Rise and premature fall of the old quantum theory

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Abstract

The old quantum theory of Bohr and Sommerfeld was abandonned for the wrong reason. Its contradictions were caused not by the orbit concept but by a mental barrier—the inconceivability that an electron might collide with the atomic nucleus. Removing that barrier resolves the theory’s main failures—incorrect orbital momenta, He atom, $H_2^+$ molecule ion. The inclusion of electron oscillations through the nucleus—a concept called “Coulomb oscillator”—renders the old quantum theory consistent with quantum mechanics (although devoid of wave character). The triple success of the Bohr-Sommerfeld model is its correct description of the $H$ atom (and one-electron ions) concerning (1) the energy levels $E_{nl}$, (2) the orbital angular momenta $L_{nl}$—if corrected as $L_{nl}^2 = l(l + 1)\hbar^2$ and with the Coulomb oscillator included—and (3) the orbits’ space quantization—with $(L_{nl})_z = ml\hbar$. These achievements are succinctly represented by the principal, angular and magnetic quantum numbers ($n, l, m_l$) and visualized by orbital ellipse geometry—major axis, vertex curvature, and tilt angle, respectively. Orbit geometry also accounts for the average orbit size. Moreover, the Coulomb oscillator provides a natural explanation of (isotropic) hyperfine interaction. The shortcomings of the old quantum theory lie in its neglect of three properties of particles—their spin, their wave nature and their quantum statistics. These deficiencies notwithstanding, the visual appeal of the Bohr-Sommerfeld model remains a pedagogical asset to complement the abstract character of quantum mechanics.
I. INTRODUCTION

Quantum theory made its debut in the fall of 1900 when Max Planck, professor at the University of Berlin, succeeded in deriving a formula for the spectral distribution of thermal radiation that agreed precisely with experiment (Planck 1900). The formula was based on the unconventional, and (at the time) unjustified assumption that electromagnetic radiation at any (visible or invisible) spectral color can be absorbed or emitted only in tiny portions of energy, called “quanta.” Planck’s formula—later called “Planck’s law”—resolved the long-standing puzzle of why all (“black”) bodies at the same temperature have the same thermal color. Fostered by advances in spectroscopy and thermodynamics, Gustav Kirchhoff, a previous professor at Berlin, had discovered, a half-century earlier, this universal relation (Kirchhoff 1859). Kirchhoff’s discovery was recognized as being of fundamental rather than technical importance—something akin to Newton’s universal law of gravity. Accordingly, much experimental and theoretical effort was devoted to thermal-radiation spectroscopy. With Planck’s successful resolution of a problem of universal scope, quantum theory, while still at the margins of physics, acquired a touch of foundational significance. More importantly, the theory’s underlying concept of stepwise change introduced a new paradigm to the description of nature. The previous paradigm—continuous change—had gained universal credibility because of its basic role in the greatest triumph of mathematics: the calculus.

The second step in the advance of quantum theory occurred in 1905 when iconoclast Albert Einstein, still patent clerk in Bern, used Planck’s quantum concept to explain the obscure photoelectric effect (Einstein 1905). Einstein assumed that light consisted of “light quanta”—later called “photons”—that would hit electrons like bullets. Both Planck and Einstein assumed a universal ratio between photon energy and radiation frequency, $\epsilon/f = h$, later called Planck’s constant. They differed, though, in its interpretation. Planck regarded merely the radiative emission and absorption process as quantized, but not, like Einstein, radiation per se. In contrast to Planck’s resolution of a universal problem (thermal radiation), Einstein’s contribution appeared less significant—an attempt to explain an experimental oddity. Einstein invoked Planck’s quantum theory in two other cases. One was his theory of the specific heat of solids at low temperatures (Einstein 1907). In the other case, Einstein calculated energy fluctuations of radiation and found that they
consisted of both wave and particle contributions (Einstein 1909).

With its next appearance, however, quantum theory moved from the margins of physics to center stage when it addressed the most important question of the day: the structure of the atom. The notion of atoms had already appeared in some natural philosophy of ancient Greece—a speculation vindicated only two and a half millennia later. However, from the late 1700s on, the concept of atoms had attracted serious consideration as it provided a simple explanation for the discovery that pure chemicals react without remainders only in certain weight (or volume) proportions (Dalton 1842). Strong support for atoms came from the related discovery that all chemicals can be broken down into (less than 100) “elements,” whose systematic relations were successfully displayed in the periodic table (Meyer 1864, Mendeleev 1869). Other support for the concept of atoms came from the gas laws and their explanation with molecular kinetics (Maxwell 1859, Boltzmann 1868). Nevertheless, in the phenomenological spirit of thermodynamics, opposition to the existence of atoms was still raised at the turn of the century by extreme proponents (Mach 1896, Ostwald 1902) of the greatest discovery in physics in the 1800s—the unifying principle of conservation of energy (Mayer 1867). The atomic adversaries (“energeticists”) conceded that atoms were useful thought patterns but not reality. Their main argument was that mechanical laws, applied to atoms, could not account for irreversibility because of the independence of the equation of motion on the direction of time. [In response to such doubts, and following Boltzmann’s footsteps, Einstein, in his doctoral thesis, put forth further arguments—molecular suspension—for the existence of atoms (Einstein 1906).]

So it was in 1913, while on a post-doctoral fellowship in Manchester under the tutelage of Ernest Rutherford, that Niels Bohr of Copenhagen proposed a model of the atom that resolved the century-old mystery of spectral lines (Bohr 1913a). Elaborating Rutherford’s recent planetary concept of the atom, Bohr combined Kepler’s laws of celestial mechanics with the Planck-Einstein quantization of energy (or alternatively, of angular momentum). The result was a frequency formula [conceived three decades earlier with numerological guesswork (Balmer 1885)] for the spectrum of the simplest atom—hydrogen—that agreed with experiment to high precision. The same method yielded a reasonable value for the ground-state energy of the next atom in the periodic table, helium, and promising results for some other atoms (Bohr 1913b). Extending the method to questions of the chemical
bond, Bohr obtained reasonable values for the binding and spacing of the hydrogen molecule, $H_2$, but instability for the hydrogen molecule ion, $H_2^+$ (Bohr 1913c).

