Computational Chemistry Course Lab Report 8

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Q1: For what properties are DFT calculations known to give accurate predictions and for what are DFT calculations known to be inaccurate?

DFT is known to provide accurate predictions of equilibrium geometries, reaction energies, vibrational frequencies and periodic trends.

✓

On the other hand, DFT is so inaccurate describing excited states, dispersion or van der Waals forces, charge transfer, etc. and energy barriers for reactions.

Q2: Give a concise description of the different types of exchange-correlation functionals mentioned above and explain qualitatively the difference between them.

LDA is the most basic approximation of the exchange correlation functional which is based on the uniform electron gas. GGA uses the electron density and its gradient (first derivative of the electron density). meta-GGA includes the ~~hessian~~ Laplacian of the electron density (second derivative). Hybrid functionals mixes exact exchange with GGA. Hybrid m-GGA mixes m-GGA with exact exchange. ✓

Perhaps better to say Fock exchange, since it is really not *exact* when using KS orbitals.

Q3: Make a table of the energy of a single hydrogen atom obtained with the various functional approximations and compare with the energy obtained using HF.

Table 1: Energy of H using HF and different DFT functionals using 6-311++G(3df,3pd) as basis set.

Functional	Energy (a.u.)
LDA	-0.478505578059
BLYP	-0.497722599053
TPSS	-0.500043908784
B3LYP	-0.498870898302
TPSSh	-0.500000365524
HF	-0.499817915359

✓

Q4: Does any of the calculations give total energy for the H atom that is lower than the exact energy? If so, is this in contradiction with the variational principle? Explain.

The results from TPPS and TPPSh functionals provide a lower energy than the exact energy of the H atom. This is not in contradiction with the variational principle ~~due to this principle set a lower limit, the calculated energy should be greater or equal than the exact result, but not lower~~ beccause the exact hamiltonian or the exact functional is being used in the calculations. ✓

Q5: Make two graphs showing the binding curves for the various functionals as well as the exact results obtained by Kolos and Wolniewicz. In the first graph, show the binding energy of the molecule as a function of the distance between the atoms. In the second graph, focus on the distance between 0.5 and 1.1 Å. How do the results obtained using the various functionals compare with the exact results? Explain why some functionals work better than others.

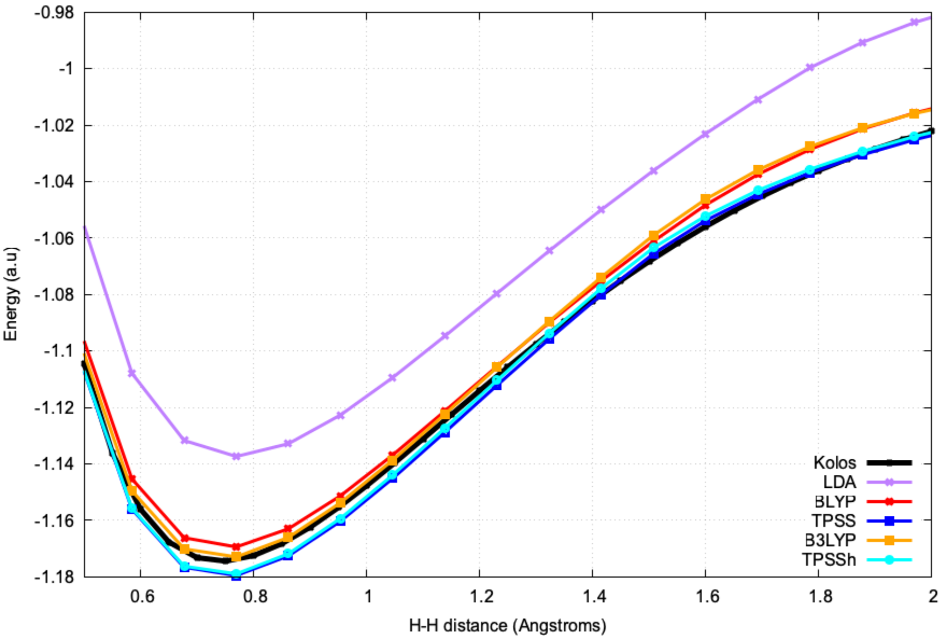

Figure 1: PES of hydrogen molecule.

As we can see in Figures 1 and 2, ~~DFT~~ B3LYP gives similar results as the exact H_2 potential energy curve. However, LDA functional is the worst result among all the functionals and the functionals TPSS and TPSSh ~~rely~~ give lower energies than the exact result. The difference between these functionals arise from the "nature" of them. In other words, they are different types of functionals which include less or more terms such as gradient of the electron density, the ~~Hessian~~ Laplacian of the electron density, etc. (See the characteristics mentioned in question 2)

Q6: What value should the energy approach as the H_2^+ bond breaks?

