Perturbation Theory

Unperturbed system : $H^0\psi_n^0 = E_n^0\psi_n^0$ w/ orthonormal basis $\{\psi_n^0\}$

New Hamiltonian $H = H^0 + \lambda \underbrace{H'}_{\text{perturbed Hamiltonian}}$ $\quad 0 \le \lambda \le 1 \quad \Rightarrow \quad \boxed{H\psi_n = E_n\psi_n}$ (*)

Use power series approximation (polynomial in λ)

$$\boxed{\begin{aligned} \psi_n &= \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots \\ E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots \end{aligned}}$$

ψ_n^k, E_n^k are order of correction

Substitution and collecting like power for (*)

(1st order λ^1) $\quad H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0 \quad$ (1)

(2nd order λ^2) $\quad H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0 \quad$ (2)

1st order theory

Obtain : (i) $\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle}$ (3)

(ii) $\boxed{\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0}$ (4)

sketch of proof

(i) $\underbrace{\langle \psi_n^0 | H^0 | \psi_n^1 \rangle}_{\langle H^0\psi_n^0 | \psi_n^1 \rangle \ \because \text{Hemitian.}} + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle$

(ii) Wave function correction from (1) Remark: want express ψ_n^1 in term of known basis $\{\psi_n^0\}$.

$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$; let $\boxed{\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m}$

note. why $m \neq n$? Both ψ_n^1, ψ_n^0 solve the above equation (Coeff is trivial 0) don't need $m = n$!

Now inner product w/ $\psi_m^0 \Rightarrow c_m^{(n)} = -\frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_m^0 - E_n^0}$

Remarks: • hold for non-degen. sys only (degen. perturbation theory need for $\underbrace{E_n^0 = E_m^0}_{\text{two diff states share same energy.}}$)

• Accurate energies $E_n \simeq E_n^0 + E_n^1$ but inaccurate wave function! (Why?) ← $[\hat{x}, \hat{H}] \neq 0$?

2nd Order theory (use of (2))

Obtain : (**) $\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$ — level repulsion! imagine $E_n^0 \gtrless E_m^0$

Consider $E_n^0 > E_m^0$, $E_n^0 < E_m^0$ for ...

sketch

Use (**) $\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$ sub into (**)

First:

$$\langle \psi_n^0 | H^0 | \psi_n^2 \rangle + \underbrace{\langle \psi_n^0 | H' | \psi_n^1 \rangle}_{(**) \neq 0} = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \underbrace{\langle \psi_n^0 | \psi_n^1 \rangle}_{(**) \to 0} + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle^{1}$$

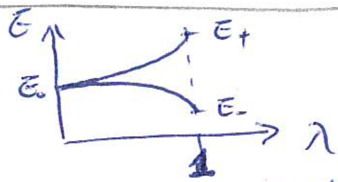
Degen. Perturbation Theory (DPT)

Degen. States, $H^0\psi_a^0 = E\psi_a^0$ where $\langle\psi_a^0|\psi_b^0\rangle = 0$

$H^0\psi_b^0 = E\psi_b^0$

Also $\boxed{\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0}$ (Good States) solves $H\psi^0 = E^0\psi^0$

Remark: Perturbation H' breaks degeneracy (but how?)



First order perturbation turns into eigenvalue prob. by solving matrix $W_{ij} \equiv \langle\psi_i^0|H'|\psi_j^0\rangle$ where ψ_i^0 for $i=1,\dots,n$ are the deg. states ie $H\psi_i = E_i\psi_i$

Sub Solve $H\psi = E\psi$ using $H = H^0 + \lambda H'$ and power series of E, ψ in power of λ: (simple ex 2 states deg)

Yield 1st order expression → the good state

$$H^0\psi' + H'\psi^0 = E^0\psi' + E'\psi^0$$

* Take inner product w/ both ψ_a^0 and ψ_b^0 w.r.t.,

Remark: "good" linear comb. states are eigenvect of $\vec{W}$ clearly!

Simplify $H' \to$ matrix rep W_{ij} st $Wv = Ev$ eig. val. prob.

$$\boxed{\begin{aligned}\alpha W_{aa} + \beta W_{ab} &= \alpha E' \\ \alpha W_{ba} + \beta W_{bb} &= \beta E'\end{aligned}}$$

where $\boxed{W_{ij} = \langle\psi_i^0|H'|\psi_j^0\rangle}$ $i,j = a,b$; $\boxed{W_{ab} = W_{ba}^*}$

Remark: set of eqn. can be used to determine α, β if $\psi_{a,b}^0$ known!

Remark: Goal is for E', so this reduces to eigenvalue problem,

$$\underset{2\times2}{W}\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb}\end{pmatrix}\begin{pmatrix}\alpha \\ \beta\end{pmatrix} = E'\begin{pmatrix}\alpha \\ \beta\end{pmatrix} \Rightarrow (E')^2 - (W_{aa}+W_{bb})E' + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0$$

we have

$$\boxed{E_\pm^1 = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa}-W_{bb})^2 + 4|W_{ab}|^2}\right]}$$

$$\frac{tr(W) \pm \sqrt{tr^2(W) - 4\det(W)}}{2}$$

Remark: • fundament results of degen. perturb. theory saying two roots correspond. two perturbed energies

• $\alpha = 0, \beta = 1$ so $W_{ab} = 0 \Rightarrow E_+^1 = \langle\psi_a^0|H'|\psi_a^0\rangle$

$E_-^1 = \langle\psi_b^0|H'|\psi_b^0\rangle$

distinct Real Roots

* $\boxed{\text{Thm}}$ Let A ops. (operator) commute w/ H^0 and H'. ψ_a^0, ψ_b^0 degen. states of H^0. A compatible w/ $H^0 \Rightarrow \psi_a^0, \psi_b^0$ also eig. func. of A but let they have distinct eig. val st. $A\psi_a^0 = \mu\psi_a^0$, $A\psi_b^0 = \nu\psi_b^0$ $\mu \neq \nu$

then $W_{ab} = 0$ and ψ_a^0, ψ_b^0 are the "good" states for DPT.

sketch of proof starts w/ $\boxed{\langle\psi_a^0|[A, H']|\psi_b^0\rangle = 0}$, details out L.H.S in terms of W_{ab}.

High order Degeneracy. Recall: $W = \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb}\end{pmatrix}$

For n-fold degen., we are looking for eigenvalues of $n\times n$ matrix

$$\boxed{W_{ij} = \langle\psi_i^0|H'|\psi_j^0\rangle} \quad i,j = 1,\dots,n$$

Remark: • In Linear Algebra, this equivalent to construct a basis that diagonalized W

• ex $W_{ij} = \langle\psi_i|H'|\psi_j\rangle$ $i,j = a,b,c$ then W is 3×3!

Fine Structure of Hydrogen

- Good Quantum number.
Given H and

2

Hamiltonian of hydrogen atom:

$$\boxed{H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}}$$

Two body problem, a correction is $m \mapsto \mu$ (reduced mass)

Recalled Bohr energy of hydrogen atom

$$\boxed{E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2}}$$ also Bohr radius $a = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$ — for completeness.

We have smaller corrections!

"Hierarchy of corrections" to hydrogen Bohr energies ($\sim$ orders)

Bohr energies	$\sim$	$\alpha^2 mc^2$
Fine structure	$\sim$	$\alpha^4 mc^2$
Lamb shift	$\sim$	$\alpha^5 mc^2$
Hyperfine splitting	$\sim$	$\left(\frac{m}{m_p}\right)\alpha^4 mc^2$

$\longrightarrow E_n = -\frac{mc^2}{2}\underbrace{\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)}_{\alpha}^2\frac{1}{n^2}$ ~~[illegible]~~

α is the fine structure constant

$$\boxed{E_n = -\alpha^2 mc^2\left(\frac{1}{2n^2}\right)}$$

$\alpha \sim \frac{1}{137}$.

BFLH
α: 2 4 5 4

Fine Structure

a tiny perturbation smaller by factor of α^2 $\boxed{\alpha \equiv \frac{e^2}{4\pi\varepsilon_0\hbar c}} \sim \frac{1}{137}$ fine structure constant

Due to two distinct mechanisms: • relativistic correction, • spin-orbit coupling.

Relativistic correction

take $c = 1$. what is the correction, what is H', good quantum number
what is E depends on n, l, m?

$H' = -\frac{1}{8}\frac{p^4}{m^3}$
commute w/ L^2, L_z
good qum # n, l, m
E'_{em}

$$E^2 = m^2 + p^2$$
$$T = E - m = \sqrt{m^2+p^2} - m$$
} relativistic setting

Classically,

$$T = \frac{p^2}{2m} \xrightarrow[\substack{\text{non relativistic} \\ \text{limit} \\ (m \gg p)}]{\text{correction on}} \simeq \frac{1}{2}\left(\frac{p}{m}\right)^2 m - \frac{1}{8}\frac{p^4}{m^3} + \cdots$$

Now, Hamiltonian of the hydrogen atom:

$$H = \frac{p^2}{2m} + V + H' \;;\; H' = -\frac{1}{8}\frac{p^4}{m^3} \text{ and } V = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

Def $[H, O] = 0$
O has eigenvect. eigenval: (simple) $O|q_j\rangle = q_j|q_j\rangle$, then q_j "" is good quantum number if $\forall |q_j\rangle$ remains eigenvec. of O w/ same q_j eigenval. as time evolves. Consider $\frac{d\langle O\rangle}{dt} = \frac{i}{\hbar}\langle[H,O]\rangle + \langle\frac{\partial O}{\partial t}\rangle$

w/ $n l m$ good eig #

Remarks • this perturbation is spherical symmetric, it commutes w/ L^2 & L_z.
• eigenfun. of L^2, L_z has distinct eigenval. for n^2 states given E_n.
• n, l, m are good quantum number (Def)

$\because p$ derivative which interchange $L(\theta,\phi)$

Recalled
$W_{ab} = W_{ba} = 0$
$E_\pm = W_{aa}, W_{bb}$

1st order correction

* These implies one can use nondegenerate perturbation theory (Why?)

$$\boxed{E_r^1 = \langle H_r'\rangle = -\frac{1}{8m^3c^2}\langle\psi|p^4|\psi\rangle \;;\; p^2\psi = 2m(E-V)\psi}$$ — Schrödinger eq E_r

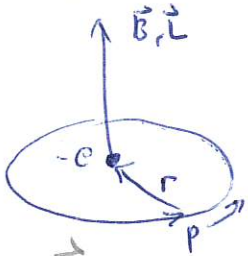
$$\Rightarrow E_r^1 = -\frac{1}{2mc^2}\langle(E-V)^2\rangle = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right];$$ $\langle\frac{1}{r}\rangle$

Yields: $$\boxed{E^1_{r(nl)} = -\frac{E_n^2}{2mc^2}\left(\frac{4n}{l+\frac{1}{2}} - 3\right)}$$ w/ n, l dependent but not m! $\Rightarrow 2l+1$ degen.

what is H'? $H' \propto \vec{L}\cdot\vec{S}$
good quantum #: J_z, J^2, L^2, S^2 commute not $\vec{L}, \vec{S}$
l, s, j, m_j

Spin-Orbit Coupling (Find H' due to these effect)

Set electron be the rest frame.



Biot-Savart $\boxed{B = \frac{\mu_0 I}{2r}}$; $I = \frac{e^+}{T}$; $\boxed{L = rmv}$; $v = \frac{2\pi r}{T}$

Then $\boxed{\vec{B} = \frac{1}{4\pi\varepsilon_0}\frac{e^+}{mc^2r^3}\vec{L}}$ recalled $C = \frac{1}{\sqrt{\mu_0\varepsilon_0}}$

Magnetic dipole moment of electron — recalled $\mu = \frac{1}{2}\int \vec{r}\times\vec{J}\, d^3x = AI = \frac{q\pi r^2}{T}$ (area)

$\vec{J} = \frac{q}{T}\delta(z-0)\delta(r-R)$

$\mu = \frac{q}{2T}\int \delta(z\cdot 0)\delta(r-R)\, r\, dr\, d\phi\, dz = \frac{qR^2}{2T}\cdot 2\pi = \frac{q}{T}\pi R^2$

① $\mu = \boxed{\frac{q\pi r^2}{T}}$ ($\mu = AI$)

$\vec{\mu} = \frac{q}{m}\vec{S} \Leftarrow$ ①

Angular momentum $\vec{S} = I\vec{\omega}$; $I = mr^2$ $\omega = \frac{2\pi}{T}$

$\vec{S} = \boxed{\frac{2\pi mr^2}{T}}$

Then gyromagnetic ratio : $g_r = \frac{\mu}{S} = \frac{q}{m}$ — $\gamma_0 = 2$ due to relativistic theory of electron by Dirac.

Classical $\boxed{\vec{\mu} = \frac{q}{2m}\vec{S}}$, indeed $\boxed{\vec{\mu} = \gamma_0\left(\frac{q}{2m}\right)\vec{S}}$

$H = \vec{\mu}\cdot\vec{B}$

Now $H = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L}$

relativistic $H = \frac{\gamma_0}{2}\left(\frac{e^2}{8\pi\varepsilon_0 m^2c^2r^3}\vec{S}\cdot\vec{L}\right)$

Thomas precession

Remarks: • Want proton not electron on Lab frame!
• Can treat electron continually boost from one ~~into~~ inertial frame to another.
• This cummulative effect of Lorentz transformation is called the Thomas precession, corrected by factor ½.

spin-orbit interaction ②

$$\boxed{H'_{so} = \frac{e^2}{8\pi\varepsilon_0}\frac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L}}$$

Remark: • γ_0 and Thomas precession cancelled each other due to torque on μ_e of spinning e^- by p's m-field.

$H = H^0 + H'$

Remark: (*). In spin-orbit coupling $[H, \vec{L}], [H, \vec{S}] \neq 0$ can this $H \to H_{so}$? w.f., eg.val depends on !
From Heisenberg equation of motion, spin and orbital ang. momentum are no longer conserved!
③ • But H_{so} does commutes w/ L^2, S^2 and $\vec{J} = \vec{L} + \vec{S}$, thus they conserved in H'_{so}.
• L^2, S^2, J^2, J_z are good states but not J_z, L_z, S_z to use in perturbation theory.

Now $J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S} \Rightarrow$ eigenvalues of $\vec{L}\cdot\vec{S}$: $\boxed{\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]}$ natural!

important

Also $\left\langle \frac{1}{r^3}\right\rangle = \frac{1}{l(l+\frac{1}{2})(l+1)n^3a^3}$

so, $\boxed{E^1_{so} = \langle H'_{so}\rangle = \frac{(E_n)^2}{mc^2}\frac{n\left[j(j+1) - l(l+1) - \frac{3}{4}\right]}{l(l+\frac{1}{2})(l+1)}}$

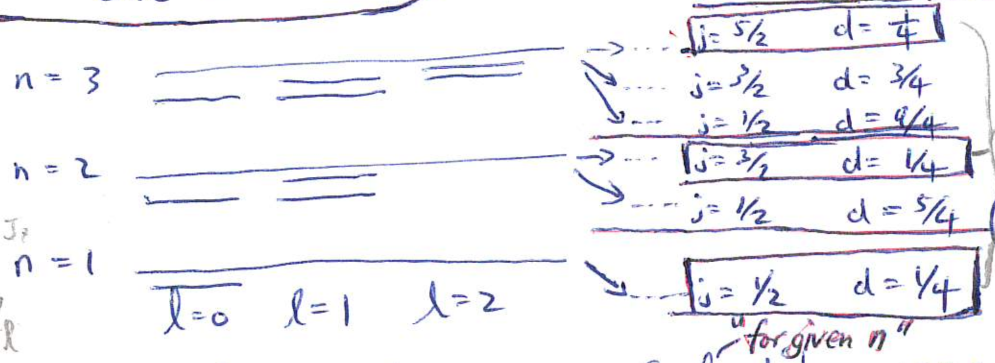
Adding both mechanism :

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)$$

$E_{nj} = E_n + E^1_{fs}$

$$\boxed{E_{nj} = -\frac{13.6\,eV}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\underbrace{\frac{n}{j+\frac{1}{2}} - \frac{3}{4}}_{d}\right)\right]}$$

fine structure Spectrum.



show degeneracy of j ⑤

note
$n=1$, $l=0$
$j = l+s$, $s = \frac{1}{2}$
$\Rightarrow j = \frac{1}{2}$
④ $n=2$ $l=0,1$
$l=0 \Rightarrow j=\frac{1}{2}$
$l=1$ & $s = \pm\frac{1}{2}$
$\Rightarrow j = \frac{3}{2}, \frac{1}{2}$
$n=3$, $l=0,1,2$
$l=2$ & $s=\pm\frac{1}{2}$, $j = \frac{5}{2}, \frac{3}{2}$

$\propto \vec{L}\cdot\vec{S}$
q.# J^2, L^2, S^2, J_z
$E = E_0 + E_R$

Remarks: • Fine structure break degeneracy of l but preserves degeneracy of j "for given n" explain
• Stationary states are linear comb. of states w/ different m_l, m_s
$\Rightarrow m_s, m_l$ no longer good quantum numb.;
n, l, s, j, m_j are good quantum # !

L, S are not separately conserved in the presence of spin-coupling. (*)

Zeeman effect . Uniform $\vec{B}_{ext}$ (External) field causes shifting of atom's energy level

The perturbation: $H_Z' = -(\vec{\mu}_s + \vec{\mu}_\ell)\cdot\vec{B}_{ext}$ where $\vec{\mu}_s = -\frac{e}{m}\vec{S}$, $\vec{\mu}_\ell = -\frac{e}{2m}\vec{L}$ (1)

- $\vec{\mu}_s$ dipole moment assoc. w/ electron spin.
- $\vec{\mu}_\ell$ " " assoc. w/ orbital motion. pure classical

$$\boxed{H_Z' = \frac{e}{2m}(\vec{L} + 2\vec{S})\cdot\vec{B}_{ext}}$$

; Recalled $H_{mB}' = \vec{\mu}_s\cdot\vec{B}_{int}$ — partial effect.

$\mu_s = -\frac{e}{m}\vec{S}$
$\mu_\ell = -\frac{e}{2m}\vec{L}$
$H_Z' \propto \vec{L} + 2\vec{S}$ due to $\vec{B}_{ext}$

Remark: • Zeeman splitting depends critically on $\vec{B}_{ext}$

(1) $B_{int} \gg B_{ext}$, $H' \gg H_Z'$ • $\vec{B}_{ext} \ll \vec{B}_{int}$ fine structure dominate, H_Z' is small perturbation.

(2) $B_{ext} \gg B_{int}$, $H' \gg H_{fs}'$ • $\vec{B}_{ext} \gg \vec{B}_{int}$ Zeeman dominate, H_{fs}' is small perturbation.

Focus on (1) weak zeeman

• Effect of $\vec{B}_{ext} \sim \vec{B}_{int}$, full machinery of DPT is needed.

Weak-Field Zeeman Effect $(\vec{B}_{ext} \ll \vec{B}_{int})$. H_Z' -perturbation.

Good Quantum # Z (2)
- n, ℓ, j, m_j are good quantum numbers (not m_ℓ, m_s since not conserved and spin-orbit effect)

not m_ℓ, m_s but $J^2, L^2, S^2, \vec{J}$

$$\boxed{E_Z^1 = \langle n\ell j m_j | H_Z' | n\ell j m_j\rangle = \frac{e}{2m}\vec{B}_{ext}\cdot\langle\vec{L}+2\vec{S}\rangle} \quad ; \quad \vec{L}+2\vec{S} = \vec{J}+\vec{S}$$

- Quest for eig. val of $\vec{L}+2\vec{S}$. Need $\vec{L}+2\vec{S}$ in terms of $J^2, L^2, S^2, \vec{J}$.
- Remarks: ~~$\vec{J}$~~ $\vec{J} = \vec{L}+\vec{S} = \text{const.}$, rapid precession of $\vec{L}, \vec{S} \Rightarrow \boxed{\vec{S}_{ave} = \frac{(\vec{S}\cdot\vec{J})}{J^2}\vec{J}}$.

Rewrite $\vec{L} = \vec{J} - \vec{S} \Rightarrow \boxed{\vec{J}\cdot\vec{S} = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - \ell(\ell+1)]}$. gives $m_j\hbar$

analyse $\vec{L}+2\vec{S}$
- $J = \text{const}$
- $\vec{L}+2\vec{S} = J + (\vec{J}\cdot\vec{S})\vec{J}$
- $\vec{S} \to \vec{S}_{ave} = \frac{(\vec{S}\cdot\vec{J})}{}\hat{J}$
- $\to L^2 = (\vec{J}-\vec{S})^2$
- Landé factor

So, $\langle\vec{L}+2\vec{S}\rangle = \left\langle\left(1 + \frac{\vec{S}\cdot\vec{J}}{J^2}\right)\vec{J}\right\rangle = \underbrace{\left[1 + \frac{j(j+1) - \ell(\ell+1) + 3/4}{2j(j+1)}\right]}_{\text{Landé g-factor } g_J}\langle\vec{J}\rangle$

Now $g_J = 1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}$

$$\boxed{E_Z^1 = \mu_B g_J B_{ext} m_j}$$

here choose $\vec{B}_{ext}$ along z-axis.

or $E_Z' = \mu_B B_{ext} m_j g_J$ (3) — easier to remember

$$\boxed{\mu_B = \frac{e\hbar}{2m} = 5.788\times10^{-5}\frac{eV}{T}}$$

Bohr magneton. (4)

Total energy is: n, ℓ, j, m_j — determine the spectrum line.

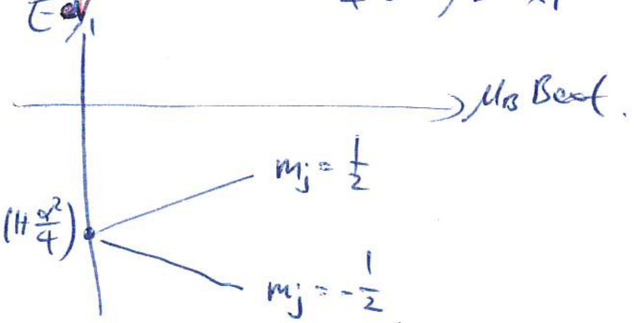
Recalled $E_{nj} = -\frac{13.6eV}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right] \Rightarrow E = E_{nj} + E_Z^1$

E_{nj} from f.s; E_Z^1 Zeeman contribution.

ex (5) Ground state $n=1$ $\ell=0$ $j=\frac{1}{2} \Rightarrow g_J = 2$, $m_j = \frac{1}{2}, -\frac{1}{2}$ ← combine w/ $2S+1$ $L(j) \to$ to inspect line splitting

ex $Z=9$ $^2P_{3/2}$

Then $E = -13.6eV(1+\frac{\alpha^2}{4}) \pm \mu_B B_{ext}$ splits into two levels.



Summary.

$H' \propto \vec{L}+2\vec{S} \to \vec{J} + (\vec{J}\cdot\vec{S})\vec{J}$

note $L^2 = (\vec{J}-\vec{S})^2$

$\to$ Landé factor: $g_J = 1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}$

$\therefore E_Z' = m_j g_J \mu_B B_{ext}$

$\mu_B = \frac{e\hbar}{2m}$ Bohr magneton.

General Pictures:

hydrogen atom: $E_n = -\left(\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right)\frac{1}{n^2}$

f.s: $H'_{rel} + H'_{so}$, $H'_{so} = \vec{\mu}_s \cdot \vec{B}$

$\vec{B} \sim \vec{L}$ $\vec{\mu}_s = \frac{q}{m}\vec{S}$

$H'_{so} \sim \vec{L}\cdot\vec{S}$ commutes w/ L^2, S^2, J

good Qnum ($\underline{n, l, s, j, m_j}$) $\Rightarrow$ break degen of l, preserve dgen of j

$E_{nj} = E_n + E'_{fs}$

zeeman; focus on $\vec{B}_{ext} \ll \vec{B}_{int}$ ($\vec{B}_{int}$ due to SO in f.s)

$H'_Z = \vec{\mu}\cdot\vec{B}_{ext}$ $\vec{\mu} = \underset{\frac{q}{m}\vec{S}}{\vec{\mu}_s} + \underset{\frac{q}{2m}\vec{L}}{\vec{\mu}_L}$

$H'_Z = \frac{q}{2m}(\vec{L}+2\vec{S})\cdot\vec{B}_{ex}$

commutes w/ $L^2, S^2, J^2, \vec{J}$

good Qnum. (n, l, j, m_j)

~~E_Z^1~~ $E_Z^1 = \mu_B B_{ex} m_j g_J$

$E = E_{nj} + E_Z^1$

generally

$\begin{cases} E = [\underbrace{E_n + E'_{fs}}_{E_{nj}}] + E'_Z & \vec{B}_{ex} \ll \vec{B}_{int} \\ E = [E_n + E_Z'] + E'_{fs} & \vec{B}_{int} \gg \vec{B}_{ex} \end{cases}$

Hyperfine perturbed energy due to B field induced by proton

$\vec{\mu}_p = \frac{g_p e}{2m}\vec{S}_p$, $H'_{hf} = \vec{\mu}_e \cdot \vec{B}_p$ $E'_{hf} \sim \langle \vec{S}_p \cdot \vec{S}_e \rangle$

$\vec{S} = \vec{S}_p + \vec{S}_e$ so $\vec{S}_p\cdot\vec{S}_e = \frac{1}{2}(S^2 - S_p^2 - S_e^2)$

ex p, e w/ spin $\frac{1}{2}$ S_p^2, S_e^2 has $\frac{3}{4}\hbar^2$

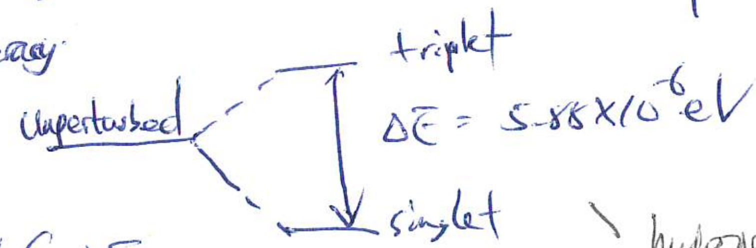
Now spin addition (adding $\frac{1}{2}$ of p & $\frac{1}{2}$ e):

triple : $S^2 = 1 \Rightarrow 2\hbar^2$

singlet : $S^2 = 0 \Rightarrow 0$

so $E'_{hf} \sim \langle \vec{S}_p \cdot \vec{S}_e \rangle = \begin{cases} \frac{1}{4} & \text{(triplet)} \\ -\frac{3}{4} & \text{(singlet)} \end{cases}$

This breaks spin degeneracy



\ hydrogen atom!

Emitted photon freq. $hf = \Delta E$

$f = 1420\ MHz$

wavelength $\lambda = \frac{c}{f} = 21\,cm$!

Lamb shift

energy difference between two energy levels: $^2S_{1/2}$ and $^2P_{1/2}$ of hydrogen atom

"not predicted by Dirac Eqn"

Stark effect

$E'_{stark} = q\vec{E}\cdot\vec{r}$

See H.W. for calculation / (4)

Variational Principle

For any normalized ψ, the ground state energy E_{gs} of a Hamiltonian system H has upper bound given by

$$\boxed{E_{gs} \le \langle \psi | H | \psi \rangle}$$

some trial wavefunc

Pf. The eig. func. of H ψ_n is completed s.t. $(H\psi_n = E_n \psi_n)$

$$\psi = \sum_n c_n \psi_n \quad ; 1 = \langle \psi | \psi \rangle = \sum_n |c_n|^2$$

so $\langle H \rangle = \sum_n E_n |c_n|^2 \ge \sum_n E_{gs} |c_n|^2 = E_{gs}$ since $E_{gs} \le E_n \; \forall n$.

Remark: ψ_n unknown, can't solve shrödinger eqn.

Summary of Variational Principle & Helium ground state

For arbitary $\hat{H}$, variational principle is a technique to use to estimate upper bound of ground state energy using a test wave function.

(1) $\langle \psi | H | \psi \rangle \ge E_{gs}$ trial wave func. ex $\psi = Ae^{-bx^2}$ Gaussian.

(2) $\langle \psi | \psi_{gs} \rangle = 0$ (orthogonal to ψ_{gs}) then $\langle \psi | H | \psi \rangle \ge E_{fs}$ — 1st excited state.

(3) i) 1st order Ptrb theory overestimate E_{gs}.

$$\langle \psi_0^0 | H^0 + H' | \psi_0^0 \rangle = E_{gs} + E' \ge E_{gs} \quad \text{assume } \langle H' \rangle > 0$$

by definition $\langle \psi_0^0 | H' | \psi_0^0 \rangle \ge E_{gs}$

ii) 2nd order Ptrb theory yields $E_0^2 < 0$ always.

(4) Helium ground state.

$$H = -\frac{\hbar^2}{2m} P_1^2 - \frac{\hbar^2}{2m} P_2^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_1} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_2} - \underbrace{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{V_{ee}}$$

V_{ee} — repulsion.

Add shielding factor Z,

$$H = T_1 + T_2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z - Z_0}{r_1} + \frac{Z - Z_0}{r_2}\right) - V_{ee}$$

$$\langle H \rangle = 2Z^2 E_1 + \frac{2e^2}{4\pi\varepsilon_0}(Z - Z_0)\left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle$$

$$\langle H \rangle = \left(2Z^2 - 4Z(Z - Z_0) - \frac{5}{4}Z\right)E_1$$

set $\frac{d\langle H \rangle}{dZ} = 0$ optimize to obtain $\langle H \rangle_{min} \ge E_{gs}$!

Variational Principle application
Helium Ground State

(1) $$H = \overbrace{-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)}^{\text{kinetic enegy of electrons}} - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}\right) + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}}_{V_{ee}\ \text{electron-electron replusion}}$$

ignored Vee yield exact solution — recall ground state of hydrogen $\frac{1}{\sqrt{\pi a^3}}e^{-r/a}$

$$\psi_0(\vec{r}_1,\vec{r}_2) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a}$$ and use this as trial solution to variation principle;

$$H\psi_0 = (8E_1 + V_{ee})\psi_0$$

(2) $$\langle H\rangle = 8E_1 + \langle V_{ee}\rangle \ ; \quad \langle V_{ee}\rangle = \frac{5}{4a}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = -\frac{5}{2}E_1$$

$\langle V_{ee}\rangle = -\frac{5}{2}E_1$

Can do better!

Remark. • ψ_0 treat electron as not interact at all.
• Add an effective nuclear charge Z due to partial shielding of electron cloud to nucleus.

Thus we try: $$\psi_1(\vec{r}_1,\vec{r}_2) = \frac{Z^3}{\pi a^3}e^{-Z(r_1+r_2)/a}$$

rewrite the Hamiltonian as: (Here $Z_0=2$ for 2 nucleus-protons)

Outmost shell w/ 2 electrons Z_0 nucleus-proton

(3) $$H = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z-Z_0}{r_1}+\frac{Z-Z_0}{r_2}+\frac{1}{|\vec{r}_1-\vec{r}_2|}\right)$$

average of $\frac{1}{r_1}$ & $\frac{1}{r_2}$

$$\langle H\rangle = 2Z^2E_1 + 2(Z-Z_0)\left(\frac{e^2}{4\pi\varepsilon_0}\right)\underbrace{\left\langle\frac{1}{r}\right\rangle}_{=\frac{Z}{a}\ \text{eq 6.55}} + \underbrace{\langle V_{ee}\rangle}_{-\frac{5Z}{4}E_1}$$

$-\frac{Z}{2}\frac{5}{2}E_1$

multiply by $\frac{Z}{2}$ due to shielding effect.

$$\langle V_{ee}\rangle \longrightarrow \frac{Z}{2}\langle V_{ee}\rangle \quad \text{ie multiply } a \text{ to } \frac{2}{Z}$$

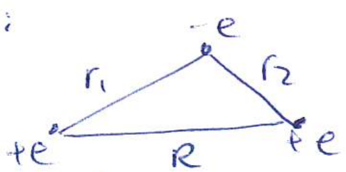
Thus, (4) $$\boxed{\langle H\rangle = \left[2Z^2 - 4Z(Z-Z_0) - \frac{5}{4}Z\right]E_1}$$

$$= \left[-2Z^2 + \left(4Z_0 - \frac{5}{4}\right)Z\right]E_1$$

(5) $$\frac{d\langle H\rangle}{dZ} = -4Z + 4Z_0 - \frac{5}{4} = 0 \Rightarrow \boxed{Z = Z_0 - \frac{5}{16}}$$

Substitute this extrema into $\langle H\rangle$ to obtain optimized $\langle H\rangle_{min} \geq E_{gs}$.

Hydrogen molecule:



$$H = \underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\text{Kinetic energy of electron}} - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$$

see H.W.

WKB (slow varying irregular $V(x)$)

Technique to time-independent Schrödinger equation solution,
In calculating
- bound state
- tunneling rate

Set up

Consider particle w/ energy E travel through potential well $V(x)$

At region s.t $V(x) =$ constant & $E > V$ (If $E<V$, we have $\psi(x) = Ae^{\pm kx}$ instead)

Wave function

$$\psi(x) = Ae^{\pm ikx} \qquad k = \frac{\sqrt{2m(E-V)}}{\hbar} \qquad \text{wavelength}: \boxed{\lambda = \frac{2\pi}{k}}$$

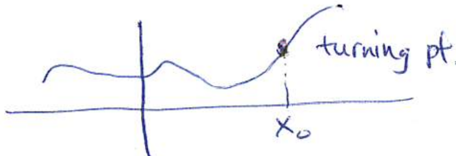
+ travel to right
− go to left

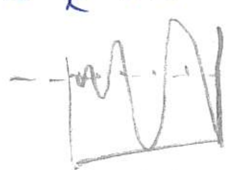
Assumption *

If $V(x)$ varies slowly w.r.t λ, over region w/ many full wavelength,
$V(x) \sim$ constant in this region.

Reasonable to state: $\psi \sim$ sinusoidal w/ slow variation of $\lambda(x)$ or k, and $A(x)$ amplitude.

Remark: Cautious: when $E \approx V$ "turning point" $\lambda = \frac{1}{k} \to \infty$ $V(x)|_{x_0}$ ~~changing rapidly~~ now hardly said to vary slowly.





$\lambda \sim \frac{1}{k}$ $k \sim (E-V)$

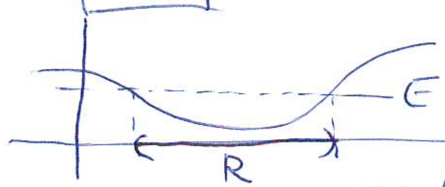
$A \sim \frac{1}{\sqrt{p}}$ $p \sim E-V$

Formalism Schrödinger Equation (SE)

$$H\psi = E\psi \longrightarrow \frac{d^2\psi}{dx^2} = -\frac{p^2}{\hbar^2}\psi \; ; \quad (1) \; \boxed{p(x) = \sqrt{2m[E-V(x)]}} \qquad \text{recalled } p = \hbar k$$

Classical Region

: For region R s.t $\boxed{E>V} \Rightarrow p$ real (particle confined to R)



W.l.o.g putdown $\boxed{\psi(x) = A(x)e^{+i\phi(x)}}$ (2) *

Apply to (SE), $\Rightarrow$

$$\boxed{\begin{aligned} A'' &= A\left[(\phi')^2 - \frac{p^2}{\hbar^2}\right] && (1) \\ (A^2\phi')' &= 0 && (2) \end{aligned}}$$

(3)

(2) $\Rightarrow$ $A = \frac{C}{\sqrt{\phi'}}$

WKB approximation: (From assumption *) A changes slowly $\Rightarrow A'' \sim 0$ negligible

(1) $\Rightarrow$ $\frac{d\phi}{dx} = \pm\frac{p}{\hbar}$

Summary – Classical region ($p>0$)

$$\boxed{\begin{aligned} \phi(x) &= \pm\frac{1}{\hbar}\int_{x_0}^{x} p(x')\,dx' \\ \text{and} \quad \psi(x) &= \frac{C}{\sqrt{p(x)}}\, e^{\pm\frac{i}{\hbar}\int_{x_0}^{x} p(x')\,dx'} \end{aligned}} \quad (4)$$

upper & lower limit for $\int$.

Note: $\boxed{|\psi(x)|^2 \simeq \frac{|C|^2}{p(x)}}$

implied probability in finding particle at $x \propto \frac{1}{v(x)}$ velocity.

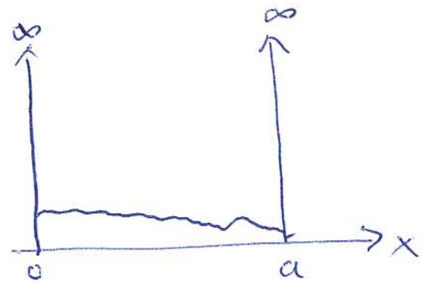
make use of

$$A(x) = \frac{C}{\sqrt{\phi'}} = \frac{C}{\sqrt{p}}$$

$$p = \sqrt{2m(E-V(x))}$$

As $x \nearrow$ $p \searrow$ $A \nearrow$

ex $E>V$



$$\psi(x) \cong \frac{1}{\sqrt{p(x)}}\left[C_+ e^{i\phi(x)} + C_- e^{-i\phi(x)}\right]$$

$$\mapsto \frac{1}{\sqrt{p(x)}}\left[C_1 \sin\phi(x) + C_2\cos\phi(x)\right]$$

& $\phi(x) = \frac{1}{\hbar}\int_0^x p(x')\,dx'$

B.C on $\psi(x)$ $\Rightarrow$ $C_2 = 0$ and $\phi(a) = n\pi$ $(n \in \mathbb{N})$

then $n\pi\hbar = \int_0^a p(x)\,dx$

Remark: For flat bottom $V=0 \Rightarrow p(x) = \sqrt{2mE}$, recovered: $E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$!

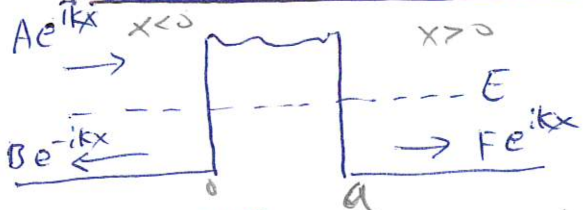
WKB

Tunneling $E<V$ (non-classical region) $\Rightarrow$ $p(x)$ imaginary.

Now,
$$\boxed{\psi(x) \simeq \frac{C}{\sqrt{|p|}} e^{\pm\frac{1}{\hbar}\int |p(x)|\,dx}} \quad (1)$$
inside

note ~~$\psi(x) = A(x)e^{\pm\phi(x)}$~~

$\leftarrow$ $\psi(x) = A(x)e^{\pm\phi(x)}$ apply to SE.



