ab initio Computational Methods for Electronic Excitations: Density-Functional and the Green’s Function

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Part 0: Introduction
  - Electronic excitations
  - Approaches

Part I: Density Functional Theory (DFT)

Part II: Orbital-Dependent DFT

Part III: Time-Dependent DFT

Part IV: GW/BSE
Photoemission: Quasiparticle Gap

Electron addition/removing

\[ E_g = IP - EA \]

Electron Affinity

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

Ionization Potential

\[ IP = E(N-1) - E(N) \]
**Quasiparticle**

- Excitations of many-electron system can often be described in terms of weakly interacting “quasiparticles”

- Quasiparticle (QP) = bare particle + polarization clouds

\[ E_{QP} = E^0 + \Sigma \]

\( \Sigma \): response of system to the excitation (self-energy)
Optical Absorption: Neutral Excitation

Optical Gap
Electron addition removing – exciton binding energy

\[ E_{\text{opt}} = E_g - E_{e-h} \]

\[ E_{e-h} \sim \frac{e^2}{2\varepsilon a_0} \]
Approaches (1)

- **Density Functional Theory (KS-states)**
  Serves as 0\textsuperscript{th}-order approximation; very efficient
  Unjustified theoretically; Underestimates gaps severely.

- **ΔSCF**
  Can be accurate for QP-gap, moderate accuracy for neutral excitation; Difficult to get the full spectrum; Only applicable for finite systems.

- **Ensemble DFT**
  Can compute the excitation energy; But ensemble LDA performs poorly - need better approximation.

- **LDA + DMFT**: strongly-correlated materials (cuprate)

- **LDA + U**: Mott insulators (NiO); U is ad hoc.
Approaches (2)

- Orbital-Dependent DFT
  - Self-Interaction Correction (SIC)
  - Hybrid DFT: B3LYP, PBE0, HSE, etc
  - Exact Exchange (EXX)
  - Screened Exchange (sx)

  Could predict good QP-gap, and more efficient than GW; But the accuracy varies strongly for different materials.

- Time-Dependent (TD) DFT
  Exact theory in principle for neutral excitations; In practice, adiabatic LDA is OK for molecules, poor for solids; No quasi-particles.
Approaches (3)

- Green-function methods: GW/BSE
  State-of-the-art for both QP and neutral excitation; scaling as $N^{4-7}$.

- Quantum chemistry post-HF methods:
  CI, CC, MP2, etc.
  Accurate for QP and neutral excitation of molecules
  But bad scaling of $N^{5-7}$; Prohibitive for solids.

- Quantum Monte Carlo
  Scaling as $N^3$: most accurate benchmarks for systems of medium size;
  Essentially ΔSCF for excitations: difficult to get the full spectrum.
Balance Between Accuracy and Applicability

- **QMC for ground and excited state materials properties**
- **Embedded post-HF quantum chemistry for structures, adsorption, diffusion, reactions, excitation energies**
- **TD-DFT or DFT/GW/BSE for band gaps and spectra of conventional semiconductors**
- **DMFT for band gaps and spectra of strongly correlated materials**
- **DFT + U for same ground state properties as DFT-GGA for strongly correlated materials**
- **DFT-GGA for structures, thermal, electrical, magnetic, and mechanical properties, diffusion and reaction kinetics, surface and defect energies of most hard materials**

PART I: Density Functional Theory
KS-States as Quasiparticles

\[
\left(-\frac{\hbar^2 \nabla^2}{2m} + v_{\text{KS}}(\vec{r})\right) \phi_i(\vec{r}) = \varepsilon \phi_i(\vec{r}),
\]

where \( v_{\text{KS}}(\vec{r}) = v_{\text{ext}}(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r}) \),

with \( v_H(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \) and \( v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})} \).

Janak’s Theorem (PRB 18, 7165):

\[
\frac{\partial E}{\partial n_i} = \varepsilon_i
\]

\[
\Rightarrow \left\{ \begin{array}{l}
E(N+1) - E(N) = \int_N^{N+1} \varepsilon_i(n) dn \approx \varepsilon_i(N+0.5) \\
E(N) - E(N-1) = \int_{N-1}^N \varepsilon_i(n) dn \approx \varepsilon_i(N-0.5)
\end{array} \right.
\]
KS-States as Quasiparticles

\[-E_A = E_{\text{min}}^\text{max}(N + 1) - E(N) \approx \varepsilon_{N+1}(N + 0.5)\]

\[-\text{IP} = E(N) - E_{\text{min}}^\text{max}(N - 1) \approx \varepsilon_N(N - 0.5)\]

For infinite KS systems (solids): \( N \to \infty \)

\[E(N + 1) - E(N) = \varepsilon_i(N) \text{ for } i > N\]

\[E(N) - E(N - 1) = \varepsilon_i(N) \text{ for } i \leq N\]

For finite KS systems (molecules):

KS eigenstates cannot be treated as quasiparticles.
KS-Eigenvalues vs $\Delta$SCF

![Graph showing KS-Eigenvalues vs $\Delta$SCF](image)

$\Delta E$ (eV) vs $1/N$

- E(N+1)-E(N)
- E(N)-E(N-1)

CBM, VBM

DFT, QMC

Si slab

PRB 79, 201309 (2009)
KS-Eigenvalues vs $\Delta$SCF

Benzene

$\varepsilon_{\text{LUMO}}^{\text{KS}} = -1.16 \text{ eV}$  
$\varepsilon_{\text{HOMO}}^{\text{KS}} = -6.25 \text{ eV}$  
$E_{g}^{\text{KS}} = 5.1 \text{ eV}$

$E_{N+1} - E_{N} = 1.10 \text{ eV}$  
$E_{N} - E_{N-1} = -9.12 \text{ eV}$  
$E_{g}^{\Delta \text{SCF}} = 10.22 \text{ eV}$  
$E_{g}^{\text{GW}} = 10.51 \text{ eV}$
Lack of Derivative Discontinuity in $E_{xc}$

\[ \frac{\partial E}{\partial n_i} = \varepsilon_i \]

CBM = \( \frac{\delta E}{\delta n} \bigg|_{n=N^+} \)

VBM = \( \frac{\delta E}{\delta n} \bigg|_{n=N^-} \)

\[ \Delta_{xc} = \frac{\delta E_{xc}}{\delta n} \bigg|_{n=N^+} - \frac{\delta E_{xc}}{\delta n} \bigg|_{n=N^-} \]

\[ \Delta^\text{DFT} = 0 \]

The DFT band gap is due to the derivative discontinuity in $E_{\text{kin}}$

\[ \Delta_{xc} = E_{\text{g}}^{\text{QP}} - E_{\text{g}}^{\text{KS}} \]

Underestimate the band gap by $\Delta_{xc}$

\[ \frac{\delta E_{xc}}{\delta n_i} = \frac{\delta E_{xc}}{\delta n_j} = \frac{\delta E_{xc}}{\delta n_{N}} \]

\[ |\varepsilon_i^{\text{KS}} - \varepsilon_j^{\text{KS}}| < |\varepsilon_i^{\text{QP}} - \varepsilon_j^{\text{QP}}| \]

Underestimate the band width

Levy et al., PRA 30, 2745 (1984)

\[ \varepsilon_N^\text{KS} (N) = -\text{IP} \]

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

Other KS eigenvalues cannot be rigorously assigned to the QP energies.
Presence of Self-Interaction

Too much Coulomb repulsion (each electron is repelled by itself) pushes electrons apart: delocalization of the KS wavefunction

FIG. 1 (color online). ISosurface of an extra electron added in the system of two distant Na$_2$ molecules, or in other words: isosurface of the highest occupied molecular orbital of the (2Na$_2$)$^-$ system. Panel (a) represents the LDA results, whereas panel (b) provides the scGW result.
**Fig. 2.** Seeing the delocalization error. The incorrect convex behavior of the LDA energy is seen for the Cl atom with fractional numbers of electrons (A). Despite good agreement with the exact values at the integer points, the convex behavior means that a lower energy can be achieved with fractional charges. This leads to an unphysical delocalization of the electrons in a simulation of the solvated anion, as shown (in blue) by the difference of the LDA density between the solvated Cl and solvated Cl\(^-\) (B).
PART II: Orbital-Dependent DFT
Why Adding Orbitals to $E_{xc}$

- Using orbitals in $E_{\text{kin}}$ is precisely what made DFT so successful.
- Using orbitals allows more flexibility and accuracy in construction of functionals.
- Orbital dependence may introduce derivative discontinuity in exchange-correlation.
- Orbital dependence can compensate for self-interaction.
- The exchange energy is formulated naturally in terms of orbitals.
Optimized Effective Potential (OEP)

\[ E_{xc}[\rho(\vec{r})] \text{ obeys the Hohenberg-Kohn principle: } \frac{\delta E_{tot}}{\delta \rho(\vec{r})} = 0 \quad \text{PR 136, B864 (1964)} \]

\[ E_{xc}[\{\phi_j\}] \text{ obeys the Sharp-Horton principle: } \frac{\delta E_{tot}}{\delta v_{KS}(\vec{r})} = 0 \quad \text{PR 90, 317 (1953)} \]

These two principles are equivalent

\[ \rho \rightarrow \nu \rightarrow \{\phi_j\} \Rightarrow \{\phi_j\} = \{\phi_j\}[\rho] \]

\[ \Rightarrow E_{xc}[\{\phi_j\}] \text{ is within the framework of KS theorem} \]

