QM3 workshop 4

Problem 1 (Problem from D. Griffiths, Introduction to QM)

A hydrogen atom is placed in a time-dependent electric field $\boldsymbol{E} = E(t)\,\hat{\boldsymbol{z}}$.
We consider the ground state ($n = 1$) and the quadruply degenerate first excited states ($n = 2$).
(a) Calculate all four matrix elements H'_{ij} of the perturbation $H' = -eEz$ between the ground state ($n = 1$) and the quadruply degenerate first excited states ($n = 2$).
Note: Only one integral is nonzero; you can realise which one it is if you exploit oddness with respect to z.
(b) Show that $H'_{ii} = 0$ for all five states.
The eigenfunctions of the hydrogen atom are: ($m = -l, \ldots, l$; $l = 0, 1, \ldots, n-1$; $n = 1, 2, \ldots$)

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_{lm}(\theta, \phi)$$

with

$$\begin{aligned} R_{10} &= \frac{2}{\sqrt{a^3}}\, e^{-r/a}, \\ R_{20} &= \frac{1}{\sqrt{2\, a^3}} \left(1 - \frac{r}{2a}\right) e^{-r/2a}, \\ R_{21} &= \frac{1}{2\sqrt{6\, a^3}}\, \frac{r}{a}\, e^{-r/2a} \end{aligned}$$

$$\begin{aligned} Y_{0,0}(\theta, \phi) &= \frac{1}{\sqrt{4\pi}} \\ Y_{1,0}(\theta, \phi) &= \sqrt{\frac{3}{4\pi}}\, \cos\theta \\ Y_{1,\pm1}(\theta, \phi) &= \mp\sqrt{\frac{3}{8\pi}}\, \sin\theta \exp(\pm i\phi) \end{aligned}$$

$$\int_0^\infty r^k \exp(-\alpha r)\, \mathrm{d}r = k!/\alpha^{k+1}.$$

Solution (a)

The aim of this problem is to find out which matrix elements vanish without doing the full integrations over r, θ, ϕ. Let's take the matrix element

$$\langle 100|H'|200\rangle = -e\, E\, \langle 100|z|200\rangle$$

It holds: $z = r\, \cos\theta$ and hence: (We need this later on.)

$$z = \sqrt{\frac{4\pi}{3}}\, r\, Y_{1,0}(\theta, \phi) \tag{1}$$

We have:

$$\langle \psi_{100}|z|\psi_{200}\rangle = 0 \text{ because integrand odd function of } z$$

$$\langle\psi_{100}|z|\psi_{21\pm1}\rangle = \phi \text{ integral gives } 0$$

We use (1) below:

$$\begin{aligned}\langle\psi_{100}|z|\psi_{210}\rangle &= \int_0^\infty dr\, r^2\, R_{10}(r)\, R_{21}(r) \int_0^\infty d\phi \int_0^{\pi/2} d\theta\, \sin\theta \left[\sqrt{\frac{4\pi}{3}}\, r\, Y_{1,0}(\theta,\phi)\right] Y_{00}\, Y_{10}(\theta,\phi) \\ &= \frac{1}{\sqrt{3}} \int_0^\infty dr\, r^3\, R_{10}(r)\, R_{21}(r) \underbrace{\int_0^\infty d\phi \int_0^{\pi/2} d\theta\, \sin\theta\, Y_{1,0}(\theta,\phi)\, Y_{10}(\theta,\phi)}_{1}\end{aligned}$$

$$= \frac{1}{\sqrt{3}} \frac{1}{\sqrt{a^3}} \frac{1}{\sqrt{6\, a^3}} \int_0^\infty dr\, r^3\, e^{-r/a}\, \frac{r}{a}\, e^{-r/2a} = \frac{a}{3\sqrt{2}} \int_0^\infty ds\, s^4\, e^{-3s/2} = \frac{a\, 2^7 \sqrt{2}}{3^5} = 0.7449a$$

So, $\langle\psi_{100}|(-eEz)|\psi_{210}\rangle = -0.7449\, e\, E\, a$.