$x<0$ $\psi(x) = Ae^{ikx} + Be^{-ikx}$

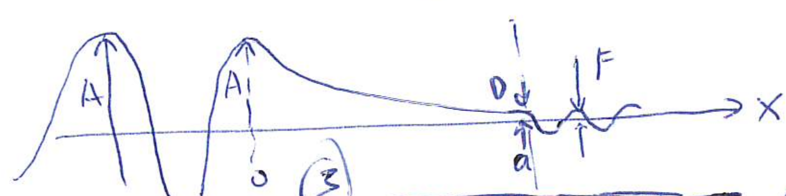
$x>a$ $\psi(x) = Fe^{ikx}$

$$\boxed{T = \left|\frac{F}{A}\right|^2}$$

in tunneling region:
$$\psi(x) = \frac{C}{\sqrt{|p(x)|}} e^{\frac{1}{\hbar}\int_0^x |p(x')|\,dx'} + \frac{D}{\sqrt{|p|}} e^{-\frac{1}{\hbar}\int_0^x |p(x)|\,dx'} \quad (2)$$

For wide & high barriers $\Rightarrow$ $C \ll 1$ ~~samely $B \ll 1$~~ $\Rightarrow$ $F \sim D$

Thus, ~~$A+B$~~



(3)

And $\left|\frac{F}{A}\right|^2 \simeq \left|\frac{D}{A}\right|^2 \Rightarrow \boxed{T \simeq e^{-2\gamma}}$ $\boxed{\gamma = \frac{1}{\hbar}\int_0^a |p(x)|\,dx}$

~~life~~ life time: $\boxed{\tau = \frac{2r_1}{v} e^{2\gamma}}$ (4)

well size

velocity from kinetic energy

$\rightarrow$ $\tau = \frac{2L}{v_0} e^{2\gamma}$

Summary of Perturbation Theory

- time independent

T1. non dgen $\mathcal{O}(1)$ $E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$; $\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$

$\mathcal{O}(2)$ $E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$

dgen $H' \rightarrow$ matrix representation $W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$
reduced to eig. values problem.

T2. <u>variation principle</u>: estimation of ground state of sys.

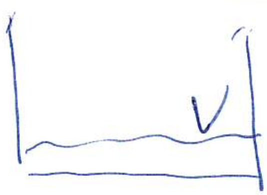
$$\langle \psi | H | \psi \rangle \geq E_{gs}$$

trial wave func ie Ae^{-bx^2}

ex Helium ground state (Helium like atom).

$$\langle H \rangle = \left(2Z - 4Z(Z - Z_0) - \frac{5}{4} Z \right) E_1 \quad E_1 = -13.6\,eV$$

- timeindependent <u>WKB</u> technique



V varies slowly w.r.t wavelength except at classical turning ie $E \sim V$

S.E : • $p = \sqrt{2m(E - V(x))}$

• $A = \frac{C}{\sqrt{\phi'}} = \frac{C}{\sqrt{p}}$ ✓ explains how amplitude behaves!

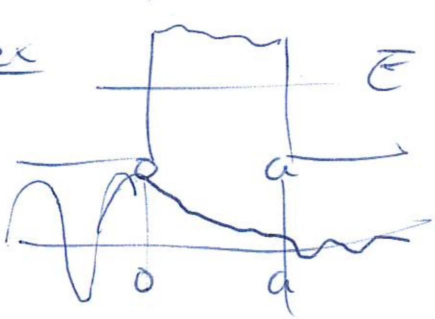
For $E > V(x) \Rightarrow \psi(x) = A(x) e^{i\phi(x)}$

• $\frac{d\phi}{dx} = \pm \frac{p}{\hbar}$ $\phi(x) = \pm \frac{1}{\hbar} \int_0^x p(x) dx$

For $E < V(x)$

$$\psi(x) = A(x) e^{\pm \phi(x)}$$

ex



$$\psi(x) = \cancel{\frac{C}{\sqrt{|p|}} e} \frac{C}{\sqrt{|p|}} e^{\pm \frac{1}{\hbar} \int |p(x)| dx}$$

Tunneling probability coefficient $T \simeq e^{-2\gamma}$ $\gamma = \frac{1}{\hbar} \int_0^a |p(x)| dx$

life time $\tau = \frac{2r_1}{v} e^{2\gamma}$ r_1 well size v velocity.

Quantum States with Quantum state in K-space

Particle in k-space

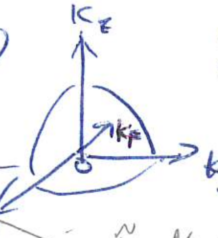
From 3D infinite well particle in the box

Volume in kspace per particle state: $\frac{\pi^3}{\gamma_s V}$ (*) $\quad \gamma_s = \begin{cases} 2 & \text{fermion} \\ 1 & \text{boson.} \end{cases}$

ex electron

N atom w/ q electrons. occupied volume.

$$Nq\frac{\pi^3}{2V} \overset{\text{equiv}}{=} \frac{1}{8}\frac{4}{3}\pi k_F^3 \Rightarrow \boxed{k_F = (3\rho\pi^2)^{1/3}}$$



k_F seperated occupied & unoccupied states.

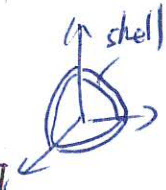
This gives Fermi energy ϵ_F (energy of free electrons)

$$(*) \boxed{\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2\left(3\frac{Nq}{V}\pi^2\right)^{2/3}}{2m}}$$

$\tilde{N} = Nq = \frac{\gamma_s V}{6\pi^2}k^3$

$\downarrow$

$\frac{d\tilde{N}}{dk}$



E_{tot} & N_{tot} (tot # states)

$dN = g(k)dk$

$\mapsto g(\epsilon)d\epsilon$

$g(k)$ density of state

3D infinite well $dk\, g(k) = \frac{\frac{4}{8}\pi k^2 dk}{\pi^3}$

equally likely

N_{tot} or simply $\boxed{dN = \frac{\frac{1}{8}4\pi k^2 dk}{\frac{\pi^3}{\gamma_s V}}} \longrightarrow \boxed{dN = \gamma_s\frac{V}{2\pi^2}k^2 dk}$ on shell.

