1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
  3.1 Separation of Variables
  3.2 Eigenfunctions of the Hamiltonian
    and Energy Levels of H atom

EXAMPLE: The hydrogen atom or hydrogen-like atom:

Two particles: N and e

$$H_{total} = \frac{-\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{r}$$

where

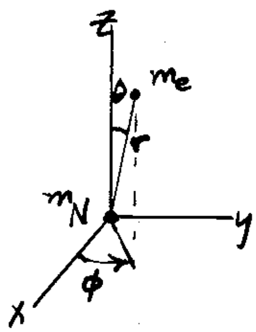
$$\nabla_e^2 \equiv \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}$$

SEPARATION of VARIABLES will be possible if we change into the center-of-mass and relative coordinates:

$$X_{CM}\, M_{total} = x_e m_e + x_N m_N$$

$$Y_{CM}\, M_{total} = y_e m_e + y_N m_N$$

$$Z_{CM}\, M_{total} = z_e m_e + z_N m_N$$



$$x = x_e - x_N$$

$$y = y_e - y_N$$

$$z = z_e - z_N$$

$M_{total} = m_e + m_N$

REDUCED MASS μ as in

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$

Substitution into H_{total} leads to:

$$H_{total} = \underbrace{\frac{-\hbar^2}{2M_{total}}\nabla_{cm}^2}_{\text{in coordinates of center of mass}} \quad \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}}_{\text{in } x,\, y,\, z \text{ coords or } r,\theta,\phi}$$

SEPARABLE as follows:

$$\frac{-\hbar^2}{2M_{total}}\left(\frac{\partial^2}{\partial X_{CM}^2} + \frac{\partial^2}{\partial Y_{CM}^2} + \frac{\partial^2}{\partial Z_{CM}^2}\right) G(X_{CM}, Y_{CM}, Z_{CM}) = E_{transl} G$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}\right)\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$

$$E_{total} = E_{transl} + E$$

The translational motion of the H atom is already solved (a particle in a three-dimensional box) by SEPARATION OF VARIABLES:

$$G(X_{cm}, Y_{cm}, Z_{cm}) = \sqrt{\frac{2}{L_1}}\sin\left(\frac{n_x\pi}{L_1}X_{cm}\right)\cdot\sqrt{\frac{2}{L_2}}\sin\left(\frac{n_y\pi}{L_2}Y_{cm}\right)\cdot$$

$$\sqrt{\frac{2}{L_3}}\sin\left(\frac{n_z\pi}{L_3}Z_{cm}\right)$$

We now have to solve the motion of the electron relative to the nucleus of the hydrogen atom: **"A PARTICLE IN A COULOMB FIELD"**

$$\left(\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}\right)\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

In spherical polar coordinates

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\left\{-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \left(\frac{1}{2\mu r^2}\right)\underbrace{-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}}_{\boldsymbol{l}^2_{op}}\right.$$

$$\left.-\frac{Ze^2}{r}\right\}\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

that is,

$$H_{op} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\boldsymbol{l}^2_{op}}{2\mu r^2} - \frac{Ze^2}{r}$$

in which we see that $\boldsymbol{l}^2_{op}$ COMMUTES with H_{op}!

Since we already know the EIGENFUNCTIONS of ℓ^2_{op} which satisfy the equation

$$\ell^2_{op} Y_{\ell m}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\phi),$$

then we can say that, except for a function of r, we already know the EIGENFUNCTIONS of H_{op} for a hydrogen atom, that is,

$$H_{op}\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$

where, $\Psi(r,\theta,\phi) = \underbrace{R(r)\cdot Y_{\ell m}(\theta,\phi)}$.

Substitute this $\longrightarrow$ product function into the Schrödinger equation and divide both sides by the product function:

$$\frac{\left\{\frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r}\right\}R(r)}{R(r)} = E$$

Like all the others, the solution of this equation requires imposing the condition that R(r) be WELL-BEHAVED, obviously important since r can have values $0 \longrightarrow \infty$.

		WAVEFUNCTION is WELL-BEHAVED if
Particle on a circle	$\frac{1}{\sqrt{2\pi}}e^{im\phi}$	$m = 0, \pm1, \pm2, \cdots$
Particle on a sphere	$\Theta_{\ell\lvert m\rvert}(\theta)\cdot\frac{1}{\sqrt{2\pi}}e^{im\phi}$	$\ell = 0, 1, 2, 3, \cdots$; $m = 0, \pm1, \pm2, \cdots \pm\ell$
Hydrogen atom (a particle in a Coulomb field)	$R_{n\ell}(r)\cdot\Theta_{\ell\lvert m\rvert}(\theta)\cdot\frac{1}{\sqrt{2\pi}}e^{im\phi}$	$n = 1, 2, 3, \cdots$; $\ell = 0, 1, 2, \cdots n-1$; $m = 0, \pm1, \pm2, \cdots \pm\ell$

The R part, the quantum number n, its relation to l

$$\left\{ -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} - E \right\} R(r) = 0$$

Use the transformation

$$g = rR$$

let $\begin{cases} r = \text{in multiples of } a = \frac{\hbar^2}{\mu e^2} \\ E = \text{in multiples of } \frac{\hbar^2}{2\mu a^2} \end{cases}$

simpler equation →

$$\frac{d^2 g}{dr^2} + \left\{ E + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right\} g = 0$$

Solve the g(r) problem

Then can go back and find R(r)

a) Large r to get asymptotic solution:

$$\frac{d^2 g}{dr^2} + E g \Longrightarrow 0$$

Asymptotic solution $g \Rightarrow A e^{-\sqrt{-E}\, r}$

for E negative (we want bound states)

for $E > 0$ we get ≈ "free particle" w/fn (Ensoidal)

Genl Solution is

$$g = \underbrace{\text{Poly}(r)}_{\text{varies slowly at infinity}} e^{-\sqrt{-E}\, r}$$

Call it $u(r)$

Let $Poly(r) = U(r)$ so that $g(r) = U(r)\exp^{-\sqrt{-E}\,r}$

$$\frac{d^2 g(r)}{dr^2} + \left\{E + \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2}\right\} g(r) = 0$$

$$\boxed{\frac{d^2 U(r)}{dr^2} - 2\sqrt{-E}\,\frac{dU}{dr} + \left[\frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2}\right] U(r) = 0}$$

Let the polynomial be written in the form

$$U(r) = r^s \sum_{N=0}^{\infty} C_N r^N = C_0 r^s + C_1 r^{s+1} + C_2 r^{s+2} + \cdots$$

$$= \sum_{N=0}^{\infty} C_N r^{(s+N)}$$

The first derivative:

$$\frac{dU(r)}{dr} = sC_0 r^{s-1} + (s+1)C_1 r^s + C_2(s+2) r^{s+1} + \cdots$$

$$= \sum_{N=0}^{\infty} (s+N) C_N\, r^{(s+N-1)}$$

The second derivative:

$$\frac{d^2U(r)}{dr^2} = s(s-1)C_0 r^{s-2} + s(s+1)C_1 r^{s-1} + (s+2)(s+1)C_2 r^s + \ldots$$

$$= \sum_{N=0}^{\infty} (s+N)(s+N-1) C_N\, r^{(s+N-2)}$$

Now put the first and second derivatives into the equation (see above)

Collect the terms in the same power of r:

The terms in the power $s+N-2$:

$$(s+N)(s+N-1)C_N r^{(s+N-2)} - 2\sqrt{-E}\,(s+N-1)C_{N-1}\, r^{(s+N-2)}$$
$$+ 2Z \cdot C_{N-1} r^{(s+N-2)} - \ell(\ell+1) C_N r^{(s+N-2)} = 0$$

$$g(r) = u(r)\, exp^{-\sqrt{E}\,r}$$

$$\frac{dg}{dr} = \frac{du}{dr} exp^{\sqrt{E}\,r} + u(r) \cdot \sqrt{-E}\, exp^{\sqrt{E}\,r}$$

$$\frac{d^2g}{dr^2} = \frac{d^2u}{dr^2} exp^{-\sqrt{E}r} - \sqrt{E}\frac{du}{dr} exp^{-\sqrt{E}r} + u(r)\left[\sqrt{-E}\right]^2 exp^{-\sqrt{E}r} + -\frac{du}{dr}\sqrt{-E}\, exp^{-\sqrt{E}\,r}$$

$$\frac{d^2g}{dr^2} = \left[\frac{d^2u}{dr^2} - 2\sqrt{-E}\frac{du}{dr} - E\,u(r)\right] exp^{-\sqrt{E}\,r}$$

most general form of polynomial
first term can be any power of r

subst

$$\frac{d^2g(r)}{dr^2} + \left\{E + \frac{2Z}{r} - \frac{l(l+1)}{r^2}\right\} g(r) = 0$$

$$\left[\frac{d^2u}{dr^2} - 2\sqrt{-E}\frac{du}{dr} - \cancel{E}\,u(r)\right] exp^{-\sqrt{E}\,r}$$ ← divide agn by exp

$$+ \left\{\cancel{E} + \frac{2Z}{r} - \frac{l(l+1)}{r^2}\right\} g(r) = 0$$

$$\frac{d^2u}{dr^2} - 2\sqrt{-E}\frac{du}{dr} + \left[\frac{2Z}{r} - \frac{l(l+1)}{r^2}\right] u(r) = 0$$

Regrouping the terms:

$$\left[(s+N)(s+N-1) - \ell(\ell+1)\right] C_N r^{(s+N-2)}$$

$$+ \left[2Z - 2\sqrt{-E}\ (s+N-1)\right] C_{N-1}\ r^{(s+N-2)} = 0$$

$$\therefore\ C_N = \frac{\left[2\sqrt{-E}\ (s+N-1) - 2Z\right]}{(s+N)(s+N-1) - \ell(\ell+1)}\ C_{N-1}$$ a recursion relation!

In order to have an acceptable $g(r)$, must truncate the polynomial series, i.e., there must be some N, call it N_{max}, for which $C_{N_{max}} = 0$ which will make all $C_{N_{max}+1}$ (or greater) equal to zero via the recursion relation.

So let us find N_{max} that will make $C_{N_{max}} = 0$

$$C_{N_{max}} = 0 = \frac{\left[2\sqrt{-E}\ (s+N_{max}-1) - 2Z\right]}{(s+N_{max})(s+N_{max}-1) - \ell(\ell+1)}\ C_{N_{max}-1}$$

$$\therefore\ 2\sqrt{-E}\ (s+N_{max}-1) = 2Z$$

$$\text{or } E = \frac{-Z^2}{(\underset{\uparrow}{s}+\underset{\uparrow}{N_{max}}-1)^2}$$

an integer an integer

3

Note that we had previously imposed $C_{-1}=0$ and $C_0 \neq 0$ so that Poly(r) can be written as $r^s \sum_{N=0}^{\infty} C_N r^N$

What are the bounds on s ?

$$R = \frac{g(r)}{r}$$

$\therefore$ g(r) should go to zero at least as fast as r so that R(r) will not blow up.

We found $g(r) = \sum_{N=0}^{N_{max}-1} C_N r^{s+N} e^{-\sqrt{E}r}$

s can not be negative because this will give for $N=0$ $R(r) = \frac{C_0}{r^{s+1}} e^{-\sqrt{E}r}$ which blows up as $r \to 0$

s can not be zero because this will give $R(r) = \frac{C_0 e^{-\sqrt{E}r}}{r}$ which still blows up as $r \to 0$

$\therefore$ $s > 0$

Apply the recursion relation to N=0

$$C_N = \frac{[2\sqrt{-E}(s+N-1) - 2Z]}{(s+N)(s+N-1) - \ell(\ell+1)} C_{N-1}$$

$$C_0 = \frac{2\sqrt{-E}\,(s-1) - 2Z}{s(s-1) - \ell(\ell+1)} C_{-1}$$

But we have imposed the condition that $C_0 \neq 0$, that is, we need to at least have the first term in our series expansion.

Also we know that we do not have a C_{-1} since N starts at 0, 1, 2, etc.

How can both be true that $C_0 \neq 0$ but $C_{-1} = 0$??

Denominator must vanish!

$$\therefore \quad s(s-1) = \ell(\ell+1)$$

$$\text{or} \quad s = \ell + 1$$

$$\therefore \quad E = \frac{-Z^2}{(\underbrace{\ell + N_{max}}_{\text{call this integer } n})^2}$$

$N_{max} \geq 1$ in order to have at least one term in $g(r)$

$n = \ell + N_{max} \geq 1$ because $\ell \geq 0$ from solving θ part

$$0 \leq l \leq n-1 \qquad l = 0, 1, \cdots n-1$$

$$n = 1, 2, 3, \cdots$$

$$\therefore \; g(r) = r^{l+1}\left(\sum_{N=0}^{n-l-1} c_N r^N\right) e^{-\frac{Zr}{n}}$$

$$\therefore \; R_{nl}(r) = r^{l}\left(\sum_{N=0}^{n-l-1} c_N r^N\right) e^{-\frac{Zr}{n}}$$

where c_N can be found from the recursion formula.

Summary:

$$\Psi(r,\theta,\phi) = R_{nl}(r) \cdot Y_{lm}(\theta,\phi)$$

r in units of $a = \frac{\hbar^2}{\mu e^2}$

$$E = -\frac{Z^2}{n^2} \text{ in units of } \frac{e^2}{2a}$$

where $n = 1, 2, 3, \cdots$

$l = 0, 1, 2, 3, \cdots, n-1$

$m = 0, \pm 1, \pm 2, \cdots \pm l$

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
   3.1 Separation of Variables
   3.2 Eigenfunctions of the Hamiltonian and Energy Levels of H atom

EIGENFUNCTIONS of the Hamiltonian for a Hydrogen-like atom: $\Psi(r,\theta,\phi)$

$$\left(\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}\right)\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$

$$\Psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\cdot \Theta_{\ell|m|}(\theta)\cdot \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$$

This function is called an "**orbital**", that is, a function which describes ONE ELECTRON under the influence of one (or more) nuclei.

n "principal" quantum number
$1, 2, 3, \ldots$

ℓ angular momentum quantum number
$0, 1, 2, \ldots n-1$

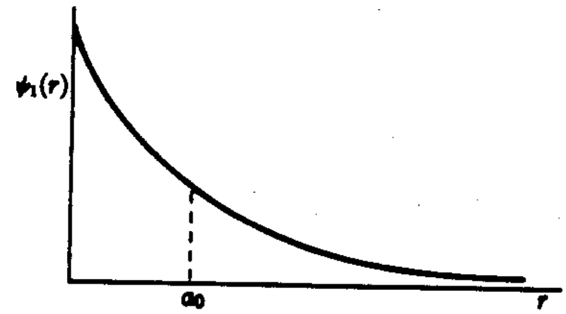
m magnetic quantum number
$0, \pm 1, \pm 2, \ldots \pm \ell$

Special names to denote functions with particular values of ℓ

$\ell = 0$ s orbital
$\ell = 1$ p orbital
$\ell = 2$ d orbital
$\ell = 3$ f orbital
$\ell = 4$ g orbital
(alphabetical)
h, i etc.

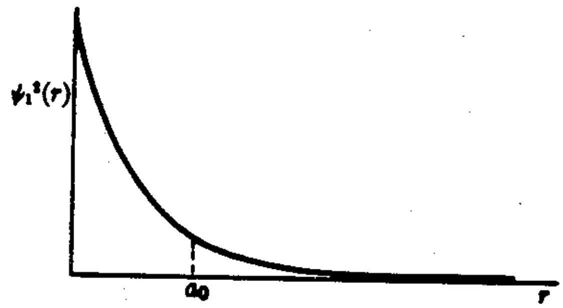
$$\psi_{100}(r,\theta,\phi) = \left(\frac{Z^3}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{Zr}{a_0}}$$

wavefunction



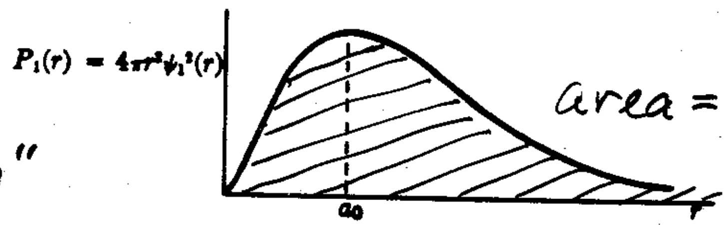
$\psi^*\psi$

probability density function



$4\pi r^2 \psi^*\psi$

"radial distribution" function



$$4\pi \int_{r=0}^{r=\infty} \psi^*\psi\, r^2 dr = 1$$

$$\underbrace{\int_0^{\pi} \sin\theta\, d\theta}_{2} \cdot \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$a_0 \equiv$ Bohr radius $\equiv \dfrac{\hbar^2}{m_e e^2}$ $\left(\text{or } \dfrac{4\pi\epsilon_0\hbar^2}{me^2} \text{ in SI units}\right)$

mass of electron

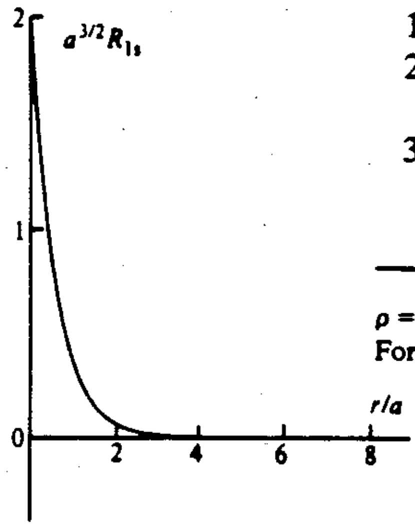
$\mu \approx m_e$ for an infinitely heavy nucleus

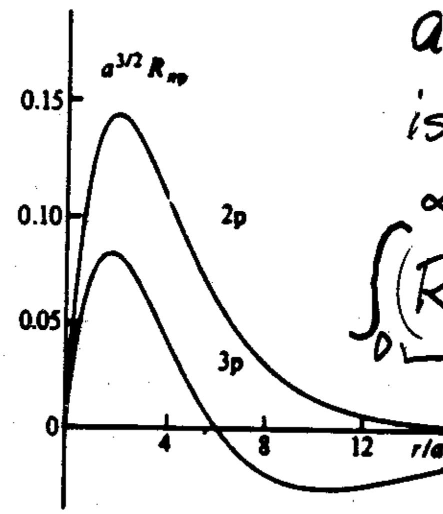
$a = \dfrac{\hbar^2}{\mu e^2}$ $\qquad \dfrac{1}{\mu} = \dfrac{1}{m_{Nucleus}} + \dfrac{1}{m_e}$

Hydrogen-like radial wavefunctions

n	l	$R_{nl}(r)$
1	0(1s)	$(Z/a)^{3/2} 2e^{-\rho/2}$
2	0(2s)	$(Z/a)^{3/2}(1/2\sqrt{2})(2-\rho)e^{-\rho/2}$
	1(2p)	$(Z/a)^{3/2}(1/2\sqrt{6})\rho e^{-\rho/2}$
3	0(3s)	$(Z/a)^{3/2}(1/9\sqrt{3})(6-6\rho+\rho^2)e^{-\rho/2}$
	1(3p)	$(Z/a)^{3/2}(1/9\sqrt{6})(4-\rho)\rho e^{-\rho/2}$
	2(3d)	$(Z/a)^{3/2}(1/9\sqrt{30})\rho^2 e^{-\rho/2}$

$\rho = (2Z/na)r$; $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$.
For an infinitely heavy nucleus $\mu = m_e$ and $a = a_0$, the Bohr radius.

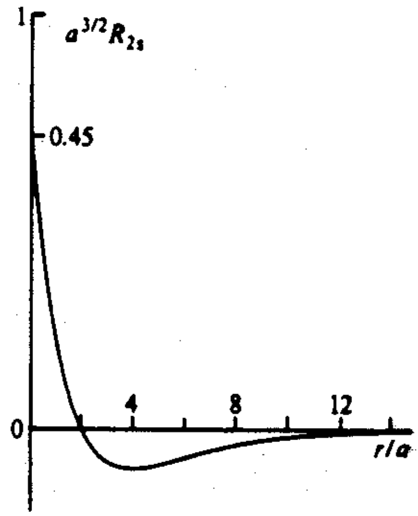


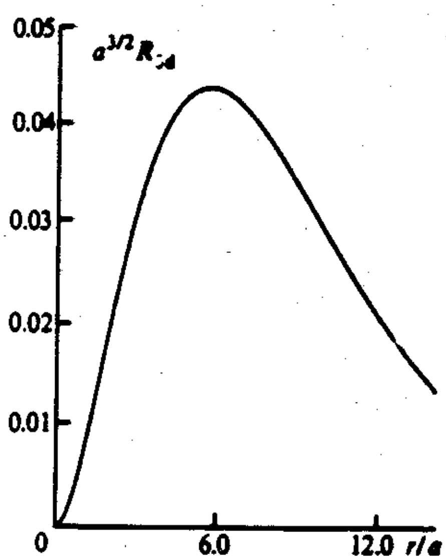


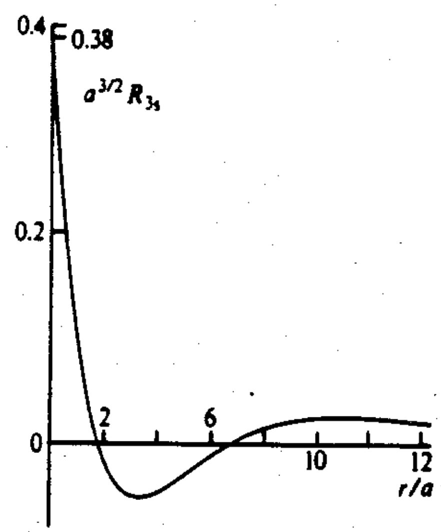
$a^{3/2} R_{n\ell}(r)$

is dimensionless

$$\int_0^\infty \underbrace{\left(R_{n\ell}(r)\right)^2}_{\frac{1}{\text{volume}}} \underbrace{r^2 dr}_{\text{volume}} = 1$$

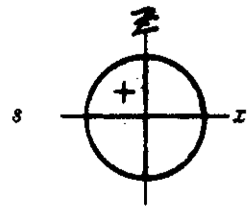






Hydrogen radial wavefunctions.

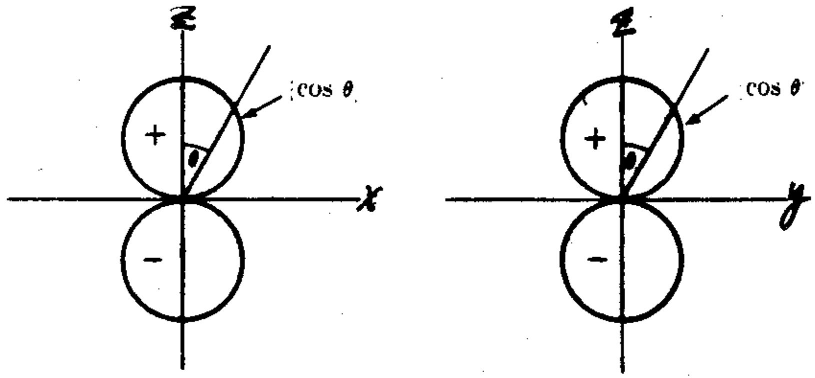
Geometric details of hydrogen-like orbitals



"s" $l=0$

$l=1$

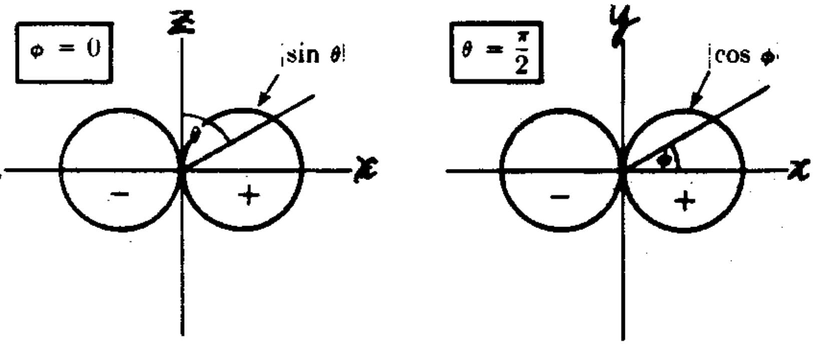
$m=0$ $p_z \sim \cos\theta$



"p_z"

LINEAR COMBINATION of $m=+1$ and $m=-1$ functions.

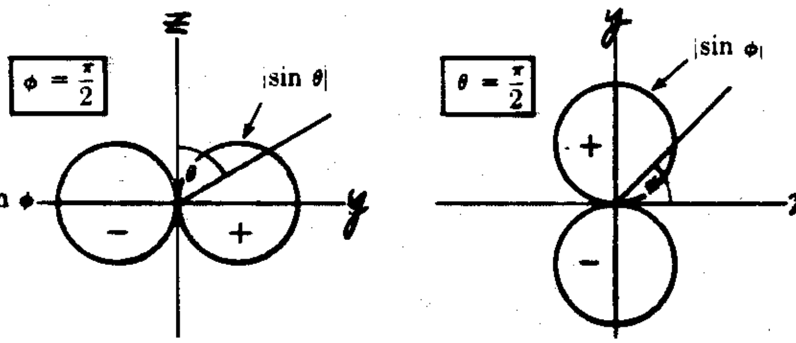
$p_x \sim \sin\theta\cos\phi$



"p_x"

OTHER LINEAR COMBINATION of $m=+1$ and $m=-1$ functions.

