3.4: Angular Momentum of an Electron in a Hydrogen Atom

The simplest classical model of the hydrogen atom is one in which the electron moves in a circular planar orbit about the nucleus as previously discussed and as illustrated in Figure 3-7. The angular momentum vector **M** in this figure is shown at an angle qwith respect to some arbitrary axis in space. Assuming for the moment that we can somehow physically define such an axis, then in the classical model of the atom there should be an infinite number of values possible for the component of the angular momentum vector along this axis. As the angle between the axis and the vector **M** varies continuously from 0°, through 90° to 180°, the component of **M** along the axis would vary correspondingly from **M** to zero to -**M**. Thus the quantum mechanical statements regarding the angular momentum of an electron in an atom differ from the classical predictions in two startling ways. First, the magnitude of the angular momentum (the length of the vector **M**) is restricted to only certain values given by:

$$M = \sqrt{l(l+1)}\,\hbar$$

with $l = 0, 1, 2, \ldots$

The magnitude of the angular momentum is quantized. Secondly, quantum mechanics states that the component of **M** along a given axis can assume only $(2l + 1)$ values, rather than the infinite number allowed in the classical model. In terms of the classical model this would imply that when the magnitude of **M** is $\sqrt{2}\,(h/2\pi)$ (the value when $l = 1$), there are only three allowed values for q, the angle of inclination of **M** with respect to a chosen axis.

The angle q is another example of a physical quantity which in a classical system may assume any value, but which in a quantum system may take on only certain discrete values. You need not accept this result on faith. There is a simple, elegant experiment which illustrates the "quantization" of q, just as a line spectrum illustrates the quantization of the energy.

If we wish to measure the number of possible values which the component of the angular momentum may exhibit with respect to some axis we must first find some way in which we can physically define a direction or axis in space. To do this we make use of the magnetism exhibited by an electron in an atom. The flow of electrons through a loop of wire (an electric current) produces a magnetic field (Figure 3.4.1). At a distance from the ring of wire, large compared to the diameter of the ring, the magnetic field produced by the current appears to be the same as that obtained from a small bar magnet with a north pole and a south pole. Such a small magnet is called a magnetic dipole, i.e., two poles separated by a small distance.
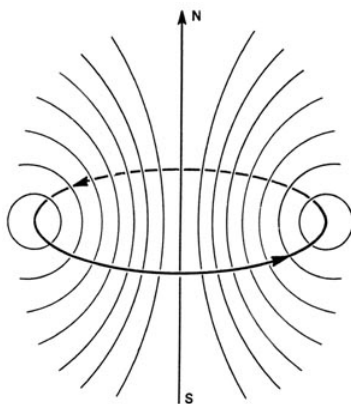

Figure $3.4.1$ *: The magnetic field produced by a current in a loop of wire.*

The electron is charged and the motion of the electron in an atom could be thought of as generating a small electric current. Associated with this current there should be a small magnetic field. The magnitude of this magnetic field is related to the angular momentum of the electron's motion in roughly the same way that the magnetic field produced by a current in a loop of wire is proportional to the strength of the current flowing in the wire.

The strength of the atomic magnetic dipole is given by m where:

$$\mu = \sqrt{l(l+1)}\,\beta_m \tag{3.4.1}$$

Just as there is a fundamental unit of negative charge denoted by e^- so there is a fundamental unit of magnetism at the atomic level denoted by b_m and called the Bohr magneton. From Equation 3.4.1 we can see that the strength of the magnetic dipole will increase as the angular momentum of the electron increases. This is analogous to increasing the magnetic field by increasing the strength of the current through a circular loop of wire The magnetic dipole, since it has a north and a south pole, will define some direction in space (the magnetic dipole is a vector quantity). The axis of the magnetic dipole in fact coincides with the direction of the angular momentum vector. Experimentally, a collection of atoms behave as though they were a collection of small bar magnets if the electrons in these atoms possess angular momentum. In addition, the axis of the magnet lies along the axis of rotation, i.e., along the angular momentum vector. Thus the magnetism exhibited by the atoms provides an experimental means by which we may study the direction of the angular momentum vector.

