STEFANO
CURTAROW

QM THEORY OF SOLIDS

- INTRODUCTION
- BORN-VON KARMAN
- FERMI ENERGY, MOM, TEMP
- FERMI-DIRAC STATISTICS
- DENSITY OF STATES
- ENERGIES
- CHEMICAL POTENTIALS
- SPECIFIC HEATS
- TWO SPINS SYSTEMS

QM1 - QM5
FD1 - FD7
SPIN 1 - SPIN 6

SOMMERFELD THEORY ELECTRON GAS
CHAP 2 AM.

Free electrons in a box

STATIONARY SCHRÖDINGER EQUATION (TIME INVARIAT (stationary)

$i\hbar\frac{\partial}{\partial t}\psi \Rightarrow$ operator

→ $\hat{H}\psi = E\psi \Rightarrow$ defines ψ (stationary)

→ real solutions are eigenvectors functions $[\psi(x)]_n$ of Hamiltonian operator (Energy) with Energies (n)

$\left(i\hbar\frac{\partial}{\partial t}\right)\psi$

$e^{i\omega t} \Rightarrow \frac{\partial}{\partial t} = i\omega$

$i\hbar\omega i = -\hbar\omega = e^{i(\vec{k}\cdot\vec{x} - \omega t)}$

n can be discrete a continuum

→ ψ is wave function $\int \psi^* \psi \, dx = 1$

$|\psi(\vec{x})|^2 d^3\vec{x} = \psi^*\psi \, dx =$ prob to have electron in $[x, dx]$ volume d^3x

→ Other properties are operators

$$O = \langle \hat{O} \rangle \equiv \int \psi^*(x) \hat{O} \psi(x) \, dx = \sum (\psi^T)(\hat{O})\begin{pmatrix}\psi\\ \downarrow\end{pmatrix}$$

O: Properties; $\langle \hat{O} \rangle$: average of an operator over the density

↳ but this is Real $\Rightarrow O^* = O \Rightarrow \hat{O} = \hat{O}^+$ self adjoint

adjoint for matrix would be — complex conjugate — transpose

$\hat{H}$ = Energy operator $\Rightarrow$ Hamiltonian $\hat{T} + \hat{V}$

$\frac{\hat{p}^2}{2m} + V \Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x}\right)^2 + V(x) = \hat{H}(x)$

$\hat{p} = -i\hbar\frac{\partial}{\partial x}$

$e^{i(\vec{k}\vec{x} - \omega t)}$

$\hat{p} \cdot = \hbar k \cdot$

$-\hbar i\left(\frac{\partial}{\partial x} = +ik\right) = \hbar k$

DE BROGLIE says: POSTULATE

$\lambda = \frac{h}{p}$ $\quad k = \frac{2\pi}{\lambda}$

$p = \frac{h}{\lambda} = \frac{hk}{2\pi} \Rightarrow p = \hbar k$

$p = mv$

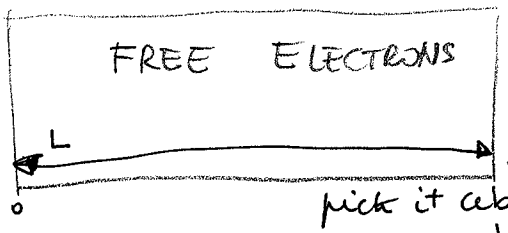
How to go to *macroscopic*

what happens at the borders?

$\psi(0) = \psi(L) = 0$?

NO!! too restrictive

METAL = HUGE BOX $\Rightarrow \infty$



pick it cubic $V = L^3$

we can state BORN-VON KARMAN

$\psi(0) = \psi(L) \Rightarrow$ & $L \to \infty$

$\psi(x,y,z) = \psi(x+L,y,z) = \psi(x,y+L,z) = \psi(x,y,z+L)$

$\Rightarrow$ S. eq is $\hat{H}\psi = E\psi$

$\hat{H} = \frac{\hat{p}^2}{2m}$ $\frac{\hat{p}^2}{2m}\psi = E\psi \Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$ free wave

$\psi \simeq \psi_0 e^{i k x}$

$1 = \int_V \psi^* \psi \, d^3x \Rightarrow \int_V \psi_0^2 e^{-i\vec{k}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}} dV = 1$

$\Rightarrow \psi_0 = \frac{1}{\sqrt{V}}$

$\psi = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V}}$ but which k

and energy $\int \psi^* \hat{H} \psi \, dx = E \Rightarrow E = -\frac{\hbar^2}{2m}(ik)^2 = \frac{\hbar^2 k^2}{2m}$ (p^2??)

