Basic Summary Notes: Advanced Quantum Physics

By Shikang Ni

DISCLAIMER

This set of notes is by far INCOMPLETE representation of the tricks and understanding you need to know about the topic

WISDOM

The purpose of this note is to give you a quick reminder/summary of what was taught when you are revising (KNOWING)
Actual understanding comes after CONNECTING and GENERALISING
This can be done by practicing, mindmapping and reading

Other great and important sources of information are:

1. Problems in Quantum Mechancis (Squires)
2. Quantum Physics (Gasiorowicz)
3. Modern Quantum Mechanics (Sakurai)
4. Past exam papers (higher order corrections, beware of over-fitting)
5. Example sheets (build awareness/first-order practice)
6. Pen and paper derivations/proofs

Course Content

1. Fundamentals of Quantum Mechanics
2. Charged particles moving in B field
   - Gauge invariance (Aharanov-Bohm effect)
   - Landau levels (2D electron gas)
   - Spin and magnetic moment (Stern-Gerlach experiment)
3. Approximate methods
   - Time-independent perturbation method (1^{st} & 2^{nd} order, non-degenerate & degenerate)
   - Variational method (Rayleigh-Ritz method)
4. Real Hydrogen atom (Application of perturbation method)
   - Fine structure: relativistic correction, spin-orbit coupling, Darwin term
   - Hyperfine structure: nuclear spin coupling
5. Symmetries
   - Temporal, translational, **rotational** invariance / parity
   - Wigner-Eckart theorem (Landé projection formula)
   - Selection rules (Atomic transitions)
6. Identical particles
   - Spin-statistics theorem
   - Slater determinants (2-electron system)
   - Exchange forces
7. Helium atom - 2 identical electrons (Application of perturbation method + exchange interactions)
8. Multi-electron atom (Central field approximation/Hartree-Fock CFA)
   - Configuration quantum numbers
   - Coupling schemes: LS coupling v.s. jj coupling
   - Hund's rule, Landé interval rule
   - E1 transition
9. Spectral lines: Zeeman effect (B-field), Stark effect (E-field)
10. Molecules (Born-Oppenheimer approximation): studying H_2^+ and H_2
11. Time-dependent systems
    - Transitions from harmonic perturbation
    - Time-dependent perturbation theory
    - Fermi's Golden Rule (transition rate)

12. Scattering (Born approximation)
13. Quantum Electrodynamics - A quantum description of EM field
    - Get photons when we quantise the Fourier expansion of the EM field.
14. Atomic transitions
    - Transition rate: computing the matrix element from Fermi's Golden Rule using QED
    - Spontaneous emission
    - Stimulated emission and absorption (Einstein coefficients)
    - Spontaneous decay: decay rate, angular distribution
    - Polarisation in atomic transitions (in B field)
15. Lasers (HeNe laser)
    - Laser rate equations
    - Steady state solutions
16. Coherent states

1 Generalised angular momentum

$$\hat{\boldsymbol{J}} = n\hat{\boldsymbol{L}} + m\hat{\boldsymbol{S}}$$

- Commutation relations:
$$[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k$$

- $\boldsymbol{J}^2$ and J_z
$$\hat{J}_z\,|j, m_j\rangle = m_j\hbar\,|j, m_j\rangle \quad \text{and} \quad \hat{\boldsymbol{J}}^2\,|j, m_j\rangle = j(j+1)\hbar^2\,|j, m_j\rangle$$
where $m_j = -j, -j+1, ..., j-1, j$ and j can be a half-integer.

- The eigenstates are orthonormal: $\langle j_1 m_1 | j_2 m_2\rangle = \delta_{j_1 j_2}\delta_{m_1 m_2}$

- Ladder operators:
$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \quad \Rightarrow \quad \hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-) \quad \text{and} \quad \hat{J}_y = \frac{1}{2i}(\hat{J}_+ - \hat{J}_-)$$
$$[\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z \quad \text{and} \quad \hat{J}^2 = \hat{J}_+\hat{J}_- + \hat{J}_z^2 - \hbar\hat{J}_z$$
$$\hat{J}_\pm\,|j, m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)}\,|j, m_j \pm 1\rangle$$

- Matrix representation:

  1. For $j = \frac{1}{2}$ (1/2-spin), we get the **Pauli matrices**, $\boldsymbol{\sigma}$. Can write $\hat{\boldsymbol{J}} = \frac{\hbar}{2}\boldsymbol{\sigma}$ or $\hat{\boldsymbol{S}} = \frac{\hbar}{2}\boldsymbol{\sigma}$.
  $$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad ; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad ; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
  It has commutation relations:
  $$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$$
  2. For other j values, just figure out the matrix elements of J_x, J_y, J_z methodically.

- Addition of angular momentum:
$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{J}}' + \hat{\boldsymbol{J}}''$$
Now, $m = m' + m''$ and $j = j' \otimes j'' = |j' - j''|, ..., j' + j''$.

  Also, the eigenstate $|jm\rangle$ of J can be expressed as a linear combinations of the product states $|j'm'\rangle \otimes |j''m''\rangle$:
  $$|JM\rangle = \sum_{m', m''} \underbrace{|j'm'\rangle\,|j''m''\rangle}_{\substack{\text{product of} \\ \text{states}}} \underbrace{\langle j'm'; j''m''|JM\rangle}_{\substack{\text{Clebsch-Gorden} \\ \text{coefficients}}}$$
  Coupled states can be expressed in terms of the uncoupled states using Clebsch-Gordan coefficients: $|njm_jls\rangle = \sum |nlm_s sm_s\rangle\,\langle lm_l; sm_s|jm_j\rangle$.

2 Charged particles in EM field

An external EM field decribed by $\mathbf{A}$ and ϕ can be introduced via the minimal substitution prescription into the Hamiltonian: $\mathbf{p} \to \mathbf{p} - q\mathbf{A}$ and $E \to E + q\phi$:

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi \quad \Longleftrightarrow \quad i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}[-i\hbar\boldsymbol{\nabla} - q\mathbf{A}]^2\psi + (q\phi)\psi$$

Gauge transformation and gauge invariance: for the Schrödinger equation to be gauge invariant, the gauge transformation requires an additional phase factor of the wavefunction:

$$\mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} f \quad ; \quad \phi' = \phi - \frac{\partial f}{\partial t} \quad ; \quad \psi' = \psi e^{i(q/\hbar)f}$$

[**Derivation**] Figure out that the Λ in phase factor $e^{i\Lambda}$ is $\frac{q}{\hbar}f(\mathbf{r}, t)$ by substitution.

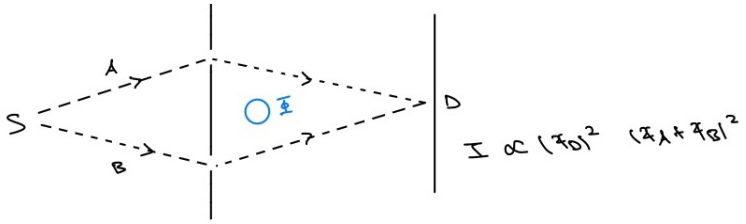
For $\mathbf{B} = \mathbf{0}$, we can choose a continuum of gauges, $\mathbf{A}(\mathbf{r}) = \boldsymbol{\nabla}\chi(\mathbf{r})$. Choosing $f = -\chi$, we have the transformation:

$$\mathbf{A}' = \mathbf{A} - \boldsymbol{\nabla}\chi = 0 \quad ; \quad \psi'(\mathbf{r}) = \psi_0(\mathbf{r}) = \psi_\chi(\mathbf{r})e^{-i(q/\hbar)\chi}$$

Thus, we can relate the wavefunction for $\mathbf{A} = 0$ with wavefunction for a general gauge, $\mathbf{A} = \boldsymbol{\nabla}\chi$:

$$\psi_\chi(\mathbf{r}) = \psi_0 e^{i(q/\hbar)\chi} = \psi_0(\mathbf{r}) \exp\left(i\frac{q}{\hbar}\int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{A}(\mathbf{s})\, d\mathbf{s}\right)$$

1. The Aharanov-Bohm Effect: is a quantum mechanical effect where a charged particle is affected by magnetic potential $\mathbf{A}$ even in regions with $\mathbf{B} = 0$. It shows up as A-B oscillations in semiconductor rings, due to periodic dependence of the electron phase on the Φ through the ring.



In the absence of flux, $\int_S \mathbf{B}\cdot d\mathbf{S} = \int_A \mathbf{A}\cdot d\mathbf{s} - \int_B \mathbf{A}\cdot d\mathbf{s} = 0$, the phase factor are equal and the interference pattern is independent of the choice of gauge.

