Response functions of correlated systems within Green's function theory

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U.S. DEPARTMENT OF ENERGY | Office of Science

Why use Green's functions as the fundamental variable ?

- Wave-function (ψ) methods are king for high-fidelity
- Density-functional (ρ) methods are very efficient (Kohn-Sham)

Goldilocks principle: Green's function (G) methods straddle the ρ- and ψ- methods, intermediate in both accuracy and efficiency.

Also, when interest lies in excitations & 2-particle properties: G- methods are natural --- intrinsic to the theory

What about fidelity ?

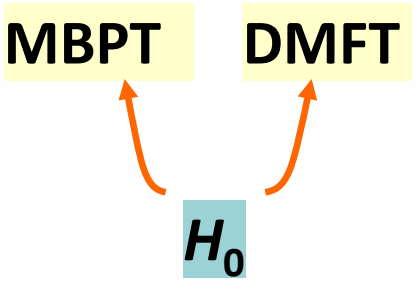
With G- methods, possible to *systematically improve* fidelity by:

✓ Adding higher order diagrams ✓ Self consistency

NREL/PR-5F00-91307

Primary tracks for implementation of G methods

Two traditional routes to extend one-body descriptions. Both traditionally start from independent-particle H_0 (e.g. DFT)



1 Many body perturbation theory (MBPT)

Usually H_0 constructed from DFT

Add low order diagrams (usu. GW)

Best for weak or moderate correlations

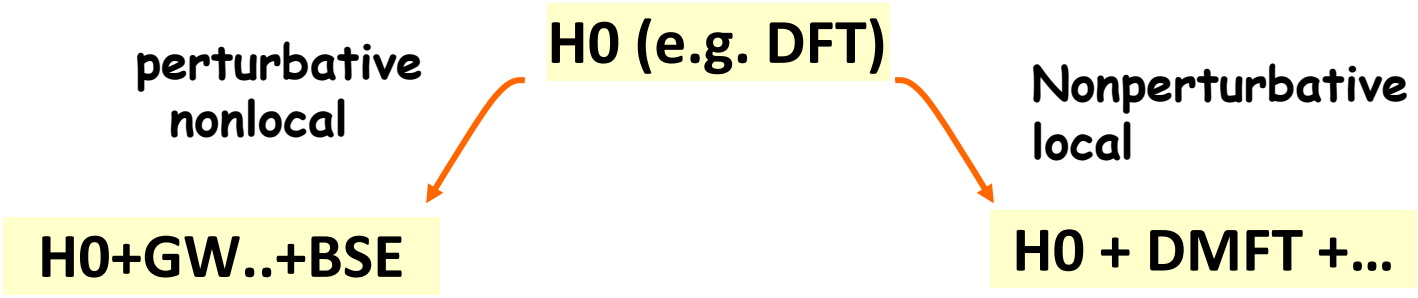
Dynamical Mean-Field Theory

2 If correlations are strong but local (DMFT)

Partition Hilbert space into strongly correlated local sector, + a weakly correlated nonlocal sector, which acts as "bath"

Solve Anderson impurity problem including all local graphs, embedded in a noninteracting bath H_0 (*usually* H_0 = DFT)

Two tracks of G originate from different energy scales



Weak spin fluctuations

Spin is adequately described by the Fock diagram (screening of spin is weak)

Charge fluctuations are high energy, and long range.

Low order MBPT will adequately capture electronic structure

Strong spin fluctuations

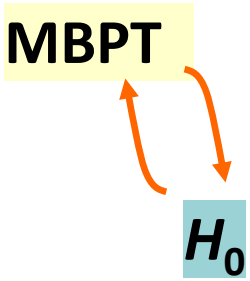
Low energy ⇒ many competing processes. Rich phase diagrams.

(Unconventional superconductors are usually bad metals)

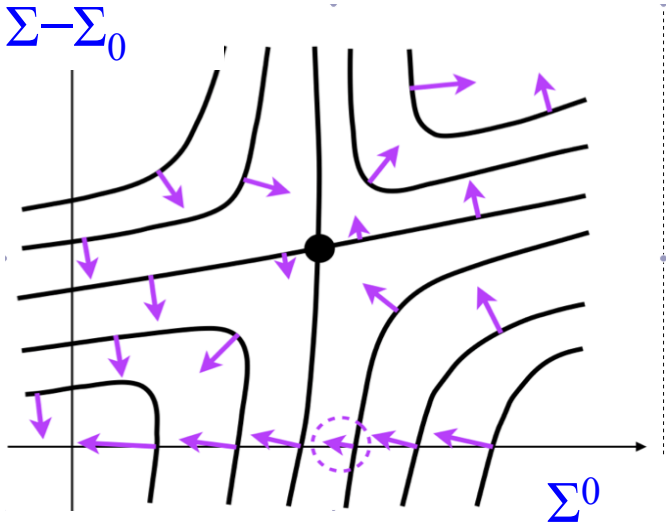
✗ nonperturbative : low order diagrams not sufficient!

✔ The effective interaction is mostly site-local (DMFT)

MBPT and Quasiparticle self-consistency



Avoid problems with self-consistency: choose an optimal noninteracting H_0.



S. Ismail-Beigi, J. Phys. C

How to find the best possible H_0 ?
Requires a prescription for minimizing the difference ΔV between H_0 and the full H :

$$\Delta V = H - H_0 = G^{-1} - G_0{}^{-1}$$

Quasiparticle Self-Consistent *GW* : a self-consistent perturbation theory where self-consistency determines the best H_0 within the GW approximation

- ✓ Surmounts starting point dependence
- ✓ Discrepancies w/ expt ⇒ uniform, their origin transparent

Prescription for Optimal G_0

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

$$H_0 = \frac{-1}{2m}\nabla^2 + V^{\text{ext}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r}) + \Sigma_0(\mathbf{r},\mathbf{r}')$$

Analog of LDA V^{xc}

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

GWA determines ΔV and thus H :

$$G_0 \xrightarrow{RPA} \varepsilon(iG_0G_0) \xrightarrow{GWA} \Sigma(\mathbf{r},\mathbf{r}',\omega) = iG_0W; \qquad \Delta V = \Sigma - \Sigma_0$$

Find a new Σ_0 that minimizes norm N, a measure of $\Delta V\, G_0$.

$$\Sigma_0 = \frac{1}{2}\sum_{ij}\langle\psi_i|\text{Re}\Big(\Sigma(E_i) + \Sigma(E_j)\Big)|\psi_j\rangle$$

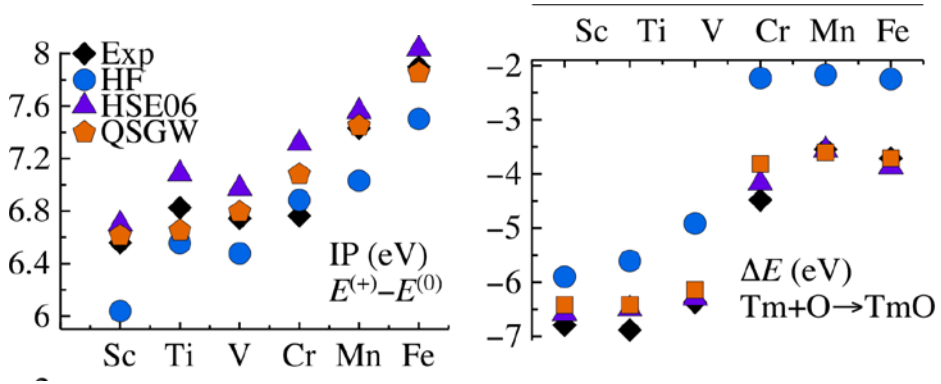
(approximate) result of min N

Iterate to self-consistency.

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

Why Self-Consistency Matters: 3 Case Studies

Ambiguities through choice of H_0
⇒ not really *ab initio* any more.

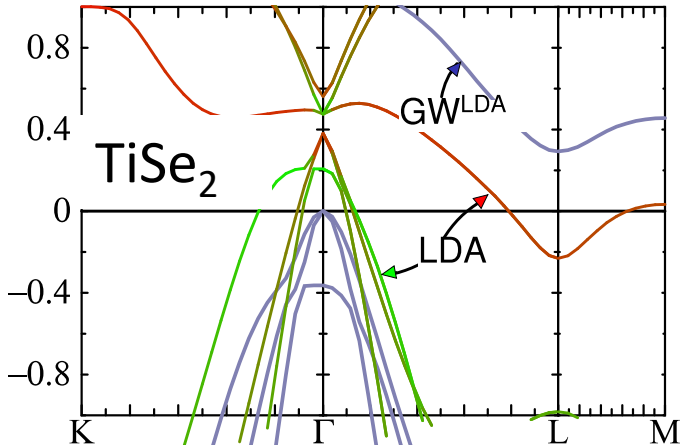


I.P (atom) **TM-O dimer**

Strong starting dependence for GW ionization potential (atom) and RPA heat of reaction (dimer)

$CuInS_2$: strong feedback between eigenvalues and W, not captured by LDA+U or hybrid functionals
PRL 104, 056401 (2010)

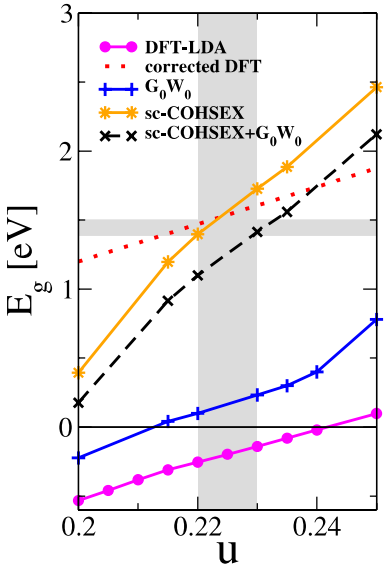
Nat. Comm. 14, 5565 (2023)



$G^{LDA}W^{LDA}$ predicts gap>0 (P3m1 phase)

QSGW gap is negative. (change in V_H)

But … Exptl gap is slightly positive. Explain later



skip

QP Renormalization by density

Turns out that the positive gap is an artifact of $G^{LDA}W^{LDA}$!

LDA eigenfunctions ψ should be different from *GW*.

