UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part II

May–June 2020 **1 hour 15 minutes**

PHYSICS (3)
PHYSICAL SCIENCES: HALF SUBJECT PHYSICS (3)

ADVANCED QUANTUM PHYSICS

*Candidates offering this paper should attempt a total of **four** questions: **three** questions from Section A and **one** question from Section B.*

*The approximate number of marks allocated to each question or part of a question is indicated in the right margin. This paper contains **four** sides, including this coversheet. You may use the formula handbook for values of constants and mathematical formulae, which you may quote without proof.*

You have 75 minutes (plus any pre-agreed individual adjustment) to answer this paper. Do not start to read the questions on the subsequent pages of this question paper until the start of the time period.

Please treat this as a closed-book exam and write your answers within the time period. Downloading and uploading times should not be included in the allocated exam time. If you wish to print out the paper, do so in advance. You can pause your work on the exam in case of an external distraction, or delay uploading your work in case of technical problems.

Section A and the chosen section B question should be uploaded as separate pdfs. Please name the files 1234X_Qi.pdf, where 1234X is your examination code and i is the number of the question/section (A or 4 or 5).

STATIONERY REQUIREMENTS	SPECIAL REQUIREMENTS
Master coversheet	Mathematical Formulae handbook Approved calculator allowed

SECTION A

*Attempt **all** questions in this Section. Answers should be concise and relevant formulae may be assumed without proof.*

1 Two spin-$\frac{1}{2}$ particles exhibit an exchange-like interaction between their spins

$$\widehat{H} = A[3(\widehat{S}_1^z \widehat{S}_2^z) - \widehat{\boldsymbol{S}}_1 \cdot \widehat{\boldsymbol{S}}_2],$$

where A is a constant. Show that the triplet and singlet states are eigenfunctions of the spin Hamiltonian with eigenvalues 0 for $|0,0\rangle$, $-\hbar^2 A$ for $|1,0\rangle$ and $\frac{\hbar^2 A}{2}$ for $|1,\pm 1\rangle$, where the first and second indices are quantum numbers of the total spin operators $\widehat{S}^2$ and $\widehat{S}^z$, respectively. [4]

We use that $\widehat{\boldsymbol{S}}_1 \cdot \widehat{\boldsymbol{S}}_2 = \frac{1}{2}(\widehat{S}^2 - \widehat{S}_1^2 - \widehat{S}_2^2)$. If s and m_s are the quantum numbers associated with $\widehat{S}^2$ and $\widehat{S}^z$, respectively, we have that

$$\widehat{S}^2 |s, m_s\rangle = s(s+1) |s, m_s\rangle$$

$$\widehat{S}_1^2 |s, m_s\rangle = \widehat{S}_2^2 |s, m_s\rangle = 3\hbar^2/4.$$

Also, since $m_s = 0$ requires the two spins to be opposite to each other, while $m_s = \pm 1$ requires that they are pointed in the same direction, we have that

$$\widehat{S}_1^z \widehat{S}_2^z |s, 0\rangle = -\hbar^2/4$$

$$\widehat{S}_1^z \widehat{S}_2^z |s, \pm 1\rangle = \hbar^2/4.$$

Putting everything together, we find that:

$$\widehat{H} |0,0\rangle = A[-\frac{3\hbar^2}{4} - \frac{1}{2}(0 - 2\frac{3\hbar^2}{4})] |0,0\rangle = 0 |0,0\rangle .$$

$$\widehat{H} |1,0\rangle = A[-\frac{3\hbar^2}{4} - \frac{1}{2}(2 - 2\frac{3\hbar^2}{4})] |1,0\rangle = -\hbar^2 A |1,0\rangle .$$

$$\widehat{H} |1,\pm 1\rangle = A[\frac{3\hbar^2}{4} - \frac{1}{2}(2 - 2\frac{3\hbar^2}{4})] |1,\pm 1\rangle = \frac{\hbar^2}{2} A |1,\pm 1\rangle .$$

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2 Calculate the three lowest energy levels together with their degeneracies for a system of three distinguishable non-interacting spin-$\frac{1}{2}$ particles with mass m in a two-dimensional square box of area L^2. [4]

