

The Bohr's Molecule

1 H₂ molecule in equilibrium

1.1 r/R and ρ/R

Let θ be the angle subtended by the proton-electron line from the proton-proton line, i.e. the angle between the lines with length R and r respectively. Then, balancing the repulsive and attractive forces,

$$\frac{ke^2}{R^2} = 2 \frac{ke^2}{r^2} \cos \theta$$

noting that $\cos \theta = \frac{r}{2R}$,

$$\begin{aligned} \frac{1}{R^2} &= \frac{r/R}{r^2} \\ \frac{1}{R^2} &= \frac{r}{R} \\ R &= r \end{aligned}$$

hence the two protons and one electron form the vertices of an equilateral triangle. This makes sense as now the forces are of equal magnitude and all are 120° from each other. Hence $\theta = \frac{\pi}{3}$ and

$$\frac{r}{R} = 1$$

$$\begin{aligned} \frac{\rho}{R} &= \sin \frac{\pi}{3} \\ &= \frac{\sqrt{3}}{2} \end{aligned}$$

1.2 E_p

Let E_{pp} be the electric potential energy between a pair of protons in the configuration, E_{pe} be the electric potential energy between a proton and an electron, and E_{ee} be that between two electrons. Then

$$\begin{aligned} E_{pp} &= \frac{ke^2}{R} \\ E_{pe} &= -\frac{ke^2}{r} \\ &= -\frac{ke^2}{R} \\ E_{ee} &= \frac{ke^2}{2\rho} \\ &= \frac{ke^2}{2R} \frac{2}{\sqrt{3}} \\ &= \frac{ke^2}{R} \frac{\sqrt{3}}{3} \end{aligned}$$

since there is one pair of protons, one of electrons and 4 proton-electron pairs,

$$\begin{aligned} E_p &= E_{pp} + E_{ee} + 4E_{pe} \\ &= \frac{ke^2}{R} \left(\frac{\sqrt{3}}{3} - 3 \right) \end{aligned}$$

1.3 E_k/E_p

Let F_c be the centripetal force pulling the electron in. Then

$$\begin{aligned} F_c &= 2 \frac{ke^2}{R^2} \cos \frac{\pi}{6} - \frac{ke^2}{(2\rho)^2} \\ &= \frac{ke^2}{R^2} \left(\sqrt{3} - \frac{1}{3} \right) \end{aligned}$$

Also,

$$\begin{aligned} F_c &= \frac{m_e v^2}{\rho} \\ &= \frac{m_e v^2}{R} \frac{2\sqrt{3}}{3} \end{aligned}$$

So

$$\begin{aligned} \frac{m_e v^2}{R} \frac{2\sqrt{3}}{3} &= \frac{ke^2}{R^2} \left(\sqrt{3} - \frac{1}{3} \right) \\ m_e v^2 &= \frac{ke^2}{R} \left(\sqrt{3} - \frac{1}{3} \right) \frac{\sqrt{3}}{2} \\ &= \frac{ke^2}{R} \left(\frac{9 - \sqrt{3}}{6} \right) \end{aligned}$$

Since there are two electrons, $E_k = 2(\frac{1}{2}m_e v^2) = m_e v^2$

$$E_k = \frac{ke^2}{R} \left(\frac{9 - \sqrt{3}}{6} \right)$$

So

$$\begin{aligned} \frac{E_k}{E_p} &= \frac{\frac{ke^2}{R} \left(\frac{9 - \sqrt{3}}{6} \right)}{\frac{ke^2}{R} \left(\frac{\sqrt{3}}{3} - 3 \right)} \\ &= -\frac{1}{2} \end{aligned}$$

1.4 R_0

Now

$$m_e v^2 = \frac{ke^2}{R} \left(\frac{9 - \sqrt{3}}{6} \right)$$

and so

$$v = \sqrt{\frac{ke^2}{m_e R} \left(\frac{9 - \sqrt{3}}{6} \right)}$$

the momentum p is

$$\begin{aligned} p &= m_e v \\ &= \sqrt{\frac{m_e k e^2}{R} \left(\frac{9 - \sqrt{3}}{6} \right)} \end{aligned}$$

since the momentum of the electron about the center of the molecule is perpendicular to the radial vector to the electron, $L = \rho p = R p \frac{\sqrt{3}}{2}$ and

$$\begin{aligned} L &= \frac{\sqrt{3}}{2} R p \\ &= \frac{\sqrt{3}}{2} \sqrt{\frac{m_e k e^2}{R} \left(\frac{9 - \sqrt{3}}{6} \right)} \\ &= \sqrt{\frac{m_e R k e^2}{8} \left(\frac{9 - \sqrt{3}}{8} \right)} \\ &= n \hbar \end{aligned}$$

