HuckelSolver.py

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I.   INTRODUCTION

This script solves the Hückel problem for a generic molecule provided in xyz format. The script used for Hückel Molecular Orbital (HMO) calculations can be found on GitHub at: `https://github.com/gorangiud/SCRIPTS/blob/main/HuckelSolver.py`
The quantities computed are:

- Molecular orbitals (MOs);

- MOs eigenenergies;

- State properties:

    - Mulliken charges;

    - Bond orders;

    - Dipole moment;

- Transition properties:

    - Excitation energies;

    - Transition dipole moment;

II.   LIST OF INPUTS

- Mandatory

    × -i, --xyz: structure file in XYZ format;

- Optional

    × -e, --excitations: text file with list of excitations to compute;

- $\times$ -H, --hamiltonian; user-defined Hamiltonian matrix;

- $\times$ -d, --cutoff: distance in angstrom under which two atoms are recognized as connected (default = 1.6 Å);

- $\times$ -q, --charge: net charge of the system (default = 0);

- $\times$ -M, --MO_size: integer to scale the size of lobes for MOs plots (default = 1000);

- $\times$ -C, --charge_size: integer to scale the size of Mulliken charges in plots (default = 500);

- $\times$ -N, --node_size: integer to scale the size of the font of labels on atoms (default = 5);

- $\times$ -E, --edge_size: integer to scale the size of the font of labels on bonds (default = 3);

- $\times$ -R, --reorient: Boolean to control reorientation of molecule on xy plane (default = True);

- $\times$ -T, --text_plot: Boolean to control printing of transition properties on plots (default = False);

- $\times$ -B, --bond_order: Boolean to control printing of bond orders on bonds (default = False);

Basic usage: `python HuckelSolver.py -i input.xyz`

The script will automatically remove all Hydrogen atoms from the input structure and build the Hückel Hamiltonian based on the connectivity of the remaining atoms. Connectivity is determined based on a cutoff distance of 1.6 Å. The molecule is also rotated onto the *xy* plane for plotting purposes. Plotting is done with the *networkx* package, so make sure to have it installed in your machine by running:

`pip install networkx[default]`

III.   EXAMPLE 1: BUTADIENE - BASICS

Run: `python HuckelSolver.py -i butadiene.xyz`

In your work directory you should find the following files as output:

- H_mat.txt (Hamiltonian matrix exported as .txt file)

- Figures for each MOs:

  - butadiene.xyz_N_4_MO_1.png

  - butadiene.xyz_N_4_MO_2.png

  - butadiene.xyz_N_4_MO_3.png

  - butadiene.xyz_N_4_MO_4.png

- butadiene.xyz_N_4_gs.png (ground state Mulliken charges and bond orders)

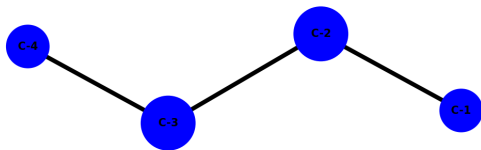- butadiene.xyz_output.txt (output file)

MO energy = 0.00 eV
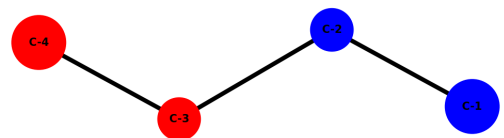Occupation = 2

MO energy = 2.62 eV
Occupation = 2

FIG. 1: MO 1

FIG. 2: MO 2

The butadiene.xyz_output.txt file will contain the structure of butadiene without Hydrogen atoms, the Hückel Hamiltonian, the MOs eigenenergies relative to the lowest value, the atomic orbitals (AOs) coefficient for each MOs (row vectors), and the ground state dipole moment.

IV. EXAMPLE 2: BUTADIENE - EXCITED STATES

Excited state calculations can be requested with an external file where the indexes of the occupied and virtual orbitals involved in the desired transition are listed. In the ground state of butadiene MO 1 and MO 2 (HOMO) are both doubly occupied. If we want to
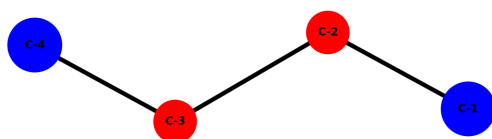
MO energy = 5.86 eV
Occupation = 0

MO energy = 8.48 eV
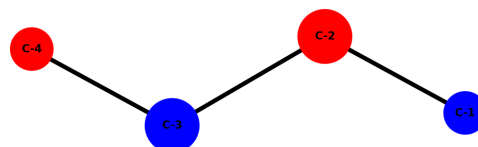Occupation = 0

FIG. 3: MO 3
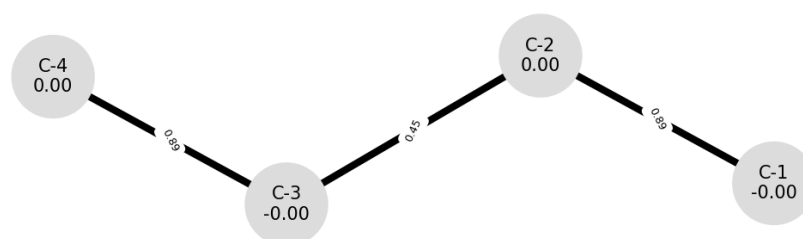
FIG. 4: MO 4

Ground state

FIG. 5: Ground state of butadiene. Labels on atoms show Mulliken charges while the ones on edges show bond orders

calculate properties for the HOMO-LUMO and HOMO-LUMO+1 transitions, we can write in a file "*excitations_butadiene.txt*" the following lines:

2 3

2 4

For each transition (i.e. each line of the external file) the code will generate a picture with Mulliken charges and bond orders like in figure 5 for the related excited state.

Run: `python HuckelSolver.py -i butadiene.xyz -e excitations_butadiene.txt` In

Excitation energy = 3.24 eV
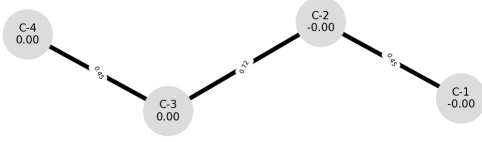Transition = MO 2 → MO 3
Tansition dipole m. = 1.171 (Å)

Excitation energy = 5.86 eV
Transition = MO 2 → MO 4
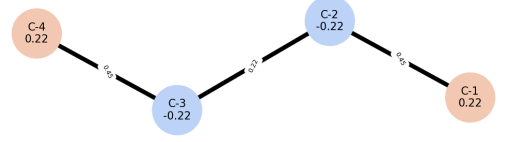Tansition dipole m. = 0.000 (Å)

FIG. 6: HOMO-LUMO transition.

FIG. 7: HOMO-LUMO+1 transition.

addition to the data described before, the script will print in the output file the excited state and transition properties for a given molecule. This includes excitation energies, state dipole moment, transition dipole moment, and dipole moment change from the ground state.

V. MOLECULAR PROPERTIES

The current implementation computes the following properties.

A. Bond Order - BO

the BO between atoms i,j is defined as:

$$BO(i,j) = \sum_{k}^{\#MO} n_k c_i^{(k)} c_j^{(k)} \tag{1}$$

where c and n are atomic orbital coefficients and occupation number of the k-th MO respectively.

B. Total π-electron energy

The total π-electron energy of a state is the sum of the MO energies multiplied by their respective occupancies:

$$E_\pi^{Tot} = \sum_k^{\#MO} n_k E_k^{MO} \qquad (2)$$

C. π-bonding energy

The π-bonding energy of a state corresponds to the difference between the π-electron energy and the π-core energy which is computed as the trace of the Hückel Hamiltonian:

$$E_\pi^{bind} = E_\pi^{Tot} - tr(\hat{H}) \qquad (3)$$

D. Mulliken Charges - q

Similarly, the Mulliken charge for each atom is:

$$q_i = 1 - \sum_k^{\#MO} n_k c_i^{(k)} c_i^{(k)} \qquad (4)$$

For excited states it is computed the Mulliken charges differences with the ground state for each atom, i.e. $q_i^{diff.} = q_i^{ex} - q_i^{gs}$

E. Dipole moment - μ

This is the dipole moment for the distribution of Mulliken (point) charges:

$$\mu = \sum_i^N q_i r_i \qquad (5)$$

i.e. the electric dipole is the vector sum of the product between Mulliken charges q_i and their position r_i.

F. Transition Dipole Moment - μ_{tr}

$$\mu_{tr}^x = \sum_l^{\#atoms} x_l c_l^{(h)} c_l^{(e)} \qquad (6)$$

Here h and e label the MOs where the electron is excited from (hole) and promoted to (electron).