Many-body perturbation theory and \textit{GW}

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What we will learn today

- Basic principles of electron spectroscopy
- The Green’s function and the self-energy
- The GW approximation to the self-energy
- Pros and cons of density-functional theory for electron spectroscopies
Spectroscopy and materials science

Experiment/Spectroscopy

[Graph showing binding energy vs. ARPES]
Spectroscopy and materials science

Experiment/Spectroscopy

ARPES

Appropriate? Accurate?
Spectroscopy and materials science

Experiment/Spectroscopy

Theoretical Spectroscopy

Appropriate? Accurate?
Spectroscopy and materials science

Experiment/Spectroscopy
- Photoemission
- Optical Absorption

Theoretical Spectroscopy
Green's function theory
- GW, BSE

Materials Science/Applications

Appropriate?
Accurate?
Applications: Light emitting diodes and lasers

inorganic

GaN

organic

sources: Nanotechnology Now, Organic Electronic Association, Samsung
Inorganics: Challenges

**LEDs - solid state lighting**
- to increase efficiency
  -> brightness
- to produce colour variability and stability

**Laser diodes**
- to produce a bright green laser diode

sources: Pixelligent
Do we know the band gap of InN?
Organics: Challenges

Photovoltaic challenge

• inorganic solar cells are expensive
• organic solar cells are inefficient

Challenges I’ll address:

• level alignment
• charge transfer

sources: Eco Friend, Nature Publishing Group
Spectroscopies

Photoemission

Inverse Photoemission

Absorption

$GW$

TDDFT

BSE

Patrick Rinke (FHI)

Excited States

Berlin 2011
Photo-electron energies

Photoemission

- electron removal
- removal energy

\[ E(N) \]

ground state total energy

\[ |N\rangle \]

vacuum level

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

Photoemission

• electron removal
  \( E(N) \)

• removal energy

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

annihilation operator

\( \epsilon_f \)

\( E_{\text{kin}} \)

vacuum level

\( \epsilon_s \)

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

**Photoemission**

- **s^{th} excited state of N-1 electron system**

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

  **total energy of s^{th} excited state of N-1 electron system**
Photo-electron energies

Photoemission

- electron removal
  \[ \psi_s(r) = \langle N - 1, s|\hat{\psi}(r)|N \rangle \]
- removal energy
  \[ \epsilon_s = E(N) - E(N - 1, s) \]
Inverse photoemission

- electron addition
  \[ \psi_s(\mathbf{r}) = \langle N | \hat{\psi}(\mathbf{r}) | N + 1, s \rangle \]
- 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

\[
A(\epsilon) = -\frac{1}{\pi} \int d\mathbf{r} \lim_{r' \to r} \Im G(\mathbf{r}, \mathbf{r'}; \epsilon)
\]
Single-particle Green’s function

- Lehmann representation of $G$

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

source: Masaki Kobayashi, PhD dissertation
Angle-resolved photoemission spectroscopy

source: 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: quasiparticle weight

$$A_k(\epsilon) = Im G_k(\epsilon) \approx \frac{Z_k}{\epsilon - (\epsilon_k + i\Gamma_k)}$$

quasiparticle peak

inverse of lifetime
Another look at quasiparticles
Another look at quasiparticles

- electron ejected
Another look at quasiparticles

electron ejected

hole is screened
Another look at quasiparticles

- electron ejected

hole is screened dynamically

screening is time dependent
Another look at quasiparticles

- electron ejected

hole is screened

dynamically

screening is time dependent

quasiparticle
The screened Coulomb interaction

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

The screened Coulomb interaction is given by the integral above, where the bare Coulomb interaction is screened by the dielectric function. The hole is screened by the system of quasiparticles.
GW approximation - screened electrons

\[ \Sigma = iGW \]

self-energy:
• energy that the quasiparticle feels due to its own presence

\[ \Sigma^{GW}(r, r', \omega) = -\frac{i}{2\pi} \int d\omega e^{i\omega \eta}G(r, r', \omega + \omega')W(r, r', \omega') \]
\[ \Sigma = iGW \]

Dyson equation:

\[ G^{-1} = G_0^{-1} - \Sigma \]

**GW approximation - screened electrons**

- **W**: screened Coulomb
- **G**: propagator

non-interacting Green’s function
Exact solution - Hedin’s equations

notation: \( 1 = (\mathbf{r}_1, \sigma_1, t_1) \)

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

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

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

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

L. Hedin, Phys. Rev. 139, A796 (1965)
Exact solution - Hedin’s equations

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\]

**Exact; therefore not tractable!**

L. Hedin, Phys. Rev. 139, A796 (1965)
Exact solution - Hedin’s equations

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\]

Do not despair!