The Hamiltonian of the system is

$$\hat{H} = \frac{1}{2m} \sum_{i=1}^{3} \hat{\boldsymbol{p}}_i^2.$$

The state factorizes and the energy levels are independent of spin and given by

$$E_{\boldsymbol{n}_i} = \frac{\pi^2\hbar^2}{2mL^2}\boldsymbol{n}_i^2,$$

for each particle i with position eigenstate $|\boldsymbol{n_i}\rangle = |n_{x,i}, n_{y,i}\rangle$. Let's define an eigenstate of the system as $|\boldsymbol{n}_1, \boldsymbol{n}_2, \boldsymbol{n}_3\rangle$. The total energy is the sum over the three particles.

The ground state is given by $|11, 11, 11\rangle$, with total energy $E_0 = 3\frac{\pi^2\hbar^2}{mL^2}$. Since there are 8 spin combinations, the degeneracy is 8.

The first excited state is given by an eigenstate like $|21, 11, 11\rangle$ or $|12, 11, 11\rangle$ where the 12 or 21 particle could be any of the three. This corresponds to energy level $E_1 = 9\frac{\pi^2\hbar^2}{2mL^2}$. The total degeneracy is $8 \times 2 \times 3 = 48$.

The second excited state is given by eigenstates like $|22, 11, 11\rangle$ or $|11, 12, 12\rangle$ or $|11, 21, 21\rangle$ or $|11, 12, 21\rangle$ and their permutations. The corresponding energy is $E_2 = 6\frac{\pi^2\hbar^2}{mL^2}$. The total number of position eigenstates is equivalent to $\binom{6}{2} = 15$. The total degeneracy is then $8 \times 15 = 120$.

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3 Using Hund's rules, find the spectroscopic term that describes the ground state of the phosphorus atom ($Z = 15$). [4]

$Z = 15$ implies an electronic structure $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3$. The quantum number S for the electrons in the outer shell can be $1/2$ or $3/2$. Hund's first rule points at the highest S for ground state, therefore $S = 3/2$ has to be the ground state.

The three electrons have to necessarily have all different m_l numbers, which leads to $L = 0$ (shell is half-full). Therefore the spectroscopic term is ${}^4S_{3/2}$.

SECTION B
Attempt one question from this section

4 An electron is in a constant magnetic field B_0 that points along the positive x-direction. At time $t = 0$ a constant magnetic field B_1 is applied in the z-direction.

(a) Briefly describe the phenomenon of spin precession in this magnetic field. [2]

The precession comes from the torque generated by the interaction between the electron's magnetic dipole moment, which is proportional to its spin, and the external magnetic field. The interaction generates a rotation about the direction of $\boldsymbol{B}$ so that the angle between the spin and the field stays constant, but the axis of the spin rotates about the axis of the magnetic field. The precession frequency ω is called the Larmor frequency of spin precession.

(b) The electron is in its ground state $|0\rangle$ before B_1 is switched on. Show that at time $t = 0$, when B_1 is turned on, the probability of finding its spin component along the new direction of the total field $\boldsymbol{B}$ with values $\pm\frac{\hbar}{2}$ is $\frac{1}{2}(1 \mp \sin\theta)$, where θ is the angle between the total field $\boldsymbol{B}$ and the z-axis. [5]

Before B_1 is switched on, $\widehat{H} = -\boldsymbol{\mu} \cdot \boldsymbol{B}_0 = -\gamma \boldsymbol{S} \cdot \boldsymbol{B}_0 = \frac{eg}{2m_e} B_0 \widehat{S}_x = \frac{eg\hbar}{4m_e} B_0 \widehat{\sigma}_x$, therefore the ground state $|0\rangle$ corresponds to the eigenstate of $\widehat{\sigma}_x$ with eigenvalue -1. In terms of eigenstates of $\widehat{S_z}$, we have

$$|0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

At time t, B_1 is turned on and the new Hamiltonian is $\widehat{H} = \frac{egB\hbar}{4m_e}(\sin\theta\widehat{\sigma}_x + \cos\theta\widehat{\sigma}_z)$, where θ is the angle between the total magnetic field $\boldsymbol{B}$ and the z-axis.