> *Thus the magnetism exhibited by the atoms provides an experimental means by which we may study the direction of the angular momentum vector.*

If we place the atoms in a magnetic field they will be attracted or repelled by this field, depending on whether or not the atomic magnets are aligned against or with the applied field. The applied magnetic field **will determine a direction in space**. By measuring the deflection of the atoms in this field we can determine the directions of their magnetic moments and hence of their angular momentum vectors with respect to this applied field. Consider an evacuated tube with a tiny opening at one end through which a stream of atoms may enter (Figure 3-12). By placing a second small hole in front of the first, inside the tube, we will obtain a narrow beam of atoms which will pass the length of the tube and strike the opposite end. If the atoms possess magnetic moments the path of the beam can be deflected by placing a magnetic field across the tube, perpendicular to the path of the atoms. The magnetic field must be one in which the lines of force diverge thereby exerting an unbalanced force on any magnetic material lying inside the field. This inhomogeneous magnetic field could be obtained through the use of N and S poles of the kind illustrated in Figure 3-12. The direction of the magnetic field will be taken as the direction of the z-axis.
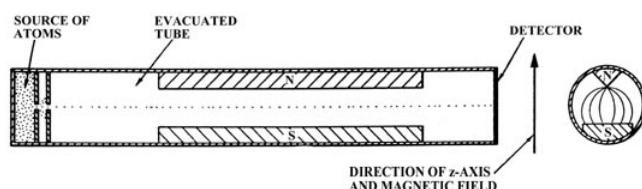

Figure 3-12. The atomic beam apparatus.

Let us suppose the beam consists of neutral atoms which possess $\sqrt{2}\,(h/2\pi)$ units of electronic angular momentum (the angular momentum quantum number $l = 1$). When no magnetic field is present, the beam of atoms strikes the end wall at a single **point** in the middle of the detector. What happens when the magnetic field is present? We must assume that before the beam enters the magnetic field, the axes of the atomic magnets are randomly oriented with respect to the z-axis. According to the concepts of classical mechanics, the beam should spread out along the direction of the magnetic field and produce a line rather than a point at the end of the tube (Figure 3-13a). Actually, the beam is split into three distinct component beams each of equal intensity producing three spots at the end of the tube (Figure 3-13b).
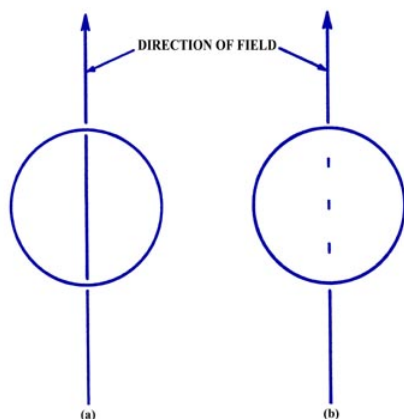

Figure 3.4.3: (a) The result of the atomic beam experiment as predicted by classical mechanics, (b) The observed result of the atomic beam experiment.

The startling results of this experiment can be explained only if we assume that while in the magnetic field each atomic magnet could assume only one of three possible orientations with respect to the applied magnetic field (Figure 3-14).
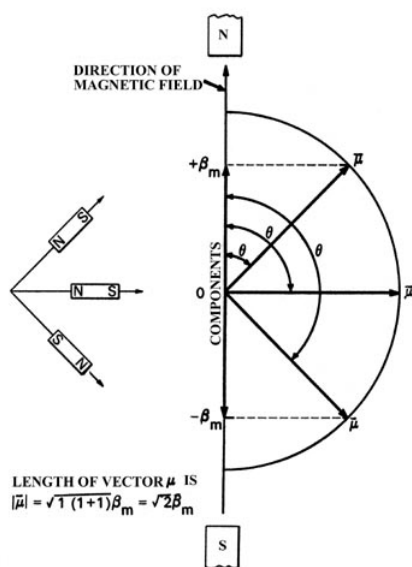

Figure $3.4.4$*: The three possible orientations for the total magnetic moment with respect to an external magnetic field for an atom with l =1.*

The atomic magnets which are aligned perpendicular to the direction of the field are not deflected and will follow a straight path through the tube. The atoms which are attracted upwards must have their magnetic moments oriented as shown. From the known strength of the applied inhomogeneous magnetic field and the measured distance through which the beam has been deflected upwards, we can determine that the component of the magnetic moment lying along the z-axis is only b_m in magnitude rather than the value of $\sqrt{2}\beta_m$ This latter value would result if the axis of the atomic magnet was parallel to the z-axis, i.e., the angle q = 0°. Instead q assumes a value such that the component of the total moment $(\sqrt{l(l+1)}\beta_m)$ lying along the z-axis is just lb_m. Similarly the beam which is deflected downwards possesses a magnetic moment along the z-axis of $-b_m$ or $-lb_m$. The classical prediction for this experiment assumes that q may equal all values from 0° to 180°, and thus all values (from a maximum of $-\sqrt{2}\beta_m$ (q = 0°) to 0 (q =90°) to $-\sqrt{2}\beta_m$ (q = 180°)) for the component of the atomic moment along the z-axis would be possible. Instead, q is found to equal only those values such that the magnetic moment along the z-axis equals $+b_m$, 0 and $-b_m$.

The angular momentum of the electron determines the magnitude and the direction of the magnetic dipole. (Recall that the vectors for both these quantities lie along the same axis.) Thus the number of possible values which the component of the angular momentum vector may assume along a given axis must equal the number of values observed for the component of the magnetic dipole along the same axis. In the present example the values of the angular momentum component are $+1(h/2p)$, 0 and $-1(h/2p)$, or since $l = 1$ in this case, $+ l(h/2p)$, 0 and $-l(h/2p)$. In general, it is found that the number of observed values is always $(2l + 1)$ the values being:

$$-l\hbar, (-l+1)\hbar, \ldots 0, \ldots, (l-1)\hbar, l\hbar$$

for the angular momentum and

$$-l\beta_m, (l-1)\beta_m \ldots, 0, \ldots, (l-1)\beta_m, l\beta_m$$

for the magnetic dipole. The number governing the magnitude of the component of $\mathbf{M}$ and $\overline{\mu}$, ranges from a maximum value of l and decreases in steps of unity to a minimum value of $-l$. This number is the third and final quantum number which determines the motion of an electron in a hydrogen atom. It is given the symbol m and is called the magnetic quantum number.

In summary, the angular momentum of an electron in the hydrogen atom is quantized and may assume only those values given by:

$\sqrt{l(l+1)}\ \dfrac{h}{2\pi}$	$l = 0, 1, 2, \ldots, n\text{-}1$

Furthermore, it is an experimental fact that the component of the angular momentum vector along a given axis is limited to $(2l + 1)$ different values, and that the magnitude of this component is quantized and governed by the quantum number m which may assume the values l, l-1, . . .,0, . . .,-l. These facts are illustrated in Figure 3-15 for an electron in a d orbital in which $l = 2$.
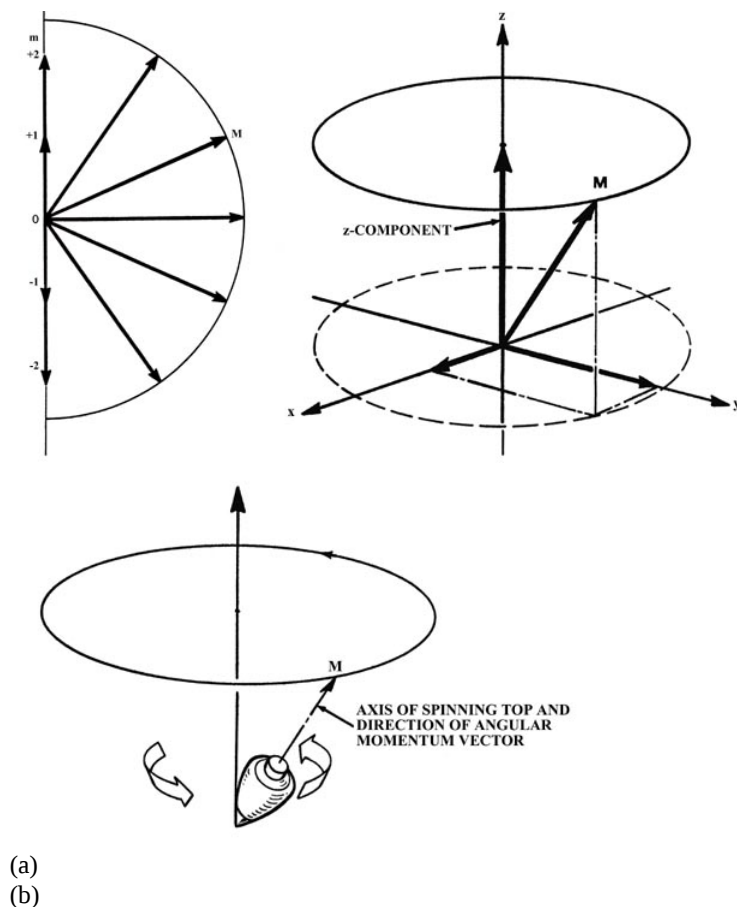
$$|\mathbf{M}| = \sqrt{2(2+1)} = \sqrt{6}$$