After placing a shielded solenoid carrying flux Φ, we still have $\mathbf{B} = 0$ everywhere but now, $\mathbf{A} = (A_\rho = 0, A_\phi = \frac{\Phi}{2\pi\rho}, A_z = 0)$ outside the solenoid. $\int_S \mathbf{B}\cdot d\mathbf{S} = \int_A \mathbf{A}\cdot d\mathbf{s} - \int_B \mathbf{A}\cdot d\mathbf{s} = \Phi \neq 0$.

$$\psi_{D,\chi} = [\psi_{A,0}e^{i(q/\hbar)\Phi} + \psi_{B,0}] \exp\left(i\frac{q}{\hbar}\int_B \mathbf{A}\cdot d\mathbf{s}\right)$$

$$I \propto |\psi_{D,\chi}|^2 = |\psi_{A,0}e^{i\delta} + \psi_{B,0}|^2$$

The interference pattern is now predicted to depend on the flux Φ contained in the solenoid.

$$\delta = 2\pi\frac{e}{h}\Phi = 2\pi\frac{\Phi}{\Phi_0} \quad \text{where} \quad \Phi_0 = \frac{h}{e} \text{ is the flux quantum}$$

2. Landau levels: at low T and high (uniform) B, cyclotron orbits of charged particles becomes quantised, occupying discrete and equidistant Landau levels. These levels are degenerate, with the number of electrons per level directly proportional to the strength of the applied magnetic field.

$$\Delta E = \hbar\omega_c = \frac{\hbar q B}{m}$$

Method 1: Rewriting the Hamiltonian as number operator

$$\text{Hamiltonian: } \hat{H} = \frac{(\hat{p} - q\hat{A})^2}{2m} = \frac{\hat{\mathbf{\Pi}}^2}{2m}$$

[**Exercise**] Commutation: $[\hat{\Pi}_x, \hat{\Pi}_y] = i\hbar q(\boldsymbol{\nabla} \times A)_z = i\hbar q B_z$. Let $\hat{a} = \frac{1}{\sqrt{2q\hbar B}}(\hat{\Pi}_x + i\hat{\Pi}_y)$. We find in uniform $\mathbf{B} = (0, 0, B)$, we get the familiar $[\hat{a}, \hat{a}^\dagger] = \frac{B_z}{B} = 1$. [**Exercise**] Finally, we can find $\hat{a}^\dagger\hat{a} = \frac{1}{2q\hbar B}(\hat{\mathbf{\Pi}}^2 - \hat{\Pi}_z^2) - \frac{1}{2}$. So,

$$\hat{H} = \hbar\omega_c\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + \frac{\hat{\Pi}_z^2}{2m} \quad \text{where} \quad E = \hbar\omega_c\left(n + \frac{1}{2}\right)$$

Method 2: Working in a different gauge, e.g. the Landau gauge: $\mathbf{A}(\mathbf{r}) = (-By, 0, 0)$,

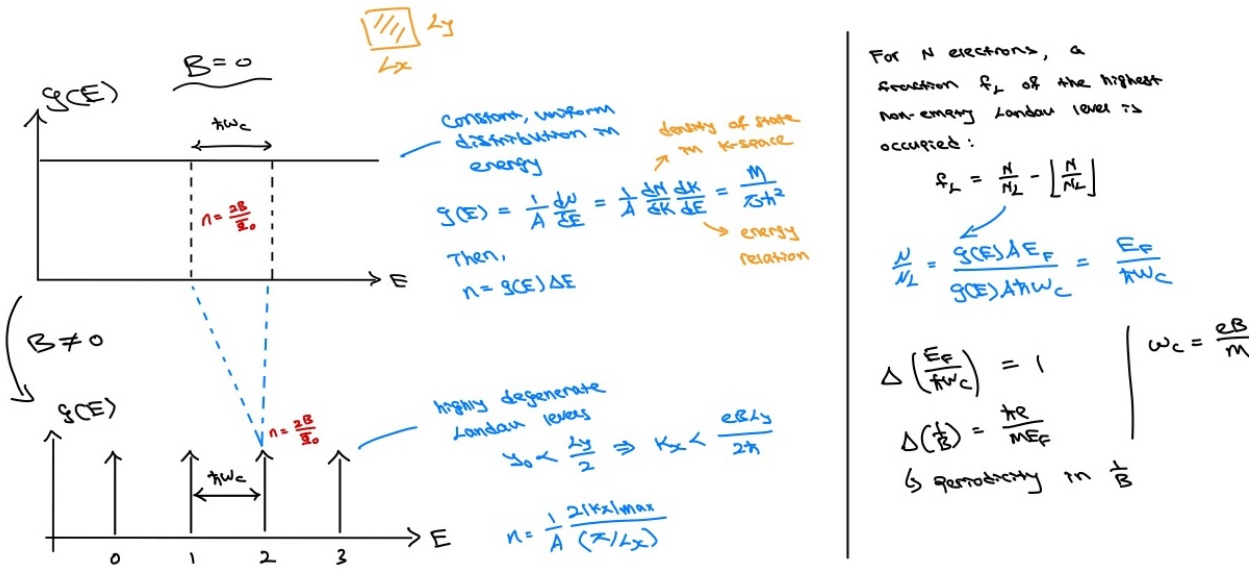
$$\text{Hamiltonian: } \hat{H} = \frac{1}{2m}[(\hat{p}_x - eBy)^2 + \hat{p}_y^2 + \hat{p}_z^2]$$

We can see that $[p_x, H] = [p_z, H] = 0$, we can write the solution to time-dependent Schrodinger's equation as: $\psi = e^{i(k_x x + k_z z)}\chi(y)$. [**Exercise**] $\hat{H}\psi = E\psi$ simplifies to:

$$\hat{H} = \frac{1}{2m}[(\hbar k_x - eBy)^2 + \hat{p}_y^2 + \hbar^2 k_z^2] = \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega_c^2(y - y_0)^2 + \frac{\hbar^2 k_z^2}{2m} \quad \text{with} \quad y_0 = \frac{\hbar k_x}{eB}$$

It has the form of a SHO shifted to y_0. As follows, $E = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m}$.

Experimental observation: 2D electron gas



3 Spin and magnetic moment interaction

$$\text{Magnetic moments: Orbital part: } \boldsymbol{m}_L = \left(\frac{g_L e}{2m}\right)\mathbf{L} \quad \text{and} \quad \text{Spin part: } \boldsymbol{m}_S = \left(\frac{g_S e}{2m}\right)\mathbf{S}$$

where the intrinsic spins has a **g-factor correction**. Define: Bohr/nuclear magneton, $\mu_{B/N} = \frac{e\hbar}{2m_{e/p}}$.

$$\text{Overall Hamiltonian: } \hat{H} = -\boldsymbol{m}\cdot\boldsymbol{B} = -\frac{e}{2m}\left(\hat{\boldsymbol{L}} + g_s\hat{\boldsymbol{S}} + g_I\hat{\boldsymbol{I}}\right)\cdot\mathbf{B}$$

and $\boldsymbol{S} = m_s\hbar$, $\boldsymbol{L} = m_l\hbar$ and $\boldsymbol{I} = m_I\hbar$.

Larmor precession - spin S particle moving in B-field

Approach 1: Operator

[**Exercise** - ES1 Qn 8] Time evolution of the spin given by Ehrenfest's theorem is: $\frac{d\hat{\boldsymbol{S}}}{dt} = \frac{1}{i\hbar}[\hat{\boldsymbol{S}}, \hat{H}] = \gamma_S\hat{\boldsymbol{S}}\times\mathbf{B}$.

This corresponds to precession of $\hat{\boldsymbol{S}}$ around $\mathbf{B}$ at the Larmor frequency ω_s,

$$\omega_s = \gamma_S B = \frac{g}{2}\omega_c \qquad \text{where } \omega_c = \frac{qB}{m} \text{ is the cyclotron frequency}$$

Consider $\hat{H}\left|s, m_s\right\rangle = E_{m_s}\left|s, m_s\right\rangle \Rightarrow E_{m_s} = -m_s\hbar\omega_s$, we obtain a set of $(2s+1)$ equally spaced energy levels, with $\Delta E = \hbar\omega_s$.

Approach 2: Wavefunction

[**Exercise**] For a particle starting out in a spin eigenstate, $\left\langle s, m_s\right|\hat{S}\left|s, m_s\right\rangle = (0, 0, m_s\hbar)$. The expectation value $\langle\hat{S}\rangle$ remains constant and directed along z-direction.

[**Derivation**] Now, for an arbitrary initial spin state, $|\psi(0)\rangle = \sum_{m_s} c_{m_s}\left|s, m_s\right\rangle$, at time t, $|\psi(t)\rangle = \sum_{m_s} c_{m_s}e^{im_s\omega_s t}\left|s, m_s\right\rangle$ by Ehrenfest's theorem.

$$\langle\hat{S}_{x,y}\rangle = \underbrace{A_{x,y}\cos\omega_s t + B_{x,y}\sin\omega_s t}_{\text{precession about B at } \omega_s} \quad \text{and} \quad \langle\hat{S}_z\rangle = \sum_{m_s}|c_{m_s}|^2 m_s\hbar = \text{const.}$$

Magnetic moment of electron - QED predicts magnetic moment as a power series in the fine structure constant α such that: $g_e = 2 + g^{(1)}\left(\frac{\alpha}{\pi}\right) + g^{(2)}\left(\frac{\alpha}{\pi}\right)^2 + g^{(3)}\left(\frac{\alpha}{\pi}\right)^3 + \ldots$ where $\alpha = \frac{1}{137}$.

Magnetic moment of muon - the difference between spin and cyclotron frequency is apparently an important quantity to measure muon magnetic moments: $\omega_a = \omega_s - \omega_c = \frac{g-2}{2}\frac{qB}{m} = a_\mu\omega_c$.

For $g = 2$, $\omega_a = 0$, the muon spin vector remains aligned with muon momentum. Nothing interesting.

For $g = 2.0023$, the muon spin precesses slightly faster than the momentum vector. In each orbit, the spin direction rotates slightly more than 360°. So, as the muons decay, e^- are preferentially emitted opposite to spin in muon's rest frame. After a γ-boost to transform to lab frame, $E^e_{lab} \approx \gamma E^*(1 + \cos\theta^*)$. The number of muons detected varies with time, with a periodic structure corresponding to the frequency $\boldsymbol{\omega_a}$ for which the spin $\mathbf{S}$ rotates relative to momentum $\mathbf{p}$.

The Stern-Gerlach Experiment

Consider a beam of neutral particles sent into a slowly varying magnetic field: $\mathbf{B}(\mathbf{r}) = \mathbf{B}_0 + \mathbf{B}_1(\mathbf{r})$. Let $\mathbf{B}_0 = (0, 0, B_0)$ and we have $\boldsymbol{m}_s = \gamma_S \hat{\boldsymbol{S}}$.

$$\text{Hamiltonian: } \hat{H} = \frac{\hat{\boldsymbol{p}}}{2m} - \boldsymbol{m}_S \cdot \mathbf{B} = \frac{\hat{\boldsymbol{p}}}{2m} - \gamma_S(\hat{S}_z B_0 + \hat{\boldsymbol{S}} \cdot \mathbf{B}_1(\mathbf{r}))$$

[**Derivation**] Ehrenfest's theorem gives:

$$\frac{d\hat{\boldsymbol{r}}}{dt} = \frac{\hat{\boldsymbol{p}}}{m} \quad \text{and} \quad \frac{d\hat{\boldsymbol{p}}}{dt} = \gamma_S(\hat{S}_x \boldsymbol{\nabla} B_{1,x} + \hat{S}_y \boldsymbol{\nabla} B_{1,y} + \hat{S}_z \boldsymbol{\nabla} B_{1,z})$$

[**Exercise**] If we neglect $\mathbf{B}_1$, the spin component evolves according to $\hat{H} = -\gamma_S \hat{S}_z B_0$, then if for initially in spin eigenstate, $\langle \hat{S}_z \rangle = m_s \hbar$:

$$\frac{d\langle \hat{\boldsymbol{p}} \rangle}{dt} = \gamma_S m_s \hbar \boldsymbol{\nabla} B_{1,z}$$

For general initial spin state:

$$\text{Equation of motion: } \mathbf{F} = \gamma_S \left(\sum_{m_s} |c_{m_s}|^2 m_s \hbar \right) \boldsymbol{\nabla} B_{1,z}$$

There are (2s+1) possible trajectories, corresponding to each m_s. The intensity of each beam is proportional to $|c_{m_s}|^2$. The equation of motion can be solved to find the actual trajectory of the particles using $z = \frac{1}{2} a t^2 = \frac{1}{2} \frac{F}{m} \left[\frac{L}{v} \right]^2$.

For an atom, the total internal angular momentum is: $\hat{\boldsymbol{F}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}} + \hat{\boldsymbol{I}}$. And $F = L \otimes S \otimes I$.
$\hat{\boldsymbol{L}}$: orbital electrons. $\hat{\boldsymbol{S}}$: spin electrons. $\hat{\boldsymbol{I}}$: spin nucleus.

4 Approximate Methods 1: Perturbation Theory

4.1 Time-independent perturbation theory (Sakurai p303/Gasiorowicz C11)

Given a perturbed Hamiltonian of the form: $\hat{H}^{(0)} + \hat{H}'$, and writing $\hat{H}' = \lambda \hat{H}^{(1)}$

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)}) \left|n\right\rangle = E_n \left|n\right\rangle$$

where as λ varies from 0 to 1, the energy change smoothly away from the unperturbed state (akin to turning on the perturbation).

We look for solutions of power series in λ:

$$E_n = E_n^{(0)} + \underbrace{\lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...}_{\text{corrections}} = \sum_m \lambda^m E_n^{(m)}$$

$$\left|n\right\rangle = \left|n^{(0)}\right\rangle + \underbrace{\lambda \left|n^{(1)}\right\rangle + \lambda^2 \left|n^{(2)}\right\rangle + ...}_{\text{corrections}} = \sum_m \lambda^m \left|n^{(m)}\right\rangle$$

where the corrections can be chosen such that they are orthogonal to the solutions of the unperturbed Hamiltonian i.e. $\left\langle n^{(k)} \middle| n^{(0)} \right\rangle = 0$.

Substituting back into the Hamiltonian and comparing same powers of λ yields:

$$\lambda^1 : \quad \hat{H}^{(0)} \left|n^{(1)}\right\rangle + \hat{H}^{(1)} \left|n^{(0)}\right\rangle = \hat{E}_n^{(0)} \left|n^{(1)}\right\rangle + \hat{E}_n^{(1)} \left|n^{(0)}\right\rangle$$

$$\lambda^2 : \quad \hat{H}^{(0)} \left|n^{(2)}\right\rangle + \hat{H}^{(1)} \left|n^{(1)}\right\rangle = \hat{E}_n^{(0)} \left|n^{(2)}\right\rangle + \hat{E}_n^{(1)} \left|n^{(1)}\right\rangle + \hat{E}_n^{(2)} \left|n^{(0)}\right\rangle$$

First-order correction (non-degenerate)

Energy correction

[**Derivation**] Consider the λ^1 term and take inner product with $\left|n^{(0)}\right\rangle$, we get the 1^{st} order correction in energy which is just the **expectation value of the perturbation in the unperturbed state**:

$$\boxed{\Delta E_n^{(1)} = \left\langle n^{(0)} \right| \hat{H}' \left|n^{(0)}\right\rangle}$$

Wavefunction correction

[**Derivation**] 1^{st} order wavefunction correction can be expressed as linear combination of the complete set of unperturbed eigenstates: $\left|n^{(1)}\right\rangle = \sum_m \left\langle m^{(0)} \middle| n^{(1)} \right\rangle \left|m^{(0)}\right\rangle$. Consider the λ^1 term and take inner product with $\left|m^{(0)}\right\rangle$, we can get the expansion coefficients, provided non-degeneracy where $E_m^{(0)} \neq E_n^{(0)}$. The perturbed eigenstate to first order is then:

$$\boxed{\Delta \left|n^{(1)}\right\rangle = \sum_m \frac{\left\langle m^{(0)} \right| \hat{H}' \left|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \left|m^{(0)}\right\rangle}$$

Second-order correction

[**Derivation**] Repeating the same procedure now for the λ^2 term and using some results from first-order correction:

$$\boxed{\Delta E_n^{(2)} = \sum_m \frac{|\left\langle m^{(0)} \right| \hat{H}' \left|n^{(0)}\right\rangle|^2}{E_n^{(0)} - E_m^{(0)}}}$$

[Example 1] Infinite square well ($-a < x < a$) with central bump ($-b < x < b$)

$$\hat{H}' = \begin{cases} \epsilon, & |x| < b \\ 0, & \text{otherwise} \end{cases}$$

Write down: $E_n^0 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{4a^2} = n^2 E_0$ and $\left|n^{(0)}\right\rangle = \psi_n(x) = \sqrt{\frac{1}{a}}\sin\left[\frac{n\pi}{2a}(x+a)\right]$.

$$[\textbf{Exercise}] \quad \Delta E_n^{(1)} = \langle \hat{H}' \rangle = \epsilon \int_{-b}^{b} |\psi_n(x)|^2 dx$$

[**Exercise**] For second-order correction, consider: $\left\langle m^{(0)}\right| \hat{H}' \left|n^{(0)}\right\rangle = \epsilon \int_{-b}^{b} \psi_m^*(x)\psi_n(x)dx$.

[Example 2] Infinite square well in E-field

$$\hat{H}' = \epsilon x = -qEx$$

$$E_n^{(1)} = \epsilon \int_{-a}^{b} x|\psi_n(x)|^2 dx \quad \text{and} \quad \Delta\left|n^{(1)}\right\rangle = \frac{\epsilon}{E_0}\sum \left|m^{(0)}\right\rangle \frac{\left\langle m^{(0)}\right| x \left|n^{(0)}\right\rangle}{n^2 - m^2}$$

$$E_n^{(2)} = \frac{\epsilon^2}{E_0}\sum \frac{|\left\langle m^{(0)}\right| x \left|n^{(0)}\right\rangle|^2}{n^2 - m^2}$$

[**Exercise**] Just do the integration and math.

[Example 3] Harmonic oscillator with linear perturbation

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \epsilon\hat{x}$$

[**Exercise**] Trick is to express $\hat{x}$ in terms of ladder operators. So, first-order energy correction is:

$$E_n^{(1)} = \epsilon \langle n|\, \hat{x}\, |n\rangle \propto \langle n|\, \hat{a}\, |n\rangle + \langle n|\, \hat{a}^\dagger\, |n\rangle = 0$$

[**Exercise**] Second-order energy correction is:

$$E_n = E_n^{(0)} + \Delta E_n^{(1)} + \Delta E_n^{(2)} = E_n^{(0)} + 0 + \epsilon^2 \sum \frac{|\langle m|\, \hat{x}\, |n\rangle|^2}{E_n^{(0)} - E_m^{(0)}} = \ldots = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{\epsilon^2}{2m\omega^2}$$

Can also be derived by completing the square for the potential, $V(x) = \frac{1}{2}m\omega^2 x^2 + \epsilon x$.

[Example 4] Van der Waal's interactions

$$\hat{H} = \hat{H}_0 + V = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2} + \frac{1}{|\mathbf{r} + \mathbf{r}_2 - \mathbf{r}_1|} - \frac{1}{|\mathbf{r} + \mathbf{r}_2|} - \frac{1}{|\mathbf{r} - \mathbf{r}_1|}\right)$$

For $r \gg a_0$, using multi-pole expansion: $V = \frac{e^2}{4\pi\epsilon_0 r^3}(x_1x_2 + y_1y_2 - 2z_1z_2) + \mathcal{O}(\frac{1}{r^4})$, which corresponds to the interaction of two electric dipoles $e\mathbf{r}_1$ and $e\mathbf{r}_2$ separated by distance r. $\Delta E_0^1 = 0$ and $\Delta E^{(2)} \propto \left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{r^3}\right)^2 \times (-1) \propto -1/r^6$.

4.2 Degenerate perturbation theory

$$\hat{H}^{(0)}\left|n_j^{(0)}\right\rangle = E_n^{(0)}\left|n_j^{(0)}\right\rangle \quad \text{where } j = 1, 2, ..., g \quad \text{(degeneracy g)}$$

We want to form a good basis using linear combinations degenerate eigenstates, such that in the subspace of those degenerate states, the perturbation matrix is diagonal.

$$\hat{H}' = \begin{pmatrix} H'_{00} & \cdots & \cdots & \cdots & . \\ \vdots & E'_{n,1} & & & . \\ . & & \ddots & & . \\ \vdots & & & E'_{n,g} & . \\ . & \cdots & \cdots & \cdots & . \end{pmatrix}$$

Method 1: Diagonalisation

Step 1: Find the matrix representation of H' in the given initial basis of eigenstates $\left|n_j^{(0)}\right\rangle$ for that energy level:

$$\hat{H}'_{jk} = \left\langle n_j^{(0)}\right| \hat{H}' \left|n_k^{(0)}\right\rangle = E'_{n,j}\delta_{jk}$$

Step 2: Diagonalise it by finding eigenvalues $E'_{n,\alpha}$ and eigenvectors $\left|n_\alpha^{(0)}\right\rangle$ of the matrix H':

$$\underbrace{\begin{pmatrix} H'_{11} & H'_{12} & \cdots & H'_{1g} \\ H'_{21} & H'_{22} & \cdots & H'_{2g} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{g1} & H'_{g2} & \cdots & H'_{gg} \end{pmatrix}}_{H'_{jk}} \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ \vdots \\ c_{g\alpha} \end{pmatrix} = E'_{n,\alpha} \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ \vdots \\ c_{g\alpha} \end{pmatrix} \qquad \text{and} \qquad \left|n_\alpha^{(0)}\right\rangle = \sum_{j=1}^{g} c_{j\alpha}\left|n_j^{(0)}\right\rangle$$

Method 2: Find an operator that commutes with $\hat{H}$

Spot a hermitian operator $\hat{A}$ that commutes with the full Hamiltonian, $\hat{H}$ (common eigenbasis). Provided they have different eigenvalues, then the basis is good. This gives us another way, hopefully easier, to find the eigenstates of H instead of diagonalising it.

