DISCUSSION ON THE BEHAVIOR OF AN ELECTRON ENCLOSED IN A SPHERE

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ABSTRACT

The quantized energy values of an electron enclosed in a spherical box are calculated by solving Schrödinger's wave equation. The energy levels are very close together if the sphere is of ordinary dimensions. But as the radius of the sphere decreases toward atomic dimensions, the value of every energy level increases and the spread between the levels also increases.

The purpose of the present note is to discuss the behavior of an electron enclosed in a sphere according to non-relativistic quantum mechanics.

We consider an electron of mass m confined in a sphere of radius r_0 by a force at the boundary. The potential V is zero within the sphere, but at the boundary it becomes infinite. We choose a spherical coordinate system with the origin at the center of the sphere. The potential energy is then

$$V=0,\ r<r_0;\ V=\infty,\ \text{for } r=r_0.$$

For the region inside the sphere the Schrödinger equation for the system is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+k^2\psi=0, \quad (1)$$

where $k^2=8\pi^2 mE/h^2$ and E is the energy of the electron. It is apparent that the variables are separable. To separate the variables in equation (1), we make the substitution

$$\psi(r,\theta,\varphi)=R(r)\,Y(\theta,\varphi).$$

obtaining

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+k^2r^2=-\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)-\frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\cdot \quad (2)$$

By the usual argument, both sides of this equation must be equal to a constant, which we call α. We then have the two equations

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}+\alpha Y=0, \quad (3)$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left\{k^2-\frac{\alpha}{r^2}\right\}R=0. \quad (4)$$

Equation (3) is quite familiar in the problem of hydrogen atom. The allowed solutions are the surface harmonics $Y=Y_{l,\ m}(\theta,\varphi)$, where $\alpha=l(l+1)$, with l and m integers, and $l\geqq|m|$. Introducing the required value $\alpha=l(l+1)$ into (4), expanding the first term, we have

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\left\{k^2-\frac{l(l+1)}{r^2}\right\}R=0. \quad (5)$$

By making the substitutions

$$R(r)=\varrho^{-\frac{1}{2}}F(\varrho),\quad \varrho=kr,$$

equation (5) is reduced to

$$\frac{d^2F}{d\varrho^2}+\frac{1}{\varrho}\frac{dF}{d\varrho}+\left\{1-\frac{(l+\frac{1}{2})^2}{\varrho^2}\right\}F=0. \quad (6)$$

This is a Bessel's equation. Its solution is the Bessel function $J_{l+\frac{1}{2}}(\varrho)$ of order $(l+\frac{1}{2})$. Hence we have

$$R(r)=C(kr)^{-\frac{1}{2}}J_{l+\frac{1}{2}}(kr), \quad (7)$$

where C is a normalizing factor.

In order that the electron is constrained to move within the sphere, we must have the boundary condition that $R(r)=0$, and hence $J_{l+\frac{1}{2}}(kr)=0$, at $r=r_0$, since the potential rises to infinity at the wall of the sphere, the probability of the electron being at the wall will be zero. For any integer l, there will be an infinite set of roots of $J_{l+\frac{1}{2}}(kr_0)$, which we shall label $\varrho_{n,l}$, $n=1,2,3,\cdots,\infty$. The permitted k's are therefore

$$k_{n,l}=\frac{\varrho_{n,l}}{r_0},\ (l,n=1,2,3,\cdots,\infty), \tag{8}$$

and hence the permitted energy is given by

$$E_{n,l}=\frac{h^2\varrho_{n,l}^2}{8\pi^2 m r_0^2}\cdot \tag{9}$$

Inserting the values for a_0, the radius of the first Bohr orbit, and E_0, the energy value of the normal H-atom, taken positively, in equation (9), it is found that

$$E_{n,l}=\left(\frac{a_0\varrho_{n,l}}{r_0}\right)^2 E_0,\ \left(a_0=\frac{h^2}{4\pi^2 m e^2},\ E_0=\frac{e^2}{2a_0}\right). \tag{10}$$

We can determine the roots of $J_{l+\frac{1}{2}}(kr_0)$ numerically. Some roots of it have been determined and tabulated in Table I. For large roots, they can be calculated from the following formula:[1]

$$\varrho_{n,l}=a-\frac{b-1}{8a}-\frac{4(b-1)(7b-31)}{3(8a)^3}-\frac{32(b-1)(83b^2-982b+3779)}{15(8a)^5}+\cdots, \tag{11}$$

where $a=\left(n+\frac{l}{2}\right)$ and $b=(2l+1)^2$.