(a)
(b)

Figure 3-15. Pictorial representation of the quantum mechanical properties of the angular momentum of a d electron for which l = 2. The z-axis can be along any arbitrary direction in space. Figure (a) shows the possible components which the angular momentum vector (of length $\sqrt{2(2+1)}\left(h/2\pi\right)$) may exhibit along an arbitrary axis in space. A d electron may possess any one of these components. There are therefore five states for a d electron, all of which are physically different. Notice that the maximum magnitude allowed for the component is less then the magnitude of the total angular momentum. Therefore, the angular momentum vector can never coincide with the axis with respect to which the observations are made. Thus the x and y components of the angular momentum are not zero. This is illustrated in Figure (b) which shows how the angular momentum vector may be oriented with respect to the z-axis for the case m = l = 2. When the atom is in a magnetic field, the field exerts a torque on the magnetic dipole of the atom. This torque causes the magnetic dipole and hence the angular momentum vector to precess or rotate about the direction of the magnetic field. This effect is analogous to the precession of a child's top which is spinning with its axis (and hence its angular momentum vector) at an angle to the earth's gravitational field. In this case the gravitational field exerts the torque and the axis of the top slowly revolves around the perpendicular direction as indicated in the figure. The angle of inclination of M with respect to the field direction remains constant during the precession. The z-component of M is therefore constant but the x and y components are continuously changing. Because of the precession, only one component of the electronic angular momentum of an atom an be determined in a given experiment.

The quantum number m determines the magnitude of the component of the angular momentum along a given axis in space. Therefore, it is not surprising that this same quantum number determines the axis along which the electron density is concentrated. When $m = 0$ for a p electron (regardless of the n value, 2p, 3p, 4p, etc.) the electron density distribution is concentrated along the z-axis (see Figure 3-10) implying that the classical axis of rotation must lie in the x-y plane. Thus a p electron with $m = 0$ is most likely to be found along one axis and has a zero probability of being on the remaining two axes. The effect of the angular

momentum possessed by the electron is to concentrate density along one axis. When $m = 1$ or -1 the density distribution of a p electron is concentrated in the x-y plane with doughnut-shaped circular contours. The $m = 1$ and -1 density distributions are identical in appearance. Classically they differ only in the direction of rotation of the electron around the z-axis; counter-clockwise for $m = +1$ and clockwise for $m = -1$. This explains why they have magnetic moments with their north poles in opposite directions.

We can obtain density diagrams for the $m = +1$ and -1 cases similar to the $m = 0$ case by removing the resultant angular momentum component along the z-axis. We can take combinations of the $m = +1$ and -1 functions such that one combination is concentrated along the x-axis and the other along the y-axis, and both are identical to the $m = 0$ function in their appearance. Thus these functions are often labelled as p_x, p_y and p_z functions rather than by their m values. The m value is, however, the true quantum number and we are cheating physically by labelling them p_x, p_y and p_z . This would correspond to applying the field first in the z direction, then in the x direction and finally in the y direction and trying to save up the information each time. In reality when the direction of the field is changed, all the information regarding the previous direction is lost and every atom will again align itself with one chance out of three of being in one of the possible component states with respect to the new direction.

We should note that the r dependence of the orbitals changes with changes in n or l, but the directional component changes with l and m only. Thus all s orbitals possess spherical charge distributions and all p orbitals possess dumb-bell shaped charge distributions regardless of the value of n.

Table 3-1: The Atomic Orbitals for the Hydrogen Atom

E_n	n	l	m	Symbol for orbital	
-K	1	0	0	1s	
$-\frac{1}{4}K$	2	0	0	2s	
	2	1	1	2p$_{+1}$	ö
	2	1	0	2p$_0$	ý p$_x$, p$_y$, p$_z$
	2	1	-1	2p$_{-1}$	þ
$-\frac{1}{9}K$	3	0	0	3s	
	3	1	1	3p$_{+1}$	ö
	3	1	0	3p$_0$	ý p$_x$, p$_y$, p$_z$
	3	1	-1	3p$_{-1}$	þ
	3	2	2	3d$_{+2}$	ö
	3	2	1	3d$_{+1}$	|
	3	2	0	3d$_0$	ý $d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz}$
	3	2	-1	3d$_{-1}$	|
	3	2	-2	3d$_{-2}$	þ

