

$$\hat{H} = \underbrace{-\sum_{I=1}^{N_N} \frac{\hbar^2}{2M_I} \nabla(I)^2}_{\text{KE of nuclei}} - \sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}} + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}}$$

Unlike the atomic systems, we now have the kinetic energy of the nuclei. We can no longer place ‘the’ nucleus at the origin and consider all coordinates relative coordinates.

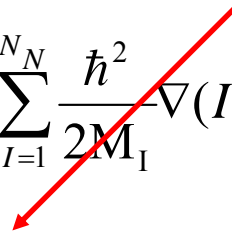
Thus, the total wave function is a function of both nuclei and electrons:

$$\Psi(q_1, q_2, \dots, q_{n_e}, Q_1, Q_2, \dots, Q_{N_N})$$

Again the lower case coordinates,  $q$ , refer to the electrons and the upper case coordinates,  $Q$ , refer to the nuclei.

# The Born-Oppenheimer Approximation

In the BO approximation, we **assume the nuclei are FIXED** as the electrons carry out their motion.

$$\hat{H} = -\sum_{I=1}^{N_N} \frac{\hbar^2}{2M_I} \nabla(I)^2 - \sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}} + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}}$$
$$\hat{T}_N = 0$$


This allows us to define an Electronic Hamiltonian, which does not contain the nuclear kinetic energy operator.

$$\hat{H}^{\text{el}} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}} + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}}$$

We are making the approximation that there is no coupling between their motions.

The total nuclear and electronic Schrodinger equation is:

$$\hat{H}\Psi(q_i, Q_I) = E\Psi(q_i, Q_I)$$

We have assumed the kinetic energy of the nuclei to be zero, so we separate our total Hamiltonian as:

$$\hat{H} = \hat{H}_{el} + \hat{T}_N$$

The Born-Oppenheimer approximation allows us to separate the total wave function as:

$$\Psi(q_i, Q_I) \approx \underbrace{\Psi^{el}(q_i : Q_I)}_{\text{electronic wave function}} \underbrace{\Psi^{NUC}(Q_I)}_{\text{nuclear wave function}}$$

This is the electronic wave function. It is a function of the coordinates of the electrons,  $q_i$ , but parametrically dependent upon the coordinates of the nuclei,  $Q_I$ .

Wave function for the nuclear motion. It depends on the nuclear coordinates,  $Q$ , only as true variables.

The resulting total nuclear and electronic Schrodinger equation is:

$$\hat{H}_{total} \Psi_{total}(q_i, Q_I) = E_{total} \Psi_{total}(q_i, Q_I)$$

$$\left( \hat{H}_{el} + \hat{T}_N \right) \Psi_{total}(q_i, Q_I) = E_{total} \Psi_{total}(q_i, Q_I)$$

Using our separation of the total wave function:  $\Psi(q_i, Q_I) \approx \Psi^{el}(q_i : Q_I) \Psi^{NUC}(Q_I)$

We have:

$$\left( \hat{H}_{el} + \hat{T}_N \right) \Psi^{el} \Psi^{NUC} = E_{total} \Psi^{el} \Psi^{NUC}$$

$$\hat{H}_{el} \Psi^{el} \Psi^{NUC} + \hat{T}_N \Psi^{el} \Psi^{NUC} = E_{total} \Psi^{el} \Psi^{NUC}$$

$$\hat{H}_{el} \Psi^{el} \Psi^{NUC} + \hat{T}_N \Psi^{el} \Psi^{NUC} = E_{total} \Psi^{el} \Psi^{NUC}$$

$\Psi^{NUC}$  does not depend on coordinates of electrons

Here we assume no coupling between the electronic state and the nuclear motion (again the BO-approximation)

$$\Psi^{NUC} \hat{H}_{el} \Psi^{el} + \cancel{\Psi^{el} \hat{T}_N \Psi^{NUC}} = E_{total} \Psi^{el} \Psi^{NUC}$$

kinetic energy of nuclei assumed to be zero in this approximation

$$\Psi^{NUC} \hat{H}_{el} \Psi^{el} = E^{el} \Psi^{el} \Psi^{NUC}$$

Divide by  $\Psi^{NUC}$

$$\hat{H}_{el} \Psi^{el} = E^{el} \Psi^{el}$$

Electronic Schrodinger equation

Thus, if the nuclear kinetic energy is zero, then the Schrodinger equation for the molecule becomes:

$$\hat{H}^{el} \Psi_n^{el}(q_i : Q_I) = E_n^{el}(Q_I) \Psi_n^{el}(q_i : Q_I)$$

Molecular Electronic Hamiltonian      Electronic wave function for the  $n^{\text{th}}$  state      Electronic energy for the  $n^{\text{th}}$  state