We will make an approximation!

L. Hedin, Phys. Rev. 139, A796 (1965)
Exact solution - Hedin’s equations

notation: \( 1 = (\mathbf{r}_1, \sigma_1, t_1) \)

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

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

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

Do not despair!  
Hedin’s GW approximation!

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

Step 1: 

- Do a DFT calculation: $\epsilon^\text{KS}_s$ and $\phi^\text{KS}_s(\mathbf{r})$
GW in practice

Step 1:

• Do a DFT calculation: $\epsilon^\text{KS}_s$ and $\phi^\text{KS}_s(\mathbf{r})$

Step 2:

• Set up Kohn-Sham Green’s function:

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

Step 1: 
- Do a DFT calculation: \( \epsilon_s^{KS} \) and \( \phi_s^{KS}(\mathbf{r}) \)

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

\[
G_0(\mathbf{r}, \mathbf{r}'; \epsilon) = \lim_{\eta \to 0^+} \sum_s \frac{\phi_s^{KS}(\mathbf{r})\phi_s^{KS}(\mathbf{r}')}{\epsilon - (\epsilon_s^{KS} + i\eta \text{ sgn}(E_f - \epsilon_s^{KS}))}
\]

Step 3: 
- Construct polarizability:

\[
P(\mathbf{r}, \mathbf{r}'; \epsilon) = -\frac{i}{2\pi} \int d\epsilon' G_0(\mathbf{r}, \mathbf{r}'; \epsilon' - \epsilon)G_0(\mathbf{r}', \mathbf{r}; \epsilon')
\]
GW in practice

Step 4:

• Dielectric function:

\[ \varepsilon(\mathbf{r}, \mathbf{r}', \epsilon) = \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}'' \nu(\mathbf{r} - \mathbf{r}'') P(\mathbf{r}'', \mathbf{r}'; \epsilon) \]
GW in practice

Step 4:
- Dielectric function:

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

Step 5:
- Screened Coulomb interaction:

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

Step 4:

- Dielectric function:

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

Step 5:

- Screened Coulomb interaction:

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

Step 6:

- Self-energy \((G_0W_0)\):

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

Step 7: Solve quasiparticle equation:

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

Step 7b: Perturbation theory:

\[ \psi_s(\mathbf{r}) = \phi_s^{KS}(\mathbf{r}) \]

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

Step 7: Solve quasiparticle equation:

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

Step 7b: Perturbation theory:

\[ \psi_s(\mathbf{r}) = \phi_s^{KS}(\mathbf{r}) \]

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

GW formal scaling \sim \text{system size}^4
Let’s get (a little bit) more real
$GW$ approximation - screened electrons

$$\Sigma = iGW$$

self-energy:
$$\Sigma = \Sigma_x + \Sigma_c$$

- $iG\nu$: exact exchange (Hartree-Fock)
- $iG(W - \nu)$: screening (due to other electrons)

$W$: screened Coulomb
$G$: propagator
On the importance of screening

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

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

\[ \text{exp: } 1.17 \text{ eV} \]
Angle resolved photoemission - ZnO

Energy relative to $E_F$ (eV)

$G_0W_0@OEPx$ (cLDA)

Band gaps of solids

![Graph showing band gaps of solids](image)

**Experimental Band Gap [eV]**

**Theoretical Band Gap [eV]**

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

Materials:
- CdS
- zb-GaN
- ZnO
- ZnS
- Ge
- InN
- wz-GaN

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

Figure adapted from Butcher and Tansley Superlattices Microstruct. 38, 1 (2005)
Do we know the band gap of InN?

Proposed reasons for band gap variation

- high carrier concentration -> Moss-Burnstein effect
- impurities, point defects, trapping centers
- non-stoichiometry
- formation of oxides and oxynitrides
- metal inclusions, formation of metal clusters

Figure adapted from Butcher and Tansley Superlattices Microstruct. 38, 1 (2005)
Do we know the band gap of InN?