We diagonalize $\widehat{H}$ to find the new eigenstates.

$$H = \frac{egB\hbar}{4m_e} \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}.$$

Its eigenvalues are given by solving

$$-(\cos^2\theta - \lambda^2) - \sin^2\theta = \lambda^2 - 1 = 0,$$

which gives $\lambda = \pm 1$.

The eigenvectors are given by solving:

$$\begin{pmatrix} \cos\theta - \lambda & \sin\theta \\ \sin\theta & -\cos\theta - \lambda \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0.$$

The eigenvector for $\lambda = 1$ gives

$$(\cos\theta - 1)\alpha + \sin\theta\beta = 0.$$

Therefore,

$$\sin\theta\beta = (1 - \cos\theta)\alpha = 2\sin^2\frac{\theta}{2}\alpha = 2\beta\sin\frac{\theta}{2}\cos\frac{\theta}{2},$$

so that

$$\sin\frac{\theta}{2}\alpha = \cos\frac{\theta}{2}\beta.$$

Because of normalization, $\alpha = \cos\frac{\theta}{2}$ and $\beta = \sin\frac{\theta}{2}$.

The eigenvector for $\lambda = -1$ gives

$$(\cos\theta + 1)\alpha + \sin\theta\beta = 0$$

Therefore,

$$2\cos^2\frac{\theta}{2}\alpha = -2\beta\sin\frac{\theta}{2}\cos\frac{\theta}{2}$$

such that,

$$\cos\frac{\theta}{2}\alpha = -\sin\frac{\theta}{2}\beta,$$

leading to $\alpha = -\sin\frac{\theta}{2}$ and $\beta = \cos\frac{\theta}{2}$

In summary the new eigenstates are:

$$|+\rangle = \begin{pmatrix} \cos\theta/2 \\ \sin\theta/2 \end{pmatrix}$$

and

$$|-\rangle = \begin{pmatrix} -\sin\theta/2 \\ \cos\theta/2 \end{pmatrix}$$

The probability of finding the spin already directed along the new direction for the two components is respectively

$$|\langle 0|+\rangle|^2 = \frac{1}{2}(\cos\theta/2 - \sin\theta/2)^2 = \frac{1}{2}(1 - \sin\theta)$$

and

$$|\langle 0|-\rangle|^2 = \frac{1}{2}(-\sin\theta/2 - \cos\theta/2)^2 = \frac{1}{2}(1 + \sin\theta)$$

(c) Show that the time-evolution operator, which describes $|\psi(t)\rangle = U(t)\,|\psi(0)\rangle$, where $|\psi(0)\rangle = |0\rangle$, can be written in the form

$$\widehat{U}(t,0) = \cos\frac{\omega t}{2}\,\widehat{I} - \mathrm{i}\sin\frac{\omega t}{2}(\sin\theta\,\widehat{\sigma}_x + \cos\theta\,\widehat{\sigma}_z),$$

where $\omega = \frac{egB}{2m_\mathrm{e}}$ is the precession frequency for electrons of mass m_e, $\widehat{I}$ is the identity matrix and $\widehat{\sigma}_i$ are the Pauli matrices. [5]

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The time-evolution operator $\widehat{U}(t) = e^{-\frac{i\widehat{H}t}{\hbar}}$, where

$$H = \frac{egB\hbar}{4m_e}\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$$

Let's define $\omega = \frac{egB}{2m_e}$, then

$$H = \frac{\hbar\omega}{2}\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$$

Then, the time operator can be written as
$\widehat{U}(t) = e^{-\frac{i\omega t}{2}\widehat{h}} = \widehat{I} - \frac{i\omega t}{2}\widehat{h} - (\frac{\omega t}{2})^2\widehat{h}^2/2 + ...$, where

$$\widehat{h} = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$$

Because $\widehat{h}^2 = \widehat{I}$, since it's a rotation matrix, the series can be divided in two parts and $\widehat{U}(t) = \cos\frac{\omega t}{2}\widehat{I} - i\sin\frac{\omega t}{2}\widehat{h}$.

