3D Ch 7

Generalization to 3D straight forward

$$i\hbar \frac{\partial \psi}{\partial t} = H \psi$$

H - total energy
"Hamiltonian"

3D

$$H \rightarrow \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V(\vec{x})$$

$$p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad \vec{p} \rightarrow \frac{\hbar}{i}\vec{\nabla}$$

Sch Eq

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi + V\psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Note ψ V now functions of $\vec{x}$ & t

Just as before, we will consider solutions

$$\Psi(\vec{x},t) = \psi(\vec{x})\, e^{-iE_n t/\hbar}$$

where $\psi(x)$ satisfies

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Questions

Infinite Cube

$$V(x,y,z) = \begin{cases} 0 & \text{if } x,y,z \text{ in } 0-a \\ \infty & \text{otherwise} \end{cases}$$

Outside of cube $\psi(x,y,z) = 0$
(Same logic as in 1D)

Inside the cube

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = E\psi$$

Assume separation of variables

$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

then (subsituting + dividing by ψ)

$$\underbrace{\frac{1}{X}\frac{d^2X}{dx^2}}_{f(x)} + \underbrace{\frac{1}{Y}\frac{d^2Y}{dy^2}}_{f(y)} + \underbrace{\frac{1}{Z}\frac{d^2Z}{dz^2}}_{f(z)} = \underbrace{-\frac{2m}{\hbar^2}E}_{\text{Constant}}$$

Only possible if the different f( )'s are equal to constants (k_x^2, k_y^2, k_z^2)

So,
$$\frac{d^2X}{dx^2} = -k_x^2, \quad \frac{d^2Y}{dy^2} = -k_y^2, \quad \frac{d^2Z}{dz^2} = -k_z^2$$

And
$$E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$\left(p = \hbar k, \quad E = \frac{p_x^2 + p_y^2 + p_z^2}{2m}\right)$$

As expected...

Now easy to solve the separated eqn's

$$X(x) = A_x \sin k_x x + \cancel{B_x \cos k_x x}$$

ψ - const at ϕ

$$k_x = \frac{n_x \pi}{a} \quad (\text{from } \psi \text{ - const at } a)$$

Ditto $Y(y)$, $Z(z)$

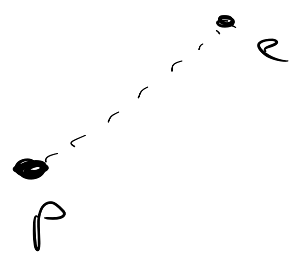
$$\psi(x,y,z) = A \sin\left(\frac{n_x \pi}{a}\right) \sin\left(\frac{n_y \pi}{a}\right) \sin\left(\frac{n_z \pi}{a}\right)$$

So $\psi_{n_x,n_y,n_z}(x,y,z)$ $\quad E_{n_x,n_y n_z} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)$

Atoms

However most physical problems in 3D have

$V(\vec{r})$



Appropriate to use

r, θ, ϕ not x, y, z.

All the complications (fancy math we'll need) arises from going to spherical coordinates not inherent in QM or in 3D Sch.

I will give a high-level view of whats going on and how I think about it.

Skip most of the math (all of the diff eq's)

<u>What I want you to pay attention to:</u>

-) Where the separation constants come from and how they are constrained.

-) Physical meaning of separation constants

-) Possible (Allowed) Quantum #'s (expect 3)

-) Qualitative understanding of ψ

Ok, need to change basis

$$(x, y, z) \to (r, \theta, \phi)$$

$$\frac{\partial \psi}{\partial x} \to \frac{\partial \psi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial \psi}{\partial \phi}\frac{\partial \phi}{\partial x}$$

+ others (Then need to "square" $\frac{\partial^2 \psi}{\partial x^2}$)

Ton of algebra, not enlightening (you do in calc 3)

Answer:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \xrightarrow{\text{goes to}}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)$$

Start by looking for seperable solutions

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

Putting this in and dividing by ψ (like always)

$$\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]}_{\text{Only depends on } r}$$

$$+\underbrace{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}}_{\text{Only cares about } \theta,\phi} = 0$$

First Separation Constant C_1

Note the equation for θ & ϕ, V independent

$\Rightarrow$ Angular Solutions universal (like $\phi(t)$)

Angular Eq well known "Laplace Eq"

It itself is separable

$$Y(\theta, \phi) = T(\theta) P(\phi)$$

Second Separation Constant. C_2

$$\frac{1}{P} \frac{d^2 P}{d\phi^2} = -C_2$$

Easy Peasy $P(\phi) = e^{i\sqrt{C_2}\phi}$

Remember ϕ periodic $\phi = \phi + 2\pi$

$$\Rightarrow e^{i\sqrt{C_2} 2\pi} = 1$$

So, $\sqrt{C_2}$ must be a real integer

$$C_2 \equiv m^2 \quad w/ \; m = 0, \pm 1, \pm 2, \ldots$$

Ok, one down. Now the Θ eq

Turns out this is a special diff eq that 19th century math figured out

<u>Solution</u>

$$T(\theta) = A P_l^m(\cos\theta)$$

where $C_1 = l(l+1)$ and l integer

where $P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_l(x)$

and $P_l \equiv \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l (x^2-1)^l$

where l is $0, 1, 2, \ldots$

(Note: you will not need these details)

Whats important:

P_l - polynomial in x of degree l.

$$\Rightarrow P_m^l \sim \left(\frac{d}{dx}\right)^{|m|} \mathcal{O}(x^l) = 0$$

if $|m| > l$

This is the take away

$\Rightarrow$ l : 0, 1, 2, ...

m : $-l$, $-l+1$ ... -1, 0, 1, ... $l-1$, l

Back to the Radial eq

Can't go further until we specify $V(r)$
Here we will only study hydrogen potential.
Most other atoms can only be solved numerically

$$V(r) \sim \frac{-\alpha}{r}$$

Again you end up w/ complicated diff eq.

<u>Note</u> that we expect:

-) Quantized states given by n, E_n

-) Link between n & l

<u>Solutions</u> $R_{nl}(r) = A e^{-r/a_0 n} r^l \mathcal{L}_{nl}\left(\frac{r}{a}\right)$

"Laguerre Polynomials"

($n > l$ from same logic as $|m| < l$, $R = 0$ otherwise)

Turns out

$$E_n = -\left(\frac{kZe^2}{\hbar}\right)^2 \frac{m}{2n^2} = -\frac{Z^2 E_1}{n^2}$$

$$E_1 = 13.6 \text{ eV}$$

Same energy levels as those in Bohr Model!!

- All upside of getting E levels right
- Now have a solid theory behind it.

$n = 1, 2, 3, \ldots$ But $n > l$

Summary of Quantum Numbers

3 as expected

$$n = 1, 2, 3, \ldots \qquad (r)$$

$$l = 0, 1, 2 \ldots, (n-1) \qquad (\theta)$$

$$m = -l, (-l+1), \ldots 0, 1, \ldots l \qquad (\phi)$$

Note E_n - only depends on n.
(special to $\frac{1}{r}$ law)

Defines overall structure of Periodic Table

P shell

n	I	II												III	IV	V	VI	VII	VIII
1	hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
2	lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
3	sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
	potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
	rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
	caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
	francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 * *	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

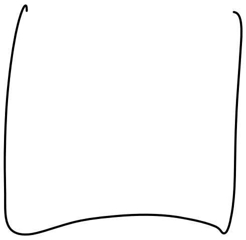
*Lanthanide series	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
* *Actinide series	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Periodic Trends

- Original structure motivated by chemical properties.

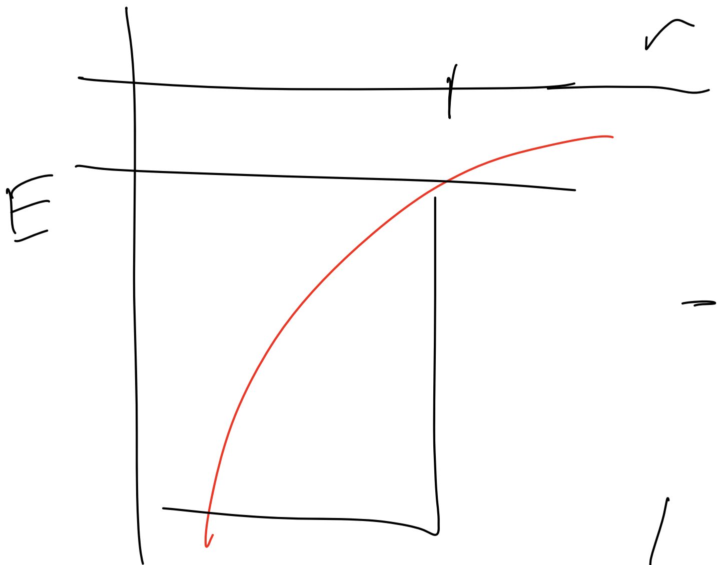
eg] similar elements in same column.

Chem. of C, Si + Ge similar



L

$$E = \frac{\hbar^2 \pi^2 n^2}{2 m L^2}$$



$$-E = \frac{\alpha}{r}$$

$$L = \frac{\alpha}{E}$$

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2 m \alpha^2} E_n^2$$

$$r_e \sim \frac{1}{m\alpha}$$

$$\Rightarrow \frac{2 m \alpha^2}{\hbar^2 \pi^2} \frac{1}{n^2}$$

$$E \sim m\alpha^2$$