For the lowest state of the electron associated with $n=1$ and $l=0$, the energy is given by

$$E_{1,0}=\left(\frac{\pi a_0}{r_0}\right)^2 E_0. \tag{12}$$

1. Cf. G. N. Watson. Theory of Bessel Function. (1922). P. 506.

TABLE I

The Roots $\varrho_{n,l}$ of the Bessel Function $J_{l+\frac{1}{2}}(\varrho)$.

n \ l	0	1	2	3	4	5
1	3.142	4.494	5.775	6.99	8.20	9.39
2	6.283	7.725	9.095	10.42	11.71	12.97
3	9.425	10.90	12.33	13.70	15.04	16.37
4	12.57	14.07	15.52	16.87	18.30	19.65
5	15.71	17.23	18.69	20.08	21.52	22.91
6	18.85	20.38	21.85	23.31	24.72	26.13
7	21.99	23.52	25.01	26.48	27.91	29.34
8	25.14	26.67	28.16	29.65	31.09	32.53
9	28.28	29.82	31.32	32.81	34.26	35.71
10	31.42	32.96	34.46	36.05	37.43	38.88

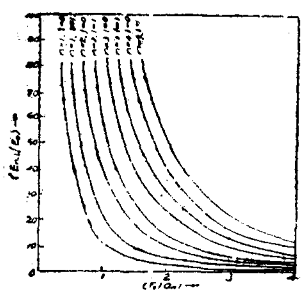

Fig. 1. The continuous curves represent $E'_{n,l}$ against r_0/a_0

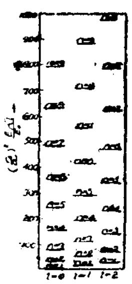

Fig. 2. Energy levels

Since the roots $\varrho_{n,l}$ in equation (10) are discrete numbers, the energy values of the electron will form a discrete spectrum. Hence the effect of enclosing the free electron is to quantize its energy. It is evident from a consideration of equation (10) or from an observation of Fig. 1, that the energy levels are very close together if the radius r_0 is of ordinary dimensions. But as r_0 decreases toward atomic dimensions, the value of every energy level increases and the spread between levels also increases.

It is interesting to point out from equation (12) that if the radius of the sphere is π times the radius of the first Bohr orbit, then the energy value of the lowest state of the electron in sphere will be exactly equal to the lowest energy value of the electron in H-atom in numerical value. But there is the difference that the energy values for the electron in the sphere are positive and that for the electron in H-atom are negative.

Fig. 2 gives the distribution of energy levels for an electron enclosed in a sphere of fixed radius r_0. It shows that the spreads between the higher energy levels are wider than that for lower levels. But for electron in the H-atom the energy levels are very close together at higher energy values. The contrary distributions of energy levels in the two cases are due to the facts that in the first case the radius of the sphere is fixed, the increasing of the kinetic energy of the electron is to increase the enclosing pressure of the sphere and hence to increase the degree of the discrete nature of energy; but in the second case, the increasing of kinetic energy of the electron is to permit electron to move in a more weak field region at a farther distance from the nucleus, and hence to decrease the degree of discrete nature of energy.