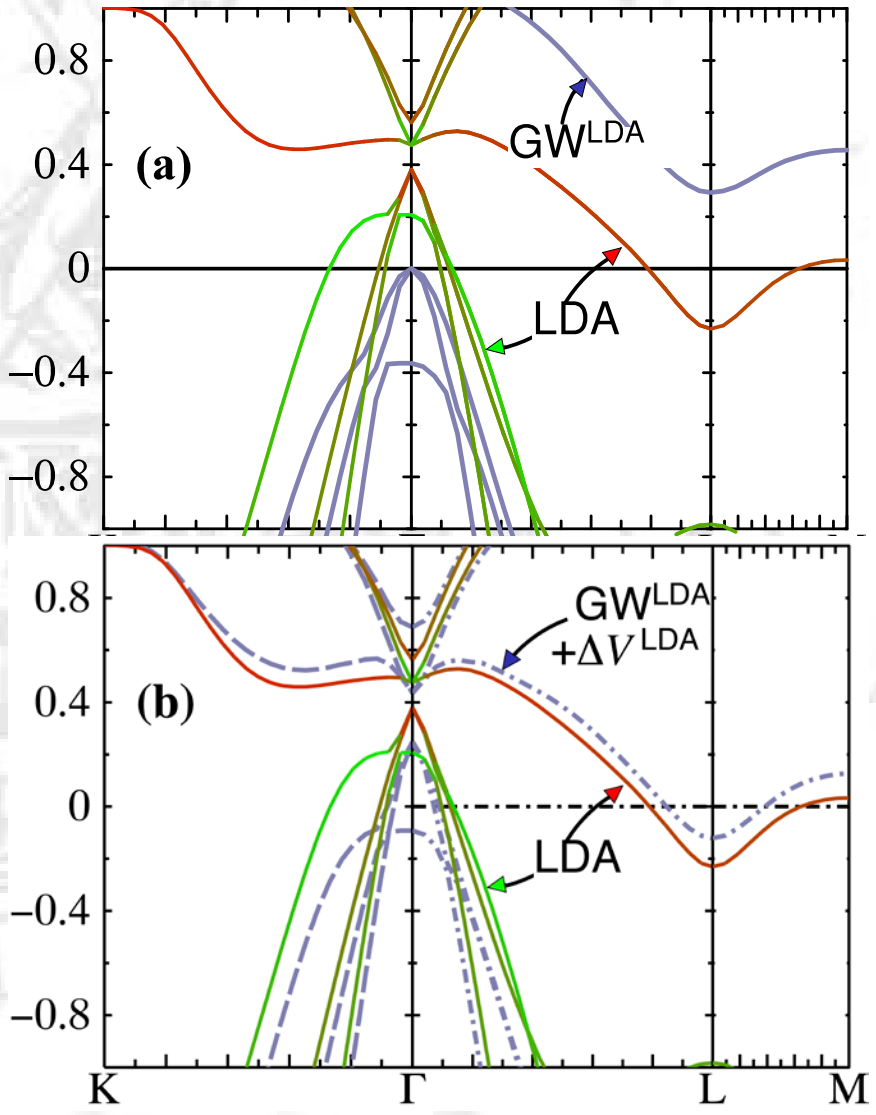
Off-diagonal self-energy $\Sigma^{n\neq n'}$ modifies ψ and density $n(\mathbf{r})$ and V (requires full matrix Σ)

Simple ansatz: assume LDA adequately yields $\delta V/\delta n$. The potential becomes

$$\Sigma - V_{\mathrm{Hxc}}{}^{\mathrm{LDA}}[n^{\mathrm{LDA}}] + V_{\mathrm{Hxc}}{}^{\mathrm{LDA}}[n^{\mathrm{GW}}]$$

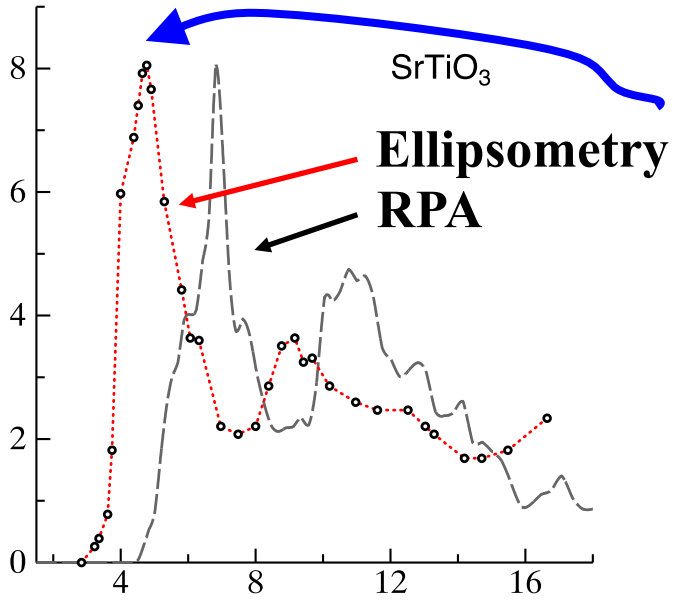
Iterate to self-consistency.

Gap becomes negative again!

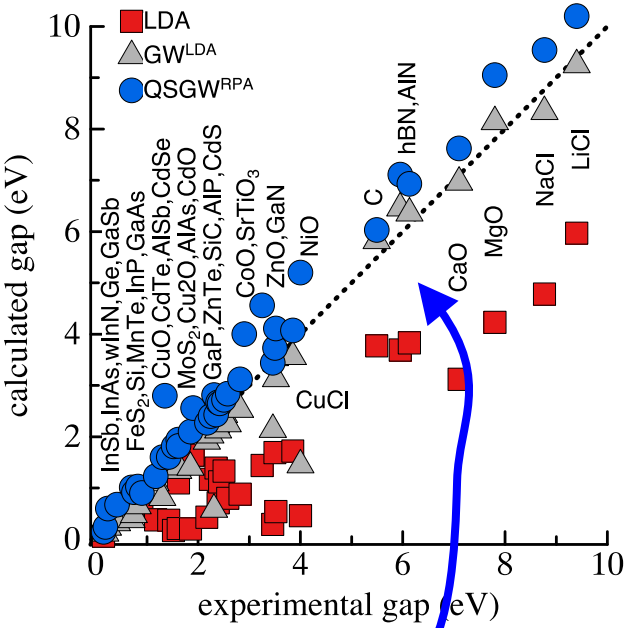


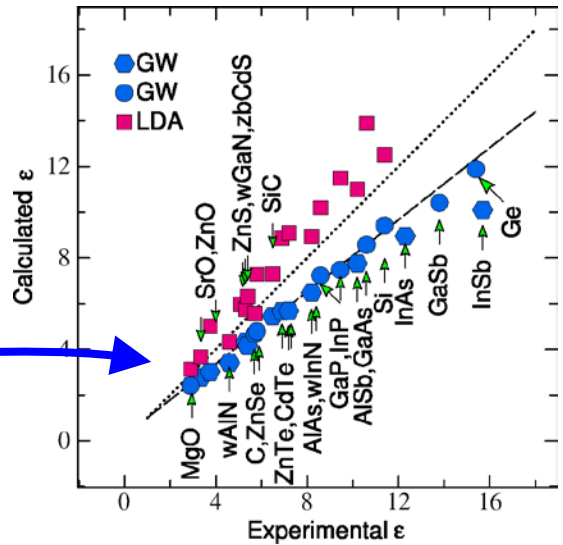
Systematics of errors in QSGW

Absent significant spin fluctuations, how well does QSGW predict spectral properties ?



- Plasmon peaks in Imε(ω) are blue shifted
- Bandgaps are systematically too large
- ε_∞ is universally underestimated by a factor 0.8





These errors are highly systematic and interconnected …

Missing diagrams in W

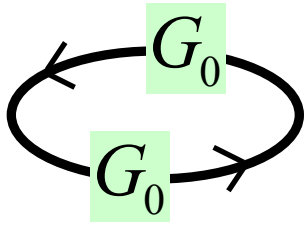
Kramer's Kronig relates real and imaginary parts of ε :

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

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

GW uses *RPA approximation* for the polarizability $\Pi = iG_0 \times G_0$, and

$$W = \left(1 - \Pi v\right)^{-1} v = \varepsilon^{-1} v$$



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

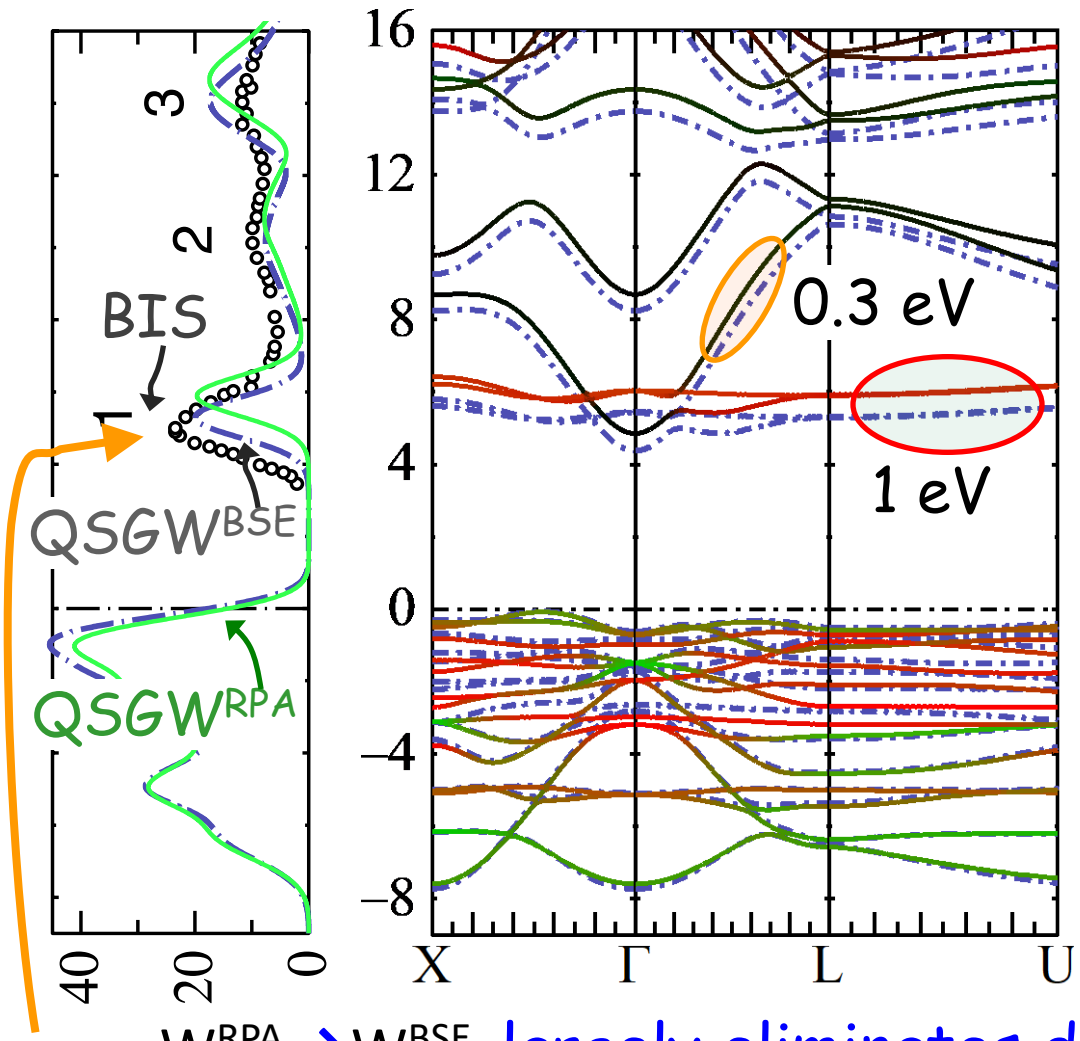
(Ladders needed for good optical spectra)

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

Also : if W is*too large* ⇒ bandgaps overestimated (towards HF)

QSGŴ : QSGW including ladders in W (NiO)

Brian Cunningham, M. Gruening added ladders to improve W.



