7-12-2006

The Runge-Lenz Vector

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(Dated: February 5, 2007)

I. SYNOPSIS

The Runge-Lenz vector is a constant of the motion which allows construction of ladder operator solutions for the Hydrogen Atom's electron eigenfunctions and energy eigenvalues. This paper discusses the precursor materials to that discussion, developing equations originally obtained by W. Pauli. It also shows how the operator form emerges without specialized arguments from the classical form.

II. INTRODUCTION

The H-atom's eigenfunctions and eigenenergies are usually obtained using differential equation methods, requiring study of Laguerre polynomials, etc.. Where other problems in elementary quantum mechanics can be solved in other ways, specifically using either ladder operators or matrices, it is possibly surprising to find that most students do not know about the availability of these (alternative) methods for the H-atom problem. In this piece, we discuss the precursor materials to the ladder operator and matrix methods which can be used to solve the H-atom problem [1].

In order to proceed, we need to develop the Runge-Lenz [2] vector, which expands the number constants of the motion of the H-atom from 4 to 7. The energy, E, is a constant of the motion, as is the angular momentum, and this latter consists of 3 constants! Now, we add the Runge-Lenz vector, which, being a vector, is going to add three more constants of the motion to the assortment.

First, we review the H-atom problem, classically, so that we can see where the Runge-Lenz vector fits in. We start with the energy, which has the form (Z is the atomic number, e is the charge on the electron):

$$\frac{p^2}{2m} + \frac{-(Ze)(e)}{r}$$

where we are writing the Coulomb potential using a charge of Ze on the nucleus, e on the electron, and the minus sign explicitly accounts for the fact that these two charges are opposite in sign. Notice, we have not yet (really) specified the coordinate system.

Now the angular momentum

$$\vec{L} = \vec{r} \times \vec{p}$$

can be written in several different coordinate systems, as can the energy, and part of our job is to pick the best one for our purposes[3]. Let's start with Cartesian coordinates (named for the mathematician Rene Descartes). In this coordinate system the energy has the form:

$$\frac{p_x^2 + p_y^2 + p_z^2}{2\mu} - \frac{Ze^2}{\sqrt{x^2 + y^2 + z^2}}$$

where we (sneakily) moved to the center of mass of the proton-electron system. The angular momentum in this same coordinate system is

$$\vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

which also can be written out in non-determinental form as

$$\vec{L} = \vec{L}_x\hat{i} + \vec{L}_y\hat{j} + \vec{L}_z\hat{k} = (yp_z - zp_y)\hat{i} + (zp_x - xp_z)\hat{j} + (xp_y - yp_z)\hat{k}$$

where we have implicitly defined the three components of $\vec{L}$ surreptitiously. Notice that we are using the unit vectors which point in the x, y, and z directions respectively.

III. THE POLAR COORDINATE REPRESENTATION OBTAINING r

Now we turn to the polar coordinate form of these equations. We do this because the problem has spherical symmetry, by virtue of the Coulomb potential form (which only depends on r). To effect the transformation, we need to remember to transformation equations between spherical polar coordinates and Cartesian coordinates. These equations are

$$\begin{aligned} x &= r\sin\theta\sin\phi \\ y &= r\sin\theta\cos\phi \\ z &= r\cos\theta \end{aligned} \tag{3.1}$$

for transforming *from* x, y, and z *to* r, θ, ϕ.The set of all six equations, in pairs, will be used over and over again in what follows, so be ready to refer back to them. The Cartesian form of the energy

$$\frac{p_x^2 + p_y^2 + p_z^2}{2\mu} - \frac{Ze^2}{\sqrt{x^2 + y^2 + z^2}}$$

depends on the definition of $\vec{r}$ in Cartesian coordinates:

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

which means that p must be

$$\vec{p} = \mu\left(\dot{x}\hat{i} + \dot{y}\hat{j} + \dot{z}\hat{k}\right)$$

[4] which implies

$$\vec{p} = \mu(\dot{v_x}\hat{i} + \dot{v_y}\hat{j} + \dot{v_z}\hat{k})$$

The kinetic energy will be the dot product of $\vec{p}$ on itself, (aside from a constant):

$$\frac{\vec{p}\cdot\vec{p}}{2\mu} = \frac{p_x^2 + p_y^2 + p_z^2}{2\mu} = \frac{1}{2}\mu\left(\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right) = \frac{1}{2}\mu\left(v_x^2 + v_y^2 + v_z^2\right)$$

all of which are saying the same thing. We finally introduce the so-called Runge-Lenz vector, employing the unit "r" vector ($\hat{r} \equiv \frac{\vec{r}}{r}$):

$$\vec{A} = \kappa\vec{L}\times\vec{p} + \hat{r}$$

(where κ is a to-be-determined constant) so

$$\frac{d\vec{A}}{dt} = \kappa\vec{L}\times\frac{d\vec{p}}{dt} + \frac{d\hat{r}}{dt}$$

since the angular momentum is itself a constant of the motion.

$$\frac{d\vec{A}}{dt} = \kappa\vec{L}\times\left(\frac{-Ze^2\hat{r}}{r^2}\right) + \frac{d\hat{r}}{dt}$$

i.e., and using the definition of the angular momentum vector, we have

$$\frac{d\vec{A}}{dt} = -\left(\frac{Ze^2}{r^2}\kappa\right)\vec{L}\times\hat{r} + \frac{d\hat{r}}{dt}$$

$$\frac{d\vec{A}}{dt} = -\left(\frac{Ze^2}{r^2}\kappa\right)(\vec{r}\times\vec{p})\times\hat{r} + \frac{d\hat{r}}{dt}$$

Now, we need a piece of calculus, viz.,

$$(\vec{A}\times\vec{B})\times\vec{C} = (\vec{A}\cdot\vec{C})\vec{B} - (\vec{B}\cdot\vec{C})\vec{A}$$

where $\vec{A}\rightarrow\vec{r}$, $\vec{B}\rightarrow\vec{p}$, and $\vec{C}\rightarrow\hat{r}$,

IV. AN ASIDE CONCERNING THE TRIPLE CROSS PRODUCT

We need to obtain the "value" of the triple cross product.

$$(\vec{A}\times\vec{B})\times\vec{C} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ A_yB_z - A_zB_y & A_zB_x - A_xB_z & A_xB_y - A_yB_x \\ C_x & C_y & C_z \end{vmatrix}$$

which expands to

$$\begin{aligned}(\vec{A}\times\vec{B})\times\vec{C} &= \\ \hat{i}\,((A_zB_x - A_xB_z)C_z &- (A_xB_y - A_yB_x)C_y) \\ +\hat{j}\,((A_xB_y - A_yB_x)C_x &- (A_yB_z - A_zB_y)C_z) \\ +\hat{k}\,((A_yB_z - A_zB_y)C_y &- (A_zB_x - A_xB_z)C_x)\end{aligned}$$

$$\begin{aligned}(\vec{A}\times\vec{B})\times\vec{C} &= \\ \hat{i}\,(A_zB_xC_z - A_xB_zC_z &- A_xB_yC_y + A_yB_xC_y) \\ +\hat{j}\,(A_xB_yC_x - A_yB_xC_x &- A_yB_zC_z - A_zB_yC_z) \\ +\hat{k}\,(A_yB_zC_y - A_zB_yC_y &- A_zB_xC_x + A_xB_zC_x)\end{aligned}$$

or, collecting terms

$$(\vec{A}\times\vec{B})\times\vec{C} =$$

$$\hat{i}\left(A_zB_xC_z + A_yB_xC_y + \underline{A_xB_xC_x} - A_xB_zC_z - A_xB_yC_y - \underbrace{A_xB_xC_x} - \underline{A_xB_xC_x} + \underbrace{A_xB_xC_x}\right)$$
$$+\hat{j}\left(A_xB_yC_x - A_yB_xC_x - A_yB_zC_z - A_zB_yC_z\right)$$
$$+\hat{k}\left(A_yB_zC_y - A_zB_yC_y - A_zB_xC_x + A_xB_z)C_x\right)$$

which is, upon inspection,

$$(\vec{A}\cdot\vec{C})\vec{B} - (\vec{B}\cdot\vec{C})\vec{A} \tag{4.1}$$

This is the end of the aside, and we now return to the main derivation.

