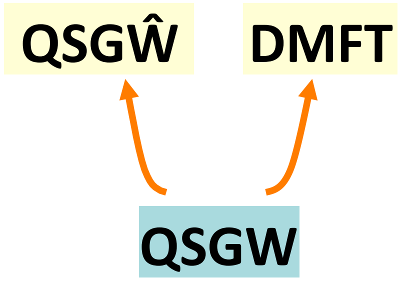
# Accurate Description of Correlated Materials

## Questaal Hands-On Workshop, May 2019

- The hard problem of correlated electrons
- Beyond the QP picture

1 Many body perturbation theory



Ladder diagrams : dominant correction to GW in charge channel

Low order $W^{RPA} \rightarrow W^{BSE}$ seems remarkably accurate, unless spin fluctuations are strong

2 Assume strong correlations mostly local (DMFT)

Partition hamiltonian into strongly correlated, local sector, and a weakly correlated nonlocal sector

Solve embedded local problem to all orders (CTQMC) in a QSGW bath.

# One-Body Hamiltonian as basis for Many-Body Theory

Pairwise interaction in Schroedinger's equation

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

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

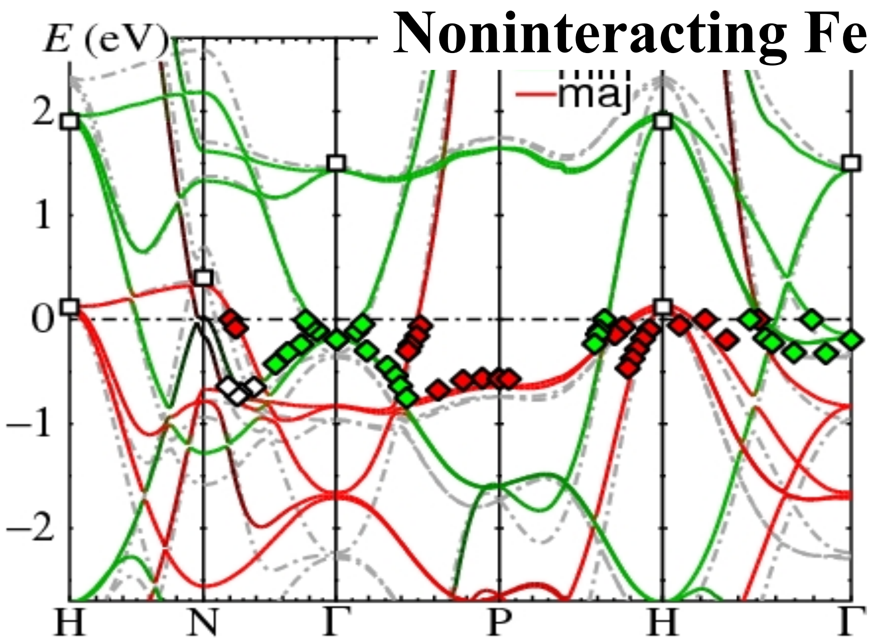
⇒ independent particle $\Psi \sim \psi_1(\mathbf{r}_1) \times \psi_2(\mathbf{r}_2) \times \ldots \times \psi_N(\mathbf{r}_N)$ is a fiction.

Screening makes the interaction weak ⇒ saves the day for independent (quasi)particle description.

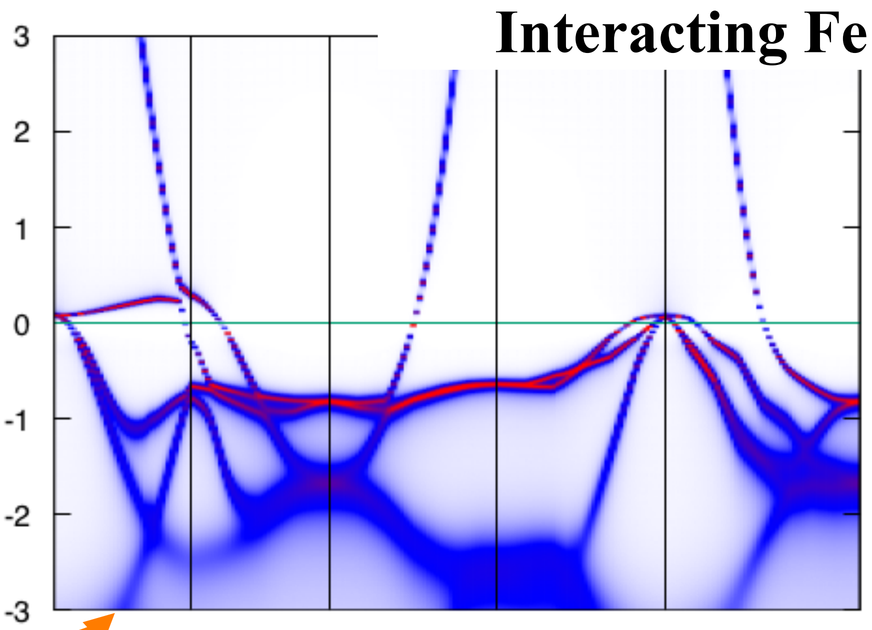
$GW$ --- a perturbative correction to IP --- is very successful.

- When correlations become strong, the QP picture fails and The perturbative approach becomes problematic.
- Typically only a part of the entire system is strongly correlated. For a workable scheme we must partition $H$.
- Treat low-level correlations globally, strong correlations locally

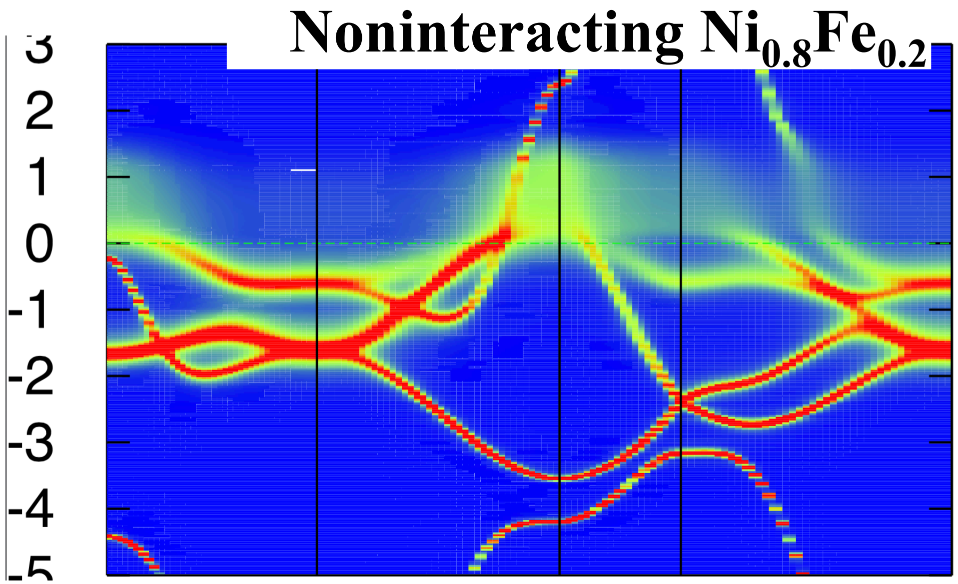
# Scattering smears out Quasiparticle Levels



**Noninteracting Fe**



**Interacting Fe**



**Noninteracting $Ni_{0.8}Fe_{0.2}$**

Broadening from $e^{-}-e^{-}$ interactions

Broadening from alloy scattering

No unique definition of noninteracting $H_0$ … but QSGW optimal by construction

# Going Beyond the 1-particle Picture

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

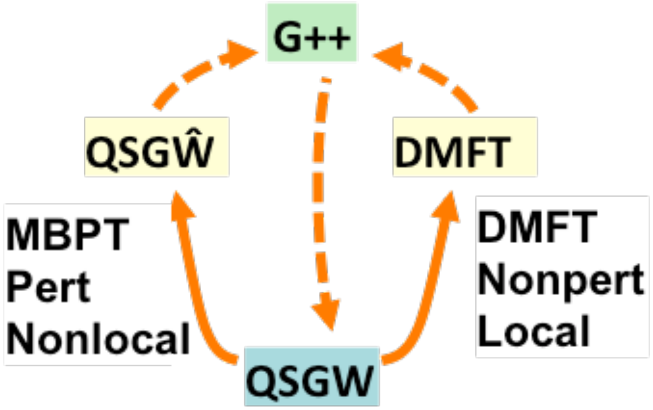
Path I. Many Body Perturbation Theory (GW, FLEX).

☑ Excellent for weak and moderate correlations

☒ Extending beyond the lowest order is a formidable task

Path II. Nonperturbative Solution on subspace (DMFT)

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



G++

QSG$\hat{W}$

DMFT

MBPT
Pert
Nonlocal

DMFT
Nonpert
Local

QSGW

☑ 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.

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 $H$

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

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

Substitute this relation to obtain an equation for $\phi_s$ alone:

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

* Note that $\hat{H}$ is $\omega$- 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 $G_{ss} = [(G_{ss}^0)^{-1} - H_{sr}G_{rr}^0 H_{rs}]^{-1}$ **where** $\begin{cases} G_{ss}^0(\omega) = [\omega - H_{ss}]^{-1} \\ G_{rr}^0(\omega) = [\omega - H_{rr}]^{-1} \end{cases}$

Call the interaction with the rest a *self-energy* $\Sigma_{\text{rest}}$ :

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

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

# Some observations

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

$\Sigma_{\text{rest}}$ "dresses" the subsystem through an $\omega$-dependent interaction with the "rest."

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

## Subsystems

The full many-body Hamiltonian is $\omega$-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. $\Sigma_{\text{rest}}$ is $\omega$- dependent and "dressing" the electron from screening by the other electrons.

We cannot solve the full problem exactly, and must make approximations. The smaller $\Sigma_{\text{rest}}$ is (especially, the smaller its $\omega$- dependence), the better the approximation.

# Mixed Approximations

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

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

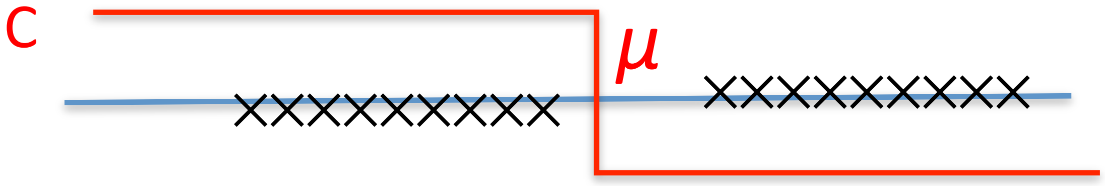
$$G^{(2)} = G^{(1)} + G^{(1)}\Sigma^{(2)}G^{(2)}$$

- $\Sigma^{(1)}$ 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 smaller $\Sigma^{(2)} - \Sigma^{(1)}$ feedback. If $\Sigma^{(1)}$ already fairly good, it may enough to calculate $\Sigma^{(2)}$ in a single shot, without updating $\Sigma^{(1)}$.

# Spectral representation of $G_0$

Construct $G_0$ from eigenfunctions of $H_0$ :

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



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

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

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

# Meaning of Quasiparticles, Interacting Case

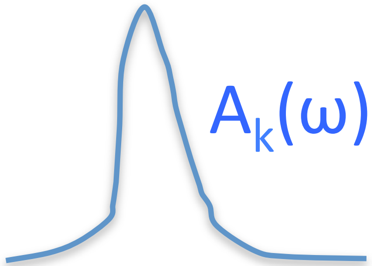
Project *G* onto 1-particle states $G_{kk'}(\omega) = \left\langle \psi_k(\mathbf{x}) \middle| G(\mathbf{x},\mathbf{x}',\omega) \middle| \psi_{k'}(\mathbf{x}') \right\rangle$

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

But the 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 $\varepsilon_k$

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 $\varepsilon_s$ coupled to a set of states $m=1\ldots N$ with eigenvalues $\varepsilon_m$ . 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 $1×N$ matrix.

Using the coupled-$G$ formalism, we obtain

$$(\omega-\varepsilon_s)G_{ss}-\sum_m^N H_{sm}G_{ms}=1$$

$$(\omega-\varepsilon_m)G_{ms}-H_{sm}G_{ss}=0$$

And

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

with

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

$\Sigma_{\mathrm{rest}}$ is the effect of the "rest" on to the subsystem. In in Dynamical Mean Field theory, $\Sigma_{\mathrm{rest}}$ is called the "hybridization function" $\Delta$.