$p_y \sim \sin\theta\sin\phi$

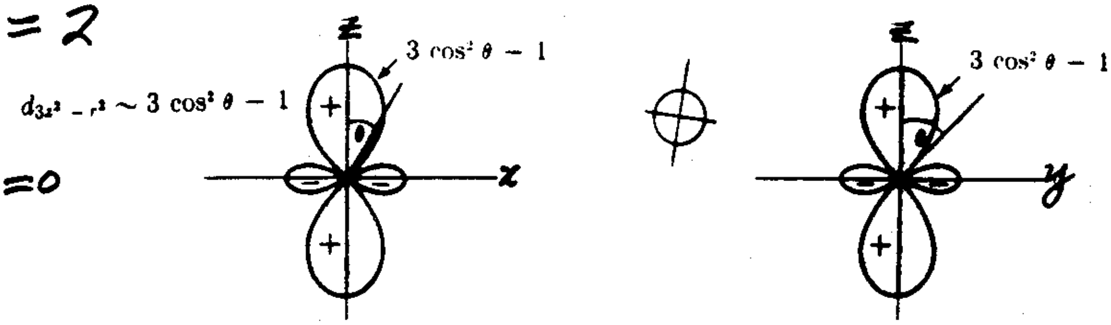


"p_y"

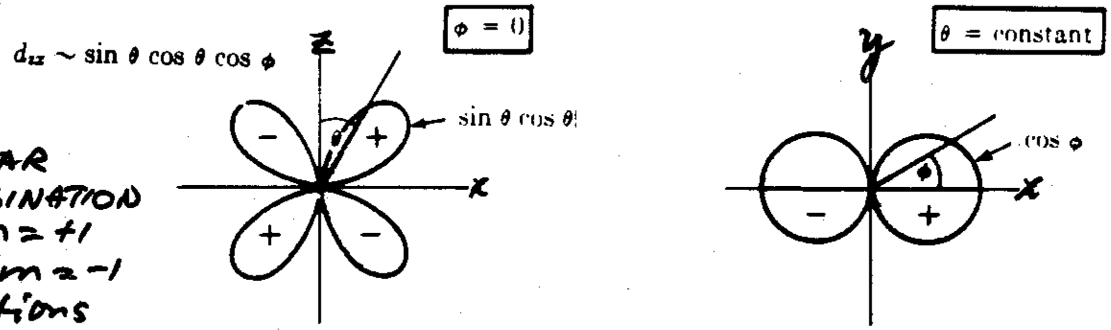
Hydrogen-atom angular wave functions; $l = 0, 1$.

$l = 2$

$m=0$

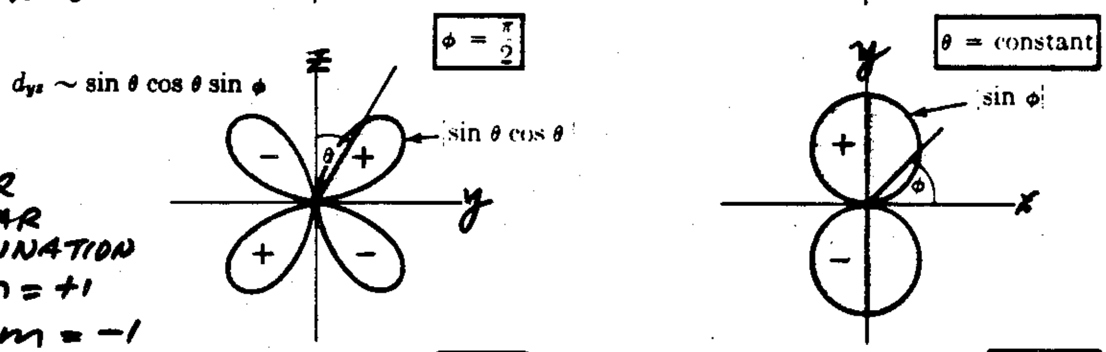


" $d_{3z^2-r^2}$ "



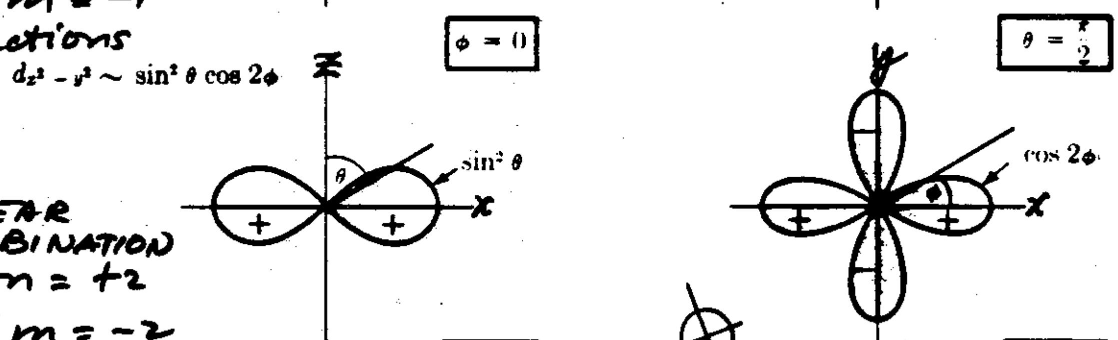
LINEAR COMBINATION of $m=+1$ and $m=-1$ functions

" d_{zx} "



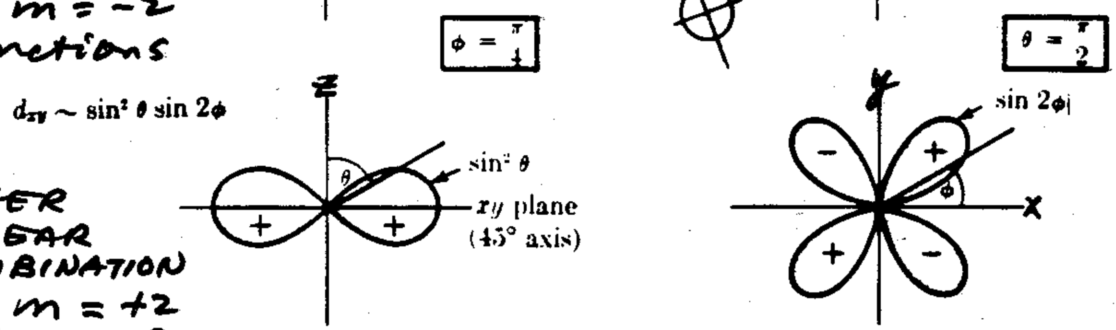
OTHER LINEAR COMBINATION of $m=+1$ and $m=-1$ functions

" d_{yz} "



LINEAR COMBINATION of $m=+2$ and $m=-2$ functions

" $d_{x^2-y^2}$ "



" d_{xy} "

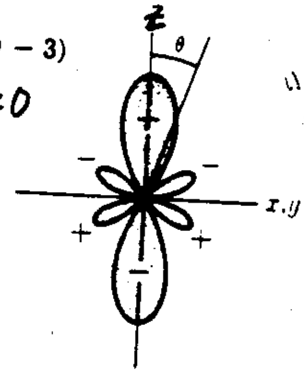
OTHER LINEAR COMBINATION of $m=+2$ and $m=-2$ functions

Hydrogen-atom angular wave functions; $l = 2$.

$l = 3$

$f_{z(5z^2-3r^2)} \sim \cos\theta\,(5\cos^2\theta - 3)$

$m=0$

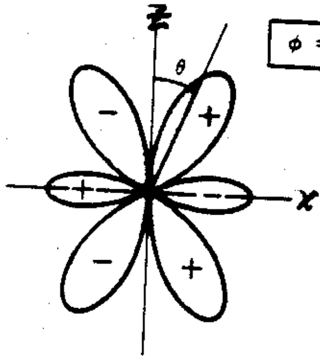


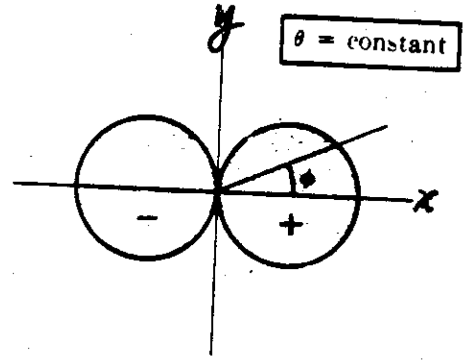
"$f_{(5z^2-3r^2)z}$"

Hydrogen-atom angular wave functions; $l = 3$.

$f_{x(5z^2-r^2)} \sim \sin\theta\,(5\cos^2\theta - 1)\cos\phi$

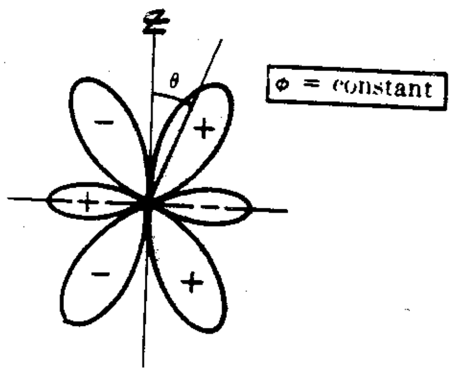
PLUS COMBINATION of $m=+1$ and $m=-1$

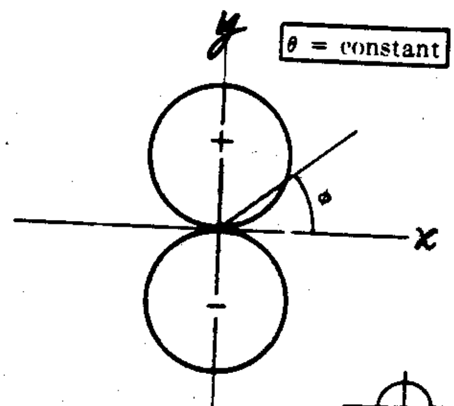




$f_{y(5z^2-r^2)} \sim \sin\theta\,(5\cos^2\theta - 1)\sin\phi$

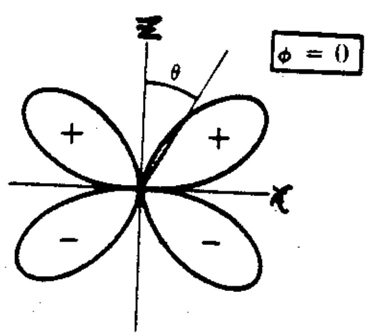
MINUS COMBINATION of $m=+1$ and $m=-1$

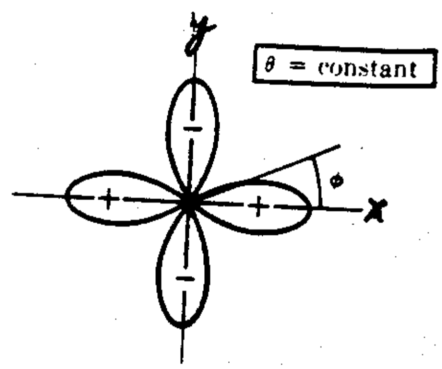




$f_{z(x^2-y^2)} \sim \sin^2\theta\cos\theta\cos 2\phi$

PLUS COMBINATION of $m=+2$ and $m=-2$

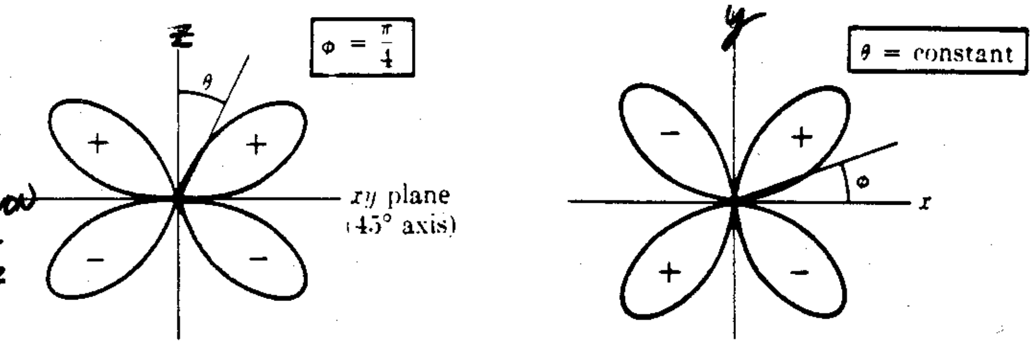




Geometric details of hydrogen-like orbitals

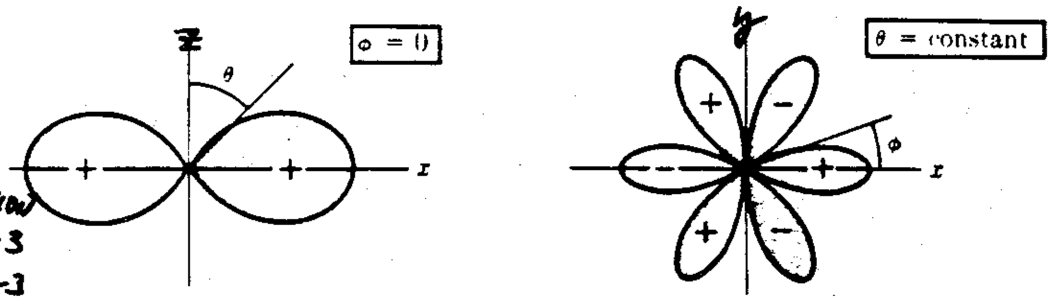
$f_{zxy} \sim \sin^2\theta \cos\theta \sin 2\phi$

MINUS COMBINATION OF $m=+2$ and $m=-2$



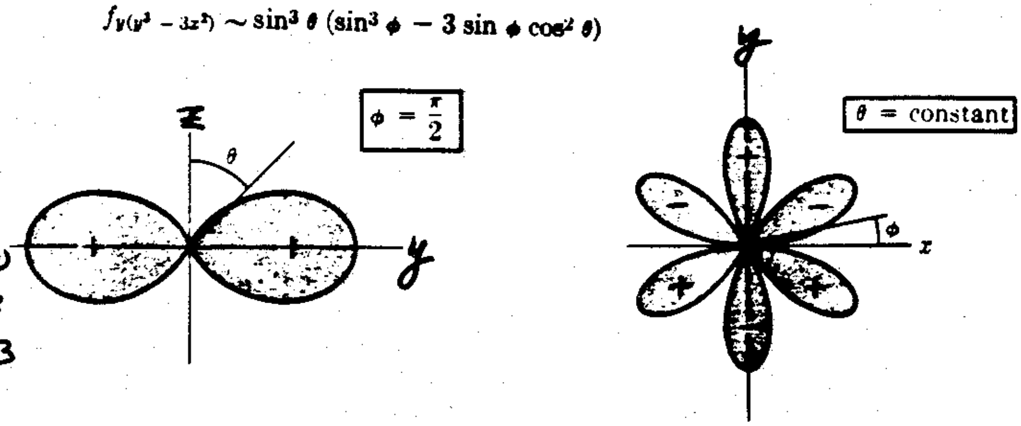
$f_{x(x^2-3y^2)} \sim \sin^3\theta\,(\cos^3\phi - 3\sin^2\phi\cos\phi)$

PLUS COMBINATION of $m=+3$ and $m=-3$

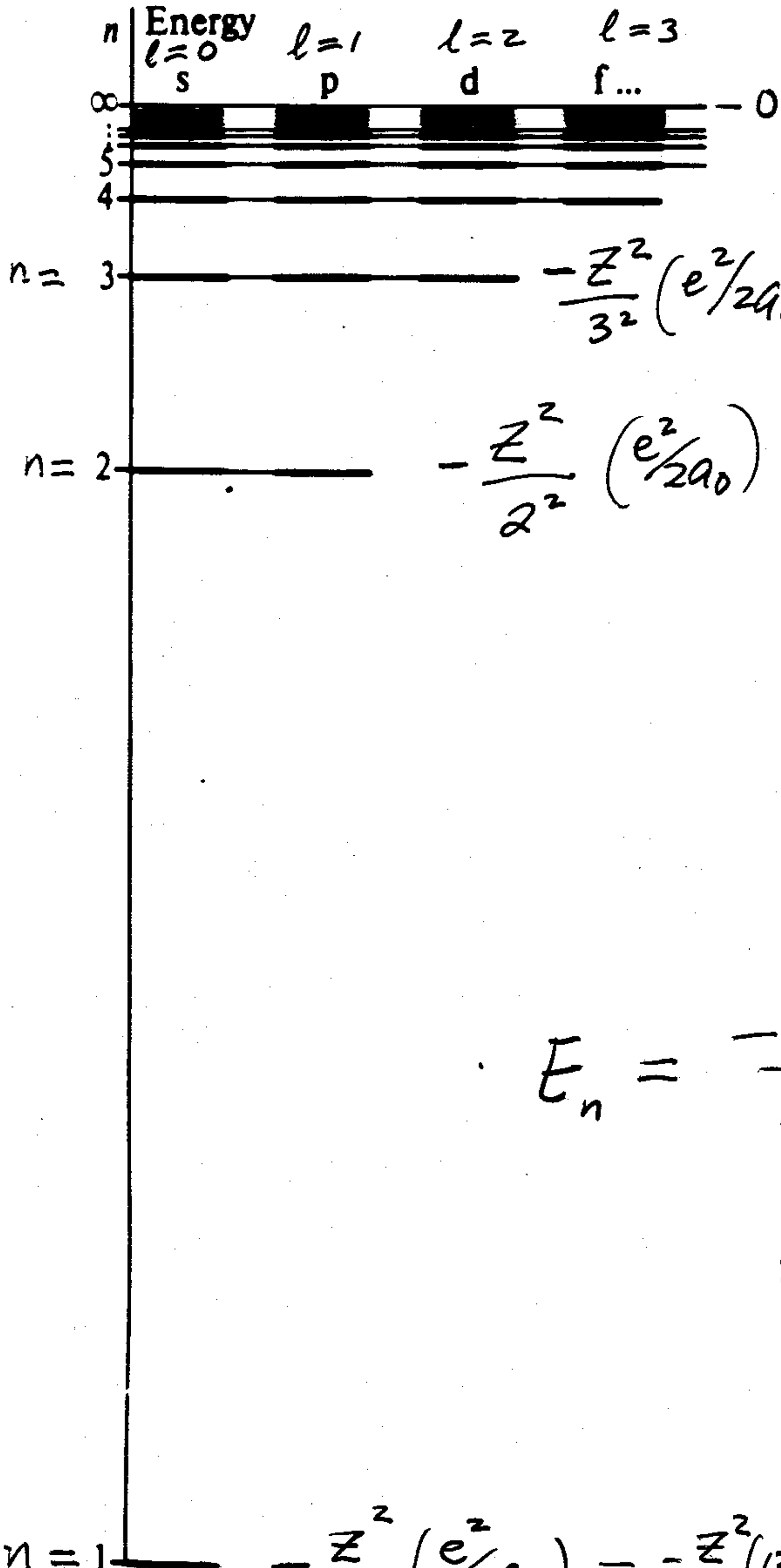


$f_{y(y^2-3x^2)} \sim \sin^3\theta\,(\sin^3\phi - 3\sin\phi\cos^2\theta)$

MINUS COMBINATION Of $m=+3$ and $m=-3$



The energy levels of atomic hydrogen.



$$-\frac{Z^2}{4^2}\left(e^2/2a_0\right)$$

$$-\frac{Z^2}{3^2}\left(e^2/2a_0\right)$$

$$-\frac{Z^2}{2^2}\left(e^2/2a_0\right)$$

$$E_n = \frac{-Z^2}{n^2}\left(e^2/2a\right)$$

where

$$a = \frac{\hbar^2}{\mu e^2} \qquad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$

$$a_0 = \frac{\hbar^2}{m_e e^2}$$

$$-\frac{Z^2}{1^2}\left(e^2/2a_0\right) = -Z^2(13.6\ \text{electronvolts})$$

States of one-electron atoms

n	l	$\lvert m\rvert$	Spectroscopic designation	E_n in units of $e^2/2a_0$	g	$\psi_{n,l,m}(r, \theta, \phi)$
1	0	0	$1s$	-1	1	$N_1 \exp(-Zr/a_0)$
2	0	0	$2s$	$-\frac{1}{4}$		$N_2(2 - Zr/a_0) \exp(-Zr/2a_0)$
2	1	0	$2p_z$	$-\frac{1}{4}$	4	$N_2(Zr/a_0) \exp(-Zr/2a_0) \cos\theta$
2	1	1, cos	$2p_x$	$-\frac{1}{4}$		$N_2(Zr/a_0) \exp(-Zr/2a_0) \sin\theta \cos\phi$
2	1	1, sin	$2p_y$	$-\frac{1}{4}$		$N_2(Zr/a_0) \exp(-Zr/2a_0) \sin\theta \sin\phi$
3	0	0	$3s$	$-\frac{1}{9}$		$N_3[27 - 18(Zr/a_0) + 2(Zr/a_0)^2] \exp(-Zr/3a_0)$
3	1	0	$3p_z$	$-\frac{1}{9}$		$N_3\sqrt{6}\,(6 - Zr/a_0)(Zr/a_0) \exp(-Zr/3a_0) \cos\theta$
3	1	1, cos	$3p_x$	$-\frac{1}{9}$		$N_3\sqrt{6}\,(6 - Zr/a_0)(Zr/a_0) \exp(-Zr/3a_0) \sin\theta \cos\phi$
3	1	1, sin	$3p_y$	$-\frac{1}{9}$	9	$N_3\sqrt{6}\,(6 - Zr/a_0)(Zr/a_0) \exp(-Zr/3a_0) \sin\theta \cos\phi$
3	2	0	$3d_{3z^2-r^2}$	$-\frac{1}{9}$		$N_3\sqrt{1/2}(Zr/a_0)^2 \exp(-Zr/3a_0)(3\cos^2\theta - 1)$
3	2	1, cos	$3d_{xz}$	$-\frac{1}{9}$		$N_3\sqrt{6}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin\theta \cos\theta \cos\phi$
3	2	1, sin	$3d_{yz}$	$-\frac{1}{9}$		$N_3\sqrt{6}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin\theta \cos\theta \sin\phi$
3	2	2, cos	$3d_{x^2-y^2}$	$-\frac{1}{9}$		$N_3\sqrt{3/2}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin^2\theta \cos 2\phi$
3	2	2, sin	$3d_{xy}$	$-\frac{1}{9}$		$N_3\sqrt{3/2}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin^2\theta \sin 2\phi$

$$N_1 = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}, \qquad N_2 = \frac{1}{4}\left(\frac{Z^3}{2\pi a_0^3}\right)^{1/2}, \qquad N_3 = \frac{1}{81}\left(\frac{Z^3}{3\pi a_0^3}\right)^{1/2}$$

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. **MATRIX REPRESENTATION OF QUANTUM MECHANICS**
   - **4.1 Matrix Representation of an Operator**
   - 4.2 Matrix Representation of an Operator Equation
   - 4.3 Solving the Matrix Equation that Represents the Operator Equation $\mathcal{H}\Psi = E\Psi$

	vectors in 3-dimensional Euclidean geometric space	vectors in n-dimensional Hilbert space
• a set of linearly independent (ORTHONORMAL) basis vectors	$\hat{\imath} \quad \hat{\jmath} \quad \hat{k}$ $\hat{\imath} \cdot \hat{\jmath} = \delta_{ij}$	$\phi_1 \quad \phi_2 \quad \phi_3 \cdots \phi_n$ $\int \phi_i^* \phi_j \, d\tau = \delta_{ij}$
• any vector can be expressed as a linear combination of basis vectors	$\vec{V} = V_x \hat{\imath} + V_y \hat{\jmath} + V_z \hat{k}$	$\Psi = \sum_i^n c_i \phi_i$
• scalar or dot product of two vectors	$\vec{V} \cdot \vec{V}' = V_x V_x' + V_y V_y' + V_z V_z'$	$\int \Psi^* \Psi' d\tau = \sum_i^n c_i^* c_i'$
• There exist transformations T which when applied to a vector, turn it into another vector. A linear transformation gives a new vector which can be expressed as linear combinations of the components of the original vector	$T\vec{V} = \vec{V}'$ when T is a counterclockwise rotation by angle θ $V_x' = V_x \cos\theta - V_y \sin\theta$ $V_y' = V_x \sin\theta + V_y \cos\theta$	$T_{op}\Psi = \Psi'$ $= \sum_i^n c_i T_{op}\phi_i$ $\sum_k^n b_{ik}\phi_k$ $= \sum_k^n \underbrace{\sum_i^n c_i b_{ik}}_{\text{call this } d_k} \phi_k$ $= \sum_k^n d_k \phi_k$
• Representation of a vector by a matrix	$\vec{V} = \begin{pmatrix} V_x \\ V_y \\ V_z \end{pmatrix}$ $\hat{\imath} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$\Psi = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{pmatrix}$ $\phi_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$
• Representation of transformations T or of operators T_{op} by a matrix	$T = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$	$T = \begin{pmatrix} T_{11} & T_{12} & T_{13} & \cdots \\ T_{21} & T_{22} & T_{23} & \cdots \\ \vdots & \vdots & \vdots & \end{pmatrix}$ where $T_{ij} = \int \phi_i^* T_{op} \phi_j \, d\tau$

MATRICES IN QUANTUM MECHANICS

A **MATRIX** is an array of <u>numbers</u> which obey certain rules.

EQUALITY
ADDITION
MULTIPLICATION by a SCALAR
MATRIX MULTIPLICATION

In Quantum Mechanics these numbers are INTEGRALS.

THE ENTIRE ARRAY OF NUMBERS REPRESENTS A QUANTUM MECHANICAL OPERATOR

For example, consider the operator F_{op} and a complete set of functions $\{\phi\}$

$$\mathbf{F} = \begin{array}{cc} & \begin{array}{cccc} \text{COLUMN } 1 & \text{COLUMN } 2 & \text{COLUMN } 3 & \end{array} \\ \begin{array}{c} \text{ROW } 1 \\ \text{ROW } 2 \\ \text{ROW } 3 \\ \\ \end{array} & \left[\begin{array}{c|c|c|c} \int \phi_1^* F_{op} \phi_1 d\tau & \int \phi_1^* F_{op} \phi_2 d\tau & \int \phi_1^* F_{op} \phi_3 d\tau & \cdots \\ \hline \int \phi_2^* F_{op} \phi_1 d\tau & \int \phi_2^* F_{op} \phi_2 d\tau & \int \phi_2^* F_{op} \phi_3 d\tau & \cdots \\ \hline \int \phi_3^* F_{op} \phi_1 d\tau & \int \phi_3^* F_{op} \phi_2 d\tau & \int \phi_3^* F_{op} \phi_3 d\tau & \cdots \\ \hline \vdots & \vdots & \vdots & \end{array} \right] \end{array}$$

$$\mathbf{F}_{32} = \int \phi_3^* F_{op} \phi_2 d\tau$$ is called a "MATRIX ELEMENT"

$\uparrow$ ROW $\uparrow$ COLUMN

The **MATRIX F** is said to REPRESENT the OPERATOR F_{op} USING AS A BASIS the SET OF FUNCTIONS $\{\phi\}$

For example:

Suppose we have the operators

$$I_x \qquad I_y \qquad I_z$$

and the complete set of functions

ORTHONORMAL COMPLETE SET $\{\alpha \quad \beta\}$ (only two in the set)

Suppose also that these are related by the following equations:

$$I_z\alpha = \left(\frac{\hbar}{2}\right)\alpha \qquad I_z\beta = \left(-\frac{\hbar}{2}\right)\beta$$

$$I_x\alpha = \left(\frac{\hbar}{2}\right)\beta \qquad I_x\beta = \left(\frac{\hbar}{2}\right)\alpha$$

$$I_y\alpha = \left(+\frac{i\hbar}{2}\right)\beta \qquad I_y\beta = \left(-\frac{i\hbar}{2}\right)\alpha$$

What are the MATRIX REPRESENTATIONS of the OPERATORS I_x, I_y, and I_z?

$$\mathbf{I_x} = \begin{bmatrix} \int\alpha^* I_x\alpha\, d\tau & \int\alpha^* I_x\beta\, d\tau \\ \int\beta^* I_x\alpha\, d\tau & \int\beta^* I_x\beta\, d\tau \end{bmatrix} = \begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix}$$

$$\mathbf{I_y} = \begin{bmatrix} \int\alpha^* I_y\alpha\, d\tau & \int\alpha^* I_y\beta\, d\tau \\ \int\beta^* I_y\alpha\, d\tau & \int\beta^* I_y\beta\, d\tau \end{bmatrix} = \begin{bmatrix} 0 & -\frac{i\hbar}{2} \\ +\frac{i\hbar}{2} & 0 \end{bmatrix}$$

$$\mathbf{I_z} = \begin{bmatrix} \int\alpha^* I_z\alpha\, d\tau & \int\alpha^* I_z\beta\, d\tau \\ \int\beta^* I_z\alpha\, d\tau & \int\beta^* I_z\beta\, d\tau \end{bmatrix} = \begin{bmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{bmatrix}$$

MATRIX REPRESENTATION means that THE OPERATORS AND THE MATRICES REPRESENTING THEM OBEY THE SAME RULES

1. MULTIPLICATION BY A SCALAR QUANTITY:

$$i\,I_y = \begin{bmatrix} i(0) & i\left(\frac{-i\hbar}{2}\right) \\ i\left(\frac{+i\hbar}{2}\right) & i(0) \end{bmatrix} = \begin{bmatrix} 0 & +\hbar/2 \\ -\frac{\hbar}{2} & 0 \end{bmatrix}$$

EVERY MATRIX ELEMENT HAS TO BE MULTIPLIED BY THE SCALAR

2. ADDITION:

$$I_x + iI_y = \begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix} + \begin{bmatrix} 0 & +\frac{\hbar}{2} \\ -\frac{\hbar}{2} & 0 \end{bmatrix} \underset{\text{ELEMENTS}}{\overset{\text{ADD}}{\underline{\text{CORRESPONDING}}}} \begin{bmatrix} 0 & \hbar \\ 0 & 0 \end{bmatrix}$$

$\int \beta^* (I_x + iI_y)\beta\, d\tau$

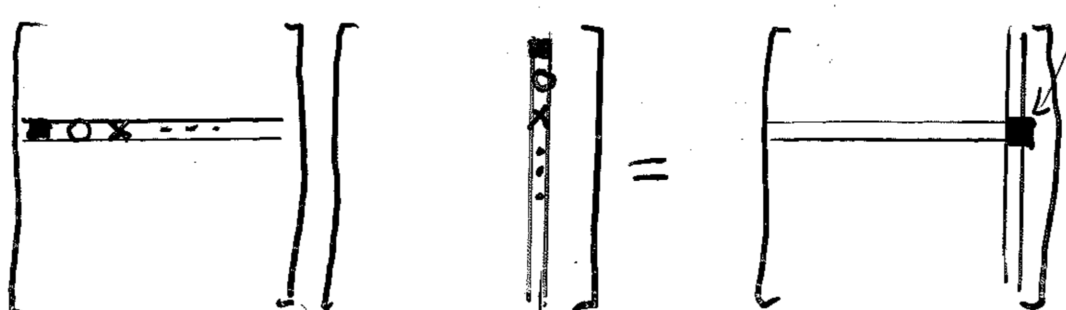
3. MATRIX MULTIPLICATION:

$$I_x I_y = \begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix} \begin{bmatrix} 0 & -\frac{i\hbar}{2} \\ +\frac{i\hbar}{2} & 0 \end{bmatrix} = ?$$

$$(FG)_{rc} = \sum_i F_{ri}\, G_{ic}$$

row column row column

$\int \phi_r^* F_{op} G_{op} \phi_c\, d\tau$



F G FG

PRODUCT

4. EQUALITY: CORRESPONDING MATRIX ELEMENTS ARE EQUAL.

$(\mathbf{FG})_{rc}$

$$\int \phi_r^* F_{op} \underbrace{G_{op} \phi_c}\, d\tau = \int \phi_r^* F_{op} (c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \dots) d\tau$$

a new function
EXPAND IT
in terms of the
COMPLETE SET

$$G_{op} \phi_c = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots$$

$$\int \phi_1^* G_{op} \phi_c \, d\tau = c_1$$

$$= \int \phi_r^* F_{op} \phi_1 d\tau \cdot \int \phi_1^* G_{op} \phi_c d\tau$$
$$+ \int \phi_r^* F_{op} \phi_2 d\tau \cdot \int \phi_2^* G_{op} \phi_c d\tau$$
$$+ \int \phi_r^* F_{op} \phi_3 d\tau \cdot \int \phi_3^* G_{op} \phi_c d\tau \quad + \cdots$$

$$(\mathbf{FG})_{rc} = \underbrace{\mathbf{F}_{r1} \mathbf{G}_{1c}} + \mathbf{F}_{r2} \mathbf{G}_{2c} + \mathbf{F}_{r3} \mathbf{G}_{3c} + \cdots$$ ALL ADDED TOGETHER

Product of element 1 of row r and element 1 of column c

element 2

element 3

MATRIX MULTIPLICATION IS <u>NOT</u> IN GENERAL COMMUTATIVE.

just as
QUANTUM MECHANICAL OPERATORS DO <u>NOT</u> IN GENERAL COMMUTE.

FG is not always
the same as **GF**

just as $F_{op} G_{op} \psi$ is not always
the same as $G_{op} F_{op} \psi$

Example: Does I_x commute with I_y?

OPERATORS: $[I_x, I_y] = I_x I_y - I_y I_x = ?$ Let us see:

$$I_x I_y \alpha = I_x\left(\frac{i\hbar}{2}\beta\right) = \frac{i\hbar}{2} I_x \beta = \frac{i\hbar}{2}\left(\frac{\hbar}{2}\alpha\right) = \frac{i\hbar^2}{4}\alpha$$

$$I_y I_x \alpha = I_y\left(\frac{\hbar}{2}\beta\right) = \frac{\hbar}{2} I_y \beta = \frac{\hbar}{2}\left(-\frac{i\hbar}{2}\alpha\right) = \frac{-i\hbar^2}{4}\alpha$$

$$\therefore (I_x I_y - I_y I_x)\alpha = \left\{\frac{i\hbar^2}{4} - \left(-\frac{i\hbar^2}{4}\right)\right\}\alpha = \frac{i\hbar^2}{2}\alpha = i\hbar I_z \alpha$$

$$[I_x, I_y] = i\hbar I_z$$

MATRICES: $\mathbf{I_x I_y - I_y I_x = ?}$

$$\mathbf{I_x I_y} = \begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix} \begin{bmatrix} 0 & -\frac{i\hbar}{2} \\ \frac{i\hbar}{2} & 0 \end{bmatrix} = \begin{bmatrix} 0\cdot 0 + \frac{\hbar}{2}\left(\frac{i\hbar}{2}\right) & 0\left(-\frac{i\hbar}{2}\right) + \frac{\hbar}{2}(0) \\ \frac{\hbar}{2}(0) + 0\left(\frac{i\hbar}{2}\right) & \frac{\hbar}{2}\left(-\frac{i\hbar}{2}\right) + 0\cdot 0 \end{bmatrix}$$

$$= \begin{bmatrix} \frac{i\hbar^2}{4} & 0 \\ 0 & -\frac{i\hbar^2}{4} \end{bmatrix}$$

$$\mathbf{I_y I_x} = \begin{bmatrix} 0 & -\frac{i\hbar}{2} \\ \frac{i\hbar}{2} & 0 \end{bmatrix} \begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix} = \begin{bmatrix} 0.0 + \left(-\frac{i\hbar}{2}\right)\left(\frac{\hbar}{2}\right) & 0\left(\frac{\hbar}{2}\right) + \left(-\frac{i\hbar}{2}\right)0 \\ \frac{i\hbar}{2}(0) + 0\left(\frac{\hbar}{2}\right) & \frac{i\hbar}{2}\left(\frac{\hbar}{2}\right) + 0.0 \end{bmatrix}$$

$$= \begin{bmatrix} -\frac{i\hbar^2}{4} & 0 \\ 0 & \frac{i\hbar^2}{4} \end{bmatrix}$$

$$\mathbf{I_x I_y - I_y I_x} = \begin{bmatrix} \frac{i\hbar^2}{2} & 0 \\ 0 & -\frac{i\hbar^2}{2} \end{bmatrix} = i\hbar \begin{bmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{bmatrix} = i\hbar \mathbf{I_z}$$

The OPERATORS I_x, I_y, I_z are represented by the

MATRICES $\mathbf{I_x}$, $\mathbf{I_y}$, and $\mathbf{I_z}$.

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
   4.1 Matrix Representation of an Operator
   4.2 Matrix Representation of an Operator Equation
   4.3 Solving the Matrix Equation that Represents the Operator Equation $\mathcal{H}\Psi = E\Psi$

MATRIX REPRESENTATION of STATE FUNCTIONS

$$\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots$$

NORMALIZE it, that is, $c_1^*c_1 + c_2^*c_2 + c_3^*c_3 + \cdots = 1$

If the ORTHONORMAL COMPLETE SET of FUNCTIONS $\{\phi\}$ is used as the BASIS for the MATRIX REPRESENTATION of OPERATORS, then the same set of functions can be used as the BASIS for the MATRIX REPRESENTATION of WAVEFUNCTIONS Ψ.

Represent Ψ by the ARRAY OF NUMBERS:

$$\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

<u>Example</u>: The EIGENFUNCTIONS of the operator I_x in MATRIX form

The functions which are the EIGENFUNCTIONS of I_x can be written as an EXPANSION in the ORTHONORMAL COMPLETE SET of FUNCTIONS which are the EIGENFUNCTIONS of I_z, that is, the functions α and β.

