Revisiting Bohr's Semiclassical Quantum Theory[†]

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Bohr's atomic theory is widely viewed as remarkable, both for its accuracy in predicting the observed optical transitions of one-electron atoms and for its failure to fully correspond with current electronic structure theory. What is not generally appreciated is that Bohr's original semiclassical conception differed significantly from the Bohr–Sommerfeld theory and offers an alternative semiclassical approximation scheme with remarkable attributes. More specifically, Bohr's original method did not impose action quantization constraints but rather obtained these as predictions by simply matching photon and classical orbital frequencies. In other words, the hydrogen atom was treated entirely classically and orbital quantized emerged directly from the Planck–Einstein photon quantization condition, $E = h\nu$. Here, we revisit this early history of quantum theory and demonstrate the application of Bohr's original strategy to the three quintessential quantum systems: an electron in a box, an electron in a ring, and a dipolar harmonic oscillator. The usual energy-level spectra, and optical selection rules, emerge by solving an algebraic (quadratic) equation, rather than a Bohr–Sommerfeld integral (or Schroedinger) equation. However, the new predictions include a frozen (zero-kinetic-energy) state which in some (but not all) cases lies below the usual zero-point energy. In addition to raising provocative questions concerning the origin of quantum-chemical phenomena, the results may prove to be of pedagogical value in introducing students to quantum mechanics.

1. Introduction

The early development of quantum mechanics was marked by over two decades of bold speculation, aimed at repairing glaring disagreements between classical predictions and experimental measurements. The ensuing debate generated a fascinating plethora of proposals regarding the fundamental constituents underlying macroscopically observable phenomena. Revisiting this early discussion can shed new light on the current canonical conception of quantum theory. One of the abandoned threads in this conversation suggests an alternative semiclassical formulation with striking attributes, in terms of both its conceptual and mathematical transparency as well as the remarkable agreement of its predictions with the stationary states of bound electrons and optical selection rules.

The most famous failure of classical electrodynamics and thermodynamics pertains to the spectra of so-called blackbodies, which in fact closely resemble coals glowing in a campfire and the light emitted by stars overhead. Classical theory predicted that the intensity of the light radiated by such bodies should increase with increasing frequency, while experiments invariably showed intensities decreasing to zero at the highest frequencies. Planck resolved the discrepancy in $1900,^3$ by postulating that the energy emitted at each blackbody frequency, ν , is quantized in packets of $h\nu$, with a universal constant of proportionality, h, which now bears his name. However, it was initially far from clear whether the required quantization should be attributed to light or to the material from which the glowing body is composed, or both.

An important clarification of the above question was suggested by Einstein in the first of his three famous papers written

in 1905,⁴ in which he presented various arguments all leading to the conclusion that light itself is quantized in packets of energy, *hv*. The following are his own words (in translation) from the introduction to that paper.⁵

It seems to me that the observations associated with blackbody radiation, fluorescence, the production of cathode rays by ultraviolet light, and other related phenomena connected with the emission or transformation of light are more readily understood if one assumes that the energy of light is discontinuously distributed in space. In accordance with the assumption to be considered here, the energy of a light ray spreading out from a point source is not continuously distributed over an increasing space but consists of a finite number of energy quanta which are localized at points in space, which move without dividing, and which can only be produced and absorbed as complete units.

At the end of the above paper, Einstein noted that the quantization of light could explain the so-called photoelectric effect, in which electrons are ejected when a metal surface is irradiated with light. The problematic feature of the associated experimental observations was that the kinetic energies of the ejected electrons were found to be proportional to the frequency of the light, rather than its intensity. Einstein pointed out that this apparently paradoxical phenomenon can readily be understood if it is assumed that light is composed of particle-like photons with energy $h\nu$. These speculations were not widely embraced for over a decade, until Millikan reported the results of additional key experiments. The following extended quotation from the introduction of Millikan's 1916 paper, entitled *A Direct*

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Photoelectric Determination of Planck's h, provides an interesting glimpse into the prevailing view of Einstein's photon postulate.

Quantum theory was not originally developed for the sake of interpreting photoelectric phenomena. It was solely a theory as to the mechanism of absorption and emission of electromagnetic waves by resonators of atomic or subatomic dimensions. It had nothing to say about the energy of an escaping electron or about the conditions under which such an electron could make its escape, and up to this day the form of the theory developed by its author has not been able to account satisfactorily for the photoelectric facts presented herewith. We are confronted, however, by the astonishing situation that these facts were correctly and exactly predicted nine years ago by a form of quantum theory which has now been pretty generally abandoned.

It was in 1905 that Einstein made the first coupling of photo effects and [sic] with any form of quantum theory by bringing forward the bold, not to say reckless, hypothesis of an electro-magnetic light copuscle of energy $h\nu$, which energy was transferred upon absorption to an electron. This hypothesis may well be called reckless first because an electro-magnetic disturbance which remains localized in space seems a violation of the very conception of an electromagnetic disturbance, and second because it flies in the face of the thoroughly established facts of interference. The hypothesis was apparently made solely because it furnished a ready explanation of one of the most remarkable facts brought to light by recent investigations, viz., that the energy with which an electron is thrown out of a metal by ultra-violet light or X-rays is independent of the intensity of the light while it depends on its frequency. This fact alone seems to demand some modification of classical theory or, at any rate, it has not yet been interpreted satisfactorily in terms of classical theory.

Even after Millikan's paper and after Einstein received a Nobel prize "for his service to theoretical physics and particularly for his discovery of the law of the photo-electric effect", the subject of photon quantization remained, and continues to be, an active and interesting area of research, all the results of which are entirely consistent with Einstein's original proposal. However, Einstein himself apparently retained some concerns about the photon concept, as illustrated by the following quotation from the end of his 1917 paper entitled *On the Quantum Theory of Radiation*7 (which is most famous for predicting stimulated emission, long before the development of lasers).

These properties of elementary particles...make the formulation of a proper quantum theory of radiation appear almost unavoidable. The weakness of the theory lies on the one hand in the fact that it does not get us any closer to making the connection with wave theory; on the other, that it leaves the duration and direction of the elementary processes to 'chance'. Nevertheless I am fully confident that the approach chosen here is a reliable one.

At around the same time that Millikan was doing his experiments (actually a couple of years earlier, and on another continent), Niels Bohr introduced his atomic theory, which deftly wed classical and quantum physics. His theory proved to be stunningly successful, not only in accurately predicting the

spectrum of hydrogen but also in correctly assigning astronomical absorption lines of previously unknown origin to helium cations. Although Bohr's atomic theory has been overshadowed by our current view of quantum mechanics, the following quotation from an interview with Einstein reveals the high regard with which he still held Bohr's theory many years after it had fallen out of favor.⁸

That this insecure and contradictory foundation was sufficient to enable a man of Bohr's unique instinct and perceptiveness to discover the major laws of the spectral lines and of the electron shells of the atom as well as their significance for chemistry appeared to me like a miracle and appears as a miracle even today. This is the highest form of musicality in the sphere of thought.

What Bohr suggested in his seminal 1913 paper9 was a deceptively simple application of the Planck-Einstein photon quantization constraint imposed on a classical electron rotating around a nucleus. Bohr simply required that the electron could only absorb or emit light in quanta of energy, hv. A key conceptual difficulty was that this required electrons to jump discontinuously from orbits of one radius and frequency to orbits of an entirely different radius and frequency, with no possibility of occupying any intervening states. A fully classical rotating electron, in contrast, was predicted to emit light whose frequency is equal to its rotational frequency, and to gradually lose energy, and thus also gradually change its emission frequency (and radius) as it did so. If an electron was to jump from one frequency to another, it was not clear what frequency of light it should emit (or absorb). Bohr suggested that it makes good sense to assume that the light that induces a transition between two states should have a frequency that is the arithmetic mean of the actual rotational frequencies of the electrons in the two states. More specifically, Bohr envisioned starting with a motionless electron that is far removed from the nucleus, so that it is no longer bound or rotating. He then imposed the Planck-Einstein photon quantization condition by requiring that the fundamental transition which such a electron could make is one which ensures both that the energy of the transition is equal to $h\nu$ and that the frequency of the electron in the final state is $v_{\rm f}=2\nu$. The latter restriction arose naturally from his meanfrequency postulate which required that $\nu = (\nu_f + \nu_i)/2$ (recalling that $v_i = 0$ is the frequency of the initial, motionless, unbound state). Moreover, he justified his mean-frequency assumption by showing that it is the only possible relationship between the photon and electron frequencies which is consistent both with the experimental Rydberg formula and with classical predictions applied to transitions between the highest energy (most closely spaced) hydrogen orbitals. With no more than the above combination of elementary assumptions, he was able to correctly predict the ground state energy of the hydrogen atom as well as the value of Rydberg's constant (in terms of Planck's constant and the charge and mass of an electron).

