

The Dirac (Bracket) Notation in the Undergraduate Physical Chemistry Curriculum: A Pictorial Introduction

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Abstract: The Dirac (bracket) notation is ubiquitous in the chemical literature, but it is rarely introduced in the undergraduate chemistry curriculum. In this article we present a pictorial approach to the bracket notation that we have successfully used for the past three years in a junior–senior-level physical chemistry course. We have found that it requires roughly 75 minutes to introduce this topic, and, upon integration into subsequent discussions, it prepares our undergraduate students to routinely use this powerful tool in the study of chemical bonding and spectroscopy. We believe that this approach, when introduced after the traditional integral treatment, enhances student learning of the abstract subject of quantum mechanics.

Introduction

In a study of atomic structure, chemical bonding, and atomic and molecular spectroscopy, expressions such as eq 1 are encountered frequently. Manipulations of such expressions

$$\int \Psi^* \hat{\Omega} \Psi d\tau \quad (1)$$

are done in a facile, elegant fashion using the bracket notation first introduced by Dirac, as shown in eq 2. In this article we present a straightforward, pictorial method that we have

$$\int \Psi^* \hat{\Omega} \Psi d\tau \equiv \langle \Psi^* | \hat{\Omega} | \Psi \rangle \quad (2)$$

successfully employed over the past three years to introduce this topic to juniors and seniors in chemistry, who are just beginning their study of elementary quantum mechanics.

It is necessary at the outset to provide a rationale for introducing this topic at the undergraduate level because almost all undergraduate textbooks in physical chemistry avoid it altogether. We note, parenthetically, that the only exception that we have found is the text by Atkins [1], wherein the notation is used but twice with no formal introduction whatsoever. We have found that it is easy for the beginner to comprehend this notation by analogy with ordinary vectors via the highly pictorial approach that we adopt. Furthermore, it can be introduced in just 75 minutes, and upon integration into subsequent discussions, this powerful tool is routinely used by our undergraduate students in the study of chemical bonding and spectroscopy. The beauty of this notation is that it is very compact, and it emphasizes the physical significance rather than the mathematical intricacies. Thus, it allows a beginner to focus on the underlying physical principles that are often lost when students laboriously keep track of the corresponding integrals used in the traditional approach. For example, the integral in eq 2 is recast into a very intuitive, physical form by regarding the action of the operator $\hat{\Omega}$ on the ket $|\Psi\rangle$ as a

vector $|\phi\rangle$ and $\langle \Psi^* | \hat{\Omega} | \Psi \rangle = \langle \Psi^* | \phi \rangle$ the as scalar product of the two vectors.

In our experience, which spans three years, the use of this notation has served as a powerful tool to enhance student learning in the abstract and often dreaded subject of elementary quantum mechanics. It also provides the student with adequate preparation to start browsing through journal articles or more advanced texts without experiencing the intimidation that most students feel when first encountering the ubiquitous bracket notation.

As we developed our pictorial approach, we did consider the possibility of adopting the presentation from any one of a number of excellent physics textbooks available on the topic of bracket notation [2]. Most of these texts assume a certain degree of mathematical maturity and may also require some familiarity with linear algebra. Not all chemistry majors have the time to adopt the formal route to the bracket notation that physics majors typically use through a sequence that includes mathematical methods and quantum mechanics. Thus, with a limited amount of time (typically one semester) available to teach elementary quantum mechanics with applications to bonding and molecular spectroscopy, we deemed it necessary to develop a very concise introduction.

In this article we present our approach in essentially the form that we have used in the classroom, along with a brief discussion of some selected illustrative examples. In addition, we present a preliminary account of the learning outcomes of this approach.

