Accurate prediction of spectroscopic properties of single molecules, molecular clusters or the solid state in combination with detailed information from apparatus-based experiments are currently paving the way to a promising revolution in the borderland between theory and experiment, namely computational spectroscopy. Though, at first sight, the term seems to contradict itself, the rapid developments in this field are opening up the study of increasingly large and chemically complex systems. At the same time, experimental molecular spectroscopy is an extremely active and fast-developing area that is heading towards the possibility of performing precise measurements on single molecules. Unique in its comprehensive coverage of not only theoretical methods but also applications in computational spectroscopy, this ready reference and handbook compiles the developments made over the last few years.

This book is a must-have for Spectroscopists, Theoretical Chemists, Libraries, and Physical Chemists wanting to catch up with the state-of-the-art in Computational Spectroscopy.

Jörg Grunenberg studied chemistry at the University Erlangen-Nürnberg. After his doctorate he moved to the Technische Universität Braunschweig and is now head of the scientific computing section at the Institute of Organic Chemistry. His interests are the in silico prediction of molecular spectroscopic properties and the quantification of covalent and non-covalent interactions. He is author and co-author of more than 80 original papers and book chapters on computational chemistry.
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Preface

...with its help, debates can be resolved forever, if they can be settled on the basis of some data; and if one took the pen it would be enough for the two disputing men to say to one another: Let’s calculate.

Leibniz in a letter to P. J. Spener, 1687

Computational chemistry has reached a high degree of maturity and comprehension making it one of the vivid research areas in modern chemical and physical research in general. This is true because an accurate simulation of spectroscopic properties is one of the major challenges and – at the same time – a precious benefit of modern theoretical chemistry. Predictions concerning single molecules, molecular clusters, or even the solid state in combination with detailed information from apparatus-based experiments are therefore providing ingredients to an auspicious revolution in the borderland between theory and experiment: computational spectroscopy. At first sight, the term seems to contradict itself: from the traditional point of view, spectroscopy (or spectrometry) belongs to the realm of the experimentalists, while computational chemistry is allocated to the domain of theory. The frantic developments in both areas during the last years have nevertheless helped build new bridges between both worlds.

This is important because until the end of the last millennium theoretical and experimental chemistry were separated by respectable gaps. Studying chemistry in the 1990s was yet sometimes accompanied by dialectical training: equipped with the sanguine knowledge that molecular orbitals are artifacts (learned from an exciting theoretical chemistry course), one stumbled into an organic chemistry exam being forced to explain the formation of a covalent bond in terms of those very orbitals. Those days are history now for several – in part ambivalent – reasons. The main cause nevertheless is a simple one: modern computational chemistry deals with observable properties and this positivistic shift does not leave too much room for “overinterpretations.” One can always try to find an experiment, which allows either falsification or confirmation of the computer simulation. This is in sharp contrast to the second major application area of computational chemistry: the underpinning of chemical concepts. Led by Coulson’s famous request, “... give us insights, not
numbers . . .,” more and more chemical perceptions as well as new molecular categories were introduced. It is, however, still unclear whether the addition of those ad hoc concepts is always helpful in characterizing the huge variety of chemical phenomena. On the contrary, many of these early chemical concepts resembled Leibniz’s voces metaphysicae, that means phrases, which we use believing that we understand entities just by pinning names on them. Or, to quote Wolfgang Pauli, many of the earlier concepts deduced from approximate quantum chemistry were so fuzzy that they were not even wrong.

In order to keep pace with new developments in terms of more rigorous solutions for Schrödinger equation, we anyhow may not demand that ideas from the early days of numerical theoretical chemistry persist permanently. The decade-long debate and struggle for a unique definition of aromaticity is only one of the many examples of those fruitless endeavors. The (in part humoristic) suggestion by Heilbronner as early as 1971 at the famous Jerusalem symposium on “Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity” to introduce the term “schizo-aromaticity” for molecules, which are aromatic by one definition and nonaromatic by another, illuminates this dilemma quite graphically.

The situation changed dramatically during the last 20 years. Reliable first-principle electronic structure calculations on the one hand and sophisticated molecular dynamic simulations for complex systems on the other hand are nowadays well-established instruments in the toolbox of theoretical chemists, and these rapid developments are paving the way for the study of increasingly large and chemically complex systems. At the same time, experimental molecular spectroscopy is also an extremely active and fast-developing field, which is evolving toward the possibility of performing precise measurements for single molecules and, even more intriguing, for the hub of chemistry itself, the individual covalent bond. The title of this book Computational Spectroscopy states its aim: From basic research to commercial applications in the area of environment relevance, we will compile the major developments during the past 5–10 years. A multitude of apparatus-driven technologies will be covered. Nevertheless, the selection of topics is of course a subjective one. Summarizing the results of so many different disciplines, I hope that this book will on the one hand attract the attention of newcomers and on the other hand inform the experts about developments in scientific areas adjacent to their own expertise.

At Wiley, I would especially like to thank Dr. Elke Maase and Dr. Martin Graf for their guidance through all phases (from the first concept of the book to the final cover design) of this challenging and fascinating project.

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1 Concepts in Computational Spectrometry: the Quantum and Chemistry

J. F. Ogilvie

1.1 Introduction

During the nineteenth century and most of the first half of the twentieth century, after Dalton’s recognition of the atomic nature of chemical matter, which is everything tangible, that matter was regarded by most chemists as a material. Even though chemists, following Couper, Kekule, van’t Hoff, and others, drew structural formulae in terms of atoms connected by bonds represented as lines, chemical samples were generally regarded as materials or “stuff”. When, after 1955, molecular spectra, particularly of organic compounds, began to be recorded routinely in the mid-infrared region and with nuclear magnetic resonance, the outlook of chemists shifted from macroscopic properties, such as density, melting point, and refractive index, to purportedly molecular properties, such as the effect of adjacent moieties on the characteristic infrared absorption associated with a carbonyl group or on the chemical shift of a proton. The first “quantum-chemical” calculations, on $\text{H}_2^+$ by Burrau and on $\text{H}_2$ by Heitler and London, all physicists, had as subjects chemical species remote from common laboratory experience, but Pauling’s brilliant insight and evangelical manner stimulated great qualitative interest in a theoretical interpretation of chemical properties, even though a large gap existed between the primitive calculations on methane and other prototypical molecules and molecules of substances of practical interest. This gap was bridged largely through the efforts of Pople and his collaborators during the second half of the twentieth century in developing computer programs that enabled efficient calculation of observable molecular properties; not coincidentally, Pople was also an early exponent of the application of nuclear-magnetic-resonance spectra in the publication in 1959 of an authoritative monograph [1] that was seminally influential in the general application of this spectral method [2].

Chemists concerned with quantitative analysis have always understood the distinction between spectroscopy and spectrometry: spectroscopy implies the use of a human eye as a visual detector with a dispersive optical instrument and hence necessarily qualitative and imprecise observations, whereas spectrometry pertains to
an instrument with an electrical detector amenable to quantitative measurement of both frequency and intensity. For spectra throughout the entire accessible range of frequencies from $10^6$ Hz, characteristic of nuclear quadrupole or nuclear magnetic resonance, to radiation in the X-ray region sufficiently energetic to cause ionization, a significant use of the numerical results of computations based nominally on quantum mechanics, such as of molecular electronic structure and properties, is to assist that spectral analysis. Pople’s programs were based, to an increasing extent over the years, on selected quantum-mechanical principles that arose from quantum theories. During the past century, the practice of chemistry has thus evolved much, from being a largely empirical science essentially involving operations in a laboratory and their discussion, to having — allegedly — an underpinning based on quantum theories.

During the nineteenth century, a standard paradigm for most chemical operations was that both matter and energy are continuous; following a philosophical point of view of Greek savants and concrete ideas of Bacon and Newton, Dalton’s contention that matter is particulate provided a basis to explain chemical composition, but Ostwald remained skeptical of the existence of atoms until 1909 [3]. The essence of the quantum concept is that both energy and matter ultimately comprise small packets, or chunks, not further divisible retaining the same properties. In Latin, quantum means *how much*? A descriptor more enlightening than quantum is discrete, so we refer to the ultimate prospective discreteness of matter and energy. (In a mathematical context, integers take discrete values, even though they number uncountably, and have a constant unit increment, whereas real numbers 1.1, 1.11, 1.111, ... vary continuously, with an increment between adjacent representatives as small as desired.) One accordingly distinguishes between the laws of discreteness, based on experiment, and various theories that have been devised to encompass or to reproduce those discrete properties. The distinctions between physical laws and theories or mathematical treatments are poorly appreciated by chemists; our objective is thus to clarify the nature of both quantum laws and quantum theories, thereby to propose an improved understanding of the purported mathematical and physical basis of chemistry and the application of computational spectrometry. After distinguishing between quantum laws and quantum theories, we apply to a prototypical problem three distinct quantum-mechanical methods that nevertheless conform to the fundamental postulate of quantum mechanics; we then consider molecular structure in relation to quantum-mechanical principles and their implications for the practice of chemistry aided by computational spectrometry.

For many chemists, the problem so called the *particle in a box* is the only purportedly quantum-mechanical calculation that they are ever required to undertake as a manual exercise, but its conventional solution is at least problematic. Any or all treatments of a harmonic oscillator in Section 1.3 serve as a viable alternative to that deficient model. The connection between quantum mechanics and chemistry might be based on a notion that “quantum mechanics governs the behavior of electrons and atoms in molecules,” which is merely supposition. While Dirac and Einstein had, to the ends of their lives, grave misgivings about fundamental aspects of quantum mechanics [4], and even Born was never satisfied with a separate — and thereby
inconsistent – treatment of the motions of electrons and atomic nuclei that underpins common quantum-chemical calculations, almost all chemists accept, as recipes, these highly mathematical theories, in a mostly qualitative manner embodied in orbitals – “for fools rush in where angels fear to tread” (Pope). For those chemists who undertake calculations, typically with standard computer programs developed by mathematically knowledgeable specialists who have no qualms about producing more or less efficient coding but who might refrain from questioning the underlying fundamental aspects, the emphasis is placed on the credibility of the results. For the molecular structures of stable species that have been established by essentially experimental methods, although a theoretical component is invariably present, the empirical nature of the computer coding – its parameters are invariably set to reproduce, approximately, various selected properties of selected calibration species – reduces its effect to a sophisticated interpolation scheme; for the molecular structures of such fabulous species as transition states, as these are inherently impossible to verify, the results of the calculations merely reinforce preconceived notions of those undertaking such calculations. We trust that reconsideration of the current paradigm in chemistry that abides such questionable content will motivate an improved understanding of the mathematical and physical bases of chemistry and a reorientation of chemistry as an experimental and logical science of both molecules and materials. For this purpose, computational spectrometry has a substantial role to play in a fertile production of information about the structure and properties of molecules and materials.

1.2 Quantum Laws, or the Laws of Discreteness

The universe comprises matter and energy; as chemists, we might ignore the possibility of their interconversion. With regard to matter, we classify anything on or above an atomic scale and that displays a rest mass as either material or molecule. Molecules exist only in a gaseous state of aggregation under conditions in which intermolecular interactions are negligible, thus describable as constituting an ideal gas; an isolated atom is simply a monatomic molecule. Molecules hence exist most purely in interstellar clouds, but even appropriate gaseous samples in a terrestrial laboratory that exhibit properties nearly characteristic of a free molecule might, to a sufficient approximation, be deemed to contain molecular entities. A material is found in a condensed phase or in a compressed gas, under which conditions rotational degrees of freedom are much hampered. A few condensed samples, such as liquid dihydrogen, have properties, such as spectra in the infrared region, that might resemble those of free molecules. In contrast, a single macroscopic crystal of diamond or sodium chloride or a sheet of “polyethylene”, for instance, might on structural grounds be regarded as constituting a single molecule. For H$_2$O, the smallest internuclear distances in the gaseous phase and in liquid water or solid ice differ by more than their experimental uncertainties, and their infrared spectra concomitantly differ. How can we consider H$_2$O to be the same species in the
molecular vapor and the material solid? For energy, we limit attention to its radiant form as constituting a free state like an interstellar molecule; a discrete unit of radiation is called a photon.

We summarize in Table 1.1 some fundamental properties of molecules and photons [5].

The experiment best known to demonstrate the discreteness of a property of a particle with rest mass is Millikan’s measurement of the charge of an electron on a drop of oil suspended in a vertical electric field. Assuming that discreteness of electric charge, one readily observes the discreteness of mass of molecular ions with a conventional mass spectrometer. The unit of charge is that on the proton or the magnitude of charge that an electron carries. Masses of individual atoms are classified with exact integers, but actual atomic masses, or masses of not too large molecules of particular isotopic composition, assume nearly integer values in terms of unified atomic mass unit or dalton. Under appropriate conditions, the total energy $W$ of a molecule confined to a finite spatial volume might take discrete values, but even for an unconfined molecule the rotational, vibrational, and electronic contributions to total energy might be observed to alter in discrete increments. The linear momentum $\mathbf{p}$ of a confined molecule is supposed to assume discrete values. Not only the total angular momentum $\mathbf{\Omega}$ of a molecule but also the separate electronic, nuclear, and rotational contributions thereto appear to assume, in a particular discrete state, integer or half-integer values in terms of Dirac constant $\hbar$ (Planck constant $\hbar$ divided by $2\pi$); these angular momenta likewise alter in unit increments in various processes.

A photon possesses neither net electric charge nor rest mass, but its energy and linear momentum are directly related to its wave attributes – frequency $\nu = E/\hbar$ and wavelength $\lambda = h/|\mathbf{p}|$; their product $\nu \lambda$ equals the speed $c$ of light. Any photon carries, independent of frequency, intrinsic angular momentum $\mathbf{\Omega}$ to the extent of one unit in terms of $\hbar$, in the direction of propagation if it be circularly polarized in one sense or opposite the direction of propagation for circular polarization in the other sense. As a limiting case of elliptical polarization, linearly polarized light as a coherent superposition of these two circular polarizations lacks net angular momentum and so imparts no total angular momentum to an absorbing target.

Even when neglecting a distinction between molecules and materials, these laws of discreteness, or quantum laws, of molecules and photons provide an ample basis for

<table>
<thead>
<tr>
<th>Property</th>
<th>Value for molecule</th>
<th>Value for photon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>$Z = 0, \pm 1e, \pm 2e, \ldots$</td>
<td>0</td>
</tr>
<tr>
<td>(Rest) mass</td>
<td>$M &gt; 0$</td>
<td>0</td>
</tr>
<tr>
<td>Energy</td>
<td>$W \approx W_{\text{tr}} + W_{\text{rot}} + W_{\text{vib}} + W_{\text{el}} + \cdots$</td>
<td>$W = h\nu$</td>
</tr>
<tr>
<td>Linear momentum</td>
<td>$</td>
<td>\mathbf{p}</td>
</tr>
<tr>
<td>Angular momentum</td>
<td>$</td>
<td>\mathbf{\Omega}</td>
</tr>
</tbody>
</table>
the conduct and explanation of chemical operations for almost all practical purposes beyond which a continuum of properties suffices.

1.3 Quantum Theories of a Harmonic Oscillator

In attempts to explain or to encompass various experimental data interpreted in terms of discrete properties at a molecular level, scientists have devised various quantum theories. Planck proposed reluctantly in 1900 the first theory to involve a discrete quantity, for which he invoked harmonic oscillators; he attempted to explain the distribution of energy, as a function of wavelength, radiated by a black body [3]. As that distribution is continuous, the requirement for a discrete quantity in a theoretical derivation is not obvious. That distribution has been derived alternatively with classical statistical thermodynamics [6], although the incorporation therein of the Planck constant remains enigmatic. The second application of a quantum condition appeared in Einstein’s treatment of the photoelectric effect in 1905, but in retrospect a recognition of the quantum laws makes that derivation almost trivial. In relation to infrared spectra of gaseous hydrogen halides, in 1911 Bjerrum, a Danish chemist, sought to develop an explicit quantum theory of molecules for vibrational and rotational motions; as this treatment preceded Rutherford’s revelation of the structure of the nuclear atom, this endeavor was bound to fail. Equally incorrect but far better known is Bohr’s theory, in 1913, of an atom with one electron for which some enhancements by Sommerfeld and Wilson failed to remedy the fundamental deficiencies [3].

In 1924, Born and Heisenberg recognized that a proper description of an atomic particle must be concerned with its mechanics and dynamics, hence with equations of motion in terms of position, momentum, and time. In Heisenberg’s development of the first enduring quantum theory in 1925 [3], the crucial particular in his paper is expressible as

\[ p_j q_k - q_k p_j = -i \hbar \delta_{j,k} \]  

(1.1)

Therein appear symbols to denote a component of momentum \( p \) or of position \( q \), \( i = \sqrt{-1} \), Dirac constant \( \hbar \), and Kronecker delta function \( \delta_{j,k} \) that equals unity if \( j = k \) or zero otherwise; the left side of this equation contains a commutator, printed as \([p_j, q_k]\). In one dimension, this equation becomes

\[ pq - qp = [p, q] = -i \hbar \]

(1.2)

From this relation are derivable both de Broglie’s relation, \( \lambda = h/p \), and Heisenberg’s principle of indeterminacy [5], \( \Delta q \Delta p \geq 1/2 \hbar \), whereas the reverse derivations are less obvious. One may thus regard this equation, as Dirac recognized directly in 1925, to constitute the fundamental postulate of quantum mechanics. A parallel postulate in the form of a commutation relation involving energy and time is less relevant here. Among quantities that naturally fail to commute are matrices, and a variable with its differential operator; such quantities to represent \( p \) and \( q \) might hence form a basis of quantum-mechanical calculations.
To illustrate and to contrast three methods of quantum mechanics in a nonrelativistic approximation, we apply this commutator to a canonical linear harmonic oscillator in one spatial dimension. According to classical mechanics, the frequency of its oscillation is independent of its amplitude, whereas according to quantum mechanics a harmonic oscillator has states of discrete energies with equal increments between adjacent states, as we derive below. Because the latter oscillator possesses no angular momentum, it behaves as a boson. The classical potential energy $V$ associated with this canonical form is expressed as

$$V(q) = \frac{1}{2} k c q^2$$  \hspace{1cm} (1.3)

in which $V$ exhibits a parabolic dependence on displacement coordinate $q$; coefficient $k c$ is also the factor of proportionality in Hooke’s law, $F(q) = -k c q$, relating a restoring force to that displacement.

### 1.3.1 Matrix Mechanics

According to matrix mechanics, each physical quantity has a representative matrix [7]. For coordinate matrix $Q$, we accordingly define its elements $q_{n,m}$. Combining the relation for the restoring force of an oscillator of mass $m$ with Newton’s second law in nonrelativistic form, we obtain

$$F(q) = -k c q = \mu \frac{d^2 q}{dt^2}$$  \hspace{1cm} (1.4)

Expressing a ratio $k c /\mu$ of parameters as a square of a radial frequency $\omega_0$, for which the units are appropriate, we rewrite this differential equation as

$$\frac{d^2 q(t)}{dt^2} = -\omega_0^2 q(t)$$  \hspace{1cm} (1.5)

For this equation to be applicable to a system described by means of matrix mechanics, each element of matrix $Q$ must separately obey this equation; we express this solution in exponential form as

$$q_{n,m}(t) = q_{n,m}^0 \exp \left(-i \omega_{n,m} t\right)$$  \hspace{1cm} (1.6)

in which appear two arbitrary constants $q_{n,m}^0$ and $\omega_{n,m}$, appropriate to an ordinary differential equation of second order. Substitution of this solution into that differential equation yields the following condition:

$$\left(\omega_0^2 - \omega_{n,m}^2\right) q_{n,m}^0 = 0$$  \hspace{1cm} (1.7)

Hence, either $q_{n,m}^0 = 0$ or $\omega_{n,m} = \pm \omega_0$. Because numbering of matrix elements is arbitrary, we apply a convention that a condition $\omega_{n,m} = + \omega_0$ corresponds to emission of a photon as the oscillator passes from a state of energy with index $n$ to another state with energy with index $n - 1$, whereas a condition $\omega_{n,m} = - \omega_0$ corresponds to absorption of a photon as the oscillator passes from a state of energy with index $n$ to another state with energy with index $n + 1$. With numbering of elements
beginning at zero, the coordinate matrix thus assumes this form,

\[
Q = \begin{pmatrix}
0 & q_{0,1}^0 & 0 & 0 & \cdots \\
q_{1,0}^0 & 0 & q_{1,2}^0 & 0 & \cdots \\
0 & q_{2,1}^0 & 0 & q_{2,3}^0 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix}
\]

(1.8)

in which nonzero elements accordingly appear only on the first diagonals above and below the principal diagonal. As momentum, in a nonrelativistic approximation, is defined as a product of a constant mass and the temporal derivative of coordinate \( q \), so that \( p = \mu \frac{dq}{dt} \), we have for each element of the momentum matrix \( p_{n,m} = i \mu \omega_{n,m} q_{n,m} \); with \( \omega_{n,m} = \pm \omega_0 \) and \( m = n \pm 1 \), we obtain

\[
P = i \mu \omega_0 \begin{pmatrix}
0 & q_{0,1}^0 & 0 & 0 & \cdots \\
q_{1,0}^0 & 0 & q_{1,2}^0 & 0 & \cdots \\
0 & q_{2,1}^0 & 0 & q_{2,3}^0 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix}
\]

(1.9)

which has nonzero elements along diagonals only directly above and below the principal diagonal.

The total energy \( W \) of a state of the oscillator is a sum of kinetic \( T \) and potential \( V \) contributions, which together constitute the Hamiltonian \( \hat{H} \) applicable to this problem,

\[
W = \hat{H} = 1/2 p^2/\mu + 1/2 k_e q^2 = 1/2 p^2/\mu + 1/2 \mu \omega_0^2 q^2
\]

(1.10)

We form accordingly an energy matrix \( W \) as a sum of squares of matrices \( P \) for momentum and \( Q \) for coordinate with their indicated multiplicands, \( 1/2 \mu^{-1} \) and \( 1/2 \mu \omega_0^2 \), respectively, which yields

\[
W = \mu \omega_0^2 \begin{pmatrix}
q_{0,1,0}^0 & q_{1,0}^0 & 0 & 0 & \cdots \\
0 & q_{0,1,0}^0 + q_{1,2,1}^0 & q_{1,1,2}^0 & 0 & \cdots \\
0 & 0 & q_{1,2,1}^0 + q_{2,3,2}^0 & q_{2,1,2}^0 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix}
\]

(1.11)

Nonzero elements appear therein only along the principal diagonal. Moreover, all factors dependent on time have vanished, which signifies that the energies of states are independent of time, thus corresponding to stationary states. Amplitude coefficients \( q_{n,m}^0 \), which originate as constants of integration, remain to be evaluated; for this purpose, we apply directly the commutation law, which here contains a unit matrix on the right side.
\[
[pq - qp] = -2i \mu \omega_0 \begin{pmatrix}
q_{1,0}^0 & q_{0,1}^0 & 0 & 0 & \cdots \\
0 & q_{2,1}^0 & q_{1,2}^0 - q_{1,0}^0 q_{0,1}^0 & 0 & \cdots \\
0 & 0 & q_{3,2}^0 & q_{2,3}^0 - q_{2,1}^0 q_{1,2}^0 & \cdots \\
& & & & \cdots \cdots \cdots \cdots \cdots
\end{pmatrix}
\]
\[
= -i \hbar \begin{pmatrix}
1 & 0 & 0 & 0 & \cdots \\
0 & 1 & 0 & 0 & \cdots \\
0 & 0 & 1 & 0 & \cdots \\
& & & & \cdots \cdots \cdots \cdots \cdots
\end{pmatrix}
\]

Therefore,
\[
q_{1,0}^0 q_{0,1}^0 = -i \hbar / (-2i \mu \omega_0) = \hbar / (2\mu \omega_0)
\]
\[
q_{2,1}^0 q_{1,2}^0 - q_{1,0}^0 q_{0,1}^0 = \hbar / (2\mu \omega_0), \ldots
\]

Solving successively these equations and consistent with microscopic reversibility, we obtain
\[
q_{n+1,n}^0 q_{n,n+1}^0 = q_{n,n+1}^0 q_{n+1,n}^0 = |q_{n,n+1}^0|^2 = (n+1)\hbar / (2\mu \omega_0)
\]

We substitute this general relation into the energy matrix. The corresponding elements \(q_{m,n}\) of coordinate matrix \(Q\) increase along each diagonal according to \([1/2 (n+1)]^{1/2}\). When we replace radial frequency \(\omega_0\) by circular frequency \(\nu_0 = \omega_0 / (2\pi)\), we derive a general result
\[
W_n \equiv W_{n,n} = (n + 1/2) \hbar \nu_0 = (n + 1/2) \hbar \nu_0
\]

This result signifies that the interval of energy between states characterized with adjacent integers is constant, equal to \(\hbar \nu_0\), and that the state of least energy, characterized with \(n = 0\), has a residual, or zero-point, energy equal to \(1/2 \hbar \nu_0\). Transitions in absorption or emission, according to type electric dipole of form charge times distance, \(e q\), are thus governed by the nonzero elements of coordinate matrix \(Q\); these transitions are hence possible only between states of adjacent energies.

In principle, the rows and columns of all matrices here number infinitely, but to form each matrix with a dozen rows and columns suffices for any practical purpose. Although these calculations by hand with matrices of even such an order are tedious, calculation with mathematical software [8] such as Maple is readily effected; according to contemporary methods of teaching mathematics, many students are introduced to such software in calculus courses, so there is no major impediment to such use for chemical applications. In the same way, one shows directly that the
numbering of matrix elements is arbitrary, so that nonzero elements \( q_{n,m}^0 \) of matrix \( Q \) might occur for \( n = m \pm k \), for instance, with \( k = 2 \) or \( 3 \) rather than \( 1 \) as above; in that case, the energies still have values \( (n + 1/2 \ h \ \nu_0) \) with nonnegative integer \( n \), and two or three states have the same energy. Transitions of type electric dipolar still occur only between states of adjacent distinct energies.

