June 2006

The Hydrogen Atom: The Bohr Model in Detail

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(Dated: June 1, 2006)

When studying the hydrogen atom's electron, the prototypical atomic problem, one should keep in mind that most of our mental impressions about atoms and their electronic structure will be gleaned from this problem. That means that paying attention to it is tantamount to laying an adequate foundation for continuing study of higher atomic number atoms, and ultimately molecules, the stuff of Chemistry.

We start with elementary Bohr theory, not because we can do it better than others, but just so that we can review the material in this appropriate place. If, to begin, we place the proton (or nucleus) at the origin, and the electron somewhere in space, and if we assume (temporarily) that the nucleus is infinitely massive, so that it doesn't ever move, then the total energy of the two particle system is contained in the energy of the electron. It has two forms of energy, as usual, potential and kinetic. Assuming the electron is located at $\vec{r}$ at time t, i.e., at

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

(where x = x(t), y = y(t), and z = z(t)) then the (classical) velocity of the electron would be

$$\vec{v} = \dot{x}\hat{i} + \dot{y}\hat{j} + \dot{z}\hat{k} = \frac{d\vec{r}}{dt} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}$$

and the kinetic energy is (by definition)

$$KE = \frac{1}{2}m_e\vec{v} \bullet \vec{v}$$

where m_e is the mass of the electron itself. This dot product produces

$$KE = \frac{1}{2}m_e\left(v_x^2 + v_y^2 + v_z^2\right)$$

which is just

$$KE = \frac{1}{2}m_e v^2$$

where v is the scalar magnitude of the velocity vector (sometimes called c), i.e., $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$.

The potential energy of the electron is given by Coulomb's law, i.e., it corresponds to the charge on the nucleus times the charge on the electron divided by the distance of separation. Since $r = \sqrt{x^2 + y^2 + z^2}$, we have that

$$PE = -\frac{(Ze)(e)}{r} = -\frac{(Ze)(e)}{\sqrt{x^2 + y^2 + z^2}}$$

where we are using the electron charge, e, and the nuclear charge of an atomic number Z, to form either an ion (Z>1) or the neutral H-atom (Z=1). The minus sign is there because the nucleus is positive and the electron carries a negative charge, and the numerator (as written) obliterates that fact. Actually, there are other reasons, but let's leave it at that for the time being.

We now have that the energy of the H-atom is

$$E_{total} = \frac{1}{2}m_e v^2 - \frac{(Ze)(e)}{r} = \frac{1}{2}m_e v^2 - \frac{Ze^2}{r} \quad (1)$$

We note in passing that this last expression will form the basis for constructing the Hamiltonian and ultimately the Schrödinger equation appropriate for this problem.

As is common in these atomic problems, we become conflicted between the Cartesian coördinate system which is the appropriate one for starting the analysis, and spherical polar coördinates, which appear to be somehow "cleaner", although much of this is in the eye of the reader. Let's recall what spherical polar coördinates are, an alternative scheme for locating a particle in space, using two angles and the distance from the origin. The definitions are

$$\begin{aligned} x &= r\sin\vartheta\cos\varphi \\ y &= r\sin\vartheta\sin\varphi \\ z &= r\cos\vartheta \end{aligned} \quad (2)$$

which is the traditional set used by physicists and chemists (mathematicians sometimes exchange ϑ and φ and it is essential when starting out to keep clear which definitions you are using). Squaring and adding these together, we recover the definition of the radius, i.e.,

$$x^2 + y^2 + z^2 = r^2$$

where we make copious use of $\cos^2 + \sin^2 = 1$.

From Figure 1 we have from the O-A-B triangle, that $\cos\varphi = \frac{x}{a}$ and $\sin\varphi = \frac{y}{a}$, while from triangle O-B-C we have $\sin\vartheta = \frac{a}{r}$ so, eliminating "a" from these gives us the transformation equations we desire. For triangle O-C-D we get $r\cos\vartheta = z$, independent of "a".

Forming

$$\frac{y}{x} = \frac{r\sin\vartheta\sin\varphi}{r\sin\vartheta\cos\varphi}$$

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we obtain

$$\tan^{-1}\frac{y}{x} = \varphi$$

and from the z-equation we obtain

$$\cos^{-1}\frac{z}{\sqrt{x^2+y^2+z^2}} = \cos^{-1}\frac{z}{r} = \vartheta$$

which we repeat (reversed) as

$$\begin{aligned} \varphi &= \tan^{-1}\frac{y}{x} \\ \vartheta = \cos^{-1}\frac{z}{\sqrt{x^2+y^2+z^2}} &= \cos^{-1}\frac{z}{r} \\ r &= \sqrt{x^2+y^2+z^2} \end{aligned} \tag{3}$$

These three equations (Equations 4) tell us, given values for x, y, and z, (on the r.h.s.) how to compute r, ϑ and φ. The first set of equations (Equations 2) gave us the opposite, i.e., knowing the values of the spherical polar coördinates of the electron (on the r.h.s.), we could calculate the x, y, and z values of that same position.

The original Bohr calculation for the electron's energy involved using circular orbits for the path of the electron around the nucleus (analogous to the Earth orbiting the Sun (elliptical orbits, hint, hint)). So we need to think about circular orbits for a bit.

In a circular orbit, r would be constant, wouldn't it? That's the meaning of circular (or spherical, if we just thought the electron stayed on the surface of a sphere). To continue this discussion then, we need to recall the angular momentum vector from elementary physics. When a particle is located at the point P(x,y,z), with instantaneous velocity v_x in the x-direction, v_y in the y-direction, and v_z in the z-direction, i.e., has a velocity vector

$$\vec{v} = v_x\hat{\imath} + v_y\hat{\jmath} + v_z\hat{k}$$

(where $v_x = \frac{dx}{dt}$ (and is itself a function of time, i.e., $v_x(t)$), with equivalent terms for the instantaneous values of y and z), and a momentum vector

$$\vec{p} = mv_x\hat{\imath} + mv_y\hat{\jmath} + mv_z\hat{k}$$

then the angular momentum is defined as the cross product of the radius vector on the momentum vector, i.e.,

$$\vec{L} = \vec{r}\otimes\vec{p} \tag{4}$$

where we remember two different definitions of the cross product. One can define it as

$$|\vec{A}\otimes\vec{B}| \equiv |\vec{A}||\vec{B}|\sin\theta$$

where θ is the angle between $\vec{A}$ and $\vec{B}$ and the vertical lines indicate "magnitude" of the enclosed vector. The added caveat is that the direction of the new vector, the cross product, is perpendicular to the plane of $\vec{A}$ and $\vec{B}$, and follows a right-hand rule analogous to $\hat{\imath}\otimes\hat{\jmath}\to\hat{k}$.

The other definition, which is caveat free, is

$$\vec{A}\otimes\vec{B} \equiv det\begin{pmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{pmatrix} \tag{5}$$

which expands to

$$\vec{A}\otimes\vec{B} = \hat{\imath}(A_yB_z - A_zB_y) + \hat{\jmath}(A_zB_x - A_xB_z) + \hat{k}(A_xB_y - A_yB_z)$$

Note that

$$\hat{\imath}\otimes\hat{\jmath} \equiv det\begin{pmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \to \hat{k}$$

as expected. In our case, we have, employing Equation 4 and Equation 5, we obtain:

$$\vec{L} \equiv \vec{r}\otimes\vec{p} = \hat{\imath}(yp_z - zp_y) + \hat{\jmath}(zp_x - xp_z) + \hat{k}(xp_y - yp_z)$$

which means that we can work with the definition of $\vec{L}$ and know that we can compute its components as needed.