E_{tot} " " $d\epsilon = \epsilon(k)dN$ $\quad \boxed{d\epsilon = \underbrace{\frac{\hbar^2 k^2}{2m}}_{\text{energy per particle state}} dN(k)} \longrightarrow \boxed{d\epsilon = \gamma_s\frac{V}{2\pi^2}\frac{\hbar^2}{2m}k^4 dk}$

generalized to $\epsilon(k)$

Integrate $\boxed{E_{tot} \sim \int_0^{k_F} k^4 dk} \to \gamma_s\frac{V}{2\pi^2}\frac{\hbar^2}{2m}\frac{k_F^5}{5} \xrightarrow{\hbar} \boxed{\epsilon_{tot} = \frac{\hbar^2(3\pi^2 Nq)^{5/3}}{10\pi^2 m}V^{-2/3}}$

Using this we can probe the degeneracy pressure

note $dW = PdV$ ie ~~$P = dE$~~ $\boxed{P = -\frac{d\epsilon}{dV}} \longrightarrow \boxed{P = \frac{2}{3}\frac{\epsilon_{tot}}{V}}$

$d\epsilon = -dW$

Quantum Statistic Distribution

Maxwell Boltzmann $\quad n(\epsilon) = e^{-(\epsilon-\mu(T))/k_B T} \quad \frac{1}{e^{(\epsilon-\mu(T))/kT}}$

logic

"case $T \to 0$"

~~As $T \to 0$~~ $\mu = \mu(T)$

As $T \to 0$ let $\mu(0)$ fixed then analysis $\epsilon < \mu(0)$, $\epsilon > \mu(0)$

Fermi-Dirac $+$
Bose-Einstein $-$ $\quad n(\epsilon) = \frac{1}{e^{(\epsilon-\mu(T))/k_B T} \pm 1}$

Remark. $n(\epsilon) \to n(k)$.

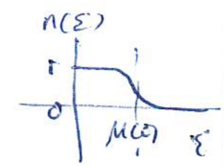
ie $\epsilon = \frac{\hbar^2 k^2}{2m}$

$\epsilon \mapsto \epsilon(k)$

Probe Fermi-Dirac: Take $T \to 0$ $\quad$ Fixed $\mu(0)$, case for ϵ vs μ For limit $T \to 0$ ie vary ϵ

$\text{arg} = \frac{\epsilon - \mu(T)}{k_B T}$

$$e^{(\epsilon-\mu(T))/k_B T} = \begin{cases} 0 & \epsilon < \mu(0), \text{arg} \to -\infty \\ \infty & \epsilon > \mu(0), \text{arg} \to +\infty \end{cases} \longrightarrow n(\epsilon) = \begin{cases} 1 \\ 0 \end{cases}$$



in Fermi-Dirac $\epsilon_F \equiv \mu(0)$.

Quantum Stat. Estimation of N & E using distribution.

Recall $dN = \frac{V}{2\pi^2} k^2 dk \xrightarrow{\text{Distribution } n(k)} N = \int_0^{k_F} \frac{V}{2\pi^2} n(k) k^2 dk.$

$\rightarrow n(k)\, dN(k)$ (are not equally likely)

$dE = \frac{V}{2\pi^2}\frac{\hbar^2}{2m} k^4 dk \longrightarrow E = \int_0^{k_F} \frac{V}{2\pi^2}\frac{\hbar^2}{2m} k^4 dk$

$dE \rightarrow E(k) n(k) dN(k)$

note ~~nce~~ only in cond? $\varepsilon = \frac{\hbar^2 k^2}{2m} \rightarrow k = \frac{\sqrt{2m\varepsilon}}{\hbar}$ and $d\varepsilon = \frac{\hbar^2 k}{m} dk.$ $g(k) = \frac{d\Gamma(k)}{dk}$

Remark: This indicates that $\int$ can be taken to $d\varepsilon$.

Plank's formula — energy density

$\cancel{\rho(\omega) d\omega = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)} d\omega}$

$$\boxed{\rho(\omega)\, d\omega = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)} d\omega}$$

Remarks: photon is boson. use Bose-Einstein

photo highly rel. $-m^2 = p^\mu p_\mu = -\frac{\varepsilon^2}{c^2} + p^2$ $\Rightarrow \varepsilon = pc$, $\varepsilon = \hbar k c = \hbar\omega$

Another method

$\Gamma(k) = \frac{V}{3\pi^2} k^3$

$\Gamma(\omega) = \frac{V}{3\pi^2}\frac{\omega^3}{c^3}$.

(photon)

note $dN = \frac{V}{(2)\pi^2} k^2 dk$; $\boxed{\varepsilon = \hbar\omega \quad \omega = kc}$ $\because$ photon

why 2 vanished? b/c Boson!

$g(\omega) d\omega = \frac{d\Gamma}{d\omega} d\omega = \frac{V\omega^2}{\pi^2 c^3} d\omega$

$dE = \varepsilon dN = \frac{V}{\pi^2} \hbar\omega k^2 dk \xrightarrow{\text{change of variable}} dE = \frac{V}{\pi^2}\frac{\hbar\omega^3}{c^3} d\omega$

$dE = E(\omega) g(\omega) d\omega = \frac{V}{\pi^2}\frac{\hbar\omega^3}{c^3} d\omega$

But photon is boson, need Bose-Einstein Distribution.

$$dE = \frac{V}{\pi^2}\frac{\hbar\omega^3}{c^3}\frac{1}{e^{\hbar\omega/k_B T} - 1} d\omega$$

$d\omega\, \rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} d\omega$

Define $d\omega\, \rho(\omega) = \frac{dE}{V} = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)} d\omega$

BE $\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$

Planck distribution

using $k = \frac{2\pi}{\lambda} = \frac{\omega}{c} \rightarrow \omega = \frac{2\pi c}{\lambda}$ & $d\omega = -\frac{2\pi c}{\lambda^2} d\lambda$

$\frac{\omega}{c} = \frac{2\pi}{\lambda}$ $|d\omega| = \frac{2\pi c}{\lambda^2} d\lambda$

we get $\bar{\rho}(\lambda) = \frac{16\pi^2 \hbar c}{\lambda^5}\frac{1}{\exp\left(\frac{2\pi\hbar c}{k_B T \lambda}\right) - 1}$ } planck distribution

$\rho(\lambda) = \frac{16\pi^2\hbar c}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$

maximum $\rightarrow$ $$\boxed{\lambda_{max} = \frac{2.90 \times 10^{-3}\, mK}{T}}$$

Wien-displacement law.

or $\Gamma(k) \mapsto \Gamma(\varepsilon) = \frac{V}{3\pi^2}\frac{\varepsilon^3}{\hbar^3 c^3}$

$g(\varepsilon) d\varepsilon = \frac{V}{\pi^2}\frac{\varepsilon^2}{\hbar^3 c^3} d\varepsilon$

$g(\omega) d\omega = \omega g(\varepsilon) d\varepsilon$
$= \frac{\omega V}{\pi^2 \hbar^3}\frac{\hbar^2\omega^2}{c^3}\hbar\, d\omega$

$\frac{g(\omega)}{V} d\omega = \frac{\hbar\omega^3}{\pi^2 c^3} d\omega$

$\hookrightarrow$ B-E

$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$

$$\rho(\lambda, T) \sim \frac{1}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$