1.3.2 Wave Mechanics

According to wave mechanics, an observable quantity might be represented with a differential operator. To conform to the fundamental postulate of quantum mechanics, either coordinate \( q \) or momentum \( p \), but not both, might be selected to be a differential operator. According to a coordinate representation, we choose momentum \( p \) to become \(-i \ \hbar \ d/dq\), whereas according to a momentum representation we choose coordinate \( q \) to become \( i \ \hbar \ d/dp\); the reason for such choices is simply to impose conformity with that fundamental postulate. A differential operator requires an operand, called an amplitude function or wavefunction; for operator \( d/dq\), we choose \( \psi \) to denote its operand, whereas \( \chi \) for operand of \( d/dp\). Among properties that \( \psi(q) \) and \( \chi(p) \) must obey are that these functions must be continuous, remain everywhere finite and singly valued, and satisfy appropriate boundary conditions; the first derivatives of \( \psi(q) \) and \( \chi(p) \) with respect to their specified arguments must likewise be well behaved except possibly at infinite discontinuities of potential energy. Amplified discussion of various properties of \( \psi(q) \) is available elsewhere [9].

Also according to wave mechanics, the possible energies \( W \) of a system in a stationary state are obtained upon solution of Schrodinger’s equation independent of time. For such a system, the coordinate representation is generally preferable to the momentum representation, because the potential energy is typically expressible more readily in terms of coordinate than in terms of momentum. For a particle of mass \( \mu \) subject to displacement \( q \), the kinetic energy according to classical formula \( T(q) = 1/2 \ p^2/\mu \) becomes operator \(-1/2 \ (h^2/\mu) \ d^2/dq^2 \) in the wave-mechanical coordinate representation. For a canonical linear harmonic oscillator, the potential energy in terms of coordinate \( q \) remains \( V(q) = 1/2 \ k_e q^2 \), as in matrix mechanics. Inserting these quantities into Schrodinger’s equation, we obtain

\[
\hat{H}(q) \psi(q) = [-1/2 \ (h^2/\mu) \ d^2/dq^2 + 1/2 \ k_e q^2] \psi(q) = W \psi(q)
\] (1.16)

in which the terms between brackets constitute the Hamiltonian operator \( \hat{H}(q) \) that is applicable to this particular problem. To solve this differential equation, of type second order with linear symmetries, we best invoke mathematical software [8], as for matrix mechanics above: with Maple the direct solution, again with \( \omega_0 \) substituted for \( \sqrt{(k_e/\mu)} \), is directly expressed as

\[
\psi(q) = c_1 W_M(\pi \ W/(h \ \omega_0), 1/4, 2\pi \ \omega_0 \ \mu \ q^2/h)/\sqrt{q} + c_2 \ W_W(\pi \ W/(h \ \omega_0), 1/4, 2\pi \ \omega_0 \ \mu \ q^2/h)/\sqrt{q}
\] (1.17)
With coefficients $c_1$ and $c_2$ as constants of integration, two independent solutions contain Whittaker M, as $W_M$, and Whittaker W, as $W_W$, functions, each with three arguments. For amplitude functions to be well behaved according to a condition specified above, namely, that $\psi_n(q) \rightarrow 0$ as $q \rightarrow \infty$, the difference between the first and second arguments must be equal to half a nonnegative integer: so $\pi W/(h \omega_0) - 1/4 = 1/2$ $n$. Replacing radial frequency $\omega_0$ by circular frequency $\nu_0$, we hence obtain

$$W_n = (n + 1/2) h \nu_0$$  \hspace{1cm} (1.18)

as in the solution according to matrix mechanics.

Plotting the part of the solution above containing the Whittaker M functions shows that, for even values of integer $n$, the curves diverge for positive and negative values of $q$; for this reason, we set $c_1$ equal to zero. In terms of Whittaker W functions, the amplitude function $\psi(q)$ thus becomes

$$\psi_n(q) = c_2 W(n/2 + 1/4, 1/4, 2\pi (k \mu)^{1/2} q^2/h)/q^{1/2}$$  \hspace{1cm} (1.19)