So, let's learn first what the time derivative of $\vec{L}$ is. Thus

$$\frac{d\vec{L}}{dt} = \frac{d\vec{r}}{dt}\otimes\vec{p} + \vec{r}\otimes\frac{d\vec{p}}{dt}$$

The first term is zero, since the time derivative of $\vec{r}$ is proportional (through the mass) to $\vec{p}$, and, we remember that the cross product of a vector on itself (or anything parallel to itself) is zero. This leaves

$$\frac{d\vec{L}}{dt} = \vec{r}\otimes\frac{d\vec{p}}{dt}$$

but the time derivative of the momentum is the force (Newton's second law), so

$$\frac{d\vec{L}}{dt} = \vec{r}\otimes\vec{F} \equiv \vec{\tau}$$

where $\vec{\tau}$ is the torque exerted by the force at $\vec{r}$. If $\vec{r}$ is parallel to $\vec{F}$ then the torque is zero, and, lo and behold, the angular momentum has a zero time derivative. And a zero time derivative means that the angular momentum is constant, and that means we have discovered one of the infamous "constants of the motion".

I. PART 2

Having established that the angular momentum is conserved, i.e., is time independent, in central force problems such as the hydrogen atom, i.e., problems in which the force vector is collinear with the radius vector, i.e., $\vec{r}$ collinear to $\vec{F}$, we turn now to the Bohr calculation of the H atom's electronic energy in the infinite nuclear mass approximation.

We have a coördinate system with the nucleus at the origin and an electron circumnavigating the nucleus at $\vec{r}(t)$. If, in that circumnavigation, the path is a circle (the Kepler problem uses ellipses), then we know that the instantaneous velocity vector $\vec{v}(t)$ of the electron at the point $\vec{r}(t)$ is perpendicular to the instantaneous force (Coulomb) between the proton (nucleus) and the electron, and therefore that the cross product becomes

$$\vec{L} = \vec{r} \otimes \vec{p} = |\vec{r}||\vec{p}| \sin \pi/2$$

Bohr's postulate consisted of quantizing angular momentum, i.e.,

$$\ell = n\hbar = \vec{r} \times \vec{p} = mvr = |\vec{r}||\vec{p}| \sin \frac{\pi}{2}$$

where n is an integer (greater than or equal to 1), and $\hbar$ (which is $\frac{h}{2\pi}$) is a constant, meaning that only integral multiples of $\hbar$ were legal values of ℓ. Note that we have used the fact that in circular motion, the angle between $\vec{r}$ and $\vec{p}$ is $\pi/2$, so the sine evaluates to one, and we get a simplified form for the angular momentum.

In the Coulomb problem of two oppositely charged particles interacting (as in our problem), the force is given by the charge on one particle times the charge on the other divided by the square of the distance of separation. This corresponds to

$$F = -\frac{Ze \times e}{r^2}$$

where $\vec{F}$ is collinear with $\vec{r}$ or, more formally

$$\vec{F} = -\frac{Ze \times e \times \hat{r}}{r^2} = -\frac{Ze \times e \times \vec{r}}{r^3} \qquad (6)$$

which is the same thing. Here, we have used the charge on the electron (e) and the atomic number of the nucleus (Z) to force the nuclear charge, Ze, and the electron charge, e, to be multiplied together in Coulomb's expression.

This force is equal and opposite to the centripetal "force" which arises from the circular motion.

It is clear from the figure that the two triangles, one involving changing r, the other involved in changing v, are similar, with the same included angle θ. From Figure 2 part (e) one sees that

$$\sin \frac{\theta}{2} = \frac{x/2}{y}$$

which, for $\theta \to 0$ (Taylor expansion for $\sin\gamma \to \gamma$) becomes

$$\frac{\theta}{2} = \frac{x/2}{y}$$

which for the "v" (velocity) triangle (d) becomes

$$\frac{\theta}{2} = \frac{|\vec{v}|/2}{v}$$

while for the "r" (radius) triangle (c) we have

$$\frac{\theta}{2} = \frac{|\vec{r}|/2}{r}$$

so, setting the two equal to each other we have

$$\frac{|\Delta\vec{v}|}{v} = \frac{|\Delta\vec{r}|}{r}$$

all in time Δt. We thus have

$$\frac{\frac{|\Delta\vec{v}|}{\Delta t}}{v} = \frac{\frac{|\Delta\vec{r}|}{\Delta t}}{r}$$

which is, in the limit $\Delta t \to 0$ becomes

$$\frac{\frac{d|\vec{v}|}{dt}}{v} = \frac{|\vec{a}|}{v} = \frac{\frac{d|\vec{r}|}{dt}}{r} = \frac{|\vec{v}|}{r}$$

i.e.,

$$|\vec{a}| = \frac{v|\vec{v}|}{r} = \frac{v^2}{r}$$

which is a classic formula. All we need now is to remember that F=ma, i.e., Newton's Second Law, and apply it to our case.

Remember that the angular momentum is conserved in this kind of "central force" model, and therefore, the vector representing the angular momentum, $\vec{L}$, is a constant. And this *means* that $\vec{L}$ has constant length *and* direction. But if the direction is fixed, then it is perpendicular to the motion at the instant, and at all future and past instants, i.e., it is perpendicular to the motion always. That means that the motion must take place in a plane, the plane to which $\vec{L}$ is perpendicular to.

So, in that plane, we can construct a local x-y coördinate system which allows us to discuss the (circular) motion in this plane. If we write

$$x = r\cos\omega t$$
$$y = r\sin\omega t$$

and takes the time derivative of these two equations, which are describing a particle moving on a circle, we obtain

$$\dot{x} = \dot{r}\cos\omega t - r\omega\sin\omega t$$
$$\dot{y} = \dot{r}\sin\omega t + r\omega\cos\omega t$$

where ω is constant, but r = r(t). We obtain, after a second differentiation:

$$\ddot{x} = \ddot{r}\cos\omega t - 2\dot{r}\omega\sin\omega t - r\omega^2\cos\omega t$$
$$\ddot{y} = \ddot{r}\sin\omega t + 2\dot{r}\omega\cos\omega t - r\omega^2\sin\omega t$$

which, by Newton's Second Law should be the force, i.e. (see Equation 6),

$$m_e\ddot{x} = F(x) = -Ze^2\frac{r\cos\omega t}{r^3} = -Ze^2\frac{\cos\omega t}{r^2}$$
$$m_e\ddot{y} = F(x) = -Ze^2\frac{r\sin\omega t}{r^3} = -Ze^2\frac{\sin\omega t}{r^2}$$

(where we have employed the Coulomb's Law force previously derived) which yields

$$-(Ze^2/m_e)\frac{r\cos\omega t}{r^3} = \ddot{r}\cos\omega t - 2\dot{r}\omega\sin\omega t - r\omega^2\cos\omega t$$
$$-(Ze^2/m_e)\frac{r\sin\omega t}{r^3} = \ddot{r}\sin\omega t + 2\dot{r}\omega\cos\omega t - r\omega^2\sin\omega t$$

so, multiplying the first of these by $\cos\omega t$ and the second by $\sin\omega t$ and adding gives us

$$m_e\left(\ddot{r} - r\omega^2\right) = -\frac{Ze^2}{r^2}$$

This led to the notion that if one re-wrote this as

$$m_e\ddot{r} = m_e r\omega^2 - \frac{Ze^2}{r^2} \to 0$$

then the r.h.s could be forced to zero if the "centrifugal force" (centripetal acceleration) balanced the gravitational (or electrostatic) attraction. Remember that $\omega = \frac{v}{r}$, so $r\omega^2 = \frac{v^2}{r}$. We then have

$$\frac{m_e v^2}{r} - \frac{Ze^2}{r^2} = 0 \tag{7}$$

as the balance between the centripetal "force" on the one hand, and the Coulomb force on the other.

We now have all three of the Bohr starting equations,

$$E_{total} = \frac{1}{2}m_e v^2 - \frac{Ze^2}{r} \tag{8}$$
$$\ell = n\hbar = m_e v r \tag{9}$$
$$\frac{m_e v^2}{r} = \frac{Ze^2}{r^2} \tag{10}$$

II. PART 3

The relevant Bohr equations are:

$$\frac{m_e v^2}{r} = \frac{Ze^2}{r^2} \tag{11}$$
$$E_{total} = \frac{1}{2}m_e v^2 - \frac{Ze^2}{r} \tag{12}$$
$$m_e v r = n\hbar \tag{13}$$

and their combination leads, irresistibly, to the Balmer formula (and others). What a bargain!

