THE MOMENTUM DISTRIBUTION IN HYDROGEN-LIKE ATOMS

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(Received April 5, 1929)

Abstract

The probability density that an electron have certain momenta is given by the square of the absolute magnitude of a *momentum eigenfunction* $\Upsilon_{nlm}(P, \Theta, \Phi)$, in which P, Θ, and Φ are spatial polar coordinates of the total momentum vector referred to the same axes as the coordinates r, θ, and ϕ of the electron. The following general expression for these functions for a hydrogen-like atom is obtained:

$$\Upsilon_{nlm}(P,\Theta,\Phi)=\left\{\frac{1}{(2\pi)^{1/2}}e^{\pm im\Phi}\right\}\left\{\left(\frac{(2l+1)(l-m)!}{2(l+m)!}\right)^{1/2}P_l^m(\cos\Theta)\right\}$$
$$\left\{\frac{\pi 2^{2l+4}l!}{(\gamma h)^{3/2}}\left(\frac{n(n-l-1)!}{(n+l)!}\right)^{1/2}\frac{\zeta^l}{(\zeta^2+1)^{l+2}}C_{n-l-1}^{l+1}\left(\frac{\zeta^2-1}{\zeta^2+1}\right)\right\}$$

in which $\zeta=(2\pi/\gamma h)P$, with $\gamma=(4\pi^2\mu e^2 Z/nh^2)=(Z/na_0)$. The probability $\Xi_{nl}(P)dP$ that the electron have a total momentum lying within the limits P and $P+dP$ is also evaluated, and it is shown that the root mean square of the total momentum is equal to the momentum of the electron in a circular Bohr orbit with the same total quantum number.

The eigenfunctions $\Psi_{nlm}(r, \theta, \phi)$ which are obtained by solving the Schrödinger wave equation for a hydrogen atom are functions of the spatial polar coordinates r, θ, and ϕ of the electron relative to the nucleus. The interpretation which has been given them is that the square of the absolute magnitude of an eigenfunction represents the probability per unit volume that on experimental investigation a hydrogen atom in the state characterized by this eigenfunction will be found to have the configuration described by r, θ, and ϕ. Thus $|\Psi_{nlm}(r, \theta, \phi)|^2$ can be called the distribution function for the electron; the probability that the electron will be found in the elementary volume dV in the region given by certain values of the coordinates relative to the nucleus is $|\Psi_{nlm}(r, \theta, \phi)|^2 dV$.

In Dirac's transformation theory the eigenfunction $\Psi_{nlm}(r, \theta, \phi)$ is the transformation function from the cartesian coordinates of the electron to the quantum numbers, and may be represented by the symbol $(x, y, z/n, l, m)$. The transformation function from the momenta p_x, p_y, p_z to the quantum numbers n, l, m, which may similarly be given the symbol $(p_x, p_y, p_z/n, l, m)$, can also be used to give a distribution function, in this case in momentum space. If this transformation function is known for a given set of values of n, l, and m, then the probability that the electron have a total momentum lying in a given range can be easily calculated. The usefulness of this transformation function is indicated by one recent application.[1]

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[1] J. W. M. DuMond, Phys. Rev. **33**, 643 (1929).

In this paper we are communicating a general expression for the transformation function from momenta to quantum numbers for a hydrogen-like atom. Weyl[2] has discussed another method of obtaining the momentum eigenfunctions as solutions of an integral equation, without, however, carrying out its application to the case of a hydrogen-like atom.[3]

2. The transformation function $(p_x, p_y, p_z/n, l, m)$ can be obtained from that $(x, y, z/n, l, m)$ by the equation[4]

$$(p_x, p_y, p_z/n, l, m) = h^{-3/2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(2\pi i/h)(xp_x+yp_y+zp_z)}(x,y,z/n,l,m)dxdydz. \quad (1)$$

Let us substitute for x, y, z the spherical polar coordinates given by the equations

