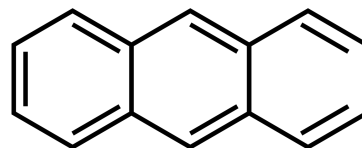


Molecule	Rings	Box Dimensions (Bohr)	π electrons
benzene	1	8 x 8 x 2	6
naphthalene	2	12 x 8 x 2	10
anthracene	3	16 x 8 x 2	14
tetracene	4	20 x 8 x 2	18
pentacene	5	24 x 8 x 2	22
hexacene	6	28 x 8 x 2	26



1 The difference between PIB and DFT

Treat the π electrons of anthracene in a 3D box as (1) non-interacting particles and (2) interacting through an LDA exchange-correlation functional by using Notebook 3, `DFT_code.ipynb` (parameters provided in above table).

Summarize the results here:

Method	HOMO-LUMO Gap (eV)	Total Energy (Ha)	max. orbital degeneracy
DFT: LDA			
PIB			

1. Which model represents a more realistic treatment of the HOMO-LUMO gap? Why?
2. Why does the PIB solution have degenerate orbitals and how do these compare with their DFT counterparts?
3. Why do the total DFT energies become progressively lower with iteration number?
4. Compare the non-interacting electron density with the DFT-optimized density. What information does this convey?

2 Jacob's Ladder

1. Repeat your DFT simulation with the GGA option (PBE) for anthracene.
 - (a) Do any of the calculated properties (KS orbital energies, exchange energy, electron density, etc.) drastically change compared to LDA? Why is this the case?
 - (b) 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 provides corrections to account for inhomogeneity. What makes the electron density inhomogeneous in a molecular system that is missing in the DFT-PIB treatment?

2. Run the code on the same system with LDA or GGA exchange but no correlation, and take note of the different terms that contribute to the total energy.
 - (a) Correlation has been described as ‘nature’s chemical glue’; in what sense is this true?
3. Now try with correlation but no exchange.
 - (a) Describe the role of exchange.
4. Try turning exchange and correlation off but keeping the classical Hartree potential on; observe how the total energy changes with iteration.

3 PAHs

1. Consider isosurface renderings of the frontier Hartree-Fock orbitals of naphthalene from notebook 2. Describe any resemblances/differences between their spatial orientations and those of the analogous PIB model system wavefunctions from notebook 1.
2. Calculate the DFT HOMO-LUMO gap for naphthalene, anthracene, and tetracene using the noninteracting PIB approach and the DFT-PIB approach; identify any trends that emerge.

4 Koopman’s Theorem

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

The relation of the orbital energies to a physical observable, ionization energy, can be achieved in an approximate sense through Koopman’s Theorem. Try calculating the frontier DFT orbitals of naphthalene using notebook 3 and observe how they change by reducing the number of electrons in increments of two.