Chain rule:

\[ v_{xc}^{\text{OEP}}(\vec{r}) = \frac{\delta E_{xc}[\{\phi_j\}]}{\delta \rho(\vec{r})} = \sum_i \int \int \frac{\delta E_{xc}[\{\phi_j\}]}{\delta \phi_i(\vec{r}')} \frac{\delta \phi_i(\vec{r}')}{\delta v_{KS}(\vec{r}'')} \frac{\delta v_{KS}(\vec{r}'')}{\delta \rho(\vec{r})} d\vec{r}' d\vec{r}'' + \text{c.c.} \]
Optimized Effective Potential (OEP)

\[
\nu_{\text{xc}}^{\text{OEP}}(\vec{r}) = \sum_i \int \int \frac{\delta E_{\text{xc}}[\{\varphi_i\}]}{\delta \varphi_i(\vec{r}')} \frac{\delta \varphi_i(\vec{r}')}{\delta \nu_{\text{KS}}(\vec{r}'')} \frac{\delta \nu_{\text{KS}}(\vec{r}'')}{\delta \rho(\vec{r})} d\vec{r}' d\vec{r}'' + \text{c.c.}
\]

First-order perturbation theory

\[
\frac{\delta \varphi_i(\vec{r}')}{\delta \nu_{\text{KS}}(\vec{r})} = \sum_{i \neq j}^{\infty} \frac{\varphi_j(\vec{r}') \varphi^*_j(\vec{r})}{\varepsilon_i - \varepsilon_j} \varphi_i(\vec{r})
\]

Response function \( \chi \)

\[
\chi_{\text{KS}}(\vec{r}, \vec{r}') \equiv \frac{\delta \rho(\vec{r}')}{\delta \nu_{\text{KS}}(\vec{r})} = \sum_i^{\text{occ}} \sum_{j \neq i}^{\infty} \varphi^*_i(\vec{r}) \varphi_i(\vec{r}') \varphi_j(\vec{r}) \varphi^*_j(\vec{r}') \frac{1}{\varepsilon_i - \varepsilon_j} + \text{c.c.}
\]

PRA 50, 196 (1994); PRB 59, 10031 (1999); PRB 68, 035103 (2003)
The OEP Equation

Multiplying $\chi_{KS}$ on both sides from the right, then integrating

$$\sum_{i}^{\text{occ}} \int \phi_i^*(\vec{r}') \left[ v_{xc}(\vec{r}') - u_{xc}^i(\vec{r}') \right] G_{KS}^i(\vec{r}', \vec{r}) \phi_i(\vec{r}) d\vec{r}' + \text{c.c.} = 0$$

where the KS Green's function $G_{KS}^i(\vec{r}', \vec{r})$ is

$$G_{KS}^i(\vec{r}', \vec{r}) = \sum_{i \neq j}^{\infty} \frac{\phi_j(\vec{r}') \phi_j^*(\vec{r})}{\varepsilon_i - \varepsilon_j}$$

and

$$u_{xc}^i(\vec{r}) = \frac{1}{\phi_i^*(\vec{r})} \frac{\delta E_{xc}[\{\phi_j\}]}{\delta \phi_i(\vec{r})}$$
Orbital-Specific Potential Approach

- Orbital-specific potential (OSP) approaches:
  - Self-interaction correction (SIC)
  - Hybrid functionals (Mixing HF with LDA/GGA)
  - Meta-GGA

- KS equation with OSP

\[
\left( -\frac{\hbar^2 \nabla^2}{2m} + v_H(\vec{r}) + v_{xc}([\rho];\vec{r}) \right) \varphi_i(\vec{r}) + F[\varphi_i(\vec{r})] = \varepsilon_i \varphi_i(\vec{r})
\]

- KS equation with OEP

\[
\left( -\frac{\hbar^2 \nabla^2}{2m} + v_H(\vec{r}) + v_{xc}([\{\varphi_j\}];\vec{r}) \right) \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})
\]
OEP versus OSP

- OEP is within KS theorem, thus no derivative discontinuity; while OSP is not within KS, but still obeys the HK theorem, and it has derivative discontinuity.

- OEP orbitals are diagonal, while OSP orbitals are non-diagonal.

- For unoccupied states, OEP is a significant improvement over OSP.

- For localization phenomena, OSP are often advantageous.

- The total energy and total electron density for both approaches are similar if the second or higher order perturbation terms for OEP are small.
Mixing LDA/GGA with HF

- **LDA/GGA**
  - Orbital delocalization
  - Convex behavior of total energy
  - Underestimation of band gap

- **HF**
  - Orbital localization
  - Concave behavior of total energy
  - Overestimation of band gap

<table>
<thead>
<tr>
<th>Band Gap (eV)</th>
<th>LDA</th>
<th>HF</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.1</td>
<td>12.1</td>
<td>5.5</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
<td>6.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Ge</td>
<td>-0.1</td>
<td>4.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Hybrid Functional: \( E_{xc}^{hyb} = bE_x^{HF} + (1 - b)E_x^{apprx} + E_c^{apprx} \)

Adiabatic connection theorem (PRB 15, 2884; PRA 26, 1200)
Hybrid Functionals

\[ E^{\text{PBE0}}_{\text{xc}} = 0.25 E^{\text{HF}}_{\text{x}} + 0.75 E^{\text{PBE}}_{\text{x}} + E^{\text{PBE}}_{\text{c}} \]

\[ E^{\text{HSE}}_{\text{xc}} = 0.25 E^{\text{HF, SR}}_{\text{x}} + 0.75 E^{\text{PBE, SR}}_{\text{x}} + E^{\text{PBE, LR}}_{\text{x}} + E^{\text{PBE}}_{\text{c}} \]

\[ E^{\text{B3LYP}}_{\text{xc}} = 0.20 E^{\text{HF}}_{\text{x}} + 0.80 E^{\text{LDA}}_{\text{x}} + 0.72 \Delta E^{\text{B88}}_{\text{x}} + 0.81 E^{\text{LYP}}_{\text{c}} + 0.19 E^{\text{LDA}}_{\text{c}} \]

More: B3P86, B1B95, B1LYP, MPW1PW91, B97, BHHLYP, B98, B971, B972, PBE1PBE, O3LYP, BHH, BMK, etc
Band Gaps from Hybrids PBE0 and HSE03

JCP 124, 154709 (2006)
B3LYP Functional

\[ E_{xc}^{\text{B3LYP}} = 0.20 E_{x}^{\text{HF}} + 0.80 E_{x}^{\text{LDA}} + 0.72 \Delta E_{x}^{\text{B88}} + 0.81 E_{c}^{\text{LYP}} + 0.19 E_{c}^{\text{LDA}} \]

Most popular functional in computational chemistry: > 12,000 citations

Si Band Structure

\( \square: \text{GW} \)
\( \bigcirc: \text{QMC} \)
\( \nabla: \text{Expt.} \)

CPL 342, 397 (2001)
B3LYP Functional

\[ E_{xc}^{\text{B3LYP}} = 0.20 E_{x}^{\text{HF}} + 0.80 E_{x}^{\text{LDA}} + 0.72 \Delta E_{x}^{\text{B88}} + 0.81 E_{c}^{\text{LYP}} + 0.19 E_{c}^{\text{LDA}} \]

A comparison of observed band gaps with those calculated using the B3LYP functional for a wide range of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Expt</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si[25]</td>
<td>\approx 3.5 (\Gamma \text{ gap})</td>
<td>3.8</td>
</tr>
<tr>
<td>Diamond[25]</td>
<td>5.5</td>
<td>5.8</td>
</tr>
<tr>
<td>GaAs[25]</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>ZnO[23]</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Al_2O_3[23]</td>
<td>\approx 9.0</td>
<td>8.5</td>
</tr>
<tr>
<td>Cr_2O_3[23]</td>
<td>3.3</td>
<td>3.4</td>
</tr>
<tr>
<td>MgO[23]</td>
<td>7.8</td>
<td>7.3</td>
</tr>
<tr>
<td>MnO[23]</td>
<td>3.6</td>
<td>3.8</td>
</tr>
<tr>
<td>NiO[23]</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td>TiO_2[23]</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>FeS_2[24]</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>ZnS[24]</td>
<td>3.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

All values are given in electron volts (eV).  
CPL 342, 397 (2001)
Screened Exchange (sx)

\[
E^{sx}_x = -\sum_{i,j} \iint \frac{\Psi^*_i(\vec{r})\Psi^*_j(\vec{r}')e^{-k_{TF}|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} \Psi_j(\vec{r})\Psi_j(\vec{r}') d\vec{r} d\vec{r}'
\]

The bare Coulomb potential is replaced with a Yukawa potential, with \(k_{TF}\) the Thomas-Fermi screening factor.

An approximation of GW theory

sx-LDA approximation

\[
\left(-\frac{\hbar^2 \nabla^2}{2m} + v_{\text{ext}}(\vec{r}) + e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{\text{xc}}^{\text{sx}}([n];\vec{r}) \right)\varphi_i(\vec{r})
\]

\[
- e^2 \sum_{j=1}^{N_{\sigma}} \int \frac{\varphi_j(\vec{r})e^{-k_{TF}|\vec{r}-\vec{r}'|}\varphi^*_j(\vec{r}')\varphi_i(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r' = \epsilon_i \varphi_i(\vec{r})
\]
Exact Exchange (EXX)

\[ E_x = -\frac{1}{2} \sum_{i,j}^{\text{occ}} \int \frac{\phi_i^*(\vec{r})\phi_j^*(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r} \]

OEP

cohesive energy

PRB 59 10031 (1999)
Is EXX Equivalent to HF?

$$E_x = -\frac{1}{2} \sum_{i,j}^{\text{occ}} \int \frac{\phi_i^*(\vec{r})\phi_j^*(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r}$$

- EXX satisfies HK theorem, but HF does not: EXX optimizes $E_{\text{tot}}$ w.r.t. density, while HF w.r.t orbitals.
- EXX potential is local and multiplicative (within KS) while HF potential is non-local and orbital-specific.
- EXX orbitals are different from HF orbitals: EXX orbitals are uniquely determined by density, HF not.
- **EXX and HF predicts different band gaps:**

<table>
<thead>
<tr>
<th>Band Gap (eV)</th>
<th>LDA</th>
<th>EXX</th>
<th>HF</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.5</td>
<td>1.4</td>
<td>6.3</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Why EXX and HF Predict Different Gaps?

