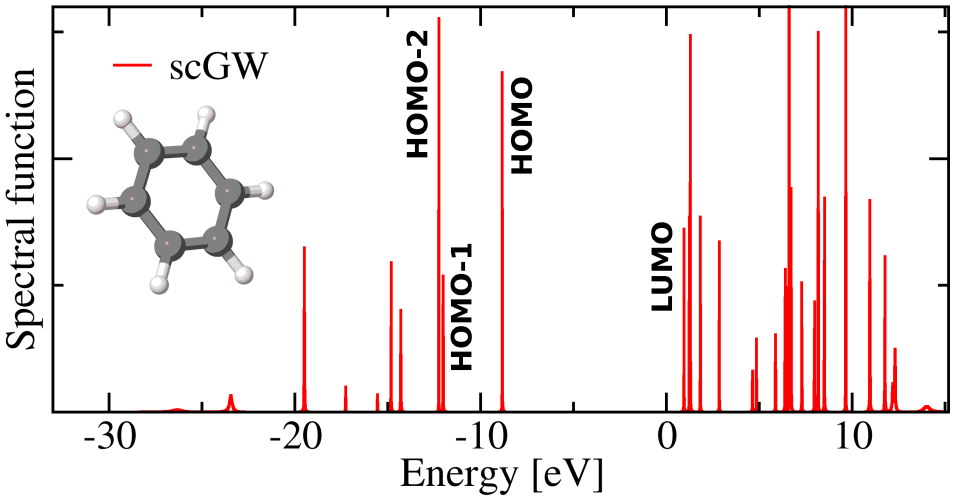
Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules

Los Angeles, July 21 - August 1, 2014



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

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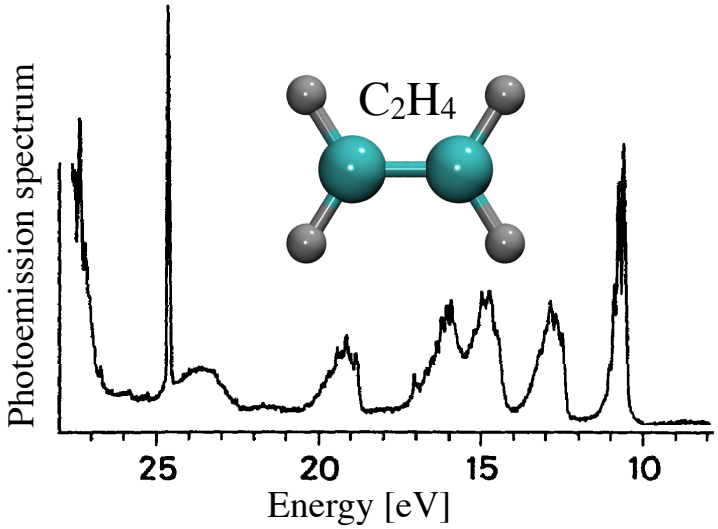
Practical Session V - Theoretical Spectroscopy and Electronic Excitations

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 `$HandsOnDFT/aimsfiles/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_2O, 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_2H_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_2H_4 will be evaluated with the delta-self-consistent-field (Δ-SCF) approach [3]. Following the definition of the ionization potential,

$$I = E_{\mathrm{tot}}^{\mathrm{PBE}}(N-1) - E_{\mathrm{tot}}^{\mathrm{PBE}}(N) \quad , \tag{1}$$

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

$$A = E_{\mathrm{tot}}^{\mathrm{PBE}}(N) - E_{\mathrm{tot}}^{\mathrm{PBE}}(N+1) \quad . \tag{2}$$

To evaluate Equation 1, $E_{\mathrm{tot}}^{\mathrm{PBE}}(N)$ can be extracted from the output file of Exercise 1. In addition we need to compute $E_{\mathrm{tot}}^{\mathrm{PBE}}(N-1)$, 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_2H_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 Σ. In the GW approximation [4] the self-energy is calculated as:

$$\Sigma^{GW}(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\int d\omega' G(\mathbf{r},\mathbf{r}',\omega')W(\mathbf{r},\mathbf{r}',\omega'+\omega) \quad , \tag{3}$$

where $G(\mathbf{r},\mathbf{r}',\omega)$ is the one-particle Green's function and $W(\mathbf{r},\mathbf{r}',\omega)$ 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:

$$\epsilon_i^{\mathrm{QP}} = \epsilon_i^{\mathrm{KS}} - \left\langle \psi_i^{\mathrm{KS}} \middle| \hat{V}_{\mathrm{xc}}^{\mathrm{KS}} - \hat{\Sigma}_{\mathrm{c}}^{GW}(\epsilon_i^{\mathrm{QP}}) - \hat{\Sigma}_{\mathrm{x}} \middle| \psi_i^{\mathrm{KS}} \right\rangle \quad , \tag{4}$$

where Σ_{c} is the exact-exchange operator, and Σ_{c}^{GW} is the correlation part of the GW self-energy. $V_{\mathrm{xc}}^{\mathrm{KS}}$ is the exchange-correlation potential of the preceding DFT/HF calculation, ϵ_i^{KS} and ψ_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 Σ. 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:

```
xc          pbe
qpe_calc    gw
```

