Physics 492 Spring 2010

M. Gold Lecture #10: Perturbation Theory II

## Degenerate perturbation theory

Consider $n^{th}$ state is d-fold degenerate:

$$\hat{H}^0 |\phi_{n,i}\rangle = E_n^0 |\phi_{n,i}\rangle \quad i = 1, \ldots d$$

Expand wave function as

$$|\psi_n\rangle = \sum^{d} C_i |\phi_{n,i}\rangle + \lambda |\varphi_n'\rangle + \cdots$$

Actually there are d first order wave function corrections, one for each of the (diagonalized) zeroth order corrections. See, for example JJ. Sakurai, "Modern Quantum Mechanics".

to first order in $\lambda$:

$$(\hat{H}_0 + \lambda \hat{H}_1)|\psi_n\rangle = (E_n^{(0)} + \lambda E_n^{(1)})|\psi_n\rangle$$

where $|\psi_n\rangle$ is expanded to first order

$$\hat{H}_1 \sum C_i |\phi_{n,i}\rangle + \hat{H}_0 |\varphi_n'\rangle = E_n^{(1)} \sum C_i |\phi_{n,i}\rangle + E_n^{(0)} |\varphi_n'\rangle$$

apply $\langle\phi_{n,j}|$ and use $\langle\phi_{n,j}|\phi_{n,i}\rangle = \delta_{ij}$

$$\sum_i C_i \langle\phi_{n,j}|\hat{H}_1|\phi_{n,i}\rangle + E_n^{(0)}\langle\phi_{n,j}|\varphi_n'\rangle$$

$$= E_n^{(1)} C_j + E_n^{(0)} \langle\phi_{n,j}|\varphi_n'\rangle$$

$$\boxed{\sum_{i=1}^{d} C_i \langle\phi_{n,j}|\hat{H}_1|\phi_{n,i}\rangle = E_n^{(1)} C_j}$$

or in matrix notation:

$$[\hat{H}_1]^n_{ij} \equiv \langle \phi_{n,j} | \hat{H}_1 | \phi_{n,i} \rangle$$

$$[\hat{H}_1]^n \cdot \vec{c} = E_n^{(1)} \vec{c}$$

d-dimensional eigenvalue problem with d (mixed) states with energy corrections $E^{(1)}_{n,i}$ $(i = 1, \dots, d)$

<u>Example: Stark effect</u>

H-atom in external electric field $\vec{\mathcal{E}}$ when $\mathcal{E}$ is small compared to Coulomb potential but large compared to relativistic correction $O(\alpha^4)$.

let $\vec{\mathcal{E}} = \mathcal{E}\,\hat{e}_z$

$$\hat{H}_1 = -\vec{\mu}_e \cdot \vec{\mathcal{E}} = e\,\hat{\vec{r}} \cdot \vec{\mathcal{E}} = e\mathcal{E}\,z = e\mathcal{E}\,r\cos\theta$$

$z$ ← operator

$$p \xrightarrow{\vec{r}} e^- \qquad \vec{\mu}_e = -e\,\vec{r} \quad \text{dipole moment operator}$$

dimensionless (small) parameter

$$\lambda = \frac{e\mathcal{E}a_0}{\frac{1}{2}\mu c^2 \alpha^2} = 2\mathcal{E}\,\frac{(\hbar c)^{3/2}}{(\mu c^2)^2}\,\frac{1}{\alpha^{5/2}}$$

(with $a_0 = \frac{\hbar}{\mu c \alpha}$, $e = \sqrt{\hbar c \alpha}$)

Physics 492, Lec 10

Ground state matrix element

$$E^{(1)}_{100} = e\mathcal{E} \langle 100 | r\cos\theta | 100 \rangle$$

angular integral $\int d\Omega \, |Y_{00}|^2 \cos\theta = \frac{2\pi}{4\pi} \int_{-1}^{1} c\,dc = 0$

$c \equiv \cos\theta$

Vanishing can also seen by invariance under Parity $\vec{r} \to -\vec{r}$ of Electromagnetic interaction.

$$\hat{H}_1 = e\vec{r}\cdot\vec{\mathcal{E}} \xrightarrow[\vec{r}\to-\vec{r}]{} -\hat{H}_1$$

but matrix (energy) cannot change sign

$$Y_{lm}(\theta,\phi) \xrightarrow[r\to-\vec{r}]{} Y_{lm}(\pi-\theta, \pi+\phi) = (-1)^l Y_{lm}(\theta,\phi)$$

thus $\langle 2lm | \hat{H}_1 | 2l'm' \rangle \xrightarrow[\vec{r}\to-\vec{r}]{} (-1)(-1)^{l+l'} \langle 2lm | \hat{H}_1 | 2l'm' \rangle$

so $(-1)^{l+l'} = -1$ non-zero matrix elements have $l+l' = 1$, Thus $E^{(1)}_{100} = 0$

For $n=2$ order $4\times4$ matrix as
$|200\rangle, |210\rangle, |211\rangle, |21-1\rangle$

$$
\begin{array}{cc|c|ccc|}
 & & l=0 & & l=1 & \\
 & m & 0 & 0 & 1 & -1 \\
\hline
l=0 & 0 & 0 & A & \checkmark & \checkmark \\
l=1 & 0 & A & 0 & 0 & 0 \\
 & 1 & \checkmark & 0 & 0 & 0 \\
 & -1 & \checkmark & 0 & 0 & 0 \\
\hline
 & m & & & &
\end{array}
$$

zeros from $l + l' = 0, 2$

$\checkmark = 0$ from $m \neq m'$

Azimuthal symmetry: $\hat{H}_1$ independent of $\phi$. Consequence of azimuthal symmetry

$$
[\hat{H}', \hat{L}_z] = e\mathcal{E}\left[r\cos\theta, \frac{\hbar}{i}\frac{\partial}{\partial\phi}\right] = 0
$$

States with $m = m'$ are orthogonal

$$
\frac{1}{2\pi}\int_0^{2\pi} e^{i(m-m')\phi}\, d\phi = \delta_{mm'} \quad \text{so } m = m'
$$

remaining $2\times 2$ matrix has number $A$ in off diagonal

$$
A = e\mathcal{E}\int_0^\infty r^2 dr\, R_{21} R_{10}\, \overbrace{r}^{\text{from } H\_1} \int d\Omega \cos\theta\, Y_{10} Y_{00}
$$

angular factor: $\int d\Omega \cos\theta\, Y_{10} Y_{00} = \frac{2\pi}{4\pi}\sqrt{3}\int_{-1}^{+1} c^2 dc$

$$
= \frac{1}{\sqrt{3}}
$$

radial factor $\rho \equiv r/a_0$

$$
R_{20} = 2\left(\frac{1}{2}\right)^{3/2}\left(1 - \frac{\rho}{2}\right)e^{-\rho/2}
$$

$$
R_{21} = \frac{1}{\sqrt{3}}\left(\frac{1}{2}\right)^{3/2} \rho\, e^{-\rho^2/2}
$$

normalized as $\int_0^\infty \rho^2 R^2 d\rho = 1$

then

$$A = \frac{1}{\sqrt{3}}(e\mathcal{E} a_0) \int_0^\infty \rho^2 d\rho \; \frac{2}{\sqrt{3}}\left(\frac{1}{2}\right)^2 \left(1 - \frac{\rho}{2}\right) \rho \cdot \rho \, e^{-\rho}$$

volume — operator — wave function

$$= \frac{1}{3}(e\mathcal{E} a_0)\frac{1}{4}\int_0^\infty \rho^4 d\rho \left(1 - \frac{\rho}{2}\right) e^{-\rho}$$

using $\int_0^\infty x^n e^{-x} dx = n!$ (integration by parts)

$$A = \frac{1}{3}(e\mathcal{E} a_0)\frac{1}{4}\left(4! - \frac{1}{2}5!\right) = -3 e a_0 \mathcal{E}$$

wave function from matrix diagonalization

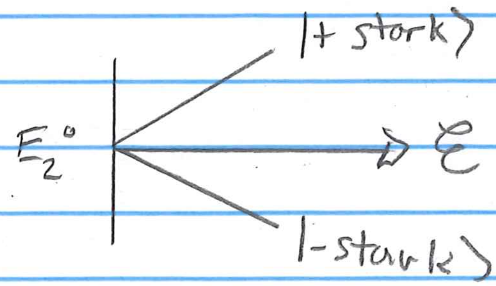
define $\epsilon = -e a_0 \mathcal{E}$

$$-3\epsilon \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E_2^{(1)} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

gives $E_2^{(1)} = \pm 3\epsilon = \pm 3 e a_0 \mathcal{E}$

and linear combination for $\pm$ energies

$$|\pm \text{stark}\rangle = \frac{1}{\sqrt{2}}\left(|200\rangle \mp |210\rangle\right)$$




$|211\rangle$, $|21\text{-}1\rangle$ unperturbed

Energy shift proportional to applied field $\mathcal{E}$

stark state have electric dipole moments.

# Electric dipole moments

$\vec{\mu}_e = -e\vec{r}$ recall $\vec{r}$ defined to go from proton to electron

$$-e \xrightarrow{-\vec{r}} +p$$

We found with $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$ $\hat{z}$ direction

important minus sign

$$\hat{H}_1 = er\cos\theta\,\mathcal{E} \qquad \langle 200|\hat{H}_1|210\rangle = -3ea_0\mathcal{E}$$

$$\& \ \langle 200|\hat{H}_1|210\rangle = 0 = \langle 210|\hat{H}_1|200\rangle$$

Stark states with energy correction

$$E_{\pm} = \pm 3ea_0\mathcal{E} \qquad \pm \text{ refer to sign of energy}$$

$$|\pm\text{stark}\rangle = \frac{1}{\sqrt{2}}\left(|200\rangle \mp |210\rangle\right)$$

then $\langle\vec{\mu}_e\rangle_{+\text{stark}} = \langle +\text{stark}|(er\cos\theta)|+\text{stark}\rangle$

$$= -\frac{2\hat{z}}{(\sqrt{2})^2}\,\underbrace{\langle 200|(er\cos\theta)|210\rangle}_{\text{dipole}}$$

from $-$ in wave function

$$= \hat{z}(-3ea_0) \qquad \text{opposite field direction}$$

higher energy

and $\langle\vec{\mu}_e\rangle_{-\text{stark}} = \hat{z}(3ea_0)$ along field direction

lower energy