

Lecture 31

Relevant sections in text: §5.1, 5.2

Example: finite size of the atomic nucleus

One improvement on the simple particle-in-a-potential model of an atom takes account of the fact that the atomic nucleus is not truly point-like but instead exhibits finite-size structure in both its mass and charge distributions. It is possible to use perturbation theory to get a quick look into the effect on atomic spectra of this feature. Of course, this effect is one of a myriad of small corrections that need to be added to the atomic model.

Let us model the nucleus as a (very massive) uniform ball of total charge Ze with radius r_0 . As a nice exercise in elementary electrostatics, you can check that the potential energy

$$V(\mathbf{r}) = -e\phi$$

for such a charge distribution takes the form

$$V(\mathbf{r}) = \begin{cases} -\frac{Ze^2}{r} & \text{for } r \geq r_0 \\ \frac{Ze^2}{2r_0} \left[\left(\frac{r}{r_0} \right)^2 - 3 \right] & \text{for } r \leq r_0. \end{cases}$$

I do not know if a closed form solution to the eigenvalue problem for the Hamiltonian

$$H = \frac{P^2}{2m} + V$$

is known, but I doubt that such a solution exists. We will treat the potential energy due to the finite size r_0 of the nucleus as a perturbation of the usual Coulomb potential. To this end we write

$$V(r) = V_0(r) + B(r),$$

where

$$V_0(r) = -\frac{Ze^2}{r}, \quad \text{for } r > 0,$$

and

$$B(r) = \begin{cases} \frac{Ze^2}{2r_0} \left[\left(\frac{r}{r_0} \right)^2 - 3 + \frac{2r_0}{r} \right] & \text{for } 0 \leq r \leq r_0, \\ 0 & \text{for } r \geq r_0. \end{cases}$$

The idea is then that, since the unperturbed energy eigenfunctions are non-trivial over a range corresponding to the Bohr radius a (for the given Z), as long as $r_0 \ll a$ we expect that the effect of the perturbation B will be small. We will make this more precise in a moment.

Recall that the energy eigenstates $|n, l, m\rangle$ have position wave functions given by

$$\langle \mathbf{r} | n, l, m \rangle \equiv \psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi),$$

where the Y_{lm} are the usual spherical harmonics and

$$R_{nl}(r) = - \left[\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3} \right]^{1/2} e^{-\frac{r}{na}} \left(\frac{2r}{na} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na} \right),$$

with

$$a = \frac{\hbar^2}{Zm_e e^2}, \quad m = \text{electron mass},$$

and L_q^p is the associated Laguerre polynomial. See the text for details. Note that a is the Bohr radius for the hydrogenic atom with a given Z ; it sets the scale for the atomic size.

Let us consider the first-order correction to the ground state of the atom due to this perturbation. We choose the ground state for simplicity and since the ground state energy is non-degenerate. The shift in the ground state energy is given by

$$\Delta E = \langle 1, 0, 0 | B | 1, 0, 0 \rangle.$$

Using the fact that

$$\psi_{100} = \frac{2}{\sqrt{4\pi a^3}} e^{-\frac{r}{a}},$$

we find that (exercise)

$$\Delta E = \int_0^{r_0} dr r^2 \frac{2Ze^2}{r_0 a^3} \left[\left(\frac{r}{r_0} \right)^2 - 3 + \frac{2r_0}{r} \right] e^{-\frac{2r}{a}}.$$

This integral can be computed explicitly. Try it! (I did it using *Maple*.) I am going to give you the answer after it has been simplified with the assumption that $r_0 \ll a$, which is needed in any case to ensure that the perturbation is sufficiently small to render our approximation scheme viable. In this case we get

$$\Delta E \approx \frac{2Ze^2 r_0^2}{5a^3} = \frac{4}{5} |E_{\text{ground}}| \left(\frac{r_0}{a} \right)^2, \quad \frac{r_0}{a} \ll 1.$$

(I got this expression by having *Maple* perform a Taylor series expansion.) Thus the effect of the finite size is to shift the energy upward and the scale of the shift is determined by $\left(\frac{r_0}{a} \right)^2$.

