2022 SUMMER SCHOOL ON ELECTRON PHONON PHYSICS
FROM FIRST PRINCIPLES AUSTIN TEXAS

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Introduction to GW, GW-Bethe-Salpeter-equation (GW-BSE), and GW perturbation theory (GWPT)

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Materials properties

**Ground-state properties**
- Total energy
- Structures
- Magnetization
- Vibrations
- ...

**Excited-state properties (Spectroscopies)**

**Single-particle excitation**
- \( N+1 \) problem
- Photoemission
- Tunneling
- Band gap
- ...

**Two-particle excitation**
- \( N+2 \) problem
- Optical responses
- Excitons
- ...

DFT/DFPT

GW

GW-BSE
## Excited-state phenomena of materials

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<td>Not the true effective potential seen by a quasiparticle</td>
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### Density functional theory (DFT)

- **Ground-state theory**
- **Exchange-correlation potential**
  
  $\hat{V}^{xc} = V^{xc}(\mathbf{r})$
  
  Not the true effective potential seen by a quasiparticle

### GW method

- **Excited-state theory**
- **Self-energy** $\leftrightarrow$ **Many-electron correlation**
  
  $\hat{\Sigma}(\mathbf{r}, \mathbf{r}'; \omega) = iGW$
  
  (G: Green’s function; $W$: screened Coulomb)
- Non-local, frequency-dependent potential

---

**Bare electron**

**Dressed electron**

$\leftrightarrow$ Quasiparticle
Spectral function and self-energy effects

Angle-resolve photoemission spectroscopy (ARPES)

- Energy shift
- Peak broadening
- Satellite features

\[ E_{nk}^{\text{QP}} = \varepsilon_{nk}^0 + \text{Re}\Sigma_{nk}(\omega) \]

\[ A_{nk}(\omega) = \frac{1}{\pi} \frac{|\text{Im}\Sigma_{nk}(\omega)|}{|\omega - \varepsilon_{nk} - \text{Re}\Sigma_{nk}(\omega)|^2 + |\text{Im}\Sigma_{nk}(\omega)|^2} \]


cf. Lec. Tue. 2. Giustino
GW approximation to electron-electron self-energy

\[ \Sigma = \Sigma^{e-e} + \Sigma^{e-ph} + \ldots \]

Electronic self-energy $GW\Gamma$

Fan-Migdal (e-ph)

Debye-Waller (e-ph)

Image from Tue.2.Giustino

Giustino, RMP 89, 015003 (2017)
GW approximation to electron-electron self-energy

- With $\Gamma = \delta(1,2)\delta(1,3)$, electron self-energy is within the **GW approximation**

  \[ \Sigma^{e-e} = iGW \]

- Dyson's equation (eigenvalue equation)

  \[ h_0(r)\psi_{nk}^{QP}(r) + \int \Sigma(r, r'; E_{nk}^{QP}) \psi_{nk}^{QP}(r')dr' = E_{nk}^{QP} \psi_{nk}^{QP} \]

  \[ h_0 = -\nabla^2 + V_{\text{ext}} + V_H \]

- Compare with Kohn-Sham DFT (with standard local functionals)

  \[ h_0(r)\psi_{nk}^{\text{DFT}}(r) + V_{xc}(r)\psi_{nk}^{\text{DFT}}(r) = \epsilon_{nk}^{\text{DFT}} \psi_{nk}^{\text{DFT}} \]
**Ab initio GW method**

- Green’s function

\[ G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{n\mathbf{k}} \frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')}{\omega - \varepsilon_{n\mathbf{k}} - i\delta_{n\mathbf{k}}} \]

- Screened and bare Coulomb interaction

\[ W(\mathbf{r}, \mathbf{r}'; \omega) = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega) v(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' \]

\[ v(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} \]

- Dielectric matrix from random-phase approximation (RPA) polarizability

\[ \varepsilon(\mathbf{r}, \mathbf{r}''; \omega) = 1 - vP^{\text{RPA}} \]

\[ P^{\text{RPA}} = -iGG \]

Ab initio GW method

- Commonly, GW self-energy is constructed with DFT starting points (eigenvalues and wavefunctions)
- GW self-energy matrix elements are computed as a many-body correction to the DFT eigenvalues

\[ E_{nk}^{GW} = \varepsilon_{nk}^{\text{DFT}} + \langle \psi_{nk} | \Sigma(E_{nk}^{GW}) - V_{xc} | \psi_{nk} \rangle \]

✓ Sum over bands: in principle to full Hilbert space, in practice hundreds to thousands for convergence

GW quasiparticle band gaps
GW-Bethe-Salpeter-equation (GW-BSE) approach

- Optical absorption processes involve two excited-state quasiparticles

- Quasi-electron and quasi-hole can bind via Coulomb interaction and form a new excitation: **Exciton**
GW-Bethe-Salpeter-equation (GW-BSE) approach

- The **Bethe-Salpeter equation** for each exciton state $S$

$$
\left(E_{ck}^{\text{QP}} - E_{vk}^{\text{QP}}\right) A_{vck}^S + \sum_{v'c'k} \langle vck | K^{e-h} | v'c'k \rangle A_{v'c'k}^S = \Omega^S A_{vck}^S
$$

- $\Omega^S$ is the excitation energy, and $A_{vck}^S$ is exciton wavefunction (in quasiparticle basis)

- Exciton wavefunction in real space

$$
\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{vck} A_{vck}^S \psi_{ck}(\mathbf{r}_e) \psi_{vk}(\mathbf{r}_h)
$$

- The **GW-BSE kernel**

$$
K^{e-h} = \frac{\delta(V_H + \Sigma_{\text{GW}})}{\delta G} = v - W
$$

Rohlfing, Louie, PRL 81, 2312 (1998)
Onida, Reining, Rubio, RMP 74, 601 (2002)
GW-Bethe-Salpeter-equation (GW-BSE) approach

- Imaginary part of the dielectric function (optical absorption)

\[
\varepsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_S |\mathbf{e} \cdot \langle 0|\mathbf{v}|S \rangle|^2 \delta(\omega - \Omega^S)
\]

\(\mathbf{e}\): photon polarization
\(\mathbf{v}\): velocity operator

Louie, Chan, Jornada, Li, and Qiu, Nature Materials 20, 728 (2021), Perspective article
Example: 2D transition-metal dichalcogenides MoS\textsubscript{2}

- Monolayer MoS\textsubscript{2}: Direct band-gap semiconductor

\[ N_b: \text{Number of bands} \]
\[ E_S: \text{Energy cutoff for dielectric matrix} \]

\textit{Convergence} is an important issue in GW calculations

Qiu, Jornada, Louie, PRL 111, 216805 (2013)
Example: 2D transition-metal dichalcogenides MoS$_2$

- Tightly bound excitons in monolayer MoS$_2$
- Strong absorbance ~ 20% at exciton excitations
- e-ph interaction introduces QP lifetimes

Theory: Qiu, Jornada, Louie, PRL 111, 216805 (2013)
Expt: Mak, Lee, Hone, Shan, Heinz, PRL 105, 136805 (2010)
Example: 2D transition-metal dichalcogenides MoS$_2$

- Rich exciton structures in 2D TMD materials

Qiu, Jornada, Louie, PRB 93, 235435 (2016)
Self-consistency in GW calculations

**Eigenvalue self-consistency GW**

- Notation: $G_n W_m$ where $n$ and $m$ label iteration steps
- **Mostly used:** one-shot $G_0 W_0$
- Self-consistency in $W$ worsens results
  - Increasing band gaps reduces screening
  - RPA-$W$ with DFT energies has error cancellation:
    vaguely speaking, mimicking excitonic effects
- **Commonly seen:** $G_n W_0$ or $GW_0$

$$ G(r, r'; \omega) = \sum_{n k} \frac{\psi_{n k}(r) \psi_{n k}^*(r')}{\omega - E_{n k}^{\text{QP}} - i \delta_{n k}} $$

$$ \psi_{n k}^{\text{QP}}(r) \approx \psi_{n k}^{\text{DFT}}(r) $$

**Eigenvector self-consistency GW**

$$ \psi_{n k}^{\text{QP}}(r) \neq \psi_{n k}^{\text{DFT}}(r) $$

- Compute off-diagonal GW matrix elements $\langle \psi_{m k} | \Sigma - V_{xc} | \psi_{n k} \rangle$
- Diagonalization gives GW-corrected QP wavefunctions

See also: Quasiparticle self-consistent GW, van Schilfgaarde, Kotani, Faleev, PRL 96, 226402 (2006)
Self-consistency in GW calculations

GW-BSE calculation of X-ray absorption spectra of liquid water

- GW-corrected quasiparticle wavefunction improves BSE absorption spectra

Tang, Li, Zhang, Louie, Car, Qiu, Wu, PNAS 119, e2201258119 (2022)
Electron-phonon coupling from lattice vibrations

\[
\frac{\delta V}{\delta R_{\text{ion}}}
\]

Potential (seen by a quasiparticle) change induced by ion displacements

**Density-functional perturbation theory (DFPT)**
- Very powerful in computing e-ph properties
- Inadequate for many-electron correlations
- Not true potential seen by quasiparticles

**GW perturbation theory (GWPT)**
- Linear-response (to phonon perturbations) theory within GW approximation
- Compute e-ph matrix elements at the GW level
- Captures many-electron correlation effects in the e-ph coupling

*cf. Lec. Mon.2.Giannozzi
Lec. Tue.2.Giustino*

GW perturbation theory (GWPT)

- Electron-phonon coupling

\[
g_{mn\nu}^{GW}(k, q) = \frac{\delta \Sigma}{\delta R_{ion}}
\]

- Electron-phonon matrix element: **building blocks** to all microscopic electron-phonon theories

\[
g_{mn\nu}^{GW}(k, q) = g_{mn\nu}^{DFT}(k, q) - \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta_{q\nu} V^{xc} | \psi_{n\mathbf{k}} \rangle + \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta_{q\nu} \Sigma | \psi_{n\mathbf{k}} \rangle
\]

- DFPT starting point to generate: \( g^{DFT}, \Delta_{q\nu} V^{xc}, \) and \( \Delta_{q\nu} \psi_{n\mathbf{k}} \) (for both valence and conduction bands)

Correlation-enhanced electron-phonon coupling and superconductivity

\( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \): experimental \( T_c = 32 \text{ K} \) at \( x = 0.4 \)

Correlation-enhanced electron-phonon coupling and superconductivity

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$: experimental $T_c = 32$ K at $x = 0.4$

McMillan–Allen-Dynes formula to estimate superconducting $T_c$ with $\mu^* = 0.16$

GW-level electron-phonon phenomena with EPW + BerkeleyGW

Fan-Migdal self-energy

Electron propagator $G$

Phonon propagator $D$

e-ph matrix elements

$g^{\text{DFT}}$ vs. $g^{\text{GW}}$

$\varepsilon^{\text{DFT}}$ vs. $E^{\text{GW}}$

DFPT phonon is based on the ground-state total energy $\Leftrightarrow$

Generally very accurate
GW-level electron-phonon phenomena with EPW + BerkeleyGW

Photoemission kink in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

Theory GWPT

Comparison

Li, Wu, Chan, Louie, PRL 126, 146401 (2021)

See also: Giustino, Cohen, Louie, Nature 452, 975 (2008)
Heid et al., PRL 100, 137001 (2008)
BerkeleyGW tutorial at the Electron-Phonon School 2022

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