

QUANTUM MECHANICS

(1st quantisation, classical)

Scalar (or sometimes vector)

$\Psi(r, t)$

$|\psi\rangle$ Dirac notation

*) Fundamentals * State of a particle is determined by its wavefunction

* Probability of finding particle in $d^3r = |\psi|^2 d^3r$

* Flux (# particles crossing unit area/unit time) = $-\frac{i\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*)$

* Classical observables \leftrightarrow Hermitean operators in QM.

Position $\rightarrow \hat{x} = x$ Momentum $\rightarrow \hat{p} = -i\hbar \nabla$

Energy $\rightarrow \hat{E} = i\hbar \frac{\partial}{\partial t}$ Angular momentum $\rightarrow \hat{L}_z = i\hbar (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$

* Most operators don't commute

c.f. conjugate variables classically.

e.g. $[x, \hat{p}_x] = i\hbar$

(z component)

classical: $L = r \times p$

$\equiv i\hbar \frac{\partial}{\partial \phi}$ \leftarrow Cartesian spherical coords.

* Possible outcomes of an observation are the (real) Eigenvalues of the operator - correspond to specific eigenstates of the operator. $\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$

* If two operators commute \rightarrow can have common eigenstates \Rightarrow measured simultaneously \rightarrow uncertainty principle for operators \hat{A}, \hat{B}

$$\Delta \hat{A} \Delta \hat{B} \geq \frac{1}{2} |\langle i[\hat{A}, \hat{B}] \rangle| \quad \Delta \hat{A} = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2$$

* Any state ψ can be expressed as a superposition of all the eigenstates of any operator i.e. if $\hat{A}|\phi_n\rangle = a_n|\phi_n\rangle$ $\psi = \sum_n b_n|\phi_n\rangle$.

* If a system is described by state ψ , measure using operator \hat{A}

\rightarrow probability of measuring eigenstate a_n is $|b_n|^2$ or

$|\langle \phi_n | \psi \rangle|^2$. ONLY IF eigenstates ϕ_n are orthonormal. $\int \phi_i^* \phi_j dt \equiv \langle \phi_i | \phi_j \rangle = \delta_{ij}$

\rightarrow After measurement system adopts state ϕ_n if a_n is measured.

* Find sets of wavefunctions by $\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$ equation. If $\{a_n\}$ are energy eigenvalues $\{|\psi_n\rangle\}$ eigenstates are found via Schrodinger Equation. $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

E = total energy. Hamiltonian \hat{H} is formed from classical statement of energy.

classical: $E = T + V$ QM: $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}$. Now ψ_n is not usually time independent, so using Hermitean operators above:

Kinetic \uparrow Potential \uparrow

\rightarrow Time dependent S.E.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t}$$

So analytical/numerical/approximate solution for ψ possible if V is known.

* usually eigenstates ψ of energy (well of \hat{H}) are time separable. i.e. $\psi(r, t) = \phi(r)\tau(t)$

\Rightarrow can utilise fact that energy eigenstates have well defined energy eigenvalues E_n to perm time independent S.E. $\hat{H}|\phi(r)\rangle = E_n|\phi(r)\rangle$ (cancel $\tau(t)$). $\Rightarrow \psi(r, t)$ must be separable in time.

cancelling $\phi(r)$ we use time dependence of $E_n|\psi_n\rangle$ to find $\tau(t)$.

$i\hbar \frac{\partial \tau}{\partial t} = E_n \tau \Rightarrow \tau_n(t) = e^{-iE_n t/\hbar}$ so $\psi_n(r, t) = \phi_n(r) \exp(-iE_n t/\hbar)$. \therefore only need to solve

time independent S.E. to find $E_n, \phi_n(r)$ to know $\psi_n(r, t)$. Note $|\psi(r, t)|^2 = |\phi(r)|^2$ "stationary states"

* observables have following time dependence $\frac{d}{dt} \langle \hat{A} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle$

For any stationary state $\langle \hat{A} \rangle = \text{const}$; \Rightarrow if $[\hat{H}, \hat{A}] = 0 \Rightarrow \langle \hat{A} \rangle$ is a constant of the system, conserved.

* Symmetry of $\hat{H} \Rightarrow$ conservation laws.

Invariance under \leftrightarrow conservation of

SPATIAL TRANSLATIONS \leftrightarrow MOMENTUM

TEMPORAL " " \leftrightarrow ENERGY

ROTATIONS \leftrightarrow ANGULAR MOMENTUM

PARITY ($r \rightarrow -r$) \leftrightarrow PARITY

* Note can use superposition principle and time dependence above to calculate

time dependence of any state ψ . (May not be an eigenstate of \hat{H} etc...)

2) Angular momentum and spin * S.E. for Spherically symmetric potential $V(r)$
 → Solutions of form $\psi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$. i.e., states characterised by integer
QUANTUM NUMBERS n, l, m . Total energy only depends on n . → For hydrogen atom
 $V(r) \propto \frac{1}{r}$, $E_n \propto -\frac{1}{n^2}$. Now GIVEN n , permitted $l = 0 \dots n-1$ → GIVEN l , permitted
 $m = -l, -l+1, \dots, l$ ← comes from solution of S.E.
 $l \in \mathbb{Z}^+ \neq 0$ \uparrow $2l+1$ possible values

* Note form of $V(r)$ only determines $R_{nl}(r)$ NOT $Y_{lm}(\theta, \phi)$
 * Important properties of angular momentum in 3D can be derived from commutation relationships.
 $[\hat{L}_x, \hat{L}_y] = i\hbar \epsilon_{xyz} \hat{L}_z$ * All components of \hat{L} commute with \hat{L}^2
 $\hat{L}^2 \equiv \hat{L} \cdot \hat{L} \Rightarrow$ can measure \hat{L}^2 and at most one component of \hat{L} . → convention \hat{L}_z .

* From S.E → eigenstates of \hat{L}_z, \hat{L}^2 are: $\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$ $\hat{L}_z Y_{lm} = m\hbar Y_{lm}$
 * Ladder operators transperm between eigenstates of \hat{L}_z $\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$ ← Not observables
 If $\hat{L}_z |\phi_m\rangle = m\hbar |\phi_m\rangle \rightarrow$ can show using commutation relations $\hat{L}_z (\hat{L}_{\pm} |\phi_m\rangle) = (m \pm 1)\hbar (\hat{L}_{\pm} |\phi_m\rangle)$
 $\Rightarrow \hat{L}_{\pm} |\phi_m\rangle = \hbar [l(l+1) - m(m \pm 1)]^{1/2} |\phi_{m \pm 1}\rangle$ (correctly normalised).

* Dirac equation (S.E. + relativistic considerations) predicts 'intrinsic angular momentum' or SPIN in addition to 'orbital' angular momentum L . Many particles have $\frac{1}{2}$ integer spin eg, electron $s = \frac{1}{2}$. → Modify wavefunction for electron in $V(r)$ potential.
 $\psi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \chi_{sm_s}$ in non relativistic limit. (i.e. "patch" to S.E.)

* s is fixed by particle type but find χ_{sm_s}, m_s in some way for l .
 i.e. $[\hat{S}_x, \hat{S}_y] = i\hbar \epsilon_{xyz} \hat{S}_z$; $\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$; $\hat{S}_{\pm} |\chi_{sm_s}\rangle = \hbar [s(s+1) - m_s(m_s \pm 1)]^{1/2} |\chi_{sm_s \pm 1}\rangle$
 $\hat{S}^2 |\chi_{sm_s}\rangle = \hbar^2 s(s+1) |\chi_{sm_s}\rangle$; $\hat{S}_z |\chi_{sm_s}\rangle = \hbar m_s |\chi_{sm_s}\rangle$; GIVEN $s, m_s = -s, -s+1, \dots, s$
 \uparrow $2s+1$ values

* Spin algebra has handy isomorphism with Pauli matrices. (In fact matrix formulation of 3D is sometimes very useful). Only for $s = \frac{1}{2}$ though...
 → If $s = \frac{1}{2}$; $\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ → Eigenstates are $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$
 $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$
 $\hat{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ $\hat{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

3) Combination of angular momentum ← Arises in many physical problems
 ← Not trivial because \hat{L}, \hat{S} are vectors with 3D restrictions on their orientation.

* Define total angular momentum operator
 $\hat{\underline{S}}$. i.e. for electron in H atom $\hat{\underline{S}} = \hat{\underline{L}} + \hat{\underline{S}}$. Quantum numbers j, m_j $m_j = -j, -j+1, \dots, j$
 \uparrow $2j+1$ values
 Properties: $[\hat{S}_x, \hat{S}_y] = i\hbar \epsilon_{xyz} \hat{S}_z$; $\hat{S}^2 |\phi_{jm_j}\rangle = j(j+1)\hbar^2 |\phi_{jm_j}\rangle$; $\hat{S}_z |\phi_{jm_j}\rangle = \hbar m_j |\phi_{jm_j}\rangle$
 $\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$ ($= \hat{L}_{\pm} + \hat{S}_{\pm}$ e.g.) ; $\hat{S}_{\pm} |\phi_{jm_j}\rangle = \hbar [j(j+1) - m_j(m_j \pm 1)]^{1/2} |\phi_{jm_j \pm 1}\rangle$ as for \hat{L}, \hat{S}

* Note $j = l+s, l+s-1, \dots, |l-s|$ for $\hat{\underline{S}} = \hat{\underline{L}} + \hat{\underline{S}}$
 * $\hat{L}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z$ mutually commute - so do $\hat{S}^2, \hat{L}^2, \hat{S}_z, \hat{L}_z$ BUT NOT TOGETHER. can't characterise angular momentum eigenstates by $|\phi_{jm_j}\rangle$ or combinations of $|Y_{lm}\rangle, |\chi_{sm_s}\rangle$
 → l, s, j coupling see later!

