Tutorial V: Theoretical Spectroscopy and Electronic Excitations
Manuscript for Exercise Problems

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Practical Session V - Theoretical Spectroscopy and Electronic Excitations

In this tutorial we will assess the suitability of density-functional theory (DFT), Hartree-Fock (HF) and many-body perturbation theory (MBPT) in the $GW$ approach for the calculation of electronic excitations. In this tutorial, most of the calculations will be performed on the ethylene molecule $C_2H_4$ (and optionally $H_2O$), with the purpose of comparing the performance of different theoretical approaches with experimental photoemission spectra (illustrated in Figure 1 for $C_2H_4$). Hence, we invite you to organise the results of each exercise in a text file, or in the table reported at the end of this document. Please note that all energies you obtain are relative to the vacuum level.

Figure 1: Photo-emission spectrum of ethylene adapted from [1].

A list of experimental ionization energies for $C_2H_4$ and $H_2O$ can be found for instance in [1] and [2], respectively.

Exercise 1: (In)adequacy of DFT eigenvalues for the description of charged electronic excitations

[Estimated total time for this exercise: 10 min. Total CPU time: <1 min.]

In this first exercise, you will perform a Kohn-Sham DFT calculation with the PBE exchange-correlation functional and Tier 2 basis set (tight settings) for ethylene $C_2H_4$. The quantities of interest in this case are the Kohn-Sham eigenvalues. You can proceed as follows:

- Generate the geometry file for ethylene from the experimental data available at http://cccbdb.nist.gov/ according to the following steps: on the home page of the CCCBDB database select “Experimental data” from the left column. Follow the link for “Summary of geometry data for one molecule” and provide the molecule name to access the geometry information. Copy the geometry specification to the geometry.in file and modify them to comply with the FHI-aims format. As in previous tutorials, the geometry data should be specified in the following format:

  atom <X> <Y> <Z> <Element>
  atom <X> <Y> <Z> <Element>
  ...

- Use the template for the control.in file, located at $HandsOnDFT/hands-on-2014-tutorials/tutorial_5/reference/DFT_total_energy.in, to set up a spin-unpolarized DFT calculation using
the PBE exchange correlation functional (flag: xc pbe).

- Copy the required basis sets from $\$\text{HandsOnDFT}/\text{aimsfiles}/\text{species\_defaults/tight}$ into your input file and start the calculation
- Compare the first four KS eigenvalues – corresponding to the highest occupied molecular orbital (HOMO), HOMO-1, HOMO-2, and HOMO-3 – with the first three experimental ionization energies given in [3].

**Optional:** Repeat the calculation for the water molecule H$_2$O, using the experimental geometry available at http://cccbdb.nist.gov/

**Exercise 2: Electron removal energies from Hartree-Fock.**

*[Estimated total time for this exercise: 10 min. Total CPU time: <1 min.]*

Modify the input files of Exercise 1 to set up a Hartree-Fock calculation by using the flag xc hf in the control.in file and compare the Hartree-Fock eigenvalues with the experimental ionization energies and with PBE.

Note that already for small molecules such as C$_2$H$_4$, the different treatment of exchange and correlation (the latter is absent in HF) may lead to differences in the energy ordering of the orbitals in DFT and HF.

**Exercise 3: Electron removal energies from delta-SCF**

*[Estimated total time for this exercise: 10 min. Total CPU time: <1 min.]*

In this exercise, the ionization energies ($I$) of C$_2$H$_4$ will be evaluated with the delta-self-consistent-field (Δ-SCF) approach [3]. Following the definition of the ionization potential,

\[
I = E_{\text{tot}}^{\text{PBE}}(N - 1) - E_{\text{tot}}^{\text{PBE}}(N) ,
\]

the total energy difference between the neutral ($E_{\text{tot}}^{\text{PBE}}(N)$) and positively ($E_{\text{tot}}^{\text{PBE}}(N - 1)$) charged species is computed from two separate DFT PBE (or HF) total energy calculations where $N$ is the number of electrons of the neutral molecule. Analogously, one can use the Δ-SCF method to evaluate the electron affinity ($A$) as:

\[
A = E_{\text{tot}}^{\text{PBE}}(N) - E_{\text{tot}}^{\text{PBE}}(N + 1) .
\]