First, we re-arrange Equation 13 to solve for v, i.e.,

$$v = \frac{n\hbar}{m_e r}$$

so, squaring, we have

$$v^2 = \frac{n^2\hbar^2}{m_e^2 r^2} \tag{14}$$

which we can substitute into Equation 11 to obtain

$$\frac{m_e v^2}{r} = \frac{Ze^2}{r^2} = \frac{m_e\frac{n^2\hbar^2}{m_e^2 r^2}}{r}$$

Simplification leads to

$$\frac{Ze^2}{r^2} = \frac{n^2\hbar^2}{m_e r^3}$$

which, solving for r gives us

$$r = \frac{n^2\hbar^2}{Ze^2 m_e}$$

which we re-write as

$$r = \frac{n^2}{Z}\frac{\hbar^2}{e^2 m_e} \tag{15}$$

isolating the quantum number and the atomic number for future use. The quantity $\frac{\hbar^2}{e^2 m_e}$ is known as the Bohr radius, a_0.

The total energy

$$E_{total} = \frac{1}{2}m_e v^2 - \frac{Ze^2}{r}$$

now becomes (using Equation 14)

$$E_{total} = \frac{1}{2}m_e\frac{n^2\hbar^2}{m_e^2 r^2} - \frac{Ze^2}{r}$$

which becomes, after substituting for r (using Equation 15),

$$E_{total} = \frac{1}{2}m_e\frac{n^2\hbar^2}{m_e^2\left(\frac{n^2}{Z}\frac{\hbar^2}{e^2 m_e}\right)^2} - \frac{Ze^2}{\frac{n^2}{Z}\frac{\hbar^2}{e^2 m_e}}$$

All it takes now is some elementary manipulations to obtain

$$E_{total} = \frac{1}{2}m_e\frac{n^2\hbar^2}{m_e^2\left(\frac{n^2}{Z}\frac{\hbar^2}{e^2 m_e}\right)^2} - \frac{Z^2 e^4 m_e}{n^2\hbar^2}$$

or

$$E_{total} = \frac{1}{2}\frac{Z^2 e^4 m_e}{n^2\hbar^2} - \frac{Z^2 e^4 m_e}{n^2\hbar^2}$$

which is

$$E_{total} = -\frac{Z^2 e^4 m_e}{2n^2\hbar^2}$$

which is the infamous Bohr result.

We have for v from Equation 14,

$$v = \frac{n\hbar}{m_e r}$$

and we have an expression for r from Equation 15, so

$$v = \frac{n\hbar}{m_e\frac{n^2\hbar^2}{Ze^2 m_e}}$$

which is,

$$v = \frac{Ze^2}{n\hbar}$$

III. PART 4

We start with the total electronic energy in the Bohr model, and seek to use an appropriate unit system which will work easily in our case. The formula for the total energy is

$$E_{total} = -\frac{Z^2 e^4 m_e}{2n^2\hbar^2}$$

where Z is the atomic number (an integer) e is the charge on the electron, m_e is the mass of an electron, n is a non-zero integer, and $\hbar$ is $\frac{h}{2\pi}$.

The normal unit of charge is the Coulomb, but we will use instead the statcoulomb, since it is appropriate in the cgs system, i.e.,

$$1statcoulomb = 1dyne^{1/2}cm$$

which means that two charges (of one statcoulomb each) separated by one centimeter would exert a force of 1 dyne ($gram - cm/sec^2$) (direction set by the charges' signs. It turns out that the charge on the electron, in statcoulombs, is $4.8 \times 10^{-10} statcoulombs$ = e, (which corresponds to $1.6 \times 10^{-19} Coulomb$). The mass of the electron, m_e is 9.1094×10^{-28} grams. h= $6.627 \times 10^{-27} erg - sec$, and $\hbar = \frac{h}{2\pi}$, so

$$E_{total} = -\frac{Z^2(4.8 \times 10^{-10})^4(9.1094 \times 10^{-28})}{2n^2(\frac{6.627\times 10^{-27}}{2\pi})^2}$$

where the units are

$$E_{total} = -\frac{Z^2(dynes^{1/2}cm)^4 grams}{2n^2(erg\ seconds)^2} \tag{16}$$

which is

$$E_{total} \rightarrow \frac{dynes^2 cm^4 grams}{(dyne\ cm\ seconds)^2}$$

which is

$$E_{total} \rightarrow \frac{dynes^2 cm^4 grams}{(grams\ (\frac{cm}{sec^2})\ cm\ sec)^2}$$

which is

$$E_{total} \rightarrow \frac{\left(\frac{gram\ cm}{sec^2}\right)^2 cm^4 grams}{(grams\ (\frac{cm}{sec})\ cm)^2}$$

which finally is

$$E_{total} \rightarrow \frac{g\ cm^2}{sec^2} = dyne\ cm = ergs$$

We know that

$$r = \frac{n^2}{Z}\frac{\hbar^2}{e^2 m_e} \tag{17}$$

$$r = \frac{n^2}{Z}\frac{(\frac{6.627\times 10^{-27}}{2\pi} erg\ sec)^2}{(4.8 \times 10^{-10} statcoulomb)^2 9.1094 \times 10^{-28} grams}$$

and it behooves us to check the units here also using the same scheme. We have

$$r \rightarrow \frac{(erg\ sec)^2}{(dynes^{-1/2}cms)^2 grams}$$

which is

$$r \rightarrow \frac{dyne^2\ cm^2\ sec^2}{dynes\ cm^2 grams}$$

which finally becomes

$$r \rightarrow \frac{dyne\ sec^2}{gm} = \frac{n^2}{Z}\frac{\frac{gm\ cm}{sec^2}\ sec^2}{gm} = cm$$