* For $\hat{\underline{S}} = \hat{\underline{L}} + \hat{\underline{S}}$ combinations use CLEBSCH-GORDAN algorithm/method to find wavefunctions
 (i) start with largest $m_j = l+s$, $j = l+s$ state (ii) Apply \hat{S}_- to find other $j = l+s$ states
 (iii) use orthogonality to find the state $j = l+s-1$ $m_j = l+s-1$ (iv) apply \hat{S}_- on this state to find other $j = l+s-1$ v) repeat until all states are found.

4) Identical particles * Symmetry depends on spin of particle → Integer spin - 'BOSONS'
 w/ symmetric under particle interchange → $\frac{1}{2}$ Integer spin - 'FERMIONS' w/ anti-sym " " "
 BOSONS can have same quantum state FERMIONS can't (w/ $\rightarrow 0$) PAULI EXCLUSION PRINCIPLE // QM (2)

Approximation methods in QM - S.E too complicated or analytical solution in most cases.

Variational method (i) Need to solve $\hat{H}\psi_n = E_n\psi_n$ $E_0 \leq E_1 \leq E_2 \dots$ (ii) consider arbitrary function ϕ . (iii) Expand in terms of ψ_n $\phi = \sum c_n \psi_n$. (iv) consider expectation value of \hat{H} in ϕ : $\langle \phi | \hat{H} | \phi \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \hat{H} | \psi_n \rangle = \sum_m \sum_n c_m^* c_n E_n \delta_{mn}$. Define $E\psi_n$ to be orthogonal s.t. $\langle \psi_m | \psi_n \rangle = \delta_{mn}$. $\langle \phi | \phi \rangle = \sum_n |c_n|^2 E_n$. (v) Also consider $\langle \phi | \phi \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2$. Now clearly $\sum_n |c_n|^2 E_n \geq \sum_n |c_n|^2 E_0$. From (ii). Now $\sum_n |c_n|^2 E_0 = E_0 \langle \phi | \phi \rangle$ so since $\sum_n |c_n|^2 E_n = \langle \phi | \hat{H} | \phi \rangle$

$\Rightarrow \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_0$ VARIATIONAL THEOREM so use TRIAL function ϕ to guess upper bound to E_0 .

Raleigh-Ritz method (i) Guess ϕ from available insight/prior knowledge. Write in terms of adjustable parameters $\alpha_1, \alpha_2, \alpha_3 \dots$ i.e. $\phi(\underline{r}, \alpha_1, \alpha_2, \dots)$. (ii) minimise $\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$ w.r.t. $\alpha_1, \alpha_2, \dots$ i.e. solve $\nabla(\dots) = 0$ using calculus phrase space of $\alpha_1, \alpha_2, \alpha_3 \dots$ substitute these values into (...) to compute 'best guess' to E_0 .

once ϕ_0 is found ^{Excited states} which minimises $\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \rightarrow$ construct orthogonal state ϕ^1 i.e. of form $\phi^1 = \phi - \langle \phi_0 | \phi \rangle \phi_0 \rightarrow$ re apply Raleigh Ritz. Note this calculation will not guarantee to $\geq E_1$ (only $\geq E_0$ guess). only works for certain if $c_0 = 0$ from symmetry, ϕ_0 is known to be exact.

Time Independent, non-degenerate, perturbation theory - write $\hat{H} = \hat{H}_0 + \lambda \hat{H}'$ (λ is a bookkeeping device - usually set = 1. $\hat{H}_0 =$ solvable Hamiltonian, $\hat{H}' =$ small perturbation (e.g. effect of small E field). known solution to $\hat{H}_0 \psi_n = E_n^0 \psi_n$. look for ϕ_n s.t. $(\hat{H}_0 + \lambda \hat{H}') \phi_n = E_n \phi_n$ (1) Expand ϕ_n, E_n in powers of λ : $\phi_n = A(\psi_n + \lambda \sum_{j \neq n} c_{jn}^{(1)} \psi_j + \lambda^2 \sum_{j \neq n} c_{jn}^{(2)} \psi_j + O(\lambda^3))$
 $E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + O(\lambda^3)$. subst. into (1):

$O(\lambda)$ (1st order) $\Rightarrow \hat{H}' \psi_n = \sum_{j \neq n} c_{jn}^{(1)} (E_n^0 - E_j^0) \psi_j + E_n^{(1)} \psi_n$ $\langle \psi_k | \Rightarrow E_n^{(1)} = \langle \psi_k | \hat{H}' | \psi_n \rangle$
 $\langle \psi_k | (k \neq n) \Rightarrow \langle \psi_k | \hat{H}' | \psi_n \rangle = c_{kn}^{(1)} (E_n^0 - E_k^0) \Rightarrow c_{kn}^{(1)} = \frac{\langle \psi_k | \hat{H}' | \psi_n \rangle}{E_n^0 - E_k^0}$
 Note non-degenerate: $E_n^0 \neq E_k^0$.

For $O(\lambda^2)$ terms use above technique to find: $E_n^{(2)} = \sum_{j \neq n} \frac{|\langle \psi_n | \hat{H}' | \psi_j \rangle|^2}{E_n^0 - E_j^0}$ (for example.)

Time independent, degenerate perturbation theory Suppose we have a set of n states which are degenerate w.r.t \hat{H}_0 , i.e. $\hat{H}_0 \psi_i = E_0 \psi_i$ $i = 1, 2, \dots, n$. Any linear combination also has energy E_0 . i.e. state $\chi_k = \sum_{i=1}^n d_{ik} \psi_i$ (define coefficient matrix d). where $\langle \chi_i | \hat{H}' | \chi_j \rangle = d_{ij}$ so $\langle \chi_i | \hat{H}' | \chi_j \rangle \neq 0$ ($= 0$ instead) \rightarrow need to DIAGONALISE \hat{H}' matrix. Procedure: $(\hat{H}_0 + \hat{H}') \chi_k = (E_0 + E_k^{(1)}) \chi_k$ from 1st order perturbation ($E_k^{(1)} = \langle \chi_k | \hat{H}' | \chi_k \rangle$). $\Rightarrow \langle \psi_j | \sum_i d_{ik} \langle \psi_j | \hat{H}' | \psi_i \rangle = E_k^{(1)} d_{jk}$
 $\Rightarrow \sum_i d_{ik} H'_{ji} = d_{jk} E_k^{(1)}$ MATRIX EIGENVALUE PROBLEM ($\underline{H}' d = E_k^{(1)} d$) \rightarrow solve $|\underline{H}' - E_k^{(1)} \underline{I}| = 0$ to find 1st order shift. Apply same tech technique for higher order terms. EXAMPLE - STARK EFFECT. Note degenerate subset of parity chop up - i.e. H atom (parity (-1)^l).

6) Transitions - Bound States (solutions to $\hat{H}_0 \psi = E \psi$) have time dependence $e^{-iEt/\hbar}$

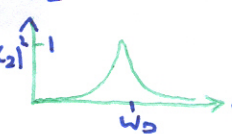
$\Rightarrow |\psi|^2$ time independent. Apply time dependent perturbation $\hat{H}'(t)$ - in general likely to get transitions between states. Examples: (1) Atomic/molecular transitions (2) Scattering (Δk)

* 2 state system ψ_1, ψ_2 $\hat{H}_0 \psi_1 = E_1 \psi_1$; $\hat{H}_0 \psi_2 = E_2 \psi_2$ let $E_1 = \hbar \omega_1$, $E_2 = \hbar \omega_2$; Apply perturbation $\hat{H}' \cos \omega t$. Write $\psi(t) = c_1(t) e^{-i\omega_1 t} \psi_1 + c_2(t) e^{-i\omega_2 t} \psi_2$. Substitute into $\hat{H} \psi = i\hbar \frac{\partial \psi}{\partial t}$ where $\hat{H} = \hat{H}_0 + \hat{H}' \cos \omega t$. Now if $\langle \psi_1 | \hat{H}' | \psi_1 \rangle = \langle \psi_2 | \hat{H}' | \psi_2 \rangle = 0$ and $\langle \psi_1 | \hat{H}' | \psi_2 \rangle = \hbar \omega'$

$\langle \psi_1 | \Rightarrow i \dot{c}_1 e^{-i\omega_1 t} = \omega' c_2 \cos \omega t e^{-i\omega_2 t}$; $\langle \psi_2 | \Rightarrow i \dot{c}_2 e^{-i\omega_2 t} = \omega' c_1 \cos \omega t e^{-i\omega_1 t}$

Now write $\omega_0 \equiv \omega_2 - \omega_1$ (Transition frequency), expand $\cos \Rightarrow (\cos \omega t = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t}))$
Neglect $e^{\pm i(\omega + \omega_0)t}$ terms (just oscillations) i.e. save near resonance $(\omega + \omega_0) \gg |\omega - \omega_0|$

Eliminating $c_1 \Rightarrow \ddot{c}_2 + i(\omega - \omega_0)\dot{c}_2 + \frac{1}{4}\omega'^2 c_2 = 0$. $\{ \dot{c}_2 = -\frac{i}{2}\omega' c_2 e^{i(\omega - \omega_0)t} \}$. DAMPED SIM (1st).

$\Rightarrow |c_2|^2 = \frac{\omega'^2}{\omega'^2 + (\omega - \omega_0)^2} \sin^2 \omega' t / 2$, $\omega_R^2 = (\omega_0 - \omega)^2 + \omega'^2$. 

BASIS OF MAGNETIC RESONANCE.

* Time-Dependent Perturbation theory (general case of above!)

