

SECOND PUBLIC EXAMINATION

Honour School of Physics Part A: 3 and 4 Year Courses

Honour School of Physics and Philosophy Part A

A3: QUANTUM PHYSICS

TRINITY TERM 2014

Friday, 20 June, 9.30 am – 12.30 pm

ion trap.

Answer all of Section A and three questions from Section B.

*For Section A start the answer to each question on a fresh page.
For Section B start the answer to each question in a fresh book.*

A list of physical constants and conversion factors accompanies this paper.

The numbers in the margin indicate the weight that the Examiners expect to assign to each part of the question.

Do NOT turn over until told that you may do so.

$$X = \frac{n_1}{n_{\text{norm}}} = \frac{\exp(-\frac{\omega t}{k_B T})}{2e} [A^\dagger A, A]$$

$\therefore \cancel{x} = 1$

$$\cancel{x} \rightarrow X = \frac{-4+2}{2}$$

Section A

$$\frac{2-4}{2} = -x$$

$$x = \frac{4}{1-x}$$

- $q = 4e^{-\frac{\omega t}{k_B T}}$
- A system at time $t = 0$ has a state vector $|\psi(0)\rangle = N(|E_1\rangle + i|E_2\rangle)$, where $|E_1\rangle$ and $|E_2\rangle$ are normalised energy eigenkets with different eigenvalues E_1 and E_2 ($E_2 > E_1$). Write down the state vector at time t , $|\psi(t)\rangle$. What are the possible values of N for this to be normalised? At what time $T > 0$ is the system first in the state $|\psi(T)\rangle = N' [|E_1\rangle + |E_2\rangle]$? (The constant N' may differ from N). [5]

- A two-state system has a Hamiltonian of the form

$$H = \begin{pmatrix} a+b & c-id \\ c+id & a-b \end{pmatrix}$$

where a, b, c and d are real numbers. Show that H is Hermitian. Find the eigenvalues of H . Hence show that the only Hamiltonians of this form with degeneracy are multiples of the identity matrix. [5]

- Operators \hat{A} and \hat{B} commute: $[\hat{A}, \hat{B}] = 0$. Operator \hat{A} has a complete set of eigenkets

$$\hat{A}|n\rangle = A_n|n\rangle$$

which are non-degenerate. Show that every eigenket of \hat{A} is an eigenket of \hat{B} . [3]

Suppose now there is a two-fold degeneracy such that $A_4 = A_5$. Show that in this case $|4\rangle$ is not necessarily an eigenket of \hat{B} , but that

$$\hat{B}|4\rangle = \alpha|4\rangle + \beta|5\rangle$$

for some constants α and β . [3]

- A particle in a (one-dimensional) box can be modelled with a confining potential $V(x)$ which is zero for $0 \leq x \leq a$, and infinite elsewhere. Write down the time-independent Schrödinger equation for the eigenfunctions $u_n(x)$, and state the boundary conditions satisfied by u_n at $x = 0$ and $x = a$. [3]

Solve to find the eigenvalues E_n and normalised eigenfunctions u_n . Hence write down the general solution to the time-dependent Schrödinger equation for a particle confined to the box. [5]

- The wavefunction for the ground state of a hydrogen-like system with nuclear charge Ze is $\psi(r) = \sqrt{\frac{Z^3}{\pi a^3}} e^{-Zr/a}$ where a is the Bohr radius and the reduced mass correction has been neglected. Show that this wavefunction is normalised. An atom of tritium (${}^3\text{H}$) in its ground state decays to singly-ionised helium (${}^3\text{He}^+$) by beta decay, in a process which can be considered instantaneous on the atomic timescale. Calculate the probability that the helium ion is left in the ground state. [7]

6. The Hamiltonian for a hydrogen-like two-particle system is

$$H = \left(\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r}$$

where $\mathbf{p}_1, \mathbf{p}_2$ are the two momentum operators, $\mathbf{r}_1, \mathbf{r}_2$ are the two position operators, and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. The centre-of-mass operator is $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$. Write down expressions for the momentum operators conjugate to \mathbf{r} and \mathbf{R} , \mathbf{p} and \mathbf{P} respectively. Show that $\mathbf{p}_1 = \frac{m_1}{m_1+m_2} \mathbf{P} - \mathbf{p}$.

[4]

Separate H into two terms $H = H_{CM} + H_{int}$, each containing only centre-of-mass or internal variables respectively. Give a physical interpretation of the two terms.

[5]

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Section B

7. The Hamiltonian of a one-dimensional harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 = \frac{1}{2}\hbar\omega(a a^\dagger + a^\dagger a)$$

where all the symbols have their usual meanings, and a is the lowering operator

$$a = \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} x + i \frac{p}{\sqrt{\hbar m\omega}} \right).$$

The action of a on the energy eigenket $|n\rangle$ is $a|n\rangle = \sqrt{n}|n-1\rangle$ for all $n \geq 0$. Find expressions for x and p in terms of a and a^\dagger . The oscillator is in the state

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} (|n-1\rangle e^{-i(n-\frac{1}{2})\omega t} + |n\rangle e^{-i(n+\frac{1}{2})\omega t}).$$

Calculate the expectation values of H , x and p for this state.

[9]

Calculate the amplitude of oscillation of a classical oscillator of this frequency and energy $E = \langle\psi(t)|H|\psi(t)\rangle$ and show that it differs from your result for $\langle\psi(t)|x|\psi(t)\rangle$ by a factor independent of n .

[4]

Find an expression for the expectation value of x^2 in the state $|\psi(t)\rangle$. Explain briefly why this state has a time-independent value for $\langle\psi(t)|x^2|\psi(t)\rangle$, whereas a superposition of more than two consecutive energy eigenstates would not.

[7]

$$\begin{aligned} & \text{in } (\frac{\partial}{\partial x}, \frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}) \\ & \text{in } (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}) \end{aligned}$$

[Turn over]

$$\frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1} \frac{\partial}{\partial x} + \frac{\partial y}{\partial x_1} \frac{\partial}{\partial y} + \frac{\partial z}{\partial x_1} \frac{\partial}{\partial z}$$

$$\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2) = \frac{1}{2} m \omega^2 (L_z^2 + L_x^2 + L_y^2)$$

$$\Rightarrow E_{\text{total}} = \hbar \omega (n_x + n_y + n_z + \frac{3}{2})$$

$$[L_z, \mathcal{E}] = 0 \quad \therefore L_z \mathcal{E}(r) = \underbrace{z L_z f(r)}_{= 0} = 0.$$

8. A three-dimensional harmonic oscillator with a spherically symmetric potential has a three-fold degenerate first excited level. A possible basis for the degenerate states is provided by the kets $|1, u\rangle$, $|1, v\rangle$ and $|1, w\rangle$ with wavefunctions

$$\langle \mathbf{r} | 1, u \rangle = x f(r) \quad \langle \mathbf{r} | 1, v \rangle = y f(r) \quad \langle \mathbf{r} | 1, w \rangle = z f(r)$$

where the explicit form of f is irrelevant. Show that $|1, w\rangle$ is an eigenstate of L_z with eigenvalue zero, so we can give it an alternative designation $|1, w\rangle = |1, 0\rangle$. Specify corresponding eigenvalue conditions satisfied by $|1, u\rangle$ and $|1, v\rangle$. Use the operators $L_x \pm iL_y$ to find the normalised eigenkets of L_z , $|1, \pm 1\rangle$, with eigenvalue $\pm \hbar$, in terms of $|1, u\rangle$ and $|1, v\rangle$. Show that there are no states $|1, \pm 2\rangle$. WTF? [9]

The oscillator is subject to a weak perturbation

$$V(\mathbf{r}) = G(2z^2 - x^2 - y^2).$$

Use degenerate perturbation theory in the $\{u, v, w\}$ basis to show that the first-order corrections to the energy are $\Delta E = 2G(K - H)$ and $G(H - K)$ where

$$H = \int x^2 y^2 f^2(r) d^3r \quad \text{and} \quad K = \int x^4 f^2(r) d^3r.$$

Normalisation of ladder operators (You may assume that
and similarly

$$H = \int x^2 y^2 f^2(r) d^3r = \int y^2 z^2 f^2(r) d^3r = \int z^2 x^2 f^2(r) d^3r$$

by symmetry.) Assign zeroth-order eigenkets to the two eigenvalues, stating which is still degenerate. [11]

$\langle 1s | -x \rangle$

$$\langle 1s | P V + V P | 1s \rangle = 0$$

\int_{SIN}

9. A hydrogen atom in the ground state $|1s\rangle$ is immersed in a radiation field with a weak electric field $\mathbf{E} = \mathcal{E}\hat{\mathbf{z}} \cos \omega t$ where ω is close to the resonant frequency for transitions to the first excited level $n = 2$. This perturbs the hydrogen atom, with interaction Hamiltonian $V(t) = e\mathcal{E}z \cos(\omega t)$. Show that V commutes with the z -component of orbital angular momentum, $[V, L_z] = 0$, and anticommutes with the parity operator $\{V, \mathcal{P}\} = 0$. Hence show that $\langle 1s | V | 1s \rangle = 0$, and that the only $n = 2$ excited state with a well-defined value for L_z having non-zero matrix element with $|1s\rangle$ is $|2p, 0\rangle$, with zero eigenvalue of L_z . (Neglect electron spin throughout.)

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[6]

At $t = 0$ the atom is in the state $|1s\rangle$, and we write the state at $t > 0$ as

$$|\psi(t)\rangle = c_1 e^{-i\omega_1 t} |1s\rangle + c_2 e^{-i\omega_2 t} |2p, 0\rangle \quad \begin{matrix} \omega_1 / \hbar \\ |3p, 0\rangle \quad |4p, 0\rangle \end{matrix}$$

(The constants $\omega_i = E_i/\hbar$, where E_i are the energy eigenvalues for hydrogen.) Show that the equations of motion for the coefficients c_i are

$$\begin{aligned} i\hbar \frac{dc_1}{dt} &= e\mathcal{E} \langle 1s | z | 2p, 0 \rangle \cos(\omega t) e^{i(\omega_1 - \omega_2)t} c_2 & c_{1(0)} = 0 \\ i\hbar \frac{dc_2}{dt} &= e\mathcal{E} \langle 2p, 0 | z | 1s \rangle \cos(\omega t) e^{i(\omega_2 - \omega_1)t} c_1. & c_{2(0)} = 0 \\ && c_{1(0)} = c_{2(0)} + \frac{dc_2}{dt} \Delta t \end{aligned}$$

Explain briefly why $\frac{dc_2}{dt}$ is first-order in \mathcal{E} but $\frac{dc_1}{dt}$ is second-order. Hence give first-order equations of motion for c_i .

