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<https://www.uni-regensburg.de/physik/evers/teaching/comp-nano-bose-2021/index.html>

Computational Nanoscience: Exercise Sheet No. 8

For this exercise sheet, the theoretical background from Chapter 14: ‘*GW* approximation for quasiparticle energies’ is needed. Chapter 13 is neither needed for this exercise sheet nor for the following exercise sheets. Thus, Chapter 13 has been shifted to the last week of the lecture period, see Youtube playlist.

Exercise 8.1: G_0W_0 @PBE for ethylene

- (a) 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” from the top menu. Follow the link for “Geometry/Experimental Geometries” 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 the previous exercise, the geometry data should be specified in the following format:

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

Start a new `control.in` file and set up a spin-unpolarized DFT calculation with zero charge using the PBE functional (flag: `xc pbe`). Include

```
qpe_calc      gw
anacon_type   1
```

into `control.in` to activate the G_0W_0 calculation.

Copy the required tight parameters for hydrogen and carbon from

```
phy318:/loctmp/comp\_nanoscience/species\_defaults/tight
```

and paste them both into your input file. Helpful command for this:

```
cat file1 >> file2
```

appends the whole content of `file1` to `file2`. 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
```

Start a parallel calculation using four cores by typing:

```
mpirun -np 4 ~/.aims.x | tee aims.out
```

A table should appear that looks as follows:

GW quasi-particle energy levels

$$e_{qp} = e_{gs} + e_x^{ex} - e_{xc}^{gs} + e_c^{nloc}$$

state	occ_num	e_gs	e_x ^{ex}	e_xc ^{gs}	e_c ^{nloc}	e_qp
1	2.0000	-269.0433	-96.9218	-61.5502	9.3514	-295.0635
2	2.0000	-269.0254	-96.9038	-61.5630	9.5102	-294.8560
3	2.0000	-18.7700	-25.6748	-16.7054	5.2793	-22.4601
4	2.0000	-14.2376	-22.3517	-15.3175	2.8906	-18.3812
5	2.0000	-11.5044	-20.1181	-14.3506	2.4518	-14.8201
6	2.0000	-10.1331	-21.1155	-15.7514	1.3993	-14.0979
7	2.0000	-8.5753	-19.2886	-14.3513	0.8708	-12.6418
8	2.0000					
9	0.0000	-1.0832	-6.4109	-11.7862	-2.2189	2.0732
10	0.0000	-0.1425	-1.0294	-3.0842	-0.5411	1.3712
11	0.0000	0.3582	-0.7849	-2.5482	-0.4608	1.6607
12	0.0000	0.4107	-0.8921	-2.7332	-0.4551	1.7966
13	0.0000	1.5596	-0.4871	-1.7665	-0.2746	2.5644
14	0.0000	2.7977	-2.0978	-5.3951	-1.0745	5.0206
15	0.0000	3.3989	-1.7048	-5.0530	-1.1114	5.6357
16	0.0000	3.5916	-3.1691	-6.9927	-1.4249	5.9903
17	0.0000	4.0348	-2.5427	-6.0026	-1.4087	6.0861
18	0.0000	4.2280	-1.8715	-5.3839	-1.1913	6.5491

Report the missing line in your solution.

- (b) For upper table, FHI-aims computes the G_0W_0 self-energy as

$$\Sigma^{G_0W_0}(\varepsilon) = \Sigma^{\text{HF}} + \Sigma^c(\varepsilon) \quad (1)$$

where Σ^{HF} is the Hartree-Fock self-energy (also called exact exchange self-energy) and $\Sigma^c(\varepsilon)$ the ‘correlation self-energy’ that includes all GW effects beyond the Hartree-Fock self-energy (the main screening effect is nonlocal since screening acts on two electrons that are on different spatial positions). Interpret upper table: Define and relate every quantity to definitions from the lecture notes. Write the equation on ‘GW quasi-particle energy levels’ in the notation of the lecture notes/Eq. (1).

Exercise 8.2: G_0W_0 basis set convergence

- (a) Report the convergence of the G_0W_0 @PBE quasi-particle energy for the G_0W_0 @PBE HOMO for ethylene using the Tier 1, Tier 1+2, and Tier 1+2+3 basis sets (by adding/removing the comment in the respective lines in the input file). Calculations with the Tier 1+2+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? Background info: There are methods to extrapolate GW calculations to the complete

basis set limit; still it is difficult to extrapolate GW for small molecules to the complete basis set limit.

- (b) Have a look at the formula for computing the polarizability P . How is an increased basis set size reflected in the computation of the polarizability? Can you explain the origin of the qualitative differences between the convergence behavior in PBE and $G_0W_0@PBE$?

Exercise 8.3: G_0W_0 starting point dependence

The purpose of this exercise is to illustrate the dependence of G_0W_0 calculations on the starting point.

- (a) Following the steps given in the previous exercises, perform a G_0W_0 calculation on ethylene using the Hartree-Fock and the PBE0 starting point (i.e. set `xc hf` and `xc pbe0`, respectively, in the `control.in` file), and compare to $G_0W_0@PBE$.
- (b) Are your conclusions from (a) also valid in the complete basis set limit? Discuss.
- (c) What is the most important origin of the strong starting point dependence of G_0W_0 ? Trace the origin back in the G_0W_0 formulas.
- (d) How can one reduce the starting point dependence of a GW calculation?