

quiz III next Tues day, allow 3 pieces of A4.

problem type: ① fill-in-the-blank, no need for derivation shown

② proving / solving - with derivation needed.

Home work (due June 4th). final exam June 11st

for the ground state of hydrogen atom, calculate $\langle r \rangle$,

$$\langle \frac{1}{r} \rangle. \text{ Hint: } \int_0^\infty e^{-sr} r^n dr = \int_0^\infty r^n de^{-sr} \quad (s \neq 0)$$

$$= \frac{r^n e^{-sr}}{(s-1)} \Big|_0^\infty + \frac{n}{s} \int_0^\infty e^{-sr} r^{n-1} dr \stackrel{n \neq 0}{=} \frac{n}{s} \int_0^\infty e^{-sr} r^{n-1} dr$$

$$\Rightarrow \int_0^\infty e^{-sr} r^n dr = \frac{n!}{s^n} \int_0^\infty e^{-sr} dr = \frac{n!}{s^{n+1}}$$

recap: Hydrogen atom

$$E_n = -\frac{\frac{e^2}{4\pi\epsilon_0 r_0^2} \cdot \frac{1}{n^2}}{2m_e c^2} \simeq -\frac{13.6 \text{ eV}}{n^2}$$

r_0 Bohr radius (effective)

$$\left\{ r_0 = \frac{4\pi\epsilon_0 e^2}{Me^2} \right\} \simeq 0.5 \text{ \AA} = 5 \times 10^{-11} \text{ m}$$

$M \sim M_e$

eV electron-volt 电子伏特

1 eV $\simeq (1.6 \times 10^{-19} \text{ C} \cdot \text{V}) = 1.6 \times 10^{-19} \text{ Joule} \leftarrow \text{energy unit, SI.}$

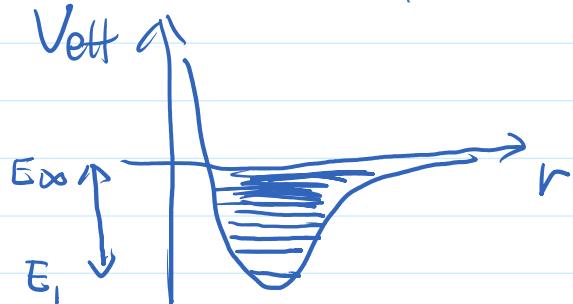
- ionization energy

$$E_{\text{ionize}} \simeq -\frac{13.6 \text{ eV}}{n^2}$$

$$E_{\text{ionize}} = E_\infty - E_{1,2,0}$$

$$= \left(\lim_{n \rightarrow \infty} -\frac{13.6 \text{ eV}}{n^2} \right) - \left(-\frac{13.6 \text{ eV}}{1^2} \right)$$

$$\simeq 13.6 \text{ eV}$$



$$= 13.6 \text{ eV}$$

when an H-atom's electron absorbs 13.6eV energy it will get excited to continuum, and no longer bound \rightarrow ionization 电离

o wavefunction

Quantum number n, l, m to describe ψ

$$\psi_{n,l,m} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2h(n+l)!}} e^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^l F_{n,l} \left(\frac{2r}{na_0}\right) Y_m^l$$

associated Laguerre polynomials

$\begin{cases} \text{exponential term} \\ \text{polynomials} \end{cases}$

$$\begin{array}{ll} r \rightarrow \infty & \gamma \rightarrow 0 \\ r \rightarrow 0 & \end{array}$$

$$\gamma \rightarrow 0$$

, when $l \geq 1$

$\gamma \neq \infty$ at $r \rightarrow 0$

Ground state $n=1, l=0, m_l=0$. ~~✓~~

$$\left\{ E_n = -\frac{13.6 \text{ eV}}{n^2} \Rightarrow \text{ground state } n=1. \right.$$

$\left. \begin{array}{l} \text{for a given } n, \text{ choice of } l = 0, 1, \dots, n-1 \\ \text{with } y=1 \Rightarrow l=0 \end{array} \right.$

