# Perturbation theory: degenerate case

Read McIntyre 10.6

PH451/551

Wednesday, February 4, 2026

# From last time:

How to find first-order energy correction in the case of degenerate energy levels?

Perturbation theory simplifies the problem **from:**

$(H_0 + H') \, |n\rangle = E_n \, |n\rangle$ (i.e. diagonalize the entire Hamiltonian to find energies $E_n$, in the entire space (which could be infinite-dimensional)

**To:**

Diagonalizing H' -only, and in the degenerate subspace (of dimensionality g, which is the degeneracy)

# Methodology

**Step 1**: identify the states corresponding to the degenerate energy level (the number of states = degeneracy g)

**Step 2**: Build a g x g matrix representing H’ in the basis formed by the states identified in Step 1

**Step 3**: Diagonalize the matrix built in Step 2 to find eigenvalues. These are the first-order energy corrections to the degenerate energy level. There should be g of these corrections.

# Example: Stark effect in H-atom (H-atom under applied electric field)

Perturbation: apply E-field along z-axis

$$H' = -\mathbf{d} \bullet \mathbf{E}$$
$$= -\left(-e\mathbf{r}\right) \bullet \mathrm{E}\hat{\mathbf{z}}$$
$$= e\mathrm{E}z$$
$$= e\mathrm{E}r\cos\theta$$

Unperturbed states:

$$\left|n\ell m^{(0)}\right\rangle \doteq R_{n\ell}\left(r\right)Y_{\ell m}\left(\theta,\phi\right)$$

# Consider 4-fold degenerate energy level with $n = 2$ (if spin is not included, $g = n^2$)

**Step 1:** identify states – what are the 4 states in this degenerate subspace for n = 2?

$$\left|2\ell m^{(0)}\right\rangle \doteq R_{2\ell}(r)Y_{\ell m}(\theta,\phi) = R_{2\ell}(r)P_{\ell}(\cos\theta)e^{im\phi}$$

$$\ell = 0, 1 \quad \text{and} \quad -\ell \leq m \leq \ell$$

So:

$$|200^{(0)}\rangle,\ |210^{(0)}\rangle,\ |211^{(0)}\rangle,\ |21-1^{(0)}\rangle$$

1 2 3 4

**Step 2:** build a 4 x 4 H’ matrix on the states identified in Step 1:

$$H'_{ij} = \left\langle 2\ell m^{(0)} \middle| H' \middle| 2\ell' m'^{(0)} \right\rangle$$
$$\ell, \ell' = 0, 1; m = -1, 0, 1$$

For example:

$$H'_{11} = \left\langle 200^{(0)} \middle| H' \middle| 200^{(0)} \right\rangle$$
$$H'_{12} = \left\langle 200^{(0)} \middle| H' \middle| 210^{(0)} \right\rangle$$
$$\dots$$
$$H'_{44} = \left\langle 21-1^{(0)} \middle| H' \middle| 21-1^{(0)} \right\rangle$$

16 matrix elements total !

Use properties of H’ and of spherical harmonics to reduce the number of elements we need to calculate !

$$H' \doteq \begin{array}{c} \begin{matrix} |200^{(0)}\rangle & |210^{(0)}\rangle & |211^{(0)}\rangle & |21-1^{(0)}\rangle \end{matrix} \\ \begin{pmatrix} & & & \\ & & & \\ & & & \\ & & & \end{pmatrix} \begin{matrix} \langle 200^{(0)}| \\ \langle 210^{(0)}| \\ \langle 211^{(0)}| \\ \langle 21-1^{(0)}| \end{matrix} \end{array}$$

H’ is Hermitian, so $H'_{ij} = H'^{*}_{ji}$

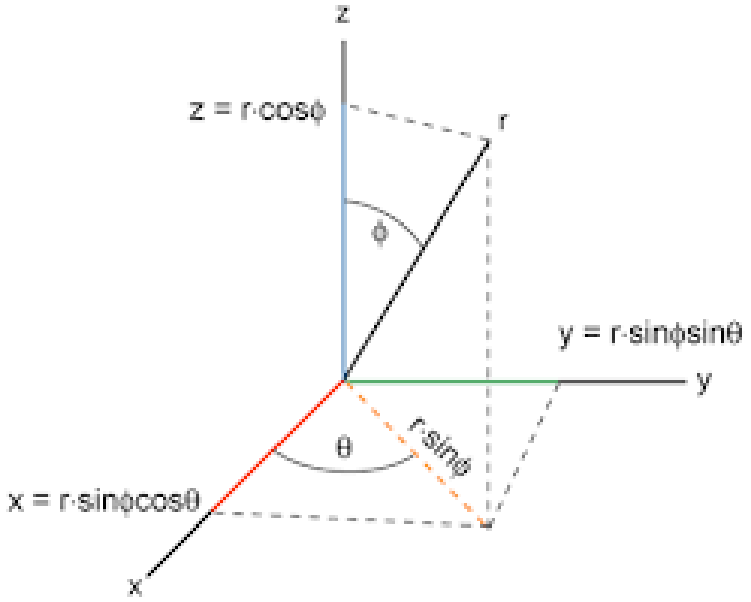
# Use parity to identify zeroes !

We can exploit parity!

$$\cos\theta = \sqrt{\frac{4\pi}{3}} Y_{1,0}$$

$$\vec{r} \to -\vec{r}$$

$$\begin{cases} x \to -x \\ y \to -y \\ z \to -z \end{cases} \quad \begin{cases} r \to r \\ \theta \to \pi - \theta \\ \phi \to \phi + \pi \end{cases}$$




Matrix elements are proportional to the integral:

$$\int_{\Omega} d\Omega\, Y^{*}_{\ell m_\ell}(\theta,\phi) Y_{1,0}(\theta,\phi) Y_{\ell' m_\ell'}(\theta,\phi) = ?$$

Parity: need different $\ell$ $(i.e. \ell \neq \ell')$; otherwise the matrix element = 0

$$H' \doteq \begin{array}{c} \begin{matrix} |200^{(0)}\rangle & |210^{(0)}\rangle & |211^{(0)}\rangle & |21-1^{(0)}\rangle \end{matrix} \\ \begin{pmatrix} 0 & & & \\ & 0 & 0 & 0 \\ & 0 & 0 & 0 \\ & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{matrix} \langle 200^{(0)}| \\ \langle 210^{(0)}| \\ \langle 211^{(0)}| \\ \langle 21-1^{(0)}| \end{matrix}$$

Also: unless m = m', the matrix element = 0

$$H' \doteq \begin{array}{c} \begin{matrix} |200^{(0)}\rangle & |210^{(0)}\rangle & |211^{(0)}\rangle & |21-1^{(0)}\rangle \end{matrix} \\ \begin{pmatrix} 0 & ? & 0 & 0 \\ ? & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{matrix} \\ \langle 200^{(0)}| \\ \langle 210^{(0)}| \\ \langle 211^{(0)}| \\ \langle 21-1^{(0)}| \end{matrix}$$

Need to calculate only one matrix element !!

$$H' \doteq \begin{array}{c} \begin{matrix} |200^{(0)}\rangle & |210^{(0)}\rangle & |211^{(0)}\rangle & |21-1^{(0)}\rangle \end{matrix} \\ \begin{pmatrix} 0 & ? & 0 & 0 \\ ? & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{matrix} \\ \langle 200^{(0)}| \\ \langle 210^{(0)}| \\ \langle 211^{(0)}| \\ \langle 21-1^{(0)}| \end{matrix}$$

Calculate one integral and find that

$$? \; = -3eEa_0$$

Next: **Step 3** – diagonalize the matrix to find first-order energy correction to each state - WS #12

# Example: Stark effect in Hydrogen

1. Perturbation ($n$=2 subspace): need different $l$, need same $m_l$

$$H' \doteq \begin{pmatrix} 0 & -3e\mathrm{E}a_0 & 0 & 0 \\ -3e\mathrm{E}a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{matrix} 200 \\ 210 \\ 211 \\ 21,-1 \end{matrix}$$

1. States:

$$E = +3e\mathrm{E}a_0, -3e\mathrm{E}a_0, 0, 0$$

$$|\psi_+\rangle = \frac{1}{\sqrt{2}}\left[|200\rangle - |210\rangle\right]$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2}}\left[|200\rangle + |210\rangle\right]$$

$$|\psi_3\rangle = |211\rangle$$

$$|\psi_4\rangle = |21,-1\rangle$$