Born-Oppenheimer Approximation

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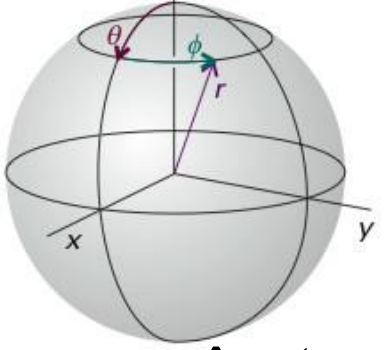


Solve the hydrogen atom

$$\hat{H}\psi(r,\theta,\phi)=\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{e^2}{4\pi\varepsilon_0 r}\right.$$

$$\left.-\frac{\hbar^2}{2\mu}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{\hbar^2}{2\mu}\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi)$$

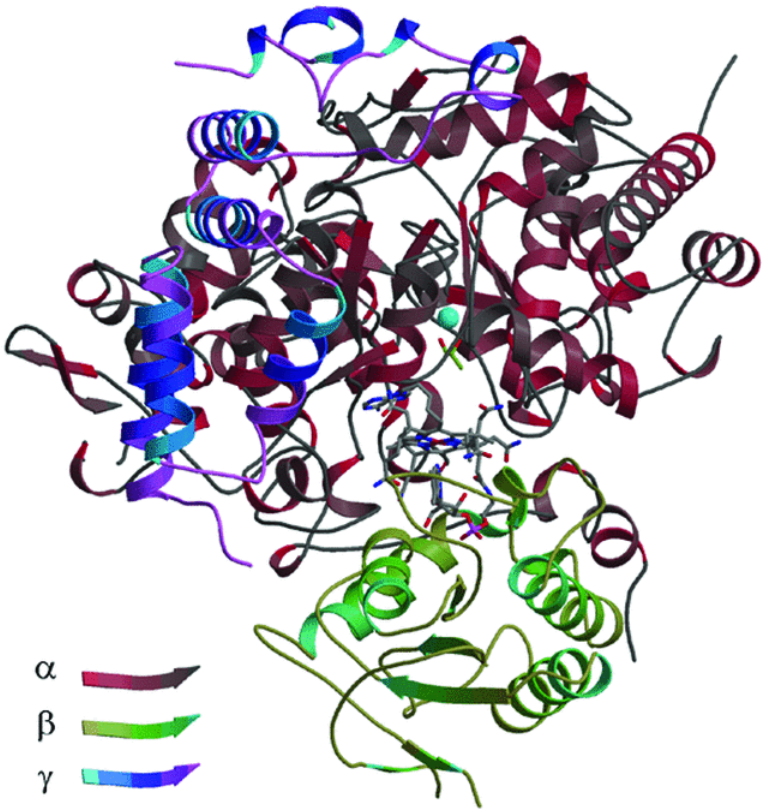
$$=E\psi(r,\theta,\phi)$$

$$E_n=-\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2}=-\frac{\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}=-\frac{e^2}{8\pi\varepsilon_0 a_0 n^2}$$

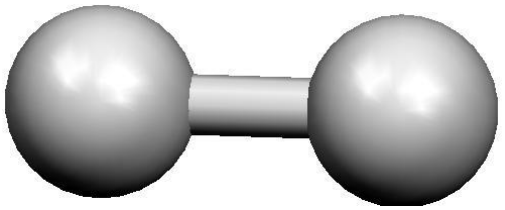
$$Y_l^{m_l}(\theta,\phi)=\frac{1}{(2\pi)^{1/2}}\exp(im\phi)\left[\frac{2l+1}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}\right]^{1/2}P_l^{|m_l|}(\cos\theta)$$

$$R_{nl}(r)=\left\{\frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{1/2}\left(\frac{2}{na_0}\right)^{3/2}\left(\frac{2r}{na_0}\right)^{l}\exp\left(-\frac{r}{na_0}\right)L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)^2$$

