6.5.2. Constant, Uniform External Electric Field $\vec{E}$: The Stark Effect

The Hamiltonian on page - - reduces to

$$H = H_0 + H_{fs} + e\vec{E}\cdot\vec{R} \quad .$$

Choosing $\vec{E}$ to lie along the z-axis $\vec{E} = E\hat{z}$, the Hamiltonian becomes

$$H = H_0 + H_{fs} + eEZ \, .$$

For simplicity we will consider $\vec{E}$ to be very much larger that H_{fs}

i.e. $|eEa_0| >> mc^2\alpha^4$

and consequently ignore H_{fs} to lowest order. Thus we have the Hamiltonian

$$H = H_0 + \underbrace{eEZ}_{=H'} \, .$$

with the effects of $H' <<$ those of H_0 $(|eEa_0| << mc^2\alpha^2)$

According to R-S degenerate perturbation we must diagonalize the unperturbed matrix elements of H' to find the first order energy level shifts,

$$E_{n\ell}(m) = E_n^0 + \Delta E_{n\ell}(m)$$

with the shifts $\Delta E_{n\ell}(m)$ the eigenvalues of

$$\langle n, \ell', m' | H' | n, \ell, m \rangle$$

$$= eE \langle n, \ell', m' | Z | n, \ell, m \rangle$$

$$= eE \int d^3r \, \psi^*_{n\ell' m'}(\vec{r}) \, z \, \psi_{n\ell m}(\vec{r}) \, .$$

Now letting $\vec{r}' = -\vec{r}$ and recalling that

$$\psi_{n\ell m}(-\vec{r}) = R_{n\ell}(r) Y_\ell^m(\pi-\theta, \varphi+\pi)$$

$$= R_{n\ell}(r) (-1)^\ell Y_\ell^m(\theta, \varphi)$$

$$= (-1)^\ell \psi_{n\ell m}(\vec{r})$$

we have the <u>parity selection rule</u>

$\langle n, l', m' | H' | n, l, m \rangle$

$$= +eE \int d^3r' \, \psi^*_{n l' m'}(-\vec{r}\,') (-z') \psi_{nlm}(-\vec{r}\,')$$

$$= eE \int d^3r' \, (-1)^{l'} \psi^*_{n l' m'}(\vec{r}\,') (-z') (-1)^{l} \psi_{nlm}(\vec{r}\,')$$

$$= (-1)^{l+l'+1} \underbrace{eE \int d^3r' \, \psi^*_{n l' m'}(\vec{r}\,') z' \psi_{nlm}(\vec{r}\,')}_{= \langle n, l', m' | H' | n, l, m \rangle}$$

$$\Rightarrow \langle n, l', m' | H' | n, l, m \rangle \left[1 - (-1)^{l+l'+1} \right] = 0$$

Hence we find that

$$\boxed{\langle n, l', m' | H' | n, l, m \rangle = 0 \quad \text{unless } (l+l'+1) = \text{even integer}.}$$

The parity selection rule.

To be concrete let $n=2$ then $l, l' = 0, 1$ and the parity selection rule implies

$$\langle 2,1,m' | H' | 2,1,m \rangle = 0$$

$$\langle 2,0,0 | H' | 2,0,0 \rangle = 0 .$$

For $n=2$ the Stark Effect Hamiltonian only connects p-states with s-states

$$\langle 2,1,m | H' | 2,0,0 \rangle$$
$$= eE \int d^3r \, \psi^*_{21m}(\vec{r}) \, z \, \psi_{200}(\vec{r})$$

Recalling that

$$\psi_{200}(\vec{r}) = R_{20}(r) Y_0^0(\theta,\varphi) = R_{20}(r) \frac{1}{\sqrt{4\pi}}$$

$$\psi_{21m}(\vec{r}) = R_{21}(r) Y_1^m(\theta,\varphi)$$

with $R_{20}(r) = \frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$

$$R_{21}(r) = \frac{1}{(2a_0)^{3/2}} \frac{1}{\sqrt{3}} \frac{r}{a_0} e^{-r/2a_0}$$

and using

$$z = r\cos\theta = \sqrt{\frac{4\pi}{3}}\, r\, Y_1^0(\theta,\varphi)$$

The integral becomes

$\langle 2,1,m | H' | 2,0,0 \rangle$

$$= eE\sqrt{\frac{1}{4\pi}}\sqrt{\frac{4\pi}{3}}\int_0^\infty dr\, r^3 R_{21}(r) R_{20}(r) \times$$

$$\times \underbrace{\int d\Omega\, Y_1^{m*}(\theta,\varphi) Y_1^0(\theta,\varphi)}_{=\delta_{m0}}$$

$$= \frac{eE}{\sqrt{3}}\delta_{m0}\int_0^\infty dr\, r^3 R_{21}(r) R_{20}(r)$$

$$= \frac{eE}{3}\delta_{m0}\frac{1}{(2a_0)^3}\frac{1}{a_0}\int_0^\infty dr\, r^4\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{a_0}}$$

let $\xi = \frac{r}{a_0}$

$$= \frac{eE\delta_{m0}}{24\, a_0^4}\, a_0^5 \underbrace{\int_0^\infty d\xi\, \xi^4 (2-\xi) e^{-\xi}}_{= 2\Gamma(5) - \Gamma(6) = 2\cdot(4!) - 5! = -3(4!)}$$

$$\boxed{\langle 2,1,m|H'|2,0,0\rangle = -3eEa_0\,\delta_{m0}}$$

The H'-matrix in the $n=2$ subspace is given by

$$(H')_{\underbrace{(l',m')}_{\text{rows}}\underbrace{(l,m)}_{\text{columns}}} = \langle 2,l',m'|H'|2,l,m\rangle$$

$$= \begin{array}{c|c} (l',m')\backslash(l,m) & \begin{array}{cccc} (1,1) & (1,-1) & (1,0) & (0,0) \end{array} \\ \begin{array}{c} (1,1) \\ (1,-1) \\ (1,0) \\ (0,0) \end{array} & \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -3eEa_0 \\ 0 & 0 & -3eEa_0 & 0 \end{pmatrix} \end{array}.$$

Thus we find the first order energy shifts by diagonalizing this ~~matrix~~ matrix. The eigenstates to zeroth order are the associated eigenvectors of the matrix.

Clearly there are 2 zero eigenvalues with ~~eigenvectors~~ eigenvectors $|2,1,1\rangle$ and $|2,1,-1\rangle$.

The 2x2-matrix in the lower right corner has eigenvalues

$$\begin{vmatrix} \lambda & -3eEa_0 \\ -3eEa_0 & \lambda \end{vmatrix} = 0 = \lambda^2 - (3eEa_0)^2$$

$$\Rightarrow \qquad \lambda = \pm 3eEa_0$$

Their orthonormal eigenvectors are just the sum and difference of the $|2,1,0\rangle$ and $|2,0,0\rangle$ states

$\frac{1}{\sqrt{2}}(|2,1,0\rangle + |2,0,0\rangle)$ has eigenvalue $-3eEa_0$

$\frac{1}{\sqrt{2}}(|2,1,0\rangle - |2,0,0\rangle)$ has eigenvalue $+3eEa_0$

i.e.
$$\begin{pmatrix} 0 & -3eEa_0 \\ -3eEa_0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = -3eEa_0 \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & -3eEa_0 \\ -3eEa_0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = +3eEa_0 \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

