Born-Oppenheimer Approximation

1. In the Born-Oppenheimer approximation the spatial wavefunction is approximated in the following manner:

$$\Psi(\vec{r}_e, \vec{R}_N, \sigma_e, \sigma_N) \approx \psi_{electronic}(\vec{r}_e; \vec{R}_N)\chi_{nuclear}(\vec{R}_N)\Gamma_{e-spin}(\sigma_e)\Gamma_{N-spin}(\sigma_N)$$

here $\Gamma_{e-spin}(\sigma_e)\Gamma_{N-spin}(\sigma_N)$ are the electronic and nuclear spin functions.

2. In the wavefunction $\psi_{electronic}(\vec{r}_e; \vec{R}_N)$ the electrons coordinates, $\vec{r}_e$, are treated as bona fide variables while the nuclear coordinates $\vec{R}_N$, are treated as parameters as elaborated below.

3. To get for $\psi_{electronic}(\vec{r}_e; \vec{R}_N)$, we solve the Schrodinger equation for electronic motion assuming some **fixed (relative) values** of the nuclear coordinates. For the H_2 molecule the electronic Hamiltonian is:

$$\mathcal{H}_{\text{electronic}}(R_{AB}) = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{Z_A Z_B}{R_{AB}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}}$$

$$\textbf{where } R_{AB} = \left|\vec{R}_A - \vec{R}_B\right|, \quad r_{A1} = \left|\vec{r}_1 - \vec{R}_A\right| \quad \cdots \quad r_{12} = \left|\vec{r}_2 - \vec{r}_1\right|$$

In applying this Hamiltonian a fixed value of $R_{AB} \equiv R$ is selected to get

$$\mathcal{H}_{el}(R)\psi_{el}(\vec{r}_e; \vec{R}) = E(R)\psi_{el}(\vec{r}_e; \vec{R})$$

Thus we get ψ's and E's for various values of R. In fact when we solve the Schrodinger equation we may get several (a manifold) of wavefunctions and energies corresponding to the ground and excited states: $\psi_i(\vec{r}_e; \vec{R})$ **and** $E_i(R)$. The values of $E_i(R)$ vs R give the intramolecular electronic energy for the electronic state i (the ground state or various excited states).

4. The nuclear wavefunction $\chi_{\text{nuclear}}(R)$ is determined by a Schrodinger equation for nuclear motion:

$$\mathcal{H}^{\text{i}}_{\text{nuclear}}\, \chi^i_{\text{v},J}(R) = E_{total}\, \chi^i_{\text{v},J}(R)$$

with $\mathcal{H}^{\text{i}}_{\text{nuclear}} = -\frac{1}{2\mu}\nabla_R^2 + E^i_{el}(R)$ **containing the kinetic energy of relative motion of the nuclei (rotation and vibration) and** $E^i_{el}(R)$**, the electronic energy of state i as a function of R, providing the potential energy for the vibrational motion of the nuclei. Note that for each electronic state i there will be a set of rotational - vibrational functions with vibrational quantum numbers v and rotational quantum numbers J.**

5. The justification for the Born-Oppenheimer approximation is that electronic motion is much more rapid than nuclear motion; the electron distribution effectively 'sees' a series of fixed nuclear positions.