The SO(4) symmetry of the hydrogen atom

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Relevant example: Kepler published his laws of planetary motion in 1609 and 1619. Newton's *Principia* was published in 1687.

Likewise, the spectrum of hydrogen was known well before the advent of quantum mechanics.

This is the Balmer series, described by the school teacher Johann Balmer in 1885.

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This was generalized by Rydberg in 1888:

$$\frac{1}{\lambda} = R_{\mathsf{H}} \left(\frac{1}{m^2} - \frac{1}{n^2} \right), n > m,$$

where $R_{\mathsf{H}} \approx 1.097373 \cdot 10^7 \mathrm{m}^{-1}$ is Rydberg's constant for hydrogen.

The energy of a photon of wavelength λ is ch/λ, where c is the speed of light and h is Planck's constant. Thus Rydberg's formula can be interpreted as saying that the hydrogen atom has a discrete spectrum with energy levels

$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, \ldots$$

In its first incarnation, quantum mechanics relied heavily on classical mechanics. Bohr's atomic model was essentially a tiny solar system, with the quantization conditions tacked on as an afterthought.

By 'the Kepler problem', one usually means the problem of determining the orbit of a mass moving a gravitational potential:

$$m\frac{d^2\mathbf{r}}{dt^2} + \frac{GMm}{r^2}\hat{\mathbf{r}} = 0,$$

but as remarked earlier, that the solutions are ellipses was known long before the form of the attraction was known.

That the orbits are closed is quite remarkable, and in fact this happens only for the two potentials

$$V(\mathbf{r}) = -\frac{k}{r} \quad \text{and} \quad V(\mathbf{r}) = kr^2,$$

that is, for the Kepler problem and for the harmonic oscillator.

The rotational symmetry of the Kepler problem means that the angular momentum $\mathbf{L}$ is a conserved quantity. It has three components, and SO(3) is indeed three-dimensional. However, it was noted early on that the vector

$$\mathbf{p} \times \mathbf{L} - mk\hat{\mathbf{r}}$$

is also a constant of motion. It is called the Laplace-Runge-Lenz vector.

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The Berry Principle: The Arnol'd Principle is applicable to itself.

The LRL vector lies in the plane of the orbit and points in the direction of the perihelion. Its magnitude depends on the eccentricity of the orbit. Thus the perihelion does not precess and the ellipse keeps its shape.

The pioneers of quantum mechanics used classical analogies extensively. In 1924, Lenz attempted to carry over perturbation theory from the classical Kepler problem to quantum mechanics. In 1925-6, Pauli constructed a quantum mechanical LRL vector:

$$\mathbf{p} \times \mathbf{L} - mk\hat{\mathbf{r}} \rightsquigarrow \frac{1}{2}(\mathbf{p} \times \mathbf{L} + \mathbf{L} \times \mathbf{p}) - mk\frac{\mathbf{r}}{r},$$

and used it to derive the hydrogen spectrum. This was before Schrödinger's equation!

The Schrödinger equation for a particle in a spherically symmetric potential is

$$\left(-\frac{\hbar^2}{2m}\Delta + V(r)\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}).$$

Using polar coordinates, one shows that the discrete spectrum is indexed by two quantum numbers n, ℓ, satisfying $0 \leq \ell \leq n-1$ and with the multiplicity of the eigenvalue $E_{n,\ell}$ being $2\ell + 1$.

The Coulomb potential is formally identical to the gravitational potential:
$$V(r) = -\frac{k}{r},$$
and in this case, the energy turns out to be independent of ℓ. The multiplicity then becomes
$$1 + 3 + 5 + \cdots + (2n - 1) = n^2.$$

The SO(3)-symmetry of the Hamiltonian leads one to expect a certain degeneracy in the energy levels. However, it is insufficient to explain the full degeneracy, and so some larger group must be in play.

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Already from Pauli's investigation, the Lie algebra of the symmetry group can be identified as $\mathfrak{so}(4)$. But where does this 'accidental' symmetry come from? This is the subject of Vladimir Fock's 1935 article, 'On the theory of the hydrogen atom' ('Zur Theorie des Wasserstoffatoms').

Fock takes as his starting point the Schrödinger equation in momentum space:

$$\frac{p^2}{2m}\psi(\mathbf{p}) - \frac{Ze^2}{2\pi^2 h}\int\frac{\psi(\mathbf{p}')d\mathbf{p}'}{|p - p'|^2} = E\psi(\mathbf{p}).$$

Mathematically, this is the Fourier transform of the ordinary Schrödinger equation. Physically, it corresponds to using a basis of momentum eigenfunctions rather than position eigenfunctions.

Taking the Fourier transform turns multiplication into convolution. With hindsight, the integral kernel is the Jacobian of a stereographic projection from a sphere to a hyperplane in $\mathbb{R}^4$:

$$\frac{p^2}{2m}\psi(\mathbf{p}) - \frac{Ze^2}{2\pi^2 h}\int\frac{\psi(\mathbf{p}')d\mathbf{p}'}{|p-p'|^2} = E\psi(\mathbf{p}).$$

This suggests changing coordinates to a sphere in four-dimensional space.

Put $p_0 = \sqrt{-2mE}$ and think of $(p_x/p_0, p_y/p_0, p_z/p_0)$ as being coordinates for a three-dimensional hyperplane in $\mathbb{R}^4$. Project stereographically to the 3-sphere

$$S^3 = \{(\xi, \eta, \zeta, \chi) \in \mathbb{R}^4 : \xi^2 + \eta^2 + \zeta^2 + \chi^2 = 1\}.$$

Explicitly,

$$\begin{cases} \xi = \frac{2p_0 p_x}{p_0^2 + p^2} = \sin\alpha \sin\vartheta \cos\varphi \\ \eta = \frac{2p_0 p_y}{p_0^2 + p^2} = \sin\alpha \sin\vartheta \sin\varphi \\ \zeta = \frac{2p_0 p_z}{p_0^2 + p^2} = \sin\alpha \cos\vartheta \\ \chi = \frac{p_0^2 - p^2}{p_0^2 + p^2} = \cos\alpha, \end{cases}$$

where ϑ and φ are the usual spherical coordinates in momentum space and $\chi = 0$ corresponds to the three-dimensional hyperplane.

The surface element on the sphere is

$$d\Omega = \sin^2 \alpha \sin \vartheta d\alpha d\vartheta d\varphi$$

and the volume element is given by

$$p^2 \sin \vartheta dp d\vartheta d\varphi = \frac{1}{8p_0^3}(p_0^2 + p^2)^3 d\Omega.$$

For brevity, write

$$\lambda = \frac{Zme^2}{hp_0} = \frac{Zme^2}{h\sqrt{-2mE}}$$

and introduce the function

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

After these substitutions, the Schrödinger equation becomes

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

where

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

so that ω is the arclength between the two points (along a great circle). This is in fact the Laplace equation.

To see this, put $x_1 = r\xi$, $x_2 = r\eta$, $x_3 = r\zeta$, $x_4 = r\chi$ and consider the Laplace equation in its usual form:

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

A harmonic function u defined in the interior of the unit sphere $S^3 \subset \mathbb{R}^4$ is determined by its values on the sphere itself:

$$u(x_1, x_2, x_3, x_4) = \frac{1}{2\pi^2} \int_{S^3} \left(\frac{\partial u}{\partial r'} + u \right) G(r, r') d\Omega'.$$

Here

$$G(r, r') = \frac{1}{2(r^2 - 2rr'\cos\omega + r'^2)} - \frac{1}{2(1 - 2rr'\cos\omega + r^2 r'^2)}$$

is Green's function.

Spherical harmonics are restrictions to spheres of harmonic polynomials. Take u of degree $n - 1$:

$$u = r^{n-1}\Psi_n(\alpha, \vartheta, \varphi).$$

Then

$$\left(\frac{\partial u}{\partial r'} + u\right)\bigg|_{r'=1} = nu.$$

Thus, for Ψ_n a spherical harmonic,

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

and letting $r = 1$ and identifying $n = \lambda$ gives back the Schrödinger equation

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

Fock then goes on to derive addition theorems for the four-dimensional spherical harmonics, and applies his method to other atoms than hydrogen by introducing an effective nuclear charge.

Fock's calculation 'explains' the SO(4)-symmetry by showing that the Schrödinger equation in $\mathbb{R}^3$ is secretly the Laplace equation on $S^3 \subset \mathbb{R}^4$, on which SO(4) acts. Why *this* should be the case remains mysterious.

This discussion applies only to bound states (energy $E < 0$). Fock remarks that for scattering states, the 'geometry of Lobaschewski applies', that is, the momentum space has negative curvature.

The equation has the following symmetry groups in the various cases:

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- $E = 0$: the Euclidean group
- $E > 0$: $\text{SO}_0(3, 1)$, the Lorentz group (identity component)

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Aside: the Lorentz group is important in special relativity. Is this also 'accidental'?