

Physical Chemistry Special

Unit 1:-

(A) Hartree Fock theory

Born Oppenheimer Approximation:

The Hamiltonian for a hydrogen molecule is given as

$$\hat{H} = \frac{-\hbar^2}{2M} (\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0 r_{1A}} - \frac{Ze^2}{4\pi\epsilon_0 r_{1B}} \\ - \frac{Ze^2}{4\pi\epsilon_0 r_{2A}} - \frac{Ze^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{Z^2 e^2}{4\pi\epsilon_0 R} \quad \text{--- (1)}$$

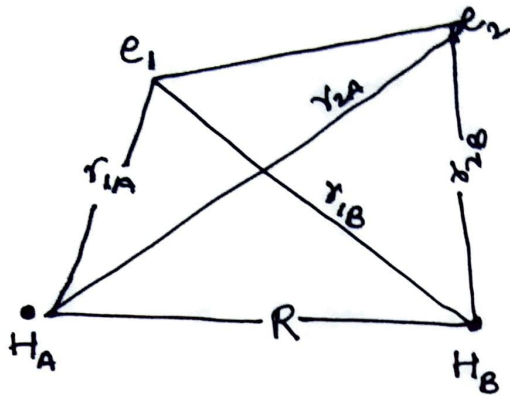
In this equation M is the mass of hydrogen ~~molecule~~ nucleus

$m \rightarrow$ electronic mass

$Z \rightarrow$ atomic number of the nucleus ($Z=1$ for Hydrogen)

∇_A^2 and ∇_B^2 are the Laplacian operators with respect to the position of nuclei A and B

∇_1^2 and ∇_2^2 are Laplacian operators for the positions of electron 1 and 2 and all these distance can be shown as:-



For Helium atom, it can be assumed that because the nuclei are so much more massive than the electrons, nuclei can be considered fixed relative to the motion of electrons.

so the terms ∇_A^2 and ∇_B^2 can be neglected and the equation can be rewritten as

$$\hat{H} = \frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0 r_{1A}} - \frac{Ze^2}{4\pi\epsilon_0 r_{1B}} - \frac{Ze^2}{4\pi\epsilon_0 r_{2A}} - \frac{Ze^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{Z^2 e^2}{4\pi\epsilon_0 R}$$

Therefore, the approximation of neglecting the nuclear motion is called Born-Oppenheimer approximation.

This approximation can be corrected by perturbation theory, using the ratio m/M as small expansion parameters.

As usual all the equations can be summed up as:-

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \quad \text{--- (3)}$$

Hartree - Fock Equation

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad \text{--- (1)}$$

The equation for He-atom.

If we introduce

$$\hbar = 1, \quad m = 1, \quad e = 1 \quad \text{and} \quad k_0 = 4\pi\epsilon_0 = 1$$

The equation becomes

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad \text{--- (2)}$$


and is independent of any physical constants.

Bohr's radius a_0 is given by

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 1 \quad (\text{atomic unit}) \quad \text{--- (3)}$$

One atomic unit of length is called a Bohr.

$$\text{and} \quad E = \frac{me^4}{16\pi^2\epsilon_0^2 \hbar^2} = 1 \quad (\text{atomic unit}) \quad \text{--- (4)}$$


 Defining the atomic energy

One atomic unit of energy is called a hartree and often is denoted by H.

In atomic units the ground-state energy of the Hydrogen atom (in the fixed nucleus approximation) is $-\frac{1}{2}$ hartree.

In equation (3) and (4) the units are called derived units as they are expressed in terms of four base units \hbar, m, e and $k_0 = 4\pi\epsilon_0$

Q: Express one hartree in units of Joule (J), kilojoules per mole ($\text{kJ} \cdot \text{mol}^{-1}$), wave numbers (cm^{-1}) and electron volts (eV).

$$\text{Hartree} = \frac{me^4}{k_0^2 \hbar^2}$$

$$\begin{aligned} \text{one hartree} &= \frac{(9.1091 \times 10^{-31} \text{ kg})(1.6021 \times 10^{-19} \text{ C})^4}{(1.1126 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})^2 (1.0545 \times 10^{-34} \text{ Js})^2} \\ &= 4.3595 \times 10^{-18} \text{ J} \end{aligned}$$

