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Eigenfunctions of the Hydrogen Atom in Momentum Space

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The Schrödinger problem of the hydrogen atom is solved using toroidal coordinates in momentum space. The wavefunctions are expressible in terms of Jacobi polynomials and ordinary trigonometric functions.

INTRODUCTION

IT is well known that the degeneracy of the energy levels of the hydrogen atom in Schrödinger's theory allows the wave equation to be separated in both spherical polar coordinates and paraboloidal coordinates. The wave equation in momentum space is similarly degenerate and therefore must allow separability in coordinates other than the usual spherical polars. It is shown below that the other system in momentum space is the toroidal system (ξ,η,φ), and that the wavefunction has the structure

$$\Psi(\xi,\eta,\varphi) = \text{const}\times F_{klm}(\operatorname{sech}^2\eta)\times\tanh^m\eta\times\operatorname{sech}^k\eta\times\begin{Bmatrix}\cos k\xi\\ \sin k\xi\end{Bmatrix}\times\begin{Bmatrix}\cos m\varphi\\ \sin m\varphi\end{Bmatrix}, \quad (1)$$

where the polynomial F_{klm}, is a Jacobi polynomial of order l. Further, just as the paraboloidal wavefunctions in position space can be written as hybrids (that is, linear combinations) of the spherical polar wavefunctions, so too, in momentum space, the toroidal wavefunctions can be written as combinations of the usual spherical wavefunctions.

The literature on the momentum eigenfunctions of the hydrogen atom dates back to the work of Podolanski and Pauling in 1929.[1] These authors carry out the elegant, but complicated, Fourier transform of the position space eigenfunctions which had been found by Schrödinger three years earlier. Their results showed that

$$\psi(p,\theta,\varphi)\sim\left(\frac{p_0^2}{p_0^2+p^2}\right)^2\times\left(\frac{2pp_0}{p^2+p_0^2}\right)^l\times C_{n-l-1}^{l+1}\left(\frac{p^2-p_0^2}{p^2+p_0^2}\right)\times Y_l^m(\theta,\varphi), \quad (2)$$

where $p_0=1/n$ reciprocal of principal quantum number (p_0 being measured in atomic units), and $C_N^\nu(x)$ is a Gegenbauer polynomial of order N, defined as the coefficient of h^N in the expansion of $(1-2hx+x^2)^{-\nu}$ is powers of h. The first factor on the right in Eq. (2) can be absorbed in a new wavefunction defined as

$$\Phi(p,\theta,\varphi)=\frac{(2pp_0)^l}{(p^2+p_0^2)^l}\times C_{n-l-1}^{l+1}\left(\frac{p^2-p_0^2}{p^2+p_0^2}\right)\times P_l^m(\cos\theta)\times\begin{Bmatrix}\cos m\varphi\\ \sin m\varphi\end{Bmatrix}. \quad (3)$$

The next advance occurred in 1935 when the Russian theoretician V. Fock recognized that the function defined by Eq. (3) is simply the stereographic projection of a hyperspherical harmonic onto the three-dimensional $p_xp_yp_z$-hyperplane.[2] In other words, by writing the quantity $2pp_0/(p_0^2+p^2)$ as $\sin\alpha$, and the quantity $(p^2-p_0^2)/(p^2+p_0^2)$ as $\cos\alpha$, (where $\cos\alpha$ is the polar angle on a hypersphere of radius p_0), one recognizes Φ to be a spherical harmonic associated with a three-dimensional spherical surface embedded in four-dimensional Euclidean momentum space. The wavefunction is simply:

$$\Phi(\alpha,\theta,\varphi)\sim(\sin\alpha)^l C_{n-l-1}^{l+1}(\cos\alpha)(\sin\theta)^m\times C_{l-m}^{m+\frac{1}{2}}(\cos\theta)\begin{Bmatrix}\cos m\varphi\\ \sin m\varphi\end{Bmatrix}. \quad (4)$$

In the above expression, we have written P_l^m in terms of a Gegenbauer polynomial. The restrictions on l and m $l\leq n-1$ $m\leq l$ are obvious.

It is clear that the momentum eigenfunctions possess the same degeneracy that characterizes the hyperspherical harmonics.

After reading Fock's work, I reasoned as follows. If one were to reorient the polar axis

[1] B. Podolanski and L. Pauling, Phys. Rev. **34**, 109 (1929).

[2] V. Fock, Z. Physik **98**, 145 (1935).

of the hypersphere, a pure spherical harmonic in this new frame can be written as a linear combination of the harmonics which relate to the original polar axis. Indeed, on a two-dimensional spherical surface, the addition theorem of spherical harmonics is simply a mathematical expression of this property. The stereographic projection of those nodal lines in the new system would be circles whose centers are displaced away from the origin. (See Fig. 1 below.) Such circles are encountered in plane bipolar coordinates,[3] and are designed by $\xi=\text{const}$ in the notation of Margenau and Murphy.

If one were to imagine a similar sort of projection applied to the hyperspherical harmonics, one sees that certain linear combinations of such harmonics possess nodal surfaces which, in stereographic projection, yield the nodal surfaces characteristic of toroidal coordinates. The latter are generated from plane bipolar coordinates by rotating the orthogonal family of circles $\xi=\text{const}$ and $\eta=\text{const}$ about the p_z axis.

The hyperspherical functions satisfy a simple eigenvalue equation (which is usually solved by separation into functions of α, θ, φ). After the transformations implied by a stereographic projection have been carried out, the new equation should be separable in toroidal coordinates in the $p_x-p_y-p_z$ space. This coordinate system is therefore analogous to the paraboloidal system of position space.

SOLUTION OF THE WAVE EQUATION

The hyperspherical harmonics satisfy the differential equation

$$\nabla^2\Phi=\lambda\Phi,$$

where

$$\nabla^2=(\sin^2\alpha)^{-1}\frac{\partial}{\partial\alpha}\left(\sin^2\alpha\frac{\partial}{\partial\alpha}\right)+(\sin^2\alpha\sin\theta)^{-1}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+(\sin^2\alpha\sin\theta)^{-1}\frac{\partial^2}{\partial\varphi^2}. \quad (5)$$

The line element ds^2 on the hypersphere is

$$ds^2=p_0^2(d\alpha^2+\sin^2\alpha d\theta^2+\sin^2\alpha\sin^2\theta d\varphi^2). \quad (6)$$

The transformation to toroidal coordinates in the $p_xp_yp_z$ hyperplane is carried out by first performing the stereographic projection of (α,θ,φ) into $(p_xp_yp_z)$ and then introducing toroidal coordinates in the usual manner.[4]

By direct calculation, we obtain the line element in the toroidal system in the hyperplane as

$$ds^2=p_0^2[\operatorname{sech}^2\eta(d\xi^2+d\eta^2)+\tanh^2\eta d\varphi^2]. \quad (7)$$

The Laplacian

$$\nabla^2=(1/\sqrt{g})(\partial/\partial x^i)[\sqrt{g}\,g^{ij}(\partial/\partial x^j)],$$

where

$$g_{ij}=\begin{bmatrix}\operatorname{sech}^2\eta & 0 & 0\\ 0 & \operatorname{sech}^2\eta & 0\\ 0 & 0 & \tanh^2\eta\end{bmatrix}.$$

Hence in the toroidal system the equation $\nabla^2\Phi=-\lambda\Phi$ reads as follows:

$$\left\{\cosh^2\eta\frac{\partial^2}{\partial\xi^2}+\frac{\cosh^3\eta}{\sinh\eta}\frac{\partial}{\partial\eta}\left(\tanh\eta\frac{\partial}{\partial\eta}\right)+\frac{\cosh^2\eta}{\sinh^2\eta}\frac{\partial^2}{\partial\varphi^2}\right\}\Phi(\xi,\eta,\varphi)=-\lambda\Phi(\xi,\eta,\varphi). \quad (8)$$

Assume a solution of the form

$$\Phi(\xi,\eta,\varphi)=F(\xi)G(\eta)\begin{Bmatrix}\cos m\varphi\\ \sin m\varphi\end{Bmatrix}.$$

We obtain readily

$$\frac{1}{F}\frac{d^2F}{d\xi^2}+\frac{1}{G}\frac{1}{\tanh\eta}\frac{d}{d\eta}\left(\tanh\eta\frac{dG}{d\eta}\right)-\frac{m^2}{\sinh^2\eta}=-\frac{\lambda}{\cosh^2\eta}. \quad (9)$$

It follows that

$$F(\xi)=\begin{Bmatrix}\cos k\xi\\ \sin k\xi\end{Bmatrix}$$

and $G(\eta)$ satisfies the equation

$$\frac{1}{\tanh\eta}\frac{d}{d\eta}\left(\tanh\eta\frac{dG}{d\eta}\right)-k^2G-\frac{m^2}{\sinh^2\eta}G=-\frac{\lambda G}{\cosh^2\eta}, \quad (10)$$

[3] H. Margenau and G. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand, Princeton, N. J. 1956), 2nd ed., Vol. I, pp. 187–191.

[4] Reference 3, p. 190.

where $G(\eta)$ depends on a quantum number l (related to λ) as well as on k and m. (This l is not the same as the l used in spherical polar coordinates.)

With the change of variable $z=\operatorname{sech}^2\eta$, the equation reads:

$$\frac{d}{dz}\left((1-z)z\times\frac{dG}{dz}\right)-\frac{k^2G}{4z}-\frac{m^2G}{4(1-z)}=-\frac{\lambda}{4}G. \quad (11)$$

This equation has singular points at $z=0$, 1. Setting $G_{klm}(z)=z^{k/2}(1-z)^{m/2}\times g(z)$, we get

$$(z^2-z)(d^2g/dz^2)+[(k+m+2)z-(k+1)](dg/dz)$$
$$-\tfrac{1}{4}[\lambda-(k+m)(k+m+2)]g=0.$$

This is of the form of the hypergeometric equation

$$(z^2-z)F''+[(1+p)z-q]F'-l(p+l)F=0 \quad (12)$$

with $p=1+k+m$, $q=1+k$, $k=0$, 1, $2\cdots$, and $l(p+l)=\frac{1}{4}[\lambda-(k+m)(k+m+2)]$.

Thus,

$$\lambda=4l(1+k+l+m)+(k+m)(k+m+2). \quad (13)$$

The solutions of Eq. (12) are Jacobi polynomials, provided l is integer.[5] Finally then, we have

$$G(\eta)=J_l(1+k+m,\ 1+k;\ \operatorname{sech}^2\eta)$$
$$\times\tanh^m\eta\times\operatorname{sech}^k\eta, \quad (14)$$

and therefore we have as the momentum-space eigenfunction in toroidal coordinates

$$\psi_{klm}(\xi,\eta,\varphi)\sim J_l(1+k+m,\ 1+k;\ \operatorname{sech}^2\eta)$$
$$\times\tanh^m\eta\cdot\operatorname{sech}^k\eta\times\begin{Bmatrix}\cos k\xi\\ \sin k\xi\end{Bmatrix}\times\begin{Bmatrix}\cos m\varphi\\ \sin m\varphi\end{Bmatrix}$$
$$\times\tfrac{1}{4}\left(1-\frac{\cos\xi}{\cosh\eta}\right)^2. \quad (15)$$

The last factor corresponds to the factor of

$$(p_0^2/p_0^2+p^2)^2,$$

which hitherto had been suppressed.

DISCUSSION OF THE WAVEFUNCTIONS

The nodal surfaces in this wavefunction can be classified as follows: there are m nodal planes corresponding to $\varphi=\text{const}\ 0\leq\varphi\leq2\pi$, k nodal planes corresponding to $\xi=\text{const}\ 0\leq\xi\leq\pi$, $2l$ nodal toroids corresponding to $\eta=\text{const}\ 0\leq\eta\leq\infty$ (the nodal toroids count twice). See Fig. 2.

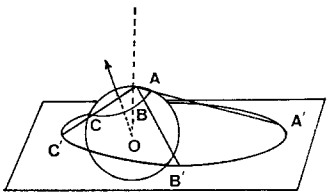

FIG. 1. Stereographic projection of nodal lines on a spherical surface.

The total number of nodal surfaces is $m+k+2l$, hence the principal quantum number n must be $n=1+m+k+2l$.

Let us consider some typical excited states of hydrogen in the momentum representation in toroidal coordinates. The first excited state $n=2$, must have the quantum number $l=0$, but either $k=1$ or $m=1$. The Jacobi polynomial $J_0(p,q;z)=1$ hence there are no toroidal nodal surfaces. The possible eigenstates are, omitting the ubiquitous factor of $\frac{1}{4}[1-(\cos\xi/\cosh\eta)]^2$

$$\Phi_{100}\sim\operatorname{sech}\eta\times\begin{cases}\cos\xi & 2s\\ \sin\xi & 2p_z\end{cases}$$

and

$$\Phi_{100}\sim\tanh\eta\times\begin{cases}\cos\varphi\\ \sin\varphi\end{cases}\quad 2p_x\quad 2p_y.$$

The correspondence with the states in spherical coordinates[6] is indicated at the right.

It is well known that application of an electric field to the $n=2$ state of hydrogen generates the hybrid states $2s\pm2p_z$ having paraboloidal nodal surfaces. A similar effect occurs in momentum space; the hybrid states are $\Phi_{100}\sim\operatorname{sech}\eta\times(\cos\xi\pm\sin\xi)$. Their nodal surfaces are the spheres $\xi=\pi/4$, $3\pi/4$ [see Fig. 3(a)]. Thus, in

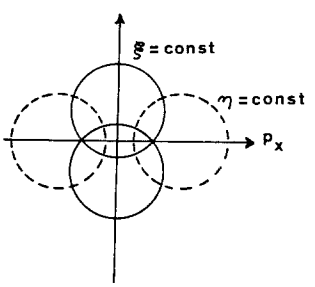

FIG. 2. Nodal surfaces in toroidal coordinates. The angle of rotation about the p_z axis is φ. The figure above is the $\varphi=0$ plane.

[5] Reference 3, p. 74.

[6] H. Bethe and E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms," *Handbuch der Physik*, S. Flugge, Ed. (Springer-Verlag, Berlin, 1957), Vol. XXXV, p. 125.

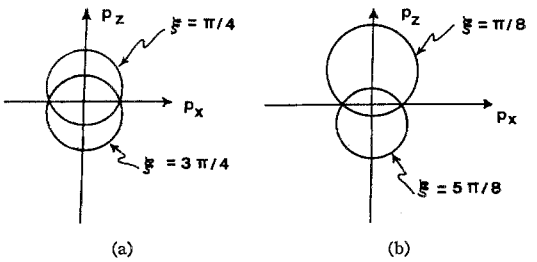

FIG. 3. (a) Nodal surfaces for $k=1$, $l=0$, $m=0$; (b) nodal surfaces for $k=2$, $l=0$, $m=0$.

momentum space, the effect of the applied field is to shift the charge distribution so that points of zero-change density lie on either of the two off-origin spheres indicated.

It is interesting to compare the situation with that which is produced by application of a magnetic field (along the z direction). In the latter case, it is the $\cos\varphi$, $\sin\varphi$ states which become hybridized, but with a phase difference in time of $\pi/2$. Thus, $\Phi_{100}\sim\tanh\eta\times(\cos\varphi\cos E_{\pm}t\pm\sin\varphi\times\sin E_{\pm}t)=\tanh\eta\times\cos(\pm\varphi+E_{\pm}t)$ i.e, in the customary complex notation $\Phi_{100}\sim\tanh\eta\times e^{\pm i\varphi}\times e^{iE\pm t}$. $E_{\pm}$ denotes the energy of the two Zeeman states $m=\pm1$, associated with the $n=2$ level.

Returning now to the discussion of the hydrogenic wavefunctions, we may consider the $n=3$ eigenfunction. Here the case $l=1$ is possible, the corresponding eigenfunction being: $\Phi_{010}\sim J_1(1,1;\operatorname{sech}^2\eta)\times1\times1=1-2\operatorname{sech}^2\eta$, the ξ and φ dependence disappears since $k=m=0$, in order that $n=1+k+m+2l$. There is a nodal toroid in this state designated as $\eta=\cosh^{-1}\sqrt{2}$, which counts as two nodal surfaces. The other eight eigenfunctions are easily seen to be

$$\Phi_{200}\sim\operatorname{sech}^2\eta\times\begin{cases}\cos2\xi\\ \sin2\xi\end{cases}\qquad k=2,\quad m=0,\quad l=0,$$

$$\Phi_{101}\sim\operatorname{sech}\eta\tanh\eta\times\begin{cases}\cos\xi\\ \sin\xi\end{cases}\times\begin{cases}\cos\varphi\\ \sin\varphi\end{cases}\quad k=1,\quad m=1,\quad l=0,$$

$$\Phi_{002}\sim\tanh^2\eta\begin{cases}\cos2\varphi\\ \sin2\varphi\end{cases}\qquad k=0,\quad m=2,\quad l=0.$$

The application of a uniform external electric field hybridizes the Φ_{200} states so as to produce states each having two nodal spheres. For example, the state $\Phi_{200}\sim\operatorname{sech}^2\eta(\cos2\xi-\sin2\xi)$ has nodal spheres designated as: $\xi=\pi/8$, $5\pi/8$, just as in position space when two nodal paraboloids are present in the hybrid state produced by the Stark effect. The position of these nodal spheres is shown in Fig. 3(b). The state $\Phi_{010}\sim1-2\operatorname{sech}^2\eta$ can be shown to be a hybrid of the $3s$ and $3d$ states, that is

$$\Phi_{010}\sim-\tfrac{1}{3}\left\{4\left(\frac{p^2-p_0^2}{p^2+p_0^2}\right)-1+\left(\frac{2pp_0}{p^2+p_0^2}\right)^2\times\frac{3\cos^2\theta-1}{2}\right\}.$$

The first two terms in brackets come from the $3s$ state; the third term, from the $3d$ state. This type of hybrid wavefunction would be produced by a quadrupole field originating at the nucleus. The quadrupole potential has the momentum-space representation

$$V'(\mathbf{p})=-\frac{4\pi}{3}Q\frac{3\cos^2\theta-1}{2}=-\frac{4\pi}{3}Q\frac{2\sin^2\xi-\sinh^2\eta}{\sin^2\xi+\sinh^2\eta}.$$

Because of the complexity of the last expression, it is not worthwhile to pursue this point further.

CONCLUSIONS

We have shown that the hydrogenic eigenfunctions are separable, in a certain sense, in both the toroidal as well as the more usual spherical polar coordinate system in momentum space. This is a result of the special Coulomb degeneracy present. It is not clear whether the toroidal system would be useful for calculation; at present these wavefunctions appear to have only pedagogical value.