Bohr’s quantum theory found rapid acceptance not only because of its promise to explain atomic structure, spectroscopy, and chemical bonding, but also because of its mathematical simplicity—a back-of-the-envelope calculation with high-school algebra. This was in contrast to Planck’s derivation of thermal radiation with demanding mathematics, applied to advanced thermodynamics and electrodynamics. In further contrast to Planck’s abstract theory, the great conceptual appeal of the Bohr model lay in its visualization with electron orbits and quantum leaps.

II. BOHR MODEL

The Bohr model of the hydrogen atom is like a miniature solar system where the nucleus plays the role of the sun and the $H$ atom’s single electron the role of a planet. Although planet and electron are held in orbit by different forces—gravitational and electric, respectively—these forces have the same distance-dependence (inverse-square law). Thus both kinds of orbit are ruled by Kepler’s laws of planetary motion. There is, however, a difference between gravity and electricity that poses a problem: According to Maxwell’s electrodynamics, any acceleration of electric charge (here, centripetal acceleration of the orbiting electron) causes a radiative loss of energy, so that the electron would spiral into the nucleus. No such instability of the hydrogen atom is observed, though—in apparent contradiction to the model. Bohr resolved the conflict with his postulate of stationary states: Defying Maxwell’s electrodynamics, the electron can move in certain orbits—called “quantum states”—without radiatively losing energy. Bohr then imposed two restrictions on the multitude of possible Kepler orbits: (i) A simplifying assumption—sufficient for energy considerations—posits that only circular orbits are permitted. (ii) A quantization condition requires that the angular momentum of the revolving electron in the $n$th orbit must equal $n$ times Planck’s (reduced) constant,

\[ L_n = n\hbar, \]  

(1)
where $\hbar = h/2\pi$. The result are quantized circular electron orbits whose radii depend on the square of the quantum number,

$$r_n = n^2 r_B,$$

shown in Fig. 1. Here the Bohr radius $r_B = \hbar^2/me^2 = 0.529 \times 10^{-10} m$ serves as a universal atomic length unit. (Traditionally, the Bohr radius has been denoted as $a_0$. For the sake of more “user friendliness,” the self-explanatory notation $r_B$ is used here.) Note that the Bohr orbits are possible orbits for the revolving electron—the electron can, of course, only be in one such orbit at a given time.

Fig. 1. Bohr orbits of quantum number $n$. 
Fig. 2. Coulomb funnel with inlaid Bohr orbits (center) and conventional energy-level diagram (left).

The quantized orbit energies are

$$E_n = -\frac{1}{n^2} R_y. \quad (3)$$

The negative sign indicates that the orbits are bound and $R_y = \frac{me^4}{2\hbar^2} = 13.6 \text{ eV}$ is the Rydberg energy—an energy unit suited to the atomic scale. Fitting, in the right part of Fig. 2, the Bohr orbits into a Coulomb-potential funnel, $V(r) \propto \frac{1}{r}$, visualizes the relation with their energy levels, Eq. (3), which are commonly displayed by the familiar level scheme in the left part of the figure.

The connection between orbit energies and spectral lines is achieved with Bohr’s postulate of quantum leaps: The electron can “jump” inward from an outer orbit $n$ to an inner orbit $n'$ by emission of a light particle (photon) whose energy $\epsilon$ is provided by the difference of the orbits’ energy,

$$E_n - E_{n'} = \epsilon = \hbar f_{nn'}, \quad (4)$$
which is, in turn, associated with the lines’ frequencies \( f_{nn'} \) through the Planck-Einstein relation. The great success of the Bohr model, achieved by combining Eqs. (4) and (3), is the Balmer formula,

\[
    f_{nn'} = \frac{R_y}{h} \left( \frac{1}{n'^2} - \frac{1}{n^2} \right),
\]

in terms of quantum numbers and, via \( R_y \), fundamental constants (electron mass \( m \) and charge \( e \), Planck’s constant \( h \)). Here \( n \) denotes the initial orbit and \( n' \) the final. A positive value of \( f_{nn'} \) signifies photon emission and a negative value photon absorption. For a connection of the Balmer formula with experiment, one converts the photon frequency to the corresponding wave length,

\[
    \lambda_{nn'} = \frac{c}{f_{nn'}}
\]

according to their relation to the speed of light \( c \). Constructive interference,

\[
    \lambda_{nn'} = D \sin \theta_{nn'}
\]

in spectroscopy with a diffraction grating of groove separation \( D \), permits observation of spectral lines at diffraction angles \( \theta_{nn'} \).

A side result of the Bohr model is the size of the hydrogen atom, Eq. (2), although no experiment was conceivable at the time to test this prediction. The Bohr model is silent, though, on the relative brightness of the spectral lines. Other predictions of the Bohr model are actually wrong: Results from quantum mechanics, obtained over a decade later, prove that the (maximum) angular momentum of the \( nth \) quantum state is

\[
    L_n = (n - 1)h
\]

instead of Eq. (1). Also disturbing, and jarring physical intuition, is the Bohr model’s spatial description of hydrogen as a ring atom instead of a space-filling, spherical entity. Nevertheless, the Bohr model has been the greatest coup in quantum physics. With bold assumptions it derived in a few, strikingly simple steps a frequency formula that historically breached the long-standing riddle of the spectral lines and provided a key to the structure of the atom. It was therefore reasonable to expect that more refined assumptions would resolve its short-comings and lead to further progress.
Fig. 3. Coaxial $nl$ Sommerfeld ellipses with correspondingly shifted nuclei. The quantum sum, $n$, characteristic for each orbit’s energy, determines its major axis. By Kepler’s 3rd law, the sorted orbits with the same major axis have the same period and energy.
III. SOMMERFELD MODEL

Such refinement occurred soon. Inspired by the fact that Planck’s constant $h$ has the same dimension as the process quantity of action, $A = \int p \, dq$, with $q$ being a generalized coordinate and $p$ the conjugate momentum, Arnold Sommerfeld, professor at the University of Munich, had previously sought a connection of quantization with the process quantity $A$—the quantity that is the backbone of the (least-) action-principle of mechanics. In this context he had coined for $h$ the term “quantum of action” (Sommerfeld 1911). Instead of Bohr’s ad hoc quantization of angular momentum, Sommerfeld subsequently proposed that atomic process action should be quantized for each degree of freedom (Sommerfeld 1916). [The same quantization conditions had been proposed independently, albeit without application to atomic structure (Wilson 1915, Ishiwara 1915).] Lifting Bohr’s special assumption of circular orbits, Arnold Sommerfeld, professor at the University of Munich, invoked the general case of Kepler motion: elliptical orbits. He quantized separately the action of the electron’s radial and angular motion,

$$\oint p_r \, dr = n_r h. \quad (7)$$

and

$$\oint p_\alpha \, d\alpha = p_\alpha \oint d\alpha = 2\pi p_\alpha = n_\alpha h. \quad (8)$$

Here $p_r = m v_r$ is the radial momentum and $p_\alpha$ is the angular momentum—a constant of the motion, denoted $L_\alpha$ in Eq. (1). The sum of the radial and angular quantum numbers,

$$1n_r + n_\alpha = n, \quad (9)$$

is the previous quantum number $n$ of the Bohr model, called (for short) “quantum sum” by Sommerfeld. The angular quantum number was soon relabeled as $k$ but will be denoted here as $n_\alpha \equiv l$ to facilitate later comparisons with quantum mechanics. The electron orbits that result from these assumptions are quantized ellipses, labeled $nl$, with semimajor axis

$$a_{nl} = n^2 r_B, \quad (n = 1, 2, ...), \quad (10)$$

semiminor axis

$$b_{nl} = n l r_B, \quad (l = 1, 2, ..., n), \quad (11)$$
and orbit energy

\[ E_{nl} = -\frac{1}{n^2}R_y. \quad (12) \]

Note in Eqs. (10, 12) that both the orbit’s semimajor axis and energy depend only on the quantum sum \( n \) and agree with the radius and energy of the \( n \)th Bohr orbit, Eqs. (2, 3), respectively. Accordingly, for a given quantum sum \( n \), all \( nl \) Sommerfeld ellipses \( (l = 1, 2, ..., n) \) have the same length of major axis and the same energy. They include the circular Bohr orbits as a special cases, \( l = n \). The lesser the angular quantum number \( l \), the sleeker the ellipse. Orbits with the same length of major axis (same energy) but of different shape (different angular momentum) are called “degenerate.” By Eqs. (10 - 12), the \( nl \) Sommerfeld orbits are \( n \)-fold degenerate. The arrangement, in Fig. 3, of Sommerfeld ellipses of the same quantum sum \( n \) by groups with coinciding major axes shows such degenerated quantum states (Sommerfeld 1931). [The elliptical orbits’ energy levels, Eq. (12), can, of course, also be visualized by the fit of their major axes into the Coulomb funnel of Fig. 2.]

The minor axis of a Sommerfeld ellipse depends on both the quantum sum \( n \) and the angular quantum number \( l \), Eq. (11). In contrast, an ellipse’s semilatus rectum,

\[ \Lambda_{nl} = l^2r_B \quad (n = 1, 2, ...) \quad (13) \]

—the distance from the focus to the perimeter, parallel to the minor axis—depends exclusively on the angular quantum number \( l \) which in turn determines the orbit’s angular momentum \( L_{nl} = lh \), Eq. (8). Geometrically, the semilatus rectum \( \Lambda_l \equiv \Lambda_{nl} \) is the radius of curvature of an ellipse at its major vertex. Thus the angular momentum of an \( nl \) Sommerfeld ellipse is represented by its vertex curvature (Mallow 1999) as the comparison in Fig. 4 shows.

Missing among the Sommerfeld orbits is one more solution of Eq. (11), \( l = 0 \)—the straight-line ellipse where the electron collides with the nucleus. Sommerfeld deliberately excluded this case as “unphysical.”
Fig. 4. Coverticil \( nl \) Sommerfeld ellipses with correspondingly shifted nuclei. The angular quantum number, \( l \), characteristic for each orbit’s angular momentum, determines its semilatus rectum \( \Lambda_l \). Geometrically, \( \Lambda_l \) is the radius of curvature of an ellipse at its vertex. Therefore, all ellipses with the same \( l \) have the same curvature.
A description of motion in three-dimensional space requires three coordinates—
Cartesian \((x, y, z)\) or, better suited for atoms, spherical \((r, \theta, \varphi)\). The use of
planar polar coordinates \((r, \alpha)\) in Eqs. (7, 8) amounts to a two-dimensional
quantization, whose coplanar ellipses serve as a conceptual stepping stone for
Sommerfeld’s quantization of motion in three “degrees of freedom” of space:

\[
\oint p_r dr = n_r h, \tag{14}
\]

\[
\oint p_\theta d\theta = n_\theta h, \tag{15}
\]

and

\[
\oint p_\varphi d\varphi = p_\varphi \oint d\varphi = 2\pi p_\varphi = n_\varphi h. \tag{16}
\]

The previous angular action integral, Eq. (8), splits now into latitudinal and
equatorial action integrals, Eqs. (15, 16), such that the angular quantum
sum is

\[
n_\theta + n_\varphi = n_\alpha \equiv l. \tag{17}
\]

Both the angular momentum \(p_\alpha\), Eq. (8), and its the axial component,
\((p_\alpha)_z \equiv p_\varphi\), Eq. (16), are constants of the motion, which justifies their
factoring out of the action integrals in these equations. The quantum number
of the latter is traditionally called “magnetic” and relabeled as \(n_\varphi \equiv m_\ell\). A
more descriptive term for \(m_\ell\) would be “tilt quantum number” which we wish
to use henceforth. The orbits that result from the 3D quantization, Eqs. (14-16), are the same Sommerfeld ellipses as from the 2D quantization, Eqs. (7, 8), but now oriented at quantized tilt angles,

\[
\tau_{m_\ell} = \arccos(m_\ell/l), \quad (m_\ell = 0, \pm 1, \pm 2, ..., \pm l), \tag{18}
\]

(“space quantization”) with respect to a reference plane—commonly equatorial—
depending on the possible values of \(m_\ell\). Accounting for all orientations, a
given \(nl\) Sommerfeld ellipse has then a \((2l+1)\)-fold orientational multiplicity.
An example of some of the possible tilts of an \(nl = (n, 3)\) Sommerfeld orbit
(here, only those above the \(xy\) reference plane, \(m_\ell = 0, +1, +2, +3\)) is shown
in the upper part of Fig. 5. The concept of space quantization is visualized
in the lower part of Fig. 5 by the projected areas of the variously tilted \(nl\)
ellipse onto the equatorial plane. The sizes of the projected areas propor-
tionally represent the equatorial action, Eq. (16). [Both the tilted \(nl\) ellipse
and each projection have the same semimajor axis, \(a_{nl}\), Eq. (10). The semi-
Fig. 5. Orbital ellipse of angular quantum number $l = 3$ in different spatial orientations and their projections onto the equatorial plane.

The hierarchy of tilted ellipses, with their ordering by quantum sum $n$ (length of major axis), angular quantum number $l = 1, 2, ..., n$ (vertex curvature), and tilt quantum number $m_l = 0, \pm 1, \pm 2, ..., \pm l$ (space quantization), has become invaluable for an understanding of the structure of all atoms—not only hydrogen—and the classification of spectroscopy, particularly in the presence of a magnetic field (Zeeman effect). Because of its electric charge, $-e$, an electron’s motion along a tilted orbit amounts to a closed-loop current and thus to an electromagnet. The field energy of such orbit-magnets in an external magnetic field $B$ lifts the orbit degeneracy by distinguishing the tilted orbits energetically (splitting of spectral lines).

Even without a magnetic field, a very minute splitting of hydrogen spectral lines had been observed already a generation before the old quantum theory (Michelson 1891). One motivation for Sommerfeld’s extension of the Bohr model was to account for this fine structure. Since Sommerfeld’s procedure, as shown above, yields the same orbit energies as Bohr’s, Eqs. (12, 3), it fails to explain the fine structure. Therefore Sommerfeld refined his previous
quantization scheme by including the electron’s relativistic mass dependence, 
\[ m = m_0 / \sqrt{1 - (v/c)^2} \], where \( m_0 \) is the electron’s rest mass. The result is, besides the strong dependence of the orbit energy on the quantum sum \( n \), a slight dependence on the angular quantum number \( l = 1, 2, ..., n \),

\[ E_{nl} = m_0 c^2 \left\{ 1 + \frac{\alpha^2}{(n - l + \sqrt{l^2 - \alpha^2})^2} \right\}^{-\frac{1}{2}} - 1 \}, \quad (19) \]
due to near cancellation of \(-l\) in Eq. (19) by the radical following it. Here \( m_0 c^2 \) is the electron’s rest energy and \( \alpha = e^2 / \hbar c \approx 1/137 \) is the fine-structure constant. A power-series expansion to order \( \alpha^2 \),

\[ E_{nl} \approx -\left[ \frac{1}{n^2} + \frac{\alpha^2}{n^4} \left( \frac{n}{l} - \frac{3}{4} \right) \right] R_y, \quad (l = 1, 2, ..., n), \quad (20) \]
contains, by the first term in the square bracket, the previous, non-relativistic orbit energy, Eq. (12), and the additional relativistic correction.

Sommerfeld’s fine-structure formula was spectroscopically confirmed for \( H \) and (in its more general form, not shown here) for hydrogenic ions (\( He^+ \), \( Li^{2+} \), ...) to the highest precision (Paschen 1916)—the greatest triumph of the old quantum theory. Over a decade later, after the electron spin had been discovered (Uhlenbeck, Goudsmit 1925), relativistic quantum mechanics (Dirac 1928) obtained the fine-structure formula (Gordon 1928) along a very different route, stated in slightly modified terms,

\[ E_{nl} = m_0 c^2 \left\{ 1 + \frac{\alpha^2}{(n - l + \sqrt{\lambda^2 - \alpha^2})^2} \right\}^{-\frac{1}{2}} - 1 \}, \quad (21) \]
The parameter \( \lambda \) depends on the electron’s total angular quantum number \( j = l \pm \frac{1}{2} \), composed of its orbital angular quantum number \( l \) and spin quantum number \( s = \frac{1}{2} \) such that \( \lambda = l + 1 \) for \( j = l + \frac{1}{2} \) and \( \lambda = l \) for \( j = l - \frac{1}{2} \). Expanded to order \( \alpha^2 \), this formula becomes

\[ E_{nl} \approx -\left[ \frac{1}{n^2} + \frac{\alpha^2}{n^4} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right] R_y, \quad \left( j = \frac{1}{2}, \frac{3}{2}, ... \right), \quad (22) \]
and yields the same energies as Sommerfeld’s formula, Eq. (20), (although with an altered ordering of quantum numbers).
Sommerfeld-like \((n, l, m_l)\) orbits, populated with electrons from the inside out, conceptually provide the backbone of the atomic \textit{Aufbau} (building-up) principle (Bohr 1923). [It would later explain, when combined with the exclusion principle (Pauli 1925b), the periodic table of the elements.] Atoms other than hydrogen constitute a many-body problem, defying closed-form solutions. Accordingly, one has to resort to approximation methods, essentially by reducing the multi-electron situation to an effective one-electron problem through shielding by the atomic core. In his initial model of the helium atom, Bohr assumed that the atom’s two electrons circulate, diametrically opposite, in a quantized ring orbit about the nucleus (Bohr 1913b), illustrated in Fig. 6. His value for the \(He\) ground-state energy was surprisingly close (within 5\%) to experiment. Much disappointment followed therefore when subsequent refinements with tools of Sommerfeld’s orbit scheme (Born and Pauli 1922, Born and Heisenberg 1923) and tremendous calculational efforts (Van Vleck 1922, Kramers 1923) failed to yield better results.

Fig. 6. Bohr’s historic “two-seat-roundabout” model of the \(He\) atom.

Similar difficulties plagued orbital calculations of other atoms. The assignment of an angular momentum to the atom core (Landé 1921), and its association with an “inner” quantum number, was eventually proved inconsistent (Pauli 1925a). Understanding the anomalous Zeeman effect remained an insurmountable barrier for the old quantum theory—desperate efforts even involved attempts with half-integer quantum numbers (vindicated after the discovery of spin).
The hydrogen molecule ion, $H_2^+$, was another proving ground for quantum theory. A one-electron problem, subject to attraction to two nuclei, it should be expected to be solvable. In exploration, Bohr (1913c) had modeled $H_2^+$ with a quantized ring orbit in the bisectorial plane between the nuclei but deemed it unstable by mechanical considerations. Sommerfeld calculated $-0.88R_y$ for the ground-state energy of this ring orbit which renders it energetically unstable. (If the energy of the $H_2^+$ ground state is higher than that of the $H$ atom, $-1R_y$, then the molecule ion is unstable and decays into a free $H$ atom and a far-away proton.) Thereupon, in 1920, Sommerfeld put his most gifted student, the prodigy Wolfgang Pauli, to the task for a more detailed analysis of the $H_2^+$ problem. Drawing on established methods of celestial mechanics (Jacobi 1866), Pauli classified possible electron orbits: four planar orbits, illustrated in Fig. 7—(a) “pendulum orbit” in the median plane perpendicular to the nuclear axis, (b) “satellite orbit,” sweeping the region about one nucleus, (c) “lemniscate orbit,” densely filling the area of an ellipse with both nuclei as foci, (d) “planetary orbit” over the interval area between two ellipses around both nuclei—and two groups of spatial orbits (not shown in Fig 7), symmetric or asymmetric to the median plane (Pauli 1922). The pendulum orbits, (a), are unstable against displacement perpendicular to their oscillation. Planetary orbits, (d), fail to satisfy a time-average equilibrium condition. Remarkably, Pauli discarded the satellite and lemniscate orbits, (b,c), because they lead arbitrarily close to a nucleus. For justification, Pauli referred to a (unstated) rule by Bohr, according to which such orbits would not occur “in reality.”

With all planar orbits excluded, Pauli analyzed the symmetric spatial orbits. (He postponed the asymmetric case because of excessive numerical effort.) Appropriate to the molecule’s symmetry, the orbits are expressed in spheroidal coordinates, $\xi = (r_1 + r_2)/R$, $\eta = (r_1 - r_2)/R$ and $\varphi$. Here $r_1$ and $r_2$ are the electron’s distance from the left and right nucleus, $R$ is the nuclear separation, and $\varphi$ is the equatorial angle in the median plane. Using these coordinates and corresponding momenta, the quantization conditions are analogues to Eqs. (14-16),

$$\oint p_j dj = n_j h, \quad (j = \xi, \eta, \varphi).$$

Pauli found that the orbit characterized by the quantum numbers $(n_\xi, n_\eta, n_\varphi) = (0, 1, 1)$ possessed the lowest energy. Accordingly he identified it as the
molecule ion’s ground state. Note that the (0, 1, 1) quantization requires two quanta of action—in contrast to 1\(\hbar\) for the ground state of the \(H\) atom. The calculated energy of the \(H_2^+\) ground state came out as \(-0.52R_y\). [The same result was obtained independently by K. F. Niessen of Holland (Niessen 1923).] As a consequence the hydrogen molecule ion would be unstable. In contrast, contemporary experiments indicated stability of \(H_2^+\), but some uncertainty remained. A few years later, though, experiments clearly confirmed that the hydrogen molecule ion was stable, with a ground-state energy of \(-1.20R_y\).

The \(H_2^+\) problem presents a paradigm for the chemical bond—two nuclei held together by an electron (Gutzwiller 1990). Pauli’s failure to find a stable ground-state of \(H_2^+\) was a serious blow to the old quantum theory. Something seemed amiss.

V. FALL OF THE OLD QUANTUM THEORY

The final straw that broke the old quantum theory was the hydrogen atom in crossed electric and magnetic fields. The spectral response of the atom to only one such field is known as the Stark effect or the Zeeman effect, respectively. In his theoretical treatment of the crossed-fields problem, Pauli
invoked Ehrenfest’s adiabatic principle whereby quantization persists under slow variation of a parameter (Ehrenfest 1916). In this way Pauli could restate the situation such that the electron would collide with the nucleus—Sommerfeld’s “unphysical” situation—and show that the old quantum theory is contradictory (Pauli 1926).

What exactly was the root of the old quantum theory’s failures? Pauli, Heisenberg and Born suspected that is was the orbit paradigm that caused the difficulties. Subsequent mathematical explorations of more abstract nature (differential operator techniques) by Born and Heisenberg led to the discovery of matrix mechanics, based solely on quantities that can be observed in principle (Heisenberg 1925, Born et al. 1925). The successful solution of the previous difficulties with the $H$ atom with the new method—called, for distinction, quantum mechanics—seemed to confirm the inappropriateness of the orbit concept (Pauli 1926). This notion acquired formal support with the discovery of the uncertainty principle (Heisenberg 1927). Henceforth the old quantum theory of Bohr and Sommerfeld was abandoned from serious calculations. Only occasionally was it employed, with many caveats and much warning, for introductory purposes (Bohr model, visual appeal of Sommerfeld orbits. [Ironically—and confusing generations of students—some texts and handbooks labeled the Sommerfeld orbits faultily (Jaworski and Detlaf 1972). They erroneously assigned the angular quantum number $l = 0$ to the circular (Bohr) orbits, and orbits of increasing $l$ to increasing eccentricity. It is not clear what caused such confusion—perhaps mistaken association of Sommerfeld’s circular ground-state orbit with the spherical symmetry of the ground state’s quantum-mechanical description? Or, paradoxically, a formal application of unvisualizable, quantum-mechanical rules to a quantum visualization by orbits, starting with the first Bohr orbit as ground state?]

Quantum mechanics, while suited to calculate atomic properties to highest precision, left little room for visualization—a serious curtailment of physical intuition. [Quantum mechanics’ few visualization tools are graphs of radial or angular wave functions $\psi$ (by themselves entities of no or vague interpretation), squared wave functions $|\psi|^2$ with their probability interpretation (Born 1926), and spatial representations of orbitals’ electron-density to serve as indicators for chemical bonding.]
VI. COULOMB OSCILLATOR

Eighty years after its demise the old quantum theory experienced a resurrection when a fatal flaw in the Sommerfeld model was recognized: the exclusion of the “unphysical” electron collision with the nucleus—Sommerfeld’s dictum $l \neq 0$, Eq. (11). If instead the electron is permitted to swing through the nucleus (“Coulomb oscillator,” $l = 0$), the correct hierarchy of orbital angular momenta in the hydrogen atom is obtained (Bucher 2006). (How I came to that revelation, I tell in the appendix.) Likewise, when the electron of $H_2^+$ swings through both nuclei with an action of $1\hbar$, stability of the molecule ion is achieved. By excluding this case, both Pauli and Niessen had missed that crucial result. The unstable orbit they found, with action of $2\hbar$,

Fig. 8. Binding energy $E$ of the hydrogen molecule ion $H_2^+$ vs nuclear separation $R$: Exact, quantum mechanical solution (curve) and Coulomb-oscillator calculation (circles). The bottom curve is the $1s\Sigma_g$ ground state, the top curve the $2p\Pi_u$ excited state. The triangle shows Pauli and Niessen’s historical calculation (at equilibrium), misinterpreted as the (unstable) ground state. Data beneath (above) the horizontal dashed line—the binding energy of a free $H$ atom—indicate stability (instability) of the molecule ion.
can today be identified as the approximate solution of an excited state of $H_2^+$, rather than their mistaken ground-state allocation (see Fig. 8). The small deviation of the Coulomb-oscillator calculation of $H_2^+$ from the exact solution, Fig. 8, is caused by the former’s neglect of the electron’s wave nature (Bucher 2006).

Applied to the helium atom (Bucher 2007), synchronized cross-oscillations of two electrons through its nucleus give the energy of the $1^1S$ ground state of He, in close agreement with experiment (see Fig. 9). In contrast, contralinear oscillations give the same energy as Bohr’s historical two-seat roundabout model, also shown in Fig. 9, and are interpreted as the forbidden $1^3S$ triplet ground state—a result beyond the reach of quantum mechanics.

Finally, Pauli’s discovery in his crossed-fields analysis of the $H$ atom—that the electron would collide with the nucleus—proves to be no contradiction but reality.
Fig. 10. Partial trajectory of an extranuclear, elliptical orbit $XX'$ and of a penetrating orbit $PP'$ through a finite-size nucleus $N$. The dotted line $S$ shows the major symmetry axis of $XX'$.

Obviously, the case of a planet colliding with the sun—and reappearing unscathed on the opposite side—is missing in the classical treatises of celestial mechanics (Jacobi 1866, Poincaré 1905, Charlier 1907). Still, it is surprising how matter-of-factly Sommerfeld dismissed this scenario on the atomic scale as “unphysical.” Likewise, the possibility of a rectilinear electron oscillation through the nuclei is never considered in Pauli’s treatment of $H_1^+$, in contrast to his systematic analysis of all other orbits.

A subtle, conceptual distinction arises for the rectilinear electron orbits, depending on the assumed size of the nucleus—finite or infinitely small. Closed electron orbits are always elliptical if they pass outside the nucleus. It is the entire nuclear charge, $+Ze$, that causes the centripetal acceleration. In the (temporarily assumed) continuous limit of maximal elliptical eccentricity, $l \to 0$, the orbit becomes a straight line of (major-axis) length $2n^2r_B$, Eqs. (10, 11), with its nuclear and empty focus at either end—provided the nucleus is a point charge! The centripetal acceleration of the electron then occurs infinitely close to the point nucleus such that the electron motion appears as a repulsion at the (point) nucleus—“Coulomb repeller.” A different situation is at hand, though, when the electron penetrates a finite-size nucleus. In this case only part of the nuclear charge affects the centripetal acceleration so that no closure of (genuine) elliptical orbits can occur (see Fig. 10). In the case of a head-on collision of the electron with a (realistic) finite nucleus, straight penetration and ensuing bilateral oscillations result—“Coulomb oscillator.” In calculations of the energy $E_{n0}$ of $l = 0$ orbits, the minuscule influence from the nucleus’ finite size (part of the Lamb shift) is
negligible for all practical purposes. In this respect the conceptually different unilateral oscillation at one side of a point nucleus (Coulomb repellor) and the bilateral Coulomb oscillator through a finite nucleus are calculationally equivalent.

A windfall from the notion of an electron’s (bilateral) Coulomb oscillation through a finite nucleus is a natural interpretation of the hyperfine splitting of $l = 0$ energy levels—the so-called Fermi contact term—

$$\Delta E_{hfs} = -\frac{8\pi}{3} < \mu_N \cdot \mu_{el} > |\psi(0)|^2. \quad (24)$$

Here $\psi(0)$ is the spatial wave function of an $l = 0$ electron at the position of the nucleus and $<\ldots>$ denotes the quantum-mechanical coupling of nuclear and electron spin. Virtually all quantum mechanics texts attribute the Fermi contact term to electron density $\psi\psi^*$ near, or “at” the nucleus. A detailed inspection of scales shows, however, that it arises not from outside “contact” of the electron with the nucleus but only from its presence within (Bucher 2000). Independently derived, this interpretation is consistent with the concept of the Coulomb oscillator.

VII. $\sqrt{l(l+1)}$ CORRECTION

Aside from the conceptual oversight of the Coulomb oscillator, a subtle mathematical error occurred in Sommerfeld’s transition of angular quantization from 2D to 3D, Eqs. (8, 15, 16). The correct angular quantum sum of the 3D quantization, $n_\theta + n_\varphi$, obtained from adding the right-hand side of Eqs. (15, 16), agrees only accidentally with the angular quantum number $n_\alpha$ of the 2D quantization in Eq. (8) because of the double degeneracy of the quantized Kepler problem, that is, the dependence of the orbit energy on only the quantum sum $n$ but not on the other quantum numbers, $l$ and $m_l$ (Schwarzschild 1916, Epstein 1916). Sommerfeld’s quantization by degrees of freedom, Eqs. (14-16), was patterned after the treatment of conditionally periodic systems with action-angle variables. It is known that spatial variables that lead to double degeneracy—here, $r$, $\theta$ and $\varphi$—are not quite appropriate and can give rise to errors (Joos 1959). (Instead, sophisticated orbit parameters, known in astronomy as Delaunay elements, have to be employed.)
In the present case, the sum of the left-hand side of Eqs. (15, 16) must not be identified with the action integral of the 2D orbit, Eq. (8). Experiment shows that the angular momentum—a constant of the motion—has
the correct magnitude \( L_{nl}/h = \sqrt{l(l+1)} \), with angular quantum numbers ranging

\[
l = 0, 1, ..., n - 1,
\]

instead of \( L_{nl}/h = l \) with \( l = 1, 2, ..., n \), as Eq. (8) erroneously implies. (This result agrees with quantum mechanics. However, no derivation from quantization of the proper Delaunay elements has been achieved yet.) Consistently, the correct length of semiminor axis must be

\[
b_{nl} = n\sqrt{l(l+1)}r_B
\]

instead of Eq. (11). Figure 11 shows Sommerfeld ellipses with correct widths, Eq. (22), including the (unilateral) Coulomb oscillator, in comparison with the contradictory historical orbits. An important consequence of this correction is the exclusion of circular (Bohr) orbits, \( l < n \). Another consequence is a corresponding modification of the tilt angle, \( \tau_{ml} = \arccos[ml/\sqrt{l(l+1)}] \), instead of Eq. (18). Therefore, a tilted Sommerfeld orbit can never lie in the equatorial plane.

With the Coulomb oscillator included and the magnitude of the angular momentum (and width of the tilted ellipses) corrected, the new Sommerfeld orbits agree in energy, angular momentum and magnetic response with quantum mechanics. Moreover, the time-average orbit size, expressed through elliptical semiaxes, Eqs. (10, 26), agrees with the corresponding results from quantum-mechanical wave functions (Bucher et al. 1998),

\[
< r_{nl} >_t = \frac{3a_{nl}^2 - b_{nl}^2}{2a_{nl}} = \frac{3n^2 - l(l+1)}{2}r_B = \int \psi^* r \psi d^3 r.
\]

Equation (27) gives \( < r_{10} > = \frac{3}{2}r_B \) instead of \( 1r_B \) as the Bohr model implies, Eq. (2). This result is easily illustrated by the distance \( FD = FP \) on the (unilateral) rectilinear \( (1,0) \) Coulomb-oscillator orbit of major-axis length \( 2r_B \), Eq. (10).
Fig. 12. Average distance \(< r > = FD\) and average position \(< R > = P\) of an electron in a Sommerfeld orbit.

The pathological aspect of the Sommerfeld quantization that affects the orbital momentum (and elliptical minor axis), also affects the fine-structure formula, Eq. (19), where \(l = 1, 2, ..., n\). Because of the \(\sqrt{l(l + 1)}\) correction with \(l = 0, 1, ..., n - 1\), the case \(l = n\) (circular orbit) is no longer admissible. On the other hand, the case \(l = 0\) (Coulomb oscillator) renders the radical in Eq. (19) imaginary [or Eq. (20) divergent] and thus physically meaningless. [The pathological behavior of Eqs. (19, 20) can, of course, not be used to justify the exclusion of \(l = 0\) in the Sommerfeld model since Sommerfeld explicitly excluded this “unphysical” case in the derivation of his fine-structure formula.]

A modified fine-structure formula for the permitted range of angular quantum numbers, \(l = 0, 1, ..., n - 1\), is

\[
E_{nl} = m_0 c^2 \left\{ \left[ 1 + \frac{\alpha^2}{(l + \sqrt{(n-l)^2 - \alpha^2})} \right]^{-\frac{1}{2}} - 1 \right\},
\]

(28)

It differs from Sommerfeld’s formula, Eq. (19), by an interchange of the radial quantum number \(n_r = n - l\) with the angular quantum number \(l\) but yields the same set of energy values. [No derivation of Eq. (28) from quantization of Delaunay elements has been achieved yet.] The remarkable agreement of Sommerfeld’s fine-structure formula, Eq. (19), with experiment arises from a serendipitous cancellation of two errors—the quantization pathology and the faulty range of \(l\).
The triple success of the orbit-based, non-relativistic Bohr-Sommerfeld quantum theory is its correct description of the $H$ atom (and one-electron ions) concerning (1) the energy levels $E_n$, (2) the orbital angular momenta $L_{nl}$—if corrected as $L_{nl}^2 = l(l+1)\hbar^2$ and with the Coulomb oscillator included—and (3) the orbits’ space quantization—with $(L_{nl})_z = m_l \hbar$. These three achievements are succinctly represented by the corresponding (principal, angular and magnetic) quantum numbers, $n$, $l$, $m_l$, and visualized by orbital ellipse geometry—major axis $2a_n$, latus rectum $2\Lambda_l$, and tilt angle $\tau_{m_l}$ (Figs. 3, 4, 5).

The shortcomings of the old quantum theory lie in its neglect of three properties of particles—their spin, their wave nature and their quantum statistics: Inclusion of spin—expressed by the spin quantum number $s$—is necessary to account for the total (instead of only orbital) angular momentum. The wave nature—expressed in Schrödinger’s formulation of quantum mechanics by the wave function $\psi$—is necessary to account for the particles’ spatial (probability) distribution, $\psi\psi^* = |\psi|^2$. Quantum statistics becomes relevant for systems with identical (indistinguishable) particles—atoms, molecules, crystals.

The nagging problems and contradictions during the last years of the old quantum theory were not caused by the orbit concept, as Pauli, Heisenberg and Born suspected but, first and foremost, by the deliberate neglect of the Coulomb oscillator. To be sure, ignorance of the electron spin compounded the difficulties with the anomalous Zeeman effect, and ignorance of quantum statistics hampered progress with the $He$ atom. All those problems were readily solved after the discovery and elaboration of matrix mechanics (Heisenberg 1925, Born et al. 1925), and more conveniently, after the discovery of wave mechanics (Schrödinger 1926)—consistent, equivalent theories, collectively called quantum mechanics. Naturally, the old quantum theory was dropped. It is understandable that the fathers of quantum mechanics kept pointing out the shortcomings of the old quantum theory, rather than seek common ground, to highlight the revolutionary character of their discoveries. (Not surprisingly, the vindication of the old quantum theory’s inherent Coulomb-oscillator concept by quantum mechanics, $l = 0$, went unnoticed: The radial component of a quantum-mechanical $s$ electron, with its finite—even maximum—probability density in the nucleus, can be regarded as a
Coulomb oscillator, besides its wave-nature supplement by an exponential “tunnel tail” beyond its classical region.) From a psychological perspective, Pauli’s failure to solve the $H_2^+$ problem correctly in his PhD thesis must have been a blow to that proud young man’s self-esteem and may well have caused his subsequent resentment toward the orbit concept. [For the rest of his career, Pauli avoided, in word or print, reference to his doctoral dissertation (Enz 2002).]

