Excited-State Properties

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Excited states in material science are ubiquitous.

Experiment/Spectroscopy

ARPES

ZnO
Excited states in material science are ubiquitous.

Experiment/Spectroscopy

appropriate? accurate?
Excited states in material science are ubiquitous.
Excited states in material science are ubiquitous.
Excited states in material science are ubiquitous

**Experiment/Spectroscopy**

**Theoretical Spectroscopy**

**Materials Science/Application**

appropriate? accurate?
Excited states in material science are ubiquitous.

Experiment/Spectroscopy
- photoemission
- optical absorption

Theoretical Spectroscopy
- Green’s function theory
  - GW, BSE

Materials Science/Application

appropriate? accurate?
Nitride-based light emitters

- blue LED
- blue ray

Challenges:
- solid state lighting
- RGP laser projectors
Do we know the band gap of InN?

until ‘06
Challenges I’ll address:

- level alignment

- donor-acceptor pairs
Spectroscopies

Photoemission

Inverse Photoemission

Absorption

GW

GW

BSE TDDFT
Photo-electron energies

Photoemission

- electron removal
  - ground state
- removal energy
  - ground state total energy

\[ E(N) \]

\[ |N\rangle \]

\[ \text{vacuum level} \]

\[ N \text{ electrons} \]
Photo-electron energies

Photoemission

- electron removal
- removal energy

\[ E(N) \]

\[ \hat{\psi}(r)|N\rangle \]

\[ \epsilon_f \]

\[ E_{\text{kin}} \]

\[ \epsilon_s \]

\[ h \nu \]

annihilation operator

vacuum level

N-1 electrons
Photo-emission

\[ \langle N - 1, s | \hat{\psi}(r) | N \rangle \]

• electron removal

\[ E(N) - E(N - 1, s) \]

• removal energy

\[ \epsilon_f \]

Self-interaction

\[ \epsilon_s \]

total energy of \( s^{th} \) excited state of N-1 electron system

\[ E_{\text{kin}} \]

vacuum level

\( N-1 \) electrons
Photo-electron energies

Photoemission

- electron removal
  \[ \psi_s(r) = \langle N - 1, s \mid \hat{\psi}(r) \mid N \rangle \]

- removal energy
  \[ \epsilon_s = E(N) - E(N - 1, s) \]
Photo-electron energies

Inverse photoemission

- electron addition
  \[ \psi_s(r) = \langle N | \hat{\psi}(r) | N + 1, s \rangle \]
- addition energy
  \[ \epsilon_s = E(N + 1, s) - E(N) \]
Single-particle Green’s function

- Lehmann representation of $G$

$$G(r, r'; \epsilon) = \lim_{\eta \to 0^+} \sum_s \frac{\psi_s(r)\psi_s^*(r')}{\epsilon - (\epsilon_s + i\eta \text{sgn}(E_f - \epsilon_s))}$$

excitation energies are poles of the Green’s function

- spectroscopically relevant quantity: spectral function

$$A(\epsilon) = -\frac{1}{\pi} \int dr \lim_{r' \to r} \text{Im} G(r, r'; \epsilon)$$
Single-particle Green’s function

- Lehmann representation of $G$

$$G(\mathbf{r}, \mathbf{r}'; \epsilon) = \lim_{\eta \to 0^+} \sum_s \frac{\psi_s(\mathbf{r})\psi_s^*(\mathbf{r}')}{\epsilon - (\epsilon_s + i\eta \text{sgn}(E_f - \epsilon_s))}$$
Angle-resolved photoemission spectroscopy

ARPES

$=+1^\circ$

Masaki Kobayashi,
PhD dissertation

ZnO

Binding Energy (eV)
Angle-resolved photoemission spectroscopy

Masaki Kobayashi, PhD dissertation
Single-particle Green’s function

- Lehmann representation of $G$

$$G(r, r'; \epsilon) = \lim_{\eta \to 0^+} \sum_s \frac{\psi_s(r)\psi^*_s(r')}{\epsilon - (\epsilon_s + i\eta \text{sgn}(E_f - \epsilon_s))}$$

single electron excitations merge into broad peak
Single-particle Green’s function

- single particle-like spectral function:

\[ A_k(\epsilon) = \text{Im} G_k(\epsilon) \approx \frac{Z_k}{\epsilon - (\epsilon_k + i\Gamma_k)} \]
Another take on quasiparticles
Another take on quasiparticles

- electron ejected
Another take on quasiparticles

- electron ejected

hole is screened
Another take on quasiparticles

- electron ejected

hole is screened

screening is time dependent

hole is screened dynamically
Another take on quasiparticles

- electron ejected

hole is screened
t

hole is screened dynamically
t

screening is time dependent

quasiparticle
The screened Coulomb interaction

\[ W(r, r', t) = \int dr'' \frac{\varepsilon^{-1}(r, r'', t)}{|r'' - r'|} \]

developed by Kohn and Sham. They divided the total energy into contributions such as the kinetic energy of the non-interacting particles, the Hartree energy, the external energy, and an unknown remainder, which is defined as the exchange-correlation energy.

Performing the variation with respect to the density then yields the effective potential.

In analogy to Hartree theory, Kohn and Sham divided the total energy into known contributions such as the kinetic energy of the non-interacting particles, the Hartree energy, the external energy, and an unknown remainder. This last term includes all electron-electron interactions beyond the Hartree mean-field and is defined as the exchange-correlation energy.
**GW approximation - screened electrons**

\[ \Sigma = iGW \]

**W: screened Coulomb**

**G: propagator**

**self-energy:**

- energy that the quasiparticle feels due to its own presence

\[ \Sigma^{GW} (\mathbf{r}, \mathbf{r}', \omega) = - \frac{i}{2\pi} \int d\omega \epsilon \eta G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') \]
$GW$ approximation - screened electrons

$$\Sigma = iGW$$

W: screened Coulomb

G: propagator

Dyson equation:

$$G^{-1} = G_0^{-1} - \Sigma$$

non-interacting Green's function
$G$ is solution of Hedin’s equations

notation:  \[ 1 = (r_1, \sigma_1, t_1) \]

\[
P(1, 2) = -i \int G(2, 3)G(4, 2^+)\Gamma(3, 4, 1)d(3, 4)
\]

\[
W(1, 2) = v(1, 2) + \int v(1, 3)P(3, 4)W(4, 2)d(3, 4)
\]

\[
\Sigma(1, 2) = i \int G(1, 4)W(1^+, 3)\Gamma(4, 2, 3)d(3, 4)
\]

\[
\Gamma(1, 2, 3) = \delta(1, 2)\delta(1, 3) + \int \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)}G(4, 6)G(7, 5)\Gamma(6, 7, 3)d(4, 5, 6, 7)
\]

L. Hedin, Phys. Rev. 139, A796 (1965)
$G$ is solution of Hedin’s equations

notation: $1 = (r_1, \sigma_1, t_1)$

$$P(1, 2) = -i \int G(2, 3)G(4, 2^+)\Gamma(3, 4, 1)d(3, 4)$$

$$W(1, 2) = v(1, 2) + \int v(1, 3)P(3, 4)W(4, 2)d(3, 4)$$

$$\Sigma(1, 2) = i \int G(1, 4)W(1^+, 3)\Gamma(4, 2, 3)d(3, 4)$$

$$\Gamma(1, 2, 3) = \delta(1, 2)\delta(1, 3) + \int \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)}G(4, 6)G(7, 5)\Gamma(6, 7, 3)d(4, 5, 6, 7)$$

exact, therefore not tractable

L. Hedin, Phys. Rev. 139, A796 (1965)
*G* is solution of Hedin’s equations

**GW approximation**

**Mathematical expressions**

- Notation: \( 1 = (r_1, \sigma_1, t_1) \)

- \( P(1, 2) = -i \int G(2, 3)G(4, 2^+) \Gamma(3, 4, 1) d(3, 4) \)

- \( W(1, 2) = v(1, 2) + \int v(1, 3) P(3, 4) W(4, 2) d(3, 4) \)

- \( \Sigma(1, 2) = i \int G(1, 4) W(1^+, 3) \Gamma(4, 2, 3) d(3, 4) \)

- \( \Gamma(1, 2, 3) = \delta(1, 2) \delta(1, 3) + \int \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3) d(4, 5, 6, 7) \)

**Do not despair**

L. Hedin, Phys. Rev. 139, A796 (1965)
GW in practice

Step 1:

- Do a DFT calculation: $\epsilon_s^{KS}$ and $\phi_s^{KS}(r)$
**GW in practice**

**Step 1:**
- Do a DFT calculation: \( \epsilon^K_S \) and \( \phi^K_S(\mathbf{r}) \)

**Step 2:**
- Set up Kohn-Sham Green’s function:

\[
G_0(\mathbf{r}, \mathbf{r}'; \epsilon) = \lim_{\eta \to 0^+} \sum_s \frac{\phi^K_S(\mathbf{r})\phi^K_S(\mathbf{r}')}{\epsilon - (\epsilon^K_S + i\eta \text{ sgn}(E_f - \epsilon^K_S))}
\]
GW in practice

Step 1:
- Do a DFT calculation: $\epsilon^KS_s$ and $\phi^KS_s(r)$

Step 2:
- Set up Kohn-Sham Green’s function:

$$G_0(r, r'; \epsilon) = \lim_{\eta \to 0^+} \sum_s \frac{\phi^KS_s(r)\phi^KS^*_s(r')}{\epsilon - (\epsilon^KS_s + i\eta \, \text{sgn}(E_f - \epsilon^KS_s))}$$

Step 3:
- Construct polarizability:

$$\chi_0(r, r'; \epsilon) = -\frac{i}{2\pi} \int \, d\epsilon' \, G_0(r, r'; \epsilon' - \epsilon) \, G_0(r', r; \epsilon')$$
GW in practice

Step 4:

• Dielectric function:

\[ \varepsilon(r, r', \epsilon) = \delta(r - r') - \int dr'' v(r - r'') \chi_0(r'', r'; \epsilon) \]
**GW in practice**

**Step 4:**
- Dielectric function:

\[
\varepsilon(r, r', \varepsilon) = \delta(r - r') - \int dr'' v(r - r'') \chi_0(r'', r'; \varepsilon)
\]

**Step 5:**
- Screened Coulomb interaction:

\[
W_0(r, r', \varepsilon) = \int dr'' \varepsilon^{-1}(r, r''; \varepsilon)v(r'' - r')
\]
**GW in practice**

**Step 4:**

- Dielectric function:

\[
\varepsilon(r, r', \epsilon) = \delta(r - r') - \int dr'' v(r - r'') \chi_0(r'', r'; \epsilon)
\]

**Step 5:**

- Screened Coulomb interaction:

\[
W_0(r, r', \epsilon) = \int dr'' \varepsilon^{-1}(r, r''; \epsilon) v(r'' - r')
\]

**Step 6:**

- Self-energy:

\[
\Sigma^{GW}(r, r', \omega) = -\frac{i}{2\pi} \int d\omega e^{i\omega\eta} G_0(r, r', \omega + \omega') W_0(r, r', \omega')
\]
**GW in practice**

**Step 7:**

- Solve quasiparticle equation:

\[
\hat{h}_0(r)\psi_s(r) + \int dr' \Sigma(r, r'; \epsilon_s^{qp})\psi_s(r') = \epsilon_s^{qp}\psi_s(r)
\]

**Step 7b:**

- Perturbation theory: \( \psi_s(r) = \phi_{s}^{KS}(r) \)

\[
\epsilon_s^{qp} = \epsilon_s^{KS} + \langle s|\Sigma(\epsilon_s^{qp})|s\rangle - \langle s|v_{xc}|s\rangle
\]
GW in practice

Step 7:

- Solve quasiparticle equation:

\[ \hat{h}_0(r)\psi_s(r) + \int dr' \Sigma(r, r'; \epsilon_{s}^{qp})\psi_s(r') = \epsilon_{s}^{qp}\psi_s(r) \]

Step 7b:

- Perturbation theory: \( \psi_s(r) = \phi_{s}^{KS}(r) \)

\[ \epsilon_{s}^{qp} = \epsilon_{s}^{KS} + \langle s | \Sigma(\epsilon_{s}^{qp}) | s \rangle - \langle s | v_{xc} | s \rangle \]

