

you really didn't get it."

8/29/12

Dr. Paulo Bedaque

→ office hours right after class

→ homeworks due Wednesdays

General Framework of Classical Mechanics

① State of the system at any given time is described by:

$$\mathbf{r}_i, \frac{d\mathbf{r}_i}{dt}, i=1,2,\dots,N$$

② Any observable can be described by

$$A(\mathbf{r}_1, \dots, \mathbf{r}_N, \frac{d\mathbf{r}_1}{dt}, \dots, \frac{d\mathbf{r}_N}{dt})$$

③ System evolves according to

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N, \frac{d\mathbf{r}_1}{dt}, \dots, \frac{d\mathbf{r}_N}{dt})$$

$\mathbf{r}_i$ = position vector

A = arbitrary function

m_i = individual mass

$\mathbf{F}_i$ = arbitrary force $\mathbf{F}(\mathbf{x})$

General Framework of Quantum Mechanics

① State of the system at any given time in linear space

(element of $\mathcal{H}$) is described by: $|\Psi\rangle$

↑ the "Hilbert space"

"In case you go to

the other building,

they may burn you

alive over your

Hilbert space."

② Every observable corresponds to an hermitian

operator: $\hat{A}$ ← operates on kets to produce other kets

• Mathematical Interlude •

$$\hat{A}^\dagger = A \text{ (Hermitian)}$$

— eigenvectors

$$\hat{A}|n\rangle = a_n|n\rangle \text{ (proportional solution)}$$

↳ Eigenvalue.

i) a_n is real

ii) $\langle n|m\rangle = \delta_{nm}$ (they are orthogonal or identical / 0 or 1)

↑ Kronecker Delta $\Rightarrow$ orthonormal

iii) $\sum_n |n\rangle\langle n| = \mathbb{I}$ ("the most useful thing in the whole world")

operator ↑ identity operator (complete basis)

$$|n\rangle\langle n|\Psi\rangle = |\varphi\rangle$$

number ↑ another vector

$$|\Psi\rangle = \mathbb{I}|\Psi\rangle = \sum_n |n\rangle\langle n|\Psi\rangle = \sum_n \langle n|\Psi\rangle |n\rangle$$

— probability of finding a_n

$$|\langle n|\Psi\rangle|^2$$

③ after measuring a_n
 $|\psi\rangle \rightarrow |n\rangle$

state of system collapses to eigenvector corresponding to eigenvalue a_n

(reduction of wave packet / von Neuman postulate)

④ System evolves in time according to Schrödinger's equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

↑ Hamiltonian

Example: point particle, mass m , in a harmonic oscillator potential

$\mathcal{H}$ = space of complex functions $\psi(x)$ (one-dimension)

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2$$

position operator $\hat{x}$: $\hat{x}\psi(x) = x\psi(x)$

- multiplies a function by its argument

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Bra's and Ket's (Q1-lecture 15)

- a ket is like a vector except:
 - it can live in any # dimension
 - it's complex

$|\psi\rangle$ ← arrow reminds us it's like a vector
 ↑ name of the vector

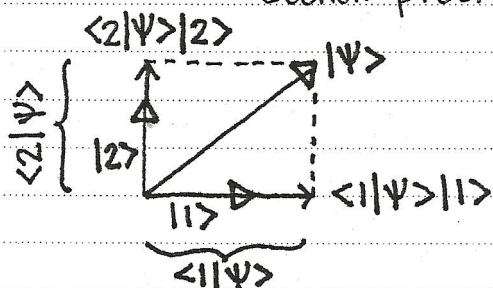
Examples: - columns of 42 numbers $\begin{pmatrix} \psi_1 \\ \vdots \\ \psi_{42} \end{pmatrix}$ } all linear spaces (latter two ∞ -dim)
 - functions of x
 - functions of x, y, z

- basis: $\{|n\rangle\}$ ← brackets indicate set of kets that form the basis
 ↓ assumed orthogonal basis

$$|\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle$$

scalar product ($\langle\psi|\psi\rangle = \langle\psi|\psi\rangle^*$)

↑ order matters in complex space!



$$\begin{aligned} |\psi\rangle &= \sum_n \langle n|\psi\rangle |n\rangle \\ &= \sum_n \psi_n |n\rangle \\ &= \sum_n \tilde{\psi}_n |\tilde{n}\rangle \end{aligned}$$

different basis = different components
 BUT STILL THE SAME KET!

- bra's: linear functional (something that takes a ket and produces a number)

$$|\psi\rangle \rightarrow \langle\psi| (|\psi\rangle) = \langle\psi|\psi\rangle$$

↑ a number!

$$\text{hermitian conjugation } |\psi\rangle^\dagger = \langle\psi|$$

↑ generic ket

$$\begin{aligned} (\alpha|\psi\rangle)^\dagger |\psi\rangle &= [\langle\psi|(\alpha|\psi\rangle)]^* = [\alpha\langle\psi|\psi\rangle]^* \\ &= \alpha^* \langle\psi|\psi\rangle^* = \alpha^* \langle\psi|\psi\rangle \end{aligned}$$

$$\Rightarrow (\alpha|\psi\rangle)^\dagger = \alpha^* \langle\psi|$$

$\dagger$ is the complex conjugate for kets

* Hermitian operators have real eigenvalues and they form an orthonormal and complete basis

• for a spinless particle moving on a (continuous) line

- position operator: $\hat{x}$

orthonormal? operator $\Rightarrow \hat{x}|x\rangle = x|x\rangle$

$$\Rightarrow \langle x|y\rangle = \delta(x-y)$$

$|x\rangle$ eigenkets (ket)

x eigenvalue (a real number)

$$\int dx |x\rangle \langle x| = \mathbb{I} \leftarrow \text{identity}$$

$\int dx$ both position values
 $\leftarrow$ ket describes the quantum behavior

$$|\psi\rangle = \mathbb{I}|\psi\rangle = \int dx |x\rangle \langle x|\psi\rangle = \int dx \langle x|\psi\rangle |x\rangle$$

$\psi(x) = \langle x|\psi\rangle$ = the wavefunction!
(in the position basis)

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More Bra's and Ket's

- $|\psi\rangle$ = element of a complex linear space
(which linear space depends on the quantum system)
- $\langle\phi|\psi\rangle$ = complex number
 $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$ linear on the right element,
 $\langle\phi|(\alpha|\psi\rangle) = \alpha\langle\phi|\psi\rangle$ anti-linear on the left
 $(\alpha|\psi\rangle)^\dagger|\psi\rangle = \alpha^*\langle\phi|\psi\rangle$
- $\langle\psi|$ aka. the dual space of the complex linear space above

 $\langle\psi|\psi\rangle$

a number

$$\langle\psi| = |\psi\rangle^\dagger \leftarrow \text{hermitian conjugation}$$

$$(|\psi_1\rangle + |\psi_2\rangle)^\dagger = \langle\psi_1| + \langle\psi_2|$$

$$(\alpha|\psi\rangle)^\dagger = \alpha^*\langle\psi|$$

- (orthonormal) basis $\{|n\rangle\}$

orthonormal - all elements are orthogonal with magnitude 1

$$\langle n|m\rangle = \delta_{nm} \text{ Kronecker delta symbolizes orthonormality}$$

$$\sum_n |n\rangle\langle n| = \mathbb{I} \text{ (completeness)}$$

$$|\psi\rangle = \mathbb{I}|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle$$

$$= \sum_n \langle n|\psi\rangle |n\rangle$$

$$\psi_n = n^{\text{th}} \text{ coordinate of } |\psi\rangle \text{ in } \{|n\rangle\}$$

$$= \sum_n \underbrace{\langle \tilde{n}|\psi\rangle}_{\psi_n} |\tilde{n}\rangle$$

- linear operators

$$\hat{A}|\psi\rangle = |\psi\rangle$$

$$\left. \begin{aligned} \hat{A}(|\psi_1\rangle + |\psi_2\rangle) &= \hat{A}|\psi_1\rangle + \hat{A}|\psi_2\rangle \\ \hat{A}(\alpha|\psi\rangle) &= \alpha\hat{A}|\psi\rangle \end{aligned} \right\} \text{linear}$$

$$\hat{A}|\psi\rangle = |\psi\rangle \Rightarrow \langle n|\hat{A}|\psi\rangle = \underbrace{\langle n|\psi\rangle}_{\psi_n}$$

$$\langle n|\hat{A}\mathbb{I}|\psi\rangle = \underbrace{\langle n|\hat{A}}_{\psi_n} \sum_m |m\rangle\langle m|\psi\rangle \quad \text{make sure these indexes are not the same!}$$

$$= \sum_m \underbrace{\langle n|\hat{A}|m\rangle}_{A_{nm}} \underbrace{\langle m|\psi\rangle}_{\psi_m}$$

 A_{nm}

matrix element

$$\sum_m A_{nm} \psi_m = \psi_n \rightarrow \text{analogous to } \rightarrow$$

$$\begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \end{pmatrix}$$

$$\underbrace{A_{11}\psi_1}_{m=1} + \underbrace{A_{12}\psi_2}_{m=2} + \dots = \underbrace{\psi_1}_{n=1}$$

• Hermitian operators

$$\langle \psi | \hat{A} | \psi \rangle = \langle \psi | \hat{A} | \psi \rangle^*$$

"the word 'sandwich' is a technical term used by grown-up physicists"

$$\hat{A} |n\rangle = a_n |n\rangle$$

- a_n is real

- $\langle n | m \rangle = \delta_{nm}$ } form an orthonormal and complete basis

$$-\sum_n |n\rangle \langle n| = \mathbb{I}$$

• Position basis

Example: one spinless particle moving on a (continuous) line

$\hat{x}$ - position operator - Hermitian because it's related to an observable

↙ eigenkets

$$\hat{x} |x\rangle = x |x\rangle \text{ (infinite-dimensional)}$$

↑ eigenvalue

$$\langle x | y \rangle = \delta_{xy} \rightarrow \text{previously assumed that } n \& m \text{ were discrete}$$

actually $\delta(x-y) \rightarrow$ delta function for continuous variables

$$-\infty \int_{-\infty}^{\infty} |x\rangle \langle x| = \mathbb{I}$$

↑ anything previously a sum becomes an integral for a continuous var.

$$|\psi\rangle = \mathbb{I} |\psi\rangle = \int dx |x\rangle \langle x | \psi \rangle = \int dx \underbrace{\langle x | \psi \rangle}_{\psi(x)} |x\rangle$$

$\psi(x) = \text{Wavefunction}$

$$\langle x | \hat{x} | y \rangle = \langle x | y | y \rangle = y \langle x | y \rangle = y \delta(x-y)$$

↑ operator $\hat{x}$ does not specifically relate to eigenket x

* note: $\alpha \langle x | \neq (\alpha | x \rangle)^*$

↙ allows you to write identity in the basis you want to work in

Suppose $\hat{x} |\psi\rangle = \langle x | \hat{x} | \psi \rangle = \langle x | \hat{x} \mathbb{I} | \psi \rangle$

$$= \int dy \underbrace{\langle x | \hat{x} | y \rangle}_{y \delta(x-y)} \underbrace{\langle y | \psi \rangle}_{\psi(y)}$$

$$= x \psi(x)$$

$$= x \psi(x)$$

• Scalar Product

$$\langle \phi | \psi \rangle = \langle \phi | \mathbb{I} | \psi \rangle = \int dx \underbrace{\langle \phi | x \rangle}_{\phi^*(x)} \underbrace{\langle x | \psi \rangle}_{\psi(x)} = \int dx \phi^*(x) \psi(x)$$

↑ puts product in basis you want

• Momentum basis:

$$\langle x | \hat{p} | \psi \rangle = -i\hbar \frac{d}{dx} \psi(x)$$

matrix element: $\langle y | \hat{p} | x \rangle$

$$= -i\hbar \frac{d}{dx} \delta(x-y)$$

eigenfunctions: $\hat{p} |p\rangle = p |p\rangle$

$$\Rightarrow \langle x | \hat{p} | p \rangle = \langle x | p | p \rangle$$

$$= -i\hbar \frac{d}{dx} \langle x | p \rangle = p \langle x | p \rangle$$

$$\Rightarrow \langle x | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

conventional normalization so $\langle p | p' \rangle = \delta(p-p')$

"You always have to have the $\hbar$, even if ψ is describing a hippopotamus. What is the momentum of a hippopotamus? I don't know, but I'm going to find out."

$$\begin{aligned}
 |\Psi\rangle &= \mathbb{I}|\Psi\rangle = \int dp |p\rangle \underbrace{\langle p|\Psi\rangle}_{\tilde{\Psi}(p)} \\
 &= \int dx \int dp |p\rangle \underbrace{\langle p|x\rangle}_{\frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}} \underbrace{\langle x|\Psi\rangle}_{\Psi(x)} \\
 &= \int dp |p\rangle \underbrace{\int dx \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \Psi(x)}_{\tilde{\Psi}(p)} \leftarrow \text{Fourier transform}
 \end{aligned}$$

Back to QM
postulate (2)

eigenbasis of $\hat{A}$: $\hat{A}|n\rangle = a_n|n\rangle$

observable: $\hat{A}, |\Psi\rangle = \sum \langle n|\Psi\rangle |n\rangle$

$\uparrow$ state of the system at time of measurement

$$\Rightarrow P_n = |\langle n|\Psi\rangle|^2$$

$\uparrow$ probability of finding a_n

Example: $\hat{A} = \hat{x}$

$$|\Psi\rangle = \int_{-\infty}^{\infty} dx \underbrace{\langle x|\Psi\rangle}_{\Psi(x)} |x\rangle$$

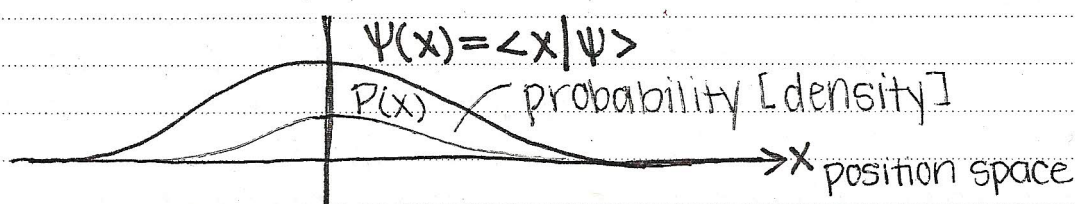
$$P(x) = |\langle x|\Psi\rangle|^2 = |\Psi(x)|^2$$

