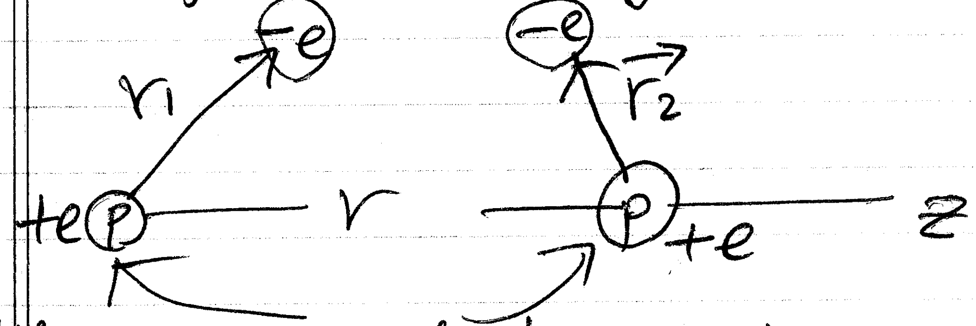
Van der Waal's Interaction

We compute the long-range interaction betwee
two hygrogen atoms in their ground states.
We shall find that they attract each other!



We assume that two protons are fixed
with the separation r along the z axis.

$\vec{r}_1$: the position vector of the electron
of the first Hydrogen.

$\vec{r}_2$: the position vector of the electro
of the second Hydrogen.

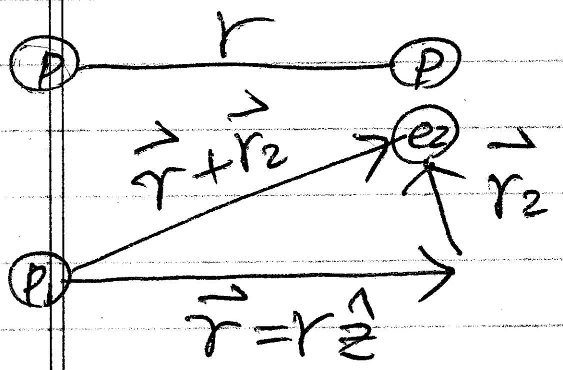
$$H_0 = \left(\frac{p_1^2}{2m} - k_1 \frac{e^2}{r_1}\right) + \left(\frac{p_2^2}{2m} - k_1 \frac{e^2}{r_2}\right)$$

$$k_1 = \frac{1}{4\pi\varepsilon_0} \text{(MKSA)}, \quad \frac{1}{4\pi} \text{(HL)}, \quad 1 \text{(G)}$$

~~We assume that~~

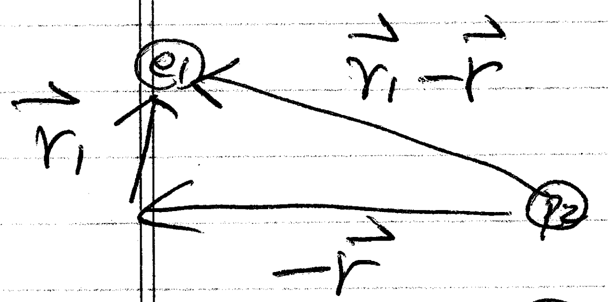
~~$r \gg r_1$ and r_2 No~~

V = Coulomb interactions
$(e_1 - e_2)$, $(p_1 - p_2)$, $(p_1 \leftrightarrow e_2)$, $(p_2 \leftrightarrow e_1)$
e_i and p_i are the electrons & proton in Hydrogen for $i=1,2$

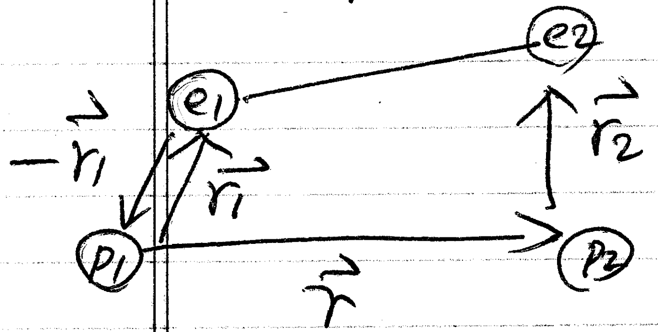


$$V_{p_1p_2} = k_1 \frac{(+e)^2}{r} = k_1 \frac{e^2}{r}$$

$$V_{p_1e_2} = k_1 \frac{(+e)(-e)}{|\vec{r}+\vec{r}_2|} = k_1 \frac{(-e}{|\vec{r}+\vec{r}}$$