$E(k) = \frac{\hbar^2 k^2}{2m}$ energy of 1 electron with wave vector k (or momentum)

~~$\psi(x,y,z)$~~ $\psi(x+L) = \psi(x) \Rightarrow \psi \sim e^{i k_x x}$ $k_x = \frac{2\pi}{L} n_x$ $e^{i k_x L} = 1$

$\Rightarrow$ BORN – VON KARMAN

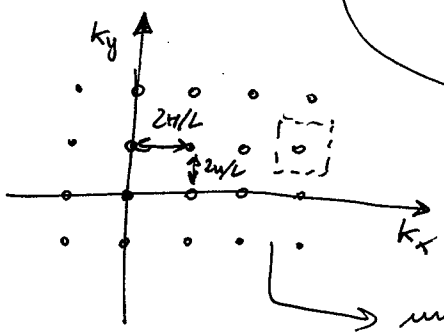
$\Rightarrow 1 = e^{i k_x L} = e^{i k_y L} = e^{i k_z L} = 1 \Rightarrow$

$k = (k_x, k_y, k_z) = \left(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L}\right)$

n_x, n_y, n_z integers

$\Rightarrow$ QUANTIZATION OF SOLUTIONS!!

in 2D

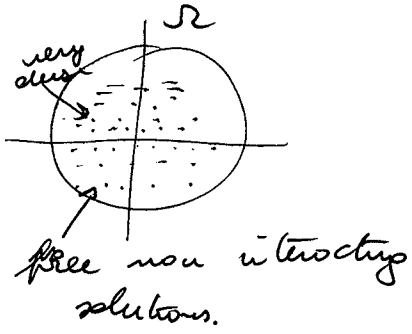


$\Rightarrow$ unit volume in k space

$(\delta k)^3 = \left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V}$!! very small

QM2.

$\Rightarrow$ a volume Ω in k space,



contains $\frac{\Omega}{(\delta k)^3} = \frac{\Omega V}{(2\pi)^3}$ points

$\Rightarrow$ SPIN $\pm\frac{1}{2}$ $\Rightarrow$ 2 electrons per state k solution of electrons

Now let's count them.

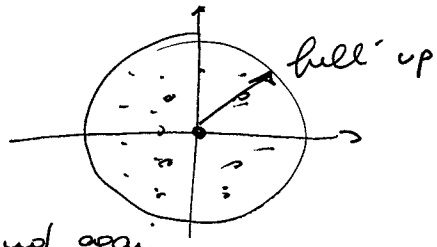
— take metal, volume V

— extract all free electrons $N = nV$ $\left(n = \frac{N}{V}\right)$ density

— put 1 $\rightarrow$ $\varepsilon = 0$, 2 $\varepsilon = 0$

— then put other 2 it to fill

$\varepsilon(n_x=1, n_y=0, n_z=0)$ and again



then full up sphere with radius k_F (Fermi MOMENTUM)

$\Rightarrow$ all states with $|k| < k_F$ are occupied (2e per point),

Volume $\Omega = \frac{4}{3}\pi k_F^3 \Rightarrow$

$$\#\,k\text{points} = \frac{\Omega}{(\delta k)^3} = \cdot\frac{4}{3}\frac{\pi k_F^3 V}{8\pi^3}$$

$$N = 2 * \#\,k\text{points}$$

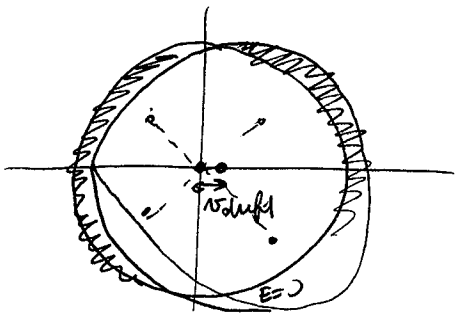
$$\Rightarrow N = 2\cdot\frac{4}{3}\frac{\pi k_F^3}{8\pi^3}V$$

$$\boxed{k_F = \sqrt[3]{3\pi^2 n}}$$

$n = \frac{N}{V} = \frac{1}{3}\frac{k_F^3}{\pi^2} \Rightarrow$

$\forall e$ with k
there is an e with $-k$
$\Rightarrow$ tot current $= 0$

$v_k = \frac{\hbar k_F}{m_e} \Rightarrow$ if apply Force (E field) $\Rightarrow v_{drift}$



