Physics 472 Lecture 17

The \( H^+ \) Ion (simplest molecule)

\[
H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{|\vec{r} - \vec{R}_1|} - \frac{e^2}{|\vec{r} - \vec{R}_2|} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|}
\]

The Schrödinger equation can be solved using elliptical coordinates, but let us use the variational approach, which is more instructive.

Trial wave function

\[
\Psi(\vec{r}) = C_1 \psi_{100}(\vec{r} - \vec{R}_1) + C_2 \psi_{100}(\vec{r} - \vec{R}_2)
\]

\( \psi_{100}(\vec{r}) = \) Hydrogenic ground state

\[
\psi_{100}(\vec{r}) = \sqrt{\frac{1}{\pi a_0^3}} e^{-1/r/a_0}
\]

\[
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\]
Since the potential is symmetric under reflection about a plane perpendicular to the molecular axis, passing through the midpoint \( \frac{1}{2} (\vec{r}_1 + \vec{r}_2) \), more appropriate trial functions are those that reflect this symmetry, namely, even- and odd-parity combinations of \( \Psi_1 \) and \( \Psi_2 \):

\[
\Psi_{\pm}(\vec{r}) = C_{\pm} \left[ \Psi_1(\vec{r}) \pm \Psi_2(\vec{r}) \right]
\]

This defines a molecular orbital, which is a linear combination of atomic orbitals (LCAO).
The normalization factors are $\sqrt{3}$

\[
\langle \gamma \pm | \gamma \pm \rangle = |C|^{-2} \left( \langle 111 \rangle + \langle 212 \rangle \pm 2 \langle 112 \rangle \right)
\]

since $\langle 112 \rangle = \langle 112 \rangle^* \in |R|$

\[
\langle \gamma \pm | \gamma \pm \rangle = (C \pm |C|^2 (2 \pm 2 S(R))),
\]

where $R = |R| = |\vec{r}_1 - \vec{r}_2|$ and

\[
S = \langle 112 \rangle = \frac{1}{\pi \rho_0^3} \int d^3 r \ e^{-\frac{|\vec{r}_1|}{\rho_0} - \frac{|\vec{r}_2 - \vec{R}|}{\rho_0}}
\]

is the overlap integral. This integral is most easily calculated using elliptical coordinates $\xi, \sigma, \phi$.
\[ S = \frac{1}{\ell} \left( |1\ell 1| + |1\ell - \ell 1| \right) \]

\[ \sigma = \frac{1}{\ell} \left( |1\ell 1| - |1\ell - \ell 1| \right) \]

\[ \int d^3r = \int d\sigma \int \rho d\sigma \int_0^{2\pi} \frac{R^3}{8} (\rho^2 - \sigma^2) \]

(see advanced calculus text)

\[ \Rightarrow S = \frac{1}{8\pi \ell a_0^2} \int_1^\infty \frac{R^3}{\ell a_0^3} \int_0^{1\pi} e^{-\frac{R}{a_0}} \rho \int_1^{2\pi} (\rho^2 - \sigma^2) d\rho d\sigma \]

\[ = \left[ 1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right] e^{-R/a_0} \]

\[ \langle H \rangle = \frac{1}{2 \pm 2s} \left[ \langle 11H11 \rangle + \langle 21H12 \rangle \pm 2 \langle 11H12 \rangle \right] \]
\[ \langle H \rangle = \frac{\langle 1 | H | 1 \rangle \pm \langle 1 | H | 2 \rangle}{1 \pm \delta} \]

\[ \langle 1 | H | 1 \rangle = \int d^3r \, \psi_i^*(r) \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{|r - q_0|} + \frac{e^2}{r} \right] \psi_i(r) \]

\[ = E_1 + \frac{e^2}{R} - e^2 \int d^3r \, \frac{|\psi_i(r)|^2}{|r - q_0|^2} \]

\[ \frac{1}{\pi a_0^3} \int d^3r \, \frac{e^{-\frac{2|\vec{r}|}{a_0}}}{|r - q_0|} = \frac{1}{R} \left[ 1 - e^{-\frac{2R}{a_0}} (1 + \frac{R}{a_0}) \right] \]

(Using elliptical coordinates)

\[ \Rightarrow \langle 1 | H | 1 \rangle = E_1 + \frac{e^2}{R} \left( 1 + \frac{R}{a_0} \right) e^{-\frac{2R}{a_0}} \]

\[ = \langle 2 | H | 2 \rangle = \text{"direct integral"} \]
\[
\langle \mathbf{H} | \mathbf{H} \rangle = \left( E_1 + \frac{e^2}{R} \right) S - e^2 \int d^3r \, \frac{\Psi_1^*(\mathbf{r}) \Psi_2(\mathbf{r})}{|\mathbf{r} - \mathbf{R}|} \\
\text{"exchange integral"} \\
= \left( E_1 + \frac{e^2}{R} \right) S - \frac{e^2}{\alpha_0} \left( 1 + \frac{R}{\alpha_0} \right) e^{-R/\alpha_0}
\]

Combining all the terms, we find
The even state has a minimum 1.8 eV below $E_1$ occurring when $R = 2.4 \ a_0 = 1.8 \ \text{Å}$. On the other hand, the odd state has no minimum. The even state is referred to as the bonding orbital and the odd state as the antibonding orbital. The antibonding orbital has a node at $\bar{r} = \frac{1}{2} (\bar{r}_1 + \bar{r}_2)$ and the force between the two protons is repulsive.
\[ F = -\frac{e\langle H \rangle}{aR} \geq 0 \]

In the even state

on the other hand, little

force between the two protons

is attractive for \( R > 1.3 \text{ \AA} \),

with a short-range repulsion,

leading to a bound state,

the H\(_2^+\) molecular ion.

It is a covalent bond,

with the electron shared

equally by both protons.
Note that the experimental value of the binding energy is 2.8 eV, greater than the 1.8 eV resulting from our variational calculation. This is not surprising, since a variational calculation overestimates the ground state energy. Nonetheless, the variational calculation correctly predicts the existence of a bound state for a symmetric wavefunction.