GW Many-Body Theory for Electronic Structure

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ETSF
Outline

• Lecture 1 (Monday)
  – Introduction to MBPT
  – The $GW$ approximation (non-SC and SC)
  – Implementation of $GW$
  – Spectral properties
• Lecture 2 (Tuesday)
  – $GW$ total energy
  – Self-consistency in $GW$
  – Vertex corrections beyond $GW$
  – Using MBPT to get better DFT functionals
• Workshop talk
  – $GW$-like approaches to quantum transport
The Basic Problem

- Electrons interact with each other as well as with the nuclei!
Quantum Mechanics

- One-electron Schrödinger equation:
  \[
  -\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r) \psi(r) = E \psi(r)
  \]
Approaches to the electron-electron interaction

- **Density-functional theory** (for ground-state properties only):
  \[
  \left[-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) - \varepsilon_i\right] \psi_i(\mathbf{r}) = 0
  \]

- **Many-body perturbation theory** based on Green’s functions:
  \[
  \left[-\frac{1}{2} \nabla^2 + V_{\text{ext}} + V_{\text{Hartree}} + \Sigma_{\text{xc}}(\omega) - \omega\right] G(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}')
  \]
  (which, *inter alia*, leads to the quasiparticle equation
  \[
  \left[-\frac{1}{2} \nabla^2 + V_{\text{ext}} + V_{\text{Hartree}} + \Sigma_{\text{xc}}(\varepsilon) - \varepsilon\right] \varphi(\mathbf{r}) = 0
  \]

Note the two ways of describing exchange and correlation:

In DFT: \( V_{\text{xc}}(\mathbf{r}) \) (local, energy-independent potential)

In many-body theory: \( \Sigma_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \) (non-local, energy-dependent potential)
Why Not Just Leave it to DFT?
Some Pathologies of the KSDFT functional

- Band-gap problem: \[ V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \]
is discontinuous (by a constant) when an electron is added to an insulator (Sham and Schlüter, Perdew and Levy 1983)

- Widely separated open-shell atoms: \( V_{xc}(\mathbf{r}) \) has a peculiar spatial variation between distant atoms so as to equalise highest occupied states (Almbladh and von Barth 1985)

- Exchange-correlation “electric field” accompanies real electric field in an insulator (Godby and Sham 1994, Gonze, Ghosez and Godby 1995)
Why Not Just Leave it to DFT?

- DFT functionals are known to have important pathologies, meaning that \textit{density-based} approximate functionals can be inadequate.
- MPBT quantities better behaved.
- MBPT role in analysing existing functionals and devising new ones (e.g. orbital functionals).
- Access to excited-state properties, some of which are inaccessible or inaccurate in (TD)DFT.
- Accurate ground-state quantities also available.
MBPT vs. (TD)DFT
MBPT vs. TDDFT

Many-body perturbation theory (e.g. $GW$)

- Based on Green’s functions
- Self-energy theories give one-particle $G$, e.g. electron addition/removal
- Natural domain: quasiparticle energies, band structure, spectral function
- Similar diagrammatic theories for two-particle $G$, e.g. optical absorption
- Other applications: ground state total energy, etc.
MBPT vs. TDDFT (2)

DFT

- Natural domain (of ordinary DFT): ground state total energy
- TDDFT permits study of time-evolution (e.g. excited states) of \( N \)-electron system
- Treatment of exchange and correlation in TDDFT requires some approximation, often based on the HEG / WIEG
## Pros and Cons

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>DFT / TDDFT</td>
<td>Inexpensive (esp. density-based functionals)</td>
<td>XC functional and $f_{xc}(r,r',\omega)$ pathological and can be difficult to approximate sufficiently accurately</td>
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<tr>
<td>[Intermediate approaches such as $GW$-based orbital functionals (KS/GKS)]</td>
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<tr>
<td>GW (+ MBPT)</td>
<td>Description of XC explicit diagrammatic series, better behaved</td>
<td>Can be expensive</td>
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</table>
Introduction to Many-Body Perturbation Theory
Electronic Excitations: $G_1$ and $G_2$

$| N,0 \rangle$  $| N+1,s \rangle$  $| N-1,s \rangle$  $| N,s \rangle$
Key ideas of many-body perturbation theory

- Electronic and optical experiments often measure some aspect of the one-particle Green’s function.
- The spectral function, \( \text{Im } G \), tells you about the single-particle-like approximate eigenstates of the system: the quasiparticles.

- \( G \) obtained from self-energy \( \Sigma(r, r', E) \)
- \( \Sigma = GW + O(W^2) \); \( W \) = screened Coulomb interaction
Second Quantisation

• Field operators add/remove an electron at \( r \) with spin \( \sigma \) \( (x=r,\sigma) \) at time \( t \)

\[ \hat{\psi}^\dagger(x,t) ; \hat{\psi}(x,t) \]

• Defined rigorously in terms of operation on Slater determinants

• Have equations of motion in the Heisenberg representation that follows from the TDSE
One-particle Green's function

\[ G(x, x'; t - t') \equiv -i \langle N | T[\hat{\psi}(x, t)\hat{\psi}^+(x', t')] | N \rangle \]

where \( x \equiv (r, \xi) \) is space+spin, \( |N\rangle = N\)-electron ground state, \( T \) = time-ordering operator
$G(x, x'; t - t') \equiv -i \langle N T[\hat{\psi}(x, t)\hat{\psi}^+(x', t')] | N \rangle$
Equation of Motion of $G$

- Using equation of motion of field operators, $G$ can be shown to satisfy

\[
\left( i \frac{\partial}{\partial t} - h(x) \right) G(xt; x't') + i \int v(r, r') \left< N \left| T [\hat{\psi}^\dagger \hat{\psi} \hat{\psi} \hat{\psi}^\dagger] \right| N \right> d^4x
\]

\[
= \delta(x - x') \delta(t - t')
\]

- defines $\Sigma$

- Then write $\Sigma \equiv V_H + \Sigma_{xc}$
Green's Functions and Self-Energies

• $G$ obeys a very similar equation to the Green’s function of the Kohn-Sham electrons in DFT, but with the non-local, time-dependent $\Sigma$ replacing $V_{xc}$:

$$\begin{align*}
\left(i \frac{\partial}{\partial t} - \left\{ h + V_H + \Sigma_{xc} \right\} \right) G(xt; x't') &= \delta(x-x') \delta(t-t') \\
\left(i \frac{\partial}{\partial t} - \left\{ h + V_H + V_{xc} \right\} \right) G_{KS}(xt; x't') &= \delta(x-x') \delta(t-t')
\end{align*}$$
Lehmann Representation for $G$

$$G(r, r', \omega) = \sum_{s} \frac{f_s(r)f_s^*(r')}{\omega - \varepsilon_s + i\delta}, \quad \varepsilon_s \leftrightarrow \mu$$

$$f_s(r) = \begin{cases} 
\langle N|\hat{\psi}(r)|N+1, s \rangle, & \varepsilon_s = E_{N+1,s} - E_N (> \mu) \\
\langle N-1, s|\hat{\psi}(r)|N \rangle, & \varepsilon_s = E_N - E_{N-1,s} (< \mu) 
\end{cases}$$

- $s$ labels the excited states of the $N+1$ or $N-1$-electron systems
- $G$ has its poles at each energy with which an electron can be added/removed
Our “Cast of Players”

- \( G \) – Green’s function
- \( \Sigma_{xc} \) – **Self-energy** (related to \( G \) as discussed)
- \( W \) – Dynamically screened Coulomb interaction
- \( P \) – Irreducible polarisation propagator
- \( \Gamma \) – Vertex function
Hedin’s Equations

\[
\begin{align*}
\Sigma (1, 2) &= i \int W \left(1^+, 3\right) G (1, 4) \Gamma (4, 2, 3) \, d (3, 4) \\
P (1, 2) &= -i \int G (2, 3) G (4, 2) \Gamma (3, 4, 1) \, d (3, 4) \\
W (1, 2) &= v (1, 2) + \int W (1, 3) P (3, 4) v (4, 2) \, d (3, 4) \\
\Gamma (1, 2, 3) &= \delta (1, 2) \delta (1, 3) \\
&\quad + \int \frac{\delta \Sigma (1, 2)}{\delta G (4, 5)} G (4, 6) G (7, 5) \Gamma (6, 7, 3) \, d (4, 5, 6, 7)
\end{align*}
\]

- With $\Sigma/G$ relation, exact closed equations for $G, \Sigma$ etc.
The GW Approximation
The GW Approximation

• Iterate Hedin’s equations once starting with $\Sigma=0$

\[
\begin{align*}
\Sigma(1,2) &= i \int W(1^+,3) G(1,4) \Gamma(4,2,3) \, d(3,4) \\
\Gamma(1,2) &= -i \int G(2,3) G(4,2) \Gamma(3,4,1) \, d(3,4) \\
W(1,2) &= \nu(1,2) + \int W(1,3) P(3,4) \nu(4,2) \, d(3,4) \\
\Gamma(1,2,3) &= \delta(1,2) \delta(1,3) \\
&\quad + \int \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3) \, d(4,5,6,7)
\end{align*}
\]
The \( \text{GW} \) Approximation

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

where \( x \equiv (r, \xi) \) is space+spin

In the time domain
\[
\Sigma(x, x'; t - t') = iW(x, x'; t - t')G(x, x'; t - t')
\]

