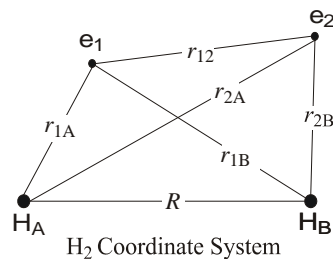


MOLECULES

Hamiltonian (in atomic units) for diatomic molecule A-B, e.g. H₂ (just 2 electrons):



$$\begin{aligned}
 \hat{H} &= -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{Z_A e^2}{4\pi\epsilon_0 r_{1A}} - \frac{Z_B e^2}{4\pi\epsilon_0 r_{1B}} - \frac{Z_A e^2}{4\pi\epsilon_0 r_{2A}} - \frac{Z_B e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} \\
 &= \hat{T}_N(\mathbf{R}) + \hat{T}_E(\mathbf{r}) + \underbrace{\frac{Z_A e^2}{4\pi\epsilon_0 r_{1A}} + \frac{Z_B e^2}{4\pi\epsilon_0 r_{1B}} + \frac{Z_A e^2}{4\pi\epsilon_0 r_{2A}} + \frac{Z_B e^2}{4\pi\epsilon_0 r_{2B}}}_{\hat{V}_{EN}(\mathbf{r}, \mathbf{R})} + \hat{V}_{EE}(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) \\
 &= -\frac{1}{2} \frac{m_e}{M} (\nabla_A^2 + \nabla_B^2) + \underbrace{-\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{Z_A}{r_{1A}} + \frac{Z_B}{r_{1B}} + \frac{Z_A}{r_{2A}} + \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}}_{\hat{H}_{el}(\mathbf{r}, \mathbf{R})} \\
 &= \hat{H}_N(\mathbf{R}) + \hat{H}_{el}(\mathbf{r}, \mathbf{R})
 \end{aligned}$$

(**r**) and (**R**) - electronic & nuclear coordinates

Atomic units - mass in units of $m_e = 1$, but we'll write m_e explicitly in 1st term

$$\hat{H}(\mathbf{r}, \mathbf{R})\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$

How to solve?? $V_{EN}(\mathbf{r}, \mathbf{R})$ e^- -nuclear attractions couple the coordinates

BORN-OPPENHEIMER APPROXIMATION

$\frac{m_e}{M} \ll 1$ Nuclei much more massive than electrons \Rightarrow nuclei are much slower

Solve electronic Schrodinger eq. for FIXED nuclear positions (**R**), e.g. (**R**₁):

$$\boxed{\hat{H}_{el}(\mathbf{r}; \mathbf{R}_1)\psi_{el}(\mathbf{r}; \mathbf{R}_1) = E_{el}(\mathbf{R}_1)\psi_{el}(\mathbf{r}; \mathbf{R}_1)}$$

No nuclear kinetic energy in \hat{H}_{el}

Includes nuclear repulsions & electron-nuclear attractions with nuclei fixed

Gives *electronic orbitals and energies* for the selected nuclear geometry

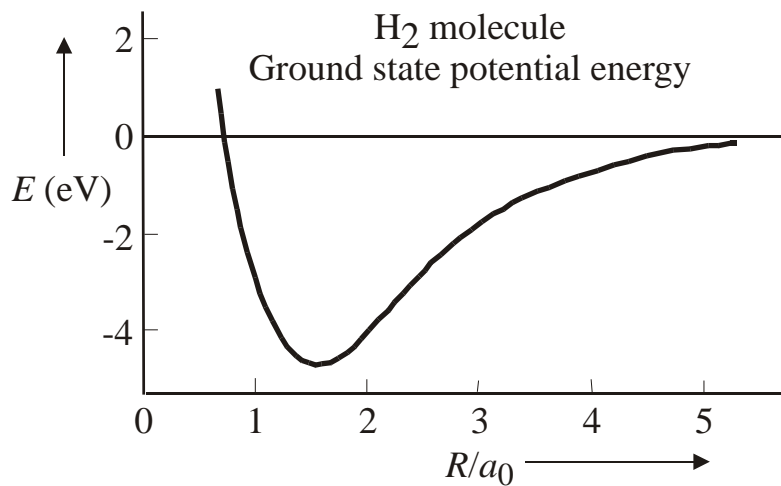
Could solve with variational (SCF-HF) or perturbation approach

Solve Schrodinger eq. for another FIXED set of nuclear positions (\mathbf{R}), e.g. (\mathbf{R}_2):

$$\hat{H}_{el}(\mathbf{r}; \mathbf{R}_2) \psi_{el}(\mathbf{r}; \mathbf{R}_2) = E_{el}(\mathbf{R}_2) \psi_{el}(\mathbf{r}; \mathbf{R}_2)$$

Repeat for lots of internuclear separations

Plot energies $E_{el}(\mathbf{R}) = E_{el}(R_{AB})$ vs. internuclear separation R_{AB} (for diatomic)



Solution of Schrodinger eq. for each value of R_{AB} yields a set of eigenvalues $E_{el_n}(R_{AB})$ and eigenfunctions $\psi_{el_n}(\mathbf{r}, R_{AB})$ (molecular orbitals)

Minimum energy - most stable nuclear geometry

$R_{AB} \rightarrow \infty$: separated *atoms*, not separated particles!