R will be minimized when n is the smallest, which occurs when $n = 1$

$$\begin{aligned} \sqrt{\frac{m_e R_0 k e^2}{8} \left(\frac{9 - \sqrt{3}}{8} \right)} &= \hbar \\ R_0 &= \frac{\hbar^2}{k m_e e^2} \left(\frac{8}{9 - \sqrt{3}} \right) \\ &= 5.82478 \times 10^{-11} \text{ m} \end{aligned}$$

1.5 E_b

The total energy of the molecule is

$$\begin{aligned} E &= E_k + E_p \\ &= \frac{k e^2}{R_0} \left(\frac{3}{2} - \frac{\sqrt{3}}{6} + \frac{\sqrt{3}}{3} - 3 \right) \\ &= -29.946 \text{ eV} \end{aligned}$$

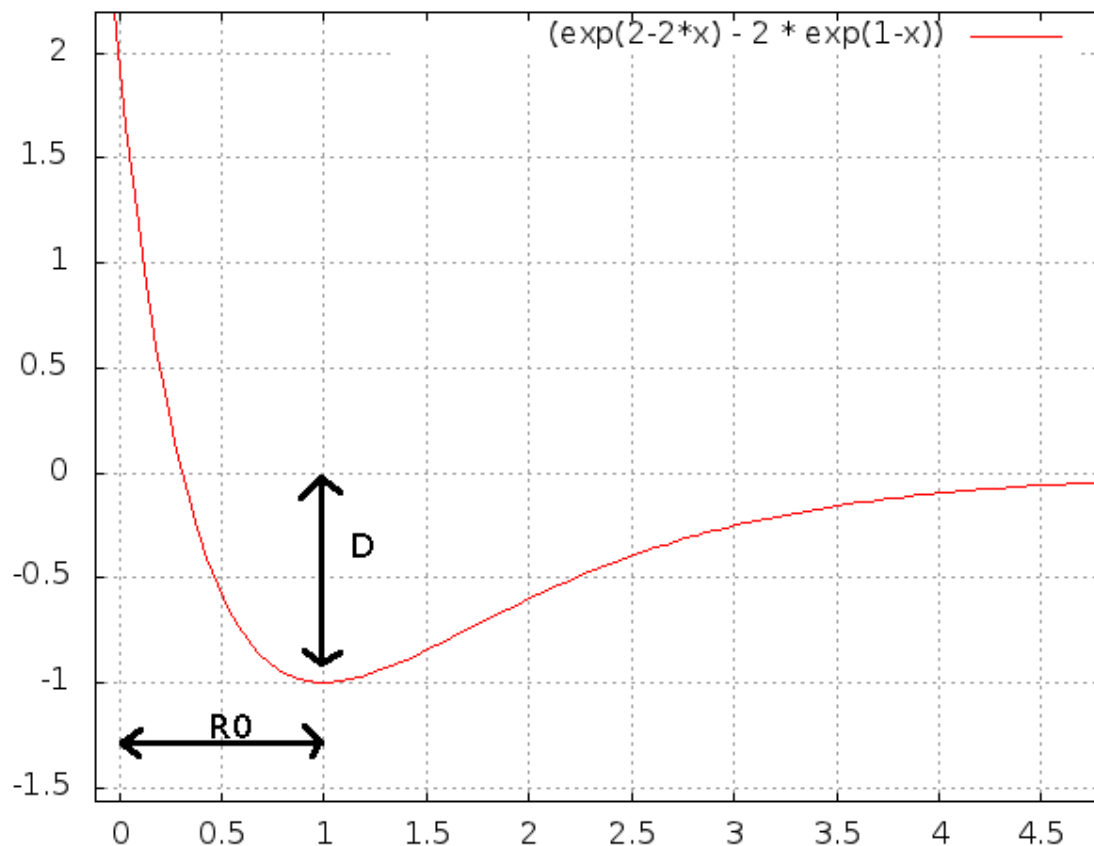
whereas the energy of the hydrogen atom is E_I . Hence the binding energy, which is the difference between the energy of a H_2 molecule and two H atoms, is

$$\begin{aligned} E_b &= -2E_I - E \\ &= 29.946 \text{ eV} - 2(13.606 \text{ eV}) \\ &= 2.73 \text{ eV} \end{aligned}$$