EXX is an approximation to GW due to screening of response-function in OEP. EXX predicts better gap than LDA/GGA and HF due to error cancellation.

\[ E_g^{KS} = \varepsilon_{N+1}(N) - \varepsilon_N(N) \]
\[ E_g = E(N + 1) + E(N - 1) - 2E(N) \]

For Si, using EXX:
\[ E_g^{KS} = 1.4 \text{ eV} \quad \Delta_{xc} = 4.5 \text{ eV} \]
\[ E_g = E_g^{KS} + \Delta_{xc} = 5.9 \text{ eV} \]
\[ E_g^{HF} = 6.3 \text{ eV} \]

The derivative discontinuity \( \Delta_{xc} \) in KS scheme can be evaluated from the GW-operator and the KS eigenvalues and orbitals:

\[ \Delta_{xc} = \langle \phi_{N+1} | \sum_{xc}^{GW} (\varepsilon_{N+1}) - \nu_{xc} | \phi_{N+1} \rangle - \langle \phi_N | \sum_{xc}^{GW} (\varepsilon_N) - \nu_{xc} | \phi_N \rangle \]

PRB 70, 245155 (2004)
FIG. 2. Minimum-energy gap for bulk Si, LiF, and Ar as calculated with EXX, HF, LDA and GW.
Exact Exchange (EXX) with Compatible Correlation

- The hyper-generalized-gradient approximation (HGGGA)
  Perdew et al., JCP 123, 062201 (2005).

\[ \tau_\alpha(r) = \frac{1}{2} \sum_i^{\text{occ.}} |\nabla \phi_{i \alpha}(r)|^2 \]

HEAVEN OF CHEMICAL ACCURACY

| unoccupied \( \{ \phi_i \} \) | generalized RPA \( E_{xc}^{\text{HGGGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r \, n \times \varepsilon_{xc}^{\text{HGGGA}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau, \tau, \varepsilon_{x\uparrow}, \varepsilon_{x\downarrow}) \) |
| \( \varepsilon_x \) | hyper-GGA |
| \( \tau \) and/or \( \nabla^2 n \) | meta-GGA |
| \( \nabla n \) | GGA |
| \( n \) | LSD |

HARTREE WORLD

Jacob’s Ladder
Exact Exchange (EXX) with Compatible Correlation

- Perturbation theory
  - Higher rung than HGGA; From construction to evaluation
  - Görling-Levy theory
    
    PRB 47, 13105 (1993); PRA 50, 196 (1994); PRA 50, 4493 (1995)

- Range-separated functionals
  - Underlies the random-phase approximation (RPA)
    
    PRB 59, 10461 (1999); PRB 61, 16430 (2000); PRB 67, 045101 (2003)
  - Generalized hybrid functionals (PRA 72, 012510; CPL 415, 100)

- Correlation factor model [Int. J. Quan. Chem. 61, 287 (1997)]
  - Model the coupling-constant-averaged xc hole

- Interaction-strength interpolation [PRA 59, 51 (1999)]
  - Model the coupling-constant integrand: $E_{xc}[^2\lambda] = \int_{0}^{1} E_{xc}[^2\lambda][\rho] d\lambda$

The forefront of present-day density-functional research

- Computationally much more demanding than LDA/GGA
Summary: Why DFT Fails to Predict Correct QP Gap?

- Is the problem due to XC approximations (LDA/GGA), or it is intrinsic due to electron density used instead of orbitals?
  - It is intrinsic to the KS scheme, which lacks the necessary derivative discontinuity in XC due to local and multiplicative potential.

- Do KS eigenvalues/states have any meaning at all?
  - KS states are QPs of the infinite KS system.
  - For real infinite systems, rigorously, only the highest occupied KS state corresponds to VBM; practically, they can be a good 0-order approximation to QPs.
  - For finite systems (molecules), KS states cannot be assigned to QP at all.
Summary: Why DFT Fails to Predict Correct QP Gap?

- Are the underestimation in gap for solids (infinite systems) and molecules (finite systems) due to the same reason?
  - No. For solids, it is mainly due to lacking derivative discontinuity in XC.
  - For molecules, KS eigenvalues can not be associated to QP energies (orbital relaxation is needed for the $N\pm1$ systems).

- If we have the holy-grail "exact XC functional", can DFT predict correct gap for solids and molecules?
  - In principle, “exact DFT” can predict correct gaps for both systems if go beyond KS scheme (even beyond HK).
  - Practically, it is doomed! Though some approaches based on DFT are fortuitous to predict correct gap for many materials.
PART III: Time-Dependent DFT

JACS 127, 1438 (2005)
1. **Time-dependent Shrödinger Equation**

\[ i \frac{\partial}{\partial t} \psi(\vec{r}, t) = \hat{H}(\vec{r}, t) \psi(\vec{r}, t) \]

\[ \hat{H}(\vec{r}, t) = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} + V_{\text{ext}}(\vec{r}, t) \]

\[ V_{\text{ext}}(\vec{r}, t) = V_{\text{e-n}}(\vec{r}, t) + V_{\text{laser}}(\vec{r}, t) \]

Coulomb interaction

\[ V_{\text{laser}} = E_0 f(t) \sin(\omega t) \sum_{i=1}^{N} \vec{r}_i \cdot \vec{z} \]

\( \vec{z} \): polarization, \( \omega \): frequency, \( E_0 \): amplitude

\( f(t) \): the envelop function.

Problem: the time to solve the equation grows exponentially with the number of particles.
2. the variational principles

**Static Shrödinger Equation:** \[ \frac{\delta E[\psi]}{\delta \psi} = 0 \]
where \[ E[\psi] = \langle \psi | \hat{H} | \psi \rangle \]

**Time-dependent Shrödinger Equation:**
the quantum mechanical Action
\[ \frac{\delta A[\psi]}{\delta \psi} = 0 \]

\[ A[\psi] = \int_{t_0}^{t_1} \langle \psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \psi(t) \rangle dt \]

At the solution point:
\[ E[\psi] = E_0 \] the ground-state energy
\[ A[\psi] = 0 \]
3) The Runge-Gross theorem

Hohenberg-Kohn theorem: the ground-state properties of a many-electron system are uniquely determined by an electron density.

\[ E = E[n] \]

Extended to time-dependent case, the Runge-Gross theorem

At any moment, the electron density uniquely determines the external potential, i.e., a one-to-one correspondence between electron density and the potential. Proof: PRL 52, 997 (1984)
4. Time-dependent Kohn-Sham (KS) Equation

KS equation: \[ \left[ -\frac{1}{2} \nabla^2 + V_{\text{KS}}(\vec{r}) \right] \Phi_i(\vec{r}) = \varepsilon_i \Phi_i(\vec{r}) \]
boundary value problem

TD-KS equation: \[ i \frac{\partial}{\partial t} \Phi_i(\vec{r}, t) = \left[ -\frac{1}{2} \nabla^2 + V_{\text{KS}}(\vec{r}, t) \right] \Phi_i(\vec{r}, t) \]
initial value problem

density: \[ n(\vec{r}, t) = \sum_i \left| \Phi_i(\vec{r}, t) \right|^2 \]

KS potential: \[ V_{\text{KS}}(\vec{r}, t) = V_{\text{ext}}(\vec{r}, t) + V_H(\vec{r}, t) + V_{\text{xc}}(\vec{r}, t) \]

\[ V_H(\vec{r}, t) = \int \frac{n(\vec{r}, t)}{|\vec{r} - \vec{r}'|} d\vec{r}' \]

\[ V_{\text{xc}}(\vec{r}, t) = \frac{\delta A_{\text{xc}}}{\delta n(\vec{r}, t)} \]
Exchange-Correlation functionals

The only fundamental approximation in TD-DFT is $V_{xc}(\vec{r},t)$.

DFT: very good $V_{xc}$ approximations exist.

TDDFT: Approximations of $V_{xc}$ are still in their infancy.

The simplest one: Adiabatic local density approximation (ALDA) ↔ DFT-LDA

$$U_{ALDA}^{ALDA}(\vec{r},t) = V_{xc}^{LDA}[n] \Big|_{n=n(\vec{r},t)}$$

1. The most used xc functional in TD-DFT.
2. Significantly improves optical absorption spectrum for finite systems over KS eigenvalue difference.
3. Works poorly for infinite systems, similar to KS.
Other functionals:
Adiabatic GGA, TD-Exact-Exchange (TD-EXX)
TD-hybrid functionals, and $V_{xc}(\vec{r},t)$ with memory
i.e. $V_{xc}(\vec{r},t) = V_{xc}[n(\vec{r},t)]$

6) Solving TD-KS Equation: Formally

An initial value problem: $t = t_0$, $\Psi_i = \Psi_i(\vec{r},t_0)$
$\Psi = \Psi_f$
Formally written by the integration:
$\Psi_i(\vec{r},t_f) = \hat{U}(t_f, t_0) \Psi_i(\vec{r},t_0)$, with $\hat{U}(t',t) = \hat{T} \exp[-i \int_t^{t'} \hat{H}_{KS}(\tau) d\tau]$
$\hat{T}$: time-ordering operator
$\hat{T}$: propagator
Numerically solving TD-KS Equation

Finite time difference from $t_0$ to $t_f$: $t_0 \rightarrow t_0 + \Delta t$, $t_0 + \Delta t \rightarrow t_0 + 2\Delta t$.

