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Perspective

Perspective on "Zur Quantentheorie der Spektrallinien"

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Abstract. Among many other results, Arnold Sommerfeld gave in his article the correct expression for the relativistic bound-state energy levels of the hydrogen atom, well before the development of wave mechanics, clear ideas about the electron spin, and Dirac's relativistic wave equation. He correctly attributed the fine structure of atomic spectra to relativistic effects, and thus published the first paper giving a quantitative perspective on relativistic quantum chemistry.

Key words: Relativistic quantum chemistry – Sommerfeld transformation

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Sommerfeld's paper features three major sections, each presenting new ideas for the explanation of the phenomenology of the spectra of hydrogen and hydrogen-like atoms. The first section develops the theory of the Balmer series in the spectrum of the hydrogen atom. The theoretical method employed is the application of Bohr–Wilson–Sommerfeld quantization rules to the nonrelativistic bound-state Kepler problem, i.e., the physics of a charged body moving in an attractive central potential. The extension of previous ad hoc quantization rules to phase integrals, enabling the application of the "old quantum theory" to nonspherical orbits, is introduced in this section. Sommerfeld uses these new rules to derive the expressions for the elliptic (bound-state) orbits, in particular the ones with nonspherical symmetry, i.e., nonvanishing eccentricity, ε.

The second section deals with the fine structure of the hydrogen spectral lines. The discussion of the bound-state Kepler problem is extended to the relativistic case. Following an idea of Bohr [1], who had already conjectured that the fine structure of the hydrogen spectrum could be a relativistic effect proportional to $e^4/\hbar^2c^2$, the fine structure of the hydrogen spectrum is thus explained using the "quantized" result of this calculation. The fine-structure constant is introduced as a measure of the size of the relativistic effects. It is subsequently used as an expansion parameter for various quantities, thus defining a "nonrelativistic limit". The separation of kinematical relativistic effects and fine-structure splitting is discussed considering the spherical orbits.

In the third section, X-ray spectra (Röntgenspektren) of the hydrogen atom are discussed. The principles developed in the first two parts of the paper are applied to inner-shell spectroscopy. The paper is characterized by a quick adaptation and rapid development of the ideas of the "old quantum theory" introduced by Bohr, which was vividly discussed in the contemporary literature [2–4]. The simultaneous treatment of relativity and quantum effects is the first of its kind.

Sommerfeld's quantization rules

$$\int p_i \, dq_i = 2\pi n_i \hbar, \quad i = 1, \ldots, D$$

for a system with D degrees of freedom are not independent of the coordinate system, and he had to carry out an explicit separation of variables in order to apply them. Einstein [5] reinvestigated the problem and, besides giving a coordinate-invariant formulation of the quantum conditions, pointed out that a quantization by means of classical action integrals is possible only for integrable systems. These quantization rules for integrable systems were later refined by Keller [6] and are known as Einstein–Brillouin–Keller rules. The method of semiclassical quantization was revived in the early 1980s, when Gutzwiller [7] found a way to apply semiclassical quantization also to nonintegrable systems. His method is based on the Feynman path integral and its expansion around closed classical paths in phase space, the "periodic orbits", and is nowadays instrumental in the context of strongly chaotic systems. For an account of these developments see the recent monograph by Grosche and Steiner [8].

In the following I shall focus on the second section of the paper, dealing with fine structure, since to some extent it survived the quantum revolutions of the 1920s, and until the end of the century still fostered interesting insight, in particular into symmetry aspects of the problem.

The results presented in Sommerfeld's papers are remarkable for three reasons. Sommerfelds tackled (and successfully solved) a problem for which the appropriate theoretical tools were only available a decade later. This fact has been called the "Sommerfeld puzzle", and a solution to the puzzle was given in a beautiful paper by Biedenharn [9], addressing this issue in the following words:

> "Clearly Sommerfeld's methods were heuristic (Bohr quantization rules), out-dated by *two* revolutions (Heisenberg–Schrödinger nonrelativistic quantum mechanics and Dirac's relativistic quantum mechanics) and his methods obviously had no place at all for the electron spin, let alone the four-components of the Dirac electron. So Sommerfeld's correct answer could only be a lucky accident, a sort of cosmic joke at the expense of serious minded physicists."

Biedenharn analyzed Sommerfeld's method and gives a surprising explanation for Sommerfeld's success, thus showing that Sommerfeld did indeed obtain the right answer for the right reason.

Biedenharn first explains the agreement of Sommerfeld's nonrelativistic quantum numbers with the exact answer. This agreement is by no means trivial, since usually Bohr–Sommerfeld quantization rules yield quantum number which are shifted by an unknown numerical constant from the exact ones. In the nonrelativistic Kepler problem there is, however, a quantum-mechanical operator corresponding to the classical eccentricity. This makes it possible to define the "spherical" orbits (i.e., those with vanishing eccentricity) in an unambiguous manner, which gives an absolute frame of reference for the Bohr–Sommerfeld quantum numbers.

Second, there is a special reason that Sommerfeld's procedure works at all in the relativistic case. In a space-fixed frame of reference, the relativistic Kepler orbit is not closed. Rather, the perihel advances in each revolution, which leads to a rosettelike orbit. Sommerfeld uses a rotating frame of reference, which effects that the relativistic orbit is again of the form a conic section (i.e., an ellipse for the bound states), albeit with an angle variable different from the nonrelativistic analogue. In this frame of reference, the phase integral

$$\int_{\phi=0}^{\phi=2\pi} p_\phi \, d\phi = 2\pi n_\phi \hbar \ ,$$

with the classical angular momentum $p_\phi = mr^2\dot{\phi}$, can be used to quantize the angular motion also in the relativistic case. Biedenharn shows that there is a quantum-mechanical counterpart to the (classical) "Sommerfeld transformation" to the moving frame, such that Sommerfeld's solution carries over to the exact treatment.

A third condition is required to explain Sommerfeld's success. Biedenharn shows that, surprisingly, the nonrelativistic problem solved by Sommerfeld is that of a nonrelativistic particle with (dynamically independent) spin, rather than a spinless nonrelativistic particle. If the spinless Schrödinger equation is used, the operator analogue for the eccentricity is given by the length of the Runge–Lenz vector

$$\mathbf{A} = \hat{r} + \frac{\hbar}{2Ze^2 m}(\mathbf{L} \times \mathbf{p} - \mathbf{p} \times \mathbf{L}) \ ,$$

where $\hat{r}$ is a unit vector in the direction of the radius vector, and the other symbols have obvious meanings. From the commutation relations of $\mathbf{A}$ with $\mathbf{L}$, the relation $L^2 + n^2A^2 + 1 = n^2$ obtains, where for simplicity we work in a basis of energy eigenfunctions, with n denoting the principal quantum number. If we solve for $\varepsilon \equiv (\mathbf{A} \cdot \mathbf{A})^{1/2}$, and replace L^2 by its eigenvalue, we get

$$\varepsilon = \left(1 - \frac{l(l+1)+1}{n^2}\right)^{\frac{1}{2}} \ .$$

From this relation we see that (except for $n = 1$) the eccentricity does not vanish for orbitals with nodeless radial probability density, which are characterized by the condition $l = n - 1$ and correspond to the classical circular orbits.

If, on the other hand, a dynamically independent spin is introduced, the appropriate orbital angular momentum operator is

$$K = \beta\left(\boldsymbol{\sigma}\mathbf{L} + \tfrac{1}{2}\right)$$

rather than $\mathbf{L}$ itself. As is well known from the Dirac treatment of the relativistic electron, this operator has eigenvalues $\kappa = \pm 1, \pm 2, \ldots,$. If the commutation relations of $\mathbf{A}$ with K are employed, one arrives at the relation

$$n^2(\boldsymbol{\sigma} \cdot \mathbf{A})^2 + K^2 = n^2 \ ,$$

and defining the operator analogue of the eccentricity as

$$(\boldsymbol{\sigma}\mathbf{A}\boldsymbol{\sigma}\mathbf{A})^{\frac{1}{2}} \equiv \varepsilon = \left(1 - \frac{\kappa^2}{n^2}\right)^{\frac{1}{2}} \ ,$$

again replacing K^2 by its eigenvalue κ, we arrive at vanishing eccentricity for orbits, which correspond to the condition $l = n - 1$ for nodeless radial probability density. Moreover, the problem of "Pendelbahnen", i.e., orbits passing through the nucleus, which had to be excluded heuristically, does not occur since κ cannot be zero. Sommerfeld himself remarked in his paper (page 21) that "at this point already a relativistic generalization is required …". In fact, the generalization required is not a relativistic one, but rather the inclusion of spin (which was unknown at the time Sommerfeld wrote his paper). Consideration of spin in the quantum-mechanical treatment resolves this problem and gives the right expectation value for the above-mentioned operator for the eccentricity of spherical orbits.

The same is true for two more special cases, namely the relativistic particle with spin (yielding the correct Dirac energy levels), and a relativistic particle without fine structure. In these cases, the Runge–Lenz vector is no longer a constant of motion, and the O_4 symmetry of the nonrelativistic problem is broken. It is, however, not "seriously" broken, and an analogue of the Runge–Lenz vector, the so-called Johnson–Lippman operator [10] can be used in lieu of **A** defined above [11]. This has the effect that a residual (super) symmetry is left in the energy levels of Dirac–Kepler problem, which has been analyzed and explained only recently [12].

The previous discussion shows that neither the spin nor the operator K are related to relativistic effects (as is often claimed), but rather they are compatible with nonrelativistic motion (Galilei group relativity) as well as relativistic motion (Poincaré group relativity). This point was also made in several of the papers by Lévy-Leblond [13].

Besides making implicit use of these really puzzling properties of the relativistic Kepler problem, the second major impact of Sommerfeld's article lies in several notions introduced which lie at the foundation of relativistic quantum chemistry and have since been instrumental in the field: the notion of scalar (kinematical) relativistic effects versus fine-structure effects, the introduction of the fine-structure constant, $\alpha = e^2/\hbar c$, and the expansion of the relativistic expressions in powers of the square of this constant. The idea that relativistic effects decisively influence the structure of the outer electrons of the atoms is at the root of relativistic quantum chemistry.

Last but not least, in Sommerfeld's article, a spirit of theoretical work is developed which is, on the one hand, deeply rooted in the experimental observations (making ample use of the spectroscopic results to derive heuristic concepts), and on the other hand, is led by the belief that there is a microscopic explanation for the experimentally observed phenomena. This paradigm is the foundation for the physics of the whole of the twentieth century, including theoretical chemistry. It is interesting to observe that it was again (this time molecular) spectroscopy which turned out to be the field of the first successes of quantum chemistry, by means of guidelines very similar to those behind Sommerfeld's work. The first one is the quest for the "right answers for the right reasons", even under the conditions of inappropriate theoretical methods and the need for heuristic concepts, and the danger that the right reasons will be fully known only decades later. The second one is the emphasis on the treatment of "real systems", i.e., systems which are of current interest for experimentalists. I am personally convinced that successful work in theoretical chemistry will continue to build on these guidelines for quite some time in the century to come.

Invoking those analogies to the development of theoretical chemistry, Sommerfeld's paper could be termed a twentieth century theoretical chemist's paper, published long before this branch of science was called into existence.

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