(d) What is the probability that at $t = T$ the electron is in the eigenstate of $\hat{S}_z$ with eigenvalue $-\hbar/2$? [4]

The eigenstate of $\widehat{S}_z$ is $(0, 1)$. Therefore the probability is

$$|(0,1)|U(T)\,|0\rangle\,|^2.$$

$$U(t)\,|0\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} \cos\frac{\omega t}{2} - i\sin\frac{\omega t}{2}\cos\theta & -i\sin\frac{\omega t}{2}\sin\theta \\ -i\sin\frac{\omega t}{2}\sin\theta & \cos\frac{\omega t}{2} + i\sin\frac{\omega t}{2}\cos\theta \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

For the probability we need only the second component:

$$|(0,1)|U(t)\,|0\rangle\,|^2 = \frac{1}{2}|-i\sin\frac{\omega t}{2}\sin\theta - \cos\frac{\omega t}{2} - i\sin\frac{\omega t}{2}\cos\theta|^2 = \frac{1}{2}|\cos\frac{\omega t}{2} + i\sin\frac{\omega t}{2}(\sin\theta + \cos\theta)|^2$$

which leads to

$$|(0,1)|U(T)\,|0\rangle\,|^2 = \frac{1}{2}[\cos^2\frac{\omega T}{2} + \sin^2\frac{\omega T}{2}(\sin\theta + \cos\theta)^2].$$

(e) At $t = 2T$ we want to bring the electron back to its initial state $|0\rangle$. Show that this can be done by switching the value of B_1 to $-B_1$ at $t = T$. [3]

MISPRINT! In order for the state to go back to $\psi(0)$ after an additional T time the total field $B_0 + B_1$ should be flipped and not just B_1. The text might

rightly be interpreted as a misprint by the students and full points should be given if this is recognised. Full points should also be given in the case in which the correct definition of the time-evolution operator is given for B_1 flipped at $t > T$.

CASE 1: Switching B_1 corresponds to moving θ to $2\pi - \theta$. Since $\sin(2\pi - \theta) = \sin\theta$ and $\cos(2\pi - \theta) = -\cos\theta$, the new Hamiltonian is going to be

$$\widehat{H}' = \frac{\omega\hbar}{2}\begin{pmatrix} -\cos\theta & \sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

The new time-evolution operator reads

$$\widehat{U'}(t,0) = \cos\frac{\omega t}{2}\,\widehat{I} - \mathrm{i}\sin\frac{\omega t}{2}(\sin\theta\,\widehat{\sigma}_x - \cos\theta\,\widehat{\sigma}_z)$$

It follows that:

$$\psi(2T) = [\cos\frac{\omega T}{2}\,\widehat{I} - \mathrm{i}\sin\frac{\omega T}{2}(\sin\theta\,\widehat{\sigma}_x - \cos\theta\,\widehat{\sigma}_z)][\cos\frac{\omega T}{2}\,\widehat{I} - \mathrm{i}\sin\frac{\omega T}{2}(\sin\theta\,\widehat{\sigma}_x + \cos\theta\,\widehat{\sigma}_z)]\psi(0)$$

CASE 2: Switching $B_0 + B_1$ reverses the direction of precession and

$$\widehat{U'}(t,0) = \cos\frac{\omega t}{2}\,\widehat{I} + \mathrm{i}\sin\frac{\omega t}{2}(\sin\theta\,\widehat{\sigma}_x + \cos\theta\,\widehat{\sigma}_z)$$

It follows that:

$$\psi(2T) = [\cos\frac{\omega T}{2}\,\widehat{I} + \mathrm{i}\sin\frac{\omega T}{2}(\sin\theta\,\widehat{\sigma}_x + \cos\theta\,\widehat{\sigma}_z)][\cos\frac{\omega T}{2}\,\widehat{I} - \mathrm{i}\sin\frac{\omega T}{2}(\sin\theta\,\widehat{\sigma}_x + \cos\theta\,\widehat{\sigma}_z)]\psi(0) = \psi(0)$$