Example: $\hat{A} = \hat{p}$

$$\tilde{\Psi}(p) = \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar} \Psi(x)$$

$$|\Psi\rangle = \int_{-\infty}^{\infty} dp \underbrace{\langle p|\Psi\rangle}_{\tilde{\Psi}(p)} |p\rangle$$

$$P(p) = |\tilde{\Psi}(p)|^2$$

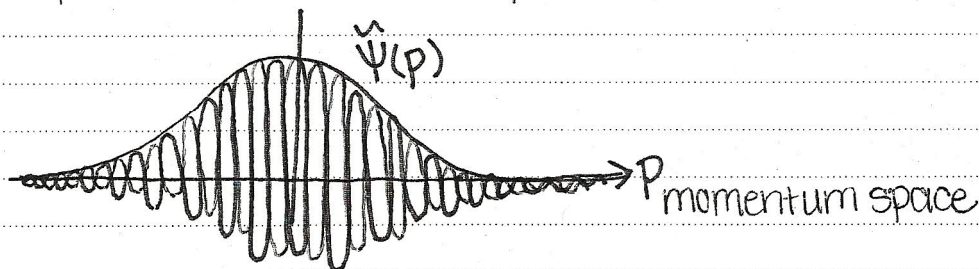


* If the position-space function is broad, the momentum

-space function is narrow

* If the position-space function is real, the momentum

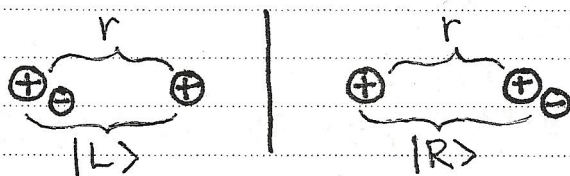
-space function is complex



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Even More Bra's and Ket's

Example: 2-dimensional Hilbert Space

 $H_2^+ \leftarrow \text{ionized}$ 

What is the Hamiltonian? (Observable representing Energy)

$$\hat{H} = E_0 (|L\rangle\langle L| + |R\rangle\langle R|) - T(r) |L\rangle\langle R| - T(r) |R\rangle\langle L|$$

operator
constant (real)

constant (real), negative on the convention on the phase of $|R\rangle$

* $|L\rangle$ and $|R\rangle$ form an orthogonal basis

Physical interpretation:

↙ ground state

 $E_0 \approx$ binding energy of the Hydrogen atom $\approx -13.6 \text{ eV}$ $|L\rangle$ and $|R\rangle$ are eigenstates of the Hamiltonian only when $T=0$ When $T \neq 0$, reference the TDSE

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \Rightarrow |\Psi(t+dt)\rangle = |\Psi(t)\rangle - i dt / \hbar \hat{H} |\Psi(t)\rangle$$

$$\frac{1}{dt} (|\Psi(t+dt)\rangle - |\Psi(t)\rangle)$$

$$|\Psi(t)\rangle = |L\rangle$$

$$|\Psi(t+dt)\rangle = |L\rangle - i dt / \hbar \hat{H} |L\rangle$$

↙ transition amplitude

$$= |L\rangle - i dt / \hbar [E_0 |L\rangle - T |R\rangle]$$

→ probability coefficient that the electron will have transitioned from $|L\rangle$ to $|R\rangle$

→ transition amplitude will be a decreasing function of r
(tunneling $\Rightarrow$ exponential)

What are the eigenstates?

— linear combinations of $|L\rangle$ and $|R\rangle$

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

$$\langle n | \hat{H} | \Psi \rangle = \langle n | E | \Psi \rangle$$

↑ insert identity

$$\sum_m \underbrace{\langle n | \hat{H} | m \rangle}_{H_{nm}} \underbrace{\langle m | \Psi \rangle}_{\Psi_m} = E \underbrace{\langle n | \Psi \rangle}_{\Psi_n}$$

here, $n = L, R$

$$\begin{pmatrix} H_{LL} & H_{LR} \\ H_{RL} & H_{RR} \end{pmatrix} \begin{pmatrix} \Psi_L \\ \Psi_R \end{pmatrix} = E \begin{pmatrix} \Psi_L \\ \Psi_R \end{pmatrix}$$

$$H_{LL} = \langle L | \hat{H} | L \rangle = E_0$$

$$H_{RR} = \langle R | \hat{H} | R \rangle = E_0$$

$$H_{LR} = \langle L | \hat{H} | R \rangle = -T$$

$$H_{RL} = \langle R | \hat{H} | L \rangle = -T$$

$$\Rightarrow \begin{pmatrix} E_0 - E & -T \\ -T & E_0 - E \end{pmatrix} \begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix} = 0 \quad (\text{moved the right to the left})$$

$$\det \begin{bmatrix} E_0 - E & -T \\ -T & E_0 - E \end{bmatrix} = 0$$

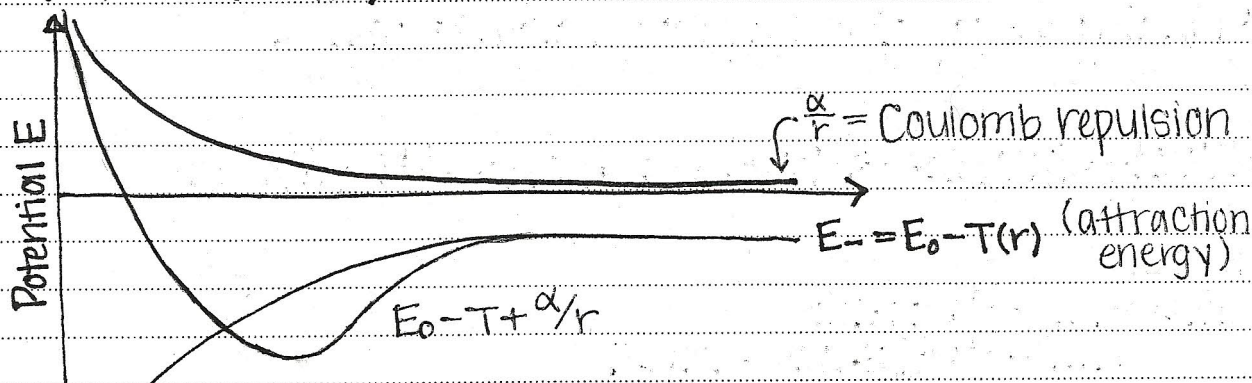
$$\Rightarrow E_{\pm} = E_0 \pm T \quad (\text{eigenvalues}) \quad (E_0 - T) \text{ is the energy of } |L\rangle \text{ due to the convention that } T \text{ is positive}$$

$$|- \rangle = \frac{1}{\sqrt{2}} (|L\rangle + |R\rangle) \quad (\text{eigenstates})$$

$$|+ \rangle = \frac{1}{\sqrt{2}} (|L\rangle - |R\rangle)$$

$$\begin{pmatrix} -T & -T \\ -T & -T \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = 0$$

$$\begin{pmatrix} T & -T \\ -T & T \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = 0$$



Remember! At all times the electron is equally on both sides (until observed)

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Spin

Angular Momentum

$$\hat{L} = \hat{r} \times \hat{p}$$

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

$$[\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij}$$

↑ commutator

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

$$[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$[\hat{L}^2, \hat{L}_x] = 0$$

$$[\hat{L}^2, \hat{L}_y] = 0$$

$$[\hat{L}^2, \hat{L}_z] = 0$$

$$[\hat{L}^2, \hat{L}_i] = 0$$

Mathematical Aside: Epsilon Tensor

$$\epsilon_{ijk} = \begin{cases} \epsilon_{123} = 1 = \epsilon_{312} = \epsilon_{231} \text{ (cyclic)} \\ \epsilon_{132} = -1 = \epsilon_{213} = \epsilon_{321} \text{ (non-cyclic)} \\ 0 \text{ otherwise} \end{cases}$$

It can be shown using only the commutation relations:

Common eigenstates of $\hat{L}^2, \hat{L}_z$

$$\hat{L}^2 |lm\rangle = \hbar^2 l(l+1) |lm\rangle$$

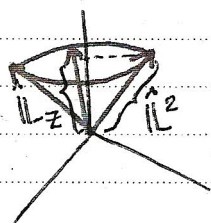
$$\hat{L}_z |lm\rangle = \hbar m |lm\rangle$$

$l = 0, 1, 2, \dots$ positive integers

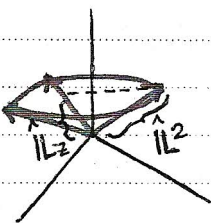
$m = -l, \dots, 0, \dots, l$ in integer steps

$$\hat{L}_{\pm} |lm\rangle = \hbar \sqrt{l(l+1) - m(m \pm 1)} |l, m \pm 1\rangle$$

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$$



$$\hat{L}_{-}$$



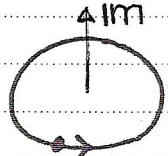
if you continued applying $\hat{L}_{-}$, this would continue getting shorter, even negative eventually

$$\langle r\theta\phi | lm \rangle = f(r) Y_{lm}(\theta, \phi)$$

spherical harmonics

↑ Wavefunction in position space (spherical coordinates)

Spin:



Charged particle orbiting around a loop

$$m = \frac{q}{2} r v$$

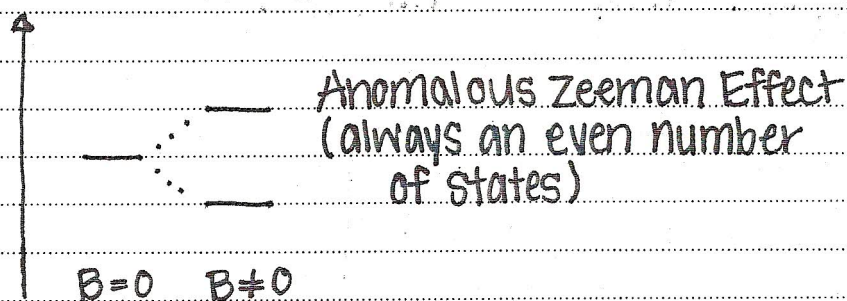
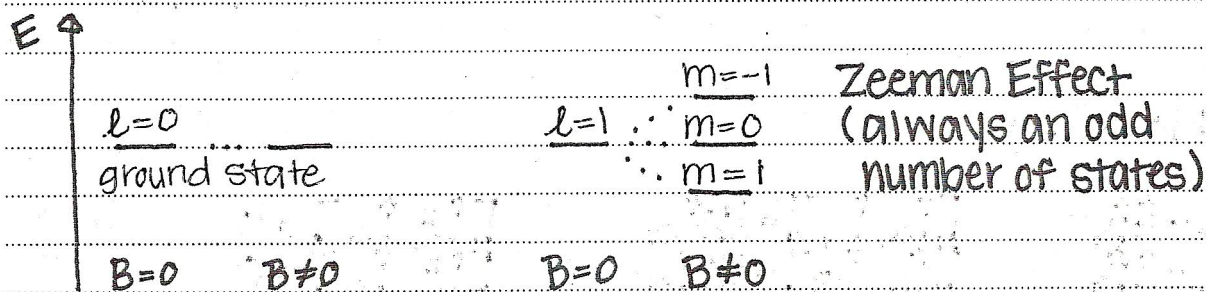
magnetic moment →

charge → radius → velocity

$$= mvr \left(\frac{q}{2m} \right)$$

$$\Delta E = mB = \left(\frac{q}{2m} \right) LB$$

assumed parallel (magnitude)



"A very drunk Pauli was once noted for saying 'Ah, you know, the Anomalous Zeeman Effect is ruining my life.'"
 "

Krönig: electrons can rotate around themselves! (a.k.a spin!)

$l = \frac{1}{2} \Rightarrow m = -\frac{1}{2}, \frac{1}{2}$ (aha! A doublet!)
 (except Pauli told him this was bullshit so he never published)

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Spin Continued

$$[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k \quad l=0, 1/2, 1, 3/2, 2, \dots; m=-l, \dots, 0, \dots, l$$

↳ Epsilon tensor

$$[\hat{L}^2, \hat{L}_z] = 0$$

$$\hat{L}^2 |lm\rangle = \hbar^2 l(l+1) |lm\rangle$$

$$\hat{L}_z |lm\rangle = \hbar m |lm\rangle$$

$$\hat{L}_\pm |lm\rangle = \hbar \sqrt{l(l+1) - m(m\pm 1)} |l, m\pm 1\rangle$$

↳ $\hat{L}_x \pm i\hat{L}_y$

$$\langle r\theta\phi | lm \rangle = f(r) \underbrace{Y_{lm}(\theta, \phi)}_{e^{im\phi}}$$

discontinuous wavefunction
@ $\phi = 0 = 2\pi$ if and only if m
is a half-integer, so it's forbidden

$$\begin{array}{c} m=1 \\ \vdots \\ m=0 \\ B=0 \end{array} \quad \begin{array}{c} m=-1 \\ \vdots \\ m=-2 \\ B \neq 0 \end{array}$$

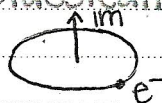
$$\begin{array}{c} \vdots \\ B=0 \end{array} \quad \begin{array}{c} \vdots \\ B \neq 0 \end{array} \quad \begin{array}{l} \text{duplet formed} \\ \text{by spin} \\ \text{(Anomalous Zeeman Effect)} \end{array}$$

