The GW approximation for single particle energies

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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

ARPES
=+1°

Binding Energy (eV)
Spectroscopy and materials science

Experiment/Spectroscopy

Appropriate? Accurate?

ARPES
=+1°

Binding Energy (eV)
Spectroscopy and materials science

Experiment/Spectroscopy

Theoretical Spectroscopy

Appropriate? Accurate?
Spectroscopy and materials science

Experiment/Spectroscopy

Theoretical Spectroscopy

Appropriate? Accurate?

Appropriate? Accurate?
Spectroscopy and materials science

Experiment/Spectroscopy

Theoretical Spectroscopy

Materials Science/Applications
Spectroscopy and materials science

Experiment/Spectroscopy
- Photoemission
- Optical Absorption

Theoretical Spectroscopy
Green’s function theory
- GW, BSE

Materials Science/Applications

Appropriate? Accurate?

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Spectroscopies

Photoemission

Inverse Photoemission

Absorption

$GW$

$GW$

BSE TDDFT
Photo-electron energies

Photoemission

- electron removal
  
  ground state $|N\rangle$

- removal energy $E(N)$

  ground state total energy

$N$ electrons
Photo-electron energies

Photoemission

- electron removal

- removal energy

\[ E(N) \]

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

\[ \epsilon_f \]

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

\[ \epsilon_s \]

\[ h\nu \]

\[ N-1 \text{ electrons} \]
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

$N$-1 electrons
Photo-electron energies

**Photoemission**

- electron removal

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

- removal energy

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

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

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

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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:

\[ A_k(\epsilon) = ImG_k(\epsilon) \approx \frac{Z_k}{\epsilon - (\epsilon_k + i\Gamma_k)} \]

\[ A(\epsilon) \]

\[ \epsilon_k \]

\[ \Gamma_k \]

quasiparticle peak

inverse of lifetime

quasiparticle weight
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

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

Coulomb interaction

dielectric function

screened

bare

screened

hole is screened by the system

quasiparticle

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 \( T_s \), the Hartree energy \( E_H[n] \), the external energy \( E_{ext}[n] \), 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 \( E_{xc}[n] \).
$\Sigma = iGW$

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

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

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

**GW approximation - screened electrons**

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

Dyson equation:

- non-interacting Green’s function

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

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

Incidentally

Hedin derived these equations by applying a small electric field perturbation to the Schrödinger equation.

Hence: many-body perturbation theory

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

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

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

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\]

Do not despair!  
Hedin’s GW approximation!

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

Step 1:

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

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

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

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

**Step 1:**
- Do a DFT calculation: $\varepsilon_s^{KS}$ and $\phi_s^{KS}(r)$

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

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

**Step 3:**
- Construct polarizability:

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

Step 4:

- Dielectric function:

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

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

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:

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

Step 7b: Perturbation theory:

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

\[ \epsilon_{sp}^q = \epsilon_{sp}^{KS} + \langle s|\sum(\epsilon_{sp}^q)|s\rangle - \langle s|v_{xc}|s\rangle \]

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

$$\Sigma = iGW$$

self-energy:

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

- exact exchange (Hartree-Fock)
  $$iGv$$
- screening (due to other electrons)
  $$iG(W - v)$$

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

\[
e_{n\mathbf{k}}^{qp} = e_{n\mathbf{k}}^{LDA} + \langle \phi_{n\mathbf{k}} | \Sigma_x + \Sigma_c (\epsilon_{n\mathbf{k}}^{qp}) - v_{xc} | \phi_{n\mathbf{k}} \rangle
\]

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

exp: 1.17 eV
Angle resolved photoemission - ZnO

$G_0W_0@OEPx$ is exact exchange + LDA correlation

Band gaps of solids

![Graph showing experimental and theoretical band gaps for various materials. The graph includes data points for materials such as CdS, ZnO, ZnS, Zb-GaN, wz-GaN, ZnSe, CdSe, and InN. The theoretical band gaps are calculated using LDA, OEPx(cLDA), and OEPx(cLDA) + $G_0 W_0$.]

*OEPx(cLDA) is exact exchange + LDA correlation

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
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
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

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

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Band structure of InN with GW corrections and Moss-Burstein effect.}
\end{figure}

InN - $GW$ band structure and Moss-Burstein

\begin{equation}
E_g(n) = \begin{cases} 
\text{parabolic} & (m_{\text{eff}} = 0.07 \, m_0) \\
G_0 W_0 @ OEPx(cLDA) & 
\end{cases}
\end{equation}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Band structure of InN with GW corrections and Moss-Burstein effect.}
\end{figure}

Organic or plastic electronics

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

... and affect or determine device properties.

