

Problem sheet - HT tutorial 4

Self-assessed questions

Q1. A quiz on hydrogenic states

States Find the errors in the following, and suggest corrections:

- (a) The ground state of hydrogen is 2s.
- (b) The 2p–1p transition in hydrogen is ultraviolet.
- (c) The angular part of the wavefunction in hydrogen depends on n and l .

[JW QM HT Q1.4]

Q2. Familiarity with hydrogenic wave functions

- (a) Treating a_0 as a parameter, write down the complete wavefunctions (including radial and angular parts) for the states 1s, 2s, and 2p (giving all three m_l possibilities in the last case). In each case draw neat graphs of the radial part of the wavefunction, $R(r)$, and also $r^2|R(r)|^2$. What is the significance of the latter? N.B. this question is not intended to test your mathematical abilities, but to produce familiarity with the wavefunctions. Look them up and copy them!
- (b) How does $R_{n,l}$ vary with r as $r \rightarrow 0$? Draw on a single plot a ‘close-up’ of $R_{n,l}$ in the region $r < 10^{-15}$ m for the states 3s, 3p, 3d. What is the significance of this region?
- (c) Consider the probability density distributions for an electron in the 2p $m_l = 0$ state and the 2p $m_l = 1$ state, where m_l is the magnetic quantum number. Which distribution is shaped like an hour-glass, and which like a doughnut? Make an “artists impression” sketch of these 3-dimensional probability density distributions. How does the wavefunction (not the probability density) carry the information about the sign of m_l when $m_l = 1$ or -1 ?

[JW QM HT Q1.5]

Q3. A very useful expectation value for the hydrogen ground state

Expectation values Show that in the ground state of hydrogen, $\langle r^n \rangle = (n+2)(a_0/2) \langle r^{n-1} \rangle$. What is $\langle r^0 \rangle$? Is there any restriction on the value of n ? Derive $\langle r \rangle$ and $\langle 1/r \rangle$ in terms of a_0 . Hence find $\langle V(r) \rangle$, where $V(r) = -e^2/4\pi\epsilon_0 r$. Given the expression for the ground state energy, use this result to deduce the mean kinetic energy of the electron in the ground state and hence its r.m.s. speed v . Express v in terms of α and the speed of light.

[JW QM HT Q1.7]

Q4. Book work derivation of the basics of non-degenerate perturbation theory

Derivation Derive the expressions for the first order shift in energy, and change in the wavefunction, in non-degenerate perturbation theory. Explain why this calculation fails if there are degenerate states in the spectrum.

[JW QM HT Q2.1]

Q5. Angular momentum addition relevant for spin-orbit coupling later

Angular momentum reminder The total angular momentum of a particle with orbital angular momentum l and spin angular momentum s is $\mathbf{j} = \mathbf{l} + \mathbf{s}$. The eigenvalues of \mathbf{j}^2 , \mathbf{l}^2 and \mathbf{s}^2 are $j(j+1)\hbar^2$, $l(l+1)\hbar^2$ and $s(s+1)\hbar^2$ respectively. State the possible values of j for the cases

- (a) $l = 0$, any s
- (b) $l = 1$, $s = 1/2$
- (c) $l = 1$, $s = 1$
- (d) $l = 1$, $s = 3/2$

What is the general rule which tells you how many values of j to expect for arbitrary l , s ?
What basic information about the fine structure of hydrogen does all this tell us?

[JW QM HT Q3.1]

Q6. Conserved quantities in this new context

Constants of motion Explain what a 'constant of the motion' is, and what is meant by a 'good quantum number'. Considering the fine structure (spin orbit coupling) of hydrogen in order to have a definite example, state the (relevant) constants of the motion and good quantum numbers. Give an example of one or more quantum numbers which are not good in this case.

[JW QM HT Q3.4]

Q7. Some practise with new notation

Spectroscopic notation Which quantum numbers are specified by the notation $3^2D_{5/2}$? Give the names and the values which are indicated. How many degenerate quantum states are together included in the level $3^2D_{5/2}$ of hydrogen?

