PHYS30201 Mathematical Fundamentals of Quantum Mechanics **Examples 5**

1. A particle of mass m moves in the 1D potential

$$V(x) = \begin{cases} -\lambda \sin(\pi x/a) & \text{for } 0 < x < a \\ \infty & \text{elsewhere} \end{cases}.$$

Treating this as a perturbation on an infinite square well, calculate the first-order shift in the ground state energy.

2. Consider each of the following two-state systems. In each case calculate the energies to second order in λ, and check your answers against the expansions of the exact results. In (ii) λ is real.

$$\text{(i)} \quad \hat{H} \longrightarrow \begin{pmatrix} E_1^{(0)} & \lambda \\ \lambda^* & E_2^{(0)} \end{pmatrix}, \qquad \text{(ii)} \quad \hat{H} \longrightarrow \begin{pmatrix} 2\lambda & \lambda \\ \lambda & E_2^{(0)} \end{pmatrix}.$$

For (i), calculate also the first-order shifts in the eigenvectors, and again compare them with the exact results. (This is easier if you don't normalise.)
[*Hint: write each Hamiltonian as* $\hat{H}^{(0)} + \hat{H}^{(1)}$*, where* $\hat{H}^{(0)} = \hat{H}(\lambda = 0)$.]

3. A two-state system has three terms in its Hamiltonian, $\hat{H}_0$, $\hat{H}_a$ and $\hat{H}_b$. In some basis, the corresponding matrices are

$$\hat{H}_0 \longrightarrow \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix}, \qquad \hat{H}_a \longrightarrow \begin{pmatrix} -a & 0 \\ 0 & a \end{pmatrix}, \qquad \hat{H}_b \longrightarrow \begin{pmatrix} b & -b \\ -b & b \end{pmatrix}.$$

For $a \gg b$, let $\hat{H}^{(0)} = \hat{H}_0 + \hat{H}_a$ and calculate the first- and second-order energy shifts due to $\hat{H}_b$.
For $a \ll b$, let $\hat{H}^{(0)} = \hat{H}_0 + \hat{H}_b$. Find the eigenvectors of $\hat{H}^{(0)}$, and then calculate the first- and second-order energy shifts due to $\hat{H}_a$.

Find the exact eigenvalues of $\hat{H}_0 + \hat{H}_a + \hat{H}_b$ and show that the previous results are obtained in the appropriate limits. Hence explain why those results fail as b and a approach the same magnitude.

4. For Q1 above, explain why the most significant part of the first-order change in the wave function is given by $-(\beta/15\pi)\sqrt{\frac{2}{a}}\sin\frac{3\pi x}{a}$, where $\beta = \lambda(2ma^2)/(\hbar^2\pi^2)$. Show that this lowers the energy compared with the first-order result, and give the corresponding estimate for the second-order energy shift.
[You may use the integral, $\int_0^\pi \sin(nx)\sin^2 x \mathrm{d}x = -\frac{4}{n(n^2-4)}$ for odd n.]

5. Consider a 1D harmonic oscillator with a perturbation $\hat{H}^{(1)} = \lambda\hat{x}$ (which could be due to an electric field). Show that there is no first-order energy shift for any state. Calculate the first-order shift in the eigenstates, and the second-order shift in their, for all states.
[*Hint: don't forget about raising and lowering operators!*]

In this case, exact results can be obtained by writing the potential in the form

$$V(x) = \tfrac{1}{2}m\omega^2 x^2 + \lambda x = \tfrac{1}{2}m\omega^2(x-\delta)^2 - \epsilon,$$

where δ and ϵ depend on λ. This is just another quadratic potential shifted to the right by δ and with an energy offset $-\epsilon$. Use this to check your results for the energies, and for the ground-state wave function.

Challenge: repeat the calculation of the ground-state energy for $\hat{H}^{(1)} = \lambda\hat{x}^3$. Comment on whether you expect this method to be reliable for all values of n, and on what might be wrong with it even for $n = 0$. [*Hint: sketch the potential.*]

6. A three-state system has an unperturbed Hamiltonian $\hat{H}^{(0)}$ and is subject to a perturbation $\hat{H}^{(1)}$. In the basis of the eigenstates of $\hat{H}^{(0)}$, the corresponding matrices are:

$$\hat{H}^{(0)} \longrightarrow \begin{pmatrix} E_1^{(0)} & 0 & 0 \\ 0 & E_2^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix}, \qquad \hat{H}^{(1)} \longrightarrow \begin{pmatrix} 0 & b & a \\ b & 0 & a \\ a & a & 0 \end{pmatrix}.$$

Calculate the first-order energy shifts and eigenstate shifts of all three states:
i) when $E_1^{(0)}$, $E_2^{(0)}$ and $E_3^{(0)}$ are all different;
ii) when $E_1^{(0)} = E_2^{(0)}$.
For case ii), compare with your results with the exact ones. (As in Q2, this is easier if you don't normalise.)

7. The unperturbed states of the symmetric 2D harmonic oscillator can be denoted $|n_x, n_y\rangle$ with energy $E^{(0)} = (n_x + n_y + 1)\hbar\omega$; states with the same $n_x + n_y$ are degenerate. Now consider a perturbation $\hat{H}^{(1)} = \lambda\hat{x}\hat{y}$. Show that there is no first-order shift in the ground-state energy.

Show that the states with $E^{(0)} = 2\hbar\omega$ are mixed by this perturbation, and that in the subspace of these states the perturbation can be written

$$\hat{H}^{(1)} \longrightarrow \frac{\hbar\lambda}{2m\omega}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Hence find the perturbed energies to first order in λ. By considering the shape of the perturbed potential and the zeroth-order wave functions of the two states, explain why this perturbation lifts the degeneracy and why one state is higher in energy than the other.

Now find the second-order energy shifts for these states.

Challenge: explain why perturbations which are functions of x or y only, or which consist of sums of such terms, do not mix the degenerate states $|n_x, n_y\rangle$, and so can be handled in non-degenerate perturbation theory. Consider the current problem using coordinates $\sqrt{\frac{1}{2}}(x \pm y)$, and (without detailed calculation) explain your results with reference to the example in section 4.1.3 of the lectures.

8. Calculate the fine-structure shifts in the energies of the $4\,^2p_{3/2}$ states of i) $^3\mathrm{Li}^{++}$ and ii) positronium.

9. *Challenge:* calculate the leading relativistic correction to the energy levels of the 1D harmonic oscillator.

10. The first excited levels of calcium have their valence electrons in a $(4s)^1\,(4p)^1$ configuration. In a particular experiment three of these are seen, with energies 1.87908 eV, 1.88555 eV and 1.89868 eV. Assuming that they are split by the spin-orbit interaction,

$$\hat{H}_{\mathrm{s.o.}} = \frac{\mathcal{E}}{\hbar^2}\,\hat{\mathbf{L}}\cdot\hat{\mathbf{S}},$$

deduce the angular-momentum quantum numbers (L, S and J) of these levels. Compare the ratio of their splittings with the prediction of first-order perturbation theory.

11. *Challenge, and extra practice with using Clebsch-Gordan coefficients:* A system has orbital angular momentum l and spin s. Its eigenstates of total angular momentum $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ are denoted $|l,s;j,m_j\rangle$. The calculation of the Landé g factor uses the result that $\langle l,s;j,m_j|\hat{S}_z|l,s;j,m_j\rangle$ must be proportional to $\langle l,s;j,m_j|\hat{J}_z|l,s;j,m_j\rangle$, which follows from the Wigner-Eckart theorem discussed in section 2.6. For a system with spin-$\frac{1}{2}$, the result can be demonstrated directly from the expressions for these states:

$$|l,\tfrac{1}{2};j,m_j\rangle = \pm\sqrt{\tfrac{l+\frac{1}{2}\pm m_j}{2l+1}}|l,m_j-\tfrac{1}{2}\rangle\otimes|\tfrac{1}{2},\tfrac{1}{2}\rangle + \sqrt{\tfrac{l+\frac{1}{2}\mp m_j}{2l+1}}|l,m_j+\tfrac{1}{2}\rangle\otimes|\tfrac{1}{2},-\tfrac{1}{2}\rangle,$$

for $j = l\pm\frac{1}{2}$. Using these, find $\langle\hat{S}_z\rangle$ and show that it is equal to $\hbar m_j\langle\hat{\mathbf{S}}\cdot\hat{\mathbf{J}}\rangle/\langle\hat{\mathbf{J}}^2\rangle$.
[*Hint: treat the cases $j = l+\frac{1}{2}$ and $j = l-\frac{1}{2}$ separately.*]

12. Two non-identical spin-$\frac{1}{2}$ particles, p and n, are in an s-wave bound state, and experience an interaction whose effective form is $\hat{H}^{(0)} = -A\hat{\mathbf{S}}^{(p)}\cdot\hat{\mathbf{S}}^{(n)}$. Write down expressions for the four spin states of the system which are eigenstates of this Hamiltonian, and give their energies.

