CHEM 310 Computational Chemistry Assignment 2025

Released 13th May and
due in at the Chemistry Office by 5pm Wednesday 28th May

Q1 **Explain** the Coulomb and Fermi holes. **Discuss** which hole relates to the potential and which to the form of the wavefunction. **Which** is more "classical" and which is more "quantum mechanical" in nature?

(10 marks)

- these "holes" relate to where electrons do not occupy the same space, there is a hole in the electron density distribution
- the Coulomb hole occurs due to Coulomb potential and is based on the negative charge (Coulomb) repulsion between electrons, and is more "classical".
- Electron e2 avoids being near e1, which is a correlation effect, ie the 2 electrons correlate so as to not occupy the same space at the same time
- the Fermi hole occurs due to Pauli Exclusion principle which is based on the antisymmetric nature of the electron wavefunction
- the Fermi hole relates to the wavefunction and is "quantum" in nature.
- 2 electrons of the same spin cannot occupy the same region of space. The Fermi hole does not apply to electrons of opposite spin, ie 2 electrons of opposite spin can occupy the same MO.

Generally well answered.
Careful: we have an antisymmetry requirement, and a Pauli principle, not an antisymmetry principle, it is anti-symmetric NOT asymemetric

Q2. **Explain** Exc[ρ]. Write out the full B3LYP functional and label the exchange and correlation parts. **Explain** the B3LYP acronym. The B3LYP functional has been effectively updated, **name** 3 of the more modern functionals, and **describe** the advanced techniques employed.

(10 marks)

- $E_{xc}[\rho]$ is the exchange correlation functional which defines DFT functionals,
- it describes the part of the molecular functional that cannot be written in terms of a density
- $E_{xc}[\rho]=T_{int}[\rho]+K_{ee}[\rho]$ which is the kinetic energy due to interacting particles and the exchange contribution.
- however in DFT $E_{xc}[\rho]$ it is written in terms of separate exchange $E_x[\rho]$ and correlation $E_c[\rho]$ contributions.
- DFT functionals are described by how they approximate the exchange and correlation functionals
- $E_{XC}^{B3LYP}\left[\rho\right]=(1-a)E_X^{LSD}+aE_{XC}^{\lambda=0}+bE_{XC}^{B88}+cE_C^{LYP}+(1-c)E_C^{LSD}$

  E_X^{LSD} is the exact exchange from the uniform electron gas

  $E_{XC}^{\lambda=0}$ is the HF exchange for a single Slater determinant

  E_{XC}^{B88} is a correction by Becke

  E_C^{LYP} is an expression for the correlation energy based on the correlation energy of a helium atom obtained using correlated wave function theory.

  E_C^{LSD} is the exact correlation from the uniform electron gas
- a=0.20, b=0.72, c=0.81
- The exchange parts are the first 3 terms and the correlation part are the last 2 terms
- B3LYP is a generalised gradient approximation GGA hybrid functional,

- B for the Becke exchange correction, LYP for the correlation contribution and 3 for the 3 parameters a, b and c.
- B3LYP is augmented with a dispersion correction including Becke-Johnson damping forming the B3LYP-D3(BJ) functional.
- B3LYP can be updated with a hybrid correlation contribution including correlation from MP2 to form the double hybrid functional B2PLYP
- B3LYP can be improved by splitting the exchange components into short and long range contributions (reducing the HF contribution at short range and increasing it at long range) in the range separated CAM-B3LYP functional

Over-all well answered. Be careful in reading the question

when you are asked to write out the **FULL** functional, include all the components and their definitions, many people missed giving a, b and c.

It was clear some answers were likely from AI responses, as a student it is best to try and make your answers as non-AI like as possible. One way to do this is to follow the lecture notes even if you do out-side reading (as you should!) to improve your understanding of the topic.

If you include terms *not discussed in the lectures,* you must define and explain what they are, otherwise I think you are copying from an alternate source and do not understand the material

When you are asked to describe how the **B3LYP functional** has been updated, your description needs to be based around that functional

Q3 **Describe** the 4-31+G(d) basis set, **explaining** each component and its purpose, **provide** an equation. **What** is the quality of this basis set, and when would it be used?

(10 marks)

- Pople basis set based on gaussian functions (G)
- Split valence is identified by the "dash" meaning the core and valence are treated differently, here a frozen core and variable valence space
- Contracted orbitals have fixed coefficients, with a single "whole group" varying coefficient.
- The 4-31 has 4 contracted Gaussian functions are used for the core orbitals and a 3-1 contraction pattern for the 4 Gaussian functions used to describe the valence orbitals.

$$\psi(4-31G) = c_{core}(a_1g_1 + a_2g_2 + a_3g_3 + a_4g_4) + c_{v1}(a_5g_5 + a_6g_6 + a_7g_7) + c_{v2}g_8$$

a are constants c_{core}, c_{v1} and c_{v2} are variables

- there are 2 variables in the valence space so this is a (valence) double zeta basis set
- The + refers to a diffuse function on all atoms but H. Diffuse functions are additional (s and p) functions with a small exponent allowing electron density to move further out from the atom.
- The (d) refers to a single set of polarisation functions per "heavy" ie non-H atom. These are functions of one higher angular momentum (so d functions are added to the first row elements) allowing electron-density to polarise around atoms.
- This is a moderate to low quality basis set, it is only double zeta, useful for obtaining a rough starting geometry, the diffuse function and polarisation functions do add some extra flexibility so it is not terrible, however this basis will misrepresent H-bonding

Some exceptional answers and some surprisingly poor answers given we have been over it twice in lectures.

When you are asked to describe something, make sure you include a development of the topic, not just bullet points without explanation

A few people missed it was a Pople basis set, with a split valence

If you write an equation *define all the terms!*

The d, means d-set function on 2nd row, but really a set of higher angular momentum functions!