$$V_{e_1p_2} = k_1 \frac{(+e)(-e)}{|\vec{r}-\vec{r}_1|} = k_1 \frac{(-e}{|\vec{r}-\vec{r}}$$



$$V_{e_1e_2} = k_1 \frac{(-e)(-e)}{|\vec{r}+\vec{r}_2-\vec{r}_1|}$$

$$\therefore V = k_1 \left[\frac{e^2}{r} + \frac{(-e^2)}{|\vec{r}_0-\vec{r}_1|} + \frac{(-e^2)}{|\vec{r}+\vec{r}_2|} + \frac{e^2}{|\vec{r}+\vec{r}_2-\vec{r}_1|} \right.$$

If we assume that $r \gg r_1, r_2$, then we can make a series expansion in powers of r_0/r.

$$\frac{1}{|\vec{r}-\vec{a}|} = \frac{1}{\sqrt{(\vec{r}-\vec{a})^2}} = \frac{1}{\sqrt{r^2-2\vec{r}\cdot\vec{a}+a^2}}$$

$$= \frac{(1/r)}{\sqrt{1-2\cos\theta\left(\frac{a}{r}\right)+\left(\frac{a}{r}\right)^2}},$$

where $\cos\theta = \hat{r}\cdot\hat{a} = \hat{z}\cdot\hat{a}$.

$$\frac{r}{|\vec{r}-\vec{a}|} = \left[1-2\cos\theta\,\frac{a}{r}+\left(\frac{a}{r}\right)^2\right]^{-\frac{1}{2}}$$

$$= 1+\cos\theta\,\frac{a}{r}-\frac{1}{2}\left(\frac{a}{r}\right)^2$$

$$+\frac{\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)}{2}\left(-2\cos\theta\,\frac{a}{r}\right)^2+O\left(\frac{a}{r}\right)^3$$

$$= 1+\cos\theta\,\frac{a}{r}-\frac{1}{2}\left(\frac{a}{r}\right)^2$$

$$+\frac{3}{2}(\cos^2\theta)\left(\frac{a}{r}\right)^2+O\left(\frac{a}{r}\right)^3$$

$$= 1+\cos\theta\left(\frac{a}{r}\right)+\frac{1}{2}(3\cos^2\theta-1)\left(\frac{a}{r}\right)^2+O\left(\frac{a}{r}\right)^3$$

Or,

$$\frac{1}{|\vec{r}-\vec{a}|} = \frac{1}{r}+\frac{a}{r^2}(\hat{z}\cdot\hat{a})+\frac{1}{2}\left[3(\hat{z}\cdot\hat{a})^2-1\right]\frac{a^2}{r^3}+\frac{1}{r}O\left(\frac{a}{r}\right)^2$$

$$\frac{1}{\left|\hat{z}+\hat{n}_2\frac{r_2}{r}\right|}=1+(\hat{z}\cdot\hat{n}_2)\left(\frac{r_2}{r}\right)+\frac{1}{2}\left[3(\hat{z}\cdot\hat{n}_2)^2-1\right]\left(\frac{r_2}{r}\right)^2+\cdots$$

$$\frac{1}{\left|\hat{z}-\hat{n}_1\frac{n}{r}\right|}=1-(\hat{z}\cdot\hat{n}_1)\left(\frac{r_1}{r}\right)+\frac{1}{2}\left[3(\hat{z}\cdot\hat{n}_1)^2-1\right]\left(\frac{r_1}{r}\right)^2+\cdots$$

$$\frac{1}{\left|\hat{z}+\hat{n}\frac{D}{r}\right|}=1+\hat{z}\cdot\hat{n}\,\frac{D}{r}+\frac{1}{2}\left[3(\hat{z}\cdot\hat{n})^2-1\right]\left(\frac{D}{r}\right)^2+\cdots$$

NOT convenient

$$\hat{n}=\frac{(\vec{r}_2-\vec{r}_1)}{|\vec{r}_2-\vec{r}_1|},\quad D=|\vec{r}_2-\vec{r}_1|$$

$$\hat{z}\cdot\hat{n}\frac{D}{r}=\frac{\hat{z}\cdot(\vec{r}_2-\vec{r}_1)}{r}$$

The following representation is more convenient:

② $$\frac{1}{|\hat{z}+(\vec{r}_2/r)|}=1+\frac{\hat{z}\cdot\vec{r}_2}{r}+\frac{1}{2}\left(\frac{3(\hat{z}\cdot\vec{r}_2)^2-r_2^2}{r^2}\right)+\cdots$$

