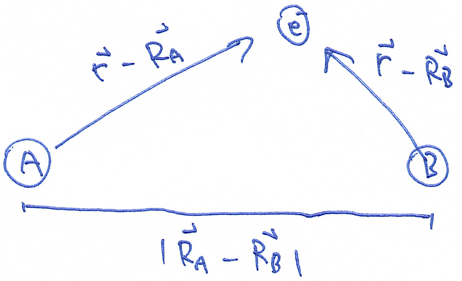
SQ 28

In a H_2^+ atom, the electron is influenced by 2 nuclei. So the ground state of the electron can be written as a linear combination of the 1s state at nucleus A, and the 1s state at nucleus B.

$$\boxed{\psi_+(\vec{r}) = C_A \psi_{1s,A} + C_B \psi_{1s,B}}$$



Note: $\psi_+(\vec{r})$, $\psi_{1s,A}(\vec{r})$, $\psi_{1s,B}(\vec{r})$ are functions in $\vec{r}$, the position vector of the electron with respect to an arbitrary reference point.

a. By symmetry argument,

$$|C_A|^2 = |C_B|^2 \quad \Rightarrow \quad C_A = \pm C_B$$

In this part, take $C_A = +C_B = \underline{C_+}$ —— that's why it is "+"

$$\therefore \psi_+(\vec{r}) = C_+(\psi_{1s,A} + \psi_{1s,B})$$

To normalise:

$$\int |\psi_+(\vec{r})|^2 \, d^3r = 1$$

Expanding $\psi_+(\vec{r})$,

$$|C_+|^2 \int d^3r \left[|\psi_A|^2 + |\psi_B|^2 + \psi_A^* \psi_B + \psi_B^* \psi_A \right] = 1$$

a. (cont.)

For $\psi_A(\vec{r})$ and $\psi_B(\vec{r})$, they should have the form of 1s state of hydrogen atom, with respect to the position of nucleus $\vec{R_A}$ and $\vec{R_B}$.

ie,

$$\psi_A(\vec{r}) = \psi_{1s}(\vec{r} - \vec{R_A}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{|\vec{r} - \vec{R_A}|}{a_0}}$$

$$\psi_B(\vec{r}) = \psi_{1s}(\vec{r} - \vec{R_B}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{|\vec{r} - \vec{R_B}|}{a_0}}$$

Note: $\psi_A(\vec{r})$ and $\psi_B(\vec{r})$ are in general not orthonormal!

Using the definition of ψ_A and ψ_B above, we got:

$$\int d^3r \, |\psi_A|^2 = \int d^3r \, |\psi_B|^2 = 1$$

Define $\int \psi_A^* \psi_B \, d^3r = \int \psi_B^* \psi_A \, d^3r = S(R)$,

The normalization equation becomes:

$$|C_+|^2 \, (1 + 1 + 2S(R)) = 1$$

Take C_+ to be real and positive,

$$C_+ = \frac{1}{\sqrt{2(1+S)}},$$

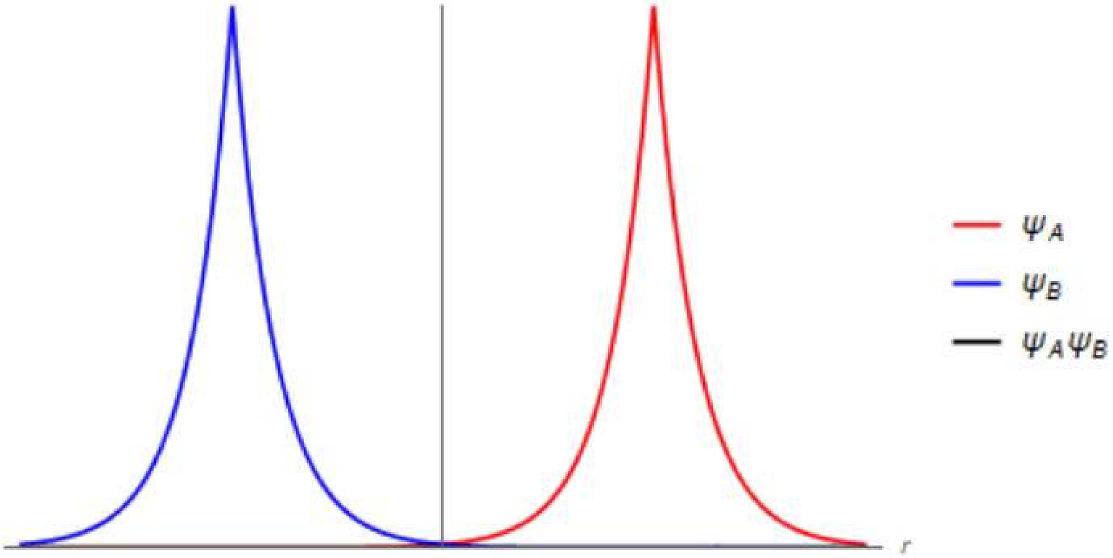
b)

The ground state wavefunction has the form of an exponential decay

$$\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

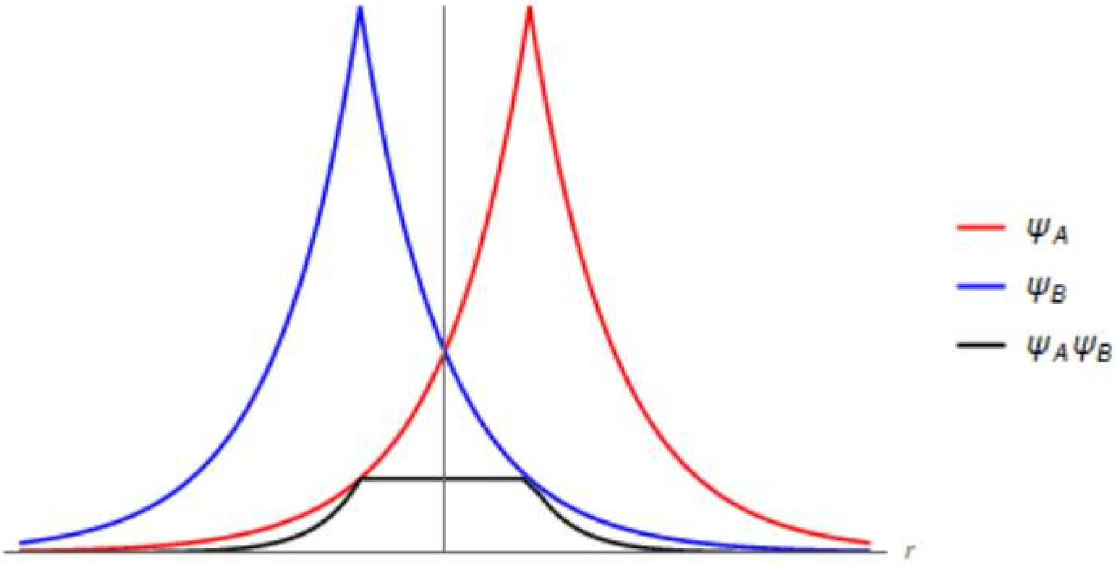
Therefore, $\psi(r)$ will be very small when r is large with respect to the constant a_0.

If the separation R between the two nuclei are large compared to the Bohr radius, ie, $R \gg a_0$, the overlapping between two wavefunctions $\psi_A(r)$ and $\psi_A(r)$ are negligible.



Therefore, $S(R) \to 0$.

If R is small, the overlapping region would be significant. Thus, $S(R) = \int d\boldsymbol{r}\, \psi_A{}^*(r)\psi_B(r)$ would be non-zero.

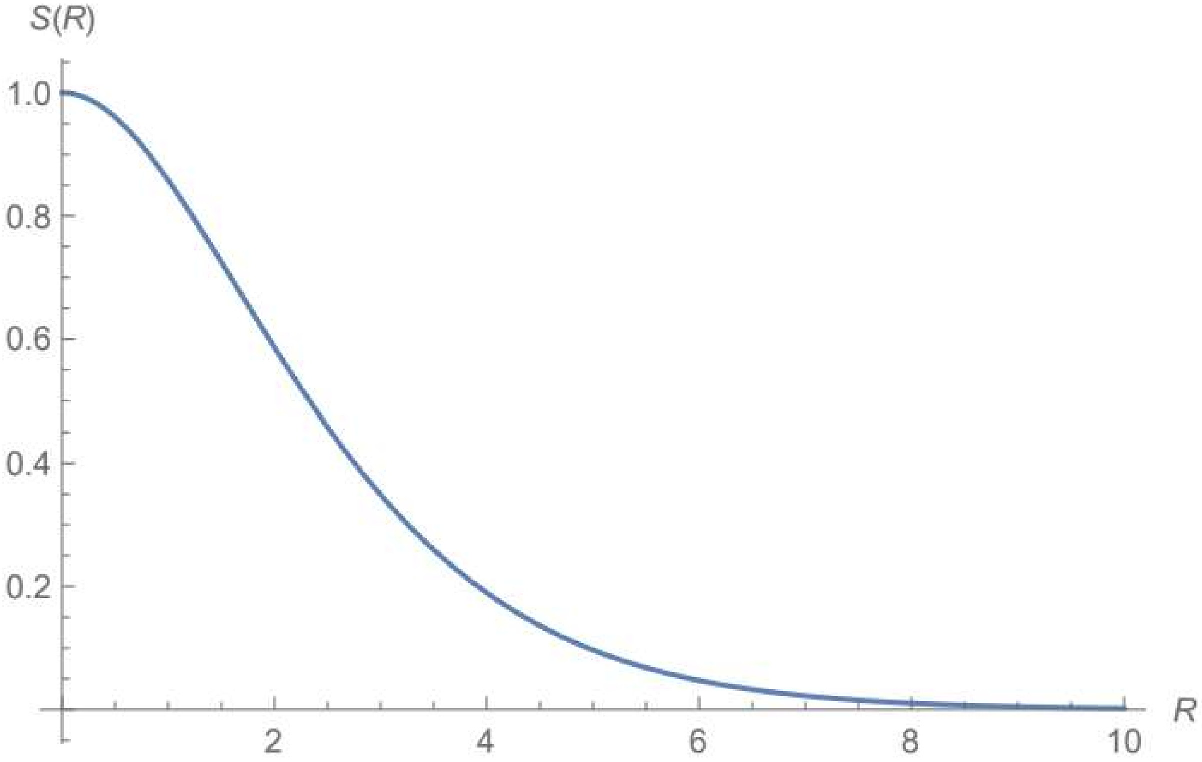

ψ_A
ψ_B
$\psi_A\psi_B$
r

c)

It can be shown that

$$S(R) = e^{-R}(1 + R + \frac{R^2}{3})$$

in atomic unit (unit of length is a_0).



You can see that $S(R)$ is decreasing with R.

At $R = 2$, which is close the the equilibrium separation of H_2^+

$$S(R = 2) = 0.586$$

d. Back to the symmetry argument in part a),

$$|C_A|^2 = |C_B|^2 ,$$

This time we take $\underline{C_A = -C_B = C_-}$ → "−" sign for this time

$$\therefore \quad \psi_-(\vec{r}) = C_-(\psi_A(\vec{r}) - \psi_B(\vec{r}))$$

The normalization condition is :

$$\int |\psi_-(\vec{r})|^2 d^3r = 1$$

$$\Rightarrow \quad |C_-|^2 \int d^3r \left[|\psi_A|^2 + |\psi_B|^2 - \psi_A^* \psi_B - \psi_B^* \psi_A \right] = 1$$

Similar to the discussion in part a),

$$|C_-|^2 (1 + 1 - 2S(R)) = 1$$

we have : $C_- = \frac{1}{\sqrt{2(1-S(R))}}$ //

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e. <u>Optional for exam purposes</u> : To evaluate $S(R)$.

$$S(R) = \int d^3r \; \psi_A^*(\vec{r}) \, \psi_B(\vec{r})$$

Step 1 : Shift the reference point to one of the nucleus position, say, nucleus A.

$$\therefore \quad \vec{R_A} = 0 , \qquad \vec{R_B} = \vec{R}$$

We use atomic unit, from now on

The wavefunctions can be written as :

$$\psi_A(\vec{r}) = \psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}} e^{-r}$$

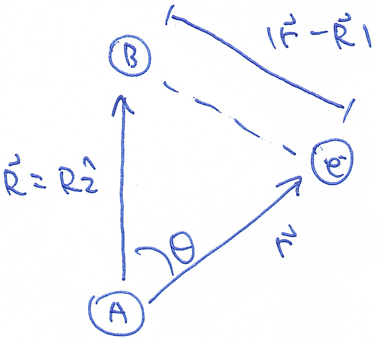
$$\psi_B(\vec{r}) = \psi_{1s}(\vec{r} - \vec{R}) = \frac{1}{\sqrt{\pi}} e^{-|\vec{r} - \vec{R}|}$$

e. (cont.)

Here, $\vec{R}$ is a constant vector, ie, nothing to deal with the integration.

We can set $\vec{R}$ to point along the $\hat{z}$-direction,

ie, $\vec{R} = R\hat{z}$.



Define the angle between $\vec{R}$ and $\vec{r}$ be θ,

By cosine law,

$$|\vec{r}-\vec{R}| = \sqrt{r^2+R^2-2rR\cos\theta}$$

$$\therefore \quad S(R) = \int d^3r \left[\frac{1}{\pi} e^{-r} e^{-|\vec{r}-\vec{R}|}\right]$$

Apply the cosine law above, and write the integral in spherical coordinates:

$$S(R) = \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr\, r^2 \left[\frac{1}{\pi} e^{-r} e^{-\sqrt{r^2+R^2-2rR\cos\theta}}\right]$$

Step 2: Evaluate the θ-integral,

Here, r and R are both constants,

$$\therefore \quad \int_0^{\pi} d\theta \sin\theta\, e^{-\sqrt{r^2+R^2-2rR\cos\theta}} = \frac{1}{2rR}\int_0^{\pi} d(r^2+R^2-2rR\cos\theta)\, e^{-\sqrt{r^2+R^2-2rR\cos\theta}}$$

put $u = \sqrt{r^2+R^2-2rR\cos\theta}$.

when $\theta = 0$, $u = |r-R|$

$\theta = \pi$, $u = r+R$

$$\therefore \quad d(r^2+R^2-2rR\cos\theta) = du^2 = 2u\,du.$$

e. (cont.)

The θ-integral becomes:

$$\frac{1}{2rR}\int_{|r-R|}^{r+R} u\,du \quad e^{-u}$$

By integration by parts,

$$= -\frac{1}{rR}\left[(1+r+R)\,e^{-(r+R)} - (1+|r-R|)\,e^{-|r-R|}\right]$$

Step 3: Evaluate the r-integral,

subst. the result of θ-integral to $S(R)$:

$$S(R) = 2\pi\int_0^\infty dr\, r^2\,\frac{1}{\pi}\,e^{-r} \quad [\,\theta\text{-integral}\,]$$

$$= 2\int_0^\infty r^2\,dr\,e^{-r}\left(-\frac{1}{rR}\right)\left[(1+r+R)\,e^{-(r+R)} - (1+|r-R|)\,e^{-|r-R|}\right]$$

$$= -\frac{2}{R}\int_0^\infty\Big[\underbrace{(r+r^2+rR)\,e^{-(2r+R)}}_{\textcircled{I}} - \underbrace{r\,(1+|r-R|)\;e^{-r-|r-R|}}_{\textcircled{II}}\Big]dr$$

$\therefore$ $S(R)$ is composed of 2 separated term, $\textcircled{I}$ and $\textcircled{II}$,

Evaluate $\textcircled{I}$:

$$\int_0^\infty (r+r^2+rR)\,e^{-(2r+R)}\,dr$$

$$= e^{-R}\left[\int_0^\infty (1+R)\,r\,e^{-2r}\,dr + \int_0^\infty r^2\,e^{-2r}\,dr\right]$$

$$= e^{-R}\left[(1+R)\,\frac{1}{2^2} + \frac{2!}{2^3}\right] \longrightarrow$$

Using Gamma integrals:

$$\int_0^\infty x^n e^{-\beta x}\,dx = n!\,\beta^{-(n+1)}$$

$$= \frac{1}{4}\,(2+R)\,e^{-R}.$$

7. (cont.)

Evaluate $\textcircled{\small II}$, separate the integration to $0<r<R$ and $R<r$,

$$\int_0^\infty r(1+|r-R|)\, e^{-|r-R|-r}\, dr$$

$$= \underbrace{\int_0^R r(1+(R-r))\, e^{-R}\, dr}_{\text{simple integration}} + \underbrace{\int_R^\infty r(1+r-R)\, e^{-2r} e^{R}\, dr}_{\text{put } y = r-R}$$

$$= e^{-R}\left(\tfrac{1}{2}R^2 + \tfrac{1}{2}R^3 - \tfrac{1}{3}R^3\right) + \int_0^\infty (y+R)(1+y)\, e^{-2(y+R)}\, e^{R}\, dy$$

$$= e^{-R}\left(\tfrac{1}{2}R^2 + \tfrac{1}{6}R^3\right) + \underbrace{e^{-R}\int_0^\infty (y^2 + (1+R)y + R)\, e^{-2y}\, dy}_{\text{Again, by Gamma integrals}}$$

$$= e^{-R}\left(\tfrac{1}{2}R^2 + \tfrac{1}{6}R^3\right) + e^{-R}\left(\tfrac{1}{2^3}2! + \tfrac{R+1}{2^2} + \tfrac{R}{2}\right)$$

$$= e^{-R}\left(\tfrac{1}{2} + \tfrac{3}{4}R + \tfrac{1}{2}R^2 + \tfrac{1}{6}R^3\right)$$

Combind $\textcircled{\small I}$ and $\textcircled{\small II}$, we have

$$S(R) = -\frac{2}{R}\left[\textcircled{\small I} - \textcircled{\small II}\right]$$

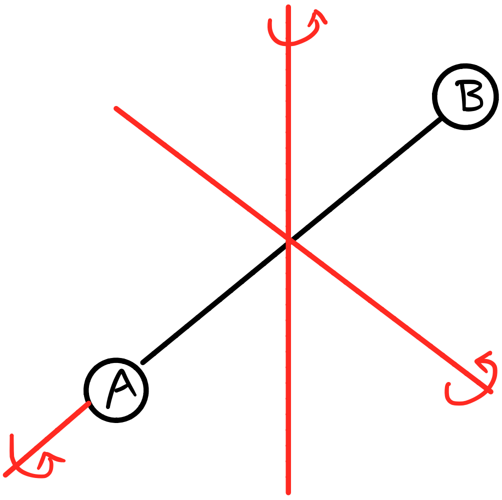
$$= -\frac{2}{R}\left[\tfrac{1}{4}(2+R)e^{-R} - \left(\tfrac{1}{2} + \tfrac{3}{4}R + \tfrac{1}{2}R^2 + \tfrac{1}{6}R^3\right)e^{-R}\right]$$

$$= e^{-R}\left(1 + R + \frac{R^2}{3}\right) \,_{\prime\prime}$$

SQ29

(a) In 3-dimensional space, the degrees of freedom of a molecule consisting of N atoms is 3N. Among the 3N degrees of freedom, there are 3 degrees of freedom for the translational motion of the molecule's center-of-mass and 2 degrees of freedom for the rotational motion of the molecule along 2 axes.

