

Wigner-Witmer Eigenfunctions in Diatomic Spectroscopy

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Received 7 August 2014, accepted 16 August 2014

ABSTRACT

Born and Oppenheimer gave an approximate separation of the molecular eigenfunction into electronic, vibrational, and rotational parts, but at the end of their paper showed that the two angles describing rotation of the nuclei in a diatomic molecule are exactly separable. A year later in a two-part work devoted strictly to diatomic molecules, Wigner and Witmer gave (1) an exact diatomic eigenfunction and (2) the rules correlating the electronic state of a diatomic molecule to the orbital and spin momenta of the separated atoms. The second part of the Wigner-Witmer became famous for its correlation rules. The first part containing the exact diatomic eigenfunction from which correlation rules were obtained has been ignored. Plausible speculation gives two explanations for why the exact Wigner-Witmer diatomic eigenfunction has been ignored for more than 80 years. First, the Wigner-Witmer diatomic eigenfunction is of no value in polyatomic theory, thus cannot serve as an introduction to polyatomic theory, and yet diatomic spectroscopy is often presented as a simplified introduction to polyatomic spectroscopy. Second, likely most significantly, the Wigner-Witmer diatomic eigenfunction is expressed in terms of Wigner's D-function, and about 40 years elapsed before Wigner's D-function was widely accepted into diatomic theory. The present work attempts to revive the Wigner-Witmer diatomic eigenfunction. In accord with the postulates of quantum mechanics, we assume that a system composed of N electrons and precisely two nuclei is fully described by an eigenfunction depending upon $3N + 6$ spatial coordinates and time. The time translation, spatial translation, and spatial rotation symmetry operators are applied to this eigenfunction. The result is the Wigner-Witmer diatomic eigenfunction which is seen to have a reasonably sound theoretical basis. Two additional symmetry operators, those for parity and the exchange of identical nuclei, are applied to the eigenfunction. The long established results for the nuclear spin statistics of a homonuclear molecule are reproduced, but the currently accepted results for diatomic parity are not. We believe that our treatment of diatomic parity is the first correct one to be given.

1. INTRODUCTION

In 1928 Wigner and Witmer [1] published a two-part article on diatomic theory. The first part gives an exact diatomic eigenfunction, and the second gives rules correlating the electronic state of a diatomic molecule to the orbital L and spin S coupling of two separated atoms. Oddly, the Wigner-Witmer correlation rules became famous but the exact Wigner-Witmer diatomic eigenfunction from which the rules were obtained has been ignored.

A year earlier, in the introduction to their paper, Born and Oppenheimer [2] allude to an exact

separation of two rotational coordinates in the diatomic molecule. In their next section, which is applicable to polyatomic molecules, they introduce a coordinate system attached to the nuclei whose orientation is set by the Euler angles, and note that there are terms in the molecular Hamiltonian in which both electronic and nuclear coordinates appear thereby preventing the exact separation of the total eigenfunction into a product of electronic and nuclear eigenfunctions. In their final section Born and Oppenheimer return to the diatomic molecule and give the details of the exact

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Keywords: Laser Induced Breakdown Spectroscopy, Wigner-Witmer diatomic eigenfunction.

separation of two of the Euler angles, angles θ and ϕ that describe rotation of the two nuclei. The spherical harmonic $Y_{\ell m}(\theta, \phi)$ is the angular momentum part of Born-Oppenheimer diatomic eigenfunction.

We are concerned here with the ignored first part of the Wigner-Witmer paper in which they show that for the diatomic molecule the Euler angles can be made exactly separable dynamical variables of the molecule, two of the angles for nuclear rotation and the third for electronic rotation. A well known relationship exists between the spherical harmonic and Wigner D-function,

$$Y_{\ell m}(\theta, \phi) = \sqrt{\frac{2\ell + 1}{4\pi}} D_{m 0}^{\ell*}(\phi, \theta, 0). \quad (1)$$

Thus, the Wigner-Witmer exact separation of the D-function depending upon all three Euler angles is the logical mathematical extension of the exact separation of $Y_{\ell m}(\theta, \phi)$ made a year earlier by Born and Oppenheimer.

In current diatomic theory the third Euler angle is excluded or considered redundant. The reasoning is that rotation about the internuclear axis of the diatomic molecule can only be electronic rotation and since by convention the Born-Oppenheimer approximation must separate nuclear coordinates from electronic coordinates, electronic rotation χ about the internuclear distance and nuclear rotation θ and ϕ of the internuclear axis must be segregated to place χ in the electronic eigenfunction and θ and ϕ in the nuclear eigenfunction.

After the Wigner-Witmer paper, the Wigner D-function mostly disappeared from diatomic literature for about four decades. Hirschfelder and Wigner [3] used the D-function in their separation of 6 coordinates (3 for the total linear momentum, 3 for the total angular momentum) for N particle systems, but do not explicitly mention the diatomic molecule. Again not specifically mentioning the diatomic molecule, Curtis et al. [4] repeat the separation of 6 coordinates for N particle systems, and consider the three-body system in detail. Davydov [5] in his quantum mechanics textbook used the D-function in his discussion of diatomic theory. At about the same time, Rubin [6] employed it for his calculations of Hönl-London factors. Park and Hirschfelder [7] used the D-function to separate two angular rotational coordinates in the diatomic eigenfunction but failed to notice that their Eq. (2.35) holds for all values of the third Euler angle, not just $\gamma = 0$. Zare et al. [8] explicitly used the D-function in their case (a) basis function. Judd [9] and Mizushima [10], in their treatments of diatomic theory, introduce the D-function and discuss its mathematical

properties, but do not explicitly display it in their Hund's cases (a) and (b) basis functions. The Wigner D-function has since become a vital mathematical component of diatomic theory. However, the exact separation of $D_{M\Omega}^{\ell*}(\phi \theta \chi)$ in the diatomic eigenfunction where the nuclear coordinates ϕ and θ appear with the electronic coordinate χ has remained essentially forgotten for eight decades.

2. DERIVATION OF THE WIGNER-WITMER DIATOMIC EIGENFUNCTION

We model the diatomic molecule as a system composed of N electrons and precisely two nuclei who are treated as point masses having spin. We consider only the low energy realm appropriate to atomic and molecular physics. In accord with the postulates of quantum mechanics we assume that the molecule is fully described by an eigenfunction Ψ_{nvJM} ,

$$\begin{aligned} &\Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b, t) \\ &\equiv \langle \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b, t | nvJM \rangle \end{aligned} \quad (2)$$

depending upon $3N + 7$ independent variables, the $3N$ spatial coordinates $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N$ of the N electrons, the 6 spatial coordinates \mathbf{R}_a and \mathbf{R}_b of the nuclei, and time t . The quantum numbers J and M are for the total angular momentum \mathbf{J} and its z-component J_z . The symbol n represents all other required quantum numbers and continuous indices except for the vibrational quantum number v. From the advantage of hindsight we include v here at the beginning. For the moment, we simply note the vast body of experimental evidence indicating that the bound states of the diatomic molecule possess a vibrational quantum number. Later we will show that v is the quantum number associated with the internuclear distance r and that the total angular momentum of the diatomic molecule is independent of r. By the process of elimination, one finds that the coordinate r can describe nothing but periodic oscillation of the diatomic molecule in a bound state.

The vibrational modes of a polyatomic molecule can contribute orbital angular momentum, but the single vibrational coordinate r of the diatomic molecule cannot. This is a fundamental difference between the diatomic molecule and all others, a fundamental difference revealed when one compares the total angular momentum states of the diatomic molecule with those of any polyatomic molecule. Rotational invariance and conservation of the total angular momentum apply, of course, to all molecules, but only for the diatomic molecule can the three variables with which one demonstrate rotational invariance and the

conservation law also, with mathematical exactness, be three internal dynamical coordinates of the molecule. The polyatomic theorist must use the Euler angles to describe rotation of the nuclear frame which means that these same Euler angles are not those with which one expresses rotational invariance and conservation of angular momentum. The diatomic theorist again uses the Euler angles to describe physical rotations in the molecule, but these same rotations are those of rotational invariance and conservation of angular momentum. This distinction might seem academic but the practical consequences are profound. In this section we explore what translational and rotational symmetry say about the eigenfunction in Eq. (2).

3. TRANSLATIONAL SYMMETRIES OF THE DIATOMIC EIGENFUNCTION

The first steps in derivation of the Wigner-Witmer diatomic eigenfunction are (1) application of the two-body reduction to the motion of the two nuclei, (2) application of the time translation (evolution) operator $U(t - t_0)$ and spatial translation operator $\mathcal{T}(\mathbf{R} - \mathbf{R}_0)$ to the eigenfunction Ψ_{nvJM} , and (3) selection of new coordinate origins t_0 and \mathbf{R}_0 which convert $U(t - t_0)$ and $\mathcal{T}(\mathbf{R} - \mathbf{R}_0)$ from being symmetry operators representing coordinate translations to operators representing physical translations in time and space. On taking these steps one finds

$$\begin{aligned} & \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, \mathbf{R}_a, \mathbf{R}_b, t) \\ &= \exp[-i(t - t_0)E_{nvJ}/\hbar] \exp[-i\mathbf{P}_{CM} \cdot \mathbf{R}_{CMab}/\hbar] \\ & \quad \times \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | nvJM \rangle \end{aligned} \quad (3)$$

The two-body reduction replaces the six coordinates of nuclei a and b, $\mathbf{R}_a(X_a, Y_a, Z_a)$ and $\mathbf{R}_b(X_b, Y_b, Z_b)$, with the three coordinates $\mathbf{r}(x, y, z)$ of a single fictitious particle of reduced mass μ .

$$\mathbf{r}(xyz) = \mathbf{r}_a - \mathbf{r}_b \quad (4a)$$

$$= \mathbf{R}_a - \mathbf{R}_0 - (\mathbf{R}_b - \mathbf{R}_0) \quad (4b)$$

$$= \mathbf{R}_a(X_a, Y_a, Z_a) - \mathbf{R}_b(X_b, Y_b, Z_b), \quad (4c)$$

$$\mu = \frac{m_a m_b}{m_a + m_b}, \quad (4d)$$

and locates the new coordinate origin \mathbf{R}_0 at the center of mass of the two particles,

$$\mathbf{R}_{CMab} = \frac{m_a \mathbf{R}_a + m_b \mathbf{R}_b}{m_a + m_b} \quad (5a)$$

$$= \frac{m_a(\mathbf{r}_a + \mathbf{R}_0) + m_b(\mathbf{r}_b + \mathbf{R}_0)}{m_a + m_b} \quad (5b)$$

$$= \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b} + \mathbf{R}_0 \quad (5c)$$

$$= \mathbf{r}_{CMab} + \mathbf{R}_0. \quad (5d)$$

This forces the center of mass of the two particles \mathbf{r}_{CMab} in the new coordinate system to be zero. Three independent variables are thereby removed from the problem allowing us to introduce the components of the center of total mass $\mathbf{R}_{CM}(X_{CM}, Y_{CM}, Z_{CM})$ without an overall increase in the number of variables.

$$\mathbf{R}_{CM} = \frac{m_a \mathbf{R}_a + m_b \mathbf{R}_b + \sum_{i=1}^N m_i \mathbf{R}_i}{m_a + m_b + \sum_{i=1}^N m_i} \quad (6)$$

Only when the new origin \mathbf{R}_0 is set at the center of mass of two nuclei \mathbf{R}_{CMab} , and the momentum operator \mathbf{P} is set equal to total linear momentum \mathbf{P}_{CM} does the spatial translation operator yield translational invariance, conservation of the total linear momentum, and separation of the three coordinates $\mathbf{R}_{CM}(X_{CM}, Y_{CM}, Z_{CM})$.

Translational invariance in time, conservation of the total energy, and separation of t is achieved if one simply chooses the time origin t_0 to be the time at which some event occurs in the system.

Separation of time and the total linear momentum in conservative systems are treated in detail in many quantum mechanics textbooks, and will not be discussed in further detail here. The following is limited to the internal eigenfunction $\Phi_{nvJM}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r})$, that part of the total eigenfunction remaining after application of the translational symmetries. We will treat rotational symmetry in considerable detail because many of the most interesting features seen in diatomic spectra come from the rotational symmetry of the internal eigenfunction.

3.1 Rotational symmetry of the diatomic eigenfunction

Symmetry operators are defined by their effect on the eigenfunction. The evolution operator translates the time coordinate,

$$U(t, t_0) \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, t) = \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, t') \quad (7)$$

$$t' = t - t_0 \quad (8)$$

and the translation operator translates spatial coordinates,

$$\mathcal{T}(\mathbf{R}, \mathbf{R}_0) \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, t) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \quad (9)$$

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0. \quad (10)$$

The rotation operator $\mathcal{R}(\alpha, \beta, \gamma)$ is similarly defined, but because it has no effect on $U(t, t_0)$ or $\mathcal{T}(\mathbf{R}, \mathbf{R}_0)$ the rotation operator acts only on the internal eigenfunction,

$$\begin{aligned} & \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | \mathcal{R}(\alpha, \beta, \gamma) | nvJM \rangle \\ &= \langle \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N, \mathbf{r}' | nvJM \rangle \end{aligned} \quad (11)$$

The primed coordinates are the result of coordinate rotation accomplished by the Euler rotations α , β , and γ . For example, the rotated coordinate vector \mathbf{r}'_1 is given by

$$\mathbf{r}'_1 = \begin{bmatrix} x'_1 \\ y'_1 \\ z'_1 \end{bmatrix} = \mathcal{D}(\alpha \beta \gamma) \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} \quad (12)$$

The coordinate rotation matrix is given by

$$\mathcal{D}(\alpha \beta \gamma) = \begin{bmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{bmatrix} \quad (13)$$

Like t_0 in the evolution operator $U(t - t_0)$, and \mathbf{R}_0 in the translation operator $\mathcal{T}(\mathbf{R} - \mathbf{R}_0)$, the Euler angles in the rotation operator $\mathcal{R}(\alpha, \beta, \gamma)$ are parameters of coordinate transformation, the arguments (independent variables) of symmetry operations. A symmetry operator can produce a new mathematical description of the system but must leave the system physically unaltered. However, if one can succeed in equating the argument of a symmetry operator to a physical variable of the system, the symmetry operator becomes an operator describing physical motion. Thus, by equating t_0 to the occurrence of some physical event, we made the evolution operator $U(t - t_0)$ become the mathematical description of the temporal evolution of the system. Similarly, by expressing the total linear momentum in terms of the coordinates of the center of total mass, we made the translation operator become a mathematical description of the total linear momentum of the system. Can one perform the analogous trick using the rotation operator $\mathcal{R}(\alpha, \beta, \gamma)$? Those of us who work with atomic and molecular system have become so accustomed to making separations of time and total linear momentum from the remainder of a conservative system we might forget that $U(t - t_0)$ and $\mathcal{T}(\mathbf{R} - \mathbf{R}_0)$ began their theoretical lives as symmetry operators, not descriptions of physical motion. Hirschfelder&Wigner attempted to find a general way of making the rotation operator $\mathcal{R}(\alpha, \beta, \gamma)$ simultaneously serve as a symmetry operator and description of physical rotation? In our estimation they failed because they express their final result in terms of “the principle axes of inertia”, a term lacking a mathematically precise quantum mechanical definition. In general, the Euler angles of rotational invariance are not angles of physical rotation. The diatomic molecule is perhaps the most complex system for which the rotation operator $\mathcal{R}(\alpha, \beta, \gamma)$ can serve as the continuous, unitary operator associated with rotational invariance and conservation of the total angular momentum and simultaneously in a

mathematically exact way describe three internal rotations of the molecule.

According to the quantum theory of angular momentum, the square of angular momentum \mathbf{J}^2 and one component of \mathbf{J} , conventionally chosen to be the z-component J_z , commute with the Hamiltonian. That is, \mathbf{J}^2 and J_z are members of the complete set of commuting observables (CSCO), and $|JM\rangle$ is an eigenvector of the operators \mathbf{J}^2 and J_z . In general, the z' axis of rotated coordinates does not coincide with the original z axis. The nature of angular momentum gives one no choice but to consider a second magnetic quantum number Ω associated with the z' component of \mathbf{J} , and equations such as

$$|JM\rangle = \sum_{\Omega=-J}^J |J\Omega\rangle \langle J\Omega | JM\rangle \quad (14)$$

which relate the $|JM\rangle$ and $|J\Omega\rangle$ states. Expressed in terms of $|J\Omega\rangle$ states and the transformation coefficients, $\langle J\Omega | JM\rangle$, the internal diatomic eigenfunction from Eq. (3) reads

$$\begin{aligned} & \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | nvJM\rangle \\ &= \sum_{\Omega=-J}^J \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | nvJ\Omega\rangle \langle J\Omega | JM\rangle \end{aligned} \quad (15)$$

On applying $\mathcal{R}(\alpha, \beta, \gamma) \mathcal{R}^\dagger(\alpha, \beta, \gamma)$ to both sides one obtains

$$\begin{aligned} & \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | nvJM\rangle \\ &= \sum_{\Omega=-J}^J \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | \mathcal{R}(\alpha, \beta, \gamma) | nvJ\Omega\rangle \\ & \quad \times \langle J\Omega | \mathcal{R}^\dagger(\alpha, \beta, \gamma) | nvJM\rangle \\ &= \sum_{J=-\Omega}^J \langle \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N, \mathbf{r}' | nvJ\Omega\rangle D_{M\Omega}^{J*}(\alpha, \beta, \gamma) \end{aligned} \quad (16)$$

The Wigner D-function or rotation matrix element is defined by

$$D_{M\Omega}^J(\alpha, \beta, \gamma) \equiv \langle JM | \mathcal{R}(\alpha, \beta, \gamma) | J\Omega \rangle. \quad (17)$$

The internuclear vector \mathbf{r} has the spherical polar coordinates $r, \theta,$ and ϕ . The angles θ and ϕ specify the direction of the internuclear vector \mathbf{r} in the laboratory coordinate system. That is, θ and ϕ describe physical rotation of the two nuclei. It is well known that the parameters of coordinate rotation α and β describe rotations taken in the same directions about the same axes as the spherical polar coordinates ϕ and θ . See, *e.g.*, Edmonds [11], p. 6, or Zare [12], p. 77. After coordinate rotation, $r, \theta,$ and ϕ become $r', \theta',$ and ϕ' , but $r' = r$ because the internuclear distance is a scalar. The physical rotation ϕ and the coordinate rotation α are both counterclockwise rotations taken about the z axis. The coordinate rotation α gives a new value to the physical rotation,

$$\phi' = \phi - \alpha. \quad (18)$$

Similarly, the physical rotation θ and the parameter of coordinate rotation β are counterclockwise rotations taken about the same axis, the first intermediate y axis of the total coordinate rotation. After coordinate rotation,

$$\theta' = \theta - \beta. \quad (19)$$

Rewritten in terms of the spherical polar coordinates of internuclear vector, Eq. (16) reads

$$\begin{aligned} & \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | JM \rangle \\ &= \sum_{J=-\Omega}^J \langle \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r, \theta', \phi' | nvJ\Omega \rangle D_{M\Omega}^{J*}(\alpha, \beta, \gamma) \end{aligned} \quad (20)$$

We are at liberty to chose α and β to serve our purposes. The choices $\alpha = \phi$ and $\beta = \theta$ remove the θ' and ϕ' dependence from $\mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r, \theta', \phi' | nvJ\Omega \rangle$ and Eq. (20) becomes

$$\begin{aligned} & \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | JM \rangle \\ &= \sum_{J=-\Omega}^J \langle \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r | nvJ\Omega \rangle D_{M\Omega}^{J*}(\phi, \theta, \gamma). \end{aligned} \quad (21)$$

The angles ϕ and θ in the Wigner D-function $D_{M\Omega}^{J*}(\phi, \theta, \gamma)$ are physical rotations but the third angle γ remains a parameter of coordinate rotation. It turns out that there is a simple way to replace γ with χ where the latter is physical rotation of an electron about the internuclear axis. We arbitrarily select one of the electrons, say the one we arbitrarily called electron 1, and express its

rotated coordinate vector \mathbf{r}'_1 in terms of its rotated cylindrical coordinates $\rho', \chi',$ and ζ' . The physical rotation χ and the coordinate rotation γ are counterclockwise rotations about the z' axis, (*i.e.*, the internuclear axis). Thus, the coordinate rotation γ gives a new value to the physical rotation χ ,

$$\chi' = \chi - \gamma \quad (22)$$

We are again at liberty to choose the Euler angle to suit our purposes (simplification of the equations). The choice $\gamma = \chi$, along with the choices $\alpha = \phi$ and $\beta = \theta$, remove, with mathematical exactness, the three Euler angles $\phi', \theta',$ and χ' from the diatomic electronic-vibrational eigenfunction $\langle \rho, \zeta, \mathbf{r}'_2, \mathbf{r}'_3, \dots, \mathbf{r}'_N, r | nv \rangle$. Primes have been dropped from ρ and ζ because they, like the internuclear distance r , are scalars. The quantum numbers J and Ω have been dropped from $\langle \rho, \zeta, \mathbf{r}'_2, \mathbf{r}'_3, \dots, \mathbf{r}'_N, r | nv \rangle$ because it is not an eigenvector of the total angular momentum. The Euler angles ϕ, θ, χ are associated with rotational invariance (under coordinate rotation) and conservation of the total angular momentum of the diatomic molecule while simultaneously being three physical rotations of the diatomic molecules. In the present context the Wigner&Witmer diatomic eigenfunction, their Eq. (6), reads,

$$\begin{aligned} & \langle \rho, \chi, \zeta, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N, r, \theta, \phi | nvJM \rangle \\ &= \sum_{\Omega=-J}^J \langle \rho, \zeta, \mathbf{r}'_2, \mathbf{r}'_3, \dots, \mathbf{r}'_N, r | nv \rangle D_{M\Omega}^{J*}(\phi, \theta, \chi). \end{aligned} \quad (23)$$

The diatomic eigenfunction is exactly separated into the product two basis functions, the electronic-vibrational eigenfunction and the Wigner D-function.

Equation (23) was obtained without consideration of the diatomic Hamiltonian. The masses, charges, and spins of the electrons and nuclei were not mentioned above. They appear, of course, in the Hamiltonian. The Wigner-Witmer eigenfunction will not yield a detailed description of a specific molecule until it is operated on by the Hamiltonian for that molecule. The mathematical form of the Wigner-Witmer eigenfunction is largely determined by the symmetries of homogeneous time and space and isotropic space. Aside from the particulars that a diatomic molecule is composed of N electrons and two nuclei, the mathematical form of the Wigner-Witmer diatomic eigenfunction is solely determined by these fundamental symmetries. It rests on a reasonably sound theoretical foundation. The following sections are concerned with its practical value in diatomic spectroscopy.

The quantum numbers J , M , and Ω are total angular momentum quantum numbers. The isotropy of space ensures that all spins are included, but advantage of this cannot be taken until one constructs angular momentum coupling models describing how the various orbital and spin momentum interact to form the total.

4. DIATOMIC PARITY

Like translational and rotational symmetry, parity is a symmetry related to coordinate transformation. The parity operator \mathcal{P} changes the sign of each Cartesian spatial coordinate.

$$\begin{aligned} & \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{r} | \mathcal{P} | nJM \rangle \\ & = \langle -\mathbf{r}_1, -\mathbf{r}_2, \dots, -\mathbf{r}_N, -\mathbf{r} | nJM \rangle. \end{aligned} \quad (24)$$

Whereas translation and rotation are continuous, the parity operation, the topic of this section, and the exchange of identical particles, the topic of the following section, are discrete. A discrete symmetry is both unitary and Hermitian, and the only possible eigenvalues are ± 1 .

Because spin is not expressible in terms of spatial coordinates, spin is unaffected by symmetry operators that act on spatial coordinates. For example, the operator that exchanges two identical particles must incorporate a spin exchange operator because merely exchanging the particles' locations does not exchange their spins (see the following section).

Comparison of the matrix equation

$$\begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (25)$$

with the equation for coordinate rotation (13) shows that the parity operation is formally a rotation but with a fundamental difference. The determinate of the coordinate rotation matrix is +1, the mark of a so-called proper rotation while the determinate of the parity matrix is -1 marking it as an improper rotation. All physical rotations are proper. Physical rotation never produces an inversion of the signs of all cartesian coordinates. Whereas actual physical motions can duplicate coordinate translations in space and time and rotations in space, physical motion cannot duplicate the parity transformation.

Equation (24) serves to define the parity operator \mathcal{P} , but a version of \mathcal{P} that can operate on the right side of Wigner-Witmer equation (23) is needed. A relationship between angular momentum and parity is seen in the multipole expansion of an electromagnetic wave wherein each term corresponds to definite a value of angular momentum and a definite value of parity. The

intimate relationship between angular momentum and coordinate rotation, and the similarity between Eqs. (13) and (25) also suggest a relationship between coordinate rotation and parity. The parity operator cannot be constructed purely from coordinate rotation because the determinant of the rotation matrix (13) is +1 while the determinant of the parity matrix (25) is -1. However, because the determinant of the product of two square matrices is the product of the individual determinants, one can construct the parity operator as the product of an improper rotation and a proper rotation. That is, the diatomic parity operator can be constructed as the product of two operators, one an improper rotation which inverts the signs of some of the cartesian coordinates while a second proper rotation inverts the sign of the remaining cartesian coordinates.

Table I shows three different discrete but proper rotations $\mathcal{P}_{\alpha\beta\gamma}$ that change the signs of two of the three components of a rotated spatial vector $\mathbf{r}'(x', y', z')$. The full parity operator can be constructed from one of the operators $\mathcal{P}_{\alpha\beta\gamma}$ from Table I and the improper operator \mathcal{P}_Σ whose function is to invert the sign of that coordinate whose sign is not inverted by $\mathcal{P}_{\alpha\beta\gamma}$,

$$\mathcal{P} = \mathcal{P}_\Sigma \mathcal{P}_{\alpha\beta\gamma}. \quad (26)$$

Table I - The sign changes on the components x' , y' and z' of a coordinate vector $\mathbf{r}'(x', y', z')$ produced by three different discrete Euler angle transformations, and the effect of these Euler angle transformations on $D_{M\Omega}^J(\alpha, \beta, \gamma)$

Group notation	Euler angle transform.	Coordinate transform.	Effect on $D_{M\Omega}^J(\alpha, \beta, \gamma)$
$C_2(x')$	$\alpha \rightarrow \pi + \alpha$	$x' \rightarrow x'$	$(-)^{J+2M} D_{M,-\Omega}^J(\alpha, \beta, \gamma)$
	$\beta \rightarrow \pi - \beta$	$y' \rightarrow -y'$	
	$\gamma \rightarrow -\gamma$	$z' \rightarrow -z'$	
$C_2(y')$	$\alpha \rightarrow \pi + \alpha$	$x' \rightarrow -x'$	$(-)^{J-\Omega} D_{M,-\Omega}^J(\alpha, \beta, \gamma)$
	$\beta \rightarrow \pi - \beta$	$y' \rightarrow y'$	
	$\gamma \rightarrow \pi - \gamma$	$z' \rightarrow -z'$	
$C_2(z')$	$\alpha \rightarrow \alpha$	$x' \rightarrow -x'$	$(-)^{-\Omega} D_{M,-\Omega}^J(\alpha, \beta, \gamma)$
	$\beta \rightarrow \beta$	$y' \rightarrow -y'$	
	$\gamma \rightarrow \pi + \gamma$	$z' \rightarrow z'$	

The first entry in Table I is chosen because in this case the effect of $\mathcal{P}_{\alpha\beta\gamma}$ is independent of Ω . Thus, $\mathcal{P}_{\alpha\beta\gamma}$ inverts the signs of y' and z' components of rotated spatial vectors which in turn means that \mathcal{P}_Σ must invert the x' components of rotated spatial vectors in order that the product $\mathcal{P}_\Sigma \mathcal{P}_{\alpha\beta\gamma}$ invert all three components of each rotated spatial vector. Application of the operator \mathcal{P}_Σ to the Wigner-Witmer eigenfunction gives

$$\begin{aligned}
 & \langle \rho, \chi, \zeta, \mathbf{r}_2, \dots, \mathbf{r}_N, r, \theta, \phi | \mathcal{P}_\Sigma | n\nu JM \rangle \\
 &= \sum_{J=-\Omega}^J \langle \rho, \zeta, -x'_2, y'_2, z'_2, \dots, -x'_N, y'_N, z'_N, r | nJM \rangle \\
 & \quad \times D_{M\Omega}^{J*}(\phi, \theta, \chi) \\
 &= p_\Sigma \sum_{J=-\Omega}^J \langle \rho, \zeta, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r | nJM \rangle D_{M\Omega}^{J*}(\phi, \theta, \chi) \quad (27)
 \end{aligned}$$

where p_Σ is the eigenvalue of \mathcal{P}_Σ . Application of $\mathcal{P}_{\alpha\beta\gamma}$ to the Wigner-Witmer eigenfunction gives

$$\begin{aligned}
 & \langle \rho, \chi, \zeta, \mathbf{r}_2, \dots, \mathbf{r}_N, r, \theta, \phi | \mathcal{P}_{\alpha\beta\gamma} | n\nu JM \rangle \\
 &= \sum_{J=-\Omega}^J \langle \rho, -\zeta, x_2, -y'_2, -z'_2, \dots, x'_N, -y'_N, -z'_N, r | nJM \rangle \\
 & \quad \times D_{M,-\Omega}^{J*}(\phi, \theta, \chi) \\
 &= p_{\alpha,\beta,\gamma} \sum_{J=-\Omega}^J \langle \rho, \zeta, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r | nJM \rangle D_{M\Omega}^{J*}(\phi, \theta, \chi). \quad (28)
 \end{aligned}$$

The eigenvalue $p_{\alpha\beta\gamma}$ is taken from Table I,

$$p_{\alpha\beta\gamma} = (-)^{J-2M} \quad (29)$$

The minus sign on Ω in $D_{M,-\Omega}^{J*}(\phi, \theta, \chi)$ was dropped because changing the sign of Ω only changes the order in which the sum in Eq. (28) is formed. The only possible eigenvalues for the Hermitian parity operator \mathcal{P} are ± 1 , but the operator $\mathcal{P}_{\alpha\beta\gamma}$ is clearly not Hermitian because its eigenvalue $p_{\alpha\beta\gamma}$ is not real when J is half-integer,

$$\mathcal{P}_{\alpha\beta\gamma} D_{M\Omega}^{J*}(\phi, \theta, \chi) = (-)^{J+2M} D_{M,-\Omega}^{J*}(\phi, \theta, \chi) \quad (30a)$$

$$= p_{\alpha\beta\gamma} D_{M,-\Omega}^{J*}(\phi, \theta, \chi) \quad (30b)$$

$$= \pm D_{M,-\Omega}^{J*}(\phi, \theta, \chi) \quad J \text{ integer} \quad (30c)$$

$$= \mp i D_{M,-\Omega}^{J*}(\phi, \theta, \chi) \quad J \text{ half - integer.} \quad (30d)$$

The factor $(-)^{2M}$ is always $+1$ for integer J and always -1 for half-integer J . This explains why the \pm in Eq. (30c) is replaced by \mp in Eq. (30d). If the eigenvalue $p_{\alpha\beta\gamma}$ is purely imaginary for half-integer J , then the eigenvalue p_Σ of the operator \mathcal{P}_Σ must also equal $\pm i$ for half-integer J to ensure that the product of eigenvalues $p_\Sigma p_{\alpha\beta\gamma}$ is real. In summary, the diatomic parity operator \mathcal{P} is the product of two operators \mathcal{P}_Σ and $\mathcal{P}_{\alpha\beta\gamma}$. The eigenvalue of \mathcal{P} is, of course, ± 1 , and the product of eigenvalues $p_\Sigma p_{\alpha\beta\gamma}$,

$$p = p_\Sigma (-)^{J+2M} \quad (31)$$

is always ± 1 as required, but for half-integer J the individual eigenvalues p_Σ and $p_{\alpha\beta\gamma}$ are purely imaginary.

A widely accepted convention allows one to treat the parity eigenvalues p_Σ and $p_{\alpha\beta\gamma}$ as real for both integer and half-integer J [13]. If one agrees to always subtract $1/2$ from half-integer values of J , then the diatomic parity can be written as

$$p = p_\Sigma (-)^J \quad J \text{ integer} \quad (32a)$$

$$= -p_\Sigma (-)^{J-\frac{1}{2}} \quad J \text{ half - integer.} \quad (32b)$$

in which $p_\Sigma = \pm 1$ is always real.

Parity is a member of the complete set of commuting observables (CSCO). If a matrix representation of the Hamiltonian can be computed in a complete basis, and the matrix representation of parity is known in this same basis, then the matrix that diagonalizes the Hamiltonian must also diagonalize the matrix representation of parity. This is the physical basis of an algorithm for computing diatomic parity during the process of fitting term differences from model upper and lower Hamiltonian matrices to experimentally recorded wavenumbers.

5. EXCHANGE SYMMETRY OF IDENTICAL NUCLEI

In previous sections of this article, the symbols J , M , and Ω refer to the true total angular momentum including all orbital and spin momenta. In this section spectroscopic nomenclature is more closely followed. Nuclear spin is excluded from J , M , and Ω , and the total angular momentum quantum numbers are F , M_F , and Ω_F . Many spectra of homonuclear diatomic molecules are recorded with spectral resolution too low to reveal hyperfine structure but the spectra nevertheless reveal an influence of nuclear spin on spectral line intensity. This common circumstance is the topic of this section.