- Time indep. unperturbed \hat{H}_0 $\hat{H}_0 \psi_n = E_n \psi_n$ / set $E_n = \hbar \omega_n$ \rightarrow Apply perturbation $\hat{H}'(t)$ for $t > 0 \rightarrow$ write $\psi(t) = \sum c_j(t) \psi_j e^{-i\omega_j t}$

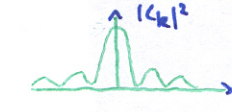
\rightarrow initial conditions $t=0, c_0=1, c_j=0$ for $j \neq 0 \rightarrow$ sub. into $\hat{H} \psi = i\hbar \frac{\partial \psi}{\partial t}$ ($\hat{H} = \hat{H}_0 + \hat{H}'(t)$).

$\rightarrow \langle \psi_k |$ and use matrix notation i.e. $\langle \psi_k | \hat{H}' | \psi_j \rangle \equiv H'_{kj} \Rightarrow \dot{c}_k = \frac{1}{i\hbar} \sum_j c_j e^{i(\omega_k - \omega_j)t} H'_{kj}(t)$

DIFFICULT TO SOLVE! Now if $\hat{H}'(t)$ is WEAK $\Rightarrow c_0 \approx 1; |c_k| \ll 1 \forall k \neq 0$ (High prob. initial state).

\rightarrow most likely transition from c_0 state. $\Rightarrow \dot{c}_k \approx \frac{1}{i\hbar} e^{i(\omega_k - \omega_0)t} H'_{k0}(t)$ $k \neq 0$

\rightarrow let $\hat{H}'(t) = \hat{H}'(t) e^{-i\omega t}$, $t > 0 \Rightarrow c_k(t) = \frac{H'_{k0}}{i\hbar} \int_0^t e^{i(\omega_k - \omega_0 - \omega)t'} dt'$. write $\delta\omega = \omega_k - \omega_0 - \omega$

$\Rightarrow |c_k(t)|^2 = 4 |H'_{k0}|^2 \frac{\sin^2 \delta\omega t / 2}{\delta\omega^2}$  Now for probability of transition to a group of closely spaced states

\rightarrow Integrate over states. Introduce "density of states" $g(E_k)$, $E_k =$ final state energy

states $E_k \rightarrow E_k + dE_k = g(E_k) dE_k = \hbar g(E_k) d\omega = \hbar g(E_k) d(\delta\omega)$

\rightarrow Assume $g(E_k)$ invariant across sharp $\text{sinc}^2(\delta\omega t / 2)$ peak and $|H'_{k0}|$ same for all states near $\omega_k \Rightarrow$ Transition probability = $4 |H'_{k0}|^2 \int \left(\frac{\sin \delta\omega t / 2}{\delta\omega} \right)^2 g(E_k) \hbar d(\delta\omega)$, let $x = \delta\omega t / 2$

$\Rightarrow \dots = 4 |H'_{k0}|^2 \frac{\hbar g(E_k) t}{2} \int_{-\infty}^{\infty} \left(\frac{\sin x}{x} \right)^2 dx$. Now $\Rightarrow \dots = \text{const. } t$. \therefore Transition rate $\frac{d}{dt}$

$\equiv \Gamma_{0 \rightarrow k} \Rightarrow \Gamma_{0 \rightarrow k} = \frac{2\pi}{\hbar} |H'_{k0}|^2 g(E_k)$ FERMI'S GOLDEN RULE

* Radiative transitions in atoms and molecules - Apply above to transitions between atomic energy levels - induced by a perturbing oscillatory EM field (photon).

- Atoms in z direction, polarized by \mathbf{E} in x direction. photon: $\lambda \sim 500 \text{ nm} \gg$ atomic dimensions

$\Rightarrow E_x = E_0 e^{i(kz - \omega t)} \Rightarrow \hat{H}' = -e_0 q x e^{i(kz - \omega t)}$, $q =$ electron charge.

kz has a value $\ll 1$ ($\sim 10^3$ typically) across atom $\Rightarrow e^{ikz} = 1 + ikz + \dots \approx 1$. {where \int compacting} $\{ H'_{k0}$ is perturbed }

$\Rightarrow \hat{H}' = -e_0 q x e^{-i\omega t}$ ELECTRIC DIPOLE APPROXIMATION ($qx =$ electric dipole operator \hat{d})

$\rightarrow \hat{H}'$ into Fermi's golden rule \rightarrow Stimulated transitions - Also spontaneous transitions.

Atomic transition rate (2 levels $E_k > E_j$) \rightarrow Balance rates: $n_k [A + B_{kj} u(\omega)] = n_j B_{jk} u(\omega)$ $n =$ atoms / level

Stimulated $j \rightarrow k = B_{jk} u(\omega)$ \rightarrow inverse eq: $n_j = \frac{e^{-E_j/k_B T}}{n_k} = e^{\hbar\omega/k_B T}$ Assume degeneracy = nil.

Stimulated $k \rightarrow j = B_{kj} u(\omega)$ $\Rightarrow A = [B_{jk} e^{\hbar\omega/k_B T} - B_{kj}] u(\omega)$ Now $u(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/k_B T} - 1}$

Spontaneous $k \rightarrow j = A$ (Planck's law) - But $A \neq A(T) \Rightarrow B_{jk} = B_{kj}$ hence $A = B_{kj} \frac{\hbar \omega^3}{\pi^2 c^3}$

where $\hbar\omega = E_k - E_j$ Now $B_{kj} = \Gamma_{k \rightarrow j} / u(\omega)$. use F.O.R but note $H' = -q E_0 x \cos \omega t$; Time av = density $= \frac{1}{2} E_0 E_0^2 \Rightarrow u(\omega) = \frac{1}{2} E_0 E_0^2 g(\omega) = \frac{1}{2} E_0 E_0^2 \hbar g(E)$

Selection rules - Transition rates between atomic energy levels depend on $\langle k | \underline{r} | j \rangle$ (Electric dipole approx.)
 Note $|\langle k | \underline{r} | j \rangle|^2 = |M_{kj}|^2 = \frac{1}{3} |\langle k | \underline{d} | j \rangle|^2$ where $\underline{d} = e \underline{r}$. Some elements of $\langle k | \underline{r} | j \rangle$ must be zero.

I - Electronic energy levels are eigenstates of parity. (\hat{H}_0 centrally symmetric). \underline{r} has odd parity.
 $\Rightarrow \langle k | \underline{r} | j \rangle = 0$ if $|k\rangle, |j\rangle$ have same parity \Rightarrow parity must change in E. dipole transitions.

II - let $|k\rangle = \psi_k(r) \chi_k$, $|j\rangle = \psi_j(r) \chi_j$; χ = spin w.f. $\therefore \langle k | \underline{r} | j \rangle = \langle \chi_k | \chi_j \rangle \int \psi_k^* \underline{r} \psi_j d^3r$
 $= 0$ unless χ_k, χ_j identical. $\Rightarrow \underline{\Delta S} = 0$


III - Consider only one electron changing state in transition. Consider $\langle k | \underline{r} | j \rangle$. $z = r \cos \theta$
 $\psi_k(r)$ is of form $R(r) Y_{lm}(\theta, \phi)$. ϕ integral: $\dots \int_0^{2\pi} d\phi e^{-im_k \phi} e^{im_j \phi} = 2\pi \delta_{m_k, m_j}$
 Consider $\langle k | \underline{r} | j \rangle$ $\alpha = r \sin \theta \cos \phi \Rightarrow \phi$ integral $\dots \int_0^{2\pi} d\phi e^{-im_k \phi} \frac{1}{2} (e^{i\phi} + e^{-i\phi}) e^{im_j \phi} = 0$
 unless $m_j - m_k = \pm 1$ (Similarly for y). $\Rightarrow \underline{\Delta M} = \pm 1, 0 \Rightarrow \underline{\Delta l} = \pm 1$. ($\Delta l = 0$ not allowed since parity = $(-1)^l$ and must change). Note $E_z \leftrightarrow \Delta m = 0$ $E_{\pm 1} \leftrightarrow \Delta m = \pm 1$ (Electric fields include Δm)
 (c.f. Zeeman effect).

IV - Atoms not necessarily eigenstates of \hat{L}_z (Spin orbit coupling) but are of \hat{J}_z .
 \Rightarrow (See Atomic/nuclear notes) $\Delta S = \pm 1, 0$. Similar argument to above?

Note: If we include ikz term in \hat{H}' i.e. $\hat{H}' \approx -E_0 \alpha (1 + ikz)$, $\langle k | \underline{r} | j \rangle$ matrix elements appear. αz - even parity \Rightarrow No parity change. $\alpha z \Rightarrow$ "Electric quadrupole" transitions. Magnetic transitions also exist/occur.

* Selection rules (a) - charged particle in 1D Harmonic oscillator w.f. $|n\rangle$ $E_n = (n + \frac{1}{2}) \hbar \omega$
 Transitions dominated by $\langle n' | x | n \rangle$. Note ladder operators $\hat{a}^{\pm} = \sqrt{\frac{m\omega}{2\hbar}} \hat{x} \pm i \frac{\hat{p}}{\sqrt{2m\hbar\omega}}$
 Property: $\hat{a}^+ |n\rangle \rightarrow |n+1\rangle$, $\hat{a}^- |n\rangle \rightarrow |n-1\rangle$. Write $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} [\hat{a}^+ + \hat{a}^-]$
 $\Rightarrow \langle n' | x | n \rangle \propto \{ \langle n' | n+1 \rangle + \langle n' | n-1 \rangle \} = 0$ unless $n' = n \pm 1$. $\Rightarrow \underline{\Delta n} = \pm 1$ selection rule.
 (Electric dipole approx again).