If we introduce Avogadro's number
one hartree = $2625 \text{ kJ} \cdot \text{mol}^{-1}$

To express one hartree in wave number (cm^{-1})

$$\begin{aligned} \bar{\nu} &= \frac{1}{\lambda} = \frac{E}{c\hbar} = \frac{(4.3595 \times 10^{-18} \text{ J})}{(2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1})(6.626 \times 10^{-34} \text{ J} \cdot \text{s})} \\ &= 2.195 \times 10^7 \text{ m}^{-1} = 2.195 \times 10^5 \text{ cm}^{-1} \end{aligned}$$

We can write the equation as

$$\text{one hartree} = 2.195 \times 10^5 \text{ cm}^{-1}$$

To express one hartree in term of electron volts, we use the conversion factor

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

using the value of one hartree in Joules, thus,

$$\text{one hartree} = (4.3595 \times 10^{-18}) \text{ J} \cdot \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right)$$

$$\boxed{\text{one hartree} = 27.21 \text{ eV}}$$

Application of Perturbation Theory and Variational Method for Helium :-

$$\hat{H} \psi = E \psi \quad \text{--- (1)}$$

$$\text{where } \hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad \text{--- (2)}$$

We can apply perturbation theory in this and consideration of interelectronic repulsion term to be a perturbation.

$$\hat{H}^{(0)} = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_2} \quad \text{--- (3)}$$

Thus zero-order ground-state wave function is

$$\psi^{(0)}(r_1, r_2) = \psi_{1s}(r_1) \psi_{1s}(r_2) \quad \text{--- (4)}$$

and $\psi^{(0)}(r_1, r_2) = \psi_{1s}^2$

$$\psi_{1s}(r_j) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr_j} \quad j = 1 \text{ and } 2 \quad \text{--- (3)}$$

Because the ground-state of a hydrogen like system is $-\frac{Z^2}{2}$, the energy $E^{(0)}$ is given by

$$E^{(0)} = -\frac{Z^2}{2} - \frac{Z^2}{2} = -Z^2 \text{ a.u.} \quad \text{--- (4)}$$

The first-order perturbation theory correction to $E^{(0)}$ is given by

$$\begin{aligned} E^{(1)} &= \iint dr_1 dr_2 \psi^{(0)*}(r_1, r_2) \hat{H}^{(1)} \psi^{(0)}(r_1, r_2) \\ &= \iint dr_1 dr_2 \psi_{1s}(r_1) \psi_{1s}(r_2) \frac{1}{r_{12}} \psi_{1s}(r_1) \psi_{1s}(r_2) \quad \text{--- (5)} \end{aligned}$$

The evaluation of the above integral and

$$E^{(1)} = \frac{5}{8} Z \text{ a.u.} \quad \text{--- (6)}$$

and so the energy of Helium atom through first order is

$$\begin{aligned} E &= E^{(0)} + E^{(1)} + \dots \\ &= -Z^2 + \frac{5}{8} Z + \dots \quad \text{--- (7)} \end{aligned}$$

For the Helium atom

$$Z = 2$$

$$E = \frac{-11}{4} \text{ au} = -2.750 \text{ au} \\ = -74.83 \text{ eV} \quad \text{--- (8)}$$

$$1 \text{ a.u.} = 27.21 \text{ eV.}$$

The experimental value of energy is -79.00 eV or -2.9033 a.u. . The first order perturbation theory gives a result that is about 5% in the error.

Scheer and Knight have calculated the energy through many orders of perturbation,

$$E = -Z^2 + \frac{5}{8}Z - \frac{0.157666254}{Z} + \frac{0.008698679}{Z^2} + \frac{0.000888302}{Z^3} + \dots$$

Yields a value of -2.9037 in a.u.

and an experimental value, -2.9033 a.u.

Note:

Students of M.Sc. sem III applying for Physical Chemistry as special paper, kindly mail on ankitaojha26@gmail.com for subject related discussions. They must attach their scanned ID for verification.

Abhishek
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