The magnetic moment of an electron $\mu = \gamma S$, where S is the spin operator and $\gamma = -\frac{ge}{2m_e}$ with $g \approx 2$ and e the absolute value of the electron charge.
The Pauli matrices are $\widehat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$; $\widehat{\sigma}_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}$; $\widehat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

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5 Consider the four degenerate levels of a non-relativistic hydrogen atom with $n = 2$. The perturbing Hamiltonian $\widehat{H}_1$ representing the application of an electric field in the z-direction can be written in the basis $|21\text{-}1\rangle$, $|211\rangle$, $|210\rangle$, $|200\rangle$ as

$$H_1 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\varepsilon \\ 0 & 0 & -\varepsilon & 0 \end{pmatrix} \qquad (\star)$$

where each state is of the form $|n\ell m\rangle$.

(a) Explain, without detailed calculation, why the only non-zero elements are $\langle 210|\widehat{H}_1|200\rangle$ and $\langle 200|\hat{H}_1|210\rangle$, with $\widehat{H}_1 = eE\widehat{z}$, and why perturbation theory cannot be applied in this case to find the corrections to the energy levels induced by the field. [4]

The perturbing Hamiltonian is odd with respect to the parity operator, therefore only combinations of even and odd eigenstates can generate non-zero elements in the matrix.

For the hydrogen wave-functions with $n = 2$, the parity is even if $l = 0$ and odd if $l = 1$. This can be seen by applying the transformation in spherical coordinates, where $r \to r$, $\theta \to 2\pi - \theta$ and $\phi \to 2\pi + \phi$. This leads to ψ_{200} not switching sign (even), while both ψ_{210} and $\psi_{21\pm1}$ switch sign (odd). As a result, the only element of the matrix that can be non-zero are $\langle\psi_{200}| H_1 |\psi_{210}\rangle$ and $\langle\psi_{200}| H_1 |\psi_{21\pm1}\rangle$. The latter term, though, leads to 0 because of the integration over ϕ.

[Bookwork]: Second-order perturbation theory gives the second-order correction to the energy levels of perturbed system.

$$E_n^2 = \sum_{m\neq n} \frac{|\langle m| H_1 |n\rangle|^2}{E_n - E_m},$$

where $|n\rangle$ and $|m\rangle$ are the unperturbed states. Because in this case the energy levels of the unperturbed states are degenerate, the basic assumption that the correction is smaller than the difference between the energy levels fails.

(b) What are the zeroth-order eigenstates and the first-order energy shifts induced by the electric field? [2]

[Bookwork]: The submatrix has eigenvalues ±1 and eigenvectors $\frac{1}{\sqrt{2}}(1, \pm1)$, therefore the zeroth-order eigenstates are $|\psi\rangle_\pm = \frac{1}{\sqrt{2}}(|200\rangle \pm |210\rangle$ with energy shifts $\mp\varepsilon$.

(c) Suppose that the unperturbed states $|210\rangle$ and $|200\rangle$ were not degenerate but had energy levels $E_0 - \Delta$ and $E_0 + \Delta$. Calculate how these energy levels

change, using second-order perturbation theory in the limit $\varepsilon \ll \Delta$. Compare your results with the exact eigenvalues. [5]

We restrict ourselves to the subspace formed by $|200\rangle$ and $|210\rangle$. In this space,

$$H_1 = \begin{pmatrix} 0 & -\varepsilon \\ -\varepsilon & 0 \end{pmatrix}.$$

If the levels are not degenerate to start with, then

$$H_0 + H_1 = \begin{pmatrix} E_0 - \Delta & -\varepsilon \\ -\varepsilon & E_0 + \Delta \end{pmatrix}.$$

If $\varepsilon \ll \Delta$, second-order perturbation theory can be applied, so the second order corrections are $E^2_{210} = -\frac{\varepsilon^2}{2\Delta}$ and $E^2_{200} = \frac{\varepsilon^2}{2\Delta}$. We then find $E_{210} \approx E_0 - \Delta - \varepsilon^2/(2\Delta)$ and $E_{200} \approx E_0 + \Delta + \varepsilon^2/(2\Delta)$.