We have with k, there is e with $-k$ only if far from surface $\Rightarrow$ ONLY electrons with $|k| \sim k_F$ are important in conduction

$v_F \sim 10^6 \frac{m}{s} \sim \frac{1}{100} c$!!!

$= \frac{1}{\left(\frac{\hbar k_F}{m}\right)}$ most surprising results

at $T=0$ all e should have $v_{TH} \simeq 0$

but for QM there are $v \approx c/100$ in all direction (conservation of mass)

$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{1}{2} m v_F^2 = k_B T_F$ $\sim$ 1.0 and 15 eV

Fermi energy $\approx$ 10–100 K HOT!!!

Total energy $\Rightarrow$ all k with $|k| \leq k_F$ are occupied

every state has energy $\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$

2e per state

$E = \int_{|k| \leq k_F}$

$E = 2 \sum_{|k| \leq k_F} \frac{\hbar^2}{2m} k^2$ so many and $(\delta k)^3$ is small

$\Rightarrow \sum_{|k| \leq k_F} \rightarrow \int_{|k| \leq k_F} \frac{d^3k}{(\delta k)^3} = \frac{1}{(2\pi)^3/V} \int d^3k$

$\sum_{|k| \leq k_F} \Leftrightarrow \frac{V}{(2\pi)^3} \int d^3k$

QM4

$$E = \frac{2V}{(2\pi)^3}\int_{|k|\le k_F} \frac{\hbar^2}{2m} k^2 \, d^3k = \frac{V\hbar^2}{8\pi^3 m}\int_{|k|\le k_F} k^2 \, d^3k$$

$|k| \le k_F \rightarrow d^3k = 4\pi k^2 dk$ (spherical symmetry)

$$= \frac{V\hbar^2 4\pi}{8\pi^3 m}\int_0^{k_F} k^4 dk = \frac{V\hbar^2}{2\pi^2 m}\,\frac{k_F^5}{5}$$

$$\int_0^{k_F} k^4 dk = \frac{k^5}{5}\Big|_0^{k_F} = k_F^5/5$$

$$E = \frac{V\hbar^2 k_F^5}{10\pi^2 m} \Rightarrow k_F = \sqrt[3]{3\pi^2 n} \Rightarrow k_F^3 = 3\pi^2 \frac{N}{V}$$

$$= \frac{V\hbar^2 k_F^2}{10\pi^2 m}\, 3\pi^2 \frac{N}{V} \Rightarrow \frac{E}{N} = \frac{3}{10}\frac{\hbar^2 k_F^2}{m} = \frac{3}{5}\varepsilon_F$$

$\Rightarrow$ $\langle E \rangle$ per electró $= \frac{3}{5}\varepsilon_F$

QMs

FERMI-DIRAC STATISTICS

$T>0$ N electrons. Thermal equilibrium

particle with energy E, probability of

occupancy states with Energy E $P_N(E) \propto e^{-\beta E}$ $\qquad \beta = \frac{1}{k_B T}$

$\Rightarrow$ sum $\forall E$ possible energy

$$P_N(E) = \frac{e^{-\beta E}}{\sum_{\text{States}} e^{-\beta E}}$$

Prob state with Energy E is occupied

$\sum_{\text{States}} \Leftrightarrow \sum_{\text{energy}}$ #states with energy $\Omega(E)$

But $S = k \log \Omega(E)$

$\Omega(E) = e^{\beta(TS)}$

$$= \frac{e^{-\beta E_i}}{\sum_{\text{states}} e^{-\beta E_j} = e^{-\beta F}}$$

$\sum_{\text{energy}} e^{-\beta(E-TS)} = e^{-\beta F}$

Helmholtz Free energy

$dE = -pdV + Tds + \mu dN$

$dF = -pdV - SdT + \mu dN$

$\Rightarrow \quad P_N(E_i^N) = e^{-\beta(E_i^N - F_N)}$

probability of a macroscopic States with N electrons in Thermal equilibrium & total energy $= E$