Phys. Rev. B 108, 165104

NiO has both dispersive *sp* bands

peak +0.3 eV too high

… and a flat *d* band

1 eV too high

Effect on dispersive *sp* bands

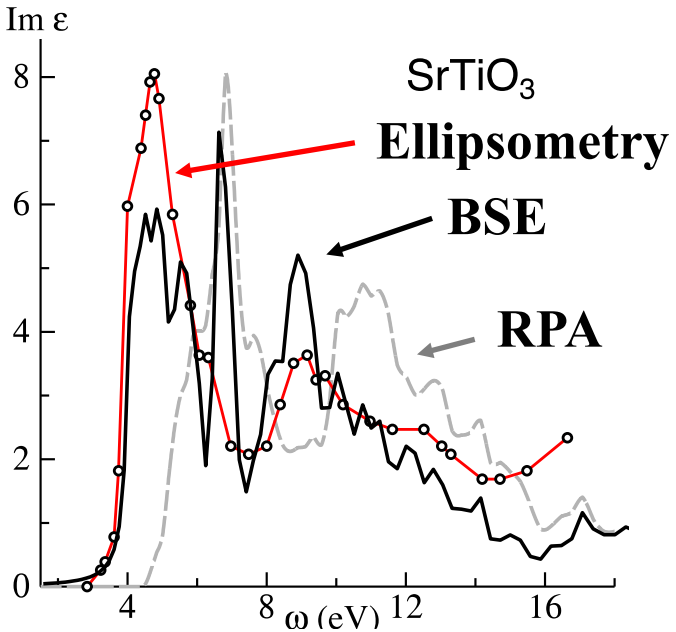
$W^{RPA} \rightarrow W^{BSE} \Rightarrow$ -0.3 eV shift

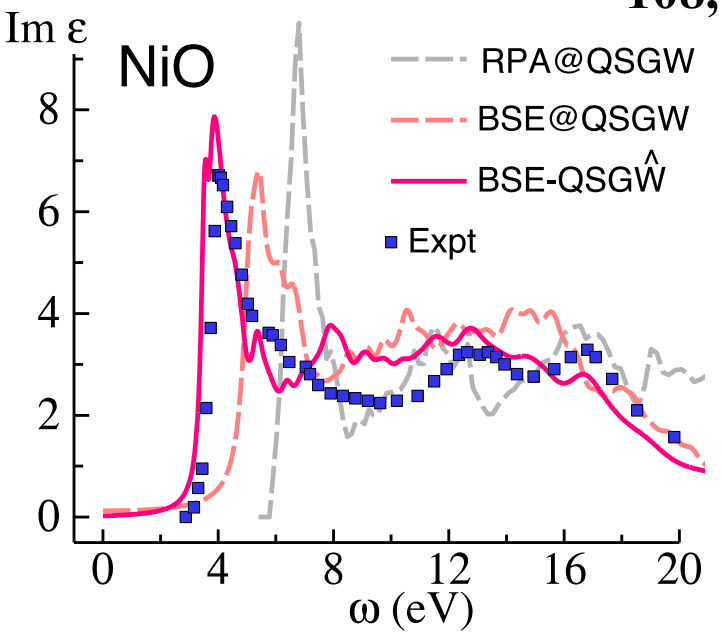
… *d* band $W^{RPA} \rightarrow W^{BSE} \Rightarrow$ -1 eV shift

… $W^{RPA} \rightarrow W^{BSE}$ largely eliminates discrepancies in BIS

Dielectric function ε^{BSE}@QSG$\hat{W}$

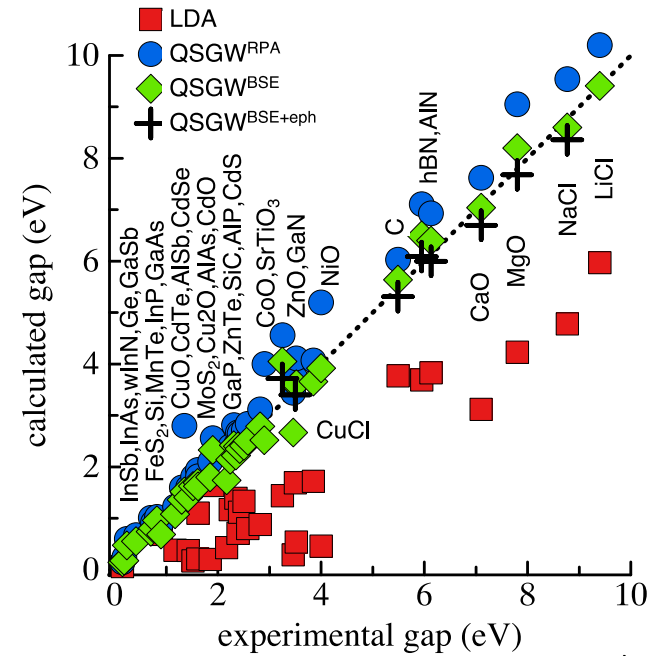
Phys. Rev. B 108, 165104

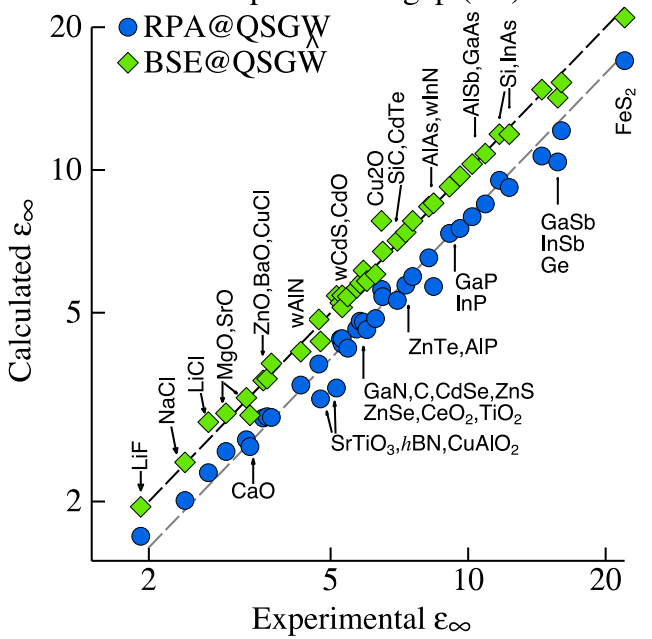




- Ladders capture main structure of $\varepsilon(\omega)$ in many systems, provided Σ generating ε is computed from QSG$\hat{W}$.
  - Short range corrections to RPA, important in correlated systems (NiO)
  - Experimental uncertainties preclude detailed comparison over full $\varepsilon(\omega)$, but ε_0 is better known
- Optical gap and fundamental gap are different ($SrTiO_3$)

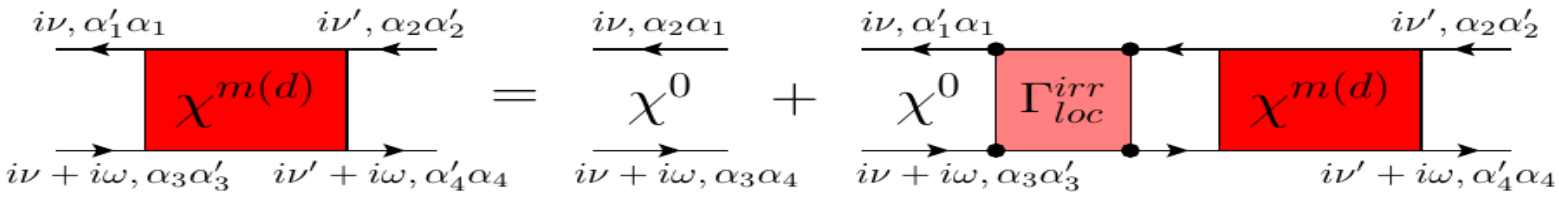
Close correspondence between E_g and ε_0

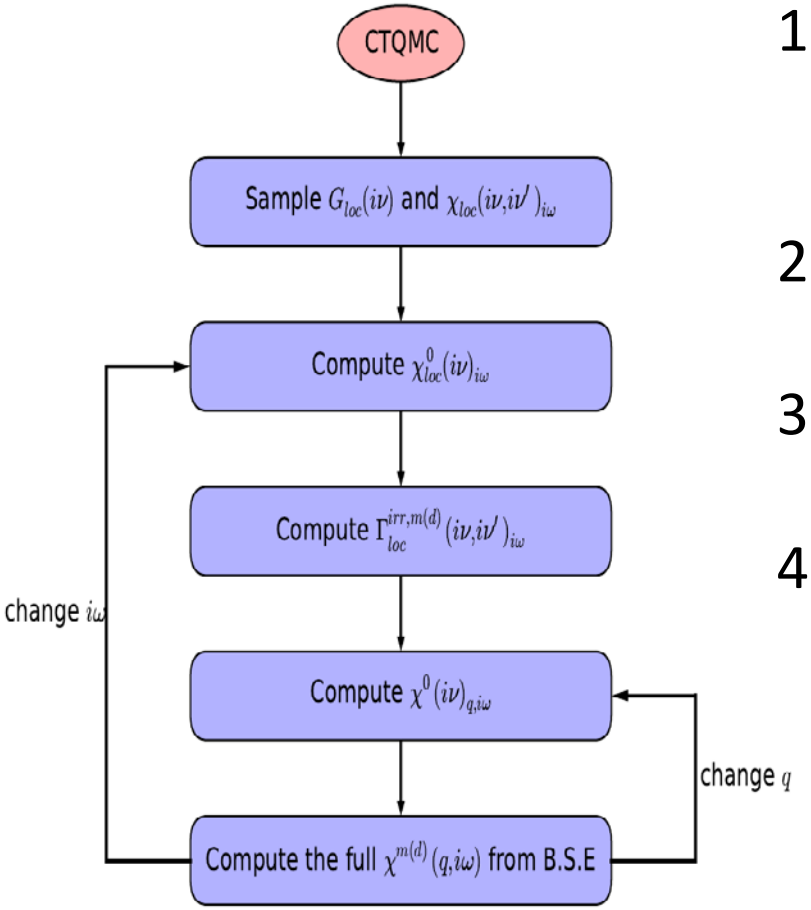




- Strong correlation betw/ E_g , ε_0
- QSG$\hat{W}$ largely eliminates systematic errors in QSGW Exceptions:
  - Renormalization from electron-lattice interaction
  - Dispersionless states near homo too high from missing vertex Γ
  - Small residual errors even in *sp* systems
  - Theory cannot account for strong spin fluctuations