Table 3-1 summarizes the allowed combinations of quantum numbers for an electron in a hydrogen atom for the first few values of n; the corresponding name (symbol) is given for each orbital. Notice that there are n^2 orbitals for each value of n, all of which belong to the same quantum level and have the same energy. There are n - 1 values of l for each value of n and there are ($2l + 1$) values of m for each value of l. Notice also that for every increase in the value of n, orbitals of the same l value (same directional dependence) as found for the preceding value of n are repeated. In addition, a new value of l and a new shape are introduced. Thus there is a repetition in the shapes of the density distributions along with an increase in their number. We can see evidence of a periodicity in these functions (a periodic re-occurrence of a given density distribution) which we might hope to relate to the

periodicity observed in the chemical and physical properties of the elements. We might store this idea in the back of our minds until later.

We can summarize what we have found so far regarding the energy and distribution of an electron in a hydrogen atom thus:

i. The energy increases as n increases, and depends only on n, the principal quantum number.
ii. The average value of the distance between the electron and the nucleus increases as n increases.
iii. The number of nodes in the probability distribution increases as n increases.
iv. The electron density becomes concentrated along certain lines (or in planes) as l is increased.

Some words of caution about energies and angular momentum should be added. In passing from the domain of classical mechanics to that of quantum mechanics we retain as many of the familiar words as possible. Examples are kinetic and potential energies, momentum, and angular momentum. We must, however, be on guard when we use these familiar concepts in the atomic domain. All have an altered meaning. Let us make this clear by considering these concepts for the hydrogen atom.

Perhaps the most surprising point about the quantum mechanical expression for the energy is that it does not involve r, the distance between the nucleus and the electron. If the system were a classical one, then we would expect to be able to write the total energy E_n as:

$$E_n = KE = PE = \frac{1}{2}mv^2 - \frac{e^2}{r} \tag{3.4.2}$$

Both the KE and PE would be functions of r, i.e., both would change in value as r was changed (corresponding to the motion of the electron). Furthermore, the sum of the PE and KE must always yield the same value of E_n which is to remain constant.
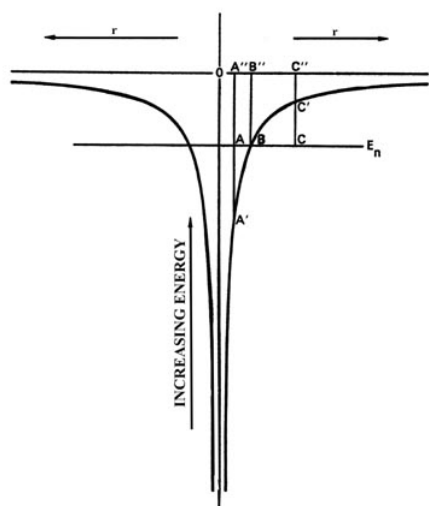

Figure3-16. The potential energy diagram for an H atom with one of the allowed energy values superimposed on it.

Fig 3-16 is the potential energy diagram for the hydrogen atom and we have superimposed on it one of the possible energy levels for the atom, E_n. Consider a classical value for r at the point A". Classically, when the electron is at the point A", its PE is given by the value of the PE curve at A'. The KE is thus equal to the length of the line A - A' in energy units. Thus the sum of $PE + KE$ adds up to E_n.

When the electron is at the point B", its PE would equal E_n and its KE would be zero. The electron would be motionless. Classically, for this value of E_n the electron could not increase its value of r beyond the point represented by B". If it did, it would be inside the "potential wall." For example, consider the point C". At this value of r, the PE is given by the value at C' which is **now greater** than E_n and hence the KE must be equal to the length of the line C - C'. But the KE must now be **negative** in sign so that the sum of PE and KE will still add up to E_n. What does a negative KE mean? It doesn't mean anything as it never occurs in a classical system. Nor does it occur in a quantum mechanical system. It is true that quantum mechanics does predict a finite probability for the electron being inside the potential curve and indeed for all values of r out to infinity. However, the quantum mechanical expression for E_n does not allow us to determine the instantaneous values for the PE and KE. Instead, we can determine only their average values. Thus quantum mechanics does not give Equation 3.4.2 but instead states only that the **average** potential and kinetic energies may be known:

$$E_n = \langle PE \rangle = \langle KE \rangle \tag{3.4.3}$$

The bracket denotes the fact that the energy quantity has been averaged over the complete motion (all values of r) of the electron.