Now pick 1 electron in level i $\quad \left(\varepsilon_i = \frac{\hbar^2 k_i^2}{2m}\right.$ for JELLO$)$

prob that there is an electron in level $i \Rightarrow$ in a system of N electrons in T. eq. is

$$f^N(i) = \sum_{\substack{\text{all states} \\ \text{with electron in state } i}} P_N(E_i^N)$$

density of prob for 1 electron

+ $f^{N}(i) = 1 - \sum_{\gamma \in \{\text{all states without electron in state } i\}} P_N(E_\gamma^N)$

+ pick $N+1$ system = energy E^{N+1}
with 1 electron in level i with energy $\varepsilon_i \Rightarrow E_\gamma^{N+1}$
↳ states with 1 electron in i

$\Rightarrow$ the N system has energy without electron in i has energy

$$E_\gamma^N = E_\gamma^{N+1} - \varepsilon_i$$

(E_γ^N: no electrons in i; E_γ^{N+1}: 1 electrons in i)

$$\Rightarrow f^{N}(i) = 1 - \sum_{\gamma \in \{\text{states of } N+1 \text{ system with 1 electron in state } i\}} P_N\left(E_\gamma^{N+1} - \varepsilon_i\right)$$

but

$$P_N(E_\gamma) = e^{-\beta(E_\gamma^N - F_N)}$$

$$P_N(E_\gamma^{N+1} - \varepsilon_i) = e^{\beta\varepsilon_i} P_N(E_\gamma^{N+1}) =$$

(P_N: N particles; energy)

$$= e^{-\beta\varepsilon_i} e^{-\beta(E_\gamma^{N+1} - F_N)}$$

$$-F_{N+1} + (F_{N+1} - F_N)$$

$\Delta F = F_{N+1} - F_N$ for 1 particle

$$e^{-\beta(E_\gamma^{N+1} - F_{N+1})} = P_{N+1}(E_\gamma^{N+1})$$

$$P_{N+1}(E_\gamma^{N+1})\, e^{\beta(\varepsilon_i - \Delta F)}$$

$$e^{\beta(\varepsilon_i - \mu)}$$

$dF = -pdV - SdT + \mu dN$

$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \Rightarrow \Delta F = \mu$

$$\Rightarrow \quad f^N(i) = 1 - \sum_{\substack{\text{i occupied}}} e^{\beta(\varepsilon_i - \mu)} \; P_{N+1}(E_x^{N+1})$$

E_x^{N+1} : i occupied

$$\Rightarrow 1 - e^{\beta(\varepsilon_i - \mu)} \; f^{N+1}(i)$$

$$\Rightarrow \quad f^N(i) = 1 - e^{\beta(\varepsilon_i - \mu)} \; f^{N+1}(i)$$

* $N \sim N_a = 10^{23}$ 1 extra electron does not change probability $\Rightarrow \quad f^N = f^{N+1}$

$$\Rightarrow \quad f^N(i)\left(1 + e^{\beta(\varepsilon_i - \mu)}\right) = 1$$

$$\boxed{f^N(i) = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}}$$

prob of state

Fermi-Dirac Distribution for 1 electron in state i with energy ε_i, in a system with a lot of electrons in thermal equilibrium

$$\boxed{N = \sum_{\substack{\text{i states}}} f(i)}$$

number of electrons = sum in all states

FD 3

$T \to 0$

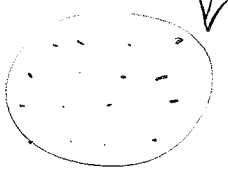
we filled up all states at $\varepsilon \leq \varepsilon_F$

$\Rightarrow$ $T=0$ $\quad f(i) \begin{cases} 1 & \varepsilon_i \leq \varepsilon_F \\ 0 & \varepsilon_i > \varepsilon_F \end{cases}$

$\lim_{T\to 0} f(i) \begin{cases} 1 & \varepsilon_i \leq \mu \\ 0 & \varepsilon_i > \mu \end{cases}$ $\Big\}$ $\varepsilon_F = \lim_{T\to 0} \mu$

