CHAPTER IV

THE HYDROGEN SPECTRUM

In this chapter we will derive the energy spectrum of the hydrogen atom by solving the system of matrix equations (3.15a) to (3.15d) in the previous chapter. In doing this, the values of the matrix elements of the time-independent vector matrix $\hat{\vec{U}}$ in these equations are to be set in accordance with the Hönl-Kronig formula for the intensities of the Zeeman components.

First, consider the case that $\hat{L}_z$ and $\hat{\vec{L}}^2$ are diagonal matrices for this case, where the degeneracy is removed by superimposing and additional central field and a weak magnetic field in the z-direction. For a given value of $\hat{\vec{L}}^2$, let the possible values of $\hat{L}_z$ be

$$\hat{L}_{z}{}^{l,m}_{l,m} = \frac{mh}{2\pi} \qquad (4.1)$$

where m runs from $-l$ to $+l$:

$$-l \leqslant m \leqslant l \qquad (4.1a)$$

Further, let the partial vibrations of $\hat{L}$, which belong to a change in m by ± 1, be left - and right-circular in the (x, y) - plane :

$$\hat{L}_{y}{}^{l,\,m}_{l,m\pm1} = \pm i\,\hat{L}_{x}{}^{l,m}_{l,m\pm1}$$

It then follows from (3.15a) that

$$\left|\hat{L}_{x\,l,m\mp1}^{\;l,m}\right|^2 = \left|\hat{L}_{y\,l,m\mp1}^{\;l,m}\right|^2 = \frac{1}{4}\frac{h^2}{4\pi^2}\cdot\left[l(l+1) - m(m\mp1)\right]$$

$$= \frac{1}{4}\frac{h^2}{4\pi^2}\,(l\pm m)(l+1\mp m)$$

and $$(\hat{L}^2)_{l,m}^{l,m} = \frac{h^2}{4\pi^2}\,l(l+1) \qquad (4.2)$$

Next we set for the matrix $\hat{\vec{U}}$,

$$\hat{U}_{y\,l',m\pm1}^{\;l,m} = \pm i\hat{U}_{x\,l',m\pm1}^{\;l,m} \qquad (l' = l+1 \text{ or } l-1), \qquad (4.3)$$

$$\left|\hat{U}_{x\,l,m\pm1}^{\;l+1,m}\right|^2 = \left|\hat{U}_{y\,l,m\pm1}^{\;l+1,m}\right|^2 = \frac{1}{4}\,C_l^{l+1}\,(l\mp m)(l\mp m+1) \qquad (4.4)$$

in accordance with the Hönl-Kronig formula for the intensities of the Zeeman components (9). These intensities are characteristic of the squares of transition elements for an atomic system when a preferred direction, the z-axis, is given, their ratios should be identical to the ratios of the absolute squares of the corresponding matrix elements of $\hat{\vec{U}}$.

When m is replaced by m-1 or m+1, it further follows that

$$\left|\hat{U}_{x\,l+1,m\pm1}^{\;l,m}\right|^2 = \left|\hat{U}_{y\,l+1,\,m\pm1}^{\;l,m}\right|^2$$

$$= \frac{1}{4}\,C_{l+1}^{l}\,(l\pm m+1)(l\pm m+2) \qquad (4.4a)$$

Finally, we have for $\hat{U}_z$

$$\left|\hat{U}_{z\,l,m}^{l+1,m}\right|^2 = C_l^{l+1}\left[(l+1)^2 - m^2\right] \tag{4.5}$$

It still remains to be seen whether m (and thus also l) is an integer or half-integer ; also, the C_l^{l+1} remain for the time being undetermined functions of l which can never take on negative values and which satisfy the symmetry relation

$$C_l^{l+1} = C_{l+1}^{l} \tag{4.6}$$

A further remark concerning the signs of $\hat{\vec{U}}$ relative to those of $\hat{\vec{L}}$: if $\hat{L}_x$ and $\hat{U}_z$ are assumed to be positive and real, then $\hat{U}_x$ has to be taken as positive or negative (and real) depending on whether one is dealing with transitions that correspond to changes of l and m in the opposite sense (as for $\hat{U}_{x\,l+1,m-1}^{\,l,m}$ and $\hat{U}_{x\,l-1,m+1}^{\,l,m}$) or in the same sense (as for $\hat{U}_{x\,l+1,m+1}^{\,l,m}$ and $\hat{U}_{x\,l-1,m-1}^{\,l,m}$). When the calculations are carried through, it is evident that this approach satisfies equations (3.15a) and (3.15b) of the previous chapter. Moreover, it follows conversely that if $\hat{\vec{L}}^2$ and $\hat{L}_z$ are assumed to be diagonal matrices, the expression chosen here for $\hat{\vec{U}}$ and $\hat{\vec{L}}$ is a necessary consequence of (3.15a) and (3.15b).