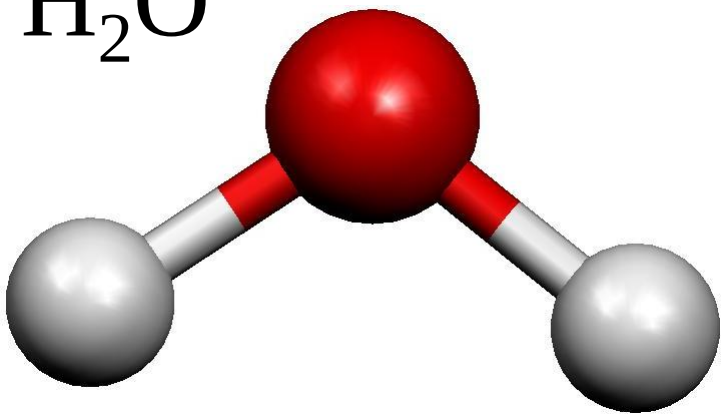
Proteins, Molecules



H_2



H_2O



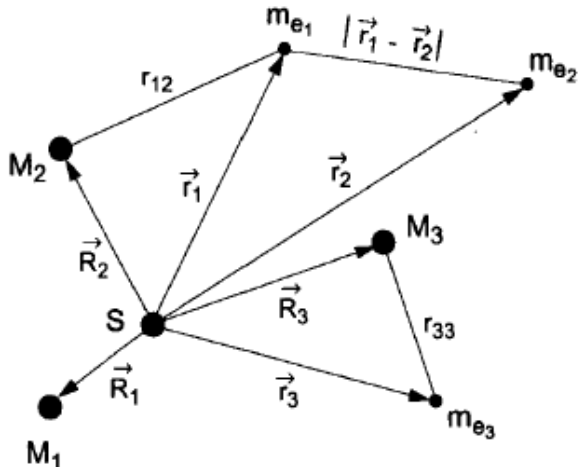
You always write where the nucleus is but you never write the electrons or the electrons are written as a line!!!
YOU ARE ALREADY ASSUMING BORN-OPPENHEIMER APPROXIMATION

Full Problem

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{r},\mathbf{R})$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^{\,2}} + \frac{\partial^2}{\partial y_i^{\,2}} + \frac{\partial^2}{\partial z_i^{\,2}} \qquad \nabla_I^2 = \frac{\partial^2}{\partial X_I^{\,2}} + \frac{\partial^2}{\partial Y_I^{\,2}} + \frac{\partial^2}{\partial Z_I^{\,2}}$$

$$V(\mathbf{r},\mathbf{R}) = \frac{e^2}{4\pi\varepsilon_0}\Big[\qquad \Big]$$



$$\mathbf{R}_I = \vec{R}_I = X_I\vec{e}_x + Y_I\vec{e}_y + Z_I\vec{e}_z$$

$$\mathbf{r}_i = \vec{r}_i = x_i\vec{e}_x + y_i\vec{e}_y + z_i\vec{e}_z$$

$$\hat{H}\Psi(\mathbf{r},\mathbf{R}) = E_{el,NU}\Psi(\mathbf{r},\mathbf{R})$$

Atomic Units

For quantum systems such as electrons and molecules it is easier to use units that fit them=ATOMIC UNIT

Use mass of electron (not kg)
Use charge of electron (not coulomb)
Use hbar for angular momentum (not kg m^2 s^{-1})
Use $4\pi\varepsilon_0$ for permittivity (not C^2 s^2 kg^{-1} m^{-3})

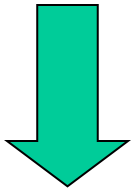
TABLE 9.1
Atomic Units and Their SI Equivalents

Property	Atomic unit	SI equivalent
Mass	Mass of an electron, m_e	9.1094×10^{-31} kg
Charge	Charge on a proton, e	1.6022×10^{-19} C
Angular momentum	Planck constant divided by 2π, $\hbar$	1.0546×10^{-34} J·s
Length	Bohr radius, $a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
Energy	$\dfrac{m_e e^4}{16\pi^2\epsilon_0^2\hbar^2} = \dfrac{e^2}{4\pi\epsilon_0 a_0} = E_h$	4.3597×10^{-18} J
Permittivity	$\kappa_0 = 4\pi\epsilon_0$	1.1127×10^{-10} $C^2 \cdot J^{-1} \cdot m^{-1}$

Born-Oppenheimer Approximation in words

Mass of electron versus mass of nucleus

1 <<< 1830 (at least)



$$\phi_n^{el}(\mathbf{r};\mathbf{R})$$

BO Approximation in equation 1

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{r},\mathbf{R})$$

$$= \hat{T}_{el} + \hat{T}_{NU} + \hat{V} = \hat{T}_{el} + \hat{V} + \hat{T}_{NU} = \hat{H}^0 + \hat{T}_{NU}$$

$$\hat{H}^0(\mathbf{r};\mathbf{R}) = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + V(\mathbf{r},\mathbf{R}) \qquad \hat{T}_{NU} = -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2$$

$$\hat{H}\Psi(\mathbf{r},\mathbf{R}) = E_{el,NU}\Psi(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_{m}^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})$$

$$\chi_m(\mathbf{R}) =$$

BO Approximation 2

$$\left(\hat{H} - E_{el,NU}\right)\Psi(\mathbf{r},\mathbf{R}) = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H} - E_{el,NU}\right)\sum_m^{\infty} \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 + \hat{T}_{NU} - E_{el,NU}\right)\sum_m^{\infty} \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 + \hat{T}_{NU} - E_{el,NU}\right)\sum_m^{\infty} \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} = 0$$