$\hat{U}(t + \Delta t, t) \approx \exp \left[ i \hat{H}_{KS}(t) \Delta t \right] = \exp \left[ -i (\hat{T} + \hat{V}_{KS}) \Delta t \right]$

For small $\Delta t$, the lowest order decompositions are

$\exp \left[ -i (\hat{T} + \hat{V}_{KS}) \Delta t \right] = \exp (-i \hat{T} \Delta t) \exp (-i \hat{V}_{KS} \Delta t) + O(\Delta t^2)$

$\exp \left[ -i (\hat{T} + \hat{V}_{KS}) \Delta t \right] = \exp (-i \hat{T} \frac{\Delta t}{2}) \exp (-i \hat{V}_{KS} \Delta t) \exp (-i \hat{T} \frac{\Delta t}{2})$

- Fourier transforms can be used to solve the TD-KS equation efficiently

- No self-consistency, only forward propagation in time.
Linear Response of TD-DFT

For small external TD-potential, no need to solve the full TD-KS. Focus: linear change of the electron density, which leads to the optical absorption spectrum.

Assumption: \( t < t_0 \), \( V_{TD} = 0 \), then potential is \( V^{(0)}_{ext} \) density is \( n^{(0)} \): in the ground state

At \( t = t_0 \), the TD-perturbation \( V^{(1)} \) is on: \( V_{ext} = V^{(0)}_{ext} + V^{(1)}_{ext} \)

\[
\begin{align*}
n(\vec{r}, t) &= n^{(0)}(\vec{r}) + n^{(1)}(\vec{r}, t) + \cdots \\
\text{linearly depends on } V^{(1)}.
\end{align*}
\]

In the frequency space,

\[
\begin{align*}
n^{(1)}(\vec{r}, \omega) &= \int X(\vec{r}, \vec{r}', \omega) V^{(1)}_{ext}(\vec{r}', \omega) \, d\vec{r}'
\end{align*}
\]

where \( X(\vec{r}, \vec{r}', \omega) \) is the linear density-density response function.
\( n^{(i)} (r, w) = \int \chi^{(i)} (r, r', w) V_{KS}^{(i)} (r', w) \, dr' \)

\[
\chi^{(i)} (r, r', w) = \lim_{y \to 0^+} \sum_{jk} (\delta_k - \delta_j) \frac{g_{\delta} (r) g^{*}_{\delta} (r') \psi_k (r) \psi^{*}_k (r)}{w - (\epsilon_j - \epsilon_k) \gamma_h + iy}
\]

\( f, g, \epsilon \) are ground-state occupation numbers, orbitals and eigenvalues of the KS system.

Random-phase Approximation (RPA)

Because the density of the interacting system of electrons can be obtained from a fictitious non-interacting electron system.
Exchange-Correlation Kernel $f_{xc}$

$U^{(1)}_{\text{KS}}(\vec{r},t) = U^{(1)}_{\text{ext}}(\vec{r},t) + U^{(1)}_{\text{H}}(\vec{r},t) + U^{(1)}_{\text{xc}}(\vec{r},t)$

where $U^{(1)}_{\text{ext}}(\vec{r},t)$ induces $U^{(1)}_{\text{H}}(\vec{r},t)$ and $U^{(1)}_{\text{xc}}(\vec{r},t)$ due to $n^{(1)}(\vec{r},t)$

$U^{(1)}_{\text{H}}(\vec{r},t) = \int \frac{n^{(1)}(\vec{r}',t)}{|\vec{r} - \vec{r}'|} \, d^3\vec{r}'$

$U^{(1)}_{\text{xc}}(\vec{r},t) = \int \int \frac{\delta U_{\text{xc}}(\vec{r},t)}{8\pi (\vec{r},t')} n^{(1)}(\vec{r}',t') \, d\vec{r}' \, dt'$

The exchange-correlation kernel $f_{xc}(\vec{r},t;\vec{r}',t') = \frac{\delta U_{\text{xc}}(\vec{r},t)}{8\pi n(\vec{r},t)}$

$f_{xc}$ is a well-known quantity in theoretical physics:

- In an electron gas, $f_{xc}$ is proportional to the "local-field correction"
- In Landau's Fermi-liquid theory, $f_{xc}$ + bare Coulomb interaction is the "effective interaction"
- kernel is a functional of only the ground-state density
11) \( x \) for the interacting system

\[
n^{(1)}(\vec{r},w) = \int x_0(\vec{r},\vec{r}',w) V^{(1)}_{KS}(\vec{r}',w) d\vec{r}'
\]

\[
= \int x_0(\vec{r},\vec{r}',w) V^{(1)}_{ext}(\vec{r}',w) d\vec{r}'
\]

\[
+ \int x_0(\vec{r},\vec{r}'',w) K(\vec{r}',\vec{r}'',w) n^{(1)}(\vec{r}',w) d\vec{r}' d\vec{r}''
\]

where \( K(\vec{r}',\vec{r}'',w) = \frac{1}{|\vec{r}' - \vec{r}''|} + f_{xc}(\vec{r}'',\vec{r},w) \)

And \( n^{(1)}(\vec{r},w) = \int x(\vec{r},\vec{r}',w) V^{(1)}_{ext}(\vec{r}',w) d\vec{r}' \)
Dyson-Like Equation

\[ X(\vec{r}, \vec{r}', \omega) = X_0(\vec{r}, \vec{r}', \omega) + \int X_0(\vec{r}, \vec{r}_1, \omega) K(\vec{r}_1, \vec{r}_2, \omega) X(\vec{r}_2, \vec{r}', \omega) \, d\vec{r}_1 \, d\vec{r}_2 \]

Formally exact linear density respect

- The frequency-dependent kernel \( f_{xc}(\vec{r}, \vec{r}', \omega) \) makes the solution of this equation yield the EXACT \( X \), including ALL Vertex corrections at every higher-order terms.

- It has to be solved iteratively to find \( X \).
Excitation / optical absorption spectrum from the Full Solution

\[ \rho^{(1)}_{ext}(\vec{r}, t) = E_0 \delta(t) \]

\[ \rho^{(k)}_{ij}(\vec{r}, t = 0^+) = \exp(-i E_0) \rho^{(k)}_{ij}(\vec{r}) \]

Let these orbitals propagate during a finite time

\[ \delta n(\vec{r}, w) = \int \left[ n(\vec{r}, t) - n(\vec{r}) \right] e^{-iwt} \, dt \]

The dynamical polarizability \( \alpha(w) \) is

\[ \alpha(w) = - \frac{2}{E_0} \int \delta n(\vec{r}, w) \, d\vec{r} \]

photo-absorption cross section \( \sigma(w) \)

\[ \sigma(w) = \frac{4\pi w}{c} \text{Im} [\alpha(w)] \]
• Computationally more demanding
• More flexible: extended to calculate the T effects and non-linear phenomena
• No kernel $f_{xc}$ is needed, only need $V_{xc}$.

Excitations from the linear response theory

$$X(r, r', w) = X_0(r, r', w) + \int X_0(r, r_1, w) K(r_1, r_2, w) X(r_2, r', w) \, dr_1 \, dr_2$$

Difficult to solve

Lehmann representation:

$$X(r, r', w) = \lim_{\eta \to 0^+} \sum_k \left[ \frac{\langle 0 | \hat{P}(r) | m \times m | \hat{P}(r') | 0 \rangle}{\omega - (E_m - E_0)^j + iy} - \frac{\langle 0 | \hat{P}(r') | m \times m | \hat{P}(r) | 0 \rangle}{\omega + (E_m - E_0)^j + iy} \right]$$
The poles of $X$ correspond to the excitation energies
\[ E^*_m = E_m - E_0 \]

$X_0$ has poles at the excitation energies of the non-interacting system
\[ E^*_KS = \varepsilon_i^{KS} - \varepsilon_j^{KS} \]

\[ n^{(1)}(\vec{r}, \omega) = \int X(\vec{r}, \vec{r}', \omega) v^{(1)}_{\text{ext}}(\vec{r}', \omega) \, d\vec{r}', \quad n^{(1)}(\vec{r}, \omega) \text{ also has the same poles as } X \]
\[ = \int X_0(\vec{r}, \vec{r}', \omega) v^{(1)}_{\text{ext}}(\vec{r}', \omega) \, d\vec{r}' \]
\[ + \iiint X_0(\vec{r}, \vec{r}', \omega) K(\vec{r}', \vec{r}'', \omega) n^{(2)}(\vec{r}'', \omega) \, d\vec{r}' \, d\vec{r}'' \]
\[ \Rightarrow \int [ \delta(\vec{y} - \vec{y}') - Q(\vec{y}, \vec{y}', \omega)] n''(\vec{y}', \omega) \, d^3\vec{y}' = \int X_0(\vec{y}, \vec{y}', \omega) \mu''(\vec{y}', \omega) \, d\vec{r}' \]

where \[ Q(\vec{y}, \vec{y}', \omega) = \int X_0(\vec{y}, \vec{y}'', \omega) K(\vec{y}'', \vec{y}'', \omega) \, d\vec{r}'' \]

when \[ \omega \to E^*/\pi \], \[ n'' \] has a pole, but the right-hand side finite

\[ \Rightarrow \delta(\vec{r} - \vec{r}') - Q(\vec{r}, \vec{r}', \omega) \] has zero eigenvalues

i.e. when \[ hw \to E^* \], \[ \lambda(\omega) \to 1 \]

\[ \int Q(\vec{r}, \vec{r}', \omega) \xi(\vec{r}, \omega) \, d\vec{r}' = \lambda(\omega) \xi(\vec{r}, \omega) \]

where \[ Q(\vec{r}, \vec{r}', \omega) \] depends on \[ X_0 \] and \[ f_{xc} \]

\[ \xi : \xi \]

\[ \zeta : \text{zeta} \]
(14) Matrix Equation for excitation Energies

\[ \tilde{\gamma}_{jk}(\omega) = \int \phi_j^*(y'') \varphi_R(y'') K(y'', y') \xi(y', \omega) \, dy' \, dy'' \]

\[ \Rightarrow \sum_{jk} \frac{(f_k - f_{j'}) \varphi_j(y) \varphi_k^*(y)}{\omega - (E_j - E_k)/\hbar + iy} \tilde{\gamma}_{jk}(\omega) = \lambda(\omega) \xi(y, \omega) \]

\[ M_{jk, j'k'}(\omega) = (f_{k'} - f_{j'}) \int \phi_j^*(y) \varphi_k(y) \varphi_{j'}(y') \varphi_{k'}^*(y') K(y, y', \omega) \, dy \, dy' \]

\[ \Rightarrow \sum_{j'k'} \frac{M_{jk, j'k'}}{\omega - (E_j - E_{k'})/\hbar + iy} \tilde{\gamma}_{j'k'}(\omega) = \lambda(\omega) \tilde{\gamma}_{jk}(\omega) \]

\[ \beta_{jk} = \frac{\tilde{\gamma}_{jk}(E^*)}{E^* - (E_j - E_k)} \text{, and } \lambda(E^*) = 1 \]

\[ \sum_{\delta k'} \left[ \tilde{\gamma}_{j' \delta k'}(E_j - E_{k'}) + M_{jk, \delta k'}(E^*) \right] \beta_{j' \delta k'} = E^* \beta_{jk} \]
Optical Absorption of the C$_6$H$_6$ Molecule

PRA 60, 1271 (1999)
Optical Absorption of the Na$_4$ Cluster

- Solid line: TDLDA
- Dotted line: TD-EXX
- Gray solid: Experiment
- Dashed line: BSE

Strength Function (1/eV) vs. Energy (eV)
Optical Absorption of the Na₄ Cluster

The lowest excitation energies
In infinite system

\[ V(q) = \frac{4\pi}{q^2} \]

\[ f_{xc}(q) \to 1 / q^2 \text{ for } q \to 0 \]

But LDA/GGA fall off exponentially

**LRC**: long range correction

\[ f_{xc}(\mathbf{r}, \mathbf{r}') = -\frac{\alpha}{4\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \]
Optical Absorption of Solid Si

\[ E_{xc}^{HSE} = 0.25 E_{x}^{HF, SR}(\mu) + 0.75 E_{x}^{PBE, SR}(\mu) + E_{c}^{PBE, LR}(\mu) + E_{c}^{PBE} \]

\[ \mu \text{ is the range separation: } \frac{1}{r} = \frac{\text{erfc}(\mu r)}{r} + \frac{\text{erf}(\mu r)}{r} \]

PRB 78, 121201 (2008)
Optical Absorption of Semiconductors

PRB 78, 121201 (2008)
\[ \Sigma_{M}^{GW}(x_1, x_2) = 1 \]
References

- Hybertsen & Louie, PRB 34, 5390 (1986).

- Books on many-particle physics
Photoemission: Quasiparticle Gap

Electron addition/removing

$E_g = IP - EA$

Electron Affinity

$EA = E(N) - E(N+1)$

Ionization Potential

$IP = E(N-1) - E(N)$
Optical Absorption: Neutral Excitation

Optical Gap
Electron addition removing — exciton binding energy

\[ E_{\text{opt}}^g = E_g - E_{e-h} \]
\[ E_{e-h} \sim \frac{e^2}{2\varepsilon a_0} \]
Corresponding Green’s Functions

- **Quasiparticle gap** ➔ **One-particle Green’s function**
  Motion of added/removed electron

  \[ G(1,1') = -i \langle N | T[\psi(1)\psi^+(1')] | N \rangle \]

  where \((1,1') \equiv (rt,r't')\)

- **Optical gap** ➔ **Two-particle Green’s function**
  Motion of added/removed electron-hole pair

  \[ G(1,2,1',2') = (-i)^2 \langle N | T[\psi(1)\psi(2)\psi^+(2')\psi^+(1')] | N \rangle \]
Why Green’s Functions?

- **Physically-motivated approach**, based on responses to well-defined excitations of the system, that includes exact exchange and nonlocal, dynamical correlation effects.

- First-principles treatment allows **correlation effects** to be assessed in a variety of environments, including solids, surfaces, interfaces, clusters, and molecules.

- **Computationally**, more intensive than DFT, but scales better \((\sim N_G^4\), where \(N_G\) is number of plane waves\) than quantum chemistry methods.
Consider a system of $N$ electrons in its ground state and define a one-electron Green’s function

$$G(x_t, x'_t) = -i < N | T[\psi(x, t)\psi^+(x', t')] | N >$$

which can be rewritten in terms of eigenstates of $H$ for the $N+1$ or $N-1$ particles, i.e.

$$G(x, x', t - t') = -i \sum_i \phi_i(x)\phi_i^*(x')\exp[-i\varepsilon_i(t - t')]$$

$$\times (\theta(t - t')\theta(\varepsilon_i - \mu) - \theta(t'-t)\theta(\mu - \varepsilon_i))$$

where $\mu$ is the Fermi level (i.e. defining minimum energies for injection of electrons or holes)
Quasiparticle

Quasiparticle energies and states

Occupied states:

\[
\begin{align*}
\varepsilon_i &= E_0(N) - E_i(N-1), \\
\phi_i(\mathbf{r}) &= \langle N-1,i | \psi(\mathbf{r}) | N,0 \rangle
\end{align*}
\]

Empty states:

\[
\begin{align*}
\varepsilon_i &= E_i(N+1) - E_0(N), \\
\phi_i(\mathbf{r}) &= \langle N,0 | \psi(\mathbf{r}) | N+1,i \rangle
\end{align*}
\]

where

\[
\begin{align*}
E_0(N) & \quad \text{Ground state energy of N-particle system} \\
E_i(N-1) & \quad \text{Excited state } i \text{ of (N-1)-particle system} \\
\psi(\mathbf{r}) & \quad \text{Field operator}
\end{align*}
\]
Excitations of many-electron system can often be described in terms of weakly interacting "quasiparticles".

Quasiparticle (QP) = bare particle + polarization clouds.

\[ E^{QP} = E^0 + \Sigma \]

\( \Sigma \): response of system to the excitation (self-energy)
Quasiparticle Equation

Fourier transform of $G$

$$G(x, x', \omega) = \sum \frac{\phi_i(x)\phi_i^*(x')}{\omega - (\varepsilon_i \pm i\delta)}$$

Equation for $G$: (Derived from the Dyson’s equation)

$$(-\frac{1}{2} \nabla^2 + V^0)G(x, x', \omega) + \int \Sigma(x, x'', \omega)G(x'', x', \omega)dx'' = \delta(x - x')$$

Schrödinger-like equation for quasiparticles

$$(-\frac{1}{2} \nabla^2 + V^0)\phi_i(x) + \int \Sigma(x, x'', \varepsilon_i)\phi_i(x'')dx'' = \varepsilon_i\phi_i(x)$$
Quasiparticle Equation

Schrödinger-like equation for quasiparticles

\[ \left( -\frac{1}{2} \nabla^2 + V^0 \right) \phi_i(x) + \int \Sigma(x, x', \epsilon_i) \phi_i(x') dx' = \epsilon_i \phi_i(x) \]

Schrödinger-like Kohn-Sham equation

\[ \left( -\frac{1}{2} \nabla^2 + V^H + V^{xc} + V^{ext} \right) \phi_i(r) = \epsilon_i \phi_i(r) \]

Where the self-energy is independent of \( \epsilon_i \) and has the form

\[ \Sigma^{\text{DFT}}(x, x'; \epsilon_i) = V^{xc}(x') \delta(x - x') \]
GW Approximation for Self-Energy

The self-energy $\Sigma$ can be regarded as a dynamical, nonlocal exchange-correlation potential

$$\Sigma(x, x', \omega) = V^{XC}(x, x', \omega)$$

DFT (Static, local self-energy):  
$$\Sigma(x, x', \omega) = V^{XC}(n(x))\delta(x, x')$$

Hartree approximation:  
$$\Sigma(x, x', \omega) = 0$$

In GWA, the self-energy is approximated by a product of the Green’s function ($G$) and the dynamically screened Coulomb interaction ($W$):

$$\Sigma^{GW}(x, x', \omega) = \frac{i}{2\pi} \int W(x, x'; \omega')G(x, x'; \omega + \omega')\exp(i\delta\omega')d\omega$$
Quasiparticle Energies

Quasiparticle energies are computed to first order as

\[
E_{i}^{\text{QP}} \approx E_{i}^{\text{KS}} + Z_{i} \left\langle \psi_{i}^{\text{KS}} \mid \Sigma(x, x'; \epsilon_{i}^{\text{KS}}) - V_{\text{XC}}^{\text{KS}} \right\rangle \psi_{i}^{\text{KS}} \right)
\]

with

\[
Z_{i} = \left[ 1 - \frac{d \Sigma(x, x', \omega)}{d \omega} \right]_{\omega=\epsilon_{i}^{\text{KS}}}^{-1}
\]

where the self-energy operator \( \Sigma \) is approximated as

\[
\Sigma = iG_{0}W = iG_{0}\epsilon^{-1}V
\]

Green’s function from KS wavefunctions

Dielectric function within the RPA and the GPP model

and \( G \) is constructed from Kohn-Sham eigenvalues & eigenstates (independent particle \( G \))

\[
G = \sum \frac{\phi_{nk}(r)\phi_{nk}^{\ast}(r')}{E - \epsilon_{nk}}
\]
From Hedin’s Equation to GW Approximation

Equation of the Green’s function $G$:

$$\left(-\frac{1}{2}\nabla^2 + V^0\right)G(x,x',\omega) + \int \Sigma(x,x'',\omega)G(x'',x',\omega)dx'' = \delta(x - x')$$