[JW QM HT Q3.7]

Q8. Hydrogen-like ions and spin-orbit coupling (consider after main Q7)

Sodium 10^+ ion Estimate the size of the fine structure of the 2p configuration in hydrogen-like sodium (i.e. sodium ions with all but the last electron removed). Why can't we use perturbation theory to calculate the effect of the spin-orbit interaction in hydrogen-like uranium?

[JW QM HT Q3.9]

Main questions

Q1. Application of perturbation theory - basic harmonic oscillator example

Example 1 A particle of charge q and mass m is in a harmonic oscillator potential $V^0 = (1/2)m\omega^2x^2$. A perturbation is introduced which changes the potential to $V = V^0 + \Delta V$ with $\Delta V = (1/2)\lambda m\omega^2x^2$ where λ is small.

(a) Use perturbation theory to compute the first order shift in the ground state energy. [The integral that you will need is given later in Question 5.2.]

(b) Of course the problem with the full potential V is exactly solvable because it's just a SHO with a shifted frequency! So write down the exact expression for the ground state energy. Now expand it in powers of λ and check that the order λ term is the same as you calculated in part (a).

[JW QM HT Q2.2]

Q2. Application of perturbation theory - slightly harder harmonic oscillator example

Example 2 †This is a classic example of – and test of – perturbation theory. A particle of charge q and mass m is in a harmonic oscillator potential $V = (1/2)m\omega^2x^2$. A weak external electric field of magnitude f is applied along the x direction. This gives an electrostatic potential $-fx$ and potential energy $V_f = -qfx$. Treating this as a small perturbation, calculate the shift in energy of all the states, as follows.

(a) Write down the energy shift to be calculated, $\delta E_n^{(1)}$, in the form of a matrix element (don't do the integral yet), by quoting the standard result of first-order perturbation theory. (Call the energy eigenstates of the unperturbed Hamiltonian $|n\rangle$ as usual.)

(b) Now have a quick look at the overall form of the integral for the matrix element, and using your general knowledge of the quantum harmonic oscillator, deduce that the first order shift is zero for every n .

(c) We will next work out the first order change in the wavefunctions (this will turn out to be non-zero). First write down the standard result, derived in question 1, involving a sum of matrix elements divided by energy differences.

(d) We could in principle write out the integrals using the Hermite polynomials and Gaussian function, but that is hard work! Let's see if we can apply our knowledge of the harmonic oscillator. First, recall that the position x can be regarded as an operator, and written in terms of raising and lowering operators:

$$x = C(a + a^\dagger)$$

where $C = (\hbar/2m\omega)^{1/2}$. The raising and lowering operators have the effects

$$\begin{aligned} a^\dagger |n\rangle &= \sqrt{n+1} |n+1\rangle \\ a |n\rangle &= \sqrt{n} |n-1\rangle \end{aligned}$$

Use this information to evaluate the matrix element $\langle n|x|k\rangle$ for arbitrary n, k (you should find that there are two cases to consider).

(e) Hence show that up to first order the state is

$$|n^{(1)}\rangle = |n\rangle + \frac{qfC}{\hbar\omega} \left((n+1)^{1/2} |n+1\rangle - n^{1/2} |n-1\rangle \right).$$

Does this formula give the correct result when $n = 0$? (f) Write down the formula for the 2nd order energy shift, and use the result of part (e) to show it is $\delta E_k^{(2)} = -q^2 f^2 / 2m\omega^2$.

(g) This is a nice test of perturbation theory, because the problem can be solved exactly by a simple insight. To get the general idea, plot a graph of $V(x)$ and also of $V(x) + V_f(x)$. (For the purpose of this graph alone, choose $m = \omega = q = f = 1$). The point is, the new potential energy is still exactly a quadratic, it is merely shifted over and down a bit. Therefore write $V(x) + V_f(x) = A(x - x_0)^2 + B$ and find A and B . Use this to deduce the exact energy eigenvalues for this problem, and hence confirm your answers from parts (b) and (f).

[JW QM HT Q2.4]

Q3. Application of degenerate perturbation theory - the 2D harmonic oscillator

Degenerate PT †The two-dimensional SHO has Hamiltonian

$$H = \frac{1}{2m}(p_x^2 + p_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2)$$

and the normalized wavefunctions for the ground state and 1st excited state of the *one-dimensional* SHO are $\phi_0(x) = N_0 e^{-\alpha x^2/2}$ and $\phi_1(x) = N_1 x e^{-\alpha x^2/2}$ respectively. Let $\Phi_{nm}(x, y) = \phi_n(x)\phi_m(y)$.

