# The 'accidental' degeneracy of the hydrogen atom is no accident! 

P.C.Deshmukh ${ }^{[1,2, *]}$, Aarthi Ganesan ${ }^{[2]}$, N. Shanthi ${ }^{[2]}$, Blake Jones ${ }^{[3]}$, James Nicholson ${ }^{[3]}$ and Andrea Soddu ${ }^{[3]}$<br>${ }^{1}$ Department of Physics<br>Indian Institute of Technology Madras<br>Chennai, 600036, India<br>${ }^{2}$ Department of Physics<br>Center for Post Graduate Studies, Jain University<br>Bengaluru, 560011, India<br>${ }^{3}$ Department of Physics and Astronomy<br>Western University<br>London, N6A3K7, Canada

PACS numbers: 01.40.Fk, 01.40.G-, 02.20.Qs, 03.65.Ca, 03.65.Ge


#### Abstract

The Schrodinger equation does not account for the $2 n^{2}$ degeneracy of the hydrogen atom which it dismisses as an 'accidental' degeneracy. The factor of ' 2 ' in the $2 n^{2}$ degeneracy is well-accounted in the relativistic formulation on account of the two spin states of the electron. The $\mathrm{n}^{2}$ degeneracy is nevertheless not quite an 'accident'; it is on account of the $\mathrm{SO}(4)$, rather than $\mathrm{SO}(3)$, symmetry of the hydrogen atom. This result is well known, but is often not adequately commented upon in most courses in quantum mechanics and atomic physics, leaving the student wondering about the origins of the $n^{2}$ degeneracy of the hydrogen atom. A pedagogical analysis of this interesting aspect, which highlights the fundamental principles of quantum mechanics is presented in this article. While doing so, not only is the $n^{2}$ degeneracy of the hydrogen atom explained, but its energy spectrum and eigenfunctions are obtained without even using the Schrodinger equation, employing only the fundamental principles of quantum mechanics rather than the Schrodinger equation.


## I. Conservation Principles from the Physical Law

[^0]One can clearly demark physics before, and after, Albert Einstein [1]. One of his outstanding contributions is the recognition of symmetry/invariance as an important principle in physics. Symmetry plays a pivotal role in nature. It has an intimate relationship with conservation principles, and with the 'Character of the Physical Law' [2]. At a fundamental level, physics deals largely with the discovery and understanding of the physical law(s) of nature. It thus becomes pertinent to ask just what is meant by a/the (physical) law(s) of nature. This quest aspires to explain the physical universe in terms of a minimum number of principles/laws. One could even perhaps hope that all physical phenomena are comprehensible in terms of just one law. We are perhaps far from this goal as yet, nonetheless, it is intriguing that most of the physical phenomena can be explained in terms of just a very few number of laws. Much of the excitement in physics is the recognition of this approach which seeks to know the most, from the least.

One does not know yet if there is then just a single law of nature which really provides the 'theory of everything'. It is nevertheless important to inquire just what is meant by a law of nature. Following early insights provided by Albert Einstein and Amalie Emmy Noether, Eugene Wigner [3] provided deep insights on these fundamental questions and elucidated just what is meant by the laws of nature and what are their connections with symmetry and invariance principles. Inspired by Wigner's perceptivity [3], these ideas can possibly be summarized in three observations:
(i) The regularities in the phenomena which physical science endeavours to uncover are called the laws of nature.
(ii) The elements of the behaviour which are not specified by the laws of nature are called initial conditions.
(iii) The invariance principles themselves depend on the dividing line between initial conditions and laws of nature.

Two questions, apparently opposite to each other, can be asked with regard to the connections between invariance/conservation principles and the laws of nature: (a) Are the conservation principles consequences of the laws of nature? Or, (b) are the laws of nature

[^1]the consequences of the symmetry principles that govern them? Following Feynman [2], we begin with the universal law of gravity as an illustration of the law of nature. We consider a mass $m_{1}$ at a point whose position vector is $\vec{R}_{1}$ in a state of gravitational interaction with another mass $m_{2}$ at a point whose position vector is $\vec{R}_{2}$. The equation of motion which describes the gravitational inverse square law for the 'relative motion' of the smaller mass relative to the larger mass, with its position vector given by $\vec{r}=\vec{R}_{2}-\vec{R}_{1}$, is then given by:
\[

$$
\begin{equation*}
\ddot{\vec{r}}+\kappa \frac{\vec{r}}{|\vec{r}|^{3}}=\overrightarrow{0} \tag{Eq. 1}
\end{equation*}
$$

\]

where $\kappa=G\left(m_{1}+m_{2}\right) \approx G m_{1}$, for $\left.\left.m_{1}\right\rangle\right\rangle m_{2}$, and has dimensions $[\kappa]=L^{3} T^{-2}$.
The scalar product of the equation of motion, Eq. 1 , with velocity vector $\overrightarrow{\mathrm{v}}=\dot{\vec{r}}$ gives $\mathrm{v} \lim _{\delta t \rightarrow 0} \frac{\delta \mathrm{v}}{\delta t}=-\frac{\kappa \lim _{\delta t \rightarrow 0} \frac{\delta r}{\delta t}}{r^{2}}$.