$T > 0$

TOTAL for N electrons internal energy $U(T)$ sum of all electronic energy



$$U(T) = \sum_{\vec{k}}^{T} 2\varepsilon(\vec{k})\, f(\varepsilon(\vec{k}))$$

2 electrons per state

at $T=0$ was 1 for $|\vec{k}| \leq k_F$

$$\sum_{\vec{k}} \Leftrightarrow \int \frac{d^3k}{(2\pi)^3} V \qquad \Rightarrow \quad v = \frac{U}{V}$$

$$U = \frac{V 2}{(2\pi)^3} \int d^3k\, \varepsilon(\vec{k})\, f(\varepsilon(\vec{k})) \quad \Rightarrow \quad v = \frac{2}{(2\pi)^3} \int \varepsilon(\vec{k})\, f(\varepsilon(\vec{k}))\, d^3k$$

smog

$$\int \frac{2}{(2\pi)^3} d^3k \Leftrightarrow \int d\varepsilon\, g(\varepsilon) \qquad \varepsilon = \frac{\hbar^2 k^2}{2m}$$

$f(\varepsilon)$ $\Rightarrow$ $d^3k \Rightarrow 4\pi k^2 dk$

density of states $\Rightarrow$ # electronic states between ε and $\varepsilon + d\varepsilon$

$\varepsilon = \frac{\hbar^2}{2m} k^2 \Rightarrow$ spherical symmetry

$$d^3k = 4\pi k^2 dk$$

$$\int \frac{2}{(2\pi)^3} 4\pi k^2 dk = \frac{1}{\pi^2} \int k^2 dk -$$

$$\varepsilon = \frac{\hbar^2}{2m} k^2 \qquad d\varepsilon = \frac{\hbar^2}{2m} k\, dk \qquad k = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

$$\Rightarrow k^2 dk = \frac{m}{\hbar^2} k\, d\varepsilon = \frac{m}{\hbar^2} \sqrt{\frac{2m}{\hbar^2}}\, \varepsilon^{1/2} d\varepsilon$$

$$\Rightarrow \int_{k^3} \frac{2}{(2\pi)^3} d^3k \Leftrightarrow \int_0^\infty g(\varepsilon)\, d\varepsilon$$

$g(\varepsilon)$ = one-electron states density in $\varepsilon, \varepsilon + d\varepsilon$ (per unit volume)

$$g(\varepsilon) = \begin{cases} \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}} & \varepsilon > 0 \\ = 0 & \varepsilon < 0 \end{cases}$$

= free electrons

$k_F = \sqrt[3]{3\pi^2 n} \Rightarrow$

$\Rightarrow \varepsilon_F = \frac{\hbar^2}{2m} k_F^2 \Rightarrow \frac{\hbar^2}{2m} \cdot \frac{\varepsilon_F}{k_F^2} = \frac{\varepsilon_F}{(3\pi^2 n)^{2/3}}$

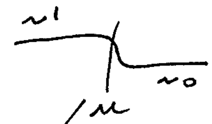
$$g(\varepsilon) = \frac{m}{\hbar^2 \pi^2} k_F \sqrt{\frac{\varepsilon}{\varepsilon_F}}$$

$$n = \frac{k_F^3}{3\pi^2} = k_F \cdot \frac{k_F^2}{3\pi^2} = \frac{k_F}{3\pi^2} \varepsilon_F \frac{2m}{\hbar^2} \Rightarrow k_F = \frac{3\pi^2 \hbar^2 n}{2m\varepsilon_F}$$

$$g(\varepsilon) = \frac{m}{\hbar^2 \pi^2} \frac{3\pi^2 \hbar^2 n}{2m\varepsilon_F} (\,) \Rightarrow$$

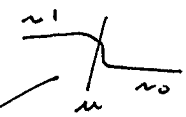
$$g(\varepsilon) = \frac{3}{2} \frac{n}{\varepsilon_F} \left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2} \quad \varepsilon > 0$$

$$U = \int \mathcal{E}(k)\, f(\mathcal{E}(k))\, \underbrace{\frac{2}{(2\pi)^3} d^3k}_{g(\mathcal{E})\,d\mathcal{E}}$$



$$U = \int_0^\infty \mathcal{E}\, g(\mathcal{E})\, f(\mathcal{E})\, d\mathcal{E} = \int_0^{\mu} \mathcal{E} f(\mathcal{E})\, g(\mathcal{E})\, d\mathcal{E}$$

energy ↑, # of states ↓, FD distrib (occupancy of 1 state) ↑



$$n = \int f(\mathcal{E}(k)) \frac{2}{(2\pi)^3} d^3k \Rightarrow \quad n = \int_0^\infty f(\mathcal{E})\, g(\mathcal{E})\, d\mathcal{E}$$

