Molecules - H²

\[ H = H_{\text{atom}, 1A} + H_{\text{atom}, 2B} + V_{ee} + V_{pp} + V_{ep} + T_N \]

\[ H_{\text{atom}, 1A} = \frac{p_1^2}{2m} - \frac{\alpha}{r_{1A}} \]
\[ H_{\text{atom}, 2B} = \frac{p_2^2}{2m} - \frac{\alpha}{r_{2B}} \]
\[ V_{ee} = \frac{\alpha}{r_{12}} \]
\[ V_{pp} = \frac{\alpha}{R_{AB}} \]
\[ V_{ep} = -\frac{\alpha}{r_{1B}} - \frac{\alpha}{r_{2A}} \]
\[ T_N = \frac{p_A^2}{2M_A} + \frac{p_B^2}{2M_B} \]

Use variational calculation

\[ \Rightarrow \text{need 1-electron basis} \]
\[
H_2^+ = \frac{P_A^2}{2m} - \frac{\alpha}{r_A} - \frac{\alpha}{r_B} + \frac{\alpha}{r_{AB}} + \frac{P_B^2}{2M}
\]

\[
\text{crude approximation LCAO}
\]

- linear combination of atomic orbitals

employ using: Born-Oppenheimer

\[
l^4_{\text{H}_2} = \left| \psi \right|_{\text{Nuclear}}^2 \left( \frac{\hat{R}}{R_0} \right) \left( \text{electrons} \right)
\]

\[
l^4_{\text{electrons}} \left( \overrightarrow{R_{AB}}, \overrightarrow{r_1}, \overrightarrow{r_2} \right) \left( \text{protons} \right)
\]

i) Fix \( \overrightarrow{R_{AB}} \)

ii) adjust \( l^4_{\text{electrons}} \) to minimize

\[
\left\langle \left( \text{N+1 electrons} \right) \left| H \right| l^4_{\text{electrons}} \right\rangle
\]

\[= \bigvee \text{protons} \left( \overrightarrow{R_{AB}} \right) \left( \text{protons} \right)
\]

iii) Solve \[
\left[ \frac{P_A^2}{2M} + \frac{P_B^2}{2M} + \bigvee \text{protons} \left( \overrightarrow{R_{AB}} \right) \right] l^4_{\text{protons}}
\]

\[= E \left| l^4_{\text{protons}} \right> \]
Fix $R_{AB}$ and approximate $L$-electron states using LCAO:

$$
|\psi_{15}^{g}\rangle = \frac{1}{\sqrt{2}} \left[ \psi_{15}^{1A} (\hat{r}) + \psi_{15}^{1B} (\hat{r}) \right]
$$

$$
|\psi_{15}^{u}\rangle = \frac{1}{\sqrt{2}} \left[ \psi_{15}^{1B} (\hat{r}) - \psi_{15}^{1A} (\hat{r}) \right]
$$

gerade = even \quad \text{exact as } R_{AB} \to \infty

ungerade = odd \quad \text{respects fact that ion is invariant under } \vec{R}_A \leftrightarrow \vec{R}_B

V_{PP}(R_{AB}) \sim \frac{a}{R_{AB}} + \langle \psi_{3,u}^{15} | \frac{P_{1}^{2}}{2m} + \frac{x}{r_{1A}} - \frac{x}{r_{1B}} | \psi_{3,u}^{15} \rangle

\begin{align*}
V_{PP} (\text{eV}) \quad &\quad & R (\text{Å}) \\
-10 \quad &\quad & 1 \\
-12 \quad &\quad & 2 \\
-14 \quad &\quad & 3
\end{align*}
\begin{align*}
\langle \Psi_{15}^g | \frac{1}{2m} \left( \frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) | \Psi_{15}^g \rangle \\
\langle \phi_A | \frac{\beta}{r_{1A}} - \frac{\alpha}{r_{1B}} | \phi_A \rangle
\end{align*}

\[
\langle \phi_A | \frac{1}{r_{1B}} | \phi_A \rangle = \frac{1}{\sqrt{2}} \left( | \phi_A \rangle + | \phi_B \rangle \right)
\]

\[
\langle \phi_A | \frac{\alpha}{r_{1A}} | \phi_A \rangle = -13.6 \text{ eV} - \langle \phi_A | \frac{\alpha}{r_{1B}} | \phi_A \rangle
\]

\[
R_{1B} = \left| \frac{\mathbf{r}}{R_{AB} + r_{1A}} \right|
\]

\[
\langle \phi_A \left| \frac{\alpha}{r_{13}} \right| \phi_A \rangle = \frac{1}{\pi a_0^3} \int \frac{e^{-2r_{1A}/a_0}}{R_{AB} + r_{1A}} \, \, d^3r_{1A}
\]

\[
\rightarrow \frac{1}{\pi a_0^3} \int \frac{e^{-2r_{1A}/a_0}}{\sqrt{r}} \, \, d^3r_{1A}
\]

where \( R = \begin{cases} 
R_{1A} & \text{if } r_{1A} > R_{AB} \\
R_{AB} & \text{if } r_{1A} < R_{AB} 
\end{cases} \)
\[ H_{2} \]

\[
\left\{ \begin{array}{c}
\frac{3A}{15,15} = \left| \begin{array}{c}
\frac{3}{15} \\
\frac{3}{15}
\end{array} \right| 100 \\
\end{array} \right.
\]

\[
= \frac{1}{2} \left[ -4_{15}(\vec{r}_{1A}) + 4_{15}(\vec{r}_{1B}) \right] \left[ -4_{15}(\vec{r}_{2A}) + 4_{15}(\vec{r}_{2B}) \right] 100
\]

\[
\approx 1.1M
\]

\[
\left\{ \begin{array}{c}
\vec{r}_{11} = 100 \\
\end{array} \right.
\]

\[
-0.5
\]

\[
R_{0} = 1.0
\]

\[
4.52 \text{eV}
\]

\[
0.0074 \text{nm}
\]
$H_2$ LCAO calculation of $V_{eff}(R)$

$H_e = \frac{P_e}{2m} - \alpha \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$

$\psi_0 (\vec{r}) = \frac{1}{\sqrt{4\pi a^3}} e^{-r/a}$

$\psi = A \left[ \psi_0 (r_1) + \psi_0 (r_2) \right]$ $1 = A^2 \int d^3r \left[ |\psi_0 (r_1)|^2 + |\psi_0 (r_2)|^2 + 2 \psi_0 (r_1) \psi_0 (r_2) \right]$ $1 = \int \left( r_1 = r \right) \left( \vec{r}_2 = \vec{R} - \vec{r}_1 \right)$

$\vec{r}_L = \sqrt{r_1^2 + R^2 - 2r_1 R \cos \theta}$

$= A^2 \left[ 2 + 2 \int d^3r \left( \frac{1}{\sqrt{4\pi a^3}} \right) e^{-r/a} - \frac{\sqrt{r^2 + R^2 - 2r_1 R \cos \theta}}{a} \right]$ 

$= 2A^2 \left[ 1 + e^{-R/a} \left[ 1 + \frac{R}{a} + \frac{1}{3} \left( \frac{R}{a} \right)^2 \right]^2 \right]$ 

$H \left| \psi \right> = -9 \text{Ryd} \left| \psi \right> - \alpha A \left( \frac{1}{r_1} \psi_0 (r_2) + \frac{1}{r_2} \psi_0 (r_1) \right)$
direct integral

\[ D = a \left< \frac{\psi_0(n_1)}{r_1} \right| \frac{1}{r_2} \left| \psi_0(n_2) \right> \]

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

exchange integral

\[ X = a \left< \frac{\psi_0(n_1)}{r_1} \right| \frac{1}{r_2} \left| \psi_0(n_2) \right> \]

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

\[ \langle H \rangle = \left[ 1 + 2 \frac{(D + X)}{(1 + X)} \right] (-\text{Ryd}) \]

add this to Coulomb repulsion

\[ \frac{1}{\text{Ryd}} \]

\[ 2.4 a = 1.3 \text{ Å} \ (\text{exp. } 1.066 \text{ Å}) \]

\[ 2 \gamma \]

\[ \text{bd energy } 1.8 \text{ eV} \]

\[ \text{exp. } 2.8 \text{ eV} \]
of $a_0$. Therefore, when the two protons are very far apart, the eigenfunctions of the Hamiltonian (13) are practically the stationary wave functions of hydrogen atoms.

