Condensed-Phase Molecular Spectroscopy and Photophysics
CONDENSED-PHASE MOLECULAR SPECTROSCOPY AND PHOTOPHYSICS
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PREFACE

Faculty members teaching advanced or graduate level courses in their specialty tend to have well-defined ideas about how such courses should be taught—what material should be covered and in what depth, how the topics should be organized, and what “point of view” should be adopted. There are probably as many different ideas about how to teach any graduate course as there are individuals doing the teaching. It is therefore no surprise that many faculty cannot find any single textbook that truly meets their needs for any given course. Most simply accept this situation, and either choose the book they like best (or dislike least) and supplement it with other textbooks and/or notes, or adopt no primary text at all. A few become sufficiently unhappy with the lack of a suitable text that they decide to write one themselves. This book is the outcome of such a decision.

Most chemistry departments offer a course in molecular spectroscopy for graduate students and advanced undergraduates. Some very good textbooks have been written for traditional molecular spectroscopy courses, but my favorite and that of many others, Walter Struve’s *Fundamentals of Molecular Spectroscopy*, is now out of print. Furthermore, most traditional textbooks focus on high-resolution spectroscopy of small molecules in the gas phase, and topics such as rotational spectroscopy and rotation–vibration interactions that are not the most relevant to much current research in chemistry programs. A great deal of modern research involves the interaction of radiation with condensed-phase systems, such as molecules in liquids, solids, and more complex media, molecular aggregates, metals and semiconductors, and their composites. There is a need for a graduate-level textbook that covers the basics of traditional molecular spectroscopy but takes a predominantly condensed-phase
perspective and also addresses optical processes in extended systems, such as metals, semiconductors, and conducting polymers.

This book aims to provide a treatment of radiation–matter interactions that is useful for molecules in condensed phases, as well as supramolecular structures and nanostructures. The book is written at a level appropriate for advanced undergraduates or beginning graduate students in physical or materials chemistry. Much of the organization and topic selection is similar to that of a traditional graduate-level molecular spectroscopy text, but atomic spectroscopy, rotational spectroscopy, and other topics relevant mainly to gas-phase systems are omitted entirely, and there is much more emphasis on the molecule–environment interactions that strongly influence spectra in condensed phases. Additions often not found in molecular spectroscopy texts include the spectroscopy and photophysics of molecular aggregates and molecular solids and of metals and semiconductors, with particular emphasis on nanoscale size regimes. Spin-resonance methods (e.g., NMR and ESR) are not covered, nor are x-ray or electron spectroscopies. Experimental techniques are addressed only to the extent needed to understand spectroscopic data.

Chapters 1 through 10 address spectroscopic fundamentals that should probably be included in any spectroscopy course or in prerequisite courses. Chapters 11 through 16 are less fundamental, and some will probably need to be omitted in a one-semester spectroscopy course, and certainly in a one-quarter course. The instructor may choose to omit all of these remaining chapters or may pick and choose among them to tailor the course. It is assumed that students using this book have already taken a course in basic quantum mechanics and many instructors may choose to omit explicit coverage of Chapter 1, but it is included for review and reference as it is essential to understanding what comes later. Instructors may also wish to omit Chapter 6 if it is assumed that students have been introduced to group theory in undergraduate inorganic chemistry or quantum chemistry courses.

Textbooks of this type inevitably reflect the experiences and biases of their authors, and this one is no exception. Group theory is discussed in less depth and is used less extensively than in most spectroscopy textbooks. Raman and resonance Raman scattering are developed in considerable detail, while most other multiphoton spectroscopies are treated only at a rather superficial level. Spectroscopies that involve circularly polarized light, such as circular dichroism, are ignored completely. These all represent choices made in an effort to keep this book a reasonable length while trying to optimize its usefulness for a wide range of students. Only time will tell how well I have succeeded.

The general structure and emphasis of this book developed largely from discussions with David Kelley, whose encouragement pushed me over the edge from thinking about writing a book to actually doing it. He would not have written the same book I did, but his input proved valuable at many stages. I would also like to acknowledge the graduate students in my Spring 2012 Molecular Spectroscopy course (Gary Abel, Joshua Baker, Ke Gong, Cheetar Lee, and Xiao Li) for patiently pointing out numerous typographical errors,
notational inconsistencies, and confusing explanations present in the first draft of this book. Their input was very helpful in bringing this project to its conclusion.

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Merced, CA
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CHAPTER 1

REVIEW OF TIME-INDEPENDENT QUANTUM MECHANICS

While some spectroscopic observations can be understood using purely classical concepts, most molecular spectroscopy experiments probe explicitly quantum mechanical properties. It is assumed that students using this text have already taken a course in basic quantum mechanics, but it is also recognized that there are likely to be some holes in the preparation of most students and that all can benefit from a brief review. As this is not a quantum mechanics textbook, many results in this chapter are given without proof and with minimal explanation. Students seeking a deeper treatment are encouraged to consult the references given at the end of this chapter.

This chapter, like most introductory quantum chemistry courses, focuses on solutions of the time-independent Schrödinger equation. Because of the importance of time-dependent quantum mechanics in spectroscopy, that topic is discussed further in Chapter 2.