To evaluate Equation 1, $E_{\text{tot}}^{\text{PBE}}(N)$ can be extracted from the output file of Exercise 1. In addition we need to compute $E_{\text{tot}}^{\text{PBE}}(N - 1)$, which requires a second DFT calculation. You can proceed as follows:

- Copy the input files from the first exercise.
- Modify the control.in file and set the necessary flags for performing a spin-polarized calculation of the charged molecule:

```
xc pbe
spin collinear
default_initial_moment 1
charge +1
```

Compute the ionization energy of C$_2$H$_4$ using Equation 1 and repeat the procedure for the electron affinity, as given in Equation 2. Also repeat the Δ-SCF calculations for Hartree-Fock.

- How do these values compare to the bare PBE eigenvalue and to experiment?
- What is the origin of the difference between the Hartree-Fock eigenvalue and the Δ-SCF value for the ionization energy?
Exercise 4: Perturbative $G_0W_0$ and quasi-particle corrections

An improved description of charged electronic excitations is obtained by the perturbative inclusion of many-body effects through the self-energy $\Sigma$. In the $GW$ approximation [4] the self-energy is calculated as:

$$\Sigma_{GW}(r, r', \omega) = i \frac{2\pi}{\omega} \int d\omega' G(r, r', \omega') W(r, r', \omega' + \omega),$$

where $G(r, r', \omega)$ is the one-particle Green's function and $W(r, r', \omega)$ is the screened Coulomb interaction (see e.g. [4, 5] for details). The $GW$ self-energy can be used to perturbatively correct the DFT or HF eigenvalues by means of the quasi-particle equation:

$$\epsilon_{i}^{QP} = \epsilon_{i}^{KS} - \langle \psi_{i}^{KS} | V_{xc}^{KS} - \Sigma_{c}^{GW}(\epsilon_{i}^{QP}) - \hat{\Sigma}_{x} \psi_{i}^{KS} \rangle,$$

where $\Sigma_{c}$ is the exact-exchange operator, and $\Sigma_{c}^{GW}$ is the correlation part of the $GW$ self-energy. $V_{xc}^{KS}$ is the exchange-correlation potential of the preceding DFT/HF calculation, $\epsilon_{i}^{KS}$ and $\psi_{i}^{KS}$ are the corresponding eigenvalues and eigenvectors. This approximation is known as $G_0W_0$ or one-shot $GW$, because the self-energy is calculated only once, whereas a more rigorous approach would require a fully self-consistent evaluation of $\Sigma$. Since the quasi-particle energies in Equation 4 are evaluated perturbatively on top of a preceding single-particle calculation (generally DFT or Hartree-Fock), the $G_0W_0$ approach depends on the initial reference calculation.

In the following we refer to PBE and Hartree-Fock based $G_0W_0$ as $G_0W_0@PBE$ and $G_0W_0@HF$, respectively, to distinguish between the different starting points.

Sub-Exercise 4.1: $G_0W_0@PBE$ quasiparticle energies

[Estimated total time for this exercise: 10 min. Total CPU time: <1 min.]

The purpose of this exercise is to perform a $G_0W_0$ calculation for the quasi-particle energies of ethylene.

For this exercise, proceed along the following steps:

- Copy the input files from Exercise 1.
- Modify the control.in file including the following flags:
  
  \begin{verbatim}
  xc pbe
  qpe_calc gw
  \end{verbatim}

In the species settings at the end of the control.in file modify the following flags (for all elements!):

\begin{verbatim}
  cut_pot 6.0 2.0 1.0
  basis_dep_cutoff 0
\end{verbatim}

The relevance of these adjustments can be explored as an optional bonus task in the next exercise. In addition to the output of the DFT PBE calculation, the output file will contain a table – similar to that in Figure 2 – with the quasi-particle corrections to the single-particle eigenvalues. Extract the quasi-particle energies for the HOMO, HOMO-1, HOMO-2, and HOMO-3 levels and compare them with the results from the previous calculations.

