

Problem IV.S . . . quantum of molecules 10 points; průměr 7,96; řešilo 46 studentů

1. At the beginning of the series, we mentioned a couple of approximations we made – fixing the nuclei and neglecting relativistic effects. For which chemical elements would you expect the motion of electrons to have the strongest influence on the motion of the nuclei, and why? In which part of the periodic table do you think relativistic effects will be most apparent? What is the reason for that? (2 pts)
2. The total energy of a water molecule, obtained from a quantum chemical calculation, is approximately -75 Ha. The energy released by the fusion of hydrogen and oxygen into water is $242 \text{ kJ}\cdot\text{mol}^{-1}$. If we calculate the energy of the reactants and products with an error of 1 %, how big will the error be in determining the reaction energy? Furthermore, try to find an analogy for this based on real-life measurements. (For example: “Weighing myself with a five-crown coin and without it to determine its weight.”) (3 pts)
3. Install the program *Psi4* and try to calculate the difference of energies of the chair and (twist-)boat conformations of cyclohexane. You can use the attached input files, where the geometry is already optimised. How much does the result differ from the experimental value $21 \text{ kJ}\cdot\text{mol}^{-1}$? (2 pts)

Note: If you encounter a problem with *Psi4*, please feel free to contact me at mikulas@fykos.cz

4. Try calculating the reaction energy for the chlorination of benzene $\text{C}_6\text{H}_6 + \text{Cl}_2 \Rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$. Compare it with the experimental value of $-134 \text{ kJ}\cdot\text{mol}^{-1}$. You can use the included geometry of the benzene molecule. (3 pts)

Bonus: Choose your favorite (or any other) chemical reaction and calculate its energy. (up to +3 pts)

Mikuláš keeps on giving even after Christmas.

As you will have noticed, quantum phenomena manifest for small things. Not surprisingly, quantum phenomena at the level of nuclear motion will be the most pronounced for the lightest elements. Finally, even if we stick to the simplest case in classical physics, then the electron and the nucleus should orbit around a common center of gravity. The heavier the nucleus, the closer the center of gravity will be to the nucleus, and thus the position of the electrons will have a smaller effect on the position of the molecule's center of gravity. Therefore, the motion of the nuclei will be most correlated with the motion of the electrons for the lightest elements. And as even the nucleus of the lightest element, hydrogen, is almost 2000 times heavier than an electron, most electronic structure calculations will make do with fixed nuclei. Conversely, if we want to study effects related to the entanglement of the motion of electrons and nuclei, or even quantum effects such as tunneling, it is sufficient to study them for hydrogen, since the nearest heavier elements do not behave as chemically interesting. (Helium is inert, lithium occurs primarily in the form of a cation Li^+ and electrostatic interaction is dominant over other occurring effects, etc.)

On the other hand, relativistic effects will be the most pronounced in situations where the electrons move the fastest. These occur in elements where the nuclei have a large charge and the electrons have to move fast to counteract the attractive force of the nucleus with the centrifugal force. Hence, we can expect relativistic effects to manifest primarily in the lower part of the table. Here, the electrons on the inner shells are already moving at a significant fraction of the speed of light, which will eventually show up in the chemical behavior of the elements. It is accepted that relativistic phenomena are absolutely fundamental to consider in the system of elements from the lanthanides onwards because there, the effect is already observable in the

macroscopic behavior of the elements. A perfect example is gold. Here, relativistic phenomena cause it to behave less like its direct neighbor above it, silver, but more like the element a tier above it, copper. Most strikingly, it is not of silver color, but rather has its distinctive color similar to copper. If it were not for relativity, gold would not be golden, mercury would not be liquid and you would not be able to start the car because the battery in the car would only have 2 V instead of 12 V.

To calculate the reaction energy in quantum chemistry, we have to calculate the total energy of the reactants and the products and subtract them from each other. But if we subtract the two values that are burdened with error, these deviations add up. Especially in this case, where the difference between the two values is small compared to the values themselves, it can lead to the error being even an order of magnitude larger than the final value itself. If we consider that the reactants and products have a total energy of approximately -75 Ha with a relative error of 1%, the magnitude of the error for both is 0.75 Ha. This means an error of 1.5 Ha in the reaction energy, or nearly 4000 $\text{kJ}\cdot\text{mol}^{-1}$. That is an order of magnitude higher than the reaction energy itself.