$$\sum_m^{\infty} \chi_m(\mathbf{R})\Big[\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Big]$$

$$+ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 0$$

BO Approximation 3

$$\sum_m^{\infty} \chi_m(\mathbf{R}) \left[\int \phi_n^{el*}(\mathbf{r};\mathbf{R}) \left(\hat{H}^0 - E_{el,NU} \right) \phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r} \right]$$

$$= \sum_m^{\infty} \chi_m(\mathbf{R}) \left[\left(E_m(\mathbf{R}) - E_{el,NU} \right) \langle n \| m \rangle_r \right] = \left(E_n(\mathbf{R}) - E_{el,NU} \right) \chi_n(\mathbf{R})$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R}) \left(\hat{T}_{NU} \right) \sum_m^{\infty} \chi_m(\mathbf{R}) \phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r}$$

$$= \int \phi_n^{el*}(\mathbf{r};\mathbf{R}) \left(-\frac{1}{2} \sum_{I=1}^{N} \frac{1}{M_I} \nabla_I^2 \right) \sum_m^{\infty} \chi_m(\mathbf{R}) \phi_m^{el}(\mathbf{r};\mathbf{R})\, d\mathbf{r}$$

$$|n\rangle = \psi_n(x) \qquad \langle m| = \psi_m{}^*(x)$$

Using Bra-Ket Notation

$$\langle n|\hat{x}|m\rangle = \int_{-\infty}^{\infty} \psi_n{}^*(x)\, x\, \psi_m(x) dx$$

$$\langle n|\hat{1}|m\rangle = \langle n|m\rangle = \langle n\|m\rangle = \int_{-\infty}^{\infty} \psi_n{}^*(x) \psi_m(x) dx$$

BO Approximation 4

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

$$= \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\sum_m^{\infty}\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_m(\mathbf{R})\right)\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

$$+$$

$$+$$

$$= \sum_m^{\infty} -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_m(\mathbf{R})\langle n\|m\rangle_r = -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_n(\mathbf{R})$$

$$+\sum_m^{\infty}\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right|m\right\rangle\chi_m(\mathbf{R})+\sum_m^{\infty}\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\right|m\right\rangle\nabla_I\chi_m(\mathbf{R})$$

BO Approximation 5

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(E_n(\mathbf{R})+\hat{T}_{NU}-E_{el,NU}\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}=0$$

$$=\left(E_n(\mathbf{R})-E_{el,NU}\right)\chi_n(\mathbf{R})-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_n(\mathbf{R})+\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})=0$$

$$\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})$$

$$\equiv$$

$$\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2+E_n(\mathbf{R})\right)\chi_n(\mathbf{R})+\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})=E_{el,NU}\chi_n(\mathbf{R})$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})=E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

BO Approximation 6

Born-Oppenheimer Approximation ignore C_{nm}

$$\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + E_n(\mathbf{R})\right)\chi_n(\mathbf{R}) = E_{el,NU}\,\chi_n(\mathbf{R})$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

Nuclear wavefunction is given by the expansion coefficient!

$$\hat{H}_{NU}(\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R}) = E_{el,NU}\,\chi_{n,v_n}^{NU}(\mathbf{R})$$

$$\hat{H}_{NU}(\mathbf{R}) = \left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{R})\right)$$

The nucleus is moving in an potential that is the result of averaging the contribution coming from the electron at a given nuclear geometry! In essence you have separated the motion of the electron and nucleus.

Separation of Variables by Time Scale

$$\hat{H}^{0}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{NU}(\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R}) = E_{el,NU}\chi_{n,v_n}^{NU}(\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \phi_n^{el}(\mathbf{r};\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R})$$

Now you can say nuclear wave function on the n-th electronic state

You can write the energy of the electron as a function of the nuclear coordinate and consider it as a potential that the nucleus feels.

Adiabatic Approximation

Include diagonal coupling term C_{nn}

$$C_{nn} = \left\langle n \left| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \right| n \right\rangle + \left\langle n \left| -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I \right| n \right\rangle \nabla_I$$

$$\langle n \| n \rangle = 1 \rightarrow \nabla_I \langle n \| n \rangle = \nabla_I \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= 2\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} = 0$$

$$\nabla_I^2 \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}$$

$$= 2\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\nabla_I^2 \phi_n^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} + 2\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\nabla_I \phi_n^{el}(\mathbf{r};\mathbf{R})\right)^2 d\mathbf{r} = 0$$

$$C_{nn} =$$