Sub-Exercise 4.2: $G_0W_0$ basis set convergence

[Estimated total time for this exercise: 15 min. Total CPU time: 6 min.]

Plot the convergence of the first $G_0W_0@PBE$ quasi-particle energy (i.e. the $G_0W_0@PBE$ HOMO level)
The purpose of this exercise is to perform a perturbative treatment of the full frequency dependence of the self-energy on the initial reference calculations. In the following we refer to PBE and Hartree-Fock based on a preliminary single-particle calculation [generally DFT or Hartree-Fock?]. The consistent evaluation of the self-energy is calculated once whereas a more rigorous approach would require a fully self-consistent treatment of the eigenvalues and eigenvectors, respectively. This approximation is known as the exchange-correlation potential of the preliminary calculation. Where HF eigenvalues by means of the linearized quasi-particle equation [see e.g. Refs. [2ru]] for details.

### Exercise 4: Perturbative

- **Total time for this exercise:** 10 minutes. **Total CPU time:** <1 min.

The purpose of this exercise is to illustrate the dependence of $G_0W_0$ calculations on the starting point. Following the steps given in the previous part of this exercise, perform a $G_0W_0$ calculation using the Hartree-Fock and the PBE0 starting point (i.e. set xc **hf** and xc **pbe0**, respectively, in the control.in file) to overcome ill-conditioning of the overlap matrix between basis functions due to the large basis set.

```
basis_threshold 1.e-4
override_illconditioning .true.
```

- How does the convergence of the ionization energy in $G_0W_0$@PBE compare to that of the PBE eigenvalue?
- What is the origin of the qualitative differences between the convergence behavior in PBE and $G_0W_0$@PBE?
- Optional: plot the convergence of the first ionization energy of C$_2$H$_4$ for different values of the onset of the cut-off potential cut_pot (1.0, 2.0, ..., 6.0) with a Tier 2 basis set.

### Sub-Exercise 4.3: $G_0W_0$@HF and $G_0W_0$@PBE0 – Starting point dependence

[Estimated total time for this exercise: 10 min. Total CPU time: <1 min.]

The purpose of this exercise is to illustrate the dependence of $G_0W_0$ calculations on the starting point. Following the steps given in the previous part of this exercise, perform a $G_0W_0$ calculation using the Hartree-Fock and the PBE0 starting point (i.e. set xc **hf** and xc **pbe0**, respectively, in the control.in file). The different colors relate terms in the output file to the corresponding quantities in the quasi-particle equation (Equation 4).

**GW quasi-particle energy levels**

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<th>state</th>
<th>occ_num</th>
<th>e_gs</th>
<th>e_x(^x)ex</th>
<th>e_x(^x)c(^\beta)g(^s)</th>
<th>e_c(^\beta)nloc</th>
<th></th>
<th>e_qp</th>
</tr>
</thead>
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<td>1</td>
<td>0.0000</td>
<td>-15.7633</td>
<td>-27.5752</td>
<td>-18.2118</td>
<td>1.8024</td>
<td>-23.3242</td>
<td></td>
</tr>
<tr>
<td>2</td>
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<td>1.5646</td>
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<td></td>
</tr>
<tr>
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<td>9.0087</td>
<td>-1.1907</td>
<td>-5.6246</td>
<td>-0.3857</td>
<td>13.0569</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0000</td>
<td>9.0087</td>
<td>-1.1907</td>
<td>-5.6246</td>
<td>-0.3857</td>
<td>13.0569</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.0000</td>
<td>9.0087</td>
<td>-1.1907</td>
<td>-5.6246</td>
<td>-0.3857</td>
<td>13.0569</td>
<td></td>
</tr>
</tbody>
</table>

For ethylene using the Tier 1, Tier 2, and Tier 3 basis sets. Calculations with the Tier 3 basis set will require the following additional settings in the control.in file to overcome ill-conditioning of the overlap matrix between basis functions due to the large basis set.

`basis_threshold 1.e-4
override_illconditioning .true.
`
file), and compare the HOMO, HOMO-1, HOMO-2, and HOMO-3 quasi-particle energy of C\textsubscript{2}H\textsubscript{4} with G\textsubscript{0}W\textsubscript{0}@PBE.

**Sub-Exercise 4.4: Visualization of the G\textsubscript{0}W\textsubscript{0} spectra**

*Estimated total time for this exercise: 5 min. Total CPU time: <1 min.*

The quasi-particle energies calculated in the previous tasks are the peak positions of the molecule’s electronic excitation spectrum. Now you will visualize the spectra for the three G\textsubscript{0}W\textsubscript{0} calculations you performed in the previous tasks.

- Use the provided script create_spectrum.py, which can be found in the folder \$HandsOnDFT/hands-on-2014-tutorials/tutorial_5/scripts, to extract the quasi-particle energies from the outputfiles and transform them into a spectrum where the energies were broadened by 0.05 eV to facilitate the comparison with experimental data. Supply the name of your FHI-aims outputfile as the first argument and call the script with
  ```
  python3 create_spectrum.py aims.out > spectrum_HF.dat
  ```
  where the output spectrum was redirected from the terminal to the file spectrum_HF.dat.
- Visualize the generated spectra (e.g. with qtiplot or xmgrace) together with the experimental photo-emission spectroscopy data provided in the file \$HandsOnDFT/hands-on-2014-tutorials/tutorial_5/data/C2H4-PES.dat.
- How large is the deviation from the experimental HOMO level? How large is the starting point dependence for lower lying quasi-particle energies (e.g. for the HOMO-3 level)?

**Exercise 5: Self-consistent G\textsubscript{W}**

In this exercise, you will perform a fully self-consistent G\textsubscript{W} calculation. Differently from G\textsubscript{0}W\textsubscript{0}, the Green’s function is calculated by solving the Dyson’s equation self-consistently. The Dyson equation relates the input Green’s function G\textsubscript{0} to the G\textsubscript{W} Green’s function G via the self-energy \( \Sigma \)

\[
G(1,2) = G_0(1,2) + \int d34 G_0(1,3) [v_H(3)\delta(3,4) + \Sigma(3,4)] G(4,2), \tag{5}
\]

or in inverted form

\[
G^{-1}(1,2) = G_0^{-1}(1,2) - v_H(1)\delta(1,2) - \Sigma(1,2), \tag{6}
\]

where we used the shorthand notation \( 1 \equiv \{r_1, t_1, \sigma_1\} \) – see e.g. [5] for an introduction. \( v_H \) is the Hartree potential. We refer to [6] for details of the scG\textsubscript{W} implementation in FHI-aims.

**Sub-Exercise 5.1: Spectral function from the self-consistent Green’s function**

*Estimated total time for this exercise: 15 min. Total CPU time: 3 min.*

To perform a self-consistent G\textsubscript{W} calculation for C\textsubscript{2}H\textsubscript{4}, create a new directory and copy the input files from Exercise 1. Modify the first part of the control.in file:

```
xc pbe
sc_self_energy scgw
spin none
```
and **choose Tier 1** settings for all species at the bottom of the `control.in` file.

After running FHI-aims, the file `spectrum_sc.dat` will be created\(^2\) The file `spectrum_sc.dat` contains the spectral function calculated from the self-consistent \(GW\) Green’s function

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

(7)

where \(G\) has been determined self-consistently from Equation 5. Figure 3 reports an example of a self-consistent \(GW\) spectral function for benzene. You can visualize the spectral function using \texttt{xmgrace}, \texttt{qtiplot} or another available plotting tool. The first three ionization energies of \(\text{C}_2\text{H}_4\) must be extracted directly from the spectral function (like in experiment) by reading of the peak positions.

