Dr. B. L. Bishwas
Associate Professor & Head
P.G. Deptt. of Chemistry
Purnea College, Purnea

Residence
Prabhat Colony,
Bhootnath Mandir Road,
Purnea

Quantum chemistry, physical spl paper, Semester-IV

Ref.: Page-①

Dated: 24.04.2020

The Born-oppenheimer Approximation:

A/c to The Born-oppenheimer approximation the electronic motion in a molecule is assumed to take place independently of the nuclear motion. Since the electronic and the nuclear motions are assumed to be separable we can write

$$\psi(r,R) = \psi_R(r)\,\phi(R) \quad \text{——— ①}$$

where $\psi_R(r)$ implies that the electronic wavefunction depends functionality on r and parametrically on R.

For simplicity we shall write ψ_e for $\psi_R(r)$ and ψ_n for $\phi(R)$

Let us define ψ_e as a function which satisfies the electronic schrondinger equation

$$\hat{H}_e\psi_e = (\hat{T}_e + V_{en} + V_{ee})\psi_e = E_e\psi_e \quad \text{——— ②}$$

Since we know that the Schrondinger equation for the molecule is

$$\hat{H}\psi(r,A) = (\hat{T}_e + \hat{T}_n + V_{en} + V_{ee} + V_{nn})\psi(r,A) = E\psi(r,R) \text{—③}$$

Substituting $\psi(r,R) = \psi_e\psi_n$ in eq^n ③ and writting the expressions for $\hat{T}_e$ and $\hat{T}_n$ explicity we get,

$$\left(-\sum_\mu \frac{\nabla_\mu^2}{2} - \sum \frac{\nabla_A^2}{2m_A} + V_{en} + V_{ee} + V_{nn}\right)\psi_e\psi_n = E\psi_e\psi_n \quad \text{——— ④}$$

Now,

$$-\sum_\mu \frac{\nabla_\mu^2}{2}(\psi_e\psi_n) = -\psi_n\sum_\mu \frac{\nabla_\mu^2}{2}\psi_e \quad \text{——— ⑤}$$

$$-\sum_A \frac{\nabla_A^2}{2m_A}(\psi_e\psi_n) = -\sum_A \frac{1}{2m_A}\left(\psi_e\nabla_A^2\psi_n + \psi_n\nabla_A^2\psi_e + 2\nabla_A\psi_e\cdot\nabla_A\psi_n\right) \quad \text{——— ⑥}$$

[Since note that $d^2(xy) = xd^2y + yd^2x + 2dxdy$]

Now using eq^n ⑤ and ⑥ in eq^n ④ gives

$$-\psi_n\sum_\mu \frac{\nabla_\mu^2}{2}\psi_e - \left[\sum_A \frac{1}{2m_A}\left(\psi_n\nabla_A^2\psi_e + 2\nabla_A\psi_e\cdot\nabla_A\psi_n\right)\right]$$

$$-\psi_e\sum_A \frac{\nabla_A^2}{2m_A}\psi_n + (V_{en} + V_{ee} + V_{nn})\psi_e\psi_n = E\psi_e\psi_n \quad \text{——— ⑦}$$

The square-bracketted terms in eq^n ⑦ describes the coupling of electronic and nuclear motion. these terms are neglected in the BO approximation.