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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:

$$H_0 = 0 \qquad |\phi_1^{(0)}\rangle = |\uparrow\rangle \qquad |\phi_2^{(0)}\rangle = |\downarrow\rangle \qquad E_1^{(0)} = E_2^{(0)} = 0$$

Now add a small perturbation and solve:

$$H = H_0 + \lambda H_1 \qquad H_1 = S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\Rightarrow \ |\psi_\pm\rangle = |\pm\rangle = \frac{1}{\sqrt{2}}\big(|\uparrow\rangle \pm |\downarrow\rangle\big) \qquad \Rightarrow \ E_\pm = \pm\lambda\frac{\hbar}{2}$$

This should be exact at order λ^1.

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

$$E_1^{(1)} = \langle\uparrow|H_1|\uparrow\rangle = 0 \qquad E_2^{(1)} = \langle\downarrow|H_1|\downarrow\rangle = 0$$

wrong answer!

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:

Want this to be finite:

$$\frac{\langle \phi_k^{(0)} | H_1 | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

Try to choose a basis such that for distinct states:

$$E_n^{(0)} - E_k^{(0)} = 0 \quad \Rightarrow \quad \langle \phi_k^{(0)} | H_1 | \phi_n^{(0)} \rangle = 0$$

This is the same as choosing unperturbed basis states so that the perturbing Hamiltonian is **diagonal** in the degenerate subspace.

Diagonalizing in a degenerate subspace

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

To ease notation, introduce:

$$|\chi_j\rangle := |\phi_E^{(0)}, j\rangle \qquad j = 1,\ldots,N \qquad H_0|\chi_j\rangle = E|\chi_j\rangle \qquad E = E^{(0)}$$

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

Projector onto degenerate subspace:

matrix element $(H_1)_{kj}$

$$\sum_{j=1}^{N} |\chi_j\rangle\langle\chi_j| = 1_E \qquad 1_E \lambda H_1 1_E = \lambda \sum_{j,k} |\chi_k\rangle\underbrace{\langle\chi_k|H_1|\chi_j\rangle}\langle\chi_j|$$

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

$$|\psi_E\rangle = \sum_j c_j|\chi_j\rangle \qquad H_0|\phi^{(1)}\rangle + H_1|\psi_E\rangle = E^{(0)}|\phi^{(1)}\rangle + E^{(1)}|\psi_E\rangle$$

Diagonalizing in a degenerate subspace

Apply the projector 1_E on the left:

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

$$\sum_k |\chi_k\rangle\langle\chi_k|H_0|\phi^{(1)}\rangle + 1_E H_1|\psi_E\rangle = E\sum_k |\chi_k\rangle\langle\chi_k|\phi^{(1)}\rangle + E^{(1)}1_E|\psi_E\rangle$$

$$\cancel{E\sum_k |\chi_k\rangle\langle\chi_k|\phi^{(1)}\rangle} + 1_E H_1 1_E|\psi_E\rangle = \cancel{E\sum_k |\chi_k\rangle\langle\chi_k|\phi^{(1)}\rangle} + E^{(1)}|\psi_E\rangle$$

$$1_E H_1 1_E|\psi_E\rangle = E^{(1)}|\psi_E\rangle$$

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:

Suppose E-field points along z axis

$$H_0 = \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{|\hat{\mathbf{r}}|} \qquad H_1 = -\boldsymbol{\mu}_e \cdot \mathbf{E} = e\,\mathbf{r}\cdot\mathbf{E} = e\,|\mathbf{E}|\,\hat{\mathbf{z}}$$

$$|\phi^{(0)}_{n,l,m}\rangle = |n,l,m\rangle$$

Non-degenerate energy for $n = 1$ only.

Degenerate energy for $n > 1$ and all $l < n$ and $|m| \leq l$

1st order energy corrections to the ground state:

$$E_1^{(1)} = \langle 1,0,0|H_1|1,0,0\rangle = e\,|\mathbf{E}|\,\langle 1,0,0|\hat{\mathbf{z}}|1,0,0\rangle = 0$$

by symmetry

2nd order energy corrections to the ground state:

$$E_1^{(2)} = \sum_{n\neq 1}\ \sum_{l<n,|m|\leq l} \frac{e^2|\mathbf{E}|^2|\langle n,l,m|\hat{\mathbf{z}}|1,0,0\rangle|^2}{E_1^{(0)} - E_n^{(0)}} \propto |\mathbf{E}|^2$$

Stark effect

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

$$H_1 = e|\mathbf{E}|\hat{\mathbf{z}} \qquad |\chi_j\rangle \in \left\{|2,0,0\rangle, |2,1,0\rangle, |2,1,1\rangle, |2,1,-1\rangle\right\}$$