Integrating Eq. 2 with respect to time yields the conservation of energy:
$\frac{\mathrm{v}^{2}}{2}-\frac{\kappa}{r}=E$,
Eq. 3
$E$ being the specific (i.e. per unit mass) energy, which has emerged as the constant of integration. Integration with respect to time as the mathematical operation that yields the conservation of energy is no accident; it comes from the fact that energy and time are canonically conjugate variables. Likewise, cross product of the equation of motion with the position vector $\vec{r}$, together with the recognition that the gravitational force is a central field force, immediately yields the conservation of ('specific', i.e. per unit mass) angular momentum $\vec{H}=\vec{r} \times \dot{\vec{r}}=\vec{r} \times \overrightarrow{\mathrm{v}}$. We see that it essentially stems from the isotropy of the interaction. Furthermore, cross product of the equation of motion with the specific angular momentum $\vec{H}$ yields, after some straight forward manipulation, the conservation of yet another vector, namely the Laplace-Runge-Lenz [4] (LRL) vector,

$$
\vec{A}=(\overrightarrow{\mathrm{v}} \times \vec{H})-\kappa \hat{e}_{\rho},
$$

where $\hat{e}_{\rho}$ is a unit vector along the radial line toward the object in motion, drawn from the origin of a plane polar coordinate system located at the centre of mass.

[^2]The LRL vector is sometimes alternatively (but equivalently) defined as

$$
\vec{A}=\frac{(\vec{p} \times \vec{L})}{\mu}-\kappa \hat{e}_{\rho},
$$

wherein the new $\kappa$ now has dimensions $M L^{3} T^{-2}$.

The constancy of the LRL vector, directed always from the focus to the perigee of the ellipse, explains the fact that in the gravitational two-body problem whose closed orbits are described by an ellipse, the major axis of the ellipse is fixed; there is no rosette motion (i.e., there is no precession). The necessary and sufficient condition that the LRL [5] vector is fixed is the fact that the gravitational potential goes as $\frac{1}{r}$, and the force as $\frac{1}{r^{2}}$. Since the inverse square law of the force appears as a necessary condition, the symmetry related to the constancy of the LRL vector and associated fixation of the ellipse's major axis is often called as the 'dynamical' symmetry. It is almost startling that straight-forward mathematics such as integration, scalar and vector products, as described above reveal the intimacy between symmetry and conservation laws. One can only perhaps attribute this to the "unreasonable power of mathematics", as Wigner [6] would say, in explaining physical laws.

We note from the above discussion that the symmetry associated with respect to temporal evolution of an isolated system (whose Lagrangian has no explicit dependence on time) is associated with the conservation of energy, symmetry associated with the isotropy of the gravitational interaction is associated with the conservation of angular momentum, and the 'dynamical' symmetry of the $\frac{1}{r}$ gravitational interaction is connected with the constancy of the LRL vector and the associated fixation of the Kepler-ellipse in the two-body problem. We find that conservation principles are derivable, quite simply, from the physical law. In the next section we ask if the reverse process is possible.

## II. Physical Laws from the Conservation Principles

[^3]We consider a system of N particles in a medium that is homogenous. An infinitesimal virtual [4] instantaneous displacement of the entire N-particle system through $\overrightarrow{\delta S}$ in this medium would result in a new configuration that would find itself in an environment that is completely indistinguishable from the previous one. No external force is applied in the virtual displacement. Denoting the force on the $\mathrm{k}^{\text {th }}$ particle by the $\mathrm{i}^{\text {th }}$ by $\vec{F}_{i k}$, we find, since internal forces do no work toward the virtual displacement, that

$$
\begin{equation*}
0=\delta W=\left\{\sum_{k=1}^{N} \vec{F}_{k}\right\} \bullet \overrightarrow{\delta s}=\left\{\sum_{k=1}^{N} \sum_{i=1, i \neq k}^{N} \vec{F}_{i k}\right\} \bullet \overrightarrow{\delta s}, \tag{Eq. 5}
\end{equation*}
$$

$\vec{F}_{k}$ being the force on the $k^{t h}$ particle due to the remaining $N-1$ particles.
The necessary and sufficient condition that Eq. 5 holds for an arbitrary displacement is that

$$
\begin{equation*}
\overrightarrow{0}=\left\{\sum_{k=1}^{N} \vec{F}_{k}\right\}=\sum_{k=1}^{N} \frac{d \vec{p}_{k}}{d t}=\frac{d}{d t} \sum_{k=1}^{N} \vec{p}_{k}=\frac{d \vec{P}}{d t} . \tag{Eq. 6}
\end{equation*}
$$

We have used, to arrive at Eq. 6 from Eq.5, the first two laws of Newton, but of course not the third. Rather, the third law follows from Eq. 6 since application of Eq. 5 to a two-body system results in

$$
\begin{equation*}
\frac{d \overrightarrow{p_{2}}}{d t}=-\frac{d \overrightarrow{p_{1}}}{d t} \text {, i.e., } \vec{F}_{12}=-\vec{F}_{21} \tag{Eq. 7}
\end{equation*}
$$

which of course is Newton's III law, that action and reaction are equal and opposite. We see here that the physical law has followed from an invariance/symmetry principle. Likewise, from the fact that the LRL vector is a constant if and only if the interaction is governed by the inverse square law, one could have deduced the $\frac{1}{r}$ form of the gravitational interaction.

