

## 8 Perturbation Theory I: Time Independent Case

We've now come about as far as we can (in this course) relying purely on symmetry principles. The dynamics of systems of genuine physical interest is rarely simple enough to hope that we can solve it exactly, just using the general constraints of symmetry. In these circumstances we need to make some sort of approximation, treating our system as being 'close to' some other system whose dynamics is sufficiently simple to be controllable. That is, we treat the difference between our actual system, whose experimental properties we care about, and our model system, whose description is simple enough that we can handle it, as a *perturbation*. The whole art of a theoretical physicist lies in striking this balance; if one's model system is too simplistic, it might not provide a reasonable guide to the behaviour of the real case<sup>65</sup>, while if the model is overly complicated it may itself prove impossible to understand.

There's nothing inherently quantum mechanical about the need to approximate a complicated system by a simpler one, but, fortunately, perturbation theory in quantum mechanics often turns out to be considerably easier than in classical dynamics, largely because of the vector space nature of  $\mathcal{H}$ . In this chapter and the next, we'll study various techniques to handle quantum mechanical perturbation theory, beginning with the simplest cases.

### 8.1 An Analytic Expansion

Let  $H$  be the Hamiltonian of the experimental system we wish to understand, and  $H_0$  be the Hamiltonian of our model system whose eigenstates and eigenvalues we already know. We hope that  $\Delta H = H - H_0$  is in some sense 'small', so that it may be treated as a perturbation. More specifically, we look for a parameter — let's call it  $\lambda$  — that our true Hamiltonian depends on such that at  $\lambda = 0$ ,  $H = H_0$ . For  $\lambda \in [0, 1]$ , define

$$H_\lambda = H_0 + \lambda \Delta H. \quad (8.1)$$

We can think of  $H_\lambda$  as the Hamiltonian of an apparatus that is equipped with a dial that allows us to vary  $\lambda$ . At  $\lambda = 0$  the system is our model case, and at  $\lambda = 1$  it's the case of genuine interest.

We now seek the eigenstates  $|E_\lambda\rangle$  of  $H_\lambda$ . This may look as though we've made the problem even harder — we now need to find the eigenstates not just of our model and experimental systems, but of a 1-parameter family of interpolating systems. Our key assumption is that *since  $H_\lambda$  depends analytically on  $\lambda$ , so too do its eigenstates*. In essence, this amounts to the assumption that small changes in the system will lead to only small changes in the outcome. Every mountain climber knows that this assumption can be dreadfully false and we'll see that it can easily fail in QM too, but for now let's see where it takes us.

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<sup>65</sup>Milk production at a dairy farm was low, so the farmer wrote to the local university, asking for help from academia. A multidisciplinary team of professors was assembled, headed by a theoretical physicist, and two weeks of intensive on-site investigation took place. The scholars then returned to the university, notebooks crammed with data, where the task of writing the report was left to the team leader. Shortly thereafter the physicist returned to the farm, saying to the farmer, "I have the solution, but it works only in the case of spherical cows in a vacuum".

If indeed  $|E_\lambda\rangle$  depends analytically in  $\lambda$ , then we can expand it as

$$|E_\lambda\rangle = |\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \dots \quad (8.2)$$

and similarly expand the eigenvalues

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots. \quad (8.3)$$

Plugging these expansions into the defining equation  $H_\lambda|E_\lambda\rangle = E(\lambda)|E_\lambda\rangle$  we obtain

$$\begin{aligned} (H_0 + \lambda\Delta H) (|\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \dots) \\ = \left( E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \right) (|\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \dots). \end{aligned} \quad (8.4)$$

Since we require this to hold as  $\lambda$  varies, it must hold for each power of  $\lambda$  separately. Thus we find an infinite system of equations

$$\begin{aligned} H_0|\alpha\rangle &= E^{(0)}|\alpha\rangle, \\ H_0|\beta\rangle + \Delta H|\alpha\rangle &= E^{(0)}|\beta\rangle + E^{(1)}|\alpha\rangle, \\ H_0|\gamma\rangle + \Delta H|\beta\rangle &= E^{(0)}|\gamma\rangle + E^{(1)}|\beta\rangle + E^{(2)}|\alpha\rangle, \\ &\vdots \end{aligned} \quad (8.5)$$

and so on.

The first of these equations simply states that  $|\alpha\rangle$  is an eigenstate of the model Hamiltonian  $H_0$  with eigenvalue  $E^{(0)}$ . This is not surprising; under our analyticity assumptions the terms of  $\mathcal{O}(\lambda^0)$  are all that would survive when the dial is set to  $\lambda = 0$ , which is indeed the model system. Henceforth, we relabel  $|\alpha\rangle \rightarrow |n\rangle$  and  $E^{(0)} \rightarrow E_n$  to reflect this understanding. (The notation  $|n\rangle$  is intended to imply the  $n^{\text{th}}$  energy eigenstate of the model Hamiltonian  $H_0$ , with eigenvalue  $E_n$ ; we will distinguish the higher-order corrections to these states with superscripts.)

To determine the first-order correction  $E_n^{(1)}$  to the  $n^{\text{th}}$  energy level of the unperturbed Hamiltonian, we contract the second of equations (8.5) with  $\langle\alpha| \equiv \langle n|$  to find

$$\langle n|H_0|\beta\rangle + \langle n|\Delta H|n\rangle = E_n\langle n|\beta\rangle + E_n^{(1)} \quad (8.6)$$

Since (as for any Hamiltonian) the model Hamiltonian is Hermitian,

$$\langle n|H_0|\beta\rangle = \overline{\langle\beta|H_0|n\rangle} = E_n\langle n|\beta\rangle, \quad (8.7)$$

so in the case that the unperturbed state is  $|n\rangle$ , equation (8.6) becomes

$$E_n^{(1)} = \langle n|\Delta H|n\rangle. \quad (8.8)$$

In other words, to first order in  $\lambda$ , the change in the energy of our system as we move away from the model system is given by the expectation value  $\langle\Delta H\rangle_n$  of the change in the Hamiltonian when the system is in its original state  $|n\rangle$ .

To find the perturbed state, to first order in  $\lambda$  we must understand  $|\beta\rangle$ . We can expand  $|\beta\rangle$  in the complete set  $\{|n\rangle\}$  of eigenstates of the original system as

$$|\beta\rangle = \sum_n b_n |n\rangle. \quad (8.9)$$

Using this expression in the second of equations (8.5) and contracting with  $\langle m|$  (where  $|m\rangle \neq |n\rangle$ , the initial state we're perturbing) gives

$$(E_n - E_m) b_m = \langle m|\Delta H|n\rangle \quad (8.10)$$

and so, provided  $E_m \neq E_n$ ,

$$b_m = \frac{\langle m|\Delta H|n\rangle}{E_n - E_m}. \quad (8.11)$$

This will hold provided the energy levels of our model system are non-degenerate; we'll examine how to handle the more general case including degeneracy in section 8.2. In the non-degenerate case, equation (8.11) determines all the expansion coefficients  $b_m$  in  $|\beta\rangle$  *except*  $b_n$ . Fortunately, one can argue that  $b_n = 0$  from the requirement that  $|E_\lambda\rangle$  remains correctly normalised — I'll leave this as an exercise, but the essential idea is that if we move a point on a unit sphere, then to first order  $\mathbf{r} \cdot \delta\mathbf{r} = 0$  so that the variation is only non-zero in directions orthogonal to the original vector. With  $b_n = 0$  we have

$$|\beta\rangle = \sum_{m \neq n} \frac{\langle m|\Delta H|n\rangle}{E_n - E_m} |m\rangle \quad (8.12)$$

as the first-order perturbation of the state when the unperturbed state is  $|n\rangle$ .

We can also examine the second-order perturbation,  $E_n^{(2)}$ , of the  $n^{\text{th}}$  energy level. To do so, contract the third of equations (8.5) with  $\langle n|$ . Using the facts that  $\langle n|H_0|\gamma\rangle = E_n \langle n|\gamma\rangle$  and  $\langle n|\beta\rangle = 0$  we have

$$\begin{aligned} E_n^{(2)} &= \langle n|\Delta H|\beta\rangle = \sum_{m \neq n} \frac{\langle n|\Delta H|m\rangle \langle m|\Delta H|n\rangle}{E_n - E_m} \\ &= \sum_{m \neq n} \frac{|\langle n|\Delta H|m\rangle|^2}{E_n - E_m}, \end{aligned} \quad (8.13)$$

using our expression (8.12) for  $|\beta\rangle$ . We could go on to higher order in  $\lambda$ , next finding  $|\gamma\rangle$  in terms of the original states  $\{|n\rangle\}$  and then finding the third-order energy shift  $E_n^{(3)}$  *etc.*, but in practice the summations become increasingly messy and we hope (!) that the first few terms already provide a good guide to the behaviour of the system near  $\lambda = 1$ . (In high-energy quantum field theory, modern experiments typically cost many millions of dollars so it's especially important to have extremely accurate theoretical predictions to compare to. Consequently, there's a whole industry of people whose life's work is to compute higher and higher order terms in perturbation series such as these.) Fortunately, in the Tripos you'll never be asked to do anything beyond 2<sup>nd</sup> order.