Consider $\left|n_p^{(0)}\right\rangle$ and $\left|n_q^{(0)}\right\rangle$ with $\hat{A}$ eigenvalue $a_p \neq a_q$,

$$\begin{aligned} 0 &= \left\langle n_p^{(0)}\right| [\hat{A}, \hat{H}'] \left|n_q^{(0)}\right\rangle \\ &= \left\langle n_p^{(0)}\right| \hat{A}\hat{H}' \left|n_q^{(0)}\right\rangle - \left\langle n_p^{(0)}\right| \hat{H}'\hat{A} \left|n_q^{(0)}\right\rangle \\ &= (a_p - a_q)\left\langle n_p^{(0)}\right| \hat{H}' \left|n_q^{(0)}\right\rangle \end{aligned}$$

$$\Rightarrow \left\langle n_p^{(0)}\right| \hat{H}' \left|n_q^{(0)}\right\rangle = 0$$

It works! But what is $\hat{A}$ though, more on this later on.

First order energy correction: $\Delta E_{n,\alpha}^{(1)} = \left\langle n_\alpha^{(0)}\right| \hat{H}' \left|n_\alpha^{(0)}\right\rangle = E'_{n,\alpha} \quad (\alpha = 1, 2, 3, ...g)$

The corrections are just the eigenvalues of H' in the good basis. Also, the energy correction for each of the g degenerate states is different so the perturbation kills the degeneracy. The original energy level $E_n^{(0)}$ splits into g distinct levels in the presence of H'.

4.3 Time-dependent perturbation theory

Given a Hamiltonian with a small time-dependent perturbation $\hat{H}(t) = \hat{H}_0 + \lambda\hat{H}(t)$.

Start with the Schrodinger's equation:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \left[\hat{H}_0 + \lambda\hat{H}(t)\right]|\psi(t)\rangle$$

Writing a state vector as a basis expansion:

$$|\psi(t)\rangle = \sum_j c_j(t)e^{-i\omega_j t}|j\rangle \quad , \quad c_j(t) = c_j^{(0)} + \lambda c_j^{(1)} + ...$$

Sub into Schrodinger's equation, expand out LHS, H_0 term cancels and take inner product with $\langle k|$:

$$i\hbar\frac{dc_k}{dt} = \sum_j c_j e^{i(\omega_k-\omega_j)t}H'_{kj}$$

Group powers of λ,

$$\lambda^0 : i\hbar\frac{d}{dt}c_k^{(0)} = 0 \implies c_k^{(0)} = c_k^{(0)}(t=0)$$

$$\lambda^1 : i\hbar\frac{d}{dt}c_k^{(1)} = \sum_j c_j^{(0)}e^{i(\omega_k-\omega_j)t}H'_{kj}(t)$$

Suppose system is initially in state $|0\rangle$, so at $t = 0$, the only non-zero term is $c_0^{(0)} = 1$:

$$\boxed{c_k(t) = \frac{1}{i\hbar}\int_0^t e^{i(\omega_k-\omega_0)t'}H'_{k0}(t')dt'}$$

The probability of transition from $|0\rangle \to |k\rangle$ is

$$P(0 \to k) = |c_k|^2$$

Fermi's Golden Rule
Consider monochromatic perturbation of the form:

$$\hat{H}' = \hat{U}e^{-i\omega t} + \hat{U}^\dagger e^{i\omega t}$$

We use time-dependent perturbation theory to find c_k:

$$c_k(t) = \frac{1}{i\hbar}\int_0^t e^{i(\omega_k-\omega_0-\omega)t'}U_{k0}dt' + \frac{1}{i\hbar}\int_0^t e^{i(\omega_k-\omega_0+\omega)t'}U_{k0}^\dagger dt' \tag{1}$$

$$= \underbrace{-\frac{1}{\hbar}U_{k0}\frac{e^{i(\omega_k-\omega_0-\omega)t}-1}{\omega_k-\omega_0-\omega}}_{\text{absorption}}\underbrace{-\frac{1}{\hbar}U_{k0}^\dagger\frac{e^{i(\omega_k-\omega_0+\omega)t}-1}{\omega_k-\omega_0+\omega}}_{\text{emission}} \tag{2}$$

Compute $|c_k|^2$ for each of the two terms and get:

$$P(0 \to k) = |c_k|^2 = \frac{1}{\hbar^2}|U_{k0}|^2\frac{\sin^2(\Delta\omega/2\cdot t)}{(\Delta\omega/2)^2} \to \frac{2\pi t}{\hbar^2}|U_{k0}|^2\delta(\omega_k-\omega_0\pm\omega) \quad \text{as} \quad t\to\infty$$

We can get the transition rate:

$$\boxed{\Gamma(0\to k) = \frac{|c_k|^2}{t} = \frac{2\pi}{\hbar}|U_{k0}|^2\delta(E_k-E_0\pm\hbar\omega) = \frac{2\pi}{\hbar}|U_{k0}|^2 g(E_k)}$$

5 Approximate Methods 2: Variational Method

For a given trial wavefunction $|\Psi_{trial}(\alpha_i)\rangle$, we can find an upper bound on ground state energy E_0,

$$E_0 \leq \min(E_\alpha) = \min_\alpha \frac{\langle\Psi_{trial}(\alpha_i)|\,\hat{H}\,|\Psi_{trial}(\alpha_i)\rangle}{\langle\Psi_{trial}(\alpha_i)|\Psi_{trial}(\alpha_i)\rangle}$$

Trial wavefunction can be parameterised by a variational parameter α_i which can be used to attempt to minimise E_α w.r.t. α. (optimisation)

Proof:
For

$$|\psi(\alpha)\rangle = \sum_n a_n(\alpha)\,|n\rangle \quad \text{and} \quad \hat{H}\,|n\rangle = E_n\,|n\rangle$$

Then,

$$E(\alpha) = \langle\psi(\alpha)|\,\hat{H}\,|\psi(\alpha)\rangle = \sum_n |a_n(\alpha)|^2 E_n$$

By definition, the ground state energy is the lowest energy,

$$E_n \geq E_0$$

So $E(\alpha)$ place an upper bound on ground state energy,

$$E(\alpha) \geq E_0 \sum_n |a_n(\alpha)|^2 = E_0$$

A wise choice of trial wavefunction would give a better bound, it should in general:

- Satisfy symmetry properties and boundary conditions.
- The closer it is to the true (but unknown) ground state function, the closer the minimum will be to the true E_0.

Rayleigh-Ritz Method

If we use a trial function of the form:

$$\psi(\mathbf{r}) = \sum_j \alpha_j \psi_j(\mathbf{r})$$

where ψ_j are a linearly independent set of wavefunctions, which do not necessarily have to be complete or orthogonal. For example, in molecular physics, states can be approximated as a Linear Combination of (single-electron) Atomic Orbitals (LCAO).

Formulation of the problem:

$$\text{min.} \quad \langle E\rangle = \frac{\langle\psi|\,\hat{H}\,|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{j,k}\alpha_j\alpha_k H_{jk}}{\sum_{j,k}\alpha_j\alpha_k S_{jk}}$$

where $H_{jk} = \langle\psi_j|\,\hat{H}\,|\psi_k\rangle = H^*_{jk}$ are the matrix elements of H in the basis $\{\psi_j\}$ and $S_{jk} = \langle\psi_j|\psi_k\rangle = S^*_{kj}$ are the overlap integrals used for normalisation, in case the wavefunctions are not orthonormal. We can

minimise $\langle E \rangle$ w.r.t. the variational parameter α_i through $\frac{\partial \langle E \rangle}{\partial \alpha_i} = 0$. [**Derivation**] After doing lots of math and simplifying, we get:

$$\boxed{\det(H - E_{min}S) = 0}$$

The lowest of the resulting set of eigenvalues E_{min} provides the best upper bound on the ground state energy.

6 Application: The 'real' hydrogen atom (Gasiorowicz C12)

1. "Switch on" **electron spin**.
2. Add leading-order **relativistic effects** [relativistic KE correction + SO coupling + Darwin term] $\rightarrow$ fine structure
3. "Switch on" **nuclear spin** [coupling of p^+ and e^- spin] $\rightarrow$ hyperfine structure

1. Switch on electron spin (trivial)

The zeroth order Hamiltonian remains as $\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$. Since H_0 does not contain the spin operator $\hat{S}$, direct products of spatial and spin states are energy eigenstates. $|nlm_s sm_s\rangle = |nlm_l\rangle \otimes |sm_s\rangle$.

$$\textbf{Energy: } E_n = -\frac{Z^2}{n^2} R_\infty \quad \text{with total degeneracy } g = 2n^2$$

2 possible basis: $|nlm_l\rangle\,|sm_s\rangle$ (uncoupled) or $|njm_j ls\rangle$ (coupled) - related by Clebsch-Gordon coeff. Each set of $\{n, l, s\}$ is degenerate.

The Hamiltonian commutes with all angular momentum operators: $\mathbf{L}$, $\mathbf{L}^2$, $\mathbf{S}$, $\mathbf{S}^2$, $\mathbf{J}$ and $\mathbf{J}^2$. So, $\{l, m_l, s, m_s, j, m_j\}$ are all good quantum numbers.

Spectroscopic notation:

$$n^{2S+1}L_j$$

where $L = \{S, P, D, F, ...\}$. E.g. $1^2S_{1/2}$ / $2^2S_{1/2}$, $2^2P_{1/2}$ and $2^2P_{3/2}$...

2. Relativistic corrections - Fine structure (Sakurai page 494)

Start with the relativistic relation: $E^2 \overset{K-G}{=} |\mathbf{p}|^2c^2 + m^2c^4 \overset{Dirac}{=} (c\,\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2)^2$

The first part of the relation gets us the Klein-Gordan equation which describes relativistic particles of 0-spin. The attempt at square-rooting in the second part gives us the Dirac equation for 1/2-spin particles:

$$i\hbar\partial_t\psi = \hat{H}\psi \quad \text{where} \quad \hat{H} = c\boldsymbol{\alpha}\cdot\hat{\boldsymbol{p}} + \beta mc^2$$

where:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix}$$

$\boldsymbol{\sigma}$ are Pauli matrices.

Now, an external EM field can be introduced via the minimal substitution prescription: $\mathbf{p} \rightarrow \mathbf{p} - q\mathbf{A}$ and $E \rightarrow E + q\phi$. Keeping terms up to v^2/c^2, the Dirac equation becomes:

$$(E' - q\phi)\psi = [\underbrace{\frac{(\hat{\boldsymbol{p}} - q\mathbf{A})^2}{2m} - \frac{q}{m}(\hat{\boldsymbol{S}}\cdot\mathbf{B})}_{(1)} \underbrace{- \frac{\hat{\boldsymbol{p}}^4}{8m^3c^2}}_{\substack{\text{relativistic} \\ \text{corr. } (\hat{H}_R)}} \underbrace{+ \frac{q\hbar^2}{8m^2c^2}(\nabla^2\phi)}_{\substack{\text{Darwin} \\ \text{corr. } (\hat{H}_D)}} \underbrace{+ \frac{q}{2m^2c^2}\hat{\boldsymbol{S}}\cdot(\boldsymbol{\nabla}\phi\times\hat{\boldsymbol{p}})}_{\substack{\text{Spin-orbit} \\ \text{coupling, } (\hat{H}_{SO})}}]\psi$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{\text{Perturbation } \hat{H}'}$$

where $E' = E - mc^2$ is the relativistic kinetic energy.

Part (1): the $\frac{(\hat{\boldsymbol{p}}-q\mathbf{A})^2}{2m}$ term includes a hidden contribution $-\frac{q}{2m}(\hat{\boldsymbol{L}}\cdot\mathbf{B})$. So the entire part (1) contains both an orbital and spin magnetic moment interaction:

$$\hat{H}_B = -\boldsymbol{m}\cdot\boldsymbol{B} \quad \text{with} \quad \boldsymbol{m} = \frac{q}{2m}(\hat{\boldsymbol{L}} + 2\hat{\boldsymbol{S}})$$

Relativistic correction:

$$E = \sqrt{\mathbf{p}^2c^2 + m^2c^4} = mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{(\mathbf{p}^2)^2}{8m^3c^2} + ...$$

Hence,

$$\hat{H}_R = -\frac{\hat{\boldsymbol{p}}^2}{8m^3c^2}$$

which can be understood physically as the first-order relativistic correction to the electron energy.

Spin-orbit interaction:

For central potential:

$$\boldsymbol{\nabla}\phi = \frac{1}{r}\frac{d\phi}{dr}\mathbf{r} \quad \text{so} \quad \boldsymbol{\nabla}\phi\times\hat{\boldsymbol{p}} = \frac{1}{r}\frac{d\phi}{dr}(\mathbf{r}\times\hat{\boldsymbol{p}}) = \frac{1}{r}\frac{d\phi}{dr}\hat{\boldsymbol{L}}$$

Hence,

$$\hat{H}_{SO} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}} \quad \text{where } V = -e\phi$$

which can be understood semi-classically as a result of relative motion between electron and proton, the electron spin interacts with apparent magnetic field of proton. For H-like atom, $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$, so:

$$\hat{H}_{SO} = \frac{1}{2m^2c^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r^3}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$$

It is a bunch of things with $\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$

Darwin term: purely quantum in origin.

$$\hat{H}_D = -\frac{e\hbar^2}{8m^2c^2}(\boldsymbol{\nabla}^2\phi)$$

All 3 additional terms are small relative to $\hat{H}_0$, i.e. their ratio $\ll 1$. So, we can regard them as perturbations, allowing us to apply **degenerate perturbation theory**. These energy corrections will break the initial degeneracy, causing energy levels to split and giving levels known as **fine structure**.

(**Exercise**) Now let's go through the machinery to calculate the energy corrections:

Relativistic correction: the trick is to express H_R in terms of H_0 and work in the uncoupled basis, $|nlm_l\rangle\,|sm_s\rangle$:

$$\hat{H}_R = -\frac{1}{2mc^2}\left(\frac{\hat{\boldsymbol{p}}^2}{2m}\right) = -\frac{1}{2mc^2}(\hat{H}_0 - V)^2$$

where only $|nlm_l\rangle$ is relevant. H_R is diagonal in this basis within each n (Wigner-Eckart theorem).

$$\Delta E^{(1)}_{n,R} = \langle nlm_l|\,\hat{H}_R\,|nlm_l\rangle$$

We then have to compute $\langle 1/r\rangle$ and $\langle 1/r^2\rangle$ that comes from V and V^2. After all the computation[1]:

$$\boxed{(\Delta E)_R = \left(\frac{3}{n} - \frac{4}{\ell + 1/2}\right)\cdot\frac{Z^4\alpha^2 R_\infty}{4n^3}}$$

Effect: relativistic energy correction splits states with different ℓ

Spin-orbit correction, we need to evaluate the matrix elements of $\hat{H}_{SO}$ in the coupled basis, $|njm_jls\rangle$ (**proof in notes 4.33**). **The trick is to express $\mathbf{L}\cdot\mathbf{S}$ in terms of squares of angular momentum operators**:

$$\hat{H}_{SO} = \xi(r)\,\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}} = \xi(r)\times\frac{1}{2}(\hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2)$$

For each n, $\hat{H}_{SO}$ is diagonal, hence the zeroth order states forms a good basis for perturbation theory,

$$\begin{aligned}\Delta E^{(1)}_{n,SO} &= \langle njm_jls|\,\xi(r)\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\,|njm_jls\rangle \\ &= \frac{1}{2}[j(j+1) - l(l+1) - s(s+1)]\hbar^2\langle\xi(r)\rangle_{nl}\end{aligned}$$

We have to compute $\langle 1/r^3\rangle$ coming from $\xi(r)$ and noting that $s = 1/2$ only. Finally, we arrive at:

$$\boxed{(\Delta E)_{SO} = \pm\frac{2}{(j+1/2)(\ell+1/2)}\cdot\frac{Z^4\alpha^2 R_\infty}{4n^3} \quad , \quad \text{for } \ell \neq 0}$$

Effect: spin-orbit energy correction splits states with different ℓ and j

---

Darwin term, knowing the identity: $\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta^{(3)}(\mathbf{r})$. We can rewrite the Hamiltonian in more convenient form:

$$\hat{H}_D = \frac{Ze}{4\pi\epsilon_0}\frac{\hbar^2 e}{8m^2c^2}4\pi\delta^{(3)}(\mathbf{r})$$

After computing the expectation value $\langle\psi|\,\hat{H}_D\,|\psi\rangle$, we obtain:

$$\boxed{(\Delta E)_D = 4\cdot\frac{Z^4\alpha^2 R_\infty}{4n^3}\cdot \quad , \quad \text{for } \ell = 0}$$

$$\boxed{\Delta E \propto Z^4 \text{ and } \sim\frac{\alpha^2 R_\infty}{n^3}}$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$ is the fine structure constant and $R_\infty \approx 13.6eV$.

[1] Trick to figure out Z dependence is to use change of variable, $u = \frac{Zr}{a_0}$

Hydrogen atom fine structure

Adding all the corrections up gives the fine structure splitting:

$$\Delta E_{FS} = \Delta E_R + \Delta E_{SO} + \Delta E_D$$

Explicitly,

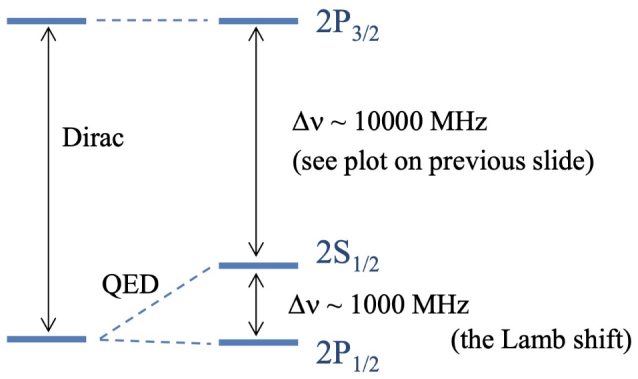
$$\Delta E_{FS} = \left(\frac{3}{n} - \frac{4}{j+1/2}\right) \cdot \frac{Z^4\alpha^2 R_\infty}{4n^3} < 0$$

Net effect: fine structure split states with different j only and lower the energies

This is what the Dirac equation got us, but the **lamb shift** is observed experimentally whereby the same j and different ℓ are not degenerate. The transition frequencies are found to be systematically smaller than Dirac prediction by:

$$\text{Lamb shift: } \Delta\nu \sim 1000 MHz$$

This can be explained with QED. Hence, QED corrections break the degeneracy in ℓ for fixed j.