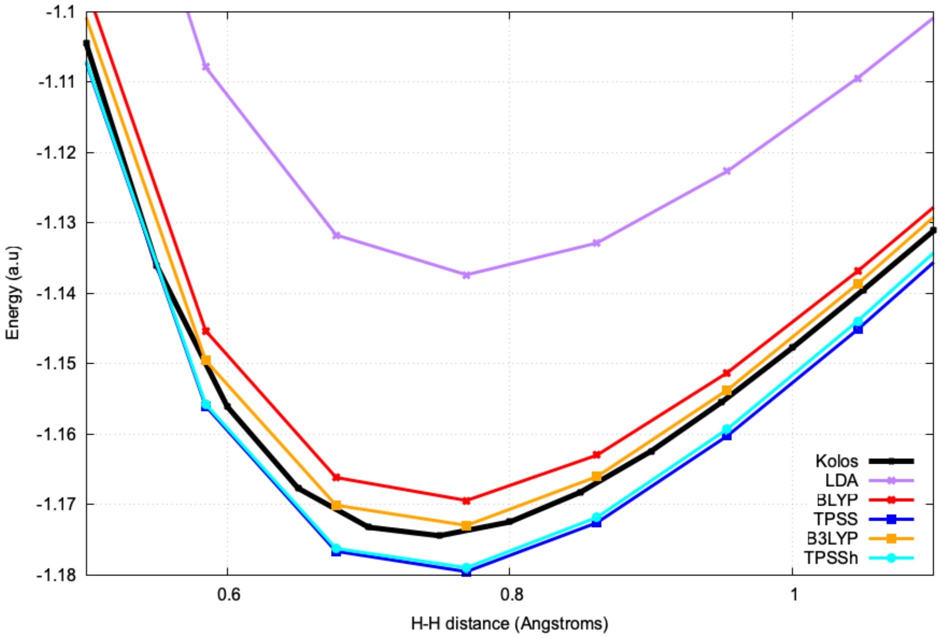

Figure 2: PES of hydrogen molecule between 0.5 and 1.1 Å.

The energy should approach to -0.5 hartree because when H_2^+ dissociates, it yields $H + H^+$. The energy of H^+ is 0, therefore, the energy should be the same as the energy of an hydrogen atom, which is -0.5 a.u. ✓

Q7: Make a graph showing the three binding curves (BLYP, B3LYP and HF). How do the results obtained by BLYP and B3LYP compare with the HF results (i) in the bonding region and (ii) when the bond has been stretched (i.e. rHH > 3.0 Å)? Explain possible discrepancies between DFT and HF results. Also, explain the difference in behaviour between BLYP and B3LYP.

In the bonding region, DFT functionals give lower ~~results~~ energy compared with the HF result. However, when the bond is stretched, above 3.0 Å, DFT provides the wrong result due to it should approximate to -0.5 a.u. This is produced because DFT tends to delocalize the electron while HF does the opposite, it tends to localize it. The difference between both functionals is that B3LYP is an hybrid functional, this means that it includes "exact" exchange in the energy. It applies the Fock operator in the Kohn-Sham orbitals and this improve the calculation. ✓

Q8: How does the geometry and singlet-triplet splitting obtained using B3LYP compare with the Hartree Fock, CI and MP2 results (from lab 4, 5 and 6) and with the experimental values of 134º (triplet)/102º (singlet) and a splitting of 9.05 kcal/mol?

The values in Table 2 show that DFT gives good approximated values based on the experimental