Integral equations relating $G$, $\Sigma$, $\Gamma$, and $W$:

$$\Gamma(12;3) = \delta(12)\delta(13) + \int \frac{\delta \Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(67;3)d(4567)$$

$$\Sigma(12) = i\int W(1^+3)G(14)\Gamma(42;3)d(34)$$

$$W(12) = \nu(12) + \int W(13)P(34)\nu(42)d(34)$$

$$P(12) = -i\int G(23)G(42)\Gamma(34;1)d(34)$$

Hardin, PR139, A796 (1965)
Hedin’s GW approximation

\[ \Gamma(12;3) \equiv \delta(12)\delta(13) \quad \rightarrow \quad \text{Neglect vertex} \]

\[ \Sigma(12) \equiv iG(12)W(1^+2) \]

\[ W(12) \equiv v(12) + \int W(13)P(34)v(42)d(34) \]

\[ P(12) \equiv -iG(12)G(21) \quad \rightarrow \quad \text{RPA} \]

First-order expansion in screened Coulomb interaction $W$. Core electron polarization, and core electron screening, are neglected.
Screened Coulomb Interaction $W$

Short hand

$$W = \varepsilon^{-1} V^{\text{Coul}}$$

where epsilon is the full frequency dependent dielectric function

$$\varepsilon(r, r', \omega) = \delta(r - r') - \int V(r, r'') P(r'', r', \omega) dr''$$

where $V$ is the bare Coulomb potential and the (irreducible) polarizability is

$$P(r, r', \omega) = \sum_{nk,n'k'} \phi^*_n(r) \phi_{n'k'}(r) \phi^*_n(r') \phi_{nk}(r')$$

$$\times \left( \frac{f_{nk}(1 - f_{n'k'})}{\varepsilon_{nk} - \varepsilon_{n'k'} + \omega + i\delta} + \frac{f_{n'k'}(1 - f_{nk})}{\varepsilon_{n'k'} - \varepsilon_{nk} - \omega + i\delta} \right)$$
Short hand \( W = \varepsilon^{-1} V \)

where \( \varepsilon^{-1} = \varepsilon^{-1}(q, \omega) \)

The dielectric function is calculated in reciprocal space, within the Random Phase Approximation (RPA):

\[
W_{GG'}(q, \omega) = \varepsilon^{-1}_{GG'}(q, \omega)V_{G'}(q)
\]

\[
V_{G'}(q) = \frac{4\pi}{|q + G'|^2}
\]

Frequency-dependent dielectric matrix

Coulomb interaction
**Screened Coulomb Interaction** \( W \)

**Random Phase Approximation (RPA)**

\[
\varepsilon_{GG'}^{RPA}(q, \omega) = \delta_{GG'} - V_G(q) \chi_{GG'}^0(q, \omega)
\]

**Independent particle polarizability (Adler-Wiser form)**

\[
\chi_{GG'}^0(q, \omega) = 2 \sum_{nn'k} \langle n, k | e^{-i(q+G)\cdot r} | n', k + q \rangle \langle n', k + q | e^{i(q+G')\cdot r'} | n, k \rangle \frac{f(\varepsilon_{n', k+q}) - f(\varepsilon_{n, k})}{\varepsilon_{n', k+q} - \varepsilon_{n, k} - \omega - i\delta}
\]

**Ingredients:** Kohn-Sham eigenvalues and eigenstates
Static Dielectric Function

In practice, we first compute the static polarizability

\[ \chi_{GG'}^0(q, \omega = 0) = 2 \sum_{nn'kk'} \langle n, k | e^{-i(q+G) \cdot r} | n', k + q \rangle \langle n', k + q | e^{i(q+G') \cdot r'} | n, k \rangle \frac{f(\varepsilon_{n',k+q}) - f(\varepsilon_{n,k})}{\varepsilon_{n',k+q} - \varepsilon_{n,k}} \]

cutting off the sum to include only a finite (but sufficient) number of empty bands. We then construct

\[ \varepsilon_{GG'}^{RPA}(q,0) = \delta_{GG'} - V_G(q) \chi_{GG'}^0(q,0) \]

invert this matrix in G and G', and extend it to finite frequency using the generalized plasmon-pole model.
Dielectric Function with Finite Frequencies

- Static dielectric function $\varepsilon(q, \omega=0)$ is a ground-state property obtainable from DFT or DFPT within RPA or beyond.

- To evaluate the GW self-energy, we need $W$, the dynamically-screened Coulomb interaction. This is a convolution of $\varepsilon^{-1}(q, \omega)$ and the bare Coulomb potential $V(q)$.

- Thus, we need to capture the **frequency dependence** of the screening.

- Evaluating the frequency-dependence is computationally-expensive, and in practice, we find that $\varepsilon(q, \omega=0)$ can be extended to finite frequency using a **plasmon-pole model** (PPM).
Plasmon-Pole Model

Physical motivation: The loss function is a peaked function of $\omega$

\[ S(q,\omega) \propto \text{Im } \varepsilon^{-1}(q,\omega) = A_q \left\{ \delta(\omega - \tilde{\omega}_q) \right\} \]

The peaks are dictated by the plasmon dispersion, $\omega(q)$


\[ \text{Im } \varepsilon^{-1}_{G,G'}(q,\omega) = A_{G,G'}(q) \left\{ \delta(\omega - \tilde{\omega}_{G,G'}(q)) \right\} \]

\[ \text{Re } \varepsilon^{-1}_{G,G'}(q,\omega) = \delta_{G,G'} + \frac{\Omega_{G,G'}^2}{\omega^2 - \tilde{\omega}_{G,G'}^2(q)} \]

Parameters $A$, $\omega$, and $\Omega$ are fixed by KK relations and the f-sum rule.

Hybertsen & Louie, PRB 34, 5390 (1986)
KK relations & \( f \)-sum rule

For a complex function \( \chi(\omega) = \chi_1(\omega) + i\chi_2(\omega) \) of the complex variable \( \omega \), analytic in the upper half plane of \( \omega \) and which vanishes faster than \( 1/|\omega| \) as \( |\omega| \to \infty \), the Kramers–Kronig relations are given by

\[
\chi_1(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{\omega' - \omega} \, d\omega' \quad \text{and} \quad \chi_2(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{\omega' - \omega} \, d\omega'
\]

where \( P \) denotes the Cauchy principal value.

**Thomas-Reiche-Kuhn (f-)sum rule**

\[
\sum_n (E_0 - E_n) \left| \langle n | x | 0 \rangle \right|^2 = \frac{\hbar^2}{2m}
\]

Oscillator strength \( f \):

\[
f_{12} = \frac{2m_e}{3\hbar^2} (E_2 - E_1) \sum_{m_2} \sum_{\alpha=x,y,z} \left| \langle 1m_1 | R_\alpha | 2m_2 \rangle \right|^2
\]
Plasmon-Pole Model

Plasmon-pole frequency

\[ \tilde{\omega}^2_{GG'}(q) = \frac{\Omega^2_{GG'}(q)}{\delta - \text{Re} \varepsilon^{-1}_{GG'}(q,0)} \]

Bare plasma frequency

\[ \Omega^2_{GG'}(q) = \omega_p^2 \frac{(q + G) \cdot (q + G')}{|q + G|^2} \frac{\rho(G - G')}{\rho(0)} \]

The Amplitude \( A \) can be determined as

\[ A_{GG'}(q) = -\frac{\pi}{2} \frac{\Omega_{GG'}(q)}{\tilde{\omega}_{GG'}(q)} \]
GW Self-Energy $\Sigma$

GW Self-Energy

$$\Sigma = \Sigma_x + \Sigma_{sx} + \Sigma_{ch}$$

Bare exchange: Fock term

Screened exchange: Poles of G

Coulomb-hole: Poles of W

Screened-exchange ($X+SX$)

$$\Sigma_{nk}^{SX}(E_{nk}) = \langle n,k | \Sigma_{nk}^{SX}(r,r';E_{nk}) | n,k \rangle$$

$$= - \sum_{n_1,q,G,G'} \langle n,k | e^{-i(q+G)\cdot r} | n_1,k-q \rangle \langle n_1,k-q | e^{-i(q+G')\cdot r'} | n,k \rangle \left[ 1 + \frac{\Omega_{GG'}^2(q)}{(E_{nk} - \epsilon_{n_1k-q})^2 - \tilde{\omega}_{GG'}^2(q)} \right] v(q+G')$$

Coulomb-Hole (CH)

$$\Sigma_{nk}^{CH}(E_{nk}) = \langle n,k | \Sigma_{nk}^{CH}(r,r';E_{nk}) | n,k \rangle$$

$$= - \sum_{n_1,q,G,G'} \langle n,k | e^{-i(q+G)\cdot r} | n_1,k-q \rangle \langle n_1,k-q | e^{-i(q+G')\cdot r'} | n,k \rangle \left[ \frac{\Omega_{GG'}^2(q)}{2\tilde{\omega}_{GG'}(q)(E_{nk} - \epsilon_{n_1k-q} - \tilde{\omega}_{GG'}(q))} \right] v(q+G')$$
The self-energy is, in general, a complex non-Hermitian operator.

The real part gives quasiparticle correction to the DFT energies, and the imaginary part is related to the quasiparticle lifetime. Here, we focus only on Re[$\Sigma$]. The GPP model prevents us from inferring much about Im[$\Sigma$].

In principle, the quasiparticle equations are coupled nonlinear equations and should be solved self-consistently.

In practice, off-diagonal corrections are relatively small, and we just compute the first-order correction to the Kohn-Sham energies.

Self-consistent GW calculations can be done self-consistently, although it is very expensive, and its merits are an issue of current debate in the literature.

GW with the vertex correction: computationally demanding and often overestimates the band gap.
Dynamic Dependence of GW Self-Energy

For this discussion, we neglect off-diagonal corrections.

