Lecture 10 Highlights

We started with the second order corrections to the perturbed Schrödinger equation:

$$\mathrm{H}\psi_n = E_n\psi_n \,, \tag{1}$$

solved assuming:

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + ... \tag{2}$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + ... \tag{3}$$

and yielding (to second order):

$$\lambda^2: \quad \mathrm{H}^0\psi_n^2 + \mathrm{H}'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0 \tag{4}$$

The second-order equation can be solved using the fact that ψ_n^1 and ψ_n^2 can each be expressed as a linear combination of all the eigenfunctions of H^0 (a postulate of QM) as,

$$\psi_n^1 = \sum_{k\neq n} a_{nk}\ \psi_k^0 \qquad\qquad \psi_n^2 = \sum_{\ell} b_{n\ell}\ \psi_\ell^0 \tag{5}$$

where the a_{nk} are known from the solution of the first-order equation in the last lecture, but the $b_{n\ell}$ are unknown at this point. Putting (5) into (4) and exploiting orthonormality (i.e. multiply both sides by ψ_j^{0*} and integrating over all space) yields (for the case $j = n$):

$$E_n^2 = \sum_{k\neq n} \frac{\left|\int \psi_k^{0*}\ \mathrm{H}'\,\psi_n^0\ d^3r\right|^2}{E_n^0 - E_k^0} \tag{6}$$

This represents the second order correction to the energy. It is often necessary to calculate this because the first-order energy correction is sometimes zero. This result again assumes that the energy eigenvalues are non-degenerate.

As an example of first-order perturbation theory we considered the relativistic correction to the kinetic energy operator. Following the discussion in Griffiths pages 267-270 we found a relativistic correction to the kinetic energy operator as:

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

The new Schrödinger equation for the Hydrogen atom can now be written as:

$$\mathrm{H}\psi = E\psi \,,$$

with $\mathrm{H} = \mathrm{H}^0 + \mathrm{H}'$, and $\mathrm{H}^0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$ is the original un-perturbed Hydrogen atom Hamiltonian, and $\mathrm{H}' = -\frac{p^4}{8m^3c^2}$ is the perturbation. We evaluate the change in energy to first order using the result derived in the last lecture:

$$E_n^1 = \iiint \psi_n^{0*}\ \mathrm{H}'\,\psi_n^0\, d^3r \,,$$

where ψ_n^0 are the unperturbed Hydrogen atom wavefunctions, and n now represents the list of H-atom quantum numbers n, ℓ, m. Evaluating the expectation value integral as in Griffiths yields the following result:

$$E_{n,\ell}^{1} = -E_n^0 \frac{\alpha^2}{2n^2}\left[\frac{4n}{\ell+\frac{1}{2}} - 3\right]$$

where the subscripts are now the principle quantum number n and angular momentum quantum number ℓ of the Hydrogen atom, and $E_n^0 = -13.6\,\text{eV}/n^2$. We have also introduced a new and very important dimension-less parameter called the fine structure constant α. This is a combination of fundamental constants from electrodynamics, quantum mechanics and relativity:

$$\alpha \equiv \frac{e^2}{4\pi\varepsilon_0 \hbar c} \cong \frac{1}{137.036}.$$

Note that the correction to the energy of the Hydrogen atom due to relativistic effects is on the scale of $\alpha^2 E_n^0$, which is roughly on the order of 10^{-3} eV, as compared to the ground state energy of order 10 eV. Also note that the ℓ dependence of the first-order corrected energy will lift some of the degeneracies of the un-perturbed hydrogen atom, and this will give rise to "fine structure" in the radiation emission spectrum of the atom. In other words some of the H-atom spectral lines will now be split into multiple lines (because of the ℓ dependence of $E_{n,\ell}^1$) with an energy splitting on order 10^{-3} eV. Such effects are visible in a spectrometer as "fine structure splitting" of the spectral lines.