We thus find that indeed it is possible to get a physical law from a symmetry/conservation principle, just as we saw in Section I that conservation principles follow from the physical law. In fact, the role of 'symmetry' as a guiding principle became firmly established when Einstein recognized that the symmetry in the expressions for the curl of the electric field and that of the magnetic field seen in Maxwell's equations was pivotal to the recognition of the constancy of the speed of light in vacuum in all inertial frames of reference and thus for the fundamental principles of the special theory of relativity.

[^4]
## III. Symmetry of the Atomic Hamiltonian, and Spectra of the I Group Atoms

In Section I we saw that conservation principles are derivable from the physical law, and in Section II we saw that the physical law is obtainable from the underlying symmetry associated with the conservation principles. As to which way the relationship has its most natural flow is best explained by Wigner [7,8]: " It is now natural for us to derive the laws of nature and to test their validity by means of the laws of invariance, rather than to derive the laws of invariance from what we believe to be the laws of nature".

We now examine the importance of symmetry with regard to specific interest in atomic physics. The discrete symmetries, namely parity ( P ), charge conjugation ( C ) and timereversal ( T ) symmetry constitute an important cornerstone of the standard model of physics. PCT symmetry has important implications in atomic physics [9,10,11,12]. Also, important physical processes to probe the atom, namely electron-atom collisions and atomic photoionization, are related to each other by the time-reversal symmetry, discussed elsewhere [11].

In the present article, we focus on an interesting consequence of the so-called 'dynamical symmetry' of the Coulomb interaction, also described by the $\frac{1}{r}$ attraction between the electron and the proton in the hydrogen atom. This symmetry, and/or its breakdown, has an important consequence on the spectra of the atoms belonging to the I Group of the periodic table.

The importance of studying the symmetry aspects of the hydrogen atom is best illustrated in the context of the well-known D1, D2 lines (Fig.1) of the sodium vapour lamp. For the present purpose, we do not get into the complexities of the alkali atom spectra arising out of the hyperfine structure and the Lamb shift. The yellow doublet lines of the sodium atom occur due to transitions from the relativistic spin-orbit split $3 \mathrm{p}_{3 / 2}$ and $3 \mathrm{p}_{1 / 2}$ levels to the 3 s level; and the fact that the energy of the 3 p level is different from that of the 3 s in the sodium atom is of fundamental consequence to these spectral line. Similar lines are seen in all the

[^5]alkali atoms of the I Group of the periodic table, except the hydrogen atom, in which the 3p and 3 s levels are degenerate; and this is because of the fact that the symmetry of the hydrogen atom is essentially different from that of the other atoms of the I Group elements, as explained below. Transitions resulting from the relativistic and Lamb shift splitting in the hydrogen atom would fall in the microwave region of the electromagnetic spectrum, not in the optical region.


Fig.1: There would be no D1,D2 lines in the sodium atom's spectrum if the energy of the 3 p state were the same as that of the 3 s state.

The reason why the spectrum of the hydrogen atom is fundamentally different amongst all elements of the I group is the degeneracy of the hydrogen atom's eigen-states with different values of the orbital angular momentum, $l$, for a given value of the principal quantum number $n$. The hydrogen atom's eigenvalues are given by the famous Balmer-RydbergBohr $\frac{1}{n^{2}}$ law, independent of $l$, whereas the eigenvalues of states of other atoms in the Group I depend not just on the principal quantum number as per the Balmer-Rydberg-Bohr law, but also on the orbital angular momentum quantum number. This $l$-dependence enables the transitions that generate the D lines, and along with the relativistic spin-orbit splitting, we get the D1,D2 transitions. What connects this problem to the symmetries in Sections I and II is the fact that degeneracy and symmetry go together in quantum mechanics. The symmetry and invariance principle responsible for the peculiar degeneracy in the hydrogen atom is that of the LRL vector describing the $\frac{1}{r}$ Coulomb potential in the electron-proton interaction. It seems not known if it is merely a coincidence that the form of

[^6]the Coulomb interaction is similar to that of the gravitational interaction, both governed by the inverse square law. As discussed in this article, it is however understood that if it were not so, planetary orbits would not really be stable, so perhaps this was natural selection by nature. Regardless, the constancy of the LRL vector has important consequences for the quantum mechanics of the hydrogen atom. However, unlike the Kepler orbit of 'classical mechanics', the quantum hydrogen atom does not have any 'orbit'. An orbit can be defined only if position and momentum are simultaneously measurable. We therefore do not talk about (Bohr-type) orbits, but quantize the LRL vector, following Pauli [13], now referred to as the Pauli-Lenz operator:
\[

$$
\begin{equation*}
\vec{A}=\vec{A}_{Q M}=\frac{1}{2 \mu}[\vec{p} \times \vec{L}-\vec{L} \times \vec{p}]-\kappa \hat{r} . \tag{Eq. 8}
\end{equation*}
$$

\]

We note that quantization results in $\vec{A}$ of Eq. 8 to be a vector operator. In contrast, the corresponding term in classical mechanics represented by Eq. 4 is not an operator; it is only a vector. The Pauli-Lenz quantum operator commutes with the Hamiltonian for the hydrogen atom.