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\} \quad (2)$$

and write for p_x, p_y, p_z

$$\left.\begin{aligned} p_x &= P\sin\Theta\cos\Phi \\ p_y &= P\sin\Theta\sin\Phi \\ p_z &= P\cos\Theta. \end{aligned}\right\} \quad (3)$$

P then is equal in magnitude to the total momentum vector, and the angles Θ and Φ give the orientation of the momentum vector relative to the cartesian axes of coordinates. The function $(p_x, p_y, p_z/n,l,m)$ then becomes a function of P, Θ, and Φ, which we may call the *momentum eigenfunction* and give the symbol $\Upsilon_{nlm}(P, \Theta, \Phi)$. Eq. (1) is transformed into

$$\Upsilon_{nlm}(P,\Theta,\Phi) = h^{-3/2}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} e^{-(2\pi i/h)[\sin\theta\sin\Theta\cos(\Phi-\phi)+\cos\theta\cos\Theta]rP}\cdot\Psi_{nlm}(r,\theta,\phi)r^2\sin\theta drd\theta d\phi \quad (4)$$

with

$$\Psi_{nlm}(r,\theta,\phi) = \left\{\frac{1}{(2\pi)^{1/2}}e^{\pm im\phi}\right\}\left\{\left(\frac{(2l+1)(l-m)!}{2(l+m)!}\right)^{1/2}P_l^m(\cos\theta)\right\}$$
$$\left\{\frac{(2\gamma)^{l+1}}{(n+l)!}\left(\frac{\gamma(n-l-1)!}{n(n+l)!}\right)^{1/2}e^{-\gamma r}r^l L_{n+l}^{2l+1}(2\gamma r)\right\}, \quad (5)$$

in which $\gamma = 4\pi^2\mu e^2Z/nh^2 = Z/na_0$.

[2] H. Weyl, Zeits. f. Physik. **46**, 1 (1928).

[3] On page 43 of his paper Weyl states that the momentum eigenfunctions are given in his dissertation, Math. Ann., **66**, 307–309, 317–324 (1908). We have, on attempting to verify this, found nothing in his dissertation that we could interpret as constituting a solution of this problem.

[4] P. Jordan, Zeits. f. Physik **40**, 809 (1927).

The symbols are the customary ones. P_l^m (cos θ) is Ferrers' associated Legendre function of degree l and order m; and L_{n+l}^{2l+1} $(2\gamma r)$ is an associated Laguerre polynomial, defined by the identity[5]

$$\sum_{\beta=0}^{\infty} \frac{L_{\alpha+\beta}^{\alpha}(\xi)}{(\alpha+\beta)!} u^\beta \equiv (-)^\alpha \frac{e^{-\xi u/(1-u)}}{(1-u)^{\alpha+1}} \cdot \qquad (6)$$

3. Let

$$I_1 = \int_0^{2\pi} e^{\pm im\phi + ib\cos(\Phi-\phi)} d\phi, \quad \text{with} \quad b = -(2\pi/h) rP \sin\theta \sin\Theta, \qquad (7)$$

and

$$I_2 = \int_0^{\pi} e^{ic\cos\theta\cos\Theta} I_1 P_l^m(\cos\theta) \sin\theta d\theta, \quad \text{with} \quad c = -(2\pi/h) rP\ ; \qquad (8)$$

then

$$\Upsilon_{nlm}(P,\Theta,\Phi) = -\frac{h^{-3/2}}{(2\pi)^{1/2}} \left(\frac{(2l+1)(l-m)!}{2(l+m)!}\right)^{1/2} \frac{(2\gamma)^{l+1}}{(n+l)!} \left(\frac{\gamma(n-l-1)!}{n(n+l)!}\right)^{1/2}$$

$$\int_0^\infty I_2 e^{-\gamma r} r^{l+2} L_{n+l}^{2l+1}(2\gamma r) dr. \qquad (9)$$

The values of the first and second integrals are known. The transformation

$$\phi - \Phi = \omega \qquad (10)$$

converts I_1 into Sommerfeld's integral,[6] which gives a Bessel function of order $\pm m$:

$$I_1 = e^{\pm im\Phi} \int_0^{2\pi} e^{\pm im\omega + ib\cos\omega} d\omega = 2\pi i^{\pm m} J_{\pm m}(b) e^{\pm im\Phi}.$$

The relation

$$J_{-m}(b) = i^{2m} J_m(b)$$

permits this to be transformed into

$$I_1 = 2\pi i^m J_m(b) e^{\pm im\Phi}. \qquad (4)$$

We shall need the relation between the associated Legendre functions and the Gegenbauer C_k^ν functions,[7] which may be defined by the generating function[8]

[5] E. Schrödinger, Ann. d. Physik **80,** 484 (1926).

