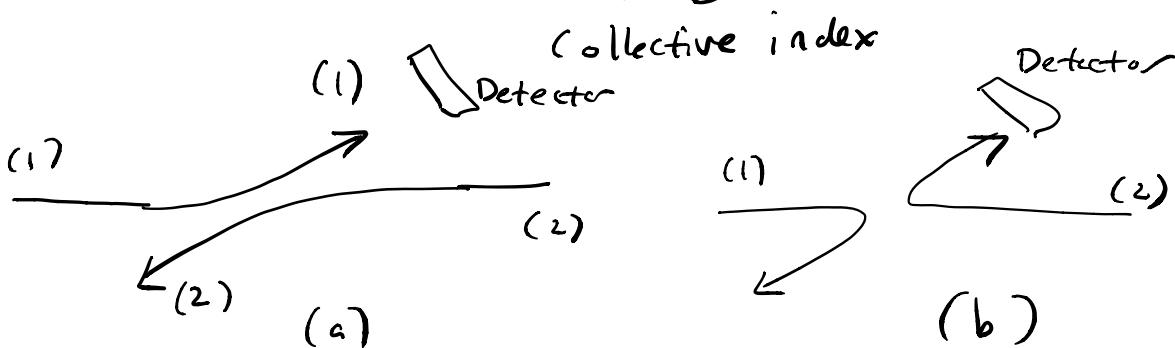


Identical Particles

Consider two identical particles scattering, they have state kets $|k'\rangle, |k''\rangle$



Classically we could label one particle "red" and one particle "blue" to determine which hit the detector.

Quantum mechanically can't define an arbitrary observable color "red" or "blue"

there is some complete set of commuting observables, each particle is in a state specified by the eigenvalues of these observables.

It's not possible even in principle to determine if (1) or (2) hit the detector.

Consider a state in the tensor product space :

$$|k'\rangle \otimes |k''\rangle$$

\nearrow \uparrow

in subspace $E(1)$ in subspace $E(2)$

$IP - 1$

the ket $|k''\rangle \otimes |k'\rangle$ is distinct from the above ket and in fact if $k' \neq k''$ it is orthogonal.

If we measure this system we can get k' for one particle, k'' for another.

All kets of form

$$c_1 |k'\rangle \otimes |k''\rangle + c_2 |k''\rangle \otimes |k'\rangle$$

lead to an identical measurement result.

This is exchange degeneracy.

Example : Consider 2 spin- $\frac{1}{2}$ particles

state space : $\{|e_1, e_2\rangle\} \quad e_1 = \uparrow, \downarrow$

If we have 2 spin observables $e_2 = \uparrow, \downarrow$

S_{1z}, S_{2z}

kets $\alpha |\uparrow, \downarrow\rangle + \beta |\downarrow, \uparrow\rangle$ all

represent a state with one spin up and another down.

Define a permutation operator P_{12}

such that $P_{12} |k'\rangle |k''\rangle = |k''\rangle |k'\rangle$

$$\text{then } P_{21} = P_{12}, \quad P_{12}^2 = 1$$

Consider our spin example S_{1z} , S_{2z}

$$S_{1z} |1\uparrow\rangle|1\uparrow\rangle = \frac{\hbar}{2} |1\uparrow\rangle|1\uparrow\rangle$$

Consider an observable A :

$$A_1 |a'\rangle|a''\rangle = a' |a'\rangle|a''\rangle$$

$$A_2 |a'\rangle|a''\rangle = a'' |a'\rangle|a''\rangle$$

$$\begin{aligned} P_{12} A_1 P_{12}^{-1} P_{12} |a'\rangle|a''\rangle &= a' P_{12} |a'\rangle|a''\rangle \\ &= a' |a''\rangle|a'\rangle \\ &= P_{12} A_2 P_{12}^{-1} |a''\rangle|a'\rangle \end{aligned}$$

$$\text{But } A_2 |a'\rangle|a''\rangle = a'' |a'\rangle|a''\rangle$$

$$\text{So } A_2 = P_{12} A_1 P_{12}^{-1}$$

P_{12} changes particle label of an observable.

$$\text{L.S. } S_{2z} = P_{12} S_{1z} P_{12}^{-1}$$

Consider a Hamiltonian w/ two identical particles!

$$\begin{aligned} H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + V_{\text{pair}}(|\vec{x}_1 - \vec{x}_2|) \\ + V_{\text{ext}}(\vec{x}_1) + V_{\text{ext}}(\vec{x}_2) \end{aligned}$$

$$P_{12} H P_{12}^{-1} = H \quad (\text{exercise})$$

$\Rightarrow P_{12}$ is a "constant of the motion"

$$[P_{12}, H] = 0$$

$$P_{12}^2 = 1. \quad \text{Eigenvalues are } \pm 1.$$

If a two particle state is symmetric (+) it remains so.

Antisymmetric (-) it also remains so.

