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Hydrogen Atom and Non-Euclidean Geometry¹

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As is known, the hydrogen atom energy levels depend on the principal quantum number n only and are independent of the azimuthal quantum number l . One can say (by using the common but not very suitable term) that there is degeneracy (i.e., the multiplicity of the level) with respect to the azimuthal quantum number. On the other hand, there is a general rule according to which the multiplicity of the Schrödinger equation eigenvalues relates to the invariance of the equation under a definite group of transformations. So, for example, the invariance under a common rotation group (spherical symmetry) leads to the energy level independence on the magnetic quantum number m . Therefore, it should be expected that the energy level independence of the azimuthal quantum number is explained by the existence of a certain transformation group that is more general than the three-dimensional rotation group. Up to now, this group of transformations for the Schrödinger equation has not been found. In the present work, we shall show that this group is equivalent to the rotation group in the four-dimensional Euclidean space.

1. Let us write the Schrödinger equation for a hydrogen atom in the momentum representation. Since the Coulomb potential energy operator $-\frac{Ze^2}{r}$ in the momentum representation is the integral operator, the Schrödinger equation will be an integral equation of the form

$$\frac{1}{2m}\mathbf{p}^2\psi(\mathbf{p}) - \frac{Ze^2}{2\pi^2\hbar} \int \frac{\psi(\mathbf{p}') (d\mathbf{p}')}{|\mathbf{p} - \mathbf{p}'|^2} = E\psi(\mathbf{p}), \quad (1)$$

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where $(d\mathbf{p}') = dp'_x dp'_y dp'_z$ is an elementary volume in the momentum space. First we consider the discrete spectrum, for which the energy E is negative, and denote mean-square momentum as p_0 :

$$p_0 = \sqrt{-2mE}. \quad (2)$$

We shall treat components of momentum \mathbf{p} divided by p_0 as rectangular coordinates on the hyperplane which is stereographic a projection of a sphere in the four-dimensional Euclidean space. The rectangular coordinates of a certain point on the sphere will be

$$\begin{aligned} \xi &= \frac{2p_0 p_x}{p_0^2 + p^2} = \sin \alpha \sin \vartheta \cos \varphi, \\ \eta &= \frac{2p_0 p_y}{p_0^2 + p^2} = \sin \alpha \sin \vartheta \sin \varphi, \\ \zeta &= \frac{2p_0 p_z}{p_0^2 + p^2} = \sin \alpha \cos \vartheta, \\ \chi &= \frac{p_0^2 - p^2}{p_0^2 + p^2} = \cos \alpha, \end{aligned} \quad (3)$$

being

$$\xi^2 + \eta^2 + \zeta^2 + \chi^2 = 1. \quad (3^*)$$

The angles α, θ , and φ are spherical coordinates of a point on a hypersphere. At the same time, angles θ and φ are ordinary spherical coordinates characterizing the momentum direction. The surface element of a hypersphere is equal to

$$d\Omega = \sin^2 \alpha d\alpha \sin \vartheta d\vartheta d\varphi. \quad (4)$$

It is related to the volume element in the momentum space by

$$(d\mathbf{p}') = dp'_x dp'_y dp'_z = p^2 dp \sin \vartheta d\vartheta d\varphi = \frac{1}{8p_0^3} (p_0^2 + p^2)^3 d\Omega. \quad (5)$$

Let us denote for brevity

$$\lambda = \frac{Zme^2}{hp_0} = \frac{Zme^2}{h\sqrt{-2mE}} \quad (6)$$

and introduce instead of $\psi(\mathbf{p})$ the function

$$\Psi(\alpha, \vartheta, \varphi) = \frac{\pi}{\sqrt{8}} p_0^{-\frac{5}{2}} (p_0^2 + p^2)^2 \psi(\mathbf{p}). \quad (7)$$

Here the factor is chosen to fulfill the normalization condition²

$$\begin{aligned} \frac{1}{2\pi^2} \int |\Psi(\alpha, \vartheta, \varphi)|^2 d\Omega &= \int \frac{p^2 + p_0^2}{2p_0^2} |\psi(\mathbf{p})|^2 (d\mathbf{p}) = \\ &= \int |\psi(\mathbf{p})|^2 (d\mathbf{p}) = 1. \end{aligned} \quad (*)$$