Solution (b)

We have to evaluate the diagonal matrix elements:

$$\langle\psi_{nlm}|z|\psi_{nlm}\rangle = \iint dx\, dy \int_{-\infty}^{\infty} dz\, z\, |\psi_{nlm}(x,y,z)|^2$$

$|\psi_{nlm}|^2$ is a function only of r when $n, l, m = 1, 0, 0$; when $n, l, m = n, 1, 0$, then $|\psi_{nlm}|^2$ is a function of r and of $\cos^2\theta$ which is proportional to z^2, so even function of z. When $n, l, m = n, 1, \pm1$, then $|\psi_{nlm}|^2$ is a function of r and of $\sin^2\theta = 1 - \cos^2\theta$, so it still depends on z^2 and is an even function of z. So, finally the integrand in $\iint dx\, dy \int_{-\infty}^{\infty} dz\, z\, |\psi_{nlm}(x,y,z)|^2$ is always odd in z and the z integration of an odd function of z vanishes.

Problem 2:

As a mechanism for downward transitions, spontaneous emission competes with thermally stimulated emission (i.e. by the blackbody radiation). Show that at room temperature, ($T = 300$K) thermal stimulation dominates for frequencies well below 5×10^{12}Hz, whereas spontaneous emission dominates for frequencies well above 5×10^{12}Hz. Which mechanism dominates for visible light?

The spontaneous emission rate is:

$$A = \frac{\omega^3 |\mathcal{P}|^2}{3\pi\, \epsilon_0 \hbar c^3}$$

Rate for emission stimulated by thermal (blackbody) radiation is:

$$R = \frac{\pi}{3\epsilon_0 \hbar^2} |\mathcal{P}|^2 \rho(\omega), \quad \rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

Solution 2

The ratio of the rates of spontaneous emission thermally stimulated emission is:

$$\frac{A}{R} = \frac{\omega^3 |\mathcal{P}|^2}{3\pi\, \epsilon_0 \hbar c^3} \frac{3\epsilon_0 \hbar^2}{\pi\, |\mathcal{P}|^2} \frac{\pi^2 c^3}{\hbar} \frac{e^{\hbar\omega/k_B T} - 1}{\omega^3} = e^{\hbar\omega/k_B T} - 1$$

The rate for spontaneous emission dominates for

$$e^{\hbar\omega/k_BT} \gg 2 \;\Rightarrow\; \omega \gg \frac{\ln 2\, k_BT}{\hbar} \Rightarrow \nu \gg \frac{\ln 2\, k_BT}{h}$$

$$\nu \gg \frac{(1.38\times 10^{-23}\mathrm{J/K})(300\mathrm{K})}{6.63\times 10^{-34}\mathrm{J\,s}}\ln 2 = 4.35\times 10^{12}\mathrm{Hz}$$

This includes visible light $\sim$ 4-8 $\times 10^{14}$Hz.

Problem 3

Calculate the rate for spontaneous emission

$$A = \frac{\omega_0^3|\mathcal{P}|^2}{3\,\pi\,\epsilon_0\,\hbar\,c^3}$$

and the lifetime, $\tau = 1/A$, for each of the four $n = 2$ states of hydrogen.

$\mathcal{P}$ is the matrix element of the dipole moment $q\boldsymbol{r}$ in the initial and final states $\mathcal{P} = \langle\psi_{\rm in}|q\boldsymbol{r}|\psi_{\rm fi}\rangle$. You will need to evaluate matrix elements of the form $\langle\psi_{100}|x|\psi_{200}\rangle$ and so on. Remember:

$$x = r\ \sin\theta\ \cos\phi,\ \ y = r\ \sin\theta\ \sin\phi,\ \ z = r\ \cos\theta.$$

Also the ground state energy of the H atom and the Bohr radius a are:

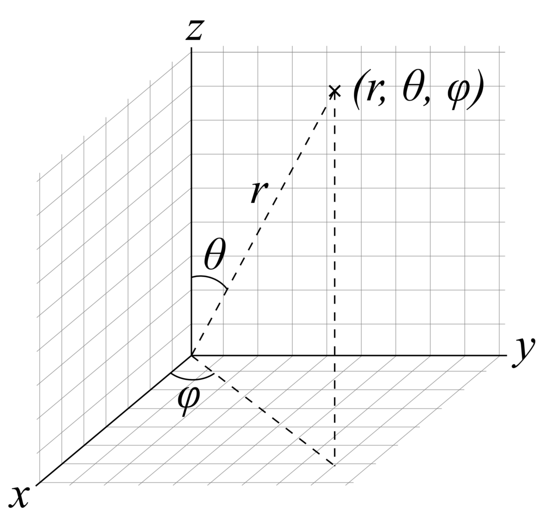
$$E_1 = -\frac{\hbar^2}{2ma^2}, \quad a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529\times 10^{-10}\mathrm{m}$$

Solution 3

We want to assess, without a calculation, whether integrals such as $\int dxdydz\, x\, f(r,\theta,\phi)$, $\int dxdydz\, y\, f(r,\theta,\phi)$ are zero.

