## Question 1: Gaussian basis sets

This question was part of an exam in a previous year. It is not about DFT, but about the basis sets that we've seen a few weeks ago.

Atomic basis sets are available online in the "EMSL basis set exchange" database. The details of the Pople 6-31G* basis set of Nitrogen are presented in this way:

```
01: #BASIS SET: (10s,4p,1d) -> [3s,2p,1d]
02: N    S
03:    4173.5110000           0.0018348
04:     627.4579000           0.0139950
05:     142.9021000           0.0685870
06:      40.2343300           0.2322410
07:      12.8202100           0.4690700
08:       4.3904370           0.3604550
09: N    SP
10:      11.6263580          -0.1149610            0.0675800
11:       2.7162800          -0.1691180            0.3239070
12:       0.7722180           1.1458520            0.7408950
13: N    SP
14:       0.2120313           1.0000000            1.0000000
15: N    D
16:       0.8000000           1.0000000
```

The first column is the line number.

**1a**. What is the meaning of line 01 ?

Answer: *It tells you how many basis functions (of s, p, d type) are used and how many independent basis functions remain after contraction.*

**1b**. What is the meaning of line 02 and the numbers in lines 03-08 ?

Answer: *line 02: it is nitrogen, so "N", and the information on the following lines is about the s-channel only. lines 03-08: the exponents* $\zeta_i$ *of the Gaussians* ($e^{-\zeta_i r^2}$) *and the weights* $c_i$ *in the contraction. As there are 6 Gaussians, this describes the* $1s$ *core orbital, as says the "6" in "6-31G*".*

**1c**. What is the meaning of lines 15 and 16 ?

Answer: *There is a single d-channel, represented by a single Gaussian. This is a polarization function, i.e. comes from the "*" in "6-31G*".*

**1d**. What is the meaning of lines 09-14 ?

Answer: *These are s and p functions, as indicated by "SP". Lines 10-12 describe a contraction of 3 Gaussians, line 14 a contraction of one Gaussian. These are added to describe the valence electrons, consistent with the split valence "31" in "6-31G*". There is an additional column, because separate contraction coefficients are given for s and p, who are evidently described by the same Gaussians, but mixed in different proportions.*

## Question 2: Applications of Density Functional Theory

The question below was part of an exam in a previous year.

**2a**. The following table shows lattice constants (in Å) calculated with PBE and LDA and compared with experiment.[1]

| Solid | I | II | Expt. |
|---|---|---|---|
| Li | 3.363 | 3.435 | 3.451 |
| Na | 4.047 | 4.196 | 4.209 |
| K | 5.045 | 5.282 | 5.212 |
| Rb | 5.374 | 5.670 | 5.577 |

Which of the columns I and II corresponds to LDA and which to PBE?

Answer: *I=LDA, II=GGA. Gradient corrected functionals, such as PBE, typically yield higher and often more accurate, bond distances (so also lattice constants) than LDA.*

**2b**. Maria has installed an electronic structure programme on her laptop. She wants to use it to calculate the band gap of InSb. The programme has a GUI.[2] In one scroll menu she has the choice between "LDA", "PBE", "HF", "PBE0" and "B3LYP". Which option(s) would you advice Maria to use? Briefly explain why. Also explain what you would expect to happen if Maria does not follow your advice.

Answer: *The hybrids PBE0 and B3LYP would probably yield reasonable gaps. Pure density functionals such as LDA and PBE would underestimate (say 50 %), HF would severely overestimate.*

**2c**. The programme can also handle molecules. Maria does a calculation on benzene. Her friend Klaas has done a very accurate calculation on benzene, converging to the exact ground state energy with an error less than 5 kJ/mole. Using the HF option in the programme, Maria finds an energy much larger than that of Klaas. This is what she expected. However, using one of the DFT methods Maria finds an energy that is 10 kJ/mole lower (than Klaas' energy). She is very angry, and wants her money back. You sold her the programme. What can you say in your defense?

Answer: *Well, DFT is based on the variational principle, but, once you approximate the density functional (and you have to!), there is no guarantee anymore that you don't get energies lower than the true ground state energy.*

## Question 3: Practice of DFT and more

The question below was part of an exam in a previous year.

**3a**. Piet has done several quantum chemical calculations with NWCHEM. They are all on the hydrogen atom. He has made a terrible mess of his notes. You have to help him sort things out. With much effort Piet has come up with the following table (Hartree units):

| | (KS) eigenvalue | Total energy | Basis set |
|---|---|---|---|
| 1 | -0.4996188 | -0.2776207 | 6-311G∗ |
| 2 | -0.3217006 | -0.5021559 | 6-311G∗ |
| 3 | -0.5021559 | -0.3217006 | 6-311G∗ |
| 4 | -0.4998098 | -0.4998098 | 6-311G∗ |
| 5 | -0.2776207 | -0.2776207 | 6-311G∗ |
| 6 | -0.2776207 | -0.4996188 | 6-311G∗ |
| 7 | -0.3217006 | -0.3217006 | 6-311G∗ |

---

[1] Data taken from Phys. Rev. B **79**, 085104 (2009).

[2] Graphical User Interface

This lists the output of his calculations. Each row is the output of one calculation. Some outputs are just wrong (Piet has a vivid imagination). Some make sense. Please find in the table the output of (a) a PBE calculation, (b) a B3LYP calculation and (c) a HF calculation. Provide a motivation for the choices you make.

Answer: *PBE has a crazy eigenvalue because of the imperfect cancellation of self-Coulomb (Hartree) and self-exchange term in the KS equation. The total energy is almost okay (the XC-hole integrates to ∼1, only the spherically averaged XC-hole matters for the energy).*

*B3LYP has a better eigenvalue (admixing of HF).*

*HF has identical eigenvalue and total energy that are practically equal to* $-0.5$ *Hartree. In the H atom there is only one electron so no Coulomb interaction with other electrons and no exchange. Hence the HF energy is the exact energy of the H atom from the textbooks:* $-0.5$ *Hartree (the small deviation points to limitations of the basis set... why could that be?). The HF eigenvalue equation for the H atom is just the Schrödinger equation for the H atom, as there are no double counting corrections (because there is only one electron there are no Coulomb and no exchange interaction) and the artificial self-Coulomb and self-exchange of the single electron with itself cancel exactly (contrary to PBE and B3LYP). Hence, in this special case, the energy and single eigenvalue are equal.*

*The other entries are nonsense.*

| | *(KS) eigenvalue* | *Total energy* | *Basis set* |
|---|---|---|---|
| | -0.4996188 | -0.2776207 | 6-311G∗ |
| *B3LYP* | -0.3217006 | -0.5021559 | 6-311G∗ |
| | -0.5021559 | -0.3217006 | 6-311G∗ |
| *HF* | -0.4998098 | -0.4998098 | 6-311G∗ |
| | -0.2776207 | -0.2776207 | 6-311G∗ |
| *PBE* | -0.2776207 | -0.4996188 | 6-311G∗ |
| | -0.3217006 | -0.3217006 | 6-311G∗ |