$\left. \begin{array}{l} \text{for a given } l, \text{ choice of } m_l = -l, -l+1, \dots, l-1, l \\ l=0 \Rightarrow m_l=0. \end{array} \right.$

don't need to write out for fill-in-the-blanks.

o degeneracy

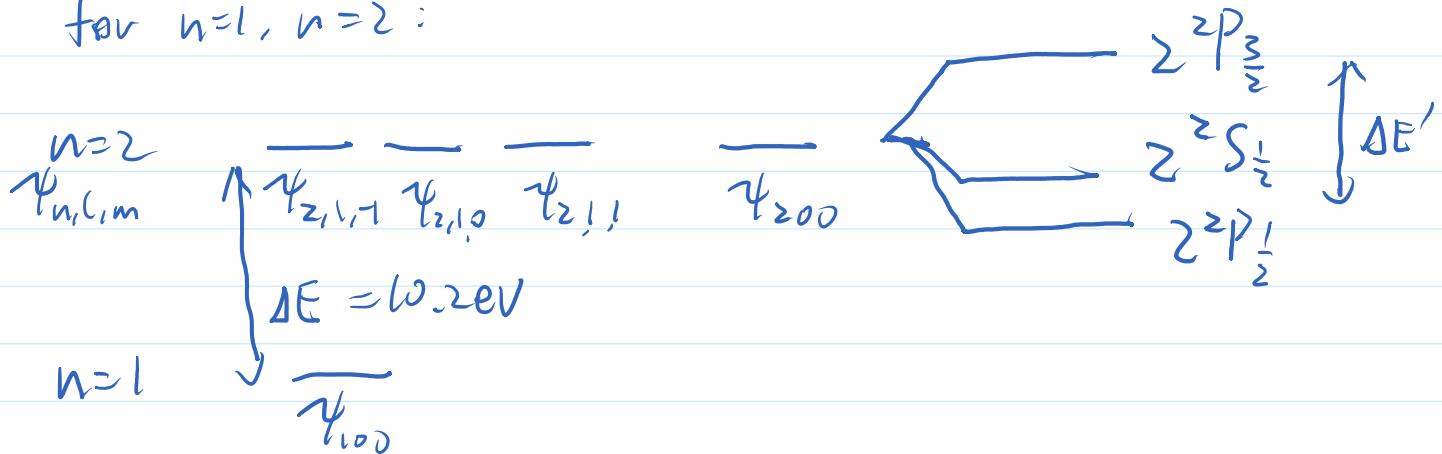
for a given n , many choices of l, m_l 's,
in general, n^2 choices

$n=1, 1^2$ choice, no degeneracy for ground state

$n=2, 2^2$ choices = 4. $\left\{ \begin{array}{cccc} l & 0 & 1 \\ m_l & 0 & -1, 0, 1 \end{array} \right. \Rightarrow 4 \text{ choices}$

energy diagram

for $n=1, n=2$:



here we ignore the spin of electron, nucleus,
also we ignore relativistic effects, etc.

if we include these effects, this introduces the
fine-structure 精细结构

term symbol $n^{2s+1}L_J$

$$\Delta E_{2 \rightarrow 1} = -\frac{13.6 \text{ eV}}{2^2} - \left(-\frac{13.6 \text{ eV}}{1^2}\right) = 10.2 \text{ eV}$$

$$\Delta E' \approx 4.5 \times 10^{-5} \text{ eV}$$

w principle quantum number.

if we further consider couplings between
electron spin + nuclear spin, and their coupling
to external weak magnetic field etc.

hyperfine structure 超精细结构

$\Delta E'' \sim 10^{-6} \text{ eV}$ or smaller in some cases.

↳ idea of approximation

more about atomic physics.
conversion of unit
energy units.

Joule

$$\text{eV} \doteq 1.6 \times 10^{-19} \text{ Joule}$$

$$\frac{\text{nm}}{\text{cm}^{-1}} \rightarrow \text{wavelength } \lambda, E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$$

example $E = 13.6 \text{ eV} = 13.6 \times 1.6 \times 10^{-19} \text{ Joule}$

$$\Rightarrow \lambda = \frac{hc}{E} \simeq 91 \text{ nm}$$

for comparison human eye visible wavelengths
400 nm - 700 nm.