1.1. STATES, OPERATORS, AND REPRESENTATIONS

A quantum mechanical system consisting of N particles (usually electrons and/or nuclei) is represented most generally by a state function or state vector \( \Psi \). The state vector contains, in principle, all information about the quantum mechanical system.
In order to be useful, state vectors have to be expressed in some basis. In the most commonly used position basis, the state vector is called the wavefunction, written as $\Psi(r_1, r_2, \ldots, r_N)$, where $r_i$ is the position in space of particle $i$. The position $r$ may be expressed in Cartesian coordinates ($x, y, z$), spherical polar coordinates ($r, \theta, \phi$), or some other coordinate system. Wavefunctions may alternatively be expressed in the momentum basis, $\Psi(p_1, p_2, \ldots, p_N)$, where $p_i$ is the momentum of particle $i$. Some state vectors cannot be expressed as a function of position, such as those representing the spin of an electron. But there’s always a state function that describes the system, even if it’s not a “function” of ordinary spatial coordinates.

The wavefunction itself, also known as the probability amplitude, is not directly measurable and has no simple physical interpretation. However, the quantity $|\Psi(r_1, r_2, \ldots, r_N)|^2 \, dr_1 \, dr_2 \ldots dr_N$ gives the probability that particle 1 is in some infinitesimal volume element around $r_1$, and so on. Integration over a finite volume then gives the probability that the system is found within that volume. A “legal” wavefunction has to be single valued, continuous, differentiable, and normalizable.

The scalar product or inner product of two wavefunctions $\Psi$ and $\Phi$ is given by $\int \Psi^* \Phi$, where the asterisk means complex conjugation and the integration is performed over all of the coordinates of all the particles. The inner product is not a function but a number, generally a complex number if the wavefunctions are complex. In Dirac notation, this inner product is denoted $\langle \Psi | \Phi \rangle$. The absolute square of the inner product, $|\langle \Psi | \Phi \rangle|^2$, gives the probability (a real number) that a system in state $\Psi$ is also in state $\Phi$. If $\langle \Psi | \Phi \rangle = 0$, then $\Psi$ and $\Phi$ are said to be orthogonal. Reversing the order in Dirac notation corresponds to taking the complex conjugate of the inner product: $\langle \Phi | \Psi \rangle = \int \Phi^* \Psi$, while $\langle \Phi | \Psi \rangle = \int \Psi^* \Phi = (\int \Phi^* \Psi)^*$. The inner product of a wavefunction with itself, $\langle \Psi | \Psi \rangle = \int \Psi^* \Psi$, is always real and positive. Usually, wavefunctions are chosen to be normalized to $\int \Psi^* \Psi = 1$. This means that the probability of finding the system somewhere in space is unity.

The quantities we are used to dealing with in classical mechanics are represented in quantum mechanics by operators. Operators act on wavefunctions or state vectors to give other wavefunctions or state vectors. Operator $A$ acting on wavefunction $\Psi$ to give wavefunction $\Phi$ is written as $A \Psi = \Phi$. The action of an operator can be as simple as multiplication, although many (not all) operators involve differentiation.

Quantum mechanical operators are linear, which means that if $\lambda_1$ and $\lambda_2$ are numbers (not states or operators), then $A(\lambda_1 \Phi_1 + \lambda_2 \Phi_2) = \lambda_1 A \Phi_1 + \lambda_2 A \Phi_2$, and $(AB) \Phi = A(B \Phi) = AB \Phi$. However, it is not true in general that $AB \Phi = BA \Phi$; the order in which the operators are applied often matters. The quantity $AB - BA$ is called the commutator of $A$ and $B$ and is symbolized $[A, B]$, and it is zero for some pairs of operators but not for all. Most of what is “interesting” (i.e., nonclassical) about quantum mechanical systems arises from the noncommutation of certain operators.
A representation is a set of basis vectors, which may be discrete (finite or infinite) or continuous. An example of a finite discrete basis is the eigenstates of the $z$-component of spin for a spin-$1/2$ particle (two states, usually called $\alpha$ and $\beta$). An example of a discrete infinite basis is the set of eigenstates of a one-dimensional harmonic oscillator, $\{\psi_v\}$, where $v$ must be an integer but can go from 0 to $\infty$. An example of a continuous basis is the position basis $\{r\}$, where $r$ can take on any real value. To be a representation, a set of basis vectors must obey certain extra conditions. One is orthonormality: $\langle u_i | u_j \rangle = \delta_{ij}$ (the Kronecker delta) for a discrete basis, or $\langle w_\alpha | w_\alpha' \rangle = \delta(\alpha-\alpha')$ (the Dirac delta function) for a continuous basis. The Kronecker delta is defined by $\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ if $i \neq j$. The Dirac delta function $\delta(\alpha-\alpha')$ is a hypothetical function of the variable $\alpha$ that is infinitely sharply peaked around $\alpha = \alpha'$ and has an integrated area of unity. Three useful properties of the Dirac delta function are:

$$\int_{-\infty}^{\infty} dke^{ikx} = 2\pi \delta(x) \quad (1.1)$$
$$\int_{-\infty}^{\infty} dxf(x)\delta(x-a) = f(a) \quad (1.2)$$
$$\delta(ax) = \delta(x)/|a|, \quad (1.3)$$

where $a$ is a constant.