Can we understand and control them?
Atomistic organic/inorganic interface

Level alignment

Interface properties

Molecular geometry

ZnO

F4TCNQ
Atomistic organic/inorganic interface

- Interface properties
- Molecular geometry

Level alignment

ZnO

F4TCNQ
Level alignment at interface

- **conduction band**
- **valence band**
- **Fermi level**

**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 surface
Molecular levels at surface

- Surface
- Gas phase

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

surface

gas phase

image effect

EA

IP

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Molecular levels at surface
Molecular levels at surface

- surface
- gas phase

Renormalization

EA

IP
Molecular levels at surface

Surface

Gas phase

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

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

\(\varepsilon\) dielectric constant

renormalization

\(z\)

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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

gap/eV | DFT (LDA) | G₀W₀@LDA | Exp.*
---|---|---|---
free CO | 6.9 | 15.1 | 15.8
CO@NaCl | 7.4 | 13.1 |


Make CO “ride the image potential”

**Ge 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

I need your input!

Take out your mobile phone (or laptop) and go to:

http://presemo.aalto.fi/peking2018gw/
Some open questions
$\Sigma = iGW$

**Accuracy:**

We have only one diagram!

Is this enough?
$\Sigma = iGW$

We have a basis representation.

Are the results reproducible?
\[ \Sigma = iGW \]

\[ \sum_{n,k} G_{0W0} \text{ depends on starting-point.} \]

- \( G_{0W0} \): correction to DFT eigenvalues:

\[ \epsilon_{np}^{pq} = \epsilon_{nk}^{\text{DFT}} + \sum_{n,k} G_{0W0}(\epsilon_{nk}^{pq}) - \nu_{nk}^{xc} \]
**GW open questions**

\[ \Sigma = iG\!W \]

- \( G_0W \) correction to DFT eigenvalues:
  \[ \epsilon_{n\mathbf{k}}^{qp} = \epsilon_{n\mathbf{k}}^{\text{DFT}} + \sum_{n\mathbf{k}} G_0W_0 (\epsilon_{n\mathbf{k}}^{qp}) - v_{n\mathbf{k}}^{xc} \]

W: screened Coulomb

G: propagator

Reference:

Which starting-point is most appropriate?

\( G_0W_0 \) depends on starting-point.
GW open questions

\[ \Sigma = iGW \]

Understanding: Complex theory with many flavors.

Do we know why GW performs the way it does?
GW open questions

\[ \Sigma = iGW \]

Beyond GW:

GW is already very expensive.

How do we go beyond GW? What alternatives do we have?
GW open questions

- Accuracy
- Reference
- Understanding
- Reliability
- Beyond GW
GW open questions

Accuracy
Reference
Reliability
Understanding
Beyond GW
Angle resolved photoemission - ZnO

Convergence of $G_0W_0$ for ZnO

Origin of the slow convergence

- Green’s function:

\[ G^0_\sigma(r, r', \omega) = \sum_n \frac{\psi_{n\sigma}(r)\psi^*_{n\sigma}(r')}{\omega - \epsilon_{n\sigma} - i\eta \ \text{sgn} (\epsilon_F - \epsilon_{n\sigma})} \]

- Polarizability:

\[ P(r, r', \omega) = \sum_\sigma \sum_m \sum_a \frac{\psi^*_{m\sigma}(r)\psi_{a\sigma}(r)\psi^*_{a\sigma}(r')\psi_{m\sigma}(r')}{\omega - (\epsilon_{m\sigma} - \epsilon_{a\sigma})} + \text{c.c.} \]
Testing the accuracy and reliability of $G_0W_0$
Testing the accuracy and reliability of $G_0W_0$

- local atomic basis
- all-electron
- local atomic basis
- small core pseudo potentials
- plane waves
- pseudo potentials

FHI-aims
TURBOMOLE
BerkeleyGW
Aalto University
School of Science
Testing the accuracy and reliability of $G_0W_0$

- imaginary frequency
- analytic continuation
- local atomic basis
- all-electron
- exact real frequency treatment
- local atomic basis
- small core pseudo potentials
- plane waves
- pseudo potentials
Testing the accuracy and reliability of $G_0W_0$

- Imaginary frequency
- Analytic continuation
- Local atomic basis
- All-electron
- Exact real frequency treatment
- Local atomic basis
- Small core pseudo potentials
- Plane waves
- Pseudo potentials
- Gaussian def2 basis sets
- Extrapolated to basis set limit
Testing the accuracy and reliability of $G_0W_0$

GW100 project

3 GW codes
3 groups
100 molecules

M. van Setten, P. Rinke, et al,
GW100: accuracy and reliability of $G_0W_0$

Baseline: FHI-aims def2-QZVP basis set

Turbomole 3 meV

M. van Setten, P. Rinke, et al,
GW100: accuracy and reliability of $G_0W_0$

Baseline: FHI-aims def2-QZVP basis set

EXTRA - BGW-GPP
AIMS-P16 - AIMS-2P
AIMS-P16 - TM-noRI

Aims different analytic cont.

FHI-Aims
0.1 eV

Turbomole
3 meV

M. van Setten, P. Rinke, et al,
GW100: accuracy and reliability of $G_0W_0$

GW100: accuracy and reliability of $G_0W_0$

BerkeleyGW full frequency

- can be further reduced by increasing the density of frequency points

BerkeleyGW plasmon pole

- $0.5 \text{ eV}$
- $0.2 \text{ eV}$
- $3 \text{ meV}$

EXTRA - BGW-GPP
AIMS-P16 - AIMS-2P
AIMS-P16 - TM-noRI

M. van Setten, P. Rinke, et al,
GW100: latest developments

<table>
<thead>
<tr>
<th>MAD (eV)</th>
<th>FHI-aims</th>
<th>TURBOMOLE</th>
<th>WEST</th>
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<tr>
<td></td>
<td>16P</td>
<td>EXTRA</td>
<td>W/ RI</td>
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<td>FHI-aims</td>
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<td>0.14</td>
<td>0.05</td>
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<td></td>
<td>0.14</td>
<td>—</td>
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<td>—</td>
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<tr>
<td>WEST</td>
<td>0.15</td>
<td>0.13</td>
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</tr>
</tbody>
</table>

M. Govoni and G. Galli
GW100: accuracy and reliability of $G_0W_0$

$G_0W_0@PBE$

0.5 eV

0.2 eV

deviation from experiment

GW100: accuracy and reliability of $G_0W_0$

Let’s go beyond $G_0W_0$! 

1: Different starting points
2: Beyond GW

deviation from experiment

$G_0W_0@PBE$
GW open questions

Accuracy
Reference
Understanding
Reliability
Beyond GW
Beyond $G_0W_0$ - Self-consistent $GW$ (sc$GW$)

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:
Beyond $GW$ - the SOSEX self-energy

\[ GW = \\text{antisymmetrization} \]

Beyond $GW$ - the SOSEX self-energy

\[
GW = \begin{array}{c}
\text{antisymmetrization} \\
\text{turned inside out}
\end{array} + \begin{array}{c}
\text{turned inside out}
\end{array} + \ldots
\]
Beyond GW - the SOSEX self-energy

\[ GW + SOSEX \]

implemented in FHI-aims

Benchmarking GW and beyond for acceptors
Benchmarking GW and beyond for acceptors

**Acceptor project**

- 5 groups
- 24 acceptors
- 3 different approaches (hybrids, GW, propagators)
- 1 coupled cluster reference set
Benchmarking GW and beyond for acceptors

MAD error of electron affinity

- scGW
- scGW₀@PBE
- G₀W₀@COHSEX
- G₀W₀@HF
- G₀W₀@PBE
- G₀W₀@PBEh
- G₀W₀@LC-ωPBE
- G₀W₀ + SOSEX@PBE

MAD in eV

0.6
0.4
0.2

anthracene
acridine
phenazine
azulene
benzoquinone
naphthalene (BQ)

cich
Benchmarking GW and beyond for acceptors

Benchmarking GW and beyond for acceptors

MAD error of electron affinity

J. Knight, T. Körzdörfer, P. Rinke N. Marom, et al,
Benchmarking GW and beyond for acceptors

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\[ G_0W_0@LC-\omega PBE \]

\[ \text{MAE} = 0.19 \text{ eV} \]
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 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
Ionisation Potential, Affinity and (Band) Gaps

$\Delta$SCF 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
$\Delta$SCF versus eigenvalues for finite systems

oligoacetylenes

Pinheiro Jr, Caldas, Rinke, Blum, Scheffler
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

Pinheiro Jr, Caldas, Rinke, Blum, Scheffler
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

data courtesy of Max Pinheiro
Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

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

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

\[ \Delta_{xc} \]

\[ E_{\text{gap}}^{KS} \]
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: \( N \gg 1 \quad \Rightarrow \quad \Delta n(r) \rightarrow 0 \text{ for } N \rightarrow N + 1 \)

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

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

- DFT: highest Kohn-Sham state exact:

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

\[ = \epsilon^{KS}_{N+1}(N+1) - \epsilon^{KS}_{N+1}(N) + \epsilon^{KS}_{N+1}(N) - \epsilon^{KS}_N(N) \]

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

- for solids

\[ \nu_{xc}: 0 \rightarrow N + 1 \]

many DFT functionals do not capture this derivative discontinuity
Band gaps of solids

Experimental Band Gap [eV]

Theoretical Band Gap [eV]

LDA
OEPx(cLDA)
OEPx(cLDA) + G_0 W_0

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

The Green’s function is versatile, it also gives us the ground state directly.
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:**

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

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

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

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

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RPA/GW
Trieste 2013 23

Caruso, Rinke, Ren, Scheffler, Rubio,
The GW density of CO

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

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

Dipole moment (in Debye):

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

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

GW total energy assessment

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