These are the EIGENFUNCTIONS OF I_x → $\psi_1 = \frac{1}{\sqrt{2}}\alpha + \frac{1}{\sqrt{2}}\beta \qquad \psi_2 = \frac{1}{\sqrt{2}}\alpha - \frac{1}{\sqrt{2}}\beta$

Let us see if these are correct:

$$I_x\psi_1 = I_x\left(\tfrac{1}{\sqrt{2}}\alpha + \tfrac{1}{\sqrt{2}}\beta\right) = \tfrac{1}{\sqrt{2}}\left(I_x\alpha + I_x\beta\right)$$
$$= \tfrac{1}{\sqrt{2}}\left(\tfrac{\hbar}{2}\beta + \tfrac{\hbar}{2}\alpha\right) = \tfrac{\hbar}{2}\left(\tfrac{1}{\sqrt{2}}\alpha + \tfrac{1}{\sqrt{2}}\beta\right) = \underbrace{\tfrac{\hbar}{2}}_{\text{EIGENVALUE}}\psi_1$$

$$I_x\psi_2 = I_x\left(\tfrac{1}{\sqrt{2}}\alpha - \tfrac{1}{\sqrt{2}}\beta\right) = \tfrac{1}{\sqrt{2}}\left(I_x\alpha - I_x\beta\right)$$
$$= \tfrac{1}{\sqrt{2}}\left(\tfrac{\hbar}{2}\beta - \tfrac{\hbar}{2}\alpha\right) = -\tfrac{\hbar}{2}\left(\tfrac{1}{\sqrt{2}}\alpha - \tfrac{1}{\sqrt{2}}\beta\right) = \underbrace{-\tfrac{\hbar}{2}}_{\text{EIGENVALUE}}\psi_2$$

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
   4.1 Matrix Representation of an Operator
   4.2 Matrix Representation of an Operator Equation
   4.3 Solving the Matrix Equation that Represents the Operator Equation $\mathcal{H}\Psi = E\Psi$

$\psi_1 = \frac{1}{\sqrt{2}}\alpha + \frac{1}{\sqrt{2}}\beta \qquad \psi_2 = \frac{1}{\sqrt{2}}\alpha - \frac{1}{\sqrt{2}}\beta$

The MATRIX REPRESENTATION of ψ_1 and ψ_2 are

ψ_1 is $\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \qquad \psi_2$ is $\begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix}$

The **MATRIX REPRESENTATION** of the equation

$$I_x \psi_1 = \frac{\hbar}{2}\psi_1$$

is

$$\begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 0\left(\frac{1}{\sqrt{2}}\right) + \frac{\hbar}{2}\left(\frac{1}{\sqrt{2}}\right) \\ \frac{\hbar}{2}\left(\frac{1}{\sqrt{2}}\right) + 0\left(\frac{1}{\sqrt{2}}\right) \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$$

$$I_x \quad \psi_1 \quad = \quad \frac{\hbar}{2}\psi_1$$

The MATRIX REPRESENTATION of the equation

$$I_x \psi_2 = -\frac{\hbar}{2}\psi_2$$

is

$$\begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 0\left(\frac{1}{\sqrt{2}}\right) + \frac{\hbar}{2}\left(-\frac{1}{\sqrt{2}}\right) \\ \frac{\hbar}{2}\left(\frac{1}{\sqrt{2}}\right) + 0\left(-\frac{1}{\sqrt{2}}\right) \end{bmatrix} = -\frac{\hbar}{2}\begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix}$$

$$I_x \quad \psi_2 \quad = \quad -\frac{\hbar}{2}\psi_2$$

IN GENERAL, for the OPERATOR F_{op} whose EIGENFUNCTION is ψ_1 with EIGENVALUE a_1 the differential equation is:

$$F_{op}\psi_1 = a_1\psi_1$$

the MATRIX REPRESENTATION

$$\mathbf{F}\psi_1 = a_1\psi_1$$

$$\begin{bmatrix} F_{11} & F_{12} & \cdots \\ F_{21} & F_{22} & \cdots \\ \vdots & \vdots & \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} = a_1 \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

reads as follows: (following the rules of MATRIX MULTIPLICATION)

row 1 → $F_{11}\boxed{c_1} + F_{12}c_2 + F_{13}c_3 + \cdots = a_1\boxed{c_1}$

row 2 $F_{21}c_1 + F_{22}c_2 + F_{23}c_3 + \cdots = a_1 c_2$

row 3 $F_{31}c_1 + F_{32}c_2 + F_{33}c_3 + \cdots = a_1 c_3$

THESE LOOK LIKE SIMULTANEOUS LINEAR EQUATIONS

$$\left.\begin{array}{l}(F_{11}-a_1)c_1 + F_{12}c_2 + F_{13}c_3 + \cdots = 0 \\ F_{21}c_1 + (F_{22}-a_1)c_2 + F_{23}c_3 + \cdots = 0 \\ F_{31}c_1 + F_{32}c_2 + (F_{33}-a_1)c_3 + \cdots = 0 \\ \vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad = 0 \\ \qquad\qquad\qquad\qquad\quad = 0 \\ \qquad\qquad\qquad\qquad\quad = 0\end{array}\right\}$$

From your algebra class,

$$\left.\begin{array}{l}b_{11}x + b_{12}y + b_{13}z = 0 \\ b_{21}x + b_{22}y + b_{23}z = 0 \\ b_{31}x + b_{32}y + b_{33}z = 0\end{array}\right\} \text{Solve for } x, y, z$$

$x=0$ $y=0$ $z=0$ is a "TRIVIAL" solution
Any others? NON-TRIVIAL solutions can be found **IF and ONLY IF**

$$\textbf{det}\begin{vmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{vmatrix} = 0$$

Similarly our simultaneous equations with unknowns $c_1, c_2, c_3 \cdots$ and a_1 has a solution other than $c_1=0, c_2=0, c_3=0, \cdots$

IF and ONLY IF

$$\textbf{det}\begin{vmatrix} F_{11}-a_1 & F_{12} & F_{13} & F_{14} & \cdots \\ F_{21} & F_{22}-a_1 & F_{23} & F_{24} & \cdots \\ F_{31} & F_{32} & F_{33}-a_1 & F_{34} & \cdots \end{vmatrix} = 0$$

Example: The operator equation to be solved is $I_x \psi_1 = a_1 \psi_1$

MATRIX REPRESENTATION is

$$\mathbf{I_x} = \begin{bmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{bmatrix} \qquad \psi_1 = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$$\mathbf{I_x} \psi_1 = a_1 \psi_1$$

reads as follows:

$$(I_x)_{11} c_1 + (I_x)_{12} c_2 = a_1 c_1$$
$$(I_x)_{21} c_1 + (I_x)_{22} c_2 = a_1 c_2$$

Rearranging we get,

$$\left.\begin{aligned} ((I_x)_{11} - a_1) c_1 + (I_x)_{12} c_2 &= 0 \\ (I_x)_{21} c_1 + ((I_x)_{22} - a_1) c_2 &= 0 \end{aligned}\right\} \text{SIMULTANEOUS LINEAR EQUATIONS}$$

Unknowns c_1, c_2, a_1. Non-trivial solution exists if and only if the determinant

$$\det \begin{vmatrix} 0-a_1 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0-a_1 \end{vmatrix} = 0$$

Evaluate the determinant:

$$(0-a_1)(0-a_1) - \left(\frac{\hbar}{2}\right)\left(\frac{\hbar}{2}\right) = 0 \quad \text{or} \quad a_1^2 = \left(\frac{\hbar}{2}\right)^2$$

$a_1 = \frac{\hbar}{2}$ ONE EIGENVALUE

OR $-\frac{\hbar}{2}$ ALSO AN EIGENVALUE.

SOLVING THE MATRIX EQUATION THAT REPRESENTS THE OPERATOR EQUATION YIELDS ALL THE EIGENVALUES OF THE OPERATOR !!!

Evaluating the 2X2 DETERMINANT leads to a quadratic equation in the EIGENVALUES of the **MATRIX** representing the OPERATOR. The ROOTS of the quadratic equation are the 2 values of the EIGENVALUES of the OPERATOR.

If it had been a 3X3 DETERMINANT, it would lead to a cubic equation:

$$\sim \underline{E}^3 + \sim \underline{E}^2 + \sim \underline{E} + \sim = 0$$

which would have 3 ROOTS, which are the 3 EIGENVALUES of the OPERATOR

Let us go back to our example:

Once the values

$$a_1 = \hbar/2$$

$$a_2 = -\hbar/2$$

are found, we can put them back into the simultaneous linear equations:

$$(0 - a_1)c_1 + \frac{\hbar}{2}c_2 = 0$$

$$\frac{\hbar}{2}c_1 + (0 - a_1)c_2 = 0$$

in order to solve for c_1 and c_2. Let us do it:

For $a_1 = \hbar/2$:

$$(0 - \frac{\hbar}{2})c_1 + \frac{\hbar}{2}c_2 = 0$$

or $c_1 = c_2$ But we also know $c_1^2 + c_2^2 = 1$

For $a_2 = -\hbar/2$:

$$(0 - -\frac{\hbar}{2})c_1 + \frac{\hbar}{2}c_2 = 0$$

or $c_1 = -c_2$

For $a_1 = \frac{\hbar}{2}$

We found $c_1 = c_2$

substitute this into

$c_1^2 + c_2^2 = 1$

we get

$c_1^2 + c_1^2 = 1$

or $c_1 = \frac{1}{\sqrt{2}}$

$c_2 = c_1 = \frac{1}{\sqrt{2}}$

$\psi_1 = c_1\phi_1 + c_2\phi_2$

Normalization condition:

$$\int \psi_1^* \psi_1 \, d\tau = 1 = \int (c_1^*\phi_1^* + c_2^*\phi_2^*)(c_1\phi_1 + c_2\phi_2)\, d\tau$$

$$= c_1^2 \underbrace{\int \phi_1^* \phi_1 \, d\tau}_{1} + c_2^2 \underbrace{\int \phi_2^* \phi_2 \, d\tau}_{1}$$

\+ all others are zero since ϕ_1 and ϕ_2 are an ORTHONORMAL set of functions

$$1 = c_1^2 + c_2^2$$

$\psi_1 = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{2}}\phi_2$ EIGENFUNCTION

$$\psi_1 = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \quad \text{for } a_1 = \frac{\hbar}{2} \text{ EIGENVALUE}$$

SUBSTITUTING THE EIGENVALUE INTO THE LINEAR EQUATIONS YIELDS THE CORRESPONDING EIGENFUNCTION

For $a_2 = -\frac{\hbar}{2}$

We found $c_1 = -c_2$

Substitute this into

$c_1^2 + c_2^2 = 1$

We get

$c_1^2 + (-c_1)^2 = 1$

or $c_1 = \frac{1}{\sqrt{2}}$

$c_2 = -c_1 = -\frac{1}{\sqrt{2}}$

$\psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_2$ EIGENFUNCTION

$$\psi_2 = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix} \quad \text{for } a_2 = -\frac{\hbar}{2} \text{ EIGENVALUE}$$

$$\det\begin{vmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{vmatrix} = D_{11}\begin{vmatrix} D_{22} & D_{23} \\ D_{32} & D_{33} \end{vmatrix} - D_{12}\begin{vmatrix} D_{21} & D_{23} \\ D_{31} & D_{33} \end{vmatrix} + D_{13}\underbrace{\begin{vmatrix} D_{21} & D_{22} \\ D_{31} & D_{32} \end{vmatrix}}_{D_{21}D_{32} - D_{31}D_{22}}$$

In general the problem

$$\underbrace{H_{op}}_{\text{Given}}\Psi = E\Psi$$

unknown!

can be represented by the matrix problem

$$\mathbf{H}\boldsymbol{\Psi}_1 = E_1\boldsymbol{\Psi}_1$$

a) Find a COMPLETE ORTHONORMAL SET OF functions $\phi_1\ \ \phi_2\ \ \phi_3\ \cdots \phi_n$

b) Determine the matrix $\mathbf{H}$

$$\mathbf{H} = \begin{vmatrix} H_{11} & H_{12} & H_{13} \cdots H_{1n} \\ H_{21} & H_{22} & H_{23} \cdots H_{2n} \\ \vdots & & \\ H_{n1} & H_{n2} & H_{n3} \cdots H_{nn} \end{vmatrix}$$

in which $H_{rc} = \int \phi_r^* H_{op} \phi_c \, d\tau$ are calculated.

c) The matrix equation is the same as a set of n simultaneous linear equations

$$H_{11}c_1 + H_{12}c_2 + H_{13}c_3 + \cdots + H_{1n}c_n = E_1 c_1$$
$$H_{21}c_1 + H_{22}c_2 + H_{23}c_3 + \cdots + H_{2n}c_n = E_1 c_2$$
$$\vdots$$
$$H_{n1}c_1 + H_{n2}c_2 + H_{n3}c_3 + \cdots + H_{nn}c_n = E_1 c_n$$

d) A non-trivial solution exist if and only if

$$\det \begin{vmatrix} H_{11}-E & H_{12} & H_{13} & \cdots H_{1n} \\ H_{21} & H_{22}-E & H_{23} & \cdots H_{2n} \\ H_{31} & H_{32} & H_{33}-E & \cdots H_{3n} \\ H_{n1} & H_{n2} & H_{n3} & \cdots H_{nn}-E \end{vmatrix} = 0$$

which is an n^{th} order polynomial equation in the unknown E. There will be n roots, that is n values of E, the EIGENVALUES of matrix **H**. These are also the EIGENVALUES of the operator H_{op}.

