Introduction to Correlated systems

Questaal Hands-On Workshop, May 2017

- The hard problem of correlated electrons
- Introduce quasiparticles, elements in one-particle theory, partitioning of the hamiltonian to frame many-body theory
- How to build 1-particle hamiltonian. Elements of Hartree Fock and Density-Functional theory.
- What screening is, how to calculate it.
- The GW approximation as extension of Hartree Fock
- Quasiparticle Self-Consistency: importance and justification.
- Formulate the many-body problem in a subspace

Many Body Hamiltonian

Schroedinger's equation

$$H = T_{\text{el}} + T_{\text{nuc}} + V_{\text{el-el}} + V_{\text{el-nuc}} + V_{\text{nuc-nuc}}$$

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_I \frac{P_I^2}{2M_I} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iI} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

has a pairwise interaction ⇒ inherently many-body.

- Easy if H separates into $V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2) + \ldots V_N(\mathbf{r}_N)$ ⇒ Ψ would factor into a product of w.f. for independent electrons: i.e.

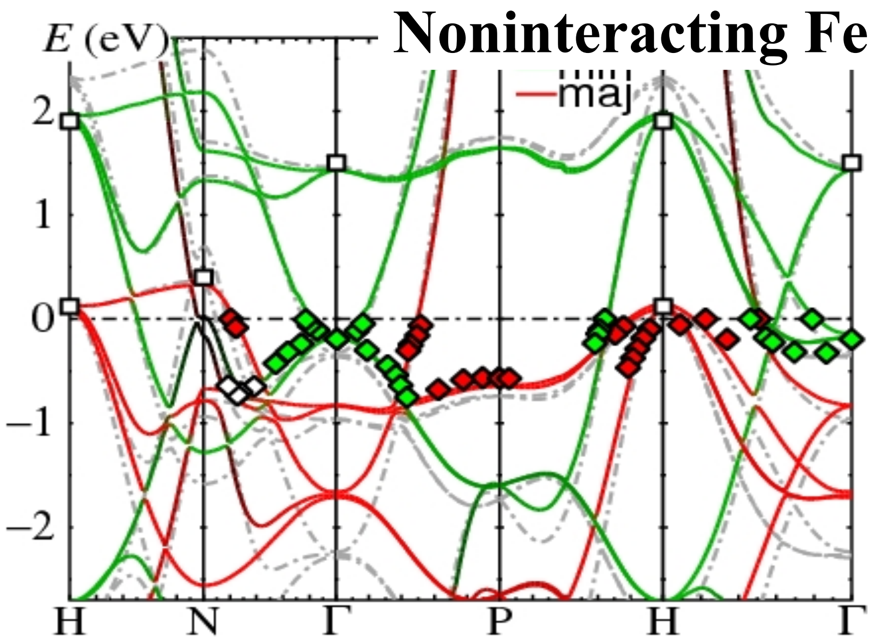
$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \rightarrow \psi_1(\mathbf{r}_1) \times \psi_2(\mathbf{r}_2) \times \ldots \times \psi_N(\mathbf{r}_N)$$

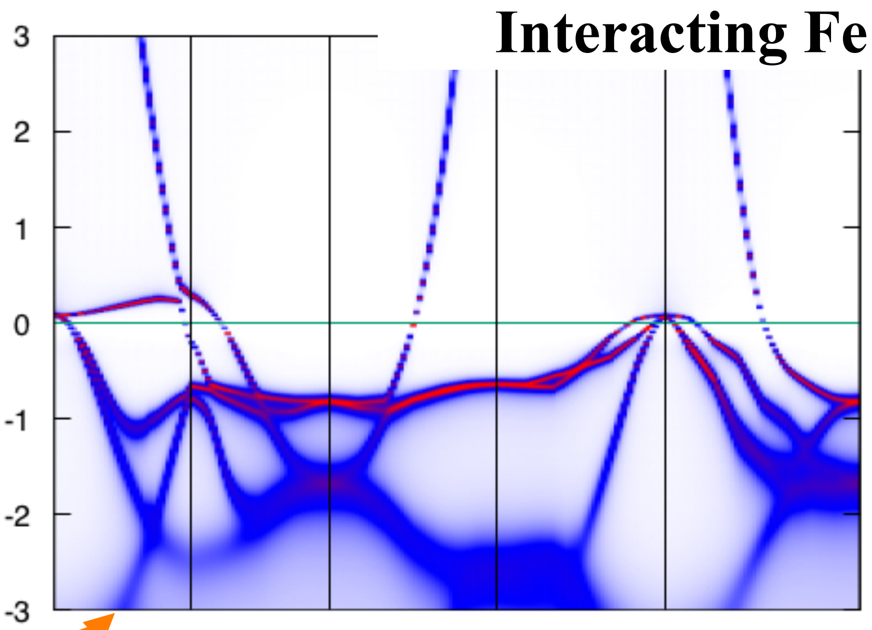
- If the pair interaction were weak, the deviation from an independent-particle description would not be large, and we could use perturbation theory.
- But the coulomb interaction $v_{ij} = e^2/|\mathbf{r}_i - \mathbf{r}_j|$ is large and long-ranged ($e^2 = 14.4$ eV-A). Also the nuclei

Quasiparticles

- Resolution: each e^- contributes some effective external field V^{eff} to the entire system. The nuclei + e^- both generate V^{eff} and are governed by it. All e^- move in the presence of V^{eff}.
- Quasiparticles (Landau): a "particle," e.g. electron, is "dressed" by a cloud of other "stuff" (e^- or maybe nuclei). The cloud strongly screens v : the renormalized v is much smaller than the bare one.
- Quasiparticles behave as though they are nearly independent of each other with residual interactions ⇒ quasiparticles decay after finite time. Lifetime cannot be too short if QP picture is meaningful.
- When correlations become strong, the QP picture fails.
  - Even so, theories for strong correlations start from an independent particle description as a basis set.
  - Typically only a part of the entire system is strongly correlated. For a workable scheme we partition H.

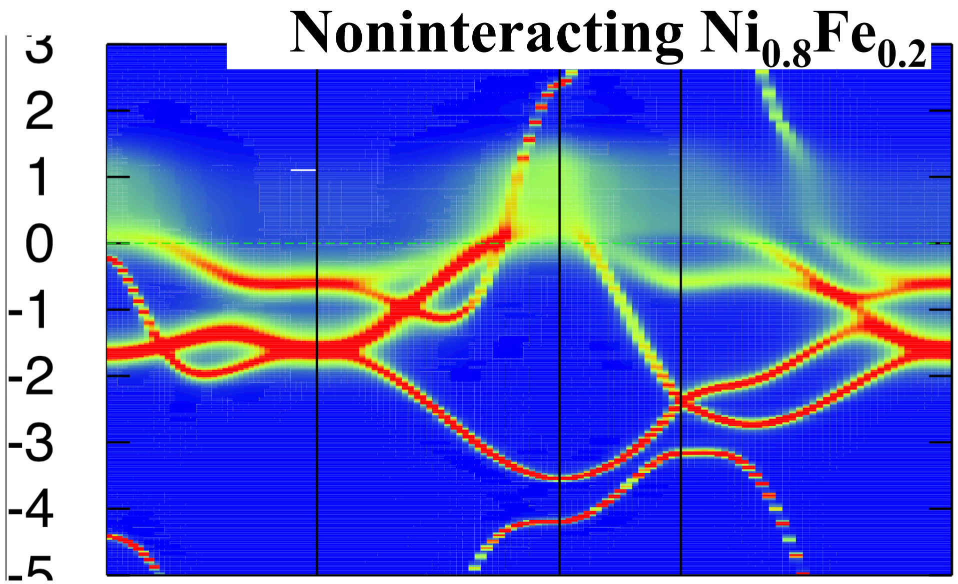
Scattering smears out Quasiparticle Levels


Noninteracting Fe


Interacting Fe

Broadening from $e^- - e^-$ interactions

Broadening from alloy scattering


Noninteracting $Ni_{0.8}Fe_{0.2}$

No unique definition of noninteracting hamiltonian.

Going Beyond the 1-particle Picture

See book by Richard Martin, Lucia Reining and David Ceperly.

Many Body Perturbation Theory (GW, FLEX).

☑ Good for weak and moderate correlations
☒ Extending beyond the lowest order is a formidable task
☒ Even if we could, it may not converge to the proper solution for strong correlation (diagrammatic Monte Carlo, Kozik et al, Phys Rev Lett 114, 156402)

But … for only a few degrees of freedom (e.g. d orbitals on some transition metals) are correlations strong.

Nonperturbative Solution on subspace (DMFT)

☑ Select a subspace to handle at a higher level of approximation.
☒ Requires a partitioning where local, correlated subsystem are treated differently … ambiguities result
☒ Work on Matsubara (imaginary frequency) axis

Partitioning the Hamiltonian

How to *decide* on what the subsystem should be is a subtle (and not fully resolved) issue, which we will return to later.

Some general considerations:

Partition a Hamiltonian H into "Subsystem" and "Rest."

$$H = \begin{pmatrix} H_{ss} & H_{sr} \\ H_{rs} & H_{rr} \end{pmatrix}$$

Spectrum from eigenvalues of H

$$\begin{pmatrix} H_{ss} & H_{sr} \\ H_{rs} & H_{rr} \end{pmatrix} \begin{pmatrix} \phi_s \\ \phi_r \end{pmatrix} = \omega \begin{pmatrix} \phi_s \\ \phi_r \end{pmatrix}$$

ϕ_s and ϕ_r are related by: $\phi_r = (H_{rr} - \omega) H_{rs} \phi_s$

Substitute this relation to obtain an equation for ϕ_s alone:

$\hat{H}_{ss}(\omega)\phi_s = \omega\phi_s$ where $\hat{H}_{ss} = H_{ss} - H_{sr}(H_{rr} - \omega)H_{rs}$

* Note that $\hat{H}$ is ω- dependent, even if H is not.

Partitioning the Green's function

The Green's function is related to the inverse of *H*.

$$\begin{pmatrix} \omega - H_{ss} & H_{sr} \\ H_{rs} & \omega - H_{rr} \end{pmatrix} \begin{pmatrix} G_{ss} & G_{sr} \\ G_{rs} & G_{rr} \end{pmatrix} = I$$

The poles of G coincide with the eigenvalues of *H*.

Use the same trick as before to obtain an expression for G_{ss}

$$G_{ss}(\omega) = [\omega - H_{ss} - H_{sr}(H_{rr} - \omega)H_{rs}]^{-1}$$

Write as $G_{ss} = [(G^0_{ss})^{-1} - H_{sr} G^0_{rr} H_{rs}]^{-1}$ **where** $\begin{cases} G^0_{ss}(\omega) = [\omega - H_{ss}]^{-1} \\ G^0_{rr}(\omega) = [\omega - H_{rr}]^{-1} \end{cases}$

Call the interaction with the rest a *self-energy* Σ_{rest} :

$G_{ss} = [(G^0_{ss})^{-1} - \Sigma_{\text{rest}}(\omega)]^{-1}$ **where** $\Sigma_{\text{rest}} = H_{sr} G^0_{rr} H_{rs}$

Called a *self-energy* because the subsystem interacts with itself by its interactions with the rest of the system.

Some observations

$G_{ss} = [(G^0_{ss})^{-1} - \Sigma_{\mathrm{rest}}(\omega)]^{-1}$ where $\Sigma_{\mathrm{rest}} = H_{sr} G^0_{rr} H_{rs}$

Σ_{rest} "dresses" the subsystem through an ω-dependent interaction with the "rest."

G can be also be written as a Dyson equation $G_{ss} = G^0_{ss} + G^0_{ss}\Sigma_{\mathrm{rest}} G_{ss}$

Subsystems

The full many-body Hamiltonian is ω-independent. The noninteracting, or 1-body Green's approximation to it may be thought of as the "rest" and the residual interactions form the subsystem. Σ_{rest} is ω- dependent and "dressing" the electron from screening by the other electrons.

We cannot solve the full problem exactly, and must make approximations. The smaller Σ_{rest} is (especially, the smaller its ω- dependence), the better the approximation.

Mixed Approximations

The Dyson form is particularly useful because we can partition Σ as a sum $\Sigma = \Sigma^{(1)} + \Sigma^{(2)}$. The Dyson equation can be carried out in two steps

$$G^{(1)} = G^{(0)} + G^{(0)}\Sigma^{(1)}G^{(1)}$$

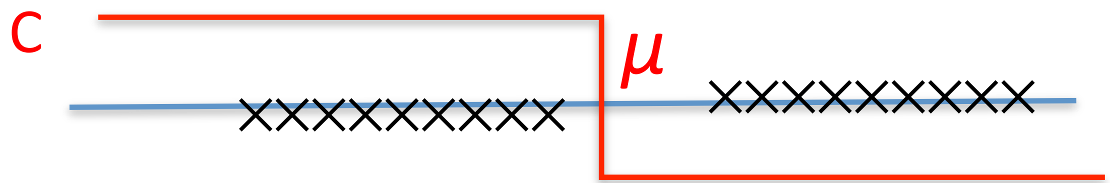
$$G^{(2)} = G^{(1)} + G^{(1)}\Sigma^{(2)}G^{(2)}$$

- $\Sigma^{(1)}$ can be a low-level approximation, e.g. Hartree Fock, GW, or Density-Functional theory applied all the electrons, carried out self-consistently; and $\Sigma^{(2)}$ a high-level theory (DMFT or a higher-order diagrammatic method), on a subspace.
- DMFT may be thought of as a (nearly) exact method of obtaining $G^{(2)}$ for a given $G^{(1)}$ (all the local graphs are summed).
- The better $\Sigma^{(1)}$ is, the weaker the feedback. If good enough, then it may *not* need be updated. This of course depends on the quality of $\Sigma^{(1)}$.

Spectral representation of G_0

Construct G_0 from eigenfunctions of H_0 :

$$G_0(\mathbf{x},\mathbf{x}',\omega)=\sum_s \frac{f_s(\mathbf{x})f_s^*(\mathbf{x}')}{\omega-\varepsilon_s+\underline{i\,\mathrm{sgn}(\varepsilon_s-\mu)\delta}}$$



Poles below E_F in bottom half of complex plane; poles above in top half.

The Spectral weight function defined:

$$A(\mathbf{x},\mathbf{x}',\omega)=\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')\delta(\omega-\varepsilon_s)$$

Easy to show that A and G are related

A is the density-of-states

$$A(\mathbf{x},\mathbf{x}',\omega)=\frac{1}{\pi}|\operatorname{Im}G(\mathbf{x},\mathbf{x}',\omega)|$$

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

Meaning of Quasiparticles, Interacting Case

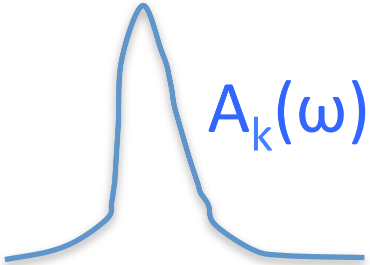
Project *G* onto 1-particle states $G_{kk'}(\omega) = \langle \psi_k(\mathbf{x}) | G(\mathbf{x},\mathbf{x}',\omega) | \psi_{k'}(\mathbf{x}') \rangle$

If non-interacting particles, $f_s(x) \longrightarrow \psi_k(x)$ and then $A_{kk}(\omega) = \delta(\varepsilon_k - \omega)$

But interacting Green's function includes self-energy

$$G_{kk}(\omega) = \sum_s \frac{1}{\omega - \varepsilon_k - \Sigma_k(\omega)}$$

This broadens out the sharp pole



Example: $\Sigma_k(\omega) = \Delta_k - i\Gamma_k$

$$G_k(t) = -i \exp\left[-i(\epsilon_k + \Delta_k)t\right] \exp\left(-\Gamma_k t\right)$$

Energy of excitation shifts from non-interacting ε_k

and decays: finite lifetime

Introduction to the Hybridization function

To see how a subsystem interacts with a host, consider a simple noninteracting case.

Let the subsystem be a single state with energy ε_s coupled to a set of states $m=1\ldots N$ with eigenvalues ε_m . State s couples to state m with hopping matrix element H_{sm}.

… H_{ss} (G_{ss}) is a 1×1 matrix, while H_{sm} (G_{sm}) is a $1\times N$ matrix.

Using the coupled-G formalism, we obtain

$$\begin{aligned}(\omega-\varepsilon_s)G_{ss}-\sum_m^N H_{sm}G_{ms} &= 1\\ (\omega-\varepsilon_m)G_{ms}-H_{sm}G_{ss} &= 0\end{aligned}$$

And

$$G_{ss}(\omega)=\frac{1}{(\omega-\varepsilon_s-\Sigma_{\text{rest}}(\omega))}$$

with

$$\Sigma_{\text{rest}}(\omega)=\sum_m^N\frac{H_{sm}H_{ms}}{\omega-\varepsilon_s}$$

Σ_{rest} is the effect of the "rest" on to the subsystem. In in Dynamical Mean Field theory, Σ_{rest} is denoted as the "hybridization function" Δ.

Effect of the Hybridization function

Δ is a special instance of Σ_{rest} where the subsystem couples to a noninteracting bath. In general the bath need not be interacting, but it is usually taken to be so in practice.

Write

$$G_{ss}(\omega) = \frac{1}{(\omega - \varepsilon_s - \Delta(\omega))}$$

with

$$\Delta(\omega) = \sum_m^N \frac{H_{sm} H_{ms}}{\omega - \varepsilon_s}$$

Suppose "rest" is a single-band tight-binding model with hopping matrix element $H_{sm}=t$. Δ becomes

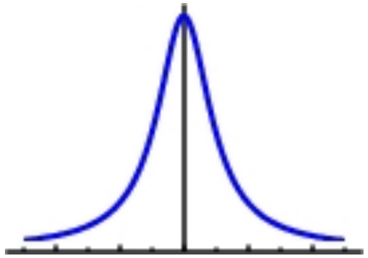
$$\Delta(\omega) = \left|t^2\right| \int d\varepsilon \, \frac{\rho(\varepsilon)}{\omega - \varepsilon}$$

If further $\rho(\varepsilon) \to$ constant, $\Delta \to -i\pi\,\rho|t|^2$ and

$$A(\omega) = -\frac{1}{\pi} G_{ss}(\omega) = \frac{2\pi|\Delta|}{(\omega - \varepsilon_s)^2 + |\Delta|^2}$$

Density-of-states

Lorentzian



$A(\omega)$ is the density-of states. What started as a sharp pole in the isolated state gets broadened ⇒ finite lifetime.

Frequency-dependent Self-Energy

Even for this noninteracting system
the self-energy is ω-dependent

$$G_{ss}(\omega) = \frac{1}{(\omega - \varepsilon_s - \Delta(\omega))}$$

Consider a more general case of an extended system. Partition the problem into a reference noninteracting effective hamiltonian given by a static self-energy $V_{xc}(k)$. The interacting system has a self-energy $\Sigma(k,\omega)$.

Write the contribution
to G from QP state j as

$$G^j(k,\omega) = \frac{1}{\omega - \omega^j - \Sigma^j(k,\omega) + V_{xc}^j(k)}$$

Linearize $\Sigma(k,\omega)$ near the pole ω^j

$$\begin{aligned}\Sigma(k,\omega) &= \Sigma(k,\omega^j) + \Sigma'(k,\omega^j)(\omega - \omega^j) \\ &= \Sigma(k,\omega^j) + (1 - \underline{(Z^j)^{-1})}(\omega - \omega^j)\end{aligned}$$

Replace ReΣ with the linearized Σ and call the resulting G the "coherent part" G^{coh} of G (next)

Definition of the Z factor:

$$(1 - (Z^j)^{-1}) = \partial\Sigma^j(k,\omega) / \partial\omega\Big|_{\omega^j}$$

Terms $\propto \omega$: $1 - (1 - Z^{-1}) = Z^{-1}$

Loss of Quasiparticle Weight

Rearrange terms

$$G^{j,\mathrm{coh}}(k,\omega)=\frac{Z}{(\omega-\omega^{j})-Z\,\mathrm{Re}\Sigma(k,\omega^{j})+ZV_{xc}^{j}(k)-iZ\,\mathrm{Im}\Sigma(k,\omega)}$$

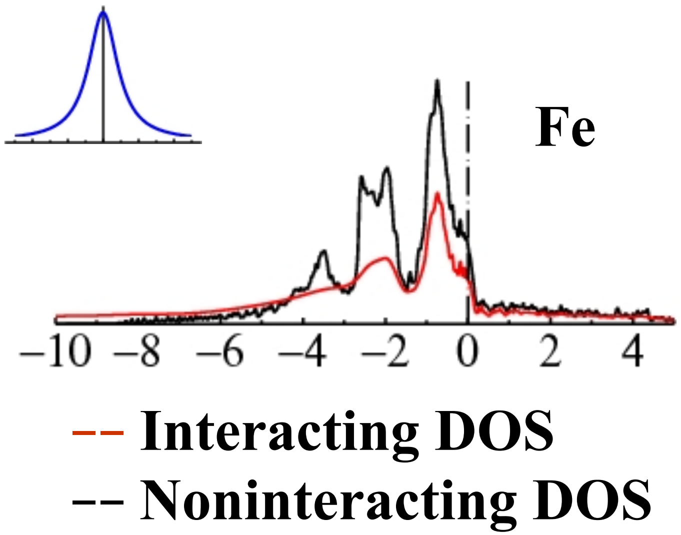
Define the QP peak as the value ω^{*} of ω where the real part of the denominator vanishes.

$$\omega^{*}=\omega^{j}+Z^{j}\left(\mathrm{Re}\Sigma(k,\omega^{j})-V_{xc}(k)\right)$$

Σ shifts ω^{*} … but the shift ω^{*}-ω^{j} depends on the reference V_{xc}. The better the V_{xc} the smaller the shift (it is zero in quasiparticle self-consistent construction; see later)

ImΣ broadens the pole at ω^{*} .

The ω-dependence of ReΣ reduces the strength of the pole by Z . QP weight gets redistributed into incoherent parts of the spectrum, Hubbard sidebands or plasmon satellites.



Quasiparticle Lifetime

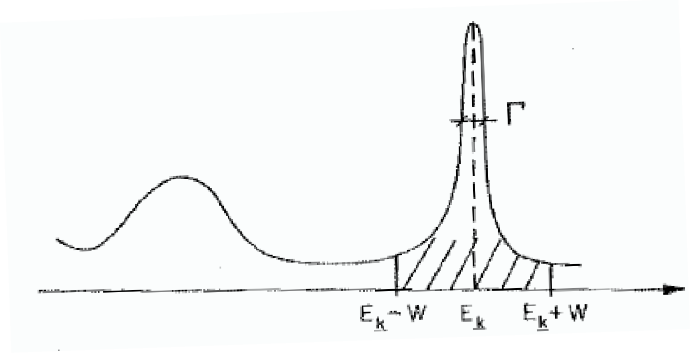
Fourier transform $G^{\mathrm{coh}}(\omega)$ into the time domain :

$$G^{\mathrm{coh}}(t) \sim iZe^{-i\omega^{*}t-(Z|\mathrm{Im}\Sigma|)t}$$

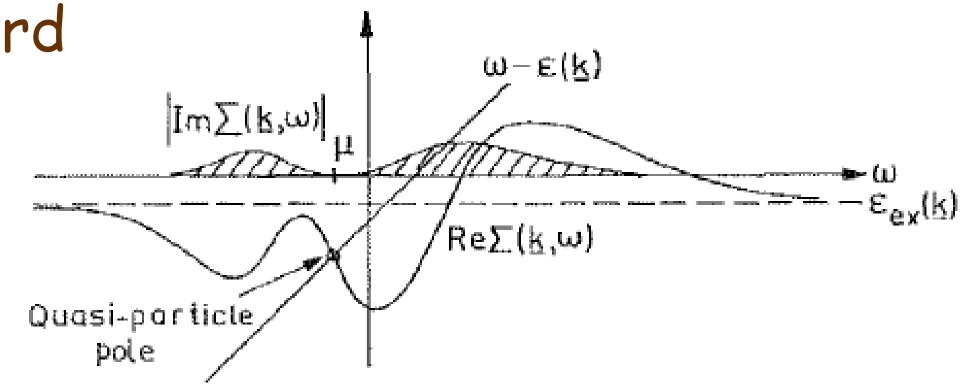
The quasiparticle decays into a continuum of infinitely closely spaced excitations near ω^{*}. The lifetime is given by ImΣ.

The corresponding spectral function A^{coh} is broadened by Σ .

$$A_{k}^{j,\mathrm{coh}}(\omega)=\frac{Z^{j}}{\pi}\frac{Z^{j}\mathrm{Im}\Sigma(k,\omega)}{(\omega-\omega^{*})^{2}+(Z^{j}\mathrm{Im}\Sigma(k,\omega))^{2}}$$



Σ can have lots of structure ...
transfer of QP weight can result in new peaks at plasmon or Hubbard satellites.



Near E_F or μ , $|\mathrm{Im}\Sigma| \sim (\omega^{*} - \mu)^2$
for a normal Fermi liquid ...
Lifetime $\tau \rightarrow \infty$ approaching E_F.

Mass Renormalization

The QP peak position is modified by $\mathrm{Re}\Sigma - V_{xc}$:

$$\omega^* = \omega^j + Z^j\left(\mathrm{Re}\Sigma(k,\omega^j) - V_{xc}(k)\right)$$

The group velocity is $d\omega^*/dk$. For the interacting case it is

$$\frac{d\omega^*}{dk} = \frac{d\omega^j}{dk} + \frac{d}{dk} Z^j\left(\mathrm{Re}\Sigma(k,\omega^j) - V_{xc}^j(k)\right)$$

The ratio $m_0/m^* = (d\omega^*/dk)/(d\omega^j/dk)$ … the “renormalization of effective mass” is often taken to be a measure of correlation.

This is a nebulous concept, because it depends on the choice of noninteracting reference V_{xc}. Still, it emphasizes that both the k- and ω - dependence of Σ modify the QP band dispersions.

Consider a reference V_{xc} constructed from a purely static theory, e.g. Hartree-Fock or DFT. Easy to show that

$$\frac{d\omega^*}{dk} = Z^j \underbrace{\frac{d\omega^j}{dk}}_{\omega\text{-dependence}} + Z^j \underbrace{\frac{\partial}{\partial k}\left(\mathrm{Re}\Sigma(k,\omega^j) - V_{xc}^j(k)\right)}_{k\text{-dependence}}$$

Important when correlations are strong → ω-dependence

k-dependence ← **Always important**

Simplest formulation of V^{eff} : Hartree Fock

How to formulate the noninteracting reference system?

Hartree-Fock was the first. Write the hamiltonian this way:

$$H = \sum_i h_0(\mathbf{x}_i) + \frac{1}{2}\sum_{i\neq j} v(\mathbf{x}_i, \mathbf{x}_j) + V_{\text{nuc}}, \qquad \mathbf{x} = (\mathbf{r}, \xi)$$

Space + spin

$$h_0(\mathbf{x}_i) = -\frac{\nabla_i^2}{2m_i} - \sum_I v(\mathbf{x}_i, \mathbf{R}_I), \qquad v(\mathbf{x}_i, \mathbf{x}_j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Define a (complete) set of one-particle orbitals $\psi_i(\mathbf{x})$.

Make a Slater Determinant of N them: $|\Psi\rangle = N^{-1/2} \det|\psi_i(\mathbf{x}_k)|$

Variational principle: vary the shape $\psi_i(\mathbf{x})$ until E is minimum

$$\delta\langle\Psi|H|\Psi\rangle = 0 \quad \text{subject to constraints} \quad \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d\mathbf{x} = \delta_{ij}$$

One Electron Hamiltonian

$\delta\langle\Psi|H|\Psi\rangle = 0$ generates effective one-body H_0:

$$(h + V_H + V_x)\psi_k = \varepsilon_k \psi_k$$

↑

nonlocal operator

$$V_x \psi_k = \int V_x(\mathbf{x},\mathbf{x}')\psi_k(\mathbf{x}')d\mathbf{x}'$$

$$V_H(\mathbf{x}) = \int v(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')d\mathbf{x}'$$

Hartree

$$V_x(\mathbf{x},\mathbf{x}') = -v(\mathbf{x},\mathbf{x}')\rho(\mathbf{x},\mathbf{x}')$$

Exchange

density

$$\rho(\mathbf{x}) = \sum_{i=1}^{N} \psi_i^*(\mathbf{x})\psi_i(\mathbf{x})$$

density matrix

$$\rho(\mathbf{x},\mathbf{x}') = \sum_{i=1}^{N} \psi_i^*(\mathbf{x})\psi_i(\mathbf{x}')$$

Ground state: only the lowest N states are filled; only the first N are ψ_i, ε_i are needed.

Koopman's theorem: the ε_i correspond to excitation energies

$$E[N] - E[N-1, i \text{ emptry}] = \varepsilon_i$$

(assumes the ψ_i does not relax after the particle is excited)

Features of the Hartree-Fock Approximation

- Build Ψ from Slater determinants of 1-particle ψ_1, ψ_2, …
  - e.g for two particles: $\Psi(\mathbf{r}_1,\mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)$
  - Satisfies self-interaction and symmetry (exclusion principle)
  - Introduces some limited correlation : $\Psi(\mathbf{r}_1,\mathbf{r}_2) = 0$ when $\mathbf{r}_1 = \mathbf{r}_2$.
  - Potential is now "Hartree" (e.s.) + "Exchange" (correlations)
  - Exchange is very important: explains origin of magnetism as a consequence of the Pauli Exclusion principle.
- Simplest ab initio theory consistent with QM.
  - What is put in, what is missing is well defined.
  - Effective potential V^{eff} is real and ω-independent ⇒ effective hamiltonian is a noninteracting, 1-body H_0 .
  - Hamiltonian is nonlocal : $V^{\text{eff}} = V_H + V^{x}(\mathbf{x},\mathbf{x}')$ ⇒ each e^- sees own V.
  - Correlation underestimated: energy > exact result
- Too simple even for H_0 : severe errors in condensed matter
  - Main value as a framework for better theories.

Problems with the Hartree-Fock Approximation

- Moderate errors in small molecules (used in chemistry)
- Severe errors in condensed matter
  - Total energy: Fe is predicted to be AFM insulator
    Magnetic moment in the FM state is much too large
  - velocity has pathological divergence at E_F in metals

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} + \frac{e^2 k_F}{\pi} f(k/k_F) \quad \text{where } f(x) = -\left[1 + \frac{1-x^2}{2x} \ln\left|\frac{1+x}{1-x}\right|\right], \quad x = \frac{k}{k_F}$$

  - Bandgaps, bandwidths much too large: 5 eV in Si, expt = 1.1 eV
- Most important : v needs to be screened!
- Even simple screening, e.g. Thomas Fermi $v(q) = 1/(q^2 + q^2_{\mathrm{TF}})$, goes a long way. (removes divergence of v_F in metals, reduces bandwidths, magnetic moments …)

$$v(r) = 1/r$$

$$v(q) = 1/q^2$$

Density-Functional Theory I

Hohnberg and Kohn (1964) proved that the total energy E can be determined solely from the density. The total energy is written:

$$E_{HK}[n] = T_s[n] + \underbrace{\int d^3r\, n(\mathbf{r}) V_{ext}(\mathbf{r}) + \int d^3r\, n(\mathbf{r}) V_H(\mathbf{r})}_{\textbf{Classical Electrostatics}} + \underbrace{E_{xc}[n]}_{\textbf{Correlations}}$$

- $E=E[n(\mathbf{r})]$ where the density $n(\mathbf{r})$ is the basic variable.
- DFT uses n alone rather than $E=E[\{\psi_i\}]$ as in Hartree-Fock.
  - A “deep” result: n can determine the many-body $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$
- Formally exact but $E[n]$ is unknown! *Must be* highly nonanalytic
- Particularly pathological is the K.E. functional $T[n]$.
  - Hard to see how any universal functional of n can reproduce, e.g. core states of an atom ⇒ discontinuities.
  - Similar problems as change occupation of 1-electron levels.
- Tradeoff: $E[n]$ has vastly fewer degrees of freedom than $E[\{\psi_i\}]$ ⇒ complication pushed onto unknown $E_{xc}[n(\mathbf{r})]$.

Density-Functional Theory II

A tractable theory: Kohn-Sham ansatz + the Local Density Approx.

1. Assume $T[n]$ is identical to T for a non-interacting system with orbitals constructed from the theory (general to DFT methods)
2. Approximate E_{xc} has some analytic form, calculated e.g. for a reference system such as the homogeneous electron gas

E_{KS} = kinetic + potential energy:

$$E_{KS} = T_s[n] + E_{\text{pot}}[n],$$

$$E_{\text{pot}}[n] = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_H[n] + E_{xc}[n]$$

Use noninteracting ansatz to get at T_{KS} through a back door.

$$H_{KS}^{\text{eff}} \psi_i = -\frac{1}{2}\nabla^2 \psi_i + V^{\text{eff}}(\mathbf{r})\psi_i = \varepsilon_i \psi_i, \qquad V^{\text{eff}}(\mathbf{r}) = \frac{\delta E_{\text{pot}}[n(\mathbf{r})]}{\delta n}$$

$$\left\langle \psi_i \middle| -\frac{1}{2}\nabla^2 + V^{\text{eff}} \middle| \psi_i \right\rangle = \left\langle \psi_i \,|\, \varepsilon_i \,|\, \psi_i \right\rangle = \varepsilon_i$$

$$T_{KS} = \sum_i \varepsilon_i - \int d\mathbf{r} V^{\text{eff}}(\mathbf{r}) \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) = E_{bs} - \int d\mathbf{r} V^{\text{in}}(\mathbf{r}) n^{\text{out}}(\mathbf{r})$$

Properties of the Local Density Approximation

We do not know $E_{\mathrm{xc}}[n]$, but must make approximations for it. DFT is very effective because $E_{\mathrm{xc}}[n]$ is much less pathological than $T[n]$. Simple approximations (e.g. $E_{\mathrm{xc}}[n]$ for the homogeneous electron gas) can give very good results (especially for ground-state properties in weakly correlated systems)

$$E_{\mathrm{xc}} \approx \int n(\mathbf{r})\varepsilon_{xc}[n(\mathbf{r})]d^3\mathbf{r}, \qquad V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})}\big(n(\mathbf{r})\varepsilon_{xc}[n(\mathbf{r})]\big)$$

Universal ⇒ calculate almost exactly for model, e.g. jellium

- LDA, variants have become standard "workhorse" --- now widely used in almost every branch of science, engineering
- An extremely simple and universal theory … all the complexity is folded into a simple and universal functional.
- Key point: all electrons see same effective potential $V^{\mathrm{eff}}(\mathbf{r})$. In contrast to Hartree-Fock (nonlocal $V_{\mathrm{x}}(\mathbf{r},\mathbf{r}')$ ⇒ each electron sees a different $V^{\mathrm{eff}}(\mathbf{r})$).

- The 3 most cited papers, and 6 of the 10 most cited papers in the Physical Review series (Phys. Rev. B, Phys. Rev. Lett., Rev. Mod. Physics) all have to do with ab initio approaches to solving the Schrodinger equation for the electrons.
- ~5 “kilopapers” are published every year, and the number is quickly increasing.

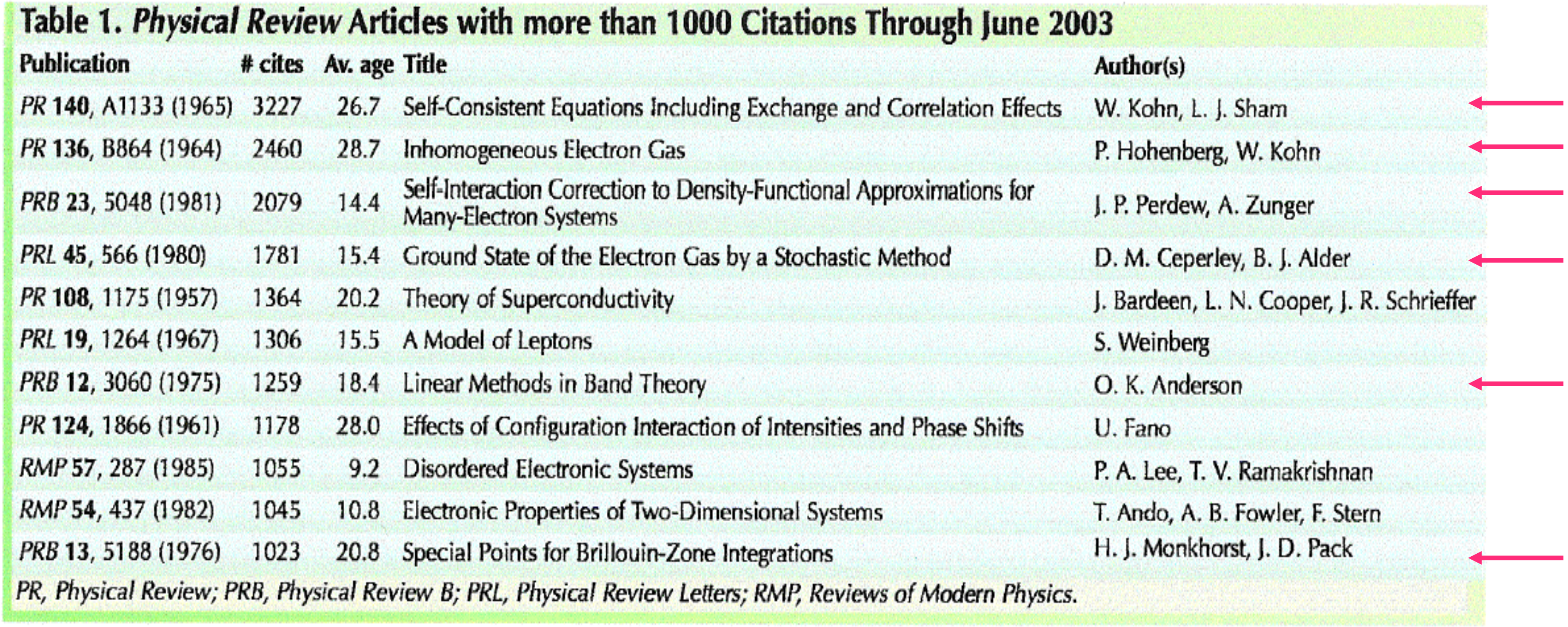


Table 1. ***Physical Review*** **Articles with more than 1000 Citations Through June 2003**

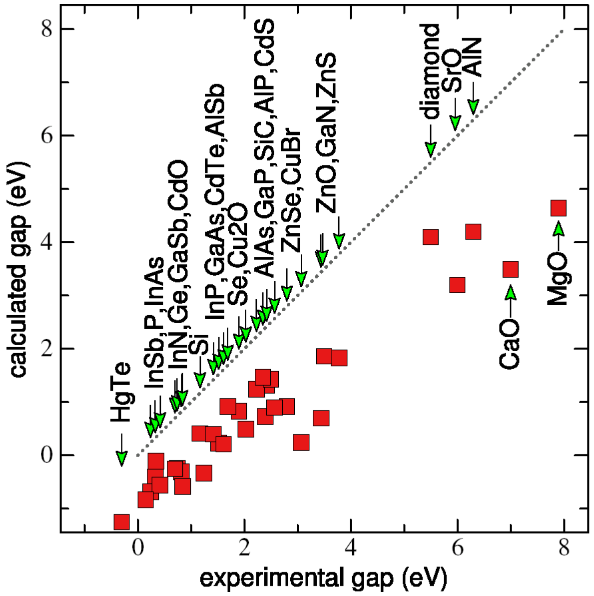
Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

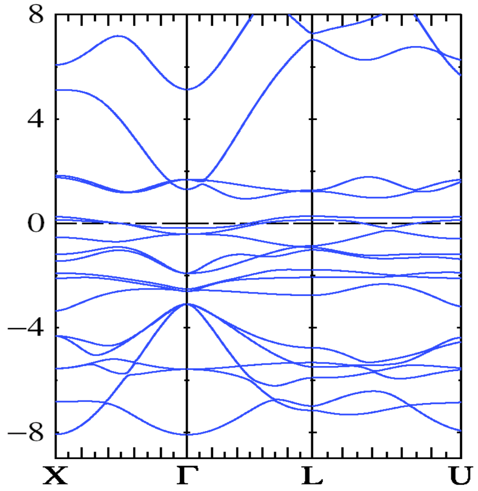
PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

- Source: Physics Today 58, 49 (2005)

Problems in the Local Density Approximation

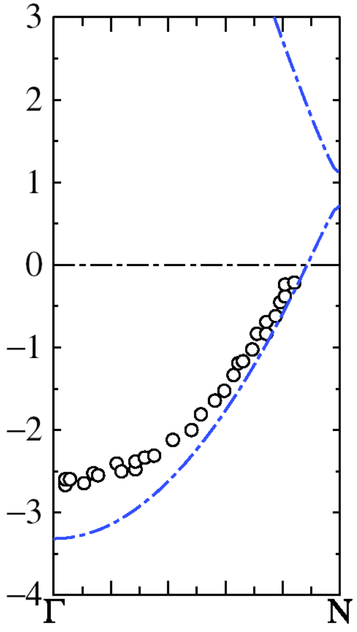
Semi. bandgaps too small

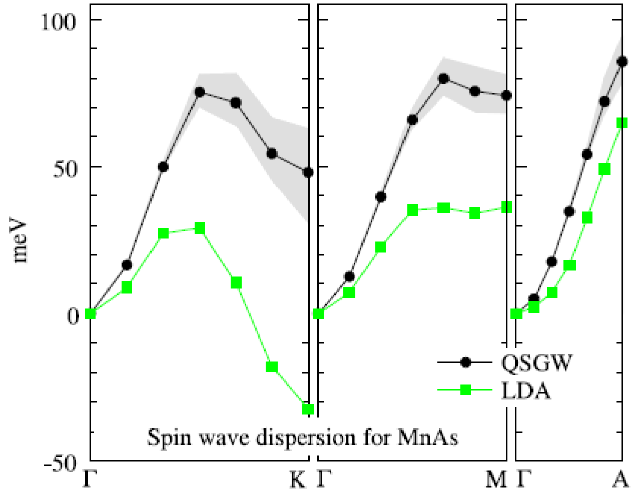




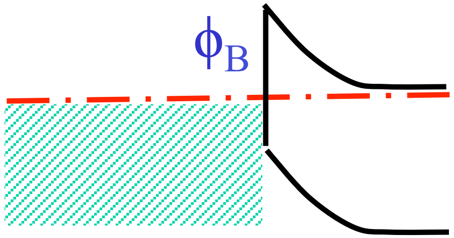
LDA CoO is metalllic but real CoO is AFM insulator w/~2.4 eV gap

Poor Na bands





Magnetism often poorly described



Schottky barriers at metal-semi contacts fall too close to Valence Band

Two possible explanations for LDA error

What is the dominant source of difficulty in the L(S)DA?

Explanation I: Ansatz for $E_{xc}[n]$ is not good enough.

Explanation II: Kohn-Sham ψ_i and eigenvalues ε_i the Lagrange multipliers of the KS hamiltonian

$$\hat{H}^{\sigma}_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + [V^{\sigma}_{KS}(\mathbf{r}) = V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) + V^{\sigma}_{xc}(\mathbf{r})]$$

are fictitious.

Q: How do we assess the source of error?

A: Density-functionalize nonlocal functionals and check.

Not a strict division (there is an interplay between them).
But roughly:

For ground state properties, I is often the primary problem

For excited state properties II is often the primary problem.

Connection between DFT and QP levels

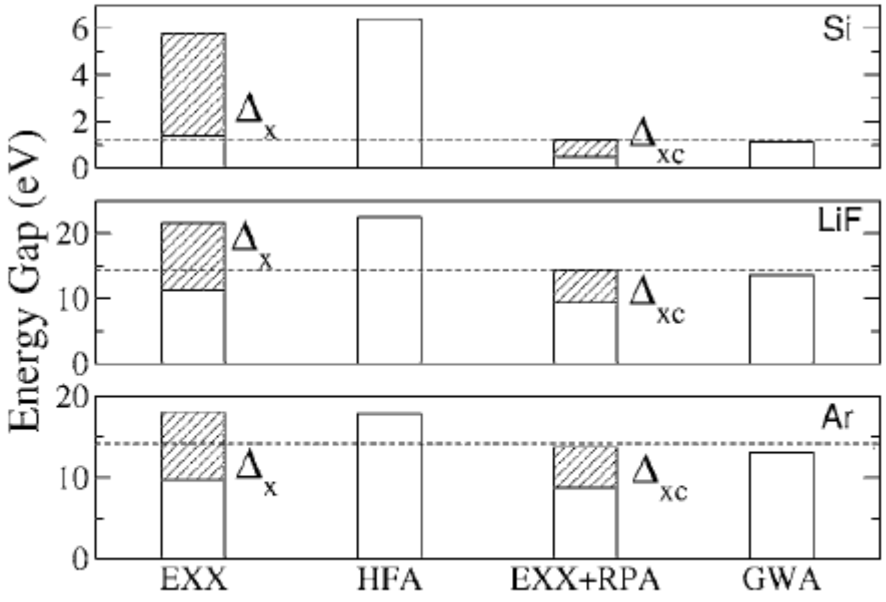
ψ_i and ε_i fictitious ⇒ discontinuity Δ_{xc} in XC potential betw/ highest occupied and lowes unoccupied state

Grüning, Marini, Rubio, (J. Chem. Phys. 124, 154108) evaluated Δ_{xc} by "density-functionalizing“ GW (OEP) for Si, LiF,Ar

$$\Delta_{\mathrm{xc}} = \langle \psi_{N+1} | \Sigma_{\mathrm{xc}}^{GW}(\varepsilon_{N+1}) - v_{\mathrm{xc}} | \psi_{N+1} \rangle - \langle \psi_N | \Sigma_{\mathrm{xc}}^{GW}(\varepsilon_N) - v_{\mathrm{xc}} | \psi_N \rangle .$$

Results show:

OEP gap (EXX+RPA) close to usual LDA gap. Thus Explanation II: the fictitious nature of ψ_i and ε_i are the primary problem



Many attempts to extend the LDA

- Good ground-state properties in weakly correlated systems.
- Excited state properties are much worse.

Many attempts to extend, improve on the LDA

- Self-Interaction Correction (Perdew, Zunger, PRB 23, 5048 (1981))
- LDA+U (Anisimov, Zaanen, Andersen, Phys. Rev. B 44, 943 (1991))
- LDA+Screened exchange, (Seidl et al, PRB 53, 3764 (1996))
- LDA+DMFT (Anisimov et al, J. Phys. C9, 7359 (1997))
- Mix Hartree-Fock with LDA (B3LYP, Becke; HSE, Scuseria)
- Optimized Effective Potential (Kotani, PRL 74, 2989 (1995))
- "Van der Waals" functionals

- All have significant successes to their credit, but improve one or another property in some special cases.
- Removing locality is essential … but LDA starts with an ill-defined ansatz. Without removing it, hard to *systematically* improve on the basic framework

Screening the Coulomb interaction

The coulomb interaction is very large and long range. In many-particle systems it is strongly renormalized by screening --- this is the essential difference between Hartree-Fock and GW.

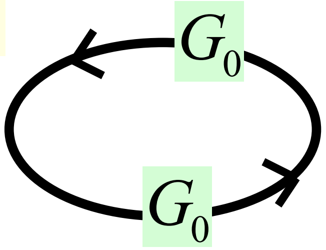
Consider a lattice of points i, with the e^- density initially in equilibrium, perturbed by external potential $\delta\phi_i = \delta V_i^0$ at site i. Supposing the screening charge did not interact with itself--- let δq_j^0 be the noninteracting screening charge at j. They are connected by the noninteracting response function

$\delta q_k^0 = P^0_{kj}\,\delta\phi_j$ ← P^0 is called the "irreducible polarizability"

Linearize Dyson's equation ($\delta G \approx G^0\,\delta\phi_i\,G^0$), to get P^0

$$\delta q_k^0 = \frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{E_F} dz\,\delta G_{kk} = \left[\frac{1}{\pi}\,\mathrm{Im}\sum_k \int_{-\infty}^{E_F} dz\,G^0_{kj}\,G^0_{jk}\right]\delta\phi_j \equiv P^0_{kj}\,\delta\phi_j$$

Write as $\boxed{P^0_{kj} = G^0_{kj}\,G^0_{jk}}$



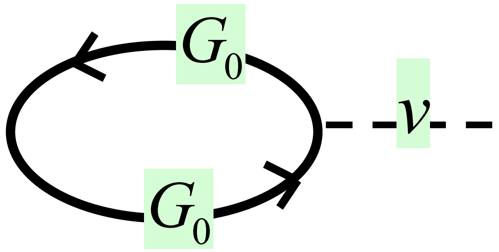
The screening charge

The independent particle picture (AKA the RPA or time-dependent Hartree approximation) assumes that the screening only interacts with it self via the classical coulomb interaction.

Then δq_j^0 would induce a potential $\delta V_k^1 = \sum_i v_{jk} \delta q_k^0 .$

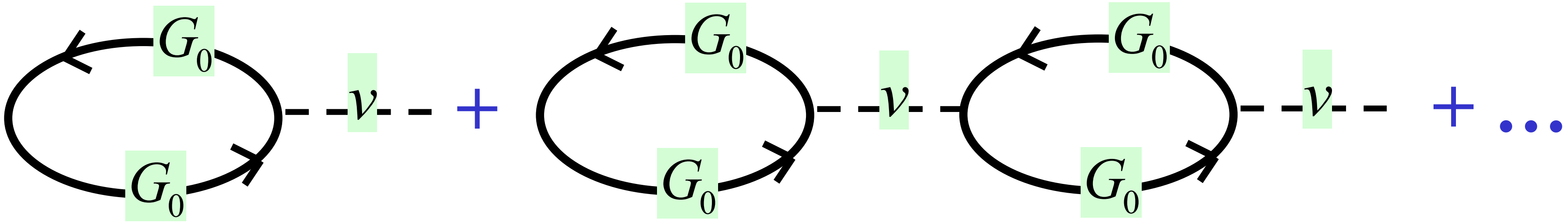
$|\mathbf{r}_j - \mathbf{r}_k|^{-1}$

$\delta V^1 =$



$\delta\phi_i = \delta V_i^0$ induces δV_i^1. δV_i^1 induces δq_j^1 which induces δV_i^2 and so on

Sum $\delta V_i^1 + \delta V_i^1 + \delta V_i^2 + \delta V_i^3 + \ldots$



The total screening charge can be summed as a geometric series

$$\delta q = \sum_n \delta q^n = \left(1 + vP^0 + vP^0 vP^0 + \ldots\right) P^0\, \delta V^0 = \left(1 - vP^0\right)^{-1} P^0\, \delta V^0$$

Rename

$\delta\phi$

The Screened Coulomb interaction

The total potential is

$$\delta V^{\text{tot}} \equiv \delta\phi + \delta V^{scr} = \sum_n \delta V^n = \left(1 - vP^0\right)^{-1} \delta\phi$$

The dielectric function is defined as the ratio

$$\varepsilon_{ij}^{-1} = \frac{\delta V_i^{\text{tot}}}{\delta\phi}$$

← **Total potential**

← **External potential**

and therefore*

$$\varepsilon^{-1} = (1 - vP^0)^{-1}$$
$$\varepsilon = 1 - vP^0$$

with $P^0 = G^0 G^0$

*This expression continues to hold in the exact description of linear response, but the irreducible polarizability P is no longer the independent particle $P^0 = G^0 G^0$.

The screened Coulomb interaction W is the potential resulting from a test charge embedded in a medium, i.e. $\delta\phi_i = v = 1/r$. Thus

$$W = (1 - vP^0)^{-1} v = \varepsilon^{-1} v$$

Beyond RPA : The Kernel in DFT

Recall

$$E_{\text{pot}}[n] = \int d\mathbf{r}\, V_{\text{ext}}(\mathbf{r})\, n^{\text{out}}(\mathbf{r}) + E_H[n] + E_{xc}[n]$$

The first variation of E_{pot} is the potential of the 1-body H_0

$$\frac{\delta E_{\text{pot}}[n]}{\delta n} = V_{\text{ext}} + V_H[n] + V_{xc}[n], \quad \begin{cases} V_H[n] = \delta E_H[n] / \delta n = \int d\mathbf{r}' \dfrac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ V_{xc}[n;\mathbf{r}] = \delta E_{xc}[n] / \delta n = \dfrac{d}{dn}\left(n\varepsilon_{xc}[n;\mathbf{r}]\right) \end{cases}$$

The second variation depends only on V_H and V_{xc} :

$$\frac{\delta^2 E_{Hxc}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \equiv K = \frac{\delta V_{Hxc}[n;\mathbf{r}]}{\delta n(\mathbf{r}')} = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r},\mathbf{r}') \;\text{ where }\; f_{xc}(\mathbf{r},\mathbf{r}') = \frac{\delta V_{xc}[n;\mathbf{r}]}{\delta n(\mathbf{r}')}$$

K is called the “Kernel.” See Richard Martin’s book Eq. D10. Very important in linear response theory. Fourier Transform:

$$K = \frac{\delta V_{Hxc}}{\delta n} = \frac{4\pi}{q^2}\delta_{\mathbf{q}\mathbf{q}'} + f_{xc}(\mathbf{q},\mathbf{q}')$$

This is v in $\mathbf{q}$ space. Fourier transform of $1/r$.

TDDFT Dielectric function

A quantity similar to P is the response function

$$\chi(1,2) = \frac{\delta n(1)}{\delta\phi(2)}$$

← **density**

← **External potential**

χ = change in n when perturbed by *external* field

Total potential change δV = external perturbation $\delta\phi$

+ δV_{ind} induced by δn, which is K.

This is *K*

$$\varepsilon^{-1} = \frac{\delta V}{\delta\phi} = \frac{\delta\phi + \delta V_{ind}}{\delta\phi} = 1 + \frac{\delta V_{ind}}{\delta n_{ind}}\frac{\delta n_{ind}}{\delta\phi} = 1 + K\left(\frac{\delta n_{ind}}{\delta\phi}\right)$$

Noninteracting susceptibility $\chi_0 = P^0$

Rewrite $\delta n_{ind}/\delta\phi$ using chain rule.

$$\varepsilon^{-1} = 1 + K\left(\frac{\delta n_{ind}}{\delta V}\frac{\delta V}{\delta\phi}\right) = 1 + K\frac{\delta n_{ind}}{\delta V}\varepsilon^{-1} = 1 + K\chi_0\varepsilon^{-1}$$

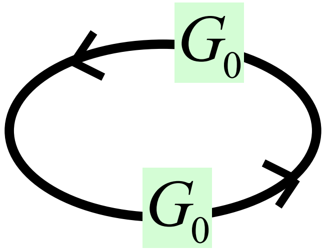
Formally exact, but K (the potential generated by δn_{ind}) is unknown.

GW: A Perturbation theory

Start from some non-interacting hamiltonian H_0.

1. $H_0 = -\frac{\nabla^2}{2} + V_{eff}(\mathbf{r},\mathbf{r}') \Rightarrow G_0 = \frac{1}{\omega - H_0}$ Usual: $H_0 = H^{\text{LDA}}$

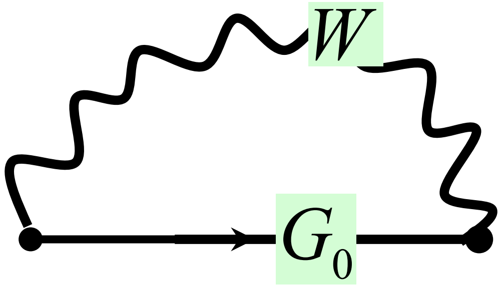
2. $\Pi = -i G_0 \times G_0$ RPA Polarization function



3. $W = \varepsilon^{-1} v = (1 - \Pi v)^{-1} v$ Dynamically screened exchange

$v(\mathbf{r},\mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$

4. $\Sigma = i G_0 W$ Self-energy $\Sigma =$

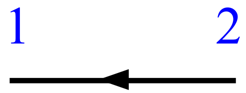


$$H(\mathbf{r},\mathbf{r}',\omega) = -\frac{\nabla^2}{2} + V^H(\mathbf{r}) + V^{ext}(\mathbf{r}) + \Sigma(\mathbf{r},\mathbf{r}',\omega)$$

This is V_{xc}

Aside : About diagrams

Feynman Diagrams are a convenient pictorial way to represent complicated chains of processes. Widely used in many-body perturbation theory



$G(\mathbf{x}_1,t_1;\mathbf{x}_2,t_2)$

The arrow represents the flow of time
A thick or double line used for an interacting G and thin line for G^0

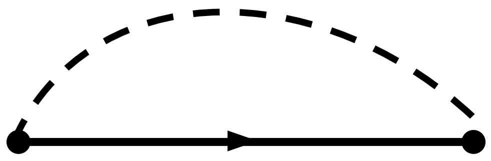
$v(\mathbf{x}_1;\mathbf{x}_2)$

The bare coulomb interaction $|\mathbf{x}_1 - \mathbf{x}_2|^{-1}$ is taken to be instantaneous

$W(\mathbf{x}_1,t_1;\mathbf{x}_2,t_2)$

The screened coulomb interaction.
W depends one time, $t_1 - t_2$.

Exchange Gv



GW

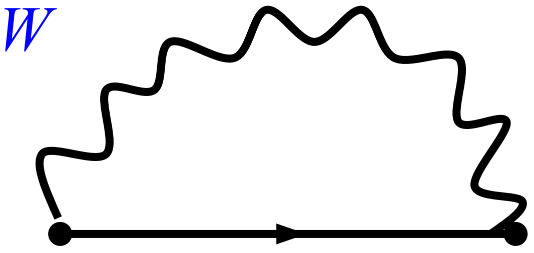
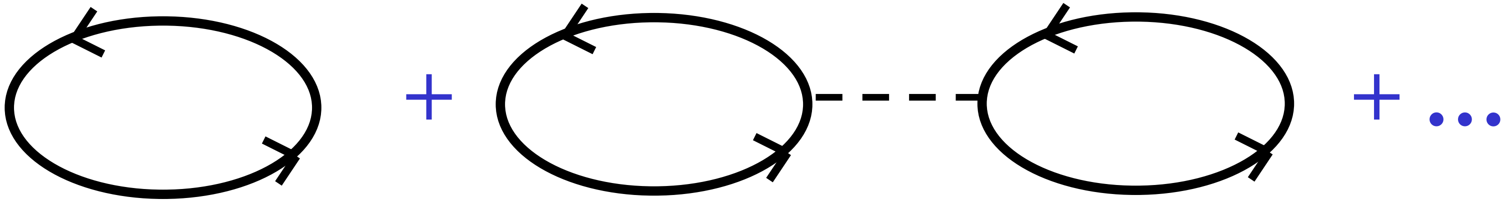


Diagram for W in the RPA

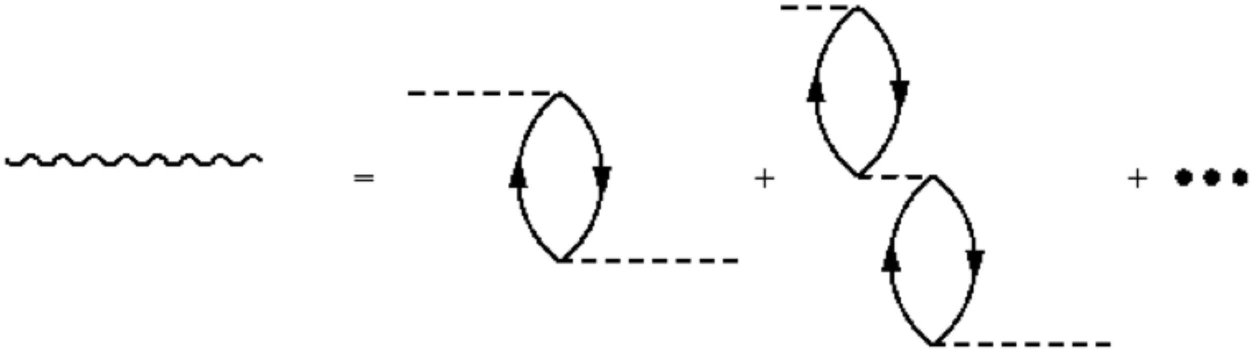
We saw how the RPA screening charge can be represented as a geometric series

$$\delta q / \delta\phi = \sum_n \delta q^n / \delta\phi = \left(1 + vP^0 + vP^0 vP^0 + \ldots\right) P^0 = \left(1 - vP^0\right)^{-1} P^0, \quad P^0 = G^0 G^0$$



which yielded ε^{-1} and W.

The diagram for W is the series of "bubbles" linked by v:



GW as Screened Hartree Fock

Hartree Fock: e^- senses an attractive potential V_x owing to correlated motion originating from antisymmetry that keeps e^- apart. Note: "correlation" is *usually* used as a term of art that means correlated motion not captured by Hartree Fock!

Write V_x in terms of Green's functions:

$$\Sigma_\mathrm{x} = V_\mathrm{x}(\mathbf{r}) = i\int G(\mathbf{r},\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' = iGv$$

GW: bare coulomb $v \rightarrow$ dynamically screened W:

$$V_\mathrm{bare}(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \rightarrow W(\mathbf{r},\mathbf{r}',\omega) = \varepsilon^{-1}v; \quad \Sigma = iGW$$

Dynamical screening is the essential difference between GW and Hartree Fock. It make both qualitative and quantitative changes to the electronic structure.

Advantages of the GW Approximation

- The GW approximation can potentially redress the worst failings inherent in both Hartree-Fock and LDA:
- HF : nonlocality is present, but not screened (disaster)
- LDA: V is local (same for all e^-) ⇒ exact V has pathologies and effective one-particle ε_i, $\psi_i(\mathbf{r})$ are fictitious. Leads to many problems, e.g. cannot break time reversal symmetry.

- But … GW is a perturbation theory: first term in an expansion in W. Perturbation theory must be carried out around some starting point H_0. How choose H_0?

- Major development (Hybertsen and Louie, 1987): use LDA as starting point

$$H_0 = H^{\mathrm{LDA}} \Rightarrow G = G^{\mathrm{LDA}}, W = W^{\mathrm{LDA}} \;;\; \Sigma = iG^{\mathrm{LDA}} W^{\mathrm{LDA}}$$

- Hugely successful in semiconductors

GW Approximation and Starting Point

G and Σ are usually generated from some effective noninteracting H_0.

Usually $H_0 = H_{\mathrm{LDA}}$

But this is often problematic … particularly when magnetism is present

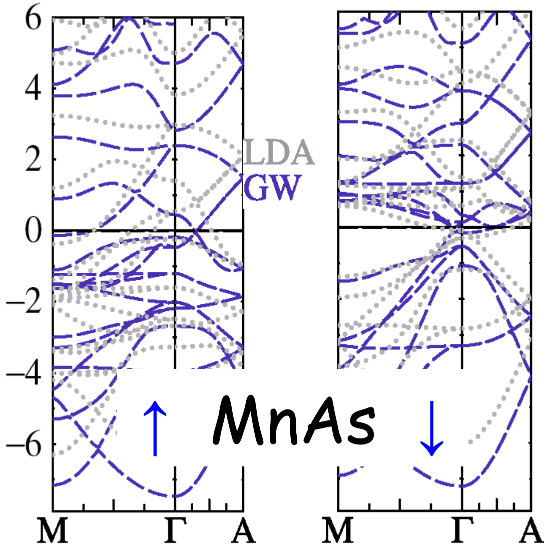
$$P(1,2) = -iGG, \quad \Sigma = iGW$$

GW neglects vertex

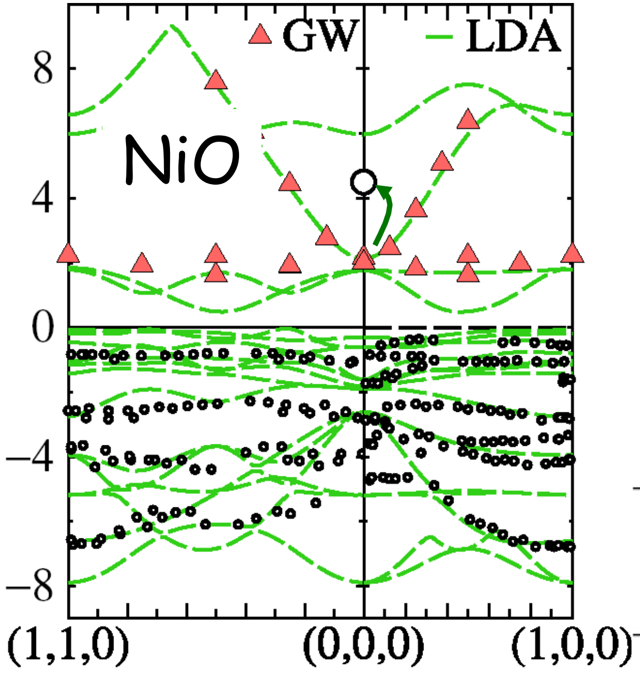
$$(h + V_H + V_{\mathrm{x}})\psi_s = \varepsilon_s \psi_s$$

$$G = \sum_s \frac{\psi_s \psi_s^*}{\omega - \varepsilon_s \pm i\delta}$$

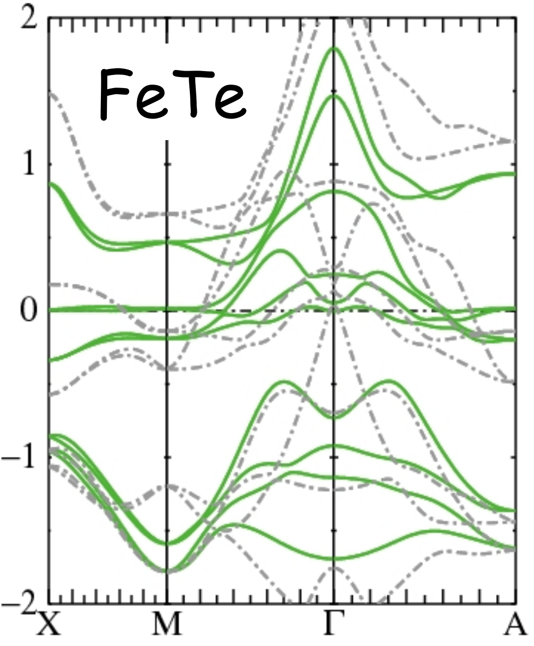
Nonsensical M, E_{x}



Severe gap errors



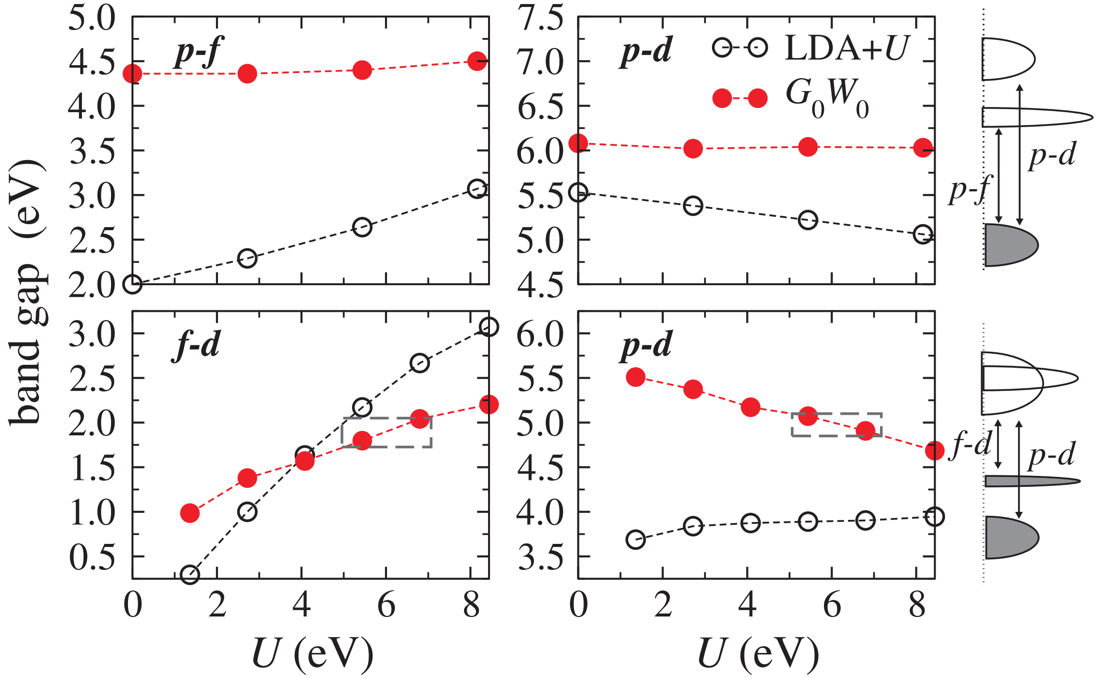
Nonsensical FS



Better GW from better G_0

W is made from G_0 , so we call this the G^0W^0 approximation.

It depends on reference G^0 . Maybe do better if choose a smarter G^0? Consider 4f elements, e.g. Ce in CeO_2



From H. Jiang et al, PRL 102, 126403

Authors use LDA+U for G^0; show GW based on it reduces the dependence of QP levels on U.

Many other kinds of G^0 have been adopted, depending on the particular material

Quasiparticle self-consistent GW Approximation

Remember : there is no unique definition of H_0.

Can we find a good starting point H_0 in place of H^{LDA} ? How to find the best possible H_0 ?

Requires a prescription for minimizing the difference between the full hamiltonian H and H_0.

QSGW : a self-consistent perturbation theory where self-consistency determines the best H_0 (within the GW approximation) PRL 96, 226402 (2006)

... Different principle than energy minimization.

QSGW: a self-consistent perturbation theory

Partition H into $H_0 + \Delta V$ and (noninteracting + residual) in such a way as to minimize ΔV :

$$G_0 = \frac{1}{\omega - H_0} \quad \xrightarrow{GWA} \quad G = \frac{1}{\omega - \left(H_0 + \Delta V(\omega)\right)}$$

G satisfies $\left(\omega - (H_0 + \Delta V(\omega))\right) G(\omega) = \delta(\mathbf{r} - \mathbf{r}')$

We seek the $G_0(\omega)$ that most closely satisfies Eqn. of motion

$$\left(\omega - (H_0 + \Delta V(\omega))\right) G_0(\omega) \approx \delta(\mathbf{r} - \mathbf{r}')$$

$$\rightarrow \Delta V(\omega) G_0(\omega) \approx 0$$

If the GWA is meaningful, $G_0 \approx G$

Q: How to find G_0 that minimizes $\Delta V\, G_0$?

Optimal G_0

Start with some trial V_{xc} (e.g. from LDA, or …). Defines G_0 :

$$H_0 = \frac{-1}{2m}\nabla^2 + V^{\mathrm{ext}}(\mathbf{r}) + V^{\mathrm{H}}(\mathbf{r}) + V^{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$$

$$H_0\psi_i = E_i\psi_i \longrightarrow G_0(\mathbf{r},\mathbf{r}',\omega) = \sum_i \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')}{\omega - E_i}$$

GWA determines ΔV and thus H :

$$G_0 \xrightarrow{RPA} \varepsilon(iG_0G_0) \xrightarrow{GWA} \Sigma(\mathbf{r},\mathbf{r}',\omega) = iG_0W; \qquad \Delta V = \Sigma - V^{\mathrm{xc}}$$

Find a new V^{xc} that minimizes norm N, a measure of $\Delta V\,G_0$.

$$V^{\mathrm{xc}} = \frac{1}{2}\sum_{ij}\langle\psi_i|\mathrm{Re}\big(\Sigma(E_i)+\Sigma(E_j)\big)|\psi_j\rangle$$

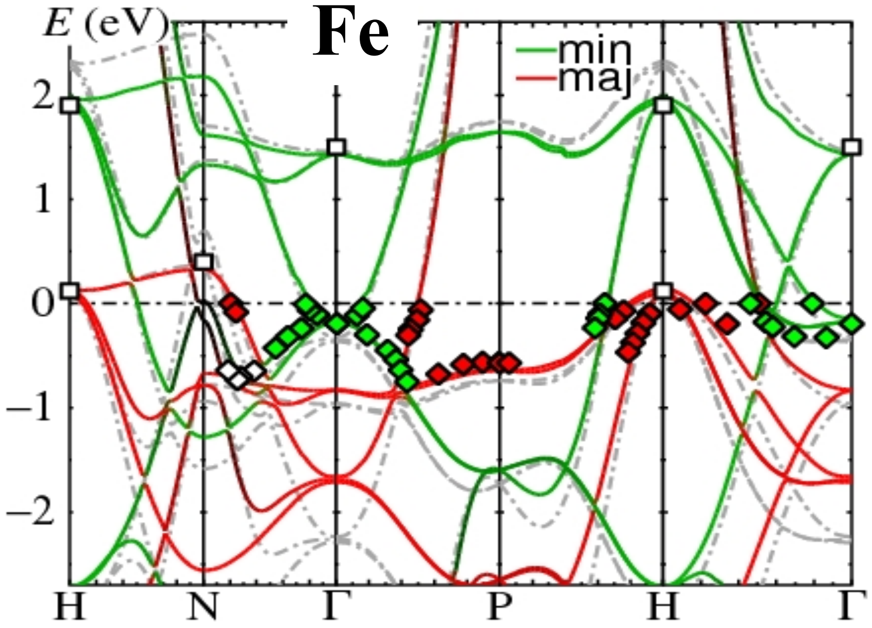
(approximate) result of min N

Iterate to self-consistency.

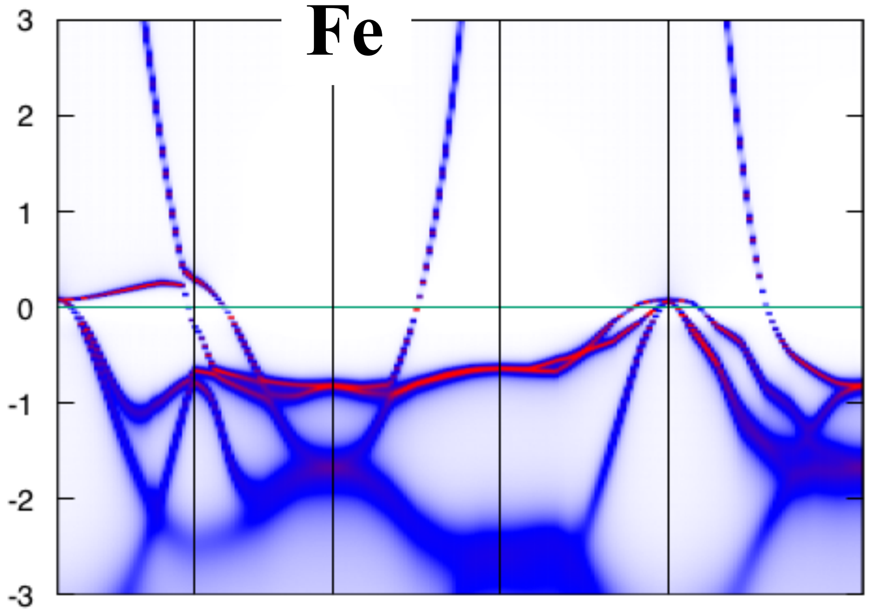
At self-consistency, E_i of G matches E_i of G_0 (real part).

Dual Nature of QS*GW*: both $G_0=(\omega-H_0)^{-1}$ and G

$E_i[G_0]$ = Re $E_i[G]$ ⇒ QS*GW* generates a nearly optimal noninteracting G_0 or H_0 for many kinds of materials classes …



G_0 majority+minority



G majority only

But … as a many-body theory QS*GW* is limited …

Primary many-body effect is a plasmon. Superconductivity, Kondo physics, spin fluctuations … not captured.

Formal Justification of QSGW

Our justification for QSGW: find the G_0 which miminizes the difference $\langle G-G_0\rangle$, according to some definition of $\langle \dots \rangle$, within the GW approximation.

Why not just find G_0 that minimizes the RPA total energy E^{RPA} ?

$$\frac{\delta E^{\mathrm{RPA}}}{\delta G_0} = 0$$

Not possible … there is no lower bound (PRB76, 165106).

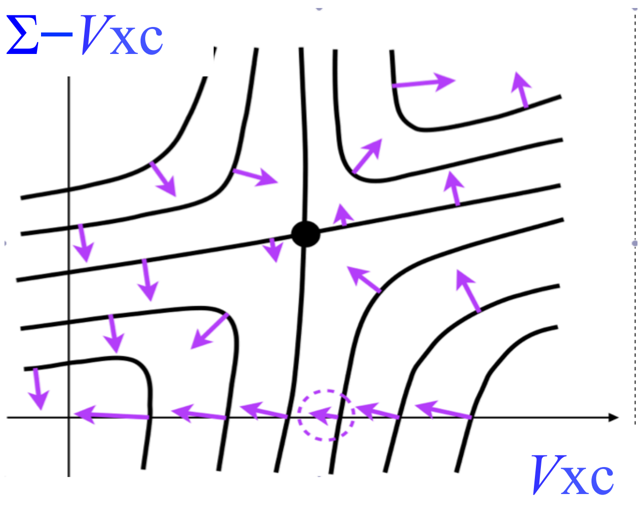
Justifying quasiparticle self-consistent schemes via gradient optimization in Luttinger-Ward theory

arXiv:1406.0772

Sohrab Ismail-Beigi

A different justification (Ismail-Beigi)
Minimize square of *gradient* of Luttinger Ward energy

$$|D|^2 \to \min \quad \text{where} \quad D = \frac{\delta F[G_0]}{\delta \Sigma}$$



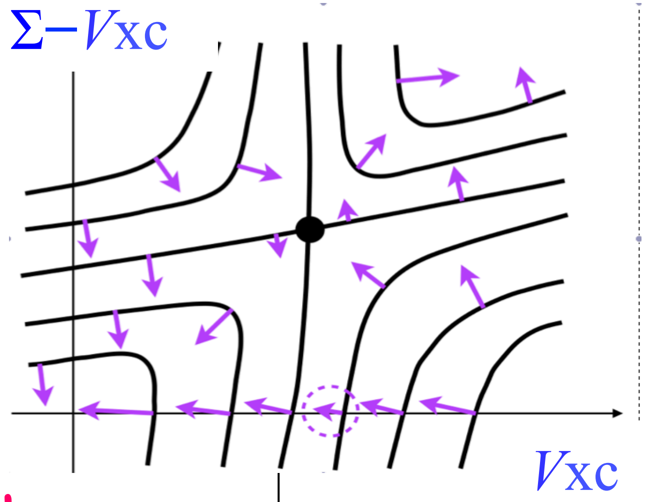
True self-consistent GW

$$G \Rightarrow P = -iGG \Rightarrow W = \varepsilon^{-1} v \Rightarrow \Sigma = iGW \Rightarrow G = \frac{1}{\omega - (T + V^{H} + V^{ext} + \Sigma_{xc})}$$

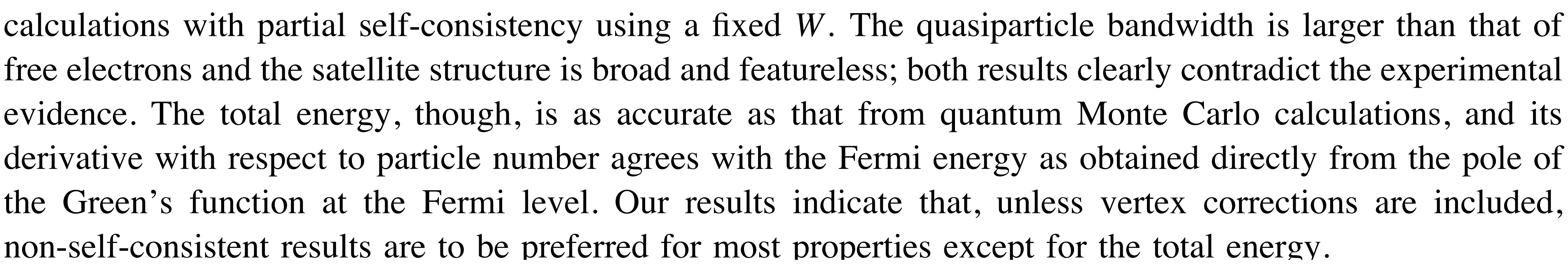
True self-consistent GW looks good
as formal theory:

→ Based on Luttinger-Ward functional.
→ Keeps symmetry for G
→ Conserving approximation

But poor in practice, even for the electron gas



B. Holm and U. von Barth, PRB57, 2108 (1998)

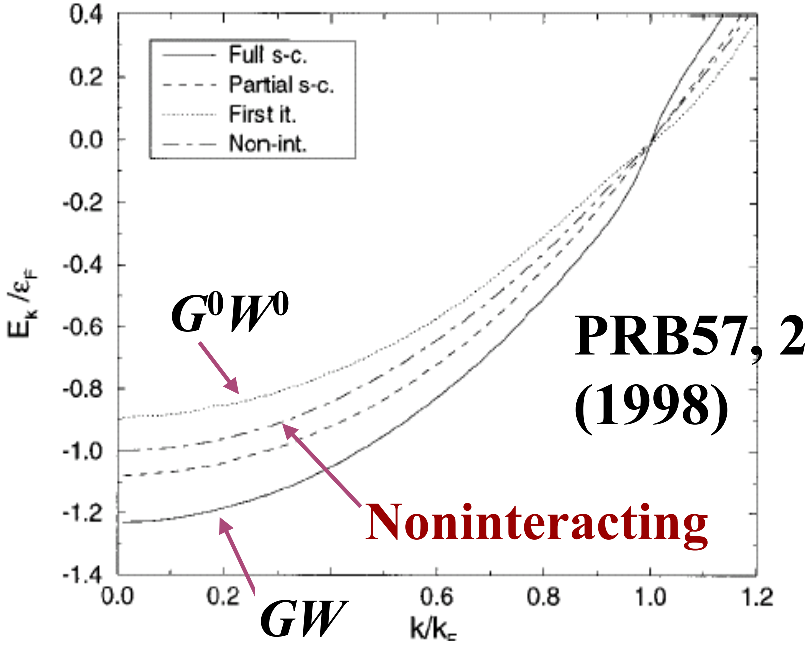

calculations with partial self-consistency using a fixed W. The quasiparticle bandwidth is larger than that of free electrons and the satellite structure is broad and featureless; both results clearly contradict the experimental evidence. The total energy, though, is as accurate as that from quantum Monte Carlo calculations, and its derivative with respect to particle number agrees with the Fermi energy as obtained directly from the pole of the Green's function at the Fermi level. Our results indicate that, unless vertex corrections are included, non-self-consistent results are to be preferred for most properties except for the total energy.

Bandwidths in scGW

Holm and von Barth compared scGW to G^0W^0 in the homogeneous electron gas.

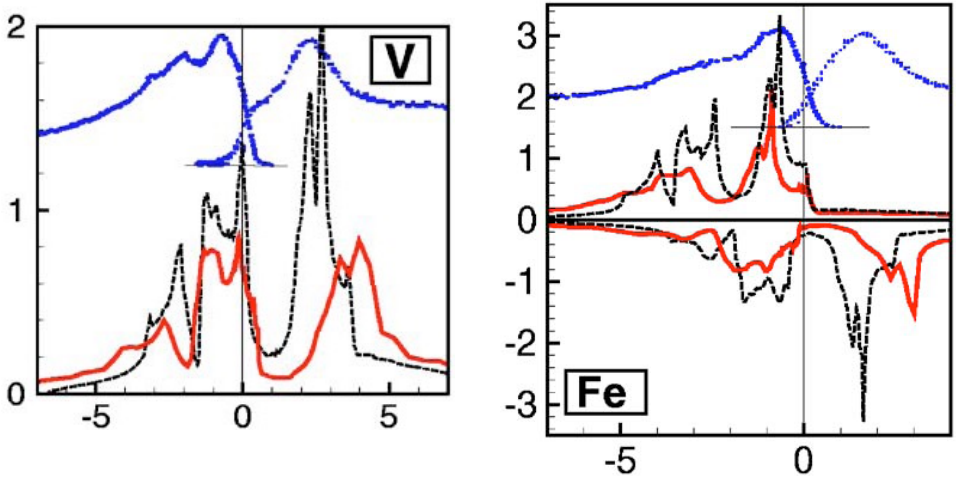
The G^0W^0 bandwidth *narrows* by ~10%.

The $scGW$ bandwidth *widens* by ~20% (30% error)



PRB57, 2108 (1998)

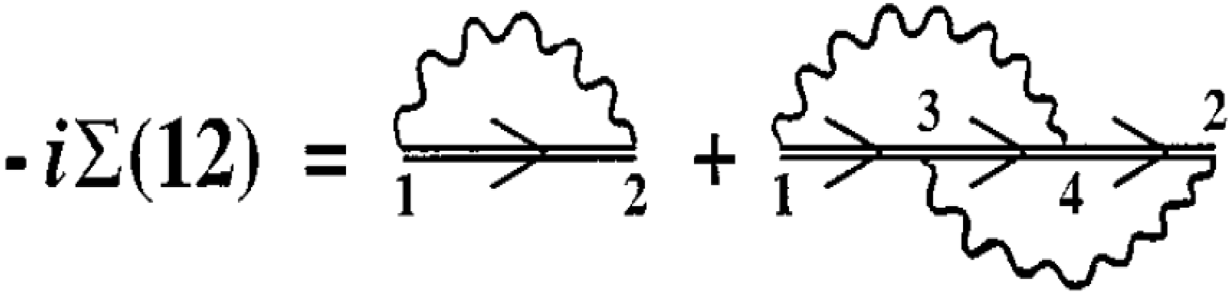
Spectral functions in real materials broaden too much and get washed out. Fares worse than LDA.



From Belashchenko et al, PRB 73, 073105

Higher order terms in Jellium

E. Shirley compared sc-GWGWG to sc-GW in Jellium:
(Phys. Rev. B 54, 7758 (1996))



"While a non-self-consistent … *GW* treatment reduces occupied bandwidths by 10–30% …, selfconsistency leads to overall increased bandwidths. Subsequent inclusion of the next-order term in *GWGWG* restores reduced bandwidths, which agree well with experiment."

Z-factor cancellation

Exact $\Sigma = iGW\Gamma$. Suppose W is exact. Then

$$G = \frac{1}{\omega - H_0 - \left[-V^{xc} + \Sigma(\omega_0) + (\partial\Sigma/\partial\omega)_{\omega_0}(\omega - \omega_0) \right] + i\delta}$$

$$Z = (1 - \partial\Sigma/\partial\omega)^{-1}$$

Residual of this pole (loss of QP weight) is reduced by Z

Write G as $G = ZG^0 + (\text{incoherent part})$ Ward identity

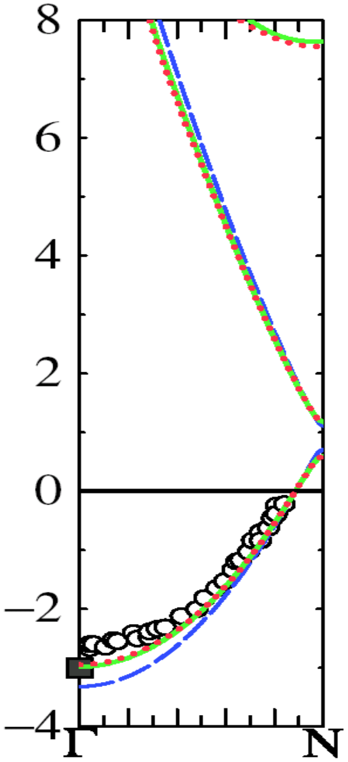
$\therefore\ GW\Gamma \approx G^0W + (\text{incoherent part})$ $\Gamma \to Z^{-1}$ for $q', \omega' \to 0$

Similar argument for W. Ishii et al (arxiv 1003.3342) reverses argument: find Γ that satisfies Ward Identity

$$\Gamma_{WI}(p, p+q) \equiv \frac{G(p+q)^{-1} - G(p)^{-1}}{G_0(p+q)^{-1} - G_0(p)^{-1}}$$

Results from $GW\Gamma_{\mathrm{WI}}$ similar to G_0W_0.

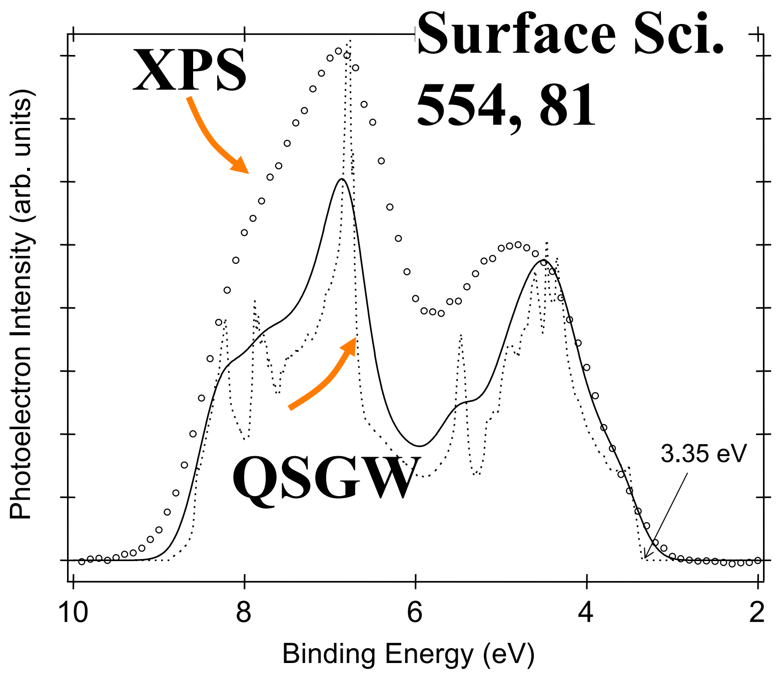
Bandwidths in QSGW



As Shirley showed, *sc:GW+GWGWG* essentially restores the G^0W^0 bandwidth

QSGW predicts the Na bandwidth to *narrow* relative to LDA by ~10%, in reasonable agreement with PE measurements.

It reliably *broadens* bandwidths in weakly correlated states, e.g. the O $2p$ band in $SrTiO_3$ and the C $2p$ band in graphene, while *narrowing* d and f bands in transition metals belonging to $4f$ and $5f$ elements

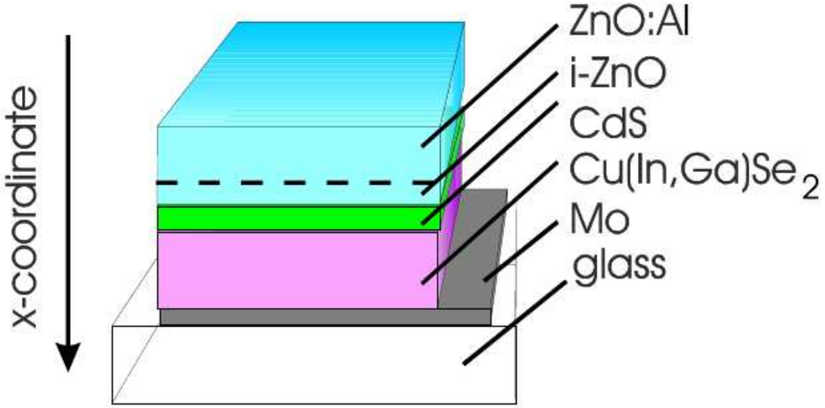

Surface Sci. 554, 81

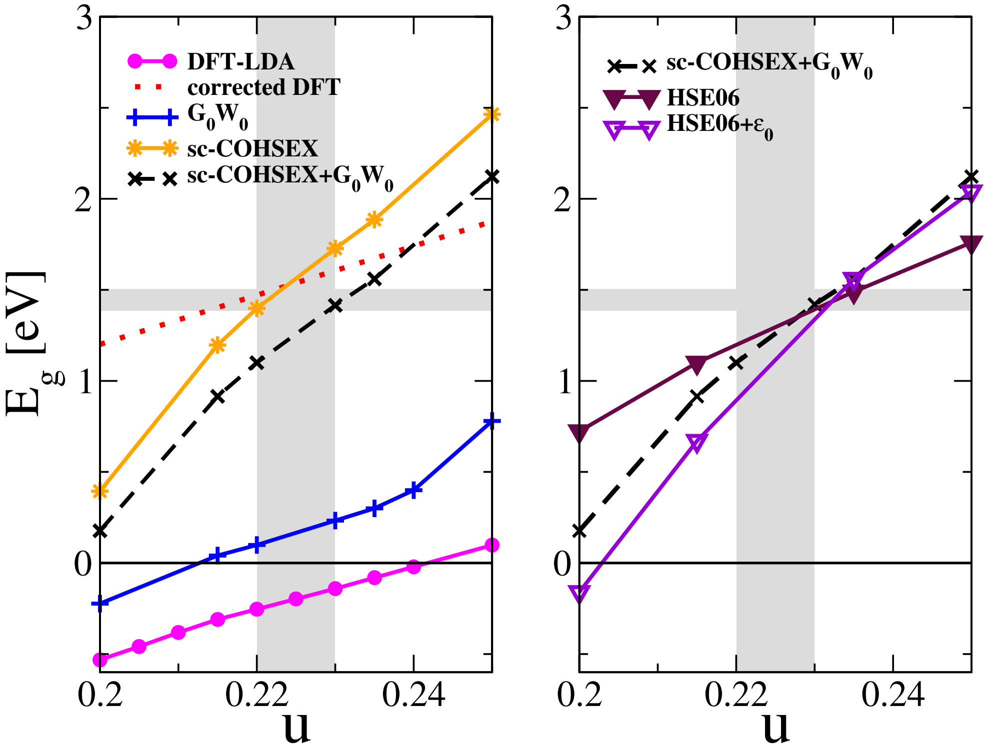
Need for Self-Consistency even in *sp* Systems

$Cu(In,Ga)Se_2$:
$d_{In\text{-}Se} \neq d_{Ga\text{-}Se}$ … but hard to measure (disorder)

$G^{LDA}W^{LDA}$ gap ~ 0 to 0.2 eV depending on (unkown) $d_{In\text{-}Se}$.
Experimental gap ~1 eV

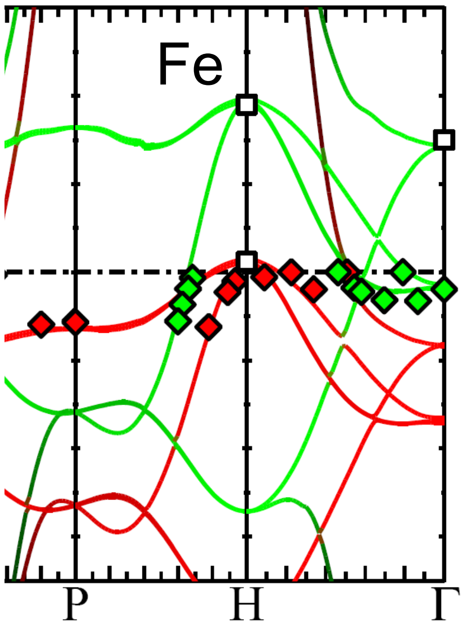
What about hybrid functionals, or LDA+U?
Strong interplay between gap, dielectric response.
Self-consistency essential to properly describe it.
Vidal et al, PRL 104, 056401 (2010)

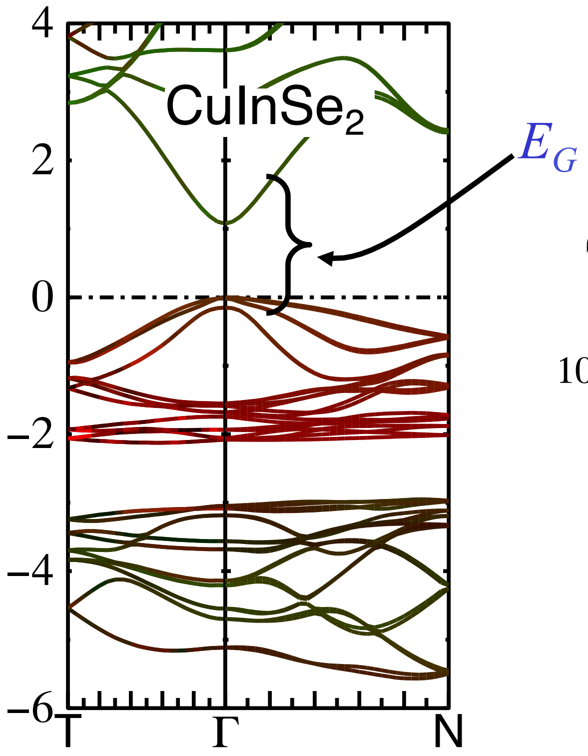




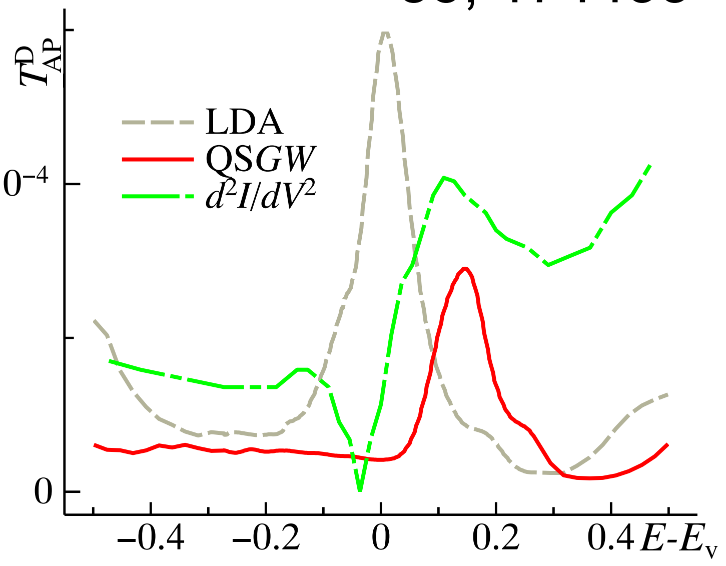
Dual Nature of QS*GW*: framework for H_0

QS*GW* generates a nearly optimal H_0 for many kinds of materials classes … often sufficient in itself





Fe/MgO tunnel junction, 0-bias anomaly (PRB 85, 174433

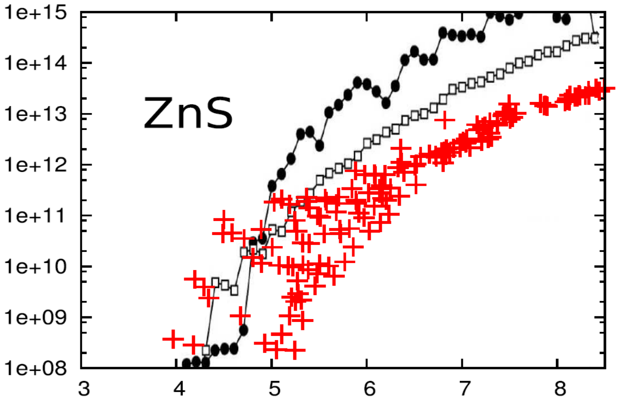


QSGW is key for distinguishing between properties accessible to a 1-particle picture (if optimally chosen), and true many-body effects that cannot be described by one Slater Determinant.

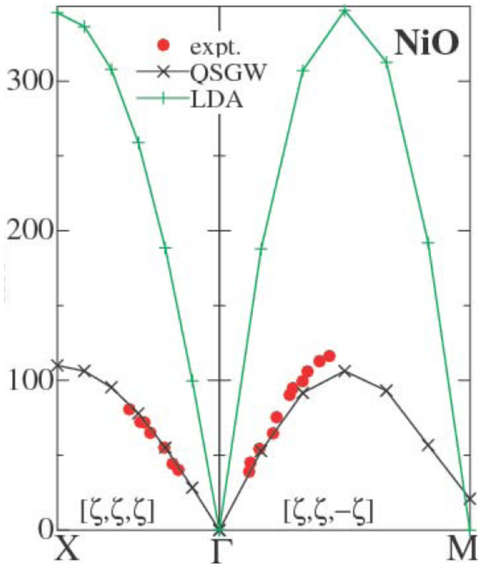
QSGW description of many body physics

QSGW also generates an interacting G with dynamical, many-body effects. It *sometimes* works very well …

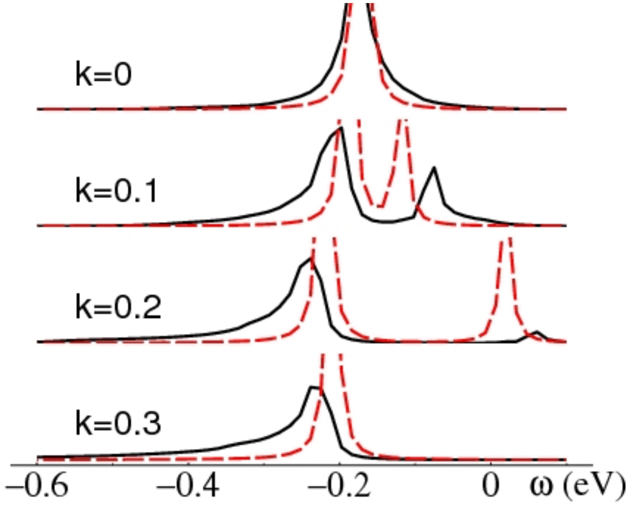
Impact ionization, ZnS



Spin waves, NiO



ARPES, Fe



GW is too simple … only real many-body effect come from plasmons in the charge channel.

QSGW is a way to choose the optimum basis set for many-body physics … strongly affects relative importance of diagrams.

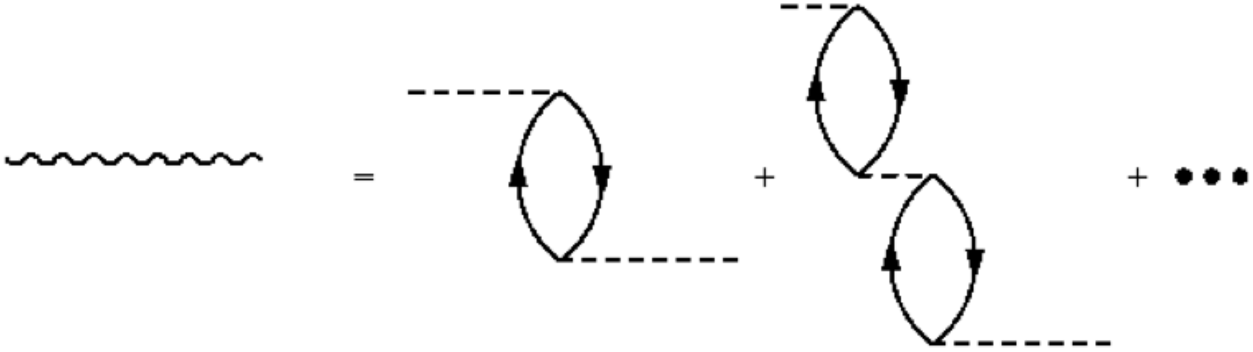
What GW does well (I)

--- No simple answer because:

- scGW is poor for spectral properties (much better for total energy; see Kutepov et al, PRB 80, 041103R),
- Starting-point dependence of $G_0W_0 \Rightarrow$ ambiguities

QSGW offers perhaps the most sensible path to eliminate ambiguities, and elucidate strengths and weaknesses in GW

1: van der Waals interactions are built into the 2nd order bubble (missing in LDA, DMFT)



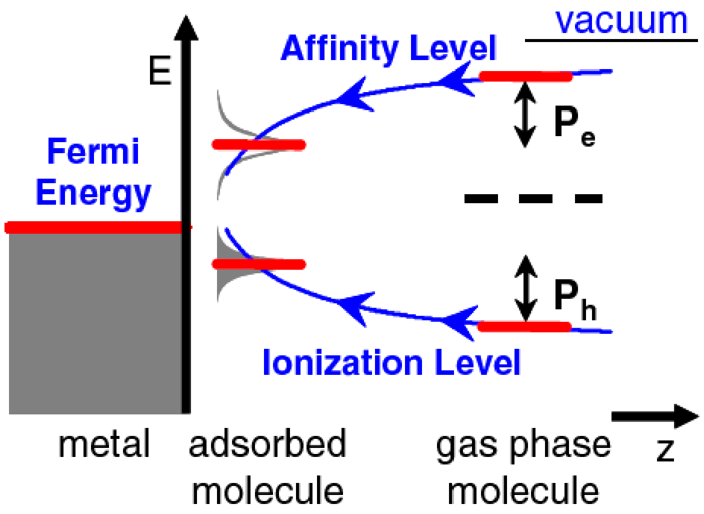
What GW does well (II)

2. Nonlocal correlation in the polarization.

Example: The benzene energy gap is predicted to be strongly renormalized from 10.5 eV (gas phase) when put on graphite (7.2 eV).

Basically like an image force.

Although correlation relatively weak here --- it has a big effect



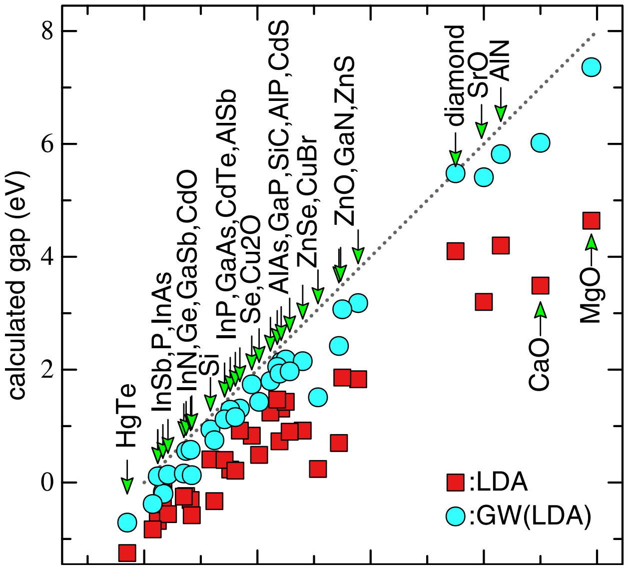
Neaton, Hybertsen and Louie, PRL 97, 216405

What GW does well (III)

3. Nonlocal correlation in the self-energy.

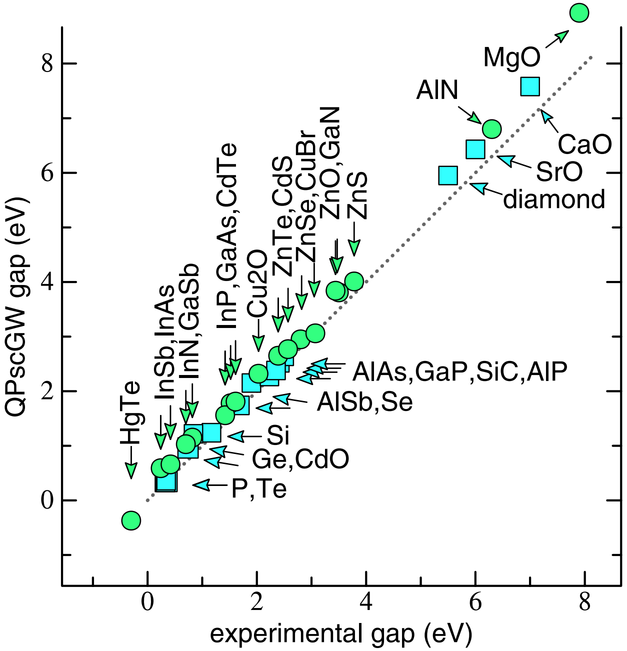
DFT gaps are too small because potential is local.

Choices: (1) make do with nonanalytic V_{xc} (problematic) or (2) allow nonlocality in the potential (practical). Most methods that resolve the bandgap problem put in some form of nonlocality. GW does it in a natural way.



← $G^{LDA}W^{LDA}$

→ QSGW



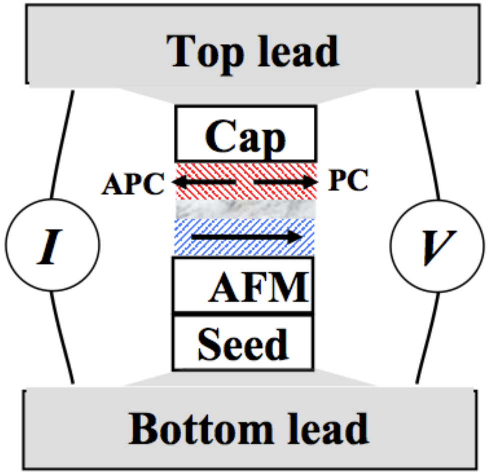
PRL 96, 226402 (2006)

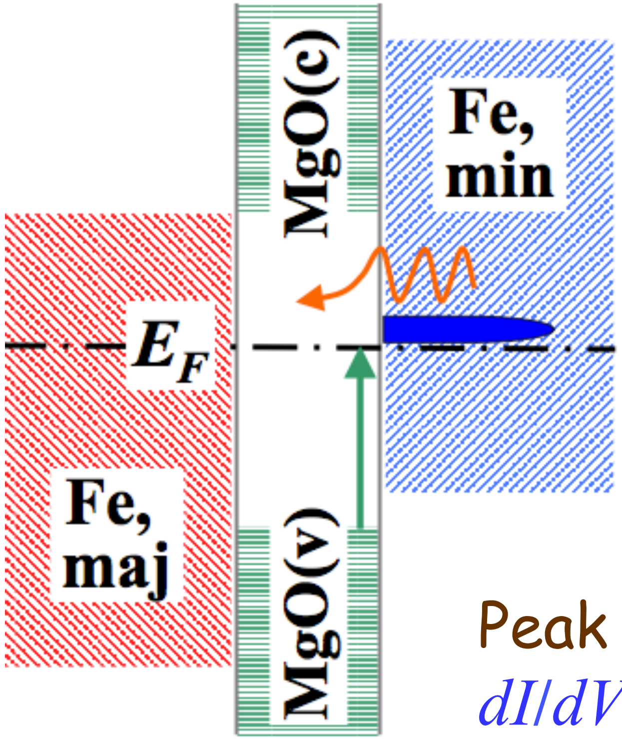
What GW does well (IV)

4. level alignments generally very good.

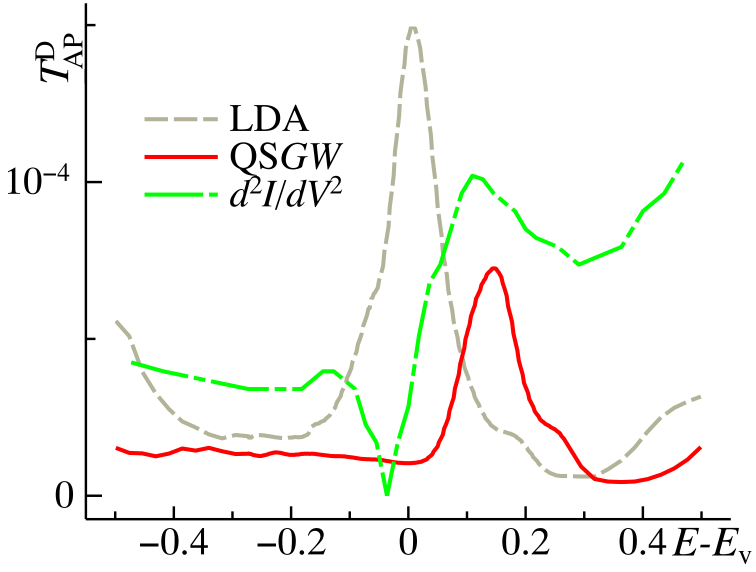
Example: Fe/MgO/Fe tunnel junctions

(Tunneling Magnetoresistance: basis for modern read heads.)





Apply V ⇒ Fe Surface state crosses E_F ⇒ current spike



Peak observed in dI/dV at 0.2 eV. LDA: dI/dV peaks at 0V

Where does QS*GW* Break Down?

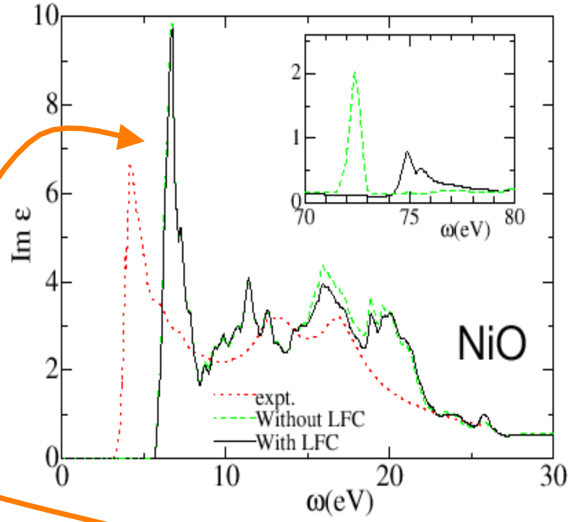
Unoccupied states *universally* too high

✓~0.2 eV for *sp* semicond;

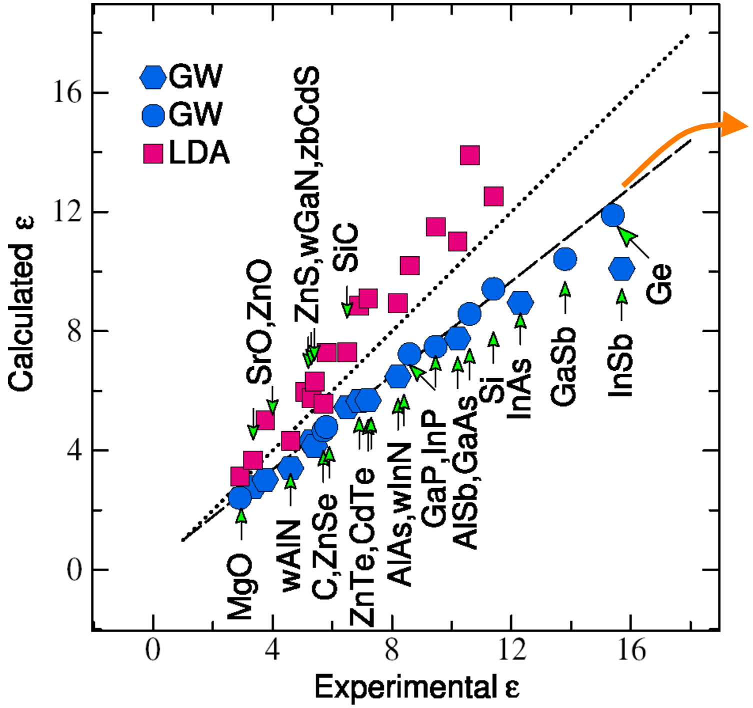
✓<~1eV for itinerant *d* $SrTiO_3$, TiO_2

✓>~1eV for less itinerant *d* NiO

✓~3 eV for *f* Gd,Er,Yb

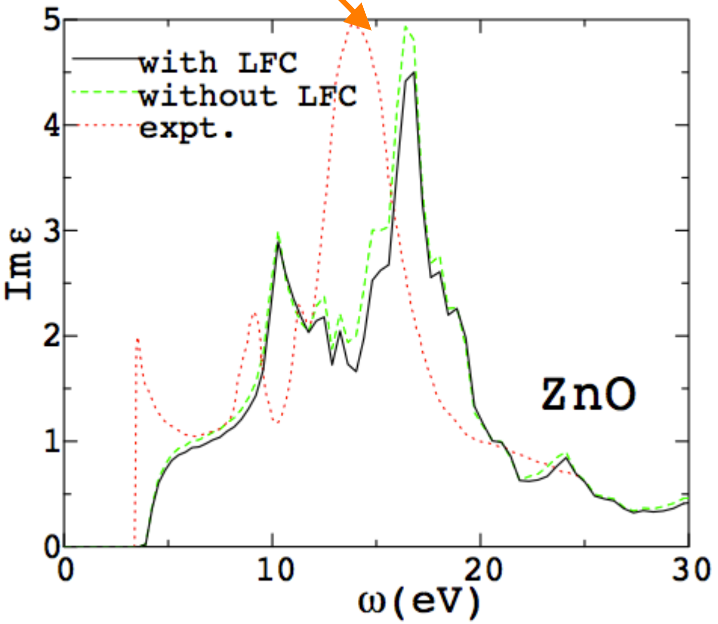


Peaks in Im ε(ω) *universally* too high

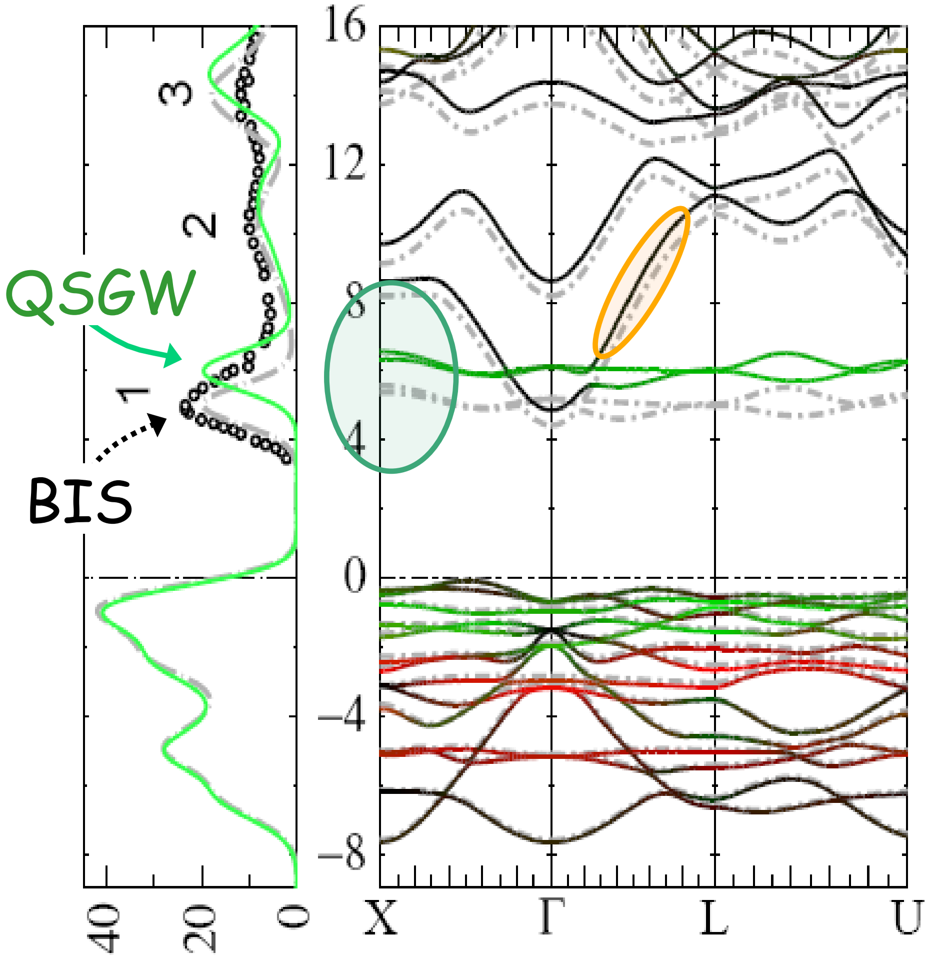


ε_∞ *universally* 20% too small.

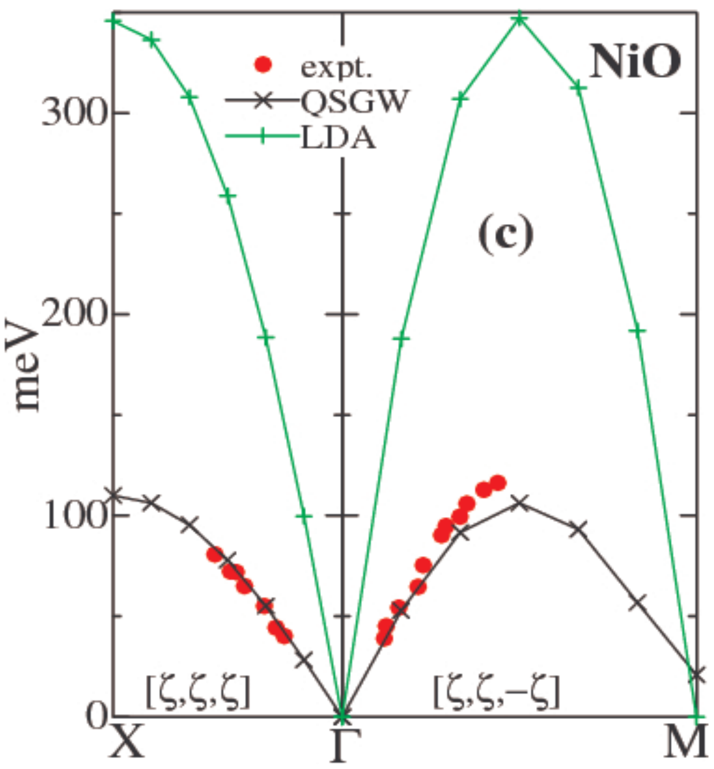
Errors are all related!



Quasiparticle Self-Consistency for NiO



NiO looks ok, but gaps too big! (clear marker of RPA overestimating W)



J. Phys. Cond. Matt. 20, 95214

Spin waves in MnO and NiO very well described. True ab initio, all electrons on same footing.

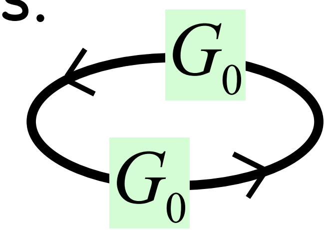
Largest Error: missing diagrams in W

A blue shift in the plasmon peak has effect on $\mathrm{Re}[\varepsilon(0)]$ (Kramer's Kronig relation). Approximate peak by δ-fn:

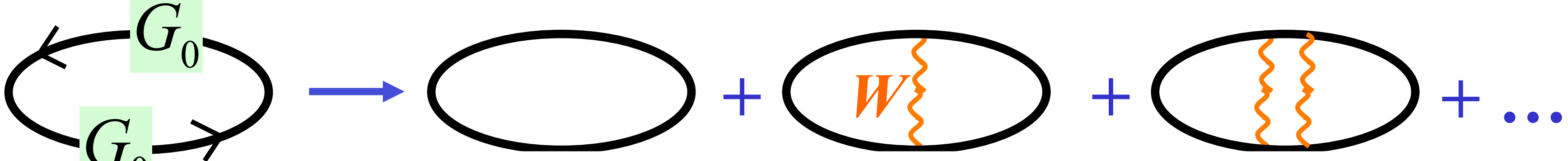
$$\Delta\,\mathrm{Re}\,\chi_1(0) = \frac{1}{\pi}\int_{-\infty}^{\infty}\left[\frac{\delta(\omega'-\omega_{\mathrm{th}})}{\omega'} - \frac{\delta(\omega'-\omega_{\mathrm{exp}})}{\omega'}\right]d\omega' = \frac{1}{\pi}\left(\frac{1}{\omega_{\mathrm{th}}} - \frac{1}{\omega_{\mathrm{exp}}}\right) < 0$$

ε_∞ too small because of *blue shifts* in plasmon peaks.

The *RPA approximation* for the polarizability $P = iG_0 \times G_0$, misses screening channels, especially:



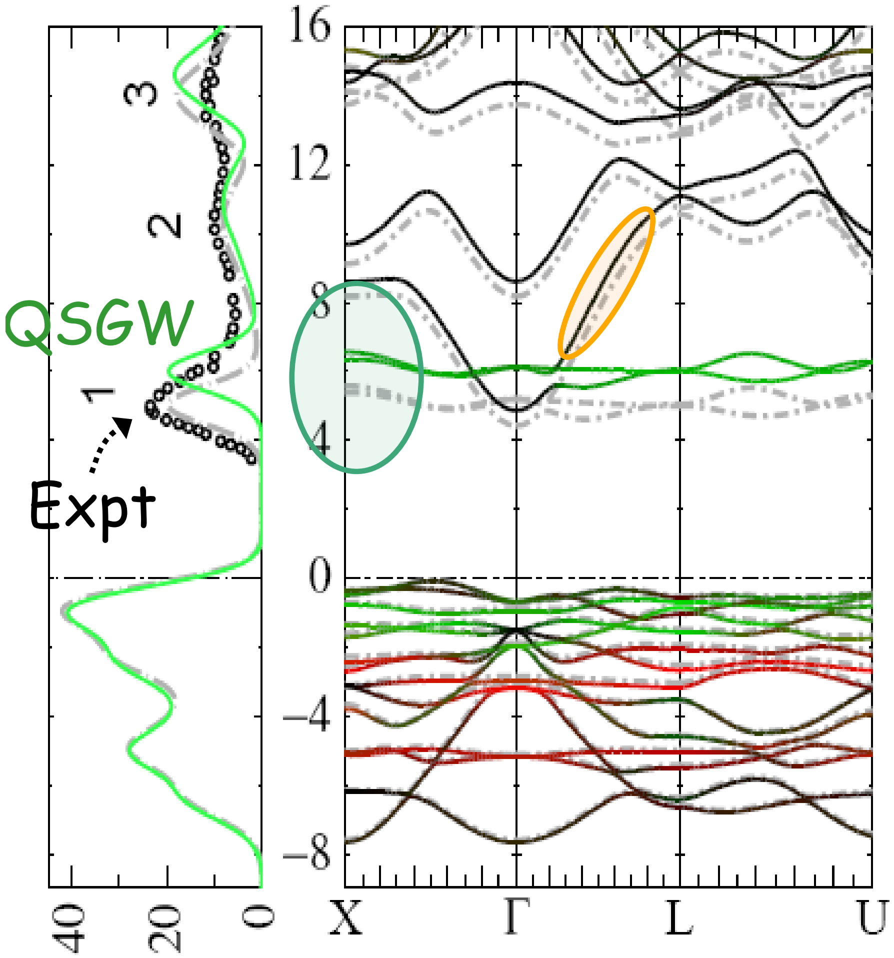
e^- and h^+ *are attracted* via W, e.g. by ladder diagrams,

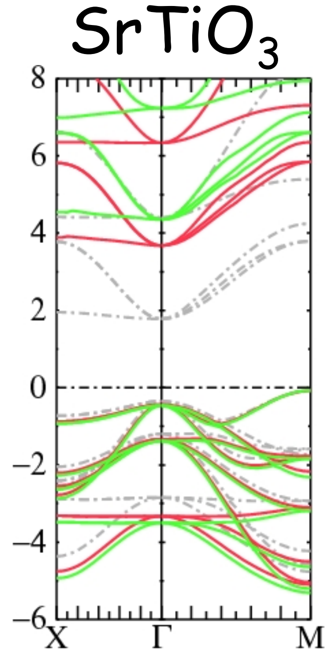


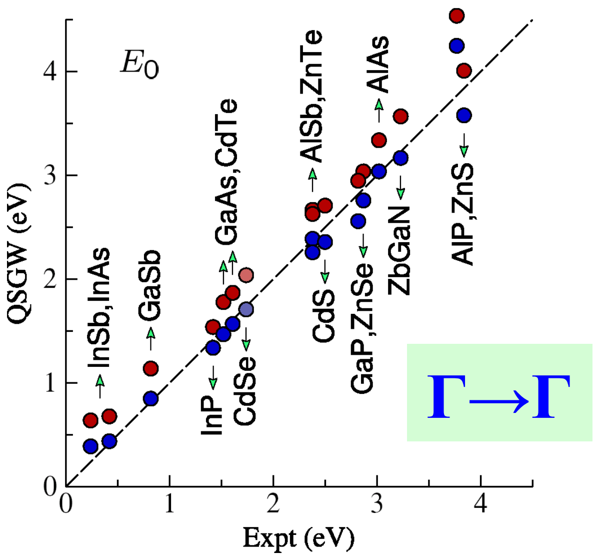
(Ladders needed for good optical spectra)

Conclusion: W calculated via RPA is *too large*, by 25% at $\omega=0$.