First-order correction depends on the quasiparticle eigenvalue

\[ E_{i}^{\text{QP}} \approx E_{i}^{\text{KS}} + \left\langle \psi_{i}^{\text{KS}} \left| \Sigma(x, x'; E_{i}^{\text{QP}}) - V_{\text{XC}}^{\text{KS}} \right| \psi_{i}^{\text{KS}} \right\rangle \]

In principle, this is a nonlinear equation that should be solved self-consistently. However, in practice, linearization is sufficient:

\[ \Sigma_{i}(E_{i}^{\text{QP}}) \approx \Sigma_{i}(E_{i}^{\text{KS}}) + \left( E_{i}^{\text{QP}} - E_{i}^{\text{KS}} \right) \frac{d\Sigma_{i}(\omega)}{d\omega} \bigg|_{E_{i}^{\text{KS}}} \]
Dynamic Dependence of GW Self-Energy

Defining the renormalization constant $Z_i$, we have

$$Z_i = \left[ 1 - \frac{d\Sigma(x, x', \omega)}{d\omega} \right]_{\omega = E_i^{KS}}^{-1}$$

The self-energy can be expressed in terms of the DFT states & energies as

$$E_i^{QP} \approx E_i^{KS} + Z_i \left\langle \psi_i^{KS} \left| \Sigma(x, x'; \epsilon_i^{KS}) - V_{XC}^{KS} \right| \psi_i^{KS} \right\rangle$$

Comments

$\frac{d\Sigma}{d\omega}$ in $Z_i$ is evaluated by finite differences, and is typically quite small. The Green’s function can be iterated, and $\Sigma$ recomputed, to further check that this procedure results in small changes in QP energies.
Neutral (Electron-Hole) Excitations

Optical excitations

\[ \epsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_s |M|^2 \delta(\omega - \Omega_s) \]

Optical gap $\Rightarrow$ Two-particle Green’s function

\[ G(1,2,1',2') = (-i)^2 \langle N | T[\psi(1)\psi(2)\psi^+(2')\psi^+(1')] | N \rangle \]
Bethe-Salpeter Formalism

Seek solutions to the BSE of the form

\[ |S\rangle = \sum_{vc,k} A_{vc,k}^S |vc,k\rangle \]

where \( |vc,k\rangle \) is taken as the product of occupied & empty quasiparticle states in the Tamm-Dancoff approximation.

This puts the BSE in the following form:

\[
(E_{ck} - E_{vk}) A_{vc,k}^S + \sum_{v'c',k'} \langle vc,k | K^{eh} | v'c',k' \rangle A_{v'c',k'}^S = \Omega_s^S A^S_{vc,k}
\]

where \( \Omega_s \) is the excitation energy of the state S
Bethe-Salpeter Formalism

Bethe-Salpeter equation (BSE)

\[ L(1,2;1',2') = G_1(1,2')G_1(2,1') + \int G_1(1,3)G_1(4,1')K^{eh}(3,5;4,6)L(6,2;5,2')d(3456) \]

where

\[ L(1,2;1',2') = -G_2(1,2;1',2') + G_1(1,1')G_1(2,2') \]

Electron-Hole correlation function

\[ K^{eh}(3,5;4,6) = \frac{\delta[V(3)\delta(3,4) + \Sigma(3,4)]}{\delta G_1(6,5)} \]

Electron-Hole interaction kernel

\[ G_2(1,2;1',2') = (-i)^2 \langle N | T[\psi(1)\psi(2)\psi^+(2')\psi^+(1')] | N \rangle \]

\[ G_1(1,1') = -i\langle N | T[\psi(1)\psi^+(1')] | N \rangle \]
Effective Two-Particle Interaction

Electron-hole interaction kernel

\[ K^{eh}(3,5;4,6) \approx K^x(3,5;4,6) + K^d(3,5;4,6), \quad \Sigma = iGW \]

- **“Exchange” term**: Bare Coulomb interaction (spin-singlet, spin-triplet splitting, etc)
- **“Direct” term**: Screened Coulomb interaction

**Comments**

As before, \( W \) is the fully dynamically-screened Coulomb interaction. However, in practice, since the exciton binding energies are much smaller than the typical plasmon energies, only static screening \( \varepsilon^{-1}(q,0) \) is used.
2-particle Green’s function

\[ G(1,2,1',2') = (-i)^2 \langle N \mid T[\psi(1)\psi(2)\psi^+(2')\psi^+(1')] \mid N \rangle \]

Define the expectation value

\[ \chi_S(x,x') = \langle N,0 \mid \psi^+(x')\psi(x) \mid N,S \rangle \]

Expand these functions in terms of single-particle states

\[ \chi_S(x,x') = \sum_v \sum_c A_v^c \psi_c(x)\psi_v^*(x') + B_v^c \psi_v(x)\psi_c^*(x') \]

Rewrite the ‘L’s’ in the BSE

\[ L(1,2;1',2') \rightarrow \chi_S(x,x') \]

Simplification of the Bethe-Salpeter Equation

Seek solutions to the BSE of the form

\[ |S\rangle = \sum_{vck} A_{vck}^S |vck\rangle \]

where \( |vck\rangle \) is taken as the product of occupied & empty quasiparticle states in the Tamm-Dancoff approximation.

This puts the BSE in the following form:

\[
(E_{ck} - E_{vk}) A_{vck}^S + \sum_{v'c'k'} \langle vck | K^{eh} | v'c'k' \rangle A_{v'c'k'}^S = \Omega_s^S A_{vck}^S
\]

where \( \Omega_s \) is the excitation energy of the state \( S \)
Optical Absorption ASpectra

Imaginary part of the transverse dielectric function:

$$\varepsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum \left| \overrightarrow{\lambda} \cdot \langle 0 | \overrightarrow{v} | S \rangle \right|^2 \delta(\omega - \Omega_S)$$

$$\overrightarrow{\lambda} = A / \overrightarrow{A}$$

Polarization vector

$$\overrightarrow{v} = i / \hbar [H, \overrightarrow{r}]$$

Single-particle velocity operator

Same thing, without electron-hole interactions:

$$\varepsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_{vc} \left| \overrightarrow{\lambda} \cdot \langle v | \overrightarrow{v} | c \rangle \right|^2 \delta(\omega - (E_c - E_v))$$

BSE optical transition matrix elements:

$$\langle 0 | \overrightarrow{v} | S \rangle = \sum_v \sum_c A_{vc}^S \langle v | \overrightarrow{v} | c \rangle$$

Coherent sum of matrix elements of contributing electron-hole transitions
GW code is often implemented in the frequency-reciprocal space with a plane wave basis and norm-conserving pseudopotentials.

- **Applicability**: Bulk systems, surfaces, clusters; ~100 atoms.

- **Input**: KS wavefunctions (of occupied and many unoccupied bands) for a converged ground state system.

- **Approximations**: GW, RPA and plasmon-pole model for the dielectric function.
GW Implementation

DFT \{\phi_{nk}, E_{nk}\} →

RPA \varepsilon^{-1}(q,0) →

\Sigma = iGW →

- SCF for ground-state (PW, NC-PPs)
- NSCF for 100’s of empty states

- Computes \chi_0(q) for G, G’
- Inverts for \varepsilon^{-1}(q) for each G, G’

- Forms matrix elements to compute \Sigma, including GPP
- Outputs \Sigma – V_{xc} for specified nk
BSE Implementation

RPA $\varepsilon^{-1}(\mathbf{q},0)$

- Computes $\chi_0(\mathbf{q})$ for $G$, $G'$
- Inverts for $\varepsilon^{-1}(\mathbf{q})$ for each $G$, $G'$

$\Sigma = iGW$

- Forms matrix elements to compute $\Sigma$, including GPP
- Outputs $\Sigma - V_{xc}$ for specified nk
  (eqp.corrections file)

$K^{eh}$, $\varepsilon_2(\omega)$

- Forms electron-hole kernel using static longitudinal dielectric function $\varepsilon^{-1}(\mathbf{q})$
- Outputs two-particle excitation energies and transverse $\varepsilon_2(\omega)$
GW/BSE Scaling Within a Planewave Implementation

**GW:** the Main cost is generating the dielectric function

- Generating $\chi_0 \sim N_G$
- Inverting $\varepsilon_{G,G'} \sim (N_G)^3$
- Total scaling $\sim (N_G)^4$

**BSE:** the QP corrections

- Diagonalization of BSE Hamiltonian
- Hamiltonian $\sim N_k \times N_{\text{cond}} \times N_{\text{val}}$, in principle, $N_{\text{cond}}$ and $N_{\text{val}}$ are small
- Need a **fine** $k$-mesh; cost of diagonalization $\sim (N_k)^3$
Band Gap and Band Energy Differences

**GW improves on the DFT gap problem** Gaps in garden variety semiconductors and insulators are under-estimated by 30~50%.