OC
[7]

WTF Separate the cosine into two complex exponentials, and explain briefly why one of the two terms in $\frac{dc_2}{dt}$ oscillates many times faster than the other. Neglect the fast term and find a first-order approximation for $c_2(t)$. Show that

$$|c_2(t)|^2 = \frac{e^2 \mathcal{E}^2 |\langle 2p, 0 | z | 1s \rangle|^2}{\hbar^2 \Delta^2} \sin^2\left(\frac{\Delta t}{2}\right) \quad PV = -VP \quad PV \langle 1s | 1s \rangle \quad PZ = \alpha P$$

where $\Delta = \omega_2 - \omega_1 - \omega$. Show that in this approximation $|c_1|^2 + |c_2|^2 \geq 1$ for all $t > 0$. Explain why $|c_1|^2 + |c_2|^2$ is expected to remain constant, and hence find a condition on \mathcal{E} and Δ for the first-order approximation to be valid.

Xp = pX
[7]

$$\frac{dc_1}{dt} \propto \mathcal{E} c_2$$

initial condition

$$\frac{dc_2}{dt} \propto \mathcal{E} c_1$$

$$c_{1(0)} = 1$$

$$c_{2(0)} = 0$$

At time $t = \Delta t$ is small, $c_2(\Delta t)$

$$c_{1(\Delta t)} = c_{1(0)} + \frac{dc_1}{dt} \Delta t + \dots \approx 1 + \frac{dc_1}{dt} \Delta t \approx 1$$

$$c_{2(\Delta t)} = c_{2(0)} + \frac{dc_2}{dt} \Delta t + \dots \approx 0 + \frac{dc_2}{dt} \Delta t + \mathcal{O}(\mathcal{E}^2)$$

$$\therefore \boxed{\frac{dc_2}{dt}} \propto c_1 \mathcal{E} \propto (\mathcal{E}(1 + \dots)) \propto \mathcal{E}$$

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5

[Turn over]

$$\boxed{\frac{dG_1}{dt}} \propto \mathcal{E} c_2 \propto \mathcal{E}(0 + \frac{dc_2}{dt} \frac{\mathcal{E}}{dt}) = 0$$

$$\propto \mathcal{E} \frac{dc_2}{dt} \propto \mathcal{E} \cdot \mathcal{E} c_1 \propto \mathcal{E}^2 c_1 \propto \underline{\mathcal{E}^2}$$

$$\frac{\partial}{\partial \phi_1} \cos(\phi_1 - \phi_2) = -\lambda \langle \mathbf{a}, \mathbf{b} | \psi \rangle = -\lambda \langle \mathbf{b}, \mathbf{a} | \psi \rangle$$

10. The Hamiltonian for helium, neglecting small spin-dependent terms and treating the nucleus as fixed, is

$$H = \frac{1}{2m} (p_1^2 + p_2^2) + \frac{e^2}{4\pi\epsilon_0} \left(-2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

where the subscripts 1 and 2 identify the two electrons and the distance between the two electrons is:

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 + 2r_1r_2 (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2))}.$$

Show that $[L_z, |\mathbf{r}_1 - \mathbf{r}_2|^2] = 0$ where L_z is the z-component of the total orbital angular momentum \mathbf{L} :

$$[|\mathbf{r}_1 - \mathbf{r}_2|, L_z] = L_z = -i\hbar \left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right).$$

Hence show that $[H, L_z] = 0$ and, assuming that $[H, L_x] = [H, L_y] = 0$, show that $[H, L^2] = 0$. [6]

In the position representation $\langle \mathbf{a}, \mathbf{b} | \psi \rangle$ denotes the amplitude for finding particle 1 at \mathbf{a} and particle 2 at \mathbf{b} . Q_{12} is a spatial symmetry operator defined by:

WTF is this? $\langle \mathbf{a}, \mathbf{b} | Q_{12} | \psi \rangle = \langle \mathbf{b}, \mathbf{a} | Q_{12} | \psi \rangle.$ $[L_z, |\mathbf{r}_1 - \mathbf{r}_2|^2] =$

WTF?

Show that $[Q_{12}, H] = 0$. Explain why H has spatial eigenstates of the form $|E, L, M_L, q\rangle$ where the eigenvalues of H , L^2 , L_z and Q_{12} are E , $\hbar^2 L(L+1)$, $\hbar M_L$ and $q = \pm 1$ respectively. The complete ket for the electrons in helium must also include a spin part. Write down possible spin kets which satisfy the symmetry requirements, in terms of the single-electron kets $|\pm\rangle_1$ and $|\pm\rangle_2$ which are eigenstates of the single electron spin operators s_{1z} and s_{2z} . [8]

WTF?

The lowest five eigenvalues of H are given in the following table together with their conventional labels, and quantum numbers for L and q .

Label	$E / (e^2 / 4\pi\epsilon_0 a_0)$	L	q	M_L
$1s^2$	-2.904	0	+1	
$1s2s$	-2.175	0	-1	
$1s2s$	-2.145	0	+1	
$1s2p$	-2.133	1	-1	
$1s2p$	-2.124	1	+1	$M_L = 1, 0, -1$

Explain why the assignment of spin parts to these spatial states is constrained by the fact that electrons are fermions. Assign spin parts and hence give degeneracies for these 5 eigenvalues of H . [6]

WTF?

$$\begin{aligned} & \langle \mathbf{a}, \mathbf{b} | \psi \rangle \\ & \langle \mathbf{a}, \mathbf{b} | \psi \rangle \text{ sym} \\ & \langle \mathbf{a}, \mathbf{b} | \psi \rangle \text{ anti} \end{aligned}$$

$$1. \because |\psi(0)\rangle = N(|E_1\rangle + |E_2\rangle)$$

$$\begin{aligned} |\psi(t)\rangle &= N(|E_1\rangle e^{-iE_1 t/\hbar} + |E_2\rangle e^{-iE_2 t/\hbar}) \\ &= N(|E_1\rangle e^{-iE_1 t/\hbar} + |E_2\rangle e^{i(\frac{\pi}{2} - \frac{E_2 t}{\hbar})}) \end{aligned}$$

$$= Ne^{-iE_1 t/\hbar} \left(|E_1\rangle + |E_2\rangle e^{i(\frac{\pi}{2} + \frac{(E_2 - E_1)t}{\hbar})} \right)$$

for $t=T$, $\cancel{\frac{\pi}{2} + \frac{E_2 - E_1}{\hbar} T = 2\pi \rightarrow 0} \quad (\because E_1 < E_2)$

$$\therefore \cancel{T = \frac{E_2 - E_1}{\hbar} T = \frac{3\pi}{2}} \rightarrow \cancel{T = \frac{3\pi}{2(E_2 - E_1)}}$$

$$c = s_b + s_d - s_{d+N} + ns - s_n \quad \therefore \quad T = \frac{\pi \hbar}{2(E_2 - E_1)}$$

$$0 = s_b - s_j - s_d - s_{d+N} + ns - s_n$$

2.

$$H = \begin{pmatrix} a+b & c-id \\ c+id & a-b \end{pmatrix}$$

$$\text{let } |\phi\rangle = \begin{pmatrix} x_1 \\ y_1 \end{pmatrix}, |\psi\rangle = \begin{pmatrix} x_2 \\ y_2 \end{pmatrix}, \text{ then}$$

$$\langle \phi | H | \psi \rangle = (x_1^*, y_1^*) \begin{pmatrix} a+b & c-id \\ c+id & a-b \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix}$$

$$= (x_1^*, y_1^*) \begin{pmatrix} (a+b)x_2 + (c-id)y_2 \\ (c+id)x_2 + (a-b)y_2 \end{pmatrix}$$

$$= ((a+b)x_1^* x_2 + (c-id)x_1^* y_2 + (c+id)y_1^* x_2 + (a-b)y_1^* y_2)$$

$$\langle \psi | H | \phi \rangle = (x_1^*, y_1^*) \begin{pmatrix} a+b & c-i\epsilon \\ c+i\epsilon & a-b \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix}$$

$$= (a+b)x_1x_1^* + (c-i\epsilon)x_1^*y_1 + (c+i\epsilon)x_1y_1^* + (a-b)y_1y_1^*$$

$\rightarrow \langle \psi | H | \phi \rangle = \langle \phi | H | \psi \rangle^* \rightarrow H \text{ is hermitian}$

$$H|\psi\rangle = \lambda |\psi\rangle$$

$$\rightarrow \det \begin{vmatrix} a+b-\lambda & c-i\epsilon \\ c+i\epsilon & a-b-\lambda \end{vmatrix} = 0$$

$$\rightarrow (a+b-\lambda)(a-b-\lambda) - (c^2+d^2) = 0$$

$$\therefore \lambda^2 - (a+b+a-b)\lambda + (a+b)(a-b) - c^2 - d^2 = 0$$

$$\therefore \lambda^2 - 2a\lambda + a^2 - b^2 - c^2 - d^2 = 0$$

$$\therefore \lambda = a \pm \frac{1}{2}\sqrt{4b^2 + 4c^2 + 4d^2}$$

$$\rightarrow \lambda = a \pm \sqrt{b^2 + c^2 + d^2}$$

2-D space \rightarrow only max. 2 linearly independent vectors. $\because H$ is hermitian, so if $\lambda_1 \neq \lambda_2$, then eigenvectors for λ_1 and λ_2 are orthogonal (thus linearly independent). \therefore for degeneracy, neither λ_1 nor λ_2 can have degeneracy. Degeneracy can occur only if $\lambda_1 = \lambda_2$, in which case $b^2 + c^2 + d^2 = 0 \rightarrow b=0, c=0, d=0$

$$H = \begin{pmatrix} a & 0 \\ 0 & a \end{pmatrix} = a \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = aI$$

QED

$$3. [\hat{A}, \hat{B}] = 0 \rightarrow \hat{A}\hat{B} = \hat{B}\hat{A}$$

$$(x_{\text{eigen}} = \text{eigen}(wV + \frac{b}{\lambda} I))$$

$$\therefore \hat{B}\hat{A}|n\rangle = \hat{A}\hat{B}|n\rangle, \hat{B}\hat{A}|n\rangle = \hat{B}A_n|n\rangle = A_n(\hat{B}|n\rangle)$$

$\therefore \hat{A}(\hat{B}|n\rangle) = A_n(\hat{B}|n\rangle)$, $\hat{B}|n\rangle$ and $|n\rangle$ are both eigenstates of \hat{A} with same eigenvalue A_n

But A_n is a non-degenerate eigenvalue

$\therefore \hat{B}|n\rangle$ and $|n\rangle$ must be linearly dependent

$\rightarrow \underbrace{\hat{B}|n\rangle = B_n|n\rangle}_{\text{non-zero}} \rightarrow$ every $|n\rangle$ is an eigenstate of \hat{B}

Now if $A_4 = A_5$, then eigenvalue A_4 has 2 linearly independent eigen vectors.