[6] A. Sommerfeld, Math. Ann. **47,** 335 (1896); see also Jahnke and Emde, "Funktionentafeln," p. 169.

[7] L. Gegenbauer, Wiener Sitzungsber. **70,** 6 (1874).

[8] An explicit expression for the C's is given in Whittaker and Watson, "Modern Analysis," p. 329.

$$Q_\nu \equiv (1-2ut+u^2)^{-\nu} \equiv \sum_{k=0}^{\infty} C_k^\nu(t) u^k. \tag{12}$$

When $\nu=\frac{1}{2}$ these functions reduce to the Legendre polynomials. On putting $\nu=\frac{1}{2}$ and differentiating m times with respect to t we obtain the relation

$$P_l^m(t) = 1\cdot 3\cdot 5 \cdots (2m-1)(1-t^2)^{m/2} C_{l-m}^{m+1/2}(t). \tag{13}$$

In 1877 Gegenbauer[9] evaluated the following definite integral

$$\int_0^\pi e^{iz\cos\theta\cos\psi} J_{\nu-1/2}(z\sin\theta\sin\psi) C_r^\nu(\cos\theta)\sin^{\nu+1/2}\theta d\theta$$
$$= \left(\frac{2\pi}{z}\right)^{1/2} i^r \sin^{\nu-1/2}\psi C_r^\nu(\cos\psi) J_{\nu+r}(z). \tag{14}$$

If we put $\nu=m+\frac{1}{2}$, $z=c$, $x=\Theta$, and $r=l-m$, this becomes, with the help of Eq. (13),

$$\int_0^\pi e^{ic\cos\theta\cos\Theta} J_m(c\sin\theta\sin\Theta) P_l^m(\cos\theta)\sin\theta a\vartheta$$
$$= \left(\frac{2\pi}{c}\right)^{1/2} i^{l-m} P_l^m(\cos\Theta) J_{l+1/2}(c). \tag{15}$$

On substitution for I_1 of its value given in Eq. (11) it is seen that I_2 is, except for a constant factor, equal to this integral, so that we may write

$$I_2 = 2\pi i^l e^{\pm im\Phi} P_l^m(\cos\Theta)\left(\frac{2\pi}{c}\right)^{1/2} J_{l+1/2}(c)$$
$$= -2\pi(-i)^l e^{\pm im\Phi} P_l^m(\cos\Theta)\left(\frac{h}{P}\right)^{1/2} r^{-1/2} J_{l+1/2}\left(\frac{2\pi rP}{h}\right). \tag{16}$$

Referring to Eqs. (9) and (16) we see that Υ_{nlm} $(P,\ \Theta,\ \Phi)$ contains the integral

$$\int_0^\infty e^{-\gamma r} r^{l+3/2} J_{l+1/2}\left(\frac{2\pi rP}{h}\right) L_{n+l}^{2l+1}(2\gamma r) dr, \tag{17}$$

which on substitution of

$$\xi = 2\gamma r \quad \text{and} \quad \zeta = 2\pi P/\gamma h \tag{18}$$

leads to

$$(2\gamma)^{-(l+5/2)} \int_0^\infty e^{-\xi/2} \xi^{l+3/2} J_{l+1/2}(\tfrac{1}{2}\zeta\xi) L_{n+l}^{2l+1}(\xi) d\xi. \tag{19}$$

[9] L. Gegenbauer, Wiener Sitzungsber. **75,** 221 (1877). The integral is also given in Watson, "Theory of Bessel Functions," p. 379.