Overview of the Course

In the physical chemistry course that covers introductory quantum chemistry, we first present a historical perspective and the detailed solution of Schrödinger's equation for the particle-in-a-box using the traditional integral approach, which includes the explicit calculation of expectation values. We then introduce operators, matrices, and the bracket notation, using the wavefunctions from the particle-in-a-box problem as illustrative examples. This is followed by a presentation of atomic and molecular structure, and rotational, vibrational, and electronic spectroscopy. The bracket notation is used

extensively, particularly in the discussion of the harmonic oscillator and chemical bonding. Our approach ensures that the students are adequately exposed to the use of appropriate integrals in the process and are expected to evaluate them, for example, in calculations of expectation values. The power of the bracket approach is that it recasts the integral approach in a format less formidable to students because it draws upon their familiarity with vectors from general physics. It also ensures to a considerable degree that they do not lose sight of the underlying physical principles, particularly when they spend considerable time and effort evaluating integrals explicitly. In our opinion, both of these approaches (the integral and bracket) are pedagogically essential in an introductory course.

The Dirac Notation: A Pictorial Introduction

Before we proceed further, we parenthetically note that because some of our students have little prior knowledge of matrices, we introduce the concepts of matrix addition, multiplication, and inversion, as well as taking the adjoint of a matrix as a brief digression prior to introducing the bracket notation. In the following paragraphs, we have, essentially, reproduced our class notes, minus the review of matrices, refined over a three-year period. The entire discussion including a review of matrices, the notation itself, and its properties in simple manipulations takes roughly 75 minutes.

The states of a quantum mechanical system are represented by ket vectors or simply kets, denoted as $|\psi\rangle$. For example, ket ψ is represented as $|\psi\rangle$. The ket vector $|\Psi\rangle$ belongs to an abstract space, referred to as the state space. Furthermore, any quantum mechanical state can be expressed as a linear combination of the elements of the state space. The properties of ket vectors can be introduced pictorially with the aid of Figure 1 by using the analogies with vectors used in classical mechanics.

While presenting the simple pictorial introduction given above, we carefully make the following distinctions between ordinary vectors and quantum mechanical states.

- The two-state system in Figure 1 is chosen as a convenient, easily understandable starting point. (We note that such a system is of particular interest in chemistry, for example, in NMR spectroscopy). In practice, the number of orthogonal basis vectors in quantum mechanics may be large, even infinite.
- In classical mechanics the coefficients c_1 and c_2 are real; however, in quantum mechanics this restriction is not necessary and c_1 and c_2 are, in general, complex numbers.

Manipulations of Ket and Bra Vectors: A Few Rules

Many of the operations involving bras and kets introduced below are analogous to operations with vectors in Euclidean space, with which students have considerable familiarity from general physics.

Manipulations using the bracket notation are governed by the following rules.

- For every ket vector $|\Psi\rangle$, there exists a bra vector, represented as $\langle\Psi|$.

b) Ket vectors can be represented as column matrices, while bra vectors can be represented as row matrices. $|\Psi\rangle$ and $\langle\Psi|$ are adjoints of one another.

c) For a ket vector $|\Psi\rangle = c_1|1\rangle + c_2|2\rangle$, the corresponding bra vector is given by $\langle\Psi| = \langle 1|c_1^* + \langle 2|c_2^*$, where c_1^* and c_2^* are the complex conjugates of c_1 and c_2 , respectively.

d) The scalar products of the basis vectors are given by

$$\langle 1|1\rangle = \langle 2|2\rangle = 1 \text{ and } \langle 1|2\rangle = \langle 2|1\rangle = 0$$

This is analogous to scalar products of unit vectors in classical mechanics,

$$\hat{i}\cdot\hat{i} = \hat{j}\cdot\hat{j} = 1 \text{ and } \hat{i}\cdot\hat{j} = \hat{j}\cdot\hat{i} = 0$$

e) The scalar product of two ket vectors $|\Psi\rangle$ and $|\phi\rangle$ is given by $\langle\phi|\Psi\rangle$.

f) $\langle\phi|\Psi\rangle^* = \langle\Psi|\phi\rangle$

Illustrative Examples

Properties of Hermitean Operators. In this exercise, we illustrate that the eigenvalues of a Hermitean operator are real, which is a key property of Hermitean operators.

Let $\hat{\Omega}$ be a Hermitean operator and $|\Psi\rangle$ a normalized ket vector satisfying

$$\hat{\Omega}|\Psi\rangle = \omega|\Psi\rangle \quad (3)$$

Multiplying eq 3 by $\langle\Psi|$,

$$\langle\Psi|\hat{\Omega}|\Psi\rangle = \omega\langle\Psi|\Psi\rangle = \omega \quad (4)$$

The adjoint of eq 3 is given by

$$\langle\Psi|\hat{\Omega}^\dagger = \langle\Psi|\omega^* \quad (5)$$

Multiplying eq 5 by $|\Psi\rangle$,

$$\langle\Psi|\hat{\Omega}^\dagger|\Psi\rangle = \langle\Psi|\omega^*|\Psi\rangle = \omega^*\langle\Psi|\Psi\rangle = \omega^* \quad (6)$$

Comparing eqs 4 and 6, with $\hat{\Omega} = \hat{\Omega}^\dagger$ for a Hermitean operator, we obtain $\omega = \omega^*$. Hence, ω must be real, and the proof is complete.

Hybrid Orbitals. In this exercise, we illustrate that the hybrid orbitals on each carbon in acetylene are orthogonal. This illustration demonstrates the compact nature of the bracket notation that we use extensively in our treatment of

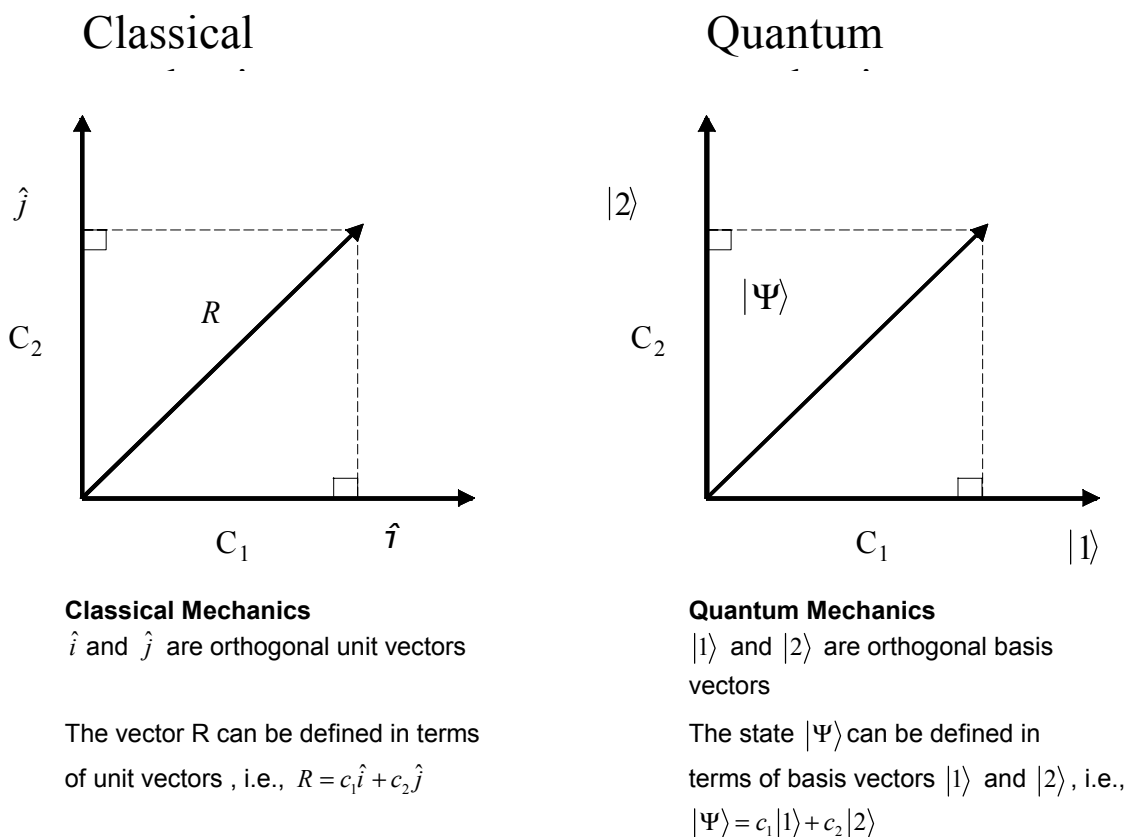


Figure 1. A pictorial introduction to the bracket notation, courtesy of ref 2.

chemical bonding. It also addresses questions that often arise in the students' minds during a first course in quantum chemistry, "are there real applications of quantum mechanics?" or "what is this material really good for?"

Following the treatment by Atkins, a standard text in Physical Chemistry [1], we construct the hybrid orbitals using the $2s$ and $2p_z$ orbitals on each carbon atom

$$h_1 = \frac{1}{\sqrt{2}}(s + p_z)$$

$$h_2 = \frac{1}{\sqrt{2}}(s - p_z)$$

We can rewrite these in the bracket notation as

$$|\Psi_1\rangle = \frac{1}{\sqrt{2}}(|\Psi_s\rangle + |\Psi_{p_z}\rangle) \quad (7)$$

$$|\Psi_2\rangle = \frac{1}{\sqrt{2}}(|\Psi_s\rangle - |\Psi_{p_z}\rangle) \quad (8)$$

Taking the adjoint of eq 7, we obtain

$$\langle\Psi_1| = \frac{1}{\sqrt{2}}(\langle\Psi_s| + \langle\Psi_{p_z}|) \quad (9)$$

Multiplying eq 8 by eq 9

$$\begin{aligned} \langle\Psi_1|\Psi_2\rangle &= \frac{1}{2}(\langle\Psi_s| + \langle\Psi_{p_z}|)(|\Psi_s\rangle - |\Psi_{p_z}\rangle) \\ &= \frac{1}{2}(\langle\Psi_s|\Psi_s\rangle - \langle\Psi_s|\Psi_{p_z}\rangle + \langle\Psi_{p_z}|\Psi_s\rangle - \langle\Psi_{p_z}|\Psi_{p_z}\rangle) \end{aligned} \quad (10)$$

We note that the orthonormality of $2s$ and $2p_z$ wavefunctions ensures that

$$\langle\Psi_s|\Psi_s\rangle = \langle\Psi_{p_z}|\Psi_{p_z}\rangle = 1 \quad (11)$$

$$\langle\Psi_s|\Psi_{p_z}\rangle = \langle\Psi_{p_z}|\Psi_s\rangle = 0 \quad (12)$$

Substitution of eqs 11 and 12 into eq 10 yields $\langle\Psi_1|\Psi_2\rangle = 0$, and the proof is complete.

Harmonic Oscillator

In this section we derive the gross and specific selection rules for vibrational spectroscopy with the aid of the bracket

notation. In addition, we determine the mean value for the potential energy of the harmonic oscillator for a given state. The derivations contained in this section can also be arrived by explicit integration, using the properties of Hermite polynomials, as illustrated in the appendix. Based on our experience with both methods, we have found the bracket approach to be more understandable for the average student.

Gross Selection Rule. The wavefunctions for a harmonic oscillator can be represented as $|\phi_m\rangle$, where the quantum number m is 0 or a positive integer. Consider a transition between vibrational states $|\phi_m\rangle$ and $|\phi_n\rangle$ with the same electronic state. The transition dipole moment is given by $\langle\phi_m|\mu|\phi_n\rangle$, where μ is the dipole moment of the molecule for that electronic state. The dipole moment is a function of the displacement x , as shown in eq 13

$$\mu = \mu_0 + \left(\frac{d\mu}{dx}\right)_0 x + \dots \quad (13)$$

where μ_0 is the dipole moment at 0 displacement, and the higher order terms have been neglected to a reasonable first approximation. The transition dipole moment can now be written as

$$\langle\phi_m|\mu|\phi_n\rangle = \langle\phi_m|\mu_0|\phi_n\rangle + \langle\phi_m|\left(\frac{d\mu}{dx}\right)_0 x|\phi_n\rangle \quad (14)$$

Because the vectors $|\phi_m\rangle$ and $|\phi_n\rangle$ are orthogonal, the first term in eq 14,

$$\langle\phi_m|\mu_0|\phi_n\rangle = \mu_0 \langle\phi_m|\phi_n\rangle = 0$$

Therefore,

$$\langle\phi_m|\mu|\phi_n\rangle = \langle\phi_m|\left(\frac{d\mu}{dx}\right)_0 x|\phi_n\rangle = \left(\frac{d\mu}{dx}\right)_0 \langle\phi_m|x|\phi_n\rangle \quad (15)$$

In order that the right hand side of eq 15 is nonzero, $\left(\frac{d\mu}{dx}\right)_0$ must be nonzero. Thus, we obtain the gross selection rule for vibrational spectroscopy: the dipole moment of the molecule must change with spatial displacement for a vibrational mode to be active.

Specific Selection Rule. In order to obtain the specific selection rule, $\Delta v = \pm 1$, we use the creation and annihilation operators as illustrated below. The treatment is essentially that presented by Cohen-Tannoudji et al [2] and Atkins [3].

The dimensionless operators \hat{X} and \hat{P} (upper case) are defined in terms of the position (x) and momentum (p) operators,

$$\hat{X} = \left(\frac{m\omega}{\hbar}\right)^{1/2} x \quad (16)$$

$$\hat{P} = \left(\frac{1}{m\omega\hbar}\right)^{1/2} p \quad (17)$$

The annihilation and creation operators, a and a^\dagger , respectively, are defined below:

$$a = \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}) \quad (18)$$

$$a^\dagger = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P}) \quad (19)$$

It can be shown that the annihilation and creation operators have the following properties:

$$a|\phi_n\rangle = n^{1/2}|\phi_{n-1}\rangle \quad (20)$$

$$a^\dagger|\phi_n\rangle = (n+1)^{1/2}|\phi_{n+1}\rangle \quad (21)$$

In order to determine $\langle\phi_m|x|\phi_n\rangle$ (Please refer to eq 15.), we use the annihilation and creation operators to express the dimensionless operator X , and hence the position operator x ,

$$\hat{X} = \frac{1}{\sqrt{2}}(a + a^\dagger) \quad (22)$$

$$x = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a + a^\dagger) \quad (23)$$

$$\begin{aligned} \langle\phi_m|x|\phi_n\rangle &= \langle\phi_m|\left(\frac{\hbar}{2m\omega}\right)^{1/2} (a + a^\dagger)|\phi_n\rangle \\ &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} \langle\phi_m|(a + a^\dagger)|\phi_n\rangle \\ &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} \langle\phi_m|a|\phi_n\rangle + \left(\frac{\hbar}{2m\omega}\right)^{1/2} \langle\phi_m|a^\dagger|\phi_n\rangle \end{aligned} \quad (24)$$

Using the properties of the annihilation operator (eq 20),

$$\langle\phi_m|a|\phi_n\rangle = \langle\phi_m|n^{1/2}|\phi_{n-1}\rangle = n^{1/2} \langle\phi_m|\phi_{n-1}\rangle = 0$$

unless $m = n - 1$, because the wavefunctions corresponding to different quantum numbers are orthogonal. In other words, $(m - n)$ must equal -1 in order that $\langle\phi_m|a|\phi_n\rangle$ be nonzero. In an analogous fashion, it can be shown that the term $\langle\phi_m|a^\dagger|\phi_n\rangle = 0$ unless $(m - n) = +1$. Thus, referring back to eq 24, $\langle\phi_m|x|\phi_n\rangle = 0$ unless $(m - n) = \pm 1$. Of course, $(m - n)$ is the difference in vibrational quantum numbers, commonly written as Δv ; thus, we have arrived at the specific selection rule, $\Delta v = \pm 1$.

Mean Potential Energy. The potential energy for a harmonic oscillator is

$$V(x) = \frac{1}{2} kx^2 \quad (25)$$

where k is the force constant defined in terms of the angular frequency ω as

$$k = m\omega^2 \quad (26)$$

The mean potential energy in a given eigenstate $|\phi_n\rangle$ is given by

$$\langle V(x) \rangle = \left\langle \frac{1}{2} kx^2 \right\rangle = \frac{1}{2} k \langle x^2 \rangle \quad (27)$$

$$= \frac{1}{2} k \langle \phi_n | x^2 | \phi_n \rangle \quad (28)$$

Rewriting x in terms of creation and annihilation operators (eq 23), the mean potential energy is

$$\langle V(x) \rangle = \frac{1}{2} k \langle \phi_n | \left[\left(\frac{\hbar}{2m\omega} \right)^{1/2} (a + a^\dagger) \right]^2 | \phi_n \rangle \quad (29)$$

$$= \frac{\hbar k}{4m\omega} \langle \phi_n | (a + a^\dagger)^2 | \phi_n \rangle$$

$$= \frac{\hbar k}{4m\omega} \left[\langle \phi_n | a^2 | \phi_n \rangle + \langle \phi_n | aa^\dagger | \phi_n \rangle + \langle \phi_n | a^\dagger a | \phi_n \rangle + \langle \phi_n | (a^\dagger)^2 | \phi_n \rangle \right] \quad (30)$$

Using the properties of annihilation operators (eq 20) and the orthogonality of the eigenstates, the expression

$$\langle \phi_n | a^2 | \phi_n \rangle = \langle \phi_n | aa | \phi_n \rangle = \langle \phi_n | an^{1/2} | \phi_{n-1} \rangle$$

$$= n^{1/2} (n-1)^{1/2} \langle \phi_n | \phi_{n-2} \rangle = 0 \quad (31)$$

Likewise, it can be shown that

$$\langle \phi_n | (a^\dagger)^2 | \phi_n \rangle = 0 \quad (32)$$

Finally, we evaluate the expression

$$\langle \phi_n | aa^\dagger | \phi_n \rangle = \langle \phi_n | a(n+1)^{1/2} | \phi_{n+1} \rangle = (n+1)^{1/2} \langle \phi_n | a | \phi_{n+1} \rangle$$

$$= (n+1)^{1/2} (n+1)^{1/2} \langle \phi_n | \phi_n \rangle = (n+1) \quad (33)$$

Using an analogous process,

$$\langle \phi_n | a^\dagger a | \phi_n \rangle = n \quad (34)$$

Substituting the results derived in eqs 31–34 in eq 30, and the definition of k , as given in eq 26, we obtain

$$\langle V(x) \rangle = \frac{\hbar k}{4m\omega} [(n+1) + n] = \frac{\hbar k}{4m\omega} (2n+1)$$

$$= \left(n + \frac{1}{2} \right) \frac{\hbar k}{2m\omega} = \frac{1}{2} \left(n + \frac{1}{2} \right) \hbar\omega \quad (35)$$

This is the expected result for a harmonic oscillator wherein the *average* potential and kinetic energies are equal.