So, we must find out if the function $f(r,\theta,\phi)$ is an even or odd function of x, y, when the function is known in terms of r,θ,ϕ.

If a function is even in x, then when we transform $x\to -x$ the function must go to itself. If it is odd, then the function must go to minus itself.



From the figure, the transformation $x \to -x$ is equivalent to

$$x \to -x \;\; \text{equivalent to} \quad \begin{cases} r \to r, \\ \theta \to \theta, \\ \phi \to \pi - \phi. \end{cases}$$

The first two are obvious, the last transformation for ϕ can also be inferred from:

$$\cos\phi' = -\cos\phi, \quad \sin\phi' = \sin\phi \;\Rightarrow\; \phi' = \pi - \phi$$

The transformation to check if the function is even in y is:

$$y \to -y \;\; \text{equivalent to} \quad \begin{cases} r \to r, \\ \theta \to \theta, \\ \phi \to 2\pi - \phi. \end{cases}$$

So, ψ_{100} is even function of x and y (obvious)!
ψ_{200} is also obviously even in both x and y.
$\psi_{210}(r, \theta, \phi)$ is also even function of x and y (independent of ϕ).

Since the states $\psi_{100}, \psi_{200}, \psi_{210}$ are all even functions of x, y, the matrix elements vanish: $\langle 100|x|200\rangle = 0$, $\langle 100|x|210\rangle = 0$, $\langle 100|y|200\rangle = 0$, $\langle 100|y|210\rangle = 0$.

The state $\psi_{211} = R_{21}(r)\, Y_{11}(\theta, \phi)$ is neither even nor odd:

$$Y_{11}(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} \;\to\; -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i(\pi-\phi)} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} = Y_{1-1}(\theta,\phi).$$

We could obtain the matrix elements for x, y directly. It is a little quicker if, instead of calculating separately the matrix elements for x and y, we combine them and find the matrix elements of $x \pm iy$:

$$x \pm i\, y = r\;\sin\theta\; e^{\pm\phi} = \mp\, r\sqrt{\frac{8\pi}{3}}\, Y_{1\pm1}(\theta\phi)$$

($d\Omega$ is shorthand for $\sin\theta\, d\theta\, d\phi$)

$$\langle 211|x \pm iy|100\rangle = \mp\sqrt{\frac{8\pi}{3}}\, Y_{00}\int dr\, r^3 R_{21}(r)\, R_{10}(r)\; \underbrace{\int d\Omega\, Y^*_{11}(\omega)\, Y_{1\pm1}(\Omega)}$$

So,

$$\langle 211|x + iy|100\rangle = -\sqrt{\frac{8\pi}{3}}\, Y_{00}\int dr\, r^3 R_{21}(r)\, R_{10}(r)\; \underbrace{\int d\Omega\, Y^*_{11}(\omega)\, Y_{11}(\Omega)}_{1}$$

$$\langle 211|x - iy|100\rangle = +\sqrt{\frac{8\pi}{3}}\, Y_{00}\int dr\, r^3 R_{21}(r)\, R_{10}(r)\; \underbrace{\int d\Omega\, Y^*_{11}(\omega)\, Y_{1-1}(\Omega)}_{0}$$

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add and subtract:

$$\langle 211|x|100\rangle = -\frac{1}{\sqrt{6}}\int dr\, r^3 R_{21}(r)\, R_{10}(r) = -\frac{2^7\, a}{3^5}$$

$$\langle 211|y|100\rangle = \frac{i}{\sqrt{6}} \int dr\, r^3 R_{21}(r)\, R_{10}(r) = i\, \frac{2^7\, a}{3^5}$$

$$\text{because : } \frac{1}{\sqrt{6}} \int dr\, r^3 R_{21}(r)\, R_{10}(r) = \frac{1}{6\, a^3} \int dr\, r^3\, \frac{r}{a}\, e^{-(3/2a)r} = \frac{a}{6} \int ds\, s^4\, e^{-(3/2)s} = \frac{2^7\, a}{3^5}$$

