III. Very Essential Quantum Mechanics[†]

- Motived by atomic spectrum (why there are Lyman, Balmer, ... series in H-atom)

  allowed energies of H-atom $-\frac{13.6}{n^2}$ eV (n=1, 2, ...)

- Electron Diffraction Experiments

  (Davisson/Germer 1923-27)

  electron has wave properties

  Given electron has wave properties, what is the governing Wave Equation?

  (de Broglie, Schrödinger, Heisenberg, Born, Dirac...)

- Photoelectric & Compton effects

  Light (EM waves) has particle properties

  [and Maxwell's Equations are the governing equations]

[†] The Quantum Mechanics assumed and required in the course is much more than that reviewed here. The purpose here is to get at a bare minimum to move on at least for a qualitative understanding of what will follow.

$\Psi(\vec{r}, t)$

↑

Quantum mechanical wavefunction of a single particle (an electron) in $\underbrace{\text{an atom/molecule/solid}}_{\text{that wave properties matter}}$

(scalar field)

Born's Interpretation

$|\Psi(\vec{r}, t)|^2 d^3r$ = Prob. of finding particle to be at $\vec{r}$ in a volume d^3r at time t (1)

$\Psi(\vec{r}, t)$ alone is Probability Amplidude

Electromagnetism

$\vec{E}(\vec{r}, t)$, $\vec{B}(\vec{r}, t)$

↑

electric field (vector field)

In EM, brightness (no negative brightness, but $\vec{E}(\vec{r}, t)$ can be +ve/-ve)

Intensity $\propto |\vec{E}(\vec{r}, t)|^2$

By interpretation,

$$\int_{\text{all space}} |\Psi(\vec{r},t)|^2 \, d^3r = 1 \qquad (2)$$

(normalization requirement)

particle must be some where !

- Single-valued
- Continuous
- Slope (Gradient) continuous

$\Psi(\vec{r},t)$ must satisfy these conditions

Various Boundary Conditions on $\vec{E}(\vec{r},t)$ and $\vec{B}(\vec{r},t)$ as they are governed by the Maxwell's equations

(e.g. $E_{\parallel}$ continuous across an interface)

$E_{\perp}$ could be discontinuous though

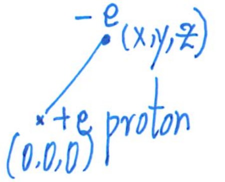
$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \qquad (3) \quad (\text{TDSE})$$

(Time-Dependent Schrödinger Equation)

$\hat{H}$ = Hamiltonian Operator of the system under consideration

Think Classical (H-atom problem)

$$H = \text{Hamiltonian} = \text{K.E.} + \text{P.E.}$$



$$= \left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}\right) - \frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}$$

and it is time-independent

$$\nabla^2 \vec{E} = \mu\varepsilon \frac{\partial^2 \vec{E}}{\partial t}$$

$$\nabla^2 \vec{B} = \mu\varepsilon \frac{\partial^2 \vec{B}}{\partial t}$$

(Maxwell's wave equations)

Go Quantum

$$p_x \rightarrow \hat{p}_x \text{ (momentum operator)} = \frac{\hbar}{i}\frac{\partial}{\partial x} \; ; \; p_y \rightarrow \hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y} \; ; \; p_z \rightarrow \hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z} \qquad (4)$$

$$x \rightarrow \hat{x} \text{ (position operator)} = x \; ; \; y \rightarrow \hat{y} = y \; ; \; z \rightarrow \hat{z} = z \qquad (5)$$

$$\hat{H}_{(H\text{-atom})} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}} \quad \text{(Cartesian Coordinates)}$$

$$= -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \quad \text{(spherical coordinates)} \qquad (6)$$

TDSE for a H-atom is:

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)\Psi(\vec{r},t) \qquad (7)$$

- "i" appears in wave equation
- $\Psi(\vec{r},t)$ is intrinsically (generally) complex

Time-Independent Schrödinger Equation

$\hat{H}$ is time-independent for many problems[+]

(carry out normal-mode analysis) → e.g.

Displacement from equilibrium

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \left(\frac{\rho}{T}\right)\frac{\partial^2 \Psi(x,t)}{\partial t^2}$$

string (tension T, mass density ρ)

What are the normal mode oscillations and frequencies?

asking intrinsic property of the string?

What are the allowed frequencies of oscillations?

