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Problem Sheet 2
Further Quantum Mechanics

May 10, 2020

Question 1

The electron in a hydrogen-like ion has a Hamiltionian

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$$

and eigenstates $|n, l, m\rangle$.

(a) Explain the origin of each term in the Hamiltionian, and the meaning of each of the quantum numbers n, l and m. On which quantum number does the energy depend? For $n = 2$, what values may l and m take?

(b) By considering the electric dipole selection rules or otherwise, identify which of the matrix elements $\langle 2, l', m'|z|2, l, m\rangle$ are non-zero.

(c) A small static electric field of strength $\mathcal{E}$ is applied in the z-direction. Write down the perturbation Hamiltonian. Calculate its non-zero matrix elements for the basis of states with $n = 2$.

(d) Identity the linear combinations of the $n = 2$ states that diagnolize the perturbation Hamiltonian and calculate the energy shifts. Hence sketch the $n = 2$ energy levels before and after the application of the perturbation. In each case, label the eigenstates and give the magnitude of any energy differences.

Solution. (a) The classical Hamiltonian of the hydrogen-like system is given by:

$$H = T + V = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$$

where $-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$ is the electrostatic potential that describes the Coulomb interaction. The Hamiltonian operator $\hat{H}$ is obtained by taking the canonical quantization $\boldsymbol{r} \mapsto \hat{\boldsymbol{r}}, \boldsymbol{p} \mapsto -\mathrm{i}\hbar\boldsymbol{\nabla}$:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$$

The quantum number n represents the eigenstates of the Hamiltonian $\hat{H}$, l the eigenstates of angular momentum $\hat{L^2}$, and m the eigenstates of angular momentum $\hat{L}_z$. The energy of the state $|n, l, m\rangle$ depends on n. More explicitly, $E_n = -\frac{R}{n^2}$, where R is the Rydberg constant.

For $n = 2$,

$$0 \leqslant l \leqslant n - 1 \Longrightarrow l = 0, 1. \qquad -l \leqslant m \leqslant l \Longrightarrow m = 1, 0, -1.$$

The eigenstates are $|2, 0, 0\rangle$, $|2, 1, 0\rangle$, $|2, 1, 1\rangle$, $|2, 1, -1\rangle$.

(b) The wave function of the state $|2, l, m\rangle$ is given by $\psi(r, \theta, \varphi) = R_{2,l}(r)Y_{l,m}(\theta, \varphi)$, where $Y_{l,m}(\theta, \varphi) \propto P_l^m(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\varphi}$. In spherical coordinates, $z = r\cos\theta$. Note that

$$\int_0^{2\pi} \mathrm{e}^{\mathrm{i}(m-m')\varphi}\,\mathrm{d}\varphi = 0 \qquad \text{for } m \neq m'$$

and that

$$\int_0^{\pi} \cos\theta\sin\theta P_l^m(\cos\theta)P_{l'}^m(\cos\theta)\,\mathrm{d}\theta = \int_{-1}^{1} tP_l^m(t)P_{l'}^m(t)\,\mathrm{d}t = 0 \qquad \text{for } l = l'$$

by the recurrance formula $tP_l^m(t) = (l - m + 1)P_{l+1}^m(t) + (l + m)P_{l-1}^m(t)$ and the orthogonal relations.

Hence

$$\langle 2, l', m'|\hat{z}|2, l, m\rangle = \int_0^{\infty} R_{2,l}(r)R_{2,l'}(r)r^3\,\mathrm{d}r \int_0^{\pi} \cos\theta\sin\theta P_l^m(\cos\theta)P_{l'}^{m'}(\cos\theta)\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{e}^{\mathrm{i}(m-m')\varphi}\,\mathrm{d}\varphi$$

is non-zero for $\langle 2, 1, 0|z|2, 0, 0\rangle$ and its complex conjugate.