Exchange symmetry, like parity, is a discrete transformation. Thus, the operator \mathcal{E}_{ab} that exchanges two identical nuclei arbitrarily labeled a and b – unrelated to Hund's cases (a) and (b) – is both unitary and Hermitian, and its only eigenvalues e_{ab} are ± 1 . However, the parity and exchange operators differ in important ways. Whereas physical motion cannot accomplish the parity operation, physical motion can exchange nucleus a and nucleus b . Also, the parity operator \mathcal{P} has no effect on spin, but the exchange operator does exchange the spins. Replacing the location of each nucleus with that of the other does not swap their spins. Construction of \mathcal{E}_{ab} requires an operator to exchange the spatial nuclear coordinate vectors and an operator to exchange their spins.

For two identical particles whose locations are given in a coordinate system whose origin lies at the center of mass of the two particles, the parity operator replaces the coordinates of each with those of the other. If an operator \mathcal{P}_{ab} that exchanges the spatial coordinates of the identical nuclei a and b can be found, then the exchange operator \mathcal{E}_{ab} can be expressed as the product $\mathcal{P}_{ab} \mathcal{J}_{ab}$,

$$\mathcal{E}_{ab} = \mathcal{P}_{ab} \mathcal{J}_{ab}, \quad (33)$$

in which \mathcal{J}_{ab} is the operator that exchanges the identical nuclear spins I_a and I_b . The operator \mathcal{P}_{ab} can be built from the total parity operator \mathcal{P} and yet another parity operator \mathcal{P}_{gu} that acts only on electronic coordinates and serves to undo what \mathcal{P} has done to the electronic coordinates,

$$\mathcal{P}_{ab} = \mathcal{P} \mathcal{P}_{gu}. \quad (34)$$

Note that our use of the letter \mathcal{P} in the symbol \mathcal{P}_{ab} might lead one to think \mathcal{P}_{ab} is a parity operator. Because \mathcal{P}_{ab} is the product to two parity operators (*i.e.*, the product of two improper rotations) \mathcal{P}_{ab} is itself a proper rotation, not a parity operator. One can call \mathcal{P}_{ab} a coordinate exchange operator. The operator \mathcal{E}_{ab} for the exchange of two identical nuclei (33) is then the product of the coordinate exchange operator \mathcal{P}_{ab} and the spin exchange operator \mathcal{J}_{ab} .

Using (26) for the total parity operator \mathcal{P} , one arrives at the following equations for the exchange operator \mathcal{E}_{ab} ,

$$\mathcal{E}_{ab} = \mathcal{P} \mathcal{P}_{gu} \mathcal{J}_{ab} \quad (35a)$$

$$= \mathcal{P}_{\Sigma} \mathcal{P}_{\alpha\beta\gamma} \mathcal{P}_{gu} \mathcal{J}_{ab}. \quad (35b)$$

and its eigenvalue e_{ab} ,

$$e_{ab} = p_{\Sigma} (-)^J p_{gu} i_{ab} \quad \text{J integer} \quad (36a)$$

$$= -p_{\Sigma} (-)^{J-\frac{1}{2}} p_{gu} i_{ab} \quad \text{J half - integer} \quad (36b)$$

$$= p p_{gu} i_{ab}, \quad (36c)$$

in terms of p_{gu} , the eigenvalue of \mathcal{P}_{gu} , and i_{ab} , the eigenvalue of \mathcal{J}_{ab} .

The Clebsch-Gordan combination of the two angular states $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$,

$$|jm\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 m_1\rangle |j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | jm\rangle \quad (37)$$

is physically correct only when $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ are independent (*i.e.*, do not interact). The magnetic moment of a nucleus is so small that

construction of total nuclear spin states $|TM_T\rangle$ states from nuclear spin states $|I_a M_a\rangle$ and $|I_b M_b\rangle$ of the nuclei is justified. The total nuclear spin is given by

$$\mathbf{T} = \mathbf{I}_a + \mathbf{I}_b, \quad (38)$$

and the combination of $|I_a M_a\rangle$ and $|I_b M_b\rangle$ states by

$$\begin{aligned} |TM_T\rangle &= \sum_{M_a=-I_a}^{I_a} \sum_{M_b=-I_b}^{I_b} |I_a M_a\rangle |I_b M_b\rangle \langle I_a M_a I_b M_b | TM_T\rangle. \end{aligned} \quad (39)$$

The interaction between $|JM\rangle$ and $|TM_T\rangle$ is also very small. The total angular momentum \mathbf{F} is given by

$$\mathbf{F} = \mathbf{J} + \mathbf{T} \quad (40)$$

and the total angular momentum states $|FM_F\rangle$ by

$$\begin{aligned} |FM_F\rangle &= \sum_{M=-J}^J \sum_{M_T=-T}^T |JM\rangle |TM_T\rangle \langle JMTM_T | FM_F\rangle. \end{aligned} \quad (41)$$

A nuclear-spin dependent version of the diatomic eigenfunction can now be written,

$$\begin{aligned} &\langle \rho, \chi, \zeta, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N, r, \theta, \phi | nvFM_F\rangle \\ &\approx \sum_{M=-J}^J \sum_{\Omega=-J}^J \langle \rho, \zeta, \mathbf{r}'_2, \mathbf{r}'_3, \dots, \mathbf{r}'_N, r | nv\rangle D_{M\Omega}^{J*}(\phi, \theta, \chi) \\ &\quad \times \sum_{M_T=-T}^T \sum_{M_a=-I_a}^{I_a} \sum_{M_b=-I_b}^{I_b} |I_a M_a\rangle |I_b M_b\rangle \\ &\quad \quad \quad \times \langle I_a M_a I_b M_b | TM_T\rangle. \end{aligned} \quad (42)$$