This is, of course, no longer true when $a_0$ is not negligible compared to $R$. We see, however, that it is convenient, for all $R$, to choose a family of trial kets constructed from atomic states centered at each of the two protons. This choice constitutes the application to the special case of the $H_+^+$ ion of a general method known as the method of linear combination of atomic orbitals. More precisely, we shall call $|\varphi_1\rangle$ and $|\varphi_2\rangle$ the kets which describe the $1s$ states of the two hydrogen atoms:

\begin{equation}
\frac{R}{j^2} (\mu^2 - \nu^2)
\end{equation}

be solved in order of the two fixed

\begin{equation}
\text{ate the variables } \mu, \nu \text{ of possible ion here, but shall}
\end{equation}

\begin{equation}
\text{the ground state oft we shall obtain in of equation (11).}
\end{equation}

with values of $r_1$

\begin{equation}
\text{an } P_1. \text{ Analogous } \text{id } r_2 \text{ of the order}
\end{equation}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Variation of the energy $E$ of the molecular ion $H_+^+$ with respect to the distance $R$ between the two protons.}
\end{figure}

- solid line: the exact total energy of the ground state (the stability of the $H_+^+$ ion is due to the existence of a minimum in this curve).
- dotted line: the diagonal matrix element $H_{11} = H_{22}$ of the Hamiltonian $H$ (the variation of this matrix element cannot explain the chemical bond).
- dashed line: the results of the simple variational calculation of §2 for the bonding and antibonding states (though approximate, this calculation explains the stability of the $H_+^+$ ion).
- triangles: the results of the more elaborate variational calculation of §3-a (taking atomic orbitals of adjustable radius considerably improves the accuracy, especially at small distances).
ns, to obtain the

\[ (54) \]

and state 1s of the

\[ \text{ent}^* \text{ of a helium} \]

\[ R = 0, \text{ with that} \]

s, this energy is

\[ (55) \]

not approach

hr orbit is twice

exact result and

ation uses atomic

h other.

\[ \text{rial kets because} \]

\[ (56) \]

us \( a_0/Z \) centered

\[ \text{try, to} \]

\[ c_1 = c_2. \]

value of \( Z \) which

\[ \text{we find (cf. fig. 5)} \]

\[ a_0, \text{ as it should.} \]

2). Table I gives

\[ \text{from the various} \]

\[ \text{e energies found} \]

\[ \text{ground state; in the} \]

\[ \text{energy.} \]

\[ \text{approach the same} \]

\[ \text{his, we shall use} \]

\[ \text{the Stark effect} \]

\[ \text{hydrogen atom (in} \]

\[ \text{at a distance} R \]

\[ \text{creates an electric} \]

\[ \text{e of two neutrons.} \]

\[ \text{FIGURE 5} \]

\[ \text{For each value of the internuclear distance, we have calculated the value of \( Z \) which minimizes the} \]

\[ \text{energy. For} \]

\[ R = 0, \text{ we have the equivalent of a He}^+ \text{ ion, and we indeed find} \]

\[ Z = 2. \] For \[ R > a_0, \]

\[ \text{we have essentially an isolated hydrogen atom, which gives} \]

\[ Z = 1. \] Between these two extremes,

\[ Z \] is a decreasing function of \( \rho \). The corresponding optimal energies are represented by triangles in figure 2.

<table>
<thead>
<tr>
<th>Method of calculation</th>
<th>Equilibrium distance between the two protons (the abscissa of the minimum of ( \Delta E_\epsilon ))</th>
<th>Depth of the minimum of ( \Delta E_\epsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variational method of § 2 (1s orbitals with ( Z = 1 ))</td>
<td>2.50 ( a_0 )</td>
<td>1.76 eV</td>
</tr>
<tr>
<td>Variational method of § 3-a (1s orbitals with variable ( Z ))</td>
<td>2.00 ( a_0 )</td>
<td>2.35 eV</td>
</tr>
<tr>
<td>Variational method of § 3-b (hybrid orbitals with variable ( Z, Z', \sigma ))</td>
<td>2.00 ( a_0 )</td>
<td>2.73 eV</td>
</tr>
<tr>
<td>Exact values</td>
<td>2.00 ( a_0 )</td>
<td>2.79 eV</td>
</tr>
</tbody>
</table>

**Table I**