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

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

Figure adapted from Butcher and Tansley Superlattices Microstruct. 38, 1 (2005)
InN - GW band structure and Moss-Burstein
InN - GW band structure and Moss-Burstein

\[ E_g(n) \text{ (eV)} \]

- parabolic \( (m_{\text{eff}} = 0.07 \, m_0) \)
- \( G_0 W_0 \@ \text{OEPx(cLDA)} \)

Organic or plastic electronics

sources (left to right): Eco Friend, Nature Publishing Group
Organic or plastic electronics

Inorganic/organic interfaces are already present...

... and affect or determine device properties.

Can we understand and control them?

sources (left to right): Eco Friend, Nature Publishing Group
Atomistic organic/inorganic interface

Level alignment

Interface properties

Molecular geometry

F4TCNQ

ZnO
Atomistic organic/inorganic interface

Level alignment

Interface properties

Molecular geometry

ZnO

F4TCNQ
Level alignment at interface

- **Fermi level**
- **conduction band**
- **valence band**
- **EIB:** electron injection barrier
- **HIB:** hole injection barrier
- **molecular states**

**Injection limited current:**

\[ j \propto AT^2 \exp \left( - \frac{\text{charge injection barrier}}{k_B T} \right) \]

**Eqs.**

1. \( G(T, V, \{ N_i \}) = E_{\text{DFT}}(T=0, V, \{ N_i \}) + F_{\text{vib}}(T, V, \{ N_i \}) + pV \) (23)
2. \( \mu_i(T, p) = E_i + \mu_i(T, p_0) + k_B T \ln \frac{p_i}{p_0} \) (24)
3. \( \mu_H, \mu_e = E_{\text{slab}} + qE_{\text{bulk}} + q(\varepsilon_{\text{VBM}}) \) (25)
4. \( I_P = E(N_1) - E(N) \) (27)
5. \( E_A = E(N) - E(N+1) \) (28)
6. \( s = E(N_1, s) - E(N) \) (29)
7. \( \varepsilon = iGW \) (30)
Molecular levels at surface

surface

gas phase

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School of Science
Molecular levels at surface

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

surface

\[ \text{image effect} \]

gas phase

\[ \text{EA} \]

\[ \text{IP} \]
Molecular levels at surface

surface

image potentials

gas phase

EA

IP

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Molecular levels at surface

surface

gas phase

renormalization

EA

IP

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Molecular levels at surface

surface

\[ \text{metal:} \quad - \frac{1}{4z} \]

\[ \text{semiconductor:} \quad \varepsilon \text{ dielectric constant} \]

\[ - \frac{(\varepsilon - 1)}{4(\varepsilon + 1)} \frac{1}{z} \]

gas phase

\[ \text{renormalization} \]

\[ z \]

\[ \text{EA} \]

\[ \text{IP} \]

\[ \text{Aalto University} \]

\[ \text{School of Science} \]
The screened Coulomb interaction

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

This is exactly what we are doing in GW!
Renormalization at insulator surfaces

**CO HOMO-LUMO gap**

<table>
<thead>
<tr>
<th>gap/eV</th>
<th>DFT (LDA)</th>
<th>$G_0W_0@$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?

Supported ultrathin films are novel nano-systems in their own rights:
CO on NaCl on Ge - layer dependent gap

- molecular levels can be tuned by polarization engineering
Why bother with GW?

What’s wrong with DFT?
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 $\Delta$SCF)

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

**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

Reference: NIST -- Atomic reference data
ΔSCF versus eigenvalues for finite systems

oligoacetylenes

Pinheiro Jr, Caldas, Rinke, Blum, Scheffler
largely the result of the delocalization or self-interaction error \( (\text{Science} \, 321, \, 792 \, (2008) )\)

the more delocalized the state, the larger the error
Band gaps of solids

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

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

\( \Delta_{\text{SCF}} \) versus eigenvalues for finite systems

oligoacetylenes

length (Å)

data courtesy of Max Pinheiro
Band gaps of semiconductors and insulators

- **DFT: highest Kohn-Sham state exact:**

\[
E_{\text{gap}} = \epsilon_{N+1}^{KS}(N + 1) - \epsilon_{N}^{KS}(N) \\
= \epsilon_{N+1}^{KS}(N + 1) - \epsilon_{N+1}^{KS}(N) + \epsilon_{N+1}^{KS}(N) - \epsilon_{N}^{KS}(N) \\
\Delta_{xc} + \epsilon_{N}^{KS}(N) - \epsilon_{N}^{KS}(N)
\]
Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

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

\[\Delta_{xc} \quad E_{gap}^{KS}\]

- For solids: \(N \gg 1 \implies \Delta n(r) \to 0 \text{ for } N \to N + 1\)

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

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

• DFT: highest Kohn-Sham state exact:

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

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

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

many DFT functionals do not capture this derivative discontinuity

\[ \nu_{xc} : \text{ density functional} \]
Band gaps of solids

Organic or plastic electronics

sources (left to right): Eco Friend, Nature Publishing Group
Charge separation at donor-acceptor pairs

Donor (D) and acceptor (A) are connected, with an electron (e) and a hole (h) pair. The energy levels are indicated by bars, with different colors representing different energy states.
Donor-acceptor pair: TTF and TCNQ

All values in eV

TTF

$C_6H_4S_4$

donor

EA

3.3

IP

6.7

exp

TCNQ

$C_{12}H_4N_4$

acceptor

EA

3.3

exp

all values in eV
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

$\text{EA} = 3.3$

$\text{IP} = 6.7$

$\text{exp} = 9.5$

$\text{exp}$
Donor-acceptor pair: TTF and TCNQ

TTF: \( C_6H_4S_4 \)

TCNQ: \( C_{12}H_4N_4 \)

donor

acceptor

EA: 3.3 exp

IP: 6.7 exp

EA: 9.5 exp
Donor-acceptor pair: TTF and TCNQ
Donor-acceptor pair: TTF and TCNQ

Donor: TTF

Kohn-Sham levels

acceptor: TCNQ

EA (Excitation Energy): 5.6

IP (Ionization Potential): 7.0

PBE exp

4.0

1.0

3.3

6.7

9.5

C₆H₄S₄

C₁₂H₄N₄
Donor-acceptor pair: TTF and TCNQ

Erroneous charge transfer in ground state!!!

PBE Kohn-Sham levels

C₆H₄S₄

donor

EA

C₁₂H₄N₄

acceptor

PBE

exp

exp

4.0

3.3

6.7

9.5

7.0

5.6

6.7
Donor-acceptor pair: TTF and TCNQ

Donor-acceptor pair: TTF and TCNQ

Correct level ordering, but how to get back to the ground state?

\[ \begin{align*}
G_0W_0 & \quad \text{exp} \\
3.3 & \quad 6.7 \\
9.5 & \quad 9.7 \\
\end{align*} \]

Donor-acceptor pair: TTF and TCNQ

Correct level ordering, but how to get back to the ground state?

We need some form of self-consistency!

 donor

acceptor

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

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

\[ G_0W_0 \]  \[ \text{exp} \]  \[ 6.7 \]  \[ 6.7 \]  \[ 3.3 \]  \[ 3.7 \]

\[ \text{IP} \]  \[ \text{exp} \]  \[ 9.5 \]  \[ 9.7 \]

Another problem: starting-point dependence

Another problem: starting-point dependence

Another problem: starting-point dependence


Find optimal starting point or remove starting-point dependence!
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:

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

implemented in FHI-aims:
Unique solution in scGW - N$_2$

Iter. 1  
- HF input
- PBE input

Iter. 2

Iter. 3

Iter. 4

spectral function (arbitrary units)

-35 -30 -25 -20 -15

Ionization potentials in scGW


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

![Graph showing spectral functions with energy in eV on the x-axis and spectral function in arbitrary units on the y-axis. The graph includes lines for PES, $G_0W_0@PBE$, $G_0W_0@PBE0$, $G_0W_0@HF$, and sc-$GW$.]

The loan pair in pyridine

The loan pair in pyridine

What the Green’s function gives us

Spectral function:

\[ A(\epsilon) = -\frac{1}{\pi} \int dr \lim_{r' \to r} \text{Im} G(r, r'; \epsilon) \]

Density:

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

Total energy:

\[ E_{GM} = -i \sum_{\sigma} \int dr \, dt \lim_{r' \to r} \lim_{t' \to t^+} \left[ i \frac{\partial}{\partial t} - \frac{\nabla^2 r}{2} + v_{\text{ext}}(r) \right] G^\sigma(r, r', t, t') \]
Return to the TTF/TCNQ dimer

What we learned today

Basic principles of electron spectroscopy

The Green’s function and the self-energy

The GW approximation to the self-energy

Pros and cons of density-functional theory for electron spectroscopies