Now we consider the radial wave function expressed in equation (7). For any integers l and n, it may be written in the form

$$R_{n,l}(r) = C_{n,l}(k_{n,l}r)^{-\frac{1}{2}} J_{l+\frac{1}{2}}(k_{n,l}r), \tag{13}$$

or, since $k_{n,l} = \varrho_{n,l}/r_0$, in the form

$$R_{n,l}(r) = C_{n,l}(\varrho_{n,l}\sigma)^{-\frac{1}{2}} J_{l+\frac{1}{2}}(\varrho_{n,l}\sigma), \tag{14}$$

where

$$\sigma = r/r_0 .$$

The normalizing factor $C_{n,l}$ in equation (13) and (14) can be determined from the normalization condition

$$\int_0^{r_0} [R(r)]^2 r^2 \, d r = 1.$$

Using the formula[2]

$$\int_0^1 x \, [J_n(a x)]^2 \, d x = \frac{1}{2} [J_{n+1}(a)]^2, \tag{15}$$

where a is the root of $J_n(x)$,
we find

$$C_{n,l} = \frac{\sqrt{2\varrho_{n,l}}}{r_0^{\frac{3}{2}} J_{l+\frac{3}{2}}(\varrho_{n,l})} . \tag{16}$$

2. Cf. Whittaker and Watson, Modern Analysis, (1935), P. 381.

The complete solution of equation (1) is

$$\psi_{n,l,m}(r,\theta,\varphi)=R_{n,l}(r)\,Y_{l,m}(\theta,\varphi), \tag{17}$$

where

$$Y_{l,m}(\theta,\varphi)=\left\{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right\}^{\frac{1}{2}}P_l^m(\cos\theta)\,e^{im\varphi}, \tag{18}$$

and

$$R_{n,l}(r)=\frac{\sqrt{2\varrho_{n,l}}}{r_0^{\frac{3}{2}}J_{l+\frac{3}{2}}(\varrho_{n,l})}(\varrho_{n,l}\sigma)^{-\frac{1}{2}}J_{l+\frac{1}{2}}(\varrho_{n,l}\sigma),\quad \sigma=r/r_0, \tag{19}$$

are the normalized surface harmonic and radial functions respectively.

The angular part of the wave function (17) is identical with that of H-atom. It is quite familiar and hence need not be discussed further here. Certain of the normalized radial wave functions $R_{n,l}$ are given in Table II. The radial wave function $R_{n,l}$ vanishes n times in the interval $0<r\leq r_0$.

Each wave function of the electron is specified by the three quantum numbers n, l and m. From equation (10) it is seen that the energy of the electron depends only on l and n but does not on m, so that all the wave functions for any given values of n and l, and all the possible values of m have all the same energy values. It is well known in the discussion of H-atom that for any given value of l, m may have the values $-l$, $-(l-1), \cdots, -2, -1, 0, 1, 2, \cdots, (l-1)$, and l. Thus for a given value of l, the degree of degeneracy is $2l+1$.

TABLE II[3]

Normalized Radial Wave Functions $R_{n,l}$ For Electron Enclosed in a Sphere of Radius r_0

$$\sigma=r/r_0$$

$$l=0,\quad R_{n,0}=\frac{2}{r_0^{\frac{3}{2}}J_{\frac{3}{2}}(\varrho_{n,0})\sqrt{\pi\varrho_{n,0}}}\,\frac{1}{\sigma}\sin(\varrho_{n,0}\sigma)$$

$$n=1,2,3,\cdots,\infty.$$

3. Cf. Whittaker and Watson, Modern Analysis, P. 365.

$$l=1, \quad R_{n,1}=\frac{2}{r_0^{\frac{3}{2}} J_{\frac{5}{2}}(\varrho_{n,1}) \sqrt{\pi \varrho_{n,1}}} \frac{1}{\sigma}\left\{\frac{\sin(\varrho_{n,1}\sigma)}{(\varrho_{n,1}\sigma)}-\cos(\varrho_{n,1}\sigma)\right\}$$

$n=1,2,3,\cdots,\infty.$

$$l=2, \quad R_{n,2}=\frac{2}{r_0^{\frac{3}{2}} J_{\frac{7}{2}}(\varrho_{n,2}) \sqrt{\pi \varrho_{n,2}}} \frac{1}{\sigma}\left\{\left[\frac{3}{(\varrho_{n,2}\sigma)^2}-1\right]\sin(\varrho_{n,2}\sigma) - \frac{3}{(\varrho_{n,2}\sigma)}\cos(\varrho_{n,2}\sigma)\right\}$$