i.e. in R-S degenerate perturbation theory notation

$$|\psi_2^{(0)}\rangle = \psi_{21}|2,1,0\rangle + \psi_{22}|2,0,0\rangle$$

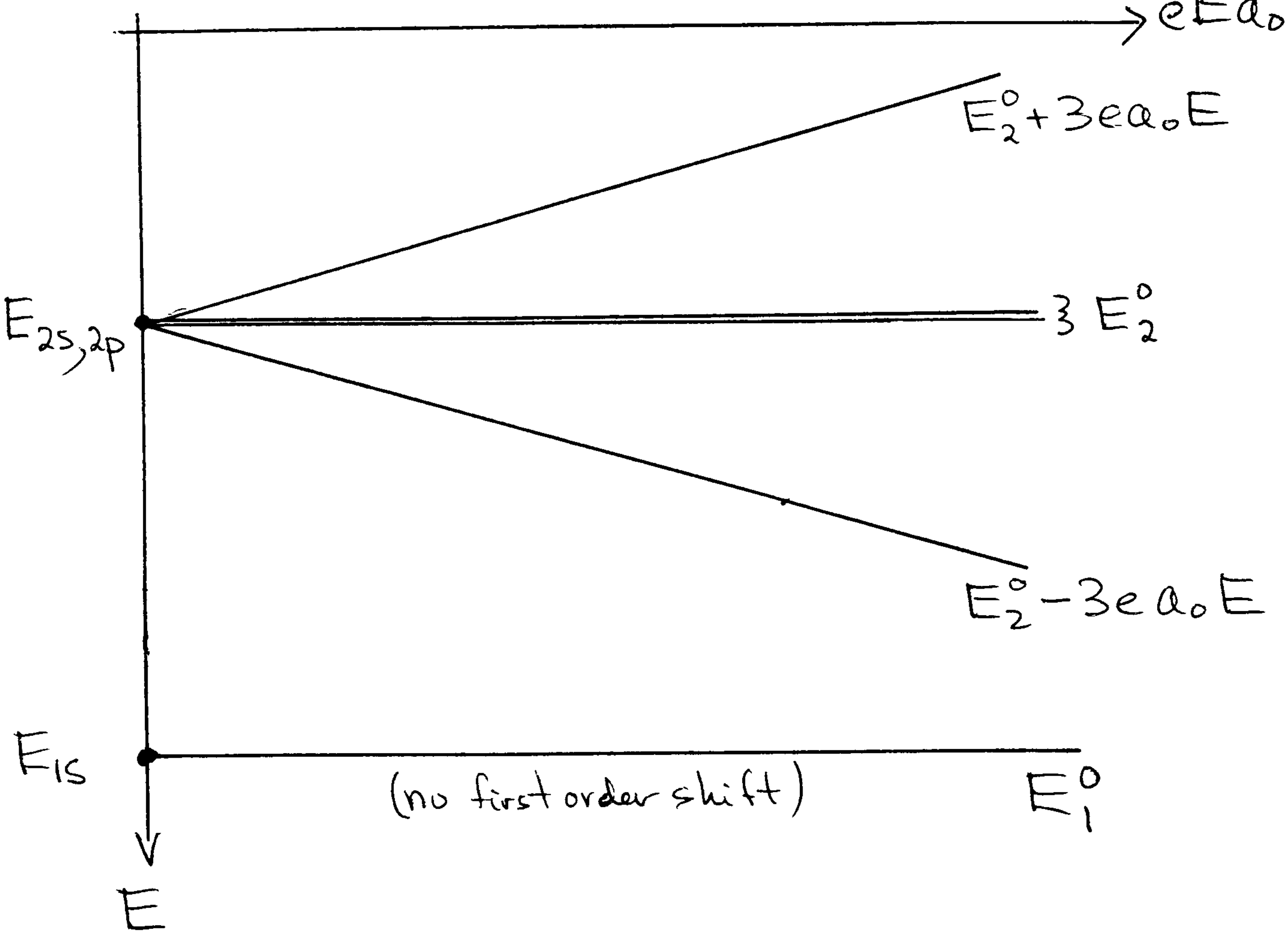
$$\begin{pmatrix}\psi_{21}\\ \psi_{22}\end{pmatrix} = \begin{cases}\begin{pmatrix}1\\1\end{pmatrix}\frac{1}{\sqrt{2}}\\ \begin{pmatrix}1\\-1\end{pmatrix}\frac{1}{\sqrt{2}}\end{cases} \quad \text{above.}$$

Hence to summarize:

Eigenstates	Energy Shift ΔE	Energy $E_2^0 + \Delta E$
$\|2,1,1\rangle$	0	$E_2^0 = -\frac{mc^2\alpha^2}{8}$
$\|2,1,-1\rangle$	0	$E_2^0 = -\frac{mc^2\alpha^2}{8}$
$\frac{1}{\sqrt{2}}\left(\|2,1,0\rangle + \|2,0,0\rangle\right)$	$-3eEa_0$	$E_2^0 - 3eEa_0$
$\frac{1}{\sqrt{2}}\left(\|2,1,0\rangle - \|2,0,0\rangle\right)$	$+3eEa_0$	$E_2^0 + 3eEa_0$

The $|2,1,\pm1\rangle$ states remain degenerate in energy while the remaining $n=2$ energy ~~shifts~~ shifts are linear in E.

Stark Diagram in first order



Note that the shifted eigenstates have an electric dipole moment

$$d_\pm = \frac{1}{\sqrt{2}}\left(\langle 2,1,0| \pm \langle 2,0,0|\right)\left[-eZ\right] \times$$

$$\times \left(|2,1,0\rangle \pm |2,0,0\rangle\right)$$

$$= \mp \frac{e}{2}\left(\langle 2,1,0|Z|2,0,0\rangle + \langle 2,0,0|Z|2,1,0\rangle\right)$$

$$d_\pm = \mp e \underbrace{\langle 2,1,0|Z|2,0,0\rangle}_{=-3a_0}$$

$$\boxed{d_\pm = \pm 3ea_0}$$

The hydrogen atom has a permanent electric dipole moment. The Stark effect energy shifts are just the effect of this electric dipole moment in an external electric field

$$\Delta E = -d_\pm E = \mp 3eEa_0 .$$