Lecture 8 Highlights
Phys 402

Degenerate Perturbation Theory

We considered the problem of degenerate perturbation theory. Degeneracy is when you have two or more distinct eigenstates of the system (i.e. distinct lists of quantum numbers) that have the same eigen-energy. We discussed three examples:

1) The un-perturbed Hydrogen atom (without spin) has degeneracy $p = n^2$, where n is the principal quantum number. The un-perturbed problem (which you studied in detail in Phys 401 and is now considered completely 'known') has eigen-energies $E_n^0 = -13.6\, eV/n^2$, and eigenfunctions $\psi^0_{n,\ell,m_\ell}(r,\theta,\varphi)$ (or $|n,\ell,m_\ell\rangle$ in ket notation), where $n = 1, 2, 3, \ldots$, and ℓ runs from 0 to $n-1$, and m_ℓ runs from $-\ell$ to $+\ell$. For $n = 2$ we saw that there are $p = 2^2 = 4$ degenerate states $|2,0,0\rangle$, $|2,1,1\rangle$, $|2,1,0\rangle$, $|2,1,-1\rangle$.
2) The two-dimensional harmonic oscillator with un-perturbed Hamiltonian $H^0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{K}{2}(x^2 + y^2)$. This problem separates in to two one-dimensional harmonic oscillators and the eigenvalues are $E^0_{n,m} = \hbar\omega(n + m + 1)$, where n, m independently run $0, 1, 2, 3, \ldots$ and the un-perturbed eigenfuctions are product wavefunctions of the 1D harmonic oscillator in the x- and y-directions $|n,m\rangle = |n\rangle_x|m\rangle_y$. These states have a degeneracy of $p = n + m + 1$. The ground state $n = m = 0$ is non-degenerate, but the first excited state with $|1,0\rangle$ and $|0,1\rangle$ is 2-fold degenerate with $E^0_{1,0} = E^0_{0,1} = 2\hbar\omega$.
3) The three-dimensional infinite cubical well has an un-perturbed Hamiltonian of $H^0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x,y,z)$, where $V(x,y,z) = \begin{cases} 0 & \text{for } 0 < x < a, \text{ and } 0 < y < a, \text{and } 0 < z < a \\ \infty & \text{otherwise} \end{cases}$. This is a cubical region of space where the particle of mass m is trapped. This problem is also separable into three one-dimensional problems. The un-perturbed eigenvlaues are $E^0_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$, where the three quantities n_x, n_y, n_z are independent positive integers. The un-perturbed eigenfunctions are the products of the 1D infinite square well eigenstates: $\psi^0_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right)\sin\left(\frac{n_z\pi}{a}z\right)$. The ground state $n_x = n_y = n_z = 1$ is non-degenerate. However the first excited state is triply degenerate ($p = 3$) since states $|2,1,1\rangle$, $|1,2,1\rangle$, and $|1,1,2\rangle$ all have the same energy, namely $6\frac{\pi^2\hbar^2}{2ma^2}$.

We note that the perturbation theory that we have developed so far will not work for these degenerate systems because of the zeros in the denominator of the first-order correction to the eigen-functions:

$$\psi^1_n = \sum_{\ell \neq n}\left(\frac{\int \psi^{0*}_\ell \, \mathrm{H}' \, \psi^0_n \, d^3r}{E^0_n - E^0_\ell}\right)\psi^0_\ell$$

To proceed with degenerate perturbation theory we focus on a particular p-fold degenerate sub-space. The degenerate eigenfunctions obey $H^0\psi^0_j = E^0\psi^0_j$ with $\langle\psi^0_j|\psi^0_l\rangle = \delta_{j,l}$ and $j, l = 1, 2, 3, \ldots p$. Note that all p states have a common un-perturbed energy E^0.

Now, we posit the existence of a "magic linear combination" of these p degenerate states that will simplify the calculation of the first-order correction to the energy:

$$\psi^0 = \sum_{j=1}^{p} \alpha_j \psi_j^0,$$

where the α_j are unknown at this point, but we expect ψ^0 to be normalized. This wavefunction has the same eigenenergy E^0 as each of its constituents ψ_j^0.

Now consider the perturbed Hamiltonian $H = H^0 + H'$ and the new Schrodinger equation $H\psi = E\psi$. We do the standard perturbation theory expansion, using this linear combination state as the zeroth-order wavefunction:

$$\psi = \psi^0 + \lambda\psi^1 + \lambda^2\psi^2 + \ldots$$
$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \ldots$$

and yielding (to first order):

$$\lambda^1: \quad \mathrm{H}^0\psi^1 + \mathrm{H}'\psi^0 = E^0\psi^1 + E^1\psi^0$$

Projecting with $\langle\psi_k^0|$ (where k is chosen arbitrarily from the degenerate sub-space) yields the following result

$\sum_{j=1}^{p} W_{k,j}\,\alpha_j = E^1\alpha_k$, where $k = 1, 2, 3, \ldots p$ and $W_{k,j} \equiv \langle\psi_k^0|H'|\psi_j^0\rangle$ is the perturbing Hamiltonian matrix element between states k and j in the unperturbed basis of degenerate states.

This is in fact a matrix-vector eigenvalue problem:

$$\bar{\bar{W}}\vec{\alpha} = E^1\vec{\alpha},$$

where the eigenvalues are the desired first-order corrections to the energies, and the eigenvectors $\vec{\alpha}$ are the coefficients in the "magic linear combination" posited above ($\vec{\alpha}$ is a vector of length p). In other words, these magic linear combinations of the degenerate eigenstates serve to diagonalize the perturbation matrix in the degenerate sub-space. These are the "good wavefunctions" in the presence of the perturbation. Note that the "magic linear combination" will be different for each choice of perturbation, in general. Also note that $\bar{\bar{W}}$ is a p by p matrix, admitting in general p eigenvalues E^1 and corresponding eigenvectors $\vec{\alpha}$.

As an example, we went back to the 2D harmonic oscillator in the first excited state with $|1,0\rangle$ and $|0,1\rangle$ and added the perturbing potential $H' = K'xy$, with $K' \ll K$ (to ensure that perturbation theory is valid). This perturbation couples the x and y motion. By examining the sign of H' we see that it tends to favor 'out of phase' motion between the x and y components of the harmonic oscillator (assuming $K' > 0$). First evaluate the $\bar{\bar{W}}$ matrix for this perturbation, writing $x = \frac{1}{\sqrt{2}\beta}(a_+ + a_-)$, and $y = \frac{1}{\sqrt{2}\beta}(b_+ + b_-)$, where $\beta^2 = \frac{m\omega}{\hbar}$, and a_+ and b_+ are the raising operators for the x-component and y-component harmonic oscillator wavefunctions, respectively. The $\bar{\bar{W}}$ matrix becomes,

$$\bar{\bar{W}} = \begin{pmatrix} 0 & \kappa \\ \kappa & 0 \end{pmatrix}, \text{ where } \kappa = K'/2\beta^2.$$

To get non-trivial solutions to the eigenvalue problem we demand that

$$det\left(\bar{\bar{W}} - E^1\bar{\bar{1}}\right) = 0.$$

This yields two eigenvalues $E^1 = \pm\kappa = \pm K'/2\beta^2$. The higher energy state is the 'symmetric mode' $\overline{\psi_1} = \frac{1}{\sqrt{2}}(|1,0\rangle + |0,1\rangle)$ with $E \simeq 2\hbar\omega + K'/2\beta^2$, and the lower

energy state is the 'beating mode' $\overline{\psi_2} = \frac{1}{\sqrt{2}}(|1,0\rangle - |0,1\rangle)$ with $E \simeq 2\hbar\omega - K'/2\beta^2$, in which the x- and y-motions are out of phase. This kind of 'anti-correlation' of the x- and y-motion is favored by the perturbing Hamiltonian. The perturbation has 'lifted the degeneracy' (or destroyed the degeneracy) and created two distinct energy eigenstates.

Note that even after including the perturbation some of the resulting eigenvalues can still be degenerate. Degeneracies arise from symmetries of the Hamiltonian. If the perturbation only partially destroys those symmetries then some degeneracies will remain. This is fine as it does not violate any assumption made in deriving these results.

Stark Effect in Hydrogen.

A Hydrogen atom placed in a uniform electric field $\vec{E} = E_0\hat{z}$ (where $\hat{z}$ is the unit vector in the z-direction, as opposed to the z-coordinate quantum operator) will be "stretched" out and have new energy eigenvalues. For small electric field we can treat this as a perturbation $\mathcal{H}' = eE_0 z = eE_0 r\cos\theta$. The un-perturbed Hydrogen atom has a non-degenerate ground state labeled by the three quantum numbers $n = 1, \ell = 0, m = 0$, with energy eigenvalue $E_1^0 = -13.6\, eV$. The first excited state ($n = 2$) is 4-fold degenerate, with states $|2\ 0\ 0\rangle, |2\ 1\ 1\rangle, |2\ 1\ 0\rangle, and\ |2\ 1\ -1\rangle$ all having energy $E_2^0 = -13.6/2^2\ eV$. The next step is to calculate the W-matrix for the perturbing Hamiltonian. Most of the matrix elements turn out to be zero for "symmetry reasons" that we will explore in more detail later. The result for the W-matrix is:

$$\bar{\bar{W}} = -3a_0 eE_0 \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

where a_0 is the Bohr radius. The rest of this problem is assigned in Homework 4.