We find the exact solutions by diagonalizing the Hamiltonian $H_0 + H_1$. This leads to

$$(E_0 - \Delta - \lambda)(E_0 + \Delta - \lambda) - \varepsilon^2 = (E_0 - \lambda)^2 - \Delta^2 - \varepsilon^2 = 0.$$

By rearranging, we get

$$\lambda^2 - 2\lambda E_0 + E_0^2 - \Delta^2 - \varepsilon^2 = 0,$$

which has solutions $\lambda = E_0 \pm \sqrt{E_0^2 - E_0^2 + \Delta^2 + \varepsilon^2} = E_0 \pm \sqrt{\Delta^2 + \varepsilon^2}$

By expanding in the limit $\varepsilon \ll \Delta$, we find
$\lambda = E_0 \pm \Delta\sqrt{1 + \varepsilon^2/\Delta^2} = E_0 \pm \Delta(1 + \frac{\varepsilon^2}{2\Delta^2}) = E_0 \pm (\Delta + \varepsilon^2/2\Delta)$.

(d) What happens if $\varepsilon \gg \Delta$? [3]

If $\varepsilon \gg \Delta$, the perturbation is larger than the energy difference and we cannot apply perturbation theory.

(e) If the unperturbed states are all degenerate, how does the matrix in ($\star$) change if the electric field points in the x-direction such that $\widehat{H}_1 = eE\widehat{x}$? Write the new elements of the matrix in terms of ε. Determine the eigenvalues and eigenstates. [5]

The parity argument is the same as in part (a), so the only terms that can be different from 0 are $\langle 200|\widehat{H}_1|210\rangle$, $\langle 200|\widehat{H}_1|21 \pm 1\rangle$. In polar coordinates, the operator $\widehat{x} = r\sin\theta\cos\phi$, while $\widehat{z} = r\cos\theta$.

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From the matrix in ($\star$), we see that

$$\begin{aligned}
\langle 200|\, eE\widehat{z}\,|210\rangle &= \frac{eE}{32\pi a_0^3}\int r^2\sin\theta dr d\theta d\phi r\cos\theta e^{-r/a_0}(2-r/a_0)r/a_0\cos\theta \\
&= \frac{eE}{32\pi a_0^3}2\pi\int dr r^4(2-r/a_0)e^{-r/a_0}\int d\theta\sin\theta\cos^2\theta \\
&= \frac{eE}{32\pi a_0^3}2\pi\int dr r^4(2-r/a_0)e^{-r/a_0}\int dy(-y^2) \\
&= \frac{eE}{32\pi a_0^3}2\pi\int dr r^4(2-r/a_0)e^{-r/a_0}(-y^3/3)|_1^{-1} \\
&= \frac{eE}{32\pi a_0^3}2\pi\int dr r^4(2-r/a_0)e^{-r/a_0}\frac{2}{3} = -\varepsilon
\end{aligned}$$

This means that

$$\frac{eE}{32\pi a_0^3}\int dr r^4(2-r/a_0)e^{-r/a_0} = -\frac{3\varepsilon}{4\pi}$$

For the new Hamiltonian $\widehat{H_1} = eE\widehat{x}$, we have to calculate

$$\begin{aligned}
\langle 200|\, eE\widehat{x}\,|210\rangle &= \frac{eE}{32\pi a_0^3}\int r^2\sin\theta dr d\theta d\phi r\sin\theta\cos\phi e^{-r/a_0}(2-r/a_0)r/a_0\cos\theta \\
&= \left[\frac{eE}{32\pi a_0^3}\int dr r^4(2-r/a_0)e^{-r/a_0}\right]\int d\theta\sin^2\theta\cos\theta\int d\phi\cos\phi \\
&= 0,
\end{aligned}$$

because of the integral in $d\phi$.