Combining our results shows that, to second order in  $\lambda$ , the energy levels of the perturbed system are given by

$$E_n(\lambda) = E_n + \lambda \langle n | \Delta H | n \rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle n | \Delta H | m \rangle|^2}{E_n - E_m} + \mathcal{O}(\lambda^3) \quad (8.14)$$

where  $E_n$  are the energies of our model system. Recall that this expression – much beloved of Tripos Examiners – is derived under the assumptions *i*) that the new energies  $E(\lambda)$  and new states  $|E_\lambda\rangle$  are analytic at  $\lambda = 0$  and *ii*) that the model system is non-degenerate so  $E_m = E_n$  iff  $|m\rangle = |n\rangle$ .

Let's now take a look at the use of this formula in a number of examples.

### 8.1.1 Fine Structure of Hydrogen

Our treatment of the hydrogen atom in the last chapter assumed the electron was moving non-relativistically in the Coulomb field of the proton. Since  $|E/\mu c^2| = \alpha^2/2n^2 \ll 1$ , non-relativistic quantum mechanics should indeed be a good approximation. Nonetheless, better agreement with experiment is obtained by describing the electron using the relativistic Dirac equation<sup>66</sup>. The energy levels obtained by assuming non-relativistic motion in a pure Coulomb potential are often called the *gross structure* of the hydrogen atom, whilst the small relativistic corrections to these energies implied by the Dirac equation are known as *fine structure*. In section 6.2.3, we understood that gross structure energies are independent of  $\ell$  because of an enhanced symmetry of the pure Coulomb potential, generated by the Runge-Lenz operator. We thus expect that relativistic corrections will lift the degeneracy among states of different  $\ell$ .

The Dirac equation itself is beyond the scope of this course, but some of its consequences are easy to understand in perturbation theory. Firstly, expanding the relativistic dispersion relation around the non-relativistic limit gives

$$E = \sqrt{\mathbf{p}^2 c^2 + \mu^2 c^4} \approx \mu c^2 + \frac{\mathbf{p}^2}{2\mu} - \frac{\mathbf{p}^4}{8\mu^3 c^2} + \dots \quad (8.15)$$

This shows that relativistic effects alter the kinetic energy by

$$\Delta H = -\frac{\mathbf{p}^4}{8\mu^3 c^2} \quad (8.16)$$

at first order. From (8.8), the first-order shift in the energy of state  $|n\ell, m\rangle$  of hydrogen due to this modified kinetic term is thus

$$E_{n,\ell}^{(1)} = \langle n, \ell, m | \Delta H | n, \ell, m \rangle. \quad (8.17)$$

(In making this claim, we should note that our perturbation (8.16) is rotationally invariant, so in particular  $[L_z, \Delta H] = 0$  and  $[\mathbf{L}^2, \Delta H] = 0$ . Therefore  $\langle n, \ell', m' | \Delta H | n, \ell, m \rangle = 0$  unless

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<sup>66</sup>A better approximation still – in precise agreement with the most accurate measurements ever performed in any branch of science – comes from quantum field theory.

$\ell' = \ell$  and  $m' = m$ . Thus our perturbation does not mix degenerate states of the gross structure, so non-degenerate perturbation theory is sufficient.)

To compute (8.17), first write  $\Delta H = -(H_0 - V(r))^2/2\mu c^2$  where  $H_0$  is the gross structure Hamiltonian and  $V(r)$  the usual Coulomb potential. Then

$$E_{n,\ell}^{(1)} = -\frac{1}{2\mu c^2} [(E_n)^2 - 2E_n \langle V(r) \rangle + \langle V(r)^2 \rangle], \quad (8.18)$$

where  $E_n = -\frac{1}{2}\mu c^2 \alpha^2/n^2$  is the original energy of our state and  $\langle V(r) \rangle = \langle n, \ell, m | V(r) | n, \ell, m \rangle$ . The virial theorem for the  $1/r$  potential tells us that  $2\langle T \rangle = -\langle V \rangle$ , so  $\langle V \rangle = 2E_n$ . Next, to compute  $\langle V^2 \rangle$ , observe that this  $1/r^2$  term just modifies the effective potential due to the electron's orbital angular momentum. Consider the Hamiltonian for the radial part of the Hydrogen atom, with an effective potential

$$V_{\text{eff}}(r) = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + \frac{\alpha}{r^2} - \frac{e^2}{4\pi\epsilon_0 r} = \frac{\hbar^2 \ell'(\ell'+1)}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r}. \quad (8.19)$$

Here we've introduced  $\ell'$  to absorb the  $\alpha/r^2$  term into the angular momentum contribution. Of course  $\ell'$  does not correspond to any actual angular momentum, it's just a trick to help us compute  $\langle V^2 \rangle$ . With this effective potential, repeating the calculations of section 6.4 would lead to just the same energy levels as before, but now in terms of  $\ell'$ . That is, in place of (6.90) we'd find

$$E(\ell') = -\frac{1}{2}\mu c^2 \alpha^2 \frac{1}{(\ell'+1)^2}. \quad (8.20)$$

using our new (non-integer)  $\ell'$ . This is the exact result for a hydrogen atom with an additional  $1/r^2$  term in its potential. However, in our perturbative context, it's only appropriate to keep the answer accurate to first order – there may be other effects we haven't yet accounted for (such as expanding (8.15) further) that contribute at higher order. Expanding  $\ell'$  around  $\ell$  we find

$$E(\ell') = E_n + \frac{1}{2}\mu c^2 \frac{\alpha^4}{n^3(\ell + \frac{1}{2})} + \dots \quad (8.21)$$

where  $n = \ell + 1$ . Combining this with the other terms in (8.18) gives

$$E_{n,\ell}^{(1)} = -\frac{1}{2}\mu c^2 \left( \frac{n}{\ell + \frac{1}{2}} - \frac{3}{4} \right) \frac{\alpha^4}{n^4} \quad (8.22)$$

as the first-order change in the energy of state  $|n, \ell, m\rangle$  due to the relativistic correction to kinetic energy. Notice that this effect is suppressed by an additional power of  $\alpha^2 \sim v^2/c^2$  compared to the gross structure, and that the degeneracy among states of different  $\ell$  is lifted, as we expected.

There's a second consequence of the Dirac equation which comes in at the same order as the above kinetic terms. Due to its spin, the electron has a magnetic dipole moment

$$\mathbf{m} = -\frac{e}{2\mu} \mathbf{S}. \quad (8.23)$$

When placed in a magnetic field, this dipole has energy  $U = -\mathbf{m} \cdot \mathbf{B}$ . Relativistically, the electron in a Hydrogen atom *does* experience a magnetic field because it moves through the electric field  $\mathbf{E}$  produced by the proton. If the electron has velocity  $\mathbf{v} = \mathbf{p}/(\mu\gamma)$ , then classically the Lorentz transformation of  $\mathbf{E}$  produces a magnetic field

$$\mathbf{B} = \frac{\gamma}{c^2} \mathbf{v} \times \mathbf{E} = \frac{1}{\mu c^2} \mathbf{p} \times \left( \frac{e\hat{\mathbf{r}}}{4\pi\epsilon_0 r^2} \right) = -\frac{e}{4\pi\epsilon_0 \mu c^2} \frac{1}{r^3} \mathbf{L} \quad (8.24)$$

### EXPLAIN THOMAS PRECESSION?

Consequently, in QM the Hamiltonian of hydrogen receives a further fine-structure correction

$$H_{\text{SO}} = -\mathbf{m} \cdot \mathbf{B} = \frac{\alpha\hbar^3}{2\mu^2 c} \frac{1}{r^3} \mathbf{S} \cdot \mathbf{L} \quad (8.25)$$

known as *spin-orbit coupling*. Since the coefficient of the operator  $\mathbf{S} \cdot \mathbf{L}$  is positive, spin-orbit coupling lowers the total energy when the spin and orbital angular momentum are antiparallel. In particular,  $\mathbf{S} \cdot \mathbf{L}$  annihilates any state of hydrogen in which  $\ell = 0$ , since then all components of  $\mathbf{L}$  act trivially. As an important special case, spin-orbit coupling does not affect the ground state. However, excited states with  $\ell \neq 0$  do generically feel the effects of spin-orbit coupling.

We first compute the effect of acting on our electron states with  $\mathbf{L} \cdot \mathbf{S}$ . To do this, clearly we must include a specification of the electron's spin. This could be done using the basis

$$|n, \ell, m\rangle \otimes |\uparrow\rangle \quad \text{and} \quad |n, \ell, m\rangle \otimes |\downarrow\rangle,$$

but it turns out to be more convenient to instead combine the electron's orbital and spin angular momenta into  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  and label states by<sup>67</sup>  $|n, j, m_j; \ell\rangle$  where  $j = \ell + \frac{1}{2}$  or  $j = \ell - \frac{1}{2}$  are the two possible values for the combined angular momentum, and  $|m_j| \leq j$ . To make use of this, we write

$$\mathbf{S} \cdot \mathbf{L} = \frac{1}{2} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2). \quad (8.26)$$

Thus

$$\begin{aligned} \mathbf{S} \cdot \mathbf{L} |n, j, m_j; \ell\rangle &= \frac{\hbar^2}{2} \left( j(j+1) - \ell(\ell+1) - \frac{3}{4} \right) |n, j, m_j; \ell\rangle \\ &= \frac{\hbar^2}{2} \begin{cases} \ell |n, j, m_j; \ell\rangle & \text{when } j = \ell + \frac{1}{2} \\ -(\ell+1) |n, j, m_j; \ell\rangle & \text{when } j = \ell - \frac{1}{2}. \end{cases} \end{aligned} \quad (8.27)$$

Consequently, according to our general expression (8.8), the first-order change in the energy of the  $|n, j, m_j; \ell\rangle$  state of hydrogen due to spin-orbit coupling is

$$E_{n,j;\ell}^1 = -\frac{1}{4\mu^2 c^2} \frac{e^2 \hbar^2}{4\pi\epsilon_0} \left\{ \begin{array}{c} \ell \\ -(\ell+1) \end{array} \right\} \left\langle \frac{1}{r^3} \right\rangle_{n,j;\ell}, \quad (8.28)$$

<sup>67</sup>Since  $[\mathbf{J}, \mathbf{L}^2] = 0$ , it's possible to find a basis of simultaneous eigenstates of  $\mathbf{J}^2$ ,  $J_z$  and  $\mathbf{L}^2$ . In this basis, we do not necessarily know the  $z$ -components of the electron's orbital and spin angular momenta separately.

with the factor of  $\ell$  or  $-(\ell + 1)$  chosen depending on whether  $j = \ell \pm \frac{1}{2}$ .

To compute the expectation value  $\langle 1/r^3 \rangle_{n,j;\ell}$  we could just perform the integral

$$\int_{\mathbb{R}^3} |\psi_{n,\ell,m}(\mathbf{x})|^2 \frac{1}{r^3} d^3x.$$

However, there's a nifty trick that allows us to short-circuit the evaluation of this integral. Recall that for states of definite  $\ell$ , the Hamiltonian for the unperturbed atom can be written

$$H_\ell = -\frac{P_r^2}{2\mu} + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r} \quad (8.29)$$

where  $P_r = (\hat{\mathbf{X}} \cdot \mathbf{P} + \mathbf{P} \cdot \hat{\mathbf{X}})/2$  is the radial momentum, given by

$$-i\hbar \left( \frac{\partial}{\partial r} + \frac{1}{r} \right)$$

in the position representation. Now, the expectation value  $\langle [P_r, H_\ell] \rangle = 0$  when evaluated in any normalizable eigenstate of  $H_\ell$ . In our case, the commutator evaluates to

$$[P_r, H_\ell] = -i\hbar \left( -\frac{\hbar^2 \ell(\ell + 1)}{\mu r^3} + \frac{e^2}{4\pi\epsilon_0 r^2} \right) \quad (8.30)$$

and therefore, provided  $\ell \neq 0$ ,

$$\left\langle \frac{1}{r^3} \right\rangle_{n,j;\ell} = \frac{1}{a_0} \frac{1}{\ell(\ell + 1)} \left\langle \frac{1}{r^2} \right\rangle_{n,j;\ell} = \frac{1}{a_0^3} \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)} \frac{1}{n^2} \quad (8.31)$$

where  $a_0 = \hbar/(\alpha\mu c)$  is the Bohr radius and the second equality follows from our previous result (8.21) for  $\langle 1/r^2 \rangle$ .

Putting this result together with the other factors in (8.28) shows that the first-order energy shifts due to spin-orbit coupling are

$$E_{n,j;\ell}^1 = +\frac{1}{2} Z^2 \alpha^4 \mu c^2 \frac{1}{2n^3(\ell + \frac{1}{2})(\ell + 1)} \quad (8.32a)$$

when  $j = \ell + \frac{1}{2}$ , whereas when  $j = \ell - \frac{1}{2}$  we have

$$E_{n,j;\ell}^1 = -\frac{1}{2} \alpha^4 \mu c^2 \frac{1}{2n^3\ell(\ell + \frac{1}{2})}. \quad (8.32b)$$

(We also recall that  $E_{n,j;\ell}^1 = 0$  if  $\ell = 0$ .) As anticipated, states whose spin and orbital angular momenta are anti-aligned ( $j = \ell - \frac{1}{2}$ ) have lower energy and so are more tightly bound than the pure Coulomb interaction, whereas if the spin and orbital angular momentum are aligned with each other ( $j = \ell + \frac{1}{2}$ ) the state is less tightly bound. Notice also that the deviation from a pure Coulombic interaction partially lifts the degeneracy between states of different  $\ell$ .

Equations (8.32a)-(8.32b) show that the spin-orbit contribution to the energy is suppressed by a factor of  $\alpha^2$  compared to the gross structure energy  $-\frac{1}{2}\mu\alpha^2 c^2/n^2$ . This is the same suppression as we found for the  $\mathbf{P}^4$  correction to the kinetic term, so it does not

really make sense to consider these two effects on the energy separately. Combining (8.22) with (8.32a) & (8.32b), we find the net energy levels

$$E_{n,j;\ell} = -\frac{1}{2}\mu\alpha^2c^2 \left[ \frac{1}{n^2} - \frac{\alpha^2}{n^3} \left( \frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right) + \dots \right] \quad (8.33)$$

incorporating fine structure correct to order  $\alpha^4$ . This formula holds regardless of whether  $j = \ell + \frac{1}{2}$  or  $j = \ell - \frac{1}{2}$ . Even better, although the spin-orbit term only contributes only when  $\ell \neq 0$ , it turns out that there is another term<sup>68</sup> that contributes only when  $\ell$  does equal zero! Even better, this remaining term has the effect that (8.33) is the correct fine structure energy levels even for states with  $\ell = 0$  where  $j = \frac{1}{2}$  just from the spin.

Proceeding down the periodic table, if we attach a single electron to an atomic nucleus containing  $Z$  protons, the bare Coulomb interaction increases by a factor of  $Z$ . The formula (8.33) remains valid provided we replace  $\alpha \sim e^2$  by  $Z\alpha$ . Hydrogen has  $Z = 1$ , so in the  $n = 1$  ground state the fine structure contribution is suppressed by a factor of  $\alpha^2 \sim 1/(137)^2$  compared to the gross structure, justifying our treatment of the fine structure as a small perturbation. However, for heavier elements with higher  $Z$ , the suppression is only by  $(Z\alpha)^2$  and the small value of  $\alpha$  can be negated by a sufficiently large  $Z$ . In particular, from (8.33) we see that the energy difference between the states with principal quantum number  $n$  but  $j = \ell \pm \frac{1}{2}$  is

$$E_{n,\ell+\frac{1}{2};\ell} - E_{n,\ell-\frac{1}{2};\ell} = \frac{1}{2}\mu c^2 \frac{1}{n^3} \frac{Z^4 \alpha^4}{\ell(\ell+1)}. \quad (8.34)$$

This gives the splitting between the two  $2p$  states of Hydrogen to be  $4.53 \times 10^{-5}$  eV, in excellent agreement with the measured value of  $4.54 \times 10^{-5}$  eV. These splittings reach around 10% of the gross energy as one reaches the middle of the periodic table, making perturbative treatments less reliable.