3. Switch on nuclear spin - Hyperfine structure (F = L + S + I)

The proton magnetic dipole $\boldsymbol{m}_{S,p}$ sets up a magnetic-field $\mathbf{B}_p$, the electron magnetic dipole $\boldsymbol{m}_{S,e}$ interacts with this B-field and has energy, $-\boldsymbol{m}_{S,e} \cdot \mathbf{B}_p$[2],

$$\begin{aligned}\hat{H}_{hf} &= \frac{\mu_B}{\hbar}(\hat{\boldsymbol{L}} + g_e\hat{\boldsymbol{S}}) \cdot \mathbf{B}_p \\ &= \frac{\mu_B}{\hbar}(\hat{\boldsymbol{L}} + g_e\hat{\boldsymbol{S}}) \cdot \frac{\mu_0}{4\pi r^3}\frac{g_p\mu_N}{\hbar}\left[3(\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}} - \hat{\boldsymbol{I}} + \frac{8\pi r^3}{3}\hat{\boldsymbol{I}}\,\delta^{(3)}(\mathbf{r})\right]\end{aligned}$$

We can use first-order perturbation theory to find the energy correction for $\ell = 0$ (S-state),

$$\Delta E_{hf} = \frac{4g_e g_p}{3}\frac{m_e}{m_p} \cdot \frac{Z^3\alpha^2 R_\infty}{n^3}$$

Net effect: hyperfine structure split states with different F into $+\frac{1}{4}\Delta E_{hf}$ and $-\frac{3}{4}\Delta E_{hf}$

The hyperfine splitting for hydrogen is $\lambda = 21cm$ known as the 21-cm line. It is a magnetic dipole (M1) transition.

[2]Electromagnetism tells us that: $\mathbf{A} = \frac{\mu_0}{4\pi}\frac{\mathbf{m}\times\hat{\mathbf{r}}}{r^2}$ and $\mathbf{B}_p = \boldsymbol{\nabla}\times\mathbf{A} = \frac{\mu_0}{4\pi r^3}\left[3(\boldsymbol{m}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}} - \boldsymbol{m} + \frac{8\pi r^3}{3}\mathbf{m}\,\delta^{(3)}(\mathbf{r})\right]$

7 Symmetry in Quantum Mechanics - Unitarity

In QM, a symmetry transformation is implemented by a unitary operator $\hat{U}$ where $\hat{U}^\dagger\hat{U} = I$.

$$|\psi\rangle \to |\psi'\rangle = \hat{U}\,|\psi\rangle$$

- Probabilities and normalisations remains unchanged after the transformation:
  $|\,\langle\phi'|\psi'\rangle\,| = |\langle\hat{U}\phi\,|\,\hat{U}\psi\rangle|^2 = |\,\langle\phi|\psi\rangle\,|^2$.

- **Continuous symmetry and generators**
  Thanks to Lie, continuous symmetries can be described by infinitesimal transformations: $\hat{U}(\epsilon) = \hat{I} + i\epsilon\hat{T}$ where $\hat{T}$ is the hermitian generator. Any arbitrary transformation is made up of many small transformations:

  $$\boxed{\hat{U}(\theta) = \lim_{N\to\infty}\left(1 + i\frac{\theta}{N}\hat{T}\right)^N = e^{i\theta\hat{T}}}$$

  For example, $\hat{T} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$ is the generator of rotation.

- **Symmetries/invariance $\longrightarrow$ Conservation laws + Degeneracies + Selection rules**:
  Symmetry operation transforms an observable $\hat{A}$ according to: $\hat{A} \to \hat{U}^\dagger\hat{A}\hat{U}$. If $\hat{A}$ is invariant under the symmetry transformation ($\hat{A} = \hat{U}^\dagger\hat{A}\hat{U}$), then $\hat{A}$ and $\hat{U}/\hat{T}$ must commute. Specifically, **if the Hamiltonian of the system is invariant under symmetry transformation**, Ehrenfest's theorem tells us that $\hat{T}$ **is conserved**.

- Examples:

Symmetry	**Generator**	**Unitary operator**
Time translation	Hamiltonian[3]	$\hat{U}(t)\,\|\psi(0)\rangle = \|\psi(t)\rangle$ and $\hat{U}(t) = e^{-i\hat{H}t/\hbar}$
Spatial translation	Total linear momentum[4]	$\hat{U}(\mathbf{a})^\dagger\hat{\boldsymbol{r}}\hat{U}(\mathbf{a}) \to \hat{\boldsymbol{r}} + \mathbf{a}$; $\hat{U}(a)\psi(x) = \psi(x-a)$ and $\hat{U}(\mathbf{a}) = e^{-i\hat{\boldsymbol{P}}\cdot\mathbf{a}/\hbar}$
Rotation	Total angular momentum[5]	$\hat{U}^\dagger\hat{V}_i\hat{U} = R_{ij}\hat{V}_j$; $\hat{U}(\phi_0)\psi(\phi) = \psi(\phi+\psi_0)$ and $\hat{U}(\omega) = e^{i\hat{\boldsymbol{J}}\cdot\boldsymbol{\omega}/\hbar}$

Spatial rotations

$$R^T R = I \quad ; \quad det(R) = \pm 1$$

For infinitesimal rotation,

$R = I + \omega + \mathcal{O}(\omega^2)$, then $\omega^T = -\omega$ (antisymmetric $\Rightarrow$ traceless): $\omega = \begin{pmatrix} 0 & \omega_3 & -\omega_2 \\ -\omega_3 & 0 & \omega_1 \\ \omega_2 & -\omega_1 & 0 \end{pmatrix}$

$\boldsymbol{\omega} = (\omega_1, \omega_2, \omega_3)$

[3] The time-dependent Schrodinger's equation is just a consequence of invariance under time translation

[4] Invariance of a system under spatial translation implies the existence of a vector operator $\hat{\boldsymbol{P}}$ satisfying the commutation relation $[\hat{r}_j, \hat{P}_k] = i\hbar\delta_{jk}$. We identify $\hat{\boldsymbol{P}}$ as the total momentum operator. Further results of $[\hat{P}_j, \hat{P}_k] = 0$ and $\hat{\boldsymbol{P}} = i\hbar\boldsymbol{\nabla}$ can be derived. For instance, by Taylor expansion of $\psi(x-a)$ or knowing commutation $\hat{U}(a)\hat{U}(b) = \hat{U}(b)\hat{U}(a)$.

[5] See notes at page 5.24

7.1 Wigner-Eckart Theorem

Rotational symmetry places a tight **constraint** on the **structure** of operator matrix elements.

For **scalar operators** $\hat{K}$, whose matrix elements are invariant under rotations i.e. $\hat{U}(R)^\dagger \hat{K} \hat{U}(R) = \hat{K}$ and commutes with all rotation operators and their generators: $[\hat{\boldsymbol{J}}, \hat{K}] = 0$.

Scalar operators COMMUTE with any form of rotation operator

E.g. of scalar operators: $\hat{\boldsymbol{r}}^2, \hat{\boldsymbol{p}}^2, V(r), \hat{\boldsymbol{L}}^2, \hat{\boldsymbol{S}}^2, \hat{\boldsymbol{J}}^2,$ $\underbrace{\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}}_{\text{only w.r.t. } \hat{\boldsymbol{J}},\, \boldsymbol{S}^2,\, \boldsymbol{L}^2}$. Examples of rotation operator: $\hat{\boldsymbol{L}}, \hat{\boldsymbol{S}}, \hat{\boldsymbol{J}}$.

$$\text{Wigner-Eckart: } \langle \alpha'' j'' m'' | \hat{K} | \alpha' j' m' \rangle = \underbrace{\langle \alpha'' j'' | | \hat{K} | | \alpha' j' \rangle}_{\substack{\text{reduced matrix element} \\ \textbf{(a common constant)}}} \underbrace{\langle \mathbf{00}; j' m' | j'' m'' \rangle}_{\delta_{j'' j'} \delta_{m'' m'}}$$

In particular, $\langle \alpha j m | \hat{K} | \alpha j m \rangle = \langle \alpha j | | \hat{K} | | \alpha j \rangle$, meaning the expectation value of a scalar operator is independent of magnetic quantum number, m. This is because m arises from the choice of a arbitrary spatial direction e.g. z-direction by convention. The matrix elements of rotationally invariant operator like $\hat{H}$ cannot possibly depend on this choice.

This m-independence creates DEGENERACIES in m

[**Proof**] As a consequence of rotational invariance $[\hat{U}^\dagger \hat{V}_i \hat{U} = R_{ij} \hat{V}_j]$, **vector operators** are defined by:

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

E.g. of vector operators: $\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}, \hat{\boldsymbol{L}}, \hat{\boldsymbol{S}}, \hat{\boldsymbol{J}}$. Examples of rotation operator: $\hat{\boldsymbol{L}}, \hat{\boldsymbol{S}}, \hat{\boldsymbol{J}}$.

It is beneficial to represent any vector operator in terms of spherical components (V_{+1}, V_{-1}, V_0):

$$V_{+1} = -\frac{1}{\sqrt{2}}(V_1 + iV_2) \quad ; \quad V_{-1} = \frac{1}{\sqrt{2}}(V_1 - iV_2) \quad ; \quad V_0 = V_3$$

$$\text{Wigner-Eckart: } \langle \alpha'' j'' m'' | \hat{V}_m | \alpha' j' m' \rangle = \underbrace{\langle \alpha'' j'' | | \hat{\boldsymbol{V}} | | \alpha' j' \rangle}_{\text{common constant}} \underbrace{\langle \mathbf{1m}; j' m' | j'' m'' \rangle}_{\text{Clebsh-Gordan coeff.}}$$

Properties of Clebsh-Gordan coefficients leads to SELECTION RULES

$$m'' = m + m' \quad ; \quad j'' = j', j' \pm 1 \quad ; \quad j'' + j' \geq 1$$

Equivalently:

$$\Delta m = 0, \pm 1 \quad ; \quad \Delta j = 0, \pm 1 \quad ; \quad j'' + j' \geq 1$$

Another symmetry that gives us more selection rules is **parity inversion**:

$$\hat{P} : \mathbf{r} \to -\mathbf{r} \quad \text{with} \quad \hat{P}\,|\psi\rangle = P\,|\psi\rangle$$

where $P = \pm 1$. For hydrogen atom with wavefunction $|nlm_l\rangle$, $P = (-1)^l$.

$\langle\psi_1(\mathbf{r})|\,\hat{\boldsymbol{r}}\,|\psi_2(\mathbf{r})\rangle = -P_1P_2\,\langle\psi_1(\mathbf{r})|\,\hat{\boldsymbol{r}}\,|\psi_2(\mathbf{r})\rangle$, meaning that the matrix elements vanishes unless the eigenstates involved have opposite parity.