Integration constant $c_2$ remains to be evaluated; for this purpose, because Maple is unable to perform a general integration for symbolic integer $n$, we integrate $\psi_n(q)^* \psi_n(q)$ over $q$ from $-\infty$ to $\infty$ for $n$ from 0 to 5, with $\psi_n(q)^*$ as complex conjugate of $\psi_n(q)$; as $\psi_n(q)$ here has no imaginary part, $\psi_n(q)^* \psi_n(q) = \psi_n(q)^2$. On inspection of those results of integration, we discern that

$$c_2 = (2^n/n!)^{1/2}/n^{1/4}$$  \hspace{1cm} (1.20)

causes each integral to become equal to unity, corresponding to normalization of amplitude function $\psi_n(q)$. After we test this result by integrating $\psi_n(q)^2$ from $-\infty$ to $\infty$ for further values of $n$ to verify our deduction, $\psi_n(q)$ becomes thereby completely defined for $n$ of arbitrary value. In Figure 1.1, with each function displaced upward $n$ units for clarity, we plot $\psi_n(q)$ in terms of Whittaker W functions for $n = 0 \ldots 3$ and with $q$ in a domain $-2.5 \ldots 2.5$; for the purpose of these plots, we take $h = k_e = \mu = 1$, but such values affect only the scales on the axes, not the shapes of the curves.

In Figure 1.2, we plot similarly a product $\psi_n(q)^2$. According to Born’s interpretation, a product $\psi_n(q)^* \psi_n(q) dq$ represents a probability of a displacement of an oscillator having a value between $q$ and $q + dq$; the unit integral for normalization is consistent with this concept.

We test two properties of these amplitude functions. When we integrate over $q$ between $-\infty$ and $\infty$ a product of the first two amplitude functions,

$$\int_{-\infty}^{\infty} \psi_1(q)^* \psi_0(q) dq = 0$$  \hspace{1cm} (1.21)

or any other two distinct functions, we obtain zero; this result verifies that these amplitude functions are orthogonal. When we integrate likewise the same product with a further multiplicand $q$ within the integrand, for the purpose of calculating
a transition probability or the intensity of a transition between the two states with which these amplitude functions are associated, we obtain a real quantity.

\[
\int_{-\infty}^{\infty} \psi_1(q)^* \psi_0(q) \, dq = \frac{1}{2} (\hbar/\pi)^{1/2}/(\mu k_e)^{1/4}
\]  

(1.22)

According to further integrals of this type, for two amplitude functions \(\psi_n(q)\) and \(\psi_m(q)\), only when \(m = n \pm 1\) does this integral differ from zero, and the values of integrals of \(\psi_{n+1}(q)^* q \psi_n(q)\) increase with \(n\) as \(\{1/2\, (n + 1)^{1/2}\}\), in accordance with the result from matrix mechanics.

With Mathematica software, the solution of this Schrödinger equation is expressed directly in terms of parabolic cylinder functions. A conventional approach to this solution yields a product of an Hermite polynomial and an exponential function of Gaussian form, to which these Whittaker W functions are equivalent. The parabolic cylinder functions are in turn related closely to Whittaker functions; both are related to confluent hypergeometric functions in a product with an exponential term. Conversion from Whittaker or parabolic cylinder functions to Hermite or hypergeometric functions is unnecessary, because the former satisfy the pertinent

**Figure 1.1** For a canonical linear harmonic oscillator according to wave mechanics and either coordinate or momentum representation, amplitude functions \(\psi_n(q)\) or \(\chi_n(p)\) in terms of Whittaker W functions on the ordinate axis versus displacement \(q\) or momentum \(p\), respectively, on the abscissal axis for \(n = 0, 1, 2, 3\), calculated with \(\hbar = k_e = \mu = 1\); each curve is displaced \(n\) units.
differential equation as effectively as the latter functions multiplied by an exponential term; avoiding that conversion makes this direct solution practicable without prior knowledge of its form. All these special functions arise in solutions of various differential equations, and their use in one or other chosen form has comparable convenience.

We repeat this calculation within the momentum representation, with amplitude function \( \chi(p) \); this representation is useful for scattering conditions such as chemical reactions. Converting coordinate \( q \) to \( i \hbar d/dp \), we obtain Schrodinger’s equation accordingly in this form:

\[
\hat{H}(p) \chi(p) = \left[ \frac{1}{2} p^2 + \frac{1}{2} k_c h^2 d^2/dp^2 \right] \chi(p) = W \chi(p)
\]

the terms between brackets constitute the Hamiltonian \( \hat{H}(p) \) applicable to this formulation. With Maple, the solution of this equation appears again in terms of Whittaker functions,

\[
\chi(p) = c_1 W_M[\pi W/(\hbar \omega_0), 1/4, 2\pi p^2/(\hbar \omega_0 \mu)]/\sqrt{p}
\]

\[
+ c_2 W_W[\pi W/(\hbar \omega_0), 1/4, 2\pi p^2/(\hbar \omega_0 \mu)]/\sqrt{p}
\]