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

April Cooper, Patrick Kreissl und Sebastian Weber

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University of Stuttgart

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1 Theoretical Task: Hückel approximation for Benzene

Due to the fact that we only consider π - electrons we have to study the p_z orbitals. The hamiltonian for the π-electrons is : $H = \sum_n -\frac{\hbar^2}{2m_0}\Delta_n + V(r_n)$ with $n = 1, 2, ..., 6$. As the hamiltonian obviously is a sum of one-electron-hamiltonians the Schrödinger equation which results from H can be solved by finding the one-electron-wavefunctions with this Schrödinger equation: $-\frac{\hbar^2}{2m_0}\Delta\psi(r) = E\psi(r)$. Where $\psi = \sum_{j=1}^{N} c_j\phi_j(r)$, with $\phi_j(r)$ being the atomic wave $2p_z$ functions of the carbon atoms. The coefficients c_j still have to be determined. To calculate them we use the variational principle trying to minimize the left side of $\frac{\int \psi^* H \psi dV}{\int \psi * \psi dV} = E$ by choosing the right set of coefficients. Using our description of ψ as a linear combination of atomic wave functions we get

$$\frac{\sum_{jj} c_j^* c_j' \int \phi_j H \phi_{jj'} dV}{\sum_{jj} c_j^* c_j' \int \phi_j \phi_{jj'} dV} = E \; (*)$$

and we define $\int \phi_j H \phi_{jj'} dV =: H_{jj'}$ and $\int \phi_j \phi_{jj'} dV =: S_{jj'}$. Therefore it is clear that the energy is a function of the coefficients c_j respectively c_j^*. Instead of using $(*)$ we can also have a look at

$$\sum_{jj'} c_j^* c_j' H_{jj'} = E \sum_{jj'} c_j^* c_j' S_{jj'} \tag{1}$$

Deriving this regarding c_j^* and keeping in mind that in order to get a minimum it is a necessary condition that they have to vanish this derivative leads us to $\sum_{j'} c_{j'} H_{jj'} = E \sum_{j'} c_{j'} S_{jj'}$. This is equal to the following matrix equation:

$$\begin{pmatrix} (H_{11} - S_{11}E)c_1 & (H_{12} - S_{12}E)c_2 & \dots & (H_{1N} - S_{1N}E)c_N \\ & \vdots & & \\ (H_{N1} - S_{N1}E)c_1 & (H_{N2} - S_{N2}E)c_2 & \dots & (H_{NN} - S_{NN}E)c_N \end{pmatrix} \times \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_6 \end{pmatrix} = 0 \tag{2}$$

As this is a homogenous system of equations the determinant has to vanish:

$$\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E & \dots & H_{1N} - S_{1N}E \\ \vdots & & & \vdots \\ H_{N1} - S_{N1}E & H_{N2} - S_{N2}E & \dots & H_{NN} - S_{NN}E \end{vmatrix} = 0$$

This is quite a complex determinant which can be avoided to be calculated using the symmetry of the benzene molecule. In order to do this we first have to show, that every atomic wave function $\phi_j(r)$ for the corresponding carbon atom j in the benzene molecule can be written as $\phi_j(r) = \phi(r - R_j)$ where R_j is the vector of the centre of the molecule to the carbon atom j. A turn if the molecule by 60° shall be described by the turning operator C_6. Using this operator in the equation for $\phi_j(r)$ we get: $C_6\phi_j(r) = \phi_j(C_6 r) = \phi(C_6 r - R_j)$. As benzene is symmetric we can also say that R_j is the vector R_{j-1}which was turned by 60° which means:$R_j = C_6 R_{j-1}$ and results in $C_6\phi_j(r) = \phi(C_6(r - R_{j-1}))$. As we're only looking at p_z orbitals and the z direction is not affected by the turn around the z axis and since $r - R_j$ stays constant under this rotation the last equation can be simplyfied to:

$C_6\phi_j(r) = \phi(r - R_{j-1}) = \phi_{j-1}(r)$. This means that the p_z wave function of the carbon atom j is merged into the one of the one of the atom j-1 by doing a turn of 60°. Having a look on the Schrödinger equation under this operator C_6 and using that the hamiltonian is not affected by turns we get: $H(r)C_6\psi(r) = EC_6\psi(r) \Leftrightarrow C_6 H(r)\psi(r) = C_6 E\psi(r)$. This means that not only $\psi(r)$ is a solution of the Schrödinger equation but also $C_6\psi(r)$. Making the assumption that the energy E is not degenerated we know that the only way that two different wave functions can belong to the same energy is when they vary by a constant factor λ alone and therefore it is $C_6\psi(r) = \lambda\psi(r)$ (+). It can be mathematically shown that this relation can be postulated in general, wherefore we don't make a mistake by doing so. Using this relation to get the coefficients c_j of ψ we get:

$$c_1 C_6\phi_1(r) + c_2 C_6\phi_2(r) + \cdots + c_6 C_6\phi_6(r) = \lambda(c_1\phi_1(r) + c_2\phi_2(r) + \cdots + c_6\phi_6(r))$$

Using (+) this equals to

$$c_1\phi_6(r) + c_2\phi_1(r) + \cdots + c_6\phi_5(r) = \lambda(c_1\phi_1(r) + c_2\phi_2(r) + \cdots + c_6\phi_6(r))$$

As the wave functions ϕ_j are linear independent this last equation can only be true if the coefficients for the same wave function ϕ_j coincide on both sides which leads us to the following equations:

$$c_1 = \lambda c_6$$

$$c_2 = \lambda c_1$$

$$\vdots$$

$$c_6 = \lambda c_5$$

To solve these equations we make the ansatz: $c_j = \lambda^j c_0$ (Δ), where c_0 is a normalization constant. If we turn the benzene molecule 6 times using C_6 the molecule is in the state in which we started which means: $\lambda^6 = 1$. Using complex numbers (Δ) has the following solution: $\lambda = exp(\frac{2\pi k i}{6})$ with $k = 0, \pm1, \pm2, \pm3$

Using these values for c_j in the system of equations (2) and taking into account that $S_{jj} = 1, S_{jj'} = 0, H_{jj} = \alpha, H_{jj\pm1} = \beta$ and otherwise $H_{jj'} = 0$ we get for example in the first line of (2) :

$$exp\left(\frac{2\pi ik}{6}\right)(\alpha - E) + exp\left(\frac{2\pi i2k}{6}\right)\beta + exp\left(\frac{2\pi i6k}{6}\right) = 0$$

Which can be directly solved for E resulting in

$$E = \alpha + \beta\left(exp\left(\frac{2\pi ik}{6}\right) + exp\left(-\frac{2\pi ik}{6}\right)\right) = \alpha + 2\beta cos\left(\frac{2\pi k}{6}\right)$$

with $k = 0, \pm1, \pm2, \pm3$ Plotting the possible energy values and the corresponding wave functions we get the following - keeping in mind that β is negative
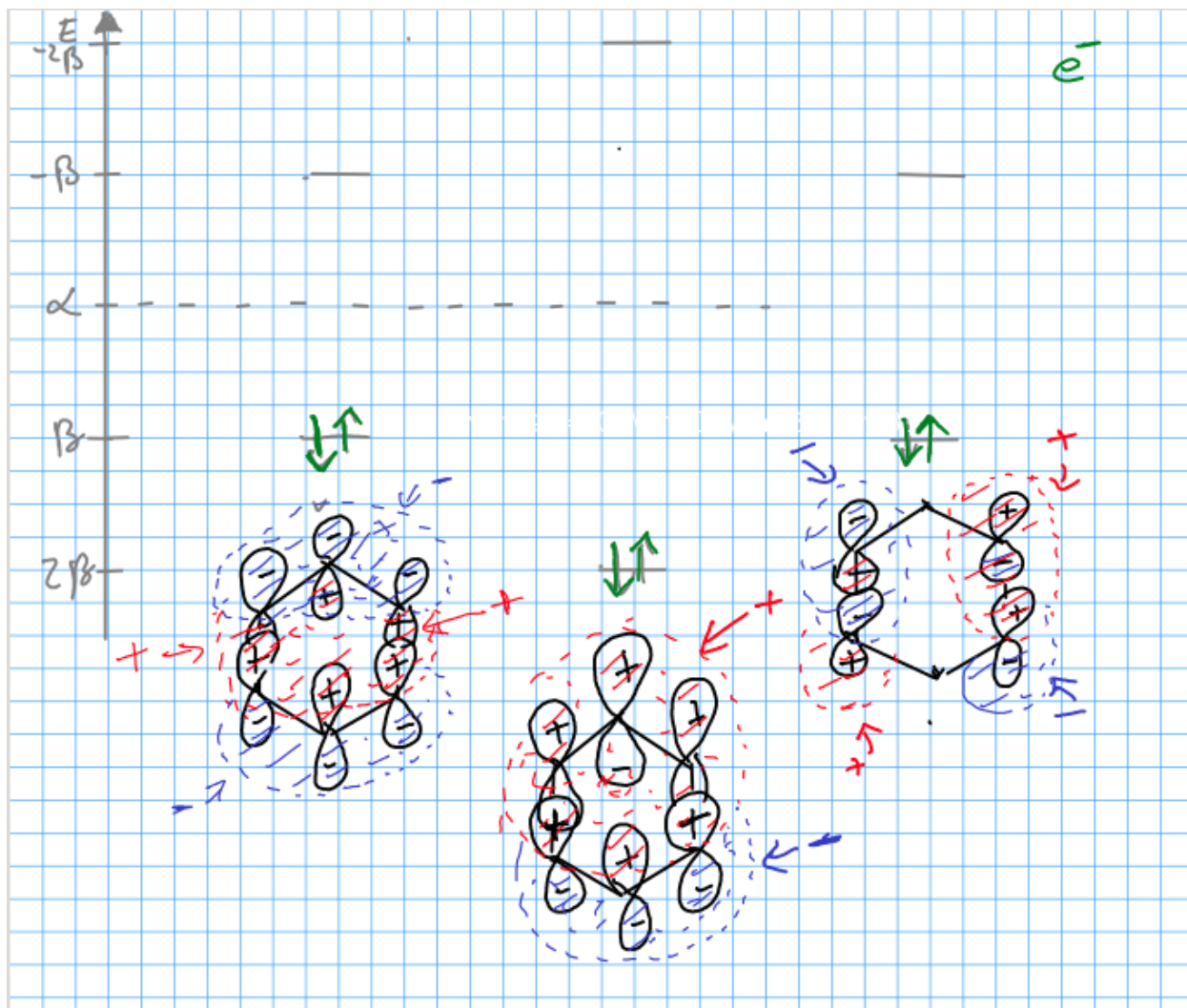
Figure 1: Plot of energy, electron distribution and corresponding wave functions

