Quantum jumps and classical harmonics

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We present an introduction to quantum mechanics based on the formal correspondence between the atomic properties of quantum jumps and the classical harmonics of the electron's periodic motion. By adding a simple quantum condition to the classical Fourier analysis, we readily find the energies of the stationary states, calculate the transition probabilities between the states, and construct the line spectrum of the emitted light. We provide examples to illustrate the asymptotic, and sometimes exact, agreement between the classical-quantum results (Fourier harmonics) and the exact quantum results (Heisenberg harmonics). © *2002 American Association of Physics Teachers.*
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I. INTRODUCTION

In quantum theory, the mechanical behavior of an atom is characterized by two fundamental quantities: E_n, the energy of the stationary state n, and A_{nm}, the probability per unit time to spontaneously jump from state n to state m. In spectroscopic experiments, the basic quantity measured is the radiation emitted by the atom—the line spectrum. Quantum theory relates the mechanical properties (E_n and A_{nm}) of the atom to the spectral properties (frequency and intensity) of the emitted light. In particular, the energy of the transition, $E_n - E_m$, determines the frequency of the emitted light, and the probability of the transition, A_{nm}, determines the intensity.

A remarkable fact is that every quantum transition between two stationary states in an atom corresponds to a certain Fourier component of the electron motion.[1] In particular, the jump energy and jump probability correspond to the harmonic frequency and harmonic amplitude, respectively. It is ironic that one of the most nonclassical concepts in quantum mechanics, namely the quantum jump, possesses properties that correspond most directly to classical properties. This correspondence played a crucial role in the development of quantum mechanics, but has lost its prominence in the modern presentation of the subject. The correspondence between classical and quantum mechanics can provide insight into both subjects.[2–5]

In an introductory course on quantum mechanics, there is much discussion of quantum states and energies, but much less discussion of transitions and line intensities. Students learn how to calculate energy levels, but seldom calculate transition probabilities. Knowledge of E_n alone allows one to calculate the frequencies, but not the intensities of the spectral lines. In the original formulation of quantum theory by Einstein, Bohr, Heisenberg, Born, and Jordan,[6] the transition probability was a central object of the theory, and the calculation of the spectral lines was a primary application of the theory. Indeed, the hallmark of quantum mechanics is its ability to explain the spectral signature of atoms.

In this paper, we present an introductory approach to quantum mechanics that focuses on quantum-jump concepts and line-spectra applications. It is based on the correspondence between quantum transitions and classical harmonics. This "classical-quantum" theory elucidates the deep connection between classical and quantum mechanics. Using this theory, a student can learn how to calculate transition rates, selection rules, and line spectra at the very beginning of the course. In the traditional quantum course, these important observables usually appear near the end, because their calculation requires heavy-duty, quantum-theoretical technology. In the classical-quantum theory, there are no wave functions, wave equations, or operators. Furthermore, there are no eigenvalue problems to solve or matrix elements to calculate. Instead, there are only Bohr postulates and Fourier series. The calculation of a quantum-mechanical observable consists of the simple quantization of a classical-mechanical Fourier series. The results of this "Bohr–Fourier" theory are in close or exact agreement with the Heisenberg–Schrödinger results.

II. HARMONIC VERSUS ATOMIC SPECTRA

Is there a relation between the orbital motion of the electron in an atom and the properties of the light emitted by the atom? The search for the answer to this question played an important part in the development of quantum mechanics.

A glimpse into the connection between orbital and optical frequencies can be obtained by considering the well-known spectrum of the hydrogen atom. The frequency of the radiation emitted by a hydrogen atom during the transition $n \to m$ is $\omega_{nm} = K(1/m^2 - 1/n^2)$, where K is a constant. For the transitions, $5 \to 4$, $5 \to 3$, $5 \to 2$, $5 \to 1$, the relative frequencies are ω', $3.2\omega'$, $9.3\omega'$, $43\omega'$, respectively ($\omega' \equiv \omega_{5,4}$). For the transitions, $500 \to 499$, $500 \to 498$, $500 \to 497$, $500 \to 496$, the relative frequencies are ω, 2.0ω, 3.0ω, 4.0ω, respectively ($\omega \equiv \omega_{500,499}$). Thus, for large quantum numbers, the atomic spectrum coincides with a harmonic spectrum. Such a harmonic spectrum, or Fourier spectrum, is the optical consequence of an underlying mechanical periodicity. Classically, the hydrogen atom is a periodic system consisting of an electron orbiting around a proton in an elliptical path. The periodic elliptical motion can be resolved into a set of harmonic vibrations of frequencies equal to ω, 2ω, 3ω, $4\omega,...$. The frequency ω of the light emitted during the quantum jump $500 \to 499$ is numerically equal to the rotational frequency of the electron in the initial (or final) elliptical orbit. The "octave" 2ω of the revolution frequency matches the radiation frequency for the quantum jump $500 \to 498$. Thus, in this region, there is an intimate connection between quantum jumps and classical harmonics: the "fundamental tone" ω of the elliptical motion is emitted during the 1-state quantum jump, while the "overtones" 2ω, 3ω, $4\omega,...$ are

emitted during the 2-state, 3-state, 4-state jumps, etc., respectively. We now turn to the general physical principles of classical and quantal spectra.

In classical physics, the emission of electromagnetic radiation is associated with the accelerated motion of an electric charge. Consider a one-dimensional system consisting of an electron undergoing periodic motion. This system represents a simple model of an atom. The periodic motion of the electron is the dynamical trademark of a classical atom. Periodic motion is synonymous with Fourier series.[7] If the fundamental frequency of the periodic motion is ω, then the position $x(t)$ of the electron can be represented by the Fourier series

$$x(t) = a_1 \cos \omega t + a_2 \cos 2\omega t + a_3 \cos 3\omega t + \cdots. \qquad (1)$$

Mechanically speaking, $x(t)$ is the solution of Newton's equation of motion. The motion $x(t)$ is expressed as a superposition of harmonic or Fourier components. The τth harmonic, $a_\tau \cos \omega_\tau t$, is characterized by an amplitude a_τ and a frequency $\omega_\tau = \tau\omega$. The spectrum of harmonic frequencies, ω, 2ω, 3ω, etc., consists of integer multiples of the fundamental frequency—the spectral trademark of a Fourier series.

According to classical electrodynamics, the spectroscopic frequencies of the radiation are identical to the mechanical frequencies ω, 2ω, 3ω, etc., that characterize the motion of the electron. The intensity of the wave of frequency $\tau\omega$ is proportional to the square of the acceleration of the τth harmonic, namely $(a_\tau \omega_\tau^2)^2 \cos^2 \omega_\tau t$. As the electron radiates, it loses mechanical energy and its motion is no longer periodic. This nonperiodic motion has a continuous spectrum of frequencies. However, if the lost energy is negligible compared to the initial energy, then the decay can be neglected. In this case, the "spiraling" motion is accurately represented by periodic motion—the same periodic motion of fundamental frequency ω which characterizes the initial state and is described by the Fourier series $x(t)$. Thus a high-energy classical atom emits a discrete (harmonic) line spectrum, ω, 2ω, 3ω, etc.

In quantum physics, the emission of radiation is due to the discontinuous jump of the electron between discrete quantum states, rather than the continuous accelerated motion of the electron. The occurrence of a quantum jump is determined by the transition probability. The radiation emitted during the transition $n \rightarrow m$ has a single frequency ω_{nm}. During the jump, the lost mechanical energy, $E_n - E_m$, appears as a light quantum (photon) of energy $\hbar\omega_{nm}$. By conservation of energy, $E_n - E_m = \hbar\omega_{nm}$. Because one photon produces an instant flash of one spectral line, the complete line spectrum is generated only if there are many atoms emitting many photons. The number of photons of frequency ω_{nm} that arrive per unit time at a given line location in the spectrometer determines the line intensity. Thus, the line intensity is determined by the number of "jumping" electrons, or equivalently, the transition rate A_{nm}. In contrast, the complete classical spectrum is generated by the deterministic motion of a single orbiting electron.

Given an ensemble of atoms each in state n, the power P_{nm} of the light associated with the transition $n \rightarrow m$ is defined as the amount of energy emitted per unit time per atom by the entire ensemble

$$P_{nm} \equiv \frac{1}{N_n} \frac{\Delta E_{nm}}{\Delta t}. \qquad (2)$$

In this expression, N_n is the number of atoms in state n, and ΔE_{nm} is the total amount of energy emitted by these atoms in time Δt due to transitions $n \rightarrow m$. By conservation of energy, it follows that $\Delta E_{nm} = \Delta N_{nm} \hbar \omega_{nm}$, where ΔN_{nm} is the number of atoms that jump from $n \rightarrow m$ in time Δt and $\hbar \omega_{nm}$ is the energy radiated per jump. For large N_n, the fraction of atoms that jump is equal to the probability for one atom to jump, $\Delta N_{nm}/N_n = A_{nm}\Delta t$. Hence, Eq. (2) becomes

$$P_{nm} = A_{nm} \hbar \omega_{nm}. \qquad (3)$$

This relation implies that bright lines are due to highly probable transitions and faint lines are due to improbable transitions.

Let us summarize the classical (harmonic) and quantal (atomic) spectra. The classical spectrum of a "Fourier atom" in a periodic state of motion consists of a harmonic series of evenly spaced lines (ω, 2ω, 3ω,...). Each line is associated with a Fourier component of the motion and labeled by the harmonic number ($\tau = 1,2,3,...$). The frequency ω_τ and relative intensity I_τ of the τth line satisfy the Fourier–Maxwell relations:

$$\omega_\tau = \tau\omega, \quad I_\tau = a_\tau^2 \omega_\tau^4. \qquad (4)$$

The mechanical quantities, ω_τ and a_τ, are calculated by solving Newton's equation of motion.

In contrast, the quantum-mechanical spectrum of a collection of atoms, initially in state n, consists of lines that are not evenly (harmonically) spaced—the optical frequencies do not equal the orbital frequencies. Each transition line is associated with a quantum jump and labeled by two quantum numbers (n, m). The frequency ω_{nm} and relative intensity I_{nm} of the nmth line satisfy the Einstein–Bohr relations:[8]

$$\omega_{nm} = \frac{1}{\hbar}(E_n - E_m), \quad I_{nm} = A_{nm}\omega_{nm}. \qquad (5)$$

The mechanical quantities, E_n and A_{nm}, are calculated by solving Schrödinger's equation.

Although the spectral frequencies, $\omega_{nm} = (E_n - E_m)/\hbar$, are not integer multiples of a fundamental frequency, they do satisfy a certain pattern of regularity. Any two frequencies can be combined (added) to produce another frequency according to the Rydberg–Ritz combination law:[9]

$$\omega_{nk} + \omega_{km} = \omega_{nm}, \qquad (6)$$

in agreement with experiment. The Rydberg–Ritz combination law is the quantum-mechanical analogue of the classical "Fourier combination law," $\omega_\tau + \omega_\sigma = \omega_{\tau+\sigma}$.

Although the harmonic spectrum in Eq. (4) differs from the atomic spectrum in Eq. (5), there is a domain where atoms radiate harmonics as illustrated in Fig. 1. One expects this classical behavior to emerge from the quantum picture as the magnitude of the quantum number increases, and in this limit, there must exist a connection between quantum jumps and classical harmonics. A comparison of Eqs. (4) and (5) suggests the following correspondence:

$$\omega_{nm} \leftrightarrow \omega_\tau, \quad A_{nm} \leftrightarrow a_\tau^2 \omega_\tau^3. \qquad (7)$$

The precise nature of this correspondence will be studied in the next two sections.
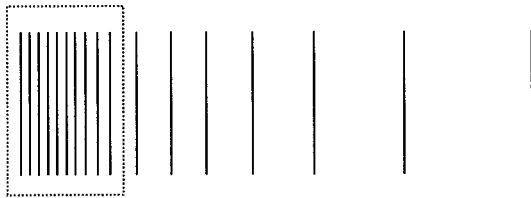
Fig. 1. For large quantum numbers (dashed box), the spectral lines are equally spaced ($\omega, 2\omega, 3\omega,...$) and thus obey Fourier's combination law—the atom radiates classical harmonics. In general, the spacing of lines obeys the Rydberg–Ritz combination law.

III. QUANTUM POSTULATES

Before introducing the postulates, we state the fundamental problem that these postulates are designed to answer. This all-encompassing problem is identical to the central problem addressed by Heisenberg in his original memoir,[10] that is, given $F(x)$, find ω_{nm} and A_{nm}. In other words, given a conservative force that binds the electron in an atom, find the quantum mechanical properties (spectral observables) associated with the transitions between the stationary quantum states.

The postulates serve as the logical foundation for an introduction to quantum mechanics, and provide insight into the connection between classical and quantum physics. They emphasize the relation between mechanical and spectral quantities and make calculations of line spectra readily accessible.

Postulate 1. Quantum states (Bohr–Wilson–Sommerfeld)

The condition that quantizes the classical states of a one-dimensional periodic system is

$$\oint p \, dx = nh. \tag{8}$$

The position x and momentum p label the classical states. The quantum number $n = 0,1,2,3,...$ labels the quantized states. The integral extends over one period of the motion and h is Planck's constant.

Postulate 2. Quantum jumps (Einstein–Bohr)

Light is emitted during a quantum jump, a probabilistic event. The frequency ω_{nm} and the power P_{nm} of the light associated with the quantum jump from state n of energy E_n to state m of energy E_m are determined by the relations

$$\omega_{nm} = \frac{1}{\hbar}(E_n - E_m), \tag{9}$$

$$P_{nm} = A_{nm}(E_n - E_m). \tag{10}$$

The transition rate A_{nm} is defined as follows: $A_{nm}\Delta t$ is the probability of a spontaneous transition $n \to m$ during the time interval Δt.

Postulate 3. Intensity correspondence (Bohr)

The power $P_{n,n-\tau}$ of the light emitted (per atom) during the quantum jump from state n to state $n - \tau$ in a collection of atoms corresponds to the power $P_\tau(n)$ of the light radi-

ated by the τth harmonic (Fourier component) of the classical motion of the electron in state n. In the limit $n \gg \tau$,

$$P_{n,n-\tau} = P_\tau(n). \tag{11}$$

Postulate 1 selects the quantum mechanically allowed stationary states from the continuum of classical states. More specifically, when the Fourier series solution $x(t)$ of the equation of motion, $F = m\ddot{x}$, is substituted into the quantum condition, $\oint m\dot{x}^2 \, dt = nh$, the classical motion becomes quantized,

$$x(t,n) = a_1(n)\cos \omega(n)t + a_2(n)\cos 2\omega(n)t$$
$$+ a_3(n)\cos 3\omega(n)t + \cdots . \tag{12}$$

The quantized Fourier series, $x(t,n)$, denotes the classical periodic motion of the electron in the quantum state n. In effect, the quantum condition replaces the classical harmonic, $a_\tau \cos \omega_\tau t$, by the quantized harmonic, $a_\tau(n)\cos \omega_\tau(n)t$. The classical (conserved) energy function $E(a_\tau, \omega_\tau)$ is replaced by the quantum energy spectrum E_n.

The quantum condition in Eq. (8) can be written in the form $2\langle K \rangle = n\hbar\omega$, where $\langle K \rangle$ is the time-average of the kinetic energy $m\dot{x}^2/2$, taken over one period $2\pi/\omega$. In terms of the potential energy $V(x)$ associated with the conservative force $F(x)$, the quantum condition is $\oint [2m(E - V(x)]^{1/2} dx = nh$. Thus, given V as a function of x, the quantum condition determines E as a function of n. In other words, the quantum condition is a rule that assigns a set of discrete energy levels E_n to a smooth potential curve $V(x)$.

As an example, consider a simple harmonic oscillator. Given the continuum of classical motions, $x(t) = a \cos \omega t$ (a is a real number), the quantum condition selects the discrete set of allowed motions, $x(t,n) = (nh/\pi m\omega)^{1/2}\cos \omega t$ ($n = 1,2,3,...$). When the classical motion $x(t)$ is replaced by the quantized motion $x(t,n)$ in the energy function, $E(x,\dot{x}) = m\dot{x}^2/2 + m\omega^2 x^2/2$, the classical energy $E(a,\omega) = m\omega^2 a^2/2$ is replaced by the quantized energy $E_n = n\hbar\omega$. Note that in general, E_n is the constant term ($\tau = 0$) in the Fourier series expansion of the energy function—all time-dependent terms disappear for a conservative system.

Postulate 2 shows clearly how the spectral (radiation) observables (ω_{nm}, P_{nm}) are related to the mechanical (atomic) parameters (E_n, A_{nm}). Note that the transition quantities (ω_{nm}, P_{nm}) between two states are proportional to the energy difference ($E_n - E_m$) between the states. The intensity relation, $P_{nm} = A_{nm}(E_n - E_m)$, introduces the fundamental notion of probability in our classical-quantum approach. Introducing a quantum probability early and in the context of a quantum jump, rather than as the square of an abstract wave function, is natural and has pedagogical advantages.

Postulate 3 is the correspondence principle for intensity, originally conjectured by Bohr.[1] Bohr's correspondence principle for frequency is not included in our postulates because it can be logically derived from Postulates 1 and 2, as we later show. Bohr's correspondence principle is steeped in the language of Fourier harmonics because the electron motion in a classical atom is periodic motion.

These three postulates introduce the basic mechanical (E_n), statistical (A_{nm}), and spectral (ω_{nm}, P_{nm}) elements of quantum mechanics, and serve as the foundation for the classical-quantum theory. They represent the minimal set of principles from which the theory of line spectra logically
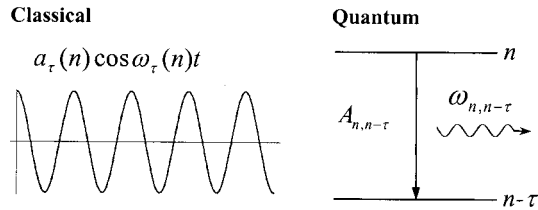
Fig. 2. The τth Fourier component of the electron motion in state n corresponds to the quantum jump from state n to state $n-\tau$. The harmonic amplitude $a_\tau(n)$ corresponds to the transition probability $A_{n,n-\tau}$. The harmonic frequency $\omega_\tau(n) = \tau\omega(n)$ of the orbiting electron corresponds to the spectroscopic frequency $\omega_{n,n-\tau}$ of the emitted light.

Fig. 3. In classical mechanics, the *sum* of the harmonics represents the periodic motion. In quantum mechanics, the *set* (matrix) of harmonics represents the quantum transitions.

unfolds. The ultimate practical power of the postulates is that they allow one to calculate quantal spectra (ω_{nm}, P_{nm}) from classical motion $x(t)$.

IV. CORRESPONDENCE THEOREMS

The correspondence theorems provide the connection between the quantum-jump quantities, ω_{nm} and A_{nm}, and the classical-harmonic quantities, $\omega_\tau(n)$ and $a_\tau(n)$. We state and discuss the theorems in this section. The proofs will be given in Sec. V.

Theorem 1. Correspondence between spectral and mechanical frequencies

The spectral frequency $\omega_{n,n-\tau}$ of the radiation emitted during the quantum jump of an electron from state n to state $n-\tau$ corresponds to the mechanical frequency $\tau\omega(n)$ of the τth harmonic of the classical motion of the electron in the state n. For $n \gg \tau$,

$$\omega_{n,n-\tau} = \tau\omega(n). \tag{13}$$

Theorem 2. Correspondence between transition probability and vibration amplitude

The transition rate $A_{n,n-\tau}$ for an electron to jump from state n to state $n-\tau$ corresponds to the square of the vibration amplitude $a_\tau(n)$ of the τth harmonic of the classical motion of the electron in the state n. For $n \gg \tau$,

$$A_{n,n-\tau} = \frac{e^2 \tau^3 \omega^3(n)}{12\pi\varepsilon_0 \hbar c^3}[a_\tau(n)]^2, \tag{14}$$

where e is the charge of the electron, ε_0 is the permittivity of free space, and c is the speed of light.

Theorem 1 was first stated and proved by Bohr.[1] The correspondence between rotation and radiation frequencies is often illustrated in textbooks[11,12] using the hydrogen atom, but only for the special case $\tau = 1$. The correspondence between transition probabilities and Fourier coefficients was first noted by Bohr.[1] An analytical form of this correspondence, similar to Eq. (14), was first stated by Van Vleck[13] and can be found in some textbooks.[14–16]

The theme of the correspondence theorems is that every possible transition between two quantum states is conjugated with a certain harmonic component of the classical motion. In particular, the transition from state n to state $n-\tau$ corresponds to the harmonic of frequency $\tau\omega(n)$ as illustrated in Fig. 2. The correspondence theorems assign a quantum
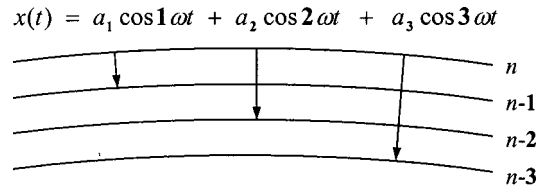
meaning to the harmonic parts, $a_1\cos\omega t$, $a_2\cos 2\omega t$, $a_3\cos 3\omega t,...,$ of the classical Fourier series, but not to the whole series. In the quantum theory, it makes no sense to combine the parts to produce a well-defined state $x(t)$ of the electron, because each part corresponds to a jump between two states, rather than a property of a single state (see Fig. 3).

Note that the classical objects, $\omega_\tau(n)$ and $a_\tau(n)$, and the quantum objects, $\omega_{n,n-\tau}$ and $A_{n,n-\tau}$, are labeled by two indices, n and τ. Classically, τ specifies a harmonic component of $x(t)$. Quantum mechanically, τ specifies the *change* Δn in the quantum number for the transition $n \to n - \Delta n$. In general, $\tau = n - m$ for the transition $n \to m$. It is important to stress that the physical meaning of the classical-harmonic number τ is completely different than the physical meaning of the quantum-jump number $n - m$. The numerical equality between τ and $n - m$ is the deep statement of the correspondence principle.

An immediate consequence of the correspondence theorems is that large quantum jumps will occur if the classical motion contains high harmonics. Furthermore, quantum jumps will be highly probable if the corresponding classical harmonics have large amplitudes. For example, if an electron moves in a circular orbit with constant speed, then only the fundamental harmonic ($\tau = 1$) exists, and thus only small quantum jumps ($n \to n - 1$) are possible. For an elliptical orbit, higher harmonics exist, and thus larger quantum jumps are possible.

A fundamental principle of quantum mechanics is that probabilities are proportional to squares of amplitudes. The correspondence relation, $A_{n,n-\tau} \sim [a_\tau(n)]^2$, clearly illustrates this principle in the framework of the classical-quantum theory. The relation between the transition *probability* $A_{n,n-\tau}$ and the vibration *amplitude* $a_\tau(n)$ makes physical sense because $A_{n,n-\tau}$ is the quantum measure of intensity (number of photons) and $[a_\tau(n)]^2$ is the classical measure of intensity (energy of vibration). The probability $A_{n,n-\tau}$ of a quantum jump and the amplitude $a_\tau(n)$ of a harmonic oscillator are more intuitive versions of probability and amplitude than those that are typically introduced in quantum mechanics.

In terms of line spectra, the correspondence theorems state that for relatively small quantum jumps ($\tau \ll n$), atoms radiate harmonics. The quantum process of jumping between two closely spaced states produces the same spectral effects as the classical process of accelerating in one of the states. In particular, the light emitted (per atom) when an actual electron makes the jump $n \to n - \tau$ is identical to the light radiated by a virtual electron oscillating with the harmonic motion $a_\tau(n)\cos\omega_\tau(n)t$. It is remarkable that the classical and
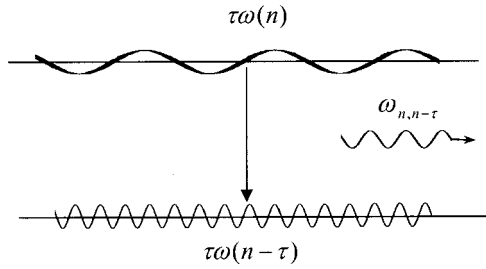
Fig. 4. When an electron changes (jumps) from orbit n to orbit $n-\tau$, the frequency of the emitted light is intermediate between the initial and final orbital (harmonic) frequencies: $\tau\omega(n)<\omega_{n,n-\tau}<\tau\omega(n-\tau)$. For relatively small jumps ($\tau\ll n$), the orbital and optical frequencies are numerically equal: $\tau\omega(n)=\omega_{n,n-\tau}=\tau\omega(n-\tau)$.

quantum predictions of line spectra can numerically coincide given the vast difference in their explanations of the emission of light from atoms.

In practice, the overlap of classical and quantum phenomena occurs for states of large quantum numbers, for example, an electron rotating at a large radius (hydrogen atom), vibrating with a large amplitude (oscillator), or moving with a large velocity (particle in a box). Because n specifies the state and τ specifies the change in state, the quantum-number condition $n\gg\tau$, or $n\gg\Delta n$, is equivalent to the electron-motion condition $x\gg\Delta x$ or $E\gg\Delta E$. States of large quantum numbers occur in Rydberg atoms, which can be found naturally in stars and stellar nebula and can be artificially created in the laboratory.[17–20]

For small quantum numbers, a transition quantity no longer corresponds to a harmonic quantity evaluated for one particular state (initial or final), but instead corresponds to a harmonic quantity averaged over the intermediate states between the initial and final states. In general, the value of the spectroscopic frequency lies between the values of the initial and final harmonic frequencies:

$$\tau\omega(n-\tau)<\omega_{n,n-\tau}<\tau\omega(n). \quad (15)$$

For some systems, the final harmonic frequency is greater than the initial frequency. This general relation is illustrated in Fig. 4. A numerical illustration for the hydrogen atom is given in Table I.

As an analytical example, consider the well-known system of a particle (electron) of mass m in a box of length L. Each state n corresponds to a one-dimensional "orbit" in which the particle translates back-and-forth at constant speed, $v(n)=nh/2mL$. The spectral frequency, $\omega_{n,n-\tau}=m[v^2(n)-v^2(n-\tau)]/2\hbar$, and the orbital frequency, $\omega(n)=\pi v(n)/L$, are

$$\omega_{n,n-\tau}=\frac{\pi h}{4mL^2}[n^2-(n-\tau)^2], \quad \omega(n)=\frac{\pi h}{2mL^2}n. \quad (16)$$

One may readily verify that these frequencies satisfy the general inequality in Eq. (15), which reduces to $n-\tau<n-(\tau/2)<n$. From the analytic functions in Eq. (16), one may also verify that the asymptotic ($n\gg\tau$) relation between the quantum and classical frequencies is $\omega_{n,n-\tau}=\tau\omega(n)$, while the exact relation is

$$\omega_{n,n-\tau}=\int_{n-\tau}^{n}\omega(s)ds. \quad (17)$$

Thus the spectral frequency is equal to an average mechanical frequency: $\omega_{n,n-\tau}=\tau\bar{\omega}(n,n-\tau)$. The average is taken over the continuous succession of intermediate states (s) that lie on an interval of width τ between the initial state (n) and the final state ($n-\tau$). In the next section, we prove that Eq. (17) is valid for all systems, thereby extending Theorem 1 to small quantum numbers.

It is natural to expect that, for all values of the quantum number, the classical and quantum expressions for the intensity (power) of the radiation satisfy the inequality $P_\tau(n-\tau)<P_{n,n-\tau}<P_\tau(n)$, which is analogous to Eq. (15). In general, the transition rate $A_{n,n-\tau}$ corresponds to the square of a mean amplitude $\bar{a}_\tau(n)$, suitably averaged over the intermediate states between n and $n-\tau$. The extension of Theorem 2 to small quantum numbers would assume the form $A_{n,n-\tau}=K\omega_{n,n-\tau}^3[\bar{a}_\tau(n)]^2$. However, unlike the average frequency, an exact averaging procedure for the amplitude does not exist within the classical-quantum theory because there does not exist a classical counterpart to the probabilistic quantum equation $P_{nm}=A_{nm}\hbar\omega_{nm}$. Kramers was the first to

Table I. Comparison of the spectral frequency, and the initial and final orbital frequencies (in Hz) for the hydrogen atom (Ref. 21).

Transition $n\rightarrow m$	Jump number $\tau=n-m$	Initial orbital frequency $\tau\nu(n)$	Spectral frequency ν_{nm}	Final orbital frequency $\tau\nu(m)$
$4\rightarrow1$	3	3.09×10^{14}	30.9×10^{14}	197×10^{14}
$4\rightarrow2$	2	2.06×10^{14}	6.17×10^{14}	16.5×10^{14}
$4\rightarrow3$	1	1.03×10^{14}	1.60×10^{14}	2.44×10^{14}
$10\rightarrow7$	3	1.97×10^{13}	3.43×10^{13}	5.76×10^{13}
$10\rightarrow8$	2	1.32×10^{13}	1.85×10^{13}	2.57×10^{13}
$10\rightarrow9$	1	6.58×10^{12}	7.72×10^{12}	9.03×10^{12}
$40\rightarrow37$	3	3.09×10^{11}	3.47×10^{11}	3.90×10^{11}
$40\rightarrow38$	2	2.06×10^{11}	2.22×10^{11}	2.40×10^{11}
$40\rightarrow39$	1	1.03×10^{11}	1.07×10^{11}	1.11×10^{11}
$100\rightarrow97$	3	1.97×10^{10}	2.07×10^{10}	2.16×10^{10}
$100\rightarrow98$	2	1.32×10^{10}	1.36×10^{10}	1.40×10^{10}
$100\rightarrow99$	1	6.58×10^{9}	6.68×10^{9}	6.78×10^{9}
$300\rightarrow297$	3	7.31×10^{8}	7.42×10^{8}	7.54×10^{8}
$300\rightarrow298$	2	4.88×10^{8}	4.92×10^{8}	4.97×10^{8}
$300\rightarrow299$	1	2.44×10^{8}	2.45×10^{8}	2.46×10^{8}

estimate the intensities of spectral lines using the correspondence between transition probabilities and Fourier amplitudes.[22]

There is a very important special case where the amplitude correspondence, $A_{n,n-\tau} \leftrightarrow a_\tau^2(n)$, predicts exact values for the transition rate, even for small quantum numbers. This is the special case where the Fourier amplitude is equal to zero. According to Theorem 2, if $a_\tau(n)=0$, then $A_{n,n-\tau}=0$. If $A_{n,n-\tau}=0$, then the quantum jump $n \to n-\tau$ does not occur—the transition is forbidden. For example, if the third harmonic ($\tau=3$) coefficient is zero, then all transitions for which the electron jumps three states ($\Delta n=3$) are strictly forbidden. *Forbidden quantum jumps* correspond to *missing classical harmonics*. This statement has powerful applications. It allows one to derive rigorous quantum mechanical selection rules for line spectra from a Fourier analysis of the classical motion. The selection rule corollary to Theorem 2 can be formally stated as follows: *If the classical Fourier amplitude of the τth harmonic is zero, both for the initial (n) and final (m) states, then the transition $n \to m$ is forbidden if $n-m=\tau$.* This corollary is valid for all quantum numbers given that the transition amplitude lies between the initial and final values of the corresponding Fourier amplitudes. Whereas the frequency condition, $\hbar \omega_{nm}=E_n-E_m$, determines only the possible values of the line frequencies, the selection rule, $A_{nm} \neq 0$, determines the allowed lines that actually occur in the spectrum.

To illustrate the correspondence theorems, consider the following example. Suppose that for a certain atom, the solution of $F=m\ddot{x}$ and $\oint p\,dx=nh$ is

$$x(t,n)=n\cos\sqrt{n}t+\sqrt{n}\cos 3\sqrt{n}t. \tag{18}$$

This dynamical function specifies the classical periodic motion of the electron in the quantum state n. The fundamental frequency is $\omega(n)=\sqrt{n}$. The motion is composed of only the first ($\tau=1$) and third ($\tau=3$) harmonics. The nonzero amplitudes are $a_1(n)=n$ and $a_3(n)=\sqrt{n}$. Because $a_\tau(n) \neq 0$ if $\tau=1,3$, the allowed transitions, $n \to n-\Delta n$, are determined by the selection rule $\Delta n=1,3$.

The basic theoretical quest is to calculate the quantum quantities, A_{nm} and ω_{nm}, from the classical motion $x(t,n)$. The predicted values will match the experimental results if the quantum jumps are relatively small. Consider the quantum jumps $100 \to 99$, $100 \to 98$, and $100 \to 97$. For $n=100$, Eq. (18) is

$$x(t,100)=100\cos 10t+10\cos 30t. \tag{19}$$

From the classical frequencies ($\omega_1=10, \omega_3=30$) and amplitudes ($a_1=100, a_3=10$), the correspondence theorems and Postulate 2 readily allow us to calculate A_{nm} and the line spectrum properties, ω_{nm}, P_{nm}. The results are

$$A_{100,99}=K \times 10^3 \times 100^2, \quad A_{100,98}=0,$$

$$A_{100,97}=K \times 30^3 \times 10^2,$$

$$\omega_{100,99}=10, \quad \omega_{100,97}=30, \tag{20}$$

$$P_{100,99}=\hbar K \times 10^4 \times 100^2, \quad P_{100,97}=\hbar K \times 30^4 \times 10^2.$$

The constant $K \equiv e^2/12\pi\varepsilon_0\hbar c^3$. The relative power is $P_{100,97}/P_{100,99}=81/100$. Figure 5 illustrates the quantum jumps and the line spectrum.
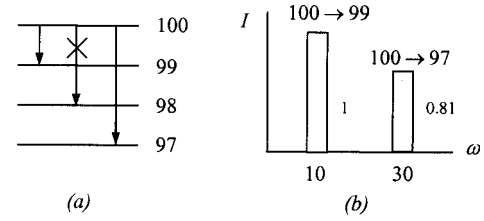
Fig. 5. The quantum transitions (a) generate the line spectrum (b). The frequencies (10, 30) and relative intensities (1, 0.81) of the lines were calculated from the motion of the electron in the state $n=100$: $x(t)=100\cos 10t+10\cos 30t$. In particular, the transition $100 \to 98$ ($\Delta n=2$) is forbidden because the second harmonic ($\tau=2$) is missing.

Classically, the state of the electron decays smoothly from $n=100$ to $n=97$ as it continuously radiates light. Because $x(t,100) \approx x(t,97)$, the relative change in the amplitude of the state is negligible. Thus the periodic function $x(t,100)$ in Eq. (19) accurately represents the quasiperiodic decaying motion. This periodic motion is characterized by only two partial vibrations—the first and third harmonics. The first vibration, $100\cos 10t$, radiates light of frequency 10 and relative intensity $(10^2 \times 100)^2=100$ million, while the third vibration, $10\cos 30t$, radiates light of frequency 30 and relative intensity $(30^2 \times 10)^2=81$ million. Note that the relative intensity is equal to the square of the maximum acceleration of the electron's partial vibration. This classical radiation is emitted continuously during the accelerated periodic motion of the electron and both frequencies are radiated simultaneously.

Quantum mechanically, the picture is quite different. The emission of light is a discontinuous process that occurs only when the electron makes a jump. The light consists of one photon and is monochromatic. Light of frequency 10 is emitted during the jump $100 \to 99$. Light of frequency 30 is emitted during the jump $100 \to 97$. The two-state jump $100 \to 98$ is forbidden because the second harmonic is missing. Because $A_{100,99}/A_{100,97}=100/27$, the jump $100 \to 99$ is $100/27$ times more likely to occur than the jump $100 \to 97$. Thus for every 100 atoms that make the jump $100 \to 99$, there are 27 atoms that make the jump $100 \to 97$ during the same time interval. The (photon) energy emitted during the jump $n \to m$ is $\hbar \omega_{nm}$. Thus the energy emitted by 100 atoms jumping $100 \to 99$ is $100 \cdot \hbar 10=1000\hbar$. For 27 atoms jumping $100 \to 97$, the energy is $27 \cdot \hbar 30=810\hbar$. This result explains why the intensity of the $100 \to 99$ line is $100/81$ times larger than the intensity of the $100 \to 97$ line.

V. PROOF OF CORRESPONDENCE THEOREMS

Proof of correspondence theorem 1

The general proof hinges on a result from classical mechanics. Consider a particle of mass m undergoing periodic motion in one dimension. The state is (x,p) and the energy of the state is $E(x,p)=p^2/2m+V(x)$. There exists a general relation between the fundamental period T of the motion and the integral of the momentum $p(x,E)=[2m(E-V(x)]^{1/2}$ over one period.[23]

Classical mechanics lemma: $T = \dfrac{d}{dE} \oint p(x,E)\,dx$.

$$(21)$$

The proof of this lemma follows. If we use $dt = dx/v$ and $1/v = \partial p/\partial E$, we can transform the relation $T \equiv \oint dt$ into Eq. (21). Moving the operator $\partial/\partial E$ outside the integral is valid because the value of $p(x,E)$ vanishes at the limits of integration (such as the turning points of an oscillator) or the limits are independent of E (such as the walls of a box).

The action variable, $J(E)$, defined by the phase integral,

$$J(E) \equiv \oint p(x,E)\,dx, \qquad (22)$$

is an important dynamical variable in the classical and quantum theory of periodic systems. In terms of $J(E)$, the classical mechanics lemma assumes the compact form, $T = dJ/dE$, or equivalently,

$$\nu = dE/dJ, \qquad (23)$$

where $\nu = 1/T$ is the fundamental linear frequency of the motion and $E(J)$ is the inverse of $J(E)$. In action language, the quantum condition is $J = h, 2h, 3h, \ldots$. For these special values of J, the smooth energy function $E(J)$ takes on the discrete values $E(h), E(2h), E(3h), \ldots$. This result explains how the quantum-mechanical energy spectrum, $E_1, E_2, E_3, \ldots$, is generated from the classical-mechanical action variable $J(E)$.

As an example, consider a simple harmonic oscillator defined by $E = p^2/2m + kx^2/2$. The result of calculating the phase integral in Eq. (22) is $J(E) = 2\pi (m/k)^{1/2} E$. Thus the period, $T = dJ/dE$, is $T = 2\pi (m/k)^{1/2}$. The inverse of $J(E)$ is $E(J) = J/T$, and thus the quantized energy, $E_n = E(J = nh)$, is $E = nh/T$.

The proof of Theorem 1 involves finding the relation between the quantum frequency, $\nu_{nm} = (E_n - E_m)/h$, and the classical frequency, $\nu = dE/dJ$. Because $E_n = E(J = nh)$ and $E_m = E(J = mh)$, the Einstein–Bohr frequency relation, $\nu_{nm} = (E_n - E_m)/h$, can be written as

$$\nu_{nm} = \frac{E(J + \Delta J) - E(J)}{h}, \qquad (24)$$

where $J + \Delta J = nh$, $J = mh$, and $\Delta J = (n-m)h$. In the limit, $J \gg \Delta J$, this difference equation can be expressed as a derivative,

$$\nu_{nm} = \frac{\Delta J}{h} \frac{dE}{dJ}. \qquad (25)$$

If we use the relations, $\Delta J = (n-m)h$ and $\nu(n) = [dE/dJ]_{J=nh}$, Eq. (25) becomes

$$\nu_{nm} = (n-m)\nu(n). \qquad (26)$$

The action condition, $J \gg \Delta J$, is equivalent to the condition, $n \gg n - m$. In terms of the angular frequency, $\omega \equiv 2\pi\nu$, and the jump number, $\tau \equiv n - m$, Eq. (26) can be written as $\omega_{n,n-\tau} = \tau\omega(n)$. This relation is valid for $n \gg \tau$. The proof of Theorem 1 is complete.

In essence, the quantum frequency $\omega_{n,n-\tau}$ is asymptotically equal to the classical frequency $\tau\omega(n)$, because in the same limit ($n \gg \tau$), the *quantum difference* $E_n - E_{n-\tau}$ is

equal to the *classical derivative* $\tau\, dE/dn$. In other words, the Einstein–Bohr relation, $\nu_{n,n-1} = (E_n - E_{n-1})/h$, is the quantum analogue of the classical relation, $\nu = dE/dJ$.

If the condition $n \gg \tau$ is not satisfied, there is no longer a one-to-one correspondence between the spectroscopic frequency $\omega_{n,n-\tau}$ and a single mechanical frequency $\tau\omega(n)$. The above proof can readily be generalized to show that, for any values of n and m, the light frequency ω_{nm} emitted during the quantum jump $n \to m$ is equal to the "jump length" $(n-m)$ multiplied by the mean electron frequency $\bar{\omega}(n,m)$, averaged over the continuum of intermediate states between n and m:

$$\omega_{nm} = (n-m)\bar{\omega}(n,m),$$

where

$$\bar{\omega}(n,m) \equiv \frac{1}{n-m} \int_m^n \omega(s)\,ds. \qquad (27)$$

The real number s is defined by the relation $J = sh$. The formula in Eq. (27) provides the most fundamental connection between the spectral frequency ω_{nm} and the mechanical frequency $\bar{\omega}(n,m)$. Within the realm of the classical-quantum theory, it is an exact formula, valid for all quantum states (n,m) and jump lengths $(n-m)$. It generalizes Eq. (26) and justifies Eq. (15).

Proof of correspondence theorem 2

Just as for the proof of Theorem 1, the proof of Theorem 2 hinges on an important classical property, in this case from Maxwell's theory of the electromagnetic field. According to Maxwell's equations, an accelerated electric charge radiates an electromagnetic wave. The electromagnetic wave propagates at the speed of light and transports energy. There exists a well-known relation (Larmor formula) between the instantaneous power $P(t)$ radiated by the electron and the acceleration $\ddot{x}$ of the electron,

Classical electrodynamics lemma:

$$P(t) = \frac{1}{4\pi\varepsilon_0} \frac{2e^2}{3c^3} \ddot{x}^2. \qquad (28)$$

A derivation of the Larmor formula can be found in most textbooks on classical electrodynamics.[24] Note that the energy of the radiation is proportional to the square of the acceleration of the electron.

For an electron undergoing periodic motion, $x(t)$ can be represented by a Fourier series and Eq. (28) becomes

$$\begin{aligned}
P(t) &= \frac{1}{4\pi\varepsilon_0} \frac{2e^2}{3c^3} \left[\sum_\tau \omega^2 \tau^2 a_\tau \cos \tau\omega t \right]^2 \\
&= \frac{e^2}{6\pi\varepsilon_0 c^3} \omega^4 \left[\sum_\tau \tau^4 a_\tau^2 \cos^2 \tau\omega t \right. \\
&\quad \left. + \sum_{\tau \neq \tau'} \tau^2 \tau'^2 a_\tau a_{\tau'} \cos \tau\omega t \cos \tau'\omega t \right]. \qquad (29)
\end{aligned}$$

Given the extremely rapid oscillations of light waves relative to the temporal response of macroscopic measuring instruments, the measurement of any light-wave observable will naturally encompass many cycles of oscillation. Instruments record time-average values rather than instantaneous values.

The average power P is defined as the time average of the instantaneous power $P(t)$ over one period. In Eq. (29), the average of $\cos^2 \tau \omega t$ is 1/2 and the average of $\cos \tau \omega t \cos \tau' \omega t$ is 0. Thus the average power is

$$P = \frac{e^2}{12\pi\varepsilon_0 c^3} \omega^4 \sum_\tau \tau^4 a_\tau{}^2. \qquad (30)$$

The average power is a sum of partial powers, one for each harmonic. The power associated with the τth harmonic is

$$P_\tau = \frac{e^2}{12\pi\varepsilon_0 c^3} \tau^4 \omega^4 a_\tau{}^2. \qquad (31)$$

This harmonic component of the power represents the average rate at which energy is radiated by the partial vibration of the electron of frequency $\tau\omega$ and amplitude a_τ.

According to Postulate 3, the electromagnetic energy radiated by the accelerating electron is asymptotically equal in value to the photonic energy emitted by the jumping electron. The precise symbolic statement of the correspondence is $P_{n,n-\tau} = P_\tau(n)$, for $n \gg \tau$. From Eqs. (3) and (31), this energy correspondence assumes the form

$$A_{n,n-\tau} \hbar \omega_{n,n-\tau} = \frac{e^2}{12\pi\varepsilon_0 c^3} [\tau\omega(n)]^4 [a_\tau(n)]^2. \qquad (32)$$

Theorem 1 says $\tau\omega(n) = \omega_{n,n-\tau}$. Thus, in the domain $n \gg \tau$, the relation between the transition probability $A_{n,n-\tau}$ and the Fourier amplitude $a_\tau(n)$ is

$$A_{n,n-\tau} = \frac{e^2 \tau^3 \omega^3(n)}{12\pi\varepsilon_0 \hbar c^3} [a_\tau(n)]^2. \qquad (33)$$

Note that the quantum mechanical relation, $A_{n,n-\tau} \sim [a_\tau(n)]^2$, originates from the classical electrodynamical relation, $P \sim \ddot{x}^2$.

VI. FOURIER SERIES AND HEISENBERG MATRICES

The theory of Fourier and the correspondence principle of Bohr played a vital role in Heisenberg's development of quantum mechanics. In essence, Heisenberg replaced the Fourier series by a "Fourier table." In his classic paper, each quantum formula was carefully crafted from the corresponding classical formula.[10] For Heisenberg, the problem with classical mechanics was not the dynamics, but the kinematics. According to Heisenberg, the equations of quantum mechanics should be relations between observable quantities such as the spectral frequencies and intensities, and not the mechanical properties of the electron motion such as the position and period. In essence, Heisenberg got rid of Bohr's orbits.

The conceptual kinematical breakthrough in the creation of quantum mechanics can be summarized as follows. Instead of representing $x(t)$ by a sum of Fourier harmonics,

$$c_1 e^{i\omega t} + c_2 e^{i2\omega t} + c_3 e^{i3\omega t} + \cdots, \qquad (34)$$

the dynamical variable x is represented by a matrix of "Heisenberg harmonics,"

$$\begin{pmatrix} c_{11}e^{i\omega_{11}t} & c_{12}e^{i\omega_{12}t} & c_{13}e^{i\omega_{13}t} & \cdots \\ c_{21}e^{i\omega_{21}t} & c_{22}e^{i\omega_{22}t} & c_{23}e^{i\omega_{23}t} & \cdots \\ c_{31}e^{i\omega_{31}t} & c_{32}e^{i\omega_{32}t} & c_{33}e^{i\omega_{33}t} & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix}. \qquad (35)$$

The Heisenberg harmonic, $x_{nm} \equiv c_{nm} \exp(i\omega_{nm}t)$, is associated with the transition $n \to m$. The transition amplitude c_{nm} provides a measure of the intensity of the light and the transition frequency ω_{nm} equals the light frequency. In particular, the Heisenberg harmonic x_{nm} uniquely determines the transition probability A_{nm} via the quantum-mechanical relation[25]

$$A_{nm} = \frac{e^2 \omega_{nm}^3}{3\pi\varepsilon_0 \hbar c^3} |x_{nm}|^2. \qquad (36)$$

The power P_{nm} of the light associated with the transition $n \to m$ is $P_{nm} = A_{nm} \hbar \omega_{nm}$, and thus

$$P_{nm} = \frac{e^2 \omega_{nm}^4}{3\pi\varepsilon_0 c^3} |x_{nm}|^2. \qquad (37)$$

Equation (37) provides the connection between the quantum mechanical "motion" of the electron, $x_{nm}(t)$, and the spectroscopic observable, P_{nm}.

Note that the exact relation between the transition probabilities and Heisenberg harmonics in Eq. (36) is identical to the correspondence relation between transition probabilities and Fourier harmonics in Eq. (14). In comparing these two equations, $\tau\omega(n)$ corresponds to $\omega_{n,n-\tau}$ and $a_\tau(n)$ corresponds to $2c_{n,n-\tau}$. The factor of 2 arises because the coefficients of the cosine Fourier series are twice those of the exponential Fourier series, due to the identity, $2\cos u = \exp(iu) + \exp(-iu)$. Thus the relation in Eq. (14), which is asymptotically valid for $n \gg \tau$, becomes valid for all n and τ if the Fourier components, $c_\tau(n)\exp[i\omega_\tau(n)t]$, are replaced by the transition components $c_{n,n-\tau}\exp(i\omega_{n,n-\tau}t)$. As a consequence, in the limit $n \gg \tau$, the Fourier amplitude is equal to the Heisenberg amplitude, $c_\tau(n) = c_{n,n-\tau}$, or equivalently, $a_\tau(n) = 2c_{n,n-\tau}$.

If one can calculate the Heisenberg harmonics, $x_{nm} = c_{nm}\exp(i\omega_{nm}t)$, then one would possess complete quantum mechanical knowledge about the line spectrum. In Schrödinger's wave mechanics, the amplitude c_{nm} and the frequency ω_{nm} are calculated as follows:[25]

$$c_{nm} = \int_{-\infty}^{\infty} \psi_n^*(x) x \psi_m(x) dx, \quad \omega_{nm} = \frac{1}{\hbar}(E_n - E_m). \quad (38)$$

The wave functions $\psi_n(x)$ and energies E_n characterize the stationary states of the system, and are solutions to the time-independent Schrödinger equation. Note that c_{nm} is equal to the matrix element $\langle \psi_n | x | \psi_m \rangle$, and x_{nm} is equal to the matrix element $\langle \Psi_n | x | \Psi_m \rangle$, where $\Psi_n(x,t) = \psi_n(x)\exp(-iE_n t/\hbar)$ are the energy-eigenstate solutions to the time-dependent Schrödinger equation.

VII. APPLICATIONS

The applications involve solving the fundamental (Heisenberg) problem of quantum mechanics: Given $F(x)$, find ω_{nm} and A_{nm}. The classical-quantum program consists of the following steps:

(1) Solve $F(x)=m\ddot{x}$ for $x(t)=a_1\cos\omega t+a_2\cos 2\omega t+\cdots$.

(2) Use $\oint p\,dx=nh$ to find $\omega(n)$, $a_\tau(n)$.

(3) Use the correspondence theorems to find ω_{nm} and A_{nm}.

A. Simple harmonic oscillator

The simple harmonic oscillator is characterized by the force function $F(x)=-kx$. The solution to the equation of motion is

$$x(t)=a\cos\omega_0 t, \tag{39}$$

where $\omega_0\equiv\sqrt{k/m}$ and the fundamental amplitude is a. Note that simple harmonic motion has no overtones.

Given the harmonic motion $x(t)$ in Eq. (39), the general quantum condition, $\oint m\dot{x}^2\,dt=nh$, assumes the specific form $ma^2\omega_0\pi=nh$. This condition determines the allowed values $a(n)$ of the vibration amplitude. The frequency of a simple harmonic oscillator is independent of the amplitude and thus independent of n. Thus, the amplitude and frequency of a simple harmonic oscillator in the state n are

$$a(n)=\sqrt{\frac{2\hbar n}{m\omega_0}},\quad \omega(n)=\omega_0. \tag{40}$$

Substituting the quantized amplitude $a(n)$ into the classical energy function, $E=m\omega_0^2a^2/2$, yields the quantum energy spectrum,

$$E_n=n\hbar\omega_0. \tag{41}$$

Because only a single Fourier harmonic term ($\tau=1$) exists, the selection rule is $\Delta n=1$. Only transitions between adjacent states ($n\rightarrow n-1$) are permitted. Using the correspondence theorems, we calculate the radiation frequency and transition probability from the classical frequency and amplitude in Eq. (40). The results are

$$\omega_{n,n-1}=\omega_0,\quad A_{n,n-1}=\frac{e^2\omega_0^2}{6\pi\varepsilon_0c^3m}n. \tag{42}$$

B. Particle in a box

Consider an electron confined to a one-dimensional region of length L that is bounded by impenetrable, rigid walls. The solution to the equation of motion is

$$x(t)=\begin{cases} vt, & 0\leqslant t\leqslant\dfrac{T}{2}, \\[2mm] 2L-vt, & \dfrac{T}{2}\leqslant t\leqslant T, \end{cases} \tag{43}$$

where v is the velocity of the electron, and $T=2L/v$ is the period of the motion. The Fourier series representation of $x(t)$ is determined by the Fourier amplitudes

$$a_\tau=\frac{\omega}{\pi}\int_0^{2\pi/\omega}x(t)\cos\tau\omega t\,dt=\begin{cases} -\dfrac{4L}{\pi^2\tau^2}, & \tau=1,3,5,... \\[2mm] 0, & \tau=2,4,6,.... \end{cases} \tag{44}$$

The constant term in the Fourier series, which represents the time average of $x(t)$, is $a_0/2=L/2$.

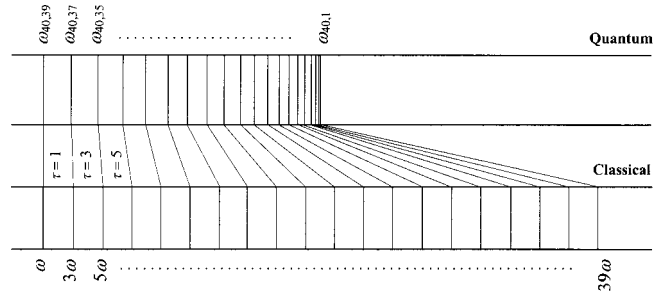The quantum condition, $\oint mv\,dx=nh$, determines the velocity of the electron in the quantum state n: $v(n)$

Fig. 6. The frequency spectrum ω_{nm}, associated with the transitions $n=40\rightarrow m=40-\tau$, of an electron in a box. The classical frequency of the back-and-forth motion of the electron in state $n=40$ is ω. For relatively small jumps, that is, $40\rightarrow35$, $40\rightarrow37$, $40\rightarrow39$, the classical and quantal spectra numerically coincide.

$=hn/2mL$. If we substitute $v(n)$ into the classical energy function, $E=mv^2/2$, we obtain the quantum energy spectrum,

$$E_n=\frac{h^2}{8mL^2}n^2. \tag{45}$$

This result is identical to that given by modern quantum mechanics, and is therefore valid for both large and small values of n. If we substitute $v(n)=hn/2mL$ into the relation $\omega=\pi v/L$, we obtain the quantized frequency

$$\omega(n)=\pi hn/2mL^2. \tag{46}$$

Note that the classical amplitude a_τ is independent of v, and thus the quantized amplitude, $a_\tau(n)=a_\tau$, is independent of n.

Because only odd harmonics ($\tau=1,3,5,...$) characterize the motion, the selection rule for allowed transitions is $\Delta n=1,3,5,...$. By using the correspondence theorems, we calculate the radiation frequency and the transition probability from the mechanical frequency in Eq. (46) and the harmonic amplitude in Eq. (44). The results, valid for $n\gg\tau$, are

$$\omega_{n,n-\tau}=\tau\frac{\pi hn}{2mL^2},\quad A_{n,n-\tau}=\frac{4\pi e^2\hbar^2n^3}{3\varepsilon_0c^3m^3L^4\tau}$$

$$(\tau=1,3,5,...). \tag{47}$$

The line spectrum of the particle in a box, based on the asymptotic spectral frequency in Eq. (47) and the exact spectral frequency calculated from Eq. (45), are compared in Fig. 6. Note that the relative intensities ($A_{n,n-\tau}\omega_{n,n-\tau}$) are independent of τ.

C. Anharmonic oscillator

We next consider the anharmonic oscillator defined by the force function $F(x)=-kx-bx^3$, where k and b are force constants. The equation of motion is

$$\ddot{x}+\omega_0^2x+\lambda x^3=0, \tag{48}$$

where $\omega_0^2\equiv k/m$ and $\lambda\equiv b/m$. The anharmonic force term λx^3 is considered a perturbation to the harmonic force term ω_0^2x. In what follows, all results are valid to first-order in the small parameter λ. The solution of Eq. (48) is the Fourier series

$$x(t)=a_1\cos\omega t+a_3\cos 3\omega t, \tag{49}$$

Table II. Comparison of classical-quantum and exact-quantum theories of the simple harmonic oscillator.

Classical-quantum energy	$E_n = n\hbar\omega_0$
Exact-quantum energy	$E_n = (n + \frac{1}{2})\hbar\omega_0$
Mechanical frequency	$\omega_1(n) = \omega_0$
Exact spectral frequency	$\omega_{n,n-1} = \omega_0$
Fourier amplitude	$a_1(n) = \sqrt{2\hbar n/m\omega_0}$
Heisenberg amplitude	$2c_{n,n-1} = \sqrt{2\hbar n/m\omega_0}$

where

$$\omega = \omega_0 + \frac{3\lambda}{8\omega_0}a_1^2, \quad a_3 = \frac{\lambda}{32\omega_0^2}a_1^3. \tag{50}$$

Note that only the first and third harmonics appear because the perturbation λx^3 in Eq. (48) generates odd harmonics via the identity $\cos^3\omega t = \frac{3}{4}\cos\omega t + \frac{1}{4}\cos 3\omega t$. If the Fourier series for the motion in Eq. (49) is substituted into the classical energy function,

$$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 + \frac{1}{4}bx^4, \tag{51}$$

the result is the Fourier series for the energy,

$$E = \frac{1}{2}m\omega_0^2 a_1^2 + \frac{9}{32}m\lambda a_1^4. \tag{52}$$

All the time-dependent terms disappear. This disappearance is the Fourier-series manifestation of energy conservation. The constant term of the energy series is the conserved energy of the anharmonic oscillator.