Contrary to presentations of Bohr's theory which are often encountered in textbooks, Bohr did not impose any additional assumptions in obtaining his original prediction of the hydrogen spectrum. For example, his conclusion that electron's have quantized values of angular momentum was a *prediction* that emerged as a natural consequence of the above assumptions, rather than an additionally imposed condition. However, he later decided that momentum quantization was a more universally applicable constraint and so elevated it to the status of a primary postulate (as further discussed in section 3). Moreover, although Bohr initially considered only circular electron orbitals, Sommerfeld later relaxed that restriction and in so doing correctly

predicted the existence of orbitals with different magnetic quantum numbers. ¹⁰ It is also noteworthy that Bohr's analysis of the hydrogen spectrum made use of the classical virial theorem, ¹¹ which requires that any particle bound by a power-law potential of the form $U(r) \propto r^a$ must obey the following relation between the time average, $\langle ... \rangle$, of its potential, V, and kinetic, K, energies: $\langle K \rangle = (a/2)\langle V \rangle$. Thus, Bohr predicted that $\langle K \rangle = -(1/2)\langle V \rangle$ for an electron in a coulomb potential, which is also consistent with current quantum theory predictions.

Although Bohr's atomic model has been superseded by modern molecular structure theory, many of his ideas continue to generate interest from various perspectives. 12-15 Particularly noteworthy is a recent flurry of activity surrounding the applications of dimensional scaling to Bohr's theory of molecular bonding. 16-18 Such studies, although quite different from those described here, clearly attest to the continued fruitfulness of Bohr's fantastic ideas.

The present paper is devoted to demonstrating that Bohr's seminal conception can be applied with remarkable success to other quantum mechanical problems which are now well-known, but to which Bohr apparently did not apply his original approach. More specifically, we focus on three fundamental systems, each of which are among the first introduced to students of modern quantum mechanics: a particle in a box, a particle in a ring, and a harmonic oscillator. The motivation for revisiting these problems from a new (old) perspective is to highlight the fact that a wide range of quantum phenomena involving atoms and molecules can emerge very naturally from the quantization of light, without attributing any wavelike properties to particles. Thus, the present results, like Bohr's original atomic theory, imply that quantizing both light (photons) and particles (wave functions) is in some respects redundant. In other words, one may quantize molecular energies simply by requiring that all electromagnetic energy exchanges obey the Planck-Einstein photon quantization conditions, without ever invoking either the de Broglie relation, the Schroedinger equation, or the Born probability postulate.

2. Quantization of Simple Model Systems

Electron in a Ring. The elementary quantum mechanical problem which is closest to the Bohr atom is that of an electron rotating in a circular ring with a fixed radius. This is clearly much simpler than the Bohr atom, as the electron in a ring is two-dimensional rather than three-dimensional and has a fixed radius. It also differs from the Bohr atom in that the electron cannot be dissociated to the nonrotating state which Bohr used as a starting point for his quantization argument. Moreover, unlike the hydrogen atom, the electron in a ring has a constant potential energy and thus is classically allowed to have any frequency, including zero, while remaining confined to the circle of fixed radius.