③ $$\frac{1}{|\hat{z}-\vec{r}_1/r|}=1-\frac{\hat{z}\cdot\vec{r}_1}{r}+\frac{1}{2}\left[\frac{3(\hat{z}\cdot\vec{r}_1)^2-r_1^2}{r^2}\right]+\cdots$$

④ $$\frac{1}{\left|\hat{z}+\frac{\vec{r}_2-\vec{r}_1}{r}\right|}=1+\frac{\hat{z}\cdot(\vec{r}_2-\vec{r}_1)}{r}+\frac{1}{2}\left(\frac{3[\hat{z}\cdot(\vec{r}_2-\vec{r}_1)]^2-|\vec{r}_2-\vec{r}_1|^2}{r^2}\right)+\cdots$$

$$V=\frac{1}{r}\left[1-②-③+④\right]$$

$\longrightarrow$ order $\left(\frac{r_i}{r}\right)^0$ and $\left(\frac{r_i}{r}\right)^1$ cancel exactly.

$$V = \frac{k_1 e^2}{2r^3}\Big[3\big[\hat{z}\cdot(\vec{r}_2-\vec{r}_1)\big]^2 - |\vec{r}_2-\vec{r}_1|^2 - 3(\hat{z}\cdot\vec{r}_2)^2 + r_2^2 - 3(\hat{z}\cdot\vec{r}_1)^2 + r_1^2\Big] + \frac{1}{r}O\left(\frac{r_i}{r}\right)^3.$$

$$\big[\hat{z}\cdot(\vec{r}_2-\vec{r}_1)\big]^2 = (\hat{z}\cdot\vec{r}_2)^2 - 2(\hat{z}\cdot\vec{r}_1)(\hat{z}\cdot\vec{r}_2) + (\hat{z}\cdot\vec{r}_1)^2$$

$$|\vec{r}_2-\vec{r}_1|^2 = r_1^2 - 2\vec{r}_1\cdot\vec{r}_2 + r_2^2$$

Therefore

$$= \frac{k_1 e^2}{2r^3}\Big[3\big[\cancel{(\hat{z}\cdot\vec{r}_2)^2} - 2(\hat{z}\cdot\vec{r}_1)(\hat{z}\cdot\vec{r}_2) + \cancel{(\hat{z}\cdot\vec{r}_1)^2}\big] - \cancel{r_1^2} + 2\vec{r}_1\cdot\vec{r}_2 - \cancel{r_2^2} \cancel{-3(\hat{z}\cdot\vec{r}_2)^2} + \cancel{r_2^2} \cancel{-3(\hat{z}\cdot\vec{r}_1)^2} + \cancel{r_1^2}\Big]$$

$$= \frac{k_1 e^2}{2r^3}\times 2\big[\vec{r}_1\cdot\vec{r}_2 - 3(\hat{z}\cdot\vec{r}_1)(\hat{z}\cdot\vec{r}_2)\big]$$

$$= k_1 e^2\left[\frac{\vec{r}_1\cdot\vec{r}_2 - 3(\hat{z}\cdot\vec{r}_1)(\hat{z}\cdot\vec{r}_2)}{r^3}\right]$$

$$\vec{r}_1 = (x_1, y_1, z_1)$$
$$\vec{r}_2 = (x_2, y_2, z_2)$$
$$\Rightarrow \vec{r}_1\cdot\vec{r}_2 = x_1x_2 + y_1y_2 + z_1z_2, \quad (\hat{z}\cdot\vec{r}_1)(\hat{z}\cdot\vec{r}_2) = z_1z_2$$

$$= \frac{k_1 e^2}{r^3}\big[x_1x_2 + y_1y_2 + z_1z_2 - 3z_1z_2\big]$$

$$= \frac{k_1 e^2}{r^3}\big[x_1x_2 + y_1y_2 - 2z_1z_2\big]$$

We have found that the perturbative potential of two-hydrogent atom system is

$$V = \frac{k_1 e^2}{r^3}\left[x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right] + \frac{1}{r} O\left(\frac{r_i}{r}\right)^3.$$

This is proportional to the electric quadrupole moment of the system.

The wavefunction $U_0^{(0)}$ of the ground state is the product of the ground-state hydrogen atom wavefunction.

$$U_0^{(0)} = \underset{nlm}{U_{100}^{(0)}}(\vec{r}_1)\ \underset{nlm}{U_{100}^{(0)}}(\vec{r}_2)$$

$$\begin{aligned}\Delta^{(1)} &= \langle U_0^{(0)} | V | U_0^{(0)} \rangle \\ &= \frac{k_1 e^2}{r^3}\Big[\langle 100|x_1|100\rangle\langle 100|x_2|100\rangle \\ &\quad + \langle '' | y_1 | '' \rangle\langle '' | y_2 | '' \rangle \\ &\quad - 2\langle '' | z_1 | '' \rangle\langle '' | z_2 | '' \rangle\Big].\end{aligned}$$

Because of parity, parity even.

$$\langle 100 | x_1 | 100 \rangle = 0.$$

parity odd

Therefore, the first-order energy shift vanishes

The scond-order energy shift is

$$\Delta^{(2)}_{100} = \sum_{|k^{(0)}\rangle \neq |100\rangle} \frac{|V_{k100}|^2}{E_0^{(0)} - E_k^{(0)}}$$

$$E^{(0)}_{100} =$$

$$\Delta^{(2)} = \frac{e^4}{r^6} \sum_{k \neq 0} \frac{|\langle k^{(0)}|(x_1x_2 + y_1y_2 - 2z_1z_2)|0^{(0)}\rangle|^2}{E_0^{(0)} - E_k^{(0)}}$$

$$E_0^{(0)} = -\frac{1}{2}mc^2 \frac{(Z\alpha)^2}{1} \times 2$$

$$E_k^{(0)} = -\frac{1}{2}mc^2 \frac{(Z\alpha)^2}{a^2} - \frac{1}{2}mc^2 \frac{(Z\alpha)^2}{b^2}$$

where $(a \geq 1$ and $b > 1)$ or $(a > 1$ and $b \geq 1)$.

Therefore, $\frac{1}{a^2} + \frac{1}{b^2} < 2$

and $E_k^{(0)} > E_0^{(0)}$.

From this, we find that

$$\Delta^{(2)} = -\frac{e^4}{r^6} \times \# \ (\leftarrow \text{positive}) < 0. \Rightarrow \text{generates an attractive force}$$

This long-range attractive force is called Van der Waals' force.

$$\Delta^{(2)} = \frac{e^4}{r^6}\sum_{k\neq 0} \frac{|\langle k^{(0)}|(x_1x_2+y_1y_2-2z_1z_2)|0^{(0)}\rangle|^2}{E_0^{(0)}-E_k^{(0)}} \qquad \left(E_0^{(0)}-E_k^{(0)}\right) < 0$$

Suppose $|k^{(0)}\rangle$ is $U_{nlm}(\vec{r}_1)U_{n'l'm'}(\vec{r}_2)$

with $n, n' \geq 2$.

$$\langle \underbrace{U^{(0)}_{nlm}}|\overset{\uparrow}{x_1}|U^{(0)}_{100}\rangle\langle U^{(0)}_{n'l'm'}|x_2|U_{100}\rangle \qquad 0^{(0)}$$

parity odd

we need a parity-odd state to have $\langle U^{(0)}_{nlm}|x_1|U^{(0)}_{100}\rangle \neq 0$.

5.4 Variational Methods

Until now, we have considered the case whose unperturbed Schrödinger equation

$$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$$

is exactly sovable.

The variation method is a method to estimate the ground state energy E_0 of a system whose solution is NOT available.

$|\tilde{0}\rangle$ is a trial ket ~~of~~ the ground state. This is not the true ground state ket but a one that has been "guessed".

$\overline{H}$ is defined by

$$\overline{H} \equiv \frac{\langle\tilde{0}|H|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle}$$

Theorem) $\overline{H} \geq E_0$: $\overline{H}$ is an upper bound of E_0

proof) If $|\tilde{0}\rangle$ is a stateket of the system, then it must be expanded as

$$|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle,$$

where $H|k\rangle = E_k|k\rangle$.

$|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle$ can be used to compute

$$\bar{H} = \frac{\langle\tilde{0}|H|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle}$$

$$\begin{aligned}
\langle\tilde{0}|H|\tilde{0}\rangle &= \sum_{k=0}^{\infty}\sum_{l=0}^{\infty} \langle\tilde{0}|l\rangle\langle l|\overset{H}{|}k\rangle\langle k|\tilde{0}\rangle \\
&= \sum_{k,l} \langle\tilde{0}|l\rangle E_k \delta_{lk} \langle k|\tilde{0}\rangle \\
&= \sum_{k=0}^{\infty} |\langle\tilde{0}|k\rangle|^2 E_k
\end{aligned}$$

$$\langle\tilde{0}|\tilde{0}\rangle = \sum_{k=0}^{\infty} |\langle\tilde{0}|k\rangle|^2$$