A set of vectors in a particular state space is a basis if every state in that space has a unique expansion, such that $\Psi = \sum_{c_i} c_i u_i$ (discrete basis) or $\Psi = \int d\alpha (\alpha) w_\alpha$ (continuous basis), where the $c_i$'s are (complex) numbers. “In a particular state space” means, for example, that if we want to describe only the spin state of a system, the basis does not have to include the spatial degrees of freedom. Or, the states of position in one dimension $\{x\}$ can be a basis for a particle in a one-dimensional box, but not a two-dimensional box, which requires a two-dimensional position basis $\{(x,y)\}$. An important property of a representation is closure:

$$\sum_{i} \langle \Phi | u_i \rangle \langle u_i | \Psi \rangle = \langle \Phi | \Psi \rangle \quad \text{or} \quad \int d\alpha \langle \Phi | w_\alpha \rangle \langle w_\alpha | \Psi \rangle = \langle \Phi | \Psi \rangle. \quad (1.4)$$

Representations of states and operators in discrete bases are often conveniently written in matrix form (see Appendix C). A state vector is represented in a basis by a column vector of numbers:

$$\begin{pmatrix} \langle u_1 | \Psi \rangle \\ \langle u_2 | \Psi \rangle \\ \vdots \end{pmatrix},$$

and its complex conjugate by a row vector: $(\langle \Phi | u_1 \rangle \langle \Phi | u_2 \rangle \cdots)$. The inner product is then obtained by the usual rules for matrix multiplication as
\begin{equation}
\langle \Phi | \Psi \rangle = \left( \langle \Phi | u_1 \rangle \langle \Phi | u_2 \rangle \cdots \right) \left( \langle u_2 | \Psi \rangle \right) = \text{a number.}
\end{equation}

An operator is represented by a square matrix having elements $A_{ij} = \langle u_i | \mathcal{A} | u_j \rangle$:

\[
\begin{pmatrix}
\langle u_1 | \mathcal{A} | u_1 \rangle & \langle u_1 | \mathcal{A} | u_2 \rangle & \cdots \\
\langle u_2 | \mathcal{A} | u_1 \rangle & \langle u_2 | \mathcal{A} | u_2 \rangle & \\
\vdots & \vdots & \\
\end{pmatrix}
\]

For Hermitian operators, $A_{ji}^* = A_{ij}$. It follows that the diagonal elements must be real for Hermitian operators, since only then can $A_{ii}^* = A_{ii}$.

The operator expression $\mathcal{A} \Psi = \Phi$ is represented in the $\{u_i\}$ basis as the matrix equation

\[
\begin{pmatrix}
\langle u_1 | \mathcal{A} | u_1 \rangle & \langle u_1 | \mathcal{A} | u_2 \rangle & \cdots \\
\langle u_2 | \mathcal{A} | u_1 \rangle & \langle u_2 | \mathcal{A} | u_2 \rangle & \\
\vdots & \vdots & \\
\end{pmatrix}
\begin{pmatrix}
\langle u_1 | \Psi \rangle \\
\langle u_2 | \Psi \rangle \\
\vdots
\end{pmatrix}
= 
\begin{pmatrix}
\langle u_1 | \Phi \rangle \\
\langle u_2 | \Phi \rangle \\
\vdots
\end{pmatrix}
\]

\section{1.2. EIGENVALUE PROBLEMS AND THE SCHRÖDINGER EQUATION}

The state $\Psi$ is an eigenvector or eigenstate of operator $\mathcal{A}$ with eigenvalue $\lambda$ if $\mathcal{A} \Psi = \lambda \Psi$, where $\lambda$ is a number. That is, operating on $\Psi$ with $\mathcal{A}$ just multiplies $\Psi$ by a constant. The eigenvalue $\lambda$ is nondegenerate if there is only one eigenstate having that eigenvalue. If more than one distinct state (wavefunctions that differ from each other by more than just an overall multiplicative constant) has the same eigenvalue, then that eigenvalue is degenerate.

To every observable (measurable quantity) in classical mechanics, there corresponds a linear, Hermitian operator in quantum mechanics. Since observables correspond to measurable things, this means all observables have only real eigenvalues. It can be shown from this that eigenfunctions of the same observable having different eigenvalues are necessarily orthogonal (orthonormal if we require they be normalized).

In Dirac notation, using basis $\{u_i\}$, the eigenvalue equation is $\langle u_i | \mathcal{A} | \Psi \rangle = \lambda \langle u_i | \Psi \rangle$. Inserting closure gives $\Sigma \langle u_i | \mathcal{A} | u_j \rangle \langle u_j | \Psi \rangle = \lambda \langle u_i | \Psi \rangle$, or in a shorter form $\Sigma A_{ij} c_j = \lambda c_i$, or in an even more compact form, $\Sigma (A_{ij} - \lambda \delta_{ij}) c_j = 0$. This is a system of $N$ equations (one for each $i$) in $N$ unknowns, which has a nontrivial solution if and only if the determinant of the coefficients is zero: $|A - \lambda 1| = 0$, where $1$ is an $N \times N$ unit matrix (1’s along the diagonal). So to find the eigenvalues, we need to set up the determinantal equation