# Effect of the Hybridization function

$\Delta$ is a special instance of $\Sigma_{\text{rest}}$ 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 $H_{sm}=t$. $\Delta$ becomes

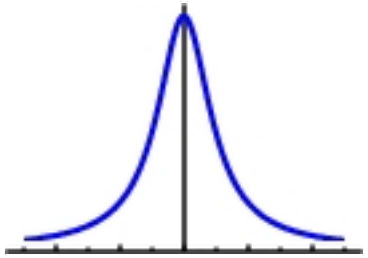
$$\Delta(\omega) = \left|t^2\right| \int d\varepsilon \frac{\rho(\varepsilon)}{\omega - \varepsilon}$$

**Density-of-states**

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

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

**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 $\omega$-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 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 $\omega^j$

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

Replace $\mathrm{Re}\Sigma$ with the linearized
$\Sigma$ and call the resulting $G$ the
"coherent part" $G^{\mathrm{coh}}$ 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

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

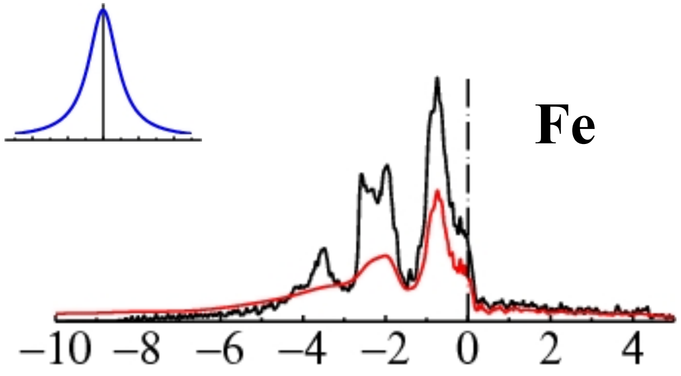
Define the QP peak as the value $\omega^*$ of $\omega$ where the real part of the denominator vanishes.

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

$\Sigma$ shifts $\omega^*$ … but the shift $\omega^*$-$\omega^j$ depends on the reference $V_{xc}$. The better the $V_{xc}$ the smaller the shift (it is zero in quasiparticle self-consistent construction!)

Im$\Sigma$ broadens the pole at $\omega^*$ .

The $\omega$-dependence of Re$\Sigma$ reduces the strength of the pole by $Z$ . QP weight gets redistributed into incoherent parts of the spectrum, such as Hubbard sidebands or plasmon satellites.



-- **Interacting DOS**
-- **Noninteracting DOS**

# Quasiparticle Lifetime

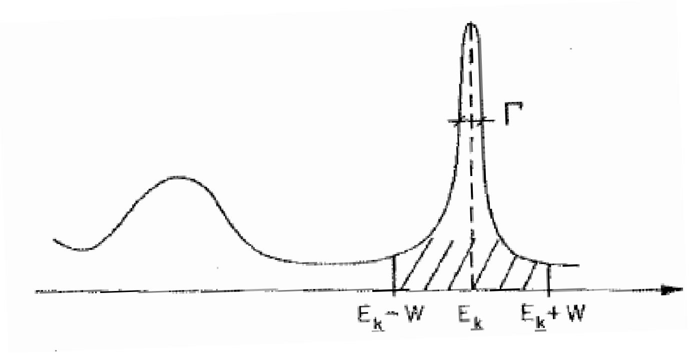
Fourier transform $G^{\mathrm{coh}}(\omega)$ into the time domain :

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

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

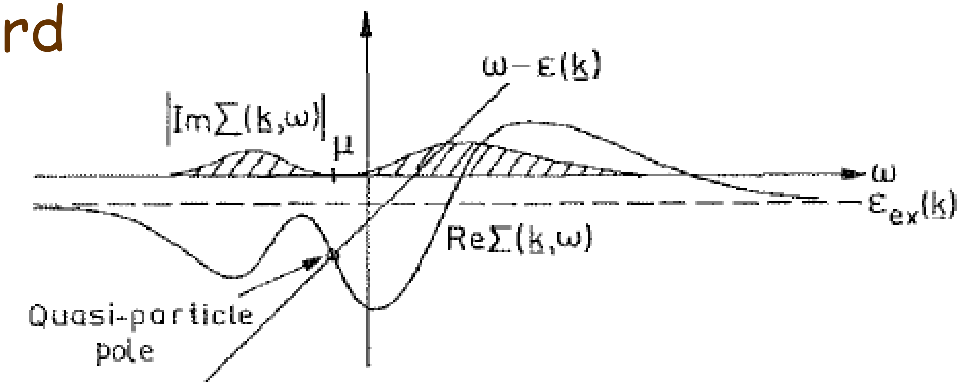
The corresponding spectral function $A^{\mathrm{coh}}$ is broadened by Σ .

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



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

Near $E_F$ or $\mu$ , $|\mathrm{Im}\Sigma| \sim (\omega^{*}-\mu)^2$ 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 $\omega$ - 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

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

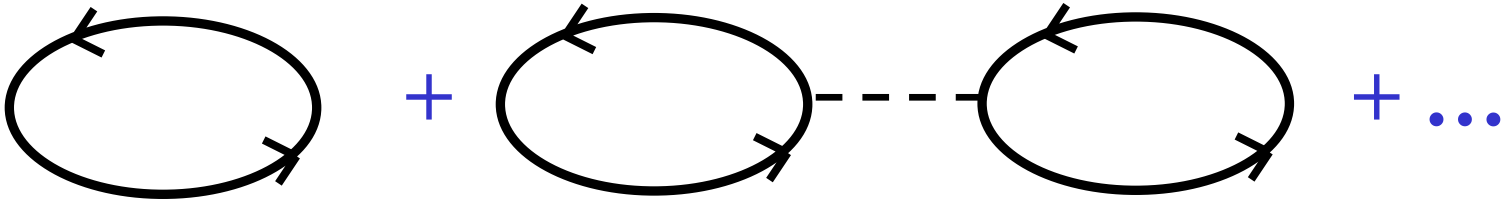
**Important when correlations are strong** → $\omega$-dependence

$k$-dependence ← **Always important; see PRL 109, 237010**

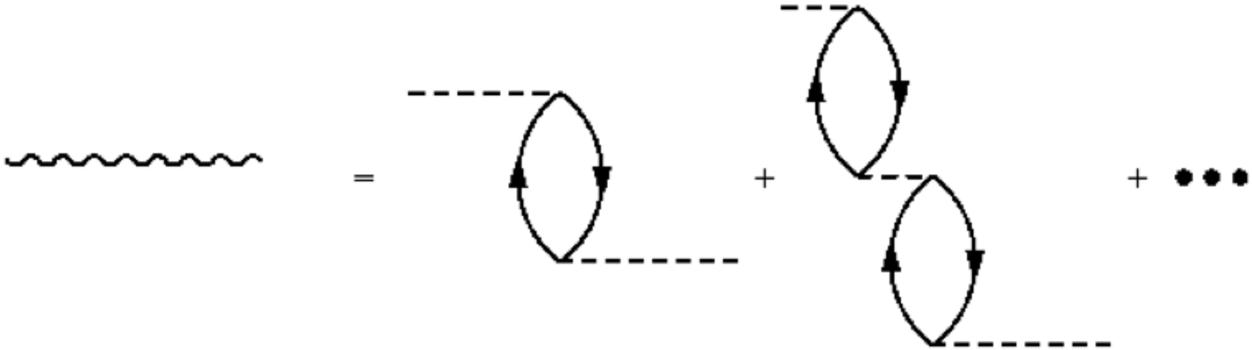
# Diagram for $W$ in the RPA

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 $\varepsilon^{-1}$ 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 $V_\mathrm{x}$ 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 $V_\mathrm{x}$ 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 $v$ → dynamically screened $W$:

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

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

# 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 $H^{\mathrm{LDA}}$ ? 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 $\Delta V$ :

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

$G$ 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 $V_{\mathrm{xc}}$ (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 $\Delta V$ 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 $V^{\mathrm{xc}}$ 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 $N$

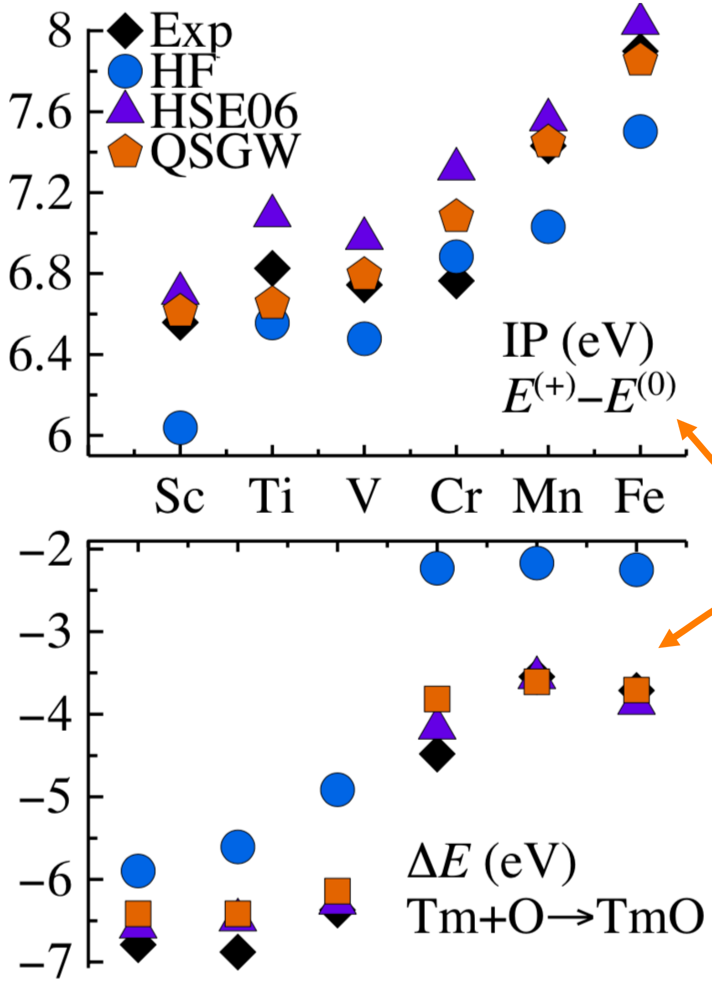
Iterate to self-consistency.

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

# Ambiguities in *GW* from starting point

*GW* is true *ab initio* (unlike many extensions to the LDA),

··· but *GW* is perturbation around $H_0$



With freedom to choose $H_0$, ambiguities
⇒ not really *ab initio* any more.

Example: TM & TM–O dimer

From RPA total energy calculate:

Ionization potential

Tm–O heat of reaction

Compare three choices for starting $H_0$:

- Hartree Fock
- HSE06
- QSGW

QSGW: optimal path of adiabatic connection within given level of approximation … best on average.

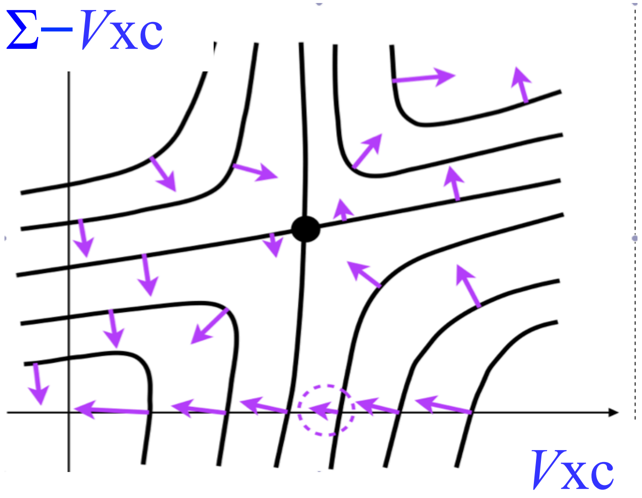
Also removes ambiguities in starting point dependence

# True self-consistent GW

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

Starting-point dependence can be also surmounted by making $G$ self-consistent

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



But …

$\varepsilon$ strongly violates *f* sum rule [Tamme, PRL '99]

$P$ loses its usual meaning as derivative $\delta n/\delta V$

**B. Holm and U. von Barth, PRB57, 2108 (1998) suggest it might be justified on empirical grounds, if it makes a better $G$.**

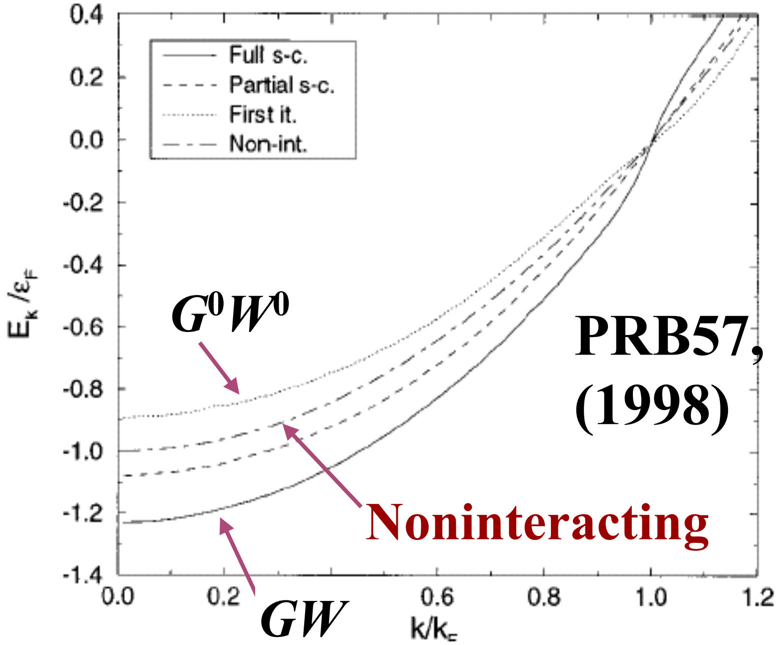
But poor in practice, even for the electron gas

# Bandwidths in scGW

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

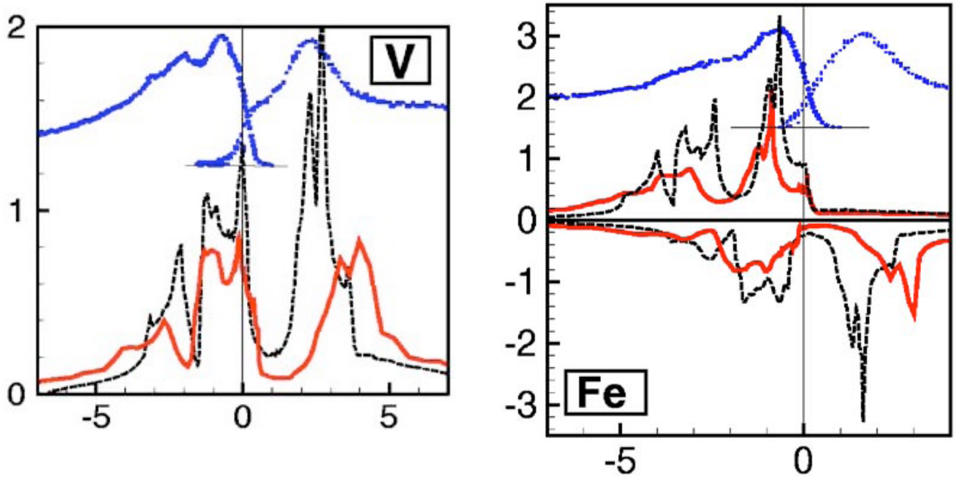
The $G^0W^0$ bandwidth *narrows* by ~10%.

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**

# 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

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

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

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

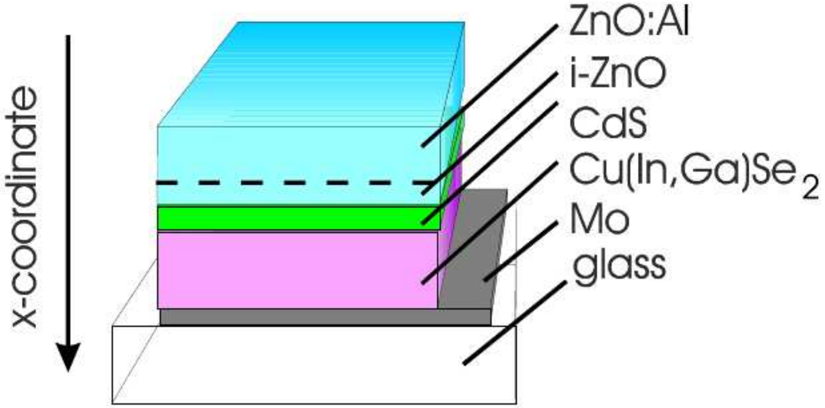
Results from $GW\Gamma_{\mathrm{WI}}$ similar to $G_0W_0$.

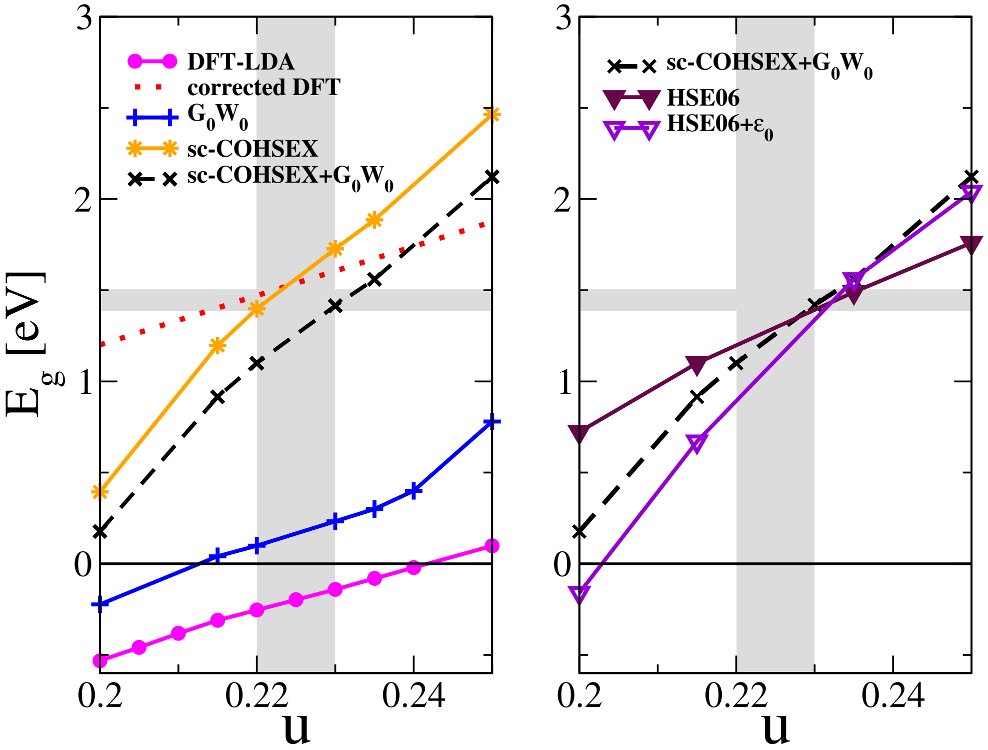
# Need for Self-Consistency even in *sp* Systems

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

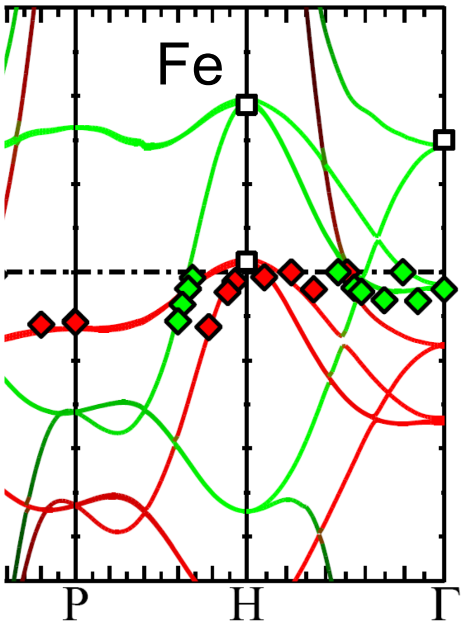
What about hybrid functionals, or LDA+U?
Strong interplay between gap, dielectric response.
Self-consistency essential to properly describe it.
Vidal et al, PRL 104, 056401 (2010)

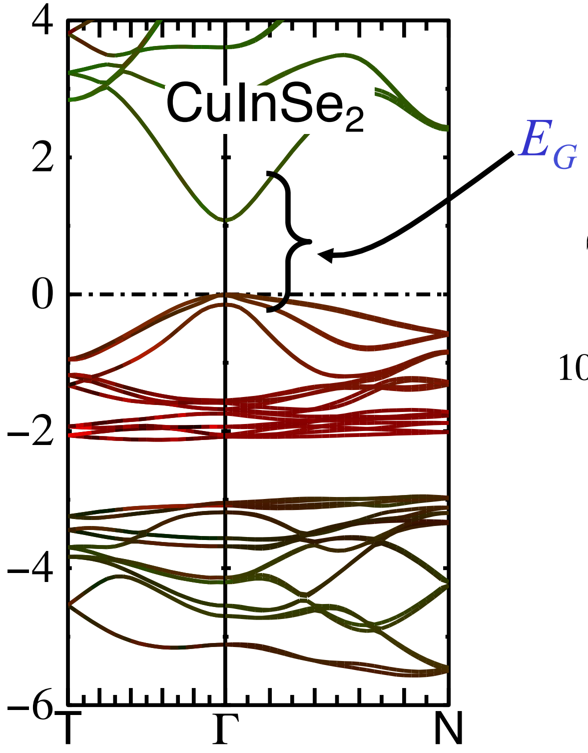




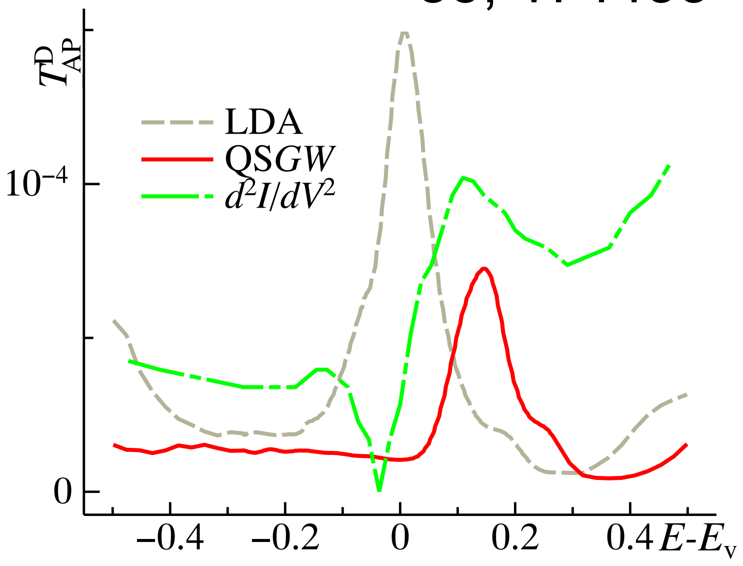
# Dual Nature of QS*GW* : framework for $H_0$

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

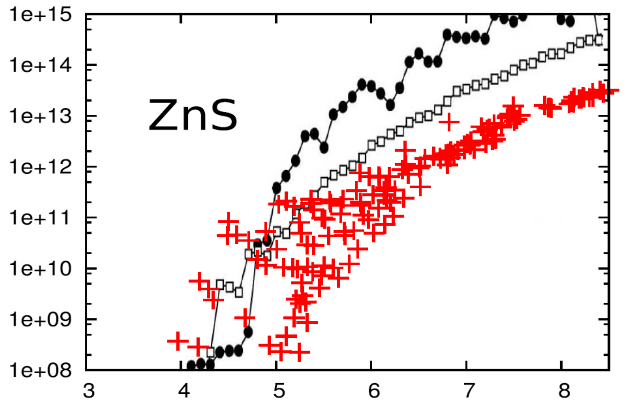


QSGW is key for distinguishing between properties accessible to a 1-particle picture (if optimally chosen), and true many-body effects that cannot be described by one Slater Determinant.

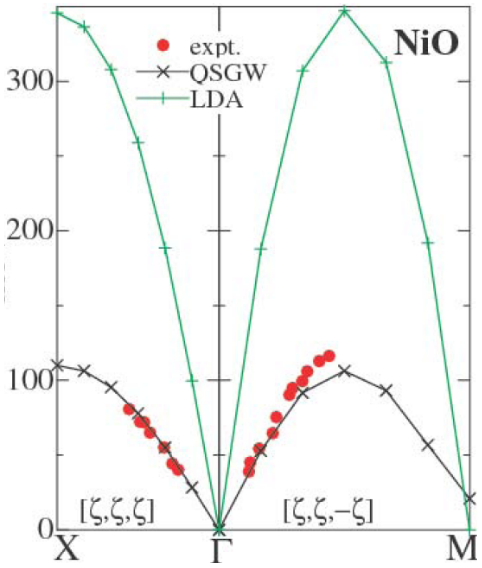
# *QSGW* description of many body physics

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

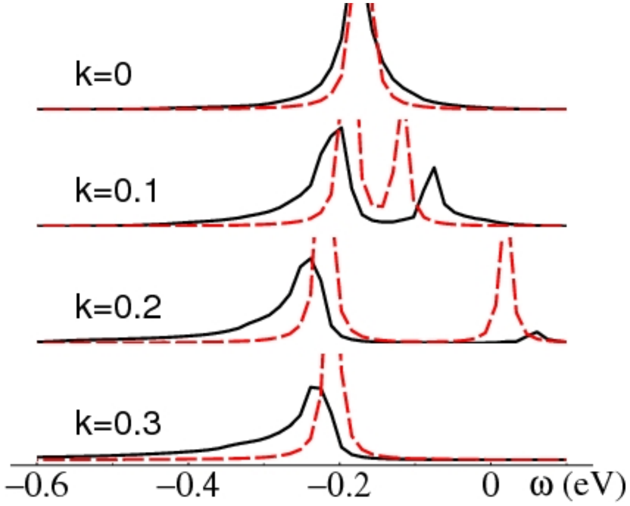
Impact ionization, ZnS



Spin waves, NiO



ARPES, Fe



But 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.

