Introduction: This problem sheet is meant to increase understanding of DFT through interactive visualizations and critical thinking. The three Google Colab Notebooks referenced throughout are hosted at this GitHub repository: https://github.com/tjz21/DFT_PIB_Code.

1 Modelling PAHs

There are different approaches to modelling the π electrons of polycyclic aromatic hydrocarbons (PAHs). Notebook 1 treats them as non-interacting particles in a rectangular 3D box. Notebook 2, on the other hand, employs a rigorous quantum mechanical method, HF/STO-3G, to find the solutions to the full system of interacting electrons and nuclei. Select any three linear PAHs of sequentially increasing size from the table in Notebook 1 and compare the HOMO-LUMO gap through the particle in a box (PIB) and Hartree-Fock (HF) approach.

Summarize the results in this table:

Molecule Name	Dimensions	PIB: H-L Gap (eV) Notebook 1	HF: H-L Gap (eV) Notebook 2

1. Do you observe any trend in relation to increasing box size and HOMO-LUMO gap? Is this trend (or lack thereof) in agreement between the two methods considered here?

2. Select the simplest of the three molecules from the above table and look at the frontier orbitals through both approaches.

   (a) How does the shape, i.e. relative phases and nodal planes, of the HOMO, HOMO-1, and LUMO of this molecule compare through the two approaches?

   (b) How does the probability density[1] of these orbitals compare?

   (c) What do these orbital comparisons tell you about the space available to the π electrons in PAHs?

3. Using the molecule from the previous question, compare the energy level plots from Notebook 1 and Notebook 2. What are the main relative and absolute differences between the diagrams?

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[1]The probability density is the square modulus of the wavefunction/orbital.

2   Density Optimization

Let's consider again any one of the simple molecules from the table of PAHs in Notebook 1 through the PIB approach. Instead of treating them as non-interacting we'll now turn on electron-electron interaction through the Kohn-Sham potential, which in this context includes the Hartree and exchange-correlation (XC) potential. This can be achieved using the DFT calculator at the end of Notebook 3. Try getting a converged SCF solution for the selected PAH-like box using three approaches: (1) non-interacting[2], so turning Hartree, exchange, and correlation OFF; (2) turning Hartree and LDA-XC potential ON; and (3) turning Hartree and PBE-XC potential ON. Record the final energy printout here and the convergence parameters used.

Method	Tot. Energy	Kinetic	Exchange	Correlation	Hartree	H-L Gap
DFT-noninter.						
DFT-LDA						
DFT-PBE						

1. Report the energy threshold, number of iterations, and amount of linear density mixing used to obtain a converged solution for

   (a) the DFT-LDA calculation.

   (b) the DFT-PBE calculation.

2. Consider the DFT-LDA or DFT-PBE calculation. Use the density analysis tools below the calculator to compare the initial non-interacting density (iteration #0) with the DFT-converged density (final iteration).

   (a) What happens to the electron density in terms of its orientation in the box as the SCF loop progresses.

   (b) Do your best to describe the difference between the initial and final density through the isodensity surface representation cell.

   (c) How reasonable would the assumption of non-interacting electrons be from your analysis in this system?

3. The terms in the LDA are derived from the uniform electron gas (UEG) model system in which the electron density is uniform in space. The PBE functional is also defined relative to the UEG, but provides corrections to account for inhomogeneity.

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[2]Due to the finite numerical grid treatment used in this code, these results will be different and not comparable to the analytic solutions from Notebook 1. They will, however, be internally comparable to other calculations within Notebook 3.

(a) What makes the electron density inhomogeneous in a molecular system that is missing in the model treatment here?

(b) Could this system be considered a UEG?

3 Exchange-Correlation

To answer the below questions, refer to the table made in **2-Density Optimization**.

1. The LDA constitutes the first rung of exchange-correlation functionals in a hierarchy known as Jacob's Ladder. As their equations indicate, the LDA depends only on the density at each grid point and is a 'local' functional in that sense; PBE depends on both the local density and its 1st derivative at each point, hence the description of 'semi-local.'

   (a) Comment on the similarity/difference between the LDA and PBE here?

   (b) What provides a more realistic treatment?

   (c) What would you naturally expect the rung above PBE to depend on?

2. Exchange and correlation have been described as 'nature's chemical glue.' In what sense is this true?

3. The Thomas-Fermi (TF) model was a predecessor of modern Kohn-Sham DFT that neglected exchange and correlation and treated kinetic energy in a very approximate way. Why might this approach be problematic for calculating the total energy and chemical bonds?

4 DFT-Koopman's Theorem

$$I \approx -\epsilon_{HOMO}$$

The connection between the orbital energies in a DFT calculation and a physical observable, ionization energy, can be achieved in an approximate sense through Koopman's Theorem. Try calculating the frontier DFT-LDA orbitals of a naphthalene-like box using Notebook 3 in different ionization states $(0, +2, +4)$, then fill out the below table.

Electrons	Orbital	Orbital Energy (Ha)
10	HOMO	
8	LUMO	
6	LUMO+1	

In the absence of orbital relaxation the energies of these orbitals would be identical. Are they similar energies? What might be going on here?