\[
\begin{vmatrix}
A_{11} - \lambda & A_{12} & \cdots \\
A_{21} & A_{22} - \lambda & \\
\vdots & \vdots & \\
\end{vmatrix}
= 0,
\]
and solve for the $N$ roots $\lambda$, then find the eigenvector corresponding to each
eigenvalue $\lambda^{(i)}$ by solving the matrix equation

$$
\begin{pmatrix}
A_{11} & A_{12} & \cdots & c_1^{(i)} \\
A_{21} & A_{22} & \cdots & c_2^{(i)} \\
\vdots & \vdots & \ddots & \vdots \\
\end{pmatrix}
= \lambda^{(i)}
\begin{pmatrix}
c_1^{(i)} \\
c_2^{(i)} \\
\vdots \\
\end{pmatrix}
$$

(see Appendix C).

Any measurement of the observable associated with operator $A$ can give only those values that are eigenvalues of $A$. If the system is in an eigenstate of the operator, then every measurement will yield the same value, the eigenvalue. If the system is not in an eigenstate, different measurements will yield different values, but each will be one of the eigenvalues.

A particularly important observable is the one associated with the total energy of the system. This operator is called the Hamiltonian, symbolized $H$, the sum of the kinetic and potential energy operators. The eigenstates of the Hamiltonian are therefore eigenstates of the energy, and the associated eigenvalues represent the only values that can result from any measurement of the energy of that system.

To find the energy eigenvalues and eigenstates, one must first write down the appropriate Hamiltonian for the problem at hand, which really amounts to identifying the potential function in which the particles move, since the kinetic energy is straightforward. One then solves the eigenvalue problem $H\psi_n = E_n\psi_n$, which is the time-independent Schrödinger equation. For most Hamiltonians, there are many different pairs of wavefunctions $\psi_n$ and energies $E_n$ that can satisfy the equation.

Two observables of particular importance in quantum mechanics are the position $Q$ and the linear momentum $P$ along the same coordinate (e.g., $x$ and $p_x$). The commutator is $[Q, P] = i\hbar$ and the action of $P$ in the $q$ representation is $-i\hbar(\partial/\partial q)$. That is, $P\Psi(q) = -i\hbar(\partial/\partial q)\Psi(q)$, where $\Psi(q)$ is the wavefunction as a function of the coordinate $q$. The operator $P^2 = PP$ in the $q$ representation is $-\hbar^2(\partial^2/\partial q^2)$.

The Schrödinger equation in the position basis, $H\Psi(q) = E\Psi(q)$, can therefore be written for a particle moving in only one dimension as

$$
[(p^2/2m) + V(q)]\Psi(q) = E\Psi(q),
$$

or

$$
-(\hbar^2/2m)[\partial^2\Psi(q)/\partial q^2] + V(q)\Psi(q) = E\Psi(q).
$$

The position operator in three dimensions is a vector, $\hat{x}\hat{x} + \hat{y}\hat{y} + \hat{z}\hat{z}$, where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors along $x$, $y$, and $z$ directions. The momentum operator is also a vector, which in the position basis is
p = -ih(\hat{x}\partial/\partial x + \hat{y}\partial/\partial y + \hat{z}\partial/\partial z) = -ih\nabla, \quad (1.7)

where \nabla is called the del or grad operator. The square of the momentum is

\[ p^2 = \mathbf{p} \cdot \mathbf{p} = -\hbar^2(\hat{x}\partial/\partial x + \hat{y}\partial/\partial y + \hat{z}\partial/\partial z) \cdot (\hat{x}\partial/\partial x + \hat{y}\partial/\partial y + \hat{z}\partial/\partial z) = -\hbar^2\nabla^2, \quad (1.8) \]

where \nabla^2 is called the Laplacian. Notice that while the momentum is a vector, the momentum squared is not.

### 1.3. EXPECTATION VALUES, UNCERTAINTY RELATIONS

When a system is in state \( \Psi \), the mean value or expectation value of observable \( A \) is defined as the average of a large number of measurements. It is given by

\[ \langle A \rangle = \langle \Psi | A | \Psi \rangle = |\Psi| A |\Psi \rangle. \]

If \( \Psi \) is an eigenfunction of \( A \), then we'll always measure the same number, the eigenvalue, for the observable \( a \). If \( \Psi \) is not an eigenfunction of \( A \), then each measurement may yield a different value, but we can calculate its average with complete certainty from the previous expression. Note that if \( A \) involves just multiplication, such as \( q \) to some power, we can just write this as \( \langle q^a \rangle = |\Psi(q)|^2 q^a dq \). But if \( A \) does something like differentiation, then we have to make sure it operates on \( \Psi(q) \) only, not also \( \Psi^*(q) \). For example, for momentum, \( p = -ih\partial/\partial q \), we have \( \langle p \rangle = -ih\int |\Psi^*(q)|^2((\partial/\partial q)\Psi(q))dq \).

The root-mean-square deviation of the value of operator \( A \) in state \( \Psi \) is

\[ \Delta A = \sqrt{\langle (A - \langle A \rangle)^2 \rangle} \quad (1.9a) \]

that is, \( \Delta A = \sqrt{\langle (A - A_{\text{avg}})^2 \rangle} \). Note that if \( \Psi \) is an eigenstate of \( A \), then \( \Delta A = 0 \), since every measurement of \( A \) gives the same result. An alternative and sometimes preferable form for \( \Delta A \) can be written by noting that since \( \langle A \rangle \) is a number, \( \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - 2\langle A \rangle \langle A \rangle + \langle A \rangle^2 = \langle A^2 \rangle - 2\langle A \rangle^2 + \langle A \rangle^2 = \langle A^2 \rangle - \langle A \rangle^2 \). So,

\[ \Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \quad (1.9b) \]

is an alternative equivalent form.

The product of the root-mean-square deviations of two operators \( A \) and \( B \), in any state, obeys the relationship

\[ \Delta A \Delta B \geq \frac{1}{2}|[A, B]|. \quad (1.10) \]

A particularly important example is for the various components of position and momentum; since \([Q, P]\) = \( i\hbar \), then \( \Delta Q \Delta P \geq \hbar/2 \). This is often known as
the Heisenberg uncertainty relation between position and momentum. The interpretation is that you cannot simultaneously know both the position and the momentum along the same direction (e.g., $x$ and $p_x$) to arbitrary accuracy; their uncertainty product, $\Delta Q \Delta P$, has a finite nonzero value. Only for operators that commute can the uncertainty product vanish (although it is not necessarily zero in any state). Note that since different components of position and momentum (e.g., $x$ and $p_y$) do commute, their uncertainty product can be zero.

Because commuting observables can have a zero uncertainty product, they are said to be compatible observables. This means that if $[A, B] = 0$, and $A \Psi = a \Psi$, ($\Psi$ is an eigenstate of the operator $A$), then the state given by $(B \Psi)$ is also an eigenstate of $A$ with the same eigenvalue. The result one gets from a measurement of $A$ is not affected by having previously measured $B$. One can have simultaneous eigenstates of $A$ and $B$. In general, this is not the case if the operators do not commute.

### 1.4. THE PARTICLE IN A BOX

The “particle in a box,” in one dimension, refers to a particle of mass $m$ in a potential defined by $V(x) = 0$ for $0 \leq x \leq a$, and $V(x) = \infty$ everywhere else. In one dimension, this may be used to model an electron in a delocalized molecular orbital, for example, the pi-electron system of a linear polyene molecule, conjugated polymer, or porphyrin. In three dimensions, it may be used to model the electronic states of a semiconductor nanocrystal.

Since the potential energy becomes infinite at the walls, the boundary condition is that the wavefunction must go to zero at both walls. Thus, the relevant Schrödinger equation becomes (in 1-D)

$$-(h^2 / 2m)(d^2 / dx^2)\psi(x) = E\psi(x) \quad \text{for } 0 \leq x \leq a.$$  \hfill (1.11)

The solutions to this equation are

$$\psi_n(x) = B \sin(n\pi x / a) \quad \text{and} \quad E_n = h^2 n^2 / 8ma^2 \quad \text{for } n = 1, 2, \ldots$$  \hfill (1.12)

The function will be a solution for any value of the constant $B$. We find $B$ by requiring that $\psi_n(x)$ be normalized: that is, the total probability of finding the particle somewhere in space must be unity. This means that $\int_0^a dx |\psi_n(x)|^2 = 1$, and we find $B = \sqrt{2 / a}$. These solutions are plotted in Figure 1.1.

The particle in a box in two or three dimensions is a simple extension of the 1-D case. The Schrödinger equation for the 3-D case is

$$-(h^2 / 2m)(\partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2)\psi(x, y, z) = -(h^2 / 2m)\nabla^2 \psi(x, y, z)\psi(x, y, z) = E\psi(x, y, z),$$  \hfill (1.13)
for \( 0 \leq x \leq a, \ 0 \leq y \leq b, \ 0 \leq z \leq c \). Since the Hamiltonian for this system is a simple sum of operators in each of the three spatial dimensions, the total energy of the system is also a simple sum of contributions from \( x, y, \) and \( z \) motions, and the wavefunctions that are eigenfunctions of the Hamiltonian are just products of wavefunctions for \( x, y, \) and \( z \) individually:

\[
\Psi(x, y, z) = \{(2/a)^{1/2} \sin(n_x \pi x/a}\} \{(2/b)^{1/2} \sin(n_y \pi y/b}\} \{(2/c)^{1/2} \sin(n_z \pi z/c}\}
\]

(1.14a)

\[
E(n_x, n_y, n_z) = (\hbar^2/8ma^2)(n_x^2/a^2) + (n_y^2/b^2) + (n_z^2/c^2)
\]

(1.14b)

\( n_x, n_y, n_z = 1, 2, 3, \ldots \)

(1.14c)

A separable Hamiltonian has eigenfunctions that are products of the solutions for the individual dimensions and energies that are sums. This result is general and important.