Susceptibilities with QSGW+DMFT+BSE



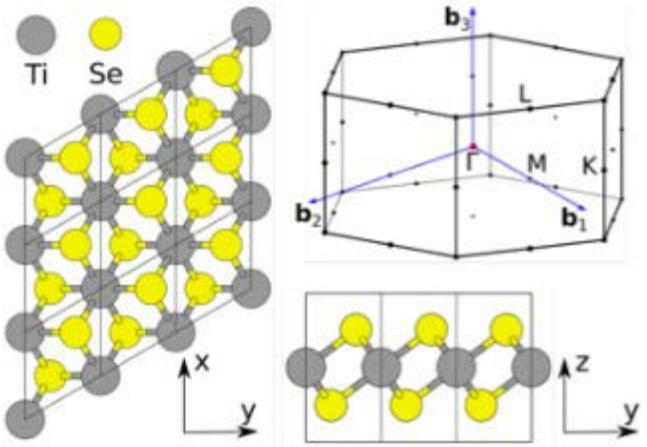


1. calculate 2-particle G .
   Generates local spin and charge particle-hole vertices $\Gamma(\omega,\omega',\Omega)$
2. Combine with bubbles (BSE) ⇒ nonlocal susceptibilities χ^S and χ^C .
3. Particle-hole vertices can yield particle-particle vertex
4. Combine with bubbles (BSE) to yield superconducting pairing field

Main assumption: local vertex, nonlocality from bubbles

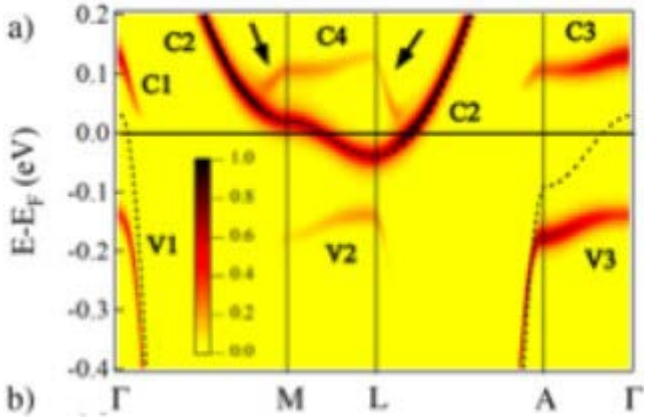
Spectral functions in $TiSe_2$

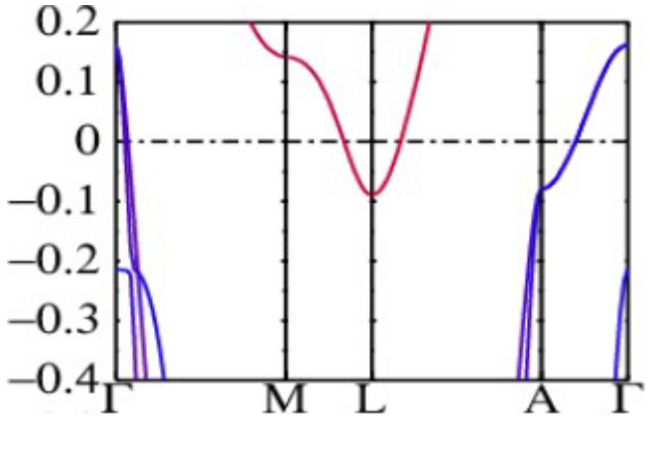
- Below 200K, $TiSe_2$ changes phase from P3c1 to a charge-density wave. The CDW is a $3q_L$ superlattice of P3c1



- Early ARPES experiments showed "shadow bands" absent in DFT

Cercellier et al, PRL 99 (2007)

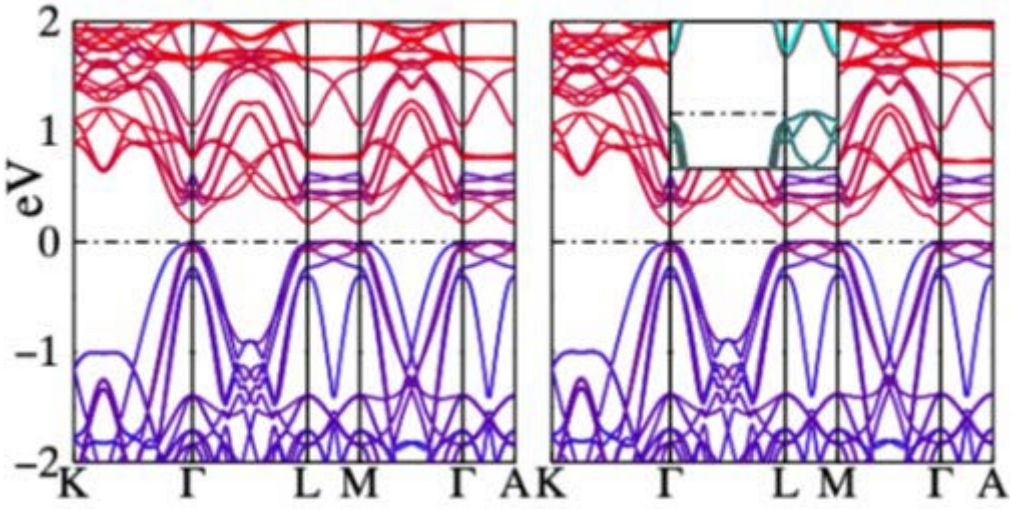




- DFT (and QSGW, for different reasons) ⇒ P3c1 is a metal.
- Shadow bands + nonmetallic state ⇒ $TiSe_2$ is excitonic insulator
- A large literature since 2007, but consensus around basic story

CDW phase, $TiSe_2$

- CDW (P3m1) : slight structural deformation of P3c1
- QSGW predicts insulating phase, gap 0.17 eV (close to expt).



QSGW **QSGŴ**

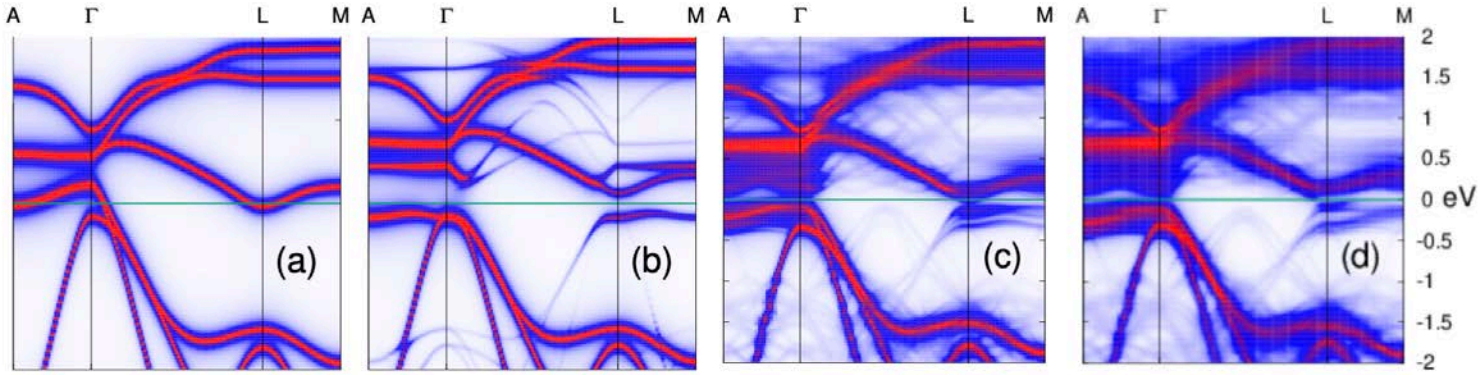
- Incorporating excitonic effects in W ($W \rightarrow \hat{W}$) has almost negligible effect. ⇒ the CDW is a band insulator.
- Recent ARPES measurements (**Watson et al, PRL 122, (2019)**) show adiabatic change in gap across T_C ⇒ gap has common origin

- But QSGW predicts high-symmetry P3m1 to be metallic.

What is missing? Do excitons play a role after all?

Why $TiSe_2$ is insulating in the high-symmetry phase

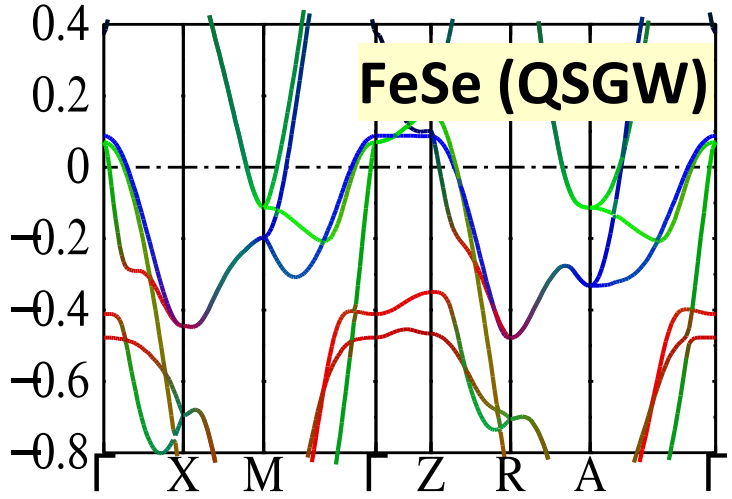
- In the CDW symmetry is broken, but statically .
- In the P3c1 phase, symmetry is broken at any instant in time: it assume the P3c1 phase only when averaged over time
- The time-averaged lattice structure assumes P3c1 symmetry, the time-averaged energy band structure is closer to the CDW. Demonstrate with MD simulations. Perform QSGW on time-separated snapshots, unfold Brillouin zone into P3c1 phase

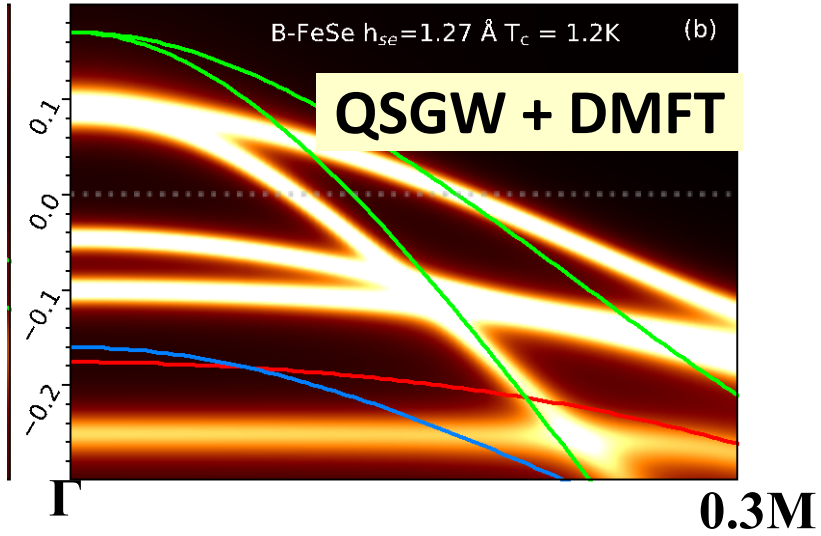


- Shadow bands & T^o dependence of gap, match ARPES nicely.
- Rare instance of a metal-insulator transition induced by dynamical symmetry breaking. Early account in **arxiv 2311.08015**

Importance of spin fluctuations

QSGW breaks down when dynamical spin fluctuations matter.





npj Quantum Mater. 8, 24 (2023)

Unconventional superconductor:

Cooper pairs bound together by something other than electron-phonon interaction.

Fe based superconductors are archetypal examples where spin fluctuations are the glue that bind Cooper pairs.

H0 (e.g. DFT) → **H0 + DMFT**

Tailor-made for DMFT provided spin fluctuations mostly driven by on-site potential.

What to do about H_0 ?

Why not DFT+DMFT?

DFT → DFT+ DMFT

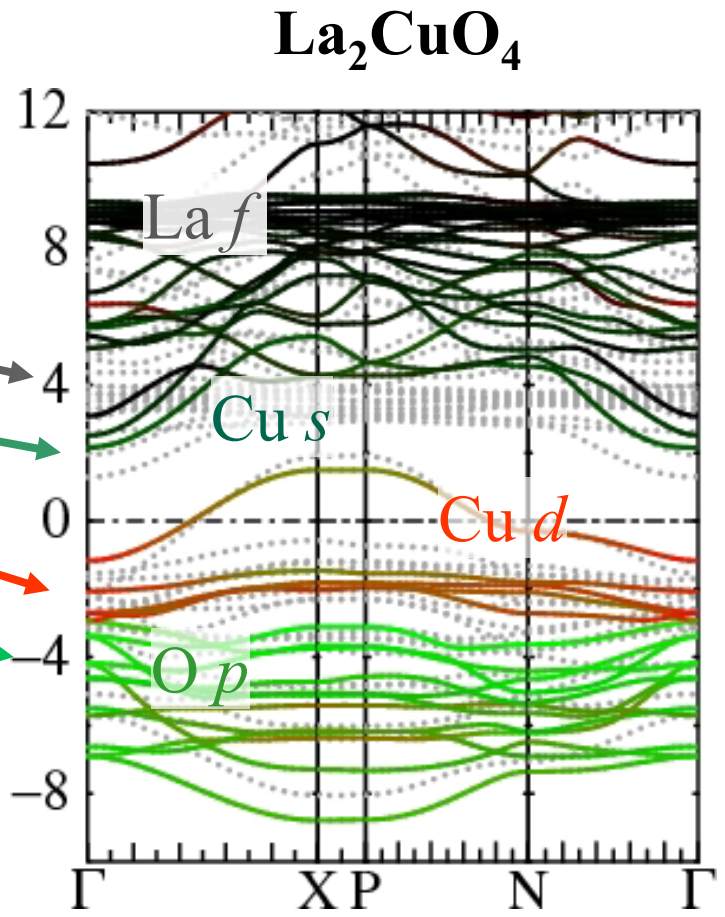
✔ DMFT is the most common approach to add strong correlations to DFT …

✘ DFT often makes poor reference H_0

Example: La_2CuO_4 (parent compound)

- La f states too low
- Cu s state is too low
- Cu d bandwidth too large
- O p states too high

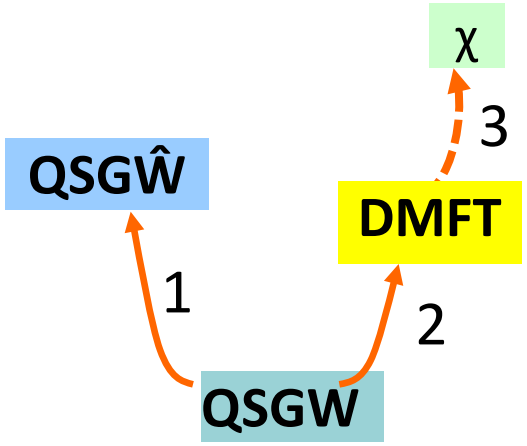
✘ Errors propagate to DMFT ⇒ large Hubbard U to stabilize insulating state, results uncertain



✔ GW + self-consistency ⇒ high fidelity H_0 with nonlocal Σ.
Augment with DMFT to pick up missing spin diagrams.

QSGW+DMFT+BSE + …

Path to tractable *ab initio* framework for strong correlations



Partition problem :

1. Charge fluctuations governed by long-range interactions … but they can be treated accurately with low-order perturbation theory (QSGW)

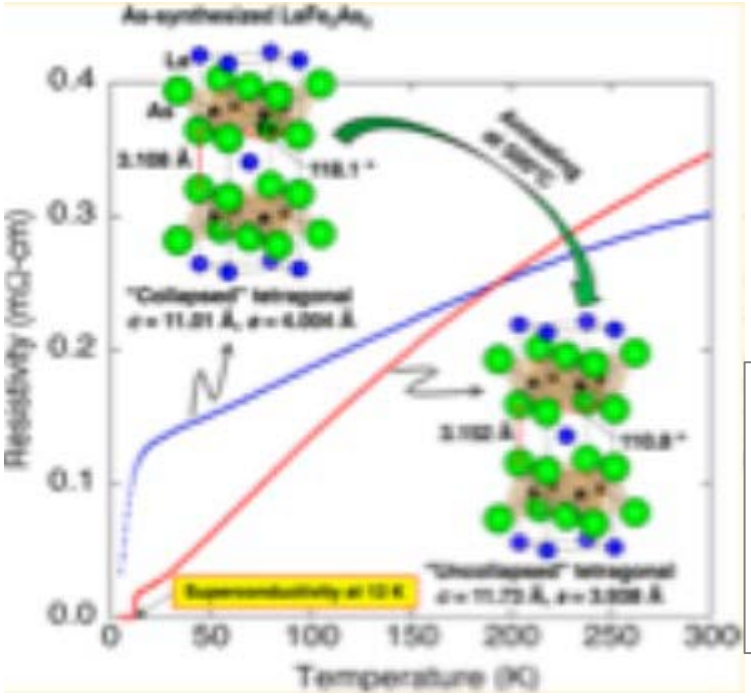
2. Spin-spin vertex mostly between orbitals on one site (nonlocality mostly carried by G connecting sites)

Solve local impurity problem with DMFT embedded in QSGW ⇒ G^{loc}.

Embed G^{loc} $[\Sigma^{DMFT}(\omega)]$ into bath

⇒ $G^{crys}(\mathbf{k};\omega)$. Iterate⇒self-consistent

$LaFe_2As_2$ and $CaFe_2As_2$: two pnictide s.c.



Both superconductors have:

(1) short *c* axis: collapsed-tet = CT

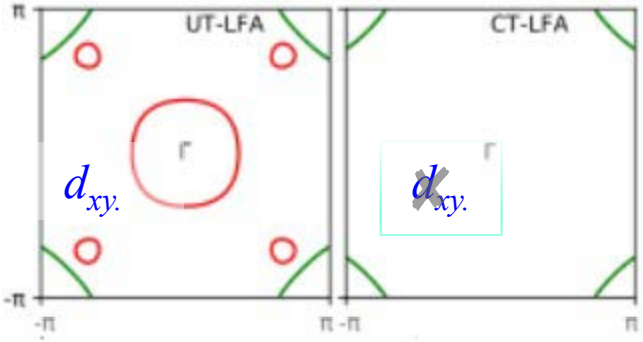
(2) long *c* axis: uncollapsed-tet = UT

No universality in the low-T_c phase

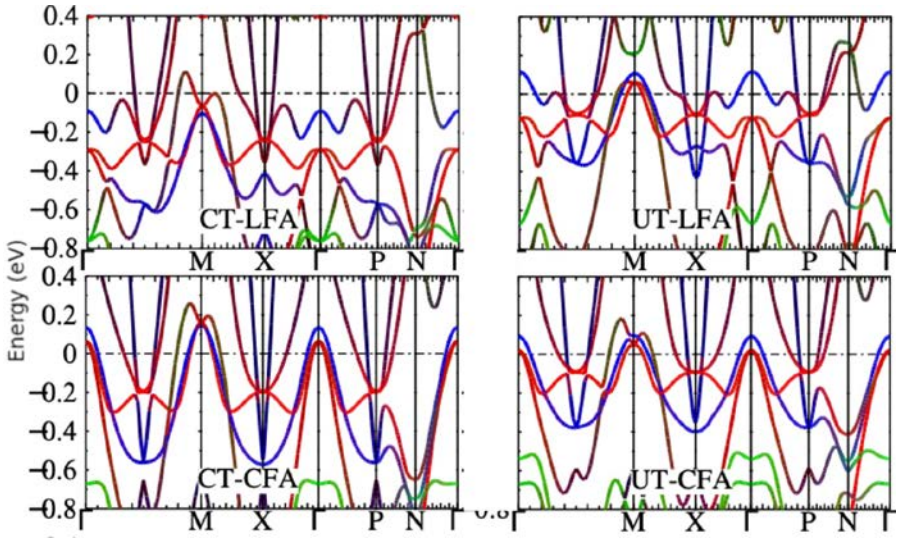
Can we explain why Tc varies so much?

	CT	UT
$LaFe_2As_2$	$T_c = 0K$	$T_c = 12K$
$CaFe_2As_2$	$T_c = 25K$	AFM

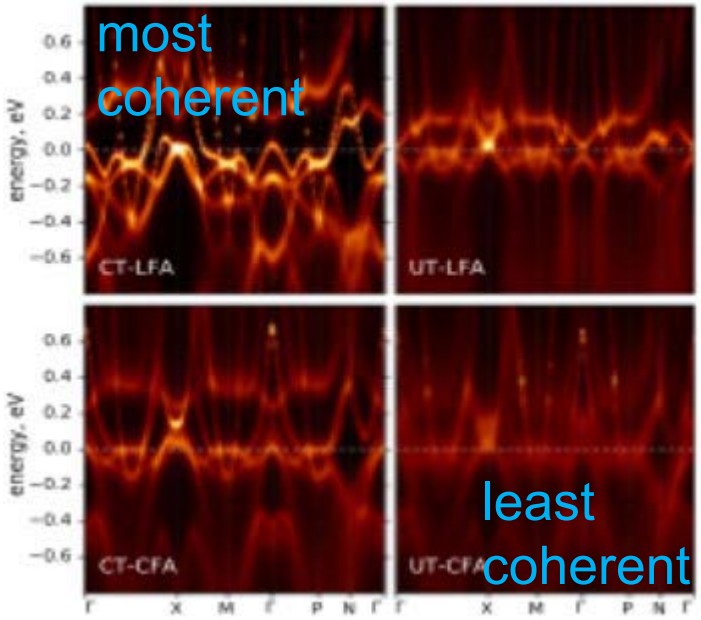
Iyo et al, J. Phys. Chem. Lett. 10 (2019)



blue = $d_{xy.}$ red = $d_{xz,yz}$ green = d_{zz}

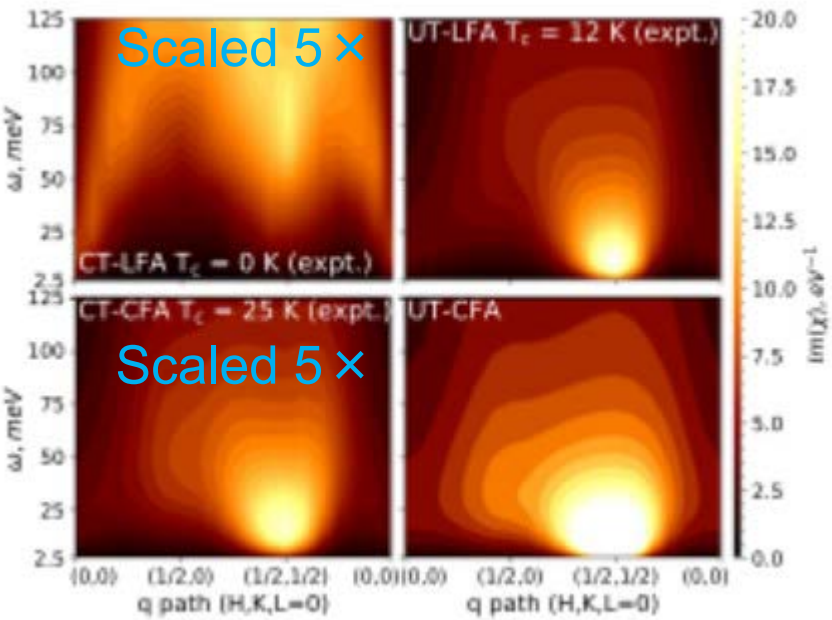


Spin susceptibility in $LaFe_2As_2$ and $CaFe_2As_2$



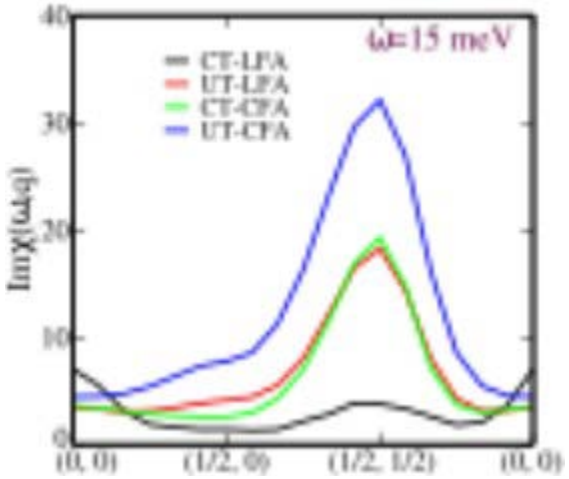
← Spectral function $A(\mathbf{q}, \omega)$ GW+DMFT

Magnetic response function $X^m(\mathbf{q}, \omega)$ →



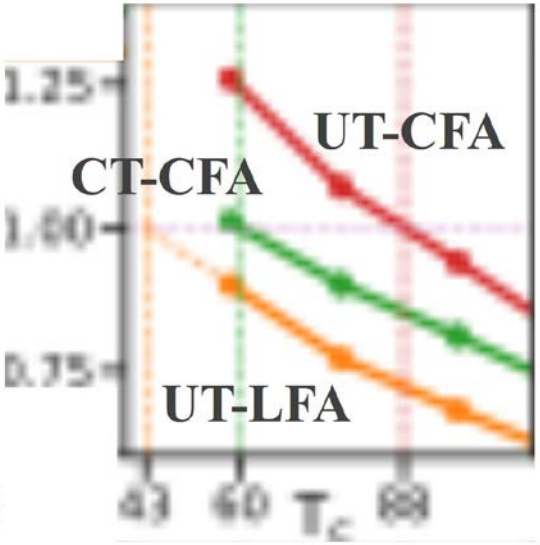
- Each system has paramagnon branches stellating from Γ .
  Strongest in CT-LFA, yet it does not superconduct
- Three have intense peaks at $\mathbf{q}=(1/2,1/2)$, ω=2-10 meV …
  not in CT-LFA because d_{xy} hole pocket at Γ is missing
- Proximity of d_{xy} to E_F drives incoherence in $A(\omega)$,
  … and also intense peak close to $\omega=0$ at $\mathbf{q}=(1/2,1/2)$,
- Intense peak is responsible for superconductivity

Superconductivity in $LaFe_2As_2$ and $CaFe_2As_2$

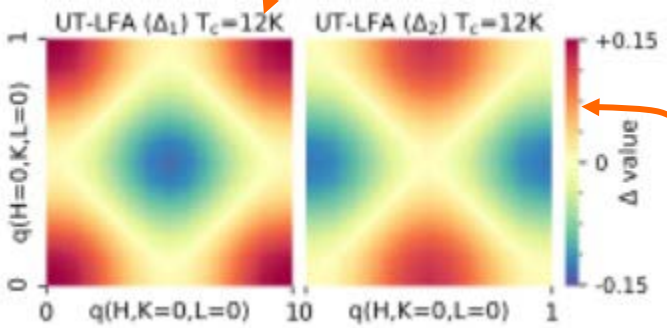


Crosscut of $X^m(q, \omega=15)$

Leading eigenvalue λ_1 of Eliashberg equation. Normal → SC @ $\lambda_1 = 1$



Leading instability is extended ***s*** wave (d_{xy})



Lagging instability (d_{x2-y2}) from d_{xz+yz}

Leading instability is strongest when : d_{xy} is proximate to E_F ⇒ incoherent $A(\omega)$ ⇒ intense, broad peak in $\chi^m(q\sim1/5, \omega<15)$

	CT	UT
$LaFe_2As_2$	$T_c = 0K$	$T_c = 12K$
$CaFe_2As_2$	$T_c = 25K$	AFM

Explains expt except UT-CFA is AFM, not SC, … because AFM overtakes SC

Spin fluctuations and superconductivity in Sr_2RuO_4

A superconductor with $T_c = 1.5K$

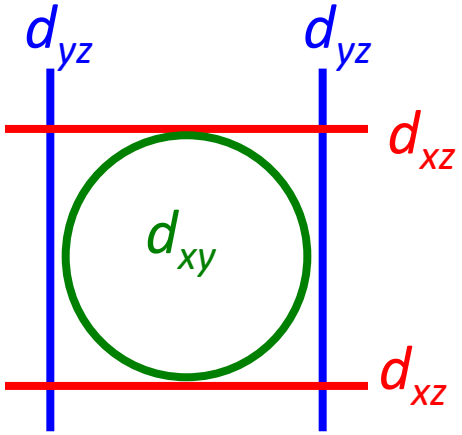
Until recently, SC thought to be a spin triplet character

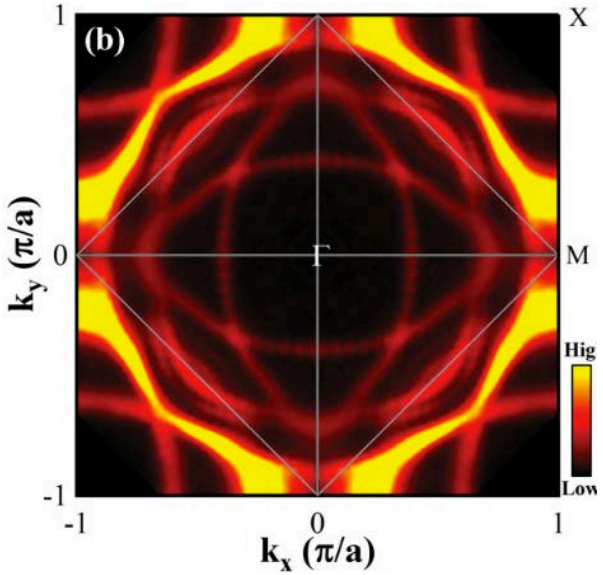
… As tensile strain ε_x increases 0.6% $T_c \rightarrow 3.4K$.

… For $\varepsilon_x > 0.6\%$, T_c falls off again

Three bands make up the Fermi surface of SRO: d_{xy}., d_{xz}, d_{yz}.

Fermi surface is approximately 2D,
quasi-2D d_{xy} superimposed on quasi-1D
d_{xz}, d_{yz}.