It should be noted that the 1-dimensional radial Schrödinger equation for the hydrogen atom does not explain the degeneracy of the hydrogen atom, as can be seen directly from it:

$$
\begin{equation*}
\frac{1}{r^{2}} \frac{d}{d r}\left(r^{2} \frac{d R}{d r}\right)-\frac{l(l+1)}{r^{2}} R+\frac{2 m}{\hbar^{2}}[E-V(r)] R=0 . \tag{Eq. 9}
\end{equation*}
$$

It is well known that in a 1-dimensional problem, none of the energy values of the discrete spectrum is degenerate. Hence, it seems natural, from Eq.9, that the energies of all states with quantum numbers $n, l$ corresponding to different values of $l$ have different energies. Eq. 9 does not therefore account for the degeneracy in the hydrogen atom with regard to the different values of $l$. One can count this degeneracy easily. It is given by:

$$
\begin{equation*}
\sum_{l=0}^{n-1}(2 l+1)=2 \sum_{l=0}^{n-1} l+\sum_{l=0}^{n-1} 1=2 \frac{n(n-1)}{2}+n=n^{2}-n+n=n^{2} . \tag{Eq. 10}
\end{equation*}
$$

[^7]The $n^{2}$-fold degeneracy of the hydrogen atom follows from the geometric (isotropic) symmetry of the Hamiltonian which provides for $(2 l+1)$ - fold degeneracy for each allowed value of $l$, together with an additional symmetry responsible for the fact that all states with $l=0,1,2,3, \ldots,(n-1)$ of the hydrogen atom are degenerate, but not so for other atoms of the I Group atoms. The radial Schrödinger equation does not account for the degeneracy in the hydrogen atom. It is therefore often referred to as 'accidental' degeneracy.

To explain the $n^{2}$ - fold degeneracy of the hydrogen atom, we must examine the symmetry group of the hydrogen atom, inclusive of the Pauli-Lenz operator of Eq.8. The three components of the Pauli-Lenz vector operator $\vec{A}$, along with the three components of the angular momentum operator $\vec{l}$ provide, a closed algebra even if only over the subspace of Hilbert space of eigenvectors belonging to a particular bound state energy eigenvalue $E$. This follows from the fact, as can be verified with some bit of patient algebra, that the following relations hold:

$$
\begin{align*}
& {\left[L_{i}, L_{j}\right]=i \hbar \varepsilon_{i j k} L_{k},} \\
& {\left[A_{i}, L_{j}\right]=i \hbar \varepsilon_{i j k} A_{k},} \\
& \text { and }\left[A_{i}, A_{j}\right]=-2 i \frac{\hbar}{\mu} H \varepsilon_{i j k} L_{k} .
\end{align*}
$$

The appearance of the Hamiltonian operator on the right hand side of Eq.11c restricts the algebra of $\vec{L}, \vec{A}$ to be closed only over the subspace of Hilbert space of eigenvectors belonging to a particular bound state energy eigenvalue $E$. The three components of the angular momentum operator $\vec{L}$, together with the three components of the Pauli-Lenz vector operator $\vec{A}$, constitute a set of six generators of the Lie Group of dimensions six, known as the $\mathrm{SO}(4)$ group, of Rank 2. Now, as per Racah's theorem, the number of Casimir [14] operators for the group is equal to the rank of the group. The two Casimir operators of the $\mathrm{SO}(4)$ group can be written as:
$C_{1}=I^{2}+K^{2} \quad$ Eq.12a
and $C_{2}=I^{2}-K^{2}$,

[^8]where $\vec{I}=\frac{1}{2}\left(\vec{L}+\vec{A}^{\prime}\right)$ and $\vec{K}=\frac{1}{2}\left(\vec{L}-\vec{A}^{\prime}\right)$, with $\vec{A}^{\prime}=\sqrt{\frac{-\mu}{2 E}} \vec{A}$.

Eq.12c

Eq.12d

Both the Casimir operators commute with each of the six generator of the $\mathrm{SO}(4)$ group. The operators $\vec{I}$ and $\vec{K}$ satisfy the commutation algebra for quantum angular momentum vector operators as can be verified:
$\left[I_{x}, I_{y}\right]_{-}=i \hbar I_{z}$ etc. and $\left[K_{x}, K_{y}\right]_{-}=i \hbar K_{z}$ etc.
$\vec{I}$ and $\vec{K}$ are referred to as quantum 'pseudo' angular momentum vector operators since they combine the polar vector $\vec{A}$ with the axial vector $\vec{L}$. The eigenvalues of $I^{2}$ and $K^{2}$ are thus given respectively by $\hbar^{2} i(i+1)$ and $\hbar^{2} k(k+1)$ as is well-known from angular momentum algebra.

Now, $i=k$, since it can be seen that $C_{2}=\vec{L} \square \vec{A}^{\prime}=0$.
Eq. 14a
The eigenvalue of the operator $C_{1}$ is therefore:
$2 \hbar^{2} k(k+1)=c_{1}=2 \hbar^{2} i(i+1)$.
Eq. 14b
Again, since $C_{1}=I^{2}+K^{2}$, we get
$c_{1}=\frac{1}{4}\left(\vec{L}^{2}+\vec{L} \square \vec{A}^{\prime}+\vec{A} \cdot \square \vec{L}+\vec{A}^{\prime^{2}}\right)+\frac{1}{4}\left(\vec{L}^{2}-\vec{L} \square \vec{A}^{\prime}-\vec{A} \cdot \square \vec{L}+\vec{A}^{\prime}{ }^{2}\right)$,
i.e., $c_{1}=\frac{1}{2}\left(\vec{L}^{2}+\vec{A}^{\prime}{ }^{2}\right)=\frac{1}{2} \vec{L}^{2}+\frac{1}{2} \vec{A}^{\prime 2}=\frac{1}{2} \vec{L}^{2}+\frac{1}{2}\left(\frac{-\mu}{2 E}\right) \vec{A}^{2}$.