GW formal scaling \( \sim \) system size\(^4\)
$\Sigma = iGW$

**GW approximation - screened electrons**

**Self-energy:**

$$\Sigma = \Sigma_x + \Sigma_c$$

- **Exact exchange** (Hartree-Fock):
  $$iG\nu$$
- **Screening** (due to other electrons):
  $$iG(W - \nu)$$
On the importance of screening

\[ \epsilon_{\text{qp}}^{nk} = \epsilon_{\text{LDA}}^{nk} + \langle \phi_{nk} | \sum_x + \sum_c (\epsilon_{\text{qp}}^{nk}) - \nu_{xc} | \phi_{nk} \rangle \]

- Hartree-Fock (HF) exact exchange gap much too large
- \( W \) is essential for solids
Angle resolved photoemission - ZnO

Convergence of $G_0W_0$ for ZnO

Band gaps of solids

Theoretical Band Gap [eV]

LDA
OEPx(cLDA)
OEPx(cLDA) + $G_0W_0$

CdS
zb-GaN
ZnS
wz-GaN
ZnO
ZnSe
CdSe
Ge
InN

Experimental Band Gap [eV]

Do we know the band gap of InN?
Band gap of InN

Figure adapted from Butcher and Tansley Superlattices Microstruct. 38, 1 (2005)
Proposed reasons for band gap variation

e.g. Butcher and Tansley Superlattices Microstruct. 38 (2005)

• high carrier concentration -> Moss-Burnstein effect
• impurities, point defects, trapping centers
• non-stoichiometry
• formation of oxides and oxynitrides
• metal inclusions, formation of metal clusters
How can first principles help?

- **Density-functional theory (DFT)**
  - atomistic control
  - stoichiometric, defect and impurity free structures

- **many-body perturbation theory (GW)**
  - method of choice for band gaps in solids

**Band gap of InN**

<table>
<thead>
<tr>
<th>Wu et al</th>
<th>Haddad et al</th>
<th>Ioffe Institute</th>
<th>Briot et al</th>
</tr>
</thead>
</table>
| Figure adapted from Butcher and Tansley

**Proposed reasons for band gap variation**

- high carrier concentration -> Moss-Burnstein effect
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- non-stoichiometry
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- metal inclusions, formation of metal clusters

**Figure adapted from**

Butcher and Tansley

Superlattices Microstruct. 38 (2005)
InN - $GW$ band structure and Moss-Burstein
InN - GW band structure and Moss-Burstein

$E_g(n)$ (eV)

- parabolic ($m_{\text{eff}} = 0.07 m_0$)
- $G_0W_0@OEPx(\text{cLDA})$

carrier concentration (cm$^{-3}$)

Organic Electronics - Plastic Electronics

sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung
Inorganic/organic interfaces are already present...

... and affect or determine device properties.

Can we understand and control them?
Atomistic understanding of molecules@surfaces

- Charge transfer
- Level alignment
- Van der Waals interaction
- Surface structure
- Adsorption geometry
Level alignment at interface

conduction band

Fermi level

valence band

EIB: electron injection barrier

HIB: hole injection barrier

molecular states

injection limited current:

\[ j \propto A T^2 \exp \left( - \frac{\text{charge injection barrier}}{k_B T} \right) \]
Molecular levels at a surface
Molecular levels at a surface

- Electron affinity (EA)
- Ionization potential (IP)
Molecular levels at a surface

surface

---

gas phase

image effect

- EA

- IP
Performing the variation with respect to the density then yields the unknown remainder. This last term includes all electron-electron actions beyond the Hartree mean-field and is defined as the exchange potential energy.

In analogy to Hartree theory, Kohn and Sham divided the total energy into known contributions such as the kinetic energy of the non-interacting and image potentials:

- **Metal:** \[-\frac{1}{4z}\]
- **Semiconductor:** \[-\frac{(\varepsilon - 1)}{4(\varepsilon + 1)}\]

\(\varepsilon\) is the dielectric constant.
Molecular levels at a surface

surface

gas phase

renormalization

metal: \(-\frac{1}{4\varepsilon}\)

semiconductor: \(-\frac{(\varepsilon - 1)}{4(\varepsilon + 1)}\frac{1}{\varepsilon}\)

\(\varepsilon\) dielectric constant
Renormalization at insulator surfaces


CO HOMO-LUMO gap

<table>
<thead>
<tr>
<th>gap/eV</th>
<th>LDA</th>
<th>G LDA</th>
<th>Exp.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>free CO</td>
<td>6.9</td>
<td>15.1</td>
<td>15.8</td>
</tr>
<tr>
<td>CO@NaCl</td>
<td>7.4</td>
<td>13.1</td>
<td></td>
</tr>
</tbody>
</table>

Make CO “ride the image potential”

- NaCl on Ge:
  ‣ prototypical semiconductor/insulator interface
- Will the CO gap depend on NaCl thickness?