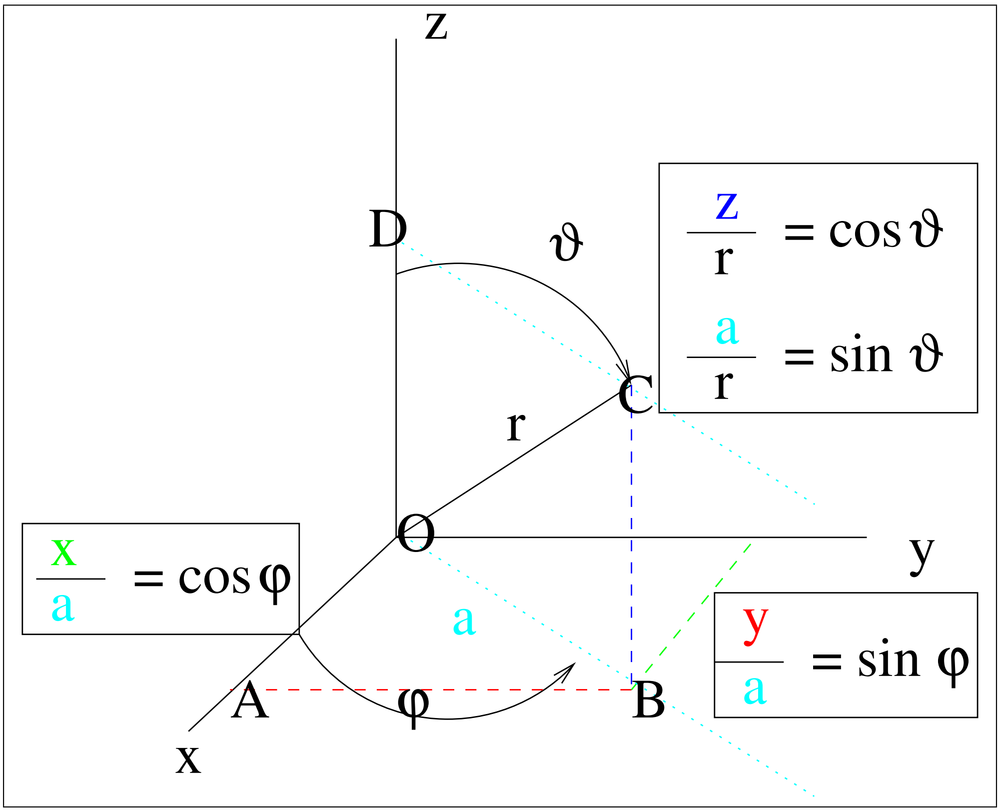

FIG. 1: If we know x and y, then we can compute a. From z and a we can compute ϑ, while from the ratio of y and x we can compute φ.

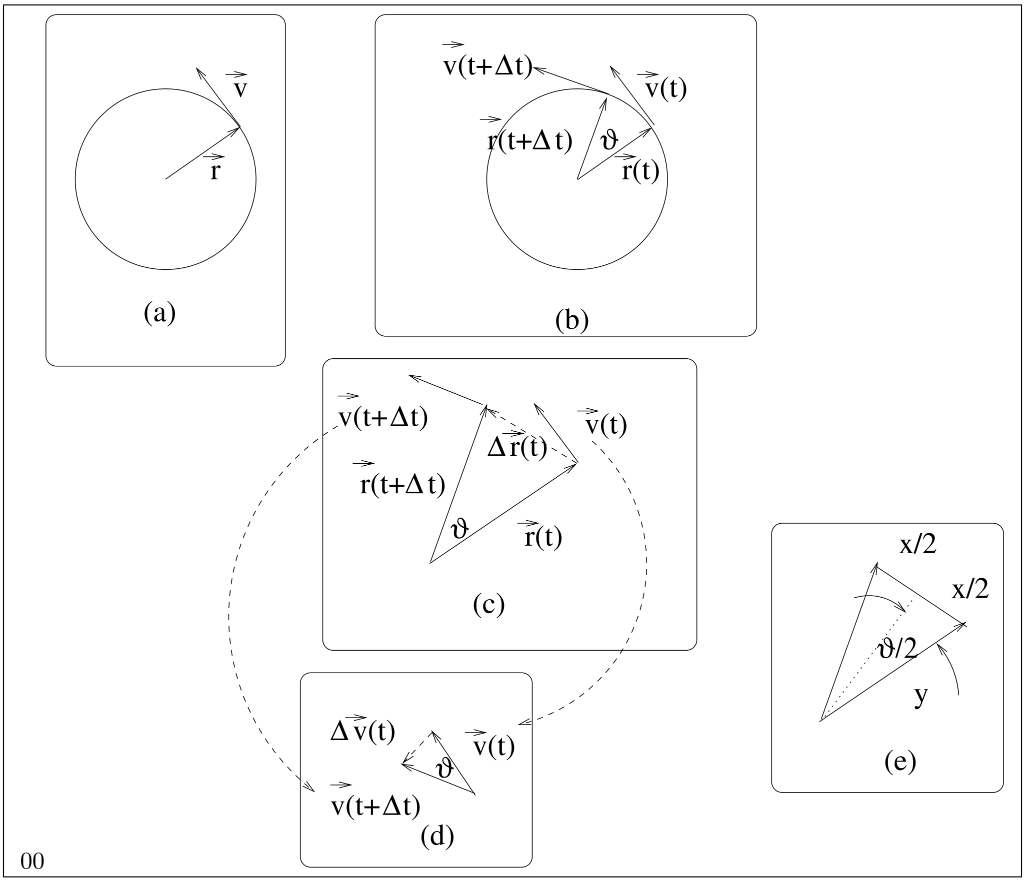

FIG. 2: Construction of the centripetal “force”.

IV. ACKNOWLEDGMENTS

This material was originally composed for interactive reading on the World Wide Web, but given the imminent demise of the site which housed the material, given my retirement, it seems worthwhile to re-edit it into coherency, attempt to remove the last little errors (there were several) and place it in a “permanent” location, if such can be said to exist.

The material is dedicated to all my students who over the years have either hated, loved, or were indifferent to, me.