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Operator Representations for Radial Wave Functions of Hydrogen-like Atoms

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SUMMARY

The author presents the operator formalism in dealing with radial wave functions of hydrogen-like atoms. The essential point rests upon that the radial wave functions can be derived by successively operating lowering operators on a radial wave function having a maximum allowed orbital angular momentum quantum number. This approach resembles the operator formalism that deals with a quantum mechanical harmonic oscillator. The results agree with the conventional coordinate representation method based upon power series expansion that leads to associated Laguerre polynomials.

The operator formalism explicitly represents the mathematical constitution of quantum mechanical systems. In this article the author shows this feature by adopting radial wave functions of hydrogen-like atoms as an example.

Key Words:　Hydrogen-like atom, Radial wave function, Operator representation, Lowering operator, Associated Laguerre polynomial

1 Introduction

Hydrogen-like atoms have been dealt with by the quantum mechanical formulation and exact analytical solutions are well-understood.[1)] The relative motion of an electron is described in spherical coordinates where a method of separation of variables is well-established. Thus the radial equation for the electron is represented in a second-order differential equation as follows:

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l}{dr}\right)+\left[\frac{\hbar^2 l(l+1)}{2\mu r^2}-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\right]R_l = ER_l, \quad (1)$$

where R_l is a radial wave function parametrized with l; μ, Z, ε_0, and E denote a reduced mass of hydrogen-like atom, atomic number, permittivity of vacuum, and eigenvalue of energy. Otherwise we follow conventions. Usually the solutions are sought by a power series expansion and given by associated Laguerre polynomials.[2–6)]

It is well-known the second-order differential equations are often solved by an operator representation method. Examples include its application to a quantum mechanical harmonic oscillator.[7)] Nonetheless, the corresponding approach to the radial equation for the electron has been less popular to date. The initial approach, however, was made by Sunakawa.[8)] The purpose of this article rests upon further improvement of that approach.

2 Operator formalism

Sunakawa[8)] introduced the following differential equation by suitable transformations of a variable, parameter, and function.

$$-\frac{d^2\psi_l(\rho)}{d\rho^2}+\left[\frac{l(l+1)}{\rho^2}-\frac{2}{\rho}\right]\psi_l(\rho)=\varepsilon\psi_l(\rho), \quad (2)$$

where $\rho=\frac{Zr}{a}$, $\varepsilon=\frac{2\mu}{\hbar^2}(\frac{a}{Z})^2E$, and $\psi_l(\rho)=\rho R_l(r)$ with a ($\equiv 4\pi\varepsilon_0\hbar^2/\mu e^2$)[9)] being Bohr radius of a hydrogen-like atom. Note that ρ and ε are dimensionless quantities.

Here we define the following operators:

$$b_l \equiv \frac{d}{d\rho}+\left(\frac{l}{\rho}-\frac{1}{l}\right). \quad (3)$$

Hence,

$$b_l^\dagger = -\frac{d}{d\rho}+\left(\frac{l}{\rho}-\frac{1}{l}\right), \quad (4)$$

where the operator $b_l^\dagger$ is an adjoint operator of b_l. Notice that these definitions are different from those of Sunakawa.[8)] However, we describe the operator formalism following his literature.[8)] The operator $\frac{d}{d\rho}$ ($\equiv A$) is formally an anti-Hermitian operator[2)] and the second terms of Eqs. (3) and (4) are Hermitian operators, which we define as H. Thus we denote $b_l = A + H$ and $b_l^\dagger = -A + H$. These representations are analogous to those appearing in the operator formalism of a quantum mechanical harmonic oscillator.[7)] Special care, however, should be taken in dealing with these

operators. First, the coordinate system we have chosen is not Cartesian coordinate but the polar (spherical) coordinate, and so $\rho > 0$. Furthermore, we should carefully examine whether $\frac{d}{d\rho}$ is in fact an anti-Hermitian operator. This is because the solution $\psi_l(\rho)$ must satisfy boundary conditions in such a way that $\psi_l(\rho)$ vanishes at $\rho \to 0$ and ∞. We will come back to this point later.

We further define an operator $H^{(l)}$ as follows:

$$H^{(l)} \equiv -\frac{d^2}{d\rho^2} + \left[\frac{l(l+1)}{\rho^2} - \frac{2}{\rho}\right]. \tag{5}$$

Hence

$$H^{(l)} = b_{l+1} b_{l+1}^{\dagger} + \varepsilon^{(l)}, \tag{6}$$

where $\varepsilon^{(l)} \equiv -\frac{1}{(l+1)^2}$. Alternatively,

$$H^{(l)} = b_l^{\dagger} b_l + \varepsilon^{(l-1)}. \tag{7}$$

If we put $l = n - 1$ in Eq. (6) with n being a fixed given integer larger than l, we obtain

$$H^{(n-1)} = b_n b_n^{\dagger} + \varepsilon^{(n-1)}. \tag{8}$$

Regarding Eq. (8) we evaluate the following inner product of both sides:

$$\begin{aligned} <\chi|H^{(n-1)}|\chi> &= <\chi|b_n b_n^{\dagger}|\chi> + \varepsilon^{(n-1)} <\chi|\chi> \\ &= <b_n^{\dagger}\chi|b_n^{\dagger}|\chi> + \varepsilon^{(n-1)} <\chi|\chi> \\ &= ||b_n^{\dagger}|\chi>||^2 + \varepsilon^{(n-1)} <\chi|\chi> \\ &\geq \varepsilon^{(n-1)}. \end{aligned} \tag{9}$$

Here we assume that χ is normalized. On the basis of the variational principle the above expected value must take a minimum $\varepsilon^{(n-1)}$ so that χ can be an eigenfunction. To satisfy this condition

$$|b_n^{\dagger}\chi> = 0. \tag{10}$$

In fact, if Eq. (10) holds,

$$H^{(n-1)}\chi = \varepsilon^{(n-1)}\chi. \tag{11}$$

We define such a function as below,

$$\psi_{n-1}^{(n)} \equiv \chi. \tag{12}$$

From Eqs. (6) and (7) we have the following relationship:

$$H^{(l)}b_{l+1} = b_{l+1}H^{(l+1)}. \tag{13}$$

Meanwhile we define the functions as shown below,

$$\psi_{n-s}^{(n)} \equiv b_{n-s+1}b_{n-s+2}\cdots b_{n-1}\psi_{n-1}^{(n)}. \tag{14}$$

With these functions (s – 1) operators have been operated on $\psi_{n-1}^{(n)}$. Here $1 \le s \le n$. Note that if s takes 1, no operation of b_l takes place. For the sake of convenience we express

$$H^{(n,s)} \equiv H^{(n-s)}. \tag{15}$$

Using this notation and Eq. (13)

$$\begin{aligned}
H^{(n,s)}\psi_{n-s}^{(n)} &= H^{(n,s)}b_{n-s+1}b_{n-s+2}\cdots b_{n-1}\psi_{n-1}^{(n)} \\
&= b_{n-s+1}H^{(n,s-1)}b_{n-s+2}\cdots b_{n-1}\psi_{n-1}^{(n)} \\
&= b_{n-s+1}b_{n-s+2}H^{(n,s-2)}\cdots b_{n-1}\psi_{n-1}^{(n)} \\
&\cdots\cdots \\
&= b_{n-s+1}b_{n-s+2}\cdots H^{(n,2)}b_{n-1}\psi_{n-1}^{(n)} \\
&= b_{n-s+1}b_{n-s+2}\cdots b_{n-1}H^{(n,1)}\psi_{n-1}^{(n)} \\
&= b_{n-s+1}b_{n-s+2}\cdots b_{n-1}\varepsilon^{(n-1)}\psi_{n-1}^{(n)} \\
&= \varepsilon^{(n-1)}b_{n-s+1}b_{n-s+2}\cdots b_{n-1}\psi_{n-1}^{(n)}
\end{aligned}$$

$$= \varepsilon^{(n-1)}\psi_{n-s}^{(n)}. \tag{16}$$

Thus total n functions $\psi_{n-s}^{(n)}$ belongs to the same eigenvalue $\varepsilon^{(n-1)}$.

If we define $l \equiv n - s$ and take account of Eq. (11), total n functions $\psi_l^{(n)}$ (l = 0, 1, 2, ····, $n - 1$) belong to the same eigenvalue $\varepsilon^{(n-1)}$. Notice that $\psi_l^{(n)}$ are associated with the operators $H^{(l)}$. Thus, the solution of Eq. (2) has been given by functions $\psi_l^{(n)}$ parametrized with n and l on condition that Eq. (10) holds. As explicitly indicated in Eqs. (14) and (16), b_l lowers the parameter l by one from l to $l - 1$, when it operates on $\psi_l^{(n)}$. The operator b_0 cannot be defined as indicated in Eq. (3), and so the lowest number of l should be zero. Operators such as b_l are known as a ladder operator (lowering operator or annihilation operator in the present case).[7] The implication is that the successive operations of b_l on $\psi_{n-1}^{(n)}$ produce various parameters l down to zero, while retaining the same integer parameter n.

3 Normalization of wave functions

Next we seek normalized eigenfunctions. Coordinate representation of Eq. (10) takes

$$-\frac{d\psi_{n-1}^{(n)}}{d\rho} + \left(\frac{n}{\rho} - \frac{1}{n}\right)\psi_{n-1}^{(n)} = 0. \tag{17}$$

The solution can be obtained as

$$\psi_{n-1}^{(n)} = c_n \rho^n e^{-\rho/n}, \tag{18}$$

where c_n is a normalization constant. This can be determined as follows:

$$\int_0^\infty |\psi_{n-1}^{(n)}|^2 d\rho = 1. \tag{19}$$

Namely,

$$|c_n|^2 \int_0^\infty \rho^{2n} e^{-2\rho/n} d\rho = 1. \tag{20}$$

Consider the following definite integral:

$$\int_0^\infty e^{-2\rho\xi} d\rho = \frac{1}{2\xi}. \tag{21}$$

Differentiating the above integral $2n$ times with respect to ξ gives

$$\int_0^\infty \rho^{2n} e^{-2\rho\xi} d\rho = (\frac{1}{2})^{2n+1} (2n)!\, \xi^{-(2n+1)}. \tag{22}$$

Substituting $1/n$ into ξ, we obtain

$$\int_0^\infty \rho^{2n} e^{-2\rho/n} d\rho = (\frac{1}{2})^{2n+1} (2n)!\, n^{(2n+1)}. \tag{23}$$

Hence,

$$c_n = \left(\frac{2}{n}\right)^{n+\frac{1}{2}} / \sqrt{(2n)!}\,. \tag{24}$$

To further normalize the other wave functions, we calculate the following inner product:

$$< \psi_l^{(n)} | \psi_l^{(n)} > = < \psi_{n-1}^{(n)} b_{n-1} \cdots b_{l+2}^\dagger b_{l+1}^\dagger | b_{l+1} b_{l+2} \cdots b_{n-1} \psi_{n-1}^{(n)} >. \tag{25}$$

From Eqs. (6) and (7) we have

$$b_l^\dagger b_l + \varepsilon^{(l-1)} = b_{l+1} b_{l+1}^\dagger + \varepsilon^{(l)}. \tag{26}$$

Applying Eq. (26) to Eq. (25) repeatedly and considering Eq. (10), we finally reach the following relationship:

$$< \psi_l^{(n)} | \psi_l^{(n)} > = \left[\varepsilon^{(n-1)} - \varepsilon^{(l)}\right] < \psi_{l+1}^{(n)} | \psi_{l+1}^{(n)} >. \tag{27}$$

Thus the normalized wave functions $\tilde{\psi}_l^{(n)}$ are expressed from Eq. (14) as

$$\tilde{\psi}_l^{(n)}=\kappa(n,l)^{-\frac{1}{2}}b_{l+1}b_{l+2}\cdots b_{n-1}\tilde{\psi}_{n-1}^{(n)}, \tag{28}$$

where $\kappa(n,l)$ is defined such that

$$\kappa(n,l)\equiv\left[\varepsilon^{(n-1)}-\varepsilon^{(n-2)}\right]\cdot\left[\varepsilon^{(n-1)}-\varepsilon^{(n-3)}\right]\cdots\cdots\left[\varepsilon^{(n-1)}-\varepsilon^{(l)}\right], \tag{29}$$

with $l\leq n-2$. More explicitly,

$$\kappa(n,l)=\frac{(2n-1)!(n-l-1)!(l!)^2}{(n+l)!(n!)^2(n^{n-l-2})^2} \tag{30}$$

and particularly

$$\tilde{\psi}_{n-1}^{(n)}=\left(\frac{2}{n}\right)^{n+\frac{1}{2}}\frac{1}{\sqrt{(2n)!}}\rho^n e^{-\rho/n}. \tag{31}$$

From Eq. (27) we define the following operator:

$$\tilde{b}_l\equiv[\varepsilon^{(n-1)}-\varepsilon^{(l-1)}]^{-\frac{1}{2}}b_l. \tag{32}$$

Then Eq. (28) becomes

$$\tilde{\psi}_l^{(n)}=\tilde{b}_{l+1}\tilde{b}_{l+2}\cdots\tilde{b}_{n-1}\tilde{\psi}_{n-1}^{(n)}. \tag{33}$$

4 Operator representations and associated Laguerre polynomials

It will be of great importance to compare the functions $\tilde{\psi}_l^{(n)}$ with conventional wave functions that are expressed using associated Laguerre polynomials. For this purpose we define the following functions $\Phi_l^{(n)}(\rho)$ such that

$$\Phi_l^{(n)}(\rho)\equiv\left(\frac{2}{n}\right)^{l+\frac{3}{2}}\sqrt{\frac{(n-l-1)!}{2n(n+l)!}}e^{-\frac{\rho}{n}}\rho^{l+1}L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right). \tag{34}$$

The associated Laguerre polynomials are described as[3)]

$$L_n^{\nu}(x) = \frac{1}{n!}x^{-\nu}e^{x}\frac{d^n}{dx^n}(x^{n+\nu}e^{-x}), (\nu > -1). \quad (35)$$

In a form of power series expansion, the polynomials are expressed for integer $k \geq 0$ as[2,4,6)]

$$L_n^k(x) = \sum_{m=0}^{n}(-1)^m \frac{(n+k)!}{(n-m)!(k+m)!m!}x^m. \quad (36)$$

The function $\Phi_l^{(n)}(\rho)$ contains multiplication factors $e^{-\frac{\rho}{n}}$ and ρ^{l+1}. The function $L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)$ is a polynomial of ρ with the highest order of ρ^{n-l-1}. Consequently, $\Phi_l^{(n)}(\rho) \to 0$ when $\rho \to 0$ and $\rho \to \infty$ (vide supra). This ensures that $\frac{d}{d\rho}$ is indeed an anti-Hermitian operator. The argument is as follows: We define $D \equiv \frac{d}{d\rho}$. An inner product between arbitrarily chosen functions *f* and *g* is

$$\begin{aligned} < f|Dg > &\equiv \int_0^{\infty} f^* D g d\rho \\ &= [f^* g]_0^{\infty} - \int_0^{\infty}(Df^*)g d\rho \\ &= [f^* g]_0^{\infty} + < -Df^*|g >, \end{aligned} \quad (37)$$

where f^* is a complex conjugate of *f*. Meanwhile,

$$< f|Dg > = < D^{\dagger} f|g >. \quad (38)$$

Therefore if the functions *f* and *g* vanish at $\rho \to 0$ and $\rho \to \infty$, $D^{\dagger} = -D$ by equating Eqs. (37) and (38). This means that *D* is anti-Hermitian. The functions $\Phi_l^{(n)}(\rho)$ we are dealing with satisfy the aforementioned boundary conditions relevant to *f* and *g*. Then the operator $\frac{d}{d\rho}$ is anti-Hermitian. The operator $H^{(l)}$ appearing in Eqs. (6) and (7) is Hermitian. This is because

$$\begin{aligned} b_l^{\dagger} b_l &= (-A + H)(A + H) \\ &= H^2 - A^2 - AH + HA; \end{aligned} \quad (39)$$

$$(b_l^{\dagger} b_l)^{\dagger} = b_l^{\dagger} b_l. \quad (40)$$

The Hermiticity is true of $b_l b_l^{\dagger}$ as well. This ensures physical meaningfulness of the eigenenergy and eigenstate (or wave function) which belongs to that eigenenergy.

Next, consider the following operation:

$$\tilde{b}_l \Phi_l^{(n)}(\rho)$$
$$= [\varepsilon^{(n-1)} - \varepsilon^{(l-1)}]^{-\frac{1}{2}} \left(\frac{2}{n}\right)^{l+\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{2n(n+l)!}} \left[\frac{d}{d\rho} + \left(\frac{l}{\rho} - \frac{1}{l}\right)\right] \{e^{-\frac{\rho}{n}} \rho^{l+1} L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)\}. \quad (41)$$

Note that $\left[\frac{d}{d\rho} + \left(\frac{l}{\rho} - \frac{1}{l}\right)\right]$ operates upon $\{e^{-\frac{\rho}{n}} \rho^{l+1} L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)\}$, and so we will be calculating differentiation of a product function, which contains again higher-order derivative of a product function. The procedure of calculation of Eq. (41) is somewhat lengthy but straightforward. Using well-known Leibnitz' theorem[2] pertinent to the higher-order differentiations of the product function, the result is expressed as

$$\begin{aligned}
\tilde{b}_l \Phi_l^{(n)}(\rho) &= \left(\frac{2}{n}\right)^{l+\frac{1}{2}} \sqrt{\frac{(n-l)!}{2n(n+l-1)!}} e^{-\frac{\rho}{n}} \rho^l L_{n-l}^{2l-1}\left(\frac{2\rho}{n}\right) \\
&= \left(\frac{2}{n}\right)^{(l-1)+\frac{3}{2}} \sqrt{\frac{[(n-(l-1)-1]!}{2n[(n+(l-1)]!}} e^{-\frac{\rho}{n}} \rho^{(l-1)+1} L_{n-(l-1)-1}^{2(l-1)+1}\left(\frac{2\rho}{n}\right) \\
&\equiv \Phi_{l-1}^{(n)}(\rho). \quad (42)
\end{aligned}$$

Thus we find out that $\Phi_l^{(n)}(\rho)$ behaves exactly like $\tilde{\psi}_l^{(n)}$. Moreover, if we replace l in Eq. (34) with $n - 1$, we find

$$\Phi_{n-1}^{(n)}(\rho) = \tilde{\psi}_{n-1.}^{(n)} \quad (43)$$

Operating $\tilde{b}_{n-1}$ on both sides of Eq. (43),

$$\Phi_{n-2}^{(n)}(\rho) = \tilde{\psi}_{n-2.}^{(n)} \quad (44)$$

Likewise successively operating $\tilde{b}_l$ $(1 \leq l \leq n-1)$,

$$\Phi_l^{(n)}(\rho) = \tilde{\psi}_l^{(n)}(\rho), \quad (45)$$

with all allowed numbers of l (i.e. $0 \leq l \leq n-1$). This permits us to identify $\Phi_l^{(n)}(\rho)$ and $\tilde{\psi}_l^{(n)}(\rho)$.

Consequently, it is clear that the parameter n introduced in Eq. (8) is identical to a principal quantum number and that the parameter l ($0 \leq l \leq n-1$) is an orbital angular momentum quantum number.[1] Although $\Phi_l^{(n)}(\rho)$ and $\tilde{\psi}_l^{(n)}(\rho)$ are identical up to the constant c_n expressed in Eq. (24), a complex constant with an absolute number of 1 (phase factor) remains undetermined.

5 Radial wave functions

The radial wave functions are derived from the following relationship as described earlier:

$$R_l^{(n)}(r) = \tilde{\psi}_l^{(n)}/\rho. \tag{46}$$

To normalize $R_l^{(n)}(r)$, we have to calculate the following integral:

$$\begin{aligned}\int_0^\infty |R_l^{(n)}(r)|^2 r^2 dr &= \int_0^\infty \frac{1}{\rho^2} |\tilde{\psi}_l^{(n)}|^2 (\frac{a}{Z}\rho)^2 \frac{a}{Z} d\rho \\ &= (\frac{a}{Z})^3 \int_0^\infty |\tilde{\psi}_l^{(n)}|^2 \, d\rho \\ &= (\frac{a}{Z})^3. \end{aligned} \tag{47}$$

Accordingly, we choose the following functions $\tilde{R}_l^{(n)}(r)$ for the normalized radial wave functions:

$$\tilde{R}_l^{(n)}(r) = \sqrt{(Z/a)^3} R_l^{(n)}(r). \tag{48}$$

Substituting Eq. (46) into Eq. (48) and taking account of Eqs. (34) and (45), we obtain[4,6,10]

$$\tilde{R}_l^{(n)}(r) = \sqrt{(\frac{2Z}{an})^3 \cdot \frac{(n-l-1)!}{2n(n+l)!}} (\frac{2Zr}{an})^l \exp\left[-\left(\frac{Zr}{an}\right)\right] L_{n-l-1}^{2l+1}\left(\frac{2Zr}{an}\right). \tag{49}$$

Equation (49) is exactly the same as the normalized radial wave functions that can be obtained as

the solution of Eq. (1) through the power series expansion.[1)] All these functions belong to the same eigenenergy E_n such that

$$E_n = -\frac{\hbar^2}{2\mu}\left(\frac{Z}{a}\right)^2 \frac{1}{n^2}. \tag{50}$$

Thus we have reached a conclusion that the operator formalism described in the present article is essentially the same as the conventional coordinate representation based upon the power series expansion that leads to associated Laguerre polynomials.[2,4,6)]

6 Conclusion

The author has developed the operator formalism in dealing with radial wave functions of hydrogen-like atoms. The essential point rests upon that the radial wave functions can be derived by successively operating the lowering operators b_l on $\tilde{\psi}_{n-1}^{(n)}$ that is parametrized with a principal quantum number n and an orbital angular momentum quantum number $l = n - 1$. This is clearly represented by Eqs. (28) and (33). The results agree with the conventional coordinate representation method based upon the power series expansion that leads to associated Laguerre polynomials.

The operator formalism explicitly represents the mathematical constitution of quantum mechanical systems. In this article the author has shown this feature by adopting radial wave functions of hydrogen-like atoms as an example.

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7 References and notes

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