We now calculate

$$\begin{aligned}
\langle 200|\, eE\widehat{z}\,|21\pm 1\rangle &= \frac{eE}{32\pi a_0^3}\frac{1}{\sqrt{2}}\int r^2\sin\theta dr d\theta d\phi r\sin\theta\cos\phi e^{-r/a_0}(2-r/a_0)r/a_0\sin\theta e^{\pm i\phi} \\
&= \frac{1}{\sqrt{2}}\left[\frac{eE}{32\pi a_0^3}\int dr r^4(2-r/a_0)e^{-r/a_0}\right]\int d\theta\sin^3\theta\int d\phi\cos\phi e^{\pm i\phi}
\end{aligned}$$

The integral in $d\theta$

$$\int d\theta\sin^3\theta = \int d\theta\sin\theta(1-\cos^2\theta) = \int d\theta\sin\theta - 2/3 = 2-2/3 = 4/3.$$

The integral in $d\phi$ gives

$$\int d\phi\cos\phi e^{\pm i\phi} = \int d\phi\frac{e^{i\phi}+e^{-i\phi}}{2}e^{\pm i\phi} = \frac{1}{2}\int d\phi(1+e^{\pm 2i\phi}) = \pi$$

Putting everything together, we get

$$\langle 200|\, eE\widehat{z}\,|21\pm 1\rangle = -\frac{1}{\sqrt{2}}\frac{3\varepsilon}{4\pi}\frac{4\pi}{3} = -\varepsilon/\sqrt{2}$$

The new matrix representing H_1 is then

$$\begin{pmatrix} 0 & 0 & 0 & -\varepsilon/\sqrt{2} \\ 0 & 0 & 0 & -\varepsilon/\sqrt{2} \\ 0 & 0 & 0 & 0 \\ -\varepsilon/\sqrt{2} & -\varepsilon/\sqrt{2} & 0 & 0 \end{pmatrix}$$

We see that $|210\rangle$ is unaffected, so we can calculate the new eigenvalues and eigenvectors in subspace generated by $|200\rangle$ and $|21\pm1\rangle$. The determinant of the corresponding 3×3 matrix gives the following equation for the eigenvalues:

$$-\lambda^3+\lambda\varepsilon^2=-\lambda(\lambda^2-\varepsilon^2),$$

which gives as eigenvalues $\lambda=0,\pm\varepsilon$.

The eigenstates are calculated by solving

$$\begin{pmatrix} 0 & 0 & -\varepsilon/\sqrt{2} \\ 0 & 0 & -\varepsilon/\sqrt{2} \\ -\varepsilon/\sqrt{2} & -\varepsilon/\sqrt{2} & 0 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}=\lambda\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

$\lambda=0$ gives $\gamma=0$ and $\alpha=-\beta$, so the eigenstate is $|0\rangle=\frac{1}{\sqrt{2}}(|211\rangle-|21-1\rangle)$, with energy E_0.

$\lambda=\varepsilon$ gives

$$-\frac{\varepsilon}{\sqrt{2}}\gamma=\varepsilon\alpha$$
$$-\frac{\varepsilon}{\sqrt{2}}\gamma=\varepsilon\beta$$
$$-\frac{\varepsilon}{\sqrt{2}}(\alpha+\beta)=\varepsilon\gamma$$

which results in $\alpha=\beta=-\gamma/\sqrt{2}$. So the eigenstate with energy $E_0+\varepsilon$ is $\frac{1}{\sqrt{5}}(\sqrt{2}\,|211\rangle+\sqrt{2}\,|21-1\rangle-|200\rangle)$

Similarly, $\lambda=-\varepsilon$ gives $\alpha=\beta=\gamma/\sqrt{2}$, so the eigenstate with energy $E_0-\varepsilon$ is $\frac{1}{\sqrt{5}}(\sqrt{2}\,|211\rangle+\sqrt{2}\,|21-1\rangle+|200\rangle)$.

The degenerate n=2 states of the hydrogen atom in spherical polar coordinates are given by:

$$\psi_{200}=\sqrt{\frac{1}{32\pi a_0^3}}e^{-r/(2a_0)}(2-\frac{r}{a_0})$$

$$\psi_{210}=\sqrt{\frac{1}{32\pi a_0^3}}e^{-r/(2a_0)}\frac{r}{a_0}\cos\theta$$

$$\psi_{21\pm1}=\sqrt{\frac{1}{64\pi a_0^3}}e^{-r/(2a_0)}\frac{r}{a_0}e^{\pm i\phi}\sin\theta$$

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