- Explain why the ground state wavefunction for the 2d SHO is $\Phi_{00}(x, y)$ and the first excited state is doubly degenerate with wavefunctions $\Phi_{10}(x, y)$ and $\Phi_{01}(x, y)$.
- A small perturbation λxy is now added to the Hamiltonian. Show that to 1st order in λ the ground state energy does not change.
- Using degenerate perturbation theory show that the degeneracy of the 1st excited state is lifted and that the wavefunctions of the two resulting states are $(\Phi_{01}(x, y) \pm \Phi_{10}(x, y))/\sqrt{2}$. What are the corresponding energies?
- Show that in this context a “small” perturbation means $\lambda \ll m\omega^2$.

[JW QM HT Q2.4]

Q4. First relativistic correction to simple hydrogen

Relativistic correction to KE Show that the first correction to the kinetic energy term in the Schrödinger equation, when one allows for special relativity in the case $v \ll c$, gives a perturbation

$$\delta H_m = -\frac{1}{2mc^2} (H^0 - V(r))^2.$$

Quoting the standard results of 1st order perturbation theory, show that for hydrogen the energy shift produced by this perturbation is

$$\delta E = -\frac{1}{2mc^2} \left(E_n^2 + 2E_n \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right)$$

Obtain the shift of the ground state of hydrogen using your results from problem set 1, Q.7. Express the result in terms of a suitable power of α and other quantities. Evaluate the shift, in GHz.

[JW QM HT Q3.2]

Q5. Another source of correction to simple hydrogen

Spin-orbit interaction

- Derive the expression for the spin-orbit interaction Hamiltonian in a one-electron atom or ion with nuclear charge Z . Use the simple method which leads to a factor of 2 error, and then put in the factor 1/2 correction due to Thomas precession, but don't spend time on the latter at this stage.
- What is the direction of the B -field experienced by the electron relative to its orbital angular momentum?
- What is the direction of the intrinsic magnetic dipole of the electron relative to its spin angular momentum?
- If the spin and orbital angular momentum vectors were described by classical mechanics, explain in qualitative terms how they would behave as a function of time.

[JW QM HT Q3.3]

Q6. Second relativistic correction to simple hydrogen

use perturbation theory to derive the spin-orbit shift

$$\Delta E_{so} = \frac{g_s}{8} mc^2 Z^4 \alpha^4 \frac{1}{n^3} \left(\frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1/2)(l+1)} \right)$$

You may quote the expression for $\langle 1/r^3 \rangle$ from a reference. The shift is of order $Z^2 \alpha^2$ times the gross structure energy of the atom. What is the significance of this?

[JW QM HT Q3.5]

Q7. Consistency check for the application of perturbation theory

This confirms a point which has been assumed above, namely that the relativistic kinetic shift can be treated using the familiar states having quantum numbers n, l, m . Since we have degeneracy, we can't take it for granted. Argue that the orbital angular momentum \hat{l}^2 is a constant of the motion under both H^0 and δH , as follows.

(a) We already know $[\hat{l}^2, H^0] = 0$ for any spherically symmetric problem, but in any case give a proof to make sure we know what we are doing. [Hint: work in spherical polar coordinates, and express the kinetic energy as an r -dependent part plus $\hat{l}^2/2mr^2$. If you actually carry out any differentiating, you have not taken the simplest route.]

(b) Show that $[\hat{l}^2, K] = 0$, where $\hat{K} = \hat{p}^2/2m$ is kinetic energy, e.g. by re-using part (a).

(c) Our perturbation is proportional to kinetic energy squared. Use a general result for commutators of the form $[A, B^2]$ to show that $[\hat{l}^2, K] = 0$ implies $[\hat{l}^2, K^2] = 0$.

(d) We have now proved both $[\hat{l}^2, H^0] = 0$ and $[\hat{l}^2, \delta H] = 0$ for our problem where $H = H^0 + \delta H$. What is the significance of these results to degenerate perturbation theory?

[JW QM HT Q3.13]