Better screening in the charge channel fixes much







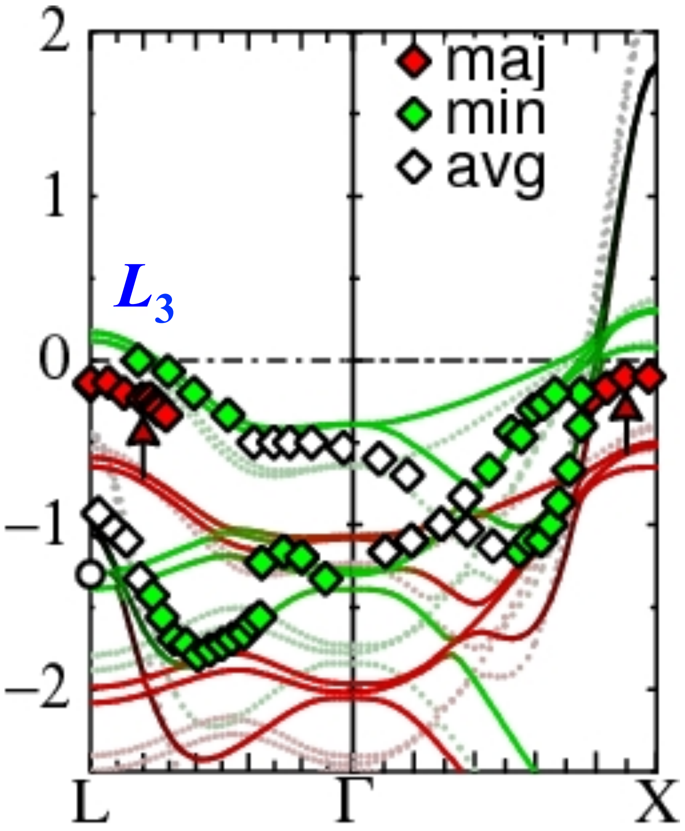
Estimate error

$W \sim [\varepsilon_\infty^{-1}(\mathrm{expt})/\varepsilon_\infty^{-1}(\mathrm{QS}GW)]\, W^{\mathrm{RPA}}$

Result: spectra aligns almost exactly with BIS. Peaks 1, 2, 3 shift different amounts

Seen in most TM oxides and universally seen in *sp* systems

QSGW and Transition Metals



W^{RPA} is screened in the charge channel only … no spin fluctuations.

QSGW : vast improvement over LDA for TM in general. But for Ni, problems appear

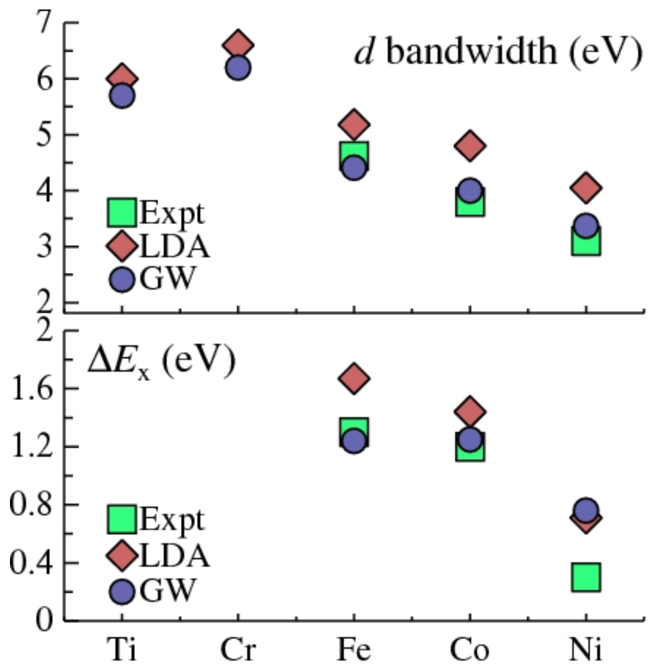
Calculated ΔE_x :

QSGW	LDA
0.76	**0.71**

Calculated M :

QSGW	LDA
0.76	**0.60**

Trends in 3*d* series

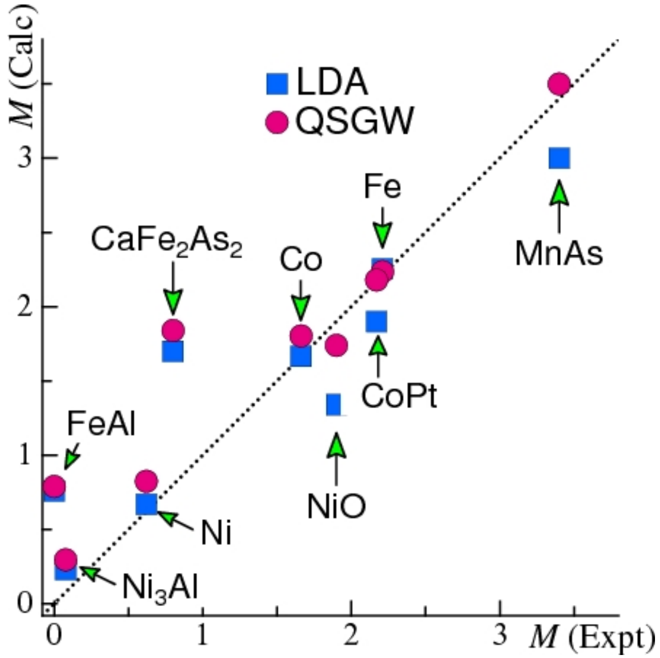


QSGW misses a satellite at -6 eV seen in photoemission

Spin Fluctuations

In Ni spin fluctuations are important (Nolting et al, 1989)
Quite generally, QSGW appears to:

- predict M in local-moment systems very well
- overestimate M in itinerant systems.



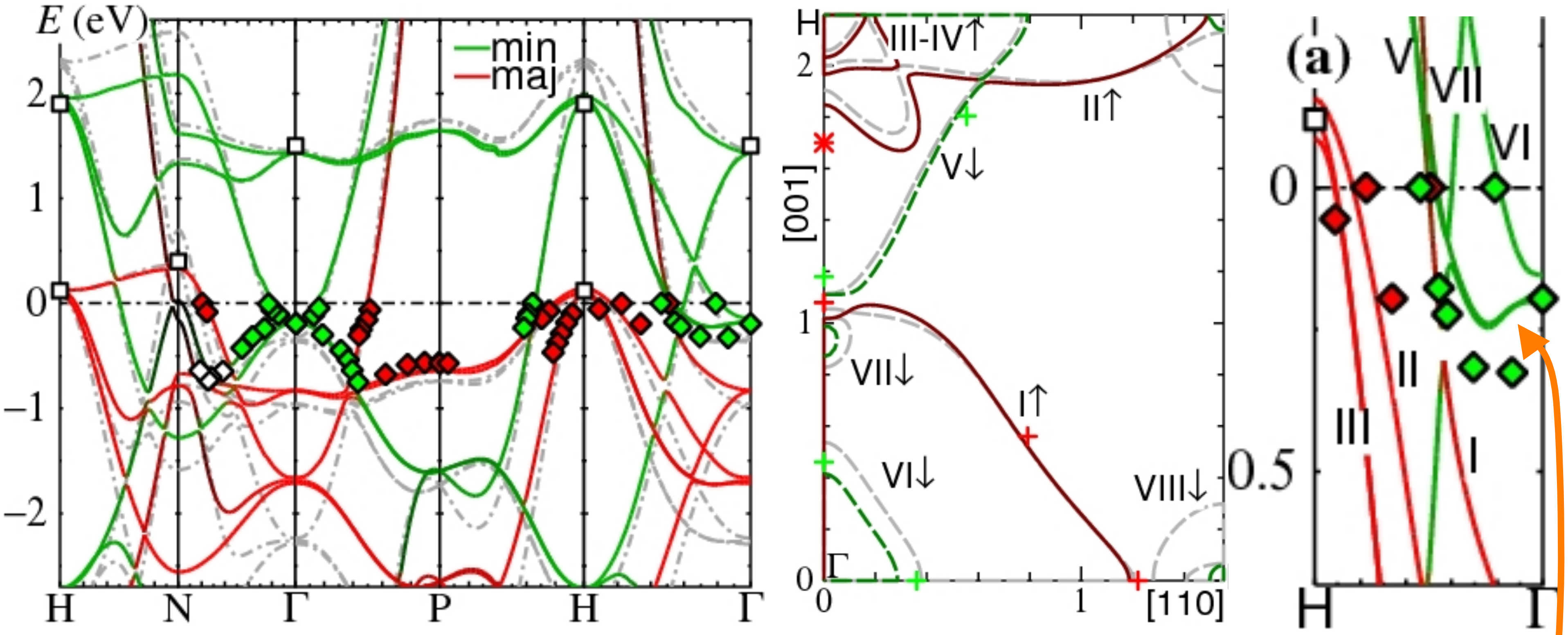
LDA has two distinct errors:
$\langle M \rangle$ is too large in itinerant materials.
$\langle M \rangle$ is too small in local-moment systems (CoPt, MnAs)

In Ni the errors cancel … $\langle M \rangle$ is fortuitously good!

Spin fluctuations reduce $\langle M \rangle$. Moriya estimated $\langle \Delta M \rangle$ from FD theorem. Requires $\int d\omega\, \mathrm{Im}\chi$ (Mazin et al PRL 2004).
… Better fluctuations are built into higher order diagrams.

Spin Fluctuations in Fe are not important

QSGW matches ARPES and inverse PE (Santoni & Himpsel, Phys. Rev. B 1991) extremely well …

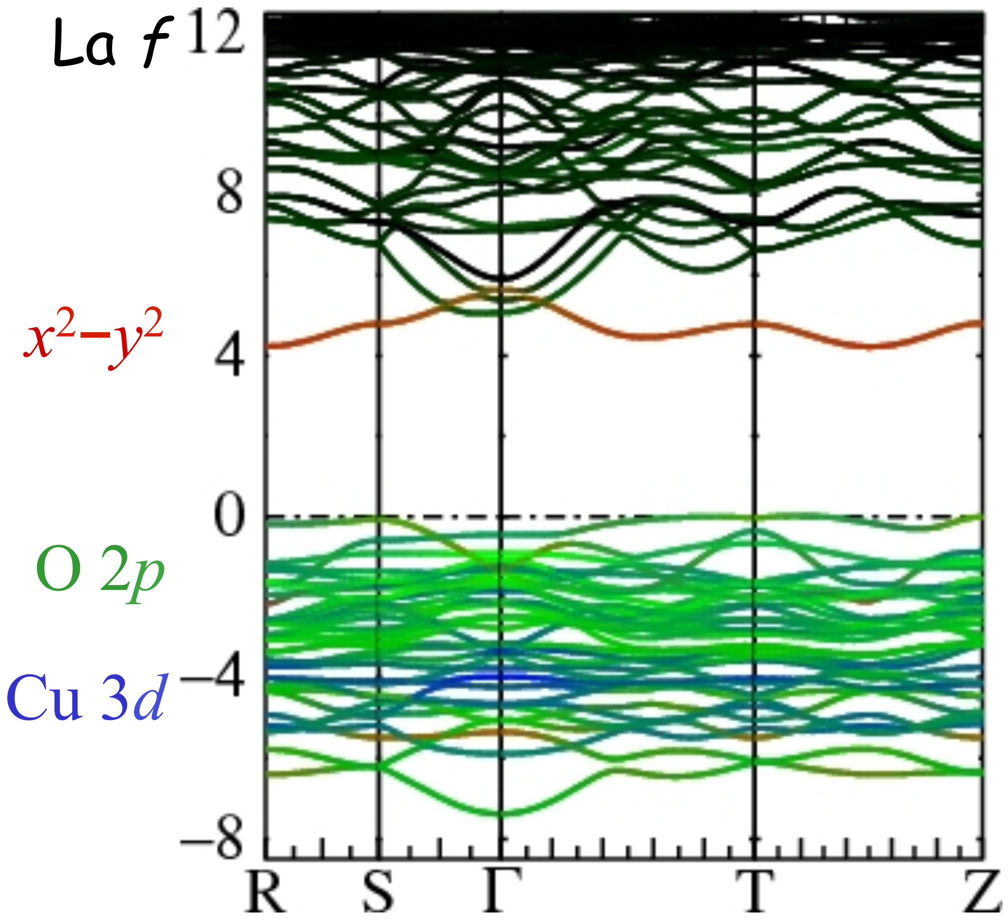


Much better than LDA+DMFT. Small discrepancies at ~0.1 eV scale: … But it turns out that differences are largely artifacts of final-state effects in PE! See Phys. Rev. B 95, 041112(R)

QSGW La_2CuO_4 ordered antiferromagnetic state

Low T° phase: AFM with (π, π) ordering

QSGW: insulating state with E_g~4eV.



Results:

- Lowest CB is Cu $x^2\!-\!y^2$ with significant O 2*p* admixed.
- VBM is O 2*p*.
- Cu $x^2\!-\!y^2$ ↑ and ↓ split by ~10eV
- Remaining Cu *d* pushed below O 2*p*.
- Magnetic moment M~0.8.

Failings:

- Gap ~4eV >> expt (2 eV)
- Disorder is expensive

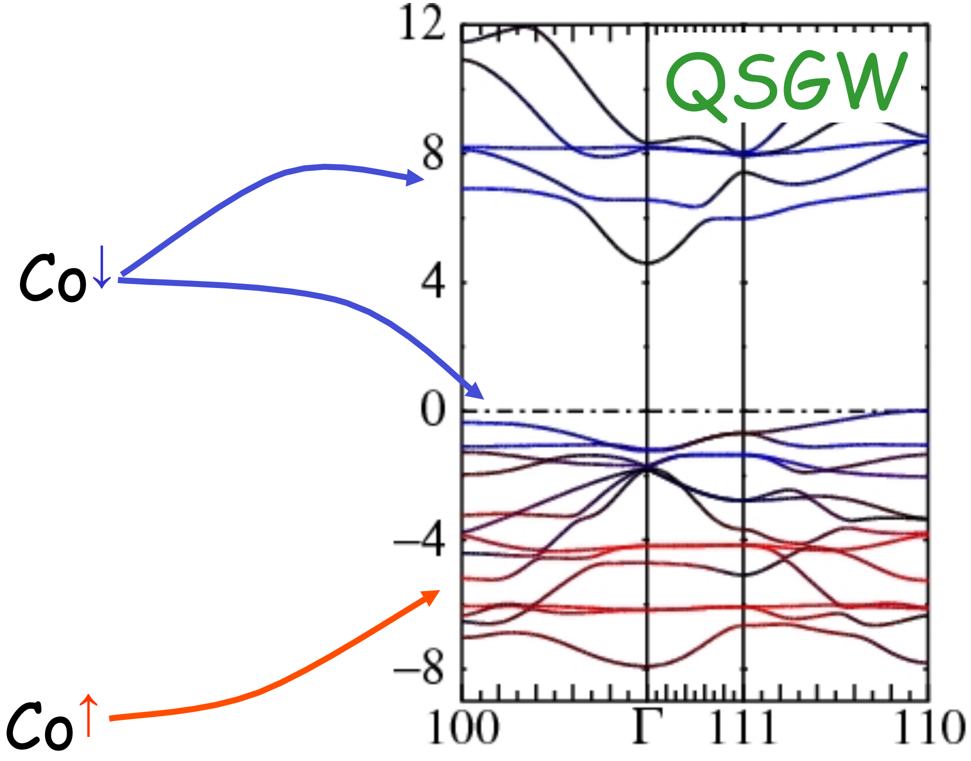
CoO shows a pattern very similar to La_2CuO_4 ….

AFM II spin configuration:
The 5 Co$^{\uparrow}$ states are filled
The 5 Co$^{\downarrow}$ states split into 3(occ)+2(unocc) separated by a gap.
The QS*GW* gap (4.4 eV) is 2 eV too big (experiment ~2.4 eV).

Gap error in CoO and La_2CuO_4 does not appear to be resolved by better screening in W.

They share in common a splitting of the d states in the minority channel into partially occupied, unoccupied groups

Gap is too large because of spin fluctuations (we think)



Summary

- Possible to construct effective noninteracting hamiltonians from a many-body hamiltonian.

  No unique choice. Common ones: Hartree Fock and Density-Functional theory. Many others …

  These methods have been tremendously successful, but they have limitations, esp in correlated systems

- Introduction to screening, and its importance as the dominant many-body effect

- The GW approximation as screened Hartree Fock

  Quasiparticle Self-Consistency to make optimal H_0.

  Dramatically improves quality of GW, but also limits.

- Partitioning : a framework to go beyond GW

  Partitioning concepts already in a one-body hamiltonian

  Rudiments of partitioning a many-body hamiltonian.