The total energy of a water molecule is approximately $200\,000$ $\text{kJ}\cdot\text{mol}^{-1}$. That is approximately a thousand times more than the reaction energy. If we follow the example in the problem statement of weighing an object in a pocket, for an 80 kg person it comes out as about 80 g, which is the weight of a small apple. Let's weigh ourselves with the apple in the pocket, then without it, and determine its weight from the difference. Surely, you can imagine how accurate such a measurement is. Moreover, if we count larger molecules, or molecules containing heavier elements (where $1s$ orbitals contribute hundreds of Hartree to the energy, although they hardly participate in the reaction), we can easily reach a state where, for a comparable value of reaction energy, we will be subtracting energies on the order of thousands to tens of thousands of Hartree. Then the instructions will make sense even with a five-crown, or an even lighter object.

To find the energy difference between the two conformations of cyclohexane, we use the attached input files. After running the file for the boat conformation in the output of the program, we find at the end of the file:

```
Nuclear Repulsion Energy = 256.0298826585392931
One-Electron Energy = -822.4160185529569844
Two-Electron Energy = 332.1735967136023646
Total Energy = -234.2125391808153836
```

We are interested in the last line, the total energy of the molecule, which is $-234.212\,539\,180\,815\,383\,6$ Hartree. Similarly, we find for the chair conformation that its energy value is $-234.223\,806\,324$ Ha. Thus, we see that the molecule comes out slightly more stable in the chair conformation, which is consistent with reality. If we subtract these two energies, we get a difference $0.011\,3$ Ha. This corresponds to 30 $\text{kJ}\cdot\text{mol}^{-1}$. That is quite in line with the experimental value of 21 $\text{kJ}\cdot\text{mol}^{-1}$, considering that the optimal precision sought after by the quantum chemists is about 1 $\text{kcal}\cdot\text{mol}^{-1}$, or 4 $\text{kJ}\cdot\text{mol}^{-1}$.

For the reaction of benzene to chlorobenzene, our calculations will get more extensive. We have to consider the whole reaction, so $\text{C}_6\text{H}_6 + \text{Cl}_2 \Rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$. If we want the final energy, we have to calculate separately the energy of all 4 molecules in the reaction, and just then will we get the total energy by

$$E_{\text{Reaction}} = E(\text{C}_6\text{H}_5\text{Cl}) + E(\text{HCl}) - E(\text{C}_6\text{H}_6) - E(\text{Cl}_2).$$

Unlike the previous problem, we have to optimize the geometries of all the molecules ourselves. Using the attached geometry, we create an input for benzene:

```
set basis cc-pVDZ
molecule {
O 1
C -0.000000000000 1.388721052559 0.000000000000
H -0.000000000000 2.470895972113 0.000000000000
C -1.202667654441 0.694360499538 0.000000000000
H -2.139858588291 1.235447933148 0.000000000000
C -1.202667654441 -0.694360499538 0.000000000000
H -2.139858588291 -1.235447933148 0.000000000000
C 0.000000000000 -1.388721052559 0.000000000000
H 0.000000000000 -2.470895972113 0.000000000000
C 1.202667654441 -0.694360499538 0.000000000000
H 2.139858588291 -1.235447933148 0.000000000000
C 1.202667654441 0.694360499538 0.000000000000
H 2.139858588291 1.235447933148 0.000000000000
}
optimize("HF")
```

Since this geometry from the assignment is already optimized with the same method and base, the program should only run through a single iteration of the geometric optimization and evaluate that the geometry is already optimal. At the end of the file listing, we find:

```
==> Convergence Check <==
```

Measures of convergence in internal coordinates in au.

Criteria marked as inactive (o), active & met (*), and active & unmet ().

```
-----
Step Total Energy Delta E Max Force RMS Force Max Disp RMS Disp
-----
Convergence Criteria 1.00e-06 * 3.00e-04 * o 1.20e-03 * o
-----
1 -230.72192588 -2.31e+02 1.44e-04 * 4.82e-05 o 3.02e-04 * 1.02e-04 o
-----
```

```
Next Geometry in Ang
Fragment 1 (Ang)
```

```
Final optimized geometry and variables:
Molecular point group: d2h
Full point group: D2h
```

Geometry (in Angstrom), charge = 0, multiplicity = 1:

```
C -0.000000000000 1.388721052559 0.000000000000
```

```

H -0.000000000000 2.470895972113 0.000000000000
C -1.202667654441 0.694360499538 0.000000000000
H -2.139858588291 1.235447933148 0.000000000000
C -1.202667654441 -0.694360499538 0.000000000000
H -2.139858588291 -1.235447933148 0.000000000000
C 0.000000000000 -1.388721052559 0.000000000000
H 0.000000000000 -2.470895972113 0.000000000000
C 1.202667654441 -0.694360499538 0.000000000000
H 2.139858588291 -1.235447933148 0.000000000000
C 1.202667654441 0.694360499538 0.000000000000
H 2.139858588291 1.235447933148 0.000000000000

```

Psi4 stopped on: Tuesday, 10 January 2023 10:48PM
Psi4 wall time for execution: 0:00:02.47

*** Psi4 exiting successfully. Buy a developer a beer!

From this, we get the energy of the benzene molecule $-230.721\,925\,88\text{ Ha}$.