$\therefore \hat{B}|n\rangle$ and $|n\rangle$ can be linearly independent and the above argument fails.

If 2 linearly independent states \rightarrow eigenstates of A_4 are $|4\rangle$ and $|5\rangle$, then since $|4\rangle, |5\rangle, \hat{B}|4\rangle, \hat{B}|5\rangle$ are all eigenstates of \hat{A} with eigenvalue A_4 , but A_4 only allow for 2-fold degeneracy

$$\rightarrow \hat{B}|4\rangle = \alpha|4\rangle + \beta|5\rangle \quad \hat{B}|5\rangle = \alpha'|4\rangle + \beta'|5\rangle$$

4. TISE: $\hat{H}\psi = \hat{E}\psi$ for $\psi \in [0, \infty]$

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi_n(x) = E_n \psi_n(x)$$

$$(\psi_n)_n = \{ \psi_n \}_{n=1}^{\infty}$$

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases}$$

analogous for $V(x) = \infty \Rightarrow \psi_n(x) = 0$ is valid

for $V(x) = 0$

analogous $\frac{d^2 \psi_n(x)}{dx^2} + \frac{2m E_n}{\hbar^2} \psi_n(x) = 0$

free-space problem and form $\lambda \rightarrow k_n = \sqrt{\frac{2m E_n}{\hbar^2}}$

example in 1D: $\psi_n(x) = \psi_1(x) = \sin(k_n x)$

$$\rightarrow \psi''_n + k_n^2 \psi_n = 0$$

and y : $\psi_n = A \cos(k_n x) + B \sin(k_n x)$ well

boundary conditions

boundary condition $\psi_n(x=0) = 0 \Rightarrow B = 0$

point boundary condition $\sin(k_n a) = 0 \Rightarrow k_n a = n\pi$

$\rightarrow k_n = \frac{n\pi}{a} \Rightarrow E_n = \frac{n^2 \pi^2 \hbar^2}{2m a^2}$

and $\psi_n(x) = B \sin\left(\frac{n\pi x}{a}\right)$

normalize $B^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$

$$\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = \int_0^a \left(\frac{1}{2}(1 - \cos\left(\frac{2n\pi x}{a}\right))\right) dx = \frac{a}{2}$$

$$\rightarrow B^2 \left(\frac{a}{2}\right) = 1 \rightarrow B = \sqrt{\frac{2}{a}}$$

$$\rightarrow \psi_n(x) = \sqrt{\frac{2}{a}} \sin^2\left(\frac{n\pi x}{a}\right) \cdot \sqrt{\frac{2}{a}}$$

General solution: $\psi(x, t) = \sum_{n=1}^{\infty} \sqrt{\frac{2}{a}} \sin^2\left(\frac{n\pi x}{a}\right) \exp\left(-\frac{i n^2 \pi^2 \hbar t}{2m a^2}\right) \cdot A_n$

arbitrary constants

$$5. \int dr \cdot r^3 \cdot \psi_1^2(r) = \frac{z^3}{\pi a^3} \int dr \cdot r^2 e^{-2zr/a}$$

$$= \frac{z^3}{\pi a^3} \left(\frac{a^2}{4z^2} \right) \left(\frac{a}{2z} \right) \int_0^\infty du \cdot u^2 e^{-u}$$

$$\begin{cases} u = \frac{2z}{a} r \\ r^2 = \frac{a^2}{4z^2} u^2 \\ dr = \frac{a}{2z} du \end{cases}$$

$$= \frac{z^3 \cdot a^2 \cdot a \cdot 2}{\pi a^3 \cdot 4 \cdot z^2 \cdot \frac{a^2}{4z^2} \cdot 2 \cdot 2} = \frac{1}{4\pi}$$

$$\therefore \langle \psi(r) | \psi(r) \rangle = \int dr d\theta d\phi r^3 \sin\theta \psi(r)^2$$

$$= \int_0^\infty dr \cdot r^3 \psi(r)^2 \int_0^\pi \underbrace{d\theta \sin\theta}_2 \int_0^{2\pi} d\phi = 1$$

$\psi(r)$ is normalised.

instantaneous process \rightarrow sudden approximation.

\rightarrow system remains in the eigenstate of H^3 ($|1\psi(r, z=1)\rangle$)

\rightarrow probability amplitude to remain in the ground state of ${}^3\text{He}^+$ ($|1\psi(r, z=2)\rangle$) is

~~$(\psi(r, z=2) | \psi(r, z=1) \rangle)$~~

$$\langle \psi(r, z=2) | \psi(r, z=1) \rangle = \sqrt{\frac{8}{\pi a^3} \cdot \sqrt{\frac{1}{\pi a^3}} \cdot \frac{4\pi}{3}}$$

$$= \left(\sqrt{\frac{8}{\pi a^3}} \right) \left(\sqrt{\frac{1}{\pi a^3}} \right) (4\pi) \int dr r^2 e^{-3r/a}$$

$$= \frac{8\pi}{a^3} \int_0^\infty \left(\frac{8\pi}{a^3} \right) \left(\frac{a^2}{9z^2} \right) \left(\frac{a}{3z} \right) \int_0^\infty u^2 e^{-u} du \quad 21$$

$$= \frac{(6\pi)^2}{27} \sqrt{\left(\frac{1}{35} \right) \left(\frac{1}{55} \right) \frac{5!}{2^{10} \pi^5}}$$

Probability $P = |(\psi(r, z=2) / \psi(r, z=1))|^2$

$$= \left(\frac{16\pi}{27} \right)^2 \approx 0.7 \int \frac{512}{729}$$

6. $H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} - \frac{Ze^2}{4\pi\epsilon_0 r}$

$$\hat{P}_1 = -i\hbar \frac{\partial}{\partial \underline{r}_1} \quad \underline{P}_1 = -i\hbar \frac{\partial}{\partial \underline{R}}$$

$$(\underline{r} = \underline{r}_2 - \underline{r}_1 , \quad \underline{R} = \frac{m_1 \underline{r}_1 + m_2 \underline{r}_2}{m_1 + m_2})$$

$$\underline{P}_1 = -i\hbar \frac{\partial}{\partial \underline{r}_1} \quad \frac{\partial}{\partial \underline{r}_1} = \frac{\partial \underline{R}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{R}} + \frac{\partial \underline{r}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{r}}$$

Notations: $\frac{\partial}{\partial \underline{r}_1} = \vec{\nabla}_{\underline{r}_1} = (\frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1})^T$

$\frac{\partial \underline{R}}{\partial \underline{r}_1}$ is a tensor, $\frac{\partial \underline{R}}{\partial \underline{r}_1} = \begin{pmatrix} \frac{\partial X}{\partial x_1} & \frac{\partial Y}{\partial x_1} & \frac{\partial Z}{\partial x_1} \\ \frac{\partial X}{\partial y_1} & \frac{\partial Y}{\partial y_1} & \frac{\partial Z}{\partial y_1} \\ \frac{\partial X}{\partial z_1} & \frac{\partial Y}{\partial z_1} & \frac{\partial Z}{\partial z_1} \end{pmatrix}$

or $(\frac{\partial \underline{R}}{\partial \underline{r}_1})_{ij} = \frac{\partial R_j}{\partial r_i}$

in this case $(\frac{\partial \underline{R}}{\partial \underline{r}_1})_{ij} = \frac{m_1}{m_1 + m_2} \delta_{ij}$

$$(\frac{\partial \underline{r}}{\partial \underline{r}_1})_{ij} = -\delta_{ij}$$

$$\therefore \left(\frac{\partial}{\partial r_i}\right)_j = \left(\frac{\partial R}{\partial r_i}\right)_{ij} \left(\frac{\partial}{\partial R}\right)_j + \left(\frac{\partial r}{\partial r_i}\right)_{ij} \left(\frac{\partial}{\partial r}\right)_j$$

$$= \frac{m_1}{m_1+m_2} \delta_{ij} \left(\frac{\partial}{\partial R}\right)_j + \delta_{ij} \left(\frac{\partial}{\partial r}\right)_j$$

$$= \frac{m_1}{m_1+m_2} \left(\frac{\partial}{\partial R}\right)_i - \left(\frac{\partial}{\partial r}\right)_i$$

$$\rightarrow \cancel{\frac{\partial}{\partial R}} + \frac{\partial}{\partial r} = \frac{m_1}{m_1+m_2} \frac{\partial}{\partial R} - \frac{\partial}{\partial r}$$