$E_{el}(R_{AB} \rightarrow \infty)$ includes atomic orbital energies, e.g. $2 \times E_{H_{1s}}$ - set to 0

WHAT ABOUT NUCLEAR MOTION?

We've neglected it - no molecular vibrations, rotations

Write complete wavefunction

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R})$$

Not complete separation of variables, but practical since we've seen we can solve for $\psi_{el}(\mathbf{r}; \mathbf{R})$ at each (\mathbf{R}) to determine $\psi_{el}(\mathbf{r}, \mathbf{R}) = \psi_{el}(\mathbf{r}, R_{AB})$.

Solve complete Schrodinger equation

$$\widehat{H}(\mathbf{r}, \mathbf{R})\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$

$$\left[\widehat{H}_{el}(\mathbf{r}, \mathbf{R}) + \widehat{H}_N(\mathbf{R}) \right] \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R}) = E \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R})$$

$$\widehat{H}_{el}(\mathbf{r}, \mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R}) + \widehat{H}_N(\mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R}) = E \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R})$$

\widehat{H}_{el} only operates on ψ_{el} . So

$$\widehat{H}_{el}(\mathbf{r}, \mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R}) = \psi_N(\mathbf{R}) \widehat{H}_{el}(\mathbf{r}, \mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R})$$

which includes the term $\psi_N(\mathbf{R}) \widehat{T}_E(\mathbf{r}) \psi_{el}(\mathbf{r}, \mathbf{R}) = \psi_N(\mathbf{R}) \left[-\frac{1}{2} (\nabla_1^2 + \nabla_2^2) \psi_{el}(\mathbf{r}, \mathbf{R}) \right]$.

$\widehat{H}_N = -\frac{1}{2} \frac{m_e}{M} (\nabla_A^2 + \nabla_B^2)$ operates on both $\psi_{el}(\mathbf{r}, \mathbf{R})$ and $\psi_N(\mathbf{R})$, but since $m_e/M \ll 1$,

$$\widehat{H}_N(\mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \ll \widehat{H}_{el}(\mathbf{r}, \mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R})$$

Born-Oppenheimer approximation:

$$\widehat{H}_N(\mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R}) \approx \psi_{el}(\mathbf{r}, \mathbf{R}) \widehat{H}_N(\mathbf{R}) \psi_N(\mathbf{R})$$

Then

$$\widehat{H}_{el}(\mathbf{r}, \mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R}) + \widehat{H}_N(\mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R})$$

$$\approx \psi_N(\mathbf{R}) \widehat{H}_{el}(\mathbf{r}, \mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) + \psi_{el}(\mathbf{r}, \mathbf{R}) \widehat{H}_N(\mathbf{R}) \psi_N(\mathbf{R})$$

$$= \psi_N(\mathbf{R}) E_{el}(\mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) + \psi_{el}(\mathbf{r}, \mathbf{R}) \widehat{H}_N(\mathbf{R}) \psi_N(\mathbf{R}) = E \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_N(\mathbf{R})$$

No more electronic coordinates!!

MOLECULES – THE NUCLEAR EQUATIONPRIMER FOR 5.33 IR EXPERIMENT!

HOW DO WE GO ABOUT SOLVING FOR MOLECULAR ENERGIES,
WAVEFUNCTIONS?

Start by solving electronic Schrodinger equation with various fixed nuclear positions

This gives us molecular orbitals $\psi_{el}(\mathbf{r}, \mathbf{R})$ and energies $E_{el}(\mathbf{R}) = U(\mathbf{R})$

Then solve nuclear Schrodinger equation using $U(\mathbf{R})$

HOW DO WE SOLVE THE NUCLEAR PART? e.g. diatomic molecule

$$\left[\hat{T}_N(\mathbf{R}) + U(R) \right] \psi_N(\mathbf{R}) = E \psi_N(\mathbf{R})$$

Go to COM coordinates, with internal spherical polar coordinates

$$\hat{T}_N = -\frac{1}{2M} (\nabla_A^2 + \nabla_B^2) \rightarrow -\frac{1}{2M_{TOT}} \nabla_{COM}^2 - \frac{1}{2\mu} \nabla_{int}^2$$

where

$$\nabla_{int}^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) = \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - \frac{\hat{L}^2(\theta, \phi)}{R^2}$$