e) For every EIGENVALUE E_i there exists an EIGENFUNCTION ψ_i

$$\psi_i = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \cdots c_n\phi_n$$

which can be found by substituting the eigenvalue E_i into the equations

use n-1 of these

$$\begin{cases} (H_{11}-E_1)c_1 + H_{12}c_2 + H_{13}c_3 + \cdots + H_{1n}c_n = 0 \\ H_{21}c_1 + (H_{22}-E_1)c_2 + H_{23}c_3 + \cdots + H_{2n}c_n = 0 \\ H_{31}c_1 + H_{32}c_2 + (H_{33}-E_1)c_3 + \cdots + H_{3n}c_n = 0 \\ \vdots \qquad\qquad \vdots \end{cases}$$

plus the NORMALIZATION condition:

$$c_1^2 + c_2^2 + c_3^3 + \cdots + c_n^2 = 1$$

Solve for the unknowns $c_1, c_2, \cdots c_n$

Now put in the next eigenvalue E_2 and solve for the $c_1, c_2, \cdots c_n$ for EIGENFUNCTION ψ_2, and so on...

f) There will be n EIGENVALUES $E_1, E_2, \cdots E_n$ and for each EIGENVALUE there will be an EIGENFUNCTION

$$\psi_i = c_{1i}\phi_1 + c_{2i}\phi_2 + c_{3i}\phi_3 + \cdots + c_{ni}\phi_n$$

$$\boldsymbol{\psi}_i = \begin{bmatrix} c_{1i} \\ c_{2i} \\ c_{3i} \\ \vdots \\ c_{ni} \end{bmatrix}$$

or $\boldsymbol{C}_i$

The ENTIRE COLLECTION of c values can be put side-by-side as follows:

$$\boldsymbol{C} = \underbrace{\begin{array}{cccc} \psi_1 & \psi_2 & \cdots & \psi_n \\ \begin{bmatrix} c_{11} \\ c_{21} \\ c_{31} \\ c_{n1} \end{bmatrix} & \begin{bmatrix} c_{12} \\ c_{22} \\ c_{32} \\ c_{n2} \end{bmatrix} & \cdots & \begin{bmatrix} c_{1n} \\ c_{2n} \\ c_{3n} \\ c_{nn} \end{bmatrix} \end{array}}_{\text{forms a matrix}}$$

g) The complete matrix equation is then

$$\boldsymbol{HC} = \boldsymbol{CE}$$

where $\boldsymbol{E} = \begin{bmatrix} E_1 & 0 & 0 & 0 & \cdots & 0 \\ 0 & E_2 & 0 & 0 & \cdots & 0 \\ 0 & 0 & E_3 & 0 & \cdots & 0 \\ 0 & 0 & 0 & E_4 & \cdots & 0 \\ \vdots & \vdots & \vdots & & & \\ 0 & 0 & 0 & 0 & \cdots & E_n \end{bmatrix}$

COMPUTERIZATION of the ABOVE PROCESS

h) The transformation of $\mathbf{H}$ into $\mathbf{E}$ requires finding the matrix $\mathbf{C}$ such that

$$\mathbf{C}^{-1}\mathbf{H}\mathbf{C} = \mathbf{E}$$

$\mathbf{C}^{-1}$ is called the INVERSE of matrix $\mathbf{C}$, that is

$$\mathbf{C}^{-1}\mathbf{C} = \mathbf{C}\mathbf{C}^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 0 & 1 & \ddots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix}$$

The transformation is called a SIMILARITY TRANSFORMATION.

Computer algorithms exist that will do this to a given matrix $\mathbf{H}$

$$\underbrace{\begin{bmatrix} H_{11} & H_{12} & H_{13} & \cdots & H_{1n} \\ H_{21} & H_{22} & H_{23} & \cdots & H_{2n} \\ \vdots & \vdots & \vdots & & \\ H_{n1} & H_{n2} & H_{n3} & \cdots & H_{nn} \end{bmatrix}}_{\text{INPUT}} \xrightarrow[\text{DIAGONALIZATION}]{\text{MATRIX}} \underbrace{\begin{bmatrix} E_1 & 0 & 0 & 0 & 0 & \vdots & 0 \\ 0 & E_2 & 0 & 0 & 0 & \vdots & 0 \\ 0 & 0 & E_3 & 0 & 0 & \vdots & 0 \\ 0 & 0 & 0 & E_4 & 0 & \vdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & & 0 \\ 0 & 0 & 0 & \cdot & 0 & \cdot\, 0 & E_n \end{bmatrix}}_{\text{OUTPUT}}$$

and at the same time find the $\mathbf{C}$ that accomplished the task:

$$\mathbf{C} = \left.\begin{bmatrix} C_{11} \\ C_{21} \\ C_{31} \\ \vdots \\ C_{n1} \end{bmatrix}\begin{bmatrix} C_{12} \\ C_{22} \\ C_{32} \\ \vdots \\ C_{n2} \end{bmatrix}\cdots\begin{bmatrix} C_{1n} \\ C_{2n} \\ C_{3n} \\ \vdots \\ C_{nn} \end{bmatrix}\right\}\text{OUTPUT}$$

$$\psi_1 \quad \psi_2 \quad \cdots \quad \psi_n$$

corresponding to EIGENVALUES

$$E_1 \quad E_2 \quad \cdots \quad E_n$$

1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
   4.1 Matrix Representation of an Operator
   4.2 Matrix Representation of an Operator Equation
   4.3 Solving the Matrix Equation that Represents the Operator Equation $\mathcal{H}\Psi = E\Psi$
   4.4 Matrix Representation of Spin Angular Momentum Operators
   4.5 Solving $\mathcal{H}\Psi = E\Psi$ for a Spin System, Comparison with NMR Experiments

EXAMPLE:

The spin portion of the hamiltonian for a hydrogen atom in a magnetic field B is

$$H = g_e \mu_B B S_z + g_N \mu_N B I_z + A\, S \cdot I$$

$g_e = 2.0023$
$g_N = 5.58556$
μ_B = Bohr magneton $\equiv e\hbar/2mc$
μ_N = nuclear magneton $\equiv e\hbar/2m_{proton}c$
$A = 1,420,405,751.786 \pm 0.010$ Hertz
or in terms of wavelength: 21 cm
(The 21 cm line emitted by hydrogen atoms in outer space is the basis of radioastronomy.)

Use MATRIX REPRESENTATIONS to solve
$H\Psi = E\Psi$

(1) First step: **Find a convenient set of functions with which to set up the matrix representation, a COMPLETE ORTHONORMAL SET.**

An easy choice is the set of eigenfunctions of the operator $(S_z + I_z)$ since the above hamiltonian contains these operators.
The eigenfunctions of $(S_z + I_z)$ are

$$\left.\begin{aligned} \psi_1 &= \alpha_e \alpha_N \\ \psi_2 &= \alpha_e \beta_N \\ \psi_3 &= \beta_e \alpha_N \\ \psi_4 &= \beta_e \beta_N \end{aligned}\right\}$$ These 4 functions form a COMPLETE ORTHONORMAL SET.

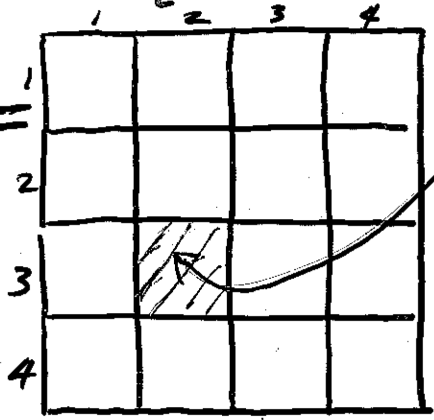
since we already know that

$S_z \alpha_e = \frac{\hbar}{2} \alpha_e$ $\qquad$ $I_z \alpha_N = \frac{\hbar}{2} \alpha_N$
$S_z \beta_e = -\frac{\hbar}{2} \beta_e$ $\qquad$ $I_z \beta_N = -\frac{\hbar}{2} \beta_N$

② Second step: **Simplify H, combine constants together, etc.**

Let $\Delta_e \equiv g_e \mu_B B \qquad \Delta_N \equiv g_N \mu_N B$

$$H = \Delta_e S_z - \Delta_N I_z + A(S_x I_x + S_y I_y + S_z I_z)$$

$H =$ 

$$\int \psi_3^* H \psi_2 \, d\tau$$

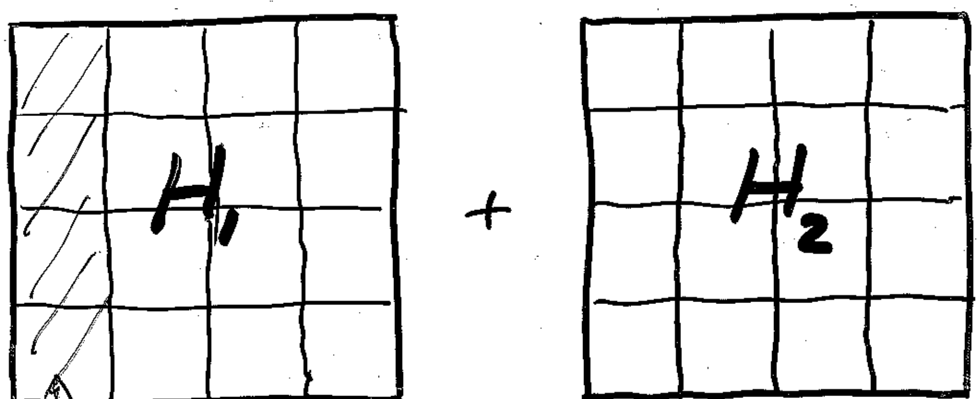
$$= \int \beta_e^* \alpha_N^* \begin{pmatrix} \Delta_e S_z \\ -\Delta_N I_z \\ +A S_x I_x \\ +A S_y I_y \\ +A S_z I_z \end{pmatrix} \alpha_e \beta_N \, d\tau_e \, d\tau_N$$

③ Do one column at a time and it may help to do the matrix in two pieces

$H = H_1 + H_2 \qquad H_1 = \Delta_e S_z - \Delta_N I_z + A S_z I_z$

$\qquad\qquad\qquad\quad H_2 = A S_x I_x + A S_y I_y$

then add the two pieces together

$H =$ 

Let us work on this column

The numbers that go into the boxes are

$$\int \psi_r^* (\Delta_e S_z - \Delta_N I_z + A S_z I_z) \psi_1 \, d\tau_e \, d\tau_N$$

$$\int \psi_r^* \underbrace{(\Delta_e S_z - \Delta_N I_z + A S_z I_z)\alpha_e \alpha_N}_{\text{OPERATE to get:}} \, d\tau_e \, d\tau_N$$

$$\underbrace{\Delta_e \frac{\hbar}{2}\alpha_e\alpha_N - \Delta_N \frac{\hbar}{2}\alpha_e\alpha_N + A\frac{\hbar}{2}\frac{\hbar}{2}\alpha_e\alpha_N}$$

$$\left(\Delta_e \frac{\hbar}{2} - \Delta_N \frac{\hbar}{2} + \frac{A\hbar^2}{4}\right)\underbrace{\alpha_e\alpha_N}$$

THIS FUNCTION IS ORTHOGONAL TO ALL of ψ_r EXCEPT FOR $\psi_1 = \alpha_e\alpha_N$

Therefore:

$$H_1 = \begin{bmatrix} \Delta_e\hbar/2 - \Delta_N\hbar/2 + A\hbar^2/4 & & & \\ 0 & & & \\ 0 & & & \\ 0 & & & \end{bmatrix}$$

Now work on column 2:

$$\int \psi_r^* \underbrace{(\Delta_e S_z - \Delta_N I_z + A S_z I_z)\alpha_e \beta_N}_{\text{OPERATE to get:}} \, d\tau_e \, d\tau_N$$

$$\underbrace{\left(\Delta_e \frac{\hbar}{2} - \Delta_N\left(-\frac{\hbar}{2}\right) + A\left(\frac{\hbar}{2}\right)\left(-\frac{\hbar}{2}\right)\right)}\underbrace{\alpha_e\beta_N}$$

THIS FUNCTION IS ORTHOGONAL TO ALL of ψ_r EXCEPT FOR $\psi_2 = \alpha_e\beta_N$

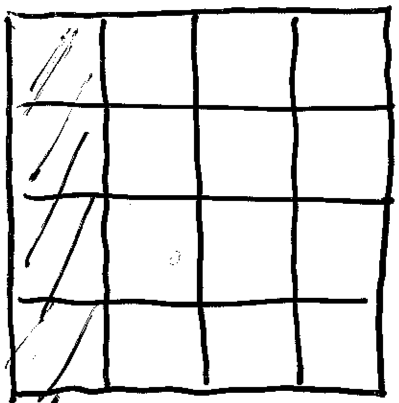
$$H_1 = \begin{bmatrix} & 0 & 0 & 0 \\ 0 & & 0 & 0 \\ 0 & 0 & & 0 \\ 0 & 0 & 0 & \end{bmatrix}$$

SIMILARLY for columns 3 + 4

$$\left(\Delta_e\left(-\frac{\hbar}{2}\right) - \Delta_N\left(\frac{\hbar}{2}\right) + A\left(-\frac{\hbar}{2}\right)\left(\frac{\hbar}{2}\right)\right)$$

$$\left(\Delta_e\left(-\frac{\hbar}{2}\right) - \Delta_N\left(-\frac{\hbar}{2}\right) + A\left(-\frac{\hbar}{2}\right)\left(-\frac{\hbar}{2}\right)\right)$$

Now work on matrix $\mathbf{H_2}$ in the same way

$\mathbf{H_2}$ = 

$S_x \alpha_e = \frac{\hbar}{2}\beta_e$

$S_x \beta_e = \frac{\hbar}{2}\alpha_e$

$S_y \alpha_e = i\frac{\hbar}{2}\beta_e$

$S_y \beta_e = -i\frac{\hbar}{2}\alpha_e$

Matrix elements in column 1 are:

$$\int \psi_r^* \underbrace{(AS_xI_x + AS_yI_y)\alpha_e\alpha_N}_{\text{OPERATE to get:}} \, d\tau_e \, d\tau_N$$

$$\underbrace{\left(A\left(\tfrac{\hbar}{2}\right)\left(\tfrac{\hbar}{2}\right) + A\left(\tfrac{i\hbar}{2}\right)\left(\tfrac{i\hbar}{2}\right)\right)}_{\text{this is zero}} \underbrace{\beta_e\beta_N}_{\text{this is } \psi_4} \, d\tau_e \, d\tau_N$$

only $\int \psi_4^* (\text{const}) \psi_4 \, d\tau_e \, d\tau_N$ survives orthogonality but the number here happens to be zero

Note that this operator makes the following conversions:

$\psi_1 \quad \alpha_e\alpha_N \longrightarrow \beta_e\beta_N \quad \psi_4$

$\psi_2 \quad \alpha_e\beta_N \longrightarrow \beta_e\alpha_N \quad \psi_3$

$\psi_3 \quad \beta_e\alpha_N \longrightarrow \alpha_e\beta_N \quad \psi_2$

$\psi_4 \quad \beta_e\beta_N \longrightarrow \alpha_e\alpha_N \quad \psi_1$

So the only non-zero elements can be

14 (but the constant happens to be zero)

23 } the constant is

32 } $A\left(\frac{\hbar}{2}\right)\left(\frac{\hbar}{2}\right) + A\left(\frac{i\hbar}{2}\right)\left(-\frac{i\hbar}{2}\right) = A\frac{\hbar^2}{2}$

41 (the constant happens to be zero)

$$H_2 = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & A\frac{\hbar}{2} & 0 \\ 0 & A\frac{\hbar}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

④ Now add the matrices:

$$H = H_1 + H_2 = \begin{bmatrix} \boxed{\Delta_e\frac{\hbar}{2} - \Delta_N\frac{\hbar}{2} + A\hbar^2/4} & 0 & 0 & 0 \\ 0 & \Delta_e\hbar/2 - A\frac{\hbar^2}{4} + \Delta_N\hbar/2 & A\frac{\hbar^2}{2} & 0 \\ 0 & A\frac{\hbar^2}{2} & \Delta_e\hbar/2 - A\frac{\hbar^2}{4} - \Delta_N\hbar/2 & 0 \\ 0 & 0 & 0 & \boxed{\Delta_e\frac{\hbar}{2} + \Delta_N\frac{\hbar}{2} + A\hbar^2/4} \end{bmatrix}$$

⑤ Look for "BLOCKING" along the diagonal!

$\mathbf{H}\Psi = E\Psi$ reads as follows:

$$H_{11}c_1 + H_{12}c_2 + H_{13}c_3 + H_{14}c_4 = E_1 c_1$$

$$\boxed{H_{11}}\, c_1 + 0 + 0 + 0 = E_1 c_1$$ This is one BLOCK

can be solved right away

as $$\underbrace{\left(\Delta_e\frac{\hbar}{2} - \Delta_N\frac{\hbar}{2} + A\frac{\hbar^2}{4}\right)}_{H_{11}} c_1 = E_1 c_1$$

only $c_1 \psi_1$ is involved!

The solution is

$$\Psi_1 = \alpha_e \alpha_N$$
$$E_1 = H_{11} \text{ itself}$$

(choose $c_1 = 1$ since $\psi_1 = \alpha_e \alpha_N$ is already normalized

Similarly

$$H_{41}c_1 + H_{42}c_2 + H_{43}c_3 + H_{44}c_4 = E\,c_4$$
$$0 + 0 + 0 + \boxed{H_{44}}c_4 = E\,c_4$$ This is a BLOCK!

The solution is

$$\Psi_4 = \beta_e \beta_N$$
$$E_4 = H_{44} \text{ itself} = -\Delta_e \frac{\hbar}{2} + \Delta_N \frac{\hbar}{2} + A\frac{\hbar^2}{4}$$

⑥ Solve the SIMULTANEOUS equations:
And the 2×2 BLOCK that is left is:

$$H_{21}c_1 + H_{22}c_2 + H_{23}c_3 + H_{24}c_4 = E\,c_2$$

$$H_{31}c_1 + H_{32}c_2 + H_{33}c_3 + H_{34}c_4 = E\,c_3$$

reduces to

$$0 + \boxed{H_{22}}c_2 + \boxed{H_{23}}c_3 + 0 = E\,c_2$$

$$0 + \boxed{H_{32}}c_2 + \boxed{H_{33}}c_3 + 0 = E\,c_3$$

which is easily solved by:

$$\det \begin{vmatrix} H_{22} - E & H_{23} \\ H_{32} & H_{33} - E \end{vmatrix} = 0$$

$$(H_{22} - E)(H_{33} - E) - H_{32}H_{23} = 0$$
$$E^2 - (H_{22} + H_{33})E - H_{32}H_{23} + H_{22}H_{33} = 0$$

The roots of the quadratic equation are:

$$E_{\pm} = \frac{(H_{22}+H_{33}) \pm \sqrt{(H_{22}+H_{33})^2 - 4(H_{22}H_{33} - H_{32}H_{23})}}{2}$$

Substitute into the equation:

$$(H_{22} - E_{\pm})c_2 + H_{23}c_3 = 0$$

$$\frac{c_3}{c_2} = \frac{H_{22} - H_{33} \mp \sqrt{}}{2H_{23}}$$

Let us drop the $\hbar$ for a while and

let $q \equiv \frac{1}{2}\Delta_e + \frac{1}{2}\Delta_N$

so that $H_{22} = q - \frac{1}{4}A$

$H_{33} = -q - \frac{1}{4}A$

$H_{23} = H_{32} = A/2$

Then

$$E_{\pm} = -\frac{A}{4} \pm \frac{1}{2}\sqrt{4q^2 + A^2}$$

$$\left(\frac{c_3}{c_2}\right)_{\pm} = \frac{2q \mp \sqrt{4q^2 + A^2}}{A}$$

a) For zero magnetic field $q = 0$

$E_+ = \frac{1}{4}A \qquad E_- = -\frac{3}{4}A$

$\left(\frac{c_3}{c_2}\right)_+ = -1 \qquad \left(\frac{c_3}{c_2}\right)_- = +1$

$\Psi_+ = \frac{1}{\sqrt{2}}\beta_e\alpha_N - \frac{1}{\sqrt{2}}\alpha_e\beta_N \qquad \Psi_- = \frac{1}{\sqrt{2}}\beta_e\alpha_N + \frac{1}{\sqrt{2}}\alpha_e\beta_N$

$\alpha_e\alpha_N \quad \beta_e\beta_N \quad \frac{1}{\sqrt{2}}(\beta_e\alpha_N + \alpha_e\beta_N) \quad E = \frac{1}{4}A$

$\Delta E = A$ (The 21 cm line emitted and absorbed by H atoms)

$\frac{1}{\sqrt{2}}(\beta_e\alpha_N - \alpha_e\beta_N) \quad E = -\frac{3}{4}A$

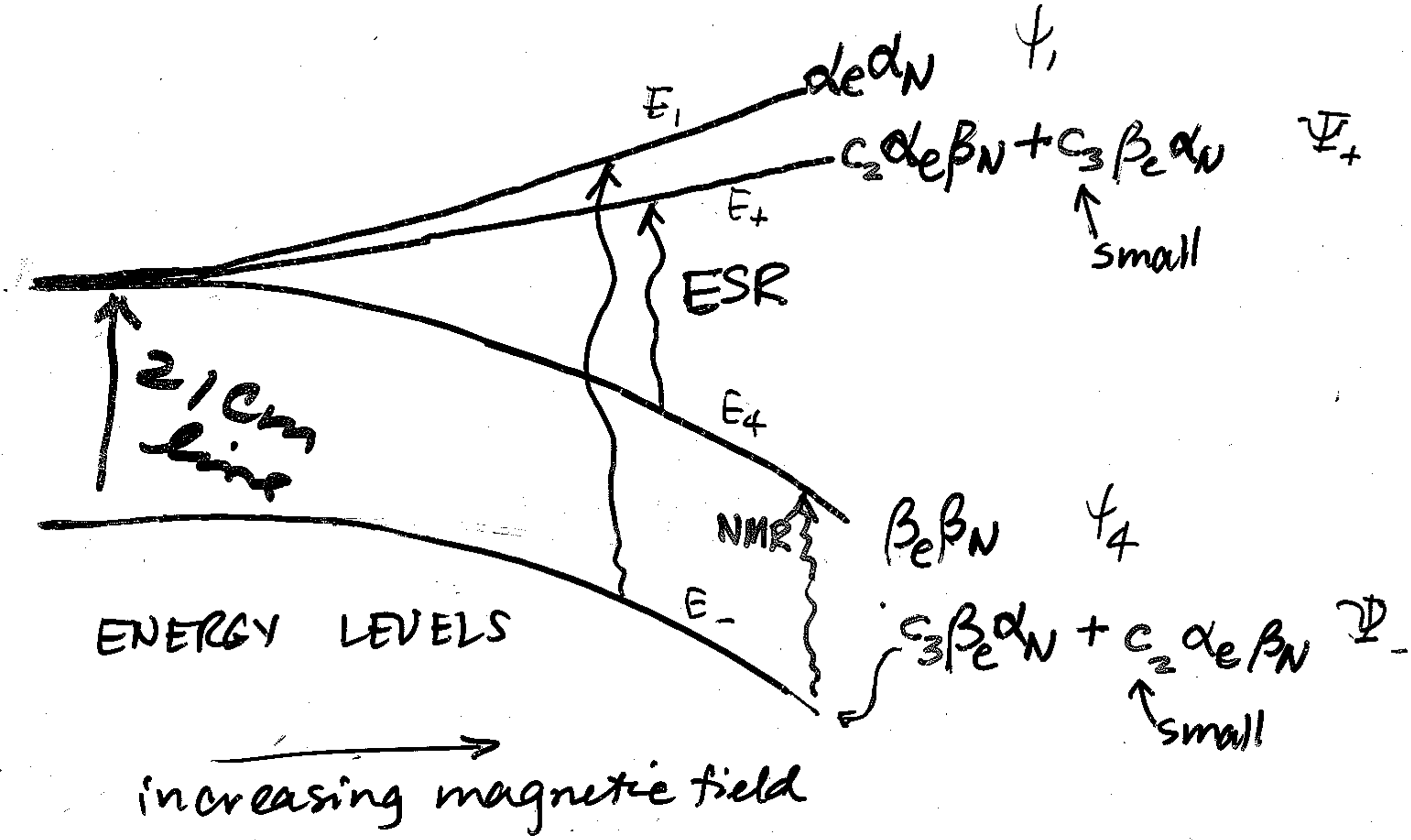
b) For very strong magnetic field $\quad g \gg A$

$$E_+ \approx -\frac{A}{4} + g \qquad E_- \approx -\frac{A}{4} - g$$

$$\frac{c_3}{c_2} \approx 0 \qquad \frac{c_2}{c_3} \approx 0$$

$\Psi_+ \approx \alpha_e\beta_N$ + only small admixture of $\beta_e\alpha_N$ $\qquad$ $\Psi_- \approx \beta_e\alpha_N$ + only a small admixture of $\alpha_e\beta_N$

c) For modest magnetic field



1. INTRODUCTION TO QUANTUM MECHANICS
2. ANGULAR MOMENTUM
3. THE HYDROGEN ATOM
4. MATRIX REPRESENTATION OF QUANTUM MECHANICS
   4.1 Matrix Representation of an Operator
   4.2 Matrix Representation of an Operator Equation
   4.3 Solving the Matrix Equation that Represents the Operator Equation $\mathcal{H}\Psi = E\Psi$
   4.4 Matrix Representation of Spin Angular Momentum Operators
   4.5 Solving $\mathcal{H}\Psi = E\Psi$ for a Spin System, Comparison with NMR Experiments