In new notations, the Schrödinger equation (1) takes the form

$$\Psi(\alpha, \vartheta, \varphi) = \frac{\lambda}{2\pi^2} \int \frac{\Psi(\alpha', \vartheta', \varphi')}{4 \sin^2 \frac{\omega}{2}} d\Omega', \quad (8)$$

where $2 \sin \frac{\omega}{2}$ is the length of a chord and ω is the length of a great circle arc joining the points α, θ, φ and $\alpha', \theta', \varphi'$ on the four-dimensional sphere, so that

$$4 \sin^2 \frac{\omega}{2} = (\xi - \xi')^2 + (\eta - \eta')^2 + (\zeta - \zeta')^2 + (\chi - \chi')^2 \quad (9)$$

or

$$\cos \omega = \cos \alpha \cos \alpha' + \sin \alpha \sin \alpha' \cos \gamma, \quad (10)$$

$\cos \gamma$ being of common value

$$\cos \gamma = \cos \vartheta \cos \vartheta' + \sin \vartheta \sin \vartheta' \cos(\varphi - \varphi'). \quad (10^*)$$

Equation (8) is nothing else but an integral equation for spherical functions of the four-dimensional sphere. To prove this, we need to recall some basic notions of the four-dimensional potential theory. Let us put

$$x_1 = r\xi, \quad x_2 = r\eta, \quad x_3 = r\zeta, \quad x_4 = r\chi \quad (11)$$

and consider the Laplace equation

$$\frac{\partial^2 u}{\partial x_1^2} + \frac{\partial^2 u}{\partial x_2^2} + \frac{\partial^2 u}{\partial x_3^2} + \frac{\partial^2 u}{\partial x_4^2} = 0. \quad (12)$$

Let us introduce the function

$$G = \frac{1}{2R^2} + \frac{1}{2R_1^2}, \quad (13)$$

where R^2 and R_1^2 are

$$R^2 = r^2 + r'^2 - 2rr' \cos \omega; \quad R_1^2 = 1 - 2rr' \cos \omega + r^2 r'^2. \quad (14)$$

²Recall that the four-dimensional sphere surface area is equal to $2\pi^2$ so that, e.g., the function $\Psi = 1$ fits this condition. (V. Fock)

This function can be called the Green's function of the third kind because it satisfies the boundary condition on the sphere surface

$$\frac{\partial G}{\partial r'} + G = 0 \quad \text{at} \quad r' = 1. \quad (15)$$

By the Green theorem the function, which is harmonic inside the sphere, can be expressed through the boundary value of $u + \frac{\partial u}{\partial r}$ as

$$u(x_1, x_2, x_3, x_4) = \frac{1}{2\pi^2} \int_{r'=1} \left(u + \frac{\partial u}{\partial r'} \right) G d\Omega'. \quad (16)$$

Let u be a homogeneous harmonic polynomial of degree $n - 1$

$$u(x_1, x_2, x_3, x_4) = r^{n-1} \Psi_n(\alpha, \vartheta, \varphi) \quad (n = 1, 2, 3, \dots). \quad (17)$$

Then we shall have

$$\left(u + \frac{\partial u}{\partial r} \right)_{r=1} = nu = n\Psi_n(\alpha, \vartheta, \varphi). \quad (18)$$

Putting these expressions into (16) and using (13) and (14) for $r' = 1$, one gets

$$r^{n-1} \Psi_n(\alpha, \vartheta, \varphi) = \frac{n}{2\pi^2} \int \frac{\Psi_n(\alpha', \vartheta', \varphi')}{1 - 2r \cos \omega + r^2} d\Omega'. \quad (19)$$

This equation is valid also for $r = 1$ and in this case can be reduced to (8); the parameter λ is equal to integer n

$$\lambda = \frac{Zme^2}{h\sqrt{-2mE}} = n, \quad (n = 1, 2, 3, \dots), \quad (20)$$

and obviously is the principal quantum number.