### 8.1.2 Hyperfine Structure of Hydrogen

A proton is a spin- $\frac{1}{2}$  particle, so like the electron it has a magnetic dipole moment  $\mathbf{m}_p$  proportional to its spin. A magnetic dipole  $\mathbf{m}_p$  placed at the origin generates its own magnetic field

$$\mathbf{B} = \frac{2\mu_0}{3} \mathbf{m}_p \delta^3(\mathbf{x}) + \frac{\mu_0}{4\pi r^3} (3(\mathbf{m}_p \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{m}_p),$$

which is (roughly) the field you saw traced out by iron filings when first playing with magnets. The dipole moment  $\mathbf{m}_e$  of the electron sits inside this field, leading to a new contribution

$$H_{\text{hfs}} = -\mathbf{m}_e \cdot \mathbf{B} \quad (8.35)$$

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<sup>68</sup>This remaining relativistic effect is known as the Darwin term and gives a contribution  $\frac{\alpha\pi\hbar^3}{2\mu^2c} \delta^3(\mathbf{x})$ . The origin of this term is rather subtle, and properly lies within QFT rather than QM. Because of the  $\delta$ -function, it only affects states which have non-zero probability to be found at  $r = 0$ . The only such states are those with  $\ell = 0$ , since all others are prevented from reaching the origin by the effective potential  $\ell(\ell+1)\hbar^2/(2mr^2)$ .

depending on both dipoles. We'll just investigate the effect of this perturbation on the  $\ell = 0$  states of hydrogen, where it turns out that only the first term  $\sim \delta^3(\mathbf{r})$  in  $\mathbf{B}$  has non-vanishing contribution. For these  $\ell = 0$  states, one finds

$$H_{\text{hfs}} = \frac{4}{3} \frac{m}{M} \alpha^4 \mu c^2 \frac{1}{n^3 \hbar^2} \mathbf{S} \cdot \mathbf{I} \quad (8.36)$$

where  $\mathbf{I}$  is the spin operator for the proton, labelled using a different letter just to avoid confusion with the electron spin operator  $\mathbf{S}$ .

The splittings in energy levels caused by this perturbation are suppressed not just by a factor of  $\alpha^4$ , but by an additional factor of the electron-to-proton mass ratio  $m/M \approx 1/1836$ . The splittings caused by accounting for nuclear spin are thus much smaller than those of the fine structure considered above, and the perturbation (8.35) is known as the *hyperfine* contribution to the energy levels. We can compute the eigenvalues in much the same way as for the spin-orbit contribution to fine structure. Let  $\mathbf{F} = \mathbf{I} + \mathbf{S}$  denote the total spin of the proton and electron. Then

$$\mathbf{S} \cdot \mathbf{I} = \frac{1}{2} (\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{S}^2) = \frac{\hbar^2}{2} \left( f(f+1) - \frac{3}{2} \right). \quad (8.37)$$

This is  $-3\hbar^2/4$  when the proton and electron spins are antiparallel so  $f = 0$ , and  $+\hbar^2/4$  when  $f = 1$ . Plugging these into (8.36) shows that the difference between the energies for the  $n = 1$  ground state of hydrogen is

$$E_{n=1;f=+1} - E_{n=1;f=0} = \frac{4}{3} \frac{m}{M} \alpha^4 \mu c^2 \approx 5.88 \times 10^{-6} \text{eV}, \quad (8.38)$$

corresponding to a frequency of 1.4GHz and a wavelength of 21cm. Thus transitions between the energy levels split by the hyperfine structure causes the hydrogen atom to have a microwave emission line.

The 21cm line provides the most powerful way of tracing diffuse gas in interstellar and intergalactic space. This wavelength is much longer than the size of typical specks of dust, so 21cm radiation can propagate with little absorption right through clouds of dust and gas that do absorb visible light. It was radiation at 1.4GHz that first revealed the large-scale structure of our galaxy. The line is intrinsically very narrow, so the temperature and radial (with the Earth as origin) velocity of the hydrogen that emitted the radiation can be accurately measured from the Doppler shift and broadening of the observed spectral line.

The hyperfine structure of hydrogen leading to this 21cm emission line was first predicted theoretically in 1944 by the Dutch physicist H.C. van de Hulst as part of his doctoral thesis, carried out in Utrecht which was then under Nazi occupation. 21cm radiation from our galaxy was first detected experimentally in 1951 by three groups working independently in the USA, Australia and the Netherlands. The Dutch group used a German radio antenna left over from the war.

### 8.1.3 The Ground State of Helium

After hydrogen, helium is the next most abundant element, making up about a quarter of the ordinary matter in the Universe. Much of this helium was created during the period of nucleosynthesis, a tiny fraction of a second after the Big Bang.

Let's use perturbation theory to find an estimate of the ground state energy of helium. Working in the centre of mass frame and treating the nucleus as stationary at the origin, the (gross structure) Hamiltonian is

$$H = \frac{\mathbf{P}_1^2}{2m} + \frac{\mathbf{P}_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0|\mathbf{X}_1|} - \frac{2e^2}{4\pi\epsilon_0|\mathbf{X}_2|} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{X}_1 - \mathbf{X}_2|} \quad (8.39)$$

where  $(\mathbf{X}_1, \mathbf{X}_2)$  are the position operators and  $(\mathbf{P}_1, \mathbf{P}_2)$  the momentum operators for the two electrons. The terms describing the electrons' kinetic energy and attraction to the nucleus are just the sum of those for Hydrogen, except with  $e^2$  replaced by  $2e^2$  since there are two protons in the nucleus of helium. We'll take these terms to be the model Hamiltonian  $H_0$ , treating the remaining electron-electron repulsion as a perturbation.

Before proceeding, we should ask what is the small, dimensionless parameter in which we're performing our perturbative expansion. One might hope that, as for the fine structure of hydrogen, this is the fine structure constant  $\alpha = e^2/\hbar c \approx 1/137$ . However, it's clear that this cannot be the case here, because both the electron-electron interaction and the electron-proton interactions both scale as  $e^2 \sim \alpha$ . Furthermore, the virial theorem says that in any state  $|\Psi\rangle$ , for the  $1/r$  hydrogenic Coulomb potential,  $2\langle T \rangle_\Psi = -\langle V \rangle_\Psi$  so the kinetic terms in the hydrogenic term are likewise of order  $\alpha$ . In fact, we'll perform a perturbation in the inverse atomic number, taking  $\lambda = 2/Z$  and treating this as a continuous parameter. We're interested in values  $\lambda \in (0, 1]$  corresponding to  $Z \in (\infty, 2]$ . Note that when  $Z \gg 1$ , corresponding to a nucleus with a large positive charge, the two electrons' attraction to this nucleus should certainly overwhelm their mutual repulsion.

In the unperturbed Hamiltonian, single-electron states are just the usual hydrogenic states  $|n, \ell, m\rangle$  with energy

$$-4 \times \frac{1}{2} mc^2 \alpha^2 \frac{1}{n^2},$$

where the factor of 4 arises because each electron's attraction to the helium nucleus is twice as strong as it was for hydrogen. Since electrons are fermions, the total state of the neutral helium atom must be antisymmetric under their exchange. In particular, the ground state is

$$|\Psi_0\rangle = |1, 0, 0\rangle \otimes |1, 0, 0\rangle \otimes \frac{1}{\sqrt{2}} (|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) \quad (8.40)$$

where the final factor is the antisymmetric spin state of the two spin- $\frac{1}{2}$  electrons. (Note that, at the level of the gross structure of helium, the Hamiltonian (8.39) is independent of the spins of the two electrons, so we are free to seek simultaneous energy and spin eigenstates.) This state is an eigenstate of the model Hamiltonian  $H_0$  with energy

$$E_1 = -\frac{4\alpha^2}{2} mc^2 - \frac{4\alpha^2}{2} mc^2 = -4\alpha^2 mc^2 \approx -108.8 \text{ eV}, \quad (8.41)$$

being the sum of the energies of the two electrons individually.

We now take account of the electron-electron repulsion. To use perturbation theory, we set

$$\lambda = \frac{2}{Z} \quad \text{and} \quad \Delta H = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{X}_1 - \mathbf{X}_2|} = \frac{\alpha\hbar c}{|\mathbf{X}_1 - \mathbf{X}_2|}. \quad (8.42)$$

Our  $\Delta H$  is chosen so that *i*) it is independent of the expansion parameter and *ii*)  $\lambda\Delta$  is precisely the electron–electron potential when  $\lambda = 1$ , appropriate for helium. Following the general results above, the first order shift in the ground state energy is

$$\begin{aligned}\langle\Psi_0|\Delta|\Psi_0\rangle &= \int \langle\Psi_0|\mathbf{x}'_1, \mathbf{x}'_2\rangle \langle\mathbf{x}'_1, \mathbf{x}'_2|\Delta H(\mathbf{X}_1, \mathbf{X}_2)|\mathbf{x}_1, \mathbf{x}_2\rangle \langle\mathbf{x}_1, \mathbf{x}_2|\Psi_0\rangle d^3x'_1 d^3x'_2 d^3x_1 d^3x_2 \\ &= \int \overline{\Psi_0(\mathbf{x}_1, \mathbf{x}_2)} \frac{\alpha\hbar c}{|\mathbf{x}_1 - \mathbf{x}_2|} \Psi_0(\mathbf{x}_1, \mathbf{x}_2) d^3x_1 d^3x_2 \\ &= \int \frac{\alpha\hbar c}{|\mathbf{x}_1 - \mathbf{x}_2|} |\psi_{100}(\mathbf{x}_1)|^2 |\psi_{100}(\mathbf{x}_2)|^2 d^3x_1 d^3x_2,\end{aligned}\tag{8.43}$$

Here  $\psi_{100}(\mathbf{x})$  are the single–electron  $n = 1$  wavefunctions

$$\psi_{100}(\mathbf{x}) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_2}\right)^{\frac{3}{2}} e^{-|\mathbf{x}|/a_2},\tag{8.44}$$

where the length scale  $a_2 = \frac{\hbar}{2\alpha mc}$  is half the Bohr radius in hydrogen. In going to the last line of (8.43), we’ve used the fact that the interaction  $\Delta$  is independent of spin, and the spin states in (8.40) have norm 1.