A good estimate of the input geometry for optimizing chlorobenzene is obtained if we replace one of the hydrogens with a chlorine atom. Thus, the input may look like this:

```

set basis cc-pVDZ
molecule {
O 1
C -0.000000000000 1.388721052559 0.000000000000
Cl -0.000000000000 2.470895972113 0.000000000000
C -1.202667654441 0.694360499538 0.000000000000
H -2.139858588291 1.235447933148 0.000000000000
C -1.202667654441 -0.694360499538 0.000000000000
H -2.139858588291 -1.235447933148 0.000000000000
C 0.000000000000 -1.388721052559 0.000000000000
H 0.000000000000 -2.470895972113 0.000000000000
C 1.202667654441 -0.694360499538 0.000000000000
H 2.139858588291 -1.235447933148 0.000000000000
C 1.202667654441 0.694360499538 0.000000000000
H 2.139858588291 1.235447933148 0.000000000000
}

```

```
optimize("HF")
```

At the end of the output, we find the line with energy again. We have to be careful to take the energy from the last iteration and not from somewhere in the optimization process of the geometry.

```
==> Convergence Check <==
```

Measures of convergence in internal coordinates in au.

Criteria marked as inactive (o), active & met (*), and active & unmet ().

```

-----
Step Total Energy Delta E Max Force RMS Force Max Disp RMS Disp
-----
Convergence Criteria 1.00e-06 * 3.00e-04 * o 1.20e-03 * o
-----
13 -689.64209882 -6.68e-07 * 5.45e-05 * 9.67e-06 o 2.98e-04 * 4.79e-05 o
-----

```

The energy in chlorobenzene will therefore be -689.64209882 Ha. The optimized geometry is:

```

C 0.000000000000 0.000000000000 0.421760303147
Cl 0.000000000000 0.000000000000 2.170797070268
C -1.207631129031 -0.000000000000 -0.256682861045
H -2.136797603674 -0.000000000000 0.293524814393
C -1.200300224567 -0.000000000000 -1.644450321492
H -2.139926866970 -0.000000000000 -2.180334147000
C 0.000000000000 0.000000000000 -2.340986942849
H 0.000000000000 0.000000000000 -3.422438848199
C 1.200300224567 0.000000000000 -1.644450321492
H 2.139926866970 0.000000000000 -2.180334147000
C 1.207631129031 0.000000000000 -0.256682861045
H 2.136797603674 0.000000000000 0.293524814393

```

Finally, we need to prepare the inputs for the chlorine and hydrogen chloride molecules. That is simple for a diatomic molecule. We keep all the coordinates at zero, except for one, which is approximately the length of the bond (let's say 1.5 Ångström). The input for chlorine will therefore be:

```

set basis cc-pVDZ
molecule {
0 1
Cl 0.000000000000 0.000000000000 0.000000000000
Cl 0.000000000000 1.500000000000 0.000000000000
}

```

```
optimize("HF")
```

And for hydrogen chloride:

```

set basis cc-pVDZ
molecule {
0 1
H 0.000000000000 0.000000000000 0.000000000000
Cl 0.000000000000 1.500000000000 0.000000000000
}

```

```
optimize("HF")
```

After running these files, we get the remaining two required energies as well as the optimal values of the bond lengths, 2.00803 Å for Cl_2 and 1.27728 Å for HCl . So we have the energies of

all the molecules in our reaction. Specifically the energy for benzene is $-230.721\,925\,88$ Ha, for chlorobenzene $-689.642\,098\,82$ Ha, for chlorine $-918.960\,678\,65$ Ha and $-460.089\,417\,40$ Ha for hydrogen chloride. If we plug them into the above-mentioned formula for the reaction energy, we get approximately -0.048 Ha, which is -128 kJ·mol⁻¹. That compared to the experimental value of -134 kJ·mol⁻¹ is not bad at all. On the contrary, we can say that it is a good match.

Mikuláš Matoušek

mikulas@fykos.org

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