\rho(\mathbf{r},\mathbf{r}';\omega)$$

$$\frac{1}{x\pm i\eta}=\hat{\mathrm{P}}\left(\frac{1}{x}\right)\mp i\pi\delta(x)$$

$$\rho(\mathbf{r},\mathbf{r}';\omega)=\mp\frac{1}{\pi}\mathrm{Im}\,G^{\mathrm{R/A}}(\mathbf{r},\mathbf{r}';\omega)=\frac{1}{2\pi}\left[G^{\mathrm{A}}(\mathbf{r},\mathbf{r}';\omega)-G^{\mathrm{R}}(\mathbf{r},\mathbf{r}';\omega)\right]$$

- Retarded Green's function as the propagator

$$\Psi(\mathbf{r},t)=\int G^{\mathrm{R}}(\mathbf{r},\mathbf{r}';t-t')\Psi(\mathbf{r}',t')d\mathbf{r}$$

Green's function for many-body systems: General formalism

Outline

- **Green's functions: definition and properties**
- Many-body perturbation theory based on Green's functions
- Hedin's equations

Representations (pictures) of quantum mechanics

Schrödinger Representation

$$i\frac{\partial}{\partial t}\Psi_S(q,t)=\hat{H}(q)\Psi_S(q,t)$$

$$\langle O(t)\rangle=\int\Psi_S^{\dagger}(q,t)\hat{O}_S(q)\Psi_S(q,t)\,dq$$

Heisenberg Representation

$$i\frac{\partial}{\partial t}\Psi_{\mathrm{H}}(q)=0$$

$$\langle O(t)\rangle=\int\Psi_{\mathrm{H}}^{\dagger}(q)\hat{O}_{\mathrm{H}}(q,t)\Psi_{\mathrm{H}}(q)\,dq$$

$$\hat{O}_{\mathrm{H}}(q,t)=e^{i\hat{H}t}\hat{O}_S(q)e^{-i\hat{H}t},\qquad \text{(assuming } \hat{H} \text{ is independent of time)}$$

$$i\frac{\partial}{\partial t}\hat{O}_{\mathrm{H}}(q,t)=\left[\hat{O}_{\mathrm{H}}(q,t),\hat{H}\right]$$

Hamiltonian in terms of field operators

Field operators

$\hat{\psi}(\mathbf{x})$ annihilation operator ➔ remove an electron at **r**

$\hat{\psi}^\dagger(\mathbf{x})$ creation operator ➔ creator an electron at **r**

$$\left[\hat{\psi}(\mathbf{x}), \hat{\psi}(\mathbf{x}')\right]_+ = \left[\hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{x}')\right]_+ = 0 \qquad \left[\hat{A}, \hat{B}\right]_+ \equiv \hat{A}\hat{B} + \hat{B}\hat{A}$$

$$\left[\hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}(\mathbf{x}')\right]_+ = \delta(\mathbf{x}, \mathbf{x}') \qquad \mathbf{x} \equiv \{\mathbf{r}, s\}, \quad s\text{: spin index}$$

Hamiltonian of *N*-electron interacting systems

$$\hat{H} = \int d\mathbf{x}_1 \hat{\psi}^\dagger(\mathbf{x}_1) h_0(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_1) + \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2) \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1).$$

$$\hat{h}_0(\mathbf{x}) \equiv -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{x})$$

Field operators in the Heisenberg representation

$$\hat{\psi}^\dagger(\mathbf{x}t) = e^{i\hat{H}t} \hat{\psi}^\dagger(\mathbf{x}) e^{-i\hat{H}t}$$

$$\hat{\psi}(\mathbf{x}t) = e^{i\hat{H}t} \hat{\psi}(\mathbf{x}) e^{-i\hat{H}t}$$

Definition of (one-body) Green's function

$$\hat{H} = \int dx \hat{\psi}^\dagger(\mathbf{x}t)\hat{h}_0(\mathbf{x})\hat{\psi}(\mathbf{x}t) + \frac{1}{2}\int d\mathbf{x}d\mathbf{x}' v(\mathbf{r}-\mathbf{r}')\hat{\psi}^\dagger(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t)\hat{\psi}(\mathbf{x}'t)\hat{\psi}(\mathbf{x}t)$$

(one-body) Green's function

$$G(\mathbf{x}t, \mathbf{x}'t') = -i\left\langle N \left| \hat{\mathrm{T}}\left[\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\right] \right| N \right\rangle$$

$|N\rangle$ the ground state of the *N*-electron systems

$\hat{\mathrm{T}}$ time-ordering operator

$$\hat{\mathrm{T}}\left[\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\right] = \begin{cases} \hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t'), & t > t' \\ \pm\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t), & t < t' \end{cases}$$

$$G(\mathbf{x}t;\mathbf{x}'t') = -i\theta(t-t')\left\langle N\right| \hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\left|N\right\rangle + i\theta(t'-t)\left\langle N\right| \hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)\left|N\right\rangle$$

Note: $G(\mathbf{x}t;\mathbf{x}'t) \equiv \lim_{t'\to t^+} G(\mathbf{x}t;\mathbf{x}'t') \equiv G(\mathbf{x}t;\mathbf{x}'t^+)$

Physical significance of Green's function (1)

$$G(\mathbf{x}t;\mathbf{x}'t') = -i\theta(t-t')\langle N|\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')|N\rangle + i\theta(t'-t)\langle N|\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)|N\rangle$$

$t > t'$ ➔ $G^{\mathrm{R}}(\mathbf{x}t;\mathbf{x}'t') = -i\theta(t-t')\langle N|\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')|N\rangle$

1) $\hat{\psi}^\dagger(\mathbf{x}',t')|N\rangle$ ➔ add an electron to the system at **x'** and *t'*

2) $\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')|N\rangle$ ➔ take an electron away from the system at **x** and *t*

3) $\langle N|\hat{\psi}(\mathbf{x},t)\hat{\psi}^\dagger(\mathbf{x}',t')|N\rangle$ ➔ project to the ground state (measure!)

Physical significance of Green's function (2)

$$iG(\mathbf{x}t,\mathbf{x}'t') = \theta(t-t')\langle N|\hat{\psi}(\mathbf{x}t)\hat{\psi}^{\dagger}(\mathbf{x}'t')|N\rangle - \theta(t'-t)\langle N|\hat{\psi}^{\dagger}(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)|N\rangle$$

$t < t'$ ➔ $G^{A}(\mathbf{x}t;\mathbf{x}'t') = i\theta(t'-t)\langle N|\hat{\psi}^{\dagger}(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)|N\rangle$

1) $\hat{\psi}(\mathbf{x},t)|N\rangle$ ➔ remove an electron from (add a hole to) the system at $(\mathbf{x},t)$

2) $\hat{\psi}^{\dagger}(\mathbf{x}',t')\hat{\psi}(\mathbf{x},t)|N\rangle$ ➔ add an electron to (annihilation of the hole) the system at $(\mathbf{x}',t')$

3) $\langle N|\hat{\psi}^{\dagger}(\mathbf{x}',t')\hat{\psi}(\mathbf{x},t)|N\rangle$ ➔ project to the ground state (measure!)

Lehmann representation (1)

$$G(\mathbf{x}t;\mathbf{x}'t') = -i\theta(t-t')\langle N|\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')|N\rangle + i\theta(t'-t)\langle N|\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)|N\rangle$$

$$\hat{\psi}(\mathbf{x}t) = e^{i\hat{H}t}\hat{\psi}(\mathbf{x})e^{-i\hat{H}t}$$

$$\begin{aligned} G(\mathbf{x}t;\mathbf{x}'t') = &- i\theta(t-t')\langle N|e^{i\hat{H}t}\hat{\psi}(\mathbf{x})e^{-i\hat{H}t}e^{i\hat{H}t'}\hat{\psi}^\dagger(\mathbf{x}')e^{-i\hat{H}t'}|N\rangle \\ &+ i\theta(t'-t)\langle N|e^{i\hat{H}t'}\hat{\psi}^\dagger(\mathbf{x}')e^{-i\hat{H}t'}e^{i\hat{H}t}\hat{\psi}(\mathbf{x})e^{-i\hat{H}t}|N\rangle \\ = &- i\theta(t-t')e^{iE_N(t-t')}\langle N|\hat{\psi}(\mathbf{x})e^{-i\hat{H}(t-t')}\hat{\psi}^\dagger(\mathbf{x}')|N\rangle \\ &+ i\theta(t'-t)e^{iE_N(t'-t)}\langle N|\hat{\psi}^\dagger(\mathbf{x}')e^{-i\hat{H}(t'-t)}\hat{\psi}(\mathbf{x})|N\rangle . \end{aligned}$$

$$\sum_{M,s}|M,s\rangle\langle M,s| = \hat{1}$$

$$\begin{aligned} G(\mathbf{x}t;\mathbf{x}'t') = &- i\theta(t-t')\sum_s e^{-i(E_{N+1,s}-E_N)(t-t')}\langle N|\hat{\psi}(\mathbf{x})|N+1,s\rangle\langle N+1,s|\hat{\psi}^\dagger(\mathbf{x}')|N\rangle \\ &+ i\theta(t'-t)\sum_s e^{-i(E_{N-1,s}-E_N)(t'-t)}\langle N|\hat{\psi}^\dagger(\mathbf{x}')|N-1,s\rangle\langle N-1,s|\hat{\psi}(\mathbf{x})|N\rangle \end{aligned}$$

Lehmann representation (2)

$$G(\mathbf{x}t;\mathbf{x}'t') = -i\theta(t-t')\sum_s e^{-i(E_{N+1,s}-E_N)(t-t')}\langle N|\hat{\psi}(\mathbf{x})|N+1,s\rangle\langle N+1,s|\hat{\psi}^\dagger(\mathbf{x}')|N\rangle$$
$$+ i\theta(t'-t)\sum_s e^{-i(E_{N-1,s}-E_N)(t'-t)}\langle N|\hat{\psi}^\dagger(\mathbf{x}')|N-1,s\rangle\langle N-1,s|\hat{\psi}(\mathbf{x})|N\rangle$$

$$f_s(\mathbf{x}) \equiv \langle N|\hat{\psi}(\mathbf{x})|N+1,s\rangle$$
$$\begin{aligned}\mathcal{E}_s &\equiv E_{N+1,s} - E_N \\ &= E_{N+1} - E_N + E_{N+1,s} - E_{N+1} \\ &= \mu_{N+1} + \varepsilon_s(N+1)\end{aligned}$$

$$f_s(\mathbf{x}) \equiv \langle N-1,s|\hat{\psi}(\mathbf{x})|N\rangle$$
$$\begin{aligned}\mathcal{E}_s &\equiv E_N - E_{N-1,s} \\ &= E_N - E_{N-1} + E_{N-1} - E_{N-1,s} \\ &= \mu_N - \varepsilon_s(N-1),\end{aligned}$$

$$\mu_{N+1} - \mu_N = E_{N+1} + E_{N-1} - 2E_N = E_g \geq 0$$

metallic systems:

$$\mu_{N+1} = \mu_N \equiv \mu$$

Insulating systems:

$$\mu = (\mu_{N+1} + \mu_N)/2$$

$$G(\mathbf{x},\mathbf{x}';\tau) \equiv G(\mathbf{x}t;\mathbf{x}'t')$$
$$= -i\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')e^{-i\mathcal{E}_s\tau}\left[\theta(\tau)\theta(\mathcal{E}_s-\mu) - \theta(-\tau)\theta(\mu-\mathcal{E}_s)\right]$$

Lehmann representation (3)

$$G(\mathbf{x},\mathbf{x}';\tau) \equiv G(\mathbf{x}t;\mathbf{x}'t')$$

$$= -i\sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}') e^{-i\mathcal{E}_s\tau}\left[\theta(\tau)\theta(\mathcal{E}_s-\mu)-\theta(-\tau)\theta(\mu-\mathcal{E}_s)\right]$$

$$G(\mathbf{x},\mathbf{x}';\omega) = \int_{-\infty}^{\infty} G(\mathbf{x},\mathbf{x}';\tau)e^{\omega\tau}d\tau$$

$$= \sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}')\left[\theta(\mathcal{E}_s-\mu)(-i)\int_{-\infty}^{\infty}\theta(\tau)e^{i(\omega-\mathcal{E}_s)\tau}d\tau + \theta(\mu-\mathcal{E}_s)i\int_{-\infty}^{\infty}\theta(-\tau)e^{i(\omega-\mathcal{E}_s)\tau}d\tau\right]$$

$$\theta(\tau) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\frac{e^{-i\omega\tau}}{\omega+i\eta}$$

$$\theta(\tau)\rightarrow\tilde{\theta}(\omega) = \frac{i}{\omega+i\eta}$$

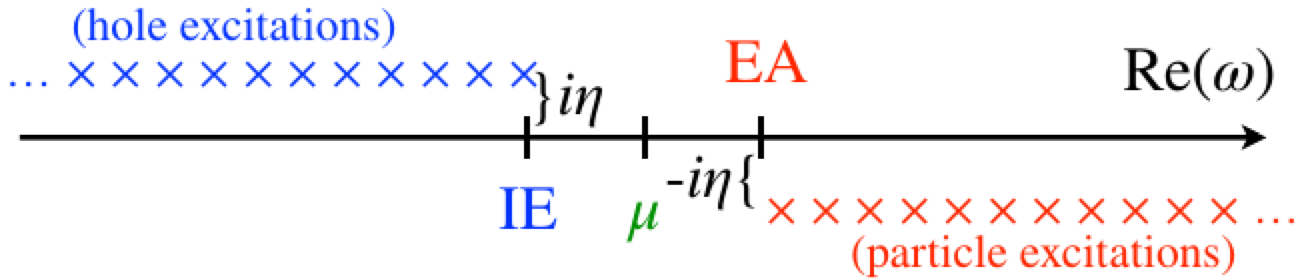
$$\theta(-\tau)\rightarrow\tilde{\theta}^*(\omega) = \frac{-i}{\omega-i\eta}$$

$$G(\mathbf{x},\mathbf{x}';\omega) = \sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}')\left[\frac{\theta(\mathcal{E}_s-\mu)}{\omega-\mathcal{E}_s+i\eta}+\frac{\theta(\mu-\mathcal{E}_s)}{\omega-\mathcal{E}_s-i\eta}\right]$$