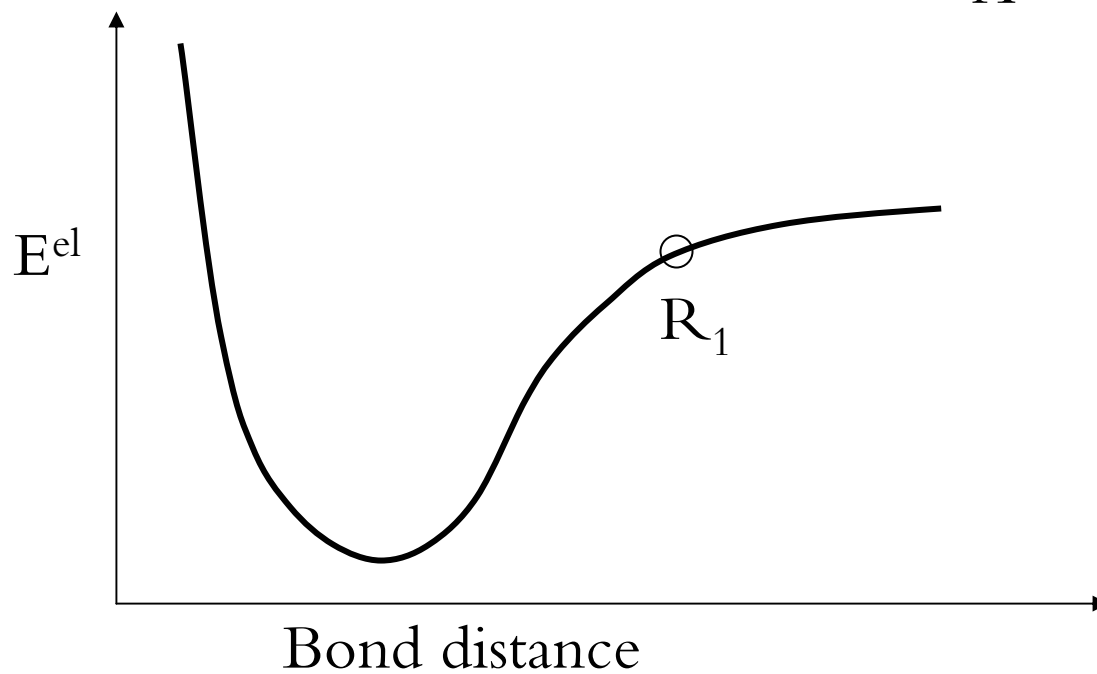
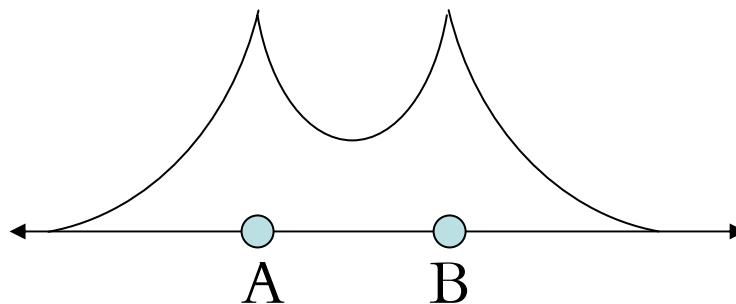
$n$  refers to the quantum state of the molecule

$H^{el}$ ,  $\Psi^{el}$  and  $E^{el}$  all depend on the nuclear coordinates,  $Q$ , as parameters. They are parametrically dependent upon what frozen nuclear framework we have chosen.

Thus, we solve for the electronic wave function, with the nuclei fixed.

