Nature of the Chemical Bond

Goal: To predict (without work) properties and structures of chemicals and materials all based on the rigorous principles of Quantum Mechanics (QM)

Why is QM so important?

→ It is why we exist!

In a Classical world:

Consider a proton and an electron at separation \( R \)

\[ \begin{array}{c}
\text{+e} \\
\text{-e} \\
\hline
\text{R}
\end{array} \]

The **CLASSICAL** energy components of the total energy is

\[ \text{Energy Terms: Potential Energy + Kinetic Energy = Total Energy} \]

\[ \hat{V} + \hat{T} = E \]

Classical Energy:

\[ \frac{-e^2}{R} + \frac{1}{2} m v^2 = E \]

The lowest energy of a system constitutes its “best” energy

\[ \text{the most negative} \]

The minimum value of \( \hat{V} \) is \( -\infty \) at \( R = 0 \)

\[ \hat{T} \geq 0 \text{ at } v = 0 \]

\[ \Box \]
If $R=0$ and $v=0$, the $e^-$ would be at the nucleus and no atoms would exist!

Luckily, QM explains atoms and bonds.

**QM points**

1. The wavefunction, $\Psi$, contains all the information we need from an electron. The wavefunction is a function of space and time: $\Psi(x,y,z,t)$

2. The probability density of a wavefunction is

$$P(x,y,z,t) = |\Psi|^2 = \Psi^\ast \Psi$$

($\Psi^\ast$ is the complex conjugate of $\Psi$)

In order to be relevant, the wavefunction must be normalized so that

$$\int P(x,y,z,t) dx = \langle \Psi | \Psi \rangle = 1$$

3. The concept of superposition allows us to make good wavefunctions out of other good wavefunctions.

\[ \Psi_{\text{new}} = \Psi_{\text{old}} + \Psi_{\text{good}} \]

Also a good wavefunction.
4 - The Hamiltonian determines the time-evolution of \( \Psi \)

\[
\frac{\partial \Psi}{\partial t} = \frac{-i}{\hbar} H \Psi
\]

5 - Phase factors don't change the state that a wavefunction represents.

\[
\langle \Psi, e^{i\alpha} \Psi \rangle = |\Psi|^2 = \Psi^\dagger \Psi = \langle \Psi | \Psi \rangle
\]

6 - If \( H \) is independent of time, then \( \Psi(x,y,z,t) = e^{-i\lambda t} \Phi(x,y,z) \)

\[
\frac{\partial}{\partial t} \Psi = -i\alpha \Psi \quad \text{(an eigenfunction!)}
\]

So \( \hat{H} \Psi = E \Psi \), the Time-Independent Schrodinger Equation.

7 - Since \( \hat{H} \Psi = E \Psi \),

\[
E = \langle \Psi | \hat{H} | \Psi \rangle
\]

and for an approximate wavefunction \( \Psi_n \)

\[
\langle E \rangle = \frac{\langle \Psi_n | \hat{H} | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} \geq E_{\text{exact}}
\]

(3)
Since \( \hat{H} = \hat{T} + \hat{V} \)

\[ E = \langle \psi | \hat{H} | \psi \rangle = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{V} | \psi \rangle \]

\[ \hat{T} = \frac{\hat{p}^2}{2m} \]

\[ \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 \]

\[ E = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{V} | \psi \rangle \]

\[ \hat{T} = \frac{\hbar^2}{2m} \nabla^2 \]

\[ E = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{V} | \psi \rangle \]

\[ \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 \]

\[ E = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{V} | \psi \rangle \]

Interpretation:

\[ KE = \langle \psi | \hat{T} | \psi \rangle \]

\[ KE = \frac{\hbar^2}{2m} \langle \psi | \nabla^2 | \psi \rangle \]

Unlike in Classical Mech., BOTH \( T \) \& \( V \) are directly related via the wavefunction.
Examples of wavefunctions

\[ \Psi_C, \quad \Psi_L, \quad \Psi_S \]

\[ R_C < R_L < R_S \]

\[ \text{best } V \approx \Psi_C \]
\[ \text{worst } R \approx \Psi_S \]

\[ \text{worst } V \approx \Psi_L \]

\[ \text{best } T \approx \Psi_S \]

\[ E = T + V \]
\[ = \frac{k^2}{2m} \left( \frac{\partial^2}{\partial x^2} \right) - \frac{e^2}{r} \]

Which \( \Psi \) has best \( V, T \)?

- KE depends on smoothness of \( \Psi \); smoother is better
  (recall \( KE \) is related to gradient of \( \Psi \))

- PE depends on average charge density; more compact is better
  (we can’t determine which \( \Psi \) is best unless we know both \( T \) and \( V \)’s dependence on \( R \))

\[ V = \frac{-e}{r} \rightarrow \frac{1}{r} \text{ relation!} \]

\[ T = \frac{k^2}{2m} \left( \frac{\partial^2}{\partial x^2} \right) \]
\[ \approx \frac{k^2}{2m} \left( \frac{1}{R^2} \right) \]

\[ \approx \frac{1}{R} \text{ relation!} \]
The higher order of $T$ dominates.

$E = H + V$

$= \frac{\hbar^2}{2m} \frac{1}{R^2} - \frac{e^2}{R}$

$\frac{\Delta E}{\Delta R} = \frac{\hbar^2}{m e^2} \equiv a_o \quad \text{(the Bohr radius)}$

$= 0.529 \text{Å}$

At $a_o = R$, $E = \frac{\hbar^2}{2m a_o} - \frac{e^2}{a_o} = -13.6 \text{ eV}$

$\frac{a^2}{a_o} = 1 \quad E_k = 27.2 \text{ eV} = 627.5 \text{ kcal/mol}$

So KE is what keeps electrons from falling into the nucleus!
Application:
- Bonding in H₂⁺

\[ \Phi_{\text{left}} \quad \Phi_{\text{right}} \]

H is on left side, H⁺ is on right.
There is one e⁻, and it's on H.

e⁻ is on right side

Also recall superposition. \( \Phi_{\text{left}}, \Phi_{\text{right}} \) are both good wave functions.

So also:

\[ \Phi_{\text{left}} + \Phi_{\text{right}} \]
and

\[ \Phi_{\text{left}} - \Phi_{\text{right}} \]

Higher e⁻ density far from nuclei means worse PE⁻.

But gradient for \( \Phi_{\text{left}} + \Phi_{\text{right}} \) is smoothest, so best KE.
Does \( \text{H}_2^+ \) remain bound?

Look at \( T, V \) for inter-nuclear distance

- \( V \) (as nuclei separate, repulsion decreases)
- \( T \) depends on \( \nabla \Phi \) change

\( \Phi_b \) nuclei on top of each other

\( R_a < R_b < R_c \)

Optimal region (note no change in \( \nabla \Phi \))

\( R_a < R_b < R_c \)

(Optimal distance is \( \approx 2a_0 \))

\( \rightarrow \) Yes! \( \text{H}_2^+ \) is bound

Nodal Theorem: A wavefunction without nodes is of lower energy.

\( \Phi_e - \Phi_r \rightarrow \) smoother

\( \Phi_e - \Phi_r \rightarrow \) less smooth