(c) The perturbed Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{V} = e\mathcal{E}z$ is the electrostatic potential induced by the external field. We know that

$$\psi_{2,0,0}(r,\theta,\varphi) = 2(2a_Z)^{-3/2}\left(1 - \frac{r}{2a_Z}\right)\mathrm{e}^{-r/2a_Z} \cdot \frac{1}{\sqrt{4\pi}} \qquad \psi_{2,1,0}(r,\theta,\varphi) = \frac{1}{\sqrt{3}}(2a_Z)^{-3/2}\frac{r}{a_Z}\,\mathrm{e}^{r/2a_Z} \cdot \sqrt{\frac{3}{4\pi}}\cos\theta$$

Therefore we have

$$\begin{aligned}
\langle 2,1,0|\hat{V}|2,0,0\rangle &= e\mathcal{E}\iiint_{\mathbb{R}^3} r\cos\theta\,\psi_{2,0,0}(\boldsymbol{r})\psi_{2,1,0}(\boldsymbol{r})\,\mathrm{d}V \\
&= e\mathcal{E}\frac{1}{2\pi}(2a_Z)^{-3}\int_0^\infty r^3\frac{r}{a_Z}\left(1 - \frac{r}{2a_Z}\right)\mathrm{e}^{-r/a_Z}\,\mathrm{d}r\int_0^\pi \cos^2\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\varphi \\
&= \frac{e\mathcal{E}}{16a_Z}\int_0^\infty\left(\frac{r^4}{a_Z} - \frac{r^5}{2a_Z}\right)\mathrm{e}^{-r/a_Z}\,\mathrm{d}r \\
&= \frac{1}{12}\left(\Gamma(5) - \frac{1}{2}\Gamma(6)\right) = -3e\mathcal{E}a_Z
\end{aligned}$$

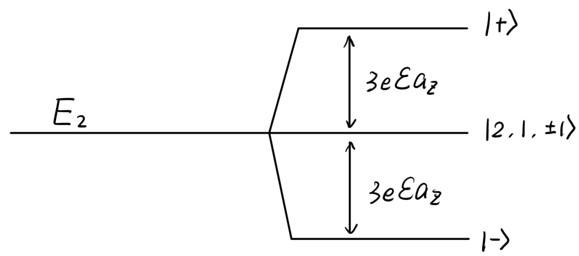
With respect to the basis $\{|2,0,0\rangle, |2,1,1\rangle, |2,1,0\rangle, |2,1,-1\rangle\}$, the matrix of $\hat{V}$ is given by

$$\begin{pmatrix} 0 & 0 & -3e\mathcal{E}a_Z & 0 \\ 0 & 0 & 0 & 0 \\ -3e\mathcal{E}a_Z & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

(d) By direct observation, we know that $\hat{V}$ is diagonalized with respect to the basis $\{|+\rangle, |-\rangle, |2,1,1\rangle, |2,1,-1\rangle\}$, where $|\pm\rangle := \frac{1}{\sqrt{2}}(|2,0,0\rangle \mp |2,1,0\rangle)$:

$$\begin{pmatrix} 3e\mathcal{E}a_Z & 0 & 0 & 0 \\ 0 & -3e\mathcal{E}a_Z & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

The first order perturbation theory gives the shift of the $n = 2$ energy levels: □



Question 2

State and prove the *variational theorem* in quantum mechanics.

Use the theorem to prove that in a one-dimensional system an attractive potential always has a bound state, by taking the following steps. We define an attractive potential $V(x)$ to be one that has finite range a and is negative on average, meaning that

$$V(x) = 0 \quad \text{for} \quad |x| \geqslant a \quad \text{and} \quad \int_{-a}^{a}\mathrm{d}x\,V(x) = -v_0$$

with $v_0 > 0$. Consider a function $f(y)$ that has its maximum at $x = 0$, is non-negative, and approaches zero for $y \to \pm\infty$, with the properties

$$\int_{-\infty}^{+\infty} \mathrm{d}y\, |f(y)|^2 = 1 \quad \text{and} \quad \int_{-\infty}^{+\infty} \mathrm{d}y \left|\frac{\mathrm{d}f(y)}{\mathrm{d}y}\right|^2 = 1$$

For the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$

use the (unnormalized) trial wave function $\psi(x) = f(x/\lambda)$ with variational parameter λ to show that

$$\langle H\rangle := \frac{\int_{-\infty}^{+\infty} \mathrm{d}x\, \psi^*(x)\hat{H}\psi(x)}{\int_{-\infty}^{+\infty} \mathrm{d}x\, |\psi(x)|^2} < 0$$

for sufficiently large λ. How is the situation different for a three-dimensional system?

Solution. We state the Variational Theorem as follows:

Theorem 1. Variational Theorem

Suppose that the Hamiltonian $\hat{H}$ has discrete spectrum, with minimum eigenvalue (ground state energy) E_0. We have $E_0 = \inf_{|\psi\rangle \in \mathscr{H}} \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$. In particular, $\langle\psi|\hat{H}|\psi\rangle \geqslant E_0$ for normalized $|\psi\rangle$.

Proof. Let the functional $g_H : \mathscr{H} \to \mathbb{R}$ given by $g_H(\psi) = \langle\psi|\hat{H}|\psi\rangle$. We shall find the extremal of g_H under the constraint $||\psi|| = 1$. By the method of Lagrange multipliers,

$$\begin{aligned} 0 &= \delta(\langle\psi|\hat{H}|\psi\rangle - \lambda\langle\psi|\psi\rangle) \\ &= \langle\delta\psi|\hat{H}|\psi\rangle + \langle\psi|\hat{H}|\delta\psi\rangle - \lambda\langle\delta\psi|\psi\rangle - \lambda\langle\psi|\delta\psi\rangle \\ &= \langle\delta\psi|(H - \lambda\,\mathrm{id})|\psi\rangle + \langle\psi|(H - \lambda\,\mathrm{id})|\delta\psi\rangle \end{aligned}$$

Since $|\delta\psi\rangle$ is arbitrary, we deduce that $(H - \lambda\,\mathrm{id})\,|\psi\rangle = 0$. That is, λ is an eigenvalue of $\hat{H}$ and $|\psi\rangle$ is an eigenstate of $\hat{H}$. It follows that $f_H(\psi) = \lambda \geqslant E_0$. Moreover, E_0 is in the image of f_H. The claim is hence proved. ☐

We shall first show that the function f satisfying all the given conditions exists. Consider $f_\sigma(x) = (2\pi\sigma)^{-1/4}\exp\left(-\frac{x^2}{4\sigma^2}\right)$. Then $f_\sigma^2(x) = \frac{1}{\sqrt{2\pi\sigma}}\exp\left(-\frac{x^2}{2\sigma^2}\right)$. We recognize that f_σ^2 is the p.d.f. of the normal distribution with mean 0 and variance σ^2. Hence $\int_{\mathbb{R}} f_\sigma^2 = 1$. We compute the derivative:

$$f_\sigma'(x) = -\frac{x}{2\sigma^2} f_\sigma(x) \Longrightarrow \int_{\mathbb{R}} |f_\sigma'|^2 = \int_{\mathbb{R}} \frac{x^2}{4\sigma^4} f_\sigma^2(x)\,\mathrm{d}x = \frac{1}{4\sigma^4}\cdot\sigma^2 = \frac{1}{4\sigma^2}$$

Therefore by taking $\sigma = \frac{1}{2}$ we find the desired function f.

Let $\psi_\lambda(x) = f(x/\lambda)$. The expectation of $\hat{H}$ is the state ψ_λ is given by:

$$\langle\hat{H}\rangle := \frac{\int_{-\infty}^{+\infty} \mathrm{d}x\, \psi^*(x)\hat{H}\psi(x)}{\int_{-\infty}^{+\infty} \mathrm{d}x\, |\psi(x)|^2}$$

$$= \frac{\displaystyle\int_{\mathbb{R}} \left(-\frac{\hbar^2}{2m\lambda^2} f''\left(\frac{x}{\lambda}\right) f\left(\frac{x}{\lambda}\right) + V(x) f\left(\frac{x}{\lambda}\right)^2\right) \mathrm{d}x}{\displaystyle\int_{\mathbb{R}} f\left(\frac{x}{\lambda}\right)^2 \mathrm{d}x}$$

$$= -\frac{\hbar^2}{2m\lambda^2} \int_{\mathbb{R}} f''(t) f(t)\, \mathrm{d}t + \int_{\mathbb{R}} V(\lambda t) f(t)^2\, \mathrm{d}t \qquad \left(\int_{\mathbb{R}} f(t)^2\, \mathrm{d}t = 1\right)$$

$$= -\frac{\hbar^2}{2m\lambda^2} f(t) f'(t)\Big|_{t=-\infty}^{t=+\infty} + \frac{\hbar^2}{2m\lambda^2} \int_{\mathbb{R}} f'(t)^2\, \mathrm{d}t + \int_{\mathbb{R}} V(\lambda t) f(t)^2\, \mathrm{d}t$$

$$= \frac{\hbar^2}{2m\lambda^2} + \int_{-a/\lambda}^{a/\lambda} V(\lambda t) f(t)^2\, \mathrm{d}t \qquad \left(\int_{\mathbb{R}} f'(t)^2\, \mathrm{d}t = 1,\ \operatorname{supp} V \subseteq [-a, a]\right)$$

