The Algebraic Hydrogen Atom

The energy levels of the non-relativistic hydrogen atom can be derived without solving for the associated states by making use of the Runge-Lenz vector which we met in the solution to the classical Kepler problem. This magical vector also provides us with ladder operators which convert states of differing l quantum number but the same principal quantum number, n.

We want to find the energy levels of the non-relativistic hydrogen atom Hamiltonian,

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2 c}{r} \tag{1}$$

where e^2 is the electron charge (possibly factored by $1/4\pi\varepsilon_0$, depending which units you prefer).

Following Chapter ? we introduce the Runge-Lenz vector, now in operator form,

$$\overline{M} = \frac{1}{2m}\left(\overline{p} \times \overline{L} - \overline{L} \times \overline{p}\right) - e^2 c\hat{r} \tag{2}$$

where the angular momentum operator is,

$$\overline{L} = \overline{r} \times \overline{p} \tag{3}$$

An explicit form for the momentum operator, $\overline{p}$, such as its representation in the spatial basis as $i\hbar\overline{\nabla}$, need not be specified. Instead we just need its commutation properties,

$$\left[x_i, x_j\right] = 0 \qquad \text{and} \qquad \left[p_i, p_j\right] = 0 \qquad \text{and} \qquad \left[x_i, p_j\right] = i\hbar\delta_{ij} \tag{4}$$

The commutators involving $\overline{L}$ and $\overline{M}$ can then be found (simply, if tediously). The result has already been given in Chapter ?,

$$\left[L_j, L_k\right] = i\hbar \in_{jkn} L_n \tag{5}$$

$$\left[M_j, L_k\right] = i\hbar \in_{jkn} M_n \tag{6}$$

$$\left[M_j, M_k\right] = -\frac{2i\hbar}{m}\hat{H} \in_{jkn} L_n \tag{7}$$

$$\left[\overline{M}, \hat{H}\right] = \left[\overline{L}, \hat{H}\right] = 0 \tag{8}$$

Equ.(8) corresponds to $\overline{L}$ and $\overline{M}$ being constants of the motion (see Chapter ?). In the context of the Kepler problem, $\overline{M}$ lies in the plane of the orbit whereas $\hat{L}$ is perpendicular to the plane of the orbit. Correspondingly we find that the operators obey,

$$\overline{L} \cdot \overline{M} = \overline{M} \cdot \overline{L} = 0 \tag{9}$$

Finally, the counterpart of the classical expression for the square of the Runge-Lenz operator, $M^2 = \dfrac{2E}{m} L^2 + K^2$, can be derived to be,

$$M^2 = \frac{2\hat{H}}{m}\left(L^2 + \hbar^2\right) + e^4 c^2 \tag{10}$$

We now confine attention to,

- a degenerate sub-space of Hilbert space for which all states have the same energy, E;

- bound states so that $E < 0$.

So long as we confine attention to this sub-space we can replace the Hamiltonian operator on the RHS of (7) simply with E and we can normalised the Runge-Lenz vector operator such that,

$$\overline{M}' = \sqrt{-\frac{m}{2E}} \cdot \overline{M} \tag{11}$$

So that (5-7) become,

$$\left[L_j, L_k\right] = i\hbar \in_{jkn} L_n \tag{12}$$

$$\left[M'_j, L_k\right] = i\hbar \in_{jkn} M'_n \tag{13}$$

$$\left[M'_j, M'_k\right] = i\hbar \in_{jkn} L_n \tag{14}$$

The substitution,

$$N_j^{\pm} = \left(L_j \pm M'_j\right)/2 \tag{15}$$

leads to a simpler set of commutators,

$$\left[N_j^+, N_k^+\right] = i\hbar \in_{jkn} N_n^+ \tag{16}$$

$$\left[N_j^-, N_k^-\right] = i\hbar \in_{jkn} N_n^- \tag{17}$$

$$\left[N_j^+, N_k^-\right] = 0 \tag{18}$$

So the algebra decomposes into two closed but independent algebras, one for $\overline{N}^+$ and one for $\overline{N}^-$, these two sub-algebras being identical and equal to the Lie algebra of the Lie group SU(2) – the universal covering group of the group of rotations in 3-dimensions, SO(3), and the group of the (non-relativistic) Pauli spinors. The utility of this is that we already understand the eigenvalue structure of the algebra of SU(2) from considerations of angular momentum. Denoting $N_+^2 \equiv \overline{N}^+ \cdot \overline{N}^+$ the eigenvalues are,

$$N_+^2 = n_+\left(n_+ + 1\right)\hbar^2 \qquad \text{and} \qquad N_-^2 = n_-\left(n_- + 1\right)\hbar^2 \tag{19}$$

where $n_{\pm}$ take half-integral values 0, ½, 1, $^3/_2$, 2, $^5/_2$,… Now it follows from (15) that,

$$N_+^2 + N_-^2 = \left(L^2 + M'^2\right)/2 \qquad \text{and} \qquad N_+^2 - N_-^2 = \left(\overline{L} \cdot \overline{M}' + \overline{M}' \cdot \overline{L}\right)/2 \tag{20}$$