Bohr's requirement that the frequency of an absorbed photon must match the mean rotational frequency of the classical electron in the initial and final states, combined with the Planck–Einstein photon energy quantization condition, $E=h\nu$, amounts to requiring that the frequencies of any optically coupled states of an electron in a ring must obey the following relation.

$$h\nu = \hbar\omega = \hbar \left(\frac{\omega_{\rm f} + \omega_{\rm i}}{2}\right) = \frac{I}{2}(\omega_{\rm f}^2 - \omega_{\rm i}^2) \tag{1}$$

If we envision starting with an electron in a frozen (zero-angular-momentum) state with $\omega_0 = 0$, just as Bohr did, then the above

expression predicts that such an electron could only absorb a photon with a circular frequency of $\omega = 2\pi\nu = (\hbar/2I)$, where $I = m_{\rm e}r^2$ is the moment of inertia of the electrons. Thus, the first excited state of an electron is predicted to have a classical rotational frequency of $\omega_1 = (\hbar/I)$, a kinetic energy of $(^1/_2)I\omega_1^2 = (\hbar^2/2I)$, and an angular momentum of $I\omega_1 = \hbar$. Notice that the above two states are precisely the same ones which arise when solving the Schroedinger equation for an electron in a ring, which is predicted to have an optically allowed transition from a ground state of energy $E_0 = 0$ to a first excited state of energy $E_1 = (\hbar^2/2I)$.

The above procedure may be repeated, starting with E_1 as the initial state, to find the next optically allowed transition to a state of energy $E_2 = (2\hbar/I)$ (obtained by assuming $\omega_i = \omega_1$ and solving the quadratic equation that emerges from eq 1 to find $\omega_f = \omega_2$). More generally, the following recursive relation predicts the frequency ω_f of each subsequent state that can be reached from a previously obtained initial state of frequency ω_f

$$\omega_{\rm f} = \frac{1}{2} \left[\frac{\hbar}{I} + \sqrt{\left(\frac{\hbar}{I}\right)^2 + 4\left(\frac{\hbar\omega_{\rm i}}{I} + \omega_{\rm i}^2\right)} \right] \tag{2}$$

Thus, we easily obtain the following series of electron stationarystate rotational frequencies and energies.

$$\omega_n = \frac{n\hbar}{I}$$

$$E_n = \frac{1}{2}I\omega_n^2 = \frac{n^2\hbar^2}{2I}$$

$$n = 0, 1, 2, 3, ...$$
(3)

Notice that all of the above energies are exactly the same as those obtained by solving the corresponding Schroedinger equation.

Electron in a Box. A classical electron confined to a onedimensional box (such as an ideal thin wire) can also be treated using Bohr's semiclassical method. Since this electron is again assumed to have a uniform potential energy, only kinetic energy distinguishes different states of the electron. A classical electron of velocity v_j has a kinetic energy of $E_j = (1/2)m_ev_j^2 = (p_j^2/2m_e)$. When confined to a box of length L, such an electron must necessarily bounce back and forth with a (nonsinusoidal) fundamental frequency of $v_j = (1/2L)v_j$ (or $\omega_j = (\pi/L)v_j$). Thus, the kinetic energy of such an electron may be expressed in terms of its frequency, $E_j = 2m_eL^2v_j^2$.

Imposing the Planck-Einstein photon quantization and Bohr mean-frequency relations, one obtains the following relation for the final states of frequency ν_f which are optically accessible to the electron in a box with an initial frequency of ν_i .

$$h\nu = h \left(\frac{\nu_{\rm f} + \nu_{\rm i}}{2}\right) = 2m_{\rm e}L^2(\nu_{\rm f}^2 - \nu_{\rm i}^2) \tag{4}$$

The lowest energy that such a classical electron can have is one with no kinetic energy, and thus with $\nu_0 = 0$ and $E_0 = 0$. By applying eq 4 to this zero-kinetic-energy state, we obtain the following electron round trip frequency and kinetic energy for the only state which is optically accessible from E_0 : $\nu_1 = (h/4m_{\rm e}L^2)$ and $E_1 = (h^2/8m_{\rm e}L^2)$.

