## Lecture 4 Highlights Phys 402

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

$$\mathbf{H}\boldsymbol{\psi}_n = E_n \boldsymbol{\psi}_n \,, \tag{1}$$

with  $H = H^0 + \lambda H'$ , solved assuming a perturbation series expansion:

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$
<sup>(2)</sup>

$$E_{n} = E_{n}^{0} + \lambda E_{n}^{1} + \lambda^{2} E_{n}^{2} + \dots$$
(3)

and yielding (to second order):

$$\lambda^{2}: \quad \mathbf{H}^{0}\psi_{n}^{2} + \mathbf{H}^{\prime}\psi_{n}^{1} = E_{n}^{0}\psi_{n}^{2} + E_{n}^{1}\psi_{n}^{1} + E_{n}^{2}\psi_{n}^{0}$$
(4)

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

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  $\psi_j^{0^*}$  and integrating over all space) yields (for the case j = n):

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

(You will derive this for HW2.) This represents the second order correction to the energy. It is sometimes necessary to calculate this because the first-order energy correction is zero. This result again assumes that the energy eigenvalues are non-degenerate.

As an example of second order perturbation theory we looked at the problem of a *planar* rigid rotator that has an electric dipole moment and is perturbed by a uniform electric field. The unperturbed problem is that of a stick with moment of inertia *I* that is in the xy-plane, rotating about the z-axis. The rotation axis passes through the center of mass of the stick, and the center of mass is stationary, i.e. it has no linear kinetic energy. It just has kinetic energy of rotation, which is given by the classical expression  $T = L_z^2/2I$ , where  $L_z$  is the angular momentum for its rotation about the z-axis. This expression is analogous to that for linear kinetic energy, which is linear momentum squared divided by twice the mass of the object. An electric dipole is a charge-neutral object that is made up of two equal and opposite charges +q and -q that are separated by a distance *s*. The electric dipole moment has a magnitude  $|\vec{d}| = qs$ . The direction of  $\vec{d}$  is along the line between the two charges, pointing from the negative charge to the positive charge. Think of a diatomic molecule in which there is charge transfer from one atom to the other. In an external electric field  $\mathcal{E}$  that is in the plane of the dipole, the dipole will have an energy of interaction given by  $\mathcal{H}' = -\vec{d} \cdot \vec{\mathcal{E}}$ . We will treat this interaction energy as a perturbation.

The unperturbed quantum problem is given by  $\hat{\mathcal{H}}^0 \psi_m^0 = E_m^0 \psi_m^0$ , with  $\hat{\mathcal{H}}^0 = \hat{L}_z^2/2I$ , and  $\psi_m^0 = \frac{1}{\sqrt{2\pi}} e^{im\phi}$  and  $E_m^0 = \frac{m^2 \hbar^2}{2I}$ , with  $m = 0, \pm 1, \pm 2, \pm 3, \dots$  We dealt with the  $\hat{L}_z =$   $-i\hbar \frac{d}{d\phi}$  operator when we treated the hydrogen atom (see Griffiths Eq. (4.128)). Recall that the integer values of *m* arise from the condition that  $\psi^0(\phi + 2\pi) = \psi^0(\phi)$ , which is the periodicity condition. The perturbation is given by  $\hat{\mathcal{H}}' = -d\mathcal{E} \cos \phi$ . The first order correction to energy gives zero:  $E_m^1 = \langle \psi_m^0 | \hat{\mathcal{H}}' | \psi_m^0 \rangle = 0$ . This reflects the fact that the inplane electric field has zero net change in the energy of the dipole when averaged over the rotation angle  $\phi \in \{0, 2\pi\}$ . We now turn to the second order correction to the energy:

$$E_{m}^{2} = \sum_{k} \frac{\left| \langle \psi_{k}^{0} | \mathcal{H}' | \psi_{m}^{0} \rangle \right|^{2}}{E_{m}^{0} - E_{k}^{0}}$$

 $H\psi = E\psi$ ,

The matrix element in the numerator is  $\langle \psi_k^0 | \mathcal{H}' | \psi_m^0 \rangle = \frac{-d\varepsilon}{4\pi} \int_0^{2\pi} \left( e^{i(m-k+1)\phi} + e^{i(m-k-1)\phi} \right) d\phi$ . The integrals are non-zero only when the exponents are zero, or in other words when  $k = m \pm 1$ , in which case the integral has a value of  $2\pi$ . This means that the infinite sum for  $E_m^2$  is reduced to just two terms! After adding them up, the result is  $E_m^2 = \frac{I\varepsilon^2 d^2}{\hbar^2} \frac{1}{4m^2-1}$ .

As an example of first-order perturbation theory consider the **relativistic correction to the kinetic energy operator** for an electron in the Hydrogen atom. Following the discussion in Griffiths pages 295-298 we found a relativistic correction to the kinetic energy operator as:

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \text{higher-order terms}$$

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

with  $H = H^0 + H'$ , and  $H^0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$  is the original un-perturbed Hydrogen atom Hamiltonian, and  $H' = -\frac{p^4}{8m^3c^2}$  is the perturbation. You know the solutions to the unperturbed problem from Phys 401 as the eigenfunctions  $\psi_{n/m}(r, \theta, \phi)$  with eigenvalues

 $E_n = -13.6 eV/n^2$ , where *n* is the principal quantum number (n = 1, 2, 3, ...),  $\ell$  is the angular momentum quantum number  $(\ell \in \{0, 1, 2, ..., n - 1\})$ , and *m* is the magnetic quantum number  $(m \in \{-\ell, -\ell + 1, ..., 0, ..., \ell - 1, \ell\})$ . We can also write the eigenfunctions in ket notation as  $|n, \ell, m\rangle$ .

We evaluate the change in energy to first order using the result derived in the last lecture:

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

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

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

where the subscripts are now the principal quantum number *n* and angular momentum quantum number  $\ell$  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**  $\alpha$ . This is a combination of four 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  $\ell$  dependence of the first-order corrected energy will <u>lift some of the degeneracies</u> 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  $\ell$  dependence of  $E_{n,\ell}^1$ ) with an energy splitting on order  $10^{-3}$  eV. The science of atomic spectroscopy is very highly refined and such effects are visible in a spectrometer as "fine structure splitting" of the spectral lines. Note that we will later calculate another contribution to fine structure splitting, namely *spin-orbit interaction*, and this will be on the same order of magnitude as the relativistic correction.