

Lenz vector operations on spherical hydrogen atom eigenfunctions

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We show that operators capable of converting certain spherical hydrogen atom eigenfunctions into others by raising the angular momentum quantum number ℓ can be constructed from components of the quantum mechanical Lenz vector operator. The derivation is performed using formalism no more sophisticated than that used to derive the properties of the angular momentum ladder operators in undergraduate quantum mechanics courses. The properties of these Lenz vector operators illustrate the accidental degeneracy of the hydrogen atom because they change the quantum number ℓ without affecting n . © 2004 American Association of Physics Teachers.

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I. INTRODUCTION

It is well-known that the Kepler/Coulomb potentials endow planetary orbits and hydrogen atoms with special properties which are not present in systems subject to other central potentials. For example, a pure Keplerian orbit does not precess. Moreover, the total energy of the system depends only on the value of the semi-major axis and not on that of the semi-minor axis. There exists, therefore, an infinity of possible orbits, all having the same energy and semi-major axis, but having different values for the semi-minor axis. While the semi-major axis is independent of the angular momentum, the semi-minor axis is determined by the angular momentum, so the energy is independent of the angular momentum. This classical degeneracy is the result of the same symmetry of the $1/r$ potential that causes the celebrated “accidental degeneracy” of the hydrogen atom, i.e., the independence of the energy eigenvalues on the angular momentum quantum number ℓ . This symmetry is different from the spatial symmetry that exists for any central potential. It is often referred to as a “dynamical symmetry.”¹ The spatial symmetry causes the energy to be independent of m , the quantum number corresponding to the z -component of the angular momentum.

Classically, the dynamical symmetry manifests itself as an additional constant of the motion, the Lenz vector \mathbf{A} , which points along the major axis of the ellipse.^{2,3} This results in an orbit that does not precess. Quantum mechanically, \mathbf{A} corresponds to an additional operator $\hat{\mathbf{A}}$ that commutes with the Hamiltonian \hat{H} as shown by Pauli in his landmark paper.⁴ Of course the magnitude of the angular momentum and each of its components also commute with \hat{H} for any central potential.

Although these consequences of the dynamical symmetry of the $1/r$ potential are rarely discussed at the undergraduate level, they provide insight into a variety of classical and quantum concepts. In this paper we will concentrate on the quantum mechanical consequences of the classical constant \mathbf{A} . We will show that it is possible to derive a set of operators consisting of components of \mathbf{A} that transform certain spherical hydrogen eigenstates into other spherical eigenstates. Spherical eigenstates are those that result from separation of the Schrödinger equation in spherical coordinates and are characterized by the quantum numbers n (energy), ℓ (angular

momentum), and m (z -component of angular momentum). The dynamical symmetry also makes it possible to separate the Schrödinger equation using parabolic coordinates.⁵ We also note that it is possible to take advantage of the dynamical symmetry to determine the energies of the hydrogen atom eigenstates using operator techniques alone.^{1,4}

II. BACKGROUND

The spherical form of any vector may be defined in terms of the Cartesian components. For the angular momentum we have

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y, \quad \hat{L}_0 = \hat{L}_z. \quad (1)$$

The fact that the \hat{L}_{\pm} change only the value of m and neither ℓ nor n when operating on a spherical eigenstate for any central potential is a manifestation of the degeneracy associated with the spatial symmetry of a central potential. Thus, the \hat{L}_{\pm} are ladder operators for *any* central potential. The spherical form of the Lenz vector operator may be similarly defined as

$$\hat{A}_{\pm} = \hat{A}_x \pm i\hat{A}_y, \quad \hat{A}_0 = \hat{A}_z. \quad (2)$$

It will be shown that \hat{A}_{\pm} and \hat{A}_0 (henceforth referred to as \hat{A}_z) effect state-to-state changes in the ℓ quantum number of certain hydrogen atom spherical eigenfunctions, *viz.* states for which $|m| = \ell$. Because \hat{A}_{\pm} and \hat{A}_z change ℓ without changing the energy they reflect the accidental degeneracy of the hydrogen atom in which the energy eigenvalues are independent of ℓ . In this paper we will derive the properties of \hat{A}_{\pm} and \hat{A}_z and obtain the exact expressions for the actions of these operators on selected eigenstates without having to resort to advanced concepts.⁶ The derivation will be carried out using formalism no more sophisticated than that used to derive the properties of \hat{L}_{\pm} in most undergraduate quantum mechanics courses. Additionally, it will be seen that, given the $\ell=0$ eigenfunction for a particular n , all eigenfunctions for that n can be obtained by judicious application of a combination of \hat{L}_{\pm} , \hat{A}_{\pm} and \hat{A}_z .

Using atomic units for which $\hbar = 1 = e = m_e$, where e is the electronic charge and m_e the electronic mass, the Lenz vector in classical mechanics is defined in atomic units as

Table I. List of some relations involving the quantum mechanical operators used in this work. ϵ_{ijk} is the Levi-Civita symbol defined as +1 for an even permutation of the i, j, k and -1 for an odd permutation; it vanishes if two or three indices are the same.

$\hat{\mathbf{L}} \cdot \hat{\mathbf{A}} = \hat{\mathbf{A}} \cdot \hat{\mathbf{L}} = 0$
$(\hat{A}_\mp)^\dagger = \hat{A}_\pm$
$(\hat{A}_\mp \hat{A}_\mu)^\dagger = \hat{A}_\pm \hat{A}_\mu$
$[\hat{L}_i, \hat{L}_j] = i\hat{L}_k \epsilon_{ijk}$
$[\hat{L}_\pm, \hat{A}_z] = \mu \hat{A}_\mp$
$[\hat{L}_i, \hat{A}_j] = i\hat{A}_k \epsilon_{ijk}$
$[\hat{A}_i, \hat{A}_j] = -2i\hat{L}_k \hat{H} \epsilon_{ijk}$
$\hat{A}^2 = 2(\hat{L}^2 + 1)\hat{H} + 1$
$\hat{A}_z = -\frac{1}{2}(\hat{L}_- \hat{A}_+ + \hat{A}_- \hat{L}_+) - \hat{A}_z \hat{L}_z$

$$\mathbf{A} = \mathbf{p} \times \mathbf{L} - \hat{\mathbf{r}}, \quad (3)$$

where \mathbf{p} is the linear momentum, \mathbf{L} is the angular momentum, and $\hat{\mathbf{r}}$ is the unit vector in the \mathbf{r} direction. The direction of \mathbf{A} , toward apocenter or pericenter, is a matter of choice. We elect the definition in Eq. (3).²

The quantum mechanical operator corresponding to \mathbf{A} cannot be constructed by merely replacing each quantity with its corresponding quantum mechanical operator because the result is a non-Hermitian operator. Pauli⁴ recognized that $\hat{\mathbf{A}}$ must be defined as

$$\hat{\mathbf{A}} = \frac{1}{2}[(\hat{\mathbf{p}} \times \hat{\mathbf{L}}) - (\hat{\mathbf{L}} \times \hat{\mathbf{p}})] - \hat{\mathbf{r}}. \quad (4)$$

Note that the quantum mechanical operators in the square brackets are not inverses of each other, i.e., $(\hat{\mathbf{p}} \times \hat{\mathbf{L}}) \neq -(\hat{\mathbf{L}} \times \hat{\mathbf{p}})$. It is easily shown that $\hat{\mathbf{A}}$ as defined in Eq. (4) is indeed Hermitian. It can also be shown, but with considerably more labor, that $[\hat{\mathbf{A}}, \hat{H}] = 0$.

It is shown in elementary quantum mechanics that the actions of \hat{L}_\pm on a spherical eigenfunction for any central potential, which we designate as $|n\ell m\rangle_C$, cause the following state-to-state conversions:

$$\hat{L}_\pm |n\ell m\rangle_C = \sqrt{(\ell \mp m)(\ell \pm m + 1)} |n\ell; (m \pm 1)\rangle_C, \quad (5)$$

where we have inserted a semi-colon between quantum numbers in the ket on the right hand side for clarity. Equation (5) is, of course, also valid for spherical hydrogen atom eigenfunctions since the Coulomb potential is a central potential.

III. THE ACTION OF \hat{A}_+

For convenience, a number of relations between the various operators to be used in this work are compiled in Table I. Some require lengthy algebraic manipulations, but the derivation of all is straightforward. We investigate the action of \hat{A}_+ on the spherical hydrogen eigenfunction $|n\ell m\rangle$. We indicate that this is a hydrogen eigenfunction by omitting the subscript C that was used to designate an eigenfunction for an arbitrary central potential. Using the relations contained in Table I we find that

$$\begin{aligned} \hat{L}_z \{\hat{A}_+ |n\ell m\rangle\} &= \hat{L}_z (\hat{A}_x + i\hat{A}_y) |n\ell m\rangle \\ &= \hat{A}_+ (\hat{L}_z + 1) |n\ell m\rangle = (m+1) \{\hat{A}_+ |n\ell m\rangle\}, \end{aligned} \quad (6)$$

which shows that $\{\hat{A}_+ |n\ell m\rangle\}$ is an eigenfunction of \hat{L}_z with eigenvalue $(m+1)$. Similarly

$$\begin{aligned} \hat{L}^2 \{\hat{A}_+ |n\ell m\rangle\} &= (\hat{A}_+ \hat{L}^2 - 2\hat{A}_z \hat{L}_+ + 2\hat{A}_+ + 2\hat{A}_+ \hat{L}_z) |n\ell m\rangle \\ &= \{\ell(\ell+1) + 2(m+1)\} \{\hat{A}_+ |n\ell m\rangle\} \\ &\quad - 2\hat{A}_z \sqrt{\ell(\ell+1) - m(m+1)} |n\ell; (m+1)\rangle. \end{aligned} \quad (7)$$

Note that the $|n\ell m\rangle$ are not eigenfunctions of \hat{A}_z , but if $m = \ell$ the term with \hat{A}_z vanishes and thus $\{\hat{A}_+ |n\ell\ell\rangle\}$ is an eigenfunction of \hat{L}^2 with eigenvalue

$$\ell(\ell+1) + 2(\ell+1) = (\ell+1)(\ell+2). \quad (8)$$

Because $\{\hat{A}_+ |n\ell\ell\rangle\}$ is an eigenfunction of \hat{L}^2 and \hat{L}_z with eigenvalues $(\ell+1)(\ell+2)$ and $(\ell+1)$ respectively, we know that

$$\hat{A}_+ |n\ell\ell\rangle = D_{\ell\ell}^+ |n; (\ell+1); (\ell+1)\rangle, \quad (9)$$

where $D_{\ell\ell}^+$ is a constant that depends on ℓ . This result is stated in the textbook by Shankar,⁷ but the derivation there employs tensor operators.

To complete the task it is necessary to evaluate $D_{\ell\ell}^+$. We begin by following a procedure similar to that used to evaluate the constants when finding the action of \hat{L}_\pm on the states $|n\ell m\rangle_C$. We consider the matrix element

$$\langle n\ell\ell | \hat{A}_- \hat{A}_+ |n\ell\ell\rangle = (D_{\ell\ell}^+)^* D_{\ell\ell}^+, \quad (10)$$

where the factor $(D_{\ell\ell}^+)^*$ was obtained by operating to the left with \hat{A}_- and noting that the Hermitian conjugate of \hat{A}_- is \hat{A}_+ . We specify for convenience, and by analogy with the assumption employed in the \hat{L}_\pm construction, that $D_{\ell\ell}^+$ is real. The operator $\hat{A}_- \hat{A}_+$ may be expanded giving

$$\begin{aligned} \hat{A}_- \hat{A}_+ &= \hat{A}^2 - \hat{A}_z^2 + 2\hat{L}_z \hat{H} \\ &= (2\hat{L}^2 \hat{H} + 2\hat{H} + 1) - \hat{A}_z^2 + 2\hat{L}_z \hat{H}. \end{aligned} \quad (11)$$

Since the $|n\ell m\rangle$ are eigenfunctions of all operators on the right hand side except \hat{A}_z we obtain

$$(D_{\ell\ell}^+)^2 = \left\{ \frac{n^2 - (\ell+1)^2}{n^2} \right\} - \langle n\ell\ell | \hat{A}_z^2 |n\ell\ell\rangle, \quad (12)$$

where we have used

$$\begin{aligned} \hat{L}^2 |n\ell\ell\rangle &= \ell(\ell+1) |n\ell\ell\rangle, \quad \hat{L}_z |n\ell\ell\rangle = \ell |n\ell\ell\rangle, \\ \hat{H} |n\ell\ell\rangle &= \left(-\frac{1}{2n^2} \right) |n\ell\ell\rangle. \end{aligned} \quad (13)$$

To complete the evaluation of $D_{\ell\ell}^+$ we must determine the matrix element $\langle n\ell\ell | \hat{A}_z^2 |n\ell\ell\rangle$. We operate on $|n\ell\ell\rangle$ with \hat{A}_z , and using a result from Table I we find

$$\begin{aligned} \hat{A}_z |n\ell\ell\rangle &= -[\frac{1}{2}\hat{L}_- \hat{A}_+ - \frac{1}{2}\hat{A}_- \hat{L}_+ + \hat{A}_z \hat{L}_z] |n\ell\ell\rangle \\ &= -\frac{1}{2} D_{\ell\ell}^+ \sqrt{2(\ell+1)} |n(\ell+1)\ell\rangle - \ell \hat{A}_z |n\ell\ell\rangle, \end{aligned} \quad (14)$$

from which we obtain

$$\hat{A}_z |n\ell\ell\rangle = -\frac{1}{\sqrt{2(\ell+1)}} D_{\ell\ell}^+ |n(\ell+1)\ell\rangle. \quad (15)$$

Thus, the matrix element $\langle n\ell\ell | \hat{A}_z^2 |n\ell\ell\rangle$ is given by

Table II. The results of operations on the specified spherical eigenfunctions of the hydrogen atom.

Operation	Result
$\hat{L}_z n\ell m\rangle$	$m n\ell m\rangle$
$\hat{L}_\pm n\ell m\rangle$	$\sqrt{(\ell \mp m)(\ell \pm m + 1)} n\ell; (m \pm 1)\rangle$
$\hat{A}_z n; \ell; (\pm \ell)\rangle$	$\frac{1}{n} \sqrt{\frac{[n^2 - (\ell + 1)^2]}{(2\ell + 3)}} n; (\ell + 1); (\pm \ell)\rangle$
$\hat{A}_+ n\ell\ell\rangle$	$-\frac{1}{n} \sqrt{\frac{2(\ell + 1)}{(2\ell + 3)}}[n^2 - (\ell + 1)^2] n; (\ell + 1); (\ell + 1)\rangle$
$\hat{A}_- n; \ell; (-\ell)\rangle$	$\frac{1}{n} \sqrt{\frac{2(\ell + 1)}{(2\ell + 3)}}[n^2 - (\ell + 1)^2] n; (\ell + 1); -(\ell + 1)\rangle$

$$\langle n\ell\ell|\hat{A}_z^2|n\ell\ell\rangle = \frac{(D_{\ell\ell}^+)^2}{2(\ell + 1)}. \quad (16)$$

Inserting Eq. (16) into Eq. (12), solving for $(D_{\ell\ell}^+)^2$ and taking the square root, we have

$$D_{\ell\ell}^+ = \pm \frac{1}{n} \sqrt{\frac{2(\ell + 1)}{(2\ell + 3)}}[n^2 - (\ell + 1)^2]. \quad (17)$$

It is important to note that, although the operator \hat{A}_- was present in our analysis of the action of \hat{A}_+ on $|n\ell\ell\rangle$, the only property of \hat{A}_- that was used was that it is the Hermitian conjugate is \hat{A}_+ . The action of \hat{A}_- on an eigenfunction was not needed. Also, because $D_{\ell\ell}^+$ was obtained by taking the square root of $(D_{\ell\ell}^+)^2$, there is no information on the sign of $D_{\ell\ell}^+$. In accordance with convention it is the minus sign that is retained.⁶

IV. THE ACTION OF \hat{A}_-

It is tempting to assume that \hat{A}_- acts as a lowering operator on certain spherical eigenfunctions. In fact, for certain state-to-state conversions it does lower the z -component of the angular momentum, but it raises the total angular momentum to $(\ell + 1)$. In a manner identical to that employed for $\{\hat{A}_+|n\ell m\rangle\}$ we find that $\{\hat{A}_-|n\ell m\rangle\}$ is an eigenfunction of \hat{L}_z with eigenvalue $(m - 1)$. Again in an analogous way we find that $\{\hat{A}_-|n\ell m\rangle\}$ is an eigenfunction of \hat{L}^2 provided $m = -\ell$, but with eigenvalue $(\ell + 1)(\ell + 2)$. We conclude therefore that

$$\hat{A}_-|n; \ell; (-\ell)\rangle = D_{\ell-\ell}^-|n; (\ell + 1); -(\ell + 1)\rangle, \quad (18)$$

where $D_{\ell-\ell}^-$ is a constant. Using a procedure analogous to that employed to evaluate $D_{\ell\ell}^+$ gives the magnitude of $D_{\ell-\ell}^-$; determination of the sign requires additional work.⁶ The result is

$$D_{\ell-\ell}^- = \frac{1}{n} \sqrt{\frac{2(\ell + 1)}{(2\ell + 3)}}[n^2 - (\ell + 1)^2] = -D_{\ell\ell}^+. \quad (19)$$

V. SUMMARY

The properties of the relevant operators are summarized in Table II. It is interesting to contrast the actions of \hat{L}_\pm and \hat{L}_z with those of \hat{A}_\pm and \hat{A}_z . For any central potential \hat{L}_\pm

change only the m quantum number, but neither n nor ℓ . This is a consequence of the spatial symmetry that causes the degeneracy in m for any central potential. \hat{L}_z , of course, does not change *any* quantum numbers because the spherical eigenfunctions are also eigenfunctions of \hat{L}_z . (Recall that the spherical eigenfunctions are obtained using the mutually commuting operators \hat{H} , \hat{L}^2 and \hat{L}_z .) On the other hand, \hat{A}_\pm change both ℓ and m . We note that in this paper we consider the actions of the \hat{A}_\pm on only eigenstates for which $|m| = \ell$. In general, however, the \hat{A}_\pm acting on $|n\ell m\rangle$ produce linear combinations of $|n(\ell + 1)(m \pm 1)\rangle$ and $|n(\ell - 1)(m \pm 1)\rangle$ as a consequence of the Wigner–Eckart theorem.

While \hat{L}_z can change neither ℓ nor m , \hat{A}_z changes ℓ but not m . \hat{A}_z cannot change m because A_z and L_z commute so $\{A_z|n\ell m\rangle\}$ must be an eigenfunction of L_z with eigenvalue m . This does not, however, preclude A_z changing ℓ (also a consequence of the Wigner–Eckart theorem). The ability to shift the angular momentum quantum number ℓ using Lenz vector operators in a manner analogous to the shift of m that can be accomplished for any central potential using angular momentum operators is a manifestation of the “extra” symmetry of the Coulomb/gravitational potential. This extra symmetry leads to an additional operator, the Lenz vector operator, that commutes with the Hamiltonian and accounts for the accidental degeneracy of the hydrogen atom.

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APPENDIX: SUGGESTED PROBLEMS

(1) Using the relations in Table I show that the commutator $[\hat{L}_z, \hat{A}_-] = -\hat{A}_-$.

Solution:

$$\begin{aligned} [\hat{L}_z, \hat{A}_-] &= [\hat{L}_z, \hat{A}_x] - i[\hat{L}_z, \hat{A}_y] \\ &= i\hat{A}_y - i\{-i\hat{A}_x\} = -\hat{A}_x + i\hat{A}_y = -\hat{A}_-. \end{aligned}$$

(2) (a) Show that $\{\hat{A}_-|n\ell m\rangle\}$ is an eigenfunction of \hat{L}_z with eigenvalue $(m - 1)$.

(b) Show that $\{\hat{A}_-|n\ell m\rangle\}$ is an eigenfunction of \hat{L}^2 if and only if $m = -\ell$ with eigenvalue $(\ell + 1)(\ell + 2)$ thus proving that the action of \hat{A}_- on $|n\ell; -\ell\rangle$ is to lower the z -component of angular momentum by one unit of angular momentum while raising the total angular momentum by one unit of angular momentum, i.e., $\{\hat{A}_-|n\ell m\rangle\} = D_{\ell\ell}^-|n; (\ell + 1); -(\ell + 1)\rangle$.

Solution:

(a)

$$\begin{aligned} \hat{L}_z\{\hat{A}_-|n\ell m\rangle\} &= \hat{L}_z(\hat{A}_x - i\hat{A}_y)|n\ell m\rangle \\ &= \hat{A}_x\hat{L}_z - [\hat{A}_x, \hat{L}_z] - i\{\hat{A}_y\hat{L}_z - [\hat{A}_y, \hat{L}_z]\}. \end{aligned}$$

Using Table I:

$$\begin{aligned}
\hat{L}_z\{\hat{A}_-|n\ell m\rangle\} &= \{\hat{A}_x\hat{L}_z + i\hat{A}_y - i(\hat{A}_y\hat{L}_z - \hat{A}_x)\}|n\ell m\rangle \\
&= \{(\hat{A}_x - i\hat{A}_y)\hat{L}_z - (\hat{A}_x - i\hat{A}_y)\}|n\ell m\rangle \\
&= \hat{A}_-(\hat{L}_z - 1)|n\ell m\rangle \\
&= (m-1)\{\hat{A}_-|n\ell m\rangle\}.
\end{aligned}$$

$$\begin{aligned}
&-1)\rangle + 2(1-m)\{\hat{A}_-|n\ell m\rangle\} \\
&= \{\ell(\ell+1) + 2(1-m)\}\{\hat{A}_-|n\ell m\rangle\} \\
&\quad + 2\hat{A}_z\sqrt{(\ell+m)(\ell-m+1)}|n;\ell;(m \\
&\quad -1)\rangle.
\end{aligned}$$

(b)

$$\hat{L}^2\{\hat{A}_-|n\ell m\rangle\} = \hat{L}^2(\hat{A}_x - i\hat{A}_y)|n\ell m\rangle.$$

Using $[\hat{X}\hat{Y}, \hat{Z}] = [\hat{X}, \hat{Z}]\hat{Y} + \hat{X}[\hat{Y}, \hat{Z}]$ and Table I we have

$$[\hat{L}^2, \hat{A}_x] = -i\hat{A}_z\hat{L}_y - i\hat{L}_y\hat{A}_z + i\hat{A}_y\hat{L}_z + i\hat{L}_z\hat{A}_y,$$

$$[\hat{L}^2, \hat{A}_y] = i\hat{A}_z\hat{L}_x + i\hat{L}_x\hat{A}_z - i\hat{A}_x\hat{L}_z - i\hat{L}_z\hat{A}_x.$$

Then $[\hat{L}^2, \hat{A}_-] = \hat{A}_z\hat{L}_- + \hat{L}_-\hat{A}_z - \hat{A}_-\hat{L}_z - \hat{L}_z\hat{A}_-$.

Using the result of problem (1) we have

$$[\hat{L}^2, \hat{A}_-] = 2\hat{A}_z\hat{L}_- + 2\hat{A}_- - 2\hat{A}_-\hat{L}_z.$$

So

$$\begin{aligned}
\hat{L}^2\{\hat{A}_-|n\ell m\rangle\} &= (\hat{A}_-\hat{L}^2 + 2\hat{A}_z\hat{L}_- + 2\hat{A}_- \\
&\quad - 2\hat{A}_-\hat{L}_z)|n\ell m\rangle \\
&= \ell(\ell+1)\hat{A}_-|n\ell m\rangle \\
&\quad + 2\hat{A}_z\sqrt{(\ell+m)(\ell-m+1)}|n;\ell;(m
\end{aligned}$$

So if $m = -\ell$ ($m = \ell + 1$ is not allowed) then $\hat{L}^2\{\hat{A}_-|n\ell; -\ell\rangle\} = (\ell+1)(\ell+2)\{\hat{A}_-|n\ell; -\ell\rangle\}$.

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