Born - Oppenheimer approximation

In order to calculating the electronic energy, we need to solve the electronic Schrodinger equation. The complete Schrodinger equation covers both the nuclear and the electronic motions.

For a system of n nuclei and p electrons whose co-ordinate are collectively denoted as R and r respectively, Hamiltonian is given by the equation.

$$\hat{H} = -\sum_{i=1}^{n} \frac{h^2}{8\pi^2 M_i} \nabla_i^2 - \sum_{j=1}^{p} \frac{h^2}{8\pi^2 m} \nabla_j^2 + V(r,R) \quad \text{—— (1)}$$

and the Potential energy $V(r,R)$ is given by

$$V(r,R) = -\sum_{k=1}^{n} \sum_{j=1}^{p} \frac{Z_k e^2}{r_{jk}} + \sum_{n\neq j} \frac{e^2}{r_{nj}} \sum \frac{Z_k Z_l e^2}{R_{kl}} \quad \text{—— (2)}$$

In equation (1) and (2). M_i is the mass of the i^{th} nucleus. m that of an electron, Z_K is the atomic number of the K^{th} nucleus. r_{jK} is the distance of the j^{th} electron from the K^{th} nucleus. r_{nj} is the distance between the n^{th} an j^{th} electrons and R_{kl} is the distance between K^{th} and the l^{th} nuclei

The first term in equation (1) represents the nuclear kinetic energy operater $\hat{T}_N$ and second and third terms together make up the electronic Hamiltonian operator $\hat{H}e$ i.e

$$\hat{H} = \hat{T}_N(R) + \hat{T}e(r,R) \quad \text{—— (3)}$$

The electronic operator describes the motion, of the electrons for fixed position of nuclei i.e it depends on the position (and not the momenta) of the nuclei.

The Schrodinger equation due to electronic motion, Max Born and J Robert Oppenheimer assumed that since the nuclei are much more heavier than the electrons. the former may be assumed to be stationary when the later moves. So the electronic wave function can be obtained by solving the electronic equations for some fixed position of the nuclei. Each choice of nuclear co-ordinate (R) will lead to a different potential energy and hence a different electronic Schrodinger equation

Thus while the electronic wave function ψ_e will depend on r as well as R, the nuclear wave function will depend on R only. The complete wave function in equation (4) can be written as.

$$\psi = \psi_e(r,R) \cdot \psi_N(R) \quad \text{—— (5)}$$

Substituting eqn (1) for $\hat{H}$ and eqn (5) for ψ in eqn (4), we get,

$$\left[-\sum_{i=1}^{n} \frac{h^2}{8\pi^2 M_i} \nabla_i^2 - \sum_{j=1}^{p} \frac{h^2}{8\pi^2 m} \nabla_j^2 + V(r,R)\right] \psi_e(r,R) \cdot \psi_N(R)$$

$$= E_T \psi_e(r,R)\, \psi_N(R) \quad \text{—— (6)}$$