Renner–Teller and Spin–Orbit Interactions between the $\tilde{A}^2A_1$ and the $\tilde{X}^2B_1$ States of NH$_2$: The Stretch-Bender Approach

Alexander Alijah* and Geoffrey Duxbury†

*Fakultät für Chemie, Universität Bielefeld, 33615 Bielefeld, Germany; †Department of Physics and Applied Physics, University of Strathclyde, Glasgow G4 0NG, Scotland, United Kingdom

Received May 7, 2001; in revised form October 29, 2001

The stretch-bender model, developed originally to describe the effects of stretch–bend interactions and Renner–Teller coupling in symmetrical triatomic molecules, has been extended to incorporate the effects of spin–orbit interaction and of overall rotation. A comparison is made between the treatment of spin–orbit interaction and of overall rotation in our model and in the MORBID approach of P. Jensen, M. Brumm, W. P. Kraemer, and P. R. Bunker (J. Mol. Spectrosc. 171, 31–57 (1995)). © 2002 Elsevier Science

Key Words: Renner–Teller; stretch-bender; electronic angular momentum; spin–orbit interaction; NH$_2$.

1. INTRODUCTION

In two previous papers (1, 2) we have described in detail the development of the stretch–bender theory for calculating the large amplitude motion and Renner–Teller coupling in symmetrical triatomic molecules. The theoretical model was then used to obtain an understanding of the effects of orbital angular momentum and vibrational resonances on the vibronic pattern of the coupled $b^1B_1$ and $\tilde{a}^1A_1$ states of singlet methylene, CH$_2$. In the present paper we extend the method to include the effects of spin–orbit coupling and overall rotation, choosing the energy level pattern of the $\tilde{A}^2A_1$ and $\tilde{X}^2B_1$ states of NH$_2$ as an example.

The NH$_2$ free radical is a particularly useful test bed for models of Renner–Teller interaction, as there exist a wealth of experimental data derived from the spectra of NH$_2$ and its isotopic modifications; see, for example, Refs. (3, 4). We have chosen to develop this theme in three phases. The present paper describes the extensions of the stretch–bender model which are necessary to incorporate the effects of spin–orbit interaction and overall rotation. The following paper describes the applications of the theory to the calculation of the structure of the rovibrational structure of the $\tilde{X}^2B_1$ state of NH$_2$ up to the barrier to linearity in the ground state. A final paper deals with the complex interactions between the $\tilde{A}^2A_1$ and $\tilde{X}^2B_1$ states which occur above the barrier to linearity of the $\tilde{X}^2B_1$ state.

2. HAMILTONIAN AND BASIS FUNCTIONS

The vibration–rotation problem in triatomic molecules in which large amplitude bending motion is occurring may be treated from the standpoint of a linear or bent molecule description. Many of the current treatments of this behavior stem from the pioneering work of Hougen et al. (5) (HBJ). They introduced the concept of a reference configuration in which large amplitude angular motion is possible, but in which the bond lengths are fixed at their equilibrium value. This is often known as the “rigid-bender” model. The stretching motion is then taken to produce small amplitude displacements from the reference frame. This contrasts with the conventional model in which rectilinear bending and stretching displacements are considered with respect to a rectilinear co-ordinate system. The stretch-bender (STRB) model which we have introduced (1) may be regarded as a development of the HBJ model (5). In the stretch–bender the bonds are allowed to stretch in such a way that, as the molecule bends, the molecule follows a “reaction type path” along the minimum of the potential energy surface defined by bending and the symmetric stretching motion. From the above it can be seen that in the standard rectilinear treatment the vibration–rotation Hamiltonian is partitioned into a three-dimensional stretching problem and an asymmetric rotor. Rotation about the nearly linear axis, $a$ (or $z$), is treated in the symmetric rotor part of the calculation, with the appropriate rotation constant being labeled $A$.

