Problem Set 1

Problem 1

Explain why the sp^2 orbitals as defined in class are at angles 120^0 from each other.

Ex

Problem 2

Consider 4 atoms arranged on a square

$$4 \qquad 3$$

$$1 \qquad 2$$

with one s-orbital per atom. Assume $H_{AA} = \alpha$, $H_{AB} = \beta$ with A, B, nearest neighbors, $H_{AC} = \gamma$ with A, C next nearest neighbors, and assume orthogonal orbitals.

(a) Find four orthogonal molecular orbitals and their energies.
(b) Discuss how your answers would change if the atomic orbitals instead of s orbitals were (i) $d_{x^2-y^2}$ orbitals and (ii) p_y orbitals, with the x and y axis connecting the atoms 1,2 and 1,4 respectively.

Problem 3

Consider the molecule NaH, and assume the bond arises from overlap of the Na 3s and the H 1s orbitals. Assume orthogonal orbitals, and matrix elements

$$H_{NaNa} = -5.13eV, \quad H_{HH} = -10.61eV, \quad H_{NaH} = -4.27eV$$

(a) Find the energy of the bonding and antibonding orbitals.
(b) Draw the energy level diagram.
(c) What is the probability that an electron in the bonding orbital will be found at the Na atom? What is it for an electron in the antibonding orbital? Which is larger, why?

Problem 4

Consider the hydrogen molecular ion H_2^+. The protons are at position $\vec{r} = 0$ and $\vec{r} = \vec{R}$.
Assume that the ground state wave function for one electron can be approximated by
$$\psi(\vec{r}) = N(a(\vec{r}) + b(\vec{r}))$$

with $a(\vec{r})$ the hydrogen 1s wave function for a proton at $\vec{r} = 0$ and $b(\vec{r}) = a(\vec{r} - \vec{R})$.

$$a(\vec{r}) = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} \text{ with } a_0 = 4\pi\varepsilon_0 \hbar^2 / (m_e e^2) \text{ the Bohr radius.}$$

(a) Find an expression for N so that $\psi(\vec{r})$ is normalized, in terms of

$$S = (a,b) = \int d^3r a(\vec{r})b(\vec{r})$$

(b) Find an expression for the expectation value of the ground state energy E(R) (including the proton-proton repulsion) in terms of S, α and β, with:

$$\alpha = \frac{e^2}{4\pi\varepsilon_0} \int d^3r a(\vec{r})^2 \frac{1}{|\vec{r} - \vec{R}|}$$

$$\beta = \frac{e^2}{4\pi\varepsilon_0}\int d^3r\, a(\vec{r})b(\vec{r})\frac{1}{|\vec{r}-\vec{R}|}$$

(c) The integrals S, α, β can be obtained analytically, they are given by:

$$S = (1+\frac{R}{a_0}+\frac{R^2}{3a_0^2})e^{-R/a_0}$$

$$\alpha = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{a_0}[\frac{a_0}{R}-(\frac{a_0}{R}+1)e^{-2R/a_0}]$$

$$\beta = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{a_0}[\frac{R}{a_0}+1]e^{-R/a_0}$$

For 232 students only: obtain the expressions given above for S, α, β.

Make a graph of E(R) vs R. Find the equilibrium distance R_0 (in A) and the binding energy in eV.

(d) Find in the literature experimental values for R_0 and the binding energy, compare with your results and discuss any differences.

(e) Find the energy of vibrational zero point motion $\hbar\omega/2$ in eV from your calculation. Compare with the experimental value.

(f) The mass of the electron, $m_e = 0.511 Mev/c^2$, is approximately 1/2000 of the mass of the proton, $m_p = 938.27 Mev/c^2$. If the mass of the electron was twice as large as it is, would you expect your answer in (e) to change by more or less than 1%? Justify.

Problem 5:
(a) Prove that the Coulomb repulsion integral for two electrons in the 1s orbital for a nucleus of charge Z, given by

$$U(Z) = \int d^3r\, d^3r'\, s(r)^2\frac{e^2}{|\vec{r}-\vec{r}'|}s(r')^2$$

with

$$s(r) = (\frac{Z^3}{\pi a_0^3})^{1/2}e^{-Zr/a_0}$$

is given by U(Z)=constant x Z x 13.6 eV, and give an expression for "constant" in terms of integrals.

(b) What is the numerical value of "constant"? Do the integral yourself or find it in Griffiths, Introduction to Quantum Mechanics, 2nd ed, p.300.

(c) Assume there are 2 electrons of opposite spin in the lowest energy state of a nucleus of charge Z. Assuming for the ground state wave function the form $\Psi(r,r') = \bar{s}(r)\bar{s}(r')$, with

$$\bar{s}(r) = (\frac{\lambda^3}{\pi a_0^3})^{1/2}e^{-\lambda r/a_0},$$

find the value of λ that minimizes the energy, in terms of Z.

(d) Compare the values of (i) the kinetic energy and (ii) electron-ion interaction energy for each electron, (iii) the electron-electron repulsion energy, and (iv) the total energy, with wavefunctions $\bar{s}(r)$, with the corresponding values with wavefunctions $s(r)$. State which are higher and which are lower and explain why.