The right side now has something on which the nuclear spin exchange operator \mathcal{J}_{ab} can operate. The nuclear exchange symmetry of a given homonuclear diatomic molecule is fixed. Depending upon whether $I = I_a = I_b$ is integer or half-integer all states will be symmetric – $e_{ab} = +1$ – or antisymmetric – $e_{ab} = -1$ – but for states of a given exchange symmetry, some will have positive (even) total parity – $p = +1$ – while others will have negative (odd) total parity – $p = -1$. One determines the influence of nuclear spin on the spectrum of a homonuclear diatomic molecule by counting the number of positive parity states g_+ and the number of negative parity states g_- . In a spectrum recorded with a resolution inadequate to show hyperfine structure, for practical purposes the nuclear spin

states are degenerate and the number of even parity states g_+ and number of odd parity states g_- can be viewed as statistical weights. The eigenvalues i_{ab} of the nuclear spin exchange operator J_{ab} ,

$$J_{ab}|TM_T\rangle = i_{ab}|TM_T\rangle \quad (43)$$

$$= (-)^{2I-T} \quad (44)$$

come from a symmetry of the Clebsch-Gordan coefficients,

$$\langle j_2 m_2 j_1 m_1 | jm \rangle = (-)^{j_1+j_2-j} \langle j_1 m_1 j_2 m_2 | jm \rangle. \quad (45)$$

for the case $j_1 = j_2$. Using the above equations one can express the parity eigenvalue for a homonuclear diatomic molecule as

$$p = \frac{e_{ab}}{p_{gu} i_{ab}}. \quad (46)$$

The eigenvalue e_{ab} is fixed for a given molecule, and the eigenvalue p_{gu} is fixed for a given electronic state of that molecule. Thus, the total parity p for a given molecule in a given electronic state is controlled by the eigenvalue of the nuclear spin exchange operator i_{ab} . Determination of the nuclear spin statistical weights consists of counting the number of states for which $i_{ab} = (-)^{2I-T}$ is positive and the number of states for which i_{ab} is negative. By counting the number of positive and negative states for various values of I , one can deduce

$$\left. \begin{aligned} g_+ &= (2I + 1)(I + 1) \\ g_- &= (2I + 1)I \end{aligned} \right\} \text{I integer}, \quad (47)$$

$$\left. \begin{aligned} g_+ &= (2I + 1)I \\ g_- &= (2I + 1)(I + 1) \end{aligned} \right\} \text{I half - integer}, \quad (48)$$

and further deduce that the ratio of statistical weights is given by

$$\frac{g_+}{g_-} = \frac{I + 1}{I}. \quad (49)$$

can produce an alternation of intensity with increasing J in diatomic spectra. Figures 1 and 2 give examples of intensity alternation for resolved Λ -doublets. A surprise that has come from using the Wigner-Witmer diatomic eigenfunction is the observation that the \mathcal{P}_Σ parity operator, seen in in Eq. (26) to be a component of the total diatomic parity operator, is applicable to all electronic types of electronic states, not just Σ states for which $\Lambda = 0$.

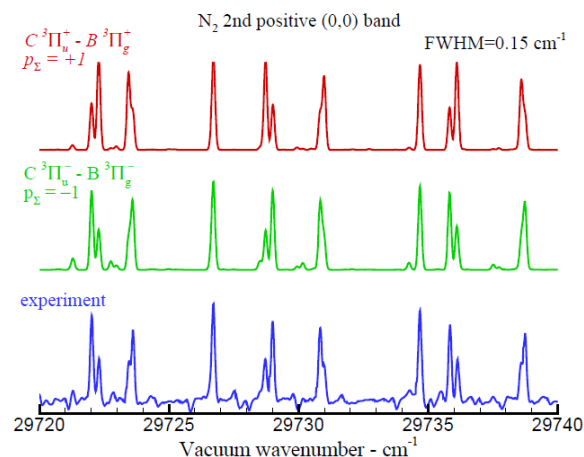


Figure 1: A comparison between an experimental spectrum [14] of $^{14}\text{N}_2$ $C^3\Pi_u^- - B^3\Pi_g^-$ and two synthetic spectra, one computed using $p_\Sigma = 1$ and the other computed using $p_\Sigma = -1$. The Λ doublets are partially resolved. p_Σ is the eigenvalue of the parity operator \mathcal{P}_Σ that changes the sign of one cartesian component of each molecule fixed electronic coordinate vector.

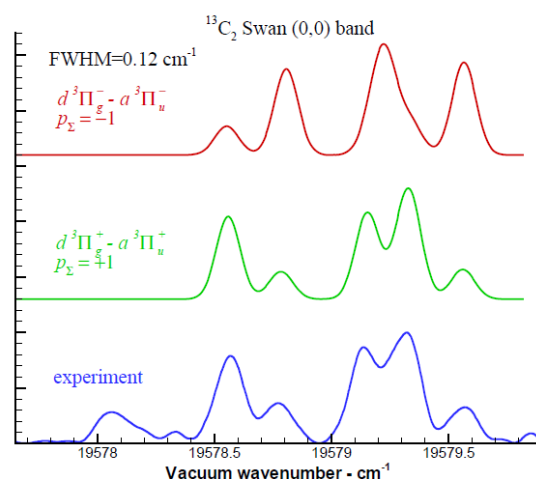


Figure 2: Two synthetic $^{13}\text{C}_2$ $d^3\Pi_g^- - a^3\Pi_u^-$ spectra compared with an experimental spectrum recorded by Amiot [15]. The comparison indicates the eigenvalue of the parity eigenvalue p_Σ is +1.

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