Since $\int_{\mathbb{R}} V(x)\, \mathrm{d}x = -v_0$ and f is continuous, $\int_{-a/\lambda}^{a/\lambda} V(\lambda t) f(t)^2\, \mathrm{d}t \to -\frac{1}{\lambda} v_0 f(0)^2$ as $\lambda \to \infty$ by mean value theorem. Hence for sufficiently large λ we have

$$\langle \hat{H} \rangle \approx \frac{\hbar^2}{2m\lambda^2} - \frac{1}{\lambda} v_0 f(0)^2 < 0$$

Finally, by variational theorem, the ground state energy $E_0 \leqslant \langle \hat{H} \rangle < 0$. We conclude that the bound states exist.

The theorem is false in the higher dimension case. An example is given in the Wikipedia: `https://en.wikipedia.org/wiki/Finite_potential_well`. ☐

Question 3

In the β decay $\mathrm{H}^3 \to (\mathrm{He}^3)^+$, the emitted electron has a kinetic energy of 16 keV. We will consider the effects on the motion of the atomic electron, i.e. the one orbiting the nucleus, which we assume is initially in the ground state of H^3.

Show by a brief justification that the perturbation is sudden, by considering the location of the emitted electron at a time around $\tau = 5 \times 10^{-17}$ s after emission. How does τ compare with the time-scale on which the wave function changes?

Show that the probability for the electron to be left in the ground state of $(\mathrm{He}^3)^+$ is $2^3(2/3)^6 \approx 0.7$.

Proof. The static energy of the electron is 510 keV $\gg$ 16 keV, so we neglect any relativistic effects. The speed of the emitted electron is $v = \sqrt{\frac{2T}{m_e}} = 0.25c$. After time τ, the electron travels a distance of $\tau c = 3.75$ nm, which is much larger than the radius of an atom. In comparison, the phase factor in the ground state wave function is $\mathrm{e}^{i\frac{E_0}{\hbar}t}$. The period is $\frac{2\pi\hbar}{E_0} = 3.04 \times 10^{-16}$ s, which is larger than τ. Therefore the perturbation is considered to be sudden.

The ground state wave function of a hydrogen-like atom is given by

$$\psi_0(x) = \frac{1}{\sqrt{\pi a_Z^3}} \mathrm{e}^{-r/a_Z}, \quad a_Z = \frac{a_0}{Z}$$

The original and perturbed ground state are given respectively by

$$\psi_0(x) = \frac{1}{\sqrt{\pi a_0^3}} \mathrm{e}^{-r/a_0}, \qquad \phi_0(x) = \sqrt{\frac{2^3}{\pi a_0^3}} \mathrm{e}^{-r/2a_0}$$

The probability of staying in the ground state is given by

$$\mathbb{P} = |\langle \psi_0 | \phi_0 \rangle|^2 = \left(\iiint_{\mathbb{R}^3} \frac{1}{\sqrt{\pi a_0^3}} \mathrm{e}^{-r/a_0} \cdot \sqrt{\frac{2^3}{\pi a_0^3}} \mathrm{e}^{-r/2a_0}\, \mathrm{d}V\right)^2 = \left(2^{3/2} \left(\frac{2}{3}\right)^3 \iiint_{\mathbb{R}^3} \psi_0(x)^2\, \mathrm{d}V\right) = 2^3 \left(\frac{2}{3}\right)^6 \approx 0.7$$

☐

Question 4

At early times ($t \sim -\infty$) a harmonic oscillator of mass m and natural angular frequency ω is in its ground state. A perturbation $\delta H = \mathcal{E} x \, \mathrm{e}^{-t^2/\tau^2}$ is then applied, where $\mathcal{E}$ and τ are constants.

What is the probability according to first-order theory that by late times the oscillator transitions to its second excited state, $|2\rangle$?

Show that to first order in δH the probability that the oscillator transitions to the first excited state, $|1\rangle$, is

$$P = \frac{\pi \mathcal{E}^2 \tau^2}{2m\hbar\omega} \, \mathrm{e}^{-\omega^2\tau^2/2}$$

Plot P as a function of τ and comment on its behaviour as $\omega\tau \to 0$ and $\omega\tau \to \infty$.

Solution. Let $\hat{H}(t) = \hat{H}_0 + \delta\hat{H}(t)$, where $\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2$. Suppose that $\{|n\rangle \,:\, n \in \mathbb{N}\}$ is the set eigenstates of $\hat{H}_0$. The state of the system is given by

$$|\psi(t)\rangle = \textstyle\sum_n c_n(t)\, \mathrm{e}^{-\frac{\mathrm{i}E_n}{\hbar}t} \, |n\rangle$$

Substitute into the time-independent Schrödinger's equation:

$$\textstyle\sum_n \mathrm{e}^{-\frac{\mathrm{i}E_n}{\hbar}t}\left(\mathrm{i}\hbar\frac{\partial c_n}{\partial t}(t) + E_n c_n(t)\right)|n\rangle = \sum_n \mathrm{e}^{-\frac{\mathrm{i}E_n}{\hbar}t}\, c_n(t)(E_n + \delta\hat{H}(t))\,|n\rangle$$

Acting $\frac{1}{\mathrm{i}\hbar}\,\mathrm{e}^{\frac{\mathrm{i}E_m}{\hbar}t}\langle m|$ on both sides:

$$\frac{\partial c_m}{\partial t} = \frac{1}{\mathrm{i}\hbar}\textstyle\sum_n \mathrm{e}^{\mathrm{i}(E_m - E_n)t/\hbar}\, c_n(t)\langle m|\delta\hat{H}(t)|n\rangle$$

The system is in the ground state $|0\rangle$ at $t = -\infty$. In the zeroth approximation of $\delta\hat{H}(t)$, we have $c_n(t) = \langle n|0\rangle = \delta_{n,0}$. Substitute it into the expression above to obtain the first order approximation:

$$\frac{\partial c_m}{\partial t} = \frac{1}{\mathrm{i}\hbar}\,\mathrm{e}^{\mathrm{i}(E_m - E_0)t/\hbar}\langle m|\delta\hat{H}(t)|0\rangle$$

First we compute the matrix element $\langle m|\delta\hat{H}(t)|0\rangle$ for $m = 2$:

$$\langle 2|\delta\hat{H}(t)|0\rangle = \mathcal{E}\,\mathrm{e}^{-t^2/\tau^2}\langle 2|\hat{x}|0\rangle = \mathcal{E}\,\mathrm{e}^{-t^2/\tau^2}\langle 2|\hat{x}|0\rangle = \mathcal{E}\,\mathrm{e}^{-t^2/\tau^2}\sqrt{\frac{\hbar}{2m\omega}}\langle 2|\hat{a} + \hat{a}^\dagger|0\rangle = 0$$

Hence $\frac{\partial c_2}{\partial t} = 0$. As $c_2 = 0$ at $t = -\infty$. We deduce that c_2 is identically zero. Hence the probability of transition to second excited state is zero.

Next we compute the matrix element $\langle m|\delta\hat{H}(t)|0\rangle$ for $m = 1$:

$$\langle 1|\delta\hat{H}(t)|0\rangle = \mathcal{E}\,\mathrm{e}^{-t^2/\tau^2}\sqrt{\frac{\hbar}{2m\omega}}\langle 1|\hat{a} + \hat{a}^\dagger|0\rangle = \mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\,\mathrm{e}^{-t^2/\tau^2}$$

We integrate c_1 over time:

$$c_1(t) = \frac{1}{\mathrm{i}\hbar}\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\int_{-\infty}^{t}\exp\left(-\frac{t'^2}{\tau^2} + \mathrm{i}\omega t'\right)\mathrm{d}t'$$

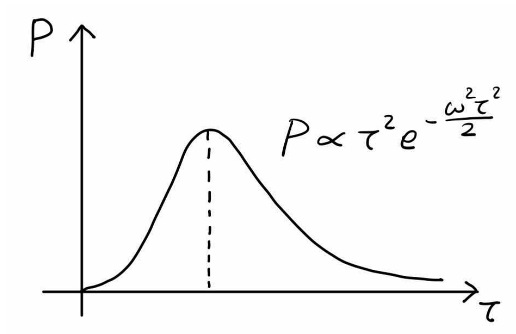
At $t \gg \tau$, approximately we have

$$\begin{aligned} c_1 &= \frac{1}{\mathrm{i}\hbar}\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\int_{-\infty}^{+\infty}\exp\left(-\frac{t^2}{\tau^2} + \mathrm{i}\omega t\right)\mathrm{d}t \\ &= \frac{1}{\mathrm{i}\hbar}\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\,\mathrm{e}^{-\omega^2\tau^2/4}\int_{-\infty}^{+\infty}\exp\left(-\frac{1}{\tau^2}\left(t - \frac{\mathrm{i}\omega\tau^2}{2}\right)^2\right)\mathrm{d}t \\ &= \frac{1}{\mathrm{i}\hbar}\mathcal{E}\sqrt{\frac{\hbar}{2m\omega}}\tau\sqrt{\pi}\,\mathrm{e}^{-\omega^2\tau^2/4} \end{aligned}$$

Hence the probability of transition to first excited state is

$$P = |c_1|^2 = \frac{\pi \mathcal{E}^2 \tau^2}{2m\hbar\omega}\, \mathrm{e}^{-\omega^2\tau^2/2}$$

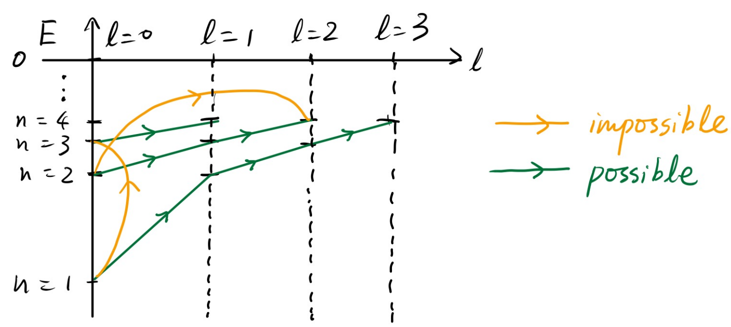
We observe that $P \to \dfrac{\pi \mathcal{E}^2 \tau^2}{2m\hbar\omega}$ as $\omega\tau \to 0$ and $P \to 0$ as $\omega\tau \to \infty$. The plot of P against τ: □



Question 5

Write down the selection rules for radiative transitions in the electric dipole approximation. Draw an energy level diagram for hydrogen (use the vertical direction for energy, and separate the states horizontally by angular momentum ℓ). Show how the selection rules apply to hydrogen by marking allowed transitions on your diagram.

Solution. The selection rules say that the radiative transitions from state $|n, l, m\rangle$ to state $|n', l', m'\rangle$ only if $|l - l'| = 1$ and $|m - m'| \leqslant 1$. Here is a diagram. □



Question 6

With $|n, l, m\rangle$ a stationary state of hydrogen, which of these matrix elements is non-zero?

$$\begin{array}{ccc} \langle 1,0,0|z|2,0,0\rangle & \langle 1,0,0|z|2,1,0\rangle & \langle 1,0,0|z|2,1,1\rangle \\ \langle 1,0,0|z|3,0,0\rangle & \langle 1,0,0|z|3,1,0\rangle & \langle 1,0,0|z|3,2,0\rangle \\ \langle 1,0,0|x|2,0,0\rangle & \langle 1,0,0|x|2,1,0\rangle & \langle 1,0,0|x|2,1,1\rangle \end{array}$$

Solution. In Question 1 we argue that $\langle n, l, m|\hat{z}|n', l', m'\rangle = 0$ unless $m = m'$ and $|l - l'| = 1$. We immediately obtain that

$$\langle 1,0,0|z|2,0,0\rangle = 0 \qquad \langle 1,0,0|z|2,1,1\rangle = 0 \qquad \langle 1,0,0|z|3,0,0\rangle = 0 \qquad \langle 1,0,0|z|3,2,0\rangle = 0$$

For $\langle 1,0,0|z|2,1,0\rangle$ and $\langle 1,0,0|z|3,1,0\rangle$, we need to compute the integral over the radial component. From Binney's book we know that the radial solutions to the TISE are

$$R_{1,0}(r) \propto a_0^{-3/2}\,\mathrm{e}^{-r/a_0} \qquad R_{2,1}(r) \propto a_0^{-3/2}\frac{r}{a_0}\,\mathrm{e}^{-r/2a_0} \qquad R_{3,1}(r) \propto a_0^{-3/2}\frac{r}{a_0}\left(1-\frac{r}{6a_0}\right)\mathrm{e}^{-r/3a_0}$$

Clearly $\int_0^\infty r^3 R_{1,0}(r)R_{2,1}(r)\,\mathrm{d}r > 0$. Therefore $\langle 1,0,0|z|2,1,0\rangle \neq 0$. For $\langle 1,0,0|z|3,1,0\rangle$,

$$\begin{aligned}\int_0^\infty r^3 R_{1,0}(r)R_{3,1}(r)\,\mathrm{d}r \propto a_0^{-3}\int_0^\infty r^3\frac{r}{a_0}\left(1-\frac{r}{6a_0}\right)\mathrm{e}^{-4r/3a_0}\,\mathrm{d}r &= \int_0^\infty \left(\frac{3^4}{4^4}\left(\frac{4r}{3a_0}\right)^4 - \frac{3^5}{6\cdot 4^5}\left(\frac{4r}{3a_0}\right)^5\right)\mathrm{e}^{-4r/3a_0}\,\mathrm{d}r \\ &= \left(\frac{3^5}{4^5}4! - \frac{3^6}{6\cdot 4^6}5!\right)a_0 \neq 0\end{aligned}$$

Therefore $\langle 1,0,0|z|3,1,0\rangle \neq 0$.

In spherical coordinates, $x = r\sin\theta\cos\varphi$. For the integral over φ component:

$$\int_0^{2\pi}\cos\varphi\,\mathrm{e}^{\mathrm{i}(m-m')\varphi}\,\mathrm{d}\varphi = \int_0^{2\pi}\cos\varphi\cos(m-m')\varphi\,\mathrm{d}\varphi = 0 \qquad \text{for } |m-m'| \neq 1$$

by the orthogonal relations. Therefore we have $\langle 1,0,0|x|2,0,0\rangle = 0$ and $\langle 1,0,0|x|2,1,0\rangle = 0$.

For $\langle 1,0,0|x|2,1,1\rangle$, the integral over φ is non-zero. As shown previously the integral over radial component is non-zero. For the integral over θ,

$$\int_0^\pi \sin^2\theta P_0^0(\cos\theta)P_1^1(\cos\theta)\,\mathrm{d}\theta = \int_0^\pi \sin^3\theta\,\mathrm{d}\theta \neq 0$$

Hence $\langle 1,0,0|x|2,1,1\rangle \neq 0$.

In conclusion, the non-zero matrix elements are $\langle 1,0,0|z|2,1,0\rangle$, $\langle 1,0,0|z|3,1,0\rangle$ and $\langle 1,0,0|x|2,1,1\rangle$. □

Question 7

With $|n,l,m\rangle$ a stationary state of hydrogen, and given that

$$Y_{1,0}(\theta,\phi) = \sqrt{\frac{6}{8\pi}}\cos\theta \quad Y_{1,1}(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta\,\mathrm{e}^{\mathrm{i}\phi} \quad Y_{1,-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta\,\mathrm{e}^{-\mathrm{i}\phi}$$

show that

$$\langle 1,0,0|x-\mathrm{i}y|2,1,1\rangle = -\sqrt{2}\langle 1,0,0|z|2,1,0\rangle$$
$$\langle 1,0,0|x-\mathrm{i}y|2,1,-1\rangle = 0$$

Write down the values of $\langle 1,0,0|x+\mathrm{i}y|2,1,-1\rangle$ and $\langle 1,0,0|x+\mathrm{i}y|2,1,1\rangle$ and hence show that with

$$|\psi\rangle := \frac{1}{\sqrt{2}}\left(|2,1,1\rangle - |2,1,-1\rangle\right),$$

$\langle 1,0,0|x|\psi\rangle = -\langle 1,0,0|z|2,1,0\rangle$, Explain the physical significance of this result.