* Scattering - can apply Fermi's Golden rule to atomic scattering as long as scattering potential is weak

- Beam of particles. Normalise in a box volume a^3 . $\psi = A e^{i\mathbf{k} \cdot \mathbf{r}}$. $|\psi|^2 = A^2 = \frac{1}{a^3}$
 - Impinge on fixed potential $V(\mathbf{r})$.  Final state $\psi' = A e^{i\mathbf{k}' \cdot \mathbf{r}}$
 - Assume energy transfer negligible (Elastic collision + massive). $\therefore |\mathbf{k}'| = |\mathbf{k}|$
 - Apply FGR: Transition $k \rightarrow k' = \frac{2\pi}{\hbar} |\langle \psi' | V(\mathbf{r}) | \psi \rangle|^2 g(E_f)$

Now $\langle \psi' | V(\mathbf{r}) | \psi \rangle = \frac{1}{a^3} \int V(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}} d^3r$ where $\mathbf{K} = \mathbf{k} - \mathbf{k}'$ Note $\mathbf{k} = 2k \sin \theta \hat{x}$
 For $g(E_f)$: Assume w.f. normalised in box size a - \mathbf{k} values are $k_x = \frac{2\pi n_x}{a}$ etc...
 \therefore each state occupies volume $(\frac{2\pi}{a})^3$ of \mathbf{k} -space. # states in solid angle $d\Omega$ and in range $k \rightarrow k + dk = k^2 dk d\Omega / (\frac{2\pi}{a})^3 \Rightarrow g(k) = k^2 dk d\Omega (\frac{a}{2\pi})^3$
 Now $E_k = \frac{\hbar^2 k^2}{2m} \Rightarrow g(E_k) = g(k) \frac{dk}{dE_k} = \frac{mk dk d\Omega}{\hbar^2} (\frac{a}{2\pi})^3$ ($g(E) dE = g(k) dk$)

DEFINE "CROSS SECTION" $\sigma = \frac{\# \text{ PARTICLES SCATTERED}}{\text{UNIT TIME} / \text{INCIDENT FLUX}}$
 AND "DIFFERENTIAL CROSS SECTION" $\frac{d\sigma}{d\Omega} = \frac{\# \text{ SCATTERED INTO } d\Omega}{\text{UNIT TIME} / \text{INCIDENT FLUX}}$

- Incident flux = $-\frac{i\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*)$ $\psi = a^{-3/2} e^{i\mathbf{k} \cdot \mathbf{r}}$ INCIDENT FLUX $\cdot d\Omega$
 \Rightarrow Incident flux = $-\frac{i\hbar}{2ma^3} (ik^2 \psi^* \psi) = \frac{\hbar k}{m} \cdot \frac{1}{a^3} (= \frac{p}{m} \cdot \frac{1}{a^3} = v/a^3)$
 \downarrow particle velocity.

$\Rightarrow \frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi \hbar^2} \right)^2 \left| \int V(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}} d^3r \right|^2$ "Born Approximation"

\rightarrow For Coulomb potential get Rutherford scattering $V(r) = \frac{Ze^2}{4\pi \epsilon_0 r}$ $\frac{d\sigma}{d\Omega} = \left[\frac{mZe^2}{8\pi \epsilon_0 p^2 \sin^2 \theta/2} \right]^2$ OM 5

7) Atomic Structure * Hydrogen atom - solve SE. for pure Coulomb potential. Solutions $R_{nl}(r) Y_{lm}(\theta, \phi)$

If $n_r = \#$ nodes of $R_{nl}(r)$ $n_r = n - l - 1$. (n, l quantum #'s). $E_n = -R_{\infty}/n^2$ R_{∞} Rydberg constant.

$R_{\infty} = 13.6 \text{ eV} = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{1}{2} m_e c^2 \alpha^2$ $a_0 = \text{Bohr radius} = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$ $\alpha = \text{"Fine structure constant"} = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$

If nuclear charge is Ze : $E_n \rightarrow Z^2 E_n$, $a_0 \rightarrow a_0/Z$.

conventional orbitals: $l = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \dots$ * \times degenerate $2s, 2p$ and $3s, 3p, 3d$ for single electron atoms
 $s \ p \ d \ f \ g \ h$

* Not so for multielectron atoms - $E = E(n, l, m)$ not $E(n)$... QM (6)

* Real Hydrogen atom has a few corrections to above. (1) FINITE nuclear size

- not Coulomb potential - heavy atoms noticeable effect. (2) NUCLEAR MASS - use reduced mass μ but need to take into account isotopes

(3) NUCLEAR SPIN - Proton's magnetic moment interacts with electron $\mu_p = g_p \mu_N \frac{S}{\hbar}$; $g_p \approx 5.58$ $\mu_N = \frac{e\hbar}{2m_p}$ (nuclear magneton). \Rightarrow "Hyperfine structure"

(4) NUCLEAR SHAPE - some non spherical i.e. deuterium - quadrupole moment \Rightarrow not Coulomb potential

(5) SPIN ORBIT INTERACTION - electron moves through \underline{E} field of nucleus - sees this as a \underline{B} field. Energy depends on orientation of spin magnetic moment with this \underline{B} .

(6) RELATIVISTIC CORRECTIONS - $KE = (p^2 c^2 + m^2 c^4)^{1/2} - mc^2 \approx \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} \dots$

* DIRAC EQUATION for electron in Coulomb potential solves many of these problems. { well, spin orbit, relativistic ... }

$\Rightarrow E = mc^2 \left[1 + \frac{\alpha^2}{[n - j - \frac{1}{2} + \sqrt{(j + \frac{1}{2})^2 - \alpha^2}]^2} \right]^{-1/2}$ In non relativistic limit - retaining leading terms of Dirac Hamiltonian yields:

$\hat{H} \approx \underbrace{\frac{\hbar^2 \nabla^2}{2m} + V(r)}_{S.E. \hat{H}_0} + \underbrace{\frac{p^4}{8m^3 c^2}}_{\text{RELATIVISTIC } \hat{H}'_1} + \underbrace{\frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr} \underline{L} \cdot \underline{S}}_{\text{SPIN ORBIT } \hat{H}'_2} + \underbrace{\frac{\pi \hbar^2 e^2}{8\pi\epsilon_0 m^2 c^2} \delta(r)}_{\text{DARWIN TERM } \hat{H}'_3}$

* Spin orbit interaction \hat{H}'_2 Energy = $-\underline{\mu} \cdot \underline{B}$ $\underline{\mu} = \frac{e}{m} \underline{S}$ \leftarrow Magnetic moment of electron

$\underline{B} = \frac{\underline{v} \times \underline{E}}{c^2}$ \leftarrow inertial motion at \underline{v} changes \underline{E} Now $\underline{E} = -\nabla\phi$ so if Energy = U :

$\Rightarrow U = \frac{e}{mc^2} \underline{S} \cdot \left(\frac{\underline{p}}{m} \times \nabla\phi \right)$
 $= \frac{e}{m^2 c^2} \underline{S} \cdot \left(\underline{p} \times \underline{r} \cdot \frac{1}{r} \frac{d\phi}{dr} \right) = -\frac{e}{m^2 c^2} \frac{1}{r} \frac{d\phi}{dr} \underline{S} \cdot \underline{L}$ ($\underline{L} = -\underline{p} \times \underline{r}$) so $\frac{1}{2}$ out. "Thomas precession" can get this.

* Note DIRAC $E_{2, j=1/2}$ predicts $2p, j=1/2$ and $2s, j=1/2$ degenerate in energy. Experimentally not so. ("Lamb shift" $\sim 10\%$ of α) \Rightarrow QED - Coulomb field needs quantising.

* Multi-electron atoms - Base on solutions for Hydrogen but need to take into account e-e repulsion, nuclear screening. - connection between e-e repulsion and w.f. Symmetry, exclusion principle. \rightarrow EXCHANGE INTERACTION. e.g. for ground state of He: $2+1s$ electrons.

w.f. $\psi = \psi_{1s}(k_1) \psi_{1s}(k_2) \cdot \frac{1}{\sqrt{2}} [\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2]$. Antisymmetric. (c.f. - each e must have opposite spins) $\Rightarrow S=0$

excited case: (1) $\psi_S = \frac{1}{2} [\psi_{1s}(k_1) \psi_{2s}(k_2) + \psi_{2s}(k_1) \psi_{1s}(k_2)] [\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2] \Rightarrow S=0$ 'singlet'

(2) $\psi_T = \frac{1}{2} [\dots] [\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2] \Rightarrow S=1$ 'Triplet'

In Triplet case electrons further apart \Rightarrow lower energy. \therefore Coulomb energy depends on spin orientation of electrons.

* Central field approximation $\hat{H} = \sum_i \left(\frac{\hbar^2 \nabla_i^2}{2m_i} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$ $r_{ij} = |\underline{r}_i - \underline{r}_j|$

\Rightarrow write $\hat{H} = \hat{H}_0 + \hat{H}'$, treat \hat{H}' as a perturbation. $\hat{H}_0 = \sum_i \left(\frac{\hbar^2 \nabla_i^2}{2m_i} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + U(r_i)$ Separable

$\hat{H}' = \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i U(r_i)$ - Tricky part is to find deriv - can only do when $\hat{H}_0 \psi = E\psi$ is solved.

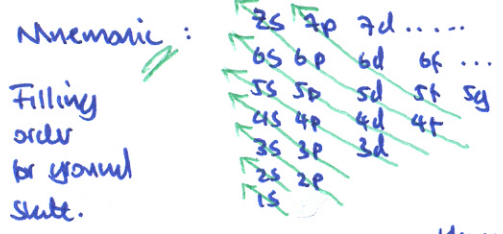
* Self consistent field approach (1) Guess deriv $\rightarrow 0$ $r_i \rightarrow 0$ (no screening) \rightarrow interpolate in between.