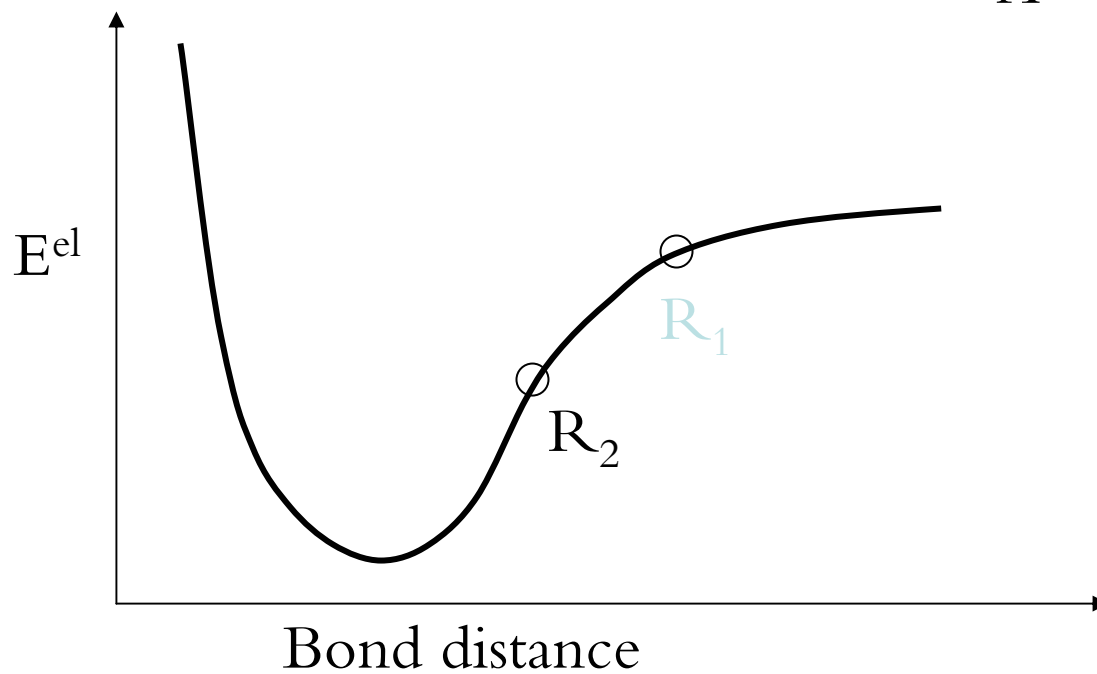
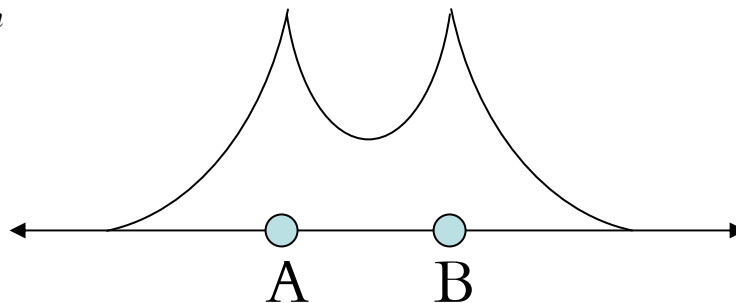
Consider a diatomic.

$$\hat{H}^{el} \Psi_n^{el} = E_n^{el}(R_1) \Psi_n^{el}$$



Consider a diatomic.

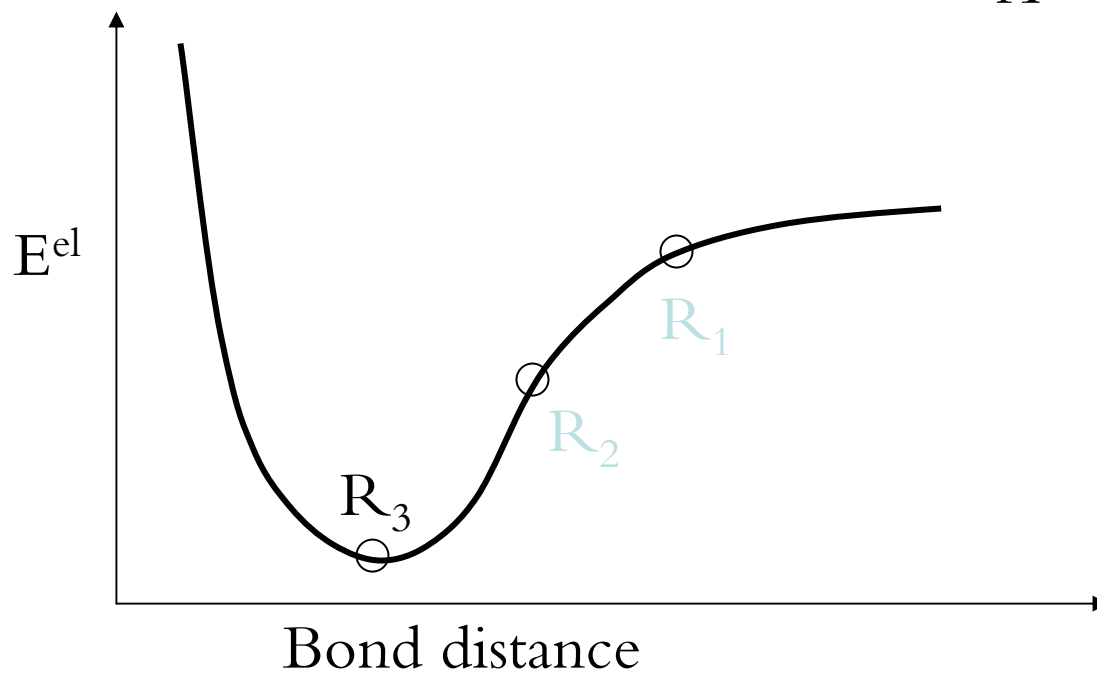
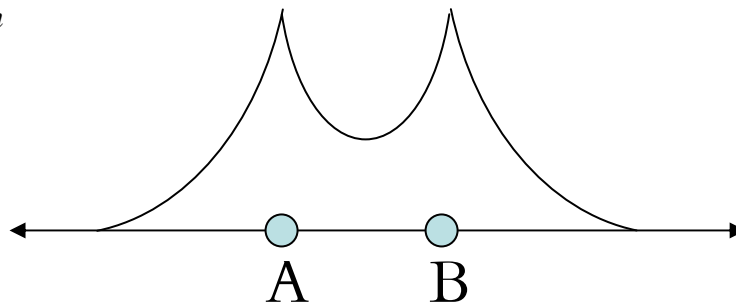
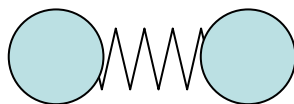
$$\hat{H}^{el} \Psi_n^{el} = E_n^{el}(R_2) \Psi_n^{el}$$





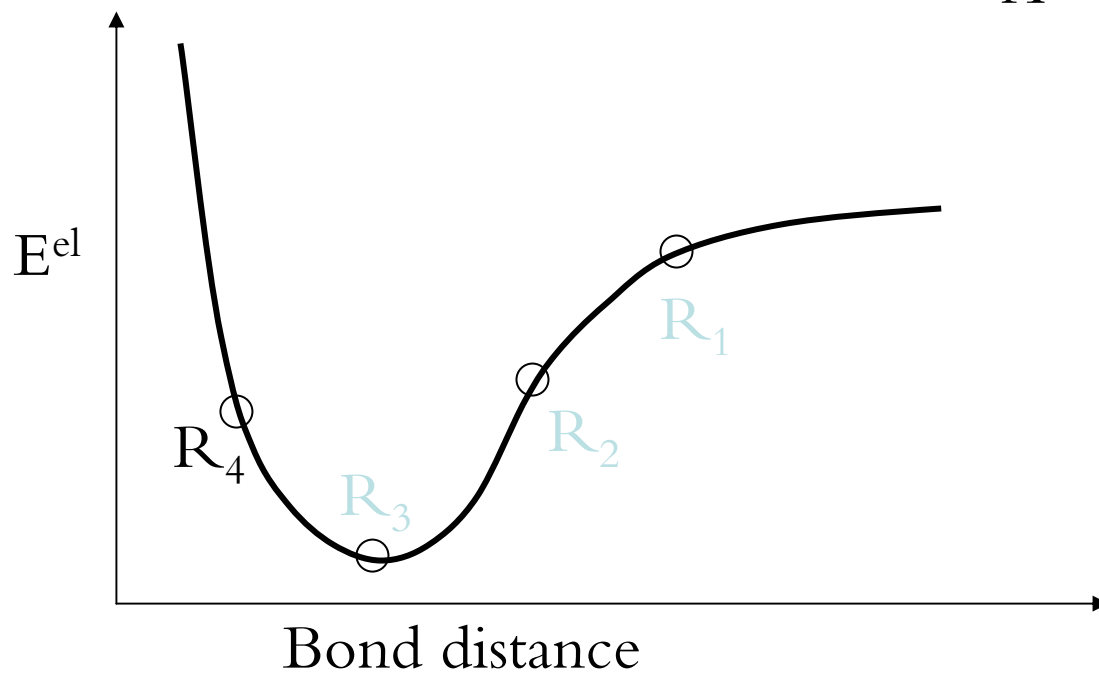
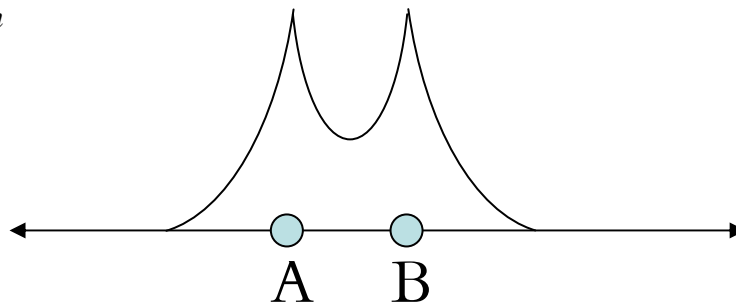
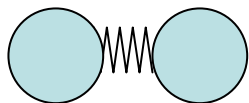
Consider a diatomic.

$$\hat{H}^{el} \Psi_n^{el} = E_n^{el}(R_3) \Psi_n^{el}$$

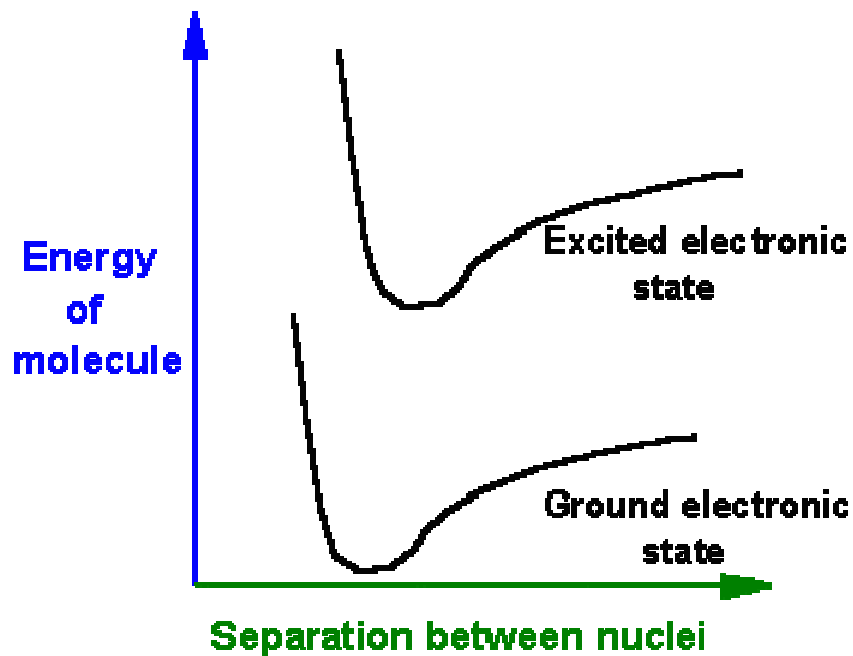


Consider a diatomic.

$$\hat{H}^{el} \Psi_n^{el} = E_n^{el}(R_4) \Psi_n^{el}$$



This leads to pictures involving more than one electronic state of the sort:



Potential energy curve for each state is different

## NOTE:

Sometimes the last term is not included in the electronic Hamiltonian.

$$\hat{H}^{\text{el}} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}} + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}}$$

This term corresponds to the nuclear-nuclear repulsion energy and is an ‘electronic’ energy term. Thus it is often dropped, such that:

$$\hat{H}^{\text{el}} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}}$$

# Compare the Electronic Hamiltonian to our Atomic Hamiltonian

With this form of the electronic Hamiltonian,

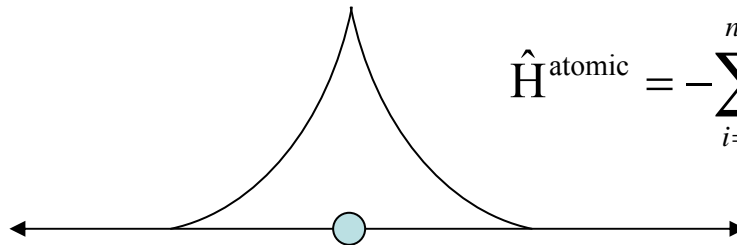
$$\hat{H}^{\text{el}} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}}$$