$f(\mathcal{E})$ → because T; $g(\mathcal{E})$ → because geometry

⇒ everything important happens ~ μ (around μ)

⇒ smooth function $H(\mathcal{E})$ (no singularities around $\mathcal{E} \sim \mu$) → Taylor around μ

$$\Rightarrow \int_0^\infty H(\mathcal{E}) f(\mathcal{E})\, d\mathcal{E} = \int_0^{\mu} H(\mathcal{E})\, d\mathcal{E} + \sum_{n=1}^{\infty} (kT)^{2n} a_n \frac{d^{2n-1}}{d\mathcal{E}^{2n-1}} H(\mathcal{E})\Big|_{\mathcal{E}=\mu}$$

SOMMERFELD EXPANSION

$$H(\mathcal{E}) < \begin{cases} \mathcal{E} g(\mathcal{E}) \sim \mathcal{E}^{3/2} & \text{for } u \\ g(\mathcal{E}) \sim \mathcal{E}^{1/2} & \text{for } n \end{cases} \quad \text{good}$$

get n, but $\frac{\partial n}{\partial T} = 0 \Rightarrow$ $\boxed{\mu = \mathcal{E}_F \left[1 - \frac{1}{3} \left(\frac{\pi k_B T}{2 \mathcal{E}_F} \right)^2 \right]}$ for free electrons

$$\mu = \mathcal{E}_F - \frac{\pi^2}{6} (kT)^2 \frac{g'(\mathcal{E}_F)}{g(\mathcal{E}_F)}$$ general

get $u \Rightarrow$ u_0 ($T \to 0$ lim)

$$\boxed{u = u_0 + \frac{\pi^2}{6} (kT)^2 g(\mathcal{E}_F)}$$ energy.

FD 6

$$dE = -pdV + TdS + \mu dN$$

δQ $\qquad C = \frac{\delta Q}{\delta T} \Rightarrow C_V = \left.\frac{\partial E}{\partial T}\right|_{V,N}$

N constant

$$\Rightarrow C_V = \left.\frac{\partial U}{\partial T}\right|_N = \frac{\pi^2}{3} k_B^2 g(\varepsilon_F) T$$

↳ ε_F constant ↳ generic $g(\varepsilon) \Rightarrow$

free electrons:

$$C_V = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B \sim \frac{T \cdot n}{\varepsilon_F} \quad \text{LINEAR}$$

n: density of free electrons

Real one is $C_V = \gamma T + AT^3$

electrons + phonon degrees of freedom

but quantum

~~$U = \frac{3}{2}(kT)$~~ electrons

$$\Rightarrow \boxed{C_V = \frac{3}{2} k n} \quad \text{CLASSIC} = \text{SHIT.}$$

per 1 electron

2 SPIN SYSTEMS: SINGLET + TRIPLET

— PAULI PRINCIPLE

‖ total wavefunction of fermion must be antysimetric an exchange of fermionic index

$$\psi^{TOT}(space, spin) = \psi^{SP}(space)\,\eta(SPIN)$$

$$\psi^{TOT}(1,2) = \psi^{SP}(r_1, r_2)\,\eta(s_1, s_2)$$

if $1 \to 2 \Rightarrow \psi(2,1) = -\psi(1,2)$

CHOICHES

a) $\psi^{SPACE}(1,2) = -\psi^{SPACE}(2,1) \Rightarrow \eta(1,2) = \eta(2,1)$

(ψ^{SPACE}: antisimetric; η: Symetric)

TRIPLET (3 solutions)

b) $\psi^{SPACE}(1,2) = \psi^{SPACE}(2,1) \Rightarrow \eta(2,1) = -\eta(1,2)$

(ψ^{SPACE}: symetric; η: antisimetric)

SINGLET (only 1 solution)

WHAT DO WE KNOW

$[\hat{H}, \hat{L}^2] = 0 \quad [\hat{H}, \hat{L}_z] = 0$ eigenfunctions of H $\psi_{n,m\ell}$

$\hat{L}_z \psi_{n\ell m} = m\hbar \psi_{n\ell m}$

$[\hat{L}_i, \hat{L}_j] = i\hbar \varepsilon_{ijk} \hat{L}_k \quad \hat{L}^2 \psi_{n\ell m} = \ell(\ell-1) \psi_{n\ell m}$

Save for S!