Nuclear Schrodinger equation is now

$$\left[\frac{-\nabla_{COM}^2}{2M_{TOT}} + \frac{-\nabla_{int}^2}{2\mu} + U(R) \right] \psi_N(\mathbf{R}) = E \psi_N(\mathbf{R})$$

Operator is separable into COM and INT coordinates

So nuclear wavefunction is separable into COM (translational) coordinates and INT (vibrational, rotational) coordinates

Energy is separable into COM and INT energies

$$\psi_N(\mathbf{R}) = \psi_{trans}(\mathbf{R}_{COM})\psi_{int}(\mathbf{R}_{int}) = \psi_{trans}(\mathbf{R}_{COM})\psi_{int}(R, \theta, \phi)$$

$$E = E_{trans} + E_{int}$$

We can write separate Schrodinger equations for COM and INT coordinates

$$\frac{-\nabla_{COM}^2}{2M_{TOT}}\psi_{trans}(\mathbf{R}_{COM}) = E_{trans}\psi_{trans}(\mathbf{R}_{COM})$$

$$\left[\frac{-\nabla_{int}^2}{2\mu} + U(R) \right] \psi_{int}(R, \theta, \phi) = E_{int}\psi_{int}(R, \theta, \phi)$$

First equation just gives translational motion, e.g. free particle or P-I-B
Not usually of interest - tells us little about the molecule itself

Second equation is separable into R and (θ, ϕ) coordinates

$$\frac{-1}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \psi_{int}(R, \theta, \phi) \right) + \frac{\hat{L}^2(\theta, \phi)}{2\mu R^2} \psi_{int}(R, \theta, \phi) + U(R)\psi_{int}(R, \theta, \phi) = E_{int}\psi_{int}(R, \theta, \phi)$$

$$\psi_{int}(R, \theta, \phi) = \chi(R)\psi_{rot}(\theta, \phi) = \chi(R)Y_l^m(\theta, \phi)$$

$$E_{int} = E_{el-vib} + E_{rot}$$

$$\frac{\hat{L}^2(\theta, \phi)}{2\mu R^2} \psi_{int}(R, \theta, \phi) = \chi(R) \frac{\hat{L}^2(\theta, \phi)}{2\mu R^2} Y_l^m(\theta, \phi) = \chi(R) \frac{J(J+1)}{2\mu R^2} Y_l^m(\theta, \phi)$$

$$\left[\frac{-1}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{J(J+1)}{2\mu R^2} + U(R) \right] \chi(R) = E_{int}\chi(R)$$

We're left with just an equation in the vibrational coordinate R

Expand $U(R)$ around equilibrium bond length R_e

$$U(R) = U(R_e) + \cancel{(R - R_e) \left(\frac{dU}{dR} \right)_{R_e}} + \frac{1}{2} (R - R_e)^2 \left(\frac{d^2U}{dR^2} \right)_{R_e} + \dots$$

$$\approx U(R_e) + \frac{1}{2} k (R - R_e)^2 \equiv U(R_e) + \frac{1}{2} k x^2 \quad \text{where } x = R - R_e$$

Define

$$\chi(R - R_e) = \psi_{\text{vib}}(R - R_e) / R$$

Then

$$\frac{-1}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \left[\frac{\psi_{\text{vib}}(R - R_e)}{R} \right] = \frac{-1}{2\mu R^2} \frac{\partial^2}{\partial R^2} \psi_{\text{vib}}(R - R_e)$$

and approximating $\frac{J(J+1)}{2\mu R^2} \approx \frac{J(J+1)}{2\mu R_e^2}$ gives

$$\left[\frac{-1}{2\mu^2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k x^2 \right] \psi_{\text{vib}}(x) = \left[E_{\text{int}} - \frac{J(J+1)}{2\mu R_e^2} - U(R_e) \right] \psi_{\text{vib}}(x) = E_{\text{vib}} \psi_{\text{vib}}(x)$$

QM HO equation of motion!

$U(R_e) = E_{\text{elec}}$ is just the electronic energy at the potential energy minimum

$\frac{J(J+1)}{2\mu R_e^2} = E_{\text{rot}}$ is the rotational energy (rigid rotor model)

$\sqrt{\frac{k}{\mu}} (n + 1/2) = E_{\text{vib}}$ is the vibrational energy (HO model)

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

Total energy as translational, rotational, vibrational, and electronic parts!!

Total wavefunction is a product

$$\psi = \psi_{el}(r, R) \psi_{vib}(R) \psi_{rot}(\theta, \phi) \psi_{trans}(R_{COM})$$

That's it!!! - to first order

Energy corrections can be derived by including anharmonic terms in the expansion of $U(R)$ and by Taylor expansion of $\frac{J(J+1)}{2\mu R^2}$ for vibration-rotation coupling, centrifugal distortion (non-rigid rotor) effects.

See Pauling & Wilson, Introduction to Quantum Mechanics, for a particularly careful treatment & discussion.