Figure 3: Example of the spectral function calculated from a self-consistent \(GW\) Green’s function for the Benzene molecule. Since the Green’s function has poles at the addition/removal energies of electrons, the position of each peak in the spectral function can be associated with these addition and removal energies.

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**Sub-Exercise 5.2: Comparison and Visualization**

*Estimated total time for this exercise: 10 min. Total CPU time: 0 min.*

Using the data collected in the previous exercises for the three highest occupied states (HOMO, HOMO-1, HOMO-2, and HOMO-3) of \(\text{C}_2\text{H}_4\), visualize the deviation from the experimental ionization energy for \(\text{DFT}, \Delta-\text{SCF}, \text{Hartree-Fock}, G_0W_0@\text{PBE}\) and self-consistent \(GW\) in a plot.

**Sub-Exercise 5.3: Independence on the starting point at self-consistency**

*Estimated total time for this exercise: 15 min. Total CPU time: 3 min.*

Perform a second self-consistent \(GW\) calculation for \(\text{C}_2\text{H}_4\) choosing Hartree-Fock as starting point in a different folder. Compare the spectral functions obtained in the previous exercise, in which a PBE starting point was used.

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\(^2\) Note, that if you had chosen to perform a spin polarized calculation it will produce a spin-resolved spectral function named `spectrum_sc_up.dat` and `spectrum_sc_do.dat` for each component of the spin moment. For closed shell systems, such as \(\text{C}_2\text{H}_4\) and \(\text{H}_2\text{O}\) both spin channels are identical.
Exercise 6: $GW$ and the self-interaction error

*Estimated total time for this exercise: 15 min. Total CPU time: 3 min.*

(Semi-)local functionals, such as LDA or PBE, suffer from the self-interaction error – the incomplete removal of the interaction of an electron with itself introduced in the Hartree term. The self-interaction error is particularly large for localized states, but plays a minor role for delocalized states. Molecules that have both localized and delocalized states that are close in energy (as for instance aromatic molecules), are particularly problematic for LDA and PBE. In such systems, the self-interaction error affects the localized and delocalized states differently, potentially leading to a wrong energetic ordering of the single particle orbitals.

In this exercise we illustrate how $G_0W_0$ establishes the correct energetic ordering by means of a proper treatment of exact exchange in the $GW$ self-energy in Equation 3.

Perform a $G_0W_0$ calculation based on an LDA calculation for the naphthalene molecule ($C_{10}H_8$, Figure 4). An unfinished template for the control.in can be found at $\$HandsOnDFT/hands-on-2014-tutorials/tutorial_5/reference/naphthalene.control.in$. The input geometry can be found at $\$HandsOnDFT/hands-on-2014-tutorials/tutorial_5/reference/naphthalene.geometry.in$.

- Plot the orbitals 27 and 28 using the following settings in the control.in file:
  
  ```
  output cube eigenstate 27
  output cube eigenstate 28
  ```

- Compare the energetic ordering of DFT orbitals and the $G_0W_0$ quasi-particle energies of naphthalene.

- Visualize the two states in VMD. For a short introduction to isosurface-plotting in VMD, see Appendix A.

Now analyze the results and answer the following questions:

- How many orbitals are energetically swapped in $G_0W_0@LDA$ compared to LDA?
- Which orbital is more localized: number 27 or number 28?
- Is the different localization of orbitals 27 and 28 consistent with the removal of the self-interaction error and the new energetic ordering?