This is the "Zeeman Effect"

$$\Delta E = \vec{m} \cdot \vec{B}$$

$$\sim \vec{L} \cdot \vec{B}$$

- Classically,



$$m = \frac{q}{2} r v = \frac{q}{2m} m r v = \frac{q}{2m} L$$

Spin 1/2

$$|\chi\rangle = \underbrace{\chi_+}_{<+|\chi>} |l=1/2, m=1/2\rangle + \underbrace{\chi_-}_{<-|\chi>} |l=1/2, m=-1/2\rangle$$

$$|+\rangle, |\uparrow\rangle$$

upspin

$$|-\rangle, |\downarrow\rangle$$

downspin

$$= \begin{bmatrix} \chi_+ \\ \chi_- \end{bmatrix}$$

"spinor"

spin is directly analogous to angular momentum

$$[\hat{S}_i, \hat{S}_j] = i\hbar \epsilon_{ijk} \hat{S}_k$$

$$\hat{S}^2 |sm\rangle = \hbar^2 s(s+1) |sm\rangle \quad s=0, 1/2, 1, 3/2, \dots$$

$$\hat{S}_z |sm\rangle = \hbar m |sm\rangle$$

$$m = -s, \dots, 0, \dots, s$$

$$\hat{S}_{\pm}|sm\rangle = \hbar\sqrt{s(s\pm 1) - m(m\pm 1)}|s, m\pm 1\rangle$$

$$\left. \begin{aligned} \hat{S}_z|+\rangle &= \frac{1}{2}\hbar|+\rangle \\ \hat{S}_z|-\rangle &= -\frac{1}{2}\hbar|-\rangle \end{aligned} \right\}$$

$$S_z = \begin{bmatrix} \langle +|\hat{S}_z|+\rangle & \langle +|\hat{S}_z|-\rangle \\ \langle -|\hat{S}_z|+\rangle & \langle -|\hat{S}_z|-\rangle \end{bmatrix}$$

$$= \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \sigma_z$$

Similarly, for S_x

$$S_x = \begin{bmatrix} \langle +|\hat{S}_x|+\rangle & \langle -|\hat{S}_x|+\rangle \\ \langle -|\hat{S}_x|+\rangle & \langle -|\hat{S}_x|-\rangle \end{bmatrix}$$

→ instead, express using $\hat{S}_{\pm}$

$$S_+ = \begin{bmatrix} \langle +|\hat{S}_+|+\rangle & \langle +|\hat{S}_+|-\rangle \\ \langle -|\hat{S}_+|+\rangle & \langle -|\hat{S}_+|-\rangle \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

$$S_+|+\rangle = 0$$

$$S_+|-\rangle = \hbar\sqrt{\frac{1}{2}(\frac{1}{2}+1) - (-\frac{1}{2})(-\frac{1}{2}+1)}|+\rangle$$

$$s = \frac{1}{2}, m = -\frac{1}{2}$$

$$= \hbar|+\rangle$$

→ using $\hat{S}_-$

$$S_- = \begin{bmatrix} \langle +|\hat{S}_-|+\rangle & \langle +|\hat{S}_-|-\rangle \\ \langle -|\hat{S}_-|+\rangle & \langle -|\hat{S}_-|-\rangle \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

$$\hat{S}_-|+\rangle = \hbar|-\rangle$$

$$s = -\frac{1}{2}, m = \frac{1}{2}$$

$$\text{Recall } \rightarrow \hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-)$$

$$\rightarrow S_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} = \sigma_x$$

$$\hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-)$$

$$\rightarrow S_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = \sigma_y$$

$$S^2 = S_x^2 + S_y^2 + S_z^2 = (\frac{1}{2}\hbar)^2(\sigma_x^2 + \sigma_y^2 + \sigma_z^2)$$

$$= \frac{1}{4}\hbar^2(\mathbf{I} + \mathbf{I} + \mathbf{I})$$

$$= \frac{3}{4}\hbar^2 \mathbf{I}$$

Electron in an External Magnetic Field

$$g \simeq 2.0028$$

$$\hat{H} = -\frac{e}{2m}g\hat{\mathbf{S}} \cdot \vec{B}$$

$$= -\left(\frac{e\hbar}{2m}\right)g\frac{1}{2}\vec{\sigma} \cdot \vec{B}$$

$$\hookrightarrow \text{Bohr magneton} = 5.78 \times 10^{-5} \text{ eV/T}$$

Initial state: $|\chi(t=0)\rangle$

$$i\hbar \frac{d}{dt} |\chi(t)\rangle = \hat{H} |\chi(t)\rangle$$

$$i\hbar \frac{d}{dt} \underbrace{\langle + | \chi(t) \rangle}_{\chi_+(t)} = \langle + | \hat{H} | \chi(t) \rangle = \langle + | -\gamma B \hat{\sigma}_z | \chi(t) \rangle$$

$$i\hbar \frac{d}{dt} \underbrace{\langle - | \chi(t) \rangle}_{\chi_-(t)} = \langle - | \hat{H} | \chi(t) \rangle = -\gamma B \langle - | \hat{\sigma}_z | \chi(t) \rangle$$

$$\hookrightarrow \mathbb{I} = |+\rangle\langle +| + |-\rangle\langle -|$$

$$\Rightarrow i\hbar \frac{d}{dt} \chi_+(t) = -\gamma B \left[\underbrace{\langle + | \hat{\sigma}_z | + \rangle}_1 \underbrace{\langle + | \chi(t) \rangle}_{\chi_+(t)} + \underbrace{\langle + | \hat{\sigma}_z | - \rangle}_0 \underbrace{\langle - | \chi(t) \rangle}_{\chi_-(t)} \right]$$

$$i\hbar \frac{d}{dt} \chi_-(t) = -\gamma B \left[\underbrace{\langle - | \hat{\sigma}_z | - \rangle}_{-1} \underbrace{\langle - | \chi(t) \rangle}_{\chi_-(t)} + \underbrace{\langle - | \hat{\sigma}_z | + \rangle}_0 \underbrace{\langle + | \chi(t) \rangle}_{\chi_+(t)} \right]$$

$$i\hbar \frac{d}{dt} \begin{bmatrix} \chi_+(t) \\ \chi_-(t) \end{bmatrix} = -\gamma B \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \chi_+(t) \\ \chi_-(t) \end{bmatrix}$$

$$\rightarrow \chi_+(t) = e^{\frac{i\gamma B}{\hbar} t} \chi_+(t=0)$$

$$\rightarrow \chi_-(t) = e^{-\frac{i\gamma B}{\hbar} t} \chi_-(t=0)$$

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Spin 1/2 Particle in an External $\vec{B}$ -field

$$|\chi(t)\rangle = e^{\frac{i\gamma B \hat{S}_z}{\hbar} t} |\chi(0)\rangle$$

$$\chi_+(t)|+\rangle + \chi_-(t)|-\rangle$$

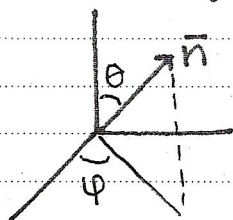
$$\begin{bmatrix} \chi_+(t) \\ \chi_-(t) \end{bmatrix} = \begin{bmatrix} e^{\frac{i\gamma B}{2} t} \chi_+(0) \\ e^{-\frac{i\gamma B}{2} t} \chi_-(0) \end{bmatrix} \quad \begin{array}{l} @ t=0, \chi_+=1, \chi_-=0 \\ \text{or} \\ @ t=0, \chi_+=\chi_-=\frac{1}{\sqrt{2}} \end{array}$$

$$\frac{\hbar}{2} \underbrace{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}}_{S_x} \underbrace{\begin{bmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{bmatrix}}_{\chi(0)} = \frac{\hbar}{2} \underbrace{\begin{bmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{bmatrix}}_{\chi(0)}$$

$$\frac{\hbar}{2} \underbrace{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}}_{S_x} \underbrace{\begin{bmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{bmatrix}}_{\chi(t)} = -\frac{\hbar}{2} \underbrace{\begin{bmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{bmatrix}}_{\chi(t)}$$

increasing the spin along $\vec{n}$: $\vec{n} \cdot \hat{\vec{S}}$

$$\begin{bmatrix} \sin(\theta)\cos(\varphi), \sin(\theta)\sin(\varphi), \cos(\theta) \end{bmatrix}$$



$$\begin{aligned} \vec{n} \cdot \hat{\vec{S}} &= \frac{\hbar}{2} (\sin(\theta)\cos(\varphi)\hat{\sigma}_x + \sin(\theta)\sin(\varphi)\hat{\sigma}_y + \cos(\theta)\hat{\sigma}_z) \\ &= \frac{\hbar}{2} \begin{bmatrix} \cos(\theta) & \sin(\theta)e^{-i\varphi} \\ \sin(\theta)e^{i\varphi} & -\cos(\theta) \end{bmatrix} \end{aligned}$$

eigenkets

$$|\vec{n}, +\rangle = \underbrace{\cos(\theta/2)}_{|\vec{z}, +\rangle} |+\rangle + e^{i\varphi} \underbrace{\sin(\theta/2)}_{|\vec{z}, -\rangle} |-\rangle, \text{ eigenvalue} = \hbar/2$$

$$|\vec{n}, -\rangle = -e^{-i\varphi} \sin(\theta/2) |+\rangle + \cos(\theta/2) |-\rangle, \text{ eigenvalue} = -\hbar/2$$

$$\rightarrow \text{get spinor: } \begin{bmatrix} \cos(\theta/2) \\ e^{i\varphi} \sin(\theta/2) \end{bmatrix}$$

$$e^{-i\alpha \hat{L}_z} |\psi\rangle = |\alpha + \psi\rangle$$

$$e^{-i\gamma \hat{P}} |x\rangle = |x + y\rangle$$

generates rotation

Rotation Operator

$$\hat{R}(\vec{n}, \alpha) = e^{-i\alpha \vec{n} \cdot \hat{\vec{S}}/\hbar} = e^{-\frac{i\alpha}{2} \hat{\sigma} \cdot \vec{n}}$$

rotation around the $\vec{n}$ axis by angle α

$$e^{i\theta \sigma_z} = 1 + i\theta \sigma_z - \frac{1}{2}\theta^2 \underbrace{\sigma_z^2}_{\text{II}} - \frac{1}{3!}\theta^3 \underbrace{\sigma_z^3}_{\sigma_z} + \frac{1}{4!}\theta^4 \underbrace{\sigma_z^4}_{\text{II}} + \dots$$

→

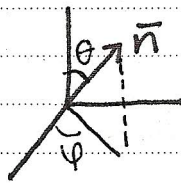
$$= \underbrace{\left(1 + \frac{1}{2!}\theta^2 + \frac{1}{4!}\theta^4 + \dots\right)}_{\cos(\theta)} \mathbb{I} + \sigma_z \underbrace{\left(i\theta + \frac{1}{3!}(-i\theta^3) + \dots\right)}_{i\sin(\theta)}$$

$$= \mathbb{I}\cos(\theta) + i\sigma_z\sin(\theta)$$

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Rotation Operator, Con't

$$\vec{n} \cdot \hat{\vec{S}} = \vec{n} \cdot \vec{S} = \frac{\hbar}{2} \begin{bmatrix} \cos(\theta) & \sin(\theta)e^{-i\varphi} \\ \sin(\theta)e^{i\varphi} & -\cos(\theta) \end{bmatrix}$$



$$\vec{n} \cdot \hat{\vec{S}} |\vec{n}, +\rangle = \hbar/2 |\vec{n}, +\rangle = \cos(\theta/2) |+\rangle + e^{i\varphi} \sin(\theta/2) |-\rangle$$

$$\vec{n} \cdot \hat{\vec{S}} |\vec{n}, -\rangle = -\hbar/2 |\vec{n}, -\rangle = -e^{-i\varphi} \sin(\theta/2) |+\rangle + \cos(\theta/2) |-\rangle$$

Rotation operator: $\hat{R}(\vec{n}, \alpha) = e^{-i\alpha \vec{n} \cdot \hat{\vec{S}} / \hbar}$

axis of rotation $\curvearrowright$ $\curvearrowright$ angle of rotation

$$= e^{-i\alpha \vec{n} \cdot \hat{\vec{\sigma}} / 2}$$

$$\hat{R}(\vec{n}, \alpha) = e^{-i\frac{\alpha}{2} \vec{n} \cdot \hat{\vec{\sigma}}}$$

$$= e^{-i\frac{\alpha}{2} (n_x \hat{\sigma}_x + n_y \hat{\sigma}_y + n_z \hat{\sigma}_z)}$$

$$= 1 - i\frac{\alpha}{2} \vec{n} \cdot \hat{\vec{\sigma}} + \frac{\alpha^2}{4!} (\vec{n} \cdot \hat{\vec{\sigma}})^2 - i\frac{\alpha^3}{8!} (\vec{n} \cdot \hat{\vec{\sigma}})^3 + \frac{\alpha^4}{16!} (\vec{n} \cdot \hat{\vec{\sigma}})^4$$

$$\curvearrowright (\vec{n} \cdot \hat{\vec{\sigma}})(\vec{n} \cdot \hat{\vec{\sigma}}) = \sum_{ij} n_i n_j \hat{\sigma}_i \hat{\sigma}_j \leftarrow$$

$$= \sum_{ij} n_i n_j (\delta_{ij} + i\epsilon_{ijk} \hat{\sigma}_k)$$

$$= \sum_i n_i n_i + i0 = \mathbb{I}$$

$$\hat{R}(\vec{n}, \alpha) = \mathbb{I} \cos(\alpha/2) - i \vec{n} \cdot \hat{\vec{\sigma}} \sin(\alpha/2)$$