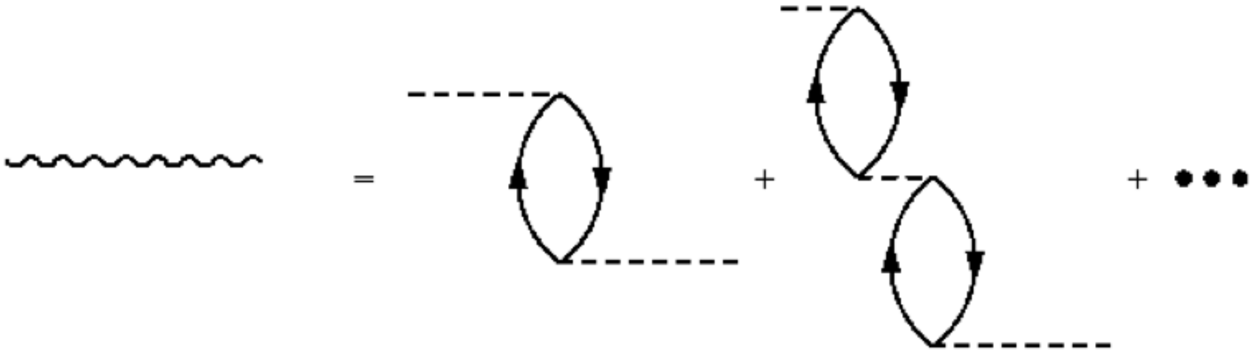
# What GW does well (I)

--- 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 $G_0W_0$ ⇒ 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)



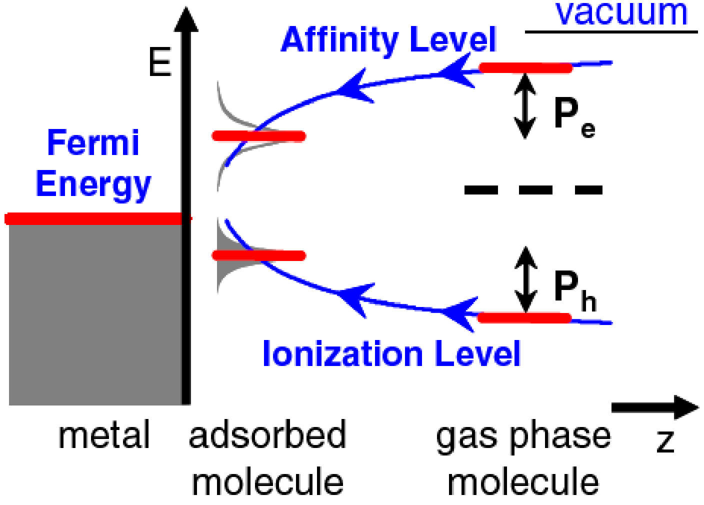
# What GW does well (II)

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 in this case --- modification of the screening has a big effect



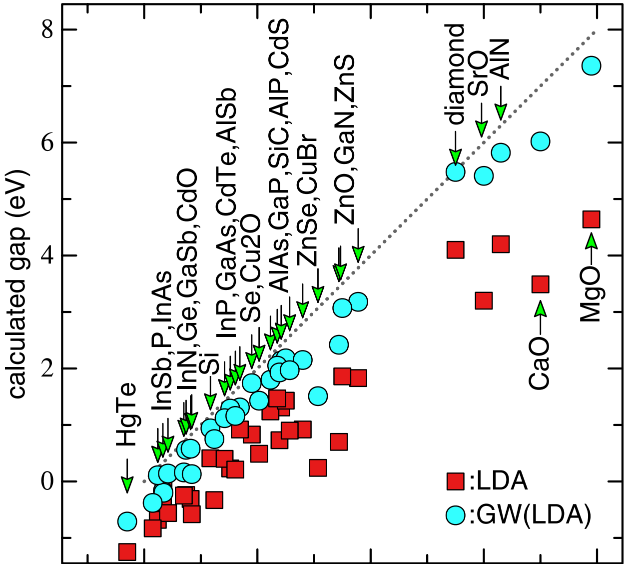
**Neaton, Hybertsen and Louie, PRL 97, 216405**

# What GW does well (III)

3. Nonlocal correlation in the self-energy.

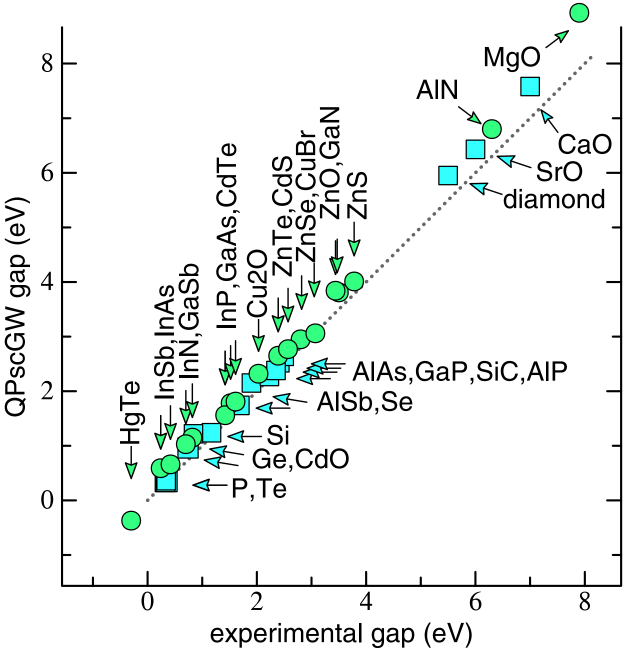
DFT gaps are too small because potential is local.

Choices: (1) make do with nonanalytic $V_{\text{xc}}$ (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.



← $G^{\text{LDA}}W^{\text{LDA}}$

→ QS$GW$



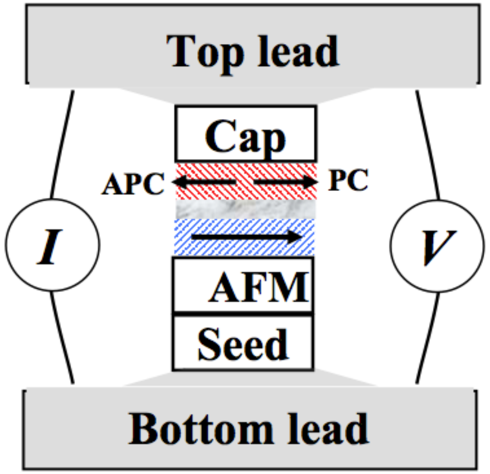
**PRL 96, 226402 (2006)**

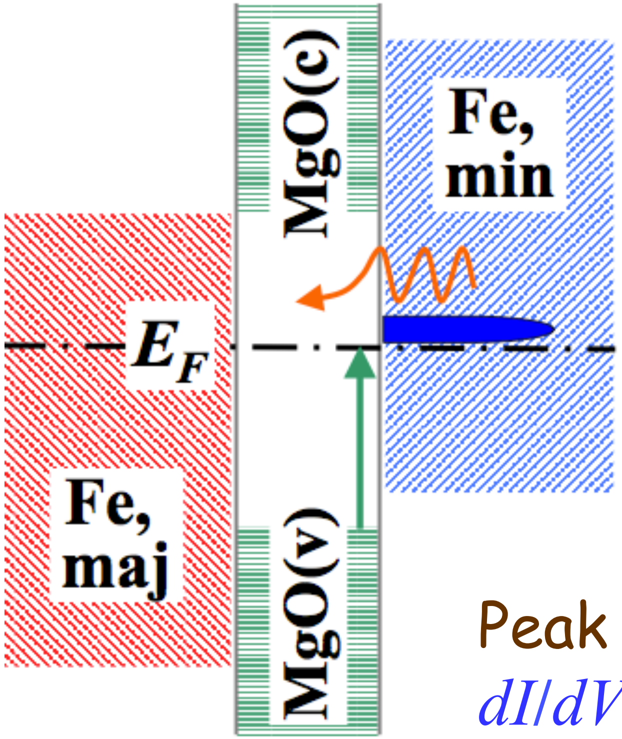
# What GW does well (IV)

4. level alignments generally very good.

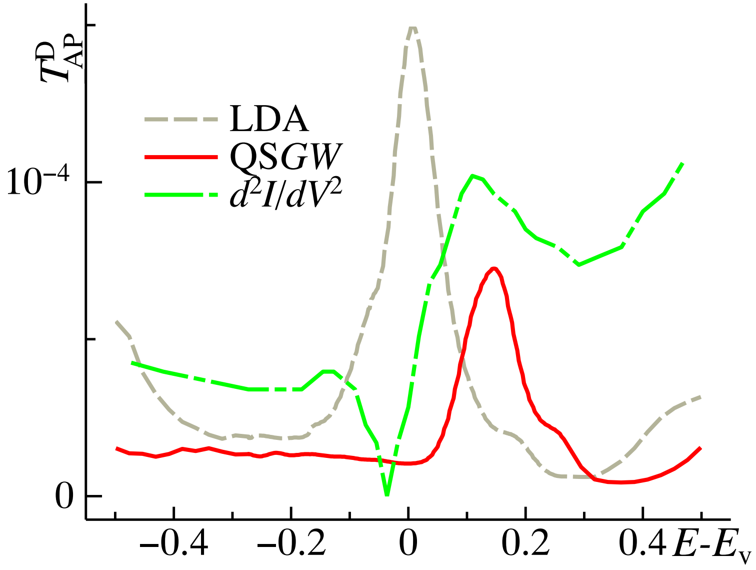
Example: Fe/MgO/Fe tunnel junctions

(Tunneling Magnetoresistance: basis for modern read heads.)





Apply $V$ ⇒ Fe Surface state crosses $E_F$ ⇒ current spike



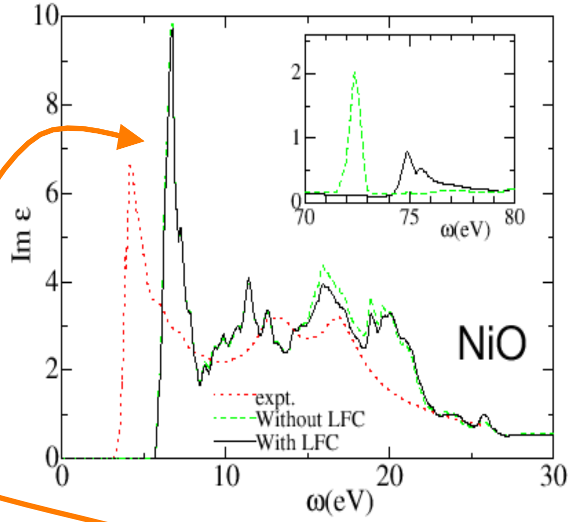
Peak observed in $dI/dV$ at 0.2 eV. LDA: $dI/dV$ peaks at 0V

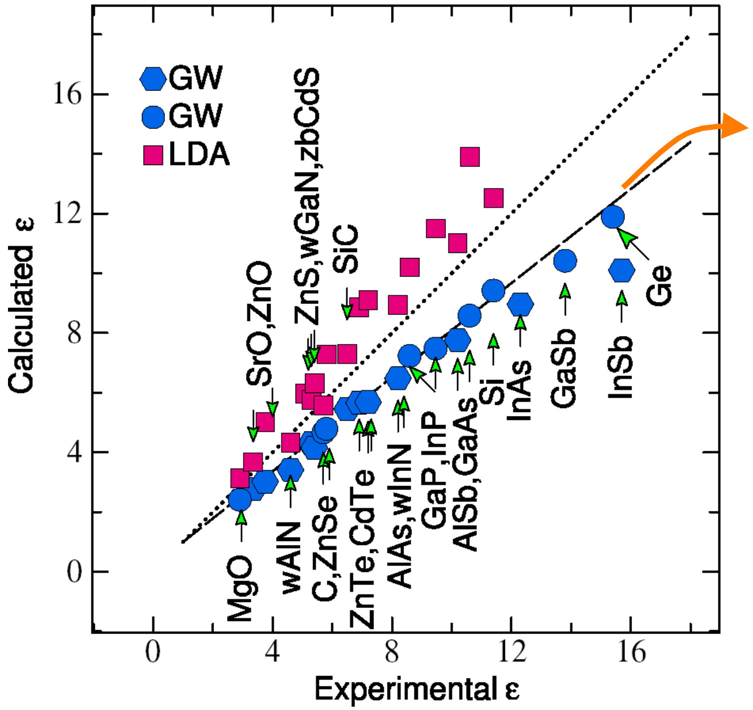
# Where does QS*GW* Break Down?

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

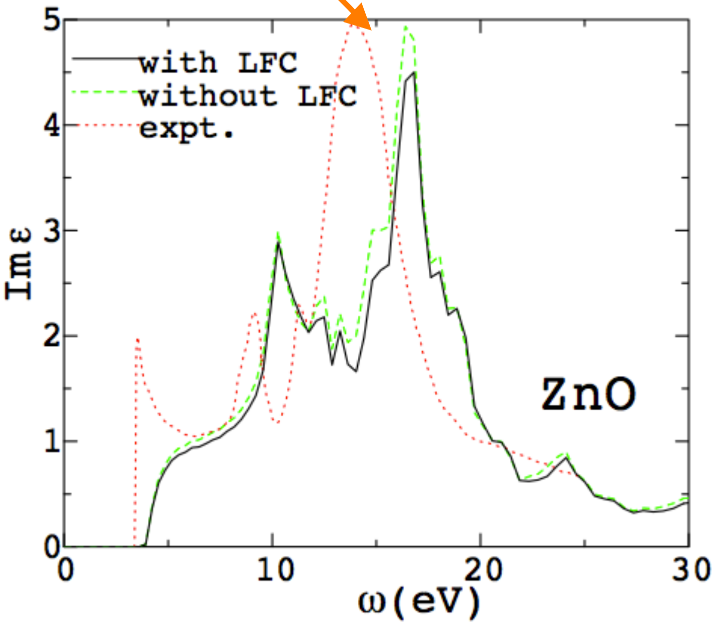
Peaks in Im ε(ω) *universally* too high



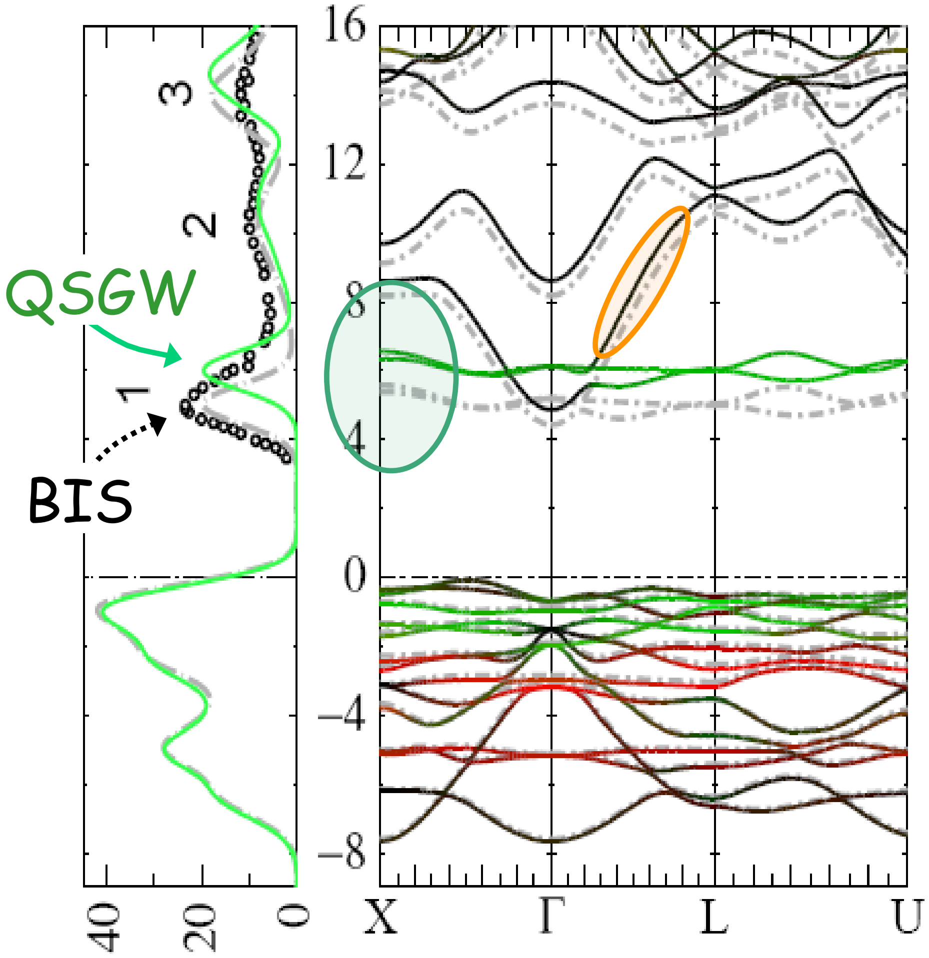


$\varepsilon_\infty$ *universally* 20% too small.

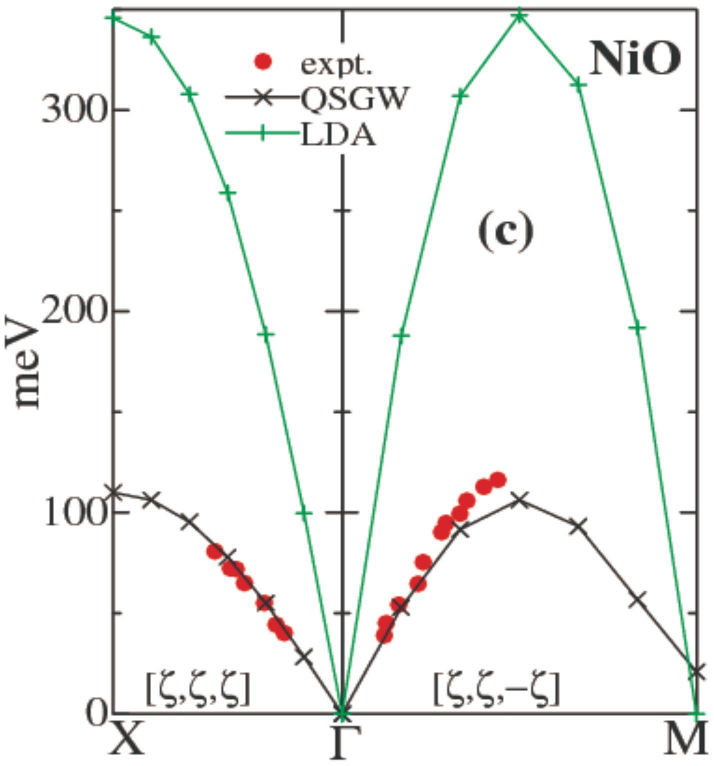
Errors are all related!



# Quasiparticle Self-Consistency for NiO



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



J. Phys. Cond. Matt. 20, 95214

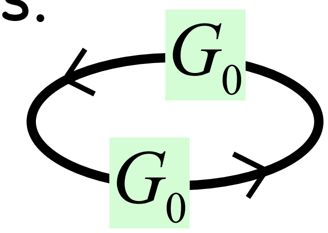
Spin waves in MnO and NiO very well described. True ab initio, all electrons on same footing.

# 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 $\delta$-fn:

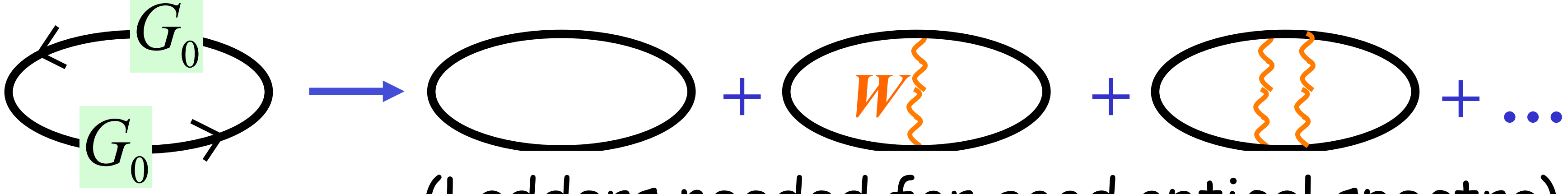
$$\Delta \mathrm{Re}\,\chi_1(0) = \frac{1}{\pi}\int_{-\infty}^{\infty}\left[\frac{\delta(\omega'-\omega_{\mathrm{th}})}{\omega'} - \frac{\delta(\omega'-\omega_{\mathrm{exp}})}{\omega'}\right]d\omega' = \frac{1}{\pi}\left(\frac{1}{\omega_{\mathrm{th}}}-\frac{1}{\omega_{\mathrm{exp}}}\right) < 0$$

$\varepsilon_\infty$ 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,

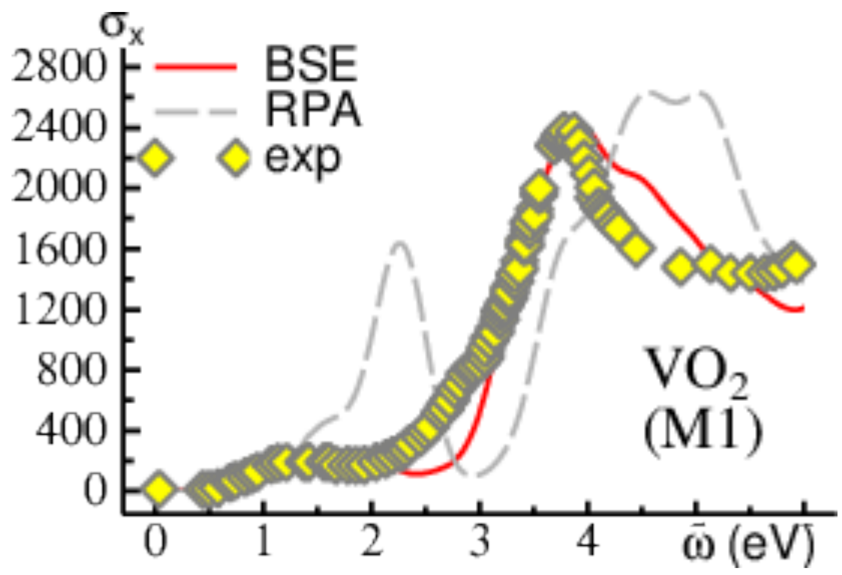


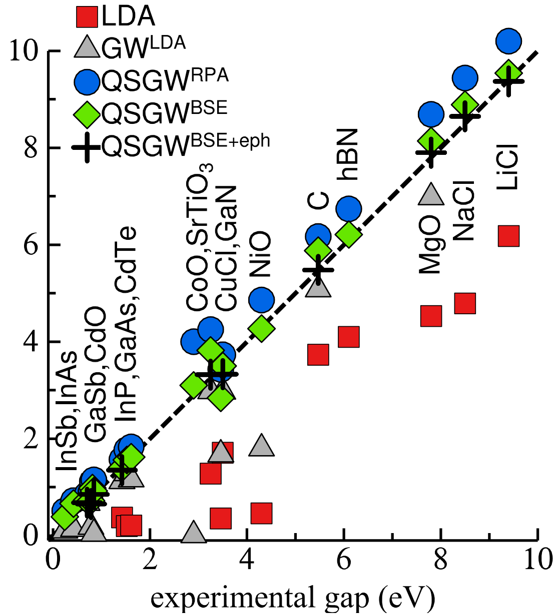
(Ladders needed for good optical spectra)

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

# Consequences of $W^{\mathrm{RPA}} \to W^{\mathrm{BSE}}$

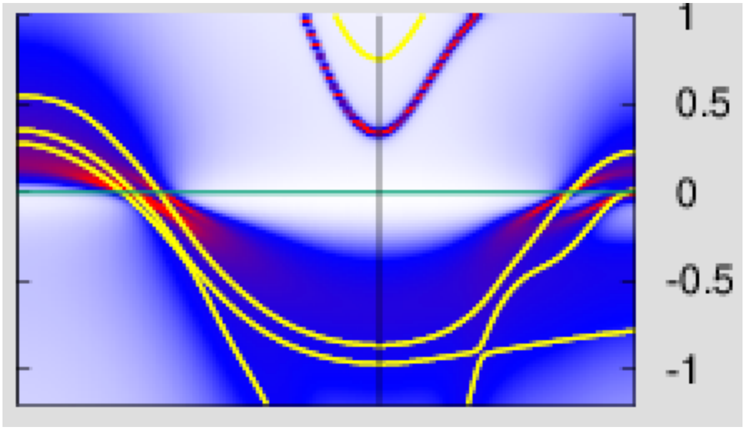
## Cunningham's work; he will talk about this tomorrow



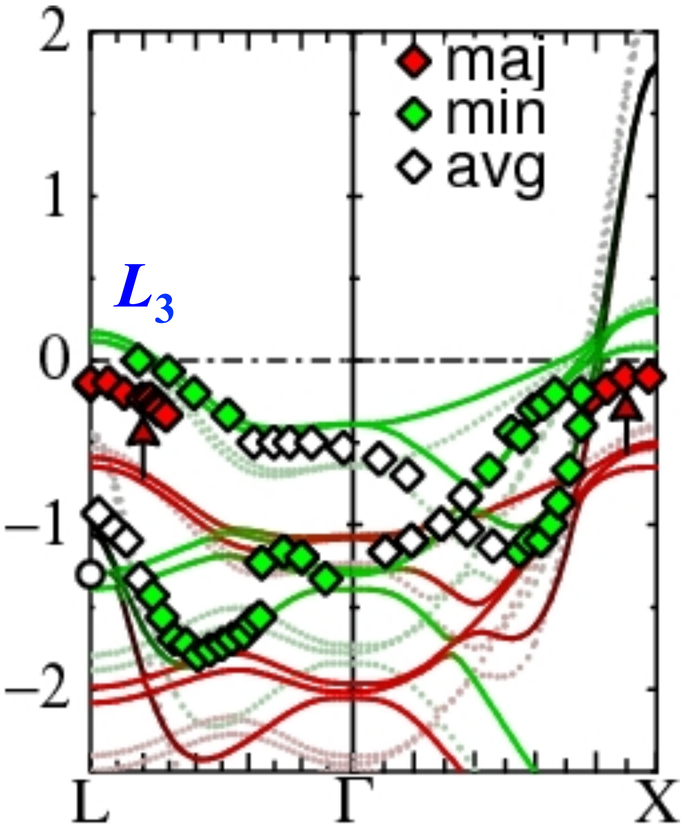


Takeaway message: $GW^{\mathrm{BSE}}$ does a stellar job at describing electronic structure in many kinds of materials, *provided* spin fluctuations are not too strong!

**Sr2RuO4**



# QSGW and Transition Metals



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

QSGW : vast improvement over LDA for TM in general.