Multiply by $-i\hbar$ gives

$$\hat{P}_1 = \frac{m_1}{m_1+m_2} \hat{P} - \hat{P}$$

$$\text{Similarly } \hat{P}_2 = \frac{m_2}{m_1+m_2} \hat{P} + \hat{P} \quad (\text{obviously } [\hat{P}, \hat{P}] = 0)$$

$$\therefore H = \frac{1}{2m_1} \left(\frac{m_1}{m_1+m_2} \hat{P} - \hat{P} \right)^2 + \frac{1}{2m_2} \left(\frac{m_2}{m_1+m_2} \hat{P} + \hat{P} \right)^2 - \frac{ze^2}{4\pi\epsilon_0 r}$$

$$= \frac{1}{2m_1} \left(\frac{m_1}{m_1+m_2} \hat{P} \right)^2 - \cancel{\frac{2}{2m_1} \frac{m_1}{m_1+m_2} \hat{P} \cdot \hat{P}} + \frac{\hat{P}^2}{2m_1}$$

$$+ \frac{1}{2m_2} \left(\frac{m_2}{m_1+m_2} \hat{P} \right)^2 + \cancel{\frac{2}{2m_2} \frac{m_2}{m_1+m_2} \hat{P} \cdot \hat{P}} + \frac{\hat{P}^2}{2m_2} - \frac{ze^2}{4\pi\epsilon_0 r}$$

$$= \left(\frac{\hat{P}^2}{2(m_1+m_2)} \right) + \left(\frac{\hat{P}^2}{2\mu} - \frac{ze^2}{4\pi\epsilon_0 r} \right)$$

Ham

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Hint

Kinetic energy
of CM

reduced mass

total
energy in the
CM frame.

$$7. \quad a = \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} X + i \frac{P}{\sqrt{\hbar m\omega}} \right) \quad (1)$$

$$a^+ = \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} X - i \frac{P}{\sqrt{\hbar m\omega}} \right) \quad (2)$$

$$(1) + (2) \rightarrow (a + a^+) = \sqrt{\frac{2m\omega}{\hbar}} X$$

$$X = \underbrace{\sqrt{\frac{\hbar}{2m\omega}} (a + a^+)}_{\checkmark}$$

$$(1) - (2) \rightarrow (a - a^+) = 2i \frac{P}{\sqrt{\hbar m\omega}} \cdot \frac{1}{\sqrt{2}}$$

$$\rightarrow P = \underbrace{\frac{1}{2i} \sqrt{\frac{\hbar m\omega}{2}} (a - a^+)}_{i \sqrt{\frac{\hbar m\omega}{2}} (a - a^+)} \quad \checkmark$$

$$\langle \psi(t) | H | \psi(t) \rangle = \frac{\hbar\omega}{4} \left(\langle n-1 | e^{i(n-\frac{1}{2})\omega t} + \langle n | e^{i(n+\frac{1}{2})\omega t} \right)$$

$$(a a^+ + a^+ a) (\langle n-1 | e^{-i(n-\frac{1}{2})\omega t} +$$

$$+ \langle n | e^{-i(n+\frac{1}{2})\omega t})$$

$$= \frac{\hbar\omega}{4} \left[\underbrace{(2n-1) + (2n+1)}_{4n} \right] = \underbrace{n\hbar\omega}_{\checkmark}$$

$$\langle \psi(t) | \times | \psi(t) \rangle$$

$$= \frac{1}{2} \cdot \sqrt{\frac{\hbar}{2m\omega}} \left(\langle n-1 | e^{i(n-\frac{1}{2})\omega t} + \langle n | e^{i(n+\frac{1}{2})\omega t} \right)$$

$$(a a^+ + a^+ a) (\langle n-1 | e^{-i(n-\frac{1}{2})\omega t} + \langle n | e^{-i(n+\frac{1}{2})\omega t})$$

$$= \frac{1}{\sqrt{2}} \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n} e^{-i\omega t} + \sqrt{n} e^{i\omega t})$$

$$\langle \psi(t) | \hat{p} | \psi(t) \rangle = \sqrt{\frac{\hbar}{2m\omega}} \cdot \sqrt{n} \cdot 2 \cos \omega t = \frac{\sqrt{n\hbar}}{\sqrt{2m\omega}} \cos \omega t.$$

$$\langle \psi(t) | \hat{p} | \psi(t) \rangle$$

$$= \frac{1}{i} \sqrt{\frac{\hbar m\omega}{2}} \cdot \frac{1}{2} (\langle n-1 | e^{i(n-\frac{1}{2})\omega t} + \langle n | e^{i(n+\frac{1}{2})\omega t})$$

$$(a - a^\dagger) (|n-1\rangle e^{-i(n-\frac{1}{2})\omega t} + |n\rangle e^{-i(n+\frac{1}{2})\omega t}).$$

$$\langle \psi_{1H} | \hat{p} | \psi_n \rangle = \frac{1}{i} \sqrt{\frac{\hbar m\omega}{2}} \cdot \frac{1}{2} (\sqrt{n} e^{-i\omega t} - \sqrt{n} e^{+i\omega t})$$

$$= \frac{1}{i} \sqrt{\frac{\hbar m\omega}{2}} \cdot \frac{1}{2} \cdot 2i \sin(-\omega t) \cdot \sqrt{n}$$

$$= -\sqrt{\frac{\hbar m\omega}{2}} \sin(\omega t)$$

$$\text{use } \frac{1}{2} m\omega^2 A^2 = E$$

$$E = \langle \psi(t) | \hat{H} | \psi(t) \rangle = n\hbar\omega$$

$$A = \sqrt{\frac{2E}{m\omega^2}}$$

As Classical amplitude A given by then substitute

$$E = n\hbar\omega$$

$$\frac{1}{2} m\omega^2 A^2 = n\hbar\omega \rightarrow A^2 = \frac{2n\hbar\omega}{m\omega^2}$$

$$\rightarrow A = \sqrt{\frac{2n\hbar}{m\omega}} \quad \begin{matrix} \text{use} \\ \hline E \end{matrix} \quad \begin{matrix} \text{directly} \\ \text{to get the ratio.} \end{matrix}$$

$$\text{ratio } \frac{|\langle x \rangle|}{A} = \frac{\sqrt{\frac{n\hbar}{2m\omega}}}{\sqrt{\frac{2n\hbar}{m\omega}}} = \frac{\left(\frac{1}{\sqrt{2}}\right)^2}{\frac{1}{2}} \text{ independant of } n$$

$$\begin{aligned}
 \langle \psi(t) | \hat{x}^2 | \psi(t) \rangle &= \frac{1}{2} \cdot \frac{\hbar}{2m\omega} \left(\langle n-1 | e^{i(n-\frac{1}{2})\omega t} \right. \\
 &\quad \left. + \langle n | e^{i(n+\frac{1}{2})\omega t} \right) (a^2 + a^{\dagger 2} + a a^{\dagger} + a^{\dagger} a) \\
 &\quad (|n-1\rangle e^{-i(n-\frac{1}{2})\omega t} + |n\rangle e^{-i(n+\frac{1}{2})\omega t}) \\
 &= \frac{\hbar}{2m\omega} \underbrace{\langle \psi(t) | H | \psi(t) \rangle}_{n\hbar\omega} \quad \langle (\psi(t) | H | \psi(t)) \rangle \\
 &= \cancel{\frac{\hbar \cdot n\hbar\omega \cdot n\hbar\omega}{\hbar\omega}} \cancel{\frac{\hbar \cdot n\hbar\omega}{m\hbar\omega^2}} = \frac{n\hbar}{m\omega} \\
 a^{\dagger}a + a a^{\dagger} &= 2n + 1
 \end{aligned}$$

$$\begin{aligned}
 &(\langle n-1 | + \langle n | + \langle n+1 |) (2n+1) (|n-1\rangle + |n\rangle + |n+1\rangle) \\
 &= \text{time independent term} \\
 \text{but } &(\langle n-1 | e^{i(n-\frac{1}{2})\omega t} + \langle n | e^{i(n+\frac{1}{2})\omega t} + \langle n+1 | e^{i(n+\frac{3}{2})\omega t}) \\
 &(a^{\dagger 2} + a^2) (|n-1\rangle e^{-i(n-\frac{1}{2})\omega t} + |n\rangle e^{-i(n+\frac{1}{2})\omega t} \\
 &+ |n+1\rangle e^{-i(n+\frac{3}{2})\omega t}) = 0
 \end{aligned}$$

term gives non-zero value
 if 3 or more consecutive states are involved. This term is time-dependent.

$$\begin{aligned}
 \text{to be independent: } & \frac{1}{\hbar} = \frac{1}{\hbar} = \frac{1}{\hbar} = \frac{1}{\hbar}
 \end{aligned}$$

$$58. \text{ To: } \langle \mathbf{r} | \mathbf{l}, w \rangle = \langle \mathbf{r}, \theta, \phi | \mathbf{l}, w \rangle = z f(r)$$

$$\therefore \langle \mathbf{r} | \hat{L}_z | \mathbf{l}, w \rangle = \hat{L}_z \langle \mathbf{r} | \mathbf{l}, w \rangle = \hat{L}_z z f(r) = z \hat{L}_z f(r)$$

$$[\hat{L}_z, \hat{z}] = 0$$

$$= z \left(-i\hbar \frac{\partial}{\partial \phi} \right) f(r) = 0$$

$$\langle \mathbf{r} | \hat{L}_z | \mathbf{l}, w \rangle = 0 \quad \leftarrow \text{eigenstate}$$

$\langle \mathbf{r} | \hat{L}_z | \mathbf{l}, w \rangle = 0$ $\Rightarrow |\mathbf{l}, w\rangle$ is an eigenstate
of \hat{L}_z with eigenvalue 0

~~$\hat{L}_z(x f(r)) = \langle \mathbf{r} | \hat{L}_z | \mathbf{l}, w \rangle$~~

~~$\langle \mathbf{r} | \hat{L}_z + i\hat{L}_y | \mathbf{l}, w \rangle = \hat{L}_z(x f(r)) = \langle \mathbf{r} | \hat{L}_z | \mathbf{l}, w \rangle$~~

$\therefore |\mathbf{l}, u\rangle$ is the eigenspace of \hat{L}_x with eigenvalue 0

~~$\langle \mathbf{r} | \hat{L}_x | \mathbf{l}, u \rangle = \langle \mathbf{r} | \hat{L}_x | \mathbf{l}, w \rangle$~~