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

$$(H_1)_{kj} = \langle \chi_k | H_1 | \chi_j \rangle$$

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

$$[L_z, H_1] \propto [L_z, \hat{\mathbf{z}}] = 0$$

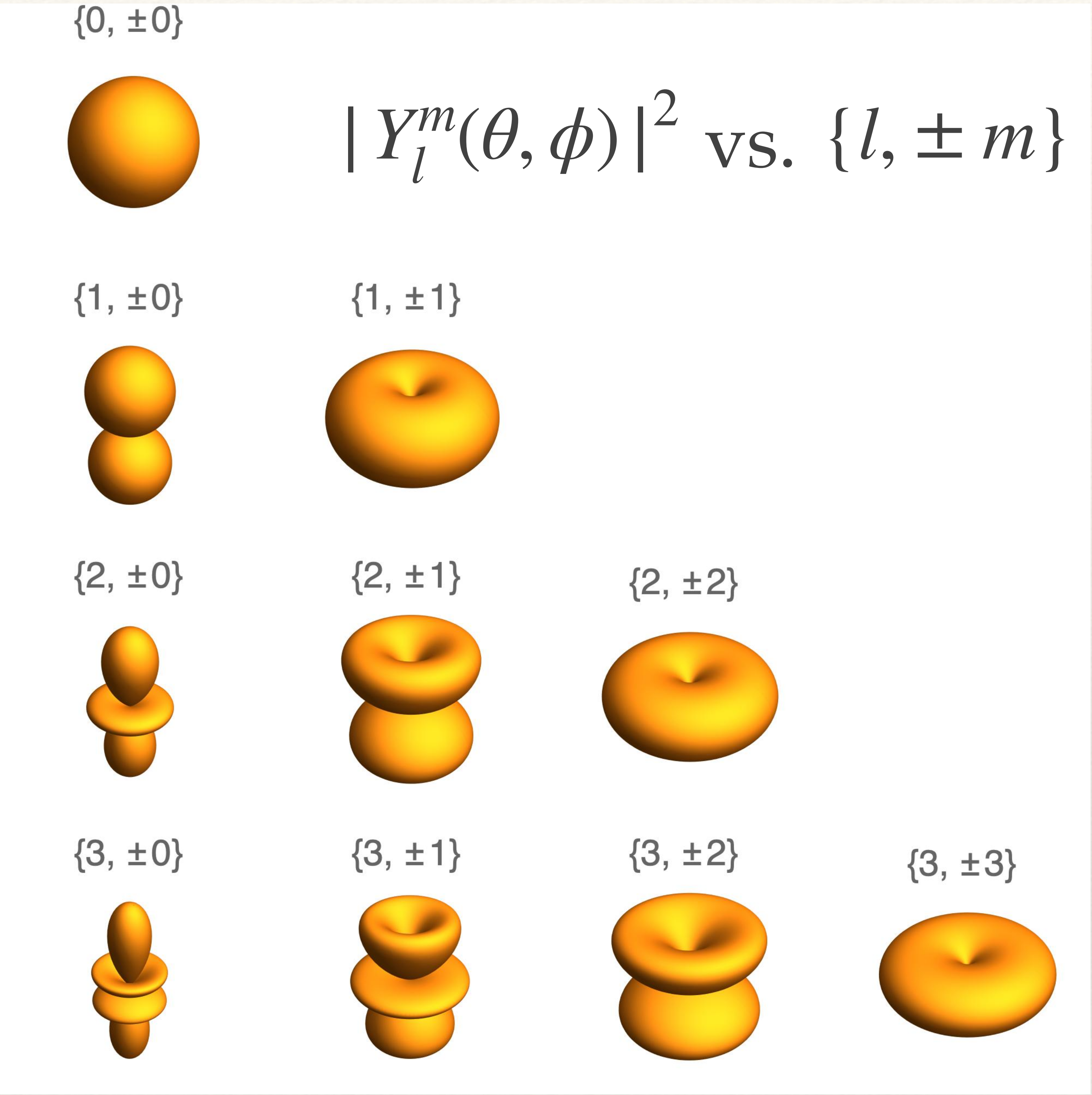
$$\begin{aligned} m'\hbar\langle n, l', m' | \hat{z} | n, l, m\rangle &= \langle n, l', m' | L_z \hat{z} | n, l, m\rangle \\ &= \langle n, l', m' | \hat{z} L_z | n, l, m\rangle \\ &= m\hbar\langle n, l', m' | \hat{z} | n, l, m\rangle \end{aligned} \qquad \Rightarrow m = m'$$

Stark effect

Therefore:

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

$m =$ 0 0 1 -1



The diagonal elements also vanish by symmetry:

$$\hat{z} \to r\cos\theta$$

$$\langle n, l, m | \hat{z} | n, l, m \rangle = f(r) \int d\Omega \cos\theta \, |Y_l^m(\theta,\phi)|^2$$

$$\propto \int_0^\pi d\theta \sin\theta \cos\theta \, |Y_l^m(\theta,\phi)|^2$$

$$= 0$$

The integral is invariant under

$$\theta \leftrightarrow \pi - \theta$$

but it also changes sign, so it must vanish.

Stark effect

Therefore:

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

$$m = \quad 0 \quad 0 \quad 1 \quad -1$$

The remaining element is nonzero:

$$\begin{aligned} H_{12} &= e|\mathbf{E}|\langle 2,0,0|\hat{z}|2,1,0\rangle \\ &= e|\mathbf{E}| \int_0^\infty \mathrm{d}r \int_0^\pi \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi (r^2 \sin\theta)(r\cos\theta) R^*_{2,0} Y^{*0}_0 R_{2,1} Y^0_1 \\ &= -3e|\mathbf{E}|a_0 \end{aligned}$$

(Bohr radius)

Stark effect

The eigenvalues and eigenvectors tell us the first order corrections:

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

$$m = \; 0 \quad 0 \quad 1 \quad -1$$

By inspection, we find:

Eigenvector:	Corresponding eigenvalue:
$\frac{1}{\sqrt{2}}\left(\vert 2,0,0\rangle \pm \vert 2,1,0\rangle\right)$	$\mp 3e\vert\mathbf{E}\vert a_0$
$\vert 2,1,\pm 1\rangle$	0

Stark shift energy level diagram: