Perturbation theory degenerate

Read McIntyre 10.6

PH451/551

Example: Stark effect in H

1. Dipole energy:

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

2. States:

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

3. Perturbation: $\left\langle n\ell m^{(0)}\right|H'\left|n\ell m^{(0)}\right\rangle$?

Matrix elements, *n* = 2

1. Dipole energy: $H' = e\mathrm{E}r\cos\theta$
2. States: $\left|2\ell m^{(0)}\right\rangle \doteq R_{2\ell}(r)Y_{\ell m}(\theta,\phi) = R_{2\ell}(r)P_{\ell}(\cos\theta)e^{im\phi}$
3. Perturbation: $\left\langle 2\ell m^{(0)}\right|H'\left|2\ell m^{(0)}\right\rangle$?
4. In groups – zero or non-zero?

$$\left\langle 200^{(0)}\right|H'\left|2\ell m^{(0)}\right\rangle$$

$$\left\langle 211^{(0)}\right|H'\left|2\ell m^{(0)}\right\rangle$$

$$\left\langle 210^{(0)}\right|H'\left|2\ell m^{(0)}\right\rangle$$

$$\left\langle 21-1^{(0)}\right|H'\left|2\ell m^{(0)}\right\rangle$$

Example: Stark effect in Hydrogen

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

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

2. States:

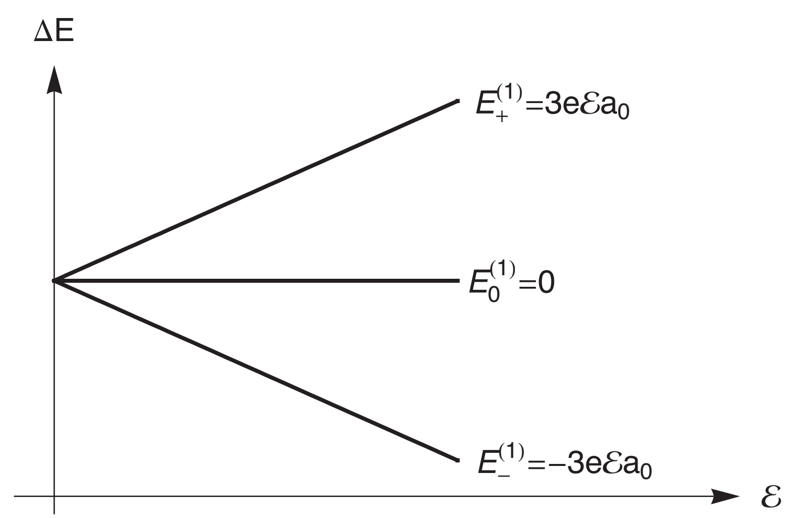
$$E = +3e\mathrm{E}a_0, -3e\mathrm{E}a_0, 0, 0$$

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

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

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

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



Degenerate perturbation theory

1. Divergence of denominator!

2. Comes about because of “wrong basis”

3. If we can find a linear combination that makes H’ diagonal, then we can use 1st order perturbation theory and avoid the divergence.

4. **Diagonalize the perturbation Hamiltonian in the degenerate subspace**

non degen $\left(H_0 - E_n^{(0)}\right)\left|n^{(1)}\right\rangle = \left(E_n^{(1)} - H'\right)\left|n^{(0)}\right\rangle$

- LHS

$$\left(H_0 - E_3^{(0)}\right)\left|3^{(1)}\right\rangle \doteq \begin{pmatrix} E_1^{(0)} - E_3^{(0)} & 0 & 0 & 0 & \cdots \\ 0 & E_2^{(0)} - E_3^{(0)} & 0 & 0 & \cdots \\ 0 & 0 & \boxed{0} & 0 & \cdots \\ 0 & 0 & 0 & E_4^{(0)} - E_3^{(0)} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{31}^{(1)} \\ c_{32}^{(1)} \\ c_{33}^{(1)} \\ c_{34}^{(1)} \\ \vdots \end{pmatrix}$$

- $$\doteq \begin{pmatrix} \left(E_1^{(0)} - E_3^{(0)}\right)c_{31}^{(1)} \\ \left(E_2^{(0)} - E_3^{(0)}\right)c_{32}^{(1)} \\ \boxed{0} \\ \left(E_4^{(0)} - E_3^{(0)}\right)c_{34}^{(1)} \\ \vdots \end{pmatrix}$$

Eqs. 10.36, 10.43

$$\text{non degen}\left(H_0 - E_n^{(0)}\right)\left|n^{(1)}\right\rangle = \left(E_n^{(1)} - H'\right)\left|n^{(0)}\right\rangle$$

- RHS

$$\left(E_3^{(1)} - H'\right)\left|3^{(0)}\right\rangle \doteq \begin{pmatrix} E_3^{(1)} - H'_{11} & -H'_{12} & -H'_{13} & -H'_{14} & \cdots \\ -H'_{21} & E_3^{(1)} - H'_{22} & -H'_{23} & -H'_{24} & \cdots \\ -H'_{31} & -H'_{32} & \boxed{E_3^{(1)} - H'_{33}} & -H'_{34} & \cdots \\ -H'_{41} & -H'_{42} & -H'_{43} & E_3^{(1)} - H'_{44} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$$

- $$\doteq \begin{pmatrix} -H'_{13} \\ -H'_{23} \\ \boxed{E_3^{(1)} - H'_{33}} \\ -H'_{43} \\ \vdots \end{pmatrix}$$

Eq. 10.36, 10.43

$$\left\langle 3^{(0)}\right|\left(H_0 - E_n^{(0)}\right)\left|3^{(1)}\right\rangle = \left\langle 3^{(0)}\right|\left(E_n^{(1)} - H'\right)\left|3^{(0)}\right\rangle$$

- LHS=RHS : the 3rd element gives the first order correction to the 3rd state energy

$$0 = E_3^{(1)} - H'_{33} \Rightarrow$$

$$E_3^{(1)} = H'_{33} = \left\langle 3^{(0)}\right| H' \left|3^{(0)}\right\rangle$$

$$\left\langle 2^{(0)} \middle| \left(H_0 - E_n^{(0)} \right) \middle| 3^{(1)} \right\rangle = \left\langle 2^{(0)} \middle| \left(E_n^{(1)} - H' \right) \middle| 3^{(0)} \right\rangle$$

- LHS=RHS : all the other elements give the first order correction to the 3rd state ket/wave function by another state (say state 2)

$$\left(E_2^{(0)} - E_3^{(0)} \right) c_{32}^{(1)} = -H'_{23} \Rightarrow$$

$$c_{32}^{(1)} = \frac{H'_{23}}{\left(E_3^{(0)} - E_2^{(0)} \right)}$$

Degenerate example $E_2^{(0)} = E_3^{(0)}$

1. First order equation:

$$\left(H_0 - E_n^{(0)}\right)\left|n^{(1)}\right\rangle = \left(E_n^{(1)} - H'\right)\left|n^{(0)}\right\rangle$$

2. LHS

$$\left(H_0 - E_2^{(0)}\right) \doteq \begin{pmatrix} E_1^{(0)} - E_2^{(0)} & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & E_4^{(0)} - E_2^{(0)} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Degenerate example $E_2^{(0)} = E_3^{(0)}$

LHS

$$\left(H_0 - E_2^{(0)}\right)\left|2^{(1)}\right\rangle \doteq \begin{pmatrix} E_1^{(0)} - E_2^{(0)} & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & E_4^{(0)} - E_2^{(0)} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{21}^{(1)} \\ c_{22}^{(1)} \\ c_{23}^{(1)} \\ c_{24}^{(1)} \\ \vdots \end{pmatrix}$$

Eq. 10.98

$$\doteq \begin{pmatrix} \left(E_1^{(0)} - E_2^{(0)}\right) c_{21}^{(1)} \\ 0 \\ 0 \\ \left(E_4^{(0)} - E_2^{(0)}\right) c_{24}^{(1)} \\ \vdots \end{pmatrix}$$

Degenerate example $E_2^{(0)} = E_3^{(0)}$

First order equation:

$$\left(H_0 - E_2^{(0)}\right)\left|2^{(1)}\right\rangle = \left(E_2^{(1)} - H'\right)\left|2^{(0)}\,?\right\rangle$$

RHS

Eq.10.99

$$\left(E_2^{(1)} - H'\right) \doteq \begin{pmatrix} E_2^{(1)} - H'_{11} & -H'_{12} & -H'_{13} & -H'_{14} & \cdots \\ -H'_{21} & E_2^{(1)} - H'_{22} & -H'_{23} & -H'_{24} & \cdots \\ -H'_{31} & -H'_{32} & E_2^{(1)} - H'_{33} & -H'_{34} & \cdots \\ -H'_{41} & -H'_{42} & -H'_{43} & E_2^{(1)} - H'_{44} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

State 2 or state 3? Or linear combo?

1. Unpert. states…

$$\left|2^{(0)}\right\rangle \doteq \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}, \qquad \left|3^{(0)}\right\rangle \doteq \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$$

2. Or

$$\alpha\left|2^{(0)}\right\rangle + \beta\left|3^{(0)}\right\rangle \doteq \begin{pmatrix} 0 \\ \alpha \\ \beta \\ 0 \\ \vdots \end{pmatrix}$$

Degenerate example $E_2^{(0)} = E_3^{(0)}$

RHS

10.104

$$\left(E_2^{(1)} - H'\right)\left|2_{new}^{(0)}\right\rangle \doteq \begin{pmatrix} E_2^{(1)} - H'_{11} & -H'_{12} & -H'_{13} & -H'_{14} & \cdots \\ -H'_{21} & \boxed{E_2^{(1)} - H'_{22}} & \boxed{-H'_{23}} & -H'_{24} & \cdots \\ -H'_{31} & \boxed{-H'_{32}} & \boxed{E_2^{(1)} - H'_{33}} & -H'_{34} & \cdots \\ -H'_{41} & -H'_{42} & -H'_{43} & E_2^{(1)} - H'_{44} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} 0 \\ \alpha \\ \beta \\ 0 \\ \vdots \end{pmatrix}$$

$$\doteq \begin{pmatrix} -H'_{12}\alpha - H'_{13}\beta \\ \boxed{\begin{matrix} \left(E_2^{(1)} - H'_{22}\right)\alpha - H'_{23}\beta \\ -H'_{32}\alpha + \left(E_2^{(1)} - H'_{33}\right)\beta \end{matrix}} \\ -H'_{42}\alpha - H'_{43}\beta \\ \vdots \end{pmatrix}$$

degenerate example $E_2^{(0)} = E_3^{(0)}$

$$\left(E_2^{(1)} - H'_{22}\right)\alpha - H'_{23}\beta = 0$$

$$-H'_{32}\alpha + \left(E_2^{(1)} - H'_{33}\right)\beta = 0$$

$$\begin{pmatrix} H'_{22} & H'_{23} \\ H'_{32} & H'_{33} \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_2^{(1)}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

Diagonalize the perturbation Hamiltonian in the degenerate subspace!

Example: Stark effect in Hydrogen

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

$$H' \doteq \begin{array}{c} \begin{pmatrix} 0 & -3e\mathrm{E}a_0 & 0 & 0 \\ -3e\mathrm{E}a_0 & 0 & 00 & 00 \\ 0 & 00 & 0 & 00 \\ 0 & 00 & 00 & 0 \end{pmatrix} \end{array} \begin{array}{c} 200 \\ 210 \\ 211 \\ 21,-1 \end{array}$$