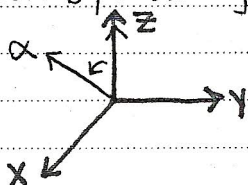
$\curvearrowright$ spin up along z

$$\hat{R}(\vec{x}, \alpha) |+\rangle \xrightarrow{\text{usual basis } \{|+\rangle, |-\rangle\}} \begin{bmatrix} \cos(\alpha/2) & -i\sin(\alpha/2) \\ -i\sin(\alpha/2) & \cos(\alpha/2) \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

rotation by α along x-axis

$$= \begin{bmatrix} \cos(\alpha/2) \\ -i\sin(\alpha/2) \end{bmatrix}$$

$$\curvearrowright \theta = \alpha, \varphi = 3\pi/2, +\rangle$$



$$\hat{R}(\vec{z}, \alpha) |+\rangle \xrightarrow{\text{usual basis}} \begin{bmatrix} \cos(\alpha/2) - i\sin(\alpha/2) & 0 \\ 0 & \cos(\alpha/2) + i\sin(\alpha/2) \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$= \begin{bmatrix} \cos(\alpha/2) - i\sin(\alpha/2) \\ 0 \end{bmatrix} = \begin{bmatrix} e^{-i\alpha/2} \\ 0 \end{bmatrix}$$

$$= e^{-i\alpha/2} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

irrelevant phase $\curvearrowright |+\rangle$

9/19/12

Recap: Spin $\frac{1}{2}$

Hilbert Space: $|x\rangle = \chi_+ |+\rangle + \chi_- |-\rangle \leftrightarrow \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix}$ - spinor

complex # $\nearrow$

$$\hat{S}_z |\pm\rangle = \pm \frac{\hbar}{2} |\pm\rangle$$

$$\hat{S}_+ |+\rangle = 0 \text{ can't go up any higher}$$

$$\hat{S}_+ |-\rangle = |+\rangle$$

$$\hat{S}_- |+\rangle = |-\rangle$$

$$\hat{S}_- |-\rangle = 0 \text{ can't go down any lower}$$

S_x, S_y , and S_z become Pauli matrices

$$S_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

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

$$S_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

* there is no quantity in quantum physics solely represented by the spinor (not a physical quantity)

Spin along an $\mathbf{n}$: $\mathbf{n} \cdot \hat{\mathbf{S}}$

$$\Rightarrow \mathbf{n} \cdot \hat{\mathbf{S}} = \frac{\hbar}{2} \begin{pmatrix} \cos(\theta) & e^{i\phi} \sin(\theta) \\ e^{-i\phi} \sin(\theta) & -\cos(\theta) \end{pmatrix}$$

eigenvectors: $\begin{pmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{pmatrix}, \begin{pmatrix} -e^{i\phi} \sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix}$

eigenvalues: $+\hbar/2, -\hbar/2$

Rotation operator: $\hat{R}(\mathbf{n}, \alpha) = e^{-i\alpha \mathbf{n} \cdot \hat{\mathbf{S}}/\hbar}$

rotation axis $\searrow$ angle of rotation

$$= \cos(\alpha/2) - i \mathbf{n} \cdot \boldsymbol{\sigma} \sin(\alpha/2)$$

Spin $\frac{1}{2}$ particle in a constant magnetic field:

$$\hat{H} = -\gamma \mathbf{B} \cdot \hat{\mathbf{S}} \quad \mathbf{B} = B \hat{\mathbf{z}}$$

$$\Rightarrow |\chi(t)\rangle = \underbrace{e^{i\gamma B t \hat{S}_z}}_{\hat{R}(-\gamma B t, \hat{\mathbf{z}})} |\chi(0)\rangle$$

Addition of Angular Momentum

$$|x\rangle = \chi_{++} |++\rangle + \chi_{--} |--\rangle + \chi_{+-} |+-\rangle + \chi_{-+} |-+\rangle$$

$$|+\rangle \otimes |+\rangle$$

direct product of two Hilbert spaces

→

1st particle spin: $\hat{S}_{1x}, \hat{S}_{1y}, \hat{S}_{1z}$:

$$\hat{S}_1^2 |m, m_2\rangle = \hbar^2 \frac{3}{4} |m, m_2\rangle$$

total spin of particle 1

$$\hat{S}_{1z} |m, m_2\rangle = \text{sign}(m_1) \hbar/2 |m, m_2\rangle$$

L ignores m_2

2nd particle spin: $\hat{S}_{2x}, \hat{S}_{2y}, \hat{S}_{2z}$:

$$\hat{S}_{2z} |m, m_2\rangle = \text{sign}(m_2) \hbar/2 |m, m_2\rangle$$

L ignores m_1

$$\hat{S}_2^2 |m, m_2\rangle = \hbar^2 \frac{3}{4} |m, m_2\rangle$$

total spin of particle 2

$$\begin{aligned} \text{Total spin: } \hat{S}^2 &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \\ &= (\hat{S}_{1x} + \hat{S}_{2x})^2 + (\hat{S}_{1y} + \hat{S}_{2y})^2 + (\hat{S}_{1z} + \hat{S}_{2z})^2 \\ &= \hat{S}_1^2 + \hat{S}_2^2 + (\hat{S}_1 \cdot \hat{S}_2) \cdot 2 \end{aligned}$$

↑ $\hat{S}_x \otimes \mathbb{I}$ ↑ $\mathbb{I} \otimes \hat{S}_x$ ↑ commutable

spins of the first + second particle

$$\begin{aligned} \hat{S}_1 \cdot \hat{S}_2 &= \frac{1}{2} (\hat{S}_{1x} + i\hat{S}_{1y})(\hat{S}_{2x} - i\hat{S}_{2y}) + \frac{1}{2} (\hat{S}_{1x} - i\hat{S}_{1y})(\hat{S}_{2x} + i\hat{S}_{2y}) + \hat{S}_{1z}\hat{S}_{2z} \\ &= \hat{S}_1^2 + \hat{S}_2^2 + \hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} \end{aligned}$$

take $|++\rangle$

$$\hat{S}_z |++\rangle = (\hat{S}_{1z} + \hat{S}_{2z}) |++\rangle = \hbar/2 |++\rangle + \hbar/2 |++\rangle = \hbar |++\rangle$$

$$\hat{S}^2 |++\rangle = [\hat{S}_1^2 + \hat{S}_2^2 + \hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}] |++\rangle$$

$$= \hbar^2 \frac{3}{4} |++\rangle + \hbar^2 \frac{3}{4} |++\rangle + \hbar^2 \frac{1}{2} \frac{1}{2} |++\rangle + 0 + 0$$

$$= 2\hbar^2 |++\rangle = \hbar^2 \cdot 1(1+1) |++\rangle$$

$|++\rangle$ is an eigenstate of $\hat{S}_z(\hbar)$, $\hat{S}^2(2\hbar^2)$

$$|++\rangle = |s=1, m=1\rangle$$

We know that $|++\rangle = |s=1, m=1\rangle$

$$|s=1, m=0\rangle = \hat{S}_- |s=1, m=1\rangle$$

$$= (\hat{S}_{1-} + \hat{S}_{2-}) |++\rangle$$

$$= |+-\rangle + |-+\rangle$$

$$|s=1, m=-1\rangle = \hat{S}_- |s=1, m=0\rangle$$

$$= (\hat{S}_{1-} + \hat{S}_{2-}) [\frac{1}{\sqrt{2}} (|+-\rangle + |-+\rangle)]$$

$$= \frac{1}{\sqrt{2}} [0 + |- - \rangle + |- - \rangle + 0]$$

$$\hookrightarrow |s=1, m=1\rangle = |++\rangle \leftarrow \hat{S}_2^2$$

$$\hat{S}_2^2 \uparrow$$

$$|s=1, m=0\rangle = \frac{1}{\sqrt{2}} (|+-\rangle + |-+\rangle)$$

$$\hat{S}_2^2 \uparrow$$

$$\hat{S}_{1z} \uparrow$$

$$|s=1, m=-1\rangle = |- - \rangle \leftarrow \hat{S}_{1z}$$

$$\hat{S}_1^2 \uparrow$$

$$|s=0, m=0\rangle = \frac{1}{\sqrt{2}} (|+-\rangle - |-+\rangle)$$

$$\hat{S}_1^2 \uparrow$$

$$\begin{aligned}\hat{S}_z \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) &= (\hat{S}_{1z} + \hat{S}_{2z}) \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) \\ &= \hbar/2 (|+-\rangle + |-+\rangle - |+-\rangle - |-+\rangle) \cdot 1/\sqrt{2} \\ &= 0 [(|+-\rangle - |-+\rangle) \cdot 1/\sqrt{2}]\end{aligned}$$

$$\begin{aligned}\hat{S}^2 \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) &= [\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}] \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) \\ &= 2 \cdot \frac{3}{4} \hbar^2 |+-\rangle - \frac{3}{4} \hbar^2 2 |+-\rangle - \hbar^2 \frac{1}{4} |+-\rangle + \hbar^2 \frac{1}{4} |-+\rangle + \hbar^2 \frac{1}{4} |+-\rangle - \hbar^2 \frac{1}{4} |-+\rangle \\ &= 0 = \hbar^2 \cdot 0(0+1) 1/\sqrt{2} (|+-\rangle - |-+\rangle)\end{aligned}$$

Without proof:

in general, add l_1 and l_2

$|l_1 - l_2| \leq l \leq l_1 + l_2$ / Clebsch-Gordan Coefficients

$$|l_1, l_2, l, m\rangle = \sum_{m_1, m_2} C_{m_1, m_2}^{lm} |l_1, l_2, l, m\rangle$$

↑ generic name for either spin or angular momentum

* adding a phase also adds a phase to the C-G coefficients

9/21/12

Many-Particle Systems

Consider two particles; spinless

Position of one particle

$$|\psi\rangle = \int d^3r \underbrace{\langle r | \psi \rangle}_{\psi(r)} |r\rangle$$

Position of two particles

$$|\psi\rangle = \int d^3r_1 d^3r_2 \underbrace{\langle r_1, r_2 | \psi \rangle}_{\psi(r_1, r_2)} |r_1, r_2\rangle$$

$\Rightarrow$ one wavefunction for the whole system

$$\hat{r}_1 |r_1, r_2\rangle = r_1 |r_1, r_2\rangle - \hat{r}_1 \text{ ignores } |r_2\rangle$$

$$\hat{r}_2 |r_1, r_2\rangle = r_2 |r_1, r_2\rangle - \hat{r}_2 \text{ ignores } |r_1\rangle$$

$$|r_1\rangle \otimes |r_2\rangle$$

- Some spatial states are indeed the product of two wavefunctions

$$\psi(r_1, r_2) = f(r_1) g(r_2)$$

- Most of the time, however, it is not

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\delta(r_1 - a) \delta(r_2 - b) + \delta(r_1 - b) \delta(r_2 - a)]$$

$\hookrightarrow$ this is an entangled state

Identical Particles

Probability of finding

$$|\psi(r_1, r_2)|^2 = |\psi(r_2, r_1)|^2 \Rightarrow \psi(r_1, r_2) = e^{i\alpha} \psi(r_2, r_1) \quad \swarrow \text{phase shift}$$

Permutation operator

$$\hat{P}_{12} \psi(r_1, r_2) = \psi(r_2, r_1)$$

$\hookrightarrow$ switches positions

$$\hat{P}_{12} \hat{P}_{21} = \mathbb{I} \rightarrow e^{i\alpha} = \pm 1$$

integer
 $\hookrightarrow$ bosons (spin = 0, 1, 2, ...)

$\hookrightarrow$ fermions (flip sign)

(spin = $\frac{1}{2}$, $\frac{3}{2}$, ...)

half-integer

electrons = fermions = deuterium

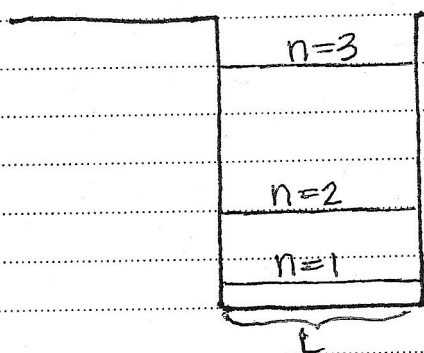
Hydrogen atom = boson

even # of fermions = boson

odd # of fermions = fermions

$\rightarrow$

Example:



single particle states
 $|n\rangle: n=1, 2, 3, \dots$

$$\Psi_B(x) = \langle x | n \rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$B_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2} \sim p \sim \hbar/L$$

Many-Particle Systems, Con't

Two-Particle review:

$$|\Psi\rangle = |\psi_1\rangle + |\psi_2\rangle = |\psi_1, \psi_2\rangle$$

└ one particle states
└ two particle state

most general state: all possible tensor product basis combinations

$$|\Psi\rangle = \sum_{n_1, n_2} \Psi_{n_1, n_2} |n_1\rangle \otimes |n_2\rangle \quad |n_1, n_2\rangle \neq |n_2, n_1\rangle$$

└ $\{|n_i\rangle\}$ basis for particle ①

Eigenbasis of Positions: $|r_1, r_2\rangle$

└ vector, x, y, and z of the particle

$$\langle r_2, r_1 | \Psi \rangle = \sum_{n_1, n_2} \Psi_{n_1, n_2} (\langle r_2 | \otimes \langle r_1 |) (|n_1\rangle \otimes |n_2\rangle)$$

└ When they become bras, flip the indexes

* Note that the Hilbert space of particle 1 does not interact with the Hilbert space of particle 2

$$= \sum_{n_1, n_2} \underbrace{\langle r_1 | n_1 \rangle}_{\Psi_{n_1}(r_1)} \underbrace{\langle r_2 | n_2 \rangle}_{\Psi_{n_2}(r_2)} \Psi_{n_1, n_2}$$

for identical particles:

$$\times |\Psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle \xrightarrow{\text{exchange}} |\psi_2\rangle \otimes |\psi_1\rangle$$

└ NOT ALLOWED

allowed:

$$|\Psi\rangle = \frac{1}{\sqrt{2}} [|\psi_A\rangle \otimes |\psi_B\rangle \pm |\psi_B\rangle \otimes |\psi_A\rangle]$$

A & B refer to states, not particle #

└ combination of two eigenstates corresponding to eigenvalues E_A and E_B , respectively

in position space

$$\langle r_1, r_2 | \Psi \rangle = \underbrace{(\langle r_2 | \otimes \langle r_1 |)}_{\langle r_2, r_1 |} \underbrace{\frac{1}{\sqrt{2}} (|\psi_A\rangle \otimes |\psi_B\rangle \pm |\psi_B\rangle \otimes |\psi_A\rangle)}_{|\Psi\rangle}$$

$$= \frac{1}{\sqrt{2}} [\underbrace{\langle r_1 | \psi_A \rangle}_{\text{wavefunction of particle one in state A } \Psi_A(r_1)} \underbrace{\langle r_2 | \psi_B \rangle}_{\Psi_B(r_2)} \pm \underbrace{\langle r_1 | \psi_B \rangle}_{\Psi_B(r_1)} \underbrace{\langle r_2 | \psi_A \rangle}_{\Psi_A(r_2)}]$$

└ Bosons (+) or Fermions (-)

$$= \frac{1}{\sqrt{2}} [\Psi_A(r_1) \Psi_B(r_2) \pm \Psi_B(r_1) \Psi_A(r_2)]$$

└ symmetric or anti-symmetric

* IF you make a measurement and find the particle in position #1, there is a 50/50 chance you will find it in either state A or state B

$|\Psi\rangle$ - arbitrary state

$\hat{H} \otimes \mathbf{I}$ - an operator that finds the energy of the first particle and ignores the second

$$\hat{H}|\Psi_B\rangle = E_B|\Psi_B\rangle$$

wrong $\left\{ \begin{array}{l} (\hat{H} \otimes \mathbf{I}) \frac{1}{\sqrt{2}} (|\Psi_A\rangle \otimes |\Psi_B\rangle \pm |\Psi_B\rangle \otimes |\Psi_A\rangle) \\ \hat{H}_1 \quad \quad \quad |\Psi\rangle \end{array} \right\}$ Ψ is NOT an eigenstate of the wavefunction

$$= E_A \frac{1}{\sqrt{2}} |\Psi_A\rangle \otimes |\Psi_B\rangle \pm E_B \frac{1}{\sqrt{2}} |\Psi_B\rangle \otimes |\Psi_A\rangle$$

correct $\rightarrow (\hat{H} \otimes \mathbf{I})(|\Psi_A\rangle \otimes |\text{any}\rangle) = E_A |\Psi_A\rangle \otimes |\text{any}\rangle$

choose $|\Psi_B\rangle \rightarrow$

$\uparrow$ Hamiltonian does nothing here

* Infinitely degenerate! You have any combination of eigenstates that still produce the same constant eigenvalue

basis $\{|\Psi_A\rangle \otimes |\Psi_B\rangle\}$, E_A - eigenvalue

50/50 probability that you will find either the state corresponding to E_A or the state corresponding to E_B , but never both

for more than 2 fermion particles $\rightarrow$ Slater determinant

$$\Psi(r_1, r_2, r_3) = \begin{vmatrix} \Psi_A(r_1) & \Psi_B(r_2) & \Psi_C(r_3) \\ \Psi_C(r_1) & \Psi_A(r_2) & \Psi_B(r_3) \\ \Psi_B(r_1) & \Psi_C(r_2) & \Psi_A(r_3) \end{vmatrix}$$

9/26/12

Many-Particles, Con't

Homework 4: Problem 1

$$|\psi\rangle, \hat{A}$$

$$\hat{A}|n\rangle = a_n|n\rangle$$

$$|\psi\rangle = \sum_n \psi_n |n\rangle$$

$$\text{probability of } a_n = |\psi_n|^2$$

$$\rightarrow S_z = \hbar/2 \text{ (spin up eigenstate)}$$

$$|\psi\rangle = |+\rangle, \text{ in } S$$

$$\rightarrow |\theta, +\rangle = \cos(\frac{\theta}{2})|+\rangle + e^{i\phi} \sin(\frac{\theta}{2})|-\rangle$$

Spin up along direction of θ

$$|\theta, -\rangle = -\sin(\frac{\theta}{2})|+\rangle + e^{i\phi} \cos(\frac{\theta}{2})|-\rangle$$

$$|+\rangle = \cos(\frac{\theta}{2})|\theta, +\rangle - \sin(\frac{\theta}{2})|\theta, -\rangle$$

$$\langle \theta, + | + \rangle$$

$$\text{probability of } \hbar/2 = \cos^2(\frac{\theta}{2})$$

* remember that if you then made another measurement, you would get $|+\rangle$ 100% of the time

Recap

$$|\Psi\rangle = \int dx_1 dx_2 \Psi(x_1, x_2) |x_1\rangle \otimes |x_2\rangle$$

identical particles

bosons ($s=0, 1, 2, \dots$)

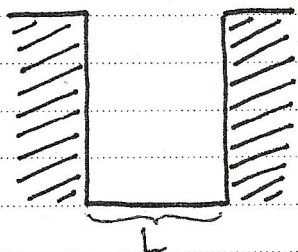
$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|A\rangle \otimes |B\rangle + |B\rangle \otimes |A\rangle)$$

fermions ($s=\frac{1}{2}, \frac{3}{2}, \dots$)

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|A\rangle \otimes |B\rangle - |B\rangle \otimes |A\rangle)$$

when you change particles for a fermion, the wavefunction must change sign

Example:



1 particle

$$|n\rangle, n=1, 2, \dots, \hat{H}|n\rangle = E_n|n\rangle$$

$$E_n = \frac{\pi^2 \hbar^2}{2mL^2} n^2, \langle x | n \rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$\text{2 particle: } \hat{H} = \hat{H}_1 \otimes \mathbf{I} + \mathbf{I} \otimes \hat{H}_2$$

$$[\hat{H}_1, \hat{H}_2] = 0 \text{ (the two Hamiltonians commute)}$$

for distinguishable particles:

$$|\Psi\rangle = |1\rangle \otimes |1\rangle - \text{ground state, particle 2}$$

↳ ground state, particle 1

$$\hat{H}|\Psi\rangle = (\hat{H} \otimes \mathbb{I} + \mathbb{I} \otimes \hat{H})|1\rangle \otimes |1\rangle = E_1|1\rangle \otimes |1\rangle + E_1|1\rangle \otimes |1\rangle \\ = 2E_1|1\rangle \otimes |1\rangle$$

→ first excited state $|1\rangle \otimes |2\rangle, E_1 + E_2$ and $|2\rangle \otimes |1\rangle, E_2 + E_1$ first excited state is degenerate!

for identical bosons:

Ground state → $|1\rangle \otimes |1\rangle, 2E_1$

1st Excited state → $\frac{1}{\sqrt{2}}(|1\rangle \otimes |2\rangle + |2\rangle \otimes |1\rangle), E_1 + E_2$

↳ must be a symmetrized linear combination, excited states must excite both particles, no degeneracies allowed

for identical fermions: (switching particles must change signs)

Ground state: $\frac{1}{\sqrt{2}}(|1\rangle \otimes |2\rangle - |2\rangle \otimes |1\rangle), E_1 + E_2$

↳ there's no way you can have two fermions in the same state, it must be a normalized anti-symmetric combination of states, no degeneracies allowed

1st Excited state: $\frac{1}{\sqrt{2}}(|1\rangle \otimes |3\rangle - |3\rangle \otimes |1\rangle), E_1 + E_3$

* this is only applicable for particles that do not interact!
- Pauli exclusion principle

Exchange "Forces"

"The problem with exchange "forces"... they don't exchange and they are not forces!"

for distinguishable particles:

$$|\Psi\rangle = |A\rangle \otimes |B\rangle \leftarrow (\langle B| \otimes \langle A|)$$

↳ single particle states

for bosons/fermions:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}[|A\rangle \otimes |B\rangle \pm |B\rangle \otimes |A\rangle]$$

$$\langle \Psi | (\hat{x}_1 - \hat{x}_2)^2 | \Psi \rangle - \text{sandwich finds the average distance between two particles}$$

distance between 1 & 2

→

Mathematical aside: Sandwich averages

$$\langle \psi | \hat{A} | \psi \rangle = \sum_{n,m} \langle \psi | m \rangle \underbrace{\langle m | \hat{A} | n \rangle}_{a_n \langle m | n \rangle} \langle n | \psi \rangle$$

$$a_n \langle m | n \rangle$$

$$\delta_{mn}$$

$$= \sum_n \langle \psi | n \rangle a_n \langle n | \psi \rangle$$

$$= \sum_n a_n |\langle n | \psi \rangle|^2$$

measurement values

probability of measuring a_n

$$\langle \psi | (\hat{x}_1 - \hat{x}_2)^2 | \psi \rangle = \langle \psi | \hat{x}_1^2 + \hat{x}_2^2 - 2\hat{x}_1\hat{x}_2 | \psi \rangle$$

Distinguishable:

$$(\langle B | \otimes \langle A |) (\hat{x}_1^2 + \hat{x}_2^2 - 2\hat{x}_1\hat{x}_2) (|A\rangle \otimes |B\rangle)$$

$$= \langle A | \hat{x}_1^2 | A \rangle + \langle B | \hat{x}_2^2 | B \rangle - 2 \underbrace{\langle A | \hat{x}_1 | A \rangle}_{\rightarrow 0} \underbrace{\langle B | \hat{x}_2 | B \rangle}_{\rightarrow 0}$$

assumption

Bosons/Fermions:

$$\frac{1}{\sqrt{2}} (\langle B | \otimes \langle A | \pm \langle A | \otimes \langle B |) (\hat{x}_1^2 + \hat{x}_2^2 - 2\hat{x}_1\hat{x}_2) \frac{1}{\sqrt{2}} (|A\rangle \otimes |B\rangle \pm |B\rangle \otimes |A\rangle)$$

L_{2nd} L_{1st}

L_{2nd} L_{1st}

$$= \pm \frac{1}{2} \langle B | \hat{x}_1^2 | A \rangle \langle A | B \rangle \pm \frac{1}{2} \langle A | \hat{x}_2^2 | B \rangle \langle B | A \rangle \pm \frac{1}{2} \cdot 2 \langle B | \hat{x}_1 | A \rangle \langle A | \hat{x}_2 | B \rangle$$

$$\pm \frac{1}{2} \langle A | \hat{x}_1^2 | B \rangle \langle B | A \rangle \pm \frac{1}{2} \langle B | \hat{x}_2^2 | A \rangle \langle A | B \rangle \pm \frac{1}{2} \cdot 2 \langle B | \hat{x}_1 | A \rangle \langle A | \hat{x}_2 | B \rangle$$

$$+ \frac{1}{2} \langle B | \hat{x}_1^2 | B \rangle + \frac{1}{2} \langle A | \hat{x}_2^2 | A \rangle$$

$$+ \frac{1}{2} \langle A | \hat{x}_1^2 | A \rangle + \frac{1}{2} \langle B | \hat{x}_2^2 | B \rangle + \frac{1}{2} \cdot 2 \underbrace{\langle A | \hat{x}_1 | A \rangle}_{\rightarrow 0} \underbrace{\langle B | \hat{x}_2 | B \rangle}_{\rightarrow 0}$$

assumption

$$= \langle A | \hat{x}_1^2 | A \rangle + \langle B | \hat{x}_2^2 | B \rangle \pm 2 |\langle A | \hat{x}_1 | B \rangle|^2$$

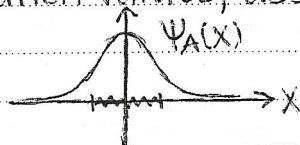
9/28/12

Exchange "Forces"

$$|\Psi\rangle = \begin{cases} |A\rangle \otimes |B\rangle & \text{distinguishable} \\ \frac{1}{\sqrt{2}}(|A\rangle \otimes |B\rangle \pm |B\rangle \otimes |A\rangle) & \text{bosons or fermions} \end{cases}$$

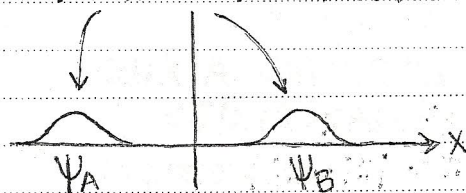
$$\langle \Psi | (\hat{x}_1 - \hat{x}_2)^2 | \Psi \rangle = \langle \Psi | \hat{x}_1^2 + \hat{x}_2^2 - 2\hat{x}_1\hat{x}_2 | \Psi \rangle$$

$$\underbrace{\langle A | \hat{x}^2 | A \rangle + \langle B | \hat{x}^2 | B \rangle}_{\text{expectation values, assumed central zero value}} + \begin{cases} 0 & \text{extra term for} \\ \mp 2|\langle A | \hat{x} | B \rangle|^2 & \text{identical particles} \end{cases}$$



- Bosons tend to want to align with each other
 - (-) makes for smaller average distance
- Fermions tend to move to avoid each other
 - (+) makes for larger average distances
- this happens even though there is no force between them, hence, exchange "forces"

$\mp 2|\langle A | \hat{x} | B \rangle|^2$ - location of Ψ_A and Ψ_B matters a lot



$$\int dx \Psi_A^*(x) \times \Psi_B(x) \approx 0$$

no overlap

→ behaves essentially like distinguishable particles

Atoms

Hydrogen atom: Kinetic energy ($\hat{p}^2/2m$)

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

— Coulomb force

— Hamiltonian in the position basis

→ assumes infinite proton mass, independent of spin, etc.

To fix this equation, must account for

- finite proton mass
- relativity
- Vacuum polarization (correction for the Coulomb force at small distances)
- spin-spin interaction
- etc...