For a state of 1 spin ↑+ or ↓- $\eta(\varepsilon) \quad \varepsilon = \pm 1$

$S_z \eta(\varepsilon) = \varepsilon \frac{\hbar}{2} \eta(\varepsilon)$ (bring $\frac{\hbar}{2}$ outside so $\varepsilon = \pm 1$)

$S^2 \eta(\varepsilon) = \frac{3}{4} \eta(\varepsilon)$

$m_z = \frac{1}{2}\varepsilon$

m_z in $-\ell_z, -\ell_z+1 \cdots, \ell_z$

for 1 state $\ell_z = \frac{1}{2}$

$m_z = -\frac{1}{2}, \frac{1}{2}$ $(\varepsilon = \pm 1)$

$\ell_z(\ell_z+1) = \frac{1}{2}\left(\frac{1}{2}+1\right) = \frac{3}{4}$

2 particles

$\Rightarrow$

$$\psi(\vec{r}_1, \vec{r}_2, \varepsilon_1, \varepsilon_2) = \psi(\vec{r}_1, \vec{r}_2)\, \eta(\varepsilon_1, \varepsilon_2)$$

basis of $\eta(\varepsilon_1, \varepsilon_2)$ = all possible configurations!

$\eta(+,+), \eta(+,-), \eta(-,+), \eta(-,-)$

how are they?

How single spin operator acts?

$$S_1^2 \eta(\varepsilon_1,\varepsilon_2) = \frac{3}{4}\hbar^2 \eta(\varepsilon_1,\varepsilon_2) \qquad S_{1z}\eta(\varepsilon_1,\varepsilon_2) = \varepsilon_1 \frac{\hbar}{2}\eta(\varepsilon_1,\varepsilon_2)$$

$$S_2^2 \eta(\varepsilon_1,\varepsilon_2) = \frac{3}{4}\hbar^2 \eta(\varepsilon_1,\varepsilon_2) \qquad S_{2z}\eta(\varepsilon_1,\varepsilon_2) = \varepsilon_2 \frac{\hbar}{2}\eta(\varepsilon_1,\varepsilon_2)$$

TOTAL SPIN

$S = S_1 + S_2$, how it commutes?

$$[S_x, S_y] = [S_{1x} + S_{1y},\ S_{2x} + S_{2y}]$$

$$= [S_{1x}, S_{1y}] + [S_{2x}, S_{2y}]$$

$$= i\hbar S_{1z} + i\hbar S_{2z} = i\hbar(S_{1z} + S_{2z}) = i\hbar S_z$$

S_1 & S_2 about spect

$[S_{1i}, S_{2j}] = 0$

$$S^2 = (S_1 + S_2)^2 = S_1^2 + S_2^2 + 2\, S_1 \cdot S_2$$

$$\overset{!}{=} S_1^2 + S_2^2 + 2\left(S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z}\right)$$

$$\overset{!}{=} S_1^2 + S_2^2 + 2\left[S_{1z}S_{2z} + \frac{1}{2}\left(S_{1+}S_{2-} + S_{1-}S_{2+}\right)\right]$$

S_+ brings spin up if down, otherwise $=0$ $\qquad S_\pm = S_+ \pm i S_y$

$$S_+\eta(+) = 0 \qquad S_+\eta(-) = \hbar\eta(+)$$

$$S_-\eta(+) = \hbar\eta(-) \qquad S_-\eta(-) = 0$$

Calculation of S_z and S^2 on total Spin

$$S_z \eta(\varepsilon_1,\varepsilon_2) = (S_{1z}+S_{2z})\eta(\varepsilon_1,\varepsilon_2) = \frac{\hbar}{2}(\varepsilon_1+\varepsilon_2)\eta(\varepsilon_1,\varepsilon_2)$$