But from (9) the second of (20) gives $N_+^2 = N_-^2$, so in this particular application (the hydrogen atom) we require $n_+ = n_-$. Hence the first of (20) becomes,

$$\left(L^2 + M'^2\right)/2 = \frac{1}{2}\left(L^2 - \frac{m}{2E}M^2\right) = 2n_+(n_+ + 1)\hbar^2 \tag{21}$$

But from (10) we have,

$$L^2 - \frac{m}{2E}M^2 = -\left(\frac{e^4 mc^2}{2E} + \hbar^2\right) \tag{22}$$

So that (21) becomes,

$$\frac{e^4 mc^2}{2E} + \hbar^2 = -4n_+(n_+ + 1)\hbar^2 \tag{23}$$

Hence,

$$\frac{e^4 mc^2}{2E} = -(2n_+ + 1)^2\hbar^2 \tag{24}$$

Hence,

$$E = \frac{e^4 mc^2}{2\hbar^2(2n_+ + 1)^2} \equiv \frac{1}{2}\frac{\alpha^2 mc^2}{n^2} \tag{25}$$

where

$$n = 2n_+ + 1 \tag{26}$$

Equ.(25) is the familiar non-relativistic solution for the energy levels of a hydrogen atom, where $\alpha = e^2/\hbar$ is the fine structure constant and n is the principal quantum number, which, since n_+ takes half-integral values 0, ½ , 1, $^3/_2$, 2, $^5/_2$,… we see that n takes integral values 1, 2, 3, 4, 5… At the same time that Schrodinger was deriving this result from the equation which was later to bear his name, Pauli derived it by the above method, Pauli (1926).

The conversion of (12-14) to (16-18) by the substitution (15) will seem eerily familiar to those who are acquainted with the finite representations of the Lorentz group, SO(3,1). Indeed exactly the same commutator structure (12-14) can apply for the Lorentz group if the generators are chosen to be Hermetian. For the Lorentz group it is more common to choose the generators of the boosts as anti-Hermetian, which is equivalent to replacing our $\overline{M}'$ with $i\overline{M}'$. Equs.(12) and (13) are unchanged whereas (14) acquires a minus sign on the RHS. However if we stick to the Hermetian generators, as in (12-14), then a six-parameter group of unitary elements is defined by,

$$U = \exp\{i\overline{\theta}\cdot\overline{L} + i\overline{\beta}\cdot\overline{M}'\} \tag{27}$$

where $\overline{\theta}$ and $\overline{\beta}$ are each real 3-vectors. The group elements (27) are unitary by virtue of $\overline{L}$ and $\overline{M}'$ being Hermetian, which follows from (2,3). In contrast, the six-parameter group defined by elements,

$$V = \exp\{i\overline{\theta}\cdot\overline{L} + \overline{\beta}\cdot\overline{M}'\} \tag{28}$$

is not unitary. The rotations, $\exp\{i\overline{\theta}\cdot\overline{L}\}$ are unitary, but the boosts, $\exp\{\overline{\beta}\cdot\overline{M}'\}$, are not. A representation of the generators as 4 x 4 matrices is,

$$\overline{L} = \hbar \left[\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \right] \tag{29}$$

$$\overline{M}' \equiv \hbar \left[\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \right] \tag{30}$$

From these it is easily confirmed that the unitary group elements, (27), leave invariant the 4-dimensional Euclidean metric $w^2 + x^2 + y^2 + z^2$ whereas the non-unitary group elements (28) preserve the Minkowski metric $t^2 - x^2 - y^2 - z^2$. There is a reason why the representation (28-30) of the Lorentz group is not unitary. There is a general theorem that non-compact Lie groups have no finite unitary representations. And the Lorentz group is non-compact because, as a result of the signature of the Minkowski metric, a boost which preserves this metric can be repeated indefinitely without reproducing a group element.

References

W.Pauli (1926) Z.Physik, **36**, 336

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