Algebraic Approach to Radial Ladder Operators in the Hydrogen Atom

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ABSTRACT: We add a phase variable and its corresponding operator to the description of the hydrogen atom. With the help of these additions, we device operators that act as ladder operators for the radial system. The algebra defined by the commutation relations between those operators has a Casimir operator coincident with the radial Hamiltonian of the problem. The algebra happens to be the well-known $su(1,1)$ Lie algebra, hence the phase-dependent eigenfunctions calculated within our scheme belong in a representation of that algebra, a fact that may be useful in certain applications. © 2007 Wiley Periodicals, Inc. Int J Quantum Chem 107: 1608 –1613, 2007

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Introduction

Operational and algebraic methods are widely used in quantum chemistry and physics [1–9]; this is so because they usually simplify the calculations required in the analysis of many chemical or physical processes. The hydrogen atom is, on the other hand, a fundamental problem whose energy eigenvalues and eigenfunctions are at the starting point of many calculations or approximations [2, 4, 10, 11]. In this work, an algebraic method for obtaining the bound states of the hydrogen atom is discussed [12].

Taking advantage of the irrelevance of global changes of phase in any quantum state, $\psi$, namely

$$\psi \rightarrow \psi' = e^{i\xi} \psi, \quad \text{and yet} \quad |\psi'|^2 = |\psi|^2,$$

we regard $\xi$ as an extra variable using it to define the phase-operator $\Omega_3$ [Eq. (7)] as an extra Hermitian op-
When we choose a specific value of the orbital quantum number $\ell$ and apply the ladder operators to the base state of the algebra—we have one base state for each $\ell$-value—we generate the transformed radial eigenfunctions of the hydrogen atom associated with the angular momentum $\ell$. Such eigenfunctions, $\Psi_{\ell m}(r, \xi)$, are thus found to belong in a representation of the $su(1,1)$ algebra, making them potentially useful in diverse quantum optics applications, in the analysis of ionization states by using nondiscrete representations of the algebra, and in the study of squeezed and coherent hydrogenic states [4, 14–17].

The commutation relations among the $\Omega$-operators comprise an $su(1,1)$ Lie algebra, $\Omega$, playing the role of its Casimir operator [13]. The use of the phase as an extra variable for solving the radial problem of the Hydrogen atom is new, this phase-extended approach has in addition other possible applications, and establishes the phase-dependent radial eigenfunctions of the system as belonging in a representation of a $su(1,1)$ algebra.

Let us note that our technique may be useful in some other quantum chemistry calculations, it may be applied to the study of ionization states by using nondiscrete representations of $su(1,1)$, it may found applications in studying squeezed and coherent states in the hydrogen atom [16], it may be used diversely in quantum optics, and it may be used to solve other quantum problems with chemical interest, as the 2D and the 3D harmonic oscillators, the Pöschl-Teller potential, or the Morse potential [4, 8, 15, 17, 19–21].

### New Operators and Their Commutation Relations

Let us use the angular variable $\xi$ relating it to the phase of a quantum state $F$. We associate it to the operator

$$\Omega_3 = -i\frac{\partial}{\partial \xi}.$$  

The eigenfunctions of the operator $\Omega_3$ are $e^{\lambda \xi}$, with the corresponding eigenvalue, $\lambda$, being any real number. As the phase of a quantum state can take any value and as $\xi$ does not correspond to any position variable, the eigenvalue $\lambda$ cannot be quantized. It should be clear that all eigenstates of the problem must be eigenstates of the operator $\Omega_3$.

Let us introduce two more operators

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\ell^2}{r} + \frac{\hbar^2}{2m} \frac{\ell(\ell + 1)}{r^2} \right] R(r) = ER(r),$$

where $\ell(= 0, 1, 2, 3, \ldots)$ is the orbital angular momentum quantum number of the atom, $e$ is the electronic charge, $m$ is the reduced mass of the system, $r$ is the radial coordinate, $\hbar$ is Planck’s constant divided by $2\pi$, and $R(r)$ is the radial part of the eigenfunction with bound energy $E < 0$ [18].

We also define

$$k^2 = -\frac{8mE}{\hbar^2}, \quad \rho = \frac{k}{2r}, \quad \lambda = \frac{2me^2}{\hbar^2\kappa},$$

introduce the transformed radial function, $F$, through

$$F(\rho) = \rho^{\ell/2} R(\rho),$$

and, finally, define the nondimensional variable $x = \log \rho$, to transform the radial equation of the hydrogen atom (2) to

$$H_x F(x) = \ell(\ell + 1) F(x).$$

We begin with the nonrelativistic radial Schrödinger equation for the hydrogen atom

$$\text{Radial Hamiltonian of the Hydrogen Atom}$$

We cast the radial Hamiltonian of the hydrogen atom in the form of an eigenvalue problem whose eigenvalues are precisely those of the nondimensional square of the angular momentum, namely, $\ell(\ell + 1)$. Furthermore, using both the phase variable, $\xi$, and a transformed radial coordinate, $x$, we introduce two more operators, $\Omega_1$ and $\Omega_2$, using them to define yet another operator, $\Omega_x$, commuting with $\Omega_i, i = 1, 2, 3$. We found the expression of the transformed Hamiltonian to be essentially the same as the operator $\Omega_c$. We also introduce two more operators $\Omega_5$ and $\Omega_6$ and show that they behave as ladder operators for the phase-extended radial part of the hydrogen atom.
\[
\Omega_{z} = i e^{\pi i/2} \left( \frac{\partial}{\partial x} - e^x + i \frac{\partial}{\partial \xi} + \frac{1}{2} \right),
\]  

(8)

depending both on \( \xi \) and on \( x \). We can easily show that

\[
[\Omega_{z}, \Omega_{z}] = \pm \Omega_{z},
\]  

(9)

and

\[
[\Omega_{z}, \Omega_{-}] = -2\Omega_{3}.
\]  

(10)

We can introduce yet two more operators, \( \Omega_{1} \) and \( \Omega_{2} \), as

\[
\Omega_{1} = \frac{1}{2}(\Omega_{+} + \Omega_{-}), \quad \Omega_{2} = \frac{1}{2i}(\Omega_{+} - \Omega_{-}),
\]  

(11)

which, together with \( \Omega_{3} \), satisfy

\[
[\Omega_{1}, \Omega_{2}] = -i \Omega_{3}, \quad [\Omega_{2}, \Omega_{3}] = i \Omega_{1}, \quad [\Omega_{1}, \Omega_{3}] = 0.
\]  

(12)

The relations (9) and (10) characterize an \( su(1,1) \) Lie algebra [13, 14]. Equations (12) are an alternative expression of the algebra [13, 14, 17].

It is not difficult to check that an operator commuting with all the elements of the algebra (12)—or (9) and (10)—is

\[
\Omega_{c} = -\Omega_{1}^{2} - \Omega_{2}^{2} + \Omega_{3}^{2} = \frac{\partial^2}{\partial x^2} - e^{2x} - 2i e^{x} \frac{\partial}{\partial \xi} + \frac{1}{4},
\]  

(13)

\( \Omega_{c} \) is the Casimir operator of the algebra.

Now, on comparing Eq. (13) with Eq. (6), we immediately see that \( \Omega_{c} \) becomes identical to the transformed radial Hamiltonian \( H_{x} \), at least if we regard it as applied to an eigenfunction of \( \Omega_{3} \) with eigenvalue \( \lambda \).

Then, to solve our problem, we need to solve the eigenvalue problem defined simultaneously by \( \Omega_{3} \) and \( \Omega_{c} \). This can be done in a manner analogous to the process used for solving the angular momentum eigenvalue problem using the operators \( L_{z} \) and \( L^{2} \) and the angular momentum algebra [4, 10, 12, 18]. This is the discussed of the next section.

### Simultaneous Eigenvalues and Eigenfunctions of \( \Omega_{c} \) and \( \Omega_{3} \)

We need to compute the complete set of eigenvalues and simultaneous eigenfunctions of \( \Omega_{c} \) and \( \Omega_{3} \). Let us write these eigenfunctions as \( \Psi^{\lambda}_{\omega}(x, \xi) \), and let us call \( \lambda \) and \( \omega \) the eigenvalues of, respectively, \( \Omega_{3} \) and \( \Omega_{c} \).

\[
\Omega_{3}\Psi^{\lambda}_{\omega}(x, \xi) = \lambda \Psi^{\lambda}_{\omega}(x, \xi) \quad \text{and} \quad \Omega_{c}\Psi^{\lambda}_{\omega}(x, \xi) = \omega \Psi^{\lambda}_{\omega}(x, \xi).
\]  

(14)

We find

\[
\Psi^{\lambda}_{\omega}(x, \xi) = e^{i\xi F_{\omega}^{\lambda}(x)};
\]  

(15)

checking with the \( \Omega_{c} \)-eigenfunctions and eigenvalues we mentioned earlier. Therefore, we can conclude that the eigenfunctions for the problem are

\[
F(x) = F_{\omega}^{\lambda}(x) \quad \text{so} \quad R(x) = e^{-x/2}F_{\omega}^{\lambda}(x);
\]  

(16)

or, in terms of \( \rho \),

\[
R(\rho) = \frac{1}{\rho^{1/2}} F_{\omega}^{\lambda}(\rho).
\]  

(17)

The eigenvalues, as we know from Eqs. (5) and (6), are \( \omega = \ell(\ell + 1) \). Thus, we have been able to recast the radial Schrödinger equation of the hydrogen atom as an eigenvalue equation for the Casimir operator of an \( su(1,1) \) algebra with eigenvalues \( \ell(\ell + 1) \).

As it should be clear from Eqs. (11) and (12), the operators \( \Omega_{c} \) are ladder operators. This feature can be easily verified from Eq. (9), since

\[
\Omega_{c}\Omega_{c}^{\lambda}_{\omega}(x, \xi) = (\Omega_{3}\Omega_{3} + \Omega_{c})\Psi^{\lambda}_{\omega}(x, \xi) = (\lambda \pm 1)\Omega_{c}\Psi^{\lambda}_{\omega}(x, \xi).
\]  

(18)

Thus, the operators \( \Omega_{c} \), change the eigenvalue \( \lambda \) to \( \lambda \pm 1 \),

\[
\Omega_{c}\Psi^{\lambda}_{\omega}(x, \xi) \propto \Psi^{\lambda_{\pm 1}}_{\omega}(x, \xi).
\]  

(19)

To check for hermiticity and other properties of the \( \Omega_{c} \) operators, we may use the product
where the functions $\phi(\xi, x)$ and $\psi(\xi, x)$ are assumed to be periodic over the interval $\xi \in [0, 2\pi]$ and also assumed to vanish as $x \to \pm \infty$. Using (20), we can check that the three $\Omega_i$ $i = 1, 2, 3$, operators are Hermitian.

Since $\Omega_2$ and $\Omega_3$ commute, we can obtain a complete orthogonal basis of their simultaneous eigenfunctions which we denote by $\Psi^\text{in}_\lambda(x, \xi) = \omega \lambda$, we assume that this basis is both orthogonal and normalized, i.e. $\langle \omega \lambda' | \omega \lambda \rangle = \delta_{\lambda\lambda'} \delta_{\lambda',\lambda}$.

The operator $\Omega_1$ is not definite positive, as can be seen from the existence of minus signs in

$$\Omega_1 = -\Omega_2^2 - \Omega_3^2.$$

(21)

Nevertheless, the operator

$$\Omega^2 = \Omega_1^2 + \Omega_2^2 + \Omega_3^2,$$

(22)

which may be regarded as the magnitude of the complex vector operator $\Omega = i \hat{l}_z + \hat{\ell} \hat{l}_z + \hat{k} \hat{l}_z$, is definitively positive. We may easily show that

$$\Omega^2 = \Omega_1^2 + \Omega_2^2 + \Omega_3^2 = 2\Omega_3 - \Omega_1,$$

(23)

and, from this relation, we easily obtain $2\lambda^2 \geq \omega$.

The consequence is that $|\lambda|$ must be bounded below; therefore, there is a minimum value, $|\lambda|_{\text{min}}$ for it.

We have then two possibilities, either $\lambda > 0$ and it itself is bounded below, or $\lambda < 0$ and then $\lambda$ is bounded above. Let us select $\lambda > 0$ and define $N = \lambda_{\text{min}}$. Since $\Omega_2$ acts over the orthogonal basis $|\omega \lambda \rangle$ as a ladder operator and $N$ is the minimum value, $\Omega_1 |\omega N \rangle = 0$, or, equivalently, $\Omega_1 \Omega_1 |\omega N \rangle = 0$.

As $\Omega_1, \Omega_2 = -\Omega_2^2 - \Omega_3^2$, then

$$-w + N^2 - N = 0 \quad \text{or} \quad w = \ell(\ell + 1) = N(N - 1).$$

(25)

If we had selected $\lambda < 0$, then $\lambda$ had to be bounded above by a certain $\lambda_{\text{max}}$. Then, using

$$\Omega_\lambda |\lambda_{\text{max}} \rangle = 0,$$

we would necessarily have been led to non-normalizable solutions of the form

$$|\lambda < 0\rangle = e^{i\lambda_{\text{max}}^\text{max}} e^{-(\lambda_{\text{max}} + 1/2)\hat{\ell}^2},$$

(26)

solutions that are totally inappropriate for describing bound states of the hydrogen atom [12, 17, 18].

Therefore, $\lambda > 0$ is the only sensible choice for the problem. Furthermore, Eq. (25) has as solutions $N = -\ell$ and $N = \ell + 1$, but the former is not allowed because we are assuming $\lambda > 0$ and also because it can be shown to lead to solutions diverging at the origin [17]. The only admissible choice is then $N = \ell + 1$. As $\ell$ varies from 0 up to infinity in unit steps, we must have $N = 1, 2, 3, \ldots$, in other words, $N$ is the principal quantum number of the hydrogen atom. Having thus found the eigenvalues of the operator algebra, we can relabel the eigenstates in a more standard way as $|\omega \lambda \rangle \to |N \ell \rangle$. However, despite using the standard symbols, these states are assumed to include their phases, that is, they necessarily depend on $\xi$.

We should notice that neither the additional variable nor the operator algebra introduced alter in any way the standard features of the hydrogen atom. For example, the angular momentum operators $\hat{l}^2 = \ell^2/\hbar$ and $\hat{l}_z = L_z/\hbar$ commute with all the $\Omega$ operators,

$$[l_z, \Omega_i] = [l_z, \Omega_i] = [l^2, \Omega_i] = [l_z, \Omega_i] = 0;$$

(27)

and, thus the degeneracy of the $s, p, d, \ldots$ orbitals, is unaffected.

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**Energy Spectrum and the Radial Eigenfunctions of the Hydrogen Atom**

The energy spectrum of the hydrogen atom follows immediately from the definition of $\lambda = N$ given in Eq. (3). The energy eigenvalues are given by the Balmer formula

$$E = -\frac{e^2}{2a_0 N^2}, \quad N = 1, 2, 3 \ldots,$$

(28)

with the Bohr radius $a_0 = h^2/\mathcal{m}e^2$.

To obtain the eigenfunctions, let us begin with the ground state $|\lambda = 1, \ell = 0\rangle$. From $\Omega_1 |\lambda = 1, \ell = 0\rangle = 0$, we have
\[ e^{-i\ell} \left( \frac{\partial}{\partial x} + e^x + i \frac{\partial}{\partial \xi} + \frac{1}{2} \right) e^{i\ell} F_0^N(x) = 0, \] (29)

whose solution is

\[ F_0^N(x) = C_1 e^{x/2} \exp(-e^x) \quad \text{or} \quad F_0^N(\rho) = C_1^{\rho/2} e^{-\rho}, \] (30)

where \( C_1 \) is a normalization constant. Using the definition (3) of \( k \), we get \( k = 2/a_0N \) and from that of \( \rho = (k/2) r = (r/a_0) \), we easily get then from (3) that the radial eigenfunction for \( N = 1 \) and \( \ell = 0 \) is given by

\[ R_1^N(r) = C_1^N e^{-(r/a_0)}, \] (31)

which is the \( N = 1, \ell = 0 \) solution of the nonrelativistic hydrogen atom.

Once we get the base state for any given \( \ell \), we can obtain, from the equation \( \Omega_+ |N\ell\rangle \sim |N + 1\ell\rangle \), the whole series of states with \( \ell \) fixed for all \( N = \ell + 1, \ell + 2, \ldots \). For instance we can obtain the state \( |N = 2\ell = 0\rangle \); from (30) we have, except for a normalization constant, that \( |100\rangle = e^{i\ell/2} \exp(-e^x) \). So,

\[ \Omega_+ |100\rangle = ie^{2\ell} \left( \frac{d}{dx} - e^x + 1 + 1/2 \right) e^{i\ell/2} e^{-e^x} \] (32)

and thus

\[ |200\rangle = C_2 e^{2\ell} F_2^0(x) = C_2^{2\ell e^{\ell/2} e^{-e^x}} (1 - e^x). \] (33)

We can continue in this way to obtain any radial eigenfunction. As a first step, we need to obtain the base state of the algebra for \( \ell \) fixed, this base state is the state that satisfies the condition \( \Omega_- |N N - 1\rangle = 0 \). Such state is precisely \( |NN - 1\rangle \). So the condition \( \Omega_- |NN - 1\rangle = 0 \), becomes

\[ ie^{-i\ell} \left( \frac{\partial}{\partial x} + e^x + i \frac{\partial}{\partial \xi} + \frac{1}{2} \right) e^{i\ell} F_{N-1}^{N-1}(x) = 0. \] (34)

Whose solution is given, except for normalization constants, by

\[ |NN - 1\rangle \sim e^{i\ell} e^{i(N-1)/2} e^{-e^x}. \] (35)

From the definitions (2) and (28), we get for \( \rho = e^x \) the general result \( \rho = (2r/a_0N) \). Going back to the definitions (3), we obtain the radial eigenfunction, with the phase dependence removed,

\[ R_{\ell}^{(\ell)}(r) = C_N^{\ell} r^{N-1} e^{-i/2(r/a_0N)}, \] (36)

where \( C_N^{\ell} \) is a normalization constant. From here we can obtain the radial wave functions for any value of \( \ell = 0, 1, 2, \ldots \) by applying successively the operator \( \Omega_+ \) to the base state (35). The method used to arrive to the radial eigenfunctions of the hydrogen atom with the phase dependence included, namely

\[ \Psi_{n\ell}(r, \xi) = C_{n\ell} e^{i\lambda \xi} R_{n\ell}(r), \] (37)

where \( \lambda \) is any real number and \( \lambda \xi \) is the phase, implies that the eigenfunctions (37) belong in a representation of the \( su(1,1) \) Lie algebra.

**CONCLUSION**

In summary, by regarding the state of a quantum state of the hydrogen atom as an additional variable, and extending the set of operators of the problem with the phase related operator, \( \Omega_+ \), plus the two additional Hermitian operators \( \Omega_i \) and \( \Omega_0 \), we have been able to define a Casimir operator \( \Omega \), commuting with all the \( \Omega_i = 1, 2, 3 \). We have additionally found that \( \Omega_0 \) essentially coincides with the radial Hamiltonian of the hydrogen atom, \( H_0 \). Such operators, plus the \( \xi \)-extended radial ladder operators \( \Omega_\xi \), we can define from them, allow us to completely solve the problem. That is, to compute both its energy spectrum and the set of radial eigenfunctions of the hydrogen atom. The operator commutation relations found can be described as comprising a \( su(1,1) \) Lie algebra. In our method, the angular momentum quantum number, \( \ell \), plays a more conspicuous role than the principal quantum number, \( N \), as we need to fix \( \ell \) first and then proceed to calculate the wave functions. The phase and its associated operator, \( \Omega_0 \), plays a crucial role since that is what makes possible the definition of the operator algebra. Hence, the method gives some operational meaning to the global phase invariance of the hydrogen atom states.

Our method also exhibits that the radial part of the hydrogen atom is a system possessing an \( su(1,1) \) symmetry. We have indeed constructed a two-dimensional realization of that Lie algebra because the \( \Omega \)-operators depend on two variables. Thus, we
can regard the phase-dependent set of the radial eigenfunctions of the hydrogen atom as belonging in a representation of $su(1,1)$. This fact may have some bearings on quantum optics applications.

We should also mention that the method discussed in this work has been successfully used for solving the Dirac relativistic hydrogen atom [19]. The algebra occurring in the relativistic case is the same as the one described here and even the algebraic details are very similar. Swainson and Drake have discussed a linear transformation relating the radial equation of the relativistic with that of non-relativistic hydrogen atom problems as an explanation of why the solution to those problems may be described in so a similar way. They also used their technique for discussing the relationship between the Green functions of both problems [22–24].

On the other hand, the importance of symmetries for understanding the Stark and Zeeman effects indicates that our method may have some bearings in these and some other related systems. It would be instructive to attempt to describe hydrogen atom in a magnetic field using our technique given that, in a way, phase invariance is included from the start in this phase-extended description.

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