\( W \) is the dynamically screened Coulomb interaction between electrons
Implementation of GW
Local-density-approximation calculation of one-electron wavefunctions and eigenvalues, using \textit{ab initio} pseudopotentials

- Compute Green's function $G$
- Compute screened Coulomb interaction $W$
- Compute self-energy $\Sigma(r,r',\omega)$
- Solve Dyson equation to obtain updated Green's function $G(r,r',\omega)$

Space-time method:
Spectral Properties
Figure 3: Comparison of characteristic direct and indirect LDA, GWA, and experimental energy gaps for all semiconductors and insulators for which first-principles GWA calculations have been reported. GWA corrects most of the LDA band gap underestimation over more
Self-Consistency

\[ \Sigma = iGW \]

Partially self-consistent

\[ \Sigma = iGW \]

Conserving

Non-self-consistent

\[ \Sigma = iG \]

Non-conserving

Kris Delaney
Tests for Be atom (QP energies)

<table>
<thead>
<tr>
<th>Method</th>
<th>All-electron</th>
<th>Pseudopotential</th>
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<tbody>
<tr>
<td>DFT-LDA</td>
<td>5.43</td>
<td>5.43</td>
</tr>
<tr>
<td>$G_0W_0$</td>
<td>9.25 ± 0.01</td>
<td>9.24 ± 0.01</td>
</tr>
<tr>
<td>$GW_0$</td>
<td>8.75 ± 0.01</td>
<td>8.75 ± 0.01</td>
</tr>
<tr>
<td>$GW$</td>
<td>8.47 ± 0.01</td>
<td>8.64 ± 0.01</td>
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Total Energy from Many-Body Perturbation Theory
**Ab initio GW total energy**

- Galitskii-Migdal expression for ground-state total energy

\[ E = \frac{1}{2} \int d\omega \int d^3r (\omega + h(r)) A(r, r', \omega)_{r' \rightarrow r} + V_{\text{nucl}} \]

- Start with LDA calculation
- Use GW space-time method to calculate self-energy \( \Sigma(r, r', it) \) using a double grid in real space, and a grid in imaginary time
- Calculate new Green’s function using

\[ G = \left(1 - G_0(\Sigma - V_{\text{xc}}^{\text{LDA}})\right)^{-1} G_0 \]

- Recalculate \( \Sigma \) using new \( G \) and new \( W \) (based on new \( G \))
- Repeat to self-consistency
- Calculate total energy using self-consistent \( G \)
Van der Waals forces

\[ e_c(d) \text{ (mHa/e)} \]

\[ e_x(d) \]

LDA

GW

RPA

\[ d \text{ (a.u.)} \]

Pablo García-González and RWG, PRL 2002
Vertex Corrections
Beyond GW
The Vertex

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

- \( \Sigma = GW \Gamma \) is exact by definition
- Vertex function \( \Gamma \) needs to be approximated; in \( GW \) start with \( \Sigma = 0 \)
- Can also start with \( \Sigma = \) simplified self-energy; simplest of all is \( V_{xc}^{LDA} \)
DFT-based Vertex

- (A)LDA vertex in $W(G_0 W_0^{\text{LDA}})$ yields slight improvement over $G_0 W_0$
- If ALDA vertex is also added into $\Sigma$, things get much worse!

Morris, Stankovski, Rinke, Delaney, RWG, PRB 2007

Morris, Stankovski et al.
DFT-based Vertex (2)

- Averaged Density Approximation (ADA) produces convenient *non-local vertex*, which gives good total energies *and* quasiparticle properties for jellium
- [Stankovski, Robinson, Morris, Rinke, Delaney, RWG]
DFT-based Vertex (3) … and restores the good results of $G_0 W_0$ for the I.P. of atoms!
DFT-based Vertex (4)

- Future question:
  - Interplay between self-consistency and vertex
Using self-energy approaches to shed light on DFT functionals
Using self-energy approaches to shed light on DFT functionals

• G.s. total energy – already discussed (e.g. van der Waals)
• Orbital functions based on $GW$ self-energies
  – Beyond “exact exchange” DFT
• From $\Sigma$ can calculate g.s. density $\rho(r)$, then determine $V_{xc}$ such that the same density is reproduced: Sham-Schlüter equation (see e.g. Godby Schlüter Sham PRL 1986): relevant to
  – Band-gap problem
  – Exchange-correlation electric field in polarised systems (and TDDFT current functionals à la R. van Leeuwen et al.)
Acknowledgements and Further Reading
Collaborators

- Pablo García-González
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- Patrick Rinke
- Martin Stankovski
- Peter Bokes
- Angel Rubio
Some starting points for further reading

- Further info at http://www-users.york.ac.uk/~rwg3