Lehmann representation (4)

$$G(\mathbf{x},\mathbf{x}';\omega) = \sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}') \left[\frac{\theta(\mathcal{E}_s - \mu)}{\omega - \mathcal{E}_s + i\eta} + \frac{\theta(\mu - \mathcal{E}_s)}{\omega - \mathcal{E}_s - i\eta} \right]$$

$$G(\mathbf{x},\mathbf{x}';\omega) = \sum_s \frac{f_s(\mathbf{x}) f_s^*(\mathbf{x}')}{\omega - \mathcal{E}_s - i\eta\,\mathrm{sgn}(\mu - \mathcal{E}_s)}$$



$f_s(\mathbf{x})$: Lehmann (quasi-particle) amplitudes

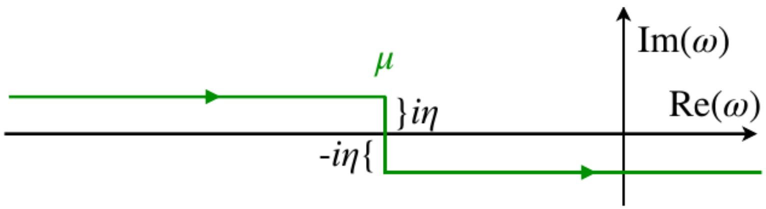
$$\sum_s f_s(\mathbf{x}) f_s(\mathbf{x}') = \langle N | \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') + \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) | N \rangle = \delta(\mathbf{x} - \mathbf{x}')$$

Spectral representation of Green's function

Spectral function
$$A(\mathbf{x},\mathbf{x}';\omega) \equiv \sum_s f_s(\mathbf{x}) f_s(\mathbf{x}')\delta(\omega - \mathcal{E}_s)$$

Spectral representation of Green's function

$$G(\mathbf{x},\mathbf{x}';\omega) = \int_C \frac{A(\mathbf{x},\mathbf{x}';\omega')}{\omega-\omega'} d\omega'$$



Alternatively,

$$G(\mathbf{x},\mathbf{x}';\omega) = \int_{-\infty}^{+\infty} \frac{A(\mathbf{x},\mathbf{x}';\omega')}{\omega-\omega' - i\eta\,\mathrm{sgn}(\mu-\omega')} d\omega'$$

$$\frac{1}{\omega \pm i\eta} = \mathcal{P}\left(\frac{1}{\omega}\right) \mp i\pi\delta(\omega)$$

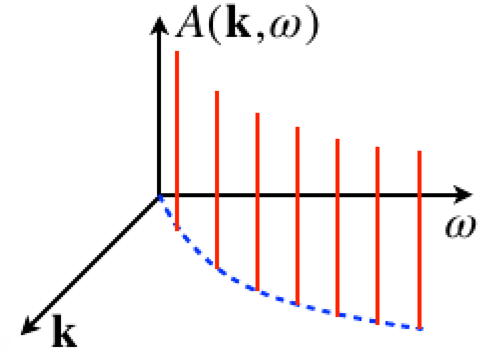
$$A(\mathbf{x},\mathbf{x}';\omega) = \mathrm{sgn}(\mu-\omega)\frac{1}{\pi}\Im G(\mathbf{x},\mathbf{x}';\omega)$$

Quasi-particles

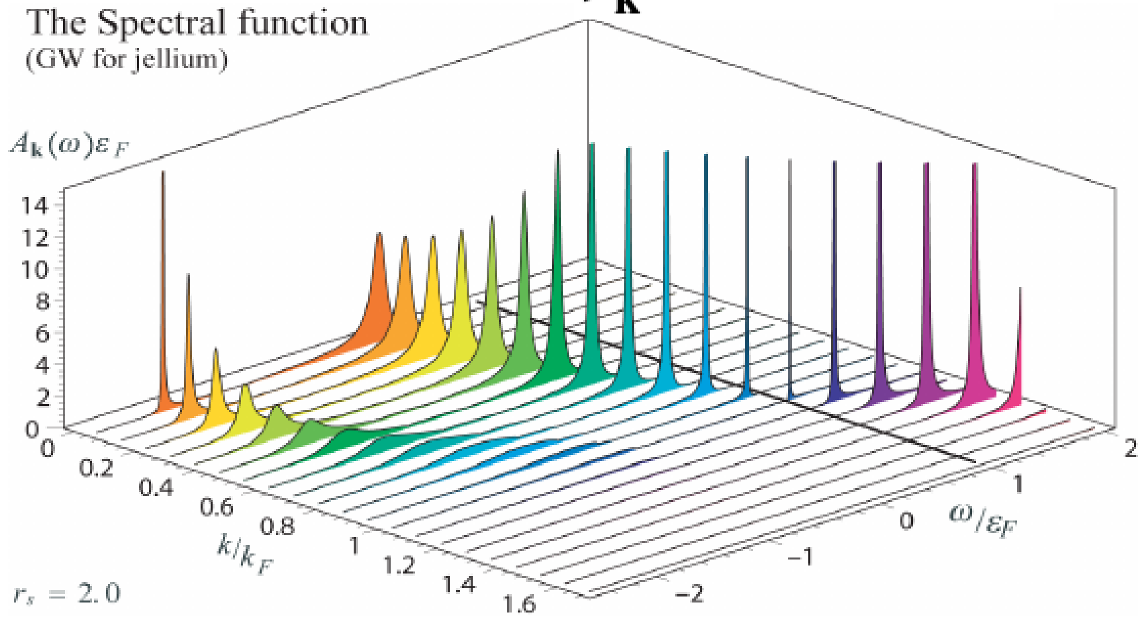
Spectral function $$A(\mathbf{x},\mathbf{x}';\omega) \equiv \sum_s f_s(\mathbf{x}) f_s(\mathbf{x}') \delta(\omega - \mathcal{E}_s)$$

Non-interacting systems

$$A(\mathbf{k},\omega) = \sum_n \delta(\omega - \varepsilon_{n\mathbf{k}})$$



Interacting systems



[courtesy of Martin Stankovski (Université Catholique de Louvain, Belgium)]

(Figures from G.-M. Rignanese's talk)

Green’s function for many-body systems: General formalism

Outline

- Green’s functions: definition and properties
- **Many-body perturbation theory and Hedin’s equations**

Equation of motion for GFs

$$\hat{H} = \int d\mathbf{x}_1 \hat{\psi}^\dagger(\mathbf{x}_1) h_0(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_1) + \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2) \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}^\dagger(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1).$$

$$G(\mathbf{x}_1 t_1; \mathbf{x}_2 t_2) = -i \langle N | \mathbf{T} \left[\hat{\psi}(\mathbf{x}_1 t_1) \hat{\psi}^\dagger(\mathbf{x}_2 t_2) \right] | N \rangle$$

$$i \frac{\delta \hat{\psi}(\mathbf{x}t)}{\delta t} = \left[\hat{\psi}(\mathbf{x}t), \hat{H} \right]$$

$$\left[i \frac{\partial}{\partial t_1} - h_0(\mathbf{x}_1) \right] G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) - i \int d\mathbf{x}_3 v(\mathbf{x}_1, \mathbf{x}_3) \langle N | \mathbf{T} \left[\hat{\psi}^\dagger(\mathbf{x}_3 t_1) \hat{\psi}(\mathbf{x}_3 t_1) \hat{\psi}(\mathbf{x}_1 t_1) \hat{\psi}^\dagger(\mathbf{x}_2 t_2) \right] | N \rangle$$

$$= \delta(\mathbf{x}_1 - \mathbf{x}_2) \delta(t_1 - t_2).$$

Equation of motion for GFs

$$\left[i\frac{\partial}{\partial t_1} - h_0(\mathbf{x}_1)\right] G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) - i\int d\mathbf{x}_3 v(\mathbf{x}_1, \mathbf{x}_3) \langle N| \mathbf{T}\left[\hat{\psi}^\dagger(\mathbf{x}_3 t_1)\hat{\psi}(\mathbf{x}_3 t_1)\hat{\psi}(\mathbf{x}_1 t_1)\hat{\psi}^\dagger(\mathbf{x}_2 t_2)\right]|N\rangle$$
$$= \delta(\mathbf{x}_1 - \mathbf{x}_2)\delta(t_1 - t_2).$$

Two-body Green's function

$$G_2(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_3, \mathbf{x}_4 t_4)$$
$$= i^2 \langle N| \mathbf{T}\left[\hat{\psi}(\mathbf{x}_1 t_1)\hat{\psi}(\mathbf{x}_3 t_3)\hat{\psi}^\dagger(\mathbf{x}_4 t_4)\hat{\psi}^\dagger(\mathbf{x}_2 t_2)\right]|N\rangle$$

$$\left[i\frac{\partial}{\partial t_1} - h_0(\mathbf{x}_1)\right] G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) + i\int d\mathbf{x}_3 v(\mathbf{x}_1, \mathbf{x}_3) G_2(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_1, \mathbf{x}_3 t_1^+)$$
$$= \delta(\mathbf{x}_1 - \mathbf{x}_2)\delta(t_1 - t_2),$$

Similar EOS can be derived for G_2 which involves G_3, and so on.

Equation of motion for GFs: Approximations

$$\left[i\frac{\partial}{\partial t_1} - h_0(\mathbf{x}_1)\right] G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) + i \int d\mathbf{x}_3 v(\mathbf{x}_1, \mathbf{x}_3) G_2(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_1, \mathbf{x}_3 t_1^+)$$

$$= \delta(\mathbf{x}_1 - \mathbf{x}_2)\delta(t_1 - t_2),$$

➔ Hartree approximation

$$G(\mathbf{x}t; \mathbf{x}t) \equiv G(\mathbf{x}t; \mathbf{x}t^+) = i\rho(\mathbf{x})$$

$$G_2(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_1, \mathbf{x}_3 t_1^+) \simeq G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) G(\mathbf{x}_3 t_1, \mathbf{x}_3 t_1^+)$$

➔ Hartree-Fock approximation

$$G_2(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t, \mathbf{x}_3 t^+) \simeq G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) G(\mathbf{x}_3 t_1, \mathbf{x}_3 t_1^+)$$

$$+ G(\mathbf{x}_1 t_1, \mathbf{x}_3 t_1^+) G(\mathbf{x}_3 t_1, \mathbf{x}_2 t_2).$$

(exchange-correlation) self-energy

Definition:

$$i \int d\mathbf{x}_3 v(\mathbf{x}_1, \mathbf{x}_3) G_2(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_1, \mathbf{x}_3 t_1^+)$$

$$\equiv - V_\mathrm{H}(\mathbf{x}_1) G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) - \int d\mathbf{x}_3 dt_3 \Sigma(\mathbf{x}_1 t_1, \mathbf{x}_3 t_3) G(\mathbf{x}_3 t_3, \mathbf{x}_2 t_2).$$

Equation of Motion

$$\left[i \frac{\partial}{\partial t_1} - h_0(\mathbf{x}_1) - V_\mathrm{H}(\mathbf{x}_1) \right] G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2)$$

$$- \int d\mathbf{x}_3 dt_3 \Sigma(\mathbf{x}_1 t_1, \mathbf{x}_3 t_3) G(\mathbf{x}_3 t_3, \mathbf{x}_2 t_2) = \delta(\mathbf{x}_1 - \mathbf{x}_2) \delta(t_1 - t_2)$$

Fourier transform

$$[\omega - h_0(\mathbf{x}_1) - V_\mathrm{H}(\mathbf{x}_1)] G(\mathbf{x}_1, \mathbf{x}_2; \omega)$$

$$- \int d\mathbf{x}_3 \Sigma(\mathbf{x}_1, \mathbf{x}_3; \omega) G(\mathbf{x}_3, \mathbf{x}_2; \omega) = \delta(\mathbf{x}_1 - \mathbf{x}_2).$$

Dyson's equation

$$[\omega - h_0(\mathbf{x}_1) - V_{\mathrm{H}}(\mathbf{x}_1)]\, G(\mathbf{x}_1, \mathbf{x}_2; \omega)$$

$$- \int d\mathbf{x}_3 \Sigma(\mathbf{x}_1, \mathbf{x}_3; \omega) G(\mathbf{x}_3, \mathbf{x}_2; \omega) = \delta(\mathbf{x}_1 - \mathbf{x}_2).$$

in matrix form

$$(\omega \mathbf{1} - \mathbf{H}_0)\, \mathbf{G} - \mathbf{\Sigma} \mathbf{G} = \mathbf{1}$$

$$\mathbf{G}_0(\omega) = (\omega \mathbf{1} - \mathbf{H}_0)^{-1}$$

➔ Hartree approximation

$$\mathbf{G}(\omega) = (\omega \mathbf{1} - \mathbf{H}_0 - \mathbf{\Sigma})^{-1}$$

$$\mathbf{G} = \mathbf{G}_0 + \mathbf{G}_0 \mathbf{\Sigma} \mathbf{G}$$

Dyson's equation (again!)