$\Rightarrow$ $\eta(\varepsilon_1,\varepsilon_2)$ eigenstate with eigenvalue

$$M_z = \frac{1}{2}(\varepsilon_1+\varepsilon_2) \qquad (*\hbar)$$

$\varepsilon_1,\varepsilon_2 = \pm 1 \Rightarrow$ $M_z = -1, 0, 1$

$(--)$ $(+-)$ $(-+)$ $(++)$

$\begin{pmatrix}1\\0\\0\\0\end{pmatrix} = (++)$ $\begin{pmatrix}0\\1\\0\\0\end{pmatrix} = (+-)$ $\begin{pmatrix}0\\0\\1\\0\end{pmatrix} = (-+)$ $\begin{pmatrix}0\\0\\0\\1\end{pmatrix} = (--)$

in this representation degenerate $\Rightarrow$ get eigenvectors linear combination

$$\Rightarrow \bar{S}_z = \hbar\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{pmatrix}$$

$S^2\eta(\varepsilon_1,\varepsilon_2) \Rightarrow$ $S^2 = S_1^2 + S_2^2 + 2S_{1z}S_{2z} + S_{1+}S_{2-} + S_{1-}S_{2+}$

$$S^2\eta(++) = \left(\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2\right)\eta(++) + \frac{1}{2}\hbar^2\eta(++) = 2\hbar^2\eta(+,+)$$

$$S^2\eta(+-) = (\quad)\eta(+-) - \frac{1}{2}\hbar^2\eta(+-) + \hbar^2\eta(-,+) \ldots = \hbar^2(\eta(+-)+\eta(-+))$$

$$S^2\eta(-+) = \hbar^2(\eta(-+)+\eta(+,-))$$

$$S^2\eta(--) = 2\hbar^2\eta(--)$$

$\Rightarrow$ $S^2 = \hbar^2$ $\begin{pmatrix}2&0&0&0\\0&1&1&0\\0&1&1&0\\0&0&0&2\end{pmatrix}$

evg $(++)$ $S^2 = 2\hbar^2$

$\rightarrow$ evg ?

evg $(--)$ $\rightarrow$ $S^2 = 2\hbar^2$

$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \Rightarrow$ eigenvalue problem

$\det \begin{pmatrix} 1-\lambda & 1 \\ 1 & 1-\lambda \end{pmatrix} = 0 \quad (1-\lambda)^2 - 1 = 0 \quad \lambda = 0, 2$

$\lambda = 0$ $\quad \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 0 \quad x_1 + x_2 = 0$

$x_1 = -x_2$

$\Rightarrow \quad \Rightarrow$ norm $\Rightarrow \left(0, \frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right)$

$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} - \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \left(\eta(+,-) - \eta(-,+) \right) \Rightarrow \lambda = 0$

$\lambda = 2 \quad \begin{pmatrix} 1-2 & 1 \\ 1 & 1-2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \Rightarrow x_1 - x_2 = 0 \quad x_1 = +x_2$

norm $\left(0, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)$

norm $\Rightarrow \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \left(\eta(+,-) + \eta(-,+) \right)$

$\Rightarrow$

SUMMARIZE

if two spin ⇒ STATES

$\frac{1}{\sqrt{2}}\left[\eta(+,-) - \eta(-,+)\right]$ = singlet $S_z = 0$ $M = 0$ $S^2 = 0$

ANTISIMMETRIC $\varepsilon_1 \Leftrightarrow \varepsilon_2$

TRIPLET

$\eta(+,+)$

$\eta(-,-)$

$\frac{1}{\sqrt{2}}\left[\eta(+,-) + \eta(+,-)\right]$

triplet

$M = 1$ $S_z = \hbar$

$M = -1$ $S_z = -\hbar$

$M = 0$ $S_z = 0$

$S^2 = 2\hbar^2$

0 + 0

SIMMETRIC

$\varepsilon_1 \Leftrightarrow \varepsilon_2$

$l_s(l_s+1)$

$1(1+1) = 2$

⇒

$M = -1, 0, 1$ Oh

$(2l_s+1)$ values

$\psi^{tot} = \psi(\quad)\eta(\quad)$ = ANTY $\varepsilon_1 \Leftrightarrow \varepsilon_2$

SIMM ANTI

ANTI SIMM