$|\mathbf{l}, v\rangle$ is the eigenspace of \hat{L}_y with eigenvalue 0

$$\langle \mathbf{r} | (\hat{L}_x + i\hat{L}_y) | \mathbf{l}, 0 \rangle = (\hat{L}_x + i\hat{L}_y) z f(r) = z i \hbar y$$

$$= \underbrace{z \hat{L}_x f(r)}_0 + \underbrace{i z \hat{L}_y f(r)}_0 + [\hat{L}_x, z] f(r) + i [\hat{L}_y, z] f(r)$$

$$= i \hbar x$$

$$= \hbar (-x - iy) f(r)$$

$$\hat{L}_z (\hat{L}_x + i\hat{L}_y) | \mathbf{l}, 0 \rangle = \hat{L}_x \hat{L}_z | \mathbf{l}, 0 \rangle + i \hat{L}_y \hat{L}_z | \mathbf{l}, 0 \rangle$$

$$+ [\hat{L}_z, \hat{L}_x] | \mathbf{l}, 0 \rangle + i [\hat{L}_z, \hat{L}_y] | \mathbf{l}, 0 \rangle$$

$$+ i \hbar \hat{L}_y = \underbrace{\langle \mathbf{r} | \hat{L}_z | \mathbf{l}, 0 \rangle}_{-i \hbar \hat{L}_x}$$

$$= \hbar (\hat{L}_x + i\hat{L}_y) | \mathbf{l}, 0 \rangle$$

$\therefore (L_x + iL_y)|1,0\rangle$ is an eigenscator of L_z

with eigenvalue $\pm \hbar = \langle w, 1, 0 | z \rangle \therefore$

$$\langle r | (L_x + iL_y) | 1,0 \rangle = (-x - iy) f(r)$$

Normalize $\rightarrow \langle r | 1,1 \rangle = \frac{1}{\sqrt{2}} (x + iy) f(r)$

$\langle r | L_x - iL_y | 1,0 \rangle = \frac{1}{\sqrt{2}} (\langle 1, u \rangle + i \langle 1, v \rangle)$

$$\langle r | L_x - iL_y | 1,0 \rangle = L_x - iL_y (L_x - iL_y)(z f(r))$$

$$= z L_x f(r) - i z L_y f(r) + [L_x, z] f(r) - i [L_y, z] f(r)$$

$$= \hbar (x - iy) f(r)$$

$$L_z (L_x - iL_y) | 1,0 \rangle = L_x L_z | 1,0 \rangle - i L_y L_z | 1,0 \rangle$$

$$= \langle w | (w + x) = \langle 0, 1 | (w + x) | 2 \rangle$$

$$+ [L_z L_x, L_x] | 1,0 \rangle - i [L_z, L_y] | 1,0 \rangle$$

$$= i \hbar L_y | 1,0 \rangle + \hbar L_x | 1,0 \rangle$$

$$= -\hbar (L_x - iL_y) | 1,0 \rangle$$

$\therefore (L_x - iL_y) | 1,0 \rangle$ is an eigenscator of L_z with eigenvalue $-\hbar$

Normalize $\rightarrow | 1, -1 \rangle = \frac{1}{\sqrt{2}} (\langle 1, u \rangle - i \langle 1, v \rangle)$

$$= \langle 0, 1 | (w + x) | 2 \rangle$$

$$\begin{aligned}
 \hat{L}^2 x_i f(r) &= L_j L_j x_i f(r) = \underbrace{L_j x_i L_j f(r)}_{=0} + L_j [L_j, x_i] f(r) \\
 &= -i\hbar \sum_{ijk} L_j x_k f(r) = -i\hbar \sum_{ijk} x_k L_j f(r) \xrightarrow{\text{if } \sum_{ijk} x_k = 0} -i\hbar \sum_{ijk} [L_j, x_k] f(r) \\
 &= -i\hbar \sum_{ijk} \hbar^2 \delta_{ijk} \sum_{jkl} x_i f(r) = 2\hbar^2 x_i f(r)
 \end{aligned}$$

∴

$|1, \pm 1\rangle, |1, -1\rangle, |1, 0\rangle, |1, u\rangle, |1, v\rangle$ are all eigenstates of \hat{L}^2 with eigenvalue $2\hbar^2$ → any linear combinations of them is also! $|1, 0\rangle, |1, u\rangle, |1, v\rangle$ are a set of basis for first energy level.

∴ if $|1, \pm 2\rangle$ exist, then they must be linear combinations of $|1, 0\rangle, |1, u\rangle, |1, v\rangle$

$$\therefore \hat{L}^2 |1, \pm 2\rangle = 2\hbar^2 |1, \pm 2\rangle$$

$$\therefore \langle 1, \pm 2 | \hat{L}^2 | 1, \pm 2 \rangle = 2\hbar^2$$

$$\text{but } \langle 1, \pm 2 | \hat{L}^2 | 1, \pm 2 \rangle = \langle 1, \pm 2 | \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 | 1, \pm 2 \rangle$$

$$\because L_i \text{ is hermitian} \quad \therefore \langle \psi | \hat{L}_i^2 | \psi \rangle = | \langle \psi | L_i | \psi \rangle |^2 \geq 0$$

$$\therefore \langle 1, \pm 2 | \hat{L}_x^2 | 1, \pm 2 \rangle \geq \langle 1, \pm 2 | \hat{L}_z^2 | 1, \pm 2 \rangle$$

$$= | \langle \hat{L}_z | 1, \pm 2 \rangle |^2 = | \pm 2\hbar |^2 = 4\hbar^2$$

$$\rightarrow 2\hbar^2 \geq 4\hbar^2 \rightarrow \text{contradiction}$$

∴ $|1, \pm 2\rangle$ does not exist.

(Eigenvalues of \hat{L}_i can only be integer $\times \hbar$)

(cont'd) But if you wish, can do this way:

$$\langle L_x + L_y + L_z | L_x + L_y + L_z \rangle = (L_x + iL_y)(L_x + iL_y) Z f(r)$$

$$= (L_x + iL_y)(x f(r) + iy f(r))$$

$$= -\hbar^2 f(r) + \hbar^2 f(r) = 0$$

$$\langle L_x - L_y + L_z | L_x - iL_y \rangle = (L_x - iL_y)(x f(r) - iy f(r))$$

$$= \hbar^2 f(r) - \hbar^2 f(r) = 0$$

but how to prove that the only way to get $|L_z\rangle$ is through the application of $L_x + iL_y$?

this is enough because eigenstates of spherically symmetric hamiltonian should include spherical harmonics and all rules for spherical harmonics work.

$$\langle S_z(1) | S_z(2) | S_z(1) \rangle = \langle S_z(1) | S_z(2) | S_z(1) \rangle$$

$$\langle S_z(1) | S_z(2) | S_z(1) \rangle \leq \langle S_z(1) | S_z(2) | S_z(1) \rangle$$

$$S_z^2 = |S_z|^2 = |\langle S_z(1) | S_z(2) | S_z(1) \rangle| =$$

not both are $\leq S_z^2 \leq S_z^2$

fixing for ab $\langle S_z(1) |$:

($\vec{r} \times \vec{p}$) $\cdot \vec{r}$ is the angular momentum

$V(r) = G(2z^2 - x^2 - y^2)$ is the perturbation

its matrix in the degenerate subspace $\{u, v, w\}$

is

$$\tilde{V} = \begin{bmatrix} V_{uu} & V_{uv} & V_{uw} \\ V_{vu} & V_{vv} & V_{vw} \\ V_{wu} & V_{vw} & V_{ww} \end{bmatrix} \quad (V_{ij} = \langle i | V | j \rangle)$$

~~$V_{uu} = V_{vv} = V_{ww} =$~~

If there are odd terms of x, y, z then

$\int_{-\infty}^{\infty}$ vanishes $\rightarrow V_{uv} = V_{vu} = 0 \quad V_{uw} = V_{wu} = 0$
 $V_{vw} = V_{rv} = 0$

$$V_{uu} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x^2 f^2(r) G(2z^2 - x^2 - y^2) dx dy dz$$

$$= G \left[2 \int x^2 z^2 f^2(r) d^3 r - \int x^4 f^2(r) d^3 r - \int x^2 y^2 f^2(r) d^3 r \right].$$

$$= G(2H - K - H) = G(H - K)$$

Similarly $V_{vv} = G(H - K)$

$$V_{ww} = G \left[2 \int z^4 f^2(r) d^3 r - \int x^2 z^2 f^2(r) d^3 r - \int y^2 z^2 f^2(r) d^3 r \right]$$

$$= 2G(K - H)$$

$$\therefore \tilde{V} = \begin{bmatrix} G(H-K) & 0 & (S^Y - S^X - S^S)R & = 2J\bar{V} \\ 0 & G(H-K) & 0 & \\ 0 & 0 & 2G(K-H) & \end{bmatrix}$$

already diagonal

$$\Delta E = G(H-K)$$

$|1,w\rangle$ ~~one~~ \rightarrow
still degenerate

$$\text{rott } \Delta E = 2G(K-H) \rightarrow b\bar{b}|1,w\rangle$$

$$0 = w\bar{w} = w\bar{v} = v\bar{w} \quad \checkmark$$

$$0 = w\bar{v} = w\bar{v}$$

$$\text{shybab } (S^Y - S^X - S^S)R (S^Y + S^X) = w\bar{v}$$

$$-r^2b(S^Y + S^X) - r^2b(S^Y + S^X) \checkmark$$

$$(H - H)R = (H - H - HS)R$$

$$(H - H)R = w\bar{v}$$

$$-r^2b(S^Y + S^X) - r^2b(S^Y + S^X) \checkmark = w\bar{v}$$

$$-r^2b(S^Y + S^X) \checkmark$$

$$(H - H)PS =$$

$$9. [L_z, z]\psi = [-i\hbar(\frac{\partial}{\partial y} - \gamma \frac{\partial}{\partial x}), z]\psi$$

$$\cancel{S''(z=0) - i\hbar \times \frac{\partial}{\partial y}(z\psi) + i\hbar y \frac{\partial}{\partial x}(z\psi) + i\hbar z \frac{\partial^2}{\partial y^2}(\psi) - i\hbar z y \frac{\partial^2}{\partial x^2}(\psi)}$$