Now, using the fact that $\vec{A} \square \vec{A}=\frac{2}{\mu} H\left(\vec{L}^{2}+\hbar^{2}\right)+\kappa^{2}$,
Eq. 16a
we get:
$c_{1}=\frac{1}{2} \vec{L}^{2}+\frac{1}{2}\left(\frac{-\mu}{2 E}\right)\left\{\frac{2 H}{\mu}\left(L^{2}+\hbar^{2}\right)+\kappa^{2}\right\}$,
Eq. 16 b
i.e., $c_{1}=-\frac{1}{2} \hbar^{2}-\frac{1}{2}\left(\frac{\mu}{2 E}\right) \kappa^{2}=-\left(\frac{\mu}{4 E}\right) \kappa^{2}-\frac{1}{2} \hbar^{2}$.

Eq. 16c

We have recognized in Eq. 16 that $\frac{H}{E}=1$, since over the domain of our exercise, which is the subspace of eigenvectors belonging to a given bound state energy eigenvalue $E$, the Hamiltonian $H$ would always return essentially the same eigenvalue $E$.

From Eq. 14 and 16, it follows that:

$$
\begin{equation*}
c_{1}=2 \hbar^{2} k(k+1)=2 \hbar^{2} i(i+1)=-\left(\frac{\mu}{4 E}\right) \kappa^{2}-\frac{1}{2} \hbar^{2}, \tag{Eq. 17}
\end{equation*}
$$

which gives the Balmer-Rydberg-Bohr expression (as shown, for example, in Ref [15], Eq. 14.35 and [16], Eq.12.85):

$$
E=-\frac{m k^{2}}{2 \mathrm{~h}^{2}\{4 i(i+1)+1\}}=-\frac{m k^{2}}{2 \mathrm{~h}^{2} n^{2}},
$$

with $n=(2 i+1)$,
recognized immediately as the principal quantum number.

Now, $i$, being a ('pseudo') angular momentum quantum number as per Eq.13, has a degeneracy which is $(2 i+1)-$ fold . Likewise, $k$ has a degeneracy which is $(2 k+1)-$ fold . The principal quantum number $n$ can get its integer value $n=2 i+1=2 k+1$, either from $i$, or from $k$ (with $i=k$ ). The quantum state with a given value of the principal quantum number $n$ therefore has a degeneracy given by $(2 i+1) \times(2 i+1)=n^{2}$, very much in accordance with Eq.10. The $n^{2}$-fold degeneracy which is peculiar only to the hydrogen atom amongst all the atoms of the I Group elements, regarded earlier only as 'accidental degeneracy' in the Schrödinger formulation, is thus not quite an 'accident'; it has a proper explanation in its $\mathrm{SO}(4)$ symmetry. This symmetry does not hold for any of the other atoms of the I Group elements, since they have $Z>1$ protons and for them only in the asymptotic

[^9]limit, $r \rightarrow \infty$, does the potential seen by the outer $n$, $l$ electron goes as $-\frac{1}{r}$; but as $r \rightarrow 0$, the potential goes as $-\frac{Z}{r}$. The potential is no longer strictly described by the $-\frac{1}{r}$ law in the entire region of space, as required for the Pauli-Lenz operator to represent a constant of motion, as discussed earlier.

The energy of all atoms with $Z>1$ is then expressed by a modified law, which goes as $E_{n}^{(Z>1)} \rightarrow E_{n, l} \rightarrow \frac{1}{\left(n-\mu_{l}\right)^{2}}$ whereas for the hydrogen atom we have $E_{n}^{(Z=1)} \rightarrow \frac{1}{n^{2}}$, independent of $l . \mu_{l}$ is called as the 'quantum defect' and it depends on the orbital angular momentum quantum number. Finally, and not surprisingly, the fact that $\vec{I}$ and $\vec{K}$ are pseudo angular momentum vector operators which combine a polar with an axial vector, is responsible for the fact that in the hydrogen atom, states with opposite parity are degenerate.

It may be noted that for atoms with $Z>1$, two types of semi-empirical modifications to the hydrogenic formula were employed in the early days of quantum mechanics. The modifications were made to both the numerator and to the denominator in the hydrogenic Balmer-Rydberg-Bohr expression for energy. Correction due to screening was indicated by screening parameters, with Z replaced by $Z-\sigma, \sigma$ being the screening parameter. The screening accounted for the effective shielding of the attractive nuclear potential by the electron cloud generated by the remaining electrons. On the other hand, modification was also introduced by replacing the principal quantum number n by $n-\mu$, with the quantum defect $\mu$ accounting for the departure from the strict $\frac{1}{r}$ potential which makes the PauliLenz vector operator a constant of motion in the hydrogen atom. The potential seen by an outer electron becomes $\frac{1}{r}$ only in the asymptotic limit, $r \rightarrow \infty$ for all atoms having more than a single electron. The hydrogen atom is the only one in the periodic table for which the potential is $\frac{1}{r}$ in the entire space, $0 \leq r<\infty$. The fact that states with different orbital angular momentum $l$ for all atoms of the first group of the periodic table, other than the
hydrogen atom, have different energies is then due to the fact that the $\mathrm{SO}(4)$ symmetry of the hydrogen atom is broken for them. Earlier works on electronic shielding and quantum defects was based on semi-empirical considerations [17,18]; these important results are now integrated comprehensively in the quantum defect theory of the atomic spectra [19,20,21,22].

The present approach underscores an important point regarding just what is meant by quantization. Explaining 'quantization' merely in terms of 'discrete energy states' is of course misleading, since the very same Schrodinger equation which admits discrete energy state solutions for bound states also admits continuum solutions for unbound states; the difference merely being in the boundary conditions imposed to solve the differential equation. Furthermore, explaining 'quantization' as a set of phenomena that require the Schrodinger equation is also inadequate, since the Schrodinger equation does not explain the degeneracy with respect to the $l$ quantum number of the hydrogen atom. Quantum mechanics is deeper than the Schrodinger equation; it requires employing operators $\left(q_{o p}, p_{o p}\right)$ instead of the classical dynamical variables $(q, p)$, followed by extraction of physical information about the system from the operator algebra by developing it further [23].

It is interesting to emphasize in this context, that since the present approach rests on the fundamental tenets of quantum theory, it explains the energy spectrum of the hydrogen atom and also its degeneracy without using the Schrodinger equation. This is akin to getting the elliptic orbit shape for the trajectory of a planet's trajectory around the sun, from the properties of the Laplace-Runge-Lenz vector, without [4] even solving the classical equation of motion. In fact, one gets not only the energies of the bound states and account for the degeneracy as explained above, one can also get $[24,25,26]$ the hydrogen atom's wavefunctions without using the Schrodinger equation, as shown in the next Section.

## IV. Hydrogen atom wave functions from the Pauli-Lenz vector operator

For the ground state $n=1$, represented as $|1\rangle$, we have from Eq. $18 \mathrm{~b} i=0=k$.

[^10]Thus: $\stackrel{1}{I}|1\rangle=0, \quad$ and also, $\quad \stackrel{1}{K}|1\rangle=0$.
Hence,

$$
\begin{align*}
& \vec{L}|1\rangle=(\vec{I}+\vec{K})|1\rangle=0 \quad \text { and } \vec{A}|1\rangle=(\vec{I}-\vec{K})|1\rangle=0 \\
& \text { i.e. } \quad \vec{A}_{Q M}|1\rangle=\left[\frac{1}{2 \mu}(\vec{p} \times \vec{L}-\vec{L} \times \vec{p})-\kappa \hat{\rho}\right]|1\rangle=0 \tag{Eq. 20}
\end{align*}
$$

Now, the $\mathrm{i}^{\text {th }}$ component of $(\vec{L} \times \vec{p})$ is given by:
$(\vec{L} \times \vec{p})_{i}=\sum_{j=1}^{3} \sum_{k=1}^{3} \epsilon_{i j k} L_{j} p_{k} \equiv \epsilon_{i j k} L_{j} p_{k}=\epsilon_{i j k} \epsilon_{j l m} \mathrm{r}_{l}\left(\mathrm{p}_{m} p_{k}\right)=\left(-\epsilon_{j i k}\right) \epsilon_{j l m}\left(r_{l} p_{k}\right) p_{m} \quad$ Eq. 21
i.e. $(\vec{L} \times \vec{p})_{i}=-\epsilon_{j i k} \epsilon_{j l m}\left(i \hbar \delta_{l k}+p_{k} r_{l}\right) p_{m}$, on account of the uncertainty principle commutation property of the position and the momentum operators.

Hence, $(\vec{L} \times \vec{p})_{i}=\left[i \hbar \epsilon_{i j k} \epsilon_{j l m} \delta_{l k} p_{m}-\epsilon_{j i k} p_{k} L_{j}\right]=\left[i \hbar\left(2 \delta_{i m}\right) p_{m}-\epsilon_{j i k} p_{k} \mathrm{~L}_{j}\right] . \quad$ Eq. 22
Inserting Eq. 22 in Eq.20, we get an equivalent form of the Pauli-Lenz vector operator:

$$
\begin{equation*}
\vec{A}=\frac{1}{\mu}[(\vec{p} \times \vec{L})-i \hbar \vec{p}]-\kappa \hat{r}, \tag{Eq. 23}
\end{equation*}
$$

Hence: $\quad\{\vec{p} \times \vec{L}-i \hbar \vec{p}-\mu \kappa \hat{r}\}|1\rangle=0$,
or, $\{i \hbar \vec{p}+\mu \kappa \hat{r}\}|1\rangle=0 \quad$ i.e. $\left\{\vec{\nabla}+\frac{\mu e^{2}}{\hbar^{2}} \hat{r}\right\}\langle\vec{r} \mid 1\rangle=\left\{\vec{\nabla}+\frac{\mu e^{2}}{\hbar^{2}} \hat{r}\right\} \psi_{1,0}(\vec{r})=0$.
Eq. 24 is a first order differential equation; it is of course not the Schrodinger equation nor has it been obtained using the Schrodinger equation. It has been obtained completely from the properties of the Pauli-Lenz vector operator. As seen readily, the Eq. 24 admits the solution $\psi_{1,0}(\vec{r})=\frac{1}{\sqrt{\pi a_{0}{ }^{3}}} e^{-r / a_{0}}$, with $a_{0}=\frac{\hbar^{2}}{\mu e^{2}}$, which is the familiar ground state of the hydrogen atom. We thus see that not merely do we get the energy states from the Pauli-Lenz vector operator, we also get the ground state wave function - without using the Schrodinger equation! In fact, one can get the excited states also following similar technique [24,25,26].

