Assignment P2-1

1. In the molecular surface reaction of N_2 interaction with iron (Fe) solid surface, the elemental iron is *bcc* in its ground state, which is metallic only due to 2 of its valence electrons. Within the free electron theory, calculate the Fermi energy (E_F in the units of eV) of elemental iron (Fe at T= 0 K). Consider the atomic radius of Fe is 1.86 Å.

> Plank constant (ħ ; read it as h-bar)= 1.05×10^{-34} J.s
> Mass of electron (m) = 9.1×10^{-31} kg
> 1 eV = 1.6×10^{-19} J

Solution:

From lecture notes, the Fermi energy can be written as:

$$\boxed{E_F = \frac{\hbar^2}{2m}\left[\frac{3\pi^2 N}{V}\right]^{2/3}}$$

Since Fe crystal is ***bcc*,** the unit cell has 2 atoms per cell.

Volume of the ***bcc*** unit cell is: $[4r/\mathrm{sqrt}(3)]^3$,

r is the radius of Fe = 1.86 Å = 1.86 x 10^{-10} m

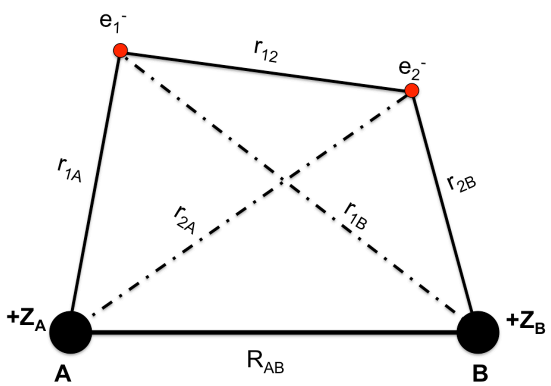
Therefore, volume of the unit cell = 7.93 x 10^{-29} m^3

Since Fe crystal has 2 atoms per unit cell, the crystal also will have 2 valence electrons per unit cell.

From this one can get the value of **N/V.**

Upon substitution of the values given for h-bar and mass of the electron, one can get the Fermi energy (E_F) = 4.98 x 10^{-19} J = **3.1 eV**

2. Write the Hamiltonian that one would need to calculate the electronic wavefunction for a system of interacting particles. The system consisting of two atoms labeled as A and B each with an electron is pictorially depicted below.



<u>Solution</u>

$$\frac{p_1^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r_{1A}} + \frac{p_2^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r_{2B}} - \frac{e^2}{4\pi\varepsilon_0 r_{1B}} - \frac{e^2}{4\pi\varepsilon_0 r_{2A}} +$$

$$\frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}} + \underline{\frac{p_A^2}{2M_A} + \frac{p_B^2}{2M_B}}$$

For the electronic Hamiltonian, the last two terms (kinetic energy of the nucleus is ignored by invoking the Born-Oppenheimer approximation, see below). Note that the nucleus may be designated with the charge Ze, for example, the charge on the two atoms labeled as A and B would be $Z_A e$ and $Z_B e$, respectively. The idea is: according to the given diagram, the notation must be strictly followed.

For electrons (i) and nuclei (α), the Schrödinger equation is approximated as (following the clamped nuclei model in other words, Born-Oppenheimer approximation)

$$\hat{H}_{el}\psi(r,R) = E_{el}\psi(r,R)$$

$$\hat{H}_{el} = \hat{T}_{el}(r) + \hat{V}_{eN}(r,R) + \hat{V}_{rr}$$

$$\hat{H}_{el} = -\tfrac{1}{2}\sum_i \nabla_i^2 - \tfrac{1}{2}\sum_{\alpha,i} \frac{Z_\alpha e^2}{r_i - R_\alpha} + \tfrac{1}{2}\sum_{i\neq j} \frac{e^2}{r_i - r_j}$$