The system is now placed in a weak magnetic field, which adds to the Hamiltonian a term

$$\hat{H}^{(1)} = \left(g_p\hat{S}_z^{(p)} + g_n\hat{S}_z^{(n)}\right)\frac{\mu_N B}{\hbar}.$$

Find the first-order energy shifts due to the magnetic field.

13. Calculate the Landé g factor for a nucleus with an unpaired nucleon, spin-$\frac{1}{2}$, in a subshell with orbital angular momentum l and total angular momentum j. [*Hint: leave the orbital and spin g factors general, so you can treat both proton and neutron cases together.*]

Extra practice: Calculate the Landé g factor for an odd-odd nucleus where the unpaired proton and neutron have angular momenta j_1 and j_2, with g factors g_1 and g_2, and are coupled to total angular momentum J.

14. Calculate the weak-field Zeeman shifts for all the $n = 1$ and $n = 2$ states of hydrogen and draw a level diagram. Mark all the transitions consistent with the $\Delta l = 1$, $\Delta m_j = -1, 0, 1$ rule, and list the frequencies.

    Now calculate the strong-field Zeeman shifts for the $n = 1, 2$ states and draw the levels for this case.
    Hint: in this case you should ignore fine structure. Think about what this implies for the basis you use.].

15. Find the magnitude of the electric field that would be required to induce a splitting of 1 meV between the $n = 2$ states of hydrogen. How large would the shift in the ground state be for that field?

16. If an electric field is very weak, we cannot ignore the fine-structure splitting when calculating the Stark effect. Consider the four degenerate states of hydrogen with $n = 2$ and $j = 1/2$: $|0, \frac{1}{2}; \frac{1}{2}, \pm\frac{1}{2}\rangle$ and $|1, \frac{1}{2}; \frac{1}{2}, \pm\frac{1}{2}\rangle$ (in the notation $|l, s; j, m_j\rangle$. Use degenerate perturbation theory in this space to show that for a very weak electric field, the Stark effect shifts the energy levels by $\pm\sqrt{3}a_0|e|\mathcal{E})$.

    [*Hint: first write the states in terms of the* $\{|l, m_l\rangle \otimes |s, m_s\rangle\}$ *basis. Show that only pairs of states with the same* m_j *are mixed. Then show that, for either pair, the perturbing term in the Hamiltonian is:*

$$\hat{H}^{(1)} \longrightarrow \sqrt{3}a_0|e|\mathcal{E} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad]$$

17. *Challenge:* the following trick allows an exact calculation of the Stark shift for the ground state of hydrogen. Starting with the more general formalism, suppose we find an operator $\hat{\Omega}$ such that $\hat{H}^{(1)}|0^{(0)}\rangle = [\hat{\Omega}, \hat{H}^{(0)}]|0^{(0)}\rangle$. Show that we can write

$$E_0^{(2)} = \sum_{m\neq 0} \frac{\langle 0^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle\langle m^{(0)}|[\hat{\Omega}, \hat{H}^{(0)}]|0^{(0)}\rangle}{E_0^{(0)} - E_m^{(0)}} = \langle 0^{(0)}|\hat{H}^{(1)}\hat{\Omega}|0^{(0)}\rangle - E_0^{(1)}\langle 0^{(0)}|\hat{\Omega}|0^{(0)}\rangle.$$

    [*Hint: use the identity* $\sum_{m\neq 0} |m^{(0)}\rangle\langle m^{(0)}| = \hat{I} - |0^{(0)}\rangle\langle 0^{(0)}|$.]

    Now show that if $\hat{H}^{(1)} \underset{\mathbf{r}}{\longrightarrow} -q_e\mathcal{E}z$, the operator $\hat{\Omega} \underset{\mathbf{r}}{\longrightarrow} (ma_0q_e\mathcal{E}/\hbar^2)(\frac{1}{2}r^2 + a_0r)\cos\theta$ works. (Don't try to construct it, just verify that it satisfies the required relation to $\hat{H}^{(1)}$.) Here the charge of the electron is $q_e = -|e|$.

    Using this result, calculate $E_0^{(2)}$.