Why can r not appear in the quantum mechanical expression for E_n, and why can we obtain only average values for the *KE* and *PE*? When the electron is in a given energy level its energy is precisely known; it is E_n. The uncertainty in the value of the momentum of the electron is thus at a minimum. Under these conditions we have seen that our knowledge of the position of the electron is very uncertain and for an electron in a given energy level we can say no more about its position than that it is bound to the atom. Thus if the energy is to remain fixed and known with certainty, we cannot, because of the uncertainty principle, refer to (or measure) the electron as being at some particular distance r from the nucleus with some instantaneous values for its *PE* and *KE*. Instead, we may have knowledge of these quantities only when they are averaged over all possible positions of the electron. This discussion again illustrates the pitfalls (e.g., a negative kinetic energy) which arise when a classical picture of an electron as a particle with a definite instantaneous position is taken literally.

It is important to point out that the classical expressions which we write for the dependence of the potential energy on distance, -e^2/r for the hydrogen atom for example, are the expressions employed in the quantum mechanical calculation. However, only the average value of the *PE* may be calculated and this is done by calculating the value of -e^2/r at every point in space, taking into account the fraction of the total electronic charge at each point in space. The amount of charge at a given point in three-dimensional space is, of course, determined by the electron density distribution. Thus the value of $\overline{PE}$ for the ground state of the hydrogen atom is the electrostatic energy of interaction between a nucleus of charge $+1e$ with the surrounding spherical distribution of negative charge.

> ⚓ Tunneling
>
> The penetration of a potential wall by the electron, into regions of negative kinetic energy, is known as "tunnelling." Classically a particle must have sufficient energy to surmount a potential barrier. In quantum mechanics, an electron may tunnel into the barrier (or through it, if it is of finite width). Tunnelling will not occur unless the barrier is of **finite height.** In the example of the H atom, the potential well is infinitely deep, but the energy of the electron is such that it is only a distance E_n from the top of the well. In the example of the electron moving on a line we assumed the potential well to be infinitely deep regardless of the energy of the electron. In this case y_n and hence P_n must equal zero at the ends of the line and no tunnelling is possible as the potential wall is infinitely high.

We can say more about the $\overline{PE}$ and $\overline{KE}$ for an electron in an atom. Not only are these values constant for a given value of $\(n\)$, but also for any value of $\(n\)$,

$$\overline{KE} = \frac{1}{2}\overline{PE} = -E_n$$

Thus the $\overline{KE}$ is always positive and equal to minus one half of the $\overline{PE}$. Since the total energy E_n is negative when the electron is bound to the atom, we can interpret the stability of atoms as being due to the decrease in the $\overline{PE}$ when the electron is attracted by the nucleus.

The question now arises as to why the electron doesn't "fall all the way" and sit right on the nucleus. When $r = 0$, the $\overline{PE}$ would be equal to minus infinity, and the $\overline{KE}$, which is positive and thus destabilizing, would be zero. Classically this would certainly be the situation of lowest energy and thus the most stable one. The reason for the electron not collapsing onto the nucleus is a quantum mechanical one. If the electron was bound directly to the nucleus with no kinetic energy, its position and momentum would be known with certainty. This would violate Heisenberg's uncertainty principle. The uncertainty principle always operates through the kinetic energy causing it to become large and positive as the electron is confined to a smaller region of space. (Recall that in the example of an electron moving on a line, the $\overline{KE}$ increased as the length of the line decreased.) The smaller the region to which the electron is confined, the smaller is the uncertainty in its position. There must be a corresponding increase in the uncertainty of its momentum. This is brought about by the increase in the kinetic energy which increases the magnitude of the momentum and thus the uncertainty in its value. In other words the bound electron must always possess kinetic energy as a consequence of quantum mechanics.

The $\overline{KE}$ and $\overline{PE}$ have opposite dependences on $\overline{r}$. The $\overline{PE}$ decreases (becomes more negative) as $\overline{r}$ decreases but the $\overline{KE}$ increases (making the atom less stable) as $\overline{r}$ decreases. A compromise is reached to make the energy as negative as possible (the atom as

stable as possible) and the compromise always occurs when $\overline{KE} = -\frac{1}{2}\overline{PE}$. A further decrease in $\bar{r}$ would decrease the $\overline{PE}$ but only at the expense of a ***larger increase*** in the $\overline{KE}$. The reverse is true for an increase in $\bar{r}$. Thus the reason the electron doesn't fall onto the nucleus may be summed up by stating that "the electron obeys quantum mechanics, and not classical mechanics."

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