

Lee 11

**Covalent Bond**

Following Feynman, Poulney & Wilson.

**Simplest example: H\textsubscript{2}+ molecule**

Assume proton separation is fixed, calculate energy, vary separation \( R \) to find minimum \( E(R) \).

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{ke^2}{r} - \frac{ke^2}{|r-R|} + \frac{e^2}{R}
\]

Approximate solution in terms of \( H \)-atom ground state wave functions

\[
\phi_{\text{Ls}}(\vec{r}) \equiv \phi(1) \quad \phi_{\text{Ls}}(\vec{r}-\vec{R}) \equiv \phi(2)
\]

\[
E_H = E_{100} = -13.6\text{eV}
\]

\( H \)-atom ground state
Then we have approximately:

\[\hat{H} \phi(1) = \left( -\frac{\hbar^2}{2m} \nabla^2 + \frac{ke^2}{r} \right) \phi(1) + \frac{e^2}{k} \phi(1) \quad (2)\]

\[= \left( E_H + \frac{e^2}{R} \right) \phi(1) + J \phi(0) - A \phi(2)\]

where \(A\) is the energy associated with the e\textsuperscript{-} tunneling, and \(J\) is an energy associated with e\textsuperscript{+} not tunneling.

Similarly,

\[\hat{H} \phi(2) = \left( E_H + \frac{ke^2}{R} + J \right) \phi(2) - A \phi(1) \quad (6)\]

It turns out that (Pauli & Wilson)

\[A = -\frac{ke^2}{\alpha_0} e^{-R/\alpha_0} \left( 1 + \frac{R}{\alpha_0} \right)\]

Show characteristic exponential tunneling behavior.
Neither \( \phi_1 \) nor \( \phi_2 \) is an energy eigenstate. However, it is easy to see that the (normalized) linear combinations are:

\[
\begin{align*}
\phi_+ &= \frac{1}{\sqrt{2}} (\phi_1 + \phi_2) \\
\phi_- &= \frac{1}{\sqrt{2}} (\phi_1 - \phi_2)
\end{align*}
\]

by adding and subtracting equations \( a, b \):

\[
\begin{align*}
\hat{H} (\frac{\phi_1 + \phi_2}{\sqrt{2}}) &= (E_+ + \frac{k e^2}{R} + J - A) \frac{\phi_1 + \phi_2}{\sqrt{2}} \\
\text{and} \quad \hat{H} (\frac{\phi_1 - \phi_2}{\sqrt{2}}) &= (E_+ + \frac{k e^2}{R} + J + A) \frac{\phi_1 - \phi_2}{\sqrt{2}}
\end{align*}
\]

The symmetric state can be bound. \( E_+ = -13.6 \text{ eV} \)

It looks like this:

\[
\begin{align*}
1.32 \text{ Å} &= \text{R}_{\text{min}} \\
E(R) &\quad \downarrow \\
-1.77 \text{ eV} &\quad \uparrow R
\end{align*}
\]
experimentally, \[ R_{\text{nu}} = 1.06 \text{Å} \]
\[ E_{\text{nu}} = 2.78 \text{ eV} \]

So the calculation is not bad. (One can do better including other effects such as the distortion of the H-atom wave function.)

The key idea is that the barrier comes from the electron tunneling. It is in this sense that the electron is “shared”.

In Feynman’s view, all forces are the result of tunneling: tunneling (“virtual”) photon

\[ \chi \]

“exchanging” or tunneling of “virtual” photon gives rise to electromagnetic force between electrons:

\[ \gamma - \text{spin } 1 \rightarrow \text{like sign repel, opposite attract} \]
\[ M_z = 0 \Rightarrow V(r) = -\frac{k e^2}{r} \text{ "infinite range} \]