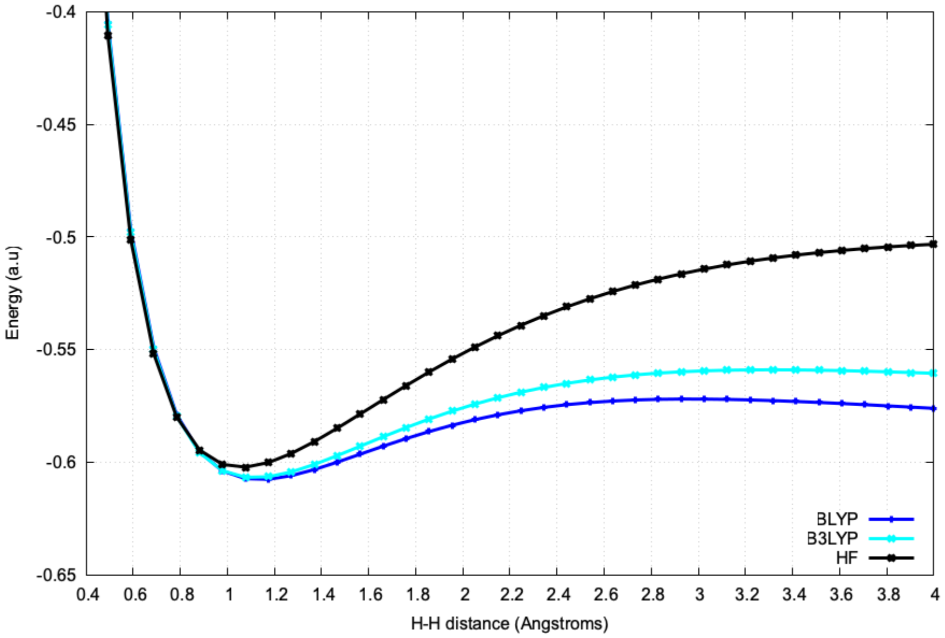

Figure 3: PES H_2^+ molecule.

Table 2: Comparison

Method	Triplet angle (°)	Singlet angle (°)	ST Splitting (kcal/mol)
DFT B3LYP	135.41	101.5	12.3
MP2	132.62	101.78	17.4
CI	132.76	122.13	17.5
HF	131.91	103.77	28.0

values. Moreover, DFT provides a better result in the Singlet-Triplet splitting compared with the previous calculations, nevertheless, it is still far from the exact value.

Q9: What would you expect the charge on the F atom to be as the C–F bond is stretched and eventually breaks? What type of molecular geometry would you expect the CH_3 moiety to assume?

Fluorine atom, as it is getting stretched from the bond with the carbon, it should have more and more negative charge (between $-1 < q < 0$) until it is fully dissociated, where it should have a negative charge (-1). The geometry of the CH_3 moiety should be trigonal planar based on VSEPR theory. ✓

Q10: Find online material/published articles and read about the Dunning basis set. Write a brief summary about this class of basis sets and also explain the (aug)-cc-pVnZ notation.

Dunning basis sets follows the next name: cc-pVnZ. cc means correlation consistent which means that the basis is constructed to converge correlated energies in a systematic way. p means that it uses polarization functions. V means valence, it expresses that only the valence electrons will be represented by the n functions, the core electrons will use fewer basis functions. nZ can be double (DZ), triple (TZ), quadruple (Q~~T~~Z), etc, at the zeta level. aug means the use of augmented by diffuse functions to improve long range interactions. ✓

Q11: Read about and explain Mulliken population analysis. Explain how the charge on a particular atom in a molecule is computed in the Mulliken approach.

Mulliken population analysis is based on atomic orbitals (AO). It sum over the contributions from each AO of the atom and take into account the electronic charge in the overlap region between the two AO of different atoms. It creates a population matrix where each row and each column corresponds to an AO. In the diagonal elements we get the population of each AO, and the off-diagonal elements give the overlap population. To calculate the charge we use the next expression:

$$q_A = \sum_{j \varepsilon A} P_{ii} + \frac{1}{2} \sum_{j \varepsilon A; i \varepsilon B} P_{ij} S_{ij} \qquad (1)$$

✓

Q12: While Mulliken population analysis is good enough when atoms are well separated as is the case here, there is a mathematical problem with this approach. Explain why.

The mathematical problem of eq. 1, the half-half splitting of the overlap terms is an arbitrary choice rather than a more physical deduction. Moreover, it is strongly dependent in the choice of the basis set and how the overlap elements are divided. ✓

Since the atomic basis set is overcomplete, the assignment of charge is somewhat arbitrary.

Q13: Why does a bond-constraint need to be applied in the constrained equilibrium structure search calculation of the dissociated fluoromethane?

The not constrained geometry optimization will not provide the dissociation of the C-F bond, therefore we need to increase the distance and constraint the bond length in the calculation. ✓

Q14: Make a table in your report with the results from the Hartree-Fock, BLYP and B3LYP calculations for the partial charge on the F atom at the equilibrium position, stretched C-F bond (3.0 Å) and the dissociated molecule (4.5 Å). ✓

Q15: Compare and contrast the charge on the F atom obtained at Hartree-Fock and B3LYP level of theory. Which is more correct and why?

HF provides a more correct solution than the B3LYP due to, our chemical intuition tell us that the fluorine atom should subtract some negative charge from the C atom, because F is the most electronegative atom in the periodic table. This behaviour is represented in the HF method but ✓

Table 3: Partial charge of F.

Method	C-F 3.0 Å	C-F 4.5 Å
HF	-0.844149	-0.938665
DFT BLYP	-0.378499	-0.287929
DFT B3LYP	-0.306353	-0.172992

✓

not using DFT.