## V. Conclusions

Symmetry plays a pivotal role in nature. From the conservation laws of energy, momentum and angular momentum that are determined by the invariance of the physical system/processes with respect to translations in time, and in homogeneous and isotropic space respectively, to the symmetry in Maxwell's equations with regard to the electric and magnetic fields, through the symmetry in nature revealed as the wave-particle duality, the subject of invariance in nature becomes only increasingly mindboggling. Other forms of symmetries such as the dynamical symmetry, discrete symmetries such as parity, timereversal and charge conjugation, also impact physical processes in the universe. The reduction of the 3 -dimensional Schrödinger equation to 1 -dimensional radial equation explains why the energies of states with different $l$ values have different energies in atoms such as sodium, but their degeneracy in the hydrogen atom requires the recognition of the SO(4) symmetry of the Hamiltonian for the hydrogen atom. This important difference between the symmetry of the hydrogen atom and that of the other atoms of the I Group elements is responsible for the appearance of the D1,D2 lines in all I Group atoms except the hydrogen atom. In the past few years, there is renewed interest in the $\mathrm{SO}(4)$ symmetry of the hydrogen atom, reflected in its relativistic [27] formulation. The present approach not merely generates the eigenvalues of the hydrogen atom and explains its degeneracy without using the Schrödinger equation, it also provides the radial wavefunctions of the hydrogen atom. That one obtains the eigenvalues and the eigenfunctions without even using the Schrödinger equation is not surprising, since we have of course used the essentials of quantum mechanics, which is to use the state vectors and the quantum operators instead of the classical representation of a system by a point in phase space.

Finally, we mention that a deviation from the inverse square law in gravitation generates apsidal precession [28,29,30]; it is a result of different reasons such as three-body interactions and/or relativistic effects.

The interested reader may go beyond the pedagogical treatment discussed above by referencing some well-known books [15,16,26,31,32]. Unfortunately, this exciting topic is

[^11]often not introduced in many courses on atomic physics and on quantum theory and thus merits, in our opinion, a pedagogical revisit.

Acknowledgment: PCD wishes to thank the Western University (London, Ontario, Canada), and especially to Dr. Shantanu Basu, Dr. Sree Ram Valluri and Dr. Kenneth Roberts, for hospitality, and as much for fruitful discussions. AG and NS wish to thank the Jain University (Bangalore, India) for partial funding of this work; and BJ and JN thank the Western University for a summer internship. This article is based on the keynote address [33] given by PCD at the National Conference on Electron Collision Processes in Atomic and Molecular Physics, held at V.P. \& R.P.T.P. Science College Charutar Vidya Mandal, Gujarat, India in March 2013.

## References

[1] Capria, Marco Mamone (Ed.) 'Physics Before and After Einstein' (IOS Press, 2005)
[2] R.P. Feynman, 'The Character of the Physical Law' ('Messenger Lectures' at Cornell University in 1964, published by Modern Library, 1994)
http://www.youtube.com/watch?v=j3mhkYbznBk [Link downloaded on 2013-08-15]
[3] E.P. Wigner, 'Events, laws of nature, and invariance principles' ('Nobel Lecture' delivered on December 12, 1963
http://www.nobelprize.org/nobel_prizes/physics/laureates/1963/wigner-lecture.pdf
[Link downloaded on 2013-08-15]
[4] H. Goldstein, Poole, C.P.(Jr.) and Safko, J.L. 'Classical Mechanics (3rd Edition)'
Addison-Wesley; 3 edition (June 25, 2001)
[5] P.C.Deshmukh, 'Special/Select Topics in Classical Mechanics', Modules 4 at the link http://nptel.ac.in/courses/115106068/; [Link downloaded on 2014-05-22]
[6] E.P. Wigner, 'The unreasonable effectiveness of mathematics in the natural sciences' Richard Courant Lecture in mathematical sciences delivered at New York University on May 11, 1959, Communications on Pure and Applied Mathematics, Vol. 13, pages 1-14, (1960).

