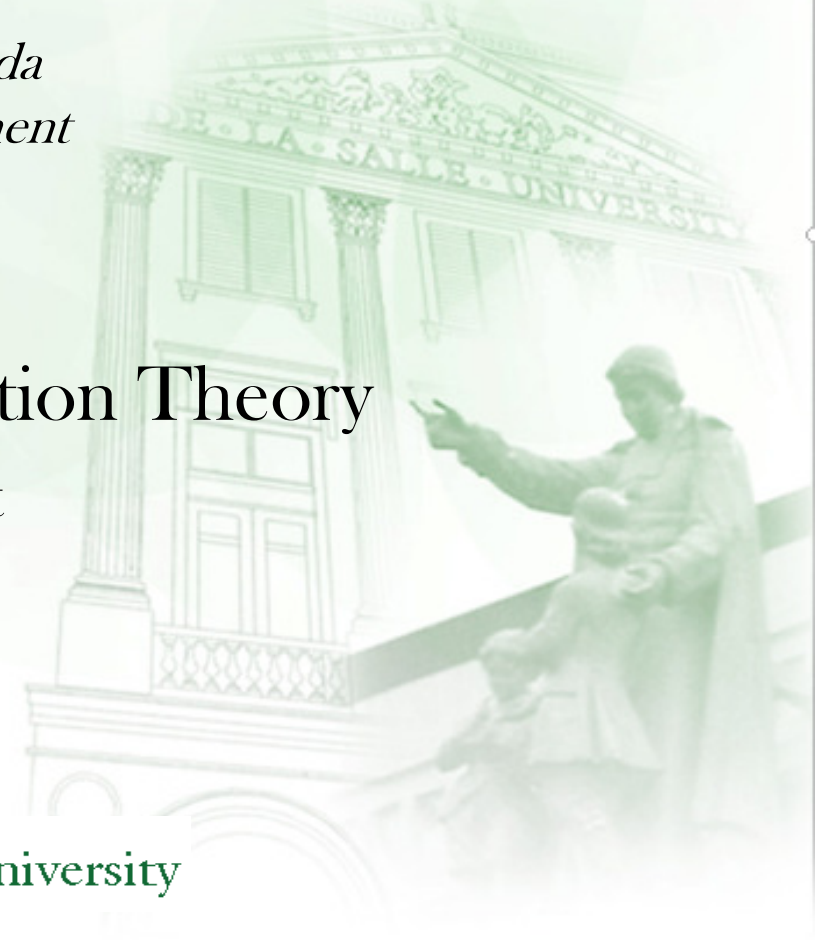
Quantum Mechanics 2

Robert C. Roleda
Physics Department

Degenerate Perturbation Theory

Stark Effect



De La Salle University

Atom in an Electric Field

Suppose a hydrogen atom is placed in a weak uniform electric field $\mathcal{E}$. What is its effect on the $n = 2$ states?

If we take the direction of the electric field as the $z-$ axis, then

$$H_I = e\mathcal{E}z$$

Excluding spin, the $n = 2$ states of a hydrogen atom are 4-fold degenerate, with the $2s, 2p_{+1}, 2p_0, 2p_{-1}$ having the same energy.

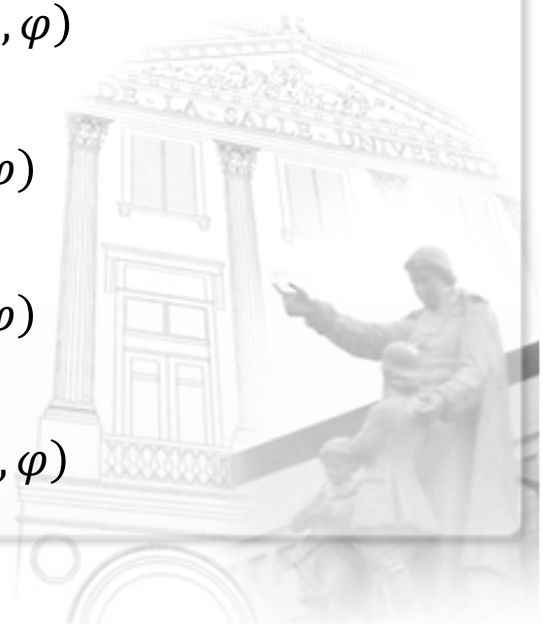
The unperturbed hydrogen eigenfunctions for these states are

$$u_{200} = (2a_0)^{-3/2} 2\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{00}(\theta, \varphi)$$

$$u_{211} = (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{11}(\theta, \varphi)$$

$$u_{210} = (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{10}(\theta, \varphi)$$

$$u_{21,-1} = (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{1,-1}(\theta, \varphi)$$



Eigenvalue Equation

The eigenvalue equation

$$\sum_i \alpha_i \langle n^{(j)} | H_I | n^{(i)} \rangle = E_n^{(1)} \alpha_j$$

is in this case expressed as

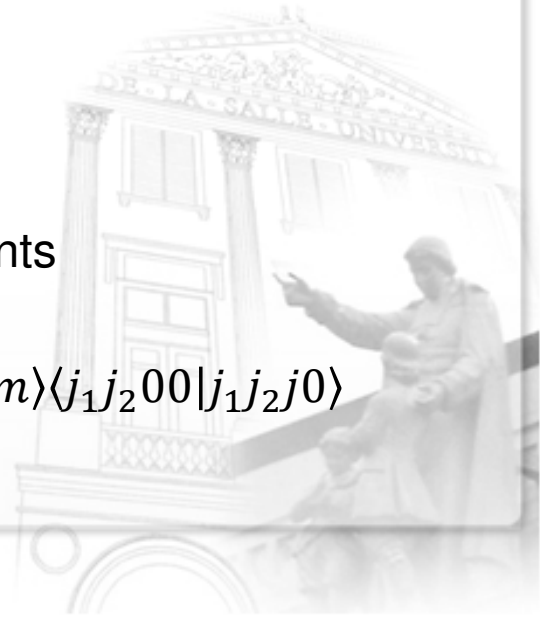
$$e\mathcal{E} \begin{pmatrix} \langle 211|z|211\rangle & \langle 211|z|210\rangle & \langle 211|z|21,-1\rangle & \langle 211|z|200\rangle \\ \langle 210|z|211\rangle & \langle 210|z|210\rangle & \langle 210|z|21,-1\rangle & \langle 210|z|200\rangle \\ \langle 21,-1|z|211\rangle & \langle 21,-1|z|210\rangle & \langle 21,-1|z|21,-1\rangle & \langle 21,-1|z|200\rangle \\ \langle 200|z|211\rangle & \langle 200|z|210\rangle & \langle 200|z|21,-11\rangle & \langle 200|z|200\rangle \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E_2^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

If we express the cartesian variable z as the spherical harmonic

$$rY_{10} = \sqrt{\frac{3}{4\pi}}\, z$$

we may use the triple Y formula to evaluate the matrix elements

$$\int Y_{jm}^* Y_{j_1 m_1} Y_{j_2 m_2} d\Omega = \sqrt{\frac{(2j_1+1)(2j_2+1)}{4\pi(2j+1)}} \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m \rangle \langle j_1 j_2 00 | j_1 j_2 j 0 \rangle$$



Triple Y Expressions

The triple Y expressions we have are

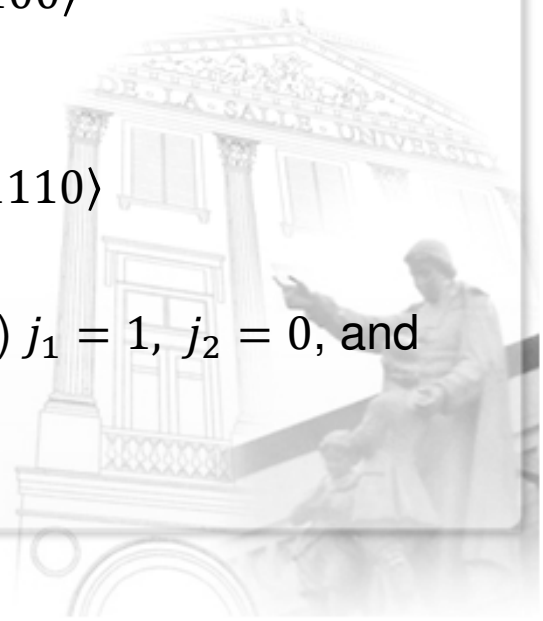
$$\int Y_{00}^{*} Y_{10}\, Y_{00} d\Omega = \sqrt{\frac{3}{4\pi}} \langle 1000|1000\rangle\langle 1000|1000\rangle$$

$$\int Y_{1m}^{*} Y_{10}\, Y_{00} d\Omega = \sqrt{\frac{1}{4\pi}} \langle 1000|101m\rangle\langle 1000|1010\rangle$$

$$\int Y_{00}^{*} Y_{10}\, Y_{1m} d\Omega = \sqrt{\frac{9}{4\pi}} \langle 110m|1100\rangle\langle 1100|1100\rangle$$

$$\int Y_{1m}^{*} Y_{10}\, Y_{1m'} d\Omega = \sqrt{\frac{3}{4\pi}} \langle 110m'|111m\rangle\langle 1100|1110\rangle$$

Clearly, we need two sets of Clebsch Gordan Coefficients: (a) $j_1 = 1,\ j_2 = 0$, and (b) (a) $j_1 = 1,\ j_2 = 1$



Clebsch-Gordan Table

The $j_1 = 1,\ j_2 = 0$ Clebsch-Gordan coefficients are easily obtained. As $j_2 = 0$, there is only one way in which the relation $m = m_1 + m_2$ can be satisfied. These are the cases where $m = m_1$.

$j_1 = 1$ $j_2 = 0$		$J = 1$		
		m		
m_1	m_2	1	0	-1
1	0	1		
0	0		1	
-1	0			1

For, $j_1 = 1,\ j_2 = 0, j = 1$. Thus, Clebsch-Gordan coefficients of the form $\langle 100m|100m'\rangle$ are zero.

The $j_1 = 1,\ j_2 = 1$ Clebsch-Gordan coefficients were evaluated in [one-one], and shown in the next slide.

Clebsch-Gordan Table

$j_1 = 1$ $j_2 = 1$		$J = 2$					$J = 1$			$J = 0$
		m								
m_1	m_2	2	1	0	-1	-2	1	0	-1	0
1	1	1								
1	0		$1/\sqrt{2}$				$-1/\sqrt{2}$			
1	-1			$1/\sqrt{6}$				$-1/\sqrt{2}$		$1/\sqrt{3}$
0	1		$1/\sqrt{2}$				$1/\sqrt{2}$			
0	0			$2/\sqrt{6}$				0		$-1/\sqrt{3}$
0	-1				$1/\sqrt{2}$				$-1/\sqrt{2}$	
-1	1			$1/\sqrt{6}$				$1/\sqrt{2}$		$1/\sqrt{3}$
-1	0				$1/\sqrt{2}$				$1/\sqrt{2}$	
-1	-1					1				

Triple Y Expressions

We then have

$$\int Y_{00}^{*} Y_{10}\, Y_{00} d\Omega = 0$$

$$\int Y_{1m}^{*} Y_{10}\, Y_{00} d\Omega = \sqrt{\frac{1}{4\pi}}\ \delta_{m,0}$$

$$\int Y_{00}^{*} Y_{10}\, Y_{1m} d\Omega = \sqrt{\frac{1}{4\pi}}\ \delta_{m,0}$$

$$\int Y_{1m}^{*} Y_{10}\, Y_{1m'} d\Omega = 0$$

Non-vanishing Terms

The only non-vanishing elements are

$$\langle 200|z|210\rangle = \langle 210|z|200\rangle = (2a_0)^{-3}\frac{2}{\sqrt{3}}\sqrt{\frac{4\pi}{3}}\sqrt{\frac{1}{4\pi}}\int r^2 dr\left(1-\frac{r}{2a_0}\right)r\left(\frac{r}{a_0}\right)e^{-r/a_0}$$

The radial integral may be evaluated using the Gamma function

$$\Gamma(n) = \int_0^\infty t^{n-1}e^{-t}dt$$

Thus,

$$\int r^2 dr\left(1-\frac{r}{2a_0}\right)r\left(\frac{r}{a_0}\right)e^{-r/a_0} = a_0^{-1}\int r^4 dr\left(1-\frac{r}{2a_0}\right)e^{-r/a_0}$$

$$= a_0^4\int\left[t^4-\tfrac{1}{2}t^5\right]e^{-t}dt = a_0^4\left[4!-\tfrac{1}{2}5!\right] = a_0^4 4!\left(1-\tfrac{5}{2}\right) = -a_0^4 4!\tfrac{3}{2} = -36a_0^4$$

and

$$\langle 200|z|210\rangle = \langle 210|z|200\rangle = -36a_0^4(2a_0)^{-3}\frac{2}{\sqrt{3}}\sqrt{\frac{4\pi}{3}}\sqrt{\frac{1}{4\pi}} = -3a_0$$

Eigenvalues

The eigenvalue equation is then

$$-3e\mathcal{E}a_0\begin{pmatrix}0&0&0&0\\0&0&0&1\\0&0&0&0\\0&1&0&0\end{pmatrix}\begin{pmatrix}\alpha_1\\\alpha_2\\\alpha_3\\\alpha_4\end{pmatrix}=E_2^{(1)}\begin{pmatrix}\alpha_1\\\alpha_2\\\alpha_3\\\alpha_4\end{pmatrix}$$

The secular equation

$$\begin{vmatrix}-\lambda&&&\\&-\lambda&&1\\&&-\lambda&\\&1&&-\lambda\end{vmatrix}=0$$

yields

$$\lambda^2(\lambda^2-1)=0$$

gives the values $\lambda=0,0,\pm1$, and the eigenvalues.

$$E_2^{(1)}=0,0,\pm3e\mathcal{E}a_0$$

Eigenvectors

The eigenvectors may be obtained from

$$-3e\mathcal{E}a_0\begin{pmatrix}0&0&0&0\\0&0&0&1\\0&0&0&0\\0&1&0&0\end{pmatrix}\begin{pmatrix}\alpha_1\\\alpha_2\\\alpha_3\\\alpha_4\end{pmatrix}=E_2^{(1)}\begin{pmatrix}\alpha_1\\\alpha_2\\\alpha_3\\\alpha_4\end{pmatrix}$$

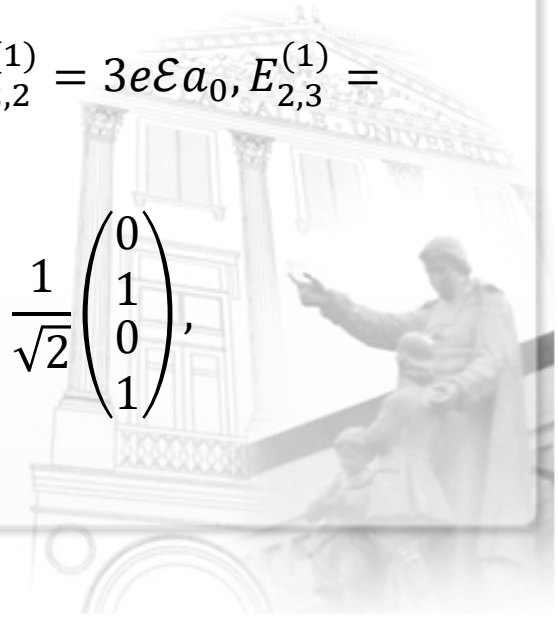
giving

$$-3e\mathcal{E}a_0\alpha_4=E_2^{(1)}\alpha_2$$

$$-3e\mathcal{E}a_0\alpha_2=E_2^{(1)}\alpha_4$$

Thus, if we arrange the eigenvalues are follows: $E_{2,1}^{(1)}=0, E_{2,2}^{(1)}=3e\mathcal{E}a_0, E_{2,3}^{(1)}=0, E_{2,4}^{(1)}=-3e\mathcal{E}a_0$, then

$$u_1=\begin{pmatrix}1\\0\\0\\0\end{pmatrix},\quad u_2=\frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\0\\-1\end{pmatrix},\quad u_3=\begin{pmatrix}0\\0\\1\\0\end{pmatrix},\quad u_4=\frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\0\\1\end{pmatrix},$$



Eigenkets

The presence of a uniform electric field breaks the degeneracy of the $n = 2$ states. In bra-ket notation,

$$|u_1\rangle = |211\rangle, \quad |u_2\rangle = \frac{1}{\sqrt{2}}[|210\rangle - |200\rangle], \quad |u_3\rangle = |21,-1\rangle, \quad |u_4\rangle = \frac{1}{\sqrt{2}}[|210\rangle + |200\rangle]$$