Proof. In spherical coordinates, $x \pm \mathrm{i}y = r\sin\theta(\cos\varphi \pm \sin\varphi) = r\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi}$ and $z = r\cos\theta$ It suffices to compute the integral over the angular coordinates.

$$\int_{\theta=0}^{\theta=\pi}\int_{\varphi=0}^{\varphi=2\pi}\sin\theta\,\mathrm{e}^{-\mathrm{i}\varphi}\,Y_{0,0}(\theta,\varphi)Y_{1,1}(\theta,\varphi)\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta = \frac{1}{\sqrt{4\pi}}\cdot\left(-\sqrt{\frac{3}{8\pi}}\right)\int_0^{2\pi}\mathrm{d}\varphi\int_0^\pi\sin^3\theta\,\mathrm{d}\theta = -\frac{\sqrt{3}}{4\sqrt{2}\pi}\cdot 2\pi\cdot\frac{4}{3} = -\frac{\sqrt{6}}{3}$$

$$\int_{\theta=0}^{\theta=\pi}\int_{\varphi=0}^{\varphi=2\pi}\sin\theta\,\mathrm{e}^{-\mathrm{i}\varphi}\,Y_{0,0}(\theta,\varphi)Y_{1,-1}(\theta,\varphi)\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta=0 \qquad \text{bacause} \int_0^{2\pi}\mathrm{e}^{-2\mathrm{i}\varphi}\,\mathrm{d}\varphi=0$$

$$\int_{\theta=0}^{\theta=\pi}\int_{\varphi=0}^{\varphi=2\pi}\cos\theta Y_{0,0}(\theta,\varphi)Y_{1,0}(\theta,\varphi)\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta=\frac{\sqrt{3}}{2}\int_0^{\pi}\cos^{\theta}\sin\theta\,\mathrm{d}\theta=\frac{\sqrt{3}}{3}$$

Hence we have $\langle 1,0,0|x-\mathrm{i}y|2,1,1\rangle=-\sqrt{2}\langle 1,0,0|z|2,1,0\rangle$ and $\langle 1,0,0|x-\mathrm{i}y|2,1,-1\rangle=0$.

Similarly we also have $\langle 1,0,0|x+\mathrm{i}y|2,1,-1\rangle=\sqrt{2}\langle 1,0,0|z|2,1,0\rangle$ and $\langle 1,0,0|x+\mathrm{i}y|2,1,1\rangle=0$. Since $x=\frac{1}{2}((x+\mathrm{i}y)+(x-\mathrm{i}y))$

$$\begin{aligned}\langle 1,0,0|x|\psi\rangle &= \frac{1}{\sqrt{2}}(\langle 1,0,0|x|2,1,1\rangle-\langle 1,0,0|x|2,1,-1\rangle)\\ &= \frac{1}{2\sqrt{2}}(\langle 1,0,0|x-\mathrm{i}y|2,1,1\rangle+\langle 1,0,0|x+\mathrm{i}y|2,1,1\rangle-\langle 1,0,0|x+\mathrm{i}y|2,1,-1\rangle-\langle 1,0,0|x-\mathrm{i}y|2,1,-1\rangle)\\ &= \frac{1}{2\sqrt{2}}(-\sqrt{2}\langle 1,0,0|z|2,1,0\rangle-\sqrt{2}\langle 1,0,0|z|2,1,0\rangle)\\ &= -\langle 1,0,0|z|2,1,0\rangle\end{aligned}$$

□

Question 8

Derive the selection rules

$$\langle n',l',m'|x_+|n,l,m\rangle=0 \quad \text{unless} \quad m'=m+1$$
$$\langle n',l',m'|x_-|n,l,m\rangle=0 \quad \text{unless} \quad m'=m-1$$

where $x_\pm=x\pm\mathrm{i}y$. From this selection rule one infers that when the atom sits in a magnetic field along the z-axis and the spectrometer looks along the z-axis, the detected photons will be circularly polarized. Show that linearly polarized photons *can* be detected from an atom that is in a magnetic field.

From the above rules it might be argued that photons emitted along the z-axis will be circularly polarized even in the absence of a magnetic field. Why is this argument bogus?

Solution. In spherical coordinates, $x_\pm=x\pm\mathrm{i}y=r\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\varphi}$. For $\langle n',l',m'|x_\pm|n,l,m\rangle$, the integral over the φ component is

$$\int_0^{2\pi}\mathrm{e}^{\pm\mathrm{i}\varphi}\cdot\mathrm{e}^{\mathrm{i}(m-m')\varphi}\,\mathrm{d}\varphi=0 \qquad \text{unless } m-m'\pm1=0$$

which gives the selection rules for m and m'.

The linearly polarized can be detected from the perpendicular direction of the magnetic field.

□