Student Responses

We have taught the introductory quantum chemistry course five times, without (1995, 1996) and with (1997, 1998, 1999) the bracket notation. In the past three years we have used the bracket notation with considerable success. We believe that there are two attributes that contribute to its success. First, it lends itself to pictorial representation. Second, it is very compact and intuitive when compared with the traditional integral formulation alone. For example, the illustration that the eigenvalues of a Hermitean operator are real is very nonintuitive with integrals, but easily handled by students with the bracket notation. In addition, students' comments reveal that the bracket notation enabled them to visualize orthonormality, perhaps the single most important concept in introductory quantum mechanics, much better than they would in the absence of the bracket approach. Feedback from students who have proceeded to graduate school is that the two class periods used for introducing creation and annihilation operators were well spent because they gave them a good foundation for further study in quantum mechanics at the graduate level.

When examining the usefulness of a new pedagogical method, it is customary to measure learning outcomes through some external yardstick. We have measured the learning outcomes using the quantum chemistry examination prepared by the American Chemical Society. The average results were 12 percentile points higher in the past three years (58th percentile, compared to national norms) as compared to the preceding two years (46th percentile). Admittedly, the sample size, (10 students in 1995 and 1996 combined and 29 students in 1997 through 1999 combined) is small; however, we believe that the increased scores are significant. We note, however, that the driving force for the continued use of this method is our belief in the pedagogical soundness of this approach, as well as the positive feedback that we have received from our former students in graduate school, as discussed above.

Many of our students have moved on from this course to undergraduate research projects using the software package, Spartan, which makes extensive, albeit implicit, use of orthonormality. They carry out energy-minimization calculations for small as well as large organic molecules that are of interest from a synthetic perspective. Students' familiarity with the bracket notation allows for a greater intuitive understanding of orthonormality as they browse through the Spartan manual, thus, it demystifies the "black box" nature of a prepackaged software program.

Conclusions

We have presented a pictorial approach that measurably enhances student learning of the abstract subject of quantum mechanics. We have included several illustrative examples of

the bracket notation that can be used alongside the traditional presentation that uses integrals. Students are appreciative of this pictorial approach, which eases their first journey into the rather elusive world of quantum mechanics.

Appendix

In this appendix, we have used the traditional integral approach to derive the expressions pertaining to the harmonic oscillator that were previously derived using the bracket notation.

I. Evaluation of conditions for a non-zero value of

$$\int_{-\infty}^{\infty} \phi_m(x) x \phi_n(x) dx$$

The analog of this expression in the bracket notation, $\langle \phi_m | x | \phi_n \rangle$, was evaluated while deriving the specific selection rules for vibrational spectroscopy using the harmonic oscillator model. To evaluate this integral, we use the functional form of the wavefunctions defined as [1]

$$\phi_n(x) = N_n H_n(y) e^{-y^2/2} \quad (\text{A1})$$

where N_n is the normalization constant

$$N_n = \frac{1}{(\alpha \pi^{1/2} 2^n n!)^{1/2}} \quad (\text{A2})$$

and y is related to x by

$$y = \frac{x}{\alpha} \quad (\text{A3})$$

$$\alpha = \left(\frac{\hbar^2}{mk} \right)^{1/4} \quad (\text{A4})$$

The Hermite polynomials $H_n(y)$ satisfy the following relations

$$\int_{-\infty}^{\infty} H_m H_n e^{-y^2} dy = 0 \quad \text{if } m \neq n$$

$$= \pi^{1/2} 2^n n! \quad \text{if } m = n \quad (\text{A5})$$

$$H_{n+1} = 2yH_n - 2nH_{n-1} \quad (\text{A6})$$

In accord with the notation adopted by Cohen-Tannoudji, we have used the subscript n as opposed to ν used in many standard textbooks when labeling the harmonic oscillator wavefunctions.

$$\int_{-\infty}^{\infty} \phi_m(x) x \phi_n(x) dx = \int_{-\infty}^{\infty} N_m H_m e^{-y^2/2} (\alpha y) N_n H_n e^{-y^2/2} \alpha dy \quad (\text{A7})$$

$$= N_m N_n \alpha^2 \int_{-\infty}^{\infty} H_m y H_n e^{-y^2} dy \quad (\text{A8})$$