Eigenstates of P_{12} :

$$|k'>|k''>_+ \equiv \frac{1}{\sqrt{2}} (|k'>|k''> + |k''>|k'>)$$

$$|k'>|k''>_- \equiv \frac{1}{\sqrt{2}} (|k'>|k''> - |k''>|k'>)$$

We can define operators

$$S_{12} \equiv \frac{1}{2} (1 + P_{12}) \quad A_{12} \equiv \frac{1}{2} (1 - P_{12})$$

\nearrow \uparrow

symmetrizes any linear
combination of $|k'>|k''>$ and $|k''>|k'>$

anti
symmetrizer

$$S_{12} [c_1 |k'>|k''> + c_2 |k''>|k'>]$$

$$= \frac{1}{2} (c_1 |k'>|k''> + c_2 |k''>|k'>) + \frac{1}{2} (c_1 |k''>|k'> + c_2 |k'>|k''>) \quad (1p-4)$$

$$= \left(\frac{C_1 + C_2}{2} \right) (|K'>|K''> + |K''>|K'>)$$

for A_{12} , we get

$$\left(\frac{C_1 - C_2}{2} \right) (|K'>|K''> - |K''>|K'>)$$

If we have N identical particles, define

P_{ij} so that

$$P_{ij} |K'>|K''> \dots |K^i>|K^{i+1}> \dots |K^j> \dots \\ = |K'>|K''> \dots |K^j>|K^{i+1}> \dots |K^i> \dots$$

then $P_{ij}^2 = 1$, eigenvalues are ± 1

But $[P_{ij}, P_{ke}] \neq 0$ in general.

Let's consider 3 particles

$$|K'>|K''>|K'''>$$

what is degeneracy in exchange? 6-fold

If we required state to be totally anti-symmetric or totally symmetric, there is only one linear combo. of each.

$$|k' k'' k''' \rangle_+ = \frac{1}{\sqrt{6}} \left(|k'\rangle |k''\rangle |k''' \rangle + |k''\rangle |k'\rangle |k''' \rangle + |k''\rangle |k''' \rangle |k'\rangle + |k''' \rangle |k''\rangle |k'\rangle + |k''' \rangle |k'\rangle |k''\rangle + |k'\rangle |k''' \rangle |k''\rangle \right)$$

$$|k' k'' k''' \rangle_- = \frac{1}{\sqrt{6}} \left(|k'\rangle |k''\rangle |k''' \rangle - |k''\rangle |k'\rangle |k''' \rangle + |k''\rangle |k''' \rangle |k'\rangle - |k''' \rangle |k''\rangle |k'\rangle + |k''' \rangle |k'\rangle |k''\rangle - |k'\rangle |k''' \rangle |k''\rangle \right)$$

These are simultaneous eigenstates of

P_{12} , P_{23} , and P_{13} with eigenvalues ± 1 ,
(here we assumed k', k'', k''' are different)

If for example $k''' = k''$ we could write

$$|k', k'', k'' \rangle_+ = \frac{1}{\sqrt{3}} \left(|k'\rangle |k''\rangle |k'' \rangle + |k''\rangle |k'\rangle |k'' \rangle + |k''\rangle |k''\rangle |k' \rangle \right)$$

There is no totally anti-symmetric state. e.g.
 $(|k'\rangle |k''\rangle)$

There is a normalization factor

generally $\sqrt{\frac{N_1! N_2! \cdots N_n!}{N!}}$ N_i is # of times
state $k^{(i)}$ occurs.

e.g. $\sqrt{\frac{2!}{6!}}$ for above example

N is total number of particles

Note: we could also define a more general permutation operator e.g. $P_{123} |k'\rangle |k''\rangle |k'''\rangle = |k''\rangle |k'''\rangle |k'\rangle$

notice $P_{123} = P_{12} P_{13}$

but we can just consider pairwise permutation for simplicity.

Note

there are also four independent states in previous example with mixed symmetry.

(not totally symmetric or anti-symmetric)

In nature there is a symmetrization postulate

Systems with N identical particles are either totally anti-symmetric or totally symmetric under the interchange of any pair.

Bose-Einstein statistics \leftrightarrow symmetric

Fermi-Dirac statistics \leftrightarrow anti-symmetric

$$P_{ij} |N \text{ identical bosons}\rangle = +1 |N \text{ identical bosons}\rangle$$

$$P_{ij} |N \text{ identical Fermions}\rangle = -1 |N \text{ identical fermions}\rangle$$

There is a spin-statistics theorem (provable in relativistic quantum theory) that shows half-integer spin particles are fermions
 integer spin particles are bosons

Pauli exclusion principle No 2 electrons can occupy the same state

The state $|k'>|k'\rangle$ is symmetric.
 Not possible for fermions.

Extremely impt. for atomic, molecular, physics & chemistry.

For 2 fermions, only possible state is :

$$\frac{1}{\sqrt{2}} (|k'>|k''\rangle - |k''>|k'\rangle)$$

Bosons

$$|k'>|k'\rangle \quad |k''>|k''\rangle \quad \frac{1}{\sqrt{2}} (|k'>|k''\rangle + |k''>|k'\rangle)$$

Classical particles :

4 independent states

$$\begin{array}{ll} k'' k' & k' k' \\ k' k'' & k'' k'' \end{array}$$

Bose-Einstein condensation : All particles can be in same ground state

with fermions this is not possible.

The symmetrization postulate limits the state space for a system of identical particles. we no longer have a tensor product of individual state spaces of particles in system.

The state space is a subspace \mathcal{E}_s or \mathcal{E}_A depending on whether the particles are bosons or fermions.

The time evolution $|n(t)\rangle$ cannot take a system out of one of these subspaces.

A physical observable G must be invariant under all permutations of the N identical particles.

e.g. observable $|\vec{r}_1 - \vec{r}_2|$ is symmetric, is allowed as a physical observable.

e.g. vector $\vec{r}_1 - \vec{r}_2$ is not invariant under P_{12} , it goes to minus itself. It is not a physical observable. (^{assumes (1) can be distinguished from (2)})

Ex: If $|n\rangle$ is completely antisymmetric
then $G|n\rangle$ also is.

Consider ground state of N identical fermions.

Energy $E_{1,2,\dots,N} = \epsilon_1 + \epsilon_2 + \dots + \epsilon_N$

\uparrow
in order of increasing energy.

You can make an antisymmetric state

$$|\Psi_{1,\dots,N}\rangle = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} |\psi_1\rangle & |\psi_2\rangle & \dots & |\psi_N\rangle \\ \vdots & \vdots & & \vdots \\ |\psi_1\rangle & |\psi_2\rangle & \dots & |\psi_N\rangle \end{pmatrix}$$

rows are particle #

columns are state vectors.

some of the energies can be degenerate

Fermi energy: highest individual energy ϵ_N .

2-electron system (fermions)

P_{12} has eigenvalue -1

coordinates $\left\{ \vec{x}_1, m_{s_1} \right\}$ spin magnetic #s
 $\left\{ \vec{x}_2, m_{s_2} \right\} \quad \pm \frac{1}{2}$

We can write the wave function as a linear combination

$$\psi = \sum_{m_{s_1}} \sum_{m_{s_2}} C(m_{s_1}, m_{s_2}) \langle \vec{x}_1, m_{s_1}; \vec{x}_2, m_{s_2} | \psi \rangle$$

Assume the Hamiltonian commutes with S_{TOT}^2

Then the energy eigenfunction is an eigenfn of S_{TOT}^2 .

If we write $\psi = \phi(\vec{x}_1, \vec{x}_2) \chi$

then the spin function χ is one of these:

$$\chi(m_{s_1}, m_{s_2}) = \begin{cases} \chi^{++} \\ \frac{1}{\sqrt{2}} (\chi_{+-} + \chi_{-+}) \\ \chi^{--} \\ \frac{1}{\sqrt{2}} (\chi_{+-} - \chi_{-+}) \end{cases} \begin{cases} \text{triplet (symmetric)} \\ \text{singlet (anti-symmetric)} \end{cases}$$

where $\chi(m_{s_1} = \frac{1}{2}, m_{s_2} = -\frac{1}{2}) \equiv \chi_{+-}$ e.s.

All triplet states are symmetric.

$$P_{12} = P_{12}^{(\text{space})} P_{12}^{(\text{spin})}$$

Notice $\langle x_1, m_{s_1}; x_2, m_{s_2} | P_{12} | \psi \rangle$

$$= \langle x_2, m_{s_2}; x_1, m_{s_1} | \psi \rangle$$

Fermi-Dirac statistics requires

$$\langle x_1, m_{s_1}; x_2, m_{s_2} | \psi \rangle = - \langle x_2, m_{s_2}; x_1, m_{s_1} | \psi \rangle$$

We can write $P_{12}^{(\text{spin})} = \frac{1}{2} (1 + \frac{4}{\hbar^2} \vec{\Sigma}_1 \cdot \vec{\Sigma}_2)$

$$\vec{\Sigma}_1 \cdot \vec{\Sigma}_2 = \left\{ \begin{array}{l} \frac{\hbar^2}{4} \text{ triplet} \\ -\frac{3\hbar^2}{4} \text{ singlet} \end{array} \right\}$$

$$|\psi\rangle \rightarrow P_{12}|\psi\rangle$$

$$\phi(\vec{x}_1, \vec{x}_2) \rightarrow \phi(\vec{x}_2, \vec{x}_1), \text{ and}$$

$$\chi(m_{s_1}, m_{s_2}) \rightarrow \chi(m_{s_2}, m_{s_1})$$

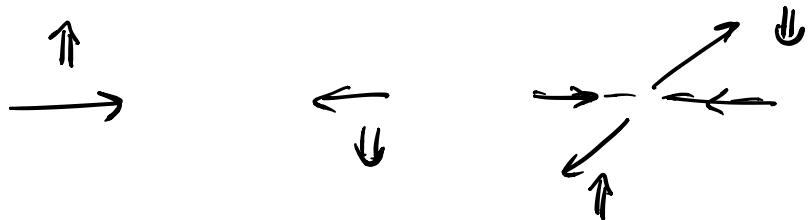
Therefore if spatial wave-function is symmetric the spin part must be anti-symmetric (and vice-versa)

e.g. electrons in a spin-triplet state must spatially avoid each other.

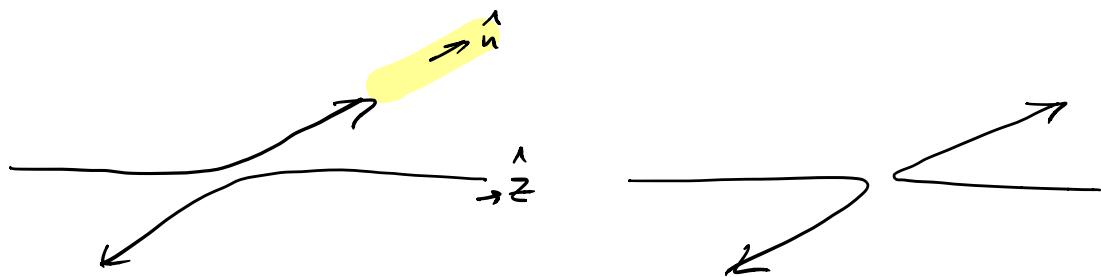
Remark

- we can effectively ignore the symmetrization postulate for identical particles situated in different regions of space, if their wave functions don't substantially overlap.
- Also can ignore it if particles are distinguishable.

Ex! orthogonal spin states in a collision and no spin-dependent interactions during the collision



Return to collision w/ 2 identical particles



Initial state :

$$|\psi_i\rangle = \frac{1}{\sqrt{2}} (|+\Sigma p_{12}\rangle |p_{e_z}; -p_{e_z}\rangle)$$

$\Sigma = 1$ if particles are bosons

$\Sigma = -1$ if particles are fermions.

Schrödinger equation

$$|\psi(t)\rangle = u(t, t_0) |\psi_i\rangle$$

After collision

$$|\psi(t_1)\rangle = u(t_1, t_0) |\psi_i\rangle$$

$$[u(t, t'), P_{12}] = 0$$

The physical ket associated with the final state

$$|\psi_f\rangle = \frac{1}{\sqrt{2}}(1 + \epsilon P_{12}) |\vec{p_n}, -\vec{p_n}\rangle$$

(assuming elastic collision, $|\vec{p}|$ unchanged)

There is a probability amplitude

$$\begin{aligned} \langle \psi_f | \psi(t_0) \rangle &= \langle \psi_f | U(t_1, t_0) | \psi_i \rangle \\ &= \frac{1}{2} \langle \vec{p_n}, -\vec{p_n} | (1 + \epsilon P_{12}^\dagger) U(t_1, t_0) (1 + \epsilon P_{12}) |\vec{p}_{e_2}, -\vec{p}_{e_2}\rangle \\ &\quad \downarrow (1 + \epsilon P_{12}^\dagger)(1 + \epsilon P_{12}) = 1 + \epsilon P_{12} + \epsilon P_{12} \\ &= \langle \vec{p_n}, -\vec{p_n} | (1 + \epsilon P_{12}^\dagger) U(t_1, t_0) |\vec{p}_{e_2}, -\vec{p}_{e_2}\rangle \\ &= \langle \vec{p_n}, -\vec{p_n} | U(t_1, t_0) |\vec{p}_{e_2}, -\vec{p}_{e_2}\rangle \\ &\quad + \epsilon \langle -\vec{p_n}, \vec{p_n} | U(t_1, t_0) |\vec{p}_{e_2}, -\vec{p}_{e_2}\rangle \end{aligned}$$

these terms correspond to the direct + exchange terms in the diagrams.

the probability amplitudes associated with these processes are added or subtracted \Rightarrow interference w/ + sign for bosons, - sign for fermions.

Ex: Helium Atom

$$H_0 = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} + V_c(R_1) + V_c(R_2)$$

Consider a perturbation

$$V = -\frac{2e^2}{R_1} - \frac{2e^2}{R_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} - V_c(R_1) - V_c(R_2)$$

The ground state and 1st excited configurations:

$$\bar{E} = E_{n, \ell} + E_{n', \ell'}$$

— 1s 2p

— 1s 2s

— 1s² ground state

Ground state:

$$|1s^2\rangle = |1, 0, 0\rangle |1, 0, 0\rangle \otimes \frac{1}{\sqrt{2}}(|\uparrow\rangle - |\downarrow\rangle)$$

wave function for electron in ground state,
other in a state n, l, m :

$$\phi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} [\psi_{100}(\vec{x}_1) \psi_{nlm}(\vec{x}_2) \pm \psi_{100}(\vec{x}_2) \psi_{nlm}(\vec{x}_1)]$$

upper sign for spin singlet

lower sign for spin triplet.

the term $\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ describes interaction w/ electrons

can be treated in pert. theory, or variational principle.

Consider the excited states :

$$E = E_{100} + E_{nlm} + \Delta E$$

In 1st-order perturbation theory ΔE can be estimated by expectation value

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = I \pm J$$

I, J are the direct and exchange integrals, resp.

$$I = \int d^3x_1 \int d^3x_2 | \psi_{100}(x_1) |^2 | \psi_{nlm}(x_2) |^2 \frac{e^2}{r_{12}}$$

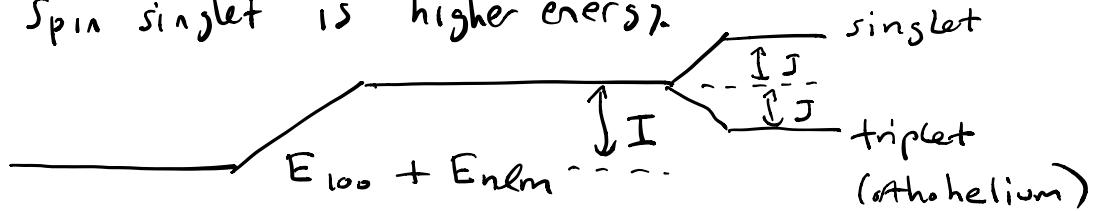
$$J = \int d^3x_1 \int d^3x_2 \psi_{100}^*(x_1) \psi_{nlm}^*(x_2) \frac{e^2}{r_{12}} \psi_{100}^*(x_2) \psi_{nlm}^*(x_1)$$

upper sign - spin singlet

lower sign - spin triplet.

$$I, J \geq 0$$

Spin singlet is higher energy.



The original Hamiltonian had no spin dependence.

Fermi-Dirac statistics gives a spin-dependent energy!

Example : Free-electron gas

Consider N electrons, neglect interactions, no external potential, in a cubic box of length L .

Infinite cubic well: $V = \begin{cases} 0 & \{(x, y, z) \in L\} \\ \infty & \text{otherwise} \end{cases}$

The energy eigenstates and eigenvalues are

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

$$n_x, n_y, n_z = 1, 2, 3, \dots$$

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

The state of electron also includes spin. The wave functions ψ_{n_x, n_y, n_z} describe the spatial part of 2 distinct states, with same energy since H is spin-independent.

In limit $L \rightarrow \infty$ spacing between levels decreases, looks more like a continuum.

Ground state (N identical fermions), must be anti-symmetric. We can anti-symmetrize the tensor product of N individual states associated with the lowest energy compatible with the Pauli exclusion principle.

If N is small, this is fairly straightforward - fill individual levels, find degree of degeneracy, construct anti-symmetrized kets which correspond to it.

e.g. $N=2$

$$|\Psi_{11}\rangle = |\Psi_{11}\rangle |\Psi_{11}\rangle \otimes \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

see also e.g. HW exercises...

In a solid, $N \approx 10^{23}$ this is not useful in practice. We can use a more global argument.

We can construct the number of individual stationary states with energy lower than E .

$$\equiv n(E)$$

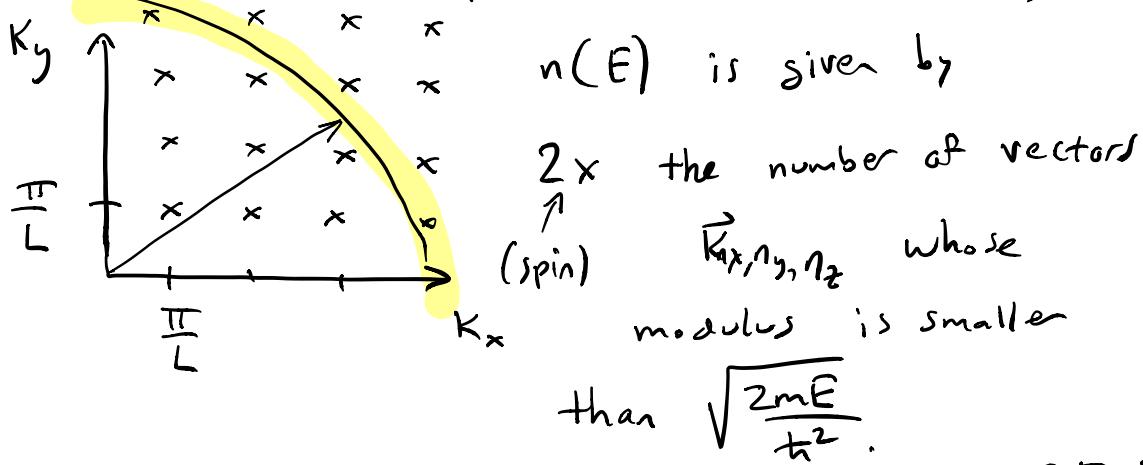
We can write $E_{n_x, n_y, n_z} = \frac{\hbar^2 k^2}{2m_e}$

$$(\vec{k}_x) = \frac{n_x \pi}{L} \quad (\vec{k}_y) = \frac{n_y \pi}{L} \quad (\vec{k}_z) = \frac{n_z \pi}{L}$$

Each vector in k -space \vec{k}_{n_x, n_y, n_z}

corresponds to a function $f_{n_x, n_y, n_z}(\vec{r})$
and vice versa.

Consider a k -space (2d for simplicity)



We can count # of cubes of volume $(\frac{\pi}{L})^3$
in 3-dimensions.

There is one vector \vec{k}_{n_x, n_y, n_z} per volume
element $(\frac{\pi}{L})^3$ of k -space.

Thus we have a sphere centered at origin
of radius $\sqrt{\frac{2mE}{\hbar^2}}$

But all n_x, n_y, n_z are positive, so all \vec{k} are positive, so only $\frac{1}{8}$ of volume is allowed.

We can find

$$n(E) = 2 \left(\frac{1}{8} \right) \underbrace{\frac{4}{3}\pi \left(\frac{2meE}{\hbar^2} \right)^{3/2}}_{\substack{\text{spin} \\ \text{only positive} \\ \vec{k}}} \underbrace{\frac{1}{\left(\frac{\pi}{L} \right)^3}}_{\substack{\text{total volume} \\ \text{of sphere in k-space} \\ \text{volume occupied} \\ \text{by 1 state} \\ (\text{cube})}}$$

$$= \frac{L^3}{3\pi^2} \left(\frac{2meE}{\hbar^2} \right)^{3/2}$$

The Fermi energy (maximal occupied level) occurs when $n(E_F) = N$

$$\Rightarrow E_F = \frac{\hbar^2}{2me} \left(3\pi^2 \frac{N}{L^3} \right)^{2/3}$$

\nearrow
density of electrons

We can also find the density of states $\rho(E)dE$ the number of states between E and $E+dE$

$$\rho(E) = \frac{dn(E)}{dE} = \frac{L^3}{2\pi^2} \left(\frac{2me}{\hbar^2}\right)^{3/2} E^{1/2}$$

$$\text{so } \rho(E) \propto E^{1/2}$$

We can rewrite this in terms of Fermi energy

$$\rho(E) = \frac{3}{2} N \frac{E^{1/2}}{E_F^{3/2}}$$

Remark

This is all valid at zero temperature.

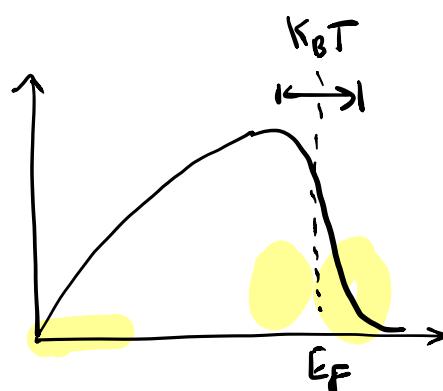
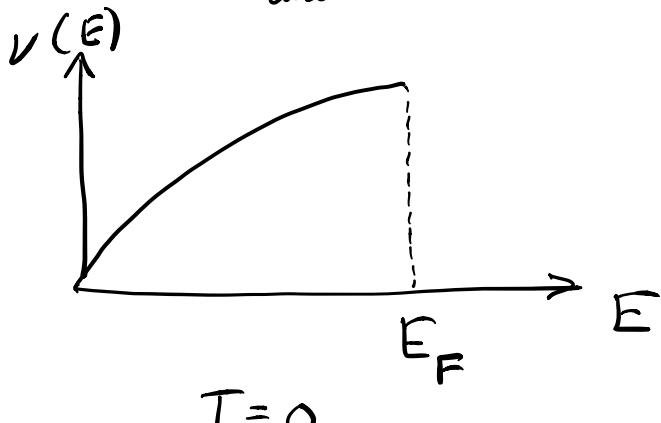
What if $T > 0$?

Specific Heat

At $T = 0$, electron gas is in ground state.

All levels under E_F are occupied.

$\nu(E) \equiv \# \text{ of electrons w/ energy between } E$
and $E + dE$



Each electron has thermal energy $k_B T$

Classically $U_{ce}(T) = \frac{N}{L^3} k_B T$

would give a constant volume specific heat

$$\frac{\partial U_{ce}}{\partial T} \text{ independent of temperature } T.$$

But QM \rightarrow Pauli exclusion principle prevents most of electrons from gaining energy. An electron w/ $E \ll E_F$ has no unfilled levels it can go to.

If $E \sim E_F$ so that $E_F - E \approx k_B T$ then electron can "heat up".

the number of these electrons is

$$\Delta N \approx \rho(E_F) k_B T = \frac{3}{2} N \frac{k_B T}{E_F}$$

since energy of each one increases by about $k_B T$

$$U(T) = \frac{N}{L^3} \frac{k_B T}{E_F} (k_B T)$$

$$\Rightarrow C_V = \frac{\partial U}{\partial T} \approx \frac{N}{L^3} \frac{k_B^2 T}{E_F} \quad \begin{matrix} \text{linear in } T. \\ (1P-22) \end{matrix}$$

For a metal, if we apply free-electron model

$E_F \sim \text{few eV}$ typically.

$K_B T \sim 0.03 \text{ eV}$ at room temperature.

the factor $\left(\frac{K_B T}{E_F}\right)$ is of order 10^{-2} .

Pauli principle greatly reduces C_V .

In Stat-Mech, # of electrons with energy between E and $E + dE$ is

$$n(E) dE = f(E, T) \rho(E) dE$$

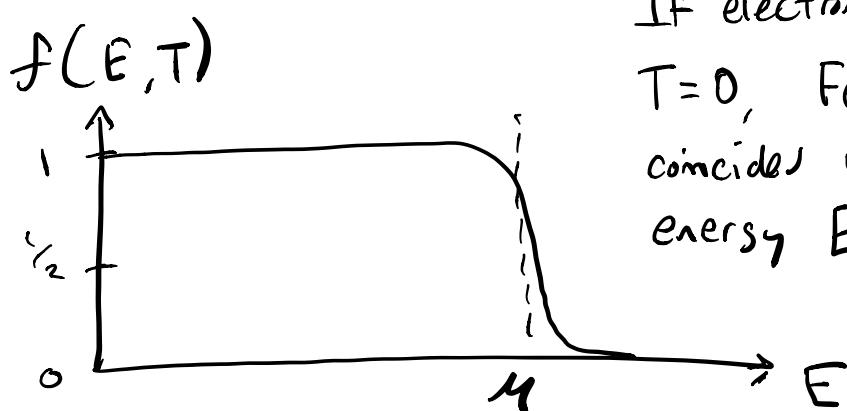
↑ ↑
probability that density of states
an energy E is
occupied if system is
at temperature T

$$f(E, T) = \frac{1}{e^{(E-\mu)/kT} + 1} \quad \text{Fermi-Dirac distribution.}$$

μ is the chemical potential. (Fermi-level ^{also called})
The fermi-level is determined by $\#_{\text{total}}$ of electrons N

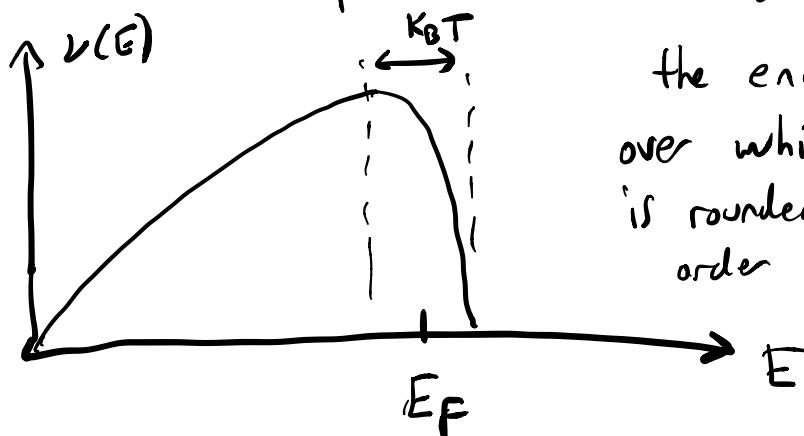
$$\int_0^{\infty} \frac{p(E) dE}{e^{(E-\mu)/k_B T} + 1} = N$$

μ can depend on T , but at low T is slowly varying



If electron gas is at $T=0$, Fermi level μ coincides w/ Fermi energy E_F .

Now we can plot $v(E)$ using $f(E, T)$



the energy interval over which the step is rounded off is order $k_B T$ as long as $k_B T \ll \mu$.

At $T=0$, μ characterizes highest individual energy E_F for free electron gas.

Remark : For a system with discrete energy spectrum ($E_1, E_2, \dots, E_i, \dots$) μ does not coincide with the highest individual energy in ground state at $T=0$.

In this case $\rho(E) dE = \sum_i \delta(E - E_i)$
 (a sum of δ -functions centered at each discrete energy E_i)

At $T=0$ μ can take any value between E_m and E_{m+1}

μ can be defined as limit of $\mu(T)$ as $T \rightarrow 0$
 ↑
 fermi-level ↑
 chemical potential

Similarly, for a system containing a series of allowed energy bands separated by forbidden bands.

The fermi level μ is in the forbidden band when the highest individual energy at $T=0$ coincides w/ upper limit of allowed band.

or $\mu = E_F$ if E_F is in middle of allowed band.

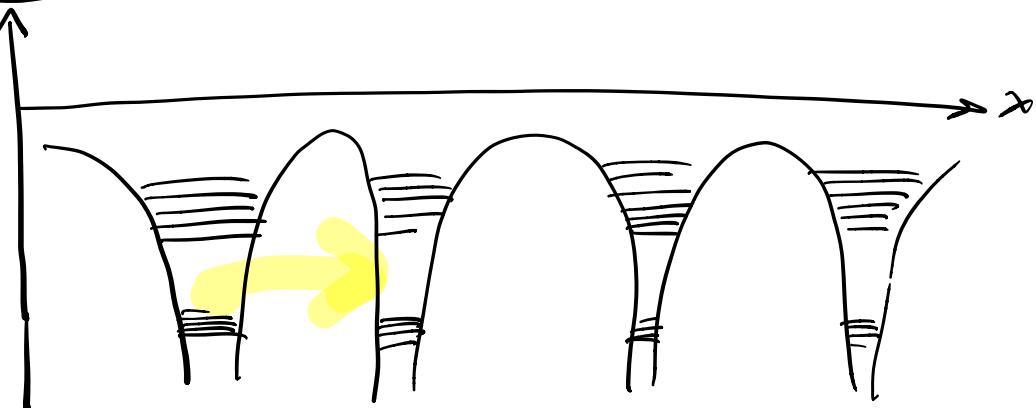
⇒ This has huge implications for resistivity of solids (varies by 10^{30} !)

A solid where Fermi-level falls in middle of a band that is allowed is called a conductor.

Applying e.g. an electric field \vec{E} , electrons can accelerate and occupy allowed higher energy states.

A solid for which Fermi level falls inside a forbidden band is an insulator.

Bands in Solids:



Energy levels for a potential w/ several regularly spaced wells.

- The stationary states of electron are all de-localized.
- widths of bands tend to get narrower the deeper they are. (since crossing the barrier by tunneling is more difficult)

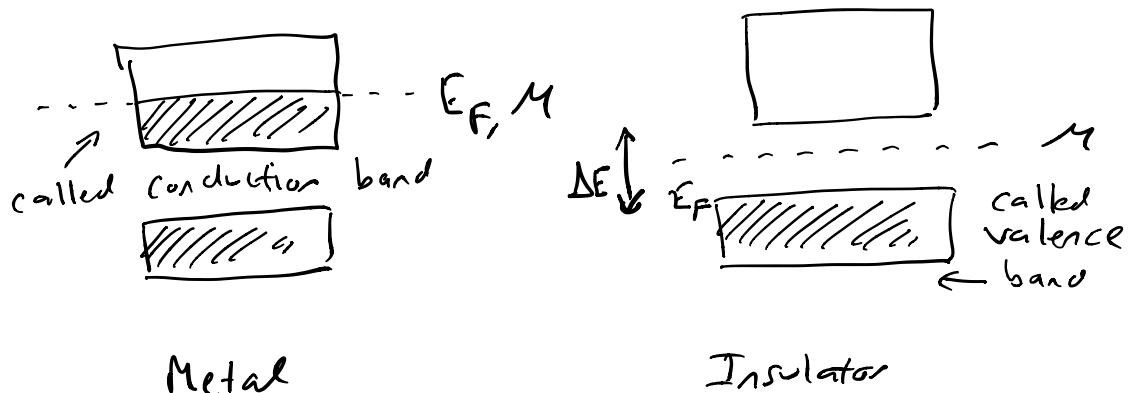
Stationary states: Bloch functions

$$\Psi_k(x+l) = e^{ikl} \Psi_k(x)$$

product of plane wave + periodic fns
 \Rightarrow electron is delocalized.

Pauli exclusion principle has profound impact on macroscopic behavior of materials

e.s. conductivity



In Insulator you need to overcome a gap in energy ΔE . Good insulator \Leftrightarrow larger ΔE

We can also have semiconductors

If $\Delta E \lesssim k_B T$ some electrons have ability to leave valence band and occupy a state at next higher band (which would be empty at $T=0$)

e.g. Silicon $\Delta E < 1\text{eV}$

Diamond (good insulator) $\Delta E = 5\text{eV}$

Quantitatively conductivity dependence:

$$e^{-\frac{\Delta E}{2k_B T}}$$

wide variability in conductivity of materials.

Magnetic Susceptibility

Free electron gas in a uniform magnetic field

$$\hat{B_z} \text{ Hamiltonian } W = -\frac{2\mu_B}{\hbar} BS_z$$

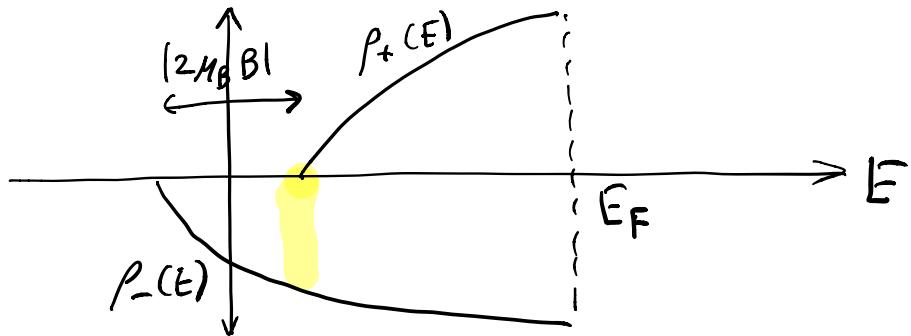
where μ_B is Bohr magneton : $\frac{g\hbar}{2m_e}$

Then energy is either increased or decreased by $\pm \mu_B B$ depending on spin-state.

The density of states $\rho_+(E)$ and $\rho_-(E)$ corresponding to $| \uparrow \rangle$, $| \downarrow \rangle$ components are

$$\rho_{\pm}(E) = \frac{1}{2} \rho(E \pm \mu_B B)$$

At $T=0$ we can plot



Typically $|\mu_B B| \ll E_F$, the difference in # of electrons $N_- - N_+ = \frac{1}{2} \rho(E_F) 2|\mu_B B|$

the moment M per unit volume

$$M = |\mu_B| \frac{1}{L^3} (N_- - N_+)$$

$$= \mu_B^2 \frac{1}{L^3} \rho(E_F) B$$

this is proportional to B , so susceptibility χ

$$\text{is } \chi = \frac{M}{B} = \mu_B^2 \frac{1}{L^3} \rho(E_F)$$

$$\rho(E) = \frac{3}{2} N \frac{E^{\frac{1}{2}}}{E_F^{3/2}}$$

$$\chi = \frac{3}{2} \frac{N}{L^3} \frac{M_B^2}{E_F}$$

This result remains valid at low temperature since modification of # of occupied states are almost same for both spin-orientations.

χ independent of T
this is what is observed in metals.

Example

From high energy physics

Quarks spin- $\frac{1}{2}$

observed hadrons must be color singlets

$$\frac{1}{\sqrt{6}} \left\{ |RBY\rangle + |BYR\rangle + |YRB\rangle - |BRY\rangle - |YBR\rangle - |RYB\rangle \right\}$$

$$P_{ij} = P_{ij}^{(\text{flavor})} P_{ij}^{(\text{spin})} P_{ij}^{(\text{space})} P_{ij}^{(\text{color})}$$

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

Postulated $SU(3)$ color to exist in order to explain this!

Sample exercises

Consider 2 spin-1 particles. Let \vec{J} be total angular momentum $\vec{J} = \vec{S}_1 + \vec{S}_2$

What are allowed values of quantum # j
if particles are identical or not identical?

Identical bosons must be in a state which is totally symmetric under exchange of their indices.

In the $|j, m\rangle$ basis, express states in the $|m_1, m_2\rangle$ basis via the Clebsch-Gordan coefficients:

$$|2, 2\rangle = |1, 1\rangle$$

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

$$|2, 0\rangle = \frac{1}{\sqrt{6}} (|1, -1\rangle + |-1, 1\rangle + 2|0, 0\rangle)$$

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

$$|2, -2\rangle = |-1, -1\rangle$$

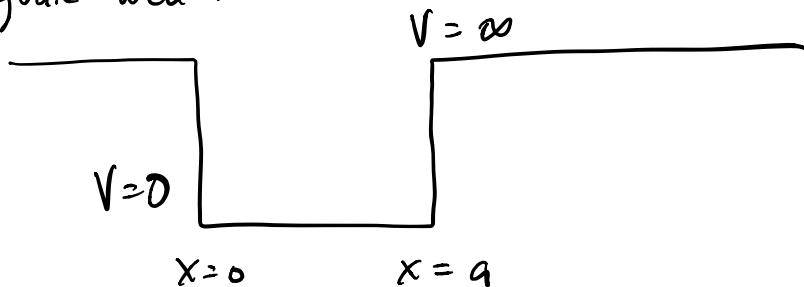
$$|1, 1\rangle = \frac{1}{\sqrt{2}} (|1, 0\rangle - |0, 1\rangle) \quad \left. \begin{array}{l} \text{symmetric} \\ \text{anti-symmetric} \end{array} \right\}$$

$$|0, 0\rangle = \frac{1}{\sqrt{3}} (|1, -1\rangle + |-1, 1\rangle + |0, 0\rangle)$$

Only $j=0, 2$ are allowed for identical bosons.

Example exercise 2

2 spin- $\frac{1}{2}$ particles (identical), in a 1-d infinite square well:



Assume particles are in a spin triplet state
what is ground state wave function and energy?
What if they were in a spin-singlet state?

Total state must be antisymmetric since they
are Fermions.

$$P_{12} = P_{12}^{(\text{spin})} P_{12}^{(\text{space})}$$

wave function must be anti-symmetric spatially

$$| \psi \rangle = \frac{1}{\sqrt{2}} (| 1 \rangle | 2 \rangle - | 2 \rangle | 1 \rangle) \otimes | \text{triplet} \rangle$$

$$\langle x | 1 \rangle = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

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

$$\text{Ground state energy} \quad \frac{\hbar^2 \pi^2}{2ma^2} + \frac{4\hbar^2 \pi^2}{2ma^2} = \frac{5\hbar^2 \pi^2}{2ma^2}$$

If we had a spin-singlet state:

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

$$E = 2 \frac{\hbar^2 \pi^2}{2ma^2} = \frac{\hbar^2 \pi^2}{ma^2}$$

lower energy
than triplet!