If all three dimensions \( a, b, \) and \( c \) are different and not multiples of each other, generally, each set of quantum numbers \( (n_x, n_y, n_z) \) will have a different energy. But if any of the box lengths are the same or integer multiples, then certain energies will correspond to more than one state, that is, more than one combination of quantum numbers. This degeneracy is a general feature of quantum mechanical systems that have some symmetry.
1.5. HARMONIC OSCILLATOR

Classically, the relative motion of two masses \( m_1 \) and \( m_2 \), connected by a Hooke’s law spring of force constant \( k \), is described by Newton’s law as

\[
\mu \ddot{x} + kx = 0,
\]

where the reduced mass is \( \mu = m_1 m_2/(m_1 + m_2) \) (\( \mu \) has units of mass). This is just \( F = ma \), where the force \( F = -kx \) and the acceleration \( a = \ddot{x} \). Here \( x \) is the deviation of the separation from its equilibrium value, \( x = (x_1 - x_2) - x_0 \), and the motion of the center of mass, \( M = m_1 + m_2 \), has been factored out.

Remember the force is just \( -dV/dx \), so \( V(x) = (1/2)kx^2 + C \); the potential energy is a quadratic function of position. The classical solution to this problem is \( x(t) = c_1 \sin \omega t + c_2 \cos \omega t \), where the constants depend on the initial conditions, and the frequency of oscillation in radians per second is \( \omega = (k/\mu)^{1/2} \).

The form \( V(x) = (1/2)kx^2 \) is the lowest-order nonconstant term in the Taylor series expansion of any potential function about its minimum:

\[
V(x) = V(x_0) + (dV/dx)_0(x - x_0) + (1/2)(d^2V/dx^2)_0(x - x_0)^2 + (1/6)(d^3V/dx^3)_0(x - x_0)^3 + \ldots.
\]

But if \( x_0 \) is the potential minimum, then by definition \( (dV/dx)_0 = 0 \), so the first nonzero term besides a constant is the quadratic one. Redefining \( x = \ell - x_0 \), we get

\[
V(x) = C + (1/2)(d^2V/dx^2)_0 x^2 + \text{higher “anharmonic” terms} \nonumber
\]

\[
= C + (1/2)kx^2 + \text{anharmonic terms}.
\]

Since the anharmonic terms depend on higher powers of \( x \), they will be progressively less important for very small displacements \( x \). So oscillations about a minimum can generally be described well by a harmonic oscillator as long as the amplitude of motion is small enough.

The quantum mechanical harmonic oscillator has a Schrödinger equation given by

\[
-(\hbar^2/2\mu)(d^2/dx^2) \Psi(x) + (1/2)kx^2 \Psi(x) = E \Psi(x).
\]

The solutions to this differential equation involve a set of functions called the Hermite polynomials, \( H_v \). The eigenfunctions and eigenvalues are:

\[
\Psi_v(x) = N_v[H_v(\alpha^{1/2} x)] \exp(-\alpha x^2/2), \quad E_v = \hbar \omega (v + 1/2), \quad v = 0, 1, 2, \ldots,
\]

with \( \alpha = (k\mu\hbar^2)^{1/2} \) and \( \omega = (k/\mu)^{1/2} \) as in the classical case. Note the units: \( k \) is a force constant in \( \text{N} \cdot \text{m}^{-1} = (\text{kg} \cdot \text{m} \cdot \text{s}^{-2}) \cdot \text{m}^{-1} = \text{kg} \cdot \text{s}^{-2} \); \( \mu \) is a mass in kg; so \( \omega \) has units of \( \text{s}^{-1} \) as it must. \( \hbar \) has units of \( \text{J} \cdot \text{s} = (\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}) \cdot \text{s} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-1} \); so \( \alpha \) has units of inverse length squared, making \( (\alpha^{1/2} x) \) a unitless quantity. This quantity is
often renamed as q, a *dimensionless coordinate*. \( N \) is a normalization constant that depends on the quantum number:

\[
N_v = (\alpha/\pi)^{1/4} (2^v v!)^{-1/2},
\]

[recall \( v! = (v)(v-1)(v-2)...(2)(1), \) and \( 0! = 1 \) by definition]. The Hermite polynomial \( H_v \) is a \( v^{th} \) order polynomial; the number of nodes equals the quantum number \( v \). The first four of them are

\[
H_0(q) = 1, \quad H_1(q) = 2q, \quad H_2(q) = 4q^2 - 2, \quad H_3(q) = 8q^3 - 12q.
\]

The quantity \( \alpha^{1/2} \) scales the displacement coordinate to the force constant and masses involved.

The energy levels of the quantum mechanical harmonic oscillator are equally spaced by an energy corresponding to the classical vibrational frequency, \( \hbar \omega \). There is a zero-point energy, \( \hbar\omega/2 \), arising from confinement to a finite region of coordinate space.

The lowest-energy wavefunction is

\[
\Psi_0(x) = (\alpha/\pi)^{1/4} \exp(-\alpha x^2/2)
\]

Its modulus squared, \( |\Psi_0(x)|^2 = (\alpha/\pi)^{1/2} \exp(-\alpha x^2) \), gives the probability of finding the oscillator at a given position \( x \). This probability has the form of a Gaussian function—it has a single peak at \( x = 0 \). This means that if this is a model for a vibrating diatomic molecule, the most probable bond length is the equilibrium length. Higher vibrational eigenstates do not all have this property. Note that the probability never goes to zero even for very large positive or negative displacements. In particular, this means that there is finite probability to find the oscillator at a position where the potential energy exceeds the total energy. This is an example of quantum mechanical tunneling.

