

# Course: Physics of Atoms and Molecules / Molecules / Born-Oppenheimer approximation

The aim of this section is to study the quantum description of the molecular bond. We are going to limit the analysis to diatomic molecules. First of all we consider a molecule composed by two atomic nuclei A and B, whose positions are defined by vectors  $\vec{R}_A$  and  $\vec{R}_B$ . The electrons positions are instead identified by  $\vec{x}_i$ . Both nuclei and electrons positions are referred to the center of mass of the two nuclei. The Hamiltonian we can write for a system like this is:

$$\hat{H} = \hat{T}_N + \hat{T}_e + U_{eN} + U_{ee} + U_{NN}$$

where  $\hat{T}_N$  and  $\hat{T}_e$  are the kinetic energies associated respectively to the nuclei and the electrons and  $U_{eN}$ ,  $U_{ee}$  and  $U_{NN}$  represent the Coulomb interactions. Now it's possible to isolate from this Hamiltonian an electron Hamiltonian:

$$\hat{H}_e = \hat{T}_e + U_{eN} + U_{ee}$$

This  $\hat{H}_e$  is a function of the nuclei positions and we can obtain an eigenvalues equation for the electrons:

$$\hat{H}_e \left( \left\{ \vec{R}_i \right\} \right) \psi_{el}^n \left( \left\{ \vec{R}_i \right\} \right) = E_{el}^n \psi_{el}^n \left( \left\{ \vec{R}_i \right\} \right)$$

It's possible to demonstrate that solving this equation for the electrons Hamiltonian leads to a solution  $\psi$  for the original complete eigenvalue equation which has the form:

$$\psi = \sum_n \chi_n \left( \left\{ \vec{R}_i \right\} \right) \psi_{el}^n \left( \left\{ \vec{R}_i \right\} \right)$$

where  $\chi_n$  is a wave function depending only on the nuclei positions. Such an equation is difficult to solve, but it can be simplified through the **Born-Oppenheimer adiabatic approximation**. This model is based on the fact that the mass of the nucleus is much greater than the electron one ( $m_p/m_e \approx 1800$ ). Being so, we can state that electrons move way faster than nuclei. Hence we can assume that electrons follow the motion of the nuclei without changing the energy level they belong to. In other words, there is no energy exchange between nuclei and electrons. In this adiabatic approximation the solution  $\psi$  becomes:

$$\psi = \chi_n \left( \left\{ \vec{R}_i \right\} \right) \psi_{el}^n \left( \left\{ \vec{R}_i \right\} \right)$$

The sum over the quantum number  $n$  disappears, because of the impossibility for



an electron to jump to an excited state. Now we can use these results to write an equation for the total Hamiltonian:

$$\langle \text{dmath} \rangle \left( \hat{T}_N + U_{NN} + \hat{H}_e \right) \chi_{\{n\}} \left( \left\{ \vec{R}_i \right\} \right) \langle \text{right} \rangle$$

At this point we can observe that  $\hat{H}_e$  only acts on  $\psi^{el}$ , which is actually an eigenstate of  $\hat{H}_e$ , so we can substitute  $\hat{H}_e$  in the equation above with the corresponding eigenvalue  $E^{el}(\vec{R}_i)$ . Moreover, again thanks to the greatness of nuclei masses in respect to electrons ones, we can assume that the application of the kinetic term  $\hat{T}_N$  to the  $\psi^{el}$  component of the total wave function gives a negligible contribution, then we can consider that  $\hat{T}_N$  acts only on  $\chi$ . Relying on this last approximation, it's possible to simplify the  $\psi^{el}$  term in order to obtain an eigenvalues equation for the sole  $\chi$  function:

$$\langle \text{dmath} \rangle \left( \hat{T}_N + U_{NN} + E^{el} \right) \chi \left( \left\{ \vec{R}_i \right\} \right) \langle \text{right} \rangle$$

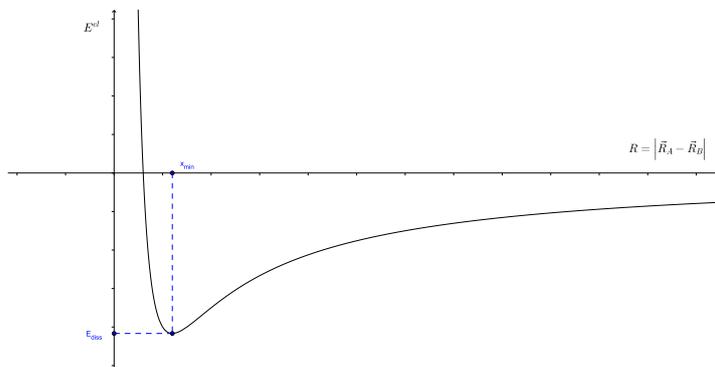
The last equation describes the nuclei dynamics and this means that the equations for  $\psi^{el}$  and  $\chi$  are now uncoupled.  $E_{tot}$  depends only on the distance between the nuclei:

$$\langle \text{dmath} \rangle E_{tot} = E_{tot} \left( \left| \vec{R}_A - \vec{R}_B \right| \right) \langle \text{right} \rangle$$

Now we can redefine the quantity  $E^{el}(\{\vec{R}_i\})$  considering that  $U_{NN}$  is just a multiplicative operator:

$$\langle \text{dmath} \rangle E^{el} \left( \left\{ \vec{R}_i \right\} \right) = E^{el} \left( \left\{ \vec{R}_i \right\} \right) + U_{NN}$$

In other words,  $E^{el}(\{\vec{R}_i\})$  is the eigenvalue for the operator  $\hat{H}_e(\{\vec{R}_i\}) + U_{NN}$  corresponding to the eigenfunction  $\psi^{el}$ . It's possible to plot  $E^{el}(\{\vec{R}_i\})$  in respect to the nuclear distance  $R = \left| \vec{R}_A - \vec{R}_B \right|$ :



In the graph, the value of the energy in correspondence of the  $x$  axis is  $E_A + E_B$ , where  $E_A$  and  $E_B$  are the energy associated to the hydrogenoid Hamiltonian for nucleus  $A$  and  $B$ . It can be seen that there is an  $R_{min}$  at which the energy is minimal. This is called **dissociation energy** and it's the energy that has to be given to the molecule in order to break the bond.



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## 1.1 Text

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