QSGW+DMFT Description of Many-body phenomena

Mark van Schilfgaarde, Real Materials Group

Starting point: GW

Importance of self-consistency: TiSe$_2$

Importance of nonlocality

Beyond GW

Benchmarks: (1) how far does low-order perturbation theory take us?
(2) Case studies: QSGW+DMFT+BSE
**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
$\Rightarrow$ 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.

Conjecture: converges most rapidly with diagram order
Quasiparticle self-consistency

Avoid problems w/ sc: perform $GW (G\hat{W})$ around optimal $G_0$.

Start with some trial $V^{xc}$ (e.g. from LDA, or ...). Defines $G_0$:

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

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

GWA determines $\Delta V$ and thus $H$:

$$G_0 \xrightarrow{\text{RPA}} \epsilon(iG_0G_0) \xrightarrow{\text{GWA}} \Sigma(r,r',\omega) = iG_0W; \quad \Delta V = \Sigma - V^{xc}$$

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

$$V^{xc} = \frac{1}{2} \sum_{ij} \langle \psi_i | \text{Re} \left( \Sigma(E_i) + \Sigma(E_j) \right) | \psi_j \rangle \quad \text{result of min } N$$

Iterate to self-consistency.

At self-consistency, $E_i$ of $G$ matches $E_i$ of $G_0$ (real part).
Justification for QSGW: find the $G_0$ which minimizes 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 $E^{\text{RPA}}$?

\[ \frac{\delta E^{\text{RPA}}}{\delta G_0} = 0 \]

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)

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

J. Phys. Cond. Matt. 29, 385501
If $T > T_c$, TiSe$_2$ has a simple unit cell. The gap is not reliably known, but it is thought to be < 0.05 eV. LDA predicts inverted gap.

Cazzaniga et al PRB 85 `12 added GW corrections to LDA ($G^\text{LDA} W^\text{LDA}$). Found an insulator with a gap ~0.5 eV ... suggests usual problem with LDA.
But the positive gap is an artifact of \( G^{LDA} W^{LDA} \)!

LDA and GW eigenfunctions should be different (missing in 1\(^{st}\) order pert theory)

Full self-energy \( \Sigma^{nn'} \) modifies density \( n(r) \) and thus \( V \).

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

\[ \Sigma - V_{xc}^{LDA}[n^{LDA}] + V_{xc}^{LDA}[n^{GW}] \]

Redo self-consistency. Gap becomes negative again!

Result similar to QSGW
TiSe$_2$ reconstructs into a $2 \times 2 \times 2$ superstructure, a superposition of three L point phonon modes, forming a "3Q" charge density wave. 3Q is thought to have a gap between 0.05 and 0.15 eV.

What does QSGW predict for CDW? Take displacement amplitudes from GGA (Bianco et al PRB 92 '15).

Trace a path from ideal to 3Q geometry. Bands evolve in a tortuous manner ... but at CDW geometry, QSGW predicts an insulator, $E_G = 0.17$ eV (including spin-orbit).

What we learn: $\delta V/\delta n$ is important, not captured by G$_{\text{LDA}}$W$_{\text{LDA}}$.
Importance of Nonlocality

\[ Z_k = \left(1 - \left(\frac{\partial \Sigma(k, \omega)}{\partial \omega}\right)\right)^{-1} \]

Dependence of NiO bandgap vs range cutoff in \( \Sigma(R, R') \).

\[ r_c = \max |R - R'| \]

\( \frac{\partial \Sigma}{\partial \omega} \) has strong band, \( k \), and \( \omega \) dependence.

\[ (1 - \frac{\partial \Sigma(k, \omega)}{\partial \omega})^{-1} \]
Electronic structure, QSG\(\hat{W}\)

Premise (1) absent significant spin fluctuations, QSG\(\hat{W}\) provides an excellent description of QP levels for most materials systems. Here \(\hat{W} = W^{RPA} + \text{low-order addition}\)

QSGW\(^{RPA}\) has well known deficiencies:
- Overestimates (unocc–occ) splitting
- Plasmon peaks blue shifted
- \(\varepsilon_{\infty} = 80\% \times \text{expt}\)
Missing diagrams in $W$

Kramer’s Kronig relates real and imaginary parts of $\varepsilon$:

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

$\varepsilon_{\infty}$ too small because of blue shifts in plasmon peaks.

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

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

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 $\omega=0$. 
Compare QSGW^{RPA}, QSGW^{BSE} bands to BIS in NiO

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

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 $W^{RPA} \rightarrow W^{BSE}$
$-0.3$ eV shift
... $d$ band $W^{RPA} \rightarrow W^{BSE}$
$-1$ eV shift

largely eliminates discrepancies in BIS
$W^{\text{RPA}} \rightarrow W^{\text{BSE}}$ mostly eliminates systematic error in QP levels.

Main part of error originates from $GW^{\text{e-ph}}$.

Residual error now small ... (but no longer systematic)
The monoclinic (M1) phase has 4 V atoms/cell: V reconstructs into two pairs of dimers.

Nonmagnetic QSGW predicts band insulator, gap ~0.7 eV (first found by Gatti et al, PRL 99, ’07). Self-consistency essential!

A (metastable) M2 phase exists : 2 V atoms dimerize, 2 do not.

NM QSGW : metal, contrary to expt.

Magnetic QSGW: no moment on dimerized V, but the other pair orders antiferromagnetically. A gap forms. Needs DMFT!
Where QSGW breaks down

QSGW describes local-moment magnetic systems remarkably well. It breaks down when spin fluctuations are strong.

Premise (2) When spin fluctuations are strong, the effective interaction is predominately local. Local vertex + bubbles describes $\chi^S$ very well.
La$_2$CuO$_4$: case study

Cool from high $T^\circ$:

Metal $\rightarrow$ PM insulator $\rightarrow$ AFM insulator

Use NM as proxy for PM.

QSGW yields metallic state, $d_{xy}$ at $E_F$

Some key differences with DFT:

- O $p$ gets pushed down
- DFT eigenfunctions near $E_F$ have lots of O $p$, Cu $s$ character
- QSGW eigenfunctions: Much closer to pure Cu $d$ character.

Very important!

Antiferromagnetic solution: small local moments form on Cu and split $d_{xy}$

Plot: Use QSGW$^{RPA}$ local moment
1. Antiferromagnetic $\text{La}_2\text{CuO}_4$: QSGW

**QSGW** bandgap is too large

**QSGW** $\hat{\mathbf{W}}$ Reduces QP gap from $3.5 \rightarrow 2.6$ eV.

**Optics:**
- BSE reasonably well predicts first peak & plateau $\Rightarrow$ lowest QP and bandgap are good.
- Subgap absorption (excitons) seem well described
- $\sigma_x, \sigma_z$ anisotropy well described $\Rightarrow$ good QP
- Rise $>5$ eV blue-shifted. Plasmon may be too high.
2. Paramagnetic La$_2$CuO$_4$: QSGW+DMFT

QSGW(NM)+DMFT yields Mott gap for paramagnetic La$_2$CuO$_4$

Originates from non-Fermi liquid structure of $\Sigma$.
Susceptibilities with QSGW+DMFT+BSE

Given one-particle $G$, use DMFT to:
1. calculate 2-particle $G$
2. generates local spin and charge particle-hole vertices $\Gamma(\omega,\omega',\Omega)$
3. Combine with bubbles to make nonlocal susceptibilities $\chi^S$ and $\chi^C$.
4. Particle-hole vertices can yield particle-particle vertex
5. Combine with bubbles to yield superconducting pairing field

Main assumption: all nonlocality from bubbles
3. Pairing Field in $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$

$\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$ has superconducting dome between $x=0.05$ and $x=0.28$. Consider underdoped case ($x=0.05$). Compare superconducting pairing field to 1-band Hubbard Model (from Park, PhD thesis, Rutgers ’11)

Gap structure in $xy$ plane
← Hubbard model (PhD thesis, Park)

QSGW+DMFT+BSE →
4. Hole-Doped LCO : \( \text{La}_{1.88}\text{Sr}_{0.12}\text{CuO}_4 \)

Neutron structure factors just above \( T_c \) at \( x=0.12 \) exhibit an intricate 4-fold-symmetric incommensurate structure around \((\pi,\pi)\). \( \chi^s \) is gapped at \((\pi,\pi)\) itself.

For each of the 4 \( q \), \( \chi^s \) has a complex energy-dependence:

A low-energy peak at 15–18 meV, a second at 40–50 meV

(The 15–18 meV peak seems to be one of the few universal features across many cuprates).

Neutron data from S. Hayden
Prediction of $\chi^s$ replicates structure factor in remarkable detail. As $T \to 145K$, gap in the spin-structure emerges.

Experimental $T^* \sim 145\,K$: peak at 50 meV vanishes at $x=0.24$. 

Appears as a result of kink in fermionic $\omega$, e.g. $\Gamma(\omega=\omega',\Omega=0)$. 

4. QSGW+DMFT+BSE Spin Susceptibilities in La$_{1.88}$Sr$_{0.12}$CuO$_4$
**Where next?**

---

**QSGW**: optimum starting point  
Accurate, minimal short range JPO  
⇒ higher order diagrams feasible

---

**Total energy**:  
Optimum path of adiabatic connection.

---

Bandgap in NiO vs nonlocality cutoff

---

Few diagrams enough for QCA?
Contributors to this work

Cedric Weber
Evgeny Plekhanov
Myrta Gruening
Brian Cunningham
Dimitar Pashov
Francois Jamet

Mainly the work of Swagata Acharya
Thanks to K. Haule and G. Kotliar!
(CTQMC from Haule)

Code is free to anyone.
https://www.questaal.org/
Conclusions

1. Many-Body Perturbation Theory (GW++)
   Low-order, but no partitioning, real axis
   \text{QS}GW \text{ resolves starting point ambiguity;}
   vastly improves consistency, reliability.
   \text{QS}GW \rightarrow \text{QS}GW \hat{W}
   removes systematic errors
   Excellent for charge fluctuations, not spin

2. Dynamical Mean Field Theory
   for spin fluctuations. QSGW+local diagrams seems describe 1- and 2-
   particle quantities remarkably well
   Nonperturbative approach essential?
   Local vertex + bubbles yields stellar \( \chi^s \) in \( \text{Sr}_2\text{RuO}_4 \) and \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \).
Non-local correlations in spin and charge: orbital characters of active band in La$_2$CuO$_4$

Cu-$d_{z^2}$, O-$p_z$ and Cu-4s are suppressed significantly in QSGW

<table>
<thead>
<tr>
<th></th>
<th>Cu $x^2-y^2$</th>
<th>Axial Orbitals</th>
<th>O $p_x+p_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>QSGW</td>
<td>0.544</td>
<td>0.108</td>
<td>0.263</td>
</tr>
<tr>
<td>LDA</td>
<td>0.401</td>
<td>0.220</td>
<td>0.280</td>
</tr>
</tbody>
</table>


Much larger orbital weight on $x^2-y^2$ relative to LDA
Closer to true 1-band description than previously thought.
Bandwidths in QSGW

As Shirley showed, $sc \cdot GW + GWGWG$ essentially restores the $G^0W^0$ bandwidth. QSGW predicts the Na bandwidth to narrow relative to LDA by $\sim 10\%$, 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.

![Graph showing bandwidths](image)