Selection rule: $P_1 \neq P_2$ or $(-1)^{l_1} \neq (-1)^{l_2}$

meaning $l_1 + l_2 = 1, 3, 5, \ldots$ i.e. $l_1 \neq l_2$

Electromagnetic interactions are invariant under parity. However, weak interactions do not conserve parity. This parity violation was observed in studies of β-decay of polarised cobalt-60 nuclei where electrons are emitted preferentially towards the direction of the ^{60}Co spin vector.

Application: selection rules for atomic transitions: Electric dipole (E1) transition between atomic states are governed by the matrix elements of the electric dipole operator, $\hat{\boldsymbol{d}} = -e\hat{\boldsymbol{r}}$.

The rate of photon absorption or emission are of the form:

$$\Gamma \propto (\Delta E)^3 \cdot |\,\langle\beta|\,\hat{\boldsymbol{d}}\,|\alpha\rangle\,|^2 = \sum_{m=0,\pm1} |\,\langle\beta|\,\hat{d}_m\,|\alpha\rangle\,|^2$$

For at least one matrix element, $\langle n_1 l_1 m_1|\,\hat{d}_m\,|n_2 l_2 m_2\rangle \neq 0$ the initial and final states of zeroth order H-atom must satisfy the selection rules:

$$\boxed{\Delta l = \pm 1 \quad ; \quad \Delta m_l = 0, \pm 1 \quad ; \quad l_1 + l_2 \geq 1}$$

The transition betwee $n = 3 \leftrightarrow 2$ is so special we call it the Balmer H_α line with $\lambda = 656.3$ nm (red). Also, the 2s level is metastable as it cannot decay to a lower energy state via an E1 transition. Hence, it has a relatively long lifetime.

(**Linear Stark effect**) For the z-component of the position operator, which is the $m = 0$ spherical component. The selection rules are:

$$\boxed{\Delta l = \pm 1 \quad ; \quad \Delta m_l = 0}$$

(L-S coupling) For fine structure H-atom, E1 selection rules apply to j and Δm_j, not to l and Δm_l: $\Delta j = 0, \pm 1$; $\Delta m_j = 0, \pm 1$; $j_1 + j_2 \geq 1$.

(L-S-I coupling) For hyperfine structure H-atom, E1 selection rules now apply to F:
$\Delta F = 0, \pm 1$; $\Delta m_F = 0, \pm 1$; $F_1 + F_2 \geq 1$.

Landé projection formula

The formula relates the matrix elements of $\mathbf{V}$ to matrix elements of the total angular momentum $\mathbf{J}$.

$$\boxed{\langle \alpha j m' | \, \hat{\boldsymbol{V}} \, | \alpha j m \rangle = \underbrace{\frac{\langle \alpha j m | \, \hat{\boldsymbol{V}} \cdot \hat{\boldsymbol{J}} \, | \alpha j m \rangle}{j(j+1)\hbar^2}}_{\text{factor}} \langle \alpha j m' | \, \hat{\boldsymbol{J}} \, | \alpha j m \rangle}$$

The derivation of the formula starts from writing down the Wigner-Eckart theorem for $\mathbf{V}$ and $\mathbf{J}$. Noting that $j' = j''$ and taking $\alpha' = \alpha''$. Then consider $\langle \alpha j m | \, \hat{\boldsymbol{V}} \cdot \hat{\boldsymbol{J}} \, | \alpha j m \rangle$ ro figure out the constant of proportionality.

For the z-component V_z:

$$\langle \alpha j m' | \, \hat{V}_z \, | \alpha j m \rangle = \frac{\langle \alpha j m | \, \hat{\boldsymbol{V}} \cdot \hat{\boldsymbol{J}} \, | \alpha j m \rangle}{j(j+1)\hbar^2} \, m \, \hbar \, \delta_{m'm}$$

Usage:

1. Combine magnetic moments

   The combined effect of two dipoles in a magnetic field $\mathbf{B}$ can be analysed by considering the Hamiltonian:

   $$\hat{H}_B = -\boldsymbol{m} \cdot \hat{\boldsymbol{B}} = -(\boldsymbol{m}_1 + \boldsymbol{m}_2) \cdot \mathbf{B} = -(\gamma_1 \hat{\boldsymbol{J}}_1 + \gamma_2 \hat{\boldsymbol{J}}_2) \cdot \mathbf{B} = -\gamma_j \hat{\boldsymbol{J}} \cdot \boldsymbol{B}$$

   where γ_j is the combined gyromagnetic ratio. Since $\boldsymbol{m}$ is a vector operator, we can use the Landé formula:

   $$\langle \alpha j m' | \, \boldsymbol{m} \, | \alpha j m \rangle = \underbrace{\frac{\langle \boldsymbol{m} \cdot \hat{\boldsymbol{J}} \rangle}{j(j+1)\hbar^2}}_{\gamma_j} \langle \alpha j m' | \, \hat{\boldsymbol{J}} \, | \alpha j m \rangle$$

   where $\langle \boldsymbol{m} \cdot \hat{\boldsymbol{J}} \rangle = \langle \gamma_1 \hat{\boldsymbol{J}}_1 \cdot \hat{\boldsymbol{J}} + \gamma_2 \hat{\boldsymbol{J}}_2 \cdot \hat{\boldsymbol{J}} \rangle$. The constant factor (Landé g-factor, $\gamma_j = -g_j \frac{\mu_B}{\hbar}$) is:

   $$\boxed{g_j = g_1 \frac{j(j+1) + j_1(j_1+1) - j_2(j_2+1)}{2j(j+1)} + g_2 \frac{j(j+1) + j_2(j_1+2) - j_1(j_1+1)}{2j(j+1)}}$$

   since $\hat{\boldsymbol{J}} = \hat{\boldsymbol{J}}_1 + \hat{\boldsymbol{J}}_2$ taking squares gives $\hat{\boldsymbol{J}}_1 \cdot \hat{\boldsymbol{J}} = \frac{1}{2}\left(\hat{\boldsymbol{J}}^2 + \hat{\boldsymbol{J}}_1^2 - \hat{\boldsymbol{J}}_2^2\right)$, similarly for $\hat{\boldsymbol{J}}_2 \cdot \hat{\boldsymbol{J}}$. This gives us a way to find any combined magnetic moments $\boldsymbol{m} = \gamma_j \hat{\boldsymbol{J}}$.

   Proton and neutron magnetic moments (Quark model)

   $$q_u = +\frac{2}{3}e \;\Rightarrow\; \mu_u = \frac{2}{3}\frac{e\hbar}{2m_u} \quad ; \quad q_d = -\frac{1}{3}e \;\Rightarrow\; \mu_d = -\frac{1}{3}\frac{e\hbar}{2m_d}$$

   Proton is (uud) and neutron is (udd). For proton, taking $j = S_p = 1/2$, $j_1 = S_{uu} = 1$ and $j_2 = S_d = 1/2$, $g_p = \frac{4}{3}\mu_u - \frac{1}{3}\mu_d$. Similarly, for neutron we obtain, $g_p = \frac{4}{3}\mu_d - \frac{1}{3}\mu_u$. Assuming mass of quarks are equal, then $\mu_u = -2\mu_d$ and sharing mass of proton equally among the quarks gives: $\mu_p = +3\mu_N$ and $\mu_n = -2\mu_N$.

2. Analyse Zeeman effect.

8 Treatment of Identical particles and its Consequences

Interchanging indistinguishable particles can differ by at most a phase factor:

$$|1,2,...,j,...,k,...,N\rangle \to e^{i\phi}\,|1,2,...,k,...,j,...,N\rangle \to e^{2i\phi}\,|1,2,...,j,...,k,...,N\rangle$$

$$e^{2i\phi} = 1 \Rightarrow e^{i\phi} = \pm 1$$

$$\begin{cases} +, \textbf{ symmetric} \text{ under exchange are } \textbf{Bosons} \\ -, \textbf{ antisymmetric} \text{ under exchange are } \textbf{Fermions} \end{cases} \quad \underbrace{\begin{cases} \text{integer spin are Bosons} \\ \text{half-integer spin are Fermions} \end{cases}}_{\text{Spin-statistics theorem}}$$

Pauli Exclusion Principle: Setting $j = k$, gives $|1,...,j,...,j,...,N\rangle = -\,|1,...,j,...,j,...,N\rangle = 0$, no two identical fermions can share an identical set of quantum numbers.

For composite systems, whether it is a boson or fermion depends only on the number of fermions:

$$\begin{cases} \text{Even number of fermions: Boson / j is integer} \\ \text{Odd number of fermions: Fermion / j is half-integer} \end{cases}$$

22We can use **Slater determinants** to construct combined wavefunctions of N non-interacting particles that obeys symmetric properties. For N fermions:

$$\text{Antisymmetric: } |\psi\rangle_A = \frac{1}{\sqrt{N!}} \begin{vmatrix} |1,\alpha_1\rangle & |2,\alpha_1\rangle & \cdots & |N,\alpha_1\rangle \\ |1,\alpha_2\rangle & |2,\alpha_2\rangle & \cdots & |N,\alpha_2\rangle \\ \cdots & \cdots & \ddots & \cdots \\ |1,\alpha_N\rangle & |2,\alpha_N\rangle & \cdots & |N,\alpha_N\rangle \end{vmatrix}$$

where the numbers $1,2,...,N$ are the particle labels. $\alpha_1,\alpha_2,...,\alpha_N$ specify the state of the particles. E.g. for particle 1 in spatial position a and spin up: $|1, a\uparrow\rangle$

Some properties:
1. Interchange of two columns gives a change of sign, $|\psi\rangle_A \to -\,|\psi\rangle_A \Rightarrow$ antisymmetric under exchange.
2. If any two rows are the same, the determinant vanishes, $|\psi\rangle_A = 0 \Rightarrow$ Pauli Exclusion.

For N bosons, we construct the symmetric wavefunction, $|\psi\rangle_S$, by using the Slater determinant and setting all the '-' sign to '+' sign.

For indistinguishable particles, we can have either particle in either state, it is just a relabelling of $\mathbf{r}_1 \longleftrightarrow \mathbf{r}_2$, there are two obvious choices for the spatial part, adjusted by normalisation:

$$1.\ \psi_-(x) = \frac{1}{\sqrt{2}}\Big[\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\Big] \quad \text{(antisymmetric)}$$

$$2.\ \psi_+(x) = \frac{1}{\sqrt{2}}\Big[\phi_1(x_1)\phi_2(x_2) + \phi_1(x_2)\phi_2(x_1)\Big] \quad \text{(symmetric)}$$

Spin part:

$$1.\ |\uparrow\rangle_1 |\uparrow\rangle_1 \quad \text{(symmetric)}$$

$$2.\ |\downarrow\rangle_1 |\downarrow\rangle_2 \quad \text{(symmetric)}$$

$$3.\ \frac{1}{\sqrt{2}}\Big[\,|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2\,\Big] \quad \text{(symmetric)}$$

$$4.\ \frac{1}{\sqrt{2}}\Big[\,|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\,\Big] \quad \text{(antisymmetric)}$$

Exchange forces

Consider mean squared separation:

$$d^2 = \langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$$

Using the corresponding wavefunction $\psi(x)$ to evaluate the expected value, $\langle \psi | \, \square \, | \psi \rangle$.

$$|\psi\rangle = \begin{cases} |1,a\rangle \, |2,b\rangle \,, & \text{for distinguishable} \\ \frac{1}{\sqrt{2}} \left[|1,a\rangle \, |2,b\rangle \pm |1,b\rangle \, |2,a\rangle \right], & \text{for identical} \end{cases}$$

For distinguishable particles:

$$d_{di}^2 = \langle x^2 \rangle_1 + \langle x^2 \rangle_2 - 2\langle x \rangle_1 \langle x \rangle_2$$

For indistinguishable particles:

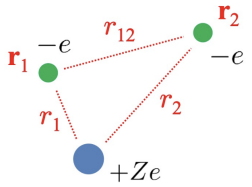
$$d_{ind}^2 = \langle x^2 \rangle_1 + \langle x^2 \rangle_2 - 2\Big(\langle x \rangle_1 \langle x \rangle_2 \; \pm |\langle x \rangle_{12}|^2 \Big) = d_{di}^2 \; \mp 2|x_{12}|^2$$

For the symmetric spatial (+)/singlet state, the particles are slightly closer together (attractive exchange force). For the antisymmetric spatial (-)/triplet state, they are further apart (repulsive exchange force) This fictitious force is the so-called **"exchange" force**

The cross term goes away if the wave functions do not significantly overlap, meaning identical particles very apart are effectively distinguishable. An indication that localization works at some level.

$$\langle x \rangle_{12} = \int \psi_1^* \, x \, \psi_2 dx \approx 0 \text{ if the wavefunctions do not overlap}$$

9 Helium atom



$$\boxed{\textbf{Hamiltonian: } \hat{H} = \frac{-\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \cancel{\frac{1}{r_{12}}}\right) = \hat{H}_1 + \hat{H}_2 + \hat{H}'} \quad (Z=2)$$

Assuming ∞ mass nucleus, non-relativistic electrons, neglecting spin-orbit and spin-spin interactions. Let's consider "Zeroth-order" Helium order by ignoring the electron-electron Coulomb interaction. It has **Energy:** $E_1 + E_2 = -\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) Z^2 R_\infty$. The **Wavefunctions** is antisymmetric overall.

$$\text{Ground state: } |\psi\rangle_0 = \frac{1}{\sqrt{2}}\Big(|100\uparrow\rangle|100\downarrow\rangle - |100\downarrow\rangle|100\uparrow\rangle\Big) \equiv |100\rangle|100\rangle \otimes \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

Single-particle excited state:

$$\text{(S=0) Para-helium: } |\psi\rangle = \frac{1}{\sqrt{2}}\Big(|100\rangle|nlm\rangle + |nlm\rangle|100\rangle\Big) \otimes \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

$$\text{(S=1) Ortho-helium: } |\psi\rangle = \frac{1}{\sqrt{2}}\Big(|100\rangle|nlm\rangle - |nlm\rangle|100\rangle\Big) \otimes \begin{cases} |\uparrow\rangle|\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle) \\ |\downarrow\rangle|\downarrow\rangle \end{cases}$$

No two-particle excited state: the lowest energy of such state is $-2R_\infty$, which is higher than the ground state energy of He^+ ion, $-4R_\infty$. If we have such state, it would rapidly auto-ionise as $He^{**} \to He^+ + e^-$.

Switch on the electron-electron interaction term (ground state)

However, we cannot treat $\hat{H}'$ as a perturbation because it is not small relative to $\hat{H}_0$. We use **variational method** instead.

$$\boxed{|\psi_{trial}(Z')\rangle = \frac{\beta^3}{\pi} e^{-\beta(r_1+r_2)} = |\psi'_{100}(\mathbf{r}_1)\rangle\,|\psi'_{100}(\mathbf{r}_2)\rangle}$$

where $\beta = \frac{Z'}{a_0}$ and parameter Z' accounts for the screening of +ve nuclear charge by e^- $(1 < Z' < 2)$. $|\psi'_{100}(\mathbf{r})\rangle$ are hydrogen-like wavefunctions. [**Exercise**] Using: $\hat{H}_{1,2} = -(a_0^2 R_\infty)\nabla^2 - (2Z a_0 R_\infty)\frac{1}{r_{1,2}}$, $\langle\psi'|\nabla^2|\psi'\rangle = -\beta^2$ and $\langle\psi|\frac{1}{r}|\psi\rangle = \beta$, we can find the expectation value of $\hat{H}_{1,2}$:

$$\boxed{E_1 = E_2 = (Z'^2 - 2ZZ')R_\infty}$$

The expectation value of the interaction term $\hat{H}_{12}$ is,

$$E_{12} = 2 \cdot \underbrace{a_0}_{Z'/\beta} \cdot R_\infty \left(\frac{\beta^3}{\pi}\right)^2 \underbrace{\int\int \frac{e^{-2\beta(r_1+r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2}_{20\pi^2 r_0^5} = \boxed{\frac{5}{4} Z' R_\infty}$$

where $r_0 = \frac{1}{2\beta}$.

With that, we can minimise $E_1+E_2+E_{12}$ w.r.t. Z' and find an upper bound on the ground state energy.

To **improve the variational method**, just add more variational parameters. For example, propose a wavefunction in the Hylleraas coordinates[6]: $\psi(s,t,u) = e^{-ks/2}(1 + c_1 ku + c_2 k^2 t^2)$ where $s \equiv r_1 + r_2$, $t \equiv r_1 - r_2$ and $u \equiv r_{12}$.

Switch on the electron-electron interaction term (excited state)

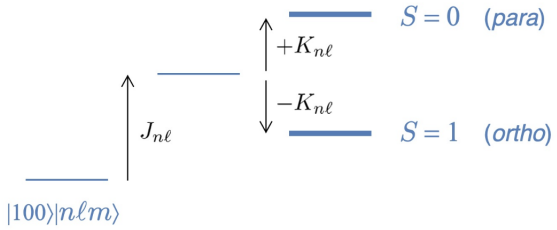
We use **perturbation theory** now.

$$\Delta E^{(1)}_{nlm} = \left\langle nlm^{(0)} \right| \hat{H}' \left| nlm^{(0)} \right\rangle = J_{nl} \pm K_{nl}$$

where $\left|nlm^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\Big(\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \pm \psi_{nlm}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\Big)$. H' is a scalar operator and by Wigner-Eckart theorem, it's matrix elements must be independent of m. Choose $m = 0$.

$J_{nl} > 0$ are the sum of square terms in the quadratic. **Coulomb repulsion breaks degeneracy in ℓ.**

$K_{nl} > 0$ are the cross terms in the quadratic. **Exchange forces breaks degeneracy in S.**



E1 transition in He atom

$$\Gamma \propto \omega^3 \left| \langle \beta | \, \hat{\boldsymbol{d}} \, | \alpha \rangle \right|^2 \quad \text{where} \quad \hat{\boldsymbol{d}} = -e\hat{\boldsymbol{r}}_1 - e\hat{\boldsymbol{r}}_2$$

Since operator d does not involve any spin operators, the **spin component of atomic state must remain unchanged** during E1 transition i.e. it obeys selection rules: $\boxed{\Delta S = 0 \text{ and } \Delta m_S = 0}$. Hydrogen selection rules still apply,

$$\Delta l = \pm 1 \quad ; \quad \Delta m_l = 0, \pm 1$$

Fine structure

For para-He, no fine structure splitting because each level is the same j. $J = L \otimes S = L \otimes 0 = L$.
For ortho-He, each level splits into 3 fine structure levels: $J = L \otimes S = L \otimes 1 = \boldsymbol{L, L \pm 1}$, for $L > 0$.

Since **d** is a vector operator, E1 transition between fine structure levels can only occurs if it obeys the selection rule:

$$\Delta J = 0, \pm 1 \quad ; \quad J_\alpha + J_\alpha \geq 1 \quad ; \quad \Delta m_J = 0, \pm 1$$

Allowed spectral lines in $S = 0$ are all singlets, and the allowed spectral lines in $S = 1$ are all mutliplets.

For **hyperfine structure**, need nuclear spin $\neq 0$, no hyperfine for ^{4}He but have for ^{3}He.

[6] https://arxiv.org/abs/math-ph/0605018

10 Multi-electron atoms

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2$$

where:

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \quad \text{(Independent H-like Hamiltonian)}$$

$$\hat{H}_1 = \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad \text{(Electron-electron repulsion)}$$

$$\hat{H}_3 = \xi_i(r_i)\hat{\boldsymbol{L}}_i \cdot \hat{\boldsymbol{S}}_i \quad \text{(Spin-orbit interaction)}$$

Relativistic corrections, hyperfine structure etc. can be included as perturbations.

No longer typing notes, changed way of learning