Do the same thing to TDSE gives

$$\boxed{\hat{H}\psi(\vec{r}) = E\,\psi(\vec{r})} \qquad (8)$$

Time-Independent Schrödinger Equation (TISE)

The most important equation in the physics of Matter (atoms/molecules/solids/nuclei)

[+] For light incident on atoms/solids, the p.E. term due to Light-Matter interaction is time-dependent.

TISE is the Equation asking for "what are the allowed energies?"

$$\underset{\nearrow \atop \text{the system}}{\hat{H}}\ \underbrace{\psi(\vec{r})}_{\text{to solve}} = \underbrace{E}_{\text{to solve}}\ \underbrace{\psi(\vec{r})}_{\text{to solve}}$$

[structure of an eigenvalue problem]

$\underbrace{\text{to solve}}$ for <u>pairs</u> of $\left(\psi(\vec{r}) \longleftrightarrow E\right)$

<u>recall</u>: the allowed <u>states</u> are those obeying $\hat{H}\psi = E\psi$ <u>AND</u> <u>boundary conditions</u>

can label (number) the solutions to TISE

$$\psi_1(\vec{r}) \leftrightarrow \underset{\uparrow}{E_1},\ \psi_2(\vec{r}) \leftrightarrow \underset{\nearrow}{E_2},\ \underset{\uparrow\uparrow\uparrow}{\cdots},\ \psi_n(\vec{r}) \leftrightarrow \underset{\nearrow}{E_n};\ \underset{\nearrow\nearrow\nearrow}{\cdots}$$

(infinitely many in principle)

see how these allowed energies distributed on energy axis

$\underbrace{\psi_i(\vec{r}) \leftrightarrow E_i}$ come in pairs

$\underbrace{\text{normal-mode analysis}}$ ⇒ $\psi_i(\vec{r})$ evolves with time as $\psi_i(\vec{r})\, e^{-\frac{iE_i t}{\hbar}}$

from TDSE to TISE <u>AND</u> time-evolution equation

<u>Linear Equation</u> (no such term as $\left(\frac{\partial \Psi}{\partial x}\right)^2$ or $\left(\frac{\partial \Psi}{\partial t}\right)^2$, just one power of 1st, 2nd derivatives)

- If time $t=0$, know that $\Psi(\vec{r},0) = \sum_n a_n \psi_n(\vec{r})$

$$\text{then } \Psi(\vec{r}, \underset{\substack{\uparrow \\ \text{later time } t}}{t}) = \sum_n a_n \psi_n(\vec{r})\, e^{-iE_n t/\hbar} \qquad (9)$$

[This is also how a string would vibrate in response to pucking it a $t=0$]

Schrödinger (1925) solved <u>the Hydrogen atom TISE</u>

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi(\vec{r}) = E\,\psi(\vec{r}) \qquad (10)$$

and found that for solutions with $E<0$ (electron bounded to nucleus), the allowed energies must be given by

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\,\frac{1}{n^2} \qquad (n=1,2,3,\cdots) \qquad (11)$$

$$= -\frac{13.6}{n^2}\ \text{eV}$$

(no more ad hoc Bohr model)

with the energy eigenstates $\psi_{\underbrace{n\ell m_\ell}}(r,\theta,\phi)$ (12)

3D problems need <u>3 labels</u>
"quantum numbers"

as listed on the following page

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\cdot Y_{\ell m_\ell}(\theta,\phi) \quad \text{[in spherical coordinates]}$$

Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2$, and 3*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r,\theta,\phi)$	
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}}e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-r/a_0}$	ψ_{100}
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\,a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$	ψ_{200}
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$	ψ_{210}
2	1	±1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$	ψ_{211} and ψ_{21-1}
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\,a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\,a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$	ψ_{300}
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\cos\theta$	ψ_{310}
3	1	±1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$	ψ_{311} and ψ_{31-1}
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}(3\cos^2\theta-1)$	ψ_{320}
3	2	±1	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$	ψ_{321} and ψ_{32-1}
3	2	±2	$\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$	ψ_{322} and ψ_{32-2}

$$U(r) \Rightarrow \underbrace{\Phi(\phi)\,\Theta(\theta)}_{Y_{\ell m_\ell}(\theta,\phi)} \quad \underbrace{R(r)}_{R_{n\ell}(r)\ \left[\text{due to } U = \frac{-e^2}{4\pi\varepsilon_0 r}\right]} \quad \underbrace{\psi(r,\theta,\phi)}_{\psi_{n\ell m_\ell}(r,\theta,\phi)}$$

Bohr radius: $a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{m_e e^2} = 5.292\times10^{-11}\,\text{m} = 0.5292\,\text{Å}$ appears naturally (roughly "half Angström")

- "1s" (H-atom ground state) $\psi_{n=1,\underbrace{l=0,\, m_l=0}_{s\text{-state}}}(r,\theta,\phi) = \psi_{100}(r,\theta,\phi) = A\, e^{-r/a_B}\cdot Y_{00}(\theta,\phi)$

  $E_{100} = -13.6\,\text{eV}$

  $= \bar{A}\, \underbrace{e^{-r/a_B}}$

  no directional dependence

  ∴ like a sphere

"s" state

dropping off exponentially but radially

- $\underbrace{\text{"2s"}}$ $E_{\underbrace{200}_{s\text{-state}}} = \frac{-13.6}{4}\,\text{eV}$

  ψ_{200} (also no directional dependence)

- "2p"'s (3 of them) $E_{211} = E_{210} = E_{21-1} = \frac{-13.6}{4}\,\text{eV}$

$$\psi_{211}(r,\theta,\phi) = R_{21}(r)\cdot \underbrace{Y_{11}(\theta,\phi)} \qquad \psi_{210}(r,\theta,\phi) = R_{21}(r)\cdot \underbrace{Y_{10}(\theta,\phi)} \qquad \psi_{21-1}(r,\theta,\phi) = R_{21}(r)\cdot \underbrace{Y_{1-1}(\theta,\phi)}$$

(see Table)

directional

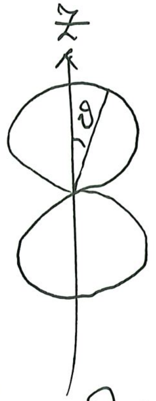
$l = 1$ gives "p-states"

$$\underset{\uparrow}{Y_{10}}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\;\underbrace{\cos\theta}_{}$$

(they are called <u>spherical harmonics</u>, there are Tables for $Y_{lm}(\theta,\phi)$)

$l=1 \Rightarrow$ "p" state

"Polar Plot"



this is the p_z state

$\psi_{210}(r,\theta,\phi)$ is H-atom's $2p_z$ state

<u>What are p_x and p_y states?</u>

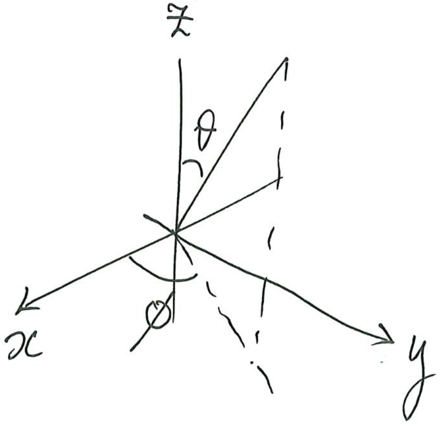
$$Y_{11}(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{i\phi} \quad ; \quad Y_{1-1}(\theta,\phi) = +\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{-i\phi}$$

complex functions

not good for visualization ("google" them for pictures)

But linear combinations of them help!

$$\frac{1}{\sqrt{2}}\left(Y_{1-1} - Y_{11}\right) = \sqrt{\frac{3}{4\pi}}\,\underbrace{\sin\theta\,\cos\phi}_{\text{go along } x} \equiv p_x \text{ state}$$



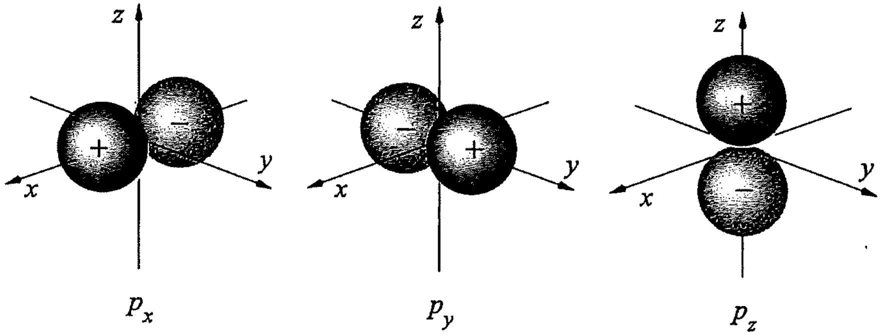
$$\frac{i}{\sqrt{2}}\left(Y_{1-1} + Y_{11}\right) = \sqrt{\frac{3}{4\pi}}\,\underbrace{\sin\theta\,\sin\phi}_{\text{go along } y} \equiv p_y \text{ state}$$

together with $Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \equiv p_x$ state