To get a feel for the size of the correction, let us consider a couple of examples. For hydrogen, we note that the charge radius of a proton is on the order of $10^{-15} m$ and that the Bohr radius is on the order of $10^{-10} m$ so that the the perturbative correction is on

the order of one part in 10^{10} . Very small! There are physical systems in which the finite size of the nucleus has a more pronounced effect. For example, one can consider “muonic hydrogen”, consisting of a proton and a μ^- muon. Muons are like electrons only much more massive. For muonic hydrogen the Bohr radius is smaller by a factor of 10^{-2} , leading to an energy shift on the order of 1 part in 10^{-6} . At the other extreme, consider a muonic lead atom (a negatively charged muon bound to a lead nucleus). There we have that both r_0 and a are on the order of $10^{-15} m$. Hence here the finite size effect is as important as the Coulombic effect. † Note, however, that our perturbative approximation is no longer valid since the effect of the perturbation is not “small” so this is at best a qualitative statement.

Let me finish this example with a few comments about the perturbative approximation to the ground state. To compute it we need to compute the matrix element $\langle n, l, m | B | 1, 0, 0 \rangle$, $n \neq 1$. Since the perturbation commutes with angular momentum, it is clear that this matrix element will be non-zero only if $l = m = 0$. We then have (exercise)

$$\langle n, l, m | B | 1, 0, 0 \rangle = \delta_{l0} \delta_{m0} \int_0^{r_0} dr r^2 R_{n0}(r) R_{10}(r) B(r).$$

Assuming that $r_0 \ll a$, we can approximate $R_{nl}(r) \approx R_{nl}(0)$. We then get (exercise)

$$\langle n, l, m | B | 1, 0, 0 \rangle \approx \frac{Ze^2}{10} r_0^2 R_{n0}(0) R_{10}(0) \delta_{l0} \delta_{m0},$$

which can be used to compute the approximate ground state wave function as a superposition of unperturbed $l = 0 = m$ hydrogenic stationary states. Note that this superposition will lead to a spherically symmetric ground state wave function which is non-vanishing for $r < r_0$. Thus there is a non-zero probability for finding the electron (or muon) *within* the nucleus!

Degenerate Perturbation Theory

We now consider the case where the unperturbed eigenvalue is degenerate, that is, there are d linearly independent eigenvectors $|E_n\rangle_i^{(0)}$, $i = 1, 2, \dots, d$ for the unperturbed eigenvalue $E_n^{(0)}$. These eigenvectors span the “degenerate subspace” D , which is a finite-dimensional vector space sitting inside the full Hilbert space of state vectors. Degeneracy is associated with a symmetry of the (unperturbed, in this case) Hamiltonian. The full Hamiltonian (with the perturbation included) will typically not have all the symmetry of the unperturbed Hamiltonian. Thus the *true* eigenvalues that are approximated by the unperturbed eigenvalue will usually not all be degenerate. Put differently, as the perturbation is “turned on”, by mathematically varying λ from 0 to 1, some of the unperturbed eigenvectors with the same unperturbed eigenvalue become eigenvectors with a distinct eigenvalue, so that the degeneracy can be lifted by the perturbation. One says that the energy levels “split” as the perturbation is “turned on”.

Consider for example an atom modeled as a particle moving in a central potential. Its excited states are degenerate because the (unperturbed) Hamiltonian H_0 is rotationally invariant. In particular, since H_0 commutes with \vec{L} , it is easy to see that all states differing only by their m values must have the same energy. In detail, if $|n, l, m\rangle$ is an eigenvector of H_0 , then so is $L_{\pm}|n, l, m\rangle$. Thus all such states will have the same energy. Suppose this atom is put in a uniform electric field (Stark effect), so that the perturbation is

$$V = e\vec{E} \cdot \vec{X}.$$

This potential breaks the rotational symmetry (to just that about \vec{E}), so that the degeneracy is lifted. States constructed as outlined above will have differing energies.

But now there is a subtlety in the perturbative account of this phenomenon. In the unperturbed system any basis for the degenerate subspace could be used to define the unperturbed states. But in the perturbed theory, the energy eigenvectors that are no longer degenerate cannot be linearly superimposed to get eigenvectors. This means that, in fact, the perturbation theory must select a preferred basis of unperturbed eigenvectors, namely, the ones that the correct eigenvectors collapse to as $\lambda \rightarrow 0$. We will see this happening in what follows. The problem is now that in perturbation theory one *begins* with the unperturbed states. But which states do we choose? The results of degenerate perturbation theory take care of this, as you will see.