6.5.2. **Constant, Uniform External Electric Field** $E$: The Stark Effect

The Hamiltonian on page 238 reduces to

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

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 than $H_{fs}$

i.e. $|eEA_0| >> mc^2 \alpha^4$

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

$$ H = H_0 + eEZ . $$

with the effects of $H' <<$ those of $H_0$ ($|eEA_0| << mc^2 \alpha^4$)
According to R-S degenerate perturbation, we must diagonalize the unperturbed matrix elements of H to find the first order energy level shifts,

\[ E_{nl}(m) = E_n^0 + \Delta E_{nl}(m) \]

with the shifts \( \Delta E_{nl}(m) \) the eigenvalues of

\[ \langle n, l', m' | H' | n, l, m \rangle \]

\[ = eE \langle n, l', m' | \Delta | n, l, m \rangle \]

\[ = eE \int d^3r \ 2l^{\ast}_{nl,m'}(\vec{r}) \Delta_{nl,m}(\vec{r}) \ 2l_{nl,m}(\vec{r}) \]

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

\[ 2l_{nl,m}(\vec{r}) = R_{nl}(r) Y^m_l(\theta - \pi, \phi + \pi) \]

\[ = R_{nl}(r) (-1)^l Y^m_l(\theta, \phi) \]

\[ = (-1)^l 2l_{nl,m}(\vec{r}) \]

we have the parity selection rule.
\[ \langle n, l', m' | H' | n, l, m \rangle \]

\[ = e E \int d^3 r' \, 2_{n l m}^* (\mathbf{r}') (-z')^2 | n l m (\mathbf{r}') \rangle \langle n l m (\mathbf{r}') | \]

\[ = (-1)^{l+l'+1} \left[ 1 - (\mathbf{r} \cdot \mathbf{r'}) \right] \]

\[ = 0 \] unless \((l+l'+1)\) = even integer.

The parity selection rule.
To be concrete let \( N = 2 \) then \( l, f = 0, 1 \) 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.

\[
\langle 2, 1, m | H' | 2, 0, 0 \rangle
\]
\[
= e E \int d^3 r \ 2_{1m}^* \ 2_{21m} \ \Phi \ \Phi^*(\vec{r})
\]
Recalling that
\[
2_{200}(\vec{r}) = R_{20}(r) Y_0^0(\theta, \phi)
\]
\[
2_{21m}(\vec{r}) = R_{21}(r) Y_1^m(\theta, \phi)
\]
with
\[
R_{20}(r) = \frac{1}{(2a_0)^{3/2}} (2 - \frac{r}{a_0}) e^{-r/2a_0}
\]
\[
R_{21}(r) = \frac{1}{(2a_0)^{3/2}} \frac{1}{\sqrt{3} i} \frac{r}{a_0} e^{-r/2a_0}
\]
and using
\[ z = r \cos \theta = \sqrt{\frac{4 \pi}{3}} \cdot r \cdot Y_{1}^0(\theta, \phi) \]
The integral becomes
\[ \langle 2, 1 | H | 2, 0, 0 \rangle \]
\[ = e E \sqrt{\frac{1}{4 \pi}} \sqrt{\frac{4 \pi}{3}} \int_0^\infty dr \ r^3 \ R_{21}(r) \ R_{20}(r) \times \]
\[ \left[ \frac{d^2}{d\Omega} \ Y_{1}^m(\theta, \phi) \right] \ Y_{1}^0(\theta, \phi) \]
\[ = \delta_{m0} \]
\[ = \frac{e E}{\sqrt{3}} \delta_{m0} \int_0^\infty dr \ r^3 \ R_{21}(r) \ R_{20}(r) \]
\[ = \frac{e E}{3} \delta_{m0} \frac{1}{(2a_0)^3} \frac{1}{a_0} \int_0^\infty dr \ r^4 \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{a_0}} \]

let \( \xi = \frac{r}{a_0} \)
\[ = \frac{e E \delta_{m0}}{24 \ a_0^4} \ a_0^5 \int_0^\infty \ d\xi \ \xi^4 \ (2 - \xi) e^{-\xi} \]
\[ = 2 \Gamma(5) - \Gamma(6) = 2 \cdot (4!) - 5! \]
\[ = -3 \ (4!) \]
\[ \langle 2, 1, m | H' | 2, 0, 0 \rangle = -3eE_0 \delta_{m0} \]

