Problem Set 1

Problem 1
Show that the Madelung constant for a linear chain is $\Lambda = 1.386$.
Hint: consider the Taylor expansion of $\ln(1+x)$.

Problem 2
Consider the molecule NaH, and assume the bond arises from overlap of the Na 3s and the H 1s orbitals, with $(\alpha_{Na} = H_{AA}, \alpha_{H} = H_{BB}, \beta = H_{AB})$. Assume orthogonal orbitals.
$\alpha_{Na} = -5.13 \text{ eV}, \alpha_{H} = -10.61 \text{ eV}, \beta = -4.27 \text{ eV}$.
(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 3
Consider 4 atoms arranged on a square

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 4  3
 1  2
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with one s-orbital per atom. Assume $H_{i,i} = \alpha$, $H_{i,i+1} = \beta$ and neglect overlap between orbitals at different atoms. Find the four possible molecular orbitals and their energies.

Problem 4
Consider the molecular ion $\text{H}_2^+$ with the protons at distance $R$ from each other. Assume the matrix elements of the Hamiltonian are $H_{11} = \alpha = -13.6 \text{ eV}, H_{12} = \beta = be^{-\lambda R}$, with $b = -40.8 \text{ eV}, \lambda = 1.3 \text{A}^{-1}$. The ion-ion repulsion is $V = e^2/(4\pi \varepsilon_0 R) = 14.4 \text{ eV A/R}$. Neglect overlap between orbitals at different atoms.
Find (i) the equilibrium separation, (ii) the binding energy, and (iii) the energy of zero-point motion.

Problem 5:
(a) Prove that the Coulomb repulsion integral for two electrons in the 1s orbital for a nucleus of charge $Z$, given by
$U(Z) = \int d^3rd^3r' s(r)^2 \frac{e^2}{|r - r'|} s(r')^2$
with
$s(r) = \left(\frac{Z^3}{\pi a_0}\right)^{1/2} e^{-Zr/a_0}$

is given by $U(Z)=\text{constant} \times Z \times 13.6 \text{ eV}$. What is the value of "constant"?

(b) Assume there are 2 electrons of opposite spin in the lowest energy state of a nucleus of charge $Z$. Assuming the ground state wave function the form $\Psi(r,r') = \bar{s}(r)\bar{s}(r')$, with $\bar{s}(r) = \left(\frac{\lambda^3}{\pi\alpha_0^2}\right)^{1/2} e^{-\lambda r/\alpha_0}$, find the value of $\lambda$ that minimizes the energy (hint: it is smaller than $Z$).

(c) 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 $s(r)$, with the corresponding values with $\bar{s}(r)$. State which are higher and which are lower and explain why.