Repeated application of eq 4 yields the following recursive expression for the electron round trip frequency of the next final state, $\nu_{\rm f}$, which is optically accessible from an initial state of frequency $\nu_{\rm i}$.

$$\nu_{\rm f} = \frac{1}{2} \left\{ \left(\frac{h}{4m_{\rm e}L^2} \right) + \sqrt{\left(\frac{h}{4m_{\rm e}L^2} \right)^2 + 4\nu_{\rm i} \left[\left(\frac{h}{4m_{\rm e}L^2} \right) + \nu_{\rm i} \right]} \right\} (5)$$

Thus, the following sequence of allowed electron round trip frequencies and energies is obtained.

$$\nu_{n} = \frac{nh}{4m_{e}L^{2}}$$

$$E_{n} = \frac{n^{2}h^{2}}{8m_{e}L^{2}}$$

$$n = 0, 1, 2, 3, ...$$
(6)

Clearly, the above energy spectrum is again identical to that obtained from the corresponding Schroedinger equation, except for the additional frozen (n = 0) state.

Harmonic Oscillator. A similar Planck-Einstein-Bohr analysis may be performed on a classical harmonic oscillator, such as an ideal dipolar diatomic molecule. In this case, the motion is equivalent to that of a mass, $\mu = (m_1 m_2/(m_1 + m_2))$ (with a partial charge, δq), moving in a central harmonic potential, $U(r) = (1/2)kr^2$ (where k is the harmonic force constant, m_1 and m_2 are the atomic masses, and r is the diatomic bond length). Thus, the total energy (Hamiltonian, H) of such a particle in a given state is the sum of its potential, V, and kinetic, K, energies, $H_i = V_i + K_i = (1/2)kR_i^2$, where R_i is the maximum amplitude of the particle. Note that the classical virial theorem further requires that for each state of the oscillator with a given total energy of $\langle V_i \rangle = \langle K_i \rangle = (1/2)H_i$ (since a = 2 for a harmonic potential). Another important feature of such a harmonic system is that the classical particle has a sinusoidal oscillation frequency of $\omega_0 = 2\pi \nu_0 = (k/\mu)^{1/2}$, which is independent of the amplitude of vibration of the particles (for any nonzero amplitude).

Imposing the usual Planck—Einstein—Bohr conditions produces the following restrictions on the optically allowed transitions of any such harmonically oscillating system.

$$h\nu = \frac{h}{2}(\nu_{\rm f} + \nu_{\rm i}) = \frac{1}{2}k(R_{\rm f}^2 - R_{\rm i}^2)$$
 (7)

If we again envision starting with the system in a frozen ($R_0 = 0$, $E_0 = 0$) state, we obtain an energy of $E_1 = (1/2)h\nu_0$ for the first optically accessible state, which is also identical to the usual zero-point energy of the harmonic oscillator. More generally, we obtain the following simple recursion relation for the sequence of final states which are accessible from a given initial state (with i > 0).

$$E_{\rm f} = E_{\rm i} + h\nu_0 \tag{8}$$

In other words, the following general expression is obtained for the allowed energy levels of the Planck-Einstein-Bohr semiclassical harmonic oscillator.

$$E_0 = 0$$

$$E_n = h\nu_0 \left(n - \frac{1}{2} \right) = h\nu_0 \left(\nu + \frac{1}{2} \right)$$

$$n = \nu + 1 = 1, 2, 3, ...$$
(9)

Note that, once again, the above energy spectrum is identical to that obtained by solving the Schroedinger equation, except

for the additional frozen (n = 0) state (and the trivial shift in n relative to the traditional harmonic oscillator quantum number label, ν).

3. Discussion

The energy-level spectra obtained using Bohr's original semiclassical procedure, when applied to three rudimentary chemical model systems, are found to be essentially identical to those obtained by solving the corresponding Schroedinger equation. A key distinction between this approach and the Bohr-Sommerfeld and Wentzel-Kramers-Brillouin (WKB) semiclassical formulations¹⁹⁻²¹ is that electrons are treated entirely classically while photon quantization imposes an algebraic restriction on optically allowed transitions. Thus, although Bohr's original conception derives from different physical assumptions than the latter theories, and leads to an entirely different mathematical formulation, the predicted optical transitions are nevertheless remarkably consistent with the corresponding Schroedinger eigenvalues. However, the semiclassical stationary-state energies include a frozen (zero-kineticenergy) state, which may or may not be experimentally observable. For the particle in a box and harmonic oscillator, these frozen states correspond to eigenfunctions of the Schroedinger Hamiltonian with zero area (and so are not normalizable). However, the semiclassical frozen state of a particle in a ring corresponds to the normalizable Schroedinger ground-state eigenfunction with zero angular momentum.