4. Let

$$I_{nl}(\zeta) \equiv \int_0^\infty e^{-\xi/2}\xi^{l+3/2}J_{l+1/2}(\tfrac{1}{2}\zeta\xi)L_{n+l}^{2l+1}(\xi)d\xi. \tag{20}$$

In order to evaluate this integral we consider a function U defined by the following identity:

$$U \equiv U_l(\zeta, u) \equiv \sum_{n=l+1}^{\infty} \frac{I_{nl}(\zeta)}{(n+l)!}u^{n-l-1}. \tag{21}$$

It turns out that we can evaluate this function by using the generating function for the associated Laguerre polynomials (Eq. (6)), and thus obtain $I_{nl}(\zeta)$ as coefficients of the expansion of $U_l(\zeta, u)$ as a power series in u.

$$\begin{aligned} U &= \int_0^\infty e^{-\xi/2}\xi^{l+3/2}J_{l+1/2}(\tfrac{1}{2}\zeta\xi)\sum_{n=l+1}^{\infty}\frac{L_{n+l}^{2l+1}(\xi)}{(n+l)!}u^{n-l-1}d\xi, \text{ by 20,} \\ &= \int_0^\infty e^{-\xi/2}\xi^{l+3/2}J_{l+1/2}(\tfrac{1}{2}\zeta\xi)\frac{(-)^{2l+1}e^{-\xi u/(1-u)}}{(1-u)^{2l+2}}d\xi, \text{ by 6,} \\ &= (1-u)^{-2l-2}\int_0^\infty e^{-\xi(1+u)/2(1-u)}J_{l+1/2}(\tfrac{1}{2}\zeta\xi)\xi^{l+3/2}d\xi. \end{aligned} \tag{22}$$

Now the last integral is a special case of a more general integral which has been evaluated by Hankel[10] and Gegenbauer,[11] who obtained the result

$$\int_0^\infty e^{-a\xi}J_\nu(z\xi)\xi^{\mu-1}d\xi = \frac{(z/2a)^\nu\Gamma(\mu+\nu)}{a^\mu\Gamma(\nu+1)}F\left(\frac{\mu+\nu}{2}, \frac{\mu+\nu+1}{2}; \nu+1; -\frac{z^2}{a^2}\right). \tag{23}$$

Putting $z=\frac{1}{2}\zeta$, $\nu=l+\frac{1}{2}$, $\mu=l+5/2$, and $a=(1+u)/2(1-u)$, this gives

$$U = \frac{4\zeta^{l+1/2}(2l+2)!}{\Gamma(l+3/2)}\,\frac{(1-u)}{(1+u)^{2l+3}}F\left(l+\frac{3}{2}, l+2; l+\frac{3}{2}; -\frac{\zeta^2(1-u)^2}{(1+u)^2}\right).$$

The hypergeometric series F is a degenerate one, equal to

$$\left\{1+\frac{\zeta^2(1-u)^2}{(1+u)^2}\right\}^{-l-2},$$

so that U can be put in the form

$$U = A\frac{1-u^2}{(1-2xu+u^2)^{l+2}}, \tag{24}$$

in which

$$A = \frac{4(2l+2)!\zeta^{l+1/2}}{\Gamma(l+3/2)(\zeta^2+1)^{l+2}}, \quad \text{and} \quad x = \frac{\zeta^2-1}{\zeta^2+1}.$$

[10] H. Hankel, Math. Ann. **8,** 467 (1875).

[11] L. Gegenbauer, Wiener Sitzungsber. **72,** 343 (1876); see also Watson, "Theory of Bessel Functions," p. 384.