Performing the integral is straightforward but somewhat tedious<sup>69</sup>, and isn’t the sort of thing I’m going to ask you to reproduce in an exam. One finds

$$\langle\Psi_0|\Delta H|\Psi_0\rangle = \frac{5}{4}\alpha^2 mc^2\tag{8.45}$$

As we suspected, this perturbation is also of order  $\alpha^2$  just like the leading–order term. Including the factor of  $\lambda = 2/Z$ , to first–order in perturbation theory the ground state of helium is

$$E_1(1/Z)_{Z=2} = -4\alpha^2 mc^2 \left(1 - \frac{5}{16} \frac{2}{Z} + \dots\right)_{Z=2} \approx -74.8 \text{ eV}.\tag{8.46}$$

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<sup>69</sup>In case you’re curious: Choose the  $z$ -axis of  $\mathbf{x}_2$  to be aligned with whatever direction  $\mathbf{x}_1$  is. Then  $|\mathbf{x}_1 - \mathbf{x}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}$ , independent of  $\phi_2$ . So

$$\langle\Psi_0|\Delta H|\Psi_0\rangle = \frac{4\alpha\hbar c}{a_2^3} \int |\psi_{100}(\mathbf{x}_1)|^2 \left[ \int \frac{r_2^2 \sin \theta_2 e^{-2r_2/a_2}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} dr_2 d\theta_2 \right] d^3x_1.$$

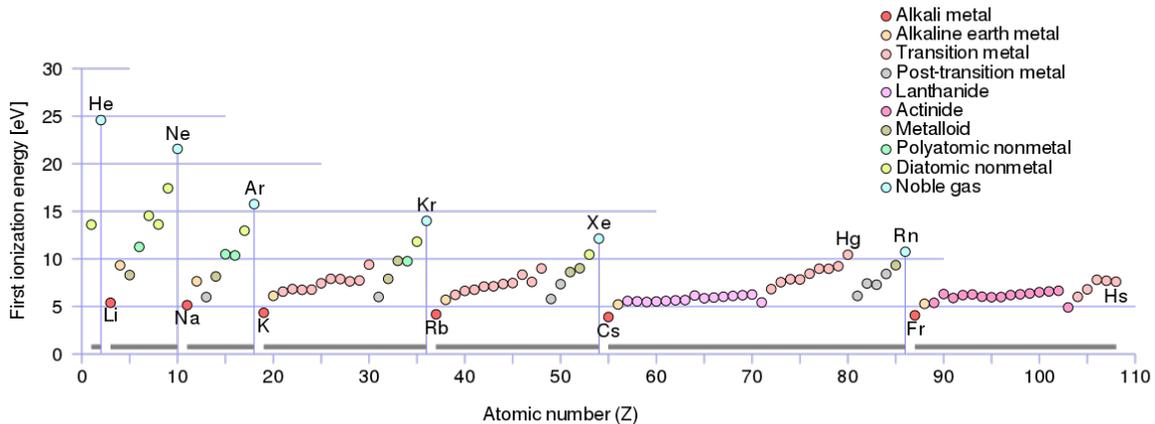
The integral in square brackets can be done using

$$\int_0^\pi \frac{\sin \theta_2 d\theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} = \frac{1}{r_1r_2} \int_0^\pi \frac{d}{d\theta_2} \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2} d\theta_2 = \begin{cases} 2/r_1 & \text{when } r_1 > r_2 \\ 2/r_2 & \text{when } r_1 < r_2 \end{cases}.$$

Thus the radial integral  $dr_2$  must be broken into two regions. Letting  $\rho_1 := 2r_1/a_2$  be a rescaled radial coordinate, we have

$$\begin{aligned}\langle\Psi_0|\Delta|\Psi_0\rangle &= \frac{8\alpha\hbar c}{a_2^3} \int |\psi_{100}(\mathbf{x}_1)|^2 \left[ \int_0^{r_1} \frac{r_2^2}{r_1} e^{-2r_2/a_2} dr_2 + \int_{r_1}^\infty r_2 e^{-2r_2/a_2} dr_2 \right] d^3x_1 \\ &= \frac{4\alpha\hbar c}{a_2} \int |\psi_{100}(\mathbf{x}_1)|^2 \frac{2 - e^{-\rho_1}(2 + \rho_1)}{\rho_1} d^3x_1 = \frac{2\alpha\hbar c}{a_2} \int_0^\infty \rho_1 e^{-\rho_1} (2 - e^{-\rho_1}(2 + \rho_1)) d\rho_1 = \frac{5\alpha\hbar c}{4a_2}.\end{aligned}$$

This is the value that was used in the text. And no, I’m not going to derive the second–order result for you.



**Figure 17:** First ionisation energies of the ground states of the first few elements. Figure by Agung Karjono at *Wikipedia*.

This is in significantly better agreement with the experimental value of  $\approx -79.0$  eV than our zeroth-order estimate (8.41). Including also the second-order term<sup>70</sup> leads to

$$E_1(1/Z) = -4\alpha^2 mc^2 \left( 1 - \frac{5}{8} \frac{1}{Z} + \frac{25}{256} \frac{1}{Z^2} + \mathcal{O}(1/Z^3) \right) \quad (8.47)$$

giving  $E_1(1/2) \approx -77.5$  eV. Given the crudity of our expansion this is in remarkably close agreement with the experimental value.

In heavy atoms, the ground state energy itself is difficult to measure experimentally since it involves computing the energy required to strip off *all* the electrons from the nucleus. Fortunately, for the same reason it's also rarely the directly relevant quantity. Instead, chemists and spectroscopists are usually more interested in the *first ionisation energy*, defined to be the energy required to liberate a single electron from the atom. Hydrogen only has one electron, so its first ionization energy is just the 13.6 eV which we must supply to eject this electron from the ground state of the atom. In the case of helium, once one electron is stripped away the remaining electron sees the full force of the Coulomb potential from the  $Z = 2$  nucleus, so will have binding energy  $-54.4$  eV. The first ionisation energy is thus the difference  $\approx (-54.4 + 79.0)$  eV = 24.6 eV. This is significantly greater than the ionisation energy of hydrogen, and in fact helium has the greatest first ionisation energy of any of the elements, reflecting its status as the first noble gas (see figure 17).

### 8.1.4 The Quadratic Stark Effect

We'll now consider a different type of perturbation, caused not by relativistic corrections to the Hamiltonian of the isolated atom, but by allowing the atom to interact with some external system.

<sup>70</sup>We could calculate this using the result (8.13) for the second-order energy shift. I'll just quote the answer.

Suppose a hydrogen atom is placed in an external electric field  $\mathbf{E} = -\nabla\phi$ . Most electric fields we can generate in the laboratory are small compared to the strength of the Coulomb field felt by the electron due to the nucleus<sup>71</sup>, so perturbation theory should provide a good estimate of the energy shifts such an external field induces. By definition of the electrostatic potential  $\Phi$ , the field changes the energy of the atom by  $\delta E = e(\phi(\mathbf{x}_p) - \phi(\mathbf{x}_e))$  where  $\mathbf{x}_p$  and  $\mathbf{x}_e$  are the locations of the proton and electron. We assume the external field varies only slowly over scales of order the Bohr radius, so

$$\delta E \approx -e\mathbf{r} \cdot \nabla\phi = -e\mathbf{r} \cdot \mathbf{E} \quad (8.48)$$

where  $\mathbf{r} = \mathbf{x}_e - \mathbf{x}_p$ . Let's choose the direction of the electric field to define the  $z$ -axis, and set  $\mathcal{E} = |\mathbf{E}|$  so as to avoid confusion with the energy. Thus  $\mathbf{E} = \mathcal{E}\hat{\mathbf{z}}$  and the effect of the external electric field is to add a new term to the Hamiltonian  $H_0$  of the unperturbed atom:

$$H = H_0 - e\mathcal{E}X_3 \quad (8.49)$$

where  $X_3$  is the position operator for the  $z$ -coordinate of the electron relative to the proton.

In this section, we'll just consider the effect of this electric field on the ground state  $|n, \ell, m\rangle = |1, 0, 0\rangle$  of the hydrogen atom. This state is non-degenerate for the unperturbed Hamiltonian (and our perturbation is blind to spin), so again non-degenerate perturbation theory will suffice. From (8.8) the first order change in the ground state energy is

$$E_1^{(1)} = -e\mathcal{E} \langle 1, 0, 0 | X_3 | 1, 0, 0 \rangle, \quad (8.50)$$

However, applying the parity operator  $\Pi$  and noting that  $\Pi^{-1}X_3\Pi = -X_3$  we have

$$\langle 1, 0, 0 | X_3 | 1, 0, 0 \rangle = -\langle 1, 0, 0 | \Pi^{-1}X_3\Pi | 1, 0, 0 \rangle = -\langle 1, 0, 0 | X_3 | 1, 0, 0 \rangle, \quad (8.51)$$

where the last equality uses the fact that  $\Pi|1, 0, 0\rangle = |1, 0, 0\rangle$  since the ground state wavefunction is spherically symmetric. Thus  $\langle 1, 0, 0 | X_3 | 1, 0, 0 \rangle = 0$  and parity symmetry ensures that, to first order in the external electric field, the ground state energy is unaffected.

To see a non-trivial effect, we must go one order further. The second order shift in the ground state energy is given by (8.13) in general. In our case, the sum is to be taken over all states of hydrogen except the ground state, so

$$E_1^{(2)} = e^2\mathcal{E}^2 \sum_{n=2}^{\infty} \sum_{\ell < n} \sum_{m=-\ell}^{\ell} \frac{|\langle 1, 0, 0 | X_3 | n, \ell, m \rangle|^2}{E_1 - E_n}. \quad (8.52)$$

In the [second problem set](#) you proved that

$$\langle n', \ell', m' | \mathbf{X} | n, \ell, m \rangle = 0 \quad \text{unless} \quad |\ell' - \ell| = 1.$$

Applying this to our case,  $\langle 1, 0, 0 | X_3 | n, \ell, m \rangle = 0$  unless  $\ell = 1$ , which greatly simplifies the sums in (8.52). Furthermore,  $[L_z, X_3] = 0$  so  $X_3|n, 0, 0\rangle$  is an eigenstate of  $L_z$  with

<sup>71</sup>With modern high intensity lasers, electric fields comparable to the nuclear Coulomb potential can be generated. The behaviour of a hydrogen atom in such a laser must be studied by other methods.

eigenvalue zero and hence it is orthogonal to  $|n, 1, m\rangle$  whenever  $m \neq 0$ . In summary, to this order the electric field causes the ground state  $|1, 0, 0\rangle$  to mix only with states  $|n, 1, 0\rangle$ . Thus the only non-vanishing terms in (8.52) are

$$E_1^{(2)} = e^2 \mathcal{E}^2 \sum_{n=2}^{\infty} \frac{|\langle 1, 0, 0 | X_3 | n, 1, 0 \rangle|^2}{E_1 - E_n} \quad (8.53)$$

involving just a single sum. This is the second-order change in the ground state energy due to the presence of the external electric field.

This change in the ground state energy is known as the *quadratic Stark effect*, after its discoverer and since it comes in at order  $\mathcal{E}^2$ . There's a good physical reason why the change in energy comes in at this order: the hydrogen atom is electrically neutral and the unperturbed ground state  $|1, 0, 0\rangle$  is spherically symmetric, so the atom in this state has no electric dipole moment. In response to the applied electric field, the electronic wavefunction changes by an amount that is proportional to the coefficients  $b_m$ , which are themselves proportional to  $\mathcal{E}$ . In other words, the applied electric field  $\mathbf{E}$  *polarizes* the atom, generating a dipole moment  $\mathbf{p} \propto \mathbf{E}$ . The energy of any dipole  $\mathbf{p}$  in an electric field is  $U_{\text{dip}} = -\mathbf{p} \cdot \mathbf{E}$  and since the dipole moment itself is  $\sim \mathcal{E}$ , for the ground state of hydrogen  $U_{\text{dip}} \sim \mathcal{E}^2$ . Higher energy states  $|n, \ell, m\rangle$  can have a permanent dipole moment due to the electron's elliptical orbits, but to study this we need degenerate perturbation theory.

## 8.2 Degenerate Perturbation Theory

Our derivation of the coefficients

$$b_m = \frac{\langle m | \Delta | n \rangle}{E_n - E_m} \quad (8.54)$$

of the first-order shift in the state breaks down if there are states  $|m\rangle$  that have the same energy as the state  $|n\rangle$  that we're attempting to perturb. Indeed, naively applying (8.54) in this case appears to show that the small perturbation can cause an extremely dramatic shift in the state of the system.

There's nothing particularly surprising about this. Consider a marble lying in the bottom of a bowl at the minimum of the gravitational potential. If we tilt the bowl slightly, the marble will move a little, resettling in the bottom of the tilted bowl as it adjusts to the new minimum of the potential. However, if the marble initially lies at rest on a smooth table, so that it initially has the same energy no matter where on the table it lies, then tilting the table even very slightly will lead to a large change in the marble's location.

To handle this degenerate situation, we first observe that the only states that will acquire a significant amplitude as a result of the perturbation are those that are initially degenerate with the original state. In other words, to good approximation, the state to which the system changes will be a linear combination of those having the same zeroth-order energy as our initial state. In many situations, there are only a finite number of these. We then diagonalise the matrix  $\langle r | \Delta | s \rangle$  of the perturbing Hamiltonian in the subspace

spanned by these degenerate states. Since this subspace was completely degenerate *wrt*  $H_0$ , in this subspace the eigenstates of the perturbation  $\Delta$  are in fact eigenstates of the full Hamiltonian  $H_0 + \Delta$ .

Let's see how this works in more detail. Suppose  $V \subset \mathcal{H}$  is an  $N$ -dimensional subspace with  $H_0|\psi\rangle = E_V|\psi\rangle$  for all  $|\psi\rangle \in V$ . For  $r = 1, \dots, N$ , we let  $\{|r\rangle\}$  be an orthonormal basis of  $V$  and define  $P_V$  to be the projection operator  $P_V : \mathcal{H} \rightarrow V$ . We can write this projection operator as

$$P_V = \sum_{r=1}^N |r\rangle\langle r| \quad (8.55)$$

in terms of our orthonormal basis. Similarly, we let  $P_\perp = 1 - P_V$  denote the projection onto  $V^\perp$ , where

$$V^\perp = \{|\chi\rangle \in \mathcal{H} : \langle\psi|\chi\rangle = 0 \ \forall \ |\psi\rangle \in V\}. \quad (8.56)$$

Note that, as projection operators,  $P_V^2 = P_V$  and  $P_\perp^2 = P_\perp$  and that  $P_V P_\perp = P_\perp P_V = 0$ . Also, we have

$$[H_0, P_V] = 0 \quad \text{and} \quad [H_0, P_\perp] = 0 \quad (8.57)$$

since  $V$  was defined in terms of a degenerate subspace of  $H_0$ .

Now let's consider a perturbed Hamiltonian  $H_\lambda = H_0 + \lambda\Delta$ . Any eigenstate  $|\psi_\lambda\rangle$  of the full Hamiltonian obeys

$$\begin{aligned} 0 &= (H_0 - E(\lambda) + \lambda\Delta)|\psi_\lambda\rangle \\ &= (H_0 - E(\lambda) + \lambda\Delta)(P_V + P_\perp)|\psi_\lambda\rangle \\ &= (E_V - E(\lambda) + \lambda\Delta)P_V|\psi_\lambda\rangle + (H_0 - E(\lambda) + \lambda\Delta)P_\perp|\psi_\lambda\rangle \end{aligned} \quad (8.58)$$

where in the second line we've separated out the terms in  $V$  from those in  $V^\perp$ . Acting on the left with either  $P_V$  or  $P_\perp$  and using (8.57), we obtain the two equations

$$0 = (E_V - E(\lambda) + \lambda P_V \Delta) P_V |\psi_\lambda\rangle + \lambda P_V \Delta P_\perp |\psi_\lambda\rangle \quad (8.59a)$$

and

$$0 = \lambda P_\perp \Delta P_V |\psi_\lambda\rangle + (H_0 - E(\lambda) + \lambda P_\perp \Delta) P_\perp |\psi_\lambda\rangle, \quad (8.59b)$$

in which we have separated out the effects of the perturbation within  $V$  and its complement.

Suppose now that we're perturbing a state  $|\psi_0\rangle$  that, in the absence of the perturbation, lies in  $V$ . We write

$$\begin{aligned} |\psi_\lambda\rangle &= |\alpha\rangle + \lambda|\beta\rangle + \lambda^2|\gamma\rangle + \dots \\ E(\lambda) &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \end{aligned} \quad (8.60)$$

just as before, noting that  $P_\perp|\psi_\lambda\rangle$  is necessarily at least first-order in  $\lambda$ . To zeroth order, equation (8.59a) tells us that  $E^{(0)} = E_V$  as expected. At first order, this equation becomes

$$(-E^{(1)} + P_V \Delta)|\alpha\rangle = 0 \quad \text{or equivalently} \quad P_V \Delta P_V |\alpha\rangle = E^{(1)}|\alpha\rangle. \quad (8.61)$$

This is a remarkable equation! It tells us that, if our assumption that the perturbation  $\Delta$  causes only a small change in the energies and states of the system is to hold and if

our zeroth-order state  $|\psi_0\rangle$  lies in some degenerate subspace, then  $|\psi_0\rangle$  can't be just any eigenstate of  $H_0$ , but must also be an eigenstate of  $P_V\Delta P_V$  – the perturbation, restricted to the degenerate subspace  $V$ . In other words, in degenerate systems, states that are stable against small perturbations are those that are already eigenstates of the perturbation. If we started with some other  $|\psi_0\rangle \in V$  that was not an eigenstate of  $\Delta$ , then as soon as the perturbation is turned on, the state would rapidly change into a  $\Delta$  eigenstate<sup>72</sup>. This large response to a small change in  $H$  would invalidate our use of perturbation theory; it's the quantum analogue of the fact that the location of a marble on a perfectly flat table is extremely sensitive to any tilt.

Let's now suppose that we've chosen our basis  $\{|r\rangle\}$  of  $V$  in such a way that  $P_V\Delta P_V|r\rangle = E_r^{(1)}|r\rangle$ , so that  $|r\rangle$  is indeed an eigenstate of the perturbation with some eigenvalue we'll call  $E_r^{(1)}$ . Then choosing our initial state  $|\alpha\rangle$  to be  $|r\rangle$ , by (8.61) the first order shift in its energy is

$$E_r^{(1)} = \langle r|P_V\Delta P_V|r\rangle = \langle r|\Delta|r\rangle. \quad (8.62)$$

This is exactly what we would have found in the non-degenerate case, but here it's very important that we're considering the effects of perturbations when we start with an eigenstate of  $\Delta$ . In fact, since  $|r\rangle$  is an eigenstate of both  $H_0$  and  $\Delta$ , we have

$$H_\lambda|r\rangle = (H_0 + \lambda\Delta)|r\rangle = (E_V + \lambda E_r^{(1)})|r\rangle \quad (8.63)$$

so that in the subspace  $V$  we've solved the perturbed spectrum *exactly*. In other words, within  $V$  we're not really doing perturbation theory at all! Fortunately, in problems of interest  $\dim(V)$  is typically rather small and finding the exact spectrum of the full Hamiltonian  $H_\lambda$  within this finite dimensional subspace is usually much easier than finding the full spectrum.

As we've seen, degeneracy in the energy spectrum often arises as a result of some symmetry. If this symmetry is dynamical, such as the enhanced  $U(d)$  symmetry of the  $d$ -dimensional harmonic oscillator, or the  $SU(2) \times SU(2)$  symmetry the Runge-Lenz vector implies for the gross structure of hydrogen, it will almost inevitably be broken by a perturbation. Even symmetries such as rotations that are inherited from transformations of space may be broken in the presence of external fields. For example, although the ground state of an atom is typically spherically symmetric, the laboratory in which one conducts an experiment likely won't be and any small stray electric and magnetic fields in the laboratory will perturb the atom away from pure spherical symmetry. For this reason, perturbations typically lift degeneracy. As we've seen, even very small perturbations can have a dramatic effect in immediately singling out a preferred set of states in an otherwise degenerate system; we'll return to this point in section 10.1.3 when trying to understand 'collapse of the wavefunction' in quantum mechanics. If you take the Applications of Quantum Mechanics course next term, you'll see that the lifting of degeneracy is also important in giving crystals their electronic properties: when a large number of identical metal atoms are brought

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<sup>72</sup>To justify this, in particular to understand what happens "as a perturbation is turned on", we'll need to consider time-dependent perturbation theory. See chapter 9.

together, ignoring the inter-atomic interactions, all the valence electrons in the different atoms will be degenerate. The small effect of the potential from nearby atoms breaks this degeneracy and makes these valence electrons prefer to delocalise throughout the crystal.

### 8.2.1 The Linear Stark Effect

As an application of degenerate perturbation theory, let's again consider the Stark effect but now for the  $2s$  state of our atom. This state is degenerate with the three<sup>73</sup>  $2p$  states, so here our degenerate subspace

$$V = \text{span}\{|2, 0, 0\rangle, |2, 1, 1\rangle, |2, 1, 0\rangle, |2, 1, -1\rangle\}. \quad (8.64)$$

As before, the electric field induces a perturbation is<sup>74</sup>  $e\mathcal{E}X_3$  and we find a diagonalise this perturbation within  $V$ . Parity implies

$$\langle 2, 0, 0 | X_3 | 2, 0, 0 \rangle = 0 \quad \text{and} \quad \langle 2, 1, m | X_3 | 2, 1, m' \rangle = 0 \quad \forall \quad m, m' \in \{1, 0, -1\}, \quad (8.65)$$

while since  $[L_z, X_3] = 0$  we also have  $\langle 2, 0, 0 | X_3 | 2, 1, \pm 1 \rangle = 0$ . Thus the matrix elements of  $\Delta$  in the basis (8.64) are

$$\Delta|_V = e\mathcal{E} \begin{pmatrix} 0 & 0 & a & 0 \\ 0 & 0 & 0 & 0 \\ a^* & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (8.66)$$

where

$$a = \langle 2, 0, 0 | X_3 | 2, 1, 0 \rangle = 2\pi \int \overline{\psi_{2,0,0}(r)} \psi_{2,1,0}(r, \theta) r \cos \theta r^2 d(\cos \theta) = -3a_0, \quad (8.67)$$

with  $a_0$  the Bohr radius. The eigenvalues of  $\Delta$  in this subspace are thus  $\{3e\mathcal{E}a_0, 0, 0, -3e\mathcal{E}a_0\}$  with corresponding eigenstates

$$\frac{1}{\sqrt{2}} (|2, 0, 0\rangle - |2, 1, 0\rangle), \quad |2, 1, 1\rangle, \quad |2, 1, -1\rangle \quad \text{and} \quad \frac{1}{\sqrt{2}} (|2, 0, 0\rangle + |2, 1, 0\rangle). \quad (8.68)$$

In the presence of the electric field, the  $n = 2$  state of lowest energy is  $(|2, 0, 0\rangle + |2, 1, 0\rangle)/\sqrt{2}$  and we conclude that even for a tiny electric field, the  $n = 2$  states will jump to this preferred state.

From our discussion of the quadratic Stark effect above, we know that a change in energy  $\propto \mathcal{E}$  requires the dipole moment  $\mathbf{D}$  of an atom to be independent of  $\mathcal{E}$ . Since this  $n = 2$  state has a first-order energy shift of  $-3e\mathcal{E}a_0$ , we conclude that the  $n = 2$  states of hydrogen do indeed have a permanent electric dipole moment of magnitude  $3ea_0$ . Classically, for an electron in an elliptical orbit, this result is expected because the electron

<sup>73</sup>Since the applied electric field does not couple to spin, we ignore the effect of spin in this discussion – at this order, the Stark effect will not lift the degeneracy of the gross structure of hydrogen *wrt* the electron's spin.

<sup>74</sup>A reminder: we define the  $z$ -direction to be the direction of the electric field, and  $X_3$  is the corresponding operator.

would spend more time at the apocentre (the point of its orbit furthest from the atom's centre of mass) than at the pericentre (the point nearest to the centre of mass). If electron's orbit was a perfect Keplerian ellipse, the atom would have a permanent electric dipole moment aligned parallel to the orbit's major axis. However, any small deviation from the  $1/r$  potential will cause the major axis of the ellipse to precess, and the time-averaged dipole moment would vanish. For hydrogen, the potential does differ from  $1/r$ , though only very slightly due to the effects of fine structure. Hence even a weak external field can prevent precession and give rise to a steady electric dipole.

