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ABSTRACT

The eigenvalues and eigenfunctions for the hydrogen atom Schrödinger equation can be easily obtained after factorizing that equation in appropriate ways. The resulting factors resemble the creation and annihilation operators that Dirac introduced for the harmonic oscillator.

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I. INTRODUCTION

The standard way of solving the hydrogen atom problem consists in relating its Schrödinger equation to associated Legendre and Laguerre equation. Thus, the wave functions can be written in terms of the corresponding polynomial solutions[1].

In this paper, I present a different approach to the hydrogen problem. This approach is, in some ways, similar to Dirac's treatment of the harmonic oscillator problem by means of the creation and annihilation (or rising and lowering) operators[2]. There, the oscillator Schrödinger equation is factorized in terms of these operators which can also be used to generate the wave functions.

For the hydrogen-like atom, the equivalent of Dirac's method was lacking. This is remedied in the present paper where I show how to treat the hydrogen atom without recourse to previous knowledge of Legendre or Laguerre associated (or otherwise) equations.

Here also, the Schrödinger equation for an hydrogen-like atom is factorized in terms of operators that generate all the wave functions. This is done for both the angular and radial parts which are treated, respectively, in sections II and III.

II. ANGULAR MOMENTUM

The first part of this section contains a totaly conventional presentation of orbital angular momentum in quantum mechanics and is only included for the sake of completeness. Then, starting with Eq. (9), I show how to obtain very easily one of the spherical harmonics of a multiplet. From it, all the other spherical harmonics can be generated.

In spherical coordinates (r,θ,ϕ) the three independent angular momentum operators can be chosen as[3]:

$$L_{\pm} = L_x \pm iL_y = \hbar\, e^{\pm i\phi}\,(\pm\frac{\partial}{\partial\theta} + i\,\cot\theta\,\frac{\partial}{\partial\phi}) \qquad (1)$$

and

$$L_z = -i\hbar \frac{\partial}{\partial \phi} \quad , \tag{2}$$

with the commutation relations

$$[L_\pm , L_z] = \mp \hbar L_\pm \quad , \quad [L_+ , L_-] = 2\hbar L_z \quad . \tag{3}$$

The operator for the angular momentum square

$$L^2 = \frac{1}{2} (L_+ L_- + L_- L_+) + L_z^2 \quad , \tag{4}$$

commutes with any one of the components of L . Let us single out L_z and call $Y_{\beta m}$ the simultaneous eigenfunctions of L_z and L^2 according to

$$L_z \, Y_{\beta m}(\theta,\phi) = \hbar \, m \, Y_{\beta m}(\theta,\phi) \tag{5}$$

and

$$L^2 \, Y_{\beta m}(\theta,\phi) = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2}\right] Y_{\beta m}$$

$$= \hbar^2 \beta \, Y_{\beta m}(\theta,\phi) \quad . \tag{6}$$

It follows that

$$Y_{\beta m}(\theta,\phi) = e^{im\phi} \, P_{\beta m}(\theta) \quad , \tag{7}$$

where m is an integer and $P_{\beta m}(\theta)$ has to be a solution of

$$\left[\sin\theta \frac{\partial}{\partial\theta}(\sin\frac{\partial}{\partial\theta}) + \beta\sin^2\theta - m^2\right] P_{\beta m}(\theta) = 0 \quad . \tag{8}$$

Looking for a simple way of solving this equation, let us try to

factor it out as

$$\left[\sin\theta\frac{\partial}{\partial\theta} + m\cos\theta\right]\left[\sin\theta\frac{\partial}{\partial\theta} + C - m\cos\theta\right]P_{\beta m} =$$

$$= C\left[\sin\theta\frac{\partial}{\partial\theta} + m\cos\theta\right]P_{\beta m}(\theta) \quad . \tag{9}$$

It is easy to see that Eq. (8) can be written in the form (9) for a particular $m=M$ such that

$$\beta = M(M+1) \quad , \tag{10}$$

a llowing for any nonvanishing constant C . In this special case, $P_{\beta M}(\theta)$ being a solution of

$$\left(\sin\theta\frac{\partial}{\partial\theta} - M\cos\theta\right)P_{\beta M} = 0 \quad , \tag{11}$$

can be readily obtained as

$$P_{\beta M}(\theta) = N_M \sin^M\theta \quad , \tag{12}$$

where N_M is a normalization factor.

From the commutators in Eqs. (3) it immediately follows that L_+ and L_- are rising and lowering operators and it is easy to verify that

$$L_+ P_{\beta M}(\theta) = 0 \quad , \tag{13}$$

which leads us to the conclusion that $M=\ell$, maximum eigenvalue of $L_z/\hbar$. Then, from Eq. (10), $\beta=\ell(\ell+1)$ which makes it convenient to change labels as follows:

$$Y_{\beta m}(\theta) \rightarrow Y_{\ell m}(\theta) \quad . \tag{14}$$

The highest eigenfunction Y of the ℓ multiplet is, according to Eqs. (7) and (12),

$$Y_{\ell\ell}(\theta,\phi) = N_\ell \, e^{i\ell\phi} \sin^\ell \theta$$

$$= (-1)^\ell \left[\frac{(2\ell+1)(2\ell)!}{4\pi \, 2^{2\ell} \, (\ell!)^2}\right]^{1/2} e^{i\ell\phi} \sin^\ell \theta \quad , \tag{15}$$

where the value of N_ℓ was calculated by normalizing $Y_{\ell\ell}$ on the unit sphere and adopting the $(-1)^\ell$ sign convention[3].

The rest is simple, all the other $Y_{\ell m}$ are obtained by repeated operations with L_-, i.e.,

$$Y_{\ell(m-1)}(\theta) = \frac{N_{(m-1)}}{N_m} \, L_- \, (\theta,\phi) \, Y_{\ell m}(\theta) \quad , \tag{16}$$

followed by normalizations.

III. HYDROGEN-LIKE ATOMS

Here, we go on to solve the problem of hydrogen-like atoms in a very simple way that does not require series expansions or having to look up Laguerre polynomials in a book.

The Schrödinger equation for an hydrogen-like atom is, in spherical coordinates[1],

$$\left[-\frac{\hbar^2}{2\mu} \, \frac{1}{r} \, \frac{d^2}{dr^2} \, r + \frac{L^2}{2\mu r^2} - \frac{Ze^2}{r}\right] \psi_{n\ell m}(r,\theta,\phi)$$

$$= E_{n\ell m} \, \psi_{n\ell m}(r,\theta,\phi) \quad , \tag{17}$$

where $(-e)$ and (Ze) are the charges of the electron and the nucleus, μ is the reduced mass, $E_{n\ell m}$ are the energy eigenvalues

which , in principle, depend on ℓ , m and, possibly, on other quantum numbers designated collectively by n .

If we separate the wave function as

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\ Y_{\ell m}(\theta,\phi) \quad , \quad R_{n\ell} = r^{-1}\ N_{n\ell}\ U_{n\ell}(r) \quad , \tag{18}$$

and solve the angular part as in section II we end up with

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + \frac{2Z}{a_o r}\right] U_{n\ell}(r) = \varepsilon^2_{n\ell}\ U_{n\ell}(r) \quad , \tag{19}$$

in which

$$a_o = (\hbar^2/me^2) \quad , \quad \varepsilon^2_{n\ell} = -2\mu\ E_{n\ell}/\hbar^2 \quad .$$

The normalization conditions

$$\int_0^\infty \left[R_{n\ell}(r)\right]^2 r^2\ dr = N^2_{n\ell} \int_0^\infty \left[U_{n\ell}(r)\right]^2 dr = 1 \tag{21}$$

fix the value of the constants $N_{n\ell}$ in (8).

For a particular eigenvalue $\ell=\lambda$ such that

$$\varepsilon^2_\lambda = Z^2/a^2_o(\lambda+1)^2 \quad , \tag{22}$$

Eq. (19) can be rewritten as

$$\left(\frac{d}{dr} - \varepsilon_\gamma + \frac{\lambda+1}{r}\right)\left(\frac{d}{dr} + \gamma - \frac{\lambda+1}{r}\right) U_{n\lambda}(r)$$

$$= (\gamma - \varepsilon_\lambda)\left(\frac{d}{dr} - \varepsilon_\lambda + \frac{\lambda+1}{r}\right) U_{n\lambda}(r) \quad , \tag{23}$$

where γ is any constant but ε_λ . In such a case, $U_{n\lambda}(r)$ is a solution of

$$\left(\frac{d}{dr} + \gamma - \frac{\lambda+1}{r}\right) U_{n\lambda}(r) = (\gamma-\varepsilon_\lambda)\, U_{n\lambda}(r) \quad , \tag{24}$$

and has to be of the form

$$U_{n\lambda}(r) = r^{\lambda+1} \; e^{-\varepsilon_\lambda r} \quad . \tag{25}$$

Let us go back to Eq. (19) and notice that it can be written in the form

$$\left[\frac{d}{dr} - \frac{Z}{a_o(\ell+1)} + \frac{\ell+1}{r}\right]\left[\frac{d}{dr} + \frac{Z}{a_o(\ell+1)} - \frac{\ell+1}{r}\right] U_{n\ell}(r) =$$

$$= \left[\varepsilon_{n\ell} - \frac{Z^2}{a_o^2(\ell+1)^2}\right] U_{n\ell}(r) \quad . \tag{26}$$

The factors

$$A_{\ell+1} = \left[\frac{d}{dr} - \frac{Z}{a_o(\ell+1)} + \frac{\ell+1}{r}\right] \tag{27}$$

and

$$B_\ell = \left[\frac{d}{dr} + \frac{Z}{a_o(\ell+1)} - \frac{\ell+1}{r}\right] \quad . \tag{28}$$

will play a very important role in the following. They are, respectively, lowering and rising operators as we will soon see.

In Eq. (26) we have the equation for the $U_{n\ell}$ eigenfunction. The equation for $U_{n(\ell+1)}$ (one more unit for angular momentum) is simply obtained by reversing the factors on the left hand side of Eq. (26), namely

$$B_\ell \; A_{\ell+1} \; U_{n(\ell+1)} = \left[\varepsilon_{n(\ell+1)} - \frac{Z^2}{a_o^2(\ell+1)^2}\right] U_{n(\ell+1)} \quad . \tag{29}$$

On the other hand, Eq. (26) multiplied on the left by B_ℓ yields

$$B_\ell \, A_{\ell+1} \, B_\ell \, U_{n\ell} = \left[\varepsilon_{n\ell} - \frac{Z^2}{a_o^2(\ell+1)^2}\right] B_\ell \, U_{n\ell} \quad , \tag{30}$$

while multiplication of Eq. (29) on the left with $A_{\ell+1}$ gives

$$A_{\ell+1} \, B_\ell \, A_{\ell+1} \, U_{n(\ell+1)} = \left[\varepsilon_{n(\ell+1)} - \frac{Z^2}{a_o^2(\ell+1)^2}\right] A_{\ell+1} \, U_{n(\ell+1)} \quad . \tag{31}$$

A comparison between Eqs. (26) and (31) and bwtween Eqs. (29) and (30) shows two things: (1) $\varepsilon_{n(\ell+1)} = \varepsilon_{n\ell}$, the eigenvalue does not change when we go from one ℓ to another in the same n multiplet; (2) we must have

$$A_\ell \, U_{n\ell}(r) = \left[\frac{d}{dr} - \frac{Z}{a_o \ell} + \frac{\ell}{r}\right] U_{n\ell} = U_{n(\ell-1)} \tag{32}$$

and

$$B_\ell \, U_{n\ell}(r) = U_{n(\ell+1)}(r) \quad . \tag{33}$$

That is, A_ℓ and B_ℓ are, as promised, lowering and rising operators.

Applying B_ℓ of Eq. (28) for $\ell=\lambda$ on the eigenfunction $U_{n\lambda}$ of Eq. (25), we see that

$$B_\lambda \, U_{n\lambda}(r) = 0 \quad . \tag{34}$$

λ appearing in Eqs. (22)-(26) is then, the maximum value of ℓ in the n multiplet[4]. It is convenient to relate the label n to λ by $n=\lambda+1$, in terms of which, from Eqs. (20) and (22), we have

$$\varepsilon_n = \frac{Z}{a_o n} \quad , \quad E_n = -\mu \frac{Z^2 \, e^4}{2h^2 \, n^2} \quad , \quad 0 \leq \ell \leq (n-1) \quad . \tag{35}$$

All the $U_{n\ell}$ functions belonging to the same multiplet can be derived by repeated application of the operator A_ℓ on the

function (25). Let me take as an example the M shell with $n=3$ and a maximum $\ell=2$ and, according to Eqs. (25) and (35),

$$u_{3,2}(r) = r^3 \, e^{-Zr/3a_o} \quad . \tag{36}$$

The next lowest function is

$$u_{3,1}(r) = A_2 \, u_{3,2} = \left(\frac{d}{dr} - \frac{Z}{2a_o} + \frac{2}{r}\right) r^3 \, e^{-Zr/3a_o}$$

$$= \frac{5}{4} \left(4 - \frac{2Zr}{3a_o}\right) r^2 \, e^{-Zr/3a_o} \quad , \tag{37}$$

and the lowest is[5]

$$u_{3,0}(r) = A_1 \, u_{31}$$

$$= \frac{5}{4} \left(\frac{d}{dr} - \frac{Z}{a_o} + \frac{1}{r}\right) \left(4 - \frac{2Zr}{3a_o}\right) r^2 \, e^{-Zr/3a_o}$$

$$= \frac{5}{2} \left(6 - \frac{4Zr}{a_o} + \frac{4 \, Z^2 r^2}{9a_o^2}\right) r \, e^{-Zr/3a_o} \quad . \tag{38}$$

The corresponding radial wave functions $R_{n\ell}$ are these, times r and the appropriate $N_{n\ell}$[6].

It is easy to see that the radial quantum numbers $n_r=(n-\ell-1)$ are equal to the number of nodes of the radial wave functions.

IV. CONCLUDING REMARKS

A new method for solving the quantum-mechanical hydrogen atom problem was presented. As compared to the traditional one, this method has the virtue of providing a simple way of

constructing the wave functions.

The method resembles Dirac's treatment of the harmonic oscillator in terms of annihilation (a) and creation (a^+) operators. Here also, one can construct lowering (A_ℓ) and rising (B_ℓ) operators that connect different wave functions. But, unlike the harmonic oscillator a and a^+ operators, A_ℓ and B_ℓ only relate eigenfunctions belonging to the same n multiplet (same energy).

The highest ℓ eigenfunction in a multiplet is obtained by solving a trivial first order differential equation that follows when Schrödinger equation is factorized in a suitable way. Then, successive operations with A_ℓ generate the rest of the wave functions.

FOOTNOTES AND REFERENCES

1. See, for instance, L.I. Schiff, "Quantum Mechanics" (McGraw-Hill, New York, 1968), pp. 76-83 and 88-94.

2. A. Messiah, "Quantum Mechanics" (North-Holland, Amsterdam, 1961), Vol. 1, pp. 432-444.

3. L.I. Schiff, "Quantum Mechanics" (McGraw-Hill, New York, 1968), pp. 76-86 and 199-204.

4. With Eqs. (22)-(25) I wanted to show an interesting way of deriving the highest radial eigenfunction of a multiplet. It is not necessary, however, to go through that procedure since condition (34) yields that eigenfunction directly.

5. A_ℓ is defined for $1 \leq \ell \leq (n-1)$, while B_ℓ for $0 \leq \ell \leq (n-1)$.

6. After working out some wave functions by her (or him)-self the reader might wish to compare results with L. Pauling and E.B. Wilson, "Introduction to Quantum Mechanics" (McGraw-Hill, New York, 1935), pp. 133-136.