Hence, we showed the solution of the Schrödinger equation to be the four-dimensional spherical function.³ So we found the Schrödinger equation transformation group as well. Obviously, this group is equivalent to the four-dimensional rotation group.

³Applications of four-dimensional spherical functions to the theory of a spherical top has been given by Hund [F. Hund, *Göttinger Nachr.*, M.-Phys. Kl., 1927, 465]. (V. Fock)

2. We will give the following explicit expression for the four-dimensional spherical function

$$\Psi_{nlm}(\alpha, \vartheta, \varphi) = \Pi_l(n, \alpha) Y_{lm}(\vartheta, \varphi), \quad (21)$$

where l and m have the usual meaning of azimuthal and magnetic quantum numbers and $Y_{lm}(\theta, \varphi)$ is a standard spherical function normalized by the condition

$$\frac{1}{4\pi} \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} |\Psi_{lm}(\vartheta, \varphi)|^2 d\varphi = 1. \quad (22)$$

If we set

$$M_l^2 = n^2(n^2 - 1) \dots (n^2 - l^2), \quad (23)$$

then the function normalized according to

$$\frac{2}{\pi} \int_0^\pi \Pi_l^2(n, \alpha) \sin^2 \alpha d\alpha = 1 \quad (24)$$

can be represented either in the integral form

$$\Pi_l(n, \alpha) = \frac{M_l}{\sin^{l+1} \alpha} \int_0^\alpha \cos n\beta \cdot \frac{(\cos \beta - \cos \alpha)^l}{l!} d\beta, \quad (25)$$

or as a derivative

$$\Pi_l(n, \alpha) = \frac{\sin^l \alpha}{M_l} \frac{d^{l+1} \cos n\alpha}{d \cos \alpha^{l+1}}. \quad (25^*)$$

At $l = 0$, both formulae give

$$\Pi_0(n, \alpha) = \frac{\sin n\alpha}{\sin \alpha}. \quad (26)$$

Note that these formulae give the determination of the function $\Pi_l(n, \alpha)$ also valid for complex n (continuous spectrum). The function Π_l satisfies the following relations:

$$-\frac{d\Pi_l}{d\alpha} + l \cot \alpha \Pi_l = \sqrt{n^2 - (l+1)^2} \Pi_{l+1}; \quad (27a)$$

$$\frac{d\Pi_l}{d\alpha} + (l+1) \cot \alpha \Pi_l = \sqrt{n^2 - 1} \Pi_{l-1}, \quad (27b)$$

where from a differential equation it follows⁴

$$\frac{d^2 \Pi_l}{d\alpha^2} + 2 \cot \alpha \frac{d \Pi_l}{d\alpha} - \frac{l(l+1)}{\sin^2 \alpha} \Pi_l + (n^2 - 1) \Pi_l = 0. \quad (28)$$

3. Let us turn now to the derivation of the addition theorem for four-dimensional spherical functions. Equation (19) is an identity relative to r . If we expand the integrand as a power series in r ,

$$\frac{1}{1 - 2r \cos \omega + r^2} = \sum_{k=1}^{\infty} r^{k-1} \frac{\sin k\omega}{\sin \omega}, \quad (29)$$

and compare the coefficients in the right- and left-hand sides of (19), we get

$$\frac{n}{2\pi^2} \int \Psi_n(\alpha', \vartheta', \varphi') \frac{\sin k\omega}{\sin \omega} d\Omega' = \delta_{kn} \Psi_n(\alpha, \vartheta, \varphi). \quad (30)$$

But the quantity $n \frac{\sin n\omega}{\sin \omega}$ as a function of α, θ, φ is a four-dimensional spherical function that can be expanded in series of functions $\Psi_{nlm}(\alpha', \theta', \varphi')$. The expansion coefficients are determined by relation (30) (at $k = n$). Thus, we arrive at the addition theorem

$$n \frac{\sin n\omega}{\sin \omega} = \sum_{l=0}^{n-1} \sum_{m=-l}^l \bar{\Psi}_{nlm}(\alpha, \vartheta, \varphi) \Psi_{nlm}(\alpha', \vartheta', \varphi'). \quad (31)$$

If we substitute here relation (21) and use the well-known addition theorem for three-dimensional spherical functions, then we can rewrite (31) in the form

$$n \frac{\sin n\omega}{\sin \omega} = \sum_{l=0}^{\infty} \Pi_l(n, \alpha) \Pi_l(n, \alpha') (2l+1) P_l(\cos \gamma), \quad (32)$$

where P_l is the Legendre polynomial, and $\cos \gamma$ is determined by (10*). We wrote the summation limits as 0 and ∞ . For integer n , series (32) is truncated at $l = n - 1$, but it is possible to prove that addition theorem (32) is also valid for the complex values of n .

⁴In his work on the wave equation for the Kepler problem, Hylleraas [E. Hylleraas, Zs. Phys. **74**, 216, 1932] derived a differential equation [see (9g) and (10b) of his paper], which can be easily reduced to that for the four-dimensional spherical functions in stereographic projection. [With the kind permission of E. Hylleraas, we correct here the following misprints in his works: in the last term of equation (9f) as well as of (9g) the magnitude E must have a factor 4]. (V. Fock)

4. We investigated integral equation (1) for the case of a discrete spectrum. For a continuous spectrum one needs to consider (instead of a four-dimensional sphere) a two-sheet hyperboloid in the four-dimensional pseudo-Euclidean space. One sheet of the hyperboloid corresponds to the momentum inside the interval $0 < p < \sqrt{2mE}$ and the other one corresponds to the interval $\sqrt{2mE} < p < \infty$. In this case, the Schrödinger equation can be written as a system of two integral equations connecting the values of the desirable functions on both sheets of the hyperboloid.

We can give the following geometrical interpretation of our results. In the momentum space in the case of a discrete spectrum, there is *the Riemann geometry* with the constant positive curvature and in the case of a continuous spectrum there is *the Lobachevskii geometry* with the constant negative curvature.

The geometrical interpretation of the Schrödinger equation for a continuous spectrum is less descriptive than that for the case of a discrete spectrum. Therefore, it is reasonable first to obtain the formulae for the point spectrum and only in the final result take the principal quantum number to be imaginary. This can be done because $\Pi_l(n, \alpha)$ are analytical functions of n and α , which for the complex values of n and α differ from those for a discrete spectrum by constant factors only.⁵

5. Now let us list briefly the problems to which the presented theory of hydrogen-like atoms can be applied.⁶ In many applications, e.g., in the theory of the Compton effect by bounded electrons [2, 3] as well as in the theory of inelastic electron collisions by atoms [4], in the mathematical sense the problem is reduced to the following. The projection norm [5] of the given function φ on the subspace of the Hilbert space, characterized by the principal quantum number n , needs to be found. In other words, one needs to find the sum

$$N = \int |P_n \varphi|^2 d\tau = \sum_{l,m} \left| \int \bar{\psi}_{nlm} \varphi d\tau \right|^2. \quad (33)$$

In calculation of this expression, the main difficulty is to sum over l , especially for the cases when the level belongs to the continuous spectrum (imaginary n) and the sum is of an infinite number of terms. Sometimes it is possible to reduce the sum to the integral by using the parabolic

⁵See [1] V.A. Fock, Basic quantum mechanics (Nachala kvantovoj mekhaniki), Leningrad, Kubuch, 1932, 162 (in Russian), eqs. (16) and (17); eq. (17) should be corrected, namely, factor $\sqrt{2}$ should be omitted. (V. Fock)

⁶We propose to treat these problems in a separate paper in more detail; it will be published in Phys. Zs. Sowjetunion. (V. Fock)

quantum numbers and make the summation in an explicit form, but corresponding manipulations turn out to be extremely complicated.

If, however, we use the group symmetry of the Schrödinger equation and the addition theorem (31) for its eigenfunctions, then the calculation is drastically simplified. The expression for the whole sum often appears to be simpler than that for its individual term.