The semiclassical analysis also reproduces exactly the same selection rules as those obtained from the Schroedinger transition dipole integrals. In other words, only transitions with quantum number changes of $\Delta n=\pm 1$ are allowed for all three of the model systems. Although only the absorption transitions have been explicitly considered, the equations are clearly symmetric with respect to absorption and emission (which simply requires swapping the frequencies ω_i and ω_f). It is also intriguing to note that the optically allowed transitions of the electron in a ring imply that only angular momentum changes of $\pm \hbar$ are optically allowed. Thus, although photon spin was not introduced, the semiclassical solution is consistent with photons having a spin quantum number of 1, as predicted by relativistic quantum field theory.²²

Notice that the stationary-state energies obtained using the Bohr semiclassical theory are not the only frequencies which satisfy the Planck—Einstein photon quantization constraint (eqs 1, 4, and 7). What makes the Bohr stationary states special is that they are the only ones which can be accessed from the frozen state of each system, by a sequence of photon absorption steps. This implies that the Schroedinger eigenfunctions correlate with classical states that are optically coupled to a state of zero kinetic energy, thus attributing an additional physical significance to the term stationary states.

A physically appealing feature of the Bohr semiclassical stationary states is that they retain information about the absolute frequencies of the associated particle motions. Note that such information is absent from the standard quantum mechanical description, as only energy differences and frequencies of the corresponding transition dipole matrix elements are predicted, while questions pertaining to the actual frequency of particles in a given stationary state are not addressed. On the other hand, as Bohr has demonstrated, the closely spaced optical transition frequencies near the dissociation limit of hydrogen approach the corresponding classical electron rotational frequencies. Moreover, the optical absorption frequencies of a dipolar harmonic oscillator exactly match the corresponding classical

vibrational frequencies. Thus, Bohr's theory extends the connection between optical and particle frequencies to all stationary states in a physically reasonable way. In other words, $\Delta E/h$ represents the classical frequency of the particle in a given stationary state (where ΔE is the energy spacing in the vicinity of that state).

Bohr's original mean-frequency postulate, which was used to obtain all of the results in section 2, was later replaced by an action quantization condition which Bohr viewed as more universally applicable. For any systems with a single degree of freedom, Bohr expressed the latter postulate as⁷

$$\oint p \, \mathrm{d}q = nh \tag{10}$$

where p and q are the conjugate momenta and position variables and the integral is performed over a single complete cycle of the periodically oscillating system. Notice that, when applied to uniform circular rotational motion, the above expression reduces to $\int_0^{2\pi} (mr\omega) r \, \mathrm{d}\phi = \int_0^{2\pi} I\omega \, \mathrm{d}\phi = 2\pi I\omega = nh$, and thus, $I\omega = n\hbar$, which is the usual Bohr angular momentum quantization condition. When applied to a particle in a box, the momentum integral becomes $\oint (2m_{\rm e}E_n)^{1/2} \, \mathrm{d}x = \int_0^{2L} (nh/2L) \, \mathrm{d}x = nh$. Thus, the mean-frequency and action quantization assumptions are apparently self-consistent, at least when applied to the above two problems.