↓ principle quantum # $n=1,2,3,\dots$ (state)

$$\Rightarrow |n, l, m, m_s\rangle$$

angular
momentum
 $l=0,1,\dots,n-1$

↑ spin $\pm 1/2$

↑ orbital angular momentum
 $-l \leq \dots \leq l$

$$|n, l, m\rangle \otimes |1/2, m_s\rangle$$

↑ spherical harmonics

$$\langle r | n, l, m \rangle = \Psi_{n, l, m}(r, \theta, \varphi) = R_{n, l}(r) Y_{l, m}(\theta, \varphi)$$

↓ position basis

↓ radial portion

↑ atomic number, here = 1

$$E_n = -\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2}$$

↓ energy eigenvalues

* this is independent of $l \Rightarrow$ accidental degeneracy

$$E_n = -13.6 \text{ eV} \frac{Z^2}{n^2} - \text{large atomic \#} \rightarrow \text{higher binding energy}$$

energy quickly approaches 0 for higher states
ground state ($n=1$)

Helium atom: ↑ Hamiltonian of the second electron

$$\hat{H} = \hat{H}_1 \otimes \mathbb{I} + \mathbb{I} \otimes \hat{H}_2 + \hat{H}_{int}$$

↑ interaction between the two electrons

↓ Hamiltonian of the first electron

r-representation (partial diff. eq. with $\mathbf{r}$ -coordinates)

$$\rightarrow \underbrace{-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_1}^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1}}_{\hat{H}_1} - \underbrace{\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_2}^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_2}}_{\hat{H}_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}}_{\hat{H}_{int}}$$

$$|\Psi\rangle = \sum_{m_{s1}, m_{s2} = \pm 1/2} \int d^3r_1 d^3r_2 \Psi_{m_{s1}, m_{s2}}(\mathbf{r}_1, \mathbf{r}_2) |\mathbf{r}_1\rangle \otimes |\mathbf{r}_2\rangle \otimes |m_{s1}\rangle \otimes |m_{s2}\rangle$$

↑ Z-components

• $\hat{H}$ doesn't depend on spin

$$\Psi_{m_{s1}, m_{s2}}(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2) \chi_{m_{s1}, m_{s2}}$$

↑ constant, generic value

• If we neglect $e^2/4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_1(\mathbf{r}_1) \Psi_2(\mathbf{r}_2) - \text{second Hamiltonian acts only here}$$

↓ first Hamiltonian acts only here

↓ Hydrogen states with $Z=2$

10/1/12

Atoms

Helium:

$$|\Psi\rangle = \sum_{m_{s1}, m_{s2}} \int d^3r_1 d^3r_2 \Psi_{m_{s1}, m_{s2}}(r_1, r_2) |r_1\rangle \otimes |r_2\rangle \otimes |m_{s1}\rangle \otimes |m_{s2}\rangle$$

↳ generic state of a two-electron system

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1}}_{\hat{H}_1} - \underbrace{\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_2}}_{\hat{H}_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_1 - r_2|}}_{\hat{H}_{int}}$$

Orbitals

$$\hat{H}_{int} \approx 0 \Rightarrow \Psi_{m_{s1}, m_{s2}}(r_1, r_2) = \psi_1(r_1) \psi_2(r_2) \chi_{m_{s1}, m_{s2}}$$

$$\hat{H}\Psi = (\hat{H}_1 + \hat{H}_2) \psi_1 \psi_2 = \underbrace{(E_1 + E_2)}_{\text{full } \hat{H} \text{ result}} \psi_1 \psi_2$$

→ if you make a wavefunction of the sub-Hamiltonian, your answer will equal the full Hamiltonian result

But the particles are fermions!

→ if you flip the particles, the sign of the wavefunction must change (one part antisymmetric)

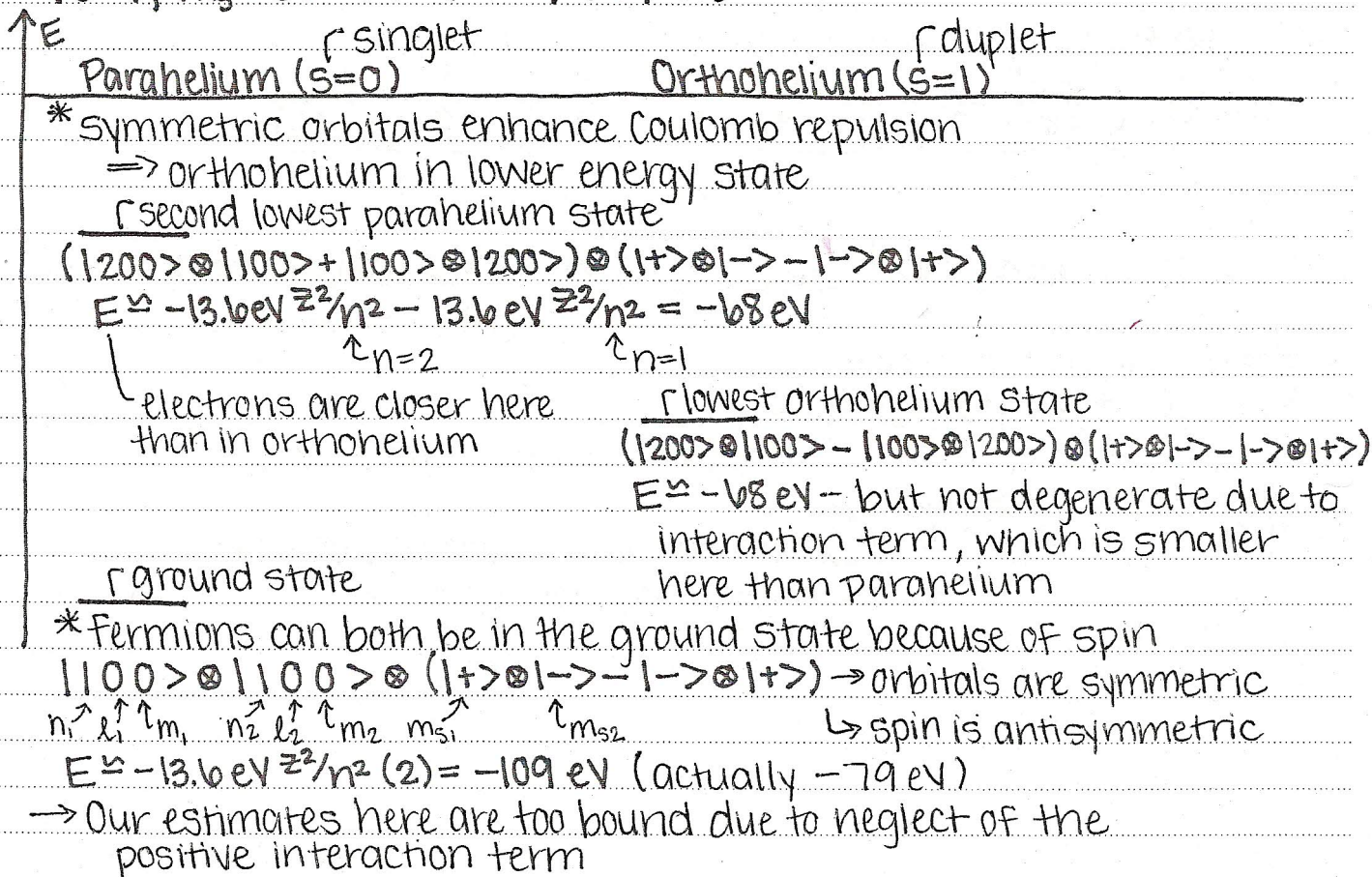
$$|S=0, m_S=0\rangle = |+\rangle \otimes |-\rangle - |-\rangle \otimes |+\rangle \sim \text{antisymmetric, spin 0}$$

$$|S=1, m_S=1\rangle = |+\rangle \otimes |+\rangle$$

$$|S=1, m_S=-1\rangle = |-\rangle \otimes |-\rangle$$

$$|S=1, m_S=0\rangle = |+\rangle \otimes |-\rangle + |-\rangle \otimes |+\rangle$$

} symmetric, spin 1



The rest of the Periodic Table

"How can I do this so quickly? Because I can't do it at all!"

You thought Helium was a lot of handwaving? Oh, boy..."

First shell (2)

$$n=1, l=0, m=0, m_s=\pm\hbar/2$$

↳ corresponds to a closed shell

↳ two states (Hydrogen and Helium) $\Rightarrow$ Noble Gas

Second shell (8)

$$n=2, l=0, m=0, m_s=\pm\hbar/2$$

Neon ($10e^-$) corresponds

$$l=1, m=-1, 0, 1, m_s=\pm\hbar/2$$

to a closed shell as well

↳ eight states

Third shell (18)

$$n=3, l=0, m=0, m_s=\pm\hbar/2$$

$$l=1, m=-1, 0, 1, m_s=\pm\hbar/2$$

$$l=2, m=-2, -1, 0, 1, 2, m_s=\pm\hbar/2$$

↳ eighteen states

$$n=4, l=0, m=0, m_s=\pm\hbar/2$$

↳ this state is preferable to $l=2$ because a large angular momentum produces a larger energy because the electron at $l=2$ is too far away to feel the specific energy of the nucleus

10/3/12

Atoms, Con't

"Everything in the Universe can be solved with Schrödinger's Equation!"

Defining properties of atoms and their states:

• principle quantum number $n=1,2,3,\dots$

• angular momentum $l=0,\dots,n-1$

$l=0$ s (sharp)

$l=1$ p ("uhh... these look like Paulo...")

$l=2$ d (diffuse)

$l=3$ f

• orbital angular momentum $m=-l,\dots,+l$

• Z # of electrons

• orbital configurations

$(2s+1) \rightarrow 2S_{1/2}$ $\left. \begin{array}{l} L \text{ (total orbital angular momentum)} \\ S_{1/2} \end{array} \right\}$ summed over all electrons
 J (spin + orbital)

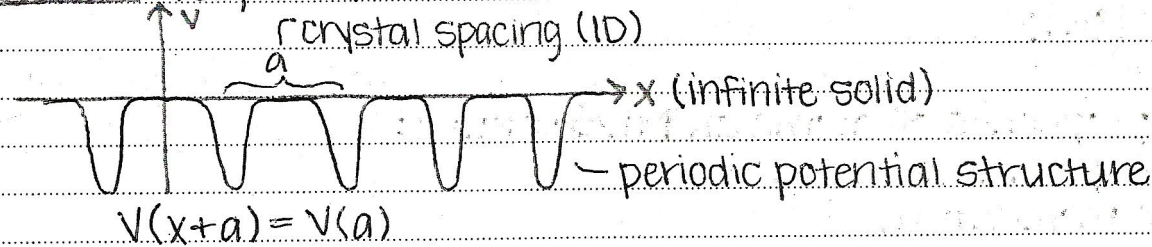
Z	element	Configuration	alt. config.
1	H	$m=1 \rightarrow 1S_{1/2}$	$2S_{1/2}$
2	He	$(1s)^2$	$1S_0$
3	Li	$(1s)^2 2s$	$2S_{1/2}$
4	Be	$(1s)^2 (2s)^2$	$1S_0$
5	B	$(1s)^2 (2s)^2 2p$	$2P_{1/2}$
6	C	$(1s)^2 (2s)^2 (2p)^2$	$3P_0$
...	...	...	...
10	Ne	$(1s)^2 (2s)^2 (2p)^6$	$1S_0$
11	Na	$(1s)^2 (2s)^2 (2p)^6 3s$	$2S_{1/2}$
...	...	...	...
19	K	$(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 4s$	
20	Ca	$(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (4s)^2$	
21	Sc	$(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (4s)^2 3d$	

Screening effect
you feel 4s before 3d

"H and Na are chemically similar. Most importantly, if you throw them both in water, they both explode!"

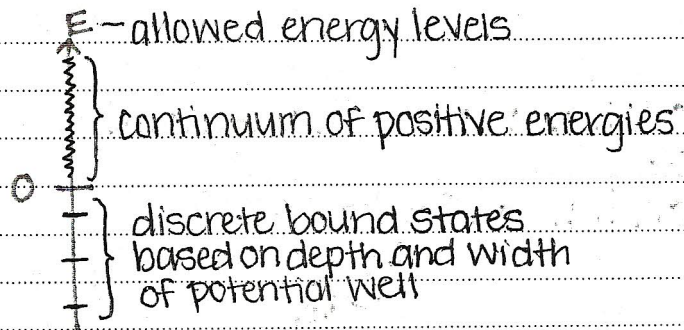
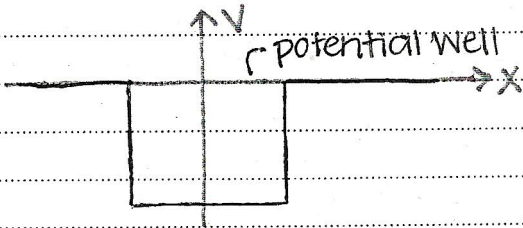
→

Solids (crystals)

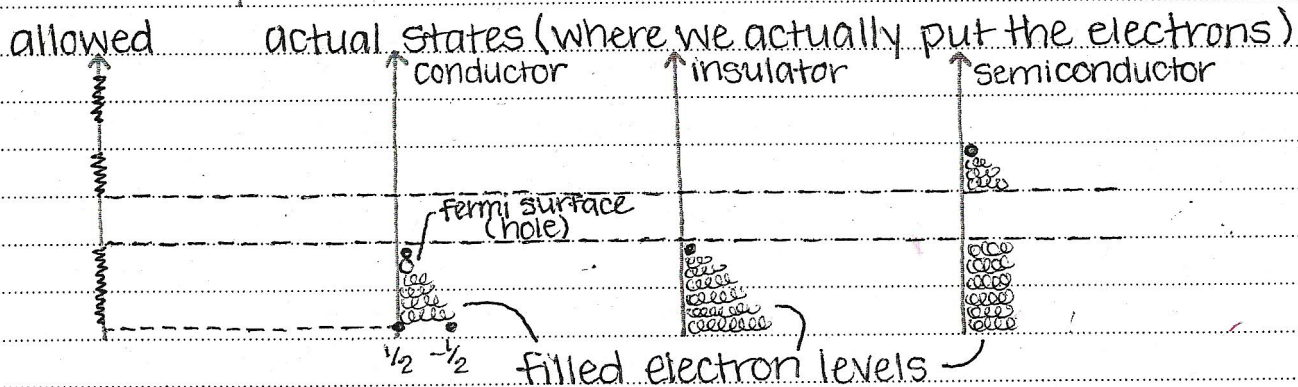
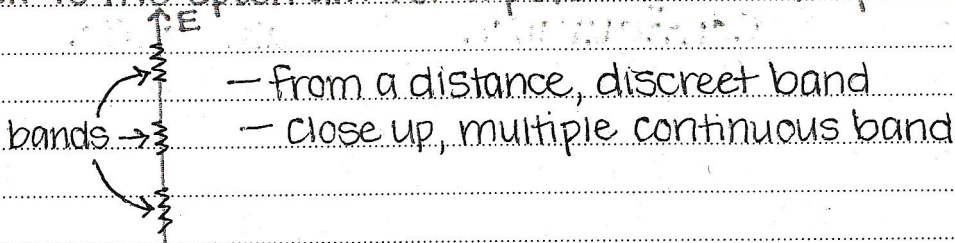


When $V=0$

$$\psi_p(x) = \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}, \quad E = \frac{p^2}{2m}$$



What is the spectrum for a potential that's periodic?