CO on NaCl on Ge - layer dependent gap

- layer-dependent CO gap due to polarization
- molecular levels can be tuned by polarization engineering

Density-functional theory and excitations

**exact DFT:**

- Ionization potential given by Kohn-Sham eigenvalue of highest occupied state

\[ I_{KS} = -\epsilon_N(N) \]
Density-functional theory and excitations

- **exact DFT:** ionization potential given by Kohn-Sham eigenvalue of highest occupied state

\[ I_{KS} = -\epsilon_N(N) \]

- **otherwise:** Janak’s theorem (PRA 18, 7165 (1978))

\[ \frac{\partial E}{\partial n_s} = \epsilon_s \]

rearranging and making mid-point approx.

\[ E(N + 1, s) - E(N) = \int_0^1 dn \epsilon_s(n) \approx \epsilon_s(0.5) \]
Ionisation Potential, Affinity and (Band) Gaps

- Could use total energy method to compute (also known as ΔSCF)

\[ \epsilon_s = E(N \pm 1, s) - E(N) \]

**Ionization potential:** minimal energy to remove an electron

\[ I = E(N - 1) - E(N) \]

**Electron affinity:** minimal energy to add an electron

\[ A = E(N) - E(N + 1) \]

**(Band) gap:**

\[ E_{gap} = I - A \]
Ionisation Potential, Affinity and (Band) Gaps

Ionisation potential in the LDA

Reference: NIST -- Atomic reference data
ΔSCF better than eigenvalues for IPs!

but:

- only justified for differences of ground states
  - ionisation potential, electron affinity
  - excited states that are ground states of particular symmetry

- difficult to find excited state density
  - excited state density is not unique

- separate calculation for every excitation needed
  - not practical for large systems or solids
$\Delta$SCF versus eigenvalues for finite systems

Data courtesy of Max Pinheiro
ΔSCF versus eigenvalues for finite systems

largely the result of the delocalization or self-interaction error (Science 321, 792 (2008))

the more delocalized the state, the larger the error

data courtesy of Max Pinheiro


\section*{ΔSCF versus eigenvalues for finite systems}

For solids:

\[ \text{Band gap: } E_{\text{gap}} = I - A = E(N + 1) - 2E(N) + E(N - 1) \]

\text{in solids: } E(N + 1) \text{ and } E(N - 1) \text{ cannot be calculated reliably}

\begin{itemize}
  \item band gap:
  \[ E_{\text{gap}} = I - A = E(N + 1) - 2E(N) + E(N - 1) \]
\end{itemize}

\text{data courtesy of Max Pinheiro}
Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

\[ E_{gap} = \epsilon_{N+1}^{KS}(N + 1) - \epsilon_{N}^{KS}(N) \]

\[ = \epsilon_{N+1}^{KS}(N + 1) - \epsilon_{N+1}^{KS}(N) + \epsilon_{N+1}^{KS}(N) - \epsilon_{N}^{KS}(N) \]

\[ \Delta_{xc} \]

\[ E_{gap}^{KS} \]
Band gaps of semiconductors and insulators

• DFT: highest Kohn-Sham state exact:

\[
E_{\text{gap}} = \epsilon_{N+1}^{KS}(N+1) - \epsilon_{N}^{KS}(N) \\
= \Delta_{xc} + E_{\text{gap}}^{KS}
\]

• for solids: \( N \gg 1 \Rightarrow \Delta n(r) \rightarrow 0 \) for \( N \rightarrow N + 1 \)

\( \nu_{xc} : \) discontinuity upon changing the particle number:

\[
\Delta_{xc} = \left( \frac{\delta E_{xc}[n]}{\delta n(r)} \bigg|_{N+1} - \frac{\delta E_{xc}[n]}{\delta n(r)} \bigg|_{N} \right) + \mathcal{O} \left( \frac{1}{N} \right)
\]
Band gaps of semiconductors and insulators

• DFT: highest Kohn-Sham state exact:

\[ E_{\text{gap}} = \epsilon_{N+1}^{KS}(N+1) - \epsilon_{N}^{KS}(N) \]

\[ = \epsilon_{\text{KS}}^{\text{N+1}}(N+1) - \epsilon_{\text{KS}}^{\text{N}}(N) - \epsilon_{N}^{\text{KS}}(N) + \epsilon_{N}^{\text{KS}}(N) \]

most DFT functionals do not capture this derivative discontinuity

• for solids:

\[ E_{\text{gap}}^{\text{KS}} \to N + 1 \]

\[ \mathcal{V}_{xc} : \text{discontinuity upon changing the particle number:} \]

\[ \Delta_{xc} = \left( \frac{\delta E_{xc}[n]}{\delta n(r)} \bigg|_{N+1} - \frac{\delta E_{xc}[n]}{\delta n(r)} \bigg|_{N} \right) + \mathcal{O} \left( \frac{1}{N} \right) \]
Band gaps of solids

In photovoltaic applications electrons and holes need to be separated!

This is done at donor-acceptor interfaces.
Charge separation at donor-acceptor pairs

[Diagram showing the separation of charge between a donor (D) and an acceptor (A) pair, with energy levels indicated by arrows and labels.]
donor-acceptor pair: TTF and TCNQ

TTF
\[ \text{C}_6\text{H}_4\text{S}_4 \]

all values in eV

EA: 2.8
IP: 6.7

TTF

TCNQ
\[ \text{C}_{12}\text{H}_4\text{N}_4 \]

EA: 4.6
IP: 9.5

donor

acceptor

exp

exp
donor-acceptor pair: TTF and TCNQ

TTF

$\text{C}_6\text{H}_4\text{S}_4$

donor

TCNQ

$\text{C}_{12}\text{H}_4\text{N}_4$

acceptor

EA

2.8

exp

IP

6.7

exp

4.6

exp

9.5
donor-acceptor pair: TTF and TCNQ

TTF

\[ C_6H_4S_4 \]

TTF

\[ C_{12}H_4N_4 \]

TCNQ

EA

2.8

IP

6.7

exp

9.5

exp

donor

acceptor
TTF and TCNQ in PBE

**TTF**

- $E_A$: 2.8 eV
- $E_P$: 6.7 eV
- $E_A$: 4.0 eV

**TCNQ**

- $E_A$: 5.6 eV
- $E_P$: 7.0 eV

All values in eV.

**Compounds**

- TTF: $C_6H_4S_4$
- TCNQ: $C_{12}H_4N_4$
TTF and TCNO in PBE Kohn-Sham levels

- PBE exp
- Kohn-Sham levels

- 4.0
- 6.7
- IP
- 9.5
- exp
- 5.6
- 9.5
- exp
- 4.6
- 2.8
- FA
- TTF

- C\textsubscript{6}H\textsubscript{4}S\textsubscript{4}
- C\textsubscript{12}H\textsubscript{4}N\textsubscript{4}

All values in eV

erroneous charge transfer in ground state!!!
TTF and TCNQ in $G_0W_0$

**TTF**

- EA: 2.8 eV
- IP: 9.5 eV

**TCNQ**

- EA: 3.7 eV
- IP: 9.7 eV

All values in eV

$G_0W_0$, $exp$
TTF and TCNQ in \( G_0W_0 \)

Correct level order, but how to get back to ground state?

\[ \Rightarrow \text{self-consistency} \]
Starting point dependence

Starting point dependence

Starting point dependence

Find optimal starting point or remove starting point dependence!
⇒ self-consistency

Self-consistent GW (scGW)

Hedin’s $GW$ equations:

\[
G(1, 2) = G_0(1, 2) \\
\Gamma(1, 2, 3) = \delta(1, 2)\delta(1, 3) \\
P(1, 2) = -iG(1, 2)G(2, 1^+) \\
W(1, 2) = v(1, 2) + \int v(1, 3)P(3, 4)W(4, 2)d(3, 4) \\
\Sigma(1, 2) = iG(1, 2)W(2, 1)
\]

Dyson’s equation:

\[
G^{-1}(1, 2) = G_0^{-1}(1, 2) - \Sigma(1, 2)
\]

Unique solution in scGW - N$_2$

spectral function (arbitrary units)

Iter. 1
- HF input
- PBE input

Iter. 2

Iter. 3

Iter. 4
Ionization potentials in scGW

Experimental IE [eV]

Theoretical IE [eV]

$G_0W_0@PBE$

$G_0W_0@HF$

KS-PBE

sc-GW

set taken from Rostgaard, Jacobsen, and Thygesen, PRB 81, 085103, (2010)
The loan pair in pyridine

Energy [eV]

Spectral function [arbitrary units]

-20

-15

-10

Energy [eV]

PES

$G_0W_0@PBE$

$G_0W_0@PBE0$

sc-$GW_0@PBE$

sc-$GW$

The loan pair in pyridine

The $GW$ density of CO

\[ \rho(PBE) - \rho(HF) \quad \rho(scGW) - \rho(HF) \]

\[ \rho(CCS\,SD) - \rho(HF) \]

- density from Green’s function: \( \rho(r) = -i \sum_\sigma G_{\sigma\sigma}(r, r, \tau = 0^+) \)

The GW density of CO

\[ \rho(PBE) - \rho(HF) \quad \text{and} \quad \rho(\text{scGW}) - \rho(HF) \]

Dipole moment (in Debye):

<table>
<thead>
<tr>
<th></th>
<th>Exp.</th>
<th>scGW</th>
<th>CCSD</th>
<th>HF</th>
<th>PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>0.11</td>
<td>0.07</td>
<td>0.06</td>
<td>-0.13</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\[ \rho(CCSD) - \rho(HF) \]

- \( \rho(r) = -i \sum_\sigma G_{\sigma\sigma}(\mathbf{r}, \mathbf{r}, \tau = 0^+) \)

Back to the TTF/TCNQ dimer

electron density difference

HOMO

LUMO

PBE

scGW
The \textit{GW} total energy

Galitskii-Migdal equation \cite{Galitskii:1958}(V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

\[
E_{GM} = -i \sum_{\sigma} \int dr \, dt \lim_{r' \to r} \lim_{t' \to t^+} \left[ i \frac{\partial}{\partial t} - \frac{\nabla^2 r}{2} + v_{\text{ext}}(r) \right] G^\sigma (rt, r't')
\]
The GW total energy

Galitskii-Migdal equation (V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

\[
E_{GM} = -i \sum \int dr \, dt \lim_{r' \to r, t' \to t^+} \left[ i \frac{\partial}{\partial t} - \frac{\nabla_r^2}{2} + v_{\text{ext}}(r) \right] G^\sigma (rt, r't')
\]

Use equation of motion to transform expression:

\[
\left[ i \frac{\partial}{\partial t} + \frac{\nabla_r^2}{2} - v_H(r) - v_{\text{ext}}(r) \right] G^\sigma (rt, r't') - \\
- \int dr'' \, dt'' \Sigma^\sigma (rt, r'' t'') G^\sigma (r'' t'', r't') = \delta(r - r') \delta(t - t')
\]
The GW total energy

Galitskii-Migdal equation (V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

\[
E_{GM} = -i \sum_{\sigma} \int dr \, dt \lim_{r' \to r, t' \to t^+} \left[ i \frac{\partial}{\partial t} - \frac{\nabla_r^2}{2} + v_{ext}(r) \right] G^\sigma(r, r', t, t')
\]

More convenient form:

\[
E_{GM} = -i \sum_{ij} \left[ 2t_{ij} + 2v_{ext}^{ij} + v_{ij}^H + \Sigma_{ij}^x \right] G_{ij}(t = 0^-)
\]

\[
- i \sum_{ij} \int \frac{d\omega}{2\pi} \Sigma_{ij}^{c}(\omega) G_{ij}(\omega) e^{i\omega \eta} = T + E_{ext} + E_H + E_x + E_c^{GW}
\]
The \(GW\) total energy

Galitskii-Migdal equation (V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

\[
E_{GM} = -i \sum \int d\mathbf{r} dt \lim_{r' \rightarrow r \atop t' \rightarrow t^+} \left[ i \frac{\partial}{\partial t} - \frac{\nabla^2_r}{2} + v_{\text{ext}}(\mathbf{r}) \right] G^\sigma(\mathbf{r}, \mathbf{r}', \mathbf{t}')
\]

More convenient form:

\[
E_{GM} = -i \sum_{ij} [2t_{ij} + 2v_{ij}^{\text{ext}} + v_{ij}^H + \Sigma_{ij}^x] G_{ij}(t = 0^-)
\]

\[
- i \sum_{ij} \int \frac{d\omega}{2\pi} \Sigma_{ij}(\omega)G_{ij}(\omega)e^{i\omega\eta}
\]

\[
= \boxed{T} + E_{\text{ext}} + E_H + E_x + \boxed{E_c^{GW}}
\]

interacting kinetic energy \hspace{1cm} \text{Coulomb correlation}
The *GW* total energy

Galitskii-Migdal equation (GM) (1958):

Our old friend, the homogenous electron gas

**correlation energy per electron:**

<table>
<thead>
<tr>
<th>r</th>
<th>scGW</th>
<th>QMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>-0.0897 Ry</td>
<td>-0.0897 Ry</td>
</tr>
<tr>
<td>4.0</td>
<td>-0.0638 Ry</td>
<td>-0.0638 Ry</td>
</tr>
</tbody>
</table>


\[
\langle \psi \rangle = \sum_{ij} \int \frac{d^3 r}{(2\pi)^3} e^{ik \cdot r} \phi_i(k) \phi_j^*(k) \delta(\epsilon_{ij} - E_{ij})
\]

\[
\frac{1}{2} \sum_{ij} \int \frac{d^3 r}{(2\pi)^3} \int \frac{d^3 r'}{(2\pi)^3} \phi_i(k) \phi_j^*(k) \phi_{i'}(k') \phi_{j'}^*(k') \delta(\epsilon_{ij} - E_{ij}) \delta(\epsilon_{i'j'} - E_{i'j'}) e^{ik \cdot r} e^{ik' \cdot r'}
\]

interacting kinetic energy  \[ T \]

Coulomb correlation  \[ E_{GW} \]

\[
E_{GW} = \frac{1}{2} \sum_{ij} \int \frac{d^3 r}{(2\pi)^3} \int \frac{d^3 r'}{(2\pi)^3} \phi_i(k) \phi_j^*(k) \phi_{i'}(k') \phi_{j'}^*(k') \delta(\epsilon_{ij} - E_{ij}) \delta(\epsilon_{i'j'} - E_{i'j'}) - \frac{1}{2} \sum_{ij} \int \frac{d^3 r}{(2\pi)^3} \phi_i(k) \phi_j^*(k) \langle \phi_{i'}(k') \phi_{j'}^*(k') \rangle
\]
GW total energy of atoms

$E_{\text{tot}} - E_{\text{Cl}}$ [eV]

- $G_0 W_0 \oplus$ PBE
- $G_0 W_0 \oplus$ HF
- sc-GW

GW total energy of atoms


(mostly) kinetic correlation
\[ GW \text{ total energy of atoms} \]

\[ E_{\text{tot}} [G_0] = T_s [G_0] + E_{\text{ext}} + E_H + E_{x}^{\text{exact}} + E_c [G_0 W_0] \]

\[ \text{scGW: } E_{\text{tot}} [G] = T [G] + E_{\text{ext}} + E_H + E_{x}^{\text{exact}} + E_c [GW] \]

GW total energy of atoms

\[ \Sigma(1, 2) = i \int G(1, 4) W(1^+, 3) \Gamma(4, 2, 3) d(3, 4) \]

\[ \Gamma(1, 2, 3) = \delta(1, 2) \delta(1, 3) + \int \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3) d(4, 5, 6, 7) \]

Further GW total energy assessment

- set of 6 dimers: LiH, LiF, HF, CO, H₂ and N₂

Summary

Photoemission

\[ \text{GW} \]

Inverse Photoemission

\[ \text{GW} \]

Absorption

\[ \text{BSE TDDFT} \]
Charge separation at donor-acceptor complex

1. **D** + **A** → **D** (hot) + **A**
2. **D** (hot) + **A** → **D** (cold) + **A**
3. **D** (cold) + **A** → **D** + **A**

- Energy from vibrations to vibrations
- Energy to vibrations

**e-h pair energy**

**Barrier**