§3. most simple molecule H_2^+

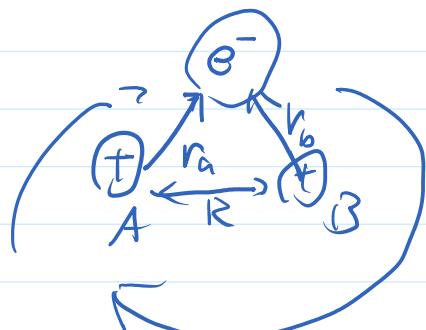
hydrogen molecular ion.

linear combination of atomic orbital (LCAO)

a bit into approximation methods.

two protons + one electron

$$H = -\frac{\frac{t^2}{2m_A} \vec{\nabla}_A^2 - \frac{t^2}{2m_B} \vec{\nabla}_B^2 - \frac{t^2}{2m} \vec{\nabla}^2}{\text{some.}} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}}_{\text{Coulomb interaction}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R}}_{\text{constant}}$$



first of all we notice mass of the proton is

much larger than e^- ~1836 times larger.

we assume proton is fixed in location.

\uparrow approximation \sum_{1th} .

$$H_{\text{effective}} \simeq -\frac{t^2}{2m} \vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B}$$

r_A, r_B include location of protons and electron.

$$\text{eigen equation } H_{\text{eff}} |\psi\rangle = E|\psi\rangle.$$

we need to find E . $|\psi\rangle$.

It's still too complicated to solve directly without using special tricks.

A simple idea (LCAO).

We have already a set of eigenstate for one atom
 $|1s\rangle$, $|2s\rangle$, $|2p, m_l = -1\rangle$, $|2p, m_l = 0\rangle$, $|2p, m_l = 1\rangle$...
 $n=1, l=0$

We label $|1s^a\rangle$ for ground state hydrogen atom wavefunction for nucleus A.

$|2s^a\rangle$, $|2p^a, m_l = -1\rangle$, $|2p^a, m_l = 0\rangle$...

$|1s^b\rangle$, $|2s^b\rangle$... for h-atom wavefunction surrounding nucleus B.

We assume

$|\Psi\rangle$ is a superposition of all the single atom wavefunction surrounding nucleus A and B.

$$|\Psi\rangle = c_{1a} |1s^a\rangle + c_{2a} |2s^a\rangle + c_{2a,-1} |2p^a, m_l = -1\rangle + \dots + c_{1b} |1s^b\rangle + c_{2b} |2s^b\rangle + c_{2b,-1} |2p^b, m_l = -1\rangle + \dots$$

We now look at ground states

We only keep $|1s^a\rangle$, $|1s^b\rangle$ components

$$|\Psi\rangle_{\text{ground state}} = c_{1a} |1s^a\rangle + c_{1b} |1s^b\rangle$$

We already simplify the system into possible superpositions between $|1s^a\rangle$, $|1s^b\rangle$

$$H|\Psi\rangle = E|\Psi\rangle \text{ with } |\Psi\rangle_{\text{ground state}}$$

$$\Rightarrow H(c_{1a}|1s^a\rangle + c_{1b}|1s^b\rangle) = E(c_{1a}|1s^a\rangle + c_{1b}|1s^b\rangle)$$

try to solve for E, c_{1a} , c_{1b} , we apply $\langle 1s^a |, \langle 1s^b |$ to the left.