We notice that it very closely resembles our many electron atomic Hamiltonian except for the extra summation over the ‘additional’ nuclei and the nuclear-nuclear repulsion:

$$\hat{H}^{\text{atomic}} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{i=1}^{n_e} \frac{Z e^2}{r_i} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}}$$

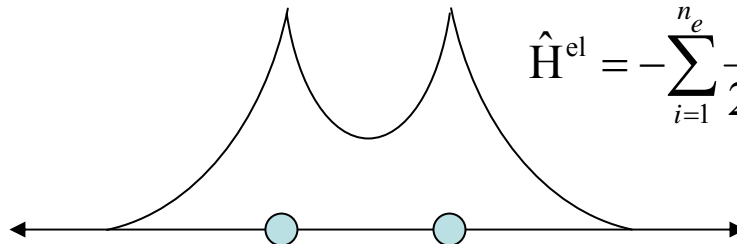
In comparison to atomic systems, we are simply solving for our electronic wave function in the potential field of more than one nucleus.

Atomic wave  
function



$$\hat{H}^{\text{atomic}} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{i=1}^{n_e} \frac{Ze^2}{r_i} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}}$$

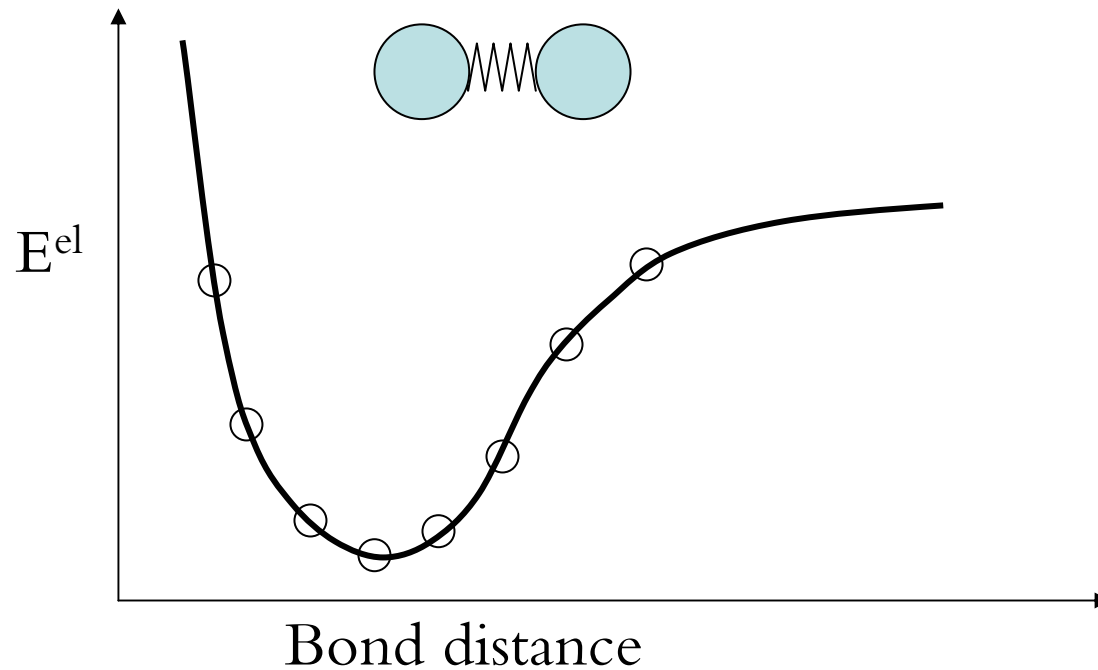
Molecular  
wave function  
with BO-  
approximation



$$\hat{H}^{\text{el}} = -\sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}}$$