Sommerfeld, a parent of the atomic models, never recognized what went wrong with his brain child. After the advent of quantum mechanics he redefined the angular quantum number (Sommerfeld 1931) from previously $n_\alpha \equiv l$ and in the range $l = 1, 2, \ldots, n$, Eqs. (17, 11), to

$$n_\alpha \equiv l + 1, \quad (l = 0, 1, \ldots, n - 1),$$

with $l$ now in the quantum-mechanical range. In this way he retained both the old theory’s exclusion of the Coulomb oscillator and inclusion of the circular Bohr orbit—along with all its problems. Giving in to quantum mechanics’ paradigm of abstraction, he considered its formal solution, $l = 0$, a “more satisfying justification” for maintaining his dictum $n_\alpha \neq 0$ than his former, orbit-based motivation of avoiding electron collision with the nucleus. Does this reveal a general psychological tendency? As a result of a visualizable (here, orbit-based) theory with celestial analogy, the solution $l = 0$ is rejected as an apparent contradiction (electron-nucleus collision). But as the result of an abstract (unvisualizable) theory, the same solution, $l = 0$, is acceptable.

Born, Heisenberg and Pauli all developed large schools where they trained virtually all quantum physicists of their era. Naturally, their collaborators, students and disciples adopted the masters’ low opinion of the old quantum theory and passed it on once they were teachers themselves—a process multitudinously repeated to the present time. In this way the old quantum theory acquired and maintained its low reputation of being conceptually naïve, logically inconsistent, and calculationally impotent.

Is the old quantum theory really that bad? No. With the Coulomb oscillator and the $\sqrt{l(l + 1)}$ correction included, it is consistent with quantum mechanics (albeit incomplete) and able to overcome its main historical stumbling blocks (with solutions exact for $H$, approximate for $H_2^+$, and plausible for $He$). This raises the question of whether quantum theory would have developed differently if the Coulomb oscillator had been included in the Som-
The remaining appeal of the Bohr-Sommerfeld model to some teachers—and virtually all students—is its visual, pedagogical asset which complements quantum mechanics’ abstraction. Combining both theories brings out the best of two worlds: visualization and physical intuition along with formal rigor and computational power. (The visual aspects of the Bohr-Sommerfeld model—the connection of orbit parameters with quantum numbers—can be traced in the wave functions of quantum mechanics. But that will be another story.) Emphasizing the difference between quantum mechanics and the old quantum theory may have been appropriate in the late 1920s but it serves little purpose today. Seeking instead common ground benefits the learning—and understanding—of quantum theory.

IX. APPENDIX: AUTOBIOGRAPHICAL NOTE

How did I get involved with the old quantum theory, eight decades after its fall? My involvement has deep roots and grew in a roundabout way. In my doctoral thesis at the University of Frankfurt, Germany, I had studied interatomic forces in silver halides—including AgBr, the traditional photographic material—in comparison with the much better understood alkali halides, like NaCl—table salt (Bucher 1984). The purpose was to employ such forces in calculations of crystal defects in order to elucidate the early stages of the photographic process (latent image). Information about certain lattice defects, such as atoms in an ionic crystal or an electron trapped at a vacancy ($F$ center), can be extracted from electron spin resonance (ESR) experiments. The ESR signal (hyperfine interaction) is proportional to the
square of the probing electron’s wave function, $|\psi(r_N)|^2$, at the position of a nucleus, $r_N$. When, as a post-doctoral fellow at the University of Kansas, I calculated such wave functions, Prof. Robert Friauf, my advisor, pointed out that ESR experiments can be regarded as “measuring” the wave function at the nuclear position. But when I searched the literature as to how close “at” the nucleus the probing electron was, I didn’t find any clarification.

A few years later, while teaching hyperfine interaction in my electrodynamics course at California State University, Fresno, I recognized that the situation can be formulated as a local-field problem in terms of atomic and nuclear scales, with averages over the latter. The formalism revealed that for an $l = 0$ electron, isotropic hyperfine interaction arises only from the presence of the electron inside its parent nucleus (Bucher 2000).

When around 2000 the opportunity arose to develop a conceptual quantum-physics course at my university, I jumped at it. Studying, in preparation, the old quantum theory’s failure to give the correct multiplet structure of the hydrogen atom, one sentence in Jammer’s magisterial treatment glared at me: “The old quantum theory could never resolve this inconsistency” (Jammer 1966). I had a strong hunch how to resolve it—and explain (isotropic) hyperfine interaction with the same stroke: by straight-line oscillations of the electron through the nucleus. Its formal development became a theory of the Coulomb oscillator (Bucher 2006). While this extension of the Bohr-Sommerfeld theory was formally pleasing, the energy of such Columb oscillators was nothing new—it agreed with those of the corresponding Bohr orbits (Bohr 1913a).

A different situation arose, however, for the hydrogen molecule ion, $H_2^+$. This entity falls into the gap between physics and chemistry. Accordingly it is little known in either community. In essence, physics stops at the hydrogen atom and chemistry starts at the hydrogen molecule, $H_2$. Hardly anybody seems responsible for $H_2^+$. Three notable exceptions are Pauling and Wilson’s classical quantum text (Pauling and Wilson 1935), Ruedenberg’s review article (Ruedenberg 1962), and Gutzwiller’s chaos text (Gutzwiller 1990). It was not until I read Enz’s biography of Wolfgang Pauli that I became aware of the history of the hydrogen molecule ion and Pauli’s failure to solve it with the old quantum theory (Enz 2002). Right away it occurred to me to apply the Coulomb oscillator to $H_2^+$—an electron swinging in a straight line through two separate protons. For large proton separations the results agreed closely with the quantum-mechanical solution, as well as with another semi-classical
treatment (Strand and Reinhardt 1979). Less satisfactory results for small proton separations alerted me to a second solution—lateral electron oscillation in the bisectorial plane—that, when taken into account, gave again good agreement with the exact, quantum-mechanical solution (Bucher 2006). It took me some time, though, to find justification for my double-solution procedure in the little-known Einstein quantization condition (Einstein 1917).

One major problem was left where the old quantum theory had failed—the helium atom. I made various, unsuccessful attempts of the Coulomb-oscillator approach. But when I finally succeeded with contra-linear oscillations, I was dumbfounded to obtain the same ground-state energy as Bohr with his original, two-seat roundabout model of $He$ (Bohr 1913b). However, subsequent explorations of both crossed and contra-linear oscillations yielded on the one hand a ground-state energy that is comparable in accuracy with the quantum-mechanical solution and, on the other hand, revealed Bohr’s historical value as the quantum-statistically forbidden triplet ground state of $He$ (Bucher 2007).

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