Rearranging eq A6, we obtain an expression for yH_n

$$yH_n = \left(\frac{1}{2} H_{n+1} + nH_{n-1} \right) \quad (\text{A9})$$

Substituting for yH_n in eq A8, the integral in eq A7 is

$$N_m N_n \alpha^2 \int_{-\infty}^{\infty} H_m \left(\frac{1}{2} H_{n+1} + nH_{n-1} \right) e^{-y^2} dy \quad (\text{A10})$$

$$= N_m N_n \alpha^2 \left(\frac{1}{2} \int_{-\infty}^{\infty} H_m H_{n+1} e^{-y^2} dy + n \int_{-\infty}^{\infty} H_m H_{n-1} e^{-y^2} dy \right) \quad (\text{A11})$$

Given the properties of Hermite polynomials (eq A5), the first integral in eq A11 is zero unless $m = n+1$. The second integral is zero unless $m = n-1$. In other words ($m - n$) must equal ± 1 in order to obtain a nonzero value for the integral $\int_{-\infty}^{\infty} \phi_m(x) x \phi_n(x) dx$, and the proof is complete.

II. Average potential energy of a harmonic oscillator

The average potential energy in a state with a vibrational quantum number n is given by

$$\langle V(x) \rangle = \left\langle \frac{1}{2} kx^2 \right\rangle = \frac{1}{2} k \langle x^2 \rangle = \frac{1}{2} k \int_{-\infty}^{\infty} \phi_n(x) x^2 \phi_n(x) dx \quad (\text{A12})$$

$$= \frac{1}{2} k \int_{-\infty}^{\infty} N_n H_n e^{-y^2/2} (\alpha y)^2 N_n H_n e^{-y^2/2} \alpha dy$$

$$= \frac{1}{2} k \alpha^3 N_n^2 \int_{-\infty}^{\infty} H_n y^2 H_n e^{-y^2} dy \quad (\text{A13})$$

Substituting for yH_n (eq A9)

$$y^2 H_n = y(yH_n) = y \left(\frac{1}{2} H_{n+1} + nH_{n-1} \right)$$

$$= \frac{1}{2} yH_{n+1} + nyH_{n-1} = \frac{1}{2} \left[\frac{1}{2} H_{(n+1)+1} + (n+1)H_{(n+1)-1} \right]$$

$$+ n \left[\frac{1}{2} H_{(n-1)+1} + (n-1)H_{(n-1)-1} \right] \quad (\text{A14})$$

$$= \frac{1}{4} H_{n+2} + H_n \left[\frac{1}{2}(n+1) + \frac{n}{2} \right] + n(n-1)H_{n-2}$$

$$= \frac{1}{4} nH_{n+2} + \left(n + \frac{1}{2} \right) H_n + n(n-1)H_{n-2}$$

Substituting eq A14 in eq A13

$$= \frac{1}{2} k \alpha^3 N_n^2 \left[\begin{array}{l} \frac{1}{4} n \int_{-\infty}^{\infty} H_n H_{n+2} e^{-y^2} dy + (n + \frac{1}{2}) \int_{-\infty}^{\infty} H_n H_n e^{-y^2} dy \\ + n(n-1) \int_{-\infty}^{\infty} H_n H_{n-2} e^{-y^2} dy \end{array} \right]$$

The first and third integrals equal zero, eq A5. Substituting $\int_{-\infty}^{\infty} H_n H_n e^{-y^2} dy = \pi^{1/2} 2^n n!$ (eq A5) and the values for N_n (eq A2) and α (eq A4), we obtain

$$\langle V(x) \rangle = \frac{1}{2} \left(n + \frac{1}{2} \right) k \alpha^2 = \frac{1}{2} \left(n + \frac{1}{2} \right) k \frac{\hbar}{(mk)^{1/2}} = \frac{1}{2} \left(n + \frac{1}{2} \right) \hbar \omega$$

and the proof is complete.

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