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Part I

Fundamentals of the diatomic molecule

Chapter 1

Primer on diatomic spectroscopy

1.1 Overview

This book describes how one uses quantum mechanics to predict the spectra of diatomic molecules in their gaseous state. The two most important attributes of a spectral line are its position in the electromagnetic spectrum and the strength with which the molecule can interact with the radiation field to produce spectral lines. Thus, a book that discusses the calculation of positions and intensities of spectral lines of a diatomic molecule equally communicates the application of quantum theory to the diatomic molecule.

The theoretically convenient measure of spectral line position is its vacuum wave number $\tilde{\nu}_{u\ell}$, which is the difference between the upper term T_u (i.e., upper energy eigenvalue expressed in the units of cm^{-1}) and the lower term T_ℓ,

$$\tilde{\nu}_{u\ell} = T_u - T_\ell. \tag{1.1}$$

In the optical region, the term difference corresponds to a specific color. However, experiments usually measure the wavelength positions in a laboratory setting at standard ambient temperature and pressure. For typical laser spectroscopy investigations of, say, optical emission spectroscopy subsequent to generation of a laser spark, spectral resolutions of the instrument spectrometer and detector amount to 0.1–0.01 nm, rarely to 0.001 nm or 1 pm. At the wavelength, λ, of 400 nm, a spectral resolution, $\Delta\lambda$, of better than 1 pm corresponds to a resolving power, R,

$$R = \lambda/\Delta\lambda \geqslant 400\,000, \tag{1.2}$$

or a wave number resolution of better than $0.05\ cm^{-1}$. The spectral resolution of diatomic molecular data computed in this book is better than $0.05\ cm^{-1}$. For laser-induced optical breakdown experiments, which is a recent application of diatomic molecular spectroscopy, resolving powers are of the order of 4000–10 000. For high-resolution, absorption measurements of stellar astrophysical objects, resolving powers of the order of 40 000 are quite common.

The theoretically most convenient measure of a molecule's ability to interact with electromagnetic radiation is its Condon and Shortley [1] line strength, $S_{u\ell}$, which describes transitions between an upper, u, and a lower level, ℓ. The line strength represents a summation over individual states that comprise upper and lower levels. Both the vacuum wave number $\tilde{\nu}_{u\ell} = \tilde{\nu}_{\ell u}$ and the line strength $S_{u\ell} = S_{\ell u}$ are symmetric with regard to the upper and lower levels. In addition, the symbols u and ℓ represent a collection of quantum numbers. In diatomic spectroscopy, upper state quantum numbers are normally denoted with a single prime, while lower states are denoted with the absence of a prime or a double prime. The absence of a double prime has become the standard way of denoting a lower state diatomic quantum number.

1.2 Reversed angular momentum

Historically, the reversed-angular-momentum (RAM) methodology has successfully predicted diatomic spectra without the use of modern digital computers. The RAM method establishes a reduced set of basis states; in other words, works with an a priori approximation. Sets of rules are introduced when applying a transformation to a molecular-fixed from the laboratory-fixed coordinate system. These rules utilize a supposed reversal of sign in the application of quantum mechanical angular momentum algebra. This section provides a brief historic account of the challenges associated with the RAM method.

The reversed-angular momentum approach is mentioned first in an article on the quantization question of the asymmetric top [2]. Klein writes in the introduction that the paper might be of interest for methods of quantization. The reversed sign is introduced for the equations of the components of angular momentum in the molecular-fixed coordinate system in order to obtain agreement with the well-established classical equations for the symmetric top. Conversely, the application of the standard, laboratory-fixed angular momentum equations would lead to the wrong classical result. This article also makes reference to canonical conjugate Euler angles that are interpreted as references to dual space.

The RAM methodology is embraced by Van Vleck in his work on the coupling of angular momentum vectors in molecules [3]. Notably, Sir Harold Kroto communicates in his acceptance lecture for the 1996 Nobel Prize in Chemistry, 'Symmetry, Space, Stars and C_{60}' [4], the importance of 'Symmetry, the Key to the Theory of Everything'. With reference to the RAM work, Sir Kroto quotes Van Vleck: '*Practically every-one (!) knows that the components of total angular momentum (NB the angular momentum operator is usually denoted by* J *and the associated quantum number by* j*) of the molecule relative to the axes [x, y, z] fixed in space satisfy the commutation relation of the form*

$$J_x J_y - J_y J_x = iJ_z \qquad (1.3)$$

Klein discovered the rather surprising fact that when total angular momentum is referred to axes mounted in the molecule which we will denote by [x', y', z'] the sign of i in the commutation relation is reversed i.e.

$$J_{x'}J_{y'} - J_{y'}J_{x'} = -iJ_{z'} \qquad (1.4)$$

Sir Kroto goes on to say: *Does practically everyone know this?—I wondered whether to check this claim out by asking everyone on the main street in Brighton whether they did. I hardly knew—or more accurately—really understood the first relation, let alone the second. However I did know that angular momentum was quantised and governed by the fundamental relations*

$$\langle j|J^2|\rangle = \hbar j(j+1) \qquad (1.5)$$

$$M_J = -j \ldots +j \qquad (1.6)$$

which means that J has $2j + 1$ possible orientations, and

$$\Delta j = 0, \pm 1 \qquad (1.7)$$

which indicates that when a transition occurs, j may only change by one unit or on occasion remain unchanged.' Previously, in 1975 and then in 1992, Sir Kroto discussed the molecule-fixed angular momentum following Van Vleck [3], leading to the reversed-angular momentum equations in his Nobel laureate lecture [4] and in his book on molecular rotation spectra [5].

However, an accurate review shows that there is no reversal of the sign when moving from a laboratory-fixed to a molecule-fixed coordinate system; in other words, there is no mathematical support of the reversed sign. Sustenance of the angular momentum equations can be explained as follows. In terms of classical mechanics, reversal of motion occurs as one goes from a rotating system to a fixed system, or vice versa. For example, motion reversal can be experienced by looking at the surroundings while on a rotating merry-go-round versus observing the rotation in the fixed reference frame. The quantum mechanical implementation of motion reversal or time reversal changes the sign and takes the conjugate complex, leading to the preservation of the sign. Reference to dual space would confuse things because clearly the standard angular momentum operator equations are not affected by a transformation from laboratory-fixed to molecule-fixed coordinates (see appendix A).

A reasonably concise treatment shows preservation of the commutator relations under a unitary transformation. Consider the operators A, B, and C which satisfy the commutation formula

$$AB - BA = iC \qquad (1.8)$$

and subject these three operators to the unitary transformation U; that is,

$$A' = U^\dagger A U \qquad (1.9a)$$

$$A = U A' U^\dagger \qquad (1.9b)$$

with similar equations holding for B and C. Then,

$$AB - BA = U A' U^\dagger U B' U^\dagger - U B' U^\dagger U A' U^\dagger \qquad (1.10a)$$

$$= U \ A' \ B' \ U^\dagger \tag{1.10b}$$

$$= iC \tag{1.10c}$$

$$iU^\dagger \ C \ U = A'B' \tag{1.10d}$$

$$iC' = A'B' - B'A'. \tag{1.10e}$$

The above result, e.g., see Davydov [6], holds for all commutators, including those for angular momentum. Thus,

$$J_{x'}J_{y'} - J_{y'}J_{x'} = i \ J_{z'} \tag{1.11a}$$

$$J_{y'}J_{z'} - J_{z'}J_{y'} = i \ J_{x'} \tag{1.11b}$$

$$J_{z'}J_{x'} - J_{x'}J_{z'} = i \ J_{y'} \tag{1.11c}$$

In summary, the RAM method is not utilized in this book for the computation of diatomic molecular spectra. RAM is avoided due, in part, to not needing approximations thanks to the availability of modern digital computers and due in part to the mathematical inconsistency of the supposed change of sign, as implied by the 'reversed-angular momentum' descriptive nomenclature.

1.3 Exact diatomic eigenfunction

An exact expression of the diatomic eigenfunction is essential for prediction of spectra. The major difference between this book and other treatments of the diatomic molecule is the use of the Wigner–Witmer diatomic eigenfunction [7] in place of invoking the Born–Oppenheimer approximation [8] from the very beginning of a theory description. In the Wigner–Witmer approach, angular coordinates are exactly separated from the electronic–vibrational coordinates. In this book, the Wigner–Witmer eigenfunction is employed for computation of the vacuum wave numbers and the rotational line strengths. If one were to instead adopt the Born–Oppenheimer approximation, then the rotational line strengths would be labeled as Hönl–London factors. The Born–Oppenheimer approximation breaks the electronic–vibrational strength into electronic and vibrational parts that correspond to r-centroids and Franck–Condon factors, and both may be functions of the total angular momentum in the upper and lower levels.

The expression *spectroscopic accuracy* refers to the accuracy with which line position measurements can be performed. Whereas wavelength measurements having an accuracy of 1 part per million are routinely performed, achieving an accuracy of 1 part per hundred in the measurement of relative intensities of a group of spectral lines is fully adequate for many purposes. Thus, one may elect to directly use the Born–Oppenheimer approximation for many practical calculations of molecular line intensity; namely, approximating the diatomic eigenfunction as a product of electronic, vibrational, and rotational factors. However, the Born–Oppenheimer approximation cannot produce diatomic term values with

spectroscopic accuracy without generalization. To achieve spectroscopic accuracy within the Born–Oppenheimer approximation, one must include sums over the many electronic states of the molecule and sums over the many vibrational states of each electronic state. Van Vleck transformations [9] or other mathematical procedures reduce the dimension of the Hamiltonian matrix prior to numerically diagonalization [10–15].

In this book, only one diatomic selection rule is used. A spectral line, i.e., a term difference, is allowed if the angular momentum part of its line strength is non-vanishing. However, a modification of the line strength computation is required if the diatomic molecule in question is homonuclear, i.e., the two nuclei are identical. An unresolved hyperfine structure in the spectrum of a homonuclear molecule causes states of positive parity and negative parity to have different nuclear spin statistical weights, g_+ and g_-. If the nuclear spin is zero, then either g_+ or g_- will be zero. Thus, exchange symmetry, the symmetry associated with the exchange of identical particles, rigorously forbids certain spectral lines, even when the rotational line strength is nonzero. However, if the rotational line strength factor vanishes, then the spectral line is rigorously forbidden.

1.4 Computation of diatomic spectra

The required steps for computation of spectra can be summarized as follows:
- An angular momentum momentum coupling model must be chosen because angular momentum theory does not tell us how the total angular momentum is formed from the orbital and spin momenta.
- The eigenfunctions for everything in the system except the total angular momentum are computed.
- With the eigenfunctions obtained in the previous step and the chosen angular momentum coupling model, upper and lower Hamiltonians are computed and diagonalized.
- From the orthogonal matrices that diagonalize the upper and lower Hamiltonians, the line strengths are computed for various possible types of transitions, e.g., electric dipole, magnetic dipole, electric quadrupole, etc. Typically, one knows precisely what type of transition dominates in the spectrum, but this is not invariably the case.
- The nonvanishing of the rotational angular momentum part of the line strength selects the subset of allowed spectral lines from the computed term differences.

Consequently, the minimal information required for computation of a spectrum includes selected term differences $\tilde{\nu}_{u\ell}$ and the computed line strengths $S_{u\ell}$. A description of a diatomic molecule having N electrons and residing in field free space requires $3N + 6$ spatial or angular coordinates, the time t, N electronic spin variables, and two nuclear spin variables. In the case of the diatomic molecule, the only exactly separable variables are the time t, the coordinates of the total mass, and three Euler angles which describe the total angular momentum. The Wigner–Witmer

diatomic eigenfunction provides the exact separation of three Euler angles, but $3N$ internal spatial coordinates and the numerous spins remain. Unless the number of electrons N is very small, the diatomic problem remains unsolvable with spectroscopic accuracy because there are $3N$ independent variables that cannot be treated with mathematical exactness.

Despite the challenges mentioned in the previous paragraph, one can, with two stringent caveats, apply the above algorithm to the diatomic molecule. The first caveat is that one must have extensive experimentally recorded wave number tables, $\tilde{\nu}_{u\ell}^{\exp}(J', J)$, versus upper and lower total angular momenta, J' and J, respectively, for many vibrational bands in the spectrum of a molecule of interest. The second caveat is associated with using trial values of semiempirical molecular parameters for each vibrational level, v, such as B_v, D_v, A_v, λ_v, γ_v, and so on. One computes term differences, $\tilde{\nu}_{u\ell}(J', J)$, from numerically diagonalized upper and lower Hamiltonians, calculates corrections to the trial values of the parameters from differences $\tilde{\nu}_{u\ell}(J', J) - \tilde{\nu}_{u\ell}^{\exp}(J', J)$, and iterates the computations until the errors in the computed line positions are comparable to the estimated errors in the experimental line positions. When successful, this procedure yields working models for the upper and lower Hamiltonians and sets of molecular parameters that predict the measured line positions.

The practical significance of molecular parameters was their appearance in term value equations, semiempirical equations with which one can compute the upper T_u and lower T_ℓ terms, and thereby the vacuum wave number $\tilde{\nu}_{u\ell}$. Herzberg [16] gives many examples of term value equations, but note that when Herzberg wrote his book the numerical diagonalization of thousands of matrices was impractical. The current significance of the molecular parameters is that they can be used to compute diatomic Hamiltonian matrix representations in one of the Hund's bases.

In this book the computation of $\tilde{\nu}_{u\ell}(J', J)$ and $S_{u\ell}(J', J)$ is based upon the Wigner–Witmer diatomic eigenfunction instead of the eigenfunction associated with the Born–Oppenheimer approximation, but computations of the electronic–vibrational strengths utilize separation of electronic from vibrational contributions familiar from the Born–Oppenheimer approximation.

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