You might ask why there are 2 but not 3 degrees of freedom for rotational motion. It is because, for a linear molecule, rotation along its own axis leaves the molecule unchanged and it is not a rotation.



Rotation along this axis leaves the molecule unchanged

Therefore, the remaining degrees of freedom comes from the vibrational motion of the molecule and we have 3N-3-2 = 3N-5 vibration normal modes.

SQ29

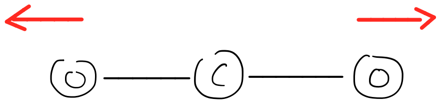
(b) $\bar{\nu} = \frac{1}{\lambda} = 380 \text{ cm}^{-1} = 38000 \text{ m}^{-1}$

$$\omega = \frac{2\pi c}{\lambda} = 7.163 \times 10^{13} \text{ s}^{-1}$$

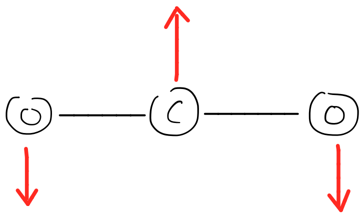
$$\mu = \left[\frac{1}{m_{Br}} + \frac{1}{m_F} \right]^{-1} = 2.518 \times 10^{-26} \text{ kg}$$

$$k = \omega^2 \mu = 129.189 \text{ kgs}^{-2}$$

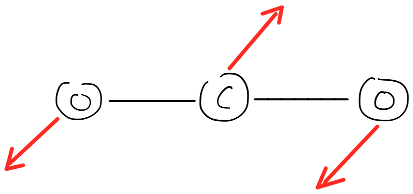
(c)

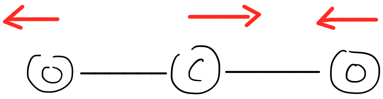


Symmetric C-O stretch



Bending along y or z direction (assume the molecule is along x-axis)





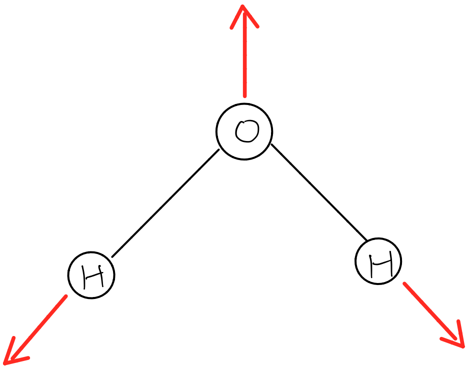
Asymmetric C-O stretch

The last three vibrational modes of CO2 are IR active because they involve a change in molecule's dipole moment.

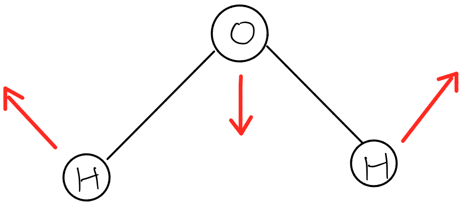
SQ29

(d) For non-linear molecules, we have 3 degrees of freedom for the rotational motion along 3 diffeent axes. Together with the 3 dregrees of freedom for the translational motion of molecule's center-of-mass, we have $3N-3-3 = 3N-6$ degrees of freedom left for the molecule's vibrational motion.

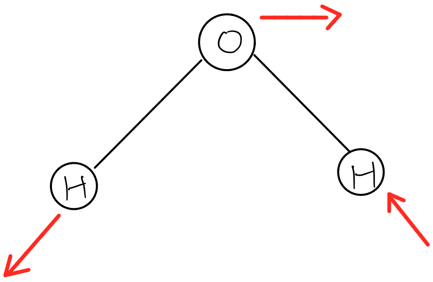
(e)



Symmetric stretching



Antisymmetric stretching



Bending

These three modes of H2O are IR active because they involve a change of molecule's dipole moment.