The harmonic oscillator is a somewhat more interesting case for several reasons. On one hand, this is the system which played a central role in Planck's blackbody radiation theory (as well as Einstein's solid heat capacity theory). In addition, this is the system which Bohr used to motivate the general validity of eq 10.7 On the other hand, the old quantum theory harmonic oscillator spectrum is usually expressed as $E_n = nh\nu_0$, rather than by eq 9, although the latter predictions were here obtained using Bohr's original mean-frequency postulate (and are in better agreement with the energy-level structure predicted using the Schroedinger equation). However, it turns out that the spectrum in eq 9 does not conform exactly with the momentum quantization condition expressed in eq 10. More specifically, the energies in eq 9 produce $\oint p \, dq = 2E_n \int_0^{1/\nu_0} \cos^2(2\pi\nu_0 t) \, dt = (n - (1/2))h$ (for $n \ge 1$). This appears to imply that the mean-frequency assumption is in some respects more consistent with Schroedinger wave mechanics than the action quantization condition. However, it should also be noted that the correct zero-point energy and action quantization are predicted for harmonic oscillators (and other potentials) using the semiclassical WKB theory²⁰ (i.e., by including the Maslov index, Langer modification, and extensions thereof).²³

As Bohr was well aware, the mean-frequency condition is also not universally applicable. For instance, in his 1918 paper entitled *On the Quantum Theory of Line Spectra*, Bohr states⁷

...we cannot expect a simple connection between the frequency...of the radiation corresponding to a transition between two stationary states and the motions of the system in these states, except in the limit where n is very large, and where the ratio between the frequencies of the motion in successive stationary states differs very little from unity....

In other words, although Bohr used the mean-frequency condition to correctly predict all of the stationary-state energies of hydrogen, he recognized the limitations of this assumption. In fact, even for the hydrogen atom, only certain optical transitions obey a strict arithmetic mean relation between the frequency of the electron in the two states and the frequency of

the light that induces the transition. The transitions that do conform with the arithmetic mean condition are those that are directly coupled to the nonrotating (frozen) state by an integral multiple of $h\nu$ as well as transitions between the highest energy states of hydrogen (near the dissociation limit). For other transitions between the classical Bohr orbits, the frequency of the light that induces the transition remains intermediate between the frequencies of the electrons in the two classical orbits, but not always at the arithmetic mean of the two. Thus, neither the mean-frequency nor the momentum quantization conditions are universally applicable.

The agreement between the results obtained in section 2 and full quantum mechanical predictions may be linked to the fact that the classical energies of such systems depend quadratically (or linearly) on the frequency of the corresponding classical motion. For any such system, an expansion of the energy about the mean frequency, $\nu_{\rm m} = (\nu_{\rm f} + \nu_{\rm i})/2$, implies that $E(\nu_{\rm f}) - E(\nu_{\rm i}) = (\partial E/\partial \nu)_{\nu_{\rm m}}(\nu_{\rm f} - \nu_{\rm i})$. Although third and higher order (odd) derivatives contribute to the corresponding expansion of non-quadratic systems, the shape invariant properties of a broad class of potentials²⁴ provide a strategy for extending the results in section 2 to such systems. More generally, it will be interesting to see whether the present method can be extended to treat multielectron systems as well as other quintessential quantum phenomena such as diffraction and tunneling, as an alternative to current semiclassical approximation strategies. $^{20,21,25-30}$

Regardless of whether the present approach proves to be of broader theoretical interest, it may be of pedagogical utility in helping students build on their classical physical intuition as they initially confront the world of quantum phenomena. In other words, Bohr's original semiclassical description provides a path along which students may gently step into quantum mechanics while initially retaining their understanding of how billiard balls and pendulums behave, as they grow to appreciate the remarkable quantum properties of light. Having gone through this exercise, perhaps students will be more receptive to appreciating the fact that the eigenvalues of the partial differential Schroedinger Hamiltonian are often identical to those obtained from a simpler semiclassical algebra. This, combined with comparisons between the Schroedinger eigenfunctions and classical vibrating guitar strings and drum heads (which arise from very similar wave equations), might serve to evoke a degree of aesthetic appreciation, or maybe even a taste of the unique satisfaction that accompanies an emerging understanding.

From a philosophical perspective, the agreement between the semiclassical and full quantum mechanical energy-level spectra appears to imply that our current view of quantum mechanics may in some sense be overconstrained, as many of the same phenomena can apparently be obtained directly from the quantization of electromagnetic energy exchanges. On the other hand, the appearance of frozen states which defy uncertainty-principle limits suggests that quantization of both particles and light may be the minimum formulation required to fully conform with experimental observations.

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