For \( v = 1 \), the probability distribution is

\[
|\Psi_1(x)|^2 = |(\alpha/\pi)^{1/4} 2^{-1/2} 2^{1/2} x \exp(-\alpha x^2/2)|^2 = 2\alpha^{3/2} \pi^{-1/2} x^2 \exp(-\alpha x^2),
\]

which has a node at the exact center and peaks on either side. The first few harmonic oscillator wavefunctions are plotted in Figure 1.2.

A classical oscillator is most likely to be found (i.e., spends most of its time) at the turning point, the outside edge where the total energy equals the potential energy. This is not true for the quantum oscillator, except at high quantum numbers. In many ways, quantum systems act like classical ones only in the limit of large quantum numbers.

All of the Hermite polynomials are either even or odd functions. The ones with even \( v \) are even and those with odd \( v \) are odd. The Gaussian function is always even. Thus, \( \Psi_v(x) \) is even for even \( v \) and odd for odd \( v \). Therefore, \( |\Psi_v(x)|^2 \) is always an even function, and
since the product of an even and an odd function is odd. The average position is always at the center (potential minimum) of the oscillator. Similarly,

\[ \langle p \rangle = \int_{-\infty}^{\infty} dx \Psi_\nu^* (x) \left( -i\hbar \frac{d}{dx} \right) \Psi_\nu (x) = 0, \]

since the derivative of an even function is always odd and vice versa, so the integrand is always odd.

It is often more convenient to work in the reduced coordinates

\[ q = \sqrt{\frac{\mu \omega}{\hbar}} x \quad \text{and} \quad P = \frac{1}{\sqrt{\mu \omega \hbar}} p. \]

Notice that the operators \( q \) and \( P \) obey the same commutation relations as \( x \) and \( p \) without the factor of \( \hbar \): \( [q, P] = (1/\hbar)[x, p] = i \). The harmonic oscillator Hamiltonian can be written in these reduced coordinates as

\[ H = \frac{1}{2} \hbar \omega (P^2 + q^2) \quad (1.23) \]
We then introduce the raising and lowering operators, $a^\dagger$ and $a$, where

$$a = \frac{1}{\sqrt{2}}(q + i\mathcal{P}) \quad (1.24a)$$

$$a^\dagger = \frac{1}{\sqrt{2}}(q - i\mathcal{P}), \quad (1.24b)$$

so the reduced position and momentum operators can be written in terms of the raising and lowering operators as

$$q = \frac{1}{\sqrt{2}}(a + a^\dagger) \quad (1.25a)$$

$$\mathcal{P} = -\frac{i}{\sqrt{2}}(a - a^\dagger). \quad (1.25b)$$

The raising and lowering operators act on the harmonic oscillator eigenstates $|\nu\rangle$ as follows:

$$a|\nu\rangle = \sqrt{\nu}|\nu - 1\rangle \quad (\nu > 0) \quad (1.26a)$$

$$a|0\rangle = 0 \quad (1.26b)$$

$$a^\dagger|\nu\rangle = \sqrt{\nu + 1}|\nu + 1\rangle. \quad (1.26c)$$

Also note

$$a^\dagger a = \frac{1}{2}(\mathcal{P}^2 + q^2 + iq\mathcal{P} - i\mathcal{P}q) = \frac{1}{2}(\mathcal{P}^2 + q^2 + i[q, \mathcal{P}]) = \frac{1}{2}(\mathcal{P}^2 + q^2 - 1),$$

so we can rewrite the Hamiltonian as

$$\mathcal{H} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) = \hbar\omega\left(N + \frac{1}{2}\right). \quad (1.27)$$

$N = a^\dagger a$ is called the number operator because the eigenstates of the Hamiltonian are also eigenstates of $N$ with eigenvalues given by the quantum numbers.

### 1.6. THE HYDROGEN ATOM AND ANGULAR MOMENTUM

The hydrogen atom consists of one electron and one proton, interacting through a Coulombic potential. If we assume that the nucleus is fixed in space, the Hamiltonian consists of the kinetic energy of the electron (mass $m_e$) plus the Coulombic attraction between the electron and the nucleus:
In spherical polar coordinates, the Schrödinger equation for the hydrogen atom is given by

\[
\mathbf{H} = -(\hbar^2/2m_e)\nabla^2 - e^2/(4\pi\epsilon_0 r).
\]  

(1.28)

The problem is most readily solved in spherical polar coordinates. Transforming the Laplacian operator into spherical polar coordinates gives the Schrödinger equation,

\[
\mathbf{H} = -(\hbar^2/2m_e)\left[(1/r^2)(\partial/\partial r)\left[(r^2(\partial/\partial r)) + \frac{1}{r^2}\sin\theta(\partial/\partial \theta)[\sin\theta(\partial/\partial \theta)]\right]\right. \\
+ \left. (1/r^2\sin^2\theta)(\partial^2/\partial \phi^2)\right]\Psi(r, \theta, \phi) = (e^2/4\pi\epsilon_0r)\Psi(r, \theta, \phi) - E\Psi(r, \theta, \phi).
\]  