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

```
cut_pot             6.0  2.0  1.0
basis_dep_cutoff    0
```

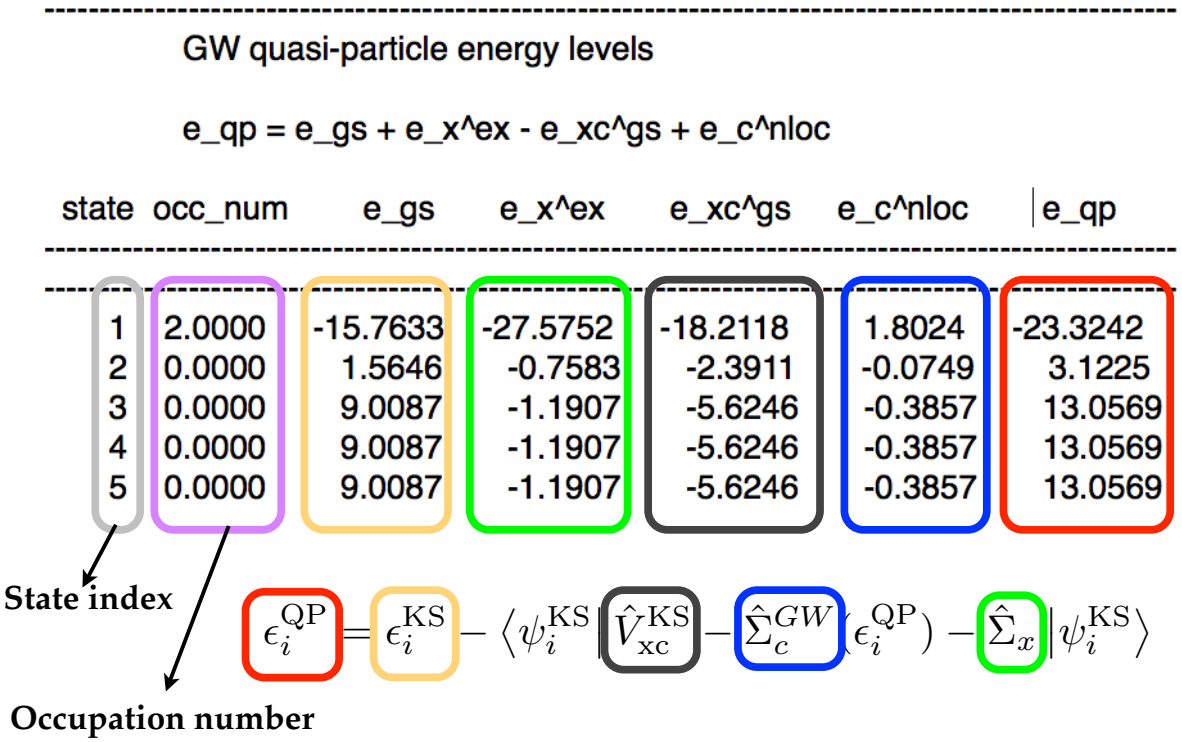
The relevance of these adjustments can be explored as an optional bonus task in the next exercise.
In addition to the output of the DFT PBE calculation, the output file will contain a table – similar to that in Figure 2 – with the quasi-particle corrections to the single-particle eigenvalues. Extract 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)

Figure 2: Sample output of a G_0W_0 quasi-particle calculation in FHI-aims for the hydrogen molecule H_2. The different colors relate terms in the output file to the corresponding quantities in the quasi-particle equation (Equation 4).



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.
```

- 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_2H_4 for different values of the onset of the cut-off potential `cut_pot` $(1.0, 2.0, \ldots, 6.0)$ with a Tier 2 basis set[1].

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`

[1] Note, that in FHI-aims the default settings for basis sets and integration grids are tuned to optimize the performance of LDA and GGA density functional calculations. Calculations beyond plain DFT may require the adjustment of such settings.

file), and compare the HOMO, HOMO-1, HOMO-2, and HOMO-3 quasi-particle energy of C_2H_4 with G_0W_0@PBE.

Sub-Exercise 4.4: Visualization of the G_0W_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_0W_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 GW

In this exercise, you will perform a fully self-consistent GW calculation. Differently from G_0W_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_0 to the GW Green's function G via the self-energy Σ

$$G(1,2) = G_0(1,2) + \int d34\, G_0(1,3)\left[v_{\mathrm{H}}(3)\delta(3,4) + \Sigma(3,4)\right] G(4,2) \quad , \tag{5}$$

or in inverted form

$$G^{-1}(1,2) = G_0^{-1}(1,2) - v_{\mathrm{H}}(1)\delta(1,2) - \Sigma(1,2) \quad , \tag{6}$$

where we used the shorthand notation $1 \equiv \{\mathbf{r}_1, t_1, \sigma_1\}$ – see e.g. [5] for an introduction. v_{H} is the Hartree potential. We refer to [6] for details of the scGW 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 GW calculation for C_2H_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
```

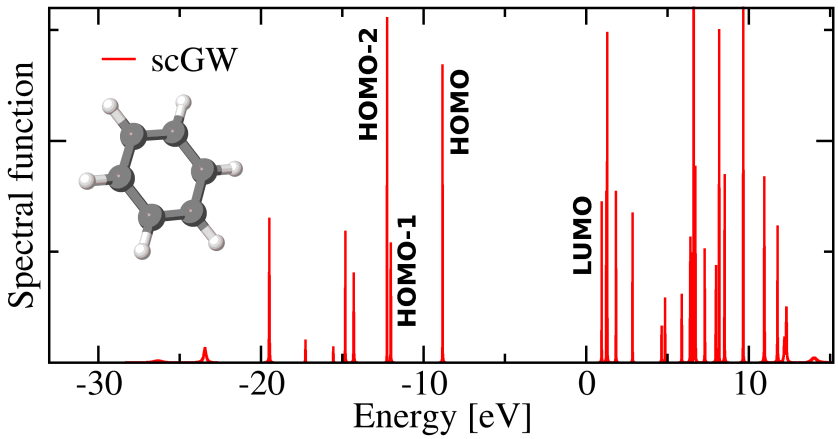
and **choose Tier 1** settings for all species at the bottom of the `control.in` file.

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

$$A(\omega) = -\frac{1}{\pi}\int \lim_{\mathbf{r}'\to\mathbf{r}} ImG(\mathbf{r},\mathbf{r}',\omega)d\mathbf{r} \tag{7}$$

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 `xmgrace`, `qtiplot` or another available plotting tool. The first three ionization energies of C_2H_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.



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 C_2H_4, visualize the deviation from the experimental ionization energy for DFT, Δ-SCF, Hartree-Fock, G_0W_0@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 C_2H_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.

[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 C_2H_4 and H_2O 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:

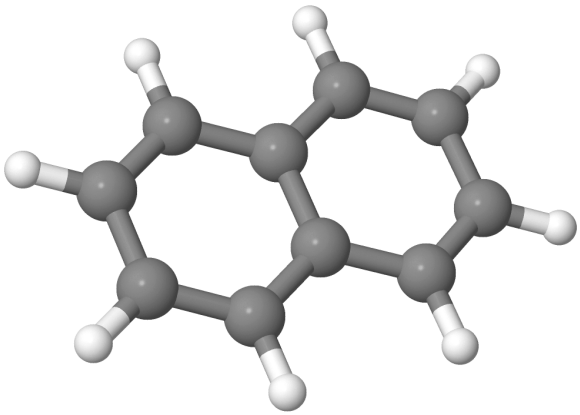
```
output cube eigenstate  27
output cube eigenstate  28
```

- 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:

$$E_{\mathrm{GM}} = -i \int \frac{d\omega}{2\pi} Tr \left\{ [\omega + h_0]\, G(\omega) \right\} + E_{ion}, \tag{8}$$

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

[1] M. E. Casida. In: *Recent Advances in Density Functional Methods* (1995).

[2] Chong, Gritsenko, and Baerends. In: *J. Chem. Phys.* 116 (2002), p. 1760.

[3] G. Bieri and L. Åsbrink. In: *J. of Electron Spectrosc. and Rel. Phenom.* 20 (1980), p. 149.

[4] Bagus. In: *Phys. Rev. A* 139 (1965), p. 619.

[5] Hedin. In: *Phys. Rev. A* 139 (1965), p. 796.

[6] F. Caruso et al. In: *Phys. Rev. B* 88 (2013), p. 75105.

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 cubefile(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)

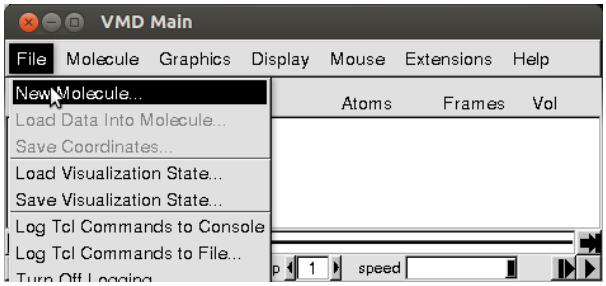


Figure 5: Step 1 - open the file import dialog

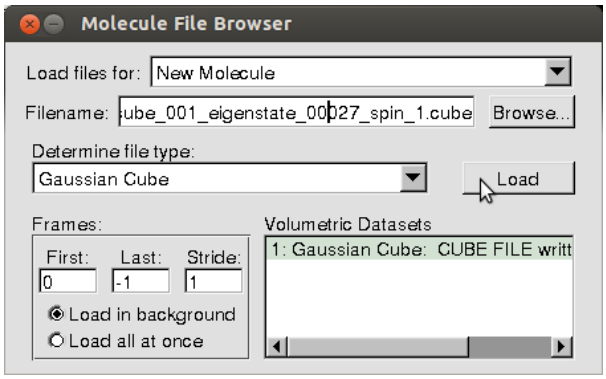


Figure 6: Step 2 - import the molecule as Gaussian Cube

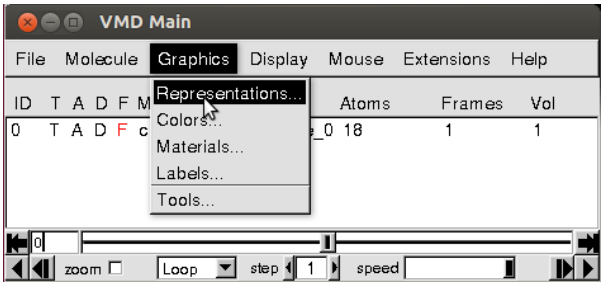


Figure 7: Step 3 - open the representation menu

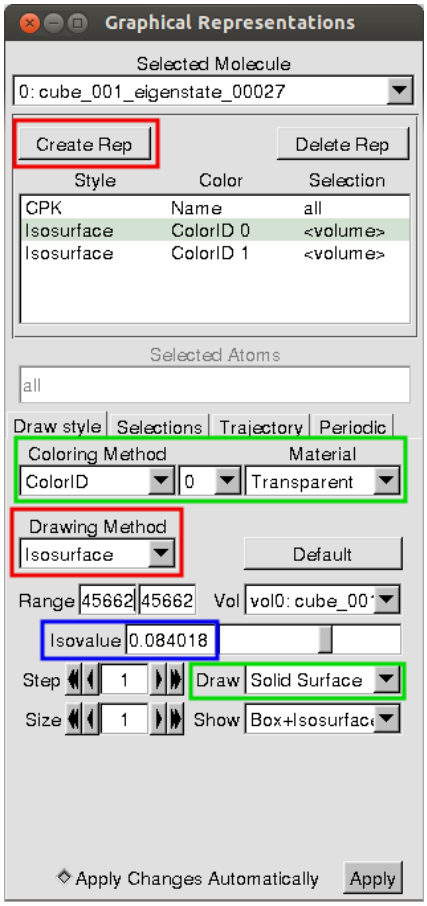


Figure 8: Step 4 - create a new represenatation as isosurface

Appendix B: Ionization energies of C_2H_4 and H_2O

C_2H_4	Experiment	DFT - PBE	Hartree-Fock	Δ-SCF (PBE)	Δ-SCF (HF)	G_0W_0@PBE	G_0W_0@HF	G_0W_0@PBE0	scGW
HOMO	10.68 eV								
HOMO-1	12.8 eV			***	***				
HOMO-2	14.8 eV			***	***				
HOMO-3	16.0 eV			***	***				

Optional: H_2O

H_2O	Experiment	DFT - PBE	Hartree-Fock	Δ-SCF (PBE)	Δ-SCF (HF)	G_0W_0@PBE	G_0W_0@HF	G_0W_0@PBE0	scGW
HOMO	12.615 eV								
HOMO-1	14.729 eV			***	***				
HOMO-2	18.550 eV			***	***				