TUTORIAL: PHOTOEMISSION SPECTRA WITH WEST

VICTOR YU, MARCO GOVONI
Materials Science Division, Argonne National Lab, USA
PHOTOELECTRON SPECTROSCOPY
\[ \hat{H}_{KS}^{\sigma} |\psi_{nk\sigma}\rangle = \varepsilon_{nk\sigma} |\psi_{nk\sigma}\rangle \]

DFT
MANY-BODY PERTURBATION THEORY

\[ \hat{H}_{\text{KS}}^{\sigma} |\psi_{n,k\sigma}\rangle = \epsilon_{n,k\sigma} |\psi_{n,k\sigma}\rangle \quad \text{DFT} \]

\[ \Sigma (r, r'; \omega) = \int \frac{d\omega}{2\pi} G(r, r'; \omega + \omega') W(r, r'; \omega') \]

\[ G(r, r'; \omega) = \langle r | \frac{1}{\omega - \hat{H}} | r' \rangle \]

\[ W(r, r'; \omega) = \int dr'' \epsilon^{-1}(r, r''; \omega) v_c(r'', r') \]

\[ E_{n,k\sigma}^{\text{QP}} = \epsilon_{n,k\sigma} + \langle \psi_{n,k\sigma} | \hat{\Sigma}^{\sigma} (E_{n,k\sigma}^{\text{QP}}) | \psi_{n,k\sigma} \rangle - \langle \psi_{n,k\sigma} | \hat{V}_{\text{xc}}^{\sigma} | \psi_{n,k\sigma} \rangle \]

Correction

Onida et al., Rev. Mod. Phys. 74, 601 (2002)
New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem

Lars Hedin†
Argonne National Laboratory, Argonne, Illinois
(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(k)$ and quasiparticle interactions $f(k,k')$. The very first approximation gives a good value for the magnitude of $E(k)$. To estimate the derivative of $E(k)$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for $f$. Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.
PHOTOELECTRON SPECTRA OF AQUEOUS SOLUTIONS

The position of both ions and water peaks is greatly improved in $G_0W_0$ on top of dielectric dependent hybrid functionals.

- Linewidths are obtained from imaginary part of the $G_0W_0$ self-energy.
- Easily generalizable to other non-metallic liquid electrolytes.

1M NaCl, 20ps simulation, PBE0, 128 snapshots average

Pham et al., *Science Advances* 3, 1603210 (2017)
GW SELF-ENERGY: OPTIMIZING OXIDE PHOTO-ABSORBERS

We investigated realistic models of oxide (WO$_3$) surfaces, with oxygen vacancies, and by coupling first principles molecular dynamics with hybrid functionals and many body electronic structure calculations.

$G_0W_0$ on top of dielectric dependent hybrid functionals provided the best agreement with experiments.

WEST ENABLES COMPUTATIONAL SPECTROSCOPY OF LARGE SYSTEMS

- WEST is an open-source software to perform large-scale many-body perturbation theory calculations

http://west-code.org
WEST ENABLES COMPUTATIONAL SPECTROSCOPY OF LARGE SYSTEMS

- Interfaces
- Liquids/Solutions
- Nanoparticles
- Defects
- Solids
- Molecules

Range of applicability:

WEST ENABLES COMPUTATIONAL SPECTROSCOPY OF LARGE SYSTEMS

- Interfaces
- Liquids/Solutions
- Nanoparticles
- Defects
- Solids
- Molecules

WEST-GPU scales to the entire Summit supercomputer

80 quasi-particle energies of the 1,728-atom silicon supercell solved in ~30 min using 25,920 V100 GPUs (94% of Summit)

Better scalability observed for bigger system (1,728-atom silicon supercell) due to a higher computation-to-communication ratio

51 EF
4320 nodes
~60 PF/s

1 Summit node = 2 IBM POWER9 CPUs + 6 NVIDIA V100 GPUs

Full-frequency $G_0W_0$ calculation of 4000 or 6912 electrons

Ground state DFT with Quantum ESPRESSO

Local density of states computed for prototypical systems representing our target applications:

- Large nanoparticles and interfaces → materials for energy conversion
- Defects in semiconductors → quantum information science

<table>
<thead>
<tr>
<th>System</th>
<th>(N_{\text{atom}})</th>
<th>(N_{\text{electron}})</th>
<th>(N_{\text{spin}})</th>
<th>(N_{\text{PW}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS/PbS</td>
<td>301</td>
<td>2,816</td>
<td>1</td>
<td>948,557</td>
</tr>
<tr>
<td>Si/Si(_3)N(_4)</td>
<td>2,376</td>
<td>10,368</td>
<td>1</td>
<td>638,633</td>
</tr>
<tr>
<td>VV(^0)</td>
<td>1,598</td>
<td>6,392</td>
<td>2</td>
<td>314,653</td>
</tr>
</tbody>
</table>

PLAN FOR TODAY

10:30-noon
Quasiparticle energies
- Full-frequency $G_0W_0$ self-energy
- Electron-phonon self-energy

Excitation processes
- Density matrix perturbation theory (BSE & TDDFT)
- Quantum defect embedding theory

1:30-3pm
Frameworks
- TensorFlow
- Qiskit

Parallelization on CPUs and GPUs

Other electronic structure codes
- Python (WestPy)
- JSON
- XML
- HDF5

Many-body perturbation theory

WEST!
FULL-FREQUENCY GW WORKFLOW

Vertical Ionization Potential (VIP): minimum energy to remove an electron

LET’S CONNECT TO LCRC...
### RESERVATION

**Day 2 – Oct 14, 2022**

<table>
<thead>
<tr>
<th>Computer</th>
<th>Time</th>
<th>Name of reservation</th>
<th>Nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bebop</td>
<td>10:15am – 12:15pm</td>
<td>miccom_day2_am</td>
<td>75</td>
</tr>
<tr>
<td>Bebop</td>
<td>1:15pm – 5:15pm</td>
<td>miccom_day2_pm</td>
<td>75</td>
</tr>
<tr>
<td>Swing</td>
<td>12:00pm – 6pm</td>
<td>miccom_2</td>
<td>3</td>
</tr>
</tbody>
</table>

[http://miccom-center.org/docs/MICCoM_Workshop_LCRC_instructions.pdf](http://miccom-center.org/docs/MICCoM_Workshop_LCRC_instructions.pdf)
START Jupyter Notebooks

---

**Terminal #1** (1)

```
# ssh to Bebop
ssh <username>@bebop.lcrc.anl.gov

# set up environment
source /lcrc/project/MICCoM-train/load_bebop_env.sh

# get a compute node
srun --pty -A MICCOM-TRAIN --reservation miccom_day2_am
   -p knlall -N 1 -t 01:30:00 /bin/bash

# launch Jupyter notebook
miccom_start_jupyter

# each person gets a different node and port number

Your compute node is: knld-0019
Your port number is: 27055
Starting Jupyter notebook ...
```

---

**Terminal #2** (2)

```
# ssh to Bebop (use the port number obtained in Terminal #1)
ssh -L 27055:localhost:27055 <username>@bebop.lcrc.anl.gov

# ssh to the compute node obtained in Terminal #1
ssh -L 27055:localhost:27055 knld-0019

# set up environment
source /lcrc/project/MICCoM-train/load_bebop_env.sh

# copy WEST tutorials to your home directory
cp -r /lcrc/project/MICCoM-train/west_tutorial $HOME
```

---

Do not copy red values from the slide!

If you have completed the instructions in **Terminal #1 AND Terminal #2**:

Open a browser and visit this link:
YOU ARE GOOD TO GO!