We also want:

$$\langle 21-1|x \pm iy|100\rangle = \mp\sqrt{\frac{8\pi}{3}}\, Y_{00} \int dr\, r^3 R_{21}(r)\, R_{10}(r)\, \underbrace{\int d\Omega\, Y^*_{1-1}(\omega)\, Y_{1\pm 1}(\Omega)}$$

So,

$$\langle 21-1|x+iy|100\rangle = -\sqrt{\frac{8\pi}{3}}\, Y_{00} \int dr\, r^3 R_{21}(r)\, R_{10}(r)\, \underbrace{\int d\Omega\, Y^*_{1-1}(\omega)\, Y_{11}(\Omega)}_{0}$$

$$\langle 21-1|x-iy|100\rangle = +\sqrt{\frac{8\pi}{3}}\, Y_{00} \int dr\, r^3 R_{21}(r)\, R_{10}(r)\, \underbrace{\int d\Omega\, Y^*_{1-1}(\omega)\, Y_{1-1}(\Omega)}_{1}$$

$$\langle 21-1|x|100\rangle = \frac{1}{\sqrt{6}} \int dr\, r^3 R_{21}(r)\, R_{10}(r) = \frac{2^7\, a}{3^5}$$

$$\langle 21-1|y|100\rangle = -\frac{i}{\sqrt{6}} \int dr\, r^3 R_{21}(r)\, R_{10}(r) = -i\, \frac{2^7\, a}{3^5}$$

Summarise all the matrix elements:

$$\langle 211|x|100\rangle = -\frac{2^7\, a}{3^5}, \quad \langle 211|y|100\rangle = i\, \frac{2^7\, a}{3^5}$$

$$\langle 21-1|x|100\rangle = \frac{2^7\, a}{3^5}, \quad \langle 21-1|y|100\rangle = -i\, \frac{2^7\, a}{3^5}$$

From Problem 1:

$$\langle 210|z|100\rangle = \frac{a\, 2^7 \sqrt{2}}{3^5}$$

So, the matrix elements of the dipole moment $q\boldsymbol{r}$ are:

$$\langle 200|q\boldsymbol{r}|100\rangle = 0 \Rightarrow |\mathcal{P}_{|200\rangle\to|100\rangle}|^2 = 0$$

$$\langle 210|q\boldsymbol{r}|100\rangle = \frac{qa\, 2^7\sqrt{2}}{3^5}\, \hat{\boldsymbol{z}} \Rightarrow |\mathcal{P}_{|210\rangle\to|100\rangle}|^2 = \frac{(qa)^2\, 2^{15}}{3^{10}}$$

$$\langle 211|q\boldsymbol{r}|100\rangle = \frac{qa\, 2^7}{3^5}\, \big(-\hat{\boldsymbol{x}} + i\hat{\boldsymbol{y}}\big) \Rightarrow |\mathcal{P}_{|211\rangle\to|100\rangle}|^2 = \frac{(qa)^2\, 2^{15}}{3^{10}}$$

$$\langle 21-1|q\boldsymbol{r}|100\rangle = \frac{qa\, 2^7}{3^5}\, \big(\hat{\boldsymbol{x}} - i\hat{\boldsymbol{y}}\big) \Rightarrow |\mathcal{P}_{|21-1\rangle\to|100\rangle}|^2 = \frac{(qa)^2\, 2^{15}}{3^{10}}$$

We have:

$$A = \frac{\omega_0^3 |\mathcal{P}|^2}{3\,\pi\,\epsilon_0\,\hbar\, c^3} = \frac{\omega_0^3}{3\,\pi\,\epsilon_0\,\hbar\, c^3}\, \frac{(ea)^2\, 2^{15}}{3^{10}}$$

The difference in energies:

$$\omega_0 = \frac{E_2 - E_1}{\hbar} = -\frac{3E_1}{4\hbar} = \frac{3\hbar}{2^3 ma^2}$$

Finally, $\tau = 1/A$. What is the final formula for A, τ?