In order to determine the normalization of m and l and the function C_{l+1}^{l} , we make use of equation (3.15c) from the preceding chapter. It suffices, however, to use just the z-component,

$$\left[\hat{U}_x, \hat{U}_y\right] = \frac{h}{2\pi i}\,\frac{2}{m_o e^4}\,\hat{E}\hat{L}_z \tag{4.7}$$

Namely, if we form the expression

$$\hat{L}_y \left[\hat{U}_x, \hat{U}_y\right] - \left[\hat{U}_x, \hat{U}_y\right] \hat{L}_y = \frac{h}{2\pi i} \cdot \frac{2}{m_o e^4} \hat{E} \left[\hat{L}_y, \hat{L}_z\right]$$

and use (3.15a) and (3.15b), we obtain an equation which agrees with the x-component of (3.15c). Similarly, the y-component of (3.15c) also follows from the z-component of this vector equation and equations (3.15a) and (3.15b).

If we form the element of equation (4.7) which occupies the (l, m) position in the diagonal series, we first obtain, for the left-hand side, from (4.3) and (4.4),

$$\left[\hat{U}_x, \hat{U}_y\right]^{l,m}_{l,m} = (\hat{U}_x\hat{U}_y - \hat{U}_y\hat{U}_x)^{l,m}_{l,m} = 2i\left\{\left|\hat{U}_{x\,l+1,m-1}^{\,l,m}\right|^2 - \left|\hat{U}_{x\,l+1,m+1}^{\,l,m}\right|^2 + \left|\hat{U}_{x\,l-1,m-1}^{\,l,m}\right|^2 - \left|\hat{U}_{x\,l-1,m+1}^{\,l,m}\right|^2\right\}$$

$$= 2i\left\{\tfrac{1}{4}C^{l}_{l+1}(l-m+1)(l-m+2) - \tfrac{1}{4}C^{l}_{l+1}(l+m+1)(l+m+2) + \tfrac{1}{4}C^{l}_{l-1}(l+m-1)(l+m) - \tfrac{1}{4}C^{l}_{l-1}(l-m-1)(l-m)\right\}$$

$$= im\left\{-(2l+3)C^{l+1}_{l} + (2l-1)C^{l}_{l-1}\right\} \qquad (4.8)$$

Noting that E has a negative sign. From equation (4.7) and (4.8) together with the value of $\hat{L}_z$ given by (4.1) yield the condition

$$m\left\{-(2l+3)C^{l+1}_{l} + (2l-1)C^{l}_{l-1}\right\} = m\left\{-\frac{h^2}{2\pi^2}\,\frac{E}{m_o e^4}\right\}$$

$$= m\left\{\frac{h^2}{2\pi^2}\,\frac{|E|}{m_o e^4}\right\} \qquad (4.9)$$

Let us consider the smallest possible value of l for a given $|E|$. Obviously the contribution from the transition $l \rightarrow l-1$ on the left-hand side vanishes for this value of l, and the coefficient of m on the left-hand side can therefore not be positive, whereas the coefficient of m on the right-hand side is positive. Hence equation (4.9) can be satisfied for the minimum value of l only if $m = 0$. But according to (4.1), this means that the minimum value of l must vanish, since otherwise m could assume other, non-zero, values. Hence l and m are necessarily integer, and l assumes the values

$$l = 0, 1, 2, \ldots, n^*, \qquad (4.10)$$

the integer n^* being the largest value of l that can be attained for a given $|E|$. Now (4.9) implies

$$(2l-1)C^l_{l-1} - (2l+3)C^{l+1}_l = \frac{h^2}{2\pi^2} \cdot \frac{|E|}{m_o e^4} \quad \text{for } l = 1, \ldots, n^* \qquad (4.11a)$$

Furthermore, we have to set

$$C^{n^*+1}_{n^*} = 0 \qquad (4.11b)$$

since obviously the contribution from the transition $l+1 \rightarrow l$ (second term) disappears for $l = n^*$. Beginning with $l = n^*$ and reducing l stepwise, we can successively calculate the values of

$$C^{n^*}_{n^*-1}, \quad C^{n^*-1}_{n^*-2}, \quad \ldots, \quad C^1_o$$

from (4.11a), i.e. for $l = n^*$ equation (4.11a) becomes

$$(2n^*-1)\,C^{n^*}_{n^*-1} - (2n^*+3)C^{n^*+1}_{n^*} = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}$$

$$\therefore\ C^{n^*}_{n^*-1} = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4\,(2n^*-1)}$$

for $l = n^*-1$,

$$(2n^*-3)C^{n^*-1}_{n^*-2} - (2n^*+1)C^{n^*}_{n^*-1} = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}$$

$$\therefore\ C^{n^*-1}_{n^*-2} = \frac{1}{(2n^*-3)}\left[\frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4} + \frac{(2n^*+1)}{(2n^*-1)}\cdot\frac{h^2}{2\pi^2}\,\frac{|E|}{m_oe^4}\right]$$

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for $l = 2$,

$$3C^2_1 - 7C^3_2 = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}$$

$$\therefore\ C^2_1 = \frac{1}{3}\left[\frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4} + 7C^3_2\right]$$

for $l = 1$,

$$C^1_o - 5C^2_1 = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}$$

$$\therefore\ C^1_o = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4} + 5C^2_1$$

The results can be expressed by the formula

$$C_l^{l+1} = \frac{h^2}{2\pi^2} \cdot \frac{|E|}{m_o e^4} \cdot \frac{n^*(n^*+2) - l(l+2)}{(2l+1)(2l+3)}$$

$$= \frac{h^2}{2\pi^2} \cdot \frac{|E|}{m_o e^4} \cdot \frac{(n^*-l)(n^*+l+2)}{(2l+1)(2l+3)} \qquad (4.12a)$$

Replacing l by $l-1$, we also obtain

$$C_{l-1}^{l} = \frac{h^2}{2\pi^2} \cdot \frac{|E|}{m_o e^4} \cdot \frac{n^*(n^*+2)-(l-1)(l+1)}{(2l-1)(2l+1)}$$

$$= \frac{h^2}{2\pi^2} \cdot \frac{|E|}{m_o e^4} \cdot \frac{(n^*-l+1)(n^*+l+1)}{(2l-1)(2l+1)} \qquad (4.12b)$$

with the help of these formulae. We can confirm directly that relations (4.11a) and (4.11b) are satisfied.

In order to derive the energy value itself, we make use of the last equation (3.15d). First of all, we determine the value of $\hat{\vec{U}}^2$ at the (l, m) position of the diagonal series.

Because of (4.4) and (4.5), we obtain

$$(\hat{U}^2)_{l,m}^{l,m} = 2\left|\hat{U}_{x\,l+1,m+1}^{\;l,m}\right|^2 + 2\left|\hat{U}_{x\,l+1,m-1}^{\;l,m}\right|^2 + \left|\hat{U}_{z\,l+1,m}^{\;l,m}\right|^2$$

$$+ 2\left|\hat{U}_{x\,l-1,m+1}^{\;l,m}\right|^2 + 2\left|\hat{U}_{x\,l-1,m-1}^{\;l,m}\right|^2 + \left|\hat{U}_{z\,l-1,m}^{\;l,m}\right|^2$$

$$= 2\cdot\frac{1}{4}\,C_{l+1}^{l}(l+m+1)(l+m+2) + 2\cdot\frac{1}{4}\,C_{l+1}^{l}(l-m+1)(l-m+2)$$

$$+ C_{l+1}^{l}\left[(l+1)^2-m^2\right] + 2\cdot\frac{1}{4}\,C_{l-1}^{l}(l+m-1)(l+m)$$

$$+ 2\cdot\frac{1}{4}C_{l-1}^{l}(l-m-1)(l-m) + C_{l-1}^{l}\,(l^2-m^2)$$

$$\therefore\ (\hat{U}^2)^{l,m}_{l,m} = (l+1)(2l+3)C^{l}_{l+1} + l(2l-1)C^{l}_{l-1}$$

and on substituting from (4.12a) and (4.12b),

$$(\hat{U}^2)^{l,m}_{l,m} = (l+1)(2l+3)\ \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}\cdot\frac{(n^*-l)(n^*+l+2)}{(2l+1)(2l+3)}$$

$$+\ l(2l-1)\ \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}\cdot\frac{(n^*-l+1)(n^*+l+1)}{(2l-1)(2l+1)}$$

$$= \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}\left[\frac{(l+1)(n^*-l)(n^*+l+2)}{(2l+1)} + \frac{l(n^*-l+1)(n^*+l+1)}{(2l+1)}\right]$$

$$= \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}\ (n^{*2}+2n^*-l^2-l)$$

$$= \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}\ \left[n^{*2}+2n^*-l(l+1)\right] \qquad (4.13)$$

This expression for $\hat{\vec{U}}^2$ and the expression (4.2) for $\hat{\vec{L}}^2$ now have to be substituted in (3.15d). it yeilds

$$1-\frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}(n^{*2}+2n^*-l^2-l) = \frac{2}{m_oe^4}\ |E|\left[\frac{h^2}{4\pi^2}l(l+1) + \frac{h^2}{4\pi^2}\right]$$

$$= \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}\ (l^2+l+1)$$

$$\therefore\quad 1 = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}(n^{*2}+2n^*+1)$$

$$1 = \frac{h^2}{2\pi^2}\cdot\frac{|E|}{m_oe^4}\ (n^*+1)^2$$

Finally,

$$|E| = \frac{2\pi^2 m_o e^4}{h^2(n^*+1)^2}$$

$$= \frac{2\pi^2 m_o e^4}{h^2 n^2} \qquad \text{(setting } n^*+1 = n\text{)}$$

or

$$E = -2\pi^2 \cdot \frac{m_o e^4}{n^2 h^2}$$

which is the well-known energy formula for the hydrogen atom.