Figure 4: The naphthalene molecule.
Exercise 7: **GW total energy from the Galitskii-Migdal formula**

As shown in Exercise 4 and Exercise 5, the single-particle Green’s function provides access to the energy of single-particle excitations. However, the Green’s function may also yield information about the ground state of a system, for instance, the total energy and the electron density. To illustrate this aspect, the purpose of this exercise is to calculate the potential energy curve of the hydrogen molecule H\(_2\) using the Galitskii-Migdal formula in the GW approximation. The Galitskii-Migdal total energy is an explicit functional of the single-particle Green’s function that can be expressed as:

\[
E_{GM} = -i \int \frac{d\omega}{2\pi} Tr \{ [\omega + h_0] G(\omega) \} + E_{ion},
\]

To evaluate the potential energy curve of H\(_2\), follow the following steps:

- Inspect the provided python3 script `generate_binding_curve.py` which can be found in the directory `$HandsOnDFT/hands-on-2014-tutorials/tutorial_5/scripts`. Call it with `-h` or `--help` to determine the parameters you need to supply.

- Prepare a geometry file in which one hydrogen atom is fixed at the origin and the other is displaced along one axis by the placeholder you supply to the script, e.g.

  ```
  atom 0.0 0.0 0.0 H
  atom 0.0 0.0 <DIST> H
  ```

  where we used the default placeholder from the script.

- Set up the `control.in` file for the calculation using the template file provided under `$HandsOnDFT/hands-on-2014-tutorials/tutorial_5/reference/scGW-Etot.control.in` and start the script with parameters to create a binding curve in the range from 0.5 to 3 Å with a grid spacing of 0.1 Å.

Once the script has finished, it creates an additional output file `<inputgeoname>_energies.dat`. The file contains the total energies of the DFT and scGW calculation for all distances. Note that the energies are given in Hartree, not electron volts.

- Visualize the PBE and self-consistent GW total energies (evaluated using the Galitskii-Migdal formula) as function of the bond length. You can use any of the available plotting tools to display the data extracted by the script.

- Compare the results with the exact data obtained by full configuration-interaction (full-CI) calculations. The full-CI curve is available in the file `$HandsOnDFT/hands-on-2014-tutorials/tutorial_5//data/H2_full-CI.dat`.

References

Appendix A: How to plot isosurfaces with VMD

To plot an isosurface with VMD, follow these simple steps:

1. Open the “New Molecule” dialog to import your cube file(s).
2. Select the file you want to import, make sure it loads files for “New Molecule” and the file type is “Gaussian Cube”.
3. Open the “Representation” dialog located in the menu graphics and create a new representation for your molecule. Then change the drawing method to “Isosurface”. (see the red boxes in Figure 8)
4. Choose a suitable isovalue. (blue box in Figure 8)
5. To improve the visualization quality, change the option Draw to “Solid Surface”, the Material to “Transparent” and finally the Colouring Method to “ColorID”. (green boxes in Figure 8)

Figure 5: Step 1 - open the file import dialog
Figure 6: Step 2 - import the molecule as Gaussian Cube
Figure 7: Step 3 - open the representation menu
Figure 8: Step 4 - create a new representation as isosurface
Appendix B: Ionization energies of C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2}O

<table>
<thead>
<tr>
<th>C\textsubscript{2}H\textsubscript{4}</th>
<th>Experiment</th>
<th>DFT - PBE</th>
<th>Hartree-Fock</th>
<th>(\Delta\text{-SCF (PBE)})</th>
<th>(\Delta\text{-SCF (HF)})</th>
<th>(G_0W_0\text{@PBE})</th>
<th>(G_0W_0\text{@HF})</th>
<th>(G_0W_0\text{@PBE0})</th>
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<tr>
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Optional: H\textsubscript{2}O

<table>
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<tr>
<th>H\textsubscript{2}O</th>
<th>Experiment</th>
<th>DFT - PBE</th>
<th>Hartree-Fock</th>
<th>(\Delta\text{-SCF (PBE)})</th>
<th>(\Delta\text{-SCF (HF)})</th>
<th>(G_0W_0\text{@PBE})</th>
<th>(G_0W_0\text{@HF})</th>
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