Problem 4 The Hamiltonian for a particle with charge q, mass m in a vector potential $\boldsymbol{A}$ is:

$$H = \frac{1}{2m}\big[\boldsymbol{p} - q\,\boldsymbol{A}(\boldsymbol{r})\big]^2. \tag{2}$$

In general, the commutator $[\boldsymbol{p}, \boldsymbol{A}(\boldsymbol{r})]$ does not vanish.
For vector operators, we define $[\boldsymbol{p}, \boldsymbol{A}(\boldsymbol{r})] = \boldsymbol{p}\cdot\boldsymbol{A}(\boldsymbol{r}) - \boldsymbol{A}(\boldsymbol{r})\cdot\boldsymbol{p}$.
(a) Obtain the commutator $\big[\boldsymbol{p}, \boldsymbol{A}(\boldsymbol{r})\big]$.
(b) Expand the Hamiltonian (2). Explain why it is convenient to choose the gauge of $\boldsymbol{A}$ to satisfy $\boldsymbol{\nabla}\cdot\boldsymbol{A}(\boldsymbol{r}) = 0$.

[Hint: Use a test function ϕ to obtain the commutator and when you expand the Hamiltonian.]

Solution: (a) Commutator $[\boldsymbol{p}, \boldsymbol{A}]$

It is useful to invoke a test function ϕ to obtain the commutator:

$$[\boldsymbol{p}, \boldsymbol{A}]\,\phi = (-i\hbar\boldsymbol{\nabla})\cdot\boldsymbol{A}\,\phi - \boldsymbol{A}\cdot(-i\hbar\boldsymbol{\nabla})\,\phi \tag{3}$$

On the 1st term on the r.h.s. the grad acts on $\boldsymbol{A}$ and on ϕ. On the 2nd term on the r.h.s. the grad acts only on ϕ.

The 1st term on the r.h.s. gives two terms, one in which grad acts on $\boldsymbol{A}$ and another term in which grad acts on ϕ:

$$(-i\hbar\boldsymbol{\nabla})\cdot\boldsymbol{A}\,\phi = -i\hbar\,\phi\,\boldsymbol{\nabla}\cdot\boldsymbol{A} - i\hbar\boldsymbol{A}\cdot\boldsymbol{\nabla}\,\phi \tag{4}$$

From (3), (4) we obtain for the commutator:

$$[\boldsymbol{p}, \boldsymbol{A}]\,\phi = -i\hbar\,\phi\,\boldsymbol{\nabla}\cdot\boldsymbol{A} \tag{5}$$

In the above, the differential operator acts only on the vector potential, not on the test function. We have then:

$$[\boldsymbol{p}, \boldsymbol{A}] = -i\hbar\,\boldsymbol{\nabla}\cdot\boldsymbol{A} \tag{6}$$

The commutator is proportional to the divergence of the vector potential.

(b) Expand H:

$$\begin{aligned} H\phi &= \frac{1}{2m}\big[\boldsymbol{p} - q\,\boldsymbol{A}(\boldsymbol{r})\big]\cdot\big[\boldsymbol{p} - q\,\boldsymbol{A}(\boldsymbol{r})\big]\phi = \frac{1}{2m}\big[p^2 - q\,\boldsymbol{p}\cdot\boldsymbol{A}(\boldsymbol{r}) - q\boldsymbol{A}(\boldsymbol{r})\cdot\boldsymbol{p} + q^2\,A^2(\boldsymbol{r})\big]\phi \\ &= \frac{1}{2m}\big[-\hbar^2\nabla^2 + 2i\hbar q\boldsymbol{A}(\boldsymbol{r})\cdot\boldsymbol{\nabla} + q^2\,A^2(\boldsymbol{r})\big]\phi + \frac{i\hbar q\phi}{2m}\big(\boldsymbol{\nabla}\cdot\boldsymbol{A}(\boldsymbol{r})\big) \end{aligned}$$

So, we conclude:

$$H = \frac{1}{2m}\big[-\hbar^2\nabla^2 + 2i\hbar q\boldsymbol{A}(\boldsymbol{r})\cdot\boldsymbol{\nabla} + q^2\,A^2(\boldsymbol{r})\big] + \frac{i\hbar q}{2m}\big(\boldsymbol{\nabla}\cdot\boldsymbol{A}(\boldsymbol{r})\big)$$

In the last term, it is understood that we take the divergence of $\boldsymbol{A}$ and the differential operator inside the parenthesis acts only inside the parenthesis.

By choosing the gauge of the vector potential to have zero divergence, the last term vanishes.