V. RETURN TO MAIN TEXT

Our last result (using Equation 4.1) means that

$$(\vec{r}\times\vec{p})\times\hat{r} = (\vec{r}\cdot\hat{r})\vec{p} - (\vec{p}\cdot\hat{r})\vec{r}$$

the r.h.s. of which is

$$\left(\frac{\vec{r}\cdot\vec{r}}{r}\right)\vec{p} - \left(\frac{\vec{p}\cdot\vec{r}}{r}\right)\vec{r}$$

$$\frac{d\vec{A}}{dt} = -\left(\frac{Ze^2}{r^2}\kappa\right)(\vec{r}\times\vec{p})\times\hat{r} + \frac{d\hat{r}}{dt}$$
$$= -\left(\frac{Ze^2}{r^2}\kappa\right)\left(\left(\frac{\vec{r}\cdot\vec{r}}{r}\right)\vec{p} - \left(\frac{\vec{p}\cdot\vec{r}}{r}\right)\vec{r}\right) + \frac{d\hat{r}}{dt} \tag{5.1}$$

A. The time derivative of $\vec{r}$

Next, we need the time derivative of $\hat{r}$, i.e.,

$$\frac{d\hat{r}}{dt} = \frac{d\frac{\vec{r}}{r}}{dt}$$

which is

$$= \frac{1}{r}\frac{\partial\vec{r}}{dt} + \vec{r}\frac{\partial\frac{1}{r}}{dt}$$

or

$$= \frac{1}{r}\frac{\vec{p}}{\mu} + \vec{r}\frac{\partial(x^2+y^2+z^2)^{-1/2}}{dt}$$

or

$$= \frac{1}{r}\frac{\vec{p}}{\mu} - \vec{r}\frac{1}{2}2\frac{1}{(x^2+y^2+z^2)^{3/2}}\left(x\frac{\partial x}{\partial t} + y\frac{\partial y}{\partial t} + z\frac{\partial z}{\partial t}\right)$$

$$\frac{1}{r}\frac{\vec{p}}{\mu} - \vec{r}\cdot\frac{\vec{r}\cdot\vec{p}}{\mu r^3}$$

$$\frac{d\vec{A}}{dt} = -\left(\frac{Ze^2}{r^2}\kappa\right)\left(\left(\frac{\vec{r}\cdot\vec{r}}{r}\right)\vec{p} - \left(\frac{\vec{p}\cdot\vec{r}}{r}\right)\vec{r}\right) + \left(\frac{1}{r}\frac{\vec{p}}{\mu} - \vec{r}\frac{\vec{r}\cdot\vec{p}}{\mu r^3}\right)$$

which becomes [5]

$$\frac{d\vec{A}}{dt} = -\left(Ze^2\kappa\right)\left(\left(\frac{1}{r}\right)\vec{p} - \left(\frac{\vec{p}\cdot\vec{r}}{r^3}\right)\vec{r}\right) + \frac{1}{\mu}\left(\frac{1}{r}\vec{p} - \vec{r}\frac{\vec{r}\cdot\vec{p}}{\mu r^3}\right)$$

which means that if we can set this time derivative equal to zero, then we can declare $\vec{A}$ to be a constant of the motion, so

$$\left(-Ze^2\kappa + \frac{1}{\mu}\right)\vec{p} = 0$$

implying that if $\vec{A}$ to have a zero time rate of change, i.e., be a constant of the motion, then κ must be chosen to make the quantity in brackets vanish, i.e.,

$$\kappa = \frac{1}{Ze^2\mu}$$

Therefore, the Runge-Lenz vector is

$$\vec{A} = \frac{1}{Ze^2\mu}\vec{L}\times\vec{p} + \hat{r}$$

which we have shown to be a constant of the motion in the Kepler problem (H-atom problem). Now, we look at the dot product of this vector on the $\vec{r}$ vector, i.e.,

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\left(\vec{L}\times\vec{p}\right)\cdot\vec{r} + \hat{r}\cdot\vec{r}$$

which is

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\left((\vec{r}\times\vec{p})\times\vec{p}\right)\cdot\vec{r} + \left(\frac{\vec{r}}{r}\right)\cdot\vec{r}$$

and since we already know that

$$(\vec{A}\times\vec{B})\times\vec{C} = (\vec{A}\cdot\vec{C})\vec{B} - (\vec{B}\cdot\vec{C})\vec{A}$$

we obtain

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\left(\vec{r}\cdot\vec{p})\vec{p} - (\vec{p}\cdot\vec{p})\vec{r}\right)\cdot\vec{r} + \left(\frac{r^2}{r}\right)$$

and defining a as the magnitude of $\vec{A}$ and r as the magnitude of $\vec{r}$, we have

$$ar\cos\theta = \frac{1}{Ze^2\mu}\left(\vec{r}\cdot\vec{p})\vec{p} - (\vec{p}\cdot\vec{p})\vec{r}\right)\cdot\vec{r} + \left(\frac{r^2}{r}\right)$$

which is

$$ar\cos\theta = \frac{1}{Ze^2\mu}\left((\vec{r}\cdot\vec{p})\vec{p}\cdot\vec{r} - (\vec{p}\cdot\vec{p})\vec{r}\cdot\vec{r}\right) + r$$

VI. L^2

Now, we need the form for L^2, i.e., what is

$$\vec{L}\cdot\vec{L} = L^2 = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ L_x & L_y & L_z \\ L_x & L_y & L_z \end{vmatrix} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ yp_z - zp_y & zp_x - xp_z & xp_y - yp_x \\ yp_z - zp_y & zp_x - xp_z & xp_y - yp_x \end{vmatrix}$$

which is,

$$\begin{aligned} L^2 = \\ (x^2+y^2)p_z^2 + (x^2+z^2)p_y^2 + (y^2+z^2)p_x^2 - 2xzp_xp_z - 2yzp_yp_z - 2yzp_yp_z = \\ r^2p^2 - (xp_x + yp_y + zp_z)^2 = r^2p^2 - (\vec{r}\cdot\vec{p})^2 \end{aligned} \quad (6.1)$$

i.e.,

$$L^2 = r^2p^2 - (\vec{r}\cdot\vec{p})^2$$

We thus have

$$ar\cos\theta = -\frac{L^2}{Ze^2\mu} + r$$

which is almost the traditional form. Rewriting, we have

$$r(a\cos\theta - 1) = -\frac{L^2}{Ze^2\mu}$$

or

$$\frac{1}{r} = \frac{Ze^2\mu}{L^2}\left(1 - a\cos\theta\right)$$

which is one of the many forms of the elliptical orbit known since Kepler.

How can we see this? Write

$$\frac{1}{r} = \frac{1}{b}\left(1 - a\cos\theta\right)$$

where $b = L^2/Ze^2\mu$. Assuming $a < 1$ we have

θ	$\frac{1}{r}$	r
0	$\frac{1}{b}(1-a)$	$\frac{b}{1-a}$
$\pi/2$	$\frac{1}{b}$	b
π	$\frac{1}{b}(1+a)$	$\frac{b}{1+a}$
$3\pi/2$	$\frac{1}{b}$	b

Figure 1 shows how this table is implemented. The ellipse is being drawn with the filled focus being F_1, i.e., the one where the Sun (proton) goes, and the other focus F_2 is "empty".

VII. SOME NEEDED COMMUTATORS

Before proceeding, we need to develop some commutators which will be useful later. We follow the paper of Pauli, whose English translation can be found at "Pauli, Sources of Quantum Mechanics, (Ed. B. L. van der Waerden), North-Holland Publ Co., 1967". This is tiresome, but necessary, work.

First, we evaluate the commutator of $\vec{L}$ with $\vec{r}$. We have, as an example

$$[L_x, x] = L_x x - xL_x = (yp_z - zp_y)x - x(yp_z - zp_y) = 0$$

i.e. $[L_i, x_i] = 0\forall i$.

What about

$$[L_x, y] = L_x y - yL_x = (yp_z - zp_y)y - y(yp_z - zp_y) = yp_z y - zp_y y - y^2 p_z + yzp_y$$

which is,

$$-z(p_y y - yp_y) = -z(-\imath\hbar) = \imath\hbar z$$

Next, we do

$$[L_x, z] = L_x z - zL_x = (yp_z - zp_y)z - z(yp_z - zp_y) = yp_z z - zp_y z - yzp_z + z^2 p_y = -\imath\hbar y$$

and

$$[L_y, x] = L_y x - xL_y = (zp_x - xp_z)x - x(zp_x - xp_z) = zp_x x - xp_z x - xzp_x + x^2 p_z$$

which is

$$z(p_x x - xp_x) = -\imath\hbar z$$

$$[L_y, z] = (zp_x - xp_z)z - z(zp_x - xp_z) = -x(pz_z - zp_z) = -x(-\imath\hbar) = +\imath\hbar x$$

Next, we need the commutators of the angular momentum with the momentum, i.e., what is

$$[L_x, p_x] = ?$$

with the clear answer, zero. Then, what is

$$[L_x, p_y] = L_x p_y - p_y L_x = (yp_z - zp_y)p_y - p_y(yp_z - zp_y) = p_z(yp_y - p_y y) = \imath\hbar p_z$$

We summarize our commutators (so far) as

$[L_x, x] = 0$	
$[L_y, y] = 0$	
$[L_z, z] = 0$	
$[L_x, y] = \imath\hbar z$	$=$ -$[Ly, x]$
$[L_y, x] =$ -$\imath\hbar z$	$= L_x, y]$
$[L_x, z] = \imath\hbar x$	$=$ - $[L_z, x]$
$[L_x, p_y] = \imath\hbar p_z$	
$[L_x, p_z] =$ -$\imath\hbar p_y$	
$[L_x, p_x] = 0$	

VIII. MORE COMMUTATORS

Next, we remind ourselves of the commutators in the $\vec{L}$ system. We had

$$\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_z & p_y & p_z \end{vmatrix}$$

as the definition of $\vec{L}$.

We then have, for example

$$[L_y, L_z] = L_y L_z - L_z L_y = (zp_x - xp_z)(xp_y - yp_x) - ((xp_y - yp_x)(zp_x - xp_z))$$

which is, expanding the two products

$$= zp_x xp_y - \underbrace{zp_x yp_x} - \overbrace{xp_z xp_y} + xp_z yp_x - (xp_y zp_x - \overbrace{xp_y xp_z} - \underbrace{yp_x zp_x} + yp_x xp_z)$$

which equals, canceling,

$$zp_y(p_x x - xp_x) - yp_z(p_x x - xp_x) = -\imath\hbar(zp_y - yp_z) = +\imath\hbar L_x$$

Now we need to obtain the commutators of the momen-

IX. SECTION 2

We have, using a sophisticated notation,

$$\vec{L} \otimes \vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ L_x & L_y & L_z \\ L_x & L_y & L_z \end{vmatrix} = \begin{vmatrix} \hat{i}(L_y z - L_z y) \\ \hat{j}(L_z x - L_x z) \\ \hat{k}(L_x y - L_y x \end{vmatrix} = \begin{vmatrix} \hat{i}\hbar L_x \\ \hat{j}\hbar L_y \\ \hat{k}\hbar L_z \end{vmatrix}$$

tum with the radius (remember, r = $|\vec{r}|$). Since $[x, r] = 0$ (and the same for y and z, we have

$$[p_x, r] = p_x r - r p_x = -\imath\hbar \frac{\partial r}{\partial x} + r p_x - r p_x$$

which is

$$[p_x, r] = -\imath\hbar \frac{x}{r} \tag{9.1}$$

from which we generalize in vector notation *(Equation 34, Pauli)*

$$[\vec{p}, \vec{r}] = -\imath\hbar \frac{\vec{r}}{r} \tag{9.2}$$

or, said another way,

$$[\vec{p}, f(r)] = -\imath\hbar \nabla f(r) \tag{9.3}$$

Following Pauli, we obtain the expression for the radial momentum, p_r. We know that and alternative form of the time dependent Schrödinger Equation involving commutators is

$$[E, \Phi(\vec{r})] = -\imath\hbar \dot{\Phi}(\vec{r}) \tag{9.4}$$

which is the way we know if something is a constant of the motion, since operators which commute with the energy are time-stationery.

So

$$[E, r] = -\imath\hbar \dot{r} = -\imath\hbar \frac{p_r}{m} \tag{9.5}$$

which means that

$$p_r = m \frac{\imath}{\hbar} [E, r]$$

and we then proceed to evaluate the commutator itself, i.e.,

$$[E, r] = \frac{1}{2\mu} \left(\left(p_x^2 + p_y^2 + p_z^2\right) r - r \left(p_x^2 + p_y^2 + p_z^2\right) \right)$$

We have (using only the first (x) term and Equation 9.1)

$$p_x^2 r - r p_x^2 = p_x (p_x r) - (r p_x) p_x$$

i.e.,

$$= p_x (r p_x - \imath\hbar \frac{x}{r}) - (p_x r + \imath\hbar \frac{x}{r}) p_x$$

$$= \underbrace{p_x r p_x} - p_x \imath\hbar \frac{x}{r} - \underbrace{p_x r p_x} - \imath\hbar \frac{x}{r} p_x$$

$$= -\imath\hbar \left(p_x \frac{x}{r} + \frac{x}{r} p_x \right)$$

which becomes, for the three components actually required

$$[E, r] = -\imath\hbar \frac{1}{2\mu} \left(\vec{p} \cdot \hat{r} + \hat{r} \cdot \vec{p} \right)$$

$$p_r = \frac{1}{2} \left(\vec{p} \cdot \hat{r} + \hat{r} \cdot \vec{p} \right) \tag{9.6}$$

Pauli's Equation 44.

X. SECTION 3

We had from Equation 9.2

$$[\vec{p}, \vec{r}] = -\imath\hbar \frac{\vec{r}}{r} = -\imath\hbar \nabla r = -\imath\hbar \hat{r} \tag{10.1}$$

and, for any function, we would have

$$[\vec{p}, f(\vec{r})] = -\imath\hbar \nabla f(\vec{r}) \tag{10.2}$$

so

$$[\vec{p}, \hat{r}] = -\imath\hbar \nabla \cdot \frac{\vec{r}}{r} \tag{10.3}$$

We know that

$$\nabla \cdot \vec{r} = \hat{i} \frac{\partial x \hat{i}}{\partial x} + \hat{j} \frac{\partial y \hat{j}}{\partial y} + \hat{k} \frac{\partial z \hat{k}}{\partial z} \tag{10.4}$$

which equals three (3)! Further

$$\nabla \frac{1}{r} = \hat{i} \frac{\partial (x^2 + y^2 + z^2)^{-1/2}}{\partial x} + \cdots \tag{10.5}$$

which yields

$$\nabla \frac{1}{r} = -\hat{i} (x^2 + y^2 + z^2)^{-3/2} x + \cdots$$

which leads to

$$\nabla \frac{1}{r} = -\hat{i} \frac{x}{r^3} + \cdots$$

which leads to

$$\nabla \frac{1}{r} = -\frac{\vec{r}}{r^3} = -\frac{\hat{r}}{r^2} \tag{10.6}$$

By explicit differentiation then, substituting Equation 10.4 into the r.h.s. of Equation 10.3 we have

$$\nabla \cdot \frac{\vec{r}}{r} = \frac{1}{r} \nabla \cdot \vec{r} + \vec{r} \cdot \nabla \frac{1}{r}$$

which is, using Equation 10.6

$$\nabla \cdot \frac{\vec{r}}{r} = \frac{3}{r} - \vec{r} \cdot \frac{\vec{r}}{r^3} = \frac{2}{r} \tag{10.7}$$

so, the commutator is

$$[\vec{p}, \hat{r}] = -2\imath\hbar \frac{1}{r} = -2\imath\hbar \hat{r} \tag{10.8}$$

Pauli's intermediate Equation between 44 and 44'.

XI. SECTION 4

We will need

$$[p_x, \frac{x}{r}] = p_z \frac{x}{r} - \frac{x}{r} p_z$$

i.e., as usual, for an arbitrary function f,

$$[p_x, \frac{x}{r}] = p_z\frac{x}{r} - \frac{x}{r}p_z = -\imath\hbar\frac{\partial \frac{x}{r} f}{\partial x} - \frac{x}{r}(-\imath\hbar)\frac{\partial f}{\partial x}$$

which is

$$-\imath\hbar\frac{f}{r} + \imath\hbar\frac{x^2}{r^3}f \tag{11.1}$$

Adding the three terms contributing to the total commutator we have

$$[\vec{p}, \hat{r}] = -3\imath\hbar\frac{1}{r} + \imath\hbar\frac{x^2+y^2+z^2}{r^3} = -2\imath\hbar\frac{1}{r}$$

This is a little deceiving, so we will work out a few terms.

$$[p_x, \frac{y}{r}]f = -\imath\hbar\frac{\partial \frac{y}{r} f}{\partial x} - \frac{y}{r}\left(-\imath\hbar\frac{\partial f}{\partial x}\right)$$

i.e.,

$$[p_x, \frac{y}{r}]f = -\imath\hbar y\frac{\partial \frac{1}{r} f}{\partial x} - \frac{y}{r}\left(-\imath\hbar\frac{\partial f}{\partial x}\right)$$

for any function "f", which is, upon expansion,

$$[p_x, \frac{y}{r}]f = -\imath\hbar y f\frac{\partial \frac{1}{r}}{\partial x} - \underbrace{\imath\hbar\frac{y}{r}\frac{\partial f}{\partial x}} - \underbrace{\frac{y}{r}\left(-\imath\hbar\frac{\partial f}{\partial x}\right)}$$

which is, upon cancellation

$$[p_x, \frac{y}{r}]f = -\imath\hbar\frac{yx}{r^3} = p_x\frac{y}{r} - \frac{y}{r}p_x \tag{11.2}$$

XII. SECTION 5

We will need the "converse" of the last result:

$$[p_y, \frac{x}{r}]f = -\imath\hbar\frac{\partial \frac{x}{r} f}{\partial y} - \frac{x}{r}\left(-\imath\hbar\frac{\partial f}{\partial y}\right)$$

which simplifies a bit to

$$[p_y, \frac{x}{r}]f = -\imath\hbar x\frac{\partial \frac{1}{r} f}{\partial y} + \imath\hbar\frac{x}{r}\frac{\partial f}{\partial y} = -\imath\hbar f\frac{\partial \frac{1}{r}}{\partial y}$$

i.e.,

$$[p_y, \frac{x}{r}] = +\imath\hbar x\frac{y}{r^3} \tag{12.1}$$

We will also need

$$[p_z, \frac{x}{r}]f = -\imath\hbar\frac{\partial \frac{x}{r} f}{\partial z} - \frac{x}{r}\left(-\imath\hbar\frac{\partial f}{\partial z}\right)$$

which simplifies:

$$[p_z, \frac{x}{r}]f = -\imath\hbar x\frac{\partial \frac{1}{r} f}{\partial z} + \imath\hbar f\frac{\partial \frac{1}{r}}{\partial z} = -\imath\hbar\frac{\partial f}{\partial z}$$

i.e.,

$$[p_z, \frac{x}{r}] = +\imath\hbar x\frac{z}{r^3} \tag{12.2}$$

XIII. SECTION 6

We will also need (doesn't this ever end?)

$$[p_x, \frac{y}{r^3}]f = -\imath\hbar\frac{\partial \frac{y}{r^3} f}{\partial x} - \frac{y}{r^3}\left(-\imath\hbar\frac{\partial f}{\partial x}\right)$$

i.e.,

$$[p_x, \frac{y}{r^3}]f = -\imath\hbar y\frac{\partial \frac{f}{r^3}}{\partial x} - \frac{y}{r^3}\left(-\imath\hbar\frac{\partial f}{\partial x}\right)$$

or

$$[p_x, \frac{y}{r^3}]f = -\imath\hbar y f\frac{\partial \frac{1}{r^3}}{\partial x}$$

which equals

$$p_x\frac{y}{r^3} - \frac{y}{r^3}p_x = -\imath\hbar\left(-\frac{3xy}{r^5}\right) \tag{13.1}$$

Also, we have

$$[p_x, \frac{x}{r^3}]f = -\imath\hbar\frac{\partial \frac{x}{r^3} f}{\partial x} - \frac{x}{r^3}\left(-\imath\hbar\frac{\partial f}{\partial x}\right)$$

$$[p_x, \frac{x}{r^3}]f = -\underbrace{\imath\hbar\frac{x}{r^3}\frac{\partial f}{\partial x}} - \imath\hbar\frac{\partial \frac{x}{r^3}}{\partial x}f - \underbrace{\frac{x}{r^3}\left(-\imath\hbar\frac{\partial f}{\partial x}\right)}$$

which equals

$$p_x\frac{x}{r^3} - \frac{x}{r^3}p_x = -\imath\hbar\left(-\frac{x}{r^3}\right) - \imath\hbar\left(-\frac{3x^2}{r^5}\right) \tag{13.2}$$

We make a table of these values for future use:

$[p_x, r]$	$p_x r - r p_x$	$-\imath\hbar\frac{x}{r}$	$Equation 9.1$
$[\vec{p}, \hat{r}]$	$\vec{p}\cdot\hat{r} - \hat{r}\cdot\vec{p}$	$-2\imath\hbar\hat{r}$	$Equation 10.8$
$[p_x, \frac{x}{r}]$	$p_x\frac{x}{r} - \frac{x}{r}p_x$	$-\imath\hbar(\frac{1}{r} - \frac{x^2}{r^3})$	$Equation 11.1$
$[p_x, \frac{y}{r}]$	$p_x\frac{y}{r} - \frac{y}{r}p_x$	$\imath\hbar\frac{yx}{r^3}$	$Equation 11.2$
$[p_y, \frac{x}{r}]$	$p_y\frac{x}{r} - \frac{x}{r}p_y$	$\imath\hbar\frac{xy}{r^3}$	$Equation 12.2$
$[p_x, \frac{y}{r^3}]$	$p_x\frac{y}{r^3} - \frac{y}{r^3}p_x$	$\imath\hbar\left(3\frac{xy}{r^5}\right)$	$Equation 13.1$
$[p_x, \frac{x}{r^3}]$	$p_x\frac{x}{r^3} - \frac{x}{r^3}p_x$	$-\imath\hbar\left(\frac{1}{r^3} - 3\frac{x^2}{r^5}\right)$	$Equation 13.2$
$[p_y, \frac{x}{r}]$	$p_y\frac{x}{r} - \frac{x}{r}p_y$	$-\imath\hbar(-\frac{xy}{r^3})$	$Equation 12.2$

XIV. USING ALL THE PRECEDING MATERIALS

So, using Equation 9.6 and Equation 10.7 we have

$$p_r = \frac{1}{2}\left(\vec{p}\cdot\hat{r} + \hat{r}\cdot\vec{p}\right) = \frac{1}{2}\left(\vec{p}\cdot\hat{r} + \vec{p}\cdot\hat{r} + \imath\hbar\frac{2}{r}\right)$$

i.e.,

$$p_r = \left(\vec{p}\cdot\hat{r} + \imath\hbar\right)\frac{1}{r}$$

while doing things in the other order we have

$$p_r = \frac{1}{r}\left(\hat{r}\cdot\vec{p} - \imath\hbar\right)$$

Right operating with r we have

$$p_r r = \left(\vec{p}\cdot\hat{r} + \imath\hbar\right)$$

while left operating with r we have

$$r p_r = \left(\hat{r}\cdot\vec{p} - \imath\hbar\right)$$

Adding these last two we have

$$\vec{p}\cdot\hat{r} + \hat{r}\cdot\vec{p} = p_r r + r p_r$$

while subtracting, we have

$$\vec{p}\cdot\hat{r} - \vec{r}\cdot\hat{p} = p_r r - r p_r + 2\imath\hbar$$

since

$$p_x x - x p_x + p_y y - y p_y + p_z z - z p_z = -3\imath\hbar$$

so

$$p_r r - r p_r = -3\imath\hbar + 2\imath\hbar = -\imath\hbar$$

Pauli's Equation 46. We know that from Equation 9.6

$$p_r = \frac{1}{2}\left(\vec{p}\cdot\hat{r} + \hat{r}\cdot\vec{p}\right)$$

and from Equation 10.8

$$[\vec{p}, \hat{r}] = -2\imath\hbar\frac{1}{r} = -2\imath\hbar\hat{r}$$

so

$$p_r = \frac{1}{2}\left(\vec{p}\cdot\hat{r} + \vec{p}\cdot\hat{r} + 2\imath\hbar\frac{1}{r}\right) = \vec{p}\cdot\hat{r} + \imath\hbar\frac{1}{r}$$

Pauli's equation 44'.

Lastly, we ask, what is

$$\frac{d\hat{r}}{dt}\ ?$$

which we answer the same way, using the commutator of the r unit vector with the energy, i.e., $[E, r]$ which we obtained in Equation 9.5, so now we form $[E, \hat{r}]$ (following Pauli, we do the x-component only):

$$\left(\frac{d\hat{r}}{dt}\right)_x = \frac{\imath}{\hbar}\frac{1}{2\mu}\left\{\left(p_x^2\frac{x}{r} - \frac{x}{r}p_x^2\right) + \left(p_y^2\frac{x}{r} - \frac{x}{r}p_y^2\right) + \left(p_z^2\frac{x}{r} - \frac{x}{r}p_z^2\right)\right\} \tag{14.1}$$

which we re-write as

$$\left(\frac{d\hat{r}}{dt}\right)_x = \frac{\imath}{\hbar}\frac{1}{2\mu}\left\{p_x\left(p_x\frac{x}{r} - \frac{x}{r}p_x\right) - \left(\frac{x}{r}p_x - p_x\frac{x}{r}\right)p_x +\right.$$

$$p_y\left(p_y\frac{x}{r}-\frac{x}{r}p_y\right)-\left(\frac{x}{r}p_y-p_y\frac{x}{r}\right)p_y+$$
$$p_z\left(p_z\frac{x}{r}-\frac{x}{r}p_z\right)-\left(\frac{x}{r}p_z-p_z\frac{x}{r}\right)p_z\Big\} \tag{14.2}$$

which is, using Equations 11.2 and 12.2

$$\left(\frac{d\hat{r}}{dt}\right)_x=\frac{\imath}{\hbar}\frac{1}{2\mu}\left\{p_x\left(-\imath\hbar\left[\frac{1}{r}-\frac{x^2}{r^3}\right]\right)-\left(\imath\hbar\left[\frac{1}{r}-\frac{x^2}{r^3}\right]\right)p_x\right.$$
$$-p_y\left(\left(\imath\hbar\frac{xy}{r^3}\right)\right)-\left(\left(\imath\hbar\frac{xy}{r^3}\right)\right)p_y$$
$$\left.-p_z\left(\imath\hbar\frac{xz}{r^3}\right)-\left(\imath\hbar\frac{xz}{r^3}\right)p_z\right\} \tag{14.3}$$

which becomes

$$\left(\frac{d\hat{r}}{dt}\right)_x=\frac{\imath}{\hbar}\frac{1}{2\mu}\left\{p_x\left(-\left(\imath\hbar\left[\frac{1}{r}-\frac{x^2}{r^3}\right]\right)\right)\frac{x}{r}+\left(-\imath\hbar\left[\frac{1}{r}-\frac{x^2}{r^3}\right]\right)p_x+\right.$$
$$p_y\left(\imath\hbar\frac{xy}{r^3}\right)-\left(\imath\hbar\frac{xy}{r^3}\right)p_y-$$
$$\left.p_z\left(\imath\hbar\frac{xz}{r^3}\right))-\left(\imath\hbar\frac{xz}{r^3}\right)p_z\right\} \tag{14.4}$$

i.e.,

$$\left(\frac{d\hat{r}}{dt}\right)_x=\frac{1}{2\mu}\left\{p_x\left(\left[\frac{x^2+y^2+z^2-x^2}{r^3}\right]\right)+\left(\left[\frac{x^2+y^2+z^2-x^2}{r^3}\right]\right)p_x+\right. \tag{14.5}$$
$$-x\left(p_y\frac{y}{r^3}-x\frac{y}{r^3}p_y\right)- \tag{14.6}$$
$$\left.-x\left(p_z\frac{z}{r^3}-\frac{z}{r^3}p_z\right)\right\} \tag{14.7}$$

which can be re-written as

$$\left(\frac{d\hat{r}}{dt}\right)_x=\frac{1}{2\mu}\left\{p_x\left(\frac{y^2+z^2}{r^3}\right)-p_y\frac{xy}{r^3}-p_z\frac{xz}{r^3}\right. \tag{14.8}$$
$$\left.+\left(\frac{y^2+z^2}{r^3}\right)p_x-\frac{xy}{r^3}p_y-\frac{xz}{r^3}p_z\right\} \tag{14.9}$$

which is Pauli's Equation, call it 46b:

$$\left(\frac{d\hat{r}}{dt}\right)_x=\frac{1}{2\mu}\left\{p_x\left(\frac{y^2+z^2}{r^3}\right)+\left(\frac{y^2+z^2}{r^3}\right)p_x-\left(p_y\frac{yx}{r^3}+\frac{yx}{r^3}p_y\right)-\left(p_z\frac{zx}{r^3}+\frac{zx}{r^3}p_z\right)\right\} \tag{14.10}$$

XV. SECTION 8

We now note the similarity between this expression and a special cross product of angular moment by deriving

$$\vec{L}\otimes\frac{\vec{r}}{r^3}=\begin{vmatrix}\hat{\imath}&\hat{\jmath}&\hat{k}\\ L_x&L_y&L_z\\ \frac{x}{r^3}&\frac{y}{r^3}&\frac{z}{r^3}\end{vmatrix}=\left(L_y\frac{z}{r^3}-L_z\frac{y}{r^3}\right)\hat{\imath}+\left(L_z\frac{x}{r^3}-L_x\frac{z}{r^3}\right)\hat{\jmath}+\left(L_x\frac{y}{r^3}-L_y\frac{x}{r^3}\right)\hat{k} \tag{15.1}$$

where we remember that

$$\vec{r}\otimes\vec{p}=\vec{L}=\begin{vmatrix}\hat{\imath}&\hat{\jmath}&\hat{k}\\ x&y&z\\ p_x&p_y&p_z\end{vmatrix}=\hat{\imath}(yp_z-zp_y)+\hat{\jmath}(zp_x-xp_z)+\hat{k}(xp_y-yp_x) \tag{15.2}$$

so, we obtain

$$\vec{L}\otimes\frac{\vec{r}}{r^3}=\begin{vmatrix}\hat{i} & \hat{j} & \hat{k}\\ (yp_z-zp_y) & (zp_x-xp_z) & (xp_y-yp_x)\\ \frac{x}{r^3} & \frac{y}{r^3} & \frac{z}{r^3}\end{vmatrix}= \tag{15.3}$$

$$\begin{aligned}&\left((zp_x-xp_z)\frac{z}{r^3}-(xp_y-yp_x)\frac{y}{r^3}\right)\hat{i}+\\ &\left((xp_y-yp_x)\frac{x}{r^3}-(yp_z-zp_y)\frac{z}{r^3}\right)\hat{j}+\\ &\left((yp_z-zp_y)\frac{y}{r^3}-(zp_x-xp_z)\frac{x}{r^3}\right)\hat{k}\end{aligned} \tag{15.4}$$

or

$$\begin{aligned}=&\left(zp_x\frac{z}{r^3}-xp_z\frac{z}{r^3}-xp_y\frac{y}{r^3}+yp_x\frac{y}{r^3}\right)\hat{i}+\\ &\left(xp_y\frac{x}{r^3}-yp_x\frac{x}{r^3}-yp_z\frac{z}{r^3}+zp_y\frac{z}{r^3}\right)\hat{j}+\\ &\left(yp_z\frac{y}{r^3}-zp_y\frac{y}{r^3}-zp_x\frac{x}{r^3}+xp_z\frac{x}{r^3}\right)\hat{k}\end{aligned} \tag{15.5}$$

which we re-write as

$$\begin{aligned}=&\left(p_x\frac{z^2}{r^3}-p_z\frac{xz}{r^3}-p_y\frac{xy}{r^3}+p_x\frac{y^2}{r^3}\right)\hat{i}+\\ &\left(p_y\frac{x^2}{r^3}-p_x\frac{xy}{r^3}-p_z\frac{yz}{r^3}+p_y\frac{z^2}{r^3}\right)\hat{j}+\\ &\left(p_z\frac{y^2}{r^3}-p_y\frac{yz}{r^3}-p_x\frac{xz}{r^3}+p_z\frac{x^2}{r^3}\right)\hat{k}\end{aligned} \tag{15.6}$$

Of course, we are "only" doing the x-component, so we have

$$\left(\vec{L}\otimes\frac{\vec{r}}{r^3}\right)_x=p_x\frac{z^2+y^2}{r^3}-p_z\frac{xz}{r^3}-p_y\frac{xy}{r^3}$$

which is half of what we need (part of Equation 14.10).

Next, we obtain $\left(\frac{\vec{r}}{r^3}\otimes\vec{L}\right)_x$ i.e.

$$\left(\frac{\vec{r}}{r^3}\otimes\vec{L}\right)_x=\left(\begin{vmatrix}\hat{i} & \hat{j} & \hat{k}\\ \frac{x}{r^3} & \frac{y}{r^3} & \frac{z}{r^3}\\ (yp_z-zp_y) & (zp_x-xp_z) & (xp_y-yp_x)\end{vmatrix}\right)_x \tag{15.7}$$

which is

$$\left(\frac{\vec{r}}{r^3}\otimes\vec{L}\right)_x=\frac{y}{r^3}(xp_y-yp_x)-\frac{z}{r^3}(zp_x-xp_z) \tag{15.8}$$

or

$$\left(\frac{\vec{r}}{r^3}\otimes\vec{L}\right)_x=-\frac{z^2+y^2}{r^3}p_x+\frac{xz}{r^3}p_z+\frac{xy}{r^3}p_y$$

which is the other half of what we need (part of Equation 14.10).

So, the final result is *Pauli's Equation 47* (in more modern notation)

$$\frac{d\vec{r}}{dt}=\frac{1}{2m}\left\{\vec{L}\otimes\frac{\vec{r}}{r^3}-\frac{\vec{r}}{r^3}\otimes\vec{L}\right\} \tag{15.9}$$

Since according to Newton's second law for the H-atom version of Coulomb's Law,

$$\dot{\vec{p}}=-\frac{Ze\times e}{r^3}\vec{r}$$

it follows that the following vector has no time derivative:

$$\vec{A}=\frac{1}{2mZe^2}\left\{\vec{L}\otimes\vec{p}-\vec{p}\otimes\vec{L}\right\}+\hat{r} \tag{15.10}$$

This is the infamous Runge-Lenz vector (in quantum mechanical operator form).

XVI. THE RUNGE-LENZ VECTOR AND THE LADDER OPERATOR FOR THE H-ATOM'S ELECTRON

The Runge-Lenz vector in operator form,

$$\vec{A} = \frac{1}{2Ze^2\mu}\left(\vec{L}\otimes\vec{p} - \vec{p}\otimes\vec{L}\right) + \hat{r} \tag{16.1}$$

turns out to be the source of the ladder operator for the H-atom problem. For extra reference to what follows, one can consult Borowitz, Fundamentals of Quantum Mechanics, W. A. Benjamin Inc., 1967, or Pauli, Sources of Quantum Mechanics, (Ed. B. L. van der Waerden), North-Holland Publ Co., 1967.

XVII. COMMUTATOR OF $\vec{A}$ WITH THE HAMILTONIAN

We are going to need the commutator of $\vec{A}$ with the Hamiltonian of the problem,

$$H_{op} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$$

where, of course, μ is the reduced mass of the proton-electron system (If Z is not one, our nucleus is not a proton, and we need to worry about the appropriate value of μ. Or, to be even more pedantic, even if Z=1 we may also have to worry about the value of μ based on which hydrogen isotope we are dealing with.) Anyway, we will be dealing with $\vec{A}$ as defined above, i.e., the three components A_x, A_y, and A_z. The ladder operators will turn out to be $A^+ = A_x + \imath A_y$ and $A^- = A_x - \imath A_y$ so we need first to obtain the components of A, and then we need to figure out the commutators of those components, both with each other, and with the Hamiltonian.

The components of $\vec{A}$ are obtained by first expanding the determinental

$$\vec{L}\otimes\vec{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ L_x & L_y & L_z \\ p_x & p_y & p_z \end{vmatrix} = \begin{pmatrix} \hat{i}(L_y p_z - L_z p_y) \\ \hat{j}(L_z p_x - L_x p_z) \\ \hat{k}(L_x p_y - L_y p_x) \end{pmatrix} \tag{17.1}$$

or

$$\vec{L}\otimes\vec{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ L_x & L_y & L_z \\ p_x & p_y & p_z \end{vmatrix} = \begin{pmatrix} \hat{i}((zp_x - xp_z)p_z - (xp_y - yp_x)p_y) \\ \hat{j}((xp_y - yp_x)p_x - (yp_z - zp_y)p_z) \\ \hat{k}((yp_z - zp_y)p_y - (zp_x - xp_z)p_x) \end{pmatrix} \tag{17.2}$$

so we have

$$\vec{L}\otimes\vec{p} = \hat{i}((zp_xp_z - xp_z^2) - (xp_y^2 - yp_xp_y)$$
$$+\hat{j}((xp_yp_x - yp_x^2) - (yp_z^2 - zp_yp_z))$$
$$+\hat{k}((yp_zp_y - zp_y^2) - (zp_x^2 - xp_zp_x)) \tag{17.3}$$

so, adding and subtracting appropriately we have

$$\begin{aligned}\vec{L}\otimes\vec{p} = \hat{i}(zp_xp_z - xp_z^2 - xp_y^2 + yp_xp_y + xp_x^2 - xp_x^2) \\ +\hat{j}(xp_yp_x - yp_x^2 - yp_z^2 + zp_yp_z + yp_y^2 - yp_y^2)) \\ +\hat{k}(yp_zp_y - z(p_y^2 + p_x^2 + p_z^2) + xp_zp_x + zp_z^2)\end{aligned} \tag{17.4}$$

so that, collecting terms, we have

$$\begin{aligned}\vec{L}\otimes\vec{p} = \hat{i}(zp_xp_z - x(p_z^2 + p_y^2 + p_x^2) + yp_xp_y + xp_x^2) \\ +\hat{j}(xp_yp_x + zp_yp_z + yp_y^2 - y(p_x^2 + p_z^2 + p_y^2)) \\ +\hat{k}(yp_zp_y - z(p_y^2 + p_x^2 + p_z^2) + xp_zp_x + zp_z^2)\end{aligned} \tag{17.5}$$

and which becomes

$$\vec{L}\otimes\vec{p} = \hat{i}(zp_xp_z + yp_xp_y + xp_x^2)$$
$$+\hat{j}(xp_yp_x + zp_yp_z + yp_y^2)$$

$$+\hat{k}(yp_zp_y + xp_zp_x + zp_z^2)$$
$$-\vec{r}(\vec{p}\cdot\vec{p}) \quad (17.6)$$

i.e.,

$$\vec{L}\otimes\vec{p} = -\vec{r}(\vec{p}\cdot\vec{p}) +$$
$$\hat{i}(p_x(zp_z + yp_y) + xp_x^2)$$
$$\hat{j}(p_y(xp_x + zp_z) + yp_y^2)$$
$$+\hat{k}(p_z(xp_x + yp_z) + zp_z^2) \quad (17.7)$$

Using the commutators similar to $p_x x - xp_x = [p_x, x] = -\imath\hbar$ we convert terms such as $xp_x^2 = xp_xp_x$ to something like p_xxp_x, i.e.,

$$\vec{L}\otimes\vec{p} = -\vec{r}(\vec{p}\cdot\vec{p})$$
$$+\hat{i}(p_x(zp_z + yp_y) + p_xxp_x + \imath\hbar p_x)$$
$$+\hat{j}(p_y(xp_x + zp_z) + p_yyp_y + \imath\hbar p_y)$$
$$+\hat{k}(p_z(xp_x + yp_z) + p_zzp_z + \imath\hbar p_z)$$

and, collecting again

$$\vec{L}\otimes\vec{p} = -\vec{r}(\vec{p}\cdot\vec{p}) + \imath\hbar\vec{p} + \vec{p}(\vec{r}\cdot\vec{p}) \quad (17.8)$$

Next we need the same operators in reverse order:

$$\vec{p}\otimes\vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ p_x & p_y & p_z \\ L_x & L_y & L_z \end{vmatrix} = \begin{pmatrix} \hat{i}(p_yL_z - p_zL_y) \\ \hat{j}(p_zL_x - p_xL_z) \\ \hat{k}(p_xL_y - p_yL_x) \end{pmatrix} \quad (17.9)$$

$$\vec{p}\otimes\vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ p_x & p_y & p_z \\ yp_z - zp_y & zp_x - xp_z & xp_y - yp_x \end{vmatrix} = \begin{pmatrix} \hat{i}(p_y(xp_y - yp_x) - p_z(zp_x - xp_z)) \\ \hat{j}(p_z(yp_z - zp_y) - p_x(xp_y - yp_x)) \\ \hat{k}(p_x(zp_x - xp_z) - p_y(yp_z - zp_y)) \end{pmatrix} \quad (17.10)$$

or, expanding

$$\vec{p}\otimes\vec{L} = \begin{pmatrix} \hat{i}(p_yxp_y - p_yyp_x - p_zzp_x + p_zxp_z) \\ \hat{j}(p_zyp_z - p_zzp_y - p_xxp_y + p_xyp_x) \\ \hat{k}(p_xzp_x - p_xxp_z - p_yyp_z + p_yzp_y) \end{pmatrix} \quad (17.11)$$

or, expanding again

$$\vec{p}\otimes\vec{L} = \begin{pmatrix} \hat{i}(x(p_y^2 + p_z^2) - p_yyp_x - p_zzp_x + xp_x^2 - xp_x^2) \\ \hat{j}(y(p_z^2 + p_x^2) - p_zzp_y - p_xxp_y + yp_y^2 - yp_y^2) \\ \hat{k}(z(p_x^2 + p_y^2) - p_xxp_z - p_yyp_z + zp_z^2 - zp_z^2) \end{pmatrix} \quad (17.12)$$

which is

$$\vec{p}\otimes\vec{L} = \begin{pmatrix} \hat{i}(x(p_y^2 + xp_z^2 + p_x^2) - p_yyp_x - p_zzp_x - xp_xp_x) \\ \hat{j}(y(p_z^2 + p_x^2 + p_y^2) - p_zzp_y - p_xxp_y - yp_yp_y) \\ \hat{k}(z(p_x^2 + p_y^2 + zp_z^2) - p_xxp_z - p_yyp_z - zp_zp_z) \end{pmatrix} \quad (17.13)$$

or, using the commutators, we obtain

$$\vec{p}\otimes\vec{L} = \begin{pmatrix} \hat{i}(x(p_y^2 + xp_z^2 + p_x^2) - p_yyp_x - p_zzp_x - (p_xx + \imath\hbar)p_x) \\ \hat{j}(y(p_z^2 + p_x^2 + p_y^2) - p_yp_zz - p_yp_xx - (p_yy + \imath\hbar)p_y) \\ \hat{k}(z(p_x^2 + p_y^2 + zp_z^2) - p_xxp_z - p_yyp_z - (p_zz + \imath\hbar)p_z) \end{pmatrix} \quad (17.14)$$

which is

$$\vec{p}\otimes\vec{L} = \begin{pmatrix} \hat{i}(x(\vec{p}\cdot\vec{p}) - p_yyp_x - p_zzp_x - (p_xx + \imath\hbar)p_x) \\ \hat{j}(y(\vec{p}\cdot\vec{p}) - p_yp_zz - p_yp_xx - (p_yy + \imath\hbar)p_y) \\ \hat{k}(z(\vec{p}\cdot\vec{p}) - p_xxp_z - p_yyp_z - (p_zz + \imath\hbar)p_z) \end{pmatrix} \quad (17.15)$$

which can be re-written as

$$\vec{p}\otimes\vec{L} = \vec{r}(\vec{p}\cdot\vec{p}) - (\vec{p}\cdot\vec{r})\vec{p} - \imath\hbar\vec{p} \quad (17.16)$$

Turning back to Equation 16.1 and substituting Equation 17.16 and Equation 17.8 we obtain

$$\vec{L}\otimes\vec{p}-\vec{p}\otimes\vec{L}= -\vec{r}(\vec{p}\cdot\vec{p})+\imath\hbar\vec{p}+\vec{p}(\vec{r}\cdot\vec{p})-[\vec{r}(\vec{p}\cdot\vec{p})-(\vec{p}\cdot\vec{r})\vec{p}-\imath\hbar\vec{p}] \quad (17.17)$$

which can be re-written as

$$\vec{L}\otimes\vec{p}-\vec{p}\otimes\vec{L}=-2\vec{r}(\vec{p}\cdot\vec{p})+2\imath\hbar\vec{p}+\vec{p}(\vec{r}\cdot\vec{p})+(\vec{p}\cdot\vec{r})\vec{p} \quad (17.18)$$

But

$$\begin{aligned}\vec{p}(\vec{r}\cdot\vec{p})+(\vec{p}\cdot\vec{r})\vec{p}=&\\ +\hat{i}(p_x(xp_x+yp_y+zp_z)+p_xxp_x+p_yyp_x+p_zzp_x)&\\ +\hat{j}(p_y(xp_x+yp_y+zp_z)+p_yyp_y+(p_xx+p_zz)p_y)&\\ +\hat{k}(p_z(xp_x+yp_y+zp_z)+p_zzp_z+(p_xx+p_yy)p_z)&\end{aligned} \quad (17.19)$$

or, re-arranging

$$\begin{aligned}\vec{p}(\vec{r}\cdot\vec{p})+(\vec{p}\cdot\vec{r})\vec{p}=&\\ +\hat{i}(p_x(xp_x+yp_y+zp_z)+p_xxp_x+p_x(yp_y-\imath\hbar+p_x(zp_z-\imath\hbar))&\\ +\hat{j}(p_y(xp_x+yp_y+zp_z)+p_yyp_y+((xp_x-\imath\hbar)+(zp_z-\imath\hbar))p_y)&\\ +\hat{k}(p_z(xp_x+yp_y+zp_z)+p_zzp_z+((xp_x-\imath\hbar)+(yp_y-\imath\hbar))p_z)&\end{aligned} \quad (17.20)$$

(why can we so blithely move p_y and p_z from the rear to the front in the above equation?) which is

$$\vec{p}(\vec{r}\cdot\vec{p})+(\vec{p}\cdot\vec{r})\vec{p}=2\vec{p}(\vec{r}\cdot\vec{p})-2\imath\hbar\vec{p}$$

so that

$$\begin{aligned}\vec{L}\otimes\vec{p}-\vec{p}\otimes\vec{L}=&\\ 2\left\{-\vec{r}(\vec{p}\cdot\vec{p})+\imath\hbar\vec{p}\right\}+\vec{p}(\vec{r}\cdot\vec{p}-2\imath\hbar\vec{p}\}&\\ =2\vec{L}\otimes\vec{p}+2\imath\hbar\vec{p}&\end{aligned} \quad (17.21)$$

where we have used Equation 17.8.

We finally obtain

$$\vec{A}=\frac{1}{2Ze^2\mu}\left(\vec{L}\otimes\vec{p}-\vec{p}\otimes\vec{L}\right)+\hat{r}=\frac{1}{Ze^2\mu}\left(\vec{L}\otimes\vec{p}-\imath\hbar\vec{p}\right)+\hat{r} \quad (17.22)$$

which is Equation 51' (according to the Pauli manuscript).

XVIII. ANOTHER PAULI EQUATION

Now we ask what is $\vec{A}\cdot\vec{r}$ where we are looking for the quantum mechanical equivalent of the conic section rule for the Runge-Lenz vector. We have

$$\vec{A}\cdot\vec{r}=\frac{1}{Ze^2\mu}\left(\vec{L}\otimes\vec{p}-\imath\hbar\vec{p}\right)\cdot\vec{r}+r$$

since $\hat{r}\cdot\vec{r}$ is $\frac{r^2}{r}$. Continuing, we have

$$\vec{A}\cdot\vec{r}=\frac{1}{Ze^2\mu}\left(\vec{L}\otimes\vec{p}\right)\cdot\vec{r}-\frac{1}{Ze^2\mu}\left(\imath\hbar\vec{p}\right)\cdot\vec{r}+r \quad (18.1)$$

which is

$$\vec{A}\cdot\vec{r}=\frac{1}{Ze^2\mu}\begin{pmatrix}\hat{i}&\hat{j}&\hat{k}\\ L_x&L_y&L_z\\ p_x&p_y&p_z\end{pmatrix}\cdot\vec{r}-\frac{1}{Ze^2\mu}\left(\imath\hbar\vec{p}\right)\cdot\vec{r}+r \quad (18.2)$$

i.e.,

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\begin{pmatrix}\hat{i} & \hat{j} & \hat{k}\\ L_x & L_y & L_z\\ p_x & p_y & p_z\end{pmatrix}\cdot\begin{pmatrix}x\\ y\\ z\end{pmatrix} - \frac{1}{Ze^2\mu}(\imath\hbar)\begin{pmatrix}p_x\\ p_y\\ p_z\end{pmatrix}\cdot\begin{pmatrix}x\\ y\\ z\end{pmatrix} + r \tag{18.3}$$

or, expanding

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\begin{pmatrix}(L_yp_z - L_zp_y)\\ (L_zp_x - L_xp_z)\\ (L_xp_y - L_yp_x)\end{pmatrix}\cdot\begin{pmatrix}x\\ y\\ z\end{pmatrix} - \frac{1}{Ze^2\mu}(\imath\hbar\vec{p})\cdot\vec{r} + r \tag{18.4}$$

which is, expanding (and watching the order of operators carefully):

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\left(L_yp_zx - L_zp_yx + L_zp_xy - L_xp_zy + L_xp_yz - L_yp_xz\right) - \frac{1}{Ze^2\mu}(\imath\hbar\vec{p})\cdot\vec{r} + r \tag{18.5}$$

which is

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\left(+L_x(p_yz - p_zy) + L_y(p_zx - p_xz) + L_z(p_xy - p_yx)\right) - \frac{1}{Ze^2\mu}\left(\imath\hbar\left(p_xx + p_yy + p_zz\right)\right) + r \tag{18.6}$$

or

$$\vec{A}\cdot\vec{r} = \frac{1}{Ze^2\mu}\left(-L_x^2 - L_y^2 - L_z^2\right) - \frac{1}{Ze^2\mu}\left(\imath\hbar\left(p_xx + p_yy + p_zz\right)\right) + r \tag{18.7}$$

and, in reverse order

$$\vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}\begin{pmatrix}x\\ y\\ z\end{pmatrix}\cdot\begin{pmatrix}(L_yp_z - L_zp_y)\\ (L_zp_x - L_xp_z)\\ (L_xp_y - L_yp_x)\end{pmatrix} - \frac{1}{Ze^2\mu}(\imath\hbar\vec{r})\cdot\vec{p} + r \tag{18.8}$$

$$\vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}\left(x\left(L_yp_z - L_zp_y\right) + y\left(L_zp_x - L_xp_z\right) + z\left(L_xzp_y - L_yp_x\right)\right) - \frac{1}{Ze^2\mu}\left(\imath\hbar\left(xp_x + yp_y + zp_z\right)\right) + r \tag{18.9}$$

and, re-arranging (expanding)

$$\vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}\left(xL_yp_z - xL_zp_y + yL_zp_x - yL_xp_z + zL_xp_y - zL_yp_x\right) - \frac{1}{Ze^2\mu}\left(\imath\hbar\left(xp_x + yp_y + zp_z\right)\right) + r \tag{18.10}$$

It is easiest if we quickly obtain the commutators of $\vec{r}$ with $\vec{L}$, i.e.,

$$[x, L_y] = x(zp_x - xp_z) - (zp_x - xp_z)x$$

which is (since $p_xx - xp_x = -\imath\hbar$)

$$[x, L_y] = xzp_x - x^2p_z - zp_xx + xp_zx = zxp_x - zp_xx = z(xp_x - p_xx) = z(\imath\hbar)$$

Similarly, we have

$$[y, L_y] = 0$$

which is true in general. Finally, we have

$$[z, L_y] = zzp_x - zxp_z - zp_xz + xp_zz = -zxp_z + xp_zz = x(p_zz - zp_z) = x(-\imath\hbar)$$

We summarize these results in the following table:

$$\begin{gathered} xL_y - L_yx = \imath\hbar z \\ yL_z - L_zy = \imath\hbar x \\ zL_x - L_xz = \imath\hbar y \\ zL_y - L_yz = -\imath\hbar x \\ xL_z - L_zx = -\imath\hbar y \\ yL_x - L_xy = -\imath\hbar z \end{gathered} \tag{18.11}$$

Returning to Equation 18.10

$$\begin{aligned} \vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}&\left((L_yx + \imath\hbar z)p_z - (L_zx - \imath\hbar y)p_y + \right. \\ &(L_zy + \imath\hbar x)p_x - (L_xy - \imath\hbar z)p_z + \\ &\left.(L_xx + \imath\hbar y)p_y - (L_yz - \imath\hbar x)p_x\right) - \\ &\frac{1}{Ze^2\mu}\left(\imath\hbar\left(xp_x + yp_y + zp_z\right)\right) + r \end{aligned} \tag{18.12}$$

or, expanding

$$\begin{aligned} \vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}&\left(L_yxp_z + \imath\hbar zp_z - L_zxp_y + \imath\hbar yp_y + \right. \\ &L_zyp_x + \imath\hbar xp_x - L_xyp_z + \imath\hbar zp_z + \\ &\left.L_xxp_y + \imath\hbar yp_y - L_yzp_x + \imath\hbar xp_x\right) - \\ &\frac{1}{Ze^2\mu}\left(\imath\hbar\left(xp_x + yp_y + zp_z\right)\right) + r \end{aligned} \tag{18.13}$$

which becomes

$$\begin{aligned} \vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}&\left(L_y(xp_z - zp_x) + 2\imath\hbar(zp_z + yp_y + xp_x)\right. \\ &\left. + L_z(yp_x - xp_y) + L_x(xp_y - yp_z)\right) - \\ &\frac{1}{Ze^2\mu}\left(\imath\hbar\left(xp_x + yp_y + zp_z\right)\right) + r \end{aligned} \tag{18.14}$$

or

$$\begin{aligned} \vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}&\left(-L_y^2 - L_z^2 - L_x^2 + 2\imath\hbar(zp_z + yp_y + xp_x)\right) - \\ &\frac{1}{Ze^2\mu}\left(\imath\hbar\left(xp_x + yp_y + zp_z\right)\right) + r \end{aligned} \tag{18.15}$$

or

$$\vec{r}\cdot\vec{A} = \frac{1}{Ze^2\mu}\left(-L^2 + 2\imath\hbar\vec{r}\cdot\vec{p}\right) - \frac{1}{Ze^2\mu}\imath\hbar\vec{r}\cdot\vec{p} + r \tag{18.16}$$

so, finally,

$$\vec{r}\cdot\vec{A} = -\frac{1}{Ze^2\mu}L^2 + \frac{\imath\hbar}{Ze^2\mu}\vec{r}\cdot\vec{p} + r \tag{18.17}$$

and we note

$$\vec{p}\cdot\vec{r} = \vec{r}\cdot\vec{p} - 3\imath\hbar$$

while from Equation 18.7

$$\vec{A}\cdot\vec{r} = -\frac{1}{Ze^2\mu}L^2 - \frac{\imath\hbar}{Ze^2\mu}\vec{p}\cdot\vec{r} + r \tag{18.18}$$

$$\vec{r}\cdot\vec{A} = -\frac{1}{Ze^2\mu}L^2 + \frac{\imath\hbar}{Ze^2\mu}\left(\vec{p}\cdot\vec{r} + 3\right) + r \tag{18.19}$$

Adding Equation 18.18 and 18.19 we have

$$\vec{A}\cdot\vec{r} + \vec{r}\cdot\vec{A} = -\frac{2}{Ze^2\mu}L^2 + \frac{\imath\hbar}{Ze^2\mu}\left(+3\imath\hbar\right) + 2r \tag{18.20}$$

i.e.,

$$\frac{\vec{A}\cdot\vec{r}+\vec{r}\cdot\vec{A}}{2} = -\frac{1}{Ze^2\mu}\left(L^2+\frac{3\hbar^2}{2}\right)+r \qquad (18.21)$$

which is Equation 51 in Pauli's manuscript.

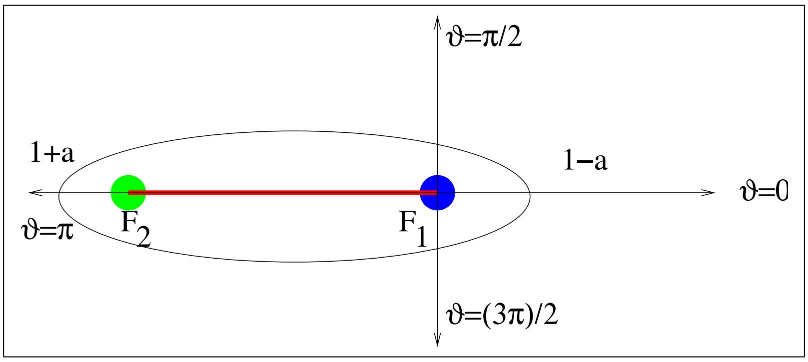

FIG. 1: The ellipse in planar polar coordinates.

[1] C. W. David, *Am. J. Phys.*, **34**,984(1966)

[2] There is some controversy about naming this vector quantity, and we will follow standard procedure, and reference C. Runge, *Vector Analysis*, E. P. Dutton, New York, 1919), Chap 11, Sec 5; and W. Lenz, *Z. Phys.* **24**,197(1924). One should also consult H. Goldstein, *Am. J. Phys.*, **44**, 1123(1976) and references therein. Finally, I need to call attention to a paper by Blinder which uses our work here, *J. Chem. Ed.*, **78**, 391(2001). Finally, in passing, in the year 2007, it seems appropriate to comment that citing materials in the chemistry education literature seems to be quite haphazard.

[3] Cartesian coordinates are the first choice, then spherical polar coordinates if we are aiming to treat the isolated atom's bound states, then cylindrical coordinates is we are interested in treating external fields, then elliptical coordinates if we are interested in dealing with H_2^+ (and we may have left out a few).

[4] the velocity can be invoked (in one dimension) we have:

$$p = \mu v = \mu\frac{dx}{dt}$$

[5] I am indebted to Prof. Liang Chen, physicist at the University of Ottawa, Canada, for pointing out an earlier error in this manuscript concerning $\vec{r}\cdot\vec{p}$, which I had declared to be zero. Although this is true for circular orbits, Keplerian orbits have this true only at certain points in space (apogee and perigee). Therefore, the longer derivation has been substituted for this spurious argument.