Given the anharmonic motion $x(t)$ in Eq. (49), the general quantum condition, $\oint m\dot{x}^2\,dt = nh$, assumes the form

$$m\omega_0\pi a_1^2 + \frac{3\pi\lambda m}{8\omega_0}a_1^4 = nh. \tag{53}$$

This condition determines the quantized fundamental amplitude $a_1(n)$. All mechanical quantities that depend on a_1 can now be quantized. In particular, substituting $a_1(n)$ into Eqs. (50) and (52), determines $\omega(n)$, $a_3(n)$, and E_n.

The results of the classical-quantum theory of the anharmonic oscillator can be summarized as follows. The classical motion in the quantum state n is given by the quantized Fourier series,

$$x(t,n) = a_1(n)\cos\omega(n)t + a_3(n)\cos 3\omega(n)t, \tag{54}$$

where the fundamental frequency is

$$\omega(n) = \omega_0 + \frac{3\hbar\lambda}{4m\omega_0^2}n, \tag{55}$$

and the harmonic amplitudes are

$$a_1(n) = \sqrt{\frac{2\hbar n}{m\omega_0}}\left(1 - \frac{3\hbar\lambda}{8m\omega_0^3}n\right),$$

$$a_3(n) = \lambda\sqrt{\frac{\hbar^3 n^3}{128m^3\omega_0^7}}. \tag{56}$$

The quantized energy is

$$E_n = n\hbar\omega_0 + \frac{3\hbar^2\lambda}{8m\omega_0^2}n^2. \tag{57}$$

We calculate the line spectrum of the anharmonic oscillator for $n \gg 1$ from the Fourier parameters in Eqs. (55) and (56) using the correspondence theorems. Because only the first ($\tau = 1$) and third ($\tau = 3$) harmonics exist, the allowed transitions obey the selection rule $\Delta n = 1,3$. For the transition $n \to n-1$, the radiation frequency and the transition probability are

$$\omega_{n,n-1} = \omega_0 + \frac{3\hbar\lambda}{4m\omega_0^2}n,$$

$$A_{n,n-1} = \frac{e^2\omega_0^2}{6\pi\varepsilon_0 c^3 m}n\left(1 + \frac{3\hbar\lambda}{2m\omega_0^3}n\right). \tag{58}$$

For the transition $n \to n-3$,

$$\omega_{n,n-3} = 3\omega_0 + \frac{9\hbar\lambda}{4m\omega_0^2}n,$$

$$A_{n,n-3} = \frac{9e^2\hbar^2\lambda^2}{512\pi\varepsilon_0 c^3 m^3\omega_0^4}n^3. \tag{59}$$

The anharmonic perturbation has two effects on the line spectrum of the harmonic oscillator. First, the frequency of the fundamental line ($n \to n-1$) is shifted slightly from ω_0 to the anharmonic value $\omega_0 + \Delta\omega_0$, where $\Delta\omega_0 = 3\hbar\lambda/4m\omega_0^2$. Second, a new line appears at the frequency $3(\omega_0 + \Delta\omega_0)$. This line corresponds to the third-harmonic jump ($n \to n-3$) and is very faint compared to the fundamental line because $A_{n,n-3}$ is a second-order quantity.

For each application in this section, we obtained the quantum energy E_n and the classical frequency $\omega(n)$. One can check that these functions satisfy the relation $dE_n/dn = \hbar\omega(n)$, or equivalently,

$$\lim_{n \gg \tau}(E_n - E_{n-\tau}) = \tau\hbar\omega(n), \tag{60}$$

which is the energy version of Theorem 1. For all values of n and m, E_n and $\omega(n)$ satisfy the exact relation

$$E_n - E_m = \hbar\int_m^n \omega(s)\,ds, \tag{61}$$

which can be interpreted as the classical-quantum version of the Einstein–Bohr relation, $E_n - E_m = \hbar\omega_{nm}$.

In Tables II, III, and IV we summarize the classical-quantum results from this section and compare them with the exact quantum-mechanical results (in the Appendix). In all cases, the selection rules are *exact*. The missing Fourier harmonics, $a_\tau(n) = 0$, in the classical theory correspond to the missing Heisenberg harmonics, $x_{nm} = 0$, in the quantum theory for $\tau = n - m$. For the nonzero harmonics, the classical quantities, $\omega_\tau(n)$ and $a_\tau(n)$, are equal to their quantum counterparts, $\omega_{n,n-\tau}$ and $2c_{n,n-\tau}$, either exactly or asymptotically. In all cases, the classical-quantum functions exhibit the same overall analytical form as the exact-quantum functions. The close agreement between the classical and quantal results is remarkable given the vast difference between the classical and quantal calculations. The classical calculations are simpler (technically and conceptually) and shorter than the quantum calculations.

Table III. Comparison of classical-quantum and exact-quantum theories of the particle in a box.

Classical-quantum energy	$E_n = \dfrac{h^2}{8mL^2} n^2$
Exact-quantum energy	$E_n = \dfrac{h^2}{8mL^2} n^2$
Mechanical frequency	$\omega_\tau(n) = \tau \dfrac{\pi h n}{2mL^2}$
Exact spectral frequency	$\omega_{n,n-\tau} = \tau \dfrac{\pi h n}{2mL^2}\left(1 - \dfrac{\tau}{2n}\right)$
Fourier amplitude	$a_\tau(n) = \begin{cases} -\dfrac{4L}{\pi^2 \tau^2}, & \tau=1,3,5,\dots \\ 0, & \tau=2,4,6,\dots \end{cases}$
Heisenberg amplitude	$2c_{n,n-\tau} = \begin{cases} -\dfrac{4L}{\pi^2 \tau^2}\dfrac{1-(\tau/n)}{[1-(\tau/2n)]^2}, & \tau=1,3,5,\dots \\ 0, & \tau=2,4,6,\dots \end{cases}$

VIII. CONCLUSION

The postulates, theorems, and applications presented in this paper can serve as an introduction to quantum mechanics. The postulates introduce and correlate the basic mechanical (E_n), statistical (A_{nm}), and spectral (ω_{nm}, P_{nm}) elements of quantum mechanics. The theorems provide insight into the classical-quantum connection and enable one to calculate transition properties (ω_{nm}, A_{nm}) from electron dynamics ($F(x)$). Furthermore, the classical-quantum theory links different areas of physics, including Newton's mechanics, Maxwell's electrodynamics, Bohr's atomic theory, Einstein's radiation theory, and Fourier's spectral analysis. Specific features that uniquely characterize the classical-quantum theory and illustrate its pedagogical usefulness are highlighted below.

(1) The classical-quantum theory reveals the precise asymptotic connection between the spectroscopic properties (A_{nm}, ω_{nm}) of the quantum jump $n \to m$ and the kinematic properties $[a_\tau(n), \omega_\tau(n)]$ of the classical harmonic $a_\tau(n) \cos \omega_\tau(n) t$. The order ($\tau$) of the harmonic is numerically equal to the length ($n-m$) of the jump.

(2) Transition rates are calculated using only Bohr theory and Fourier analysis, without having to introduce Schrödinger's equation or time-dependent perturbation theory. The calculation of an atomic line spectrum is reduced to the calculation of a quantized Fourier series.

(3) The classical-quantum calculations are much simpler and shorter than the exact-quantum calculations, and yet the classical-quantum results match the exact-quantum results, asymptotically (for large n) and in some cases perfectly (for all n).

(4) The selection rules derived from the Bohr–Fourier theory agree exactly with those of the Heisenberg–Schrödinger theory. Forbidden quantum transitions rigorously correspond to missing classical harmonics.

(5) A simple and powerful consequence of the postulates is "Fourier's golden rule:"

$$A_{n,n-\tau} = K\omega_{n,n-\tau}^3 [a_\tau(n)]^2, \tag{62}$$

which is the classical-quantum analogue of Fermi's golden rule. It is an intuitive version of the general relation, probability $\sim |\text{amplitude}|^2$, which is a paradigm of modern quantum mechanics.

(6) The classical-quantum theory illuminates the connection between the Newtonian orbital frequency, $\nu = dE/dJ$, and the Einstein–Bohr optical frequency, $\nu_{nm} = \Delta E/h$. The optical frequency is equal to the orbital frequency, averaged over the electronic orbits occupying the "jumped space" between n and m:

$$\nu_{nm} = \int_m^n \nu(s)\,ds. \tag{63}$$

(7) The classical-quantum theory illustrates the connection between the harmonic components of Heisenberg matrices and Fourier series:

$$\lim_{n \gg \tau} c_{n,n-\tau} \exp(i\omega_{n,n-\tau}t) = c_\tau(n)\exp(i\tau\omega(n)t). \tag{64}$$

Table IV. Comparison of classical-quantum and exact-quantum theories of the anharmonic oscillator.