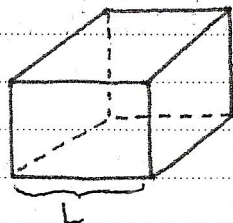
Apply an electric field $\rightarrow$ investigate whether the electrons can move within their band

— amount of available movement indicates conductivity levels

10/5/12

Free-Electron (Fermions) Gas

Homework note: if the fermions don't interact, the Hamiltonian will not have any terms that concern the coordinates of both particles.



single particle states:

$$|n_x, n_y, n_z, m_s\rangle$$

(1, 2, 3, ...)

z-component of the spin $\pm 1/2$

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

energy independent of spin

eigenfunctions of position

$$\langle x, y, z | n_x, n_y, n_z, m_s \rangle$$

$$\psi_{n_x n_y n_z}(x, y, z)$$

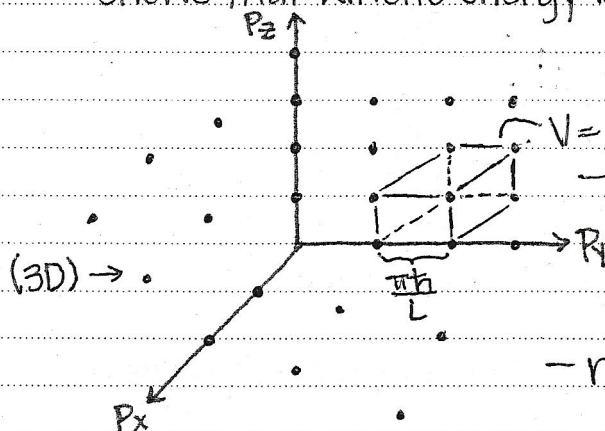
$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \begin{Bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{Bmatrix}$$

multiply by the spinor $\rightarrow$

$\rightarrow$ Rewrite energy eigenvalues in terms of momentum

$$E_{n_x n_y n_z} = \frac{p_x^2 + p_y^2 + p_z^2}{2mL^2}, \quad p_x = \frac{\pi \hbar n_x}{L} \text{ - restricted to integer } L's$$

shows that kinetic energy is the only allowable energy



$$V = (\pi \hbar / L)^3$$

- each state corresponds to a cube

$\rightarrow$ one point for each $(\pi \hbar / L)^3$

- Only interested in $+p_x, p_y, p_z$ (one octant)

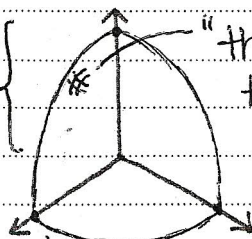
- momentum values are quantized into multiples of $(\pi \hbar / L)$

- least amount of energy is on the axis

note that $p_x = 0$ does not exist

* each cube has 8 vertices, but only one vertex has the minimum p_x, p_y, p_z value

radius - k_F
Fermi momentum



"this is three-dimensional. This little spot, this is like the orange where it shines on the surface! Don't laugh at me! You couldn't draw this better either!"

↑ Fermi Sphere - "the orange"

the edge is the Fermi Surface

The higher the number of particles, the smoother the Fermi sphere.

needed for "smoothness" in terms of the radius

$$N = \# \text{ of particles} \approx \underbrace{\frac{1}{8}}_{\text{one octant}} (2) \underbrace{\frac{4}{3} \pi k_F^3}_{\text{sphere volume}} \left(\frac{L}{\pi \hbar} \right)^3$$

"Though it's not really smooth, it's like a ball of Legos. Ever try to make a ball of Legos? You can't!"

$$= \frac{k_F^3}{3\pi^2 \hbar^3} V \sim L^3$$

$$\Rightarrow \frac{N}{V} = \frac{k_F^3}{3\pi^2 \hbar^3}$$

n - density

$$k_F = (3\pi^2 \hbar^3 n)^{1/3}$$

After you write things in terms of the density, you can forget you had a box - you can fill the whole universe and find the Fermi momentum still using this density value.

Total energy: $\left\{ \begin{array}{l} \text{spin } \pm \\ p = \hbar k \end{array} \right.$

$$E = \int_{\text{octant}} d^3p \left(\frac{L}{\pi \hbar} \right)^3 2 \frac{p^2}{2m} = 2V \int_0^{k_F} \frac{d^3p}{(2\pi \hbar)^3} \frac{p^2}{2m}$$

density of points in p -space

energy of each particle

$\int$ normalization of a plane wave in 3D

→ The energy density (E/V) can be seen as continuous so long as you include the $(2\pi \hbar)^3$ normalization to represent the octant-cube in real space → sphere in momentum space

$$\mathcal{E} = \frac{E}{V} = 2 \int_0^{k_F} \frac{d^3p}{(2\pi \hbar)^3} \frac{p^2}{2m} = \frac{2}{2\pi^2 \hbar^3} \frac{1}{2m} \frac{k_F^5}{5}$$

$\int$ solid angle

$$= \frac{k_F^5}{10\pi^2 m \hbar^3} = \frac{(3\pi^2 \hbar^3 n)^{5/3}}{10\pi^2 \hbar^3 m}$$

→ Degenerate pressure!

degenerate Fermi gas:

$$k_B T \ll k_F^2 / 2m \Rightarrow \approx \text{ground state (white dwarfs)}$$

energy density depends on particle density to the $5/3$ power

10/8/12

Approximation Methods

Time-Independent Perturbation Theory

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

known λ a "small" number

$$\hat{H}_0 |n^0\rangle = E_n^0 |n^0\rangle$$

$$\hat{H} |n\rangle = E_n |n\rangle$$

unknown

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad \text{— corrections to the eigenvalues}$$

$$|n\rangle = |n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \dots \quad \text{& eigenkets}$$

power series

$$\hat{H} |n\rangle = (\hat{H}_0 + \lambda \hat{V})(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \dots)$$

$$= (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \dots)$$

$$\Rightarrow \mathcal{O}(\lambda^0): \hat{H}_0 |n^0\rangle = E_n^0 |n^0\rangle$$

$$\mathcal{O}(\lambda^1): \hat{H}_0 |n^1\rangle + \hat{V} |n^0\rangle = E_n^0 |n^1\rangle + E_n^1 |n^0\rangle$$

$$\mathcal{O}(\lambda^2): \hat{H}_0 |n^2\rangle + \hat{V} |n^1\rangle = E_n^0 |n^2\rangle + E_n^1 |n^1\rangle + E_n^2 |n^0\rangle$$

$$\rightarrow \langle n^0 | \hat{H}_0 |n^1\rangle + \langle n^0 | \hat{V} |n^0\rangle = E_n^0 \langle n^0 | n^1\rangle + E_n^1$$

$$E_n^0 \langle n^0 | n^1\rangle$$

$$\Rightarrow E_n^1 = \langle n^0 | \hat{V} |n^0\rangle$$

$\hookrightarrow$ the energy of the first perturbation is the sandwich of the first tier perturbation on the unperturbed state

$$\lambda E_n^1 = \langle n^0 | \lambda \hat{V} |n^0\rangle$$

$\hookrightarrow$ perturbation theory algorithm

$$\langle m^0 | \hat{H}_0 |n^1\rangle + \langle m^0 | \hat{V} |n^0\rangle = E_n^0 \langle m^0 | n^1\rangle + E_n^1 \langle m^0 | n^0\rangle$$

$$E_m^0 \langle m^0 | n^1\rangle$$

$\mathcal{O}$ -orthonormal

$m \neq n$ — just a different state

$$\Rightarrow \langle m^0 | n^1\rangle = \frac{\langle m^0 | \hat{V} |n^0\rangle}{E_n^0 - E_m^0}$$

$\hookrightarrow$ only valid for m different from n

(n^1 should not have a component in the direction of m^0)

but,

$$(\langle n^0 | + \lambda \langle n^1 |)(|n^0\rangle + \lambda |n^1\rangle) = 1 + \lambda \langle n^0 | n^1\rangle + \lambda \langle n^1 | n^0\rangle + \mathcal{O}(\lambda^2)$$

$$= 1 + \mathcal{O}(\lambda^2)$$

$\hookrightarrow$ by normalization

$\hookrightarrow$ first perturbed eigenstate for order λ

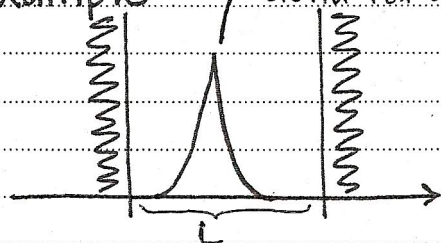
$$\Rightarrow |n^1\rangle = \sum_{m \neq n} \frac{\langle m^0 | \hat{V} |n^0\rangle}{E_n^0 - E_m^0} |m^0\rangle$$

$\hookrightarrow$ sum over all values except $m=n$

$$\rightarrow E_n^2 = \sum_{m \neq n} \frac{|\langle n^0 | \hat{V} |m^0\rangle|^2}{E_n^0 - E_m^0}$$

$\hookrightarrow$ second-order correction for the eigenvalue of order λ^2

Example: delta function potential in an infinite square well



$$V(x) = \begin{cases} \infty & x > L \text{ or } x < 0 \\ \lambda \delta(x - L/2) & 0 < x < L \end{cases}$$

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2m}}_{\hat{H}_0} + \underbrace{V_{\text{square well}}(x)}_{\lambda \hat{V}} + \lambda \delta(x - L/2)$$

$$\langle x | n \rangle^0 = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n^0 = \frac{\pi^2 \hbar^2 n^2}{2mL^2}, \quad n = 1, 2, 3, \dots$$

First-Order Correction:

$$\lambda E_n^1 = \langle n | \hat{V} | n \rangle^0 = \int_0^L dx \sqrt{\frac{2}{L}}^2 \sin^2\left(\frac{n\pi x}{L}\right) \lambda \delta(x - L/2)$$

$$= \left(\frac{2}{L}\right) \lambda \sin^2\left(\frac{n\pi}{2}\right) = \begin{cases} 2/L, & n \text{ odd} \\ 0, & n \text{ even} \end{cases}$$

$$\text{II} = \int dy |y\rangle \langle y| \quad \text{I} = \int dx |x\rangle \langle x|$$

$$\langle y | V(\hat{x}) | x \rangle = V(x) \langle y | x \rangle$$

$\uparrow$ x of the ket, not the original argument

$$= \int dx dy \langle n | y \rangle \underbrace{\langle y | V(\hat{x}) | x \rangle}_{V(x) \langle y | x \rangle} \langle x | n \rangle^0$$

shifting energy

$$= \int dx \underbrace{\langle n | x \rangle}_{\sin(n\pi x/L)} \underbrace{V(x)}_{\lambda \delta(x - L/2)} \underbrace{\langle x | n \rangle^0}_{\sin(n\pi x/L)}$$

10/10/12

An Alternative Perspective on Perturbation Theory

Guest lecturer - Professor Applebaum

You know how to solve:

$$\hat{H}_0 \vec{\Psi} = E \vec{\Psi} \text{ - describes an orthonormal basis set}$$

You want to know:

how to find eigenvectors/eigenvalues of $\hat{H}_0 + \lambda \hat{H}_1$
small compared to $\hat{H}_0$

Knowing eigenvectors Ψ_n means

$$\langle \Psi_n | \hat{H}_0 | \Psi_m \rangle = \delta_{nm} E_n$$

due to orthonormality (eigenvectors diagonalize a Hamiltonian)

i.e. $\hat{H}_0$ is diagonal in the Ψ_n basis

In general $\hat{H}_0 + \lambda \hat{H}_1$ is not diagonal

$$\langle \Psi_n | \hat{H}_0 + \lambda \hat{H}_1 | \Psi_m \rangle \neq \delta_{nm} E_n$$

→ However, the off-diagonal $n \neq m$ values are small

$\hat{H}_0 + \lambda \hat{H}_1$ is nearly diagonalized by original Ψ_n

→ Take diagonal elements as approximations to eigenvalues

2x2 Example: spin $\frac{1}{2}$

$$\hat{H}_0 = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}, \text{ with } \vec{\Psi}_1, E_1 \text{ and } \vec{\Psi}_2, E_2$$

What are the eigenvalues of $\hat{H}_0 + \lambda \hat{H}_1$?

In the nearly-diagonalizing basis $\vec{\Psi}_1, \vec{\Psi}_2$, we have

$$\begin{bmatrix} \langle \Psi_1 | \hat{H}_0 + \lambda \hat{H}_1 | \Psi_1 \rangle & \langle \Psi_1 | \hat{H}_0 + \lambda \hat{H}_1 | \Psi_2 \rangle \\ \langle \Psi_2 | \hat{H}_0 + \lambda \hat{H}_1 | \Psi_1 \rangle & \langle \Psi_2 | \hat{H}_0 + \lambda \hat{H}_1 | \Psi_2 \rangle \end{bmatrix}$$

$$= \begin{bmatrix} E_1^{(0)} & \Delta \\ \Delta^* & E_2^{(0)} \end{bmatrix} \quad \Delta \sim 0$$

- first order approximation to eigenvalues
(nearly diagonal → off elements assumed ≈ 0)

We can do better!

→ directly calculate the true eigenvalues

Second-order approximation:

eigenvalues are given by

$$\det \begin{bmatrix} E_1^{(0)} - E & \Delta \\ \Delta^* & E_2^{(0)} - E \end{bmatrix} = 0$$

$$(E_1^{(0)} - E)(E_2^{(0)} - E) - |\Delta|^2 = 0$$

$$E^2 - (E_1^{(0)} + E_2^{(0)})E + E_1^{(0)}E_2^{(0)} - |\Delta|^2 = 0$$

Quadratic formula: $E = \frac{(E_1 + E_2) \pm \sqrt{(E_1 + E_2)^2 - 4E_1E_2 + 4|\Delta|^2}}{2(1)}$

$$E = \frac{(E_1 + E_2) \pm \sqrt{(E_1 - E_2)^2 + 4|\Delta|^2}}{2}$$

Since $|\Delta|^2 \ll (E_1^{(1)} - E_2^{(1)})^2$, it makes sense to write

$$E = \frac{1}{2} \left[(E_1 + E_2) \pm (E_1 - E_2) \sqrt{1 + 4 \frac{|\Delta|^2}{(E_1 - E_2)^2}} \right]$$

only for the non-degenerate case, $E_1 \neq E_2$

$$\approx \frac{1}{2} \left[(E_1 + E_2) \pm (E_1 - E_2) \left(1 + 2 \frac{|\Delta|^2}{(E_1 - E_2)^2} \right) \right]$$

Taylor series approximation of square root

$$\approx \frac{1}{2} \left[(E_1 + E_2) \pm \left((E_1 - E_2) + 2 \frac{|\Delta|^2}{(E_1 - E_2)} \right) \right]$$

$$\Rightarrow (+): E_1^{(1)} + |\Delta|^2 / (E_1 - E_2)$$

$$(-): E_2^{(1)} - |\Delta|^2 / (E_1 - E_2) = E_2^{(1)} + |\Delta|^2 / (E_2 - E_1)$$

first-order contribution

second-order contribution

Compare: $\sum_{m \neq n} \frac{|\langle \Psi_n | \lambda \hat{H}_1 | \Psi_m \rangle|^2}{E_n - E_m}$
With

Degeneracy

What if $E_1 = E_2$? Then the second-order correction has a problem (is undefined)

→ Our previous expansion is invalid under degenerate conditions

$$\frac{1}{2} [(E_1 + E_2) \pm \sqrt{(E_1 - E_2)^2 + 4|\Delta|^2}] - \text{no longer needs expansion}$$

$$\Rightarrow E = \frac{1}{2} [(E_1 + E_2) \pm 2|\Delta|]$$

$$= E_{1,2}^{(1)} \pm |\Delta|$$

In general, for $N > 2$ degenerate states, find eigenvalues of a matrix constructed of subspace:

$$\begin{bmatrix} E_1 & & & \\ & E_2 & \alpha & \delta \\ & \alpha^* & E_3 & \Delta \\ & \delta^* & \Delta^* & E_4 \\ & & & & E_5 \end{bmatrix}$$

E_2, E_3, E_4 are degenerate

→ find eigenvalues of submatrix

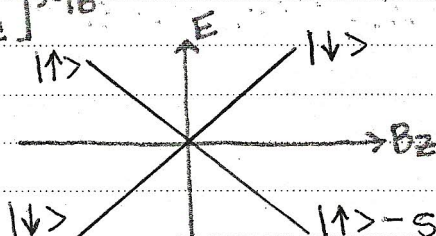
Level Splitting

This is what happens at "level crossing"

in field $\vec{B} = B_z \hat{z}$, $\hat{H}_0 = -g\mu_B \vec{\sigma} \cdot \vec{B}$ (unperturbed)

$$\rightarrow \begin{bmatrix} -B_z & 0 \\ 0 & +B_z \end{bmatrix} \mu_B$$

Pauli spin matrices $\vec{\sigma} = \sigma_x \hat{x} + \sigma_y \hat{y} + \sigma_z \hat{z}$



|↑⟩ - spin up is more energetically favorable

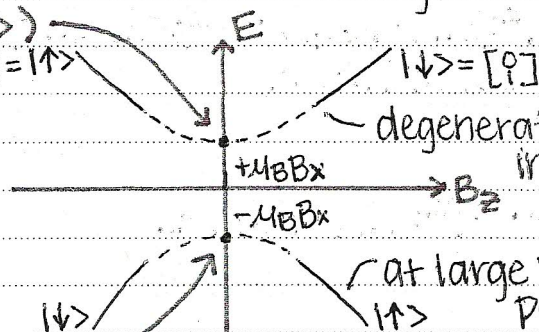
With perturbation $B_x \hat{x}$

$$\lambda \hat{H}_1 = -B_x \sigma_x$$

$$\hat{H}_0 + \lambda \hat{H}_1 = \mu_B \begin{bmatrix} -B_z & B_x \\ B_x & +B_z \end{bmatrix} \text{ - degeneracy broken}$$

$$\frac{1}{2}(|\uparrow\rangle + |\downarrow\rangle)$$

$$[0] = |\uparrow\rangle$$



degenerate crossing has been split by influence of the perturbation

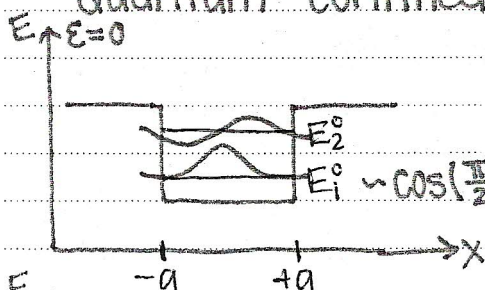
at large values of $|B_z|$ the perturbation is negligible

$$\frac{1}{2}(|\uparrow\rangle - |\downarrow\rangle)$$

The perturbation has instilled a requirement that the state, when the perturbation value is non-negligible, be a superposition of spin states!

Example: Non-degenerate perturbation theory

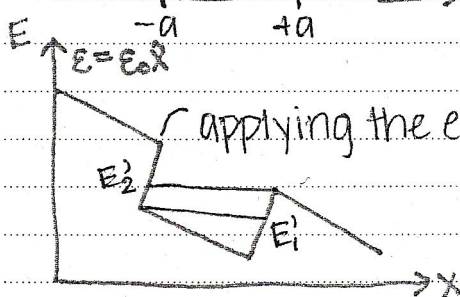
"Quantum-Confined Stark Effect"



Two states in a semi-conducting finite well with an applied electric field

$$U(x) = -qE_0 x$$

assumed "small" perturbation



applying the electric field slopes your potential

What happens to the first bound state E_1 ?

$$E_1^1 = E_1^0 + \underbrace{\langle \psi_1^0 | U(x) | \psi_1^0 \rangle}_{\text{1st order correction}} + \underbrace{\sum_{m \neq n} \frac{|\langle \psi_m^0 | U(x) | \psi_1^0 \rangle|^2}{E_n - E_m}}_{\text{2nd order correction}} + \dots$$

by symmetry

1st order: $\langle \psi_1^0 | U(x) | \psi_1^0 \rangle = \frac{1}{a} \int_{-a}^a \cos\left(\frac{\pi x}{2a}\right) (-q\epsilon_0 x) \cos\left(\frac{\pi x}{2a}\right) dx = 0$

an odd function integrated over a symmetric interval

2nd order: $\frac{|\langle \psi_2^0 | -q\epsilon_0 x | \psi_1^0 \rangle|^2}{E_1 - E_2} < 0$

dominant term is the state w/ the closest energy

So, ground state moves down in energy independent of the sign of the field!

$$\frac{|\langle \psi_2^0 | -q\epsilon_0 x | \psi_1^0 \rangle|^2}{E_1 - E_2} \approx \frac{(\frac{1}{a} - a \int_{-a}^a \sin(\pi x/2a) (-q\epsilon_0 x) \cos(\pi x/2a) dx)^2}{(\hbar^2 \pi^2 / 2m(2a)^2)(1^2 - 2^2)}$$

numerical solution under the infinite square well case

Numerator: $= \frac{2}{a} - a \int_{-a}^a \sin(\pi x/2a) \cos^2(\pi x/2a) (-q\epsilon_0 x) dx$

($\int u dv = uv - \int v du$) $u = x$ $dv = \cos^2(\pi x/2a) \sin(\pi x/2a) dx$

$du = dx$ $v = -\frac{1}{3} \cos^3(\pi x/2a) (2a/\pi)$

$$\frac{2ax}{3\pi} \cos^3(\pi x/2a) \Big|_{-a}^a - \frac{2a}{3\pi} - a \int_{-a}^a \cos^3(\pi x/2a) dx = -\frac{2a}{3\pi} - a \int_{-a}^a \cos(\pi x/2a) (1 - \sin^2(\pi x/2a)) dx$$

$$= -\frac{2a}{3\pi} \cdot \frac{2a}{\pi} \left(\sin(\pi x/2a) - \frac{1}{3} \sin^3(\pi x/2a) \right) \Big|_{-a}^a$$

$$= -\frac{4a^2}{3\pi^2} \left(\frac{2}{3} - \left(-\frac{2}{3} \right) \right) = \left(\frac{2(2a)}{3\pi} \right)^2$$

$$\frac{|\langle \psi_2^0 | -q\epsilon_0 x | \psi_1^0 \rangle|^2}{E_1 - E_2} \approx - \left(\frac{4q\epsilon_0}{2a} \right)^2 \frac{2m(2(2a)/3\pi)^4}{3\pi^2 \hbar^2}$$

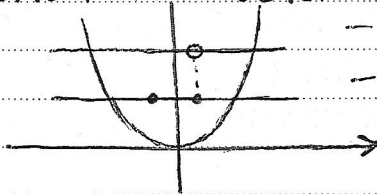
$$\approx -24 \left(\frac{2}{3\pi} \right)^6 \frac{q^2 \epsilon_0 m L^4}{\hbar^2} \quad -L = 2a$$

10/12/12

"Real" Hydrogen Atom

More time-independent perturbation theory

Homework 6 - Problem 1



- 1D harmonic oscillator
- no particle interaction

Single Particle States

$$|n, m_s\rangle = |n\rangle \otimes |m_s\rangle, \quad n=0, 1, 2, \dots, \quad m_s = \pm 1/2$$

$$E_n = \hbar\omega(n + 1/2) \quad (\text{independent of spin})$$

$$|\text{ground}\rangle = \frac{1}{\sqrt{2}} [|0, 1/2\rangle \otimes |0, -1/2\rangle - |0, -1/2\rangle \otimes |0, 1/2\rangle]$$

$$= \frac{1}{\sqrt{2}} [|00\rangle] [|1/2, -1/2\rangle - | -1/2, 1/2\rangle]$$

$S=0$

$$E_{\text{ground}} = E_0 + E_0 = \hbar\omega$$

$$|1^{\text{st}} \text{ ex. } 1\rangle = \frac{1}{\sqrt{2}} [|0\rangle \otimes |1/2\rangle \otimes |1\rangle \otimes |1/2\rangle - |1\rangle \otimes |1/2\rangle \otimes |0\rangle \otimes |1/2\rangle]$$

$$= \frac{1}{\sqrt{2}} [|01\rangle - |10\rangle] [|1/2\rangle \otimes |1/2\rangle]$$

$S=1, m_s=1$

$$|1^{\text{st}} \text{ ex. } 2\rangle = \frac{1}{\sqrt{2}} [|0\rangle \otimes |\pm 1/2\rangle \otimes |1\rangle \otimes |\mp 1/2\rangle - |1\rangle \otimes |\mp 1/2\rangle \otimes |0\rangle \otimes |\pm 1/2\rangle]$$

$$|1^{\text{st}} \text{ ex. } 3\rangle = \frac{1}{\sqrt{2}} [|0\rangle \otimes |\mp 1/2\rangle \otimes |1\rangle \otimes |\pm 1/2\rangle - |1\rangle \otimes |\pm 1/2\rangle \otimes |0\rangle \otimes |\mp 1/2\rangle]$$

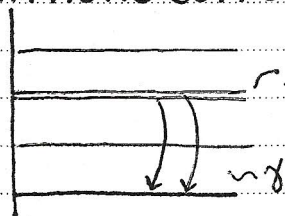
$$E_{1^{\text{st}} \text{ ex.}} = E_0 + E_1 = 2\hbar\omega$$

$$E_n \sim \alpha^2 mc^2 \quad \left(\alpha = \frac{e^2}{4\pi\epsilon_0 c} \approx \frac{1}{137.0} \right)$$

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

Corrections we neglected:

- relativistic corrections + spin-orbit = fine structure



fine structure lines

$$\Delta E_{fs} \sim \alpha^4 mc^2$$

electron/photon interaction

- Lamb shift ($\gamma \sim \text{electron}$, $\gamma \sim \text{positron}$, $\gamma \sim \text{photon}$)

$$\Delta E_{\text{Lamb}} \sim \alpha^5 mc^2$$

proton magnetic moment μ_p $\swarrow$ $\nwarrow$ electron magnetic moment μ_e

• hyperfine structure $\Delta E_{\text{hyp}} \sim \frac{m}{M} \alpha^5 mc^2$
 $\downarrow$ electron, $\downarrow$ proton mass ratio

→ Use perturbation theory to calculate these effects

Relativistic correction

"When did you take relativity? ... You haven't! This is so fucked up!

Now you just have to take my word for it, which is always a bad idea."

$$E = \sqrt{p^2 c^2 + m^2 c^4}$$

$$K = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \quad \text{-- rest-mass energy}$$

$\downarrow$ kinetic energy $\downarrow$ total energy

$$= mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots - mc^2$$

Taylor series expansion

$$\Rightarrow \Delta \hat{H} = \frac{-\hat{p}^4}{8m^3 c^2} \quad \text{-- perturbation correction to Hamiltonian}$$

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m}}_{\hat{H}_0} - \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{1}{\hat{r}}}_{\hat{V}_C} - \underbrace{\frac{\hat{p}^4}{8m^3 c^2}}_{\Delta \hat{H}}$$

$$\Delta E_n = \langle n l m m_s | \underbrace{\Delta \hat{H}}_{-\hat{p}^4/8m^3 c^2} | n l m m_s \rangle$$

$$\left[\frac{\hat{p}^2}{2m} + V_C(\hat{r}) \right] | n l m m_s \rangle = E_n^0 | n l m m_s \rangle$$

$\downarrow$ Coulomb potential negative $-(-V_C(\hat{r}))$

$$\hat{p}^2 | n l m m_s \rangle = 2m [E_n^0 - V_C(\hat{r})] | n l m m_s \rangle$$

$$\hat{p}^4 | n l m m_s \rangle = 4m^2 [E_n^0 - V_C(\hat{r})]^2 | n l m m_s \rangle$$

$$E_n^{02} - 2E_n^0 V_C(\hat{r}) + V_C^2(\hat{r})$$

$$- \frac{e^2}{4\pi\epsilon_0} \frac{1}{\hat{r}}$$

$$\langle n l m m_s | \hat{p}^4 | n l m m_s \rangle = 4m^2 [E_n^{02} - 2E_n^0 \langle n l m m_s | V_C(\hat{r}) | n l m m_s \rangle + \langle n l m m_s | V_C^2(\hat{r}) | n l m m_s \rangle]$$

$$(-\frac{e^2}{4\pi\epsilon_0})^2 \frac{1}{\hat{r}^2}$$