5. We now return to Eq. (12). Operating on both sides with $u^{-\nu+1}(\partial/\partial u)u^{\nu}$ we obtain

$$\frac{\nu(1-u^2)}{(1-2ut+u^2)^{\nu+1}} \equiv \sum_{k=0}^{\infty}(\nu+k)C_k^{\nu}(t)u^k. \tag{25}$$

Putting $\nu=l+1$ and $t=x$, we may rewrite Eq. (24) as

$$U=\frac{A}{l+1}\sum_{k=0}^{\infty}(l+k+1)C_k^{l+1}(x)u^k=\frac{A}{l+1}\sum_{n=l+1}^{\infty}nC_{n-l-1}^{l+1}(x)u^{n-l-1}. \tag{26}$$

Comparing Eqs. (26) and (21), we see that

$$I_{nl}(\zeta)=\frac{An(n+l)!}{l+1}C_{n-l-1}^{l+1}\left(\frac{\zeta^2-1}{\zeta^2+1}\right). \tag{27}$$

6. Thus the momentum eigenfunctions are found to be given by the expression

$$\Upsilon_{nlm}(P,\Theta,\Phi)=\left\{\frac{1}{(2\pi)^{1/2}}e^{\pm im\Phi}\right\}\left\{\left(\frac{(2l+1)(l-m)!}{2(l+m)!}\right)^{1/2}P_l^m(\cos\Theta)\right\}$$
$$\left\{-\frac{(-i)^l\pi 2^{2l+4}l!}{(\gamma h)^{3/2}}\left(\frac{n(n-l-1)!}{(n+l)!}\right)^{1/2}\frac{\zeta^l}{(\zeta^2+1)^{l+2}}C_{n-l-1}^{l+1}\left(\frac{\zeta^2-1}{\zeta^2+1}\right)\right\}, \tag{28}$$

in which $\zeta=2\pi P/\gamma h=nP/Zp_0=P/p_n$. p_0, which is equal to $2\pi\mu e^2/h$, is the momentum of the electron in a circular Bohr orbit with $n=1$ and $Z=1$, corresponding to a hydrogen atom in the normal state, and $p_n=Zp_0/n$ is the momentum of the electron in a circular Bohr orbit characterized by the total quantum number n and the nuclear charge Ze. The factor $-(-i)^l$ in Υ may be omitted, since its absolute value is unity.

Some of the Gegenbauer C functions which enter in this expression are given below. Others can be obtained from these by the application of the recursion formula

$$C_r^{\nu}(x)=\frac{2\nu}{r}\left\{xC_{r-1}^{\nu+1}(x)-C_{r-2}^{\nu+1}(x)\right\}.$$

	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
$n=1$	$C_0^1(x)=1$				
$n=2$	$C_1^1(x)=2x$	$C_0^2(x)=1$			
$n=3$	$C_2^1(x)=4x^2-1$	$C_1^2(x)=4x$	$C_0^3(x)=1$		
$n=4$	$C_3^1(x)=8x^3-4x$	$C_2^2(x)=12x^2-2$	$C_1^3(x)=6x$	$C_0^4(x)=1$	
$n=5$	$C_4^1(x)=16x^4-12x^2+1$	$C_3^2(x)=32x^3-12x$	$C_2^3(x)=24x^2-3$	$C_1^4(x)=8x$	$C_0^5(x)=1$
$n=6$	$C_5^1(x)=32x^5-32x^3+6x$	$C_4^2(x)=80x^4-48x^2+3$	$C_3^3(x)=80x^3-24x$	$C_2^4(x)=40x^2-4$	$C_1^5(x)=10x$

Gegenbauer[12] has shown that his $C_r^{\nu}(x)$ functions with a given upper index when multiplied by the factor $(1-x^2)^{\nu/2-1/4}$ form an orthogonal set, for they satisfy the equations

$$\int_{-1}^{+1}(1-x^2)^{\nu-1/2}C_r^{\nu}(x)C_{r'}^{\nu}(x)dx=\frac{2^{2\nu-1}\Gamma(r+2\nu)}{(r+\nu)\Gamma(r+1)}\left[\frac{\Gamma(\nu+1/2)}{\Gamma(2\nu)}\right]^2\delta_{rr'}. \tag{29}$$

[12] L. Gegenbauer, Wiener Sitzungsber. **70,** 6 (1874), Eq. (16).