2. States:

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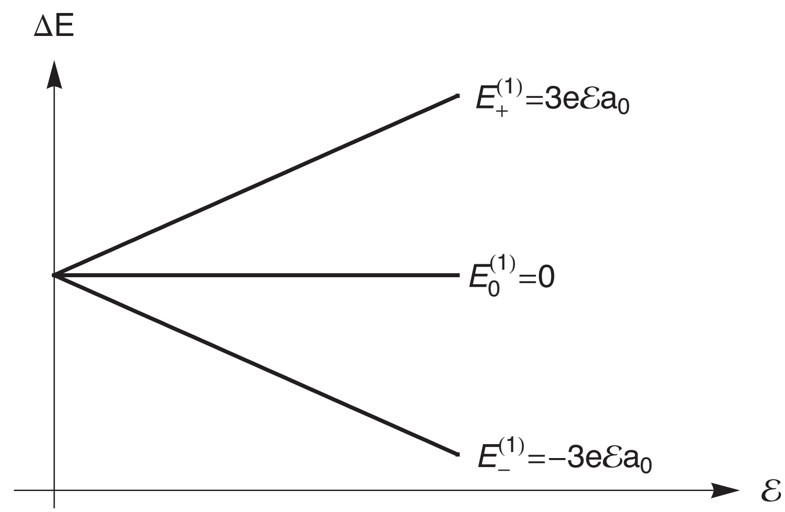
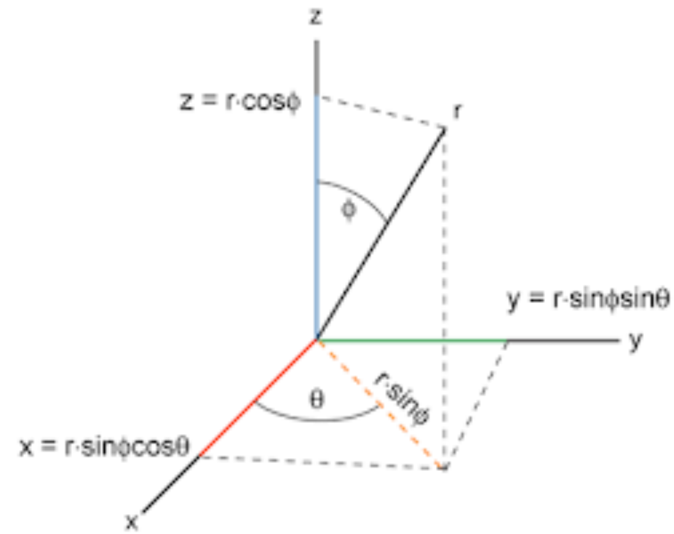


Parity – even or odd?

1. Even parity means a function remains the same if $\vec{r} \to -\vec{r}$
   Odd parity means the function changes sign.

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

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



2. Example: $$\int_{\Omega} d\Omega\, Y^{*}_{\ell m_\ell}(\theta,\phi) Y_{\ell' m_\ell'}(\theta,\phi) = \delta_{\ell\ell'}\delta_{m_\ell m_\ell'}$$

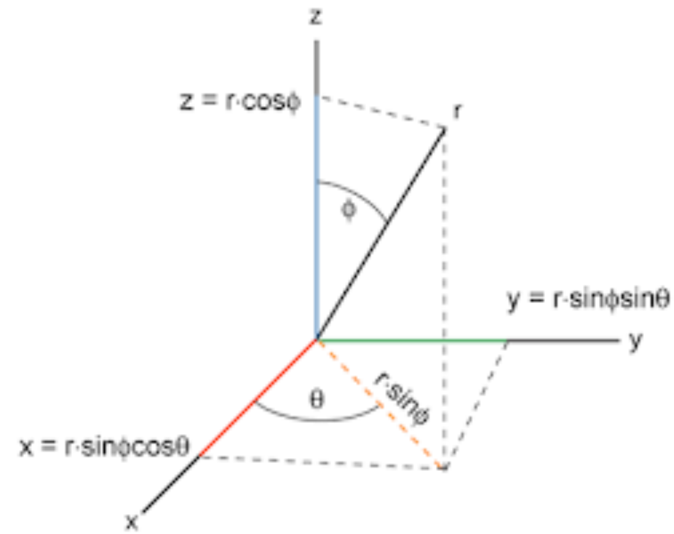
Parity – even or odd?

1. We can exploit parity!

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

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

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



2. New integral:

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