Quasi-particle Equation (?)

$$(\omega 1 - \mathrm{H}_0)\,\mathrm{G} - \Sigma\mathrm{G} = 1$$

$$\left[h_0(\mathbf{x}_1) + V_{\mathrm{H}}(\mathbf{x}_1)\right]\Psi_n(\mathbf{x}_1;\omega) + \int d\mathbf{x}_2 \Sigma(\mathbf{x}_1,\mathbf{x}_2;\omega)\Psi_n(\mathbf{x}_2;\omega) = E_n(\omega)\Psi_n(\mathbf{x}_1;\omega).$$

$$\left[h_0(\mathbf{x}_1) + V_{\mathrm{H}}(\mathbf{x}_1)\right]\Psi_n(\mathbf{x}_1;\omega) + \int d\mathbf{x}_2 \Sigma^\dagger(\mathbf{x}_1,\mathbf{x}_2;\omega)\Psi_n^\dagger(\mathbf{x}_2;\omega) = E_n^*(\omega)\Psi_n^\dagger(\mathbf{x}_1;\omega)$$

$$G(\mathbf{x},\mathbf{x}';\omega) = \sum_n \frac{\Psi_n(\mathbf{x};\omega)\Psi_n^\dagger(\mathbf{x}';\omega)}{\omega - \mathcal{E}_n(\omega)}$$

Quasi-particles

➔ $\omega = \mathcal{E}_n(\omega) \equiv \mathcal{E}_n$

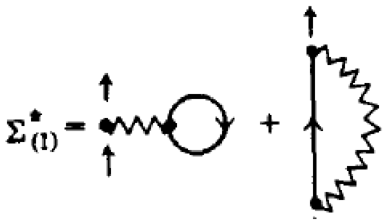
$$E_n \equiv E_n(\omega_n)$$

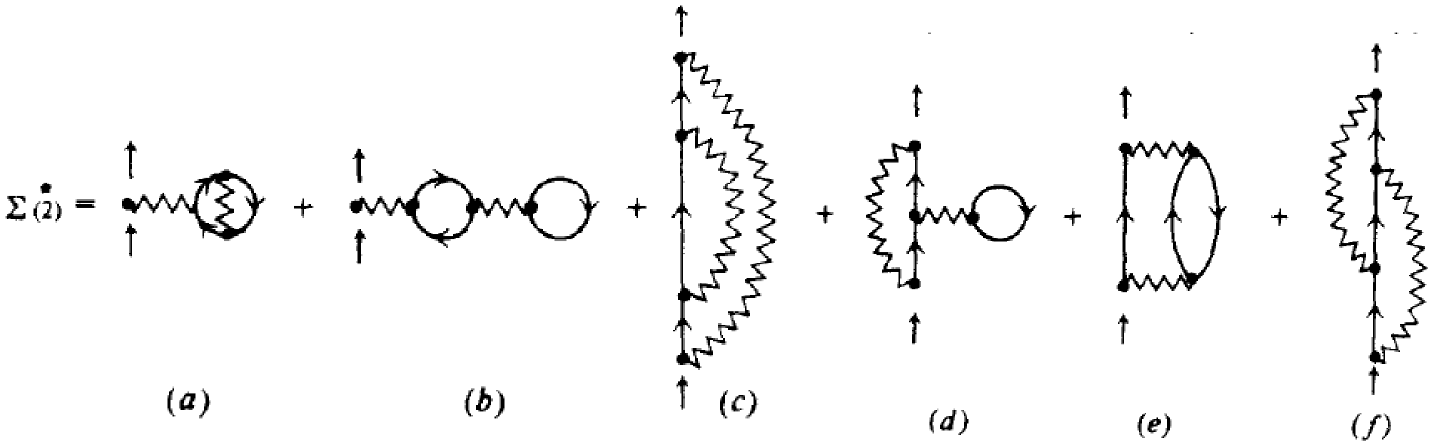
$$\Psi_n(\mathbf{x}) \equiv \Psi_n(\mathbf{x};\omega_n) = \Psi_n(\mathbf{x};\Re\mathcal{E}_n)$$

$$\left[h_0(\mathbf{x}) + V_{\mathrm{H}}(\mathbf{x})\right]\Psi_n(\mathbf{x}) + \int d\mathbf{x}'\Sigma(\mathbf{x},\mathbf{x}';\mathcal{E}_n)\Psi_n(\mathbf{x}') = \mathcal{E}_n\Psi_n(\mathbf{x})$$

Two major approaches to obtain approximate Σ_{xc}

- Diagrammatic expansion (Wick's theorem)



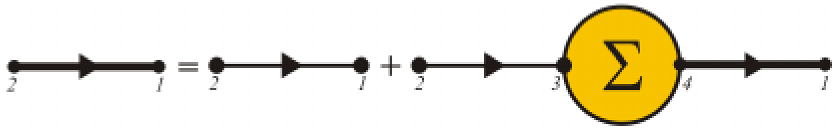


- Equation of motion and functional derivatives

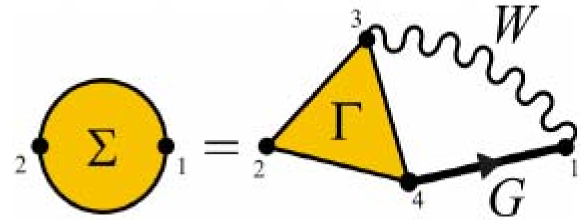
$$\left[i\frac{\delta}{\delta t} - h_0(\mathbf{x}) - V_{\mathrm{H}}(\mathbf{x}) + \phi(\mathbf{x},t) \right] G(\mathbf{x}t,\mathbf{x}'t') - \int d\mathbf{x}''dt''\Sigma(\mathbf{x}t,\mathbf{x}''t'')G(\mathbf{x}''t'',\mathbf{x}'t') = \delta(\mathbf{x}-\mathbf{x}')\delta(t-t')$$

Hedin's Equations

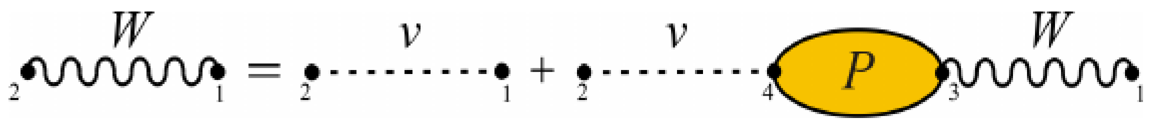
$$G(1,2) = G_0(1,2) + \int d(3)d(4)G_0(1,3)\Sigma(3,4)G(4,2)$$



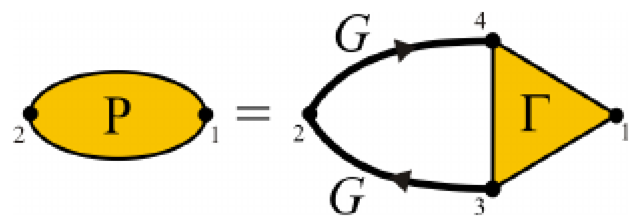
$$\Sigma(1,2) = i\int d(34)G(1,3)W(4,1)\Gamma(3,2,4),$$



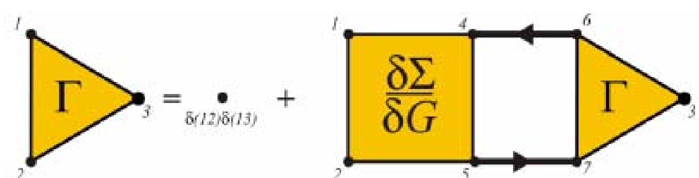
$$W(1,2) = v(1,2) + \int d(34)v(1,3)P(3,4)W(4,2),$$



$$P(1,2) = -i\int d(34)G(1,3)\Gamma(3,4,2)G(4,1^+),$$



$$\Gamma(1,2,3) = \delta(1,2)\delta(2,3) + \int d(4567)\frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\Gamma(6,7,3),$$



(Figures from G.-M. Rignanese's talk)

Hedin's Equations: Derivation (1)

$$\hat{H} = \int d\mathbf{x}_1 \hat{\psi}^\dagger(\mathbf{x}_1)\left[h_0(\mathbf{x}_1) + \phi(\mathbf{x}_1, t)\right]\hat{\psi}(\mathbf{x}_1)$$

$$+ \frac{1}{2}\int d\mathbf{x}_1 d\mathbf{x}_2 v(\mathbf{x}_1, \mathbf{x}_2)\hat{\psi}^\dagger(\mathbf{x}_1)\hat{\psi}^\dagger(\mathbf{x}_1)\hat{\psi}(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_1)$$

adiabatic small perturbation

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

$$i\int d\mathbf{x}_3 v(\mathbf{x}_1, \mathbf{x}_3) G_2(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_1, \mathbf{x}_3 t_1^+)$$

$$\equiv -V_{\mathrm{H}}(\mathbf{x}_1) G(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) - \int d\mathbf{x}_3 dt_3 \Sigma(\mathbf{x}_1 t_1, \mathbf{x}_3 t_3) G(\mathbf{x}_3 t_3, \mathbf{x}_2 t_2)$$

$$\int d(3)\Sigma(1,3)G(3,2) = i\int d(3)v(1,3)\frac{\delta G(1,2)}{\phi(3)}$$

$$\Rightarrow \Sigma(1,2) = i\int d(34)v(1,3)\frac{\delta G(1,4)}{\phi(3)}G^{-1}(4,2)$$

Hedin's Equations: Derivation (2)

$$\Sigma(1,2) = i\int d(34)v(1,3)\frac{\delta G(1,4)}{\phi(3)}G^{-1}(4,2)$$

$$\mathbf{G}^{-1}\mathbf{G} = 1$$

$$\Rightarrow \quad \frac{\delta\left(\mathbf{G}^{-1}\mathbf{G}\right)}{\delta\phi} = 0$$

$$\Rightarrow \quad \frac{\delta\mathbf{G}^{-1}}{\delta\phi}\mathbf{G} + \mathbf{G}^{-1}\frac{\delta\mathbf{G}}{\delta\phi} = 0$$

$$\Rightarrow \quad \frac{\delta\mathbf{G}}{\delta\phi} = -\mathbf{G}\frac{\delta\mathbf{G}^{-1}}{\delta\phi}\mathbf{G}$$

$$\Sigma(1,2) = -i\int d(34)v(1,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta\phi(3)}$$

Hedin's Equations: Derivation (3)

$$\Sigma(1,2) = -i \int d(34) v(1,3) G(1,4) \frac{\delta G^{-1}(4,2)}{\delta \phi(3)}$$

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

$$V(1) \equiv V_H(1) + \phi(1)$$

$$\left[i \frac{\partial}{\partial t_1} - h_0(1) - V(1) \right] G_0(1,2) = \delta(1,2)$$

$$G_0^{-1}(1,2) = \left[i \frac{\partial}{\partial t_1} - h_0(1) - V(1) \right] \delta(1,2)$$

$$G^{-1}(1,2) = \left[i \frac{\partial}{\partial t_1} - h_0(1) - V(1) \right] \delta(1,2) - \Sigma(1,2)$$

Hedin's Equations: Derivation (4)

$$\Sigma(1,2) = -i\int d(34)v(1,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta\phi(3)}$$

$$V(1) \equiv V_H(1) + \phi(1)$$

$$\Gamma(1,2,3) \equiv -\frac{\delta G^{-1}(1,2)}{\delta V(3)}$$

$$\varepsilon^{-1}(1,2) \equiv \frac{\delta V(1)}{\delta\phi(2)}$$

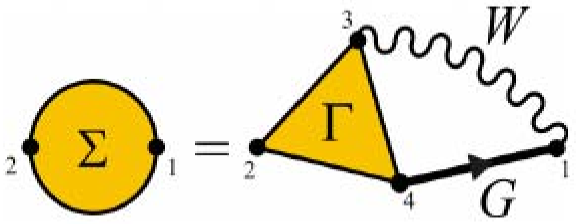
$$W(1,2) \equiv \int d(3)\varepsilon^{-1}(1,3)v(3,2)$$

$$\Sigma(1,2) = -i\int d(345)v(1,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta V(5)}\frac{\delta V(5)}{\delta\phi(3)}$$

$$\equiv i\int d(345)v(1,3)G(1,4)\Gamma(4,2,5)\varepsilon^{-1}(5,3)$$

$$\equiv i\int d(45)G(1,4)W(5,1)\Gamma(4,2,5)$$

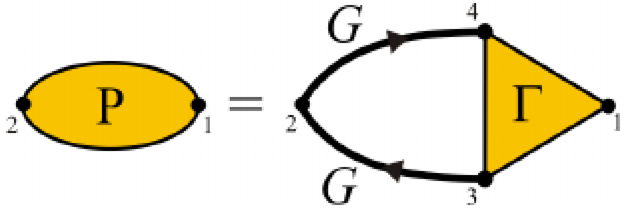
$$\equiv i\int d(34)G(1,3)W(4,1)\Gamma(3,2,4)$$



Hedin's Equations: Derivation (5)

$$P(1,2) \equiv \frac{\delta \rho(1)}{\delta V(2)} \qquad \rho(1) = -iG(1,1^+)$$

$$\begin{aligned} P(1,2) &= -i\frac{\delta G(1,1^+)}{\delta V(2)} \\ &= i\int d(34) G(1,3) \frac{\delta G^{-1}(3,4)}{\delta V(2)} G(4,1^+) \\ &\equiv i\int d(34) G(1,3)\Gamma(3,4,2)G(4,1^+) \end{aligned}$$



Hedin's Equations: Derivation (6)

$$\varepsilon^{-1} = \frac{\delta \mathbf{V}}{\delta \phi} = 1 + \frac{\delta \mathbf{V_H}}{\delta \phi}$$

$$= 1 + \frac{\delta \mathbf{V_H}}{\delta \rho}\frac{\delta \rho}{\delta \phi} = 1 + \mathbf{v}\frac{\delta \rho}{\delta \phi}$$

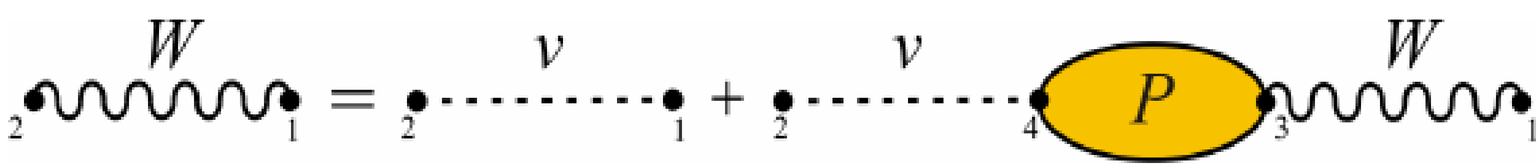
$$= 1 + \mathbf{v}\frac{\delta \rho}{\delta \mathbf{V}}\frac{\delta \mathbf{V}}{\delta \phi}$$

$$= 1 + \mathbf{vP}\varepsilon^{-1}$$

$$V(1) \equiv V_H(1) + \phi(1)$$

$$\varepsilon = 1 - \mathbf{vP}$$

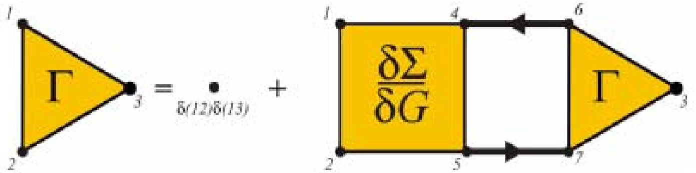
$$\mathbf{W} = \mathbf{v} + \mathbf{vPW}$$



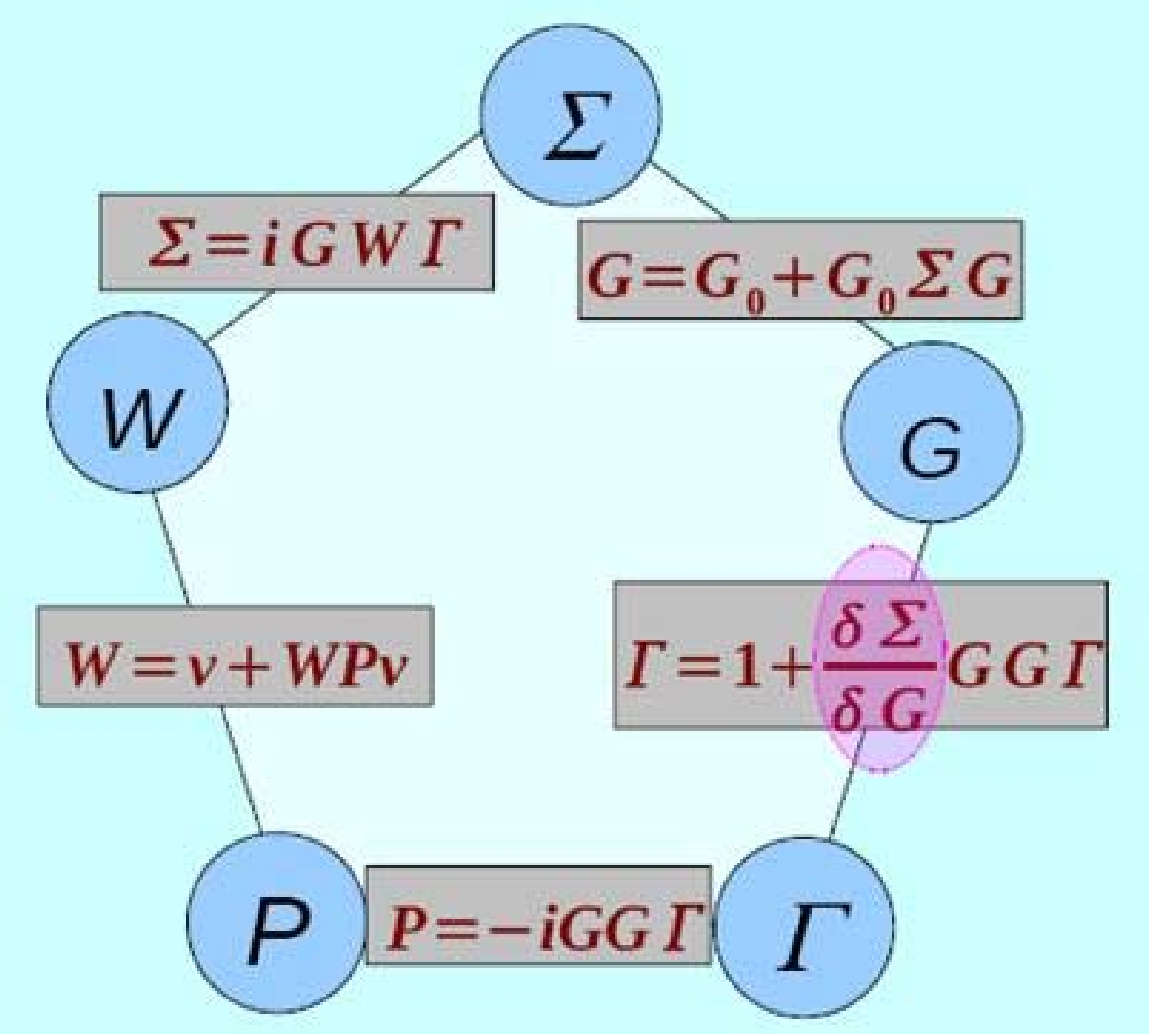
Hedin's Equations: Derivation (7)

$$G^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma(1,2)$$
$$= \left[i\frac{\partial}{\partial t_1} - h_0(1) - V(1) \right] \delta(1,2) - \Sigma(1,2)$$

$$\Gamma(1,2,3) \equiv -\frac{G^{-1}(1,2)}{\delta V(3)}$$
$$= \delta(1,2)\delta(1,3) + \frac{\delta\Sigma(1,2)}{\delta V(3)}$$
$$= \delta(1,2)\delta(1,3) + \int d(45) \frac{\delta\Sigma(1,2)}{\delta G(4,5)} \frac{\delta G(4,5)}{\delta V(3)}$$
$$= \delta(1,2)\delta(1,3) - \int d(4567) \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6) \frac{\delta G^{-1}(6,7)}{\delta V(3)} G(7,5)$$
$$= \delta(1,2)\delta(1,3) + \int d(4567) \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3)$$



Hedin's Equations: the "grand pentagon"



Ground state properties from Green's function (1)

The expectation value of one-body operator

$$\hat{J} = \sum_i j(\mathbf{x}_i) \rightarrow \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x},t) j(\mathbf{x}) \hat{\psi}(\mathbf{x},t)$$

$$\begin{aligned}
\langle \hat{J} \rangle &\equiv \langle N | \hat{J} | N \rangle \\
&= \int d\mathbf{x} \langle N | \hat{\psi}^\dagger(\mathbf{x},t) j(\mathbf{x}) \hat{\psi}(\mathbf{x},t) | N \rangle \\
&= \int d\mathbf{x} j(\mathbf{x}) \langle N | \hat{\psi}^\dagger(\mathbf{x}',t) \hat{\psi}(\mathbf{x},t) | N \rangle_{\mathbf{x}' \rightarrow \mathbf{x}} \\
&= - \int d\mathbf{x} j(\mathbf{x}) \langle N | \hat{T} \hat{\psi}(\mathbf{x},t) \hat{\psi}^\dagger(\mathbf{x}',t^+) | N \rangle_{\mathbf{x}' \rightarrow \mathbf{x}} \\
&= -i \int d\mathbf{x} \left[j(\mathbf{x}) G(\mathbf{x}t, \mathbf{x}'t^+) \right]_{\mathbf{x}' \rightarrow \mathbf{x}}
\end{aligned}$$

Examples:

$$\langle \hat{T} \rangle \equiv \langle N | \hat{T} | N \rangle = -i \int d\mathbf{x} \left[-\frac{1}{2} \nabla^2 G(\mathbf{x}t, \mathbf{x}'t^+) \right]_{\mathbf{x}' \rightarrow \mathbf{x}}$$

$$\rho(\mathbf{r}) \equiv \langle N | \hat{\rho}(\mathbf{r}) | N \rangle \equiv \langle N | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | N \rangle = -i \int G(\mathbf{x}t, \mathbf{x}t^+) ds$$

Ground state properties from Green's function (2)

In general, two-body physical properties cannot be obtained directly from one-body Green's function.

$$\hat{\mathbf{S}}^2 = \left[\sum_i \hat{\mathbf{S}}_i\right]^2 = \sum_{i,j} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$

Exception:

$$i\frac{\partial\hat{\psi}(\mathbf{x}t)}{\partial t} = \left[\hat{\psi}(\mathbf{x}t), \hat{H}\right] = h_0(\mathbf{x})\hat{\psi}(\mathbf{x}t) + \int d\mathbf{x}' v(\mathbf{r},\mathbf{r}')\hat{\psi}^\dagger(\mathbf{x}'t)\hat{\psi}(\mathbf{x}'t)\hat{\psi}(\mathbf{x}t)$$

$$\langle V_{ee}\rangle = -\frac{i}{2}\int d\mathbf{x} \lim_{\mathbf{x}'\to\mathbf{x},t'\to t^+} \left[i\frac{\partial}{\partial t} - h_0(\mathbf{x})\right] G(\mathbf{x}t,\mathbf{x}'t')$$

Galitskii-Migdal formula

$$E_0 = \langle N|\,\hat{H}\,|N\rangle == -\frac{i}{2}\int d\mathbf{x} \lim_{\mathbf{x}'\to\mathbf{x},t'\to t^+} \left[i\frac{\partial}{\partial t} + h_0(\mathbf{x})\right] G(\mathbf{x}t,\mathbf{x}'t')$$

GW approximation and implementations

Outline

- GW approximation
- Implementations of the GW approach

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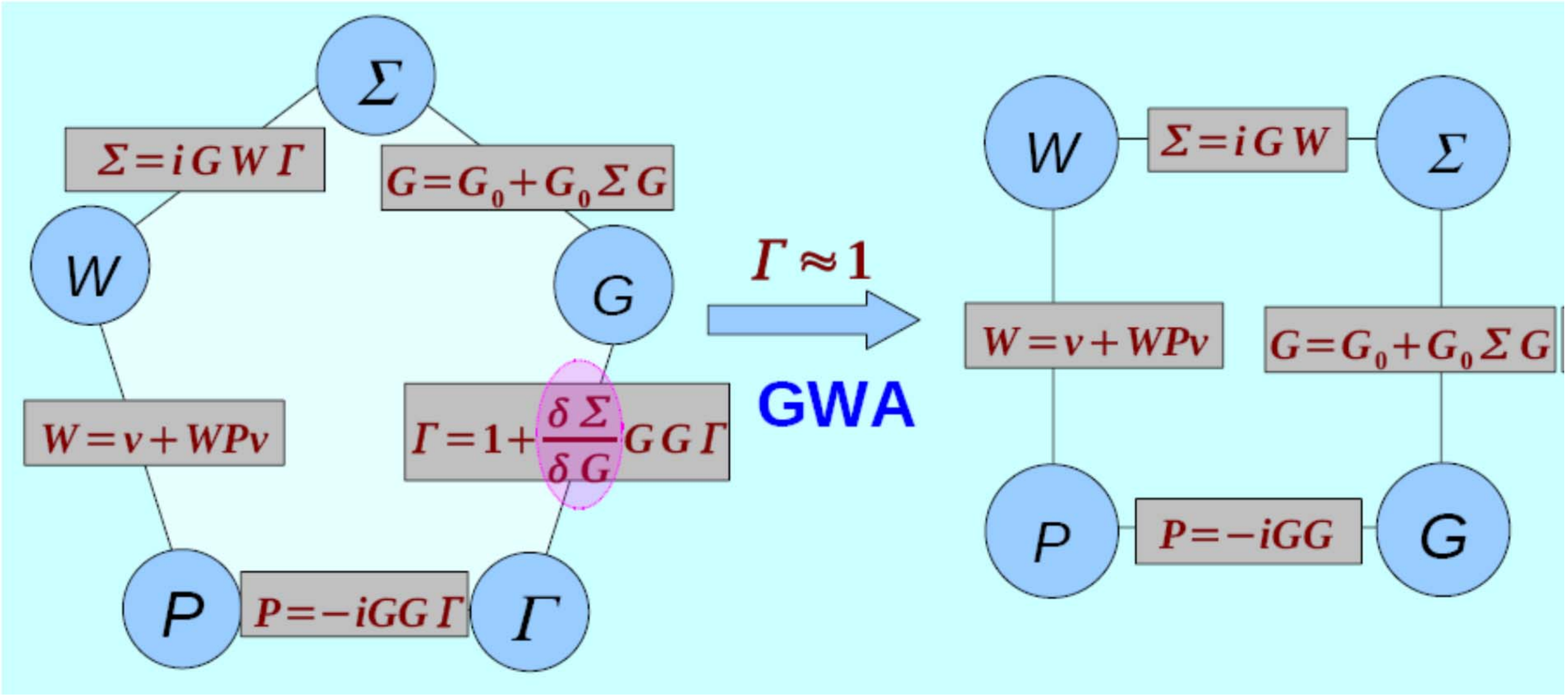
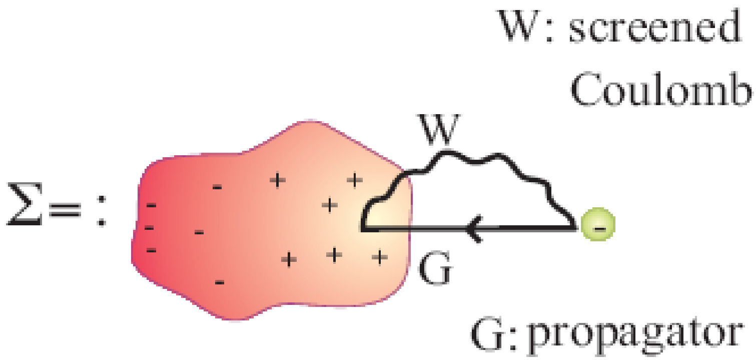
GW Approximation





"best G best W" : G_0W_0 Approximation

$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

$$G_0(\mathbf{x},\mathbf{x}';\omega) = \sum_n \frac{\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')}{\omega - \epsilon_n}$$

$$W_0(\mathbf{x},\mathbf{x}';\omega) = \int d\mathbf{x}''\varepsilon^{-1}(\mathbf{x},\mathbf{x}'';\omega)v(\mathbf{r}''-\mathbf{r}')$$

$$\varepsilon(\mathbf{x},\mathbf{x}';\omega) = 1 - \int d\mathbf{x}''v(\mathbf{r},\mathbf{r}'')P_0(\mathbf{x}'',\mathbf{x}';\omega)$$

$$P_0(\mathbf{x},\mathbf{x}';\omega) = -\frac{i}{2\pi}\int G_0(\mathbf{x},\mathbf{x}';\omega+\omega')G_0(\mathbf{x}',\mathbf{x};\omega')d\omega'$$

$$\Sigma_{\text{xc}}(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int G_0(\mathbf{r},\mathbf{r}';\omega'+\omega)W_0(\mathbf{r}',\mathbf{r};\omega')e^{i\eta\omega'}d\omega'$$

$$\mathcal{E}_n = \epsilon_n + Z_n(\epsilon_n)\Re\langle\psi_n|\Sigma(\epsilon_n) - V_{\text{xc}}|\psi_n\rangle$$

$$\equiv \epsilon_n + Z_n(\epsilon_n)\delta\Sigma_n(\epsilon_n)$$

$$Z_n(E) = \left[1 - \left(\frac{\partial}{\partial\omega}\langle\psi_n|\Sigma(\omega)|\psi_n\rangle\right)_{\omega=E}\right]^{-1}$$

Hybertsen and Louie(1985); Godby, Schlüter and Sham (1986)

Implementation: main ingredients

Polarization function

$$P_0(\mathbf{x},\mathbf{x}';\omega) = -\frac{i}{2\pi}\int G_0(\mathbf{x},\mathbf{x}';\omega+\omega')G_0(\mathbf{x}',\mathbf{x};\omega')d\omega'$$

$$= \sum_{n,m} f_n(1-f_m)\psi_n(\mathbf{x})\psi_m^*(\mathbf{x})\psi_n^*(\mathbf{x}')\psi_m(\mathbf{x}')\left\{\frac{1}{\omega-\varepsilon_m+\varepsilon_n+i\eta}-\frac{1}{\omega+\varepsilon_m-\varepsilon_n-i\eta}\right\}$$

$$\equiv \sum_{n,m} F_{nm}(\omega)\Phi_{nm}(\mathbf{x})\Phi_{nm}^*(\mathbf{x}')$$

Self-energy

$$\langle\psi_m|\Sigma_{\mathrm{xc}}(\omega)|\psi_n\rangle = \sum_k \frac{i}{2\pi}\int d\omega' \frac{\langle\psi_m\psi_k|W_0(\omega)|\psi_k\psi_n\rangle}{\omega'+\omega-\tilde{\varepsilon}_k}$$

$$\tilde{\varepsilon}_k = \varepsilon_k + i\eta\,\mathrm{sgn}(\mu-\varepsilon_k)$$

$$\langle\psi_i\psi_j|W_0(\omega)|\psi_k\psi_l\rangle = \int\int \psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')W_0(\mathbf{r},\mathbf{r}';\omega)\psi_k(\mathbf{r})\psi_l(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

Key ingredients:

- ◆ How to expand the products of two orbitals ➔ the product basis
- ◆ How to treat frequency dependency

Matrix representation

$$\epsilon_{n\mathbf{k}}^{\mathrm{qp}} = \epsilon_{n\mathbf{k}} + \left\langle \psi_{n\mathbf{k}}(\mathbf{r}) \,|\, \Re\left[\Sigma\left(\mathbf{r},\mathbf{r}';\epsilon_{n\mathbf{k}}^{\mathrm{qp}}\right)\right] - V_{\mathrm{xc}}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}') \,|\, \psi_{n\mathbf{k}}(\mathbf{r}')\right\rangle$$

Product basis: $\psi_{n\mathbf{k}}(\mathbf{r})\,\psi_{m\mathbf{k}-\mathbf{q}}^{*}(\mathbf{r}) = \sum_{i} M_{nm}^{i}(\mathbf{k},\mathbf{q})\,\chi_{i}^{\mathbf{q}}(\mathbf{r})$

$$O(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{q}}^{\mathrm{BZ}} \sum_{i,j} O_{ij}(\mathbf{q})\,\chi_{i}^{\mathbf{q}}(\mathbf{r})\left[\chi_{j}^{\mathbf{q}}(\mathbf{r}')\right]^{*}$$

$$\boldsymbol{O} = \boldsymbol{v}, \boldsymbol{P}, \boldsymbol{\varepsilon}, \boldsymbol{W}^{c}\left(\equiv \boldsymbol{W} - \boldsymbol{v}\right)$$

$$\Sigma_{n\mathbf{k}}^{\mathrm{x}} = -\frac{1}{N_c}\sum_{\mathbf{q}}^{BZ}\sum_{i,j} v_{ij}(\mathbf{q}) \sum_{m}^{\mathrm{occ}} \left[M_{nm}^{i}(\mathbf{k},\mathbf{q})\right]^{*} M_{nm}^{j}(\mathbf{k},\mathbf{q})$$

$$X_{nm}(\mathbf{k},\mathbf{q};\omega')$$

$$\Sigma_{n\mathbf{k}}^{\mathrm{c}}(\omega) = \frac{1}{N_c}\sum_{\mathbf{q}}^{\mathrm{BZ}}\sum_{m}\sum_{i,j}\frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega' \frac{\left[M_{nm}^{i}(\mathbf{k},\mathbf{q})\right]^{*} W_{ij}^{c}(\mathbf{q},\omega') M_{nm}^{j}(\mathbf{k},\mathbf{q})}{\omega + \omega' - \tilde{\varepsilon}_{m\mathbf{k}-\mathbf{q}}}$$

GW implementations

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GW approximation

From Wikipedia, the free encyclopedia

The **GW approximation** (GWA) is an approximation made in order to calculate the self-energy of a many-body system of electrons. The approximation is that the expansion of the self-energy Σ in terms of the single particle Green's function G and the screened Coulomb interaction W (in units of $\hbar = 1$)

$$\Sigma = iGW - GWGWG + \cdots$$

Software implementing the GW approximation [edit]

- ABINIT - plane-wave pseudopotential method
- BerkeleyGW - plane-wave pseudopotential method
- FHI-aims - Numeric atom-centered orbitals method
- Fiesta - Gaussian pseudopotential method
- Quantum ESPRESSO - Wannier-function pseudopotential method
- SaX - plane-wave pseudopotential method
- Spex - full-potential (linearized) augmented plane-wave (FP-LAPW) method
- TURBOMOLE - Gausssian all-electron method
- VASP - projector-augmented-wave (PAW) method
- YAMBO code - plane-wave pseudopotential method
- GAP - an all-electron GW code based on augmented plane-waves, currently interfaced with WIEN2k
- west - large scale GW
- molgw - small gaussian basis code

Implementation: the product basis (1)

- Planewaves

$$\chi_i^{\mathbf{q}}(\mathbf{r}) \rightarrow \chi_{\mathbf{G}}^{\mathbf{q}}(\mathbf{r}) \equiv \frac{1}{\sqrt{V}} \exp\left[i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}\right]$$

$$\psi_{n\mathbf{k}} = \sum_{\mathbf{G}} c_{n\mathbf{k};\mathbf{G}} \chi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) \qquad M_{nm}^{\mathbf{G}}(\mathbf{k},\mathbf{q}) = V^{-1/2} \sum_{\mathbf{G}'} C_{n\mathbf{k};\mathbf{G}'} C_{m\mathbf{k}-\mathbf{q};\mathbf{G}'-\mathbf{G}}^{*}$$

$$v_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \frac{1}{|\mathbf{q}+\mathbf{G}|}\delta_{\mathbf{G},\mathbf{G}'}. \qquad \varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}'} - \frac{4\pi}{|\mathbf{q}+\mathbf{G}\|\mathbf{q}+\mathbf{G}'|} P_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega).$$

Codes: abinit, yambo, BerkeleyGW, SaX, vasp

- Atomic-like orbitals

$$\chi_{\alpha}^{\mathbf{q}}(\mathbf{r}) = \frac{1}{N_c^{1/2}} \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{t}_\alpha)} \phi_\alpha(\mathbf{r}-\mathbf{R}-\mathbf{t}_\alpha)$$

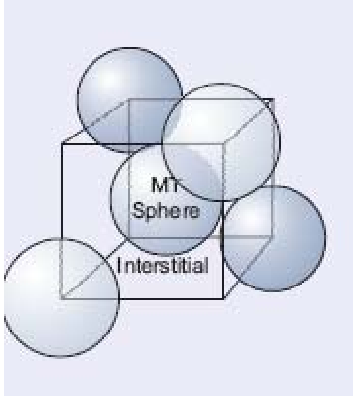
$$X(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{q}} \sum_{\alpha,\beta} \chi_{\alpha}^{\mathbf{q}}(\mathbf{r}) \langle \mathbf{X} \rangle_{\alpha\beta}(\mathbf{q}) \chi_{\beta}^{\mathbf{q}^*}(\mathbf{r}). \qquad \langle \mathbf{X} \rangle(\mathbf{q}) = \mathbf{S}^{-1}(\mathbf{q})[\mathbf{X}](\mathbf{q})\mathbf{S}_{\mathbf{q}}^{-1}(\mathbf{q})$$

$$S_{\alpha\beta}(\mathbf{q}) \equiv \int_V d\mathbf{r} \left[\chi_{\alpha}^{\mathbf{q}}(\mathbf{r})\right]^* \chi_{\beta}^{\mathbf{q}}(\mathbf{r}). \qquad [\mathbf{X}]_{\alpha\beta}(\mathbf{q}) \equiv \int_V d\mathbf{r} \int_V d\mathbf{r}' \chi_{\alpha}^{*}(\mathbf{r}) X(\mathbf{r},\mathbf{r}') \chi_{\beta}^{\mathbf{q}}(\mathbf{r}').$$

Codes: FHI-aims, FIESTA

Implementation: the product basis (2)

◆ Mixed basis



(L)APW+lo(+LO) basis

$$\phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{\zeta lm} A_{\alpha\zeta lm}(\mathbf{k}+\mathbf{G}) u_{\alpha\zeta l}(r^\alpha) Y_{lm}(\hat{r}^\alpha) & r^\alpha < R_{\mathrm{MT}}^\alpha. \\ \frac{\theta_{\mathbf{G}}^{\mathrm{LO}}}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & \mathbf{r} \in I. \end{cases}$$

$$\left\{u_{\alpha\zeta l}(r) u_{\alpha\zeta' l'}(r)\right\} \xrightarrow[|l-l'|\le L \le l+l']{l,l' \le l_{\max}^{\mathrm{MB}}} \left\{v_{NL}(r)\right\}$$

$$\chi_i^{\mathbf{q}}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{R}\alpha} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{r}_\alpha)} v_{NL}(r^\alpha) Y_{LM}(\hat{\mathbf{r}}^\alpha), & \mathbf{r} \in \text{MT spheres} \\ \frac{1}{\sqrt{V}} \sum_{|\mathbf{G}|<G_{\max}^{\mathrm{MB}}} S_{i,\mathbf{G}} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}, & \mathbf{r} \in \text{Interstitial} \end{cases}$$

Codes: GAP, SPEX

Implementation: frequency dependence

- Static approximations
  - Coulomb hole-screened exchange (COHSEX)

$$\mathrm{Re}\Sigma(\mathbf{r},\mathbf{r}';\omega) = -\sum_{n\mathbf{k}}^{occ}\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}'}(\mathbf{r}')\Re W(\mathbf{r}',\mathbf{r};\omega-\varepsilon_{n\mathbf{k}}) - \sum_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')\frac{1}{\pi}\mathcal{P}\int_0^\infty d\omega'\frac{\Im W_c(\mathbf{r}',\mathbf{r};\omega')}{\omega-\varepsilon_{n\mathbf{k}}-\omega'}$$

$$\simeq -\sum_{n\mathbf{k}}^{occ}\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}'}(\mathbf{r}')\Re W(\mathbf{r}',\mathbf{r};0) + \frac{1}{2}\delta(\mathbf{r}'-\mathbf{r})W_c(\mathbf{r},\mathbf{r}';0)$$

$$\equiv \Sigma^{\mathrm{SEX}}(\mathbf{r},\mathbf{r}') + \Sigma^{\mathrm{COH}}(\mathbf{r},\mathbf{r}')$$

- Generalized plasmon pole (GPP) model
- Full frequency treatment
  - Imaginary frequency + analytic continuation
  - real frequency Hilbert transform
  - Contour deformation

frequency treatment: GPP models

Plasmon pole model for homogeneous electron gas

$$\mathrm{Im}\,\varepsilon^{-1}(q,\omega) \approx A(q)\delta(\omega - \omega_p(q))$$

Generalized plasmon pole models

$$\mathrm{Im}\,\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = A_{\mathbf{GG'}}(\mathbf{q})\delta\left(\omega - \tilde{\omega}_{\mathbf{GG'}}(\mathbf{q})\right)$$

$$\mathrm{Re}\,\varepsilon^{-1}(\mathbf{q},\omega) = \mathbf{1} + \frac{2}{\pi}\mathcal{P}\int_0^\infty d\omega' \frac{\omega'\,\mathrm{Im}\,\varepsilon^{-1}(\mathbf{q},\omega)}{\omega'^2 - \omega^2} = \delta_{\mathbf{GG'}} + \frac{2}{\pi}\frac{\tilde{\omega}_{\mathbf{GG'}}(\mathbf{q})A_{\mathbf{GG'}}(\mathbf{q})}{\tilde{\omega}^2_{\mathbf{GG'}}(\mathbf{q}) - \omega^2}.$$

- **Hybertsen-Louie (HL) model**
- **Godby-Needs (GN) model**
- von der Linden-Horsch (vdLH) model
- Engel-Farid model

frequency treatment : Hybertsen-Louie model

$$\mathrm{Im}\,\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = A_{\mathbf{GG'}}(\mathbf{q})\delta\left(\omega - \tilde{\omega}_{\mathbf{GG'}}(\mathbf{q})\right)$$

Two parameters for each G, G' are determined by

1) Static dielectric function ω=0

2) The *f*-sum rule

$$\int_0^\infty \omega\,\mathrm{Im}\,\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega)d\omega = -\frac{\pi}{2}\Omega^2_{\mathbf{GG'}}(\mathbf{q})$$

$$\Omega^2_{\mathbf{GG'}}(\mathbf{q}) = \frac{4\pi(\mathbf{q}+\mathbf{G})\cdot(\mathbf{q}+\mathbf{G'})}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G'}|}\rho(\mathbf{G}-\mathbf{G'})$$

$$A_{\mathbf{GG'}}(\mathbf{q}) = \frac{\pi}{2}\left[\delta_{\mathbf{GG'}} - \varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},0)\right]^{1/2}|\Omega_{\mathbf{GG'}}|$$

$$\tilde{\omega}_{\mathbf{GG'}}(\mathbf{q}) = \frac{|\Omega_{\mathbf{GG'}}|}{\left[\delta_{\mathbf{GG'}} - \varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},0)\right]^{1/2}}$$

frequency treatment : the GN model

$$\mathrm{Im}\,\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega) = A_{\mathbf{GG}'}(\mathbf{q})\delta\left(\omega - \tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})\right)$$

Two parameters for each G, G' are determined by

1) Static dielectric function $\omega=0$

2) Inverse dielectric at a chosen imaginary frequency, $\omega = i\omega_p$

$$A_{\mathbf{GG}'}(\mathbf{q}) = \frac{\pi}{2}\omega_p^{1/2}\left[\left(\delta_{\mathbf{GG}'} - \varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},0)\right)\left(\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},0) - \varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},i\omega_p)\right)\right]^{1/2}$$

$$\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q}) = \omega_p^{1/2}\left[\frac{\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},0) - \varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},i\omega_p)}{\delta_{\mathbf{GG}'} - \varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},0)}\right]^{1/2}$$

frequency dependence: IF+AC approach

- Imaginary frequency plus analytic continuation (IF-AC)

$$P_{ij}(\mathbf{q},iu) = 2\sum_{\mathbf{k}}^{BZ}\sum_{n}^{occ}\sum_{m}^{unocc} \frac{-2(\varepsilon_{n\mathbf{k}}-\varepsilon_{n\mathbf{k}-\mathbf{q}})}{u^2+(\varepsilon_{n\mathbf{k}}-\varepsilon_{n\mathbf{k}-\mathbf{q}})^2} \times M_{nm}^{i}(\mathbf{k},\mathbf{q})\left[M_{nm}^{j}(\mathbf{k},\mathbf{q})\right]^*$$

$$\Sigma_{n\mathbf{k}}^{c}(iu) = \sum_{\mathbf{q}}^{BZ}\sum_{m}\int_0^\infty \frac{du'}{2\pi}\frac{2\left(\varepsilon_{m\mathbf{k}-\mathbf{q}}-iu\right)X_{nm}(\mathbf{k},\mathbf{q};iu')}{u'^2+\left(\varepsilon_{m\mathbf{k}-\mathbf{q}}-iu\right)^2}.$$

$$\Sigma_{n\mathbf{k}}^{c}(iu) = \sum_{p}^{N_\mathrm{p}}\frac{a_{p;n\mathbf{k}}}{iu-b_{p;n\mathbf{k}}}$$

$$\Sigma_{n\mathbf{k}}^{c}(\omega) = \sum_{p}^{N_\mathrm{p}}\frac{a_{p;n\mathbf{k}}}{\omega-b_{p;n\mathbf{k}}}$$

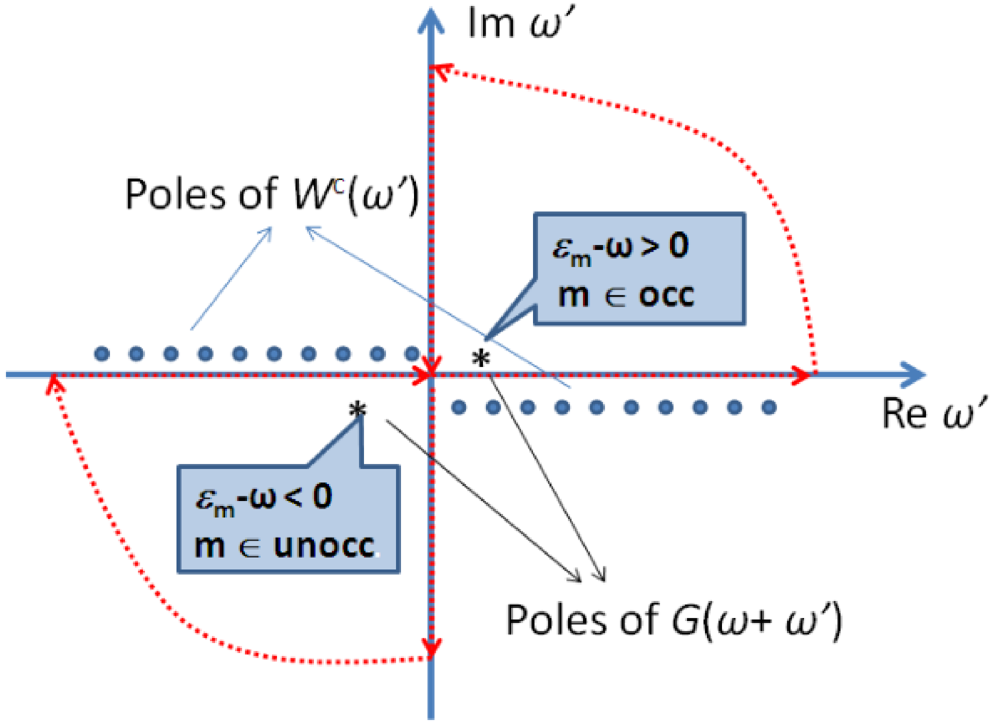
frequency dependence : the CD approach

◆ Contour deformation (CD) approach

$$\Sigma_n^{\mathrm{c}}(\omega) = \sum_m \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \frac{X_{nm}(\omega')}{\omega+\omega'-\varepsilon_m - i\eta\,\mathrm{sgn}(\varepsilon_{\mathrm{F}}-\varepsilon_m)}.$$

$$\Sigma_n^{\mathrm{c}}(\omega) = \sum_m \int_0^{\infty} \frac{du}{2\pi} X_{nm}(iu)\frac{2(\varepsilon_m-\omega)}{(\varepsilon_m-\omega)^2+u^2}$$

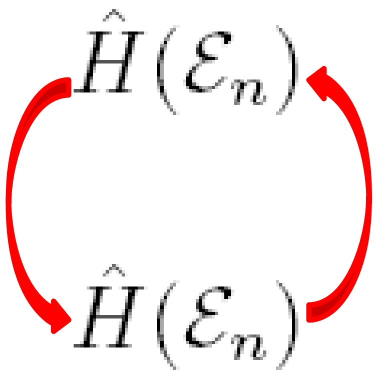
$$+X_{nm}(\varepsilon_m-\omega)[\theta(\varepsilon_m-\varepsilon_{\mathrm{F}})\theta(\omega-\varepsilon_m)-\theta(\varepsilon_{\mathrm{F}}-\varepsilon_m)\theta(\varepsilon_m-\omega)]$$



Self-consistency: full vs approximate SCGW

$$\hat{H}(\mathcal{E}_n)\,|\Psi_n\rangle \equiv \left[\hat{H}_0 + \hat{\Sigma}(\mathcal{E}_n)\right]|\Psi_n\rangle = \mathcal{E}_n\,|\Psi_n\rangle$$

Full SCGW



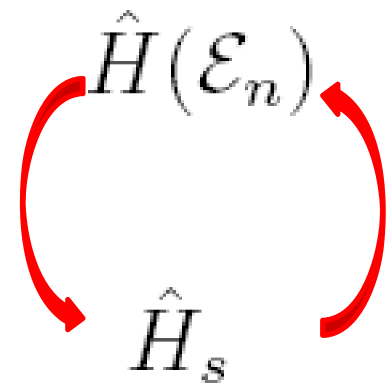
$$\hat{H}_s\,|\psi_\nu\rangle = \epsilon_\nu\,|\psi_\nu\rangle$$

$$|\Psi_n\rangle = \sum_\nu C_{\nu n}\,|\psi_\nu\rangle$$

$$\sum_\nu \left[H_{\mu\nu}(\mathcal{E}_n) - \mathcal{E}_n\delta_{\mu\nu}\right] C_{\nu n} = 0$$

$$H_{\mu\nu}(\mathcal{E}_n) = \langle\psi_\mu|\,\hat{H}_0\,|\psi_\nu\rangle + \Sigma_{\mu\nu}(\mathcal{E}_n)$$

Approx. SCGW



Faleev-van Schilfgaarde-Kotani (QSGW) scheme (PRL 2004)

$$\hat{H}_s \Rightarrow \overline{H}^{(i)}_{\mu\nu} \equiv \langle\psi_\mu|\,\hat{H}_0\,|\psi_\nu\rangle + \frac{1}{2}\left[\overline{\Sigma}_{\mu\nu}(\epsilon_\mu) + \overline{\Sigma}_{\mu\nu}(\epsilon_\nu)\right]$$

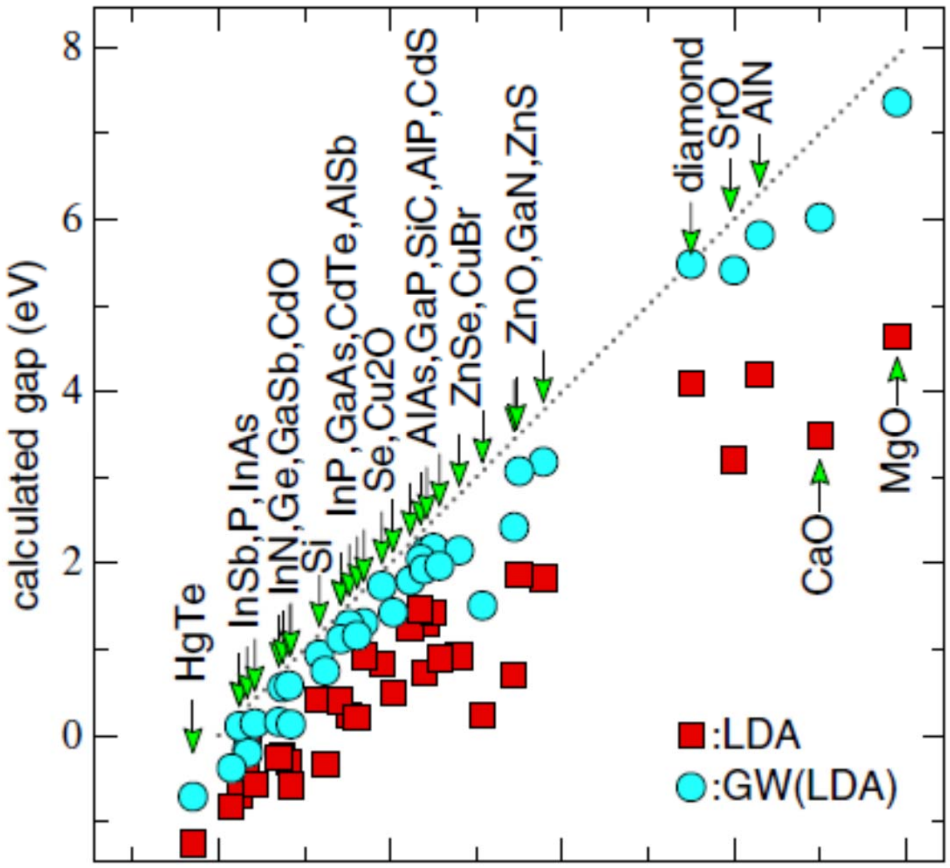
Main technical parameters in *GW* implementation

- Parameters for KS DFT:
  - pseudopotentials, PAW or LAPW?
  - basis for Kohn-Sham orbitals
- Quality of product basis
- Number of unoccupied states considered (P & Σ_c)
- The integration in the Brillouin zone: the number of **k**/**q**-points
- The frequency treatment and related parameters

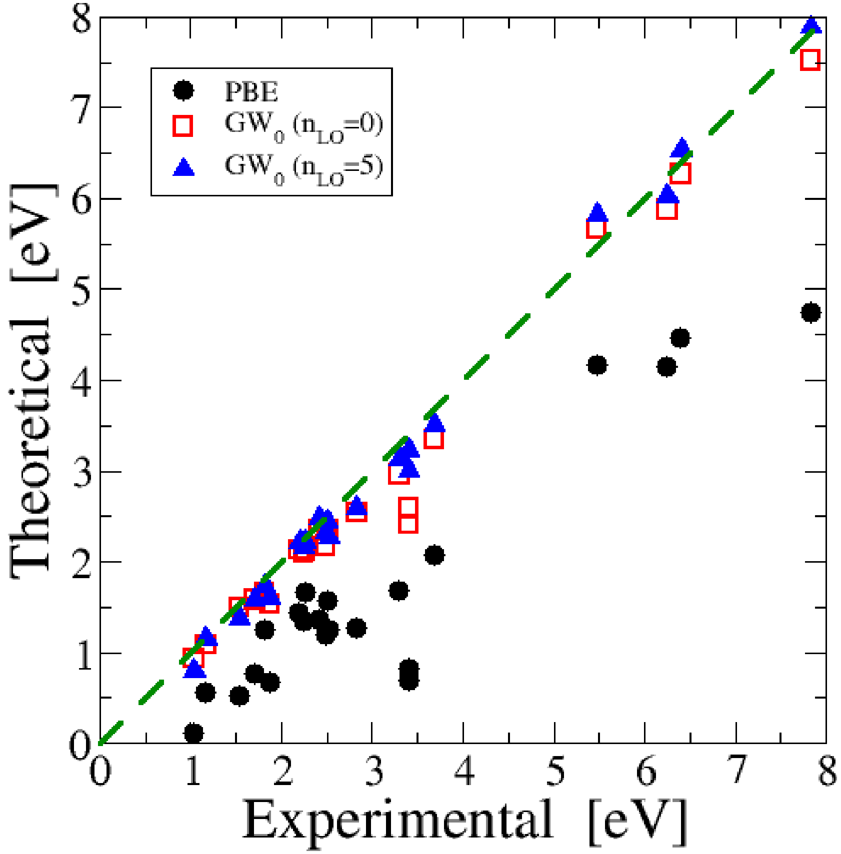
H. Jiang, *Front. Chem. China* 6(4): 253–268 (2011)

Examples for applications of the *GW* approach

Band gaps of semiconductors

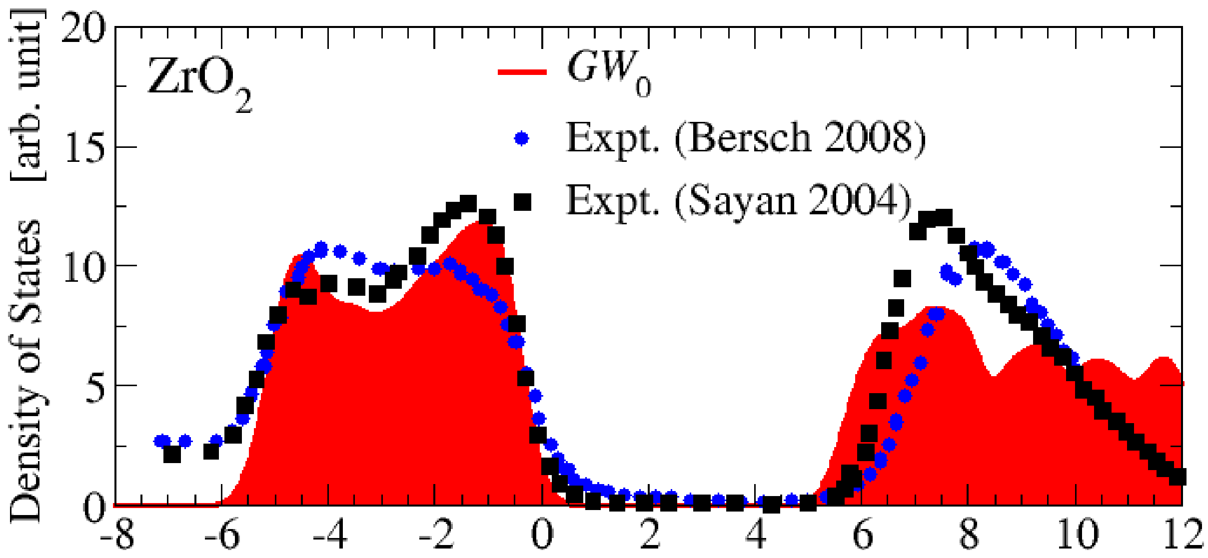


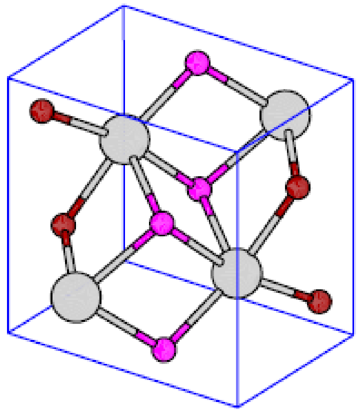
M. van Schilfgaarde et al. PRL 96, 226402 (2006)

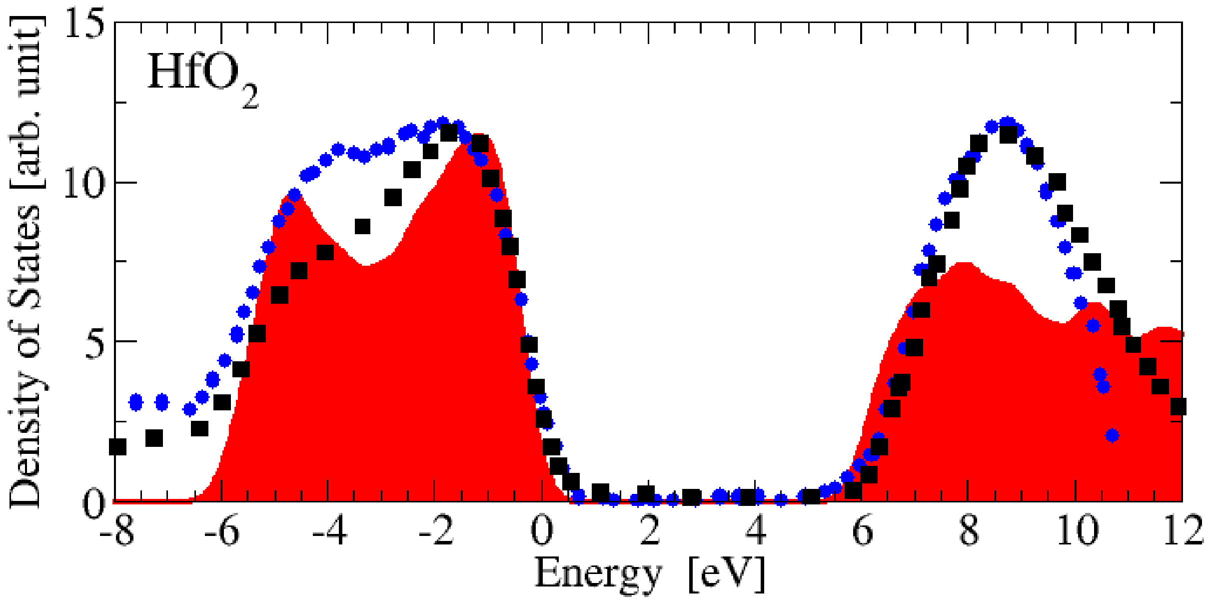


H. Jiang: *GW* with HLOs-enhanced LAPW (unpublished)

GW_0@LDA for ZrO_2 and HfO_2

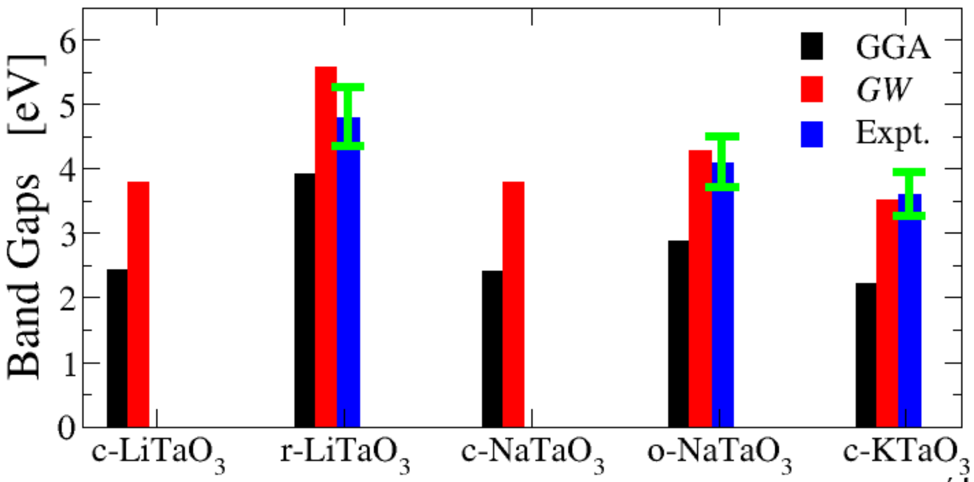


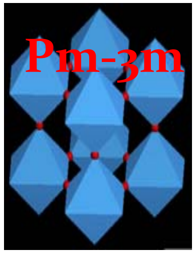


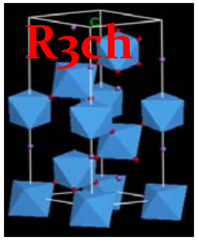


Jiang, H. *et al. Phys. Rev. B* **81**, 085119 (2010)

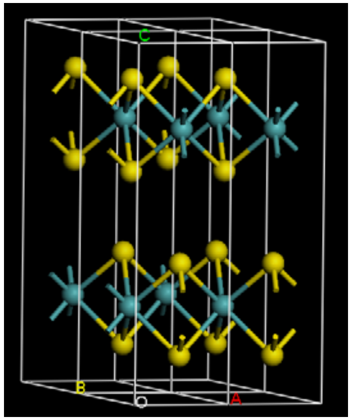
Band gaps of MX_2 and $ATaO_3$

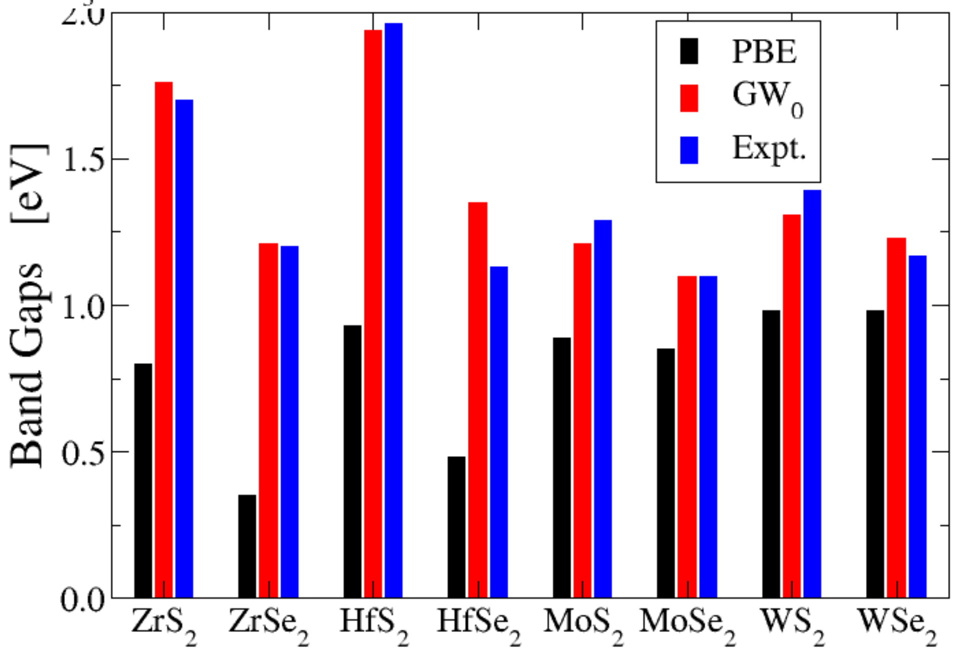






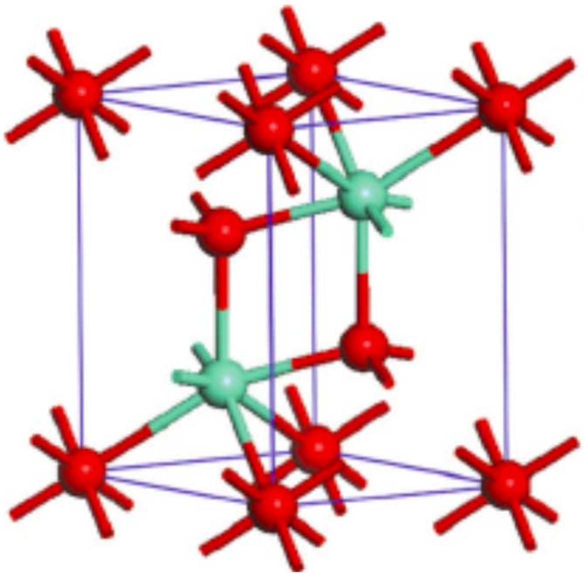
H. Wang, F. Wu and H. Jiang, *J. Phys. Chem. C*, **115**, 16180, (2011)

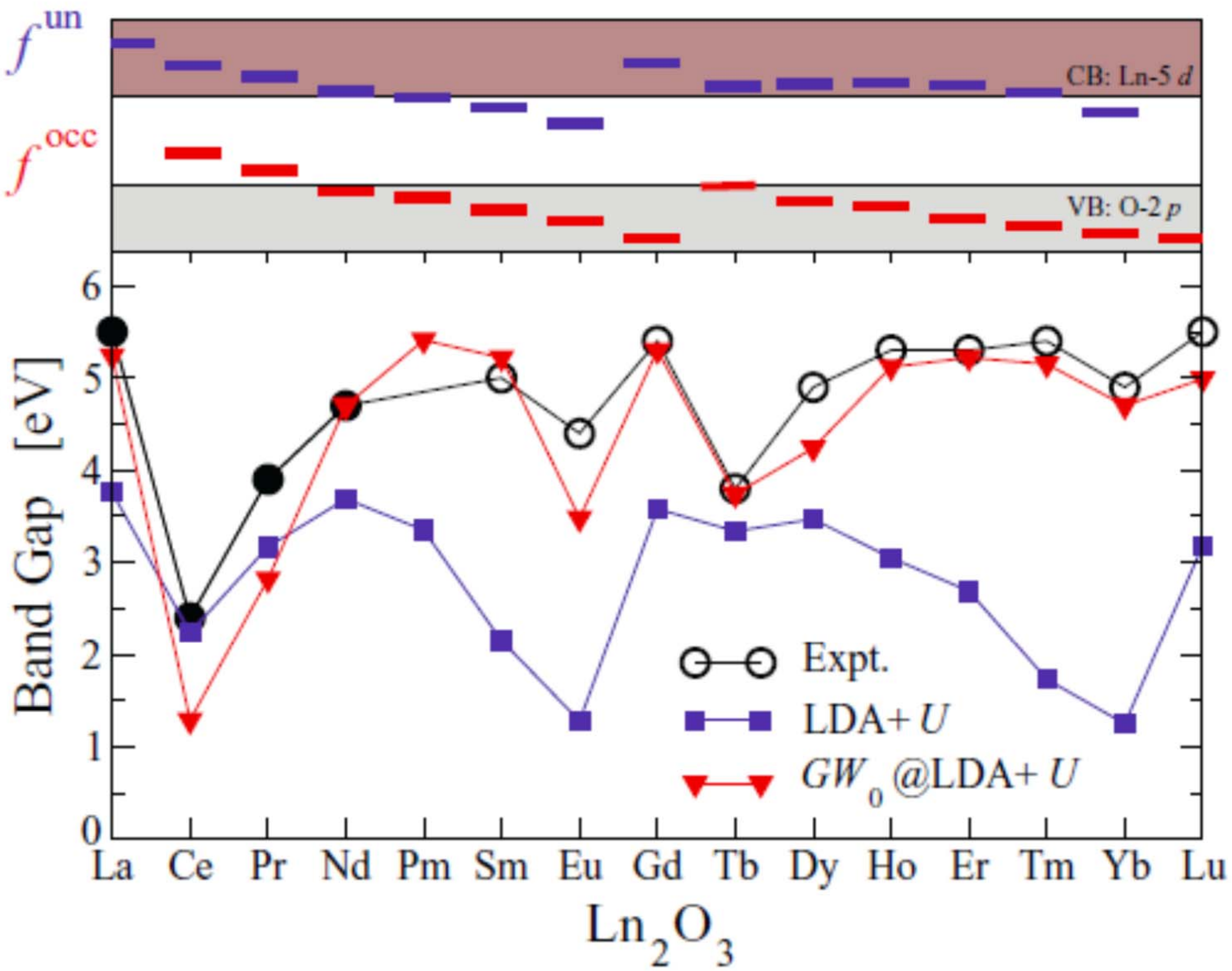




Jiang, H., *J. Chem. Phys* , **134**, 204705 (2011);
Jiang, H. *J. Phys. Chem. C*, **116**, 7664 (2012).

Ln_2O_3 band gaps: GW_0@LDA+U vs Expt.

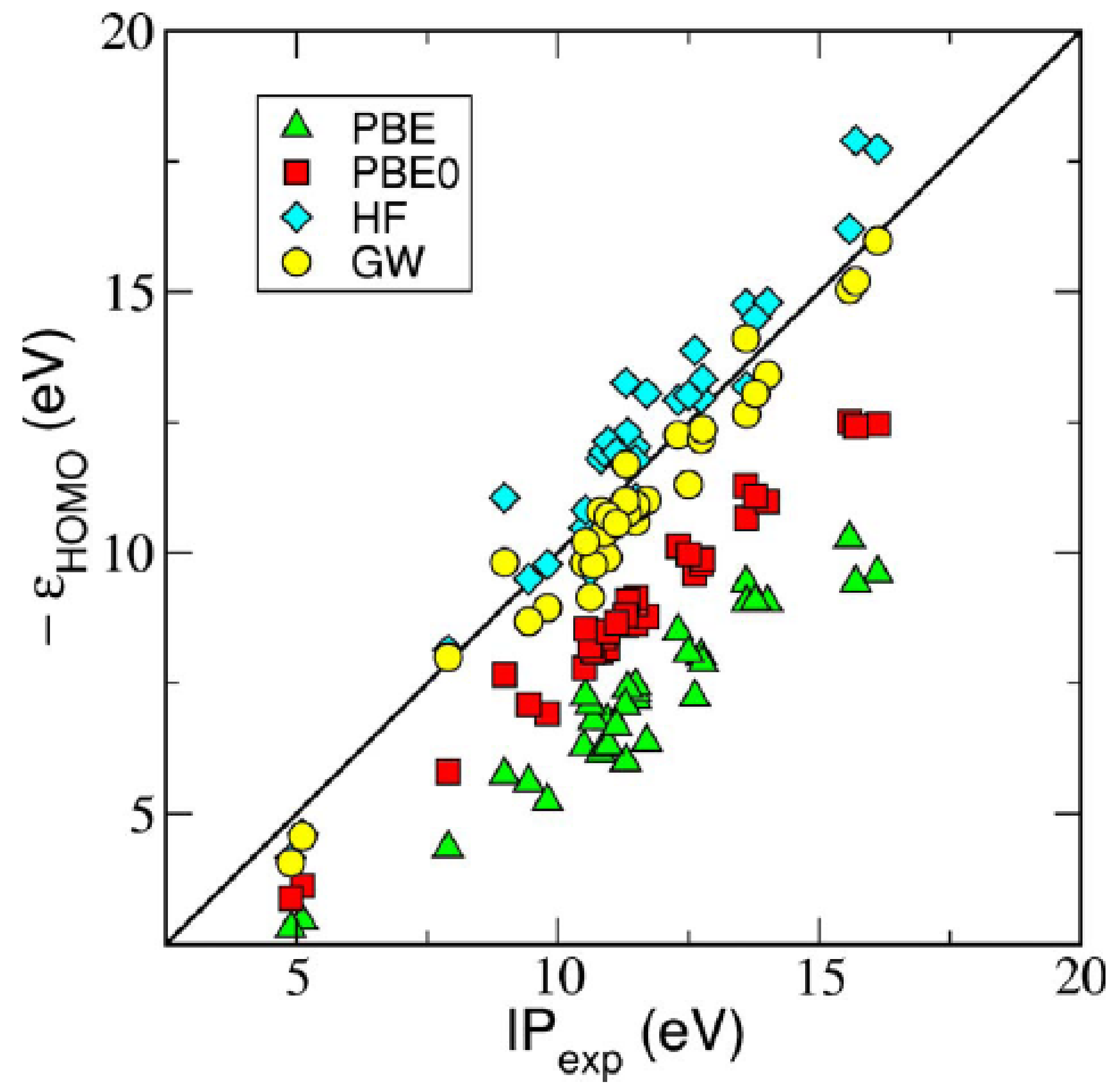




H. Jiang *et al*. **Phys. Rev. Lett. 102**, 126403(2009);

Phys. Rev. B **86**, 125115(2012).

Fully self-consistent *GW* for molecules



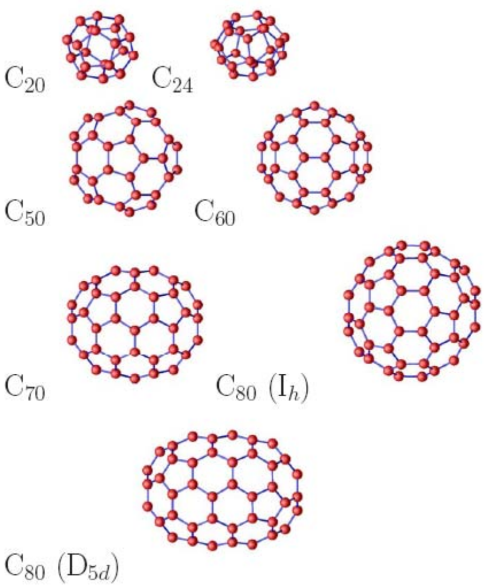
Rostgaard, Jacobsen and Thygesen, PRB 81, 085103 (2010)

GW for fullerenes

THE JOURNAL OF CHEMICAL PHYSICS **129**, 084311 (2008)

Neutral and charged excitations in carbon fullerenes from first-principles many-body theories

Murilo L. Tiago,[1,a)] P. R. C. Kent,[1] Randolph Q. Hood,[2] and Fernando A. Reboredo[1]



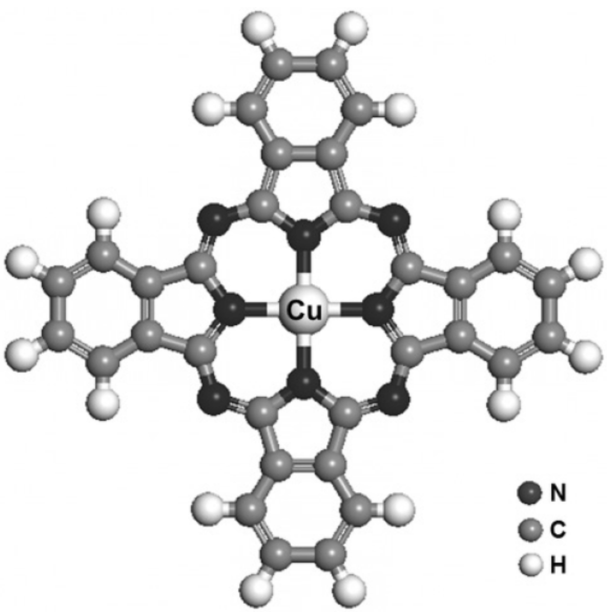
	ΔSCF-DFT	QMC	GW_0	GW_f	$scGW_f$	Expt.
	7.31	7.27(11)	7.99	7.35	7.41	
	7.77	7.70(10)	8.49	7.86	7.81	
	7.29	7.29(14)	7.97	7.33	7.35	7.61[a]
C_{60}	7.61	7.86(11)	8.22	7.70	7.86	7.6[b]
C_{70}	7.54	7.69(12)	8.12	7.53	7.45	7.47[c]
C_{80} (D_{5d})	6.67	6.30(10)	7.24	6.59	6.65	6.84[a]
C_{80} (I_h)	6.86	6.91(10)	7.45	6.90	6.95	
Average error	−0.10	−0.09	0.51	−0.09	−0.05	
Root mean square error	0.18	0.36	0.52	0.20	0.21	

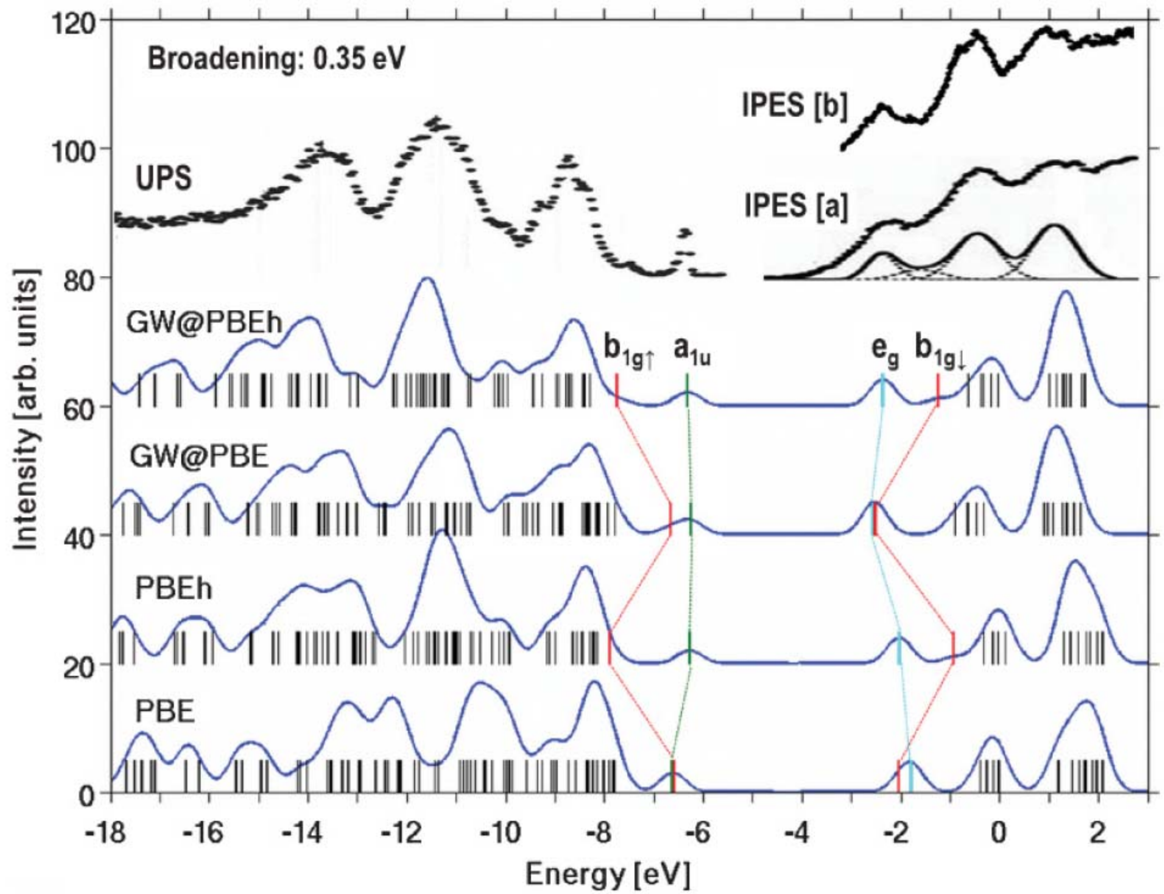
GW for CuPc

PHYSICAL REVIEW B **84**, 195143 (2011)

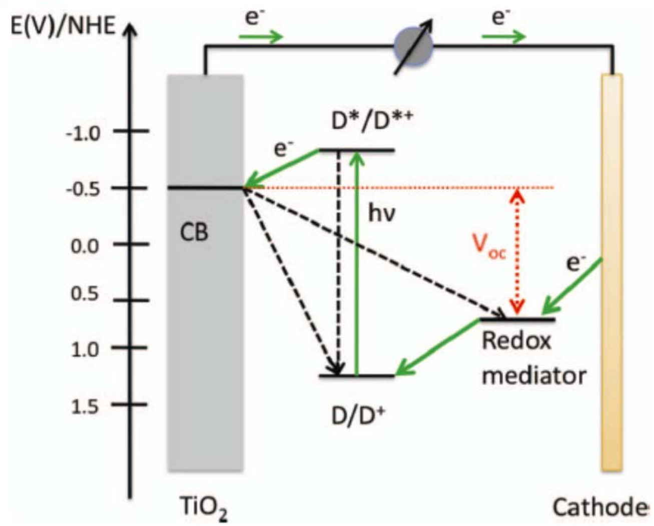
Electronic structure of copper phthalocyanine from G_0W_0 calculations

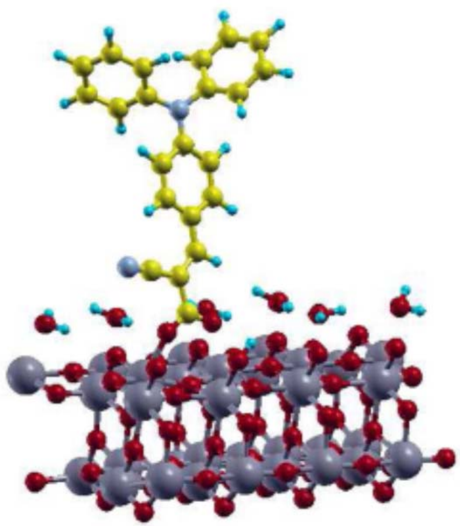
Noa Marom,[1,*] Xinguo Ren,[2] Jonathan E. Moussa,[1] James R. Chelikowsky,[1,3] and Leeor Kronik[4]

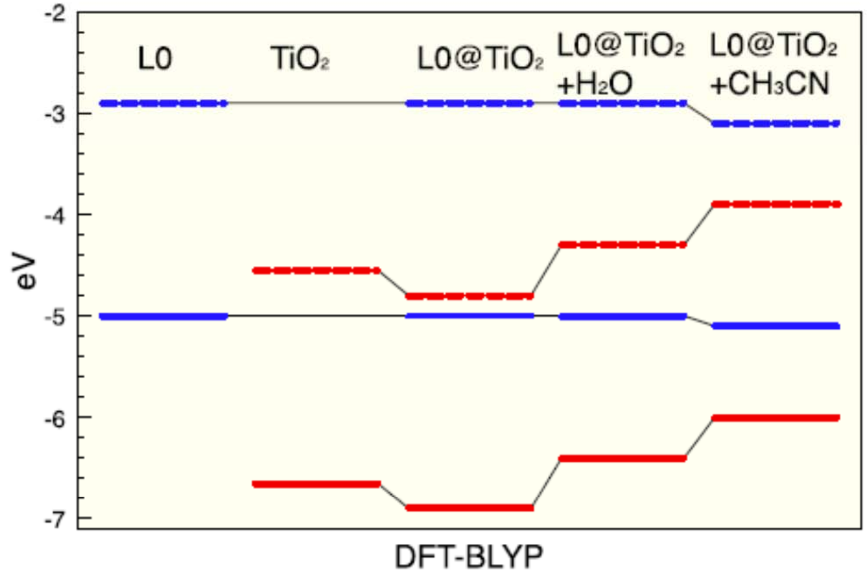


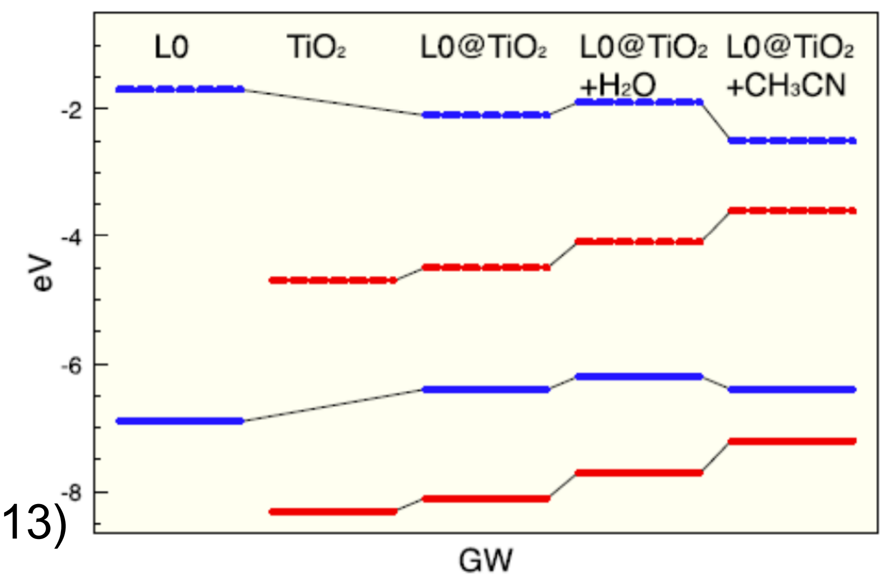


Level alignment in dye-sensitized solar cells









P. Umari et al. J. Chem. Phys. 139, 014709 (2013)
C. Verdi et al, Phys. Rev. B 90, 155410 (2014)