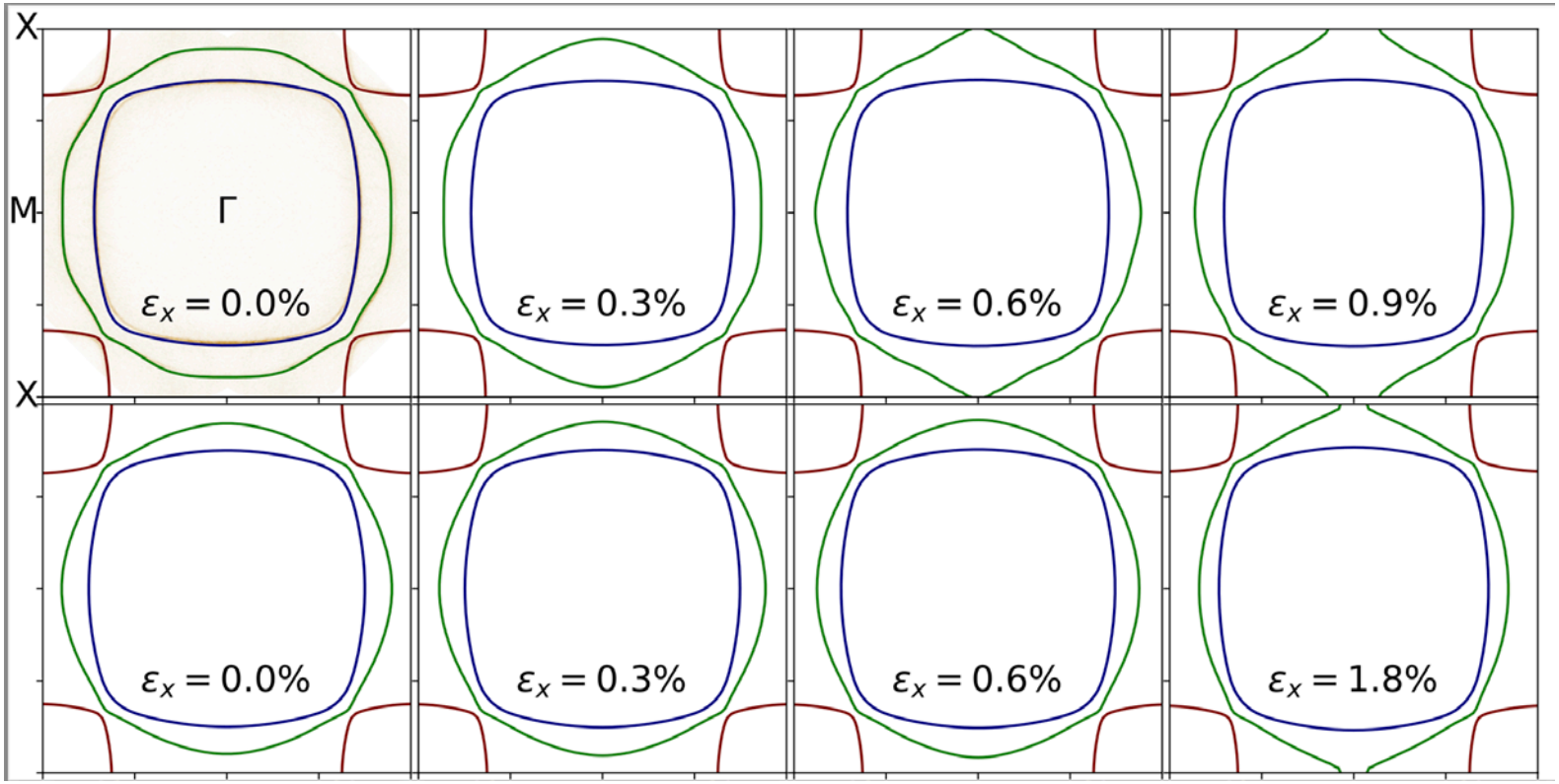


Fermi Surface of Sr_2RuO_4 as function of strain

A. Tamai, *et al.*, Phys. Rev. X 9 (2019) overlaid on QSGW

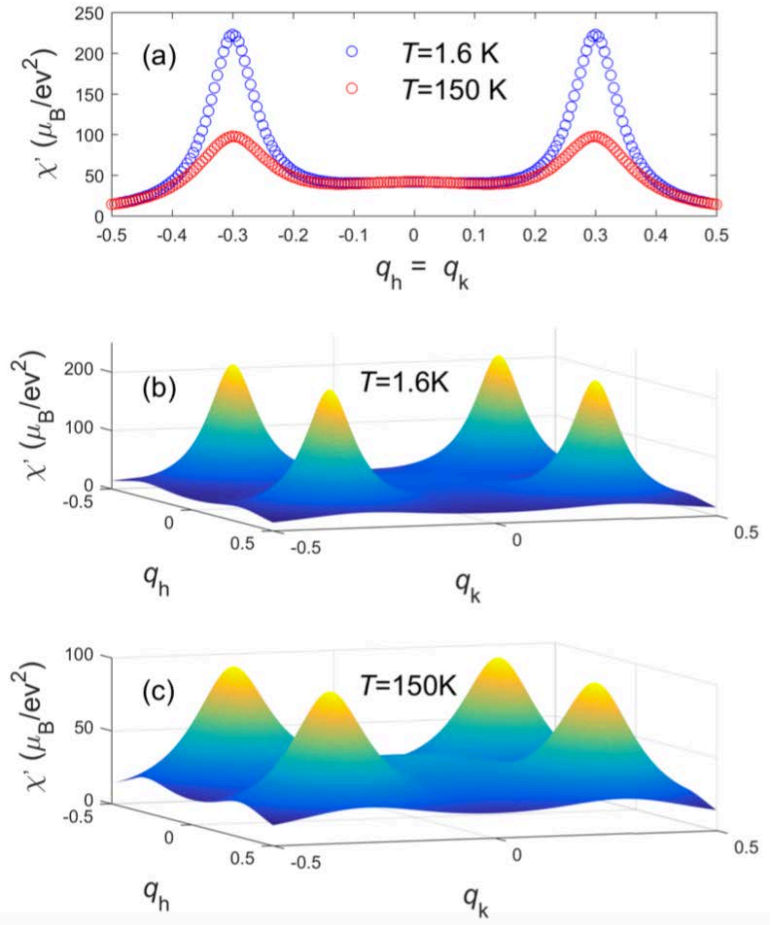
Van Hove singularity @ ε_x = 0.6%.

FS changes topology



QSGW Fermi surface essentially perfect ⇒ spin fluctuations small
Fermi velocities equally well described (Appl. Sci. 11, 508 (2021))

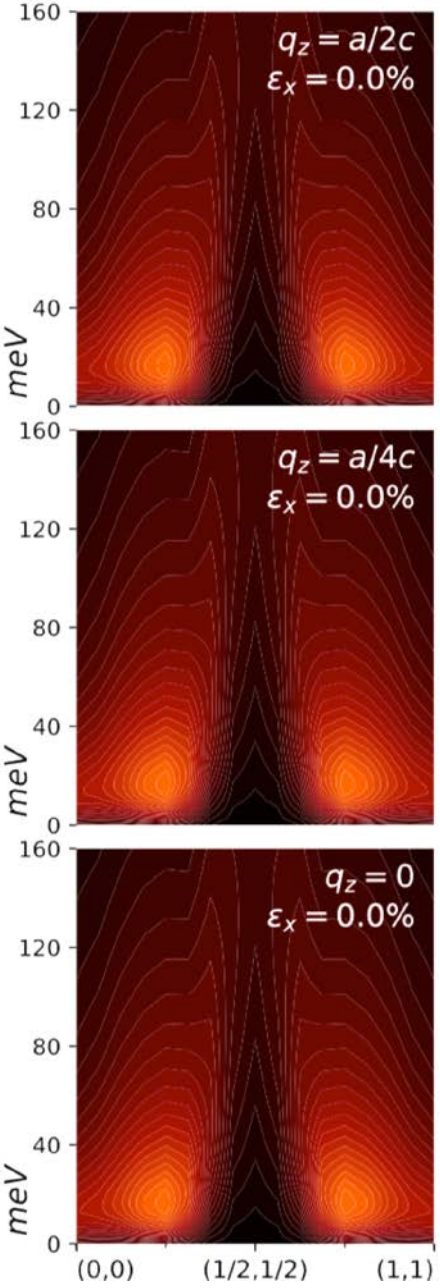
Spin susceptibility I



P. Steffens et al, arXiv:1808.05855

Inelastic neutron scattering shows strong peaks at incommensurate q = q* = (0.3, 0.3, 0) with ω_{max}≈10 meV, spread to ≈80 meV, extending to q = 0.

QSGW+DMFT χ^s is nearly identical. Peaks from more than nesting ! Full vertex $\Gamma(\omega,\omega',\Omega)$ seems to be crucial



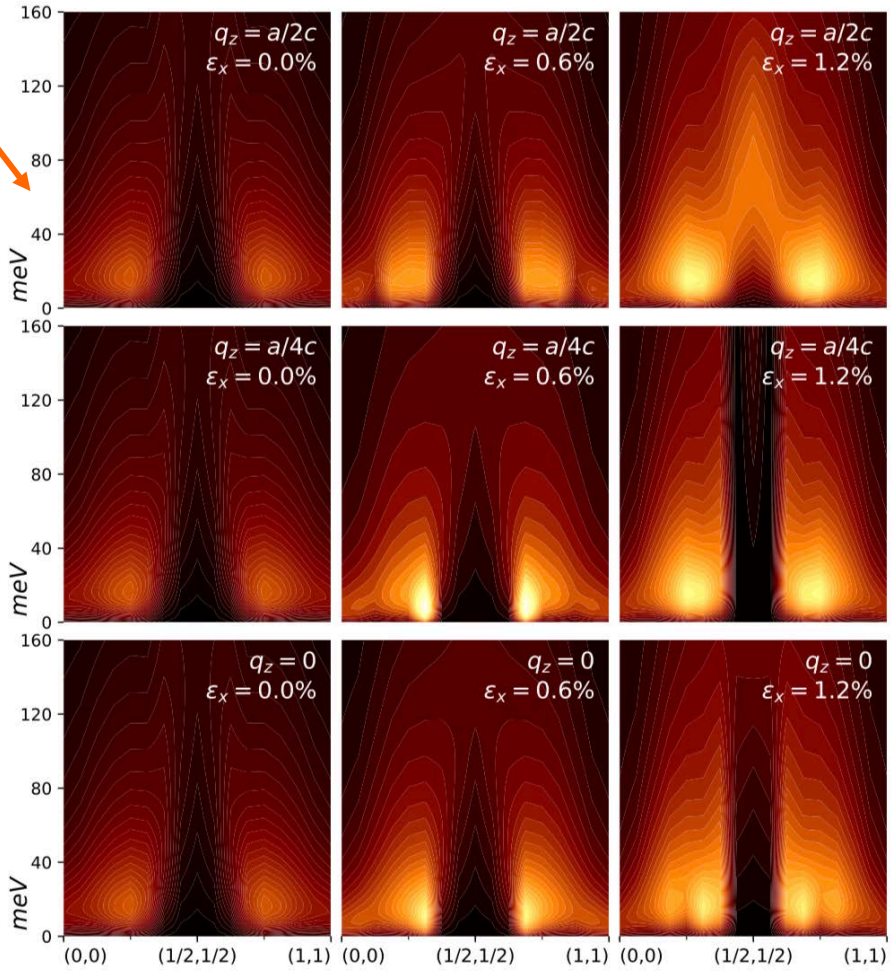
Spin susceptibility II

@ ε_x=0, diffuse paramagnons stellate from q=0 …
suggests SC is spin triplet
No q_z dependence … 2D-like

ε_x → 0.6% : Peaks sharpen and become intense around q=0.3.
No more fully 2D-like

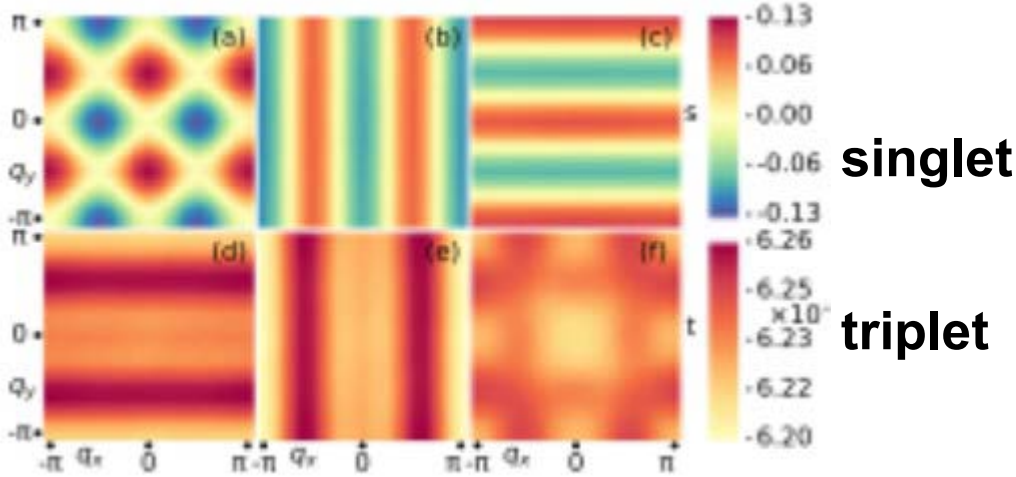
ε_x > 0.6% : Peaks become diffuse, strongly 3D-like

Explains qualitatively why T_c is maximum at $\varepsilon=\varepsilon^*$:
Spin fluctuations are main origin of superconductivity



But it is not the whole story!