Similar simplifications appear in the application of our theory to the calculation of the projection norm of a certain operator \mathbf{L} on the n -subspace, i.e., to the calculation of the double sum

$$N(L) = \sum_{lm} \sum_{l'm'} \left| \int \bar{\psi}_{nlm} L \psi_{nl'm'} d\tau \right|^2. \quad (34)$$

The expressions of the type (34) arise, e.g., in the calculation of the so-called atomic form-factors. Here the operator \mathbf{L} in the momentum representation is of the form

$$L = e^{-\mathbf{k} \frac{\partial}{\partial \mathbf{p}}}; \quad L\psi(\mathbf{p}) = \psi(\mathbf{p} - \mathbf{k}). \quad (35)$$

The calculation of (33) and (34) is based on its invariance to the choice of an orthogonal system of functions Ψ_{nlm} in the n -space. The orthogonal transformation of coordinates ξ, η, ζ, χ (four-dimensional rotation) corresponds to the introduction of a new orthogonal system of functions only and, therefore, does not change the values of sums (33) and (34). But this four-dimensional rotation can be chosen in such a manner so as to simplify integrals in these formulae or to put them to zero (except a definite number of them). Note that in (34) we can apply two different rotations of arguments of functions Ψ_{nlm} and $\Psi_{nl'm'}$ that correspond to two independent orthogonal substitutions of these functions.

6. The expression for projection $\mathbf{P}_n \varphi$ of function φ onto the n -subspace, entering (33), is of the form

$$\mathbf{P}_n \varphi = \sum_{lm} \psi_{nlm} \int \bar{\psi}_{nlm} \varphi d\tau. \quad (36)$$

In the momentum representation, a kernel of the projector \mathbf{P}_n is

$$\varrho_n(\mathbf{p}', \mathbf{p}) = \sum_{lm} \bar{\psi}_{nlm}(\mathbf{p}') \psi_{nlm}(\mathbf{p}). \quad (37)$$

By relation (7) we can express the function Ψ_{nlm} through the four-dimensional spherical functions. Since the mean-square momentum p_0

depends on the principal quantum number n , we shall denote it by p_n and rewrite (7) as

$$\Psi_{nlm}(\alpha, \vartheta, \varphi) = \frac{\pi}{\sqrt{8}} p_n^{-5/2} (p_n^2 + p^2)^2 \psi_{nlm}(\mathbf{p}). \quad (38)$$

By substituting this expression into (37) and using the addition theorem (31), we get

$$\varrho_n(\mathbf{p}', \mathbf{p}) = \frac{8p_n^5}{\pi^2(p^2 + p_n^2)^2(p'^2 + p_n^2)^2} \cdot n \frac{\sin n\omega}{\sin \omega}. \quad (39)$$

In the particular case of $\mathbf{p}' = \mathbf{p}$, a simple result follows:

$$\varrho_n(\mathbf{p}, \mathbf{p}) = \frac{8p_n^5}{\pi^2(p^2 + p_n^2)^4}. \quad (40)$$

The integral

$$4\pi \int \varrho_n(\mathbf{p}, \mathbf{p}) p^2 dp = n^2 \quad (41)$$

is equal to the dimension of a given subspace.

7. The success of Bohr's scheme for the Mendeleev periodic system and good applicability of the Rietz formula for energy levels show that the assumption that the atomic electrons are in the Coulomb field can give a satisfactory approximation.

Therefore, it is interesting to consider the following simplified variant of the Bohr model of an atom. The atomic electrons are subdivided on "large layers"; all electrons with the same principal quantum number n belong to the large n -layer. Electrons of the large n -layer are described by hydrogen-like functions with the effective nuclear charge Z_n .

Instead of Z_n , one can also introduce the mean-square momentum p_n connected with Z_n by

$$Z_n = np_n \frac{a}{h} \quad (a \text{ is "the hydrogen radius"}). \quad (42)$$

Under these assumptions, one can express the atomic energy as a function of the nuclear charge and parameters p_n and then determine these parameters from a variational principle. Here one needs to take into account the following. Although our wave functions of electrons belonging to the same large n -layer are orthogonal to each other, they are not orthogonal to the wave functions of other large layers. Therefore, in this

approximation we have to neglect the quantum exchange energy between electrons of different large layers and take into account the exchange energy between electrons of the same large layer only.

Application of this calculation method to atoms with two large layers gave very satisfactory results. For a Na^+ atom ($Z = 11$) we obtained the following values of the parameters p_1 and p_2 (in atomic units):

$$p_1 = 10.63; \quad p_2 = 3.45 \quad (Z = 11), \quad (43)$$

while for Al^{+++} ($Z = 14$) they are

$$p_1 = 12.62; \quad p_2 = 4.45. \quad (44)$$

A simple analytical expression follows for a screening potential in this method. If we substitute in it the above obtained numerical values of p_1 and p_2 , then its value practically does not differ from the self-consistent field obtained in Hartree's method by an incomparably complete way of numerical integration of the system of differential equations. For the sodium atom, our analytical result gives the value of the potential lying between the self-consistent potential obtained with and without quantum exchange [6].

Therefore, it is very probable that the accuracy of the proposed method for many-electron atoms will be pretty high at least for not very heavy atoms.

So far as this description corresponds to reality, the "mixed charge density" in the momentum space can be represented by a sum of expressions (39) for different large layers in an atom. The knowledge of the mixed charge density — as it has been stressed by Dirac [7] — allows one to give answers to all atomic problems, in particular on the light scattering by atoms and the inelastic electron scattering (atomic form-factors). For example, we present here an explicit expression of the atomic factor F_n for a large n -layer. In atomic units, we have

$$F_n = \int e^{i\mathbf{k}\mathbf{r}} \varrho_n(\mathbf{r}, \mathbf{r})(d\tau) = \int \varrho_n(\mathbf{p}, \mathbf{p} - \mathbf{k})(d\mathbf{k}). \quad (45)$$

If we substitute here instead of $\varrho_n(\mathbf{p}, \mathbf{p} - \mathbf{k})$ its expression that follows from (39), then the integral can be expressed in an explicit form. Putting for brevity

$$x = \frac{4p_n^2 - k^2}{4p_n^2 + k^2}, \quad (46)$$

we obtain

$$F_n(x) = \frac{1}{4n^2} T'_n(x) (1+x)^2 \{P'_n(x) + P'_{n-1}(x)\}, \quad (47)$$

where $T'_n(x)$ is a derivative of the Chebyshev polynomial with the minimum deviation from zero

$$T_n(x) = \cos(n \arccos x) \quad (48)$$

and P'_n is a derivative of the Legendre polynomial $P_n(x)$. Obviously, for $k = 0$ it will be $x = 1$ and $F_n(1) = n^2$.

The sum of expressions (40) over all large layers in an atom is proportional to the charge density in the momentum space. It can be compared with that obtained by the Fermi statistical model of an atom; the latter appears to be less accurate than ours. For Ne ($Z = 10$) and Na^+ ($Z = 11$) atoms; we obtained a good coincidence for large values of p , while for small p ($p < 2$ in atomic units) Fermi's result gives a too high value of the charge density.

Note in conclusion that though our method can be applied rigorously to atoms with complete large layers only, it can serve as a basis for calculation of an atom with uncompleted layers.

References

1. V.A. Fock, Basic quantum mechanics (Nachala kvantovoj mekhaniki), Leningrad, Kubuch, 1932 (in Russian).
2. G. Wentzel, Zs. Phys. **68**, 348, 1929.
3. F. Bloch, *Contribution to the Theory of the Compton Lines*, Phys. Rev. **46**, 674, 1934.
4. H. Bethe, *Zur Theory des Durchgangs schneller Korpuskularstrahlen durch Materie*, Ann. Phys. **5**, 325, 1930.
5. J. v. Neumann, Mathematische Grundlagen der Quantenmechanik, Berlin, Jul. Springer, 1932.
6. V. Fock and M. Petrashen, *On the Numerical Solution of the Generalized Equation of the Self-Consistent Field*, Phys. Zs. Sowjetunion **6**, 368, 1934. (See also [34-1] in this book. (Editors))
7. P.A.M. Dirac, *Note on Interpretation of the Density Matrix in the Many-Electron Problem*, Proc. Cambr. Phil. Soc. **28**, 240, 1931.

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