Classical-quantum energy	$E_n = n\hbar\omega_0 + \dfrac{3\hbar^2\lambda}{8m\omega_0^2}n^2$	
Exact-quantum energy	$E_n = \left(n+\dfrac{1}{2}\right)\hbar\omega_0 + \dfrac{3\hbar^2\lambda}{8m\omega_0^2}\left(n^2+n+\dfrac{1}{2}\right)$	
Mechanical frequency	$\omega_1(n) = \omega_0 + \dfrac{3\hbar\lambda}{4m\omega_0^2}n$	$\omega_3(n) = 3\omega_0 + \dfrac{9\hbar\lambda}{4m\omega_0^2}n$
Exact spectral frequency	$\omega_{n,n-1} = \omega_0 + \dfrac{3\hbar\lambda}{4m\omega_0^2}n$	$\omega_{n,n-3} = 3\omega_0 + \dfrac{9\hbar\lambda}{4m\omega_0^2}(n-1)$
Fourier amplitude	$a_1(n) = \sqrt{\dfrac{2\hbar n}{m\omega_0}}\left(1 - \dfrac{3\hbar\lambda}{8m\omega_0^3}n\right)$	$a_3(n) = \lambda\sqrt{\dfrac{\hbar^3}{128m^3\omega_0^7}n^3}$
Heisenberg amplitude	$2c_{n,n-1} = \sqrt{\dfrac{2\hbar n}{m\omega_0}}\left(1 - \dfrac{3\hbar\lambda}{8m\omega_0^3}n\right)$	$2c_{n,n-3} = \lambda\sqrt{\dfrac{\hbar^3}{128m^3\omega_0^7}n(n-1)(n-2)}$

The theory also vividly illustrates the connection between quantum amplitudes (matrix elements) and classical amplitudes (Fourier coefficients):

$$\lim_{n \gg \tau} \int_{-\infty}^{\infty} \psi_n^*(x) x \psi_{n-\tau}(x) dx$$

$$= \frac{\omega(n)}{2\pi} \int_0^{2\pi/\omega(n)} x(t,n) \cos(\tau \omega(n) t) dt. \qquad (65)$$

Equation (65) provides a remarkable analytical relation between the stationary states $\psi_n(x)$ of quantum mechanics and the periodic states $x(t,n)$ of classical mechanics.

APPENDIX: EXACT QUANTUM MECHANICAL RESULTS

1. Simple harmonic oscillator

For a simple harmonic oscillator of mechanical frequency ω_0, the energy[26] of the stationary state $|n\rangle$ is $E_n = (n + \frac{1}{2})\hbar\omega_0$. The matrix element,[27] $c_{nl} = \langle n|x|l\rangle$, is $c_{nl} = \sqrt{\hbar n/2m\omega_0}\, \delta_{l,n-1}$ for $n \geq l$. The radiation frequency, $\omega_{nl} = (E_n - E_l)/\hbar$, is $\omega_{n,n-1} = \omega_0$. Thus, the quantum motion of a simple harmonic oscillator is characterized by the Heisenberg harmonic

$$x_{n,n-1}(t) = \sqrt{\frac{\hbar n}{2m\omega_0}} e^{i\omega_0 t}. \qquad (A1)$$

2. Particle in a box

The stationary states of a particle of mass m in a box of length L are characterized by the following energies and wave functions:[28]

$$E_n = \frac{\pi^2 \hbar^2}{2mL^2} n^2, \quad \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \qquad (A2)$$

The Heisenberg harmonics, $x_{nk} = c_{nk} \exp(i\omega_{nk}t)$, are characterized by the frequencies $\omega_{nk} = (E_n - E_k)/\hbar$,

$$\omega_{nk} = \frac{\pi^2 \hbar}{2mL^2}(n^2 - k^2), \qquad (A3)$$

and the amplitudes $c_{nk} = \langle \psi_n|x|\psi_k\rangle$,

$$c_{nk} = \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right) x \sin\left(\frac{k\pi x}{L}\right) dx$$

$$= \begin{cases} -\dfrac{8L}{\pi^2}\dfrac{nk}{(n^2-k^2)^2}, & n-k = 1,3,5,..., \\ \\ 0, & n-k = 2,4,6,.... \end{cases} \qquad (A4)$$

3. Anharmonic oscillator

We solve the quantum mechanical problem of the anharmonic oscillator to first-order in perturbation theory. The Hamiltonian is

$$H = H_0 + \varepsilon x^4, \qquad (A5)$$

where $H_0 \equiv p^2/2m + kx^2/2$ is the unperturbed Hamiltonian describing the simple harmonic oscillator. The anharmonic interaction εx^4 is treated as a small perturbation to H_0. Note that the small energy parameter ε is related to the small force parameter λ used in the text by $\varepsilon = m\lambda/4$.

We first calculate the energies E_n of the stationary states $|\psi_n\rangle$ defined by the eigenvalue problem, $H|\psi_n\rangle = E_n|\psi_n\rangle$. According to perturbation theory,[29]

$$E_n = E_n^0 + \varepsilon \langle \psi_n^0|x^4|\psi_n^0\rangle, \qquad (A6)$$

where $E_n^0 = (n + \frac{1}{2})\hbar\omega_0$ and $|\psi_n^0\rangle$ are solutions of $H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$. To calculate the matrix elements $\langle \psi_n^0|x^4|\psi_n^0\rangle$ in Eq. (A6), we use the orthonormality relation, $\langle \psi_n^0|\psi_l^0\rangle = \delta_{nl}$, and the operator identity,[30]

$$x|\psi_n^0\rangle = \sqrt{\frac{\hbar}{2m\omega_0}}[\sqrt{n+1}|\psi_{n+1}^0\rangle + \sqrt{n}|\psi_{n-1}^0\rangle]. \qquad (A7)$$

The effect of x^4 operating on $|\psi_n^0\rangle$ is obtained by iterating Eq. (A7). The result of these calculations is the following energy function of the anharmonic oscillator:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 + \frac{3\hbar^2\lambda}{8m\omega_0^2}\left(n^2 + n + \frac{1}{2}\right). \qquad (A8)$$

Note that if $n \gg 1$, this quantum mechanical energy coincides with the classical-quantum energy in Eq. (57).

We now calculate the amplitude, $c_{nl} = \langle \psi_n|x|\psi_l\rangle$, of the Heisenberg harmonic, $x_{nl} = c_{nl}\exp(i\omega_{nl}t)$. In perturbation theory, the anharmonic-oscillator eigenstates $|\psi_n\rangle$ are represented as a superposition of harmonic-oscillator eigenstates $|\psi_n^0\rangle$:

$$|\psi_n\rangle = |\psi_n^0\rangle + \varepsilon \sum_{k \neq n} \frac{\langle \psi_k^0|x^4|\psi_n^0\rangle}{E_n^0 - E_k^0} |\psi_k^0\rangle. \qquad (A9)$$

Thus, our ultimate goal of finding the "anharmonic position elements" $\langle \psi_n|x|\psi_l\rangle$ requires an intermediate calculation of the "harmonic energy elements" $\langle \psi_k^0|x^4|\psi_n^0\rangle$. We find that the matrix elements $\langle \psi_k^0|x^4|\psi_n^0\rangle$ vanish unless $k = n$, $n \pm 2$, $n \pm 4$. The nonzero elements are

$$\langle \psi_{n-4}^0 | x^4 | \psi_n^0 \rangle = \left(\frac{\hbar}{2m\omega_0} \right)^2 \sqrt{n(n-1)(n-2)(n-3)},$$

$$\langle \psi_{n-2}^0 | x^4 | \psi_n^0 \rangle = \left(\frac{\hbar}{2m\omega_0} \right)^2 (4n-2) \sqrt{n(n-1)},$$

$$\langle \psi_n^0 | x^4 | \psi_n^0 \rangle = \left(\frac{\hbar}{2m\omega_0} \right)^2 (6n^2 + 6n + 3), \tag{A10}$$

$$\langle \psi_{n+2}^0 | x^4 | \psi_n^0 \rangle = \left(\frac{\hbar}{2m\omega_0} \right)^2 (4n+6) \sqrt{(n+1)(n+2)},$$

$$\langle \psi_{n+4}^0 | x^4 | \psi_n^0 \rangle = \left(\frac{\hbar}{2m\omega_0} \right)^2 \sqrt{(n+1)(n+2)(n+3)(n+4)}.$$

The matrix element $\langle \psi_n | x | \psi_l \rangle$ is assembled from the expansion of $|\psi_n\rangle$ in Eq. (A9), the expansion coefficients in Eq. (A10), and the operator identity in Eq. (A7). The results of this lengthy calculation are as follows. The amplitude $\langle \psi_n | x | \psi_l \rangle$ vanishes unless $l = n \pm 1$, $n \pm 3$. The nonzero amplitudes are

$$\langle \psi_n | x | \psi_{n-1} \rangle = \sqrt{\frac{\hbar n}{2m\omega_0}} \left(1 - \frac{3\hbar\lambda}{8m\omega_0^3} n \right),$$

$$\langle \psi_n | x | \psi_{n-3} \rangle = \lambda \sqrt{\frac{\hbar^3}{512 m^3 \omega_0^7} n(n-1)(n-2)}. \tag{A11}$$

The two amplitudes for absorption ($l = n+1, n+3$) are related to the above amplitudes for emission ($l = n-1, n-3$) via the Hermitian property of the matrix, $x_{nl} = x_{ln}^*$.

The frequencies of the radiation emitted during the allowed transitions, $n \to n-1$ and $n \to n-3$, are obtained by substituting the anharmonic oscillator energies from Eq. (A8) into the Einstein–Bohr relation, $\omega_{n,n-\tau} = (E_n - E_{n-\tau})/\hbar$. The results are

$$\omega_{n,n-1} = \omega_0 + \frac{3\hbar\lambda}{4m\omega_0^2} n,$$

$$\tag{A12}$$

$$\omega_{n,n-3} = 3\omega_0 + \frac{9\hbar\lambda}{4m\omega_0^2} (n-1).$$

Equations (A8), (A11), and (A12) constitute the main results of our quantum mechanical solution of the anharmonic oscillator problem. The results are exact to first order in λ.

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