It can easily be seen that the HOMO is $E = \beta$ and the LUMO is $E = -\beta$.

2 Computational Task: DFT calculations with Siesta

2.1 Geometry optimization of adenine

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.

With both used methods (generalized gradient approximation GGA and local density approximation LDA) the results predicted by siesta are quite close to the experimental data (table 1). In general for the bond lengths the with LDA predicted data is quite close to the experimental results while the GGA data always overestimate the bond lengths.

For nearly all predicted bond angles the GGA data is closer to the experiments than the LDA data. However the LDA results vary only a litte from the GGA results.

So from this little trial run it seem that if one is looking for bond lengths using LDA for predictions would be a better choice than using GGA. Also the predicted angles would be pretty close to the experimental data. For more accuracy computing the bond angles GGA would possibly be an even better choice.

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[1]source: Attachment1a.pdf

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

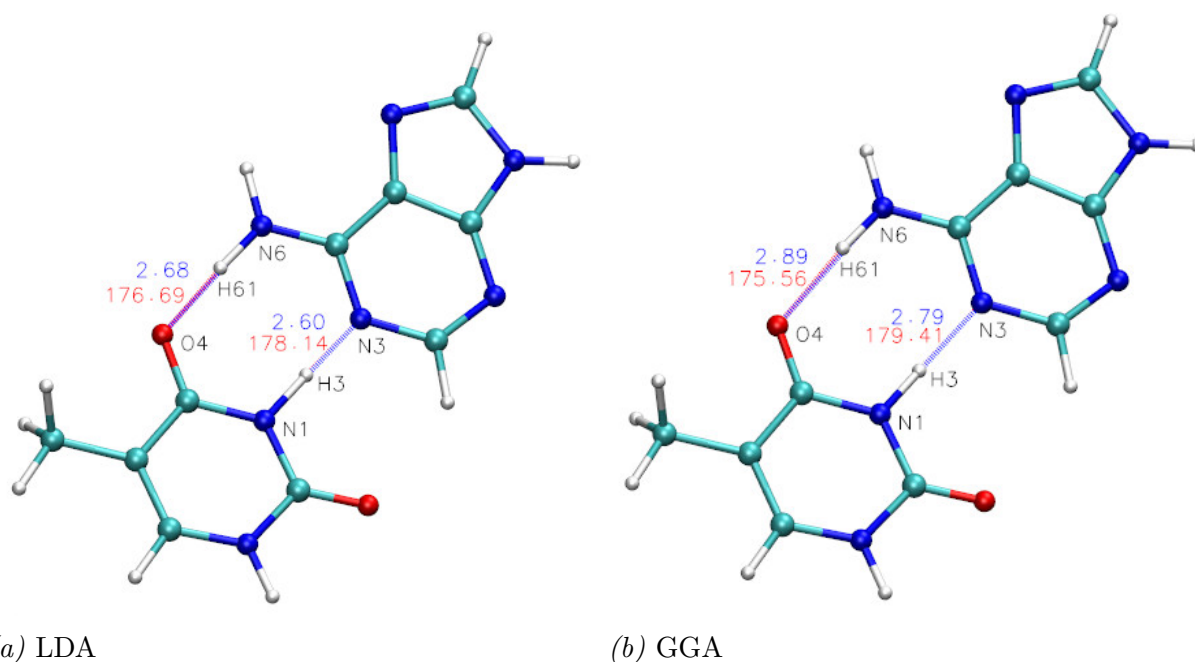*(a)* LDA   *(b)* GGA

Figure 2: Results for two flavours of XC functional. Blue numbers show bond lengths and red ones show bond angles.

Angle in degrees	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 3) 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 2). 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.