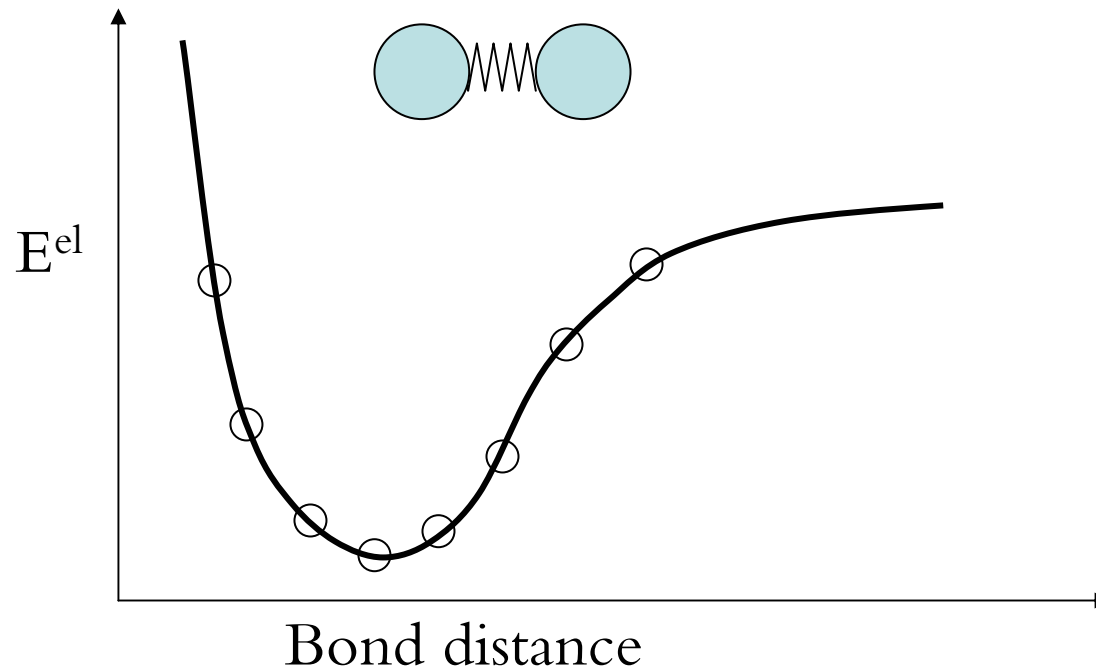
Indeed most of the methods that we used to obtain approximate wave functions to many electron atoms can be applied straightforwardly to molecular systems!

Consider a diatomic where we calculate the electronic energy for various bond distances.



This procedure, gives us what is called the **potential energy surface**. of a molecule which relates the energy of a molecular system to its nuclear geometry.

The potential energy surface is a fundamental concept. Many important properties of molecular systems can be derived if one knows the potential energy surface of the system.



## The Potential Energy Surface.

- Relates the potential energy of a molecular system to its nuclear geometry.
- It does not include the kinetic energy of the nuclei
- It is often given the symbol,  $U = U(Q_I)$  or  $V = V(Q_I)$
- The potential energy surface is a fundamental concept. Many important properties of molecular systems can be derived if one knows the potential energy surface of the system.



# What is the Physical Reasoning Behind the BO approximation?

The B-O approximation takes advantage of the fact that the mass of the electron is much smaller than the mass of the nuclei.

electron to proton mass ratio  $m_e : M_{p^+} = 1:1280$

*(all other nuclei will have even larger ratios)*

Thus, the nuclei will move much, much slower than the electrons. Why?

Consider the classical picture, where a well equilibrated system suggests that the electrons and nuclei have the same kinetic energy:

$$\frac{1}{2}m_e V_e^2 = \frac{1}{2}M_N V_N^2$$

Thus,

$$\frac{m_e}{M_N} = \frac{V_N^2}{V_e^2}$$

Another way of thinking of it is, that as the nuclei move (vibrate), we assume the electronic system can instantaneously adjust.

# How Good is the Born-Oppenheimer Approximation?

The BO approximation is in general a very good approximation.

In general the lighter the nuclei, the more severe the error.

## Example:

Consider the H<sub>2</sub> molecule, an unfavorable case (light molecule)

Energy for the ground state accurate to 2 cm<sup>-1</sup> out of 36113.6 cm<sup>-1</sup>

0.01% error!

1 cm<sup>-1</sup> = 1.24x10<sup>-4</sup> eV

The approximation can be less accurate for excited states.

## Example:

Consider the first excited bound state of H<sub>2</sub>

The exact dissociation energy is = 28852.8 cm<sup>-1</sup>

Accurate calculation using the BO approximation = 28896.3 cm<sup>-1</sup>

0.1% error!