2 Vibrating H₂ molecule

2.1 Morse potential

We sketch the morse potential with $D = R_0 = \alpha = 1$.



Clearly the potential reaches a minimum at $R = R_0$ where it has the minimum value of D . We can see this more clearly by writing $E(R) = (1 - e^{1-x})^2 - 1$. There is a horizontal asymptote at $E = 0$. α seems to control the ‘width’ of the dip.

2.2 D and E_b

When $R = R_0, E = -D$

As $R \rightarrow \infty, E \rightarrow 0$

Hence the bonding energy $E_b = D$.

2.3 Linear frequency of vibration

Let $F(R)$ be the force exerted on the electron. Then

$$\begin{aligned} F(R) &= -\frac{dE}{dR} \\ &= \frac{2\alpha D}{R_0} \left(e^{2\alpha(1-R/R_0)} - e^{\alpha(1-R/R_0)} \right) \end{aligned}$$

as expected, $F(R_0) = 0$, so R_0 is an equilibrium position and the system will oscillate around it. Let r be a small increase in R ; then

$$F(R_0 + r) = \left. \frac{dF}{dR} \right|_{R_0} r$$

so

$$\begin{aligned}\left.\frac{dF}{dR}\right|_{R_0} &= -\frac{2\alpha^2 D}{R_0^2} \left(2e^{2\alpha(1-R/R_0)} - e^{\alpha(1-R/R_0)} \right) \Big|_{R_0} \\ &= -\frac{2\alpha^2 D}{R_0^2}\end{aligned}$$

Let the acceleration be \ddot{r}

$$\ddot{r} = \frac{F}{m_p} = -\frac{2\alpha^2 D}{m_p R_0^2} r$$

Let ω be the angular frequency; then

$$\begin{aligned}\omega &= \sqrt{\frac{2\alpha^2 D}{m_p R_0^2}} \\ &= \frac{\alpha}{R_0} \sqrt{\frac{2E_b}{m_p}}\end{aligned}$$

$$\begin{aligned}v_{vib} &= \frac{\omega}{2\pi} \\ &= \frac{\alpha}{2\pi R_0} \sqrt{\frac{2E_b}{m_p}}\end{aligned}$$

2.4 α constant

The energy of a photon is hc/λ ; hence the photon lost in the Raman process is

$$\frac{hc}{\lambda_i} - \frac{hc}{\lambda_s} = hv_{vib}$$

so

$$\begin{aligned}v_{vib} &= c \left(\frac{1}{514 \text{ nm}} - \frac{1}{664 \text{ nm}} \right) \\ &= 1.32 \times 10^{14} \text{ s}^{-1}\end{aligned}$$

and the energy lost was 0.54 eV.

$$\begin{aligned}\alpha &= 2\pi R_0 v_{vib} \sqrt{\frac{m_p}{2E_b}} \\ &= 2.11\end{aligned}$$

2.5 Minimum amplitude

We approximate E by a taylor series

$$E(R_0 + r) = E(R_0) + \frac{1}{2} \left. \frac{d^2 E}{dR^2} \right|_{R_0} r^2 + O(r^3)$$

and

$$\begin{aligned}\frac{1}{2} \frac{d^2 E}{dR^2} \Big|_{R_0} &= \frac{\alpha^2 D}{R_0^2} \\ &= 3.58 \times 10^{21} \text{ eV m}^{-2}\end{aligned}$$

We know that $E(R_0 + A_{min}) = 0.54 \text{ eV}$; hence

$$\begin{aligned}A_{min} &= \sqrt{\frac{0.54 \text{ eV}}{3.58 \times 10^{21} \text{ eV m}^{-2}}} \\ &= 1.23 \times 10^{-11} \text{ m}\end{aligned}$$