<table>
<thead>
<tr>
<th>Material</th>
<th>LDA (eV)</th>
<th>GWA$^\text{(a)}$ (eV)</th>
<th>Exp (eV)</th>
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<td>Diamond</td>
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<td>5.6</td>
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<td>Silicon</td>
<td>0.52</td>
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<td>~0</td>
<td>0.75</td>
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<tr>
<td>LiC</td>
<td>6.0</td>
<td>9.1</td>
<td>9.4</td>
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Band energy difference between high symmetry points (in eV)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>LDA (eV)</th>
<th>GWA (eV)</th>
<th>Exp (eV)</th>
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<tr>
<td>Ge</td>
<td>Γ$<em>{8v}$→Γ$</em>{7c}$</td>
<td>-0.26</td>
<td>0.85</td>
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<td>Γ$<em>{8v}$→X$</em>{5c}$</td>
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<td>1.09</td>
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<td></td>
<td>Γ$<em>{8v}$→L$</em>{6c}$</td>
<td>-0.05</td>
<td>0.73</td>
</tr>
<tr>
<td>GaAs</td>
<td>Γ$<em>{8v}$→Γ$</em>{7c}$</td>
<td>0.13</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>Γ$<em>{8v}$→X$</em>{5c}$</td>
<td>1.21</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>Γ$<em>{8v}$→L$</em>{6c}$</td>
<td>0.70</td>
<td>1.75</td>
</tr>
</tbody>
</table>


Hybertsen & Louie, PRB 34, 5390 (1986)
Band Structure of Copper

Onida, Reining, Rubio, RMP 74, 6015 (2002)
FIG. 1 (color online). Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface.
Benzene/Graphite Interface

\( E - E_F \) (eV)

-4
-2
0
2
4

\( \Gamma \)

\( \pi \)

\( \pi^* \)

\( K' \)

\( \Gamma \)

LDA

GW

\( \pi \)

\( \pi^* \)

Gas phase

PRL 97, 216405 (2006)
Optical Absorption Spectra

Si

PRL 88, 066404 (2002)
Optical Absorption Spectra

SiO$_2$

PRL 95, 156401 (2005)
FIG. 1. Ball-and-stick models of silicon nanowires (SiNWs) along the [110] (right) and [111] (left) directions viewed from the top (upper panels) and the side (lower panels). Filled circles stand for Si atoms, and open circles for H atoms.

FIG. 2 (color online). LDA band gaps calculated for [110] (empty squares) and [111] (empty circles) wires, and the GW-corrected gaps (filled squares) for the two thinnest [110] wires and bulk Si, compared with the measured gaps for [112] wires (+) and a [110] wire (*). The dotted, dashed, and long-dashed lines are fitted to the data points (see text). The LDA band gap of bulk Si is indicated by the solid line, and the bulk GW gap is marked around $d = 8.0$ nm for convenience.

Zhao et al., PRL92, 236805 (2004)
Si Nanowires

Solid symbols: GW
Open symbols: LDA

Yan et al., PRB 76, 115319 (2007)
FIG. 3. Absorption spectrum of the silicon nanowire calculated with a smearing width of 0.1 eV. The arrows marked by $A$ and $A_1$ indicate the fundamental gap and the lowest-energy exciton locations, respectively. The extremely small absorption for polarization perpendicular to the axis illustrates the depolarization effect.

FIG. 4. (Color online) The density of the electron for several excitonic states with the hole fixed at the center of the wire between two nearest-neighbor Si atoms. From top to bottom, four representative states are shown with energy values of 2.1 eV, 3.3 eV, 4.2 eV, and 4.2 eV, respectively. Corresponding cross-section plots on the $xz$ plane are shown on the right, while the three-dimensional plots for the same data are shown on the left. Lengths are in atomic units.

Yang et al., PRB75, 186401 (2008)
Graphene Nanoribbon

Armchair

Zigzag

Yang et al., PRL99, 186801 (2007)
Graphene Nanoribbon

FIG. 2 (color online). (a) Optical absorption spectra, (b) density of excited states, (c) absorbance of graphene with and without excitonic effects included; and (d) comparison with experiments. In (d), rough colored curves within the small rectangular box are measurements from Ref. [11], and open circles are from those from Ref. [10].

FIG. 4 (color online). (a) Absorbance of bilayer graphene and (b) imaginary part of the dielectric function of graphite with and without excitonic effects included. Experiment data of graphite [29] are included in (b).

Yang et al., PRL103, 186802 (2009)
Self-Consistency in GW

\[ \Sigma^{GW} (x, x', \omega) = \frac{i}{2\pi} \int W(x, x'; \omega') G(x, x'; \omega + \omega') \exp(i\delta\omega') d\omega \]

\[ (-\frac{1}{2} \nabla^2 + V^0) G(x, x', \omega) + \int \Sigma(x, x'', \omega) G(x'', x', \omega) dx'' = \delta(x - x') \]

\( G_0 W_0 \): NO self-consistency, using \( G_0 \) and \( W_0 \) constructed from KS wave functions and eigenvalues.

Why NOT going beyond \( G_0 W_0 \):

- Large computational cost: a formidable task.
- A full self-consistent solution often **worsens** band structures.
- Better results from \( G_0 W_0 \) than self-consistent \( GW \) is due to an error cancellation between the dressing of Green functions and the vertex corrections.
- Levels of self-consistency: \( G_0 W_0 \) → \( GW_0 \) → \( GW \)
GW Vertex Correction

\[ \Gamma(12;3) = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(67;3)d(4567) \]

**GW**T: including the vertex gamma, which is expressed in terms of functional derivative \( \delta V_{xc}/\delta \rho \)

DFT-Based

**GW**T:

\[ \Gamma = \frac{1}{1 - f_{xc}P_0}, \]

\[ W = W_1 = \frac{(1 - f_{xc}P_0)v}{1 - (v + f_{xc})P_0}, \quad G = G_0 \]

\[ \Sigma = iG_0W_1\Gamma = iG_0\frac{v}{1 - (v + f_{xc})P_0} \]

Onida, Reining, Rubio, RMP 74, 6015 (2002)
GW Vertex Correction

**Systematic $GWT$**: iterative solution of Hedin’s equations.

\[
\Gamma^{(n+1)}(123) = \delta(12) \delta(13) + \int d(4567) \frac{\delta \Sigma^{(n)}(12)}{\delta G^{(n-1)}(45)}
\times G^{(n)}(46) G^{(n)}(75) \Gamma^{(n+1)}(673)
\]

The lowest-order version:

\[
\Gamma^{(2)}(123) = \delta(12) \delta(13) + \int d(4567) \frac{\delta \Sigma^{(1)}(12)}{\delta G^{(0)}(45)}
\times G^{(1)}(46) G^{(1)}(75) \Gamma^{(2)}(673).
\]

- The second equation is the starting point for the Bethe-Salpeter equation.
- Practically, very few systematic $GWT$ calculations for real materials.

Schindlmayr and Godby, PRL **80**, 1702 (1998)
## Self-Consistent GW Calculations

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>$G_0W_0$</th>
<th>$GW_0$</th>
<th>$GW$</th>
<th>Expt.</th>
<th>$a$</th>
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<td>MRE</td>
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<td>−9.8%</td>
<td>−3.6%</td>
<td>4.7%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PRB 8075, 235102 (2007)
Si/SiO₂ Interface

TABLE I. Quasiparticle corrections (in eV) at the VBM ($\delta E_v$), at the CBM ($\delta E_c$), and for the band gap ($\delta E_g$) for Si and c-SiO₂. The corrections are calculated within $GW$ using the PPMs proposed by Hybertsen and Louie (HL) [27], von der Linden and Horsch (vdLH) [28], Godby and Needs (GN) [29], Engel and Farid (EF) [30], and without PPM.

<table>
<thead>
<tr>
<th></th>
<th>HL</th>
<th>vdLH</th>
<th>GN</th>
<th>EF</th>
<th>no PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$\delta E_v$</td>
<td>-0.6</td>
<td>-0.6</td>
<td>-0.4</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td>$\delta E_c$</td>
<td>+0.1</td>
<td>+0.1</td>
<td>+0.2</td>
<td>+0.1</td>
</tr>
<tr>
<td></td>
<td>$\delta E_g$</td>
<td>+0.7</td>
<td>+0.7</td>
<td>+0.6</td>
<td>+0.7</td>
</tr>
<tr>
<td>c-SiO₂</td>
<td>$\delta E_v$</td>
<td>-2.6</td>
<td>-2.5</td>
<td>-2.0</td>
<td>-2.3</td>
</tr>
<tr>
<td></td>
<td>$\delta E_c$</td>
<td>+1.3</td>
<td>+1.1</td>
<td>+1.5</td>
<td>+1.2</td>
</tr>
<tr>
<td></td>
<td>$\delta E_g$</td>
<td>+3.9</td>
<td>+3.6</td>
<td>+3.5</td>
<td>+3.5</td>
</tr>
</tbody>
</table>

QSGW: quasiparticle self-consistent $GW$

GWΓ: $GW$ with the vertex correction

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TABLE II. Quasiparticle corrections (in eV) at the VBM ($\delta E_v$), at the CBM ($\delta E_c$), and for the band gap ($\delta E_g$) for Si, c-SiO₂, and s-SiO₂. The corrections are calculated within $GW$, GWT, and QSGW.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>c-SiO₂</th>
<th>s-SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta E_v$</td>
<td>$GW$</td>
<td>GWT</td>
<td>QSGW</td>
</tr>
<tr>
<td>$\delta E_c$</td>
<td>$GW$</td>
<td>GWT</td>
<td>QSGW</td>
</tr>
<tr>
<td>$\delta E_g$</td>
<td>$GW$</td>
<td>GWT</td>
<td>QSGW</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>HL</th>
<th>vdLH</th>
<th>GN</th>
<th>EF</th>
<th>no PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$\delta E_v$</td>
<td>-0.4</td>
<td>+0.1</td>
<td>-0.6</td>
<td>-1.9</td>
</tr>
<tr>
<td></td>
<td>$\delta E_c$</td>
<td>+0.2</td>
<td>+0.7</td>
<td>+0.2</td>
<td>+1.5</td>
</tr>
<tr>
<td></td>
<td>$\delta E_g$</td>
<td>+0.6</td>
<td>+0.6</td>
<td>+0.8</td>
<td>+3.4</td>
</tr>
</tbody>
</table>

TABLE III. Quasiparticle band offsets (eV) for cubic and strained SiO₂ using $GW$, GWT, and QSGW.

<table>
<thead>
<tr>
<th></th>
<th>Cubic</th>
<th>Strained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model</td>
<td>DFT $GW$</td>
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<tr>
<td>VBO</td>
<td>I</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>2.5</td>
</tr>
<tr>
<td>CBO</td>
<td>I</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.8</td>
</tr>
</tbody>
</table>