But for Ni, problems appear

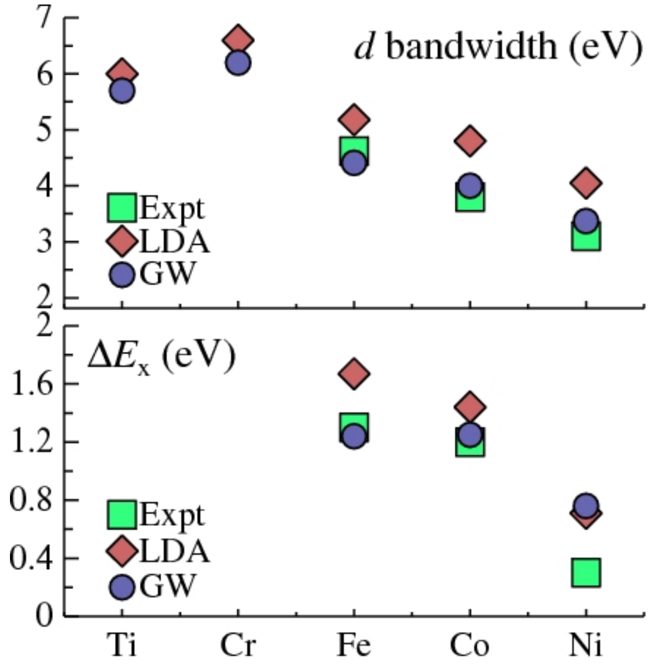
Calculated $\Delta E_x$ :

| QSGW | LDA |
|---|---|
| **0.76** | **0.71** |

Calculated $M$ :

| QSGW | LDA |
|---|---|
| **0.76** | **0.60** |

Trends in 3*d* series

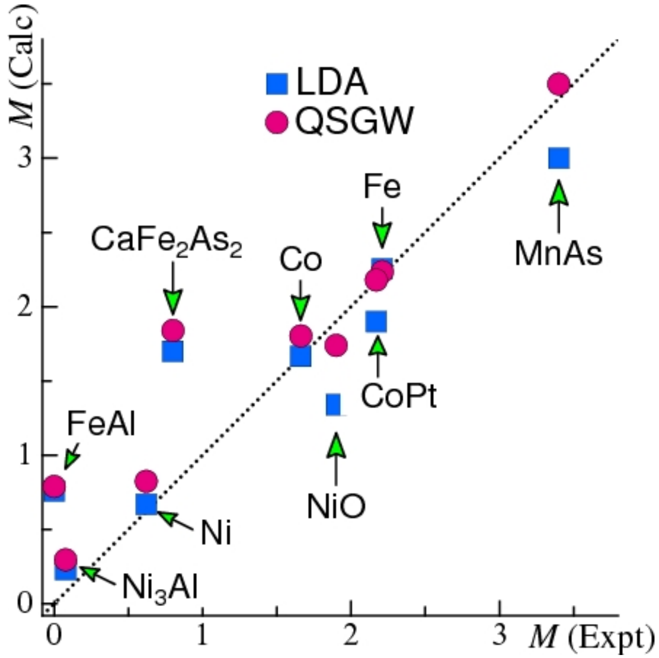


QSGW misses a satellite at -6 eV seen in photoemission

# 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.



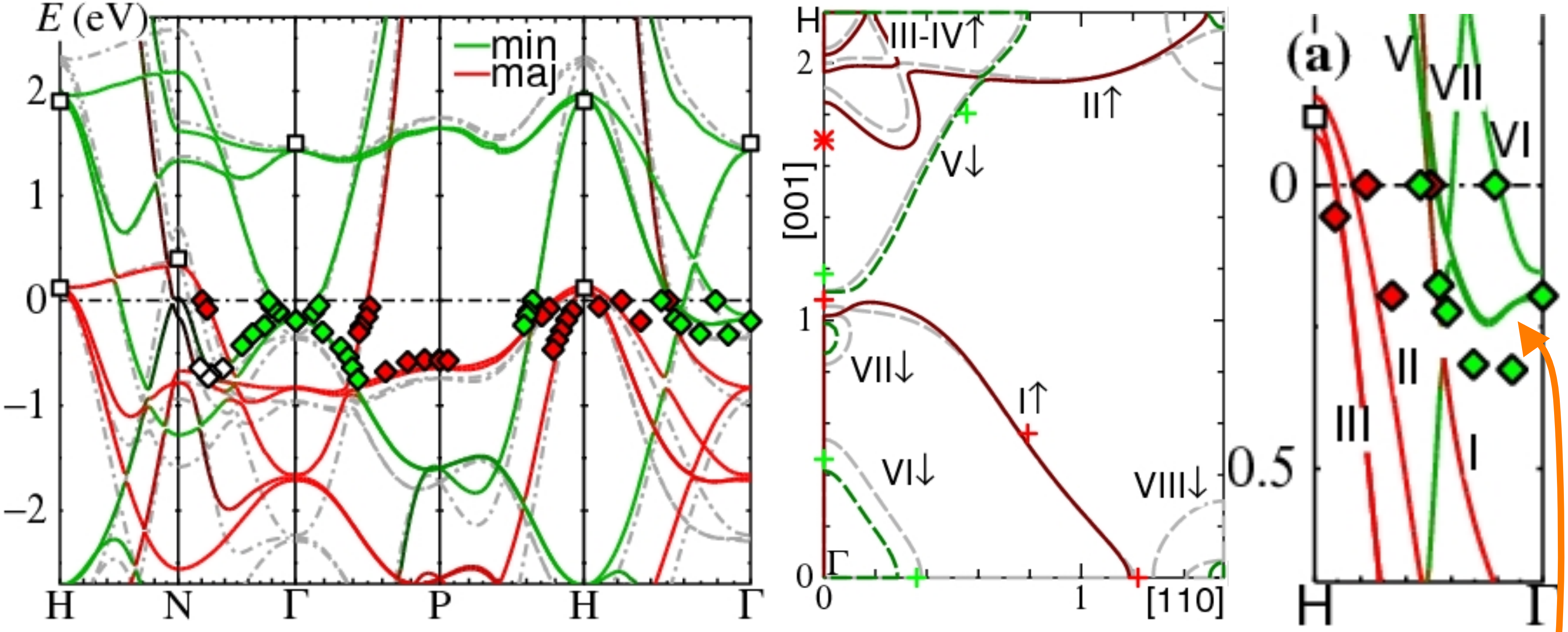
LDA has two distinct errors:
$\langle M\rangle$ is too large in itinerant materials.
$\langle M\rangle$ is too small in local-moment systems (CoPt, MnAs)

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 …

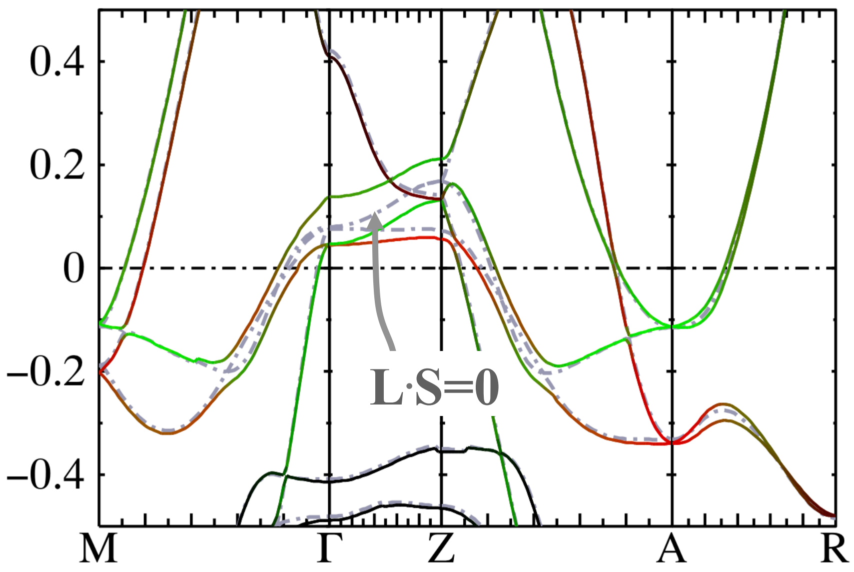


Much better than LDA+DMFT.  Small discrepancies at ~0.1 eV scale: … But it turns out that differences are largely artifacts of final-state effects in PE!     See Phys. Rev. B 95, 041112(R)

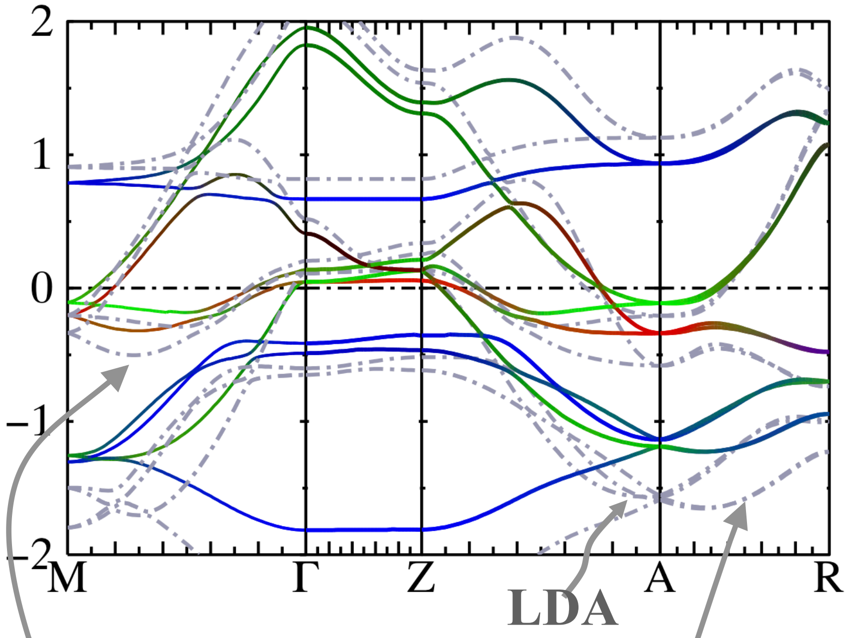
# FeSe: Strongly correlated unconventional SC

FeSe has no magnetic order. Start from nonmagnetic QSGW

Important role of SO



Small QSGW bandwidths



**L·S** generates ~30 meV shifts

**LDA → QSGW:**

- $e^-$ and $h^+$ pockets shift by ~100 meV
- Bandwidths are reduced

# Nonlocality in Self-Energy

## Compare QSGW and LDA to ARPES

| | Γ | | M | | Z | | A | |
|---|---|---|---|---|---|---|---|---|
| LDA,nm | +109 | +113 | −204 | −337 | +254 | +141 | −208 | −582 |
| QSGW,nm | +41 | +44 | −107 | −202 | +131 | +56 | −113 | −334 |
| ARPES[39–41] | +9 | −18 | −22 | −42 | +7 | +34 | −16 | −25 |

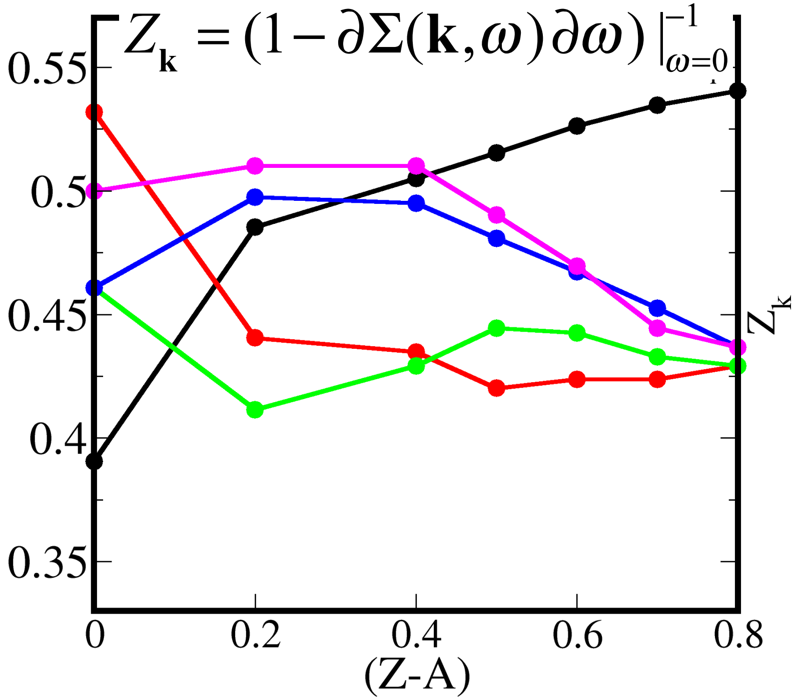
GW has:

✓ Spatial nonlocality $\Sigma(\mathbf{r},\mathbf{r}',\omega)$

✓ Nonlocality in $\Sigma(r,r',\boldsymbol{\omega})$

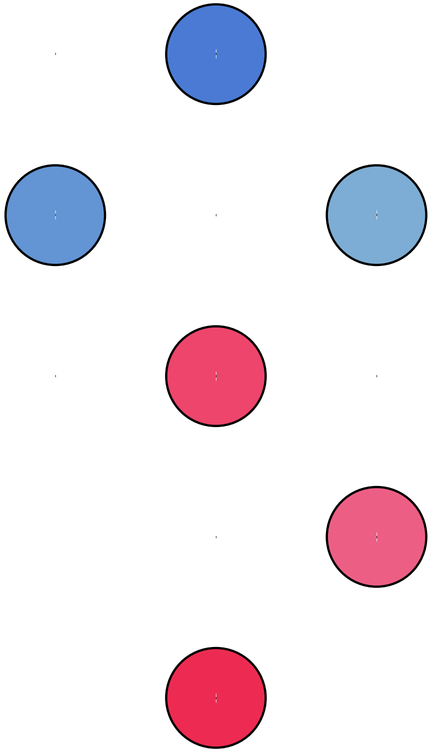
✓ (but quasiparticlized)

But pockets at Γ and M are still too deep. Why?



# Spin Fluctuations in FeSe

Simulate paramagnetism with SQS6 structure
A low moment QSGW solution can be stabilized with $\langle \mathbf{M} \rangle = 0.2 \pm 0.15\ \mu_B$ .



Levels shift towards ARPES data, but still significant discrepancy.

| | Γ | | M | | Z | | A | |
|---|---|---|---|---|---|---|---|---|
| LDA,nm | +109 | +113 | −204 | −337 | +254 | +141 | −208 | −582 |
| QSGW,nm | +41 | +44 | −107 | −202 | +131 | +56 | −113 | −334 |
| SQS6 | +45 | (60) | −52 | −70 | +31 | +68 | −59 | −72 |
| ARPES | +9 | −18 | −22 | −42 | +7 | +34 | −16 | −25 |

Shows spin fluctuations are important but (QS)*GW* does not adequately capture them.

Use DMFT to get higher order diagrams in spin channel

# Generic approach to strong correlations: partitioning

A universal theory that handles all electrons on an even footing is not feasible. So … we do higher level physics in subspace where correlations are strong. What is required?

1. A starting noninteracting hamiltonian (or $G^0$) with a family of states $\{i\}$ and a subspace of it
2. We saw that we could partition $G$ into a subspace $G_{ss}$ and the "rest", and that the effect of the "rest" on $G_{ss}$ can be cast in terms of a self-energy

$$G_{ss} = G^0_{ss} + G^0_{ss}\Sigma_{\text{rest}}G_{ss}$$

3. We need the effective interaction $W^{\text{eff}}$ in the subspace. This defines the effective local hamiltonian. Solve ~exactly.
4. If the subspace were the full space, $W^{\text{eff}}$ would be just the bare Coulomb $v$. If you could solve the full problem exactly, $W$ would be a byproduct of calculation … but not feasible.

# Dyson Equation for $W$

Remember that we developed a formula for $W$ in the RPA.

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

This formula carries over to the exact many-body system with a suitable redefinition of $P$ (see Myrta's talk).

$W$ can be equivalently expressed as a Dyson equation

$$W = (1 - vP)^{-1} v = v + vPW$$

If $P$ is divided into separate contributions $P = P^{(1)} + P^{(2)}$, then $W$ can be similarly partitioned

$$W^{(1)} = v + vP^{(1)} W^{(1)}$$

$$W^{(2)} = W^{(1)} + W^{(1)} P^{(2)} W^{(2)}$$

So … if $W^{(1)}$ is $W$ from a low-level theory like $GW$, we can calculate $W^{(2)}$ if we can calculate $P^{(2)}$. We will see that $P^{(2)}$ can be obtained from a pair correlation function.

Note: no one actually does this today, but it tells you what to do in principle. For now, we just choose a local $U$, $J$.

# General Framework for the Many-Body Problem

Partition using the "dual Dyson equation" for $G$ and $W$

$$G^{(1)} = G^{(0)} + G^{(0)}\Sigma^{(1)}G^{(1)} \qquad W^{(1)} = v + vP^{(1)}W^{(1)}$$

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

Treat entire system at a low level approximation (for definiteness, take low level approximation as GW) and deal with the interactions of a subsystem at a higher level.

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

0. Begin with a noninteracting $H_0 \Rightarrow G^{(0)} = \omega - H_0$

Make $P$ and $\Sigma^{(1)}$ and for the entire system.

- At the $GW$ level, $P \rightarrow P^0 = G^0G^0$ and $\Sigma^{(1)} \rightarrow iG_0W$.
- This defines an initial $G^{(1)} = (\omega - H_0 - \Sigma^{(1)})^{-1}$
- Note: this is typically performed in $k$-space .

For us, this is just a standard QSGW calc. (Could be LDA)

# Framework II

1. Choose a subspace, defined by one-particle orbitals $|j\rangle$.

Make the projection of $G^{(1)}, P^{(1)}, W^{(1)}$ onto this subspace, e.g. projections $G_{ij}=\langle i|G|j\rangle$, $W_{ijkl}=\langle ij|W|kl\rangle$, $P_{ijkl}=\langle ij|P|kl\rangle$

For the Questaal code, subspace = *d* or *f* partial waves

2. Build the effective interaction $U_{ijkl}$ for the subspace.

Recall relation between $W$ and polarizability $P$:

$$W=(1-vP)^{-1}v \Rightarrow W^{-1}=v^{-1}-P \Rightarrow v^{-1}=W^{-1}+P$$

Full system $v^{-1}=W^{-1}+P$ ← $P$ removes screening from $W$

Partition $P$ into $P=P_{\text{rest}}+P_{ijkl}$. Remove $P_{ijkl}$ part of screening in $W_{ijkl}$ to get effective interaction partially screened by the "rest." Partially unscreened interaction is customarily called $U$.

$$U^{-1}=W_{\text{rest}}^{-1}=W_{ijkl}^{-1}+P_{ijkl}$$

# Framework III

3. $G_{ij}^{(1)}$ and $U^{(1)}$ define the many-body hamiltonian for the system. Use a high-level solver (e.g. CTQMC) to obtain $\Sigma_{ij}^{(2)}$ and $G_{ij}^{(2)} = (G_{ij}^{(1)} - \Sigma_{ij}^{(2)})^{-1}$

4. (Almost never done in practice, but possible in principle).

~~Update full system $P$ and $W$ in full space~~

~~Get improved local $P_{ijkl}$ from DMFT so we have three quantities:~~

~~$P^{(1)}$ Polarizability of whole system at low level, eg. *GW*, approx~~

~~$P^{(1)}{}_{ijkl}$ projection of $P^{(1)}$ onto subsystem~~

~~$P_{ijkl}$ A better calculation of $P$ in the subsystem.~~

~~Improve the system $P$ with the construction~~

$$P^{(1,\mathrm{new})} = P^{(1,\mathrm{old})} + P_{\mathrm{ijkl}} - P^{(1,\mathrm{old})}{}_{ijkl}$$

~~From $P^{(1,\mathrm{new})}$, obtain $W^{(1,\mathrm{new})}$ from Dyson's equation for $W$.~~

# Framework IV

5. Determine a better $\Sigma^{(1)}$ to determine a new $G$.

$$\Sigma^{(1,\mathrm{new})} = \Sigma^{(1,\mathrm{old})} + \Sigma - \Sigma^{(1,\mathrm{old})}$$

6. ~~(Rarely done in practice, but possible in principle).~~
~~Update the low-level (e.g. GW) using better $G$ to make GW.~~

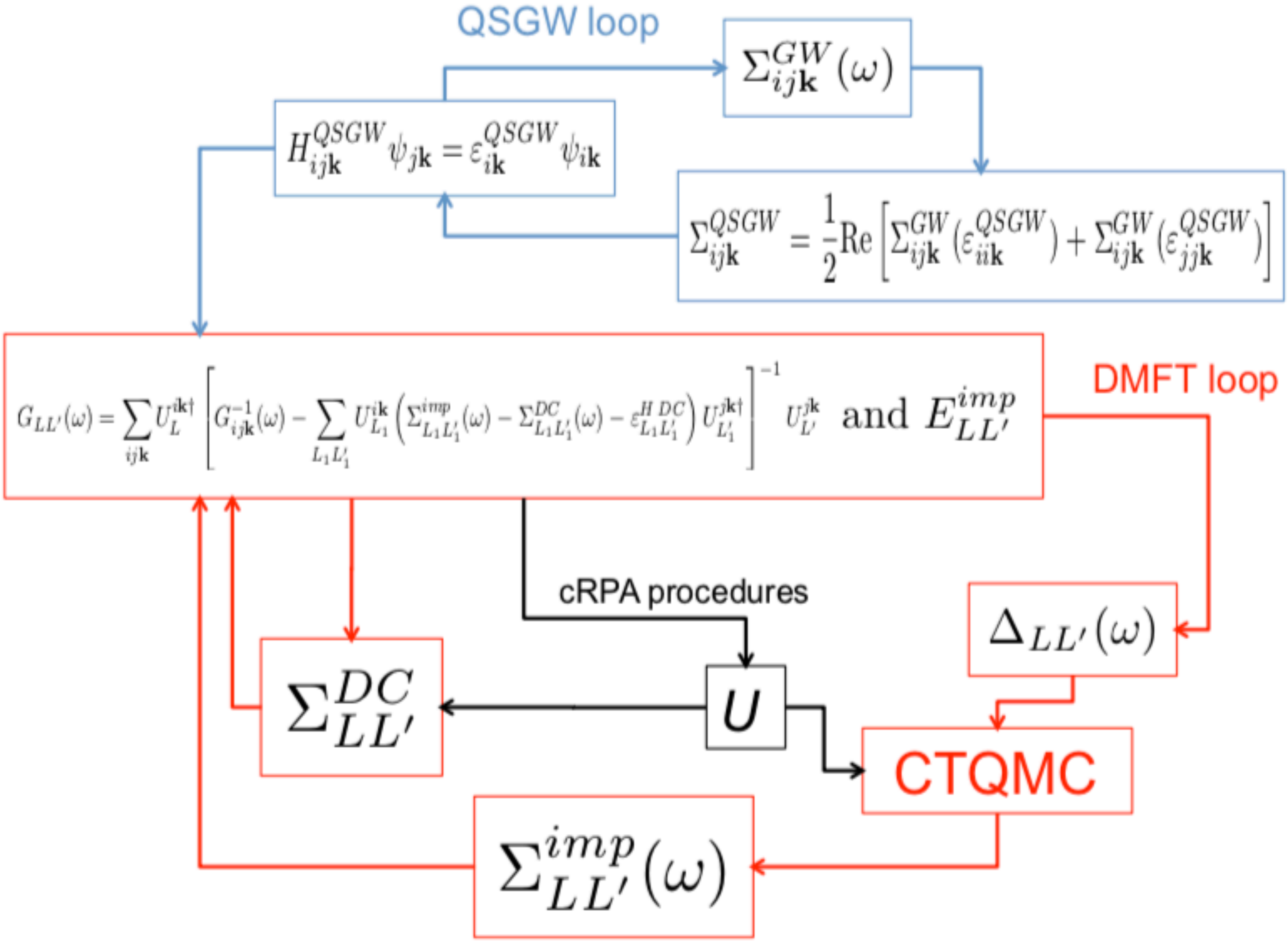
~~Iterate the parts or all of the cycle: The pair ($\Sigma$,$P$) gets~~
successively refined

Approximately this procedure was outlined in Phys Rev Lett 90, 086402 (Aryasetiawan, Biermann and Georges)
Standard practice today: LDA+DMFT: $\Sigma_{xc}{}^{(1)} = V_{xc}{}^{\mathrm{LDA}}$

Questaal partially implements QSGW+DMFT.

New ability to calculate 2-particle properties with local two-particle vertex + BSE.

Basic formalism still evolving

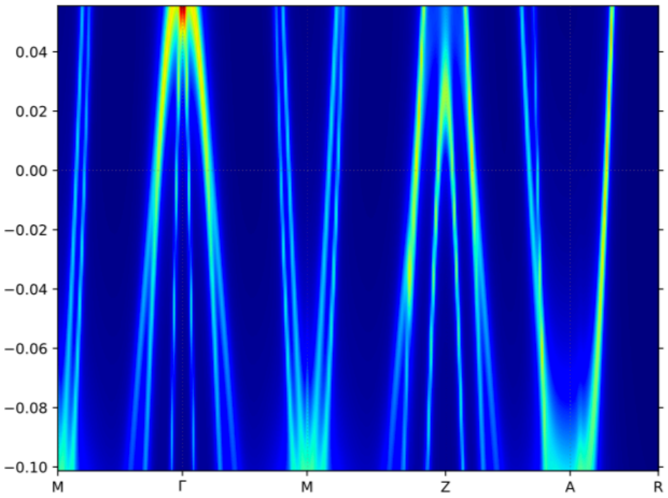

QSGW loop
$\Sigma^{GW}_{ij\mathbf{k}}(\omega)$
$H^{QSGW}_{ij\mathbf{k}}\psi_{j\mathbf{k}} = \varepsilon^{QSGW}_{i\mathbf{k}}\psi_{i\mathbf{k}}$
$\Sigma^{QSGW}_{ij\mathbf{k}} = \frac{1}{2}\mathrm{Re}\left[\Sigma^{GW}_{ij\mathbf{k}}(\varepsilon^{QSGW}_{ii\mathbf{k}}) + \Sigma^{GW}_{ij\mathbf{k}}(\varepsilon^{QSGW}_{jj\mathbf{k}})\right]$
$G_{LL'}(\omega) = \sum_{ij\mathbf{k}} U^{i\mathbf{k}\dagger}_{L}\left[G^{-1}_{ij\mathbf{k}}(\omega) - \sum_{L_1L_1'} U^{i\mathbf{k}}_{L_1}\left(\Sigma^{imp}_{L_1L_1'}(\omega) - \Sigma^{DC}_{L_1L_1'}(\omega) - \varepsilon^{H\,DC}_{L_1L_1'}\right)U^{j\mathbf{k}\dagger}_{L_1'}\right]^{-1} U^{j\mathbf{k}}_{L'}$ and $E^{imp}_{LL'}$
DMFT loop
cRPA procedures
$\Delta_{LL'}(\omega)$
$\Sigma^{DC}_{LL'}$
$U$
CTQMC
$\Sigma^{imp}_{LL'}(\omega)$

# FeSe, QSGW+DMFT

With QSGW as a bath, DMFT describes ARPES very well!

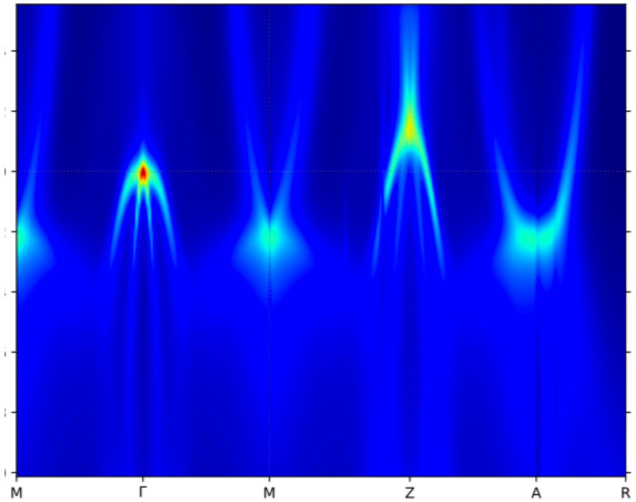
| | Γ | | M | | Z | | A | |
|---|---|---|---|---|---|---|---|---|
| LDA,nm | +109 | +113 | −204 | −337 | +254 | +141 | −208 | −582 |
| LDA+DMFT | +30 | +45 | −110 | −125 | +42 | +65 | −112 | −128 |
| QSGW,nm | +41 | +44 | −107 | −202 | +131 | +56 | −113 | −334 |
| nm+DMFT | +1 | +10 | −21 | −40 | +10 | +32 | −22 | −35 |
| ARPES | +9 | −18 | −22 | −42 | +7 | +34 | −16 | −25 |

LDA+DMFT is not adequate because errors propagate to the DMFT solver via deficiencies in the hybridization function.



← LDA+DMFT

QSGW+DMFT →



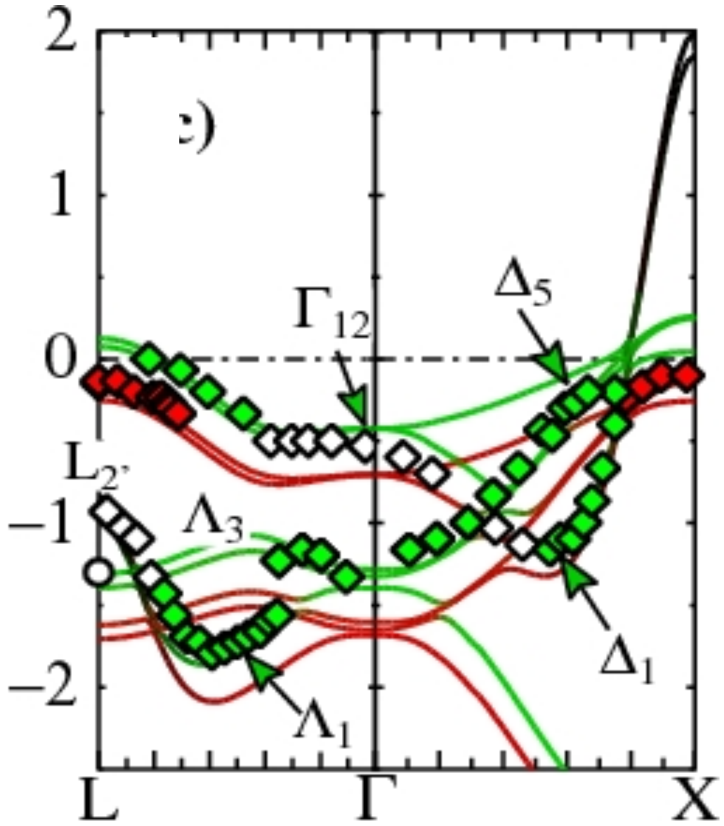
# QSGW + Magnetic DMFT, Applied to Ni

Basic idea : combine
charge $\Sigma^{\mathrm{QSGW}}(k)$ with
spin $\Sigma^{\mathrm{DMFT}}(\omega)$.

$$\Sigma^{\pm} = \bar{\Sigma}^{\mathrm{QSGW}}(k) + \Sigma^{\mathrm{DMFT},\pm}(\omega)$$

$$\bar{\Sigma}^{\mathrm{QSGW}} = [\Sigma^{+}(k) + \Sigma^{-}(k)]/2$$

$$\Sigma^{\mathrm{DMFT},\pm} = \pm[\Sigma^{+}(\omega) - \Sigma^{-}(\omega)]/2$$



| | $\Delta E_x$ | $M$: |
|---|---|---|
| LDA | 0.71 | 0.60 |
| QSGW | 0.76 | 0.76 |
| QSGW+DMFT | 0.3 | 0.51 |
| QSGW+DMFT(QP) | 0.3 | 0.55 |
| Experiment | 0.3 | 0.57 |

Exchange splitting well described by QP

Self-consistency has minimal effect

# Summary

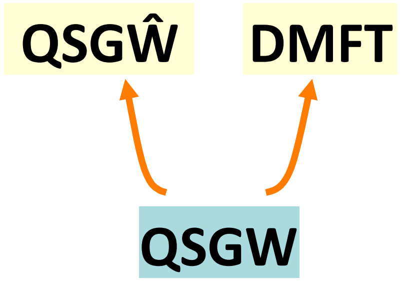
- QSGW: use GW to generate effective noninteracting hamiltonian $H_0$ to use in diagrammatic theory.

No unique choice. Density-Functional theory is popular, but QSGW is an optimum choice by construction.

Dramatically improves quality of GW, but also limits.

- When spin fluctuations are weak:

RPA+ladders work very well!



- When spin fluctuations are strong:

Many diagrams are needed, but they are mostly local. Requires nonperturbative but local approach

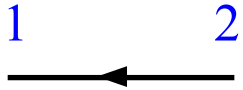
- Use partitioning and combine QSGW+DMFT

Best approach to strong correlations to date.

Nonlocality restored perturbatively via diagrams connecting local vertex.

# Aside : About diagrams

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

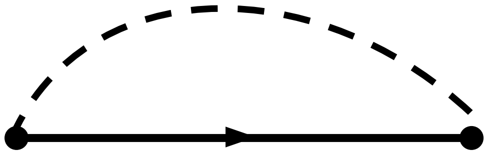


$G(\mathbf{x}_1,t_1;\mathbf{x}_2,t_2)$ The arrow represents the flow of time
A thick or double line used for an interacting $G$ and thin line for $G^0$

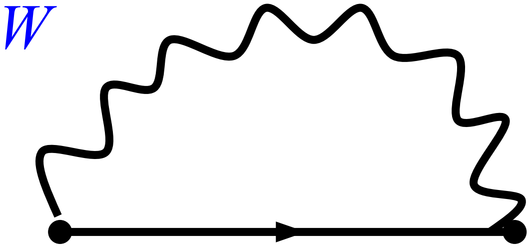
$v(\mathbf{x}_1;\mathbf{x}_2)$ The bare coulomb interaction $|\mathbf{x}_1 - \mathbf{x}_2|^{-1}$ is taken to be instantaneous

$W(\mathbf{x}_1,t_1;\mathbf{x}_2,t_2)$ The screened coulomb interaction.
$W$ depends one time, $t_1 - t_2$.

Exchange $Gv$



$GW$



# Alternative Justification of QSGW

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

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

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

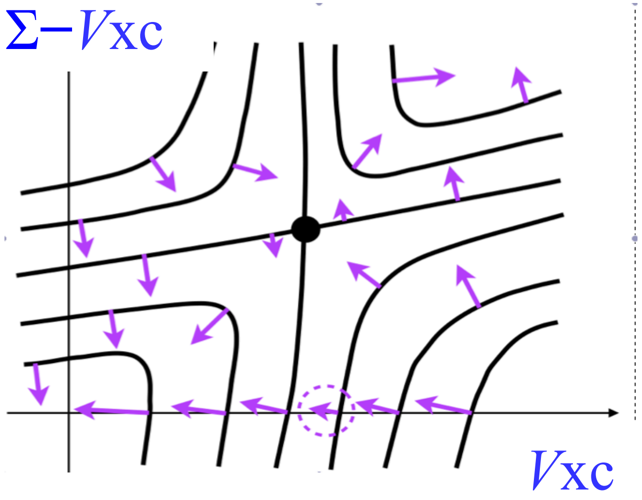
Not possible … there is no lower bound (PRB76, 165106).

A justification based on energy minimization

Minimize square of *gradient* of Klein energy functional (Ismail-Beigi)

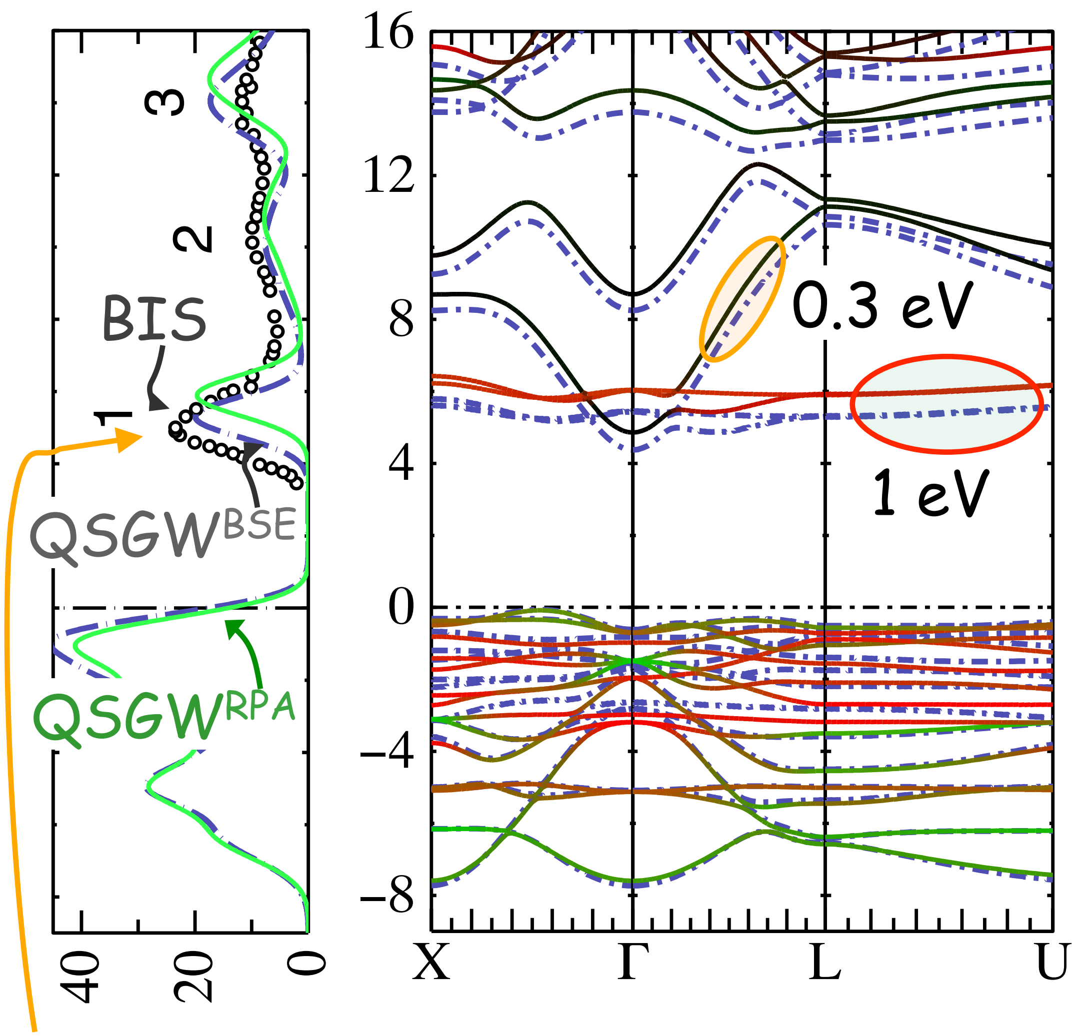
$$\left|D\right|^2 \rightarrow \min \quad \text{where} \quad D = \frac{\delta F[G_0]}{\delta \Sigma}$$

J. Phys. Cond. Matt. 29, 385501



# Compare QSGW$^{RPA}$ ,QSGW$^{BSE}$ bands to BIS in NiO

Cunningham's work; he will talk about this tomorrow



NiO has both dispersive *sp* bands

$W^{RPA} \rightarrow W^{BSE} \Rightarrow$

−0.3 eV shift

⋯ and a flat *d* band

$W^{RPA} \rightarrow W^{BSE} \Rightarrow$

−1 eV shift

Shifts get reflected in movement of DOS peaks **(1), (2), (3)**

Compare to BIS ⋯