[^12][7] Brading, Katherine and Castellani, Elena, "Symmetry and Symmetry Breaking", The Stanford Encyclopedia of Philosophy (Spring 2013 Edition), Edward N. Zalta (ed.), http://plato.stanford.edu/archives/spr2013/entries/symmetry-breaking/
[Link downloaded on 2013-08-15]
[8] E.P. Wigner, 'Symmetries and Reflections', (Bloomington, Indiana: Indiana University Press, 1967).
[9] Marie-Anne Bouchiat and Claude Bouchiat 'Parity violation in atoms' Rep. Prog. Phys. 601351 (1997)
[10] B. E. Sauer, J. A. Devlin, J. J. Hudson, D. M. Kara, I. J. Smallman, M. R. Tarbutt and E. A. Hinds 'Time reversal symmetry violation in the YbF molecule'Hyperfine Interact 214:119-126 (2013)
[11] P. C. Deshmukh, Dilip Angom and Alak Banik 'Symmetry in Electron-Atom Collision and Photoionization Process', DST-SERC-School publication (Narosa, November 2011); collection of articles based on lecture course given at the DST-SERC School at the Birla Institute of Technology, Pilani, January 9-28, 2011.
[12] P. C. Deshmukh and J. Libby 'Symmetry Principles and Conservation Laws in Atomic

- and Subatomic Physics' Resonance, 15, 832 (2010) and Resonance, 15, 926 (2010)
- [13] W. Z. Pauli, Phys. 36 336-363 (1926)
[14] H.B.G. Casimir, Proc. Roy. Soc. Amsterdam 34844 (1931)
[15] Walter Greiner and Berndt Muller. 'Quantum Mechanics - Symmetries (2 ${ }^{\text {nd }}$ Revised Edition)', Springer, Chapter 14, page 457 (1994)
[16] Eugen Merzbacher, 'Quantum Mechanics, (3rd Edition)', John Wiley \& Sons, International Edition, Chapter 12, page 269 (1998)
- [17] J.C.Slater, Phys. Rev. 3657 (1930)
[18] H.E.White. 'Introduction to Atomic Spectra', McGraw Hill, (1934)
- [19] C. H. Greene, A. R. P. Rau, and U. Fano, Phys. Rev. A 26, 2441 (1982)
$-[20]$ M. J. Seaton, Rep. Prog. Phys. 46, 167 (1983)
[21] U. Fano, and A.R.P Rau, 'Theory of Atomic Collisions and Spectra', Academic Press, (1986)
- [22] C.M.Lee and W.R.Johnson, Phys. Rev. A., 22, 979 (1980)
[23] P.A.M. Dirac, 'Principles of Quantum Mechanics’

[^13][24] C.E.Burkhardt and J.J.Leventhal: 'Lenz vector operations on spherical hydrogen atom -eigenfunction' Am. J. Phys. 72, 1013 (2004).
[25] P.C.Deshmukh, 'Special/Select Topics in Atomic Physics', Unit 1, at the link http://nptel.ac.in/courses/115106057/; [Link downloaded on 2014-05-22]
[26] Robert Gilmore: 'LIE GROUPS, PHYSICS, AND GEOMETRY - An Introduction for Physicists, Engineers and Chemists',Section 14.6, page 230 (Cambridge University Press, 2008)
[27] Jing-Ling Chen, Dong-Ling Deng, and Ming-Guang Hu, 'SO(4) symmetry in the -relativistic hydrogen atom', Phys. Rev. A 77, 034102 (2008)
[28] S.R.Valluri, C. Wilson and W. Harper 'Newton's Apsidal Precession Theorem and Eccentric Orbits’, Journal of the History of Astronomy 28: 13-27 (1997).
[29] S. R. Valluri, R. G. Biggs, W. L. Harper, and Curtis Wilson 'The Significance of the Mathieu-Hill Differential Equation for Newton's Apsidal Precession Theorem', Canadian Journal of Physics, 77, 393-407, (1999)
[30] S.R.Valluri, P. Yu, G.E. Smith, and P.A. Wiegert (2005) 'An Extension of Newton's Apsidal Precession Theorem', Monthly Notices of the Royal Astronomical Society 358 (4): 1273-1284 (2005)
[31] Leonard I. Schiff. 'Quantum Mechanics (3 ${ }^{\text {rd }}$ Edition, page 236)' McGraw-Hill Book Company; (January 1, 1968)
[32] Brian R. Judd. 'Angular Momentum Theory for Diatomic Molecules' Academic press Inc., Sections 3.5-3.8, (1975)
[33] P.C.Deshmukh, 'Invariance principles and spectra of the first group atoms', Keynote address delivered at the National Conference on Electron Collision Processes in Atomic and Molecular Physics (ECPAMP-2013), March 7-9, 2013, V. P. \& R. P. T. P. Science College Charutar Vidya Mandal, Gujarat, India (Narosa, 2013).

[^14]
[^0]:    *pcd@physics.iitm.ac.in
    Proof checked 14'th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 1

[^1]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 2

[^2]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 3

[^3]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 4

[^4]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 5

[^5]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education’ Section of the Canadian Journal of Physics Page 6

[^6]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 7

[^7]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 8

[^8]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 9

[^9]:    *pcd@physics.iitm.ac.in
    Proof checked 14'th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 11

[^10]:    *pcd@physics.iitm.ac.in
    Proof checked 14'th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 13

[^11]:    *pcd@physics.iitm.ac.in
    Proof checked 14'th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 15

[^12]:    *pcd@physics.iitm.ac.in
    Proof checked 14'th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 16

[^13]:    *pcd@physics.iitm.ac.in
    Proof checked 14'th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 17

[^14]:    *pcd@physics.iitm.ac.in
    Proof checked 14th Aug 2014 Article for the 'Physics Education' Section of the Canadian Journal of Physics Page 18