(1.29)

The solution to this equation is described in nearly all basic quantum mechanics textbooks. The wavefunctions are products of an \(r\)-dependent part and a \((\theta, \phi)\)-dependent part, and they depend on three quantum numbers, \(n\), \(\ell\), and \(m\):

\[
\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell}^m(\theta, \phi),
\]  

(1.30)

with allowed values for the quantum numbers of

\[
n = 1, 2, 3, \ldots \quad (1.31a)
\]

\[
\ell = 0, 1, 2, \ldots (n-1) \quad (1.31b)
\]

\[
m = -\ell, (-\ell+1), \ldots (\ell-1), \ell. \quad (1.31c)
\]

The quantum number \(m\) is often designated \(m\) to distinguish it from the spin quantum number \(m_s\) (see Section 1.8).

The associated energy eigenvalues depend only on \(n\) and are given by

\[
E_n = -e^2/(8\pi\epsilon_0 a_0 n^2).
\]  

(1.32)

The quantity \(a_0 = 4\pi\epsilon_0\hbar^2/(m_e e^2)\) is the Bohr radius. It has the numerical value 0.529 Å. It defines an intrinsic length scale for the H-atom problem, much as the constant \(\alpha\) does for the harmonic oscillator.

The angle-dependent functions \(Y_{\ell}^m(\theta, \phi)\) are known as the spherical harmonics. They are normalized and orthogonal. The first few spherical harmonics are

\[
Y_0^0 = \frac{1}{\sqrt{4\pi}} \quad (1.33a)
\]

\[
Y_1^0 = \frac{3}{\sqrt{4\pi}} \cos \theta \quad (1.33b)
\]

\[
Y_1^\pm = \mp \frac{3}{\sqrt{8\pi}} \sin \theta e^{\pm i\theta}. \quad (1.33c)
\]


The quantum number $\ell$ refers to the total angular momentum, while $m$ refers to its projection onto an arbitrary space-fixed axis. The spherical harmonics are eigenfunctions of both the total angular momentum (or its square, $L^2$) and the $z$-component of the angular momentum, $L_z$, but not of $L_x$ or $L_y$. Also note that the energy depends only on $L^2$. So the $z$-component of angular momentum is quantized, but this quantization affects only the degeneracy of each energy level. The spherical harmonics satisfy the eigenvalue equations

$$\begin{align*}
L^2 Y^m(\theta, \phi) &= \hbar^2 \ell (\ell + 1) Y^m(\theta, \phi) \\
L_z Y^m(\theta, \phi) &= \hbar m Y^m(\theta, \phi).
\end{align*}$$

The radial part of the wavefunction is given by

$$R_n(\ell)(r) = -\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \left(\frac{2r}{na_0}\right) \exp\left(-\frac{r}{na_0}\right) L^{2\ell+1}_{n\ell}(\frac{2r}{na_0}),$$

where the $L^{2\ell+1}_{n\ell}(2r/na_0)$ are called the associated Laguerre polynomials. The functions $R_n(\ell)(r)$ are normalized with respect to integration over the radial coordinate, such that $\int_0^\infty r^2 dr |R_n(\ell)(r)|^2 = 1$. Note that the radial part of the volume element in spherical polar coordinates is $r^2 dr$.

The H-atom wavefunctions depend on three quantum numbers. The principal quantum number $n$, the only one on which the energy depends, mainly determines the overall size of the wavefunction (larger $n$ gives a larger average distance from the nucleus). The angular momentum quantum number $\ell$ determines the overall shape of the wavefunction; $\ell = 0, 1, 2, 3, \ldots$ correspond to s, p, d, f . . . orbitals. The magnetic quantum number $m$ determines the orientation of the orbital and causes each degenerate energy level to split into $2\ell + 1$ different energies in the presence of a magnetic field.

Recall that in general, the more nodes in a wavefunction, the higher its energy. The number of radial nodes [nodes in $R_n(\ell)$] is given by $(n - \ell - 1)$, and the number of nodal planes in angular space is given by $\ell$, so the total number of nodes is $(n - 1)$, and the energy goes up with increasing $n$. For $\ell = 0$, there is no $(\theta, \phi)$ dependence. The orbital is spherically symmetric and is called an s orbital. For $\ell = 1$, there is one nodal plane, and the orbital is called a p orbital. Since in spherical polar coordinates $z = r \cos \theta$, $Y^m_1$ points along the $z$-direction and we refer to the $\ell = 1, m = 0$ orbitals as $p_z$ orbitals. $Y^m_1$ and $Y^m_{-1}$ are harder to interpret because they are complex. However, since they’re degenerate, any linear combination of them will also be an eigenstate of the Hamiltonian. Therefore, it’s traditional to work with the linear combinations

$$\begin{align*}
p_x &= 2^{-1/2}(Y^1_1 + Y^{-1}_1) = (3/4 \pi)^{1/2} \sin \theta \cos \phi \\
p_y &= -i 2^{-1/2}(Y^1_1 - Y^{-1}_1) = (3/4 \pi)^{1/2} \sin \theta \sin \phi,
\end{align*}$$