The \( H' \)-matrix in the \( n=2 \) subspace is given by

\[
(H')_{(\ell', m') (\ell, m)} = \langle 2, \ell', m' | H' | 2, \ell, m \rangle
\]

\[
= \begin{pmatrix}
(1, 1) & (1, -1) & (1, 0) & (0, 0) & (0, 0) \\
(1, 1) & 0 & 0 & 0 & 0 \\
(1, -1) & 0 & 0 & 0 & 0 \\
(1, 0) & 0 & 0 & 0 & -3eE_0 \\
(0, 0) & 0 & 0 & -3eE_0 & 0 \\
\end{pmatrix}
\]

Thus we find the first order energy shifts by diagonalizing this matrix. The eigenstates at zeroth order are the associated eigenvectors of the matrix.
Clearly there are 2 zero eigenvalues with eigenvectors \( |2,1,1\rangle \) and \( |2,1,-1\rangle \). The \( 2 \times 2 \) matrix in the lower right corner has eigenvalues

\[
\begin{vmatrix}
\lambda & -3eE_o \\
-3eE_o & \lambda
\end{vmatrix} = 0 = \lambda^2 - (3eE_o)^2
\]

\[
\Rightarrow 
\lambda = \pm 3eE_o
\]

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

\[
\frac{1}{\sqrt{2}} (|2,1,0\rangle + |2,0,0\rangle) \text{ has eigenvalue } -3eE_o
\]

\[
\frac{1}{\sqrt{2}} (|2,1,0\rangle - |2,0,0\rangle) \text{ has eigenvalue } +3eE_o
\]

\[
\begin{pmatrix}
0 & -3eE_o \\
-3eE_o & 0
\end{pmatrix}
\begin{pmatrix} 1 \\ 1 \end{pmatrix} = -3eE_o \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]

\[
\begin{pmatrix}
0 & -3eE_o \\
-3eE_o & 0
\end{pmatrix}
\begin{pmatrix} 1 \\ -1 \end{pmatrix} = +3eE_o \begin{pmatrix} 1 \\ -1 \end{pmatrix}
\]
in R-S degenerate perturbation theory.

\[ \left| 2,1,1,0 \right> = \frac{1}{\sqrt{2}} \left( \left| 2,1,1,0 \right> + \left| 2,1,-1,0 \right> \right) \]

\[
\begin{cases}
(\frac{1}{\sqrt{2}}) & \text{above} \\
(1) \frac{1}{\sqrt{2}} & \\
(-1) \frac{1}{\sqrt{2}} &
\end{cases}
\]

Hence to summarize:

<table>
<thead>
<tr>
<th>Eigenstate</th>
<th>Energy Shift ( \Delta E )</th>
<th>Energy ( E^0 + \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2,1,1,1 )</td>
<td>0</td>
<td>( E_2^0 = -\frac{mc^2\lambda^2}{8} )</td>
</tr>
<tr>
<td>( 2,1,-1 )</td>
<td>0</td>
<td>( E_2^0 = -\frac{mc^2\lambda^2}{8} )</td>
</tr>
<tr>
<td>( \frac{1}{\sqrt{2}} (\left</td>
<td>2,1,0 \right&gt; + \left</td>
<td>2,0,0 \right&gt; ) )</td>
</tr>
<tr>
<td>( \frac{1}{\sqrt{2}} (\left</td>
<td>2,1,0 \right&gt; - \left</td>
<td>2,0,0 \right&gt; ) )</td>
</tr>
</tbody>
</table>

The \( 2,1,\pm 1 \) states remain degenerate in energy, while the remaining \( N=2 \) energy shifts are linear in \( E \).
Note that the shifted eigenstates have an electric dipole moment

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

\[ \times \left( 1,2,1 \rangle \pm 1,2,0 \rangle \right) \]

\[ = \frac{e}{2} \left( \langle 2,1,0 | Z | 2,0,0 \rangle + \langle 2,0,0 | Z | 2,1,0 \rangle \right) \]
\[ d_+ = \mp e \langle 2\,l_{1,0} | z | 2\,l_{0,0} \rangle \]
\[ = -3a_0 \]

\[ d_+ = \pm 3e a_0. \]

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

\[ \Delta E = -d_+ E = \mp 3eEa_0. \]