$$\therefore \bar{H} = \frac{\langle\tilde{0}|H|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle} = \frac{\sum_{k=0}^{\infty} E_k |\langle\tilde{0}|k\rangle|^2}{\sum_{k=0}^{\infty} |\langle\tilde{0}|k\rangle|^2}.$$

$$E_k = (E_k - E_0) + E_0$$

$$= \frac{\sum_{k=0}^{\infty} |\langle\tilde{0}|k\rangle|^2 (E_k - E_0)}{\sum_{k=0}^{\infty} |\langle\tilde{0}|k\rangle|^2} + E_0$$

$$\bar{H} - E_0 = \frac{\sum_{k=0}^{\infty} |\langle\tilde{0}|k\rangle|^2 (E_k - E_0)}{\sum_{k=0}^{\infty} |\langle\tilde{0}|k\rangle|^2}$$

we know that $|\langle\tilde{0}|k\rangle|^2 > 0$ for all k and $(E_k - E) > 0$ for all k.

$$\therefore \bar{H} - E_0 > 0 \Rightarrow \bar{H} > E_0$$

We know that the ground-state wavefunction of the Hydrogen atom is

$$\langle \vec{x} | 100 \rangle = R_{10}(r) Y_{00}(\theta, \phi),$$

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

We assume that we have guessed a trial wavefunction

$$\langle \vec{x} | \tilde{0} \rangle = \psi_{100} = C e^{-r/a}.$$

We can compute $\overline{H}$ as a function of a and find the value of a that minimizes $\overline{H}$.

$$\overline{H} = \frac{\langle \tilde{0} | H | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}$$

① $$\langle \tilde{0} | \tilde{0} \rangle = C^2 \int_0^\infty dr\, r^2 e^{-\frac{2r}{a}} \int d\Omega \qquad t \equiv \frac{2r}{a}$$

$$= \frac{C^2}{8} \times 4\pi \int_0^\infty dt\, t^2 e^{-t}$$

$$= \frac{C^2}{8} \times 4\pi \times 2!$$

$$= C^2 \pi \quad \rightarrow \quad C = \frac{1}{\sqrt{\pi}}$$

$$\langle \vec{x} | \tilde{0} \rangle = \frac{1}{\sqrt{\pi}} e^{-\frac{r}{a}}.$$

② $\langle \tilde{0} | H | \tilde{0} \rangle =$

Note that $H = \frac{\hbar^2}{2m}\left[\frac{\vec{L}^2}{r^2\hbar^2} - \frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r}\right] - \frac{Ze^2}{r}k_1$

Because $\vec{L}^2$ is composed of the angle derivatives $\frac{\partial}{\partial\theta}$ and $\frac{\partial}{\partial\phi}$, the contribution of $\vec{L}^2$ must vanish!

$$\therefore \quad H = \frac{\hbar^2}{2m}\left[-\frac{\partial^2}{\partial r^2} - \frac{2}{r}\frac{\partial}{\partial r}\right] - \frac{Ze^2}{r}k_1$$

$$-\frac{\partial^2}{\partial r^2}e^{-\frac{r}{a}} = \frac{1}{a^2}e^{-\frac{r}{a}}$$

$$-\frac{2}{r}e^{-\frac{r}{a}} = +\frac{2}{ar}e^{-\frac{r}{a}}$$

$$\therefore \quad \langle \vec{x} | H | \tilde{0} \rangle = \left[\frac{\hbar^2}{2m}\left(\frac{1}{a^2} + \frac{2}{ar}\right) - \frac{Ze^2}{r}k_1\right] e^{-\frac{r}{a}} \frac{1}{\sqrt{\pi}}$$

$$\therefore \langle \tilde{0} | H | \tilde{0} \rangle = \frac{1}{\pi}\int_0^\infty \left[\frac{\hbar^2}{2m}\left(\frac{1}{a^2} + \frac{2}{ar}\right) - \frac{Ze^2}{r}k_1\right] r^2 e^{-\frac{2r}{a}} d$$

$$\times \int d\Omega$$

$$= 4\int_0^\infty \left[\frac{\hbar^2}{2m}\left(\frac{r^2}{a^2} + \frac{2r}{a}\right) - Ze^2k_1 r\right] e^{-\frac{2r}{a}}$$

$t = \frac{2r}{a}$

$$= \frac{a}{2} \times 4 \int_0^\infty \left[\frac{\hbar^2}{2m}\left(\frac{t^2}{4} + t\right) - \frac{Ze^2k_1 t}{2}\right] e^{-t} dt$$

Show that $a = a_0$ is the answer that $\frac{\text{minimiz}}{H}$!

2011.

Graduate QM2

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