$$(z=0) \rightarrow [L_z, z] = 0 \quad \checkmark$$

$$[V, L_z] = [e\varepsilon z \cos(\omega t), L_z] = -e\varepsilon \cos(\omega t) [L_z, z]$$

$$= 0 \quad \checkmark$$

$\Rightarrow [V, P] = e\varepsilon z \cos(\omega t) P$

$$\{\hat{z}, \hat{P}\}\psi = \hat{z}\hat{P}\psi + \hat{P}\hat{z}\psi = zP\psi(x, y, z) + P(z\psi(x, y, z))$$

$$= z\psi(-x, -y, -z) - z\psi(-x, -y, -z) = 0$$

$$\rightarrow \{\hat{z}, \hat{P}\} = 0$$

$$\therefore \{V, P\} = \{e\varepsilon z \cos(\omega t), P\}$$

$$= e\varepsilon \cos(\omega t) \{\hat{z}, \hat{P}\} = 0 \quad \checkmark$$

Consider $P|n\ell m\rangle$, $\langle \pm | n\ell m \rangle = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$

$$\langle \pm | P | n\ell m \rangle = \langle -\pm | n\ell m \rangle = R_{n\ell}(r) Y_{\ell m}(\pi - \theta, \phi + \pi)$$

$$= (-1)^{\ell} R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

Proof: We know $= Y_{\ell m}$ in general

$$Y_{11}(\theta, \phi) = (\sin^l(\theta)) e^{il\phi} = \psi_{+,-} \cdot P$$

$$\begin{aligned} P Y_{11}(\theta, \phi) &= Y_{11}(\theta + \pi, \phi) = \sin^l(\pi - \theta) e^{i\pi l\phi} \\ &= (-1)^l Y_{11}(\theta, \phi) \end{aligned}$$

$$[L_i]_{ijk} = \epsilon_{ijk} x_j p_k \quad (P L_i P = \underbrace{\epsilon_{ijk} P^+}_{-x_j P} \underbrace{x_j P P^+}_{I} \underbrace{P p_k P}_{-P p_k}) \\ = \epsilon_{ijk} x_j p_k = L_i$$

$$\therefore L_i P + P L_i = 0 \rightarrow [P, L_i] = 0$$

parity operator commutes with angular momentum (any component)

$$\rightarrow \hat{L}_- = L_x - i L_y \text{ commutes with } P$$

$$\therefore P L_- = L_- P \rightarrow P L_- Y_{lm} = L_- P Y_{lm} = (-1)^l L_- Y_{lm}$$

$$\rightarrow P |n_l m_l\rangle = (-1)^l |n_l m_l\rangle \rightarrow \text{orbital}$$

$$\therefore P V + V P = 0 \quad \text{i.e., } P^+ = P = P^{-1}$$

$$P^+ V P = -V$$

$$\therefore \langle 1s | V | 1s \rangle = \langle 100 | V | 100 \rangle = -\langle 100 | P^+ V P | 100 \rangle$$

$$= -[(-1)^0]^2 \langle 100 | V | 100 \rangle = -\langle 100 | V | 100 \rangle = -\langle 1s | V | 1s \rangle$$

$$\rightarrow \langle 100 | V | 100 \rangle = 0 \quad \text{and SW: for}$$

$$\langle 2lm \mid V | 2lm \rangle = -\langle 2lm \mid p^\dagger V p | 2lm \rangle$$

$$\Rightarrow \langle 1s \mid V | 2lm \rangle = \langle 100 \mid V | 2lm \rangle$$

$$= -\langle 100 \mid p^\dagger V p | 2lm \rangle = (-1)(-1)^0(-1)^\ell \langle 100 \mid V | 2lm \rangle$$

$$= (-1)^{\ell+1} \langle 1s \mid V | 2lm \rangle$$

\rightarrow if $\ell+1$ is even \rightarrow can be non-zero

if $\ell+1$ is odd \rightarrow must be zero

$$\therefore n=2 \quad \therefore \ell=1 \text{ or } 0 \quad \begin{matrix} 1 & \checkmark \\ 0 & \times \end{matrix}$$

\therefore consider $\langle 1s \mid V | 2p, m \rangle \quad m = -1, 0, 1$

$$\because [\hat{l}_z, \hat{V}] = 0 \quad \therefore L_z(V | 2p, m) = V L_z(2p, m) \\ = m(V | 2p, m)$$

$\therefore V | 2p, m \rangle$ is an eigenstate of L_z with eigenvalue m .

$\therefore |1s\rangle$ is an eigenstate of L_z with eigenvalue 0

\therefore if $m \neq 0$, eigenstates of L_z with different eigenvalues are orthogonal

$$\rightarrow \langle 1s \mid V | 2p, m \rangle = 0 \text{ for } m \neq 0$$

\rightarrow only non-zero is $\langle 1s \mid V | 2p, 0 \rangle$

Why no $|3p_{10}\rangle, |4p_{10}\rangle, \dots$?

$$|\psi\rangle = |\psi(0)\rangle = C_1 e^{-i\omega_1 t} |1s\rangle + C_2 e^{-i\omega_2 t} |2p_0\rangle$$
$$(E_1 = \omega_1 \hbar, \quad E_2 = \hbar \omega_2)$$

$$\text{TDSE} \quad i\hbar \frac{d|\psi(t)\rangle}{dt} = \hat{H}|\psi(t)\rangle + \tilde{V}|\psi(t)\rangle$$

\downarrow hydrogen \uparrow perturbation.

$$i\hbar \left(\frac{dc_1}{dt} - i\omega_1 C_1 \right) e^{-i\omega_1 t} |1s\rangle + i\hbar \left(\frac{dc_2}{dt} - i\omega_2 C_2 \right) e^{-i\omega_2 t} |2p_0\rangle$$
$$= (C_1 (\hbar\omega_1 + V|1s\rangle)) e^{-i\omega_1 t} + C_2 (\hbar\omega_2 + V|2p_0\rangle) e^{-i\omega_2 t}$$
$$= C_1 (\hbar\omega_1 + V) |1s\rangle e^{-i\omega_1 t} + C_2 (\hbar\omega_2 + V) |2p_0\rangle e^{-i\omega_2 t}$$

$$\langle 1s | \cdot \rightarrow e^{-i\omega_1 t} \cdot i\hbar \frac{dc_1}{dt} = C_1 e^{-i\omega_1 t} \underbrace{\langle 1s | V | 1s \rangle}_{0} + C_2 e^{-i\omega_1 t} \langle 1s | V | 2p_0 \rangle$$

$$\Rightarrow i\hbar \frac{dc_1}{dt} = C_2 \langle 1s | V | 2p_0 \rangle e^{i(\omega_1 - \omega_2)t}$$

$$\Rightarrow i\hbar \frac{dc_1}{dt} = eE \langle 1s | V | 2p_0 \rangle \cos(\omega_2 t) e^{i(\omega_1 - \omega_2)t}$$

$$\langle 2p_0 | \cdot \rightarrow$$

$$i\hbar e^{-i\omega_2 t} i\hbar \frac{dc_2}{dt} = C_1 e^{-i\omega_1 t} \langle 2p_0 | V | 1s \rangle$$
$$+ C_2 e^{-i\omega_2 t} \langle 2p_0 | V | 2p_0 \rangle$$

$$\langle 2p_0 | V | 2p_0 \rangle = - \langle 2p_0 | P^\dagger V P | 2p_0 \rangle$$
$$= -(-1)^2 \langle 2p_0 | V | 2p_0 \rangle \rightarrow \langle 2p_0 | V | 2p_0 \rangle = 0$$

$$\therefore i\hbar \frac{dc_2}{dt} = eE \langle 2p_0 | V | 1s \rangle \cos(\omega_1 t) e^{i(\omega_1 - \omega_2)t}$$

initial condition $C_1(t=0) = 1 = C_2(t=0) = 0$

$$\frac{dC_1}{dt} + \varepsilon C_2 = \frac{dC_2}{dt} \propto \varepsilon C_1$$

for $t = \delta t$ is small, we have

$$C_2(t=\delta t) = C_2(t=0) + \left. \frac{dC_2}{dt} \right|_{t=0} \delta t \dots$$

$$= \left. \frac{dC_2}{dt} \right|_{t=0} \times \delta t \propto \varepsilon C_1 \rightarrow \frac{dC_1}{dt} \propto \varepsilon^2 C_1(0)$$

$$C_1(t=\delta t) = C_1(t=0) + \left. \frac{dC_1}{dt} \right|_{t=0} \delta t \approx 1$$

$$\propto \varepsilon^2 C_1(t=0) \approx \varepsilon^2$$

$$\frac{dC_2}{dt} \propto \varepsilon C_1(t=0) \propto \varepsilon C_1(t=0) \propto \varepsilon$$

$$\left. \frac{dC_1}{dt} \right|_{t=\delta t} \propto \varepsilon C_2(t=\delta t) \propto \varepsilon^2 C_1(t=0) \propto \varepsilon^2$$

→ First order equations! (ignore $\frac{dC_1}{dt}$ it is too small)

$$C_1 = 1 +$$

$$\text{if } \frac{dC_2}{dt} = e^{\varepsilon (2p, 0 | 3, 1, 1, 5)} \cos(\omega t) e^{i(\omega_L - \omega_I)t}$$

$$\Rightarrow \text{ignore } \int \sin(s) \cos(b) ds = \frac{\pi b}{j b}$$

Why is that?

Why faster can be ignored

$$\cos(\omega t) e^{i(\omega_2 - \omega_1)t}$$

$$= \frac{1}{2} (e^{i\omega t} + e^{-i\omega t}) e^{i(\omega_2 - \omega_1)t}$$

$$= \frac{1}{2} (e^{i(\omega_2 - \omega_1 + \omega)t} + e^{i(\omega_2 - \omega_1 - \omega)t})$$

\downarrow
 $\omega t + \omega$

\downarrow
 $\Delta\omega - \omega$

$c_2(t)$ is the probability amplitude for transition from $|1S\rangle$ into $|2P, 0\rangle$

$\therefore \omega$ needs to be close to $\Delta\omega$, which is the resonant frequency

$\therefore \Delta\omega + \omega \approx \Delta\omega - \omega \therefore$ the first term

oscillates much faster

$$\rightarrow \frac{d(c_2(t))}{dt} = \frac{e\epsilon}{2it} \langle 2P, 0 | 2 | 1S \rangle e^{i(\omega_2 - \omega_1 - \omega)t}$$

$$\because c_2(t=0) = 0$$

$$\therefore c_2(t) = \int_{t=0}^t \frac{e\epsilon}{2it} \langle 2P, 0 | 2 | 1S \rangle e^{i(\omega_2 - \omega_1 - \omega)t} dt.$$

$$= \frac{e\epsilon \langle 2P, 0 | 2 | 1S \rangle}{2it \cdot i\Delta\omega} (e^{i\Delta\omega t} - 1)$$

$$\cancel{\frac{1}{i^2} (e^{i\Delta\omega t} - 1)} = 0 + e^{i\Delta\omega t}$$

$$\therefore \cancel{|c_2(t)|^2} = |e^{i\Delta\omega t} - 1|^2 = ((\cos(\Delta\omega t) - 1) + i\sin(\Delta\omega t))^2$$

$$= \cos^2(\Delta\omega t) - 2\cos(\Delta\omega t) + 1 + \sin^2(\Delta\omega t)$$

$$= 2 - 2\cos(\Delta\omega t) = 4\sin^2\left(\frac{\Delta\omega t}{2}\right)$$

$$|c_2(t)|^2 = \frac{e^{2\epsilon^2} |\langle 2p, 0 | z | 1s \rangle|^2}{\hbar^2 \Delta^2} \left(\frac{1}{2} + \sin^2(\frac{\Delta t}{2}) \right)$$

$$\rightarrow |c_2(t)|^2 = \frac{e^{2\epsilon^2} |\langle 2p, 0 | z | 1s \rangle|^2}{\hbar^2 \Delta^2} \sin^2(\frac{\Delta t}{2})$$

$$\therefore |c_1(t)| \approx 1 \quad \therefore |c_2(t)| = 1$$

~~$$|\langle c_1(t) \rangle|^2 = P[1] \quad |c_2(t)|^2 \geq 0$$~~

~~$$|\langle c_1(t) \rangle|^2 + |c_2(t)|^2 \geq 1$$~~

$|c_1|^2 + |c_2|^2$ is expected to be a constant ($= 1$) because the probability of being in both states $|1s\rangle$ and $|2p, 0\rangle$ should sum to 1.

$$\text{So need } |c_2(t)|^2 \leq |c_1(t)|^2 = 1$$

$$\therefore \frac{e^{2\epsilon^2} |\langle 2p, 0 | z | 1s \rangle|^2}{\hbar^2 \Delta^2} \ll 1$$

$$|\langle 2p, 0 | z | 1s \rangle|^2 = |\langle 1s | z | 2p, 0 \rangle|^2$$

$$(j_{2p}^2 \langle 1s | z | 2p \rangle)^2 + (j_{2p}^2 \langle 2p | z | 1s \rangle)^2 - (j_{1s}^2 \langle 1s | z | 1s \rangle)^2 = \\ (\frac{j_{2p}}{2})^2 \langle 1s | z | 2p \rangle^2 + (\frac{j_{1s}}{2})^2 \langle 1s | z | 1s \rangle^2 =$$

$$10. H = \frac{1}{2m} (P_1^2 + P_2^2) + \frac{e^2}{4\pi\epsilon_0} \left(-2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{|r_1 - r_2|} \right)$$

$$|r_1 - r_2|^2 = r_1^2 + r_2^2 + 2r_1 r_2 (\cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2))$$

$$\left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right) |r_1 - r_2|^2 \neq 0$$

$$0 = \left[-r_1^2 \frac{\partial \Psi}{\partial \phi_1} + r_2^2 \frac{\partial \Psi}{\partial \phi_1} + 2r_1 r_2 \cos\theta_1 \cos\theta_2 \frac{\partial \Psi}{\partial \phi_1} \right]$$

$$+ r_1^2 \frac{\partial \Psi}{\partial \phi_2} + r_2^2 \frac{\partial \Psi}{\partial \phi_2} + 2r_1 r_2 \cos\theta_1 \cos\theta_2 \frac{\partial \Psi}{\partial \phi_2}$$

$$+ 2r_1 r_2 \sin\theta_1 \sin\theta_2 \left[\frac{\partial}{\partial \phi_1} \cos(\phi_1 - \phi_2) \Psi + \frac{\partial}{\partial \phi_2} \cos(\phi_1 - \phi_2) \Psi \right]$$

$$= -\sin(\phi_1 - \phi_2) \cancel{\Psi} + \cos(\phi_1 - \phi_2) \frac{\partial \Psi}{\partial \phi_1}$$

~~$$-\cancel{\sin(\phi_1 - \phi_2)} \Psi + \cos(\phi_1 - \phi_2) \frac{\partial \Psi}{\partial \phi_2}$$~~

$$= |r_1 - r_2|^2 \left(\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2} \right) \Psi$$

$$\rightarrow \left[\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2}, |r_1 - r_2|^2 \right] = 0$$

$$\rightarrow [L_z, |r_1 - r_2|^2] = 0$$

$$\therefore D = [L_z, |r_1 - r_2|^2] = |r_1 - r_2| [L_z, |r_1 - r_2|^2] + [|L_z, |r_1 - r_2|^2| / h \cdot r_1]$$

$$\therefore \therefore [|r_1 - r_2|^2, [L_z, |r_1 - r_2|^2]] = 0$$

(let $|r_1 - r_2|^2 = B$) then \therefore

$$\therefore [B, [L_z, B]] = 0$$

$$[L_z, f(B)] = [L_z, B] \frac{df}{dB}$$

$$(5 \text{ rot } \sin\theta) + \text{for other components}$$

$$\text{Consider } f(B) = \frac{1}{\sqrt{B}} \frac{df}{dB} = -\frac{1}{2} B^{-3/2}$$

$$(\cos \theta \sin \phi, \sin \theta \sin \phi, \cos \phi) \cdot r_1, r_2 + (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \phi) \cdot r_1, r_2 = |\sin \theta|$$

$$\therefore [L_z, f(B)] = \underbrace{[L_z, B]}_{\psi(r_1, r_2)} (-\frac{1}{2} B^{-3/2}) = 0$$

$$\therefore f(B) = \frac{1}{|r_1 - r_2|} \underbrace{[L_z, \frac{1}{|r_1 - r_2|}]}_{\psi(r_1, r_2)} = 0 \quad (1)$$

~~$L_z \neq 0$~~ : $L_z = -i\hbar (\frac{\partial}{\partial \phi_1} + \frac{\partial}{\partial \phi_2})$ does not act on r_1 and r_2

$$\therefore \underbrace{[L_z, (\frac{1}{r_1} + \frac{1}{r_2})]}_{\psi(r_1, r_2)} = 0 \quad (2)$$

$$[L_{z_1}, P_{x_1}] \psi = -\hbar^2 \left[\frac{\partial^2}{\partial x_1^2} - \hbar^2 \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \right] \psi$$

$$= -\hbar^2 \left(\frac{\partial^2}{\partial y^2} \psi - \frac{\partial^2}{\partial z^2} \psi + \frac{\partial^2}{\partial x^2} \psi - \frac{\partial^2}{\partial x \partial y} \psi - \frac{\partial^2}{\partial x \partial z} \psi + \frac{\partial^2}{\partial y \partial z} \psi \right)$$

$$[L_{z_1}, P_{y_1}] \psi = -\hbar^2 \left[\frac{\partial^2}{\partial y^2} \psi - \frac{\partial^2}{\partial z^2} \psi + \frac{\partial^2}{\partial x^2} \psi \right] \psi$$

$$= -\hbar^2 (x^2)$$

L_z commutes with spherical symmetry expression.

$$\therefore [L_i, P_j] = i\hbar \sum_{k=1}^3 P_k$$

$$\circ = [[1, 0, 0], [0, 1, 0], [0, 0, 1]]$$

$$\therefore [L_z, P_x^2 + P_y^2] = [L_{z_1} + L_{z_2}, P_{x_1}^2 + P_{y_1}^2 + P_{x_2}^2 + P_{y_2}^2]$$

$$\Phi = P_{x_1} [L_{z_1}, P_{x_1}] + [L_{z_1}, P_{x_1}] P_{x_1}$$

$$+ P_{x_2} [L_{z_2}, P_{x_2}] + [L_{z_2}, P_{x_2}] P_{x_2}$$

commutes automatically

+ (same for 2)

$$= P_{ix} i \hbar P_{iy} + P_{iy} i \hbar P_{ix} - P_{iy} i \hbar P_{ix} - P_{ix} i \hbar P_{iy}$$

$$\therefore [L_z, P_i^2] = 0$$

$$\therefore [L_z, P_1^2 + P_2^2] = 0 \quad (3)$$

$$\therefore [L_z, H] = 0$$

$$\therefore [H, L_z] = 0 \quad \text{QED.}$$

$$\text{Assuming } [H, L_x] = [H, L_y] = 0$$

$$\rightarrow [H, L^2] = [H, L_i L_i] = L_i [\underbrace{[H, L_i]}_0 + \underbrace{[H, L_i] L_i}_0] = 0$$

sum over i

$$\rightarrow \langle a, b | Q_{12} | \psi \rangle = \langle b, a | Q_{12} | \psi \rangle \Rightarrow \langle a, b | Q_{12} | \psi \rangle = \langle b, a | Q_{12} | \psi \rangle$$

$$\therefore \langle a, b | Q_{12} H | \psi \rangle = \langle b, a | Q_{12} H | \psi \rangle$$

$$\text{A typo} \quad \langle a, b | H Q_{12} | \psi \rangle = \langle b, a | \cancel{H} Q_{12} | \psi \rangle$$

WTF!!! $\langle a, b | H Q_{12} | \psi \rangle$ and $H Q_{12} | \psi \rangle$ are both symmetric

Q_{12} can be represented by the transformation

~~$$Q_{12} \quad \langle a, b | \psi \rangle \rightarrow \frac{1}{\sqrt{2}} \langle a, b | \psi \rangle + \frac{1}{\sqrt{2}} \langle b, a | \psi \rangle$$~~

for $a \neq b$ $\langle a, b | \psi \rangle \neq \langle b, a | \psi \rangle$

and $\langle \underline{a}, \underline{b} | \underline{c} \rangle \xrightarrow{\mathcal{Q}_{12}} \langle \underline{a}, \underline{b} | \underline{c} \rangle$

for $\langle \underline{a}, \underline{b} | \underline{c} \rangle = \langle \underline{b}, \underline{a} | \underline{c} \rangle$

$\therefore H$ is symmetric under exchange of $\underline{r}_1, \underline{r}_2$

$$(P_{1,2} = -i\hbar \frac{\partial}{\partial r_{1,2}}) \rightarrow \hat{H}(\underline{r}_2, \underline{r}_1) = \hat{H}(\underline{r}_1, \underline{r}_2)$$

\therefore

consider $\psi(\underline{r}_1, \underline{r}_2)$

$$\mathcal{Q}_{12} \hat{H}(\underline{r}_1, \underline{r}_2) \psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\hbar^2} (\hat{H}(\underline{r}_2, \underline{r}_1) \psi(\underline{r}_1, \underline{r}_2) + \hat{H}(\underline{r}_1, \underline{r}_2) \psi(\underline{r}_1, \underline{r}_2))$$

$$= \hat{H}(\underline{r}_1, \underline{r}_2) \frac{1}{\hbar^2} (0 \psi(\underline{r}_2, \underline{r}_1) + \psi(\underline{r}_1, \underline{r}_2)) [\hat{H}, \hat{Q}_{12}] = 0$$

$$= -\hat{H} \mathcal{Q}_{12} \psi(\underline{r}_1, \underline{r}_2) \quad \mathcal{Q}_{12} \hat{H}(\underline{r}_1, \underline{r}_2) \psi(\underline{r}_1, \underline{r}_2) = 0$$

$$\rightarrow [\mathcal{Q}_{12}, \hat{H}] = 0 = \hat{H}(\underline{r}_1, \underline{r}_2) \psi(\underline{r}_2, \underline{r}_1)$$

Similarly $\therefore L^2, L_z$, are both symmetric
under exchange of \underline{r}_1 and \underline{r}_2

$$\therefore [\mathcal{Q}_{12}, \hat{L}^2] = 0, [\mathcal{Q}_{12}, \hat{L}_z] = 0$$

$\therefore H, \hat{L}^2, \hat{L}_z, \mathcal{Q}_{12}$ ~~are~~ mutually
commutes.

$|E, L, M_L, \underline{q}\rangle$ can be a good

non-interacting quantum state.

(but eigenvalues of \mathcal{Q}_{12} are 1 and 0
not 1 and -1. WTF!!!)

possible spin kets for 2 electrons.

$$S_B = 1 \quad |+\rangle_1 |+\rangle_2 \quad \checkmark$$

$$S_L = 0 \quad \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 + |-\rangle_1 |+\rangle_2) \quad \checkmark \quad \left. \right\} \begin{array}{l} \text{symmetric} \\ \text{triplet} \end{array} S=1$$

$$S_B = -1 \quad |-\rangle_1 |-\rangle_2 \quad \checkmark$$

$$S_L = 0 \quad \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2) \quad \rightarrow \quad \begin{array}{l} \text{anti-symmetric} \\ \text{singlet} \end{array} S=0$$

Assignment of spin part is constrained by the fact that since electrons are fermions, they obey pauli-exclusion principle so that the overall wavefunction must be ~~anti~~ anti-symmetric

→ spin part must have ~~opposite~~
opposite symmetry to the spatial part.

$$\begin{array}{llll} ls^2 & L=0 & q=+1 & M_L=0 \\ & & & \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2) \\ ls^2s & L=0 & q=-1 & M_L=0 \end{array}$$

degeneracy = $\boxed{d=1}$

$$\frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 + |-\rangle_1 |+\rangle_2)$$

$$|-\rangle_1 |+\rangle_2$$

$$\boxed{d=3}$$

$$|S^2 S_{\text{net}} \rangle |L=0\rangle |q=+1\rangle |M_L=0\rangle \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2)$$

$$\boxed{J=1} \quad \checkmark \quad l=2$$

$$|S^2 P\rangle |L=1\rangle |q=-1\rangle |M_L=+1, 0, -1\rangle \quad \cancel{\checkmark}$$

$$J=3 \times 3 = \boxed{9} \quad \begin{matrix} 3 \\ 3 \end{matrix} \quad \left\{ \begin{array}{l} |+\rangle_1 |-\rangle_2 \\ |-\rangle_1 |+\rangle_2 \\ |-\rangle_1 |-\rangle_2 \end{array} \right.$$

~~labeled~~

but not ~~labeled~~

$$|S^2 P\rangle |L=1\rangle |q=+1\rangle |M_L=+1, 0, -1\rangle \quad \cancel{\checkmark}$$

but not ~~labeled~~

$$|S^2 P\rangle |L=3\rangle |q=+1\rangle |M_L=+1, 0, -1\rangle \quad \cancel{\checkmark} \quad \frac{1}{\sqrt{2}} (|+\rangle_1 |-\rangle_2 - |-\rangle_1 |+\rangle_2)$$

$$\boxed{J=3} \quad \checkmark$$

$$(\sqrt{1}, \sqrt{-1} + \sqrt{-1}, \sqrt{1}) \frac{1}{\sqrt{3}}$$

$$\boxed{l=5} = \text{polynomial}$$

$$a=M \quad b=3 \quad c=l \quad d=2$$

$$(\sqrt{1}, \sqrt{-1} + \sqrt{-1}, \sqrt{1}) \frac{1}{\sqrt{3}}$$

$$d=1, c=1$$

$$\text{Quantum} \quad \boxed{\Sigma = b}$$

A3 2014 Tutorial notes

$$8. \langle \hat{L} | l, m \rangle = \begin{pmatrix} x \\ y \\ z \end{pmatrix} f(r)$$

$$\hat{L}_z |l, m\rangle = \hat{L}_z z f(r) = z \hat{L}_z f(r) = z \cdot 0 = 0.$$

$$\hat{L}_x |l, m\rangle = 0$$

$$\hat{L}_y |l, m\rangle = 0$$

$$(L_x + iL_y) |l, m\rangle = \hbar \sqrt{l(l+1) - m(m+1)} |l, m+1\rangle$$

$$|l, l\rangle = \sqrt{\hbar} |l, l\rangle$$

$$L_x z f = -i\hbar (y \partial_z - z \partial_y) z f = -\frac{i\hbar}{j_0}$$

$$= -i\hbar y f$$

$$L_y z f = +i\hbar x f$$

$$= -i\hbar (l v) - \hbar |l m\rangle$$

$$(L_x + iL_y) z f = \sqrt{\hbar} \hbar |l, l\rangle$$

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

$$|l, -l\rangle = \frac{1}{\sqrt{2}} (|l, m\rangle - i|l, m\rangle)$$

$$\vec{H} = \hat{\vec{r}} + \hat{\vec{v}}$$

$$\varphi \sim R_{nl}(r) Y_{lm}(\theta, \varphi)$$

$$\langle 1, \downarrow | \psi | 1, \downarrow \rangle = G (K-H) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

$$2(K-H)G \rightarrow \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$G(H-K) \rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$q. \quad T=0, \quad C_1=1, \quad C_2=0$$

$$\frac{dC_1}{dt} \sim O(\epsilon^2)$$

$$\frac{dC_1}{dt} = 0$$

$$\frac{dC_2}{dt} = -\left| \frac{ie\epsilon}{\hbar} \right| \langle 2P, 0 | z | 1S \rangle \underbrace{\cos(\omega t)}_{i(\omega_2 - \omega)t} e$$

$$\frac{1}{2} (e^{i\omega t} + e^{i(\omega_2 - \omega)t})$$

$$C_2(t) = -\frac{e\epsilon}{2\hbar\omega} \left| e^{i\omega t} - 1 \right| \langle 2P | \dots \rangle$$

$$|C_2|^2 = \left(\frac{e\epsilon}{\hbar\omega} \right)^2 |\langle \dots \rangle|^2 \cancel{\sin^2(\frac{\omega t}{2})}$$

$$\Rightarrow |C_2|^2 \ll 1$$

$$|C_2|^2 \ll 1 \quad \left| \frac{e\epsilon}{\hbar\omega} \right|^2 \ll \frac{\hbar}{e|\langle \dots \rangle|^2}$$

close to the resonant frequency.

$$L_z = \partial - i\hbar (\partial\phi_1 + \partial\phi_2)$$

$$[L_z, |r_1 - r_2|^2]$$

$$= -i\hbar \partial\phi_1 (2r_1 r_2 \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2))$$

$$= -i\hbar (\dots \sin(\phi_1 - \phi_2)) - \sin(\phi_1 - \phi_2) - 1$$

$$= 0$$

if $[A, B] = 0 \Rightarrow [A, f(B)] = 0$

* $[A, f(B)] = [A, B] \frac{df}{dB}$

if $(B, [A, B]) = 0$

$$\langle a, b | \alpha_{12} | \gamma \rangle = \langle b, a | \alpha_{12} | \gamma \rangle$$

$$H = \sum_{a, b, c} (b, c) \langle b, c | H | a, b \rangle \langle a, b |$$

=

swap

operator

Fucking

Type!

$$|4\rangle = P|4\rangle$$

$$\begin{aligned} -\langle 4 | \cancel{V} | 4 \rangle &= P \langle 4 | \cancel{V} | 4 \rangle \\ &= \langle 4' | \cancel{V} | 4' \rangle \\ &= \langle 4 | P^t \cancel{V} | 4 \rangle \end{aligned}$$

$$O = [(\sigma_0 + A) \cdot e^{-i\omega t}, O = [S, A]]$$

$$\Rightarrow \frac{\partial}{\partial t} [S, A] = [(\sigma_0 + A), A]$$

$$\langle V_{12} \cdot S_0 | \Omega \cdot S \rangle = \langle V_{12} \cdot S_0 | S \cdot \Omega \rangle$$

$$(A \cdot \Omega) \langle S_0 | H | \Omega \cdot S \rangle \stackrel{H = H}{=} 0$$