$n=1,2,3,\cdots,\infty.$

$$l=3, \quad R_{n,3}=\frac{2}{r_0^{\frac{3}{2}} J_{\frac{9}{2}}(\varrho_{n,3}) \sqrt{\pi \varrho_{n,3}}} \frac{1}{\sigma}\left\{\left[\frac{15}{(\varrho_{n,3}\sigma)^3}-\frac{6}{(\varrho_{n,3}\sigma)}\right]\sin(\varrho_{n,3}\sigma) - \left[\frac{15}{(\varrho_{n,3}\sigma)^2}-1\right]\cos(\varrho_{n,3}\sigma)\right\}.$$

$n=1,2,3,\cdots,\infty.$

$$l=4, \quad R_{n,4}=\frac{2}{r_0^{\frac{3}{2}} J_{\frac{11}{2}}(\varrho_{n,4}) \sqrt{\pi \varrho_{n,4}}} \frac{1}{\sigma}\left\{\left[\frac{105}{(\varrho_{n,4}\sigma)^4}-\frac{45}{(\varrho_{n,4}\sigma)^2}+1\right]\sin(\varrho_{n,4}\sigma) - \left[\frac{105}{(\varrho_{n,4}\sigma)^3}-\frac{10}{(\varrho_{n,4}\sigma)}\right]\cos(\varrho_{n,4}\sigma)\right\}.$$

$n=1,2,3,\cdots,\infty.$

$$l=5, \quad R_{n,5}=\frac{2}{r_0^{\frac{3}{2}} J_{\frac{13}{2}}(\varrho_{n,5}) \sqrt{\pi \varrho_{n,5}}} \frac{1}{\sigma}\left\{\left[\frac{945}{(\varrho_{n,5}\sigma)^5}-\frac{420}{(\varrho_{n,5}\sigma)^3} + \frac{15}{(\varrho_{n,5}\sigma)}\right]\sin(\varrho_{n,5}\sigma) - \left[\frac{945}{(\varrho_{n,5}\sigma)^4} - \frac{105}{(\varrho_{n,5}\sigma)^2}+1\right]\cos(\varrho_{n,5}\sigma)\right\}.$$

$n=1,2,3,\cdots,\infty.$

The probability of finding the electron at a distance between r and $r+dr$ from the nucleus, with its angular coodinates having values between θ and $\theta+d\theta$, φ and $\varphi+d\varphi$, is

$$\psi^*_{nlm}\psi_{nlm}\,d\tau=[R_{nl}(r)]^2[Y_{l,\pm m}(\theta,\varphi)]^2 r^2\sin\theta\,dr\,d\theta\,d\varphi. \tag{20}$$

To determine the probability that the electron be between the distances r and $r+dr$, regardless of angle, we must integrate over θ and φ. Since the spherical harmonics are normalized to unity, this integration gives us simply

$$P(r)\,dr=[R_{n,l}(r)]^2 r^2\,dr. \tag{21}$$

The average distance of the electron from the center of the sphere is given by the integral

$$\bar{r}_{n,l}=\int \psi^*_{nlm}\,\psi_{nlm}\,d\tau=\int_0^\infty [R_{n,l}(r)]^2 r^3\,dr. \tag{22}$$

For any state with zero angular momentum ($l=0$), the average value of r is calculated to be

$$\bar{r}_{n,0}=\frac{r_0}{n[\pi J_{\frac{3}{2}}(n\pi)]^2}. \tag{23}$$

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中 文 提 要

電子在球形範圍內運動情況之討論

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本文以波力學討論電子在球形範圍內運動時之情況。由計算得知。如球形大時，則電子之能層甚爲密接，如球形之半徑縮小至原子大小之程度，則其每一能層之值增大而能層與能層間之間隔亦增大。