(2) Solve $\left[\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} + U(r) \right] \psi_{nlm} = E \psi_{nlm}$ for ψ_{nlm} (3) work out overall w.f. using SUTTER

DETERMINANT $\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \dots & \psi_k(r_1) \\ \psi_2(r_1) & \psi_2(r_2) & \dots & \psi_k(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \dots & \psi_k(r_N) \end{vmatrix}$ Need Wigner scheme (4) calculate deriv $\psi_{nlm} = -e/|\psi|^2 \rightarrow$ Gauss $\rightarrow E(r)$ from $\psi \rightarrow \frac{-\hbar^2 \nabla^2 \psi}{2m\psi} \rightarrow$ iterate to convergence

Note contains sizeable central (spherically sym) component of closed shells.

* Results of self-consistent field approach → filling order to predict ground state of multi-electron atoms.



"Fill from bottom" - Aufbau principle. - understand periodic table - elements with similar outer electron configurations (i.e. last \leftarrow) - VALENCY have similar chemical properties.

Filling order for ground state.
 \hat{H}_0 - central field, solved above
 \hat{H}_1 - Residual Coulomb between unpaired electrons
 \hat{H}_2 - Spin orbit interaction.

* Coupling schemes - Need to consider spin-orbit interaction as well as Coulomb repulsion between electrons.

Hamiltonian has general form $\hat{H} = \hat{H}_0 + \underbrace{\sum_{i,j} \frac{e^2}{|r_i - r_j|}}_{\hat{H}_1} + \sum_i \underbrace{\xi_i(r_i)}_{\hat{H}_2} \hat{L}_i \cdot \hat{S}_i$

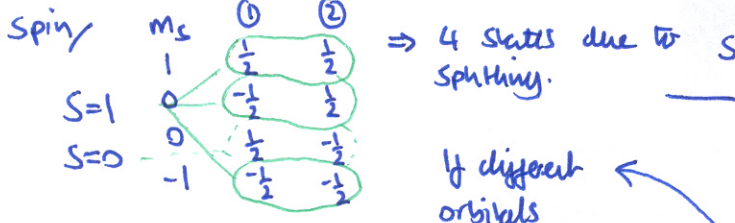
2 scenarios (1) $\hat{H}_1 \gg \hat{H}_2$: light atoms usually; → eigenstates of $\hat{H}_0 + \hat{H}_1$, \hat{H}_2 as perturbation ⇒ LS coupling. (2) $\hat{H}_2 \gg \hat{H}_1$: v. heavy atoms / highly ionized light atoms - relativistic effects more important. ⇒ jj coupling.

* LS coupling. \hat{H}_1 commutes with $\hat{S}, \hat{L}, \hat{S}^2, \hat{L}^2$ ⇒ energy levels characterized by TOTAL A.M. Quantum numbers L, S, J . order via MUND'S RULES.

- Combine spin ⇒ possible values of S. MAX S lies lowest in energy. Reason: MAX S ⇒ spin w.f. symmetric ⇒ spatial w.f. antisym. ⇒ Coulomb repulsion reduced.
- Combine orbital A.M. for each S, accounting for exclusion principle ⇒ L. MAX L lies lowest in energy. Reason: MAX L keeps electron apart ↑ ↓ ↑ ↓ (MAX L) (MIN L)
- Combine L, S ⇒ J. If shell ≤ 1/2 FULL ⇒ MIN J lies lowest. " " > 1/2 " ⇒ MAX J " " . Reason: result of \hat{H}_2 treated as perturbation. "Wigner-Eckart Theorem" used.

* Use Spectroscopists notation to label states $|S, L, J\rangle \equiv 2S+1 L_J$ (L = S, P, D, F, G, H, 0, 1, 2, 3, 4, 5)

Method: Eigen $|n, l\rangle$ states of two electrons / holes (1) work out multiplicity of spin states. e.g. for electron ① = 3p ⇒ $|3, 1\rangle$, electron ② = 4s ⇒ $|4, 0\rangle$



⇒ 4 states due to SAME ORBITAL, each S state will have different L values. In that case do L calculation separately for S=0, S=1. Note for S=0 v.f. antisym so spatial w.f. can be the same to satisfy Pauli E.P. ⇒ any pair of m_l ok. For S=1 only different m_l pairs are allowed.

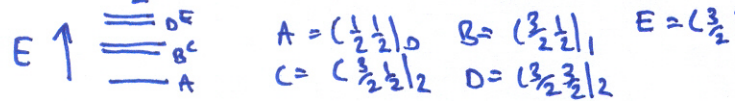
equivalent → L same for S=0, S=1 states. simply find all m_l combinations. e.g. m_l

	①	②	m_l
For each $ S, L\rangle$ state work out J values using $S = L+S, \dots, L-S $	-1	0	-1 ⇒ L=1.
	0	0	0
	-1	0	-1

→ e.g. States $|S, L\rangle = |0, 1\rangle$ and $|1, 1\rangle$ so far. $|0, 1\rangle: S=1$ $|1, 1\rangle: S=2, L=0$

→ Hund's rule for ordering: ⇒ E ↑ * jj coupling - consider eigenstates of $\hat{H}_0 + \hat{H}_2 = \hat{H}_0 + \sum_i \xi_i(r_i) \hat{L}_i \cdot \hat{S}_i$

- Hamiltonian commutes with \hat{S}^2 and with \hat{S}_i^2 since $L_i \cdot S_i = \frac{1}{2} (\hat{S}_i^2 - \hat{L}_i^2 - \hat{S}_i^2)$ ∴ characterize eigenstates by $|S, j_1, j_2, j_3, \dots, j_n\rangle$ * compute allowed j for individual electrons - split according to S-O interaction. * compute allowed S → (j_1, j_2) set with split according to S. No HUND rules expect however $j_1 > S$ (j) > E. i.e. $(\frac{3}{2}, \frac{3}{2}) > E$ than $(\frac{1}{2}, \frac{1}{2})$. Example: $(3p)^2$ - each electron can have $j = l + s, |l-s| = \frac{3}{2}, \frac{1}{2}$. Possibilities: $j_1 = j_2 = \frac{3}{2} \Rightarrow S = j_1 + j_2, \dots, |j_1 - j_2| = 3, 2, 1, 0$
 → each electron must be distinct (Pauli) so S must be even. (Antisymmetric) ⇒ S = 2, 0
 $j_1 = j_2 = \frac{1}{2} \Rightarrow S = 1, 0 \Rightarrow S=0$ allowed. $j_1 = \frac{3}{2}, j_2 = \frac{1}{2} \Rightarrow S = 2, 1$. $j_1 \neq j_2$ so all S allowed.



* Atomic Spectra - transitions between electronic states of atoms via emission/absorption of photons. - rate of spontaneous emission $\propto \omega^3 |\langle k | \hat{d} | j \rangle|^2$ in electric dipole approx.
 - selection rules: (Dipole transitions) * Parity change * $\Delta S = \pm 1, 0 \neq 0$ * $\Delta M_S = \pm 1, 0$
 Now for LS coupling ^{EXTRA!} $\Delta S = 0 \Rightarrow \Delta L = \pm 1, 0 \neq 0$ * $\Delta M_L = \pm 1, 0$ * $\Delta L_i = \pm 1$ if only electron i involved in transition. (parity change rule simplified).

8) Molecular Structure - examples of H_2^+ ion and H_2 molecule to illustrate techniques used.

* H_2^+ ion (Exact solution possible but hard) if protons have coords. R_a, R_b , electron r
 \rightarrow Full Hamiltonian is: $\hat{H} = \frac{-\hbar^2}{2m_p} (\nabla_{R_a}^2 + \nabla_{R_b}^2) - \frac{\hbar^2}{2m_e} \nabla_r^2 + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|R_a - R_b|} - \frac{1}{|r - R_a|} - \frac{1}{|r - R_b|} \right)$

- Simplify using "Born-Oppenheimer Approx". $m_p \gg m_e \therefore$ by given bond acceleration of electrons \gg protons. \therefore assume electrons respond to changes in proton position INSTANTANEOUSLY.
 \Rightarrow Try to solve $\hat{H}\psi = E\psi$ for R_a, R_b fixed \Rightarrow Energy of system.

\therefore in B.O. approx SE. is $\left\{ \frac{-\hbar^2}{2m_e} \nabla_r^2 + \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{1}{R} - \frac{1}{|r - R_a|} - \frac{1}{|r - R_b|} \right\} \right\} \psi(r, R_a, R_b) = E\psi(r, R_a, R_b)$
 Note only need to solve radial bit - i.e. think!! - Best to include full AO in variational calculations and trial function i.e. $\psi = \psi(r, R_a, R_b)$
 \rightarrow No obviously small term so use variational method. Trial function - when e is very close to one p - other will have negligible effect \Rightarrow expect w.f. close to p's to be \propto atomic orbitals.

Ground state $\psi_0(r) = \left(\frac{1}{\pi a_0} \right)^{1/2} e^{-r/a_0}$. Try $\psi = \alpha\psi_a + \beta\psi_b$
 where $\psi_{a,b} = \left(\frac{1}{\pi a_0} \right)^{1/2} e^{-|r - R_{a,b}|/a_0}$. Variational $E_0 \leq \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$ \leftarrow minimize w.r.t R . Now let $S = \langle \psi_a | \psi_b \rangle$ "overlap integral".
 and let $H_{ab} = \langle \psi_a | \hat{H} | \psi_b \rangle \Rightarrow E_0 \leq \frac{\alpha^2 H_{aa} + \beta^2 H_{bb} + 2\alpha\beta H_{ab}}{\alpha^2 + \beta^2 + 2\alpha\beta S}$. Now \hat{H} symmetric w.r.t R_a, R_b

$\Rightarrow H_{aa} = H_{bb}$. Potential symmetric about mid point between two protons $\bullet \quad \vdots \quad \bullet \rightarrow z$
 $\Rightarrow |\psi|^2$ symmetric $\Rightarrow \alpha = \beta, \alpha = -\beta$. $\Rightarrow E_0 \leq \frac{H_{aa} \pm H_{ab}}{1 \pm S}$ w.f. are $\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (\psi_a \pm \psi_b)$ \leftarrow "gerade" - even \leftarrow "ungerade" - odd
 normalised $\psi \Rightarrow \psi_g = \frac{1}{\sqrt{2(1+S)}} (\psi_a + \psi_b)$ \leftarrow let α .. normalise ψ i.e. $\langle \psi | \psi \rangle = 1$
 \rightarrow Not such a good fit to real data but could improve trial function with adjustable parameters etc. \rightarrow Rayleigh-Ritz...

* labelling MO's - g, u notation applies to all homonuclear diatomic molecules (H_2, O_2, \dots)
 Note diatomic not spherically symmetric \rightarrow eigenstates of \hat{L}_z not L^2 . label $|m_l|$ values by Greek letters: $|m_l| = 0 \ 1 \ 2 \dots \rightarrow$ in case of H_2^+ ion: $\psi_g \leftrightarrow 1s\sigma_g$ $\psi_u \leftrightarrow 1s\sigma_u^*$
 $\sigma \ \pi \ \delta$ \leftarrow ^{orbitals used} \leftarrow ANTI BONDING.

* H_2 molecule - in B.O. approx: $\hat{H} = \frac{-\hbar^2}{2m_e} (\nabla_{r_1}^2 + \nabla_{r_2}^2) + \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{1}{r_{12}} + \frac{1}{r_{1a}} + \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right\}$
 where $r_{ia} = |r_i - R_a|$ etc... \Rightarrow two H_2^+ ion Hamiltonians + SMALL term $\frac{e^2}{4\pi\epsilon_0} \left\{ \frac{1}{r_{12}} + \frac{1}{r_{1a}} + \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right\}$
 (e.e., pp repulsion). \therefore Product of 2 H_2^+ MO's could be a good start.

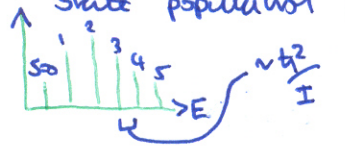
- particularly for ground state. i.e. $\psi = \psi_g(r_1)\psi_g(r_2) \rightarrow \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$ minimize w.r.t $R = R_{ab}$
 - NOT THAT GOOD. why? $\psi_g(r_1)\psi_g(r_2) \sim (\psi_a(r_1) + \psi_b(r_1))(\psi_a(r_2) + \psi_b(r_2)) \sim \underbrace{\psi_a(r_1)\psi_a(r_2)}_{\psi_{VB}} + \underbrace{\psi_a(r_1)\psi_b(r_2)}_{\psi_{IB}} + \underbrace{\psi_b(r_1)\psi_a(r_2)}_{\psi_{IB}} + \underbrace{\psi_b(r_1)\psi_b(r_2)}_{\psi_{VB}}$
 \rightarrow 1st term ψ_{VB} - "Valence Bond" - electrons shared between protons
 \rightarrow 2nd term ψ_{IB} - "Ionic Bond" - electrons ^{not} shared but associated with same proton. i.e. $H^+ - H^+$
 Equal symmetry / ionically unreasonable so try $\psi = \psi_{VB} + \lambda\psi_{IB}$ (λ is small - actually $\sim 1/6$).
 \rightarrow put into $\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$ and minimize w.r.t. λ and R . \rightarrow Fairly good agreement.

* MO's have their own "Spectroscopic Notation" $2s+1 \Lambda_{u/g}$ $2s+1 = \#$ spin substates (M_S values)
 $\Lambda = |L_z| = \sum \pi \Delta$ \leftarrow $\Delta = 0 \ 1 \ 2$

9) Molecular Spectra - analogous to electronic transitions in atomic spectra though $\Delta E \sim eV$. (optical)
 molecules can rotate and vibrate as well as rotate protons during 'orbital transitions'.
 Rotation $\sim \frac{L^2}{2I} \sim \frac{\hbar^2}{2I} \ll 10^4 eV$ vibration $\Delta E \sim 0.1 eV$

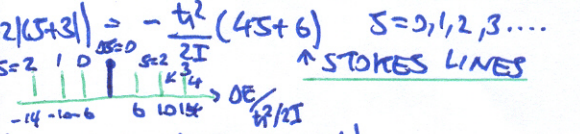
* Molecular rotation - Hamiltonian has $\frac{1}{2}I\omega^2 = \frac{1}{2} \frac{L^2}{I}$ ($L = I\omega$). S.E is $\frac{1}{2I} L^2 \psi = E_{rot} \psi$
 - eigenstates of L^2 are spherical harmonics Y_{lm} , energy $E_{rot} = \frac{\hbar^2 J(J+1)}{2I}$ (c.f. $L^2 \psi = \hbar^2 J(J+1) \psi$)
 Note $I = \mu R_0^2$, R_0 eq. separation, μ reduced mass.

→ Rotative transitions between rot. states: Dipole transitions PARITY, $\Delta S = \pm 1, 0$
 But parity = $(-1)^J \Rightarrow \Delta S = \pm 1$. ∴ Possible energies of emitted/absorbed photons $\neq 1 \rightarrow 5$
 ($J = 0, 1, 2, 3, \dots$) $\Delta E = \frac{\hbar^2}{2I} [J(J+1) - (J-1)J] = \frac{\hbar^2}{2I} (2J+1)$. Spontaneous emission slow
 (FGR - energy small) - absorption better method of study. Absorption spectrum:
 lines spaced $\sim \frac{\hbar^2}{I}$. (I sometimes varies $\rightarrow R_0$ at large J - centrifugal potential)

State population given by Boltzmann distribution. $n_J \propto (2J+1) \exp[-\frac{\hbar^2 J(J+1)}{2Ik_B T}]$

 * Homomuclear molecules - if some atoms in molecule are identical - restrictions on symmetry of wavefunction. e.g. H_2 : 2 protons, each $s = \frac{1}{2} \rightarrow$ FERMIONS ∴ Antisym. w.f. under particle exchange. Symmetry of rotational w.f. is $(-1)^J$ ∴ 2 possibilities: (1) $J = \text{even}$: spatial w.f. sym.

⇒ Spin w.f. antisym. ⇒ $S = 0$. "PARAHYDROGEN". (2) $J = \text{odd}$: spatial w.f. antisym ⇒ spin w.f. sym. ⇒ $S = 1$ "ORTHOPYDROGEN". Now - Electric dipole selection rules ⇒ $\Delta S = 0$. ∴ $S = 0 \rightarrow S = 1$ not possible. Hence H_2 will have $\Delta S = \pm 1$ pure rot. transition. (Possible for HCl, HD etc though!)
 - transitions via collision. relative populations of S, S states $\propto (2S+1)(2S+1) \exp[-\frac{S(S+1)\hbar^2}{2Ik_B T}]$
 so at high temp ratio ortho/para $\rightarrow 3:1$. CO_2 : nuclear spin 0 \rightarrow zero. ⇒ Bosons. Sym w.f. as well. ⇒ turns out S must be odd for O_2 . More complicated: $O_2 \rightarrow$ electron w.f. symmetry needed

* Raman Spectroscopy - scattering of photon from molecule - usually some photon energy change. - arises from 2nd order perturbation theory (time and dependent). Matrix element in FGR is $\langle i | \hat{H}' | j \rangle + \sum_k \frac{\langle i | \hat{H}' | k \rangle \langle k | \hat{H}' | j \rangle}{E_j - E_k}$ i.e. transition $j \rightarrow k, k \rightarrow i$. (\sum over k pr. level. If $\hat{H}' =$ Electric dipole operator)
 - selection rules: $\langle k |, |j \rangle$ differ by ± 1 , parity unil of S . $|k \rangle, |i \rangle$ same. ⇒ $|i \rangle, |j \rangle$: $\Delta S = \pm 2, 0$ (Parity ⇒ ± 1)

Also parity change in both $j \rightarrow k$ and $k \rightarrow i$ ⇒ RAMAN SELECTION RULES $\Delta S = \pm 2, 0$ / NO PARITY CHANGE
 $\Delta E_{photon} = 0$ if $\Delta S = 0$; $J \rightarrow J+2 \Rightarrow \Delta E = \frac{\hbar^2}{2I} (J(J+1) - (J+2)(J+3)) = -\frac{\hbar^2}{2I} (4J+6)$ $J = 0, 1, 2, 3, \dots$
 ⇒ $\Delta E = \frac{\hbar^2}{2I} [4J-2]$, $J = 2, 3, 4, \dots$ ← ANTI-STOKES LINES.


- good way to observe rot. transitions (Any photon can be used - pick convenient wavelength).
 * Vibrational transitions - diatomic molecules - expand $E_0(R)$ about R_0
 - approximate as harmonic oscillator potential $\frac{1}{2}\mu\omega^2(R-R_0)^2$. $\omega^2 = \frac{1}{\mu} \frac{\partial^2 E_0}{\partial R^2} \Big|_{R_0}$
 Energies are $(n + \frac{1}{2})\hbar\omega + E_0(R_0)$. Typical energy $\sim \frac{1}{50} E_{atom}$. Selection rules: Dipole ⇒ $\Delta n = \pm 1 \Rightarrow \Delta E = \hbar\omega$ (pure vib). Note pot. not purely harmonic $\sim (R-R_0)^3$ etc... $\Delta n = \pm 1$ not strictly true. Polyatomic molecules - more modes ($3N-6$) for N atoms. → Normal mode analysis.

* Vib. rotation of diatomic molecule - vib. transitions often accompanied by rot. Because microatomic potential is not exactly harmonic ⇒ $R_0 \sim$ different in two different vib. states. ⇒ I larger in state of higher n . Consider absorption: $n \rightarrow n+1$ $\Delta E = \hbar\omega$. Define $B = \frac{\hbar^2}{2I}$, $B' = \frac{\hbar^2}{2I'}$, $B' = B + \delta B$ ($\delta B < 0$)
 + rot. change I I' → 3 possibilities: (1) $\Delta S = +1, J \rightarrow J+1$ $\Delta E = \hbar\omega + 2B(J+1) + \delta B(J+1)(J+2)$ $S = 0, 1, 2, \dots$
 (2) $\Delta S = -1, \Delta E = \hbar\omega - 2B(J+1) + \delta B(J+1)(J+2)$ $S = 1, 2, 3, \dots$ (3) $\Delta S = 0, \Delta E = \hbar\omega + \delta B J(J+1)$ $S = 0, 1, 2, 3$.
 Now $|\delta B| \ll B \rightarrow$ observe: \sim equally spaced lines above $\hbar\omega$ "R Branch" $\Delta S = +1$
 \sim " " " " below $\hbar\omega$ "P Branch" $\Delta S = -1$ | "Q Branch" $\Delta S = 0$
 → In P-Branch spacing increases \sim with J , decreases with J for R. (δB). NOT SEEN (at low) - No parity change.


* Electronic transitions - if electrons make transitions in a molecule → include vib and rot.
 - Franck-Condon principle: Heavy nuclei - Electronic transition leaves nuclei unaffected.
 → initial - final state: not vib level: $n\hbar\omega \sim \frac{1}{2}\mu\omega^2(R_0^f - R_0^i)^2$. ΔI sizable. - δB not that small. (Analysis above still valid though). ΔE in UV spectrum. - observe in emission
 - Note Q-Branch may be seen if electronic transition satisfies parity selection rule.
 - energy in R branch may increase @ small J + decrease at large J ⇒ "BAND HEAD".

$\Delta E \propto J \Rightarrow$ "FORTRAN DIAGRAM" $J \uparrow \dots \leftarrow \Delta E$ QM 9

E.M. Fields in QM * Hamiltonian operator in QM based on formulation of classical mechanics. For a system of N particles (coordinates x_i ($i=1, \dots, 3N$), p_i = momentum) $H = T + V$. $\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i}$, $\frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i}$ if replace p_i by $p_i - qA_i$ (vector potential \underline{A})
 \Rightarrow generate Lorentz non-Hamiltonian equations - $m\ddot{x} = qE + q\dot{x} \times B$. So in general use $p = -i\hbar \nabla - qA$ M.S.E. if $V = q\phi \Rightarrow$ S.E. $\frac{1}{2m} (-\hbar^2 \nabla^2 \psi + i\hbar q (\nabla A + A \nabla) \psi + q^2 A^2 \psi) + q\phi \psi = E\psi$ (or $i\hbar \frac{\partial \psi}{\partial t}$)
 - can neglect A^2 term in weak fields.

* Uniform magnetic field - choose potentials $\underline{A} = -\frac{1}{2} \underline{r} \times \underline{B}$, $\phi = 0$. (Note $\underline{B} = \nabla \times \underline{A}$ ✓)
 Take $\underline{B} = (0, 0, B_z) \Rightarrow \underline{A} = \frac{B_z}{2} (-y, x, 0)$. Note "subtle gauge" $\nabla \cdot \underline{A} = 0$ if $\nabla \cdot \underline{r} = 2$ or $\rho = 0$.
 $\Rightarrow \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{q}{2m} B_z \hat{L}_z + \frac{q^2 B_z^2}{8m} (x^2 + y^2)$ noting $\hat{L}_z = i\hbar (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) \equiv x \hat{p}_y - y \hat{p}_x$
 \Rightarrow 3D generalize to $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{q}{2m} \underline{B} \cdot \hat{L} + \frac{q^2}{8m} [B^2 r^2 - (\underline{B} \cdot \underline{r})^2]$ Now B^2 term negligible for $B \leq 10^4$ T

\Rightarrow important term is $-\frac{q}{2m} \underline{B} \cdot \hat{L}$. "magnetic moment associated with e orbital interacting with \underline{B} " i.e. $-\underline{\mu} \cdot \underline{B}$ with $\hat{\underline{\mu}} = \frac{q}{2m} \hat{L}$.
 (Denote $\underline{\mu}$ classically considering particle in circular motion \Leftrightarrow current loop.)

 $L = m r^2 \omega$. current = $I = q \omega / 2\pi \Rightarrow \underline{\mu} = I \pi r^2 = \pi r^2 \frac{q \omega}{2\pi} = \frac{q L}{2m}$.
 Define BOHR MAGNETON $\mu_B = \frac{e \hbar}{2m_e}$ $\therefore \hat{H}_{\text{magnetic}} = -\frac{q}{2m} B_z \hat{L}_z = \mu_B \frac{q}{\hbar} B_z \hat{L}_z$
 \therefore if $\hat{H}_{\text{mag}} \psi = \lambda \psi$, $\lambda = \mu_B B_z m_l$ ($m_l = -l, -(l-1), \dots, +l$).

* Larmor precession and Landau levels - magnetic moment associated with \underline{L}
 \rightarrow classically expect PRECESSION about \underline{B} (Euler equation etc). Also occurs in QM.

if $\underline{B} = B_z \hat{z} \Rightarrow \frac{d}{dt} \langle \hat{L}_x \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{L}_x] \rangle = \frac{i}{\hbar} \frac{e B_z}{2m} \langle [\hat{L}_y, \hat{L}_x] \rangle = -\frac{e B_z}{2m} \langle \hat{L}_y \rangle = -\omega_L \langle \hat{L}_y \rangle$
 $\omega_L = \frac{e B_z}{2m} =$ 'Larmor frequency'. Also $\frac{d}{dt} \langle \hat{L}_y \rangle = \omega_L \langle \hat{L}_x \rangle \Rightarrow \langle L_x \rangle = A \cos(\omega_L t + \alpha)$ i.e. precess
 $\langle L_y \rangle = A \sin(\omega_L t + \alpha)$

Now consider electron in eigenstate of \hat{L}_z in uniform $\underline{B} = B_z \hat{z}$.

NOT SMALL. $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \mu_B \frac{B_z}{\hbar} \hat{L}_z + \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{e^2 B_z^2}{8m} x^2 \right) + \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{e^2 B_z^2}{8m} y^2 \right)$
 Harmonic oscillator parts have frequency $\frac{1}{2} m \omega^2 = \frac{e^2 B_z^2}{8m} \Rightarrow \omega = \frac{e B_z}{2m} = \omega_L$. Energies $(n_x + \frac{1}{2}) \hbar \omega_L$, $(n_y + \frac{1}{2}) \hbar \omega_L$.
 Here motion in z direction, $\underline{L} \cdot \underline{B}$ interaction, 1-D harmonic oscillators in y and x.

$\therefore E_{\text{TOT}} = \frac{p_z^2}{2m} + (m_l + n_x + n_y + \frac{1}{2}) \hbar \omega_L$ "LANDAU LEVELS". Now by parity of \hat{L}_z , Harmonic oscillator w.f. $\Rightarrow m_l + n_x + n_y = \text{even} = 2u$. Also $E > 0$ ($\hat{H} = \frac{(p - qA)^2}{2m}$ is a square)
 $\Rightarrow n \geq 0$. So $E = \frac{p_z^2}{2m} + (2u + 1) \hbar \omega_L$, $n \geq 0$.

* Spin Magnetic moment - Dirac equation predicts POINTLIKE spin $\frac{1}{2}$ particle has magnetic moment $\underline{\mu} = g \cdot \frac{q}{2m} \underline{S}$ with $g = 2$. (OED $\Rightarrow g = 2.002$).
 \therefore for electron $M_z = \pm \frac{e}{m_e} \frac{\hbar}{2} = \pm \mu_B$. \therefore modify (+) from SE to $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \underline{\mu} \cdot \underline{B} + \frac{q^2}{8m} (B^2 r^2 - (\underline{B} \cdot \underline{r})^2)$.
 where $\underline{\mu} = \frac{q}{2m} (\hat{L} + \hat{S})$. Note $\underline{\mu}$ is not \parallel to $\underline{S} = \underline{L} + \underline{S}$ in general. Note proton has $g = 5.58$ i.e. NOT POINT LIKE.

* ZEEMAN EFFECT - when atoms are placed in a magnetic field spectral lines are observed to split. Including SPIN ORBIT INTERACTION (not inc. in (H)) \rightarrow atom in B_z field has Hamiltonian: $\hat{H} = \hat{H}_0 + \xi \hat{L} \cdot \hat{S} + \frac{e}{2m} B_z (\hat{L}_z + 2\hat{S}_z)$. \hat{H}_0 commutes with $L^2, L_z, S^2, S_z, J^2, J_z$ but $\underline{L} \cdot \underline{S} \neq$ commute with \hat{L}_z or \hat{S}_z in general. \Rightarrow TWO REGIMES:

(1) STRONG FIELD $\mu_B B \gg \xi \underline{L} \cdot \underline{S}$ \rightarrow B large OR $L=0$ OR $S=0$ \rightarrow ignore this term.
 (2) WEAK FIELD $\mu_B B \ll \xi \underline{L} \cdot \underline{S}$ Find eigenstates of $\hat{H}_0 + \xi \underline{L} \cdot \underline{S}$ then treat $\mu_B B (\hat{L}_z + 2\hat{S}_z)$ as a perturbation. **'ANOMALOUS ZEEMAN EFFECT'**

* STRONG FIELD EXAMPLE $2p \rightarrow 1s$ transition. in H.