Nature of Superconductivity in Sr_2RuO_4

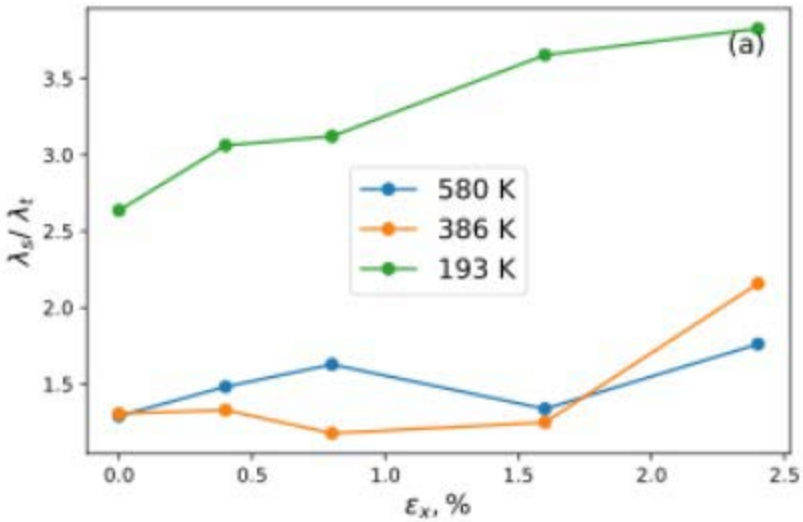


Structure of superconducting pairing field for 6 instabilities

Theory predicts 6 modes of instability: … 3 singlet + 3 triplet.

But the leading singlet is always stronger than the leading triplet, and ratio increases with ε_x

Charge susceptibility also plays a role … charge/spin cooperate increasingly so when $\varepsilon_x > 0$.



Support for Experimental Facilities

What developments are needed to support large facilities?

1. Fidelity is very important … many cases where wrong conclusions are drawn because theory is DFT or DFT based
2. QSGW+DMFT+BSE seems to provide solid foundation to predict properties of strongly correlated systems *ab initio*, including unconventional superconductivity

What is needed to make a practical tool?

1. Lowering barriers to use

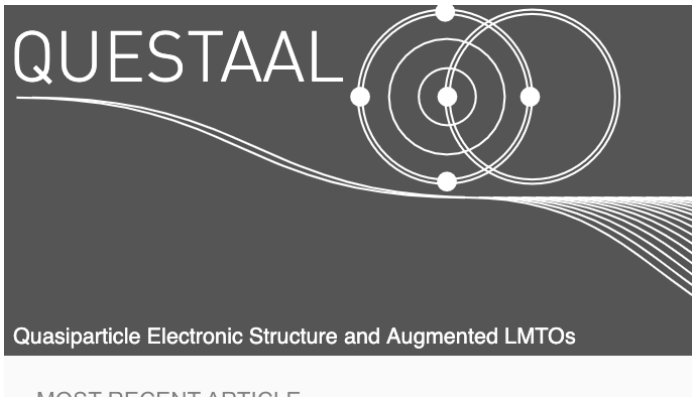
   … Can we avoid DMFT? (sufficient spin diagrams in MBPT)
2. Direct connection to facilities, e.g. ISIS… someone on site w/ expertise in modeling ... Perring's increasing output "flux"
2. Electron-phonon interaction that does not depend on DFT
3. Adequate description of RIXS … at least direct RIXS (Sotille)
4. Many-body effects beyond excitons (Louie)

Contributors to this work

Mainly the work of Swagata Acharya

All calculations were performed using Questaal. Code is free to anyone!.

https://www.questaal.org/



Made possible because of Dimitar Pashov (Questaal manager)

Most of the theory was adapted from Kristjian Haule and Hyowon Park

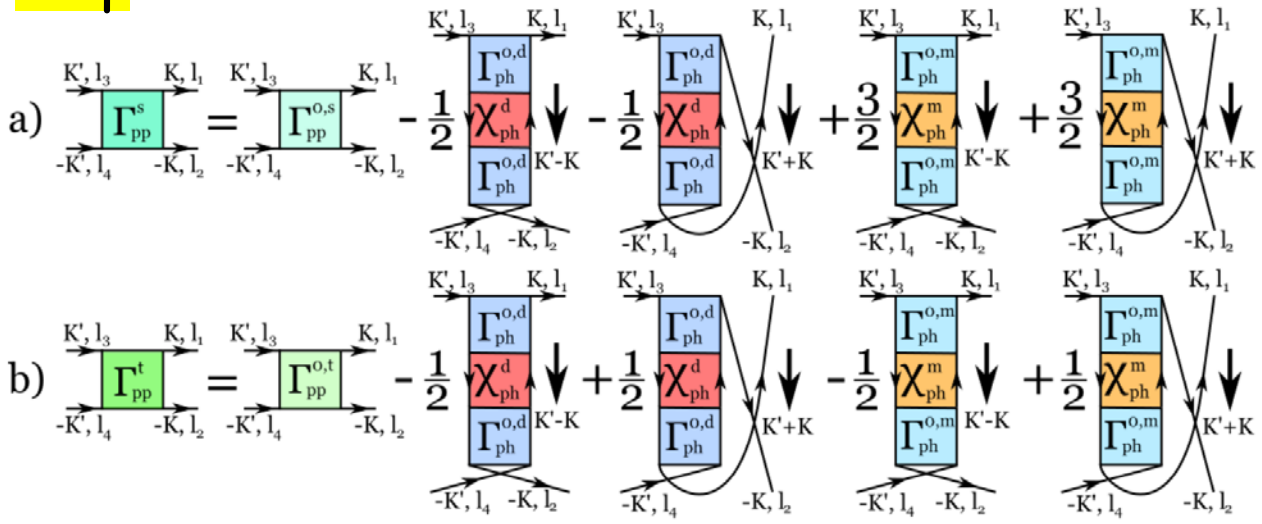
S. Aharya et al, Symmetry 13, 169
S. Aharya et al, PRB 105, 144507
S. Acharya et al npj Quantum Mater. 8, 24

} **Detailed exposition of the theory**

Comp. Phys. Comm. 249, 107065 ← **Questaal methods paper**

Superconducting pairing vertex from spin and charge fluctuations

skip



$$\chi^{p-p} = \chi^{0,p-p} \cdot [\mathbf{1} + \Gamma^{irr,p-p} \cdot \chi^{0,p-p}]^{-1}$$

iplet (t) channels are obtained from the ma

$$\Gamma^{irr,p-p,s}_{\substack{\alpha_2,\alpha_4\\ \alpha_1,\alpha_3}}(\mathbf{k}, i\nu, \mathbf{k}', i\nu') = \Gamma^{f-irr}_{\substack{\alpha_2,\alpha_4\\ \alpha_1,\alpha_3}}(i\nu, i\nu')$$
$$+ \tfrac{1}{2}[\tfrac{3}{2}\widetilde{\Gamma}^{p-h,(m)}$$
$$- \tfrac{1}{2}\widetilde{\Gamma}^{p-h,(d)}]^{\alpha_2,\alpha_3}_{\alpha_1,\alpha_4}(i\nu, -i\nu')_{\mathbf{k}'-\mathbf{k}, i\nu'-i\nu}$$
$$+ \tfrac{1}{2}[\tfrac{3}{2}\widetilde{\Gamma}^{p-h,(m)}$$
$$- \tfrac{1}{2}\widetilde{\Gamma}^{p-h,(d)}]^{\alpha_4,\alpha_3}_{\alpha_1,\alpha_2}(i\nu, i\nu')_{-\mathbf{k}'-\mathbf{k}, -i\nu'-i\nu}$$

Hyowon Park's PhD thesis,
Phys. Rev. Lett. 123, 217005 (2019)

$$\Gamma^{irr,p-p,t}_{\substack{\alpha_2,\alpha_4\\ \alpha_1,\alpha_3}}(\mathbf{k}, i\nu, \mathbf{k}', i\nu') = \Gamma^{f-irr}_{\substack{\alpha_2,\alpha_4\\ \alpha_1,\alpha_3}}(i\nu, i\nu')$$
$$- \tfrac{1}{2}[\tfrac{1}{2}\widetilde{\Gamma}^{p-h,(m)}$$
$$+ \tfrac{1}{2}\widetilde{\Gamma}^{p-h,(d)}]^{\alpha_2,\alpha_3}_{\alpha_1,\alpha_4}(i\nu, -i\nu')_{\mathbf{k}'-\mathbf{k}, i\nu'-i\nu}$$
$$+ \tfrac{1}{2}[\tfrac{1}{2}\widetilde{\Gamma}^{p-h,(m)}$$
$$+ \tfrac{1}{2}\widetilde{\Gamma}^{p-h,(d)}]^{\alpha_4,\alpha_3}_{\alpha_1,\alpha_2}(i\nu, i\nu')_{-\mathbf{k}'-\mathbf{k}, -i\nu'-i\nu}$$

→ Note: we keep the full structure of the CTQMC/ED vertex functions and its fermionic frequency dependences and entire momentum and orbital structure

Main approximation: p-p pairs with vanishing center of mass momentum-frequency (q=0,iΩ=0)
→ it can be written as an eigenvalue problem (Linearized-Eliashberg equation) in the normal state to find instability to the SC state.