$$\Rightarrow \langle ls^a | :$$

$$C_{1a} \langle ls^a | H | ls^a \rangle + C_{1b} \langle ls^a | H | ls^b \rangle \\ = EC_{1a} \langle ls^a | ls^a \rangle + EC_{1b} \langle ls^a | ls^b \rangle$$

$$\langle ls^b | :$$

$$C_{1a} \langle ls^b | H | ls^a \rangle + C_{1b} \langle ls^b | H | ls^b \rangle \\ = EC_{1a} \langle ls^b | ls^a \rangle + EC_{1b} \langle ls^b | ls^b \rangle$$

$$\text{let } H_{11} = \langle ls^a | H | ls^a \rangle, H_{12} = \langle ls^a | H | ls^b \rangle$$

$$H_{21} = \langle ls^b | H | ls^a \rangle, H_{22} = \langle ls^b | H | ls^b \rangle$$

$$S_{11} = \langle ls^a | ls^a \rangle, S_{12} = \langle ls^a | ls^b \rangle$$

$$S_{21} = \langle ls^b | ls^a \rangle, S_{22} = \langle ls^b | ls^b \rangle$$

$$\Rightarrow \begin{cases} C_{1a} (H_{11} - ES_{11}) + C_{1b} (H_{12} - ES_{12}) = 0 \\ C_{1a} (H_{21} - ES_{21}) + C_{1b} (H_{22} - ES_{22}) = 0 \end{cases}$$

$$\Rightarrow \begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \begin{pmatrix} C_{1a} \\ C_{1b} \end{pmatrix} = 0.$$

for a non-trivial solution of C_{1a}, C_{1b} , we require
the determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$H_{ij}, S_{ij} \text{ are all known. } \Rightarrow \begin{cases} E_+ = \frac{H_{11} + H_{12}}{S_{11} + S_{12}} \\ E_- = \frac{H_{11} - H_{12}}{S_{11} - S_{12}} \end{cases}$$

and solve for $\begin{pmatrix} C_{1a} \\ C_{1b} \end{pmatrix}$ accordingly.

$$E_+ : \begin{pmatrix} C_{1a} \\ C_{1b} \end{pmatrix} = \frac{1}{\sqrt{2S_{11} + 2S_{12}}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$|C_{1a}| \quad |C_{1b}|$$

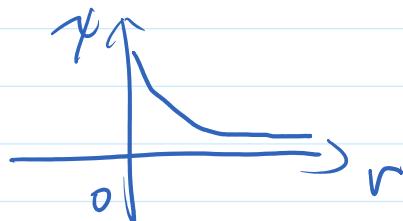
$$E^- : \begin{pmatrix} C_{1a} \\ C_{1b} \end{pmatrix} = \frac{1}{\sqrt{2S_{11}-2S_{12}}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$E^- \quad \psi = C_{1a}|1s^a\rangle + C_{1b}|1s^b\rangle$$

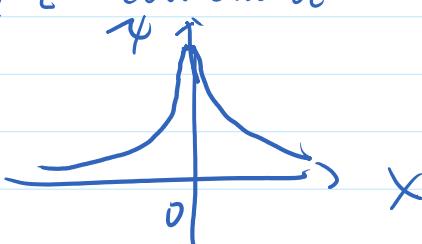
$$E^+ = \frac{H_{11} + H_{12}}{S_{11} + S_{12}} \quad t\psi_+ = \frac{1}{\sqrt{2S_{11} + 2S_{12}}} (|1s^a\rangle + |1s^b\rangle) \rightarrow \sigma$$

$$E^- = \frac{H_{11} - H_{12}}{S_{11} - S_{12}} \quad (\psi_-) = \frac{1}{\sqrt{2S_{11} - 2S_{12}}} (|1s^a\rangle - |1s^b\rangle) \rightarrow \delta^*$$

for a single hydrogen $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$



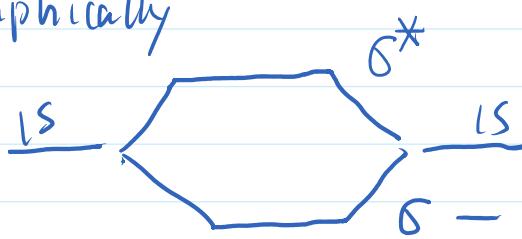
in XY-Z coordinate



$$\psi_+ \approx |1s^a\rangle + |1s^b\rangle$$

$$\psi_- \sim |1s^a\rangle - |1s^b\rangle$$

graphically



σ - true ground state.

