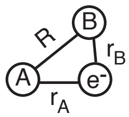
The Born-Oppenheimer approximation

Electronic Hamiltonian:



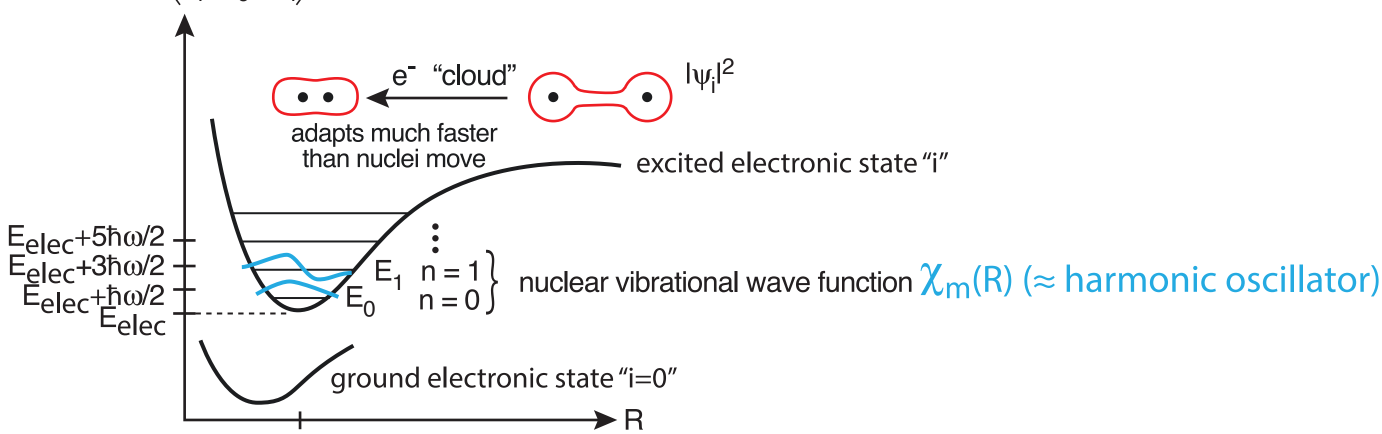
$$\hat{H} \neq \frac{\vec{p}_1^{\,2}}{2m_e} - \frac{e^2 Z_A}{4\pi\varepsilon_0 r_{1A}} - \frac{e^2 Z_B}{4\pi\varepsilon_0 r_{1B}} + \frac{e^2 Z_A Z_B}{4\pi\varepsilon_0 R}$$

Something is missing!

$$\hat{K}_{nuc} = \frac{\vec{p}_A^{\,2}}{2m_A} + \frac{\vec{p}_B^{\,2}}{2m_B} \qquad \langle K_{nuclei}\rangle \ll \langle K_{electrons}\rangle$$

So we are calculating a "Born-Oppenheimer" potential surface when we calculate the "electronic potential surface" $E_i(R)$

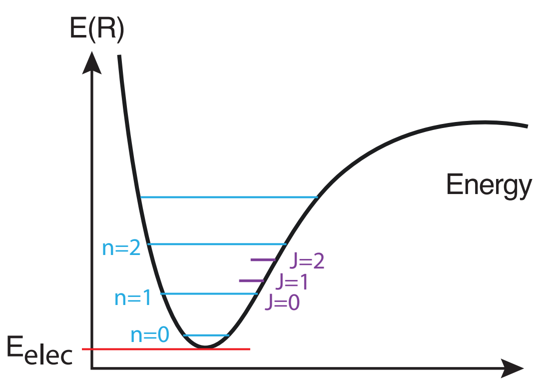
$E_i(R) = \langle \psi_i | H_{e-} | \psi_i \rangle$



$\Psi_{total}(r, R) \approx$ (electronic wavefunction)·(nuclear wavefunction)

$$\Psi_{total}(\vec{r}, R) \approx \Psi_n(\vec{r}) \cdot \chi_m(R) \cdot Y_{JM_J}(\theta,\varphi)$$

Nuclei vibrate and rotate, just like electrons



Energy = Electronic energy + vibrational energy + rotational energy

$$E \approx E_{elec} + \hbar\omega(n + 1/2) + \frac{\hbar^2 J(J+1)}{2I}$$