The functions of P which occur in the momentum eigenfunctions with a given value of l also form an orthogonal set; but they are not the Gegenbauer orthogonal functions. Since the volume element involves P^2dP, the orthogonal functions are in this case

$$\frac{\pi 2^{2l+4}l!}{(\gamma h)^{3/2}}\left(\frac{n(n-l-1)!}{(n+l)!}\right)^{1/2}\frac{\zeta^l}{(\zeta^2+1)^{l+2}}C_{n-l-1}^{l+1}\left(\frac{\zeta^2-1}{\zeta^2+1}\right)P,$$

in which $\zeta=ZP/np_0$ is different for different functions of the set, since it involves the quantum number n. That these functions are normalized can be shown with the aid of Gegenbauer's integral (29). The normalization integral

$$\left[\frac{\pi 2^{2l+4}l!}{(\gamma h)^{3/2}}\left(\frac{n(n-l-1)!}{(n+l)!}\right)^{1/2}\right]^2\int_0^\infty\left[\frac{\zeta^l}{(\zeta^2+1)^{l+2}}C_{n-l-1}^{l+1}\left(\frac{\zeta^2-1}{\zeta^2+1}\right)P\right]^2dP \qquad (30)$$

becomes on substituting x for $(\zeta^2-1)/(\zeta^2+1)$, and omitting the factor before the integral sign,

$$\int_{-1}^{+1}(1-x)(1-x^2)^{l+1/2}[C_{n-l-1}^{l+1}(x)]^2dx=\int_{-1}^{+1}(1-x^2)^{l+1/2}[C_{n-l-1}^{l+1}(x)]^2dx$$
$$-\int_{-1}^{+1}x(1-x^2)^{l+1/2}[C_{n-l-1}^{l+1}(x)]^2dx.$$

On substituting for $x\,C_{n-l-1}^{l+1}(x)$ its value given by the recursion formula

$$x\,C_r^\nu(x)=\frac{1}{2(r+\nu)}[(r+1)C_{r+1}^\nu(x)+(r+2\nu-1)C_{r-1}^\nu(x)]$$

the second integral is converted into two, each of which vanishes by Eq. (29). The value of the first integral as given by Eq. (29) is just that required to make (30) equal to unity.

7. The probability that the electron have a momentum lying in the range between P and $P+dP$ can be written as $\Xi_{nl}(P)dP$, in which $\Xi_{nl}(P)$, the momentum distribution function, is given by

$$\Xi_{nl}(P)=\int_0^\pi\int_0^{2\pi}|\Upsilon_{nlm}(P,\Theta,\Phi)|^2P^2\sin\Theta d\Theta d\Phi. \qquad (31)$$

On carrying out the integration this is found to become

$$\Xi_{nl}(P)=\frac{a_0}{Zh}\frac{2^{4l+6}n^2(l!)^2(n-l-1)!}{(n+l)!}\frac{\zeta^{2l+2}}{(\zeta^2+1)^{2l+4}}\left[C_{n-l-1}^{l+1}\left(\frac{\zeta^2-1}{\zeta^2+1}\right)\right]^2. \qquad (32)$$

8. It is of interest to evaluate the diagonal elements of the P^2 matrix, which are equal to the average values of the square of the momentum in the various quantum states:

$$\overline{P_n^2}=\int_0^\infty P^2\Xi_{nl}(P)dP. \qquad (33)$$

On substituting for P^2 its value $p_n^2(1+x)/(1-x)$, it is found that this integral, aside from the constant factor p_n^2, differs from the normalization integral only in having the factor $(1+x)$ in place of $(1-x)$; and since the integral involving x vanishes, and the normalization integral is equal to unity, we obtain

$$\overline{P_n^2} = p_n^2 = \left(\frac{2\pi\mu e^2 Z}{nh}\right)^2. \tag{34}$$

Now p^2_n is just the average value of the square of the momentum of the electron in a Bohr orbit with total quantum number n; so that the root mean square momentum for a hydrogen-like atom is the same in the quantum mechanics as in the old quantum theory, in each case depending only on the principal quantum number n.