(knowing the atomic s, atomic p_x, p_y, p_z states are essential for making sense of bonding)

$\underbrace{p_x\ ,\ p_y\ ,\ p_z}_{\text{real functions}}$ are orthonormal [∵ Y_{10}, Y_{11}, Y_{1-1} are orthonormal]

[identical shape but along different directions]



p_x p_y p_z

Three-dimensional polar plots of the angular part of the real representation of the hydrogen atomic wave functions for $l = 1$

These are the p_x, p_y, p_z in Chemistry courses.

[No $R_{nl}(r)$ yet]

$$\underbrace{p_x \qquad\qquad p_y}_{Y_{11}\ ,\ Y_{1-1}}$$

[real, useful in understanding bonding in molecules and solids, easier to visualize]

[complex, math solutions to θ-ϕ equation, not easier to visualize, known math properties]

$\hat{H}\psi = E\psi$ is also good for

- Many-particle problems (many-electrons + many-ions)
- Single electron in a complicated potential energy function
- Many electrons in one nucleus (atoms beyond Hydrogen)

We know the governing equation (TISE), but the equation is hard to solve. (impossible to solve).

Need clever approximations!

But for $\underbrace{\text{many-electron}}_{}$ atoms, we need to handle $\underbrace{\text{the spin of an electron}}_{}$

need to know how to put electrons into 1s, 2s, 2p, ... states

- electron is $\underbrace{\text{spin-}1/2 \text{ particle}}_{\text{a fermion}}$
- $s = 1/2$ and has spin angular momentum of $|S| = \sqrt{\frac{3}{4}}\,\hbar$ (a constant)
- z-components (any direction called $\hat{z}$) are $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$

  ($m_s = 1/2$) (up) ($m_s = -1/2$) (down)

$$\psi_{n l m_l}(r,\theta,\phi) \xrightarrow[\text{extended to}]{} \psi_{n l m_l,\underbrace{m_s}_{+1/2 \text{ or } -1/2}}$$

Pauli Exclusion Rule

- One state satisfied by (n, l, m_l, m_s) can only be occupied by one electron

e.g. 3s ($n=3$, $l=0$, $m_l=0$, $m_s=+1/2$ or $-1/2$)

can be occupied by one electron each for $m_s=+1/2$ and $m_s=-1/2$

$\Rightarrow$ a total of two electrons

3s ↑↓ (just a picture)

(the wavefunction is more complicated)

3p $\left(n=3,\ l=1,\ m_l=\begin{Bmatrix}1\\0\\-1\end{Bmatrix},\ m_s=\begin{Bmatrix}1/2\\-1/2\end{Bmatrix}\right)$ can hold up to 6 electrons

Examples

- Si (ground state description) $1s^2\ 2s^2\ 2p^6\ \boxed{\overbrace{3s^2}^{\text{two electrons in 3s}}\ \underbrace{3p^2}_{\text{two electrons in 3p states}}}$
- Ge (ground state description) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ \boxed{\underbrace{4s^2}_{}\ \underbrace{4p^2}_{}}$

(electronic configuration)

$\boxed{}$ need these electrons to understand "sp^3 hybridization" and the crystal structure (diamond)

- Ga : $[\mathrm{Ar}]\ 3d^{10}\ 4s^2\ 4p^1$
- As: $[\mathrm{Ar}]\ 3d^{10}\ 4s^2\ 4p^3$
- P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
- Al : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

It will be very difficult to move on if you don't have some basic QM with you.

References

- The very basics:
  - Chapters in "Modern Physics for Scientists and Engineers" by Taylor, Zafiratos, Dubson
  - Chapters in "Electronic Properties of Engineering Materials" by Livingston
- Good preparation for this course
  - PHYS 3021 Quantum Mechanics I
  - A.I.M. Rae, "Quantum Mechanics" (1st - 3rd edition) [first 7 chapters, 150 pages Only!]
- Very Good preparation
  - D. McQuarrie, "Quantum Chemistry"