$1s$	$m_s = +\frac{1}{2}$	$E - E_0 = +\mu_B B_z$	$2p$	$m_l = +1$	$m_s = \frac{1}{2}$	$E - E_0 = 2\mu_B B_z$
	$-\frac{1}{2}$	$-\mu_B B_z$		$+1$	$-\frac{1}{2}$	0
				0	$+\frac{1}{2}$	$\mu_B B_z$
				0	$-\frac{1}{2}$	$-\mu_B B_z$
				-1	$+\frac{1}{2}$	0
				-1	$-\frac{1}{2}$	$-2\mu_B B_z$

$|E_0 - E| \quad \xrightarrow{\mu_B B_z} \quad |E_0 - E| \rightarrow E$

- Selection rules: $\Delta m_s = 0$ $\Delta m_l = \pm 1, 0$
 \Rightarrow allowed transitions are $\Delta E = |E_0 - E|, |E_0 - E| \pm \mu_B B_z$
 i.e. spectral line split into 3 components.

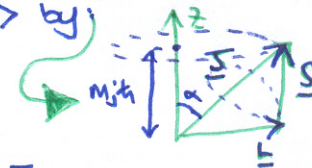
* WEAK FIELD ANALYSIS + EXAMPLE

Firstly consider $\underline{L} \perp \underline{S}$ term. Write $\underline{L} \cdot \underline{S} = \frac{1}{2}(\underline{J}^2 - \underline{L}^2 - \underline{S}^2)$ since $\underline{J}^2 = \underline{L}^2 + \underline{S}^2 + 2\underline{L} \cdot \underline{S}$
 \Rightarrow eigenstates of H_0 + $\underline{L} \cdot \underline{S}$ are eigenstates of $\underline{J}^2, \underline{L}^2, \underline{S}^2, J_z$ BUT NOT L_z, S_z . \Rightarrow state $|jls\rangle$.

$\therefore \Delta E$ due to $\underline{L} \cdot \underline{S} = \langle jls | \underline{L} \cdot \underline{S} | jls \rangle = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1))$ c.f. $\langle jls | \hat{H} | jls \rangle = E + \Delta E$.
 Now using 1st order perturbation theory ΔE due to $\frac{e}{2m} B_z (L_z + 2S_z)$ is $\langle jls | \frac{e}{2m} B_z (L_z + 2S_z) | jls \rangle$ needed.

Evaluate this using 'vector model'. - represent state $|lsjm_j\rangle$ by

- lengths of $\underline{L}, \underline{S}$ fixed by (e.g.) $|\underline{L}| = \hbar \sqrt{l(l+1)}$
- angles between \underline{S} and \underline{J} fixed and between any pair of $\underline{L}, \underline{L}, \underline{S}$ e.g. $\cos \alpha = \frac{S_z}{|\underline{S}|} = \frac{m_j}{(l+1)\frac{1}{2}}$



$M_z = \frac{e}{2m} (\underline{L} + 2\underline{S}) \cdot \underline{J}$
 so M_z not fixed. BUT angle between $\underline{M}, \underline{J}$ (β) is fixed so M moves around with \underline{J}
 Prog: $|\underline{M}| |\underline{J}| \cos \beta = \underline{M} \cdot \underline{J} \propto (\underline{L} + 2\underline{S}) \cdot (\underline{L} + \underline{S})$
 $= \underline{L}^2 + 2\underline{S}^2 + 3\underline{L} \cdot \underline{S} = \frac{1}{2} (3\underline{J}^2 - \underline{L}^2 + \underline{S}^2)$ Fixed.

- Can i. calculate M_z as $M_z = |\underline{M}| \cos \beta \cos \alpha = \underline{M} \cdot \underline{S} \frac{S_z}{|\underline{S}|^2} \Rightarrow \langle M_z B_z \rangle_{jls m_j} = g \mu_B m_j B_z$
 where $g = \frac{3j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$ LANDE g-FACTOR. (using $\underline{M} \cdot \underline{J} = \frac{1}{2} (3\underline{J}^2 - \underline{L}^2 + \underline{S}^2) \cdot \frac{g}{2m}$)

so (e.g.) for S state of H: $(l=0, s=\frac{1}{2}) \Rightarrow j=\frac{1}{2} \Rightarrow g=2$ so NS: $E = E_0 + \Delta E$
 $\Delta E = 2 \times g \mu_B m_j \max B_z = 4 \mu_B \frac{1}{2} B_z = 2 \mu_B B_z$
 { Note selection rules $\Delta m_s = \pm 1, 0$ or transitions }

* Polarisation in Zeeman effect

- Selection rules $\Delta m_s = 0$ for z-dipoles i.e. $\underline{E} \parallel \underline{z}$ $\Delta m_s = \pm 1$ for x,y dipoles.
- photon travelling $\parallel \underline{z}$ can only have x,y components of \underline{E} . \therefore if view spectrum $\parallel \underline{B}$ only see $\Delta m_s = \pm 1$ transitions. (4, 2 lines)
- photon travelling $\parallel \underline{x}$ can have y,z components of $\underline{E} \Rightarrow$ all Δm_s possible. NOTE $B_z = B_z \hat{z}$
- view $\parallel \underline{B}$, $\Delta m_s = \pm 1$ transitions will have OPPOSITE CIRCULAR POLARISATIONS.
 $\Delta m_s = +1 \Rightarrow \alpha + i\gamma$, $\Delta m_s = -1 \Rightarrow \alpha - i\gamma$.
- view $\perp \underline{B}$ i.e. using \underline{x} : $\Delta m_s = 0 \rightarrow$ plane polarised $\parallel \underline{z}$, $\parallel \underline{B}$. \rightarrow MORE ABOUT THIS IN ATOMIC PHYSICS!
 $= \pm 1 \rightarrow$ " " $\parallel \underline{y} \perp \underline{B}$.

* Magnetic susceptibility

- magnetic moments of atoms have discrete values $g \mu_B m_s$, typical energy for $B \sim 1T$ $\approx 10^{-23} J \ll k_B T$ @ room temp. ($\sim k_B T$ @ 1K). \therefore normally m_s values populated ~ equally.
 - Probability of being in state $m_s = \exp(-g \mu_B m_s / k_B T) / \sum_j \exp(-g \mu_B m_s / k_B T)$
 \Rightarrow average $M \parallel B$ is $\langle M_z \rangle = -g \mu_B \sum_j m_j e^{-\epsilon_j} / \sum_j e^{-\epsilon_j}$ if $\mu_B B / k_B T = \epsilon$. m_s (general sense)
 if $\epsilon \ll 1$ get Curie's law for χ_c / atom.
 $\chi_c = M \langle M_z \rangle / B = \frac{\mu_0 g^2 \mu_B^2}{4k_B T} j(j+1)$. Note have neglected B^2 term in $H \Rightarrow$ DIAMAGNETISM
 with $\Delta E \propto B^2$. contributes $3k_B T$ even if $(l=s=0)$. Energy $\langle \frac{e^2 B^2}{6m} (x^2 + y^2) \rangle = \frac{e^2 B^2}{12m} \langle r^2 \rangle$
 so if $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \langle r^2 \rangle \Rightarrow$ induced dipole energy $= -\frac{1}{2} \mu_B \frac{e^2 B^2}{6m} \langle r^2 \rangle$ with $\mu = \frac{e^2 B}{6m} \langle r^2 \rangle$
 \therefore DIAMAGNETIC SUSCEPTIBILITY / ATOM $\chi_0 = \mu_0 \frac{e^2}{6m} \sum_{\text{all electrons in atom}} \langle r^2 \rangle$ AM (11)

extra // * More correct treatment of EM waves in QM.

consider travelling wave polarized $\parallel z$ $E_z = E_0 e^{i(kz - \omega t)}$ (travels in z direction)
 vector potential is $\underline{A} = (0, 0, A_z)$ $A_z = A_0 e^{i(kz - \omega t)}$; $\phi = 0$
 $\underline{E} = -\frac{\partial \underline{A}}{\partial t} \Rightarrow E_0 = i\omega A_0 \Rightarrow \underline{B} = (0, B_y, 0)$; $B_y = ikA_0 e^{i(kz - \omega t)} = \frac{k}{\omega} E_0 = \frac{1}{c} E_0$

Now, neglecting A^2 term in \hat{H} , $\hat{H} = \hat{H}_0 + \hat{H}'$ for hydrogen like atom
 with $\hat{H}' = \frac{iq\hbar}{m} \cdot \underline{A} \cdot \nabla = \frac{iq\hbar}{m} A_0 \frac{\partial}{\partial z}$. (Note $\nabla \cdot \underline{A} = 0$; electric dipole approx $\Rightarrow \text{not } \times 0$; also omit $e^{-i\omega t}$ for clarity).

- use TRICK $[\hat{H}_0, z] = -\frac{\hbar^2}{m} \frac{\partial}{\partial z}$

$$\begin{aligned} \Rightarrow \langle k | \hat{H}' | j \rangle &= -\frac{iq\hbar}{m} \cdot \frac{mA_0}{\hbar^2} \langle k | \hat{H}_0 z - z \hat{H}_0 | j \rangle \\ &= -\frac{iq}{\hbar} A_0 (E_k - E_j) \langle k | z | j \rangle \\ &= -i\omega q A_0 \langle k | z | j \rangle \quad \text{with } \hbar\omega = E_k - E_j \\ &= -q E_0 \langle k | z | j \rangle \end{aligned}$$

As postulated previously (QM (4) - (5)).