Prof. Steven Flammia

Quantum Mechanics

Lecture 10

Degenerate perturbation theory;
Example: the Stark effect.

A quick recap

Suppose a complicated Hamiltonian splits into two pieces,

$$H = H_0 + \lambda H_1$$

And suppose we can solve the simple part:

$$H_0 |\phi_n^{(0)}\rangle = E_n^{(0)} |\phi_n^{(0)}\rangle$$

Assume that the full system can be solved as a power series:

$$H|\psi_n\rangle = E_n|\psi_n\rangle \qquad E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \qquad |\psi_n\rangle = |\phi_n^{(0)}\rangle + \lambda|\phi_n^{(1)}\rangle + \lambda^2|\phi_n^{(2)}\rangle + \ldots$$

The first few terms are given by:

$$E_n^{(1)} = \langle\phi_n^{(0)}|H_1|\phi_n^{(0)}\rangle \qquad |\phi_n^{(1)}\rangle = \sum_{k\neq n} |\phi_k^{(0)}\rangle \frac{\langle\phi_k^{(0)}|H_1|\phi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} \qquad E_n^{(2)} = \sum_{k\neq n} \frac{|\langle\phi_k^{(0)}|H_1|\phi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

Degeneracy

We run into problems with this prescription when there is degeneracy:

$$E_n^{(0)} - E_k^{(0)} = 0$$

The 1st order eigenstate corrections (and 2nd order energy corrections, too) are singular in this case!

$$|\phi_n^{(1)}\rangle = \sum_{k \neq n} |\phi_k^{(0)}\rangle \frac{\langle \phi_k^{(0)} | H_1 | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \qquad E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \phi_k^{(0)} | H_1 | \phi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

A simple example will illustrate the reason for the singularity and suggest a possible resolution to the problem.

Degeneracy

Consider a two-state system with a trivial Hamiltonian and eigenstates:

Now add a small perturbation and solve:

Perturbation theory gives the wrong answer, even at 1st order!

Degeneracy

Problem: Our initial choice of basis "didn't know" about the new basis after the perturbation, leading to large changes in the state for small perturbations.

Solution: In a degenerate subspace there is no preferred basis, so we should make a basis choice that is sensitive to how the symmetry breaks.

To have a hope of a solution, we should try a basis such that:

Diagonalizing in a degenerate subspace

Consider a complete set of states with a given degenerate energy E:

A resolution of the identity within the degenerate subspace is given by:

Let's focus on just the 1st order energy equations for a general state in 1_E:

Diagonalizing in a degenerate subspace

Apply the projector 1_E on the left:

$$|\psi_E\rangle = \sum_j c_j |\chi_j\rangle \qquad H_0|\phi^{(1)}\rangle + H_1|\psi_E\rangle = E|\phi^{(1)}\rangle + E^{(1)}|\psi_E\rangle \qquad 1_E|\psi_E\rangle = |\psi_E\rangle$$

The 1st-order energy shifts are **eigenvalues** of H_1 in the degenerate subspace, and the 1st-order eigenstates are the **eigenstates** of H_1.

Stark effect

Electric dipole coupling:

1st order energy corrections to the ground state:

2nd order energy corrections to the ground state:

Stark effect

Need degenerate perturbation theory for n=2 subspace; it contains 4 states:

We need to write out all 16 elements of the 4 x 4 matrix:

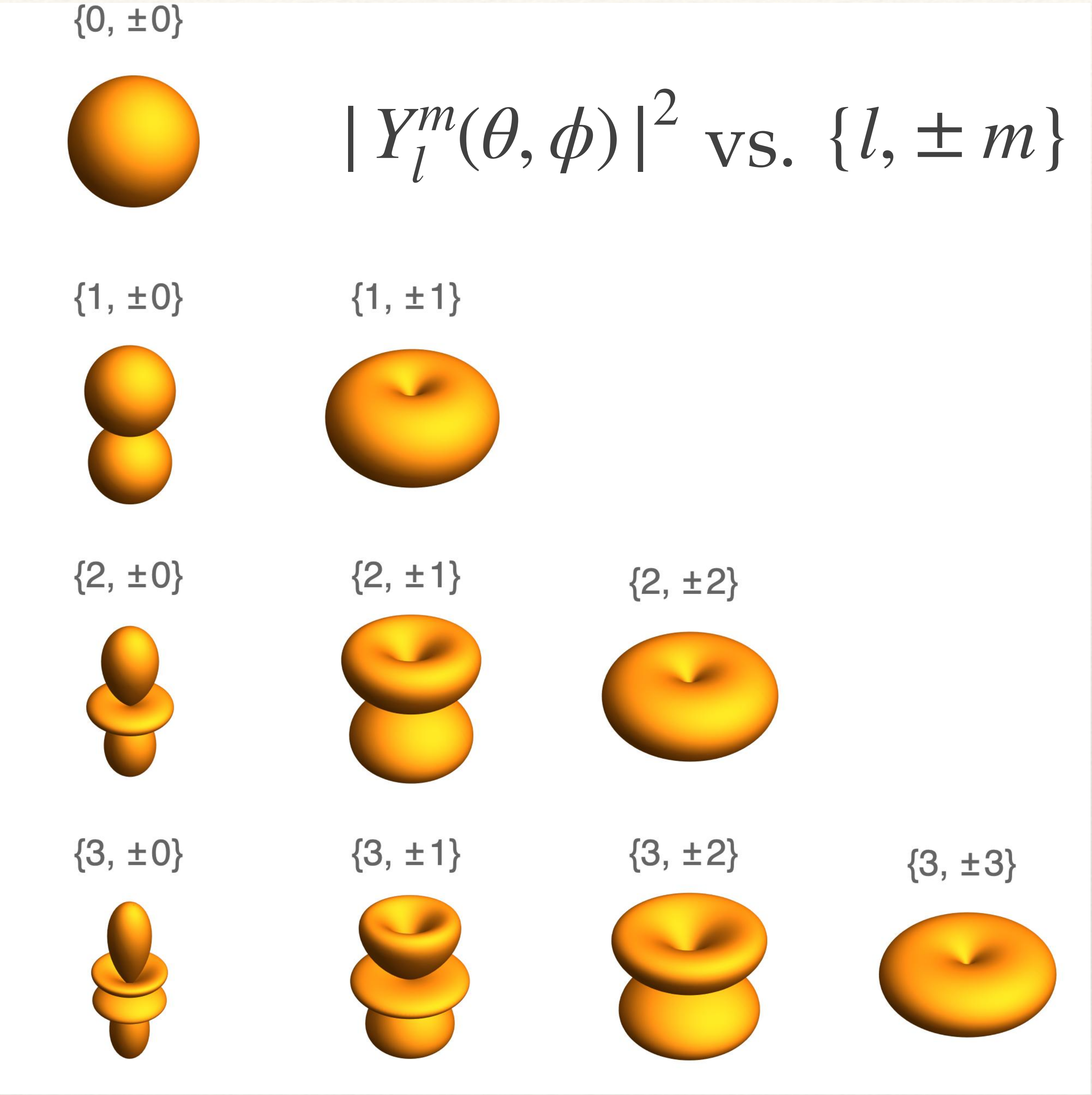
Fortunately, symmetry helps us. Many terms vanish because L_z is conserved:

Stark effect

Therefore:

$$1_E H_1 1_E \xrightarrow{E=E_2} \begin{array}{c|c} \begin{pmatrix} H_{11} & H_{12} & 0 & 0 \\ H_{21} & H_{22} & 0 & 0 \\ 0 & 0 & H_{33} & 0 \\ 0 & 0 & 0 & H_{44} \end{pmatrix} & \begin{matrix} m' = \\ 0 \\ 0 \\ 1 \\ -1 \end{matrix} \\ \begin{matrix} m = & 0 & 0 & 1 & -1 \end{matrix} & \end{array}$$

The diagonal elements also vanish by symmetry:



Stark effect

Therefore:

$$1_E H_1 1_E \xrightarrow{E=E_2} \begin{pmatrix} H_{11} & H_{12} & 0 & 0 \\ H_{21} & H_{22} & 0 & 0 \\ 0 & 0 & H_{33} & 0 \\ 0 & 0 & 0 & H_{44} \end{pmatrix} \longrightarrow \begin{array}{cc} \begin{pmatrix} 0 & H_{12} & 0 & 0 \\ H_{21} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} & \begin{matrix} m' = \\ 0 \\ 0 \\ 1 \\ -1 \end{matrix} \\ \begin{matrix} m = & 0 & 0 & 1 & -1 \end{matrix} & \end{array}$$

The remaining element is nonzero:

Stark effect

The eigenvalues and eigenvectors tell us the first order corrections:

$$1_E H_1 1_E \xrightarrow{E=E_2} -3e|\mathbf{E}|a_0 \begin{array}{c c} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} & \begin{array}{c} m' = \\ 0 \\ 0 \\ 1 \\ -1 \end{array} \\ m = \begin{array}{cccc} 0 & 0 & 1 & -1 \end{array} & \end{array}$$

By inspection, we find:

Stark shift energy level diagram: