

# MEST - Assignment 5

Due date: 12/05/2024

(For each solution, show your work through a set of important steps.)

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1. For the hydrogen atom, plot the radial wavefunction for (i) the exact 1s AO, and (ii) approximate AOs using CGTOs (a)STO-3G and (b) STO-6G. Comment on the relative accuracy of STO-6G and STO-3G basis function.
2. For the HMn(CO)<sub>5</sub> molecule, enumerate the total number of CGTOs that constitute the 6-31G and STO-3G basis sets. Try to answer this without and with the help of the basis-set website (<https://www.basissetexchange.org/>). How many spatial MOs will be occupied and how many will be empty?
3. For NH<sub>3</sub> molecule, the five lowest-energy spatial MOs in terms of AOs are:

$$\begin{aligned}\psi_1 &= 0.99339\phi_{N_{1s}} + 0.03182\phi_{N_{2s}} - 0.00440\phi_{N_{2p_z}} - 0.00658(\phi_{H_{1s}} + \phi_{H_{2s}} + \phi_{H_{3s}}) \\ \psi_2 &= -0.22026\phi_{N_{1s}} + 0.73925\phi_{N_{2s}} - 0.12153\phi_{N_{2p_z}} + 0.16182(\phi_{H_{1s}} + \phi_{H_{2s}} + \phi_{H_{3s}}) \\ \psi_3 &= 0.58945\phi_{N_{2p_x}} + 0.42798(\phi_{H_{2s}} - \phi_{H_{3s}}) \\ \psi_4 &= 0.58945\phi_{N_{2p_y}} + 0.49419\phi_{H_{1s}} - 0.24710(\phi_{H_{2s}} + \phi_{H_{3s}}) \\ \psi_5 &= -0.08049\phi_{N_{1s}} + 0.40462\phi_{N_{2s}} + 0.91261\phi_{N_{2p_z}} - 0.11245(\phi_{H_{1s}} + \phi_{H_{2s}} + \phi_{H_{3s}})\end{aligned}$$

For this configuration, calculate the individual AO electronic population, Gross electronic population on each atom, and the net charges. All AOs are normalized while the overlap integrals are given by:

$$\begin{aligned}\langle\phi_{N_{1s}}|\phi_{N_{2s}}\rangle &= 0.235038, \langle\phi_{N_{2p_y}}|\phi_{H_{1s}}\rangle = 0.411956 \\ \langle\phi_{N_{1s}}|\phi_{H_{1s}}\rangle &= \langle\phi_{N_{1s}}|\phi_{H_{2s}}\rangle = \langle\phi_{N_{1s}}|\phi_{H_{3s}}\rangle = 0.0573208 \\ \langle\phi_{N_{2s}}|\phi_{H_{1s}}\rangle &= \langle\phi_{N_{2s}}|\phi_{H_{2s}}\rangle = \langle\phi_{N_{2s}}|\phi_{H_{3s}}\rangle = 0.489927 \\ \langle\phi_{N_{2p_z}}|\phi_{H_{1s}}\rangle &= \langle\phi_{N_{2p_z}}|\phi_{H_{2s}}\rangle = \langle\phi_{N_{2p_z}}|\phi_{H_{3s}}\rangle = -0.145649 \\ \langle\phi_{H_{1s}}|\phi_{H_{2s}}\rangle &= \langle\phi_{H_{1s}}|\phi_{H_{3s}}\rangle = \langle\phi_{H_{2s}}|\phi_{H_{3s}}\rangle = 0.201445 \\ \langle\phi_{N_{2p_y}}|\phi_{H_{2s}}\rangle &= \langle\phi_{N_{2p_y}}|\phi_{H_{3s}}\rangle = -0.205978 \\ \langle\phi_{N_{2p_x}}|\phi_{H_{2s}}\rangle &= -\langle\phi_{N_{2p_x}}|\phi_{H_{3s}}\rangle = 0.356765\end{aligned}$$

4. (a) Construct the Hückel secular determinantal equation for benzene. Then calculate the energy values for all the levels.  
(Hint: The six roots for the equation  $x^6 - 6x^4 + 9x^2 - 4 = 0$  are  $x = \pm 1, \pm 1, \pm 2$ ).
- (b) Also explain why benzene is more stable than three ethene molecules? Quantify the amount of delocalization energy.
5. (a) Derive how the expectation values of kinetic energy and electron-electron interaction energy vary with the coordinate scaling factor  $\lambda$ .

- (b) Suppose kinetic energy is expressed in terms of density as follows  $T[\rho] = \int |\delta\rho^{1/2}/\delta r|^2 dr$ . Then show how does it vary with  $\lambda$ ?
6. The  $U(R)$  curve for a repulsive electronic-state of a diatomic molecule can be approximated by the function  $ae^{-bR} - c$ , where a,b, and c are positive constants with  $a > c$ . (Note: This function omits the Van der Waals minimum and fails to go to infinity at  $R = 0$ .) Sketch  $U$ ,  $\langle T_{el} \rangle$ , and  $\langle V \rangle$  as functions of  $R$  for this function. ( $V = V_{el} + V_{nn}$ ).