Worksheet 1: Quantum mechanical approaches: Hückel approximation and DFT methods

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Distance in Å	GGA	LDA	Exp[1]	Angle in degrees	GGA	LDA	Exp[1]
C2-N3	1.353	1.338	1.332	N3-C4-C5	127.37	127.17	126.9
N1-C2	1.357	1.343	1.338	C2-N3-C4	110.51	111.13	110.8
C6-N1	1.356	1.342	1.349	N9-C4-C5	104.16	104.16	105.7
C5-C6	1.427	1.415	1.409	C8-N9-C4	106.94	107.01	105.9
C4-C5	1.415	1.406	1.382	N7-C8-N9	113.51	113.28	113.8
N3-C4	1.351	1.336	1.342	C5-N7-C8	103.60	103.88	103.9

Table 1: Bond lengths and bond angles predicted by siesta and experimental data.

1 Computational Task: DFT calculations with Siesta

1.1 Geometry optimization of adenine

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[1]source: Attachment1a.pdf

1.2 Theoretical Prediction of Watson-Crick Hydrogen-bond length in adenine-thymine base pair
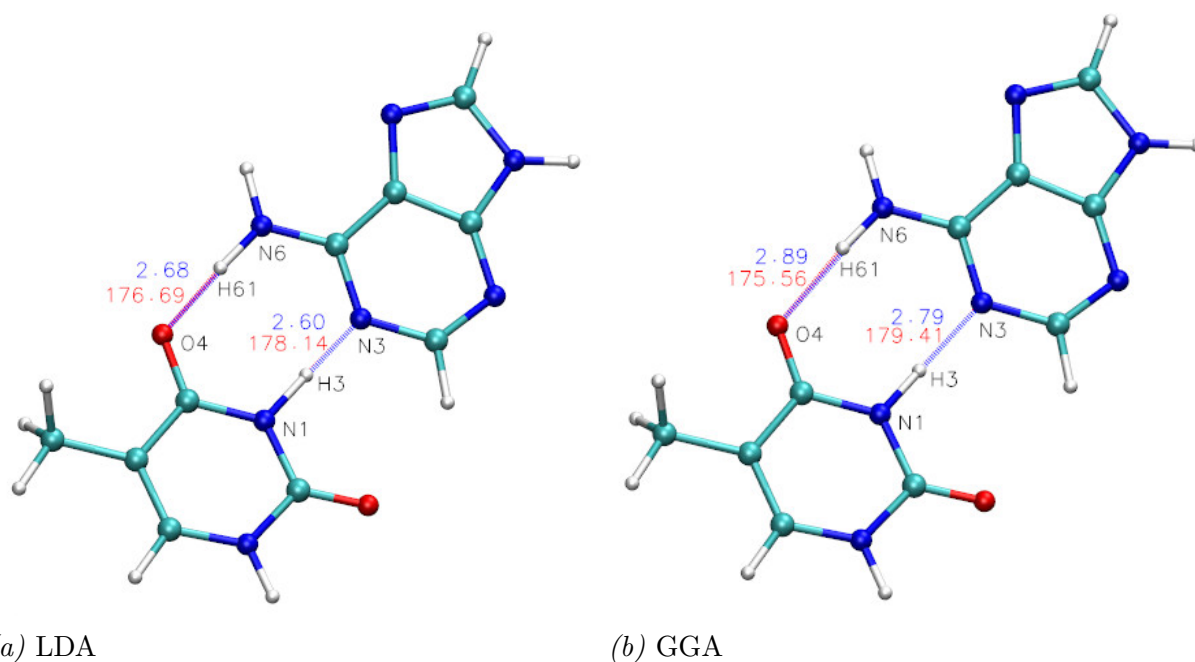

(a) LDA   *(b)* GGA

Figure 1: Results for two flavours of XC functional. Blue numbers show bond lengths and red ones show bond angles.

Angle in Å	LDA	GGA	Literature [2]
O4-H61-N6	176.7	175.6	175.8
N1-H3-N3	178.1	179.4	178.1

Table 2: Bond angles

Distance in Å	LDA	GGA	Experiment 1 [2]	Experiment 2 [2]
O4-N6	2.68	2.89	2.95	2.93
N1-N3	2.60	2.79	2.82	2.85

Table 3: Bond lengths

With LDA (local density approximation) and GGA (generalized gradient approximation) you get decent results. Both show that the O4-N6 bound is around $8 - 10\,$Å longer than the N1-N3 bound. The comparison with experimental data (see table **??**) illustrates that GGA is more precise than LDA. For GGA the deviation is around $2\,\%$ and for LDA around $10\,\%$. However the exact error can't be specified because you don't have an isolated adenine-thymine base pair in the real world and the experimental results depend on the chemical environment.

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[2]source: Attachment1b.pdf

The high precision of GGA can be explained by the fact that it uses the gradient which is non-local. In contrast LDA is a local approximation. It overestimates the bond strength regularly. Therefor the bond lengths are to short. LDA is highly precise only if you have a structure with uniform electron density.

The calculated bond angles are in conformity with calculated values that were found in Attachment1b.pdf (see Table **??**). It's virtually impossible to figure out whether their calculation is more exact than ours.

For convergence GGA needed 64 steps and LDA 70 steps. A GGA step is more time consuming than a LDA step due to the use of the gradient. Therefore GGA ran for 52 min and LDA for 49 min. As you can see the difference in run time is very small so that you should use GGA for all similar problems because of higher precision.