Quantum mechanically, in the presence of the electric field the lowest energy  $n = 2$  state  $(|2, 0, 0\rangle + |2, 1, 0\rangle)/\sqrt{2}$  is no longer an eigenstate of  $\mathbf{L}^2$ , because the field applies torque to the atom, changing its total orbital angular momentum. However, this lowest energy state is still an eigenstate of  $L_z$  with eigenvalue zero. Recalling that we took the  $z$ -direction to be the direction of the applied field, we see that the angular momentum is perpendicular to  $\mathbf{E}$ , as expected from the classical picture of an ellipse with major axis aligned along  $\mathbf{E}$ . Note also that the electric field does not lift the degeneracy between the  $|2, 1, 1\rangle$  and  $|2, 1, -1\rangle$  states. These two states have their orbital angular momentum maximally aligned or anti-aligned with  $\mathbf{E}$ ; classically, they correspond to orbits confined to a plane perpendicular to  $\mathbf{E}$ .

### 8.3 Does Perturbation Theory Converge?

We began our study of perturbation theory by assuming that the states and energy eigenvalues of the full Hamiltonian depended *analytically* on a dimensionless parameter  $\lambda$  controlling the perturbation. Even when the individual coefficients of powers of  $\lambda$  are finite, this is often not the case because the infinite perturbative series itself may fail to converge, or may converge only for some range of  $\lambda$ . The issue is that we really have an expansion in

$$\left| \lambda \frac{\langle m | \Delta | n \rangle}{E_m - E_n} \right| \quad \text{where } m \neq n,$$

and the *coefficients* of  $\lambda$  may grow too rapidly. Heuristically, the condition for convergence is thus that the typical energy splitting  $|\langle m | \Delta | n \rangle|$  induced by the perturbation should be much smaller than the initial energy difference  $E_m - E_n$ . However, a detailed criterion is often hard to come by since the higher terms in the perturbation expansion involve complicated sums (or integrals) over many different intermediate states.

To illustrate this in a simple context, let's consider in turn the following three perturbations of a  $1d$  harmonic oscillator potential

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 + \begin{cases} -\lambda m \omega^2 x_0 X \\ +\frac{1}{2}\lambda m \omega^2 X^2 \\ +\lambda \epsilon X^4 \end{cases} \quad (8.69)$$

where  $x_0$  and  $\epsilon$  are constants. Of course, the first two can be solved exactly — we'd never really use perturbation theory to study them.

In the first case, we have

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2(X - \lambda x_0)^2 - \frac{\lambda^2}{2}m\omega^2 x_0^2 \quad (8.70)$$

from which we easily see that the exact energies are

$$E_n(\lambda) = \left(n + \frac{1}{2}\right) \hbar\omega - \frac{\lambda^2}{2}m\omega^2 x_0^2, \quad (8.71)$$

with corresponding position space wavefunction  $\langle x|n_\lambda\rangle = \langle x - \lambda x_0|n\rangle$ , just a translation of the usual harmonic oscillator wavefunction  $|n\rangle$ . If we instead tackled this problem using perturbation theory, we'd find

$$\begin{aligned} E_n(\lambda) &= E_n - \lambda m\omega^2 x_0 \langle n|X|n\rangle + \lambda^2 m^2 \omega^4 x_0^2 \sum_{k \neq n} \frac{|\langle k|X|n\rangle|^2}{(n-k)\hbar\omega} + O(\lambda^3) \\ &= \left(n + \frac{1}{2}\right) \hbar\omega - \frac{\lambda^2}{2}m\omega^2 x_0^2 + O(\lambda^3). \end{aligned} \quad (8.72)$$

To obtain this result, we note that the first-order term vanishes (*e.g.* by parity), while since  $X$  is a linear combination of creation and annihilation operators  $A^\dagger$  and  $A$ , the only  $|k\rangle = |n+1\rangle$  and  $|k\rangle = |n-1\rangle$  terms can contribute to the sum in the second-order term. Going further, we'd find that there are no higher corrections in  $\lambda$  – the  $O(\lambda^3)$  terms are in fact zero – though this is not easy to see directly. Thus, in this case, the perturbative result converges to the exact result, and the radius of convergence is infinite. This reflects the fact that the perturbation  $-\lambda m\omega^2 x_0 X$  didn't really change the character of the original Hamiltonian. No matter how large  $\lambda$  is, for large enough  $x$  the perturbation remains negligible.

Turning to the second case, it's again immediate that the exact energy levels are

$$E_n(\lambda) = \left(n + \frac{1}{2}\right) \hbar\omega(\lambda) \quad (8.73)$$

where  $\omega(\lambda) = \omega\sqrt{1+\lambda}$  is the modified frequency. This has a branch cut starting at  $\lambda = -1$ , so the energy is only analytic in the disc  $|\lambda| < 1$ . Again using perturbation theory, we find

$$\begin{aligned} E_n(\lambda) &= E_n + \frac{\lambda}{2}m\omega^2 \langle n|X^2|n\rangle + O(\lambda^3) \\ &= \left(n + \frac{1}{2}\right) \hbar\omega \left(1 + \frac{\lambda}{2} - \frac{\lambda^2}{8} + O(\lambda^3)\right) \end{aligned} \quad (8.74)$$

agreeing to this order with the Taylor expansion of the exact answer. Continuing further, we'd find that this Taylor series does indeed converge provided  $|\lambda| < 1$ , and that it then converges to the exact answer. The physical reason why the perturbation series diverges when  $|\lambda| \geq 1$  is simply that if  $\lambda = -1$ , the 'perturbation' has completely cancelled the original harmonic oscillator potential, so we're no longer studying a system that can be treated as a harmonic oscillator in the first instance. Once  $\lambda < -1$  the harmonic oscillator

potential is turned upside down, and we do not expect our system to possess any stable bound states.

Finally, consider the case

$$H = H_{\text{SHO}} + \lambda \epsilon X^4. \quad (8.75)$$

I do not know whether this model has been solved exactly, but it can be treated perturbatively. After a fair amount of non-trivial calculation<sup>75</sup> one obtains the series

$$E_0(\lambda) = \hbar\omega + \sum_{n=1}^{\infty} (\lambda\epsilon)^n a_n \quad (8.76)$$

for the ground state energy including the quartic interaction, where the coefficients behave as

$$a_n = \frac{(-1)^{n+1} \sqrt{6}}{\pi^{3/2}} 3^n \Gamma(n + \frac{1}{2}) \left( 1 - \frac{95}{72} \frac{1}{n} + O(n^{-2}) \right). \quad (8.77)$$

On account of the  $\Gamma$ -function, these grow faster than factorially with  $n$ , so the series (8.76) has *zero* radius of convergence in  $\lambda$ ! Once again, this is easy to see from the form of the perturbed Hamiltonian: even though we may only care about  $\lambda > 0$ , our assumption that the perturbation expansion is analytic in  $\lambda$  at  $\lambda = 0$  means that, if it converges, it will do so for a disc  $\lambda \in D \subset \mathbb{C}$ . For any  $\lambda \in \mathbb{R}_{<0}$ , the Hamiltonian of the quartic oscillator is unbounded below, so there cannot be any stable bound states that are analytic in  $\lambda$  at  $\lambda = 0$ .

Let me comment that even when perturbative series do not converge, they may still provide very useful information as an *asymptotic series*. You'll learn far more about these if you take the Part II course on Asymptotic Methods next term, but briefly, we say a series  $S_N(\lambda) = \sum_{n=0}^N a_n \lambda^n$  is *asymptotic to* an exact function  $S(\lambda)$  as  $\lambda \rightarrow 0^+$  (written  $S_N(\lambda) \sim S(\lambda)$  as  $\lambda \rightarrow 0^+$ ) if

$$\lim_{\lambda \rightarrow 0^+} \frac{1}{\lambda^N} \left| S(\lambda) - \sum_{n=0}^N a_n \lambda^n \right| = 0. \quad (8.78)$$

In other words, if we just include a fixed number  $N$  of terms in our series, then for small enough  $\lambda \geq 0$  these first  $N$  terms differ from the exact answer by less than  $\epsilon \lambda^N$  for *any*  $\epsilon > 0$  (so the difference is  $o(\lambda^N)$ ). However, if we instead try to fix  $\lambda$  and improve our accuracy by including more and more terms in the series, then an asymptotic series will eventually diverge. Most of the perturbative series one meets in the quantum world (including most Feynman diagram expansions of Quantum Field Theory) are only asymptotic series. Just as in our toy examples above, the radius of convergence of such series is often associated with interesting physics.

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<sup>75</sup>I don't expect you to reproduce it – if you're curious you can find the details in Bender, C. and Wu, T.T., *Anharmonic Oscillator II: A Study of Perturbation Theory in Large Order*, Phys. Rev. **D7**, 1620-1636 (1973).