However, in the rigid-bender or stretch-bender the partitioning is into a four-dimensional vibrational Hamiltonian and a two-dimensional rotational part, akin to the treatment of a linear molecule. The “$a$-axis rotation” may then be thought of as part of a two-dimensional anharmonic bending oscillator, in which case it can be considered as part of the $g$-matrix, $g_{\phi\phi}$. As a result there is an ambiguity of the labelling of the “$a$-axis rotation” term, depending upon which standpoint has been adopted. In our original description of the STRB model we concentrated principally on the effects of stretch–bend interaction in the vibronic part of the coupling in triatomic molecules. This was exemplified by the form of the kinetic energy operator in the

1 Present address: Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal.
stretch–bend part of the Hamiltonian, which was derived to be
\[
T = -\frac{\hbar^2}{2} \left[ -g^{\rho \rho} f(\rho) + g^{\rho \rho} \frac{\partial^2}{\partial \rho^2} + g^{ss} \frac{\partial^2}{\partial S_s^2} + g^{aa} \frac{\partial^2}{\partial S_a^2} + g^{\phi \rho} \frac{\partial^2}{\partial \phi^2} \right],
\]
where
\[
f(\rho) = g^{-\frac{1}{2}} g^{\rho \rho} - \frac{1}{2} \frac{\partial^2}{\partial \rho^2} g^{\rho \rho} f(\rho)^2.
\]
and \(g^{ss}, g^{aa}, g^{\rho \rho},\) and \(g^{\phi \rho}\) are defined in Table 1. In the present paper we wish to consider overall rotation so that, in the absence of vibronic coupling, the complete vibration–rotation Hamiltonian may be written as
\[
\hat{H}_{vr} = \hat{H}_{strb} + \hat{H}_{rot}^{h,c}. \tag{3}
\]

In order to make a parallel with the small-amplitude treatment of vibration–rotation, and also to facilitate the introduction of electronic angular momentum coupling, we wish to rewrite the \(a\)-axis rotation term in terms of an \(A\) “rotation constant” rather than the \(g^{\phi \phi}\) \(g\)-matrix element. Our starting point is therefore
\[
\hat{H}_{strb} = -\frac{\hbar^2}{2} \left[ -g^{\rho \rho} f(\rho) + g^{\rho \rho} \frac{\partial^2}{\partial \rho^2} + g^{ss} \frac{\partial^2}{\partial S_s^2} + g^{aa} \frac{\partial^2}{\partial S_a^2} \right]
\]
\[+ A' \hat{J}_a^2 + V(\rho, S_s, S_a). \tag{4}\]
with
\[A' = \frac{1}{2} g^{\phi \rho} \tag{5}\]
and
\[
\hat{H}_{rot}^{h,c} = B' \hat{J}_b^2 + C' \hat{J}_c^2. \tag{6}
\]

In our method, the “rotational constants” are expressed, like the \(g\)-functions, in terms of the bending coordinate, \(\rho\), and the bond length, \(r^0\), which is itself assumed to be a function of \(\rho\). The particular ways in which this bond length variation could be derived were described in detail by Duxbury et al. (1, 2). It should be noted that the operators appearing in Eqs. [4] and [6] are different for any two electronic states, e.g., a Renner–Teller pair, since the variation of \(r^0\) with bending coordinate depends

<p>| Table 1 |
|----------------------------------------|--------|-------------------|------------------|
| The Angle-Dependent Functions for the Angle-Dependent (g) Values, (g^{\alpha \alpha}), Which Are Used in the Stretch-Bender (STRB) Model of a Symmetrical Triatomic Molecule (I) |</p>
<table>
<thead>
<tr>
<th>Effective rotational constant(^a)</th>
<th>Angular dependent (g) values( ^b ) ((g^{\alpha \alpha}))</th>
<th>Inverse moments of inertia( ^c ) ((\mu_{\alpha \alpha}))</th>
<th>Angle dependent function( ^d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric stretching vibration</td>
<td>(g^{ss})</td>
<td>(\mu_{ss})</td>
<td>(\frac{1}{2m}R_{g(ss)}(\rho))</td>
</tr>
<tr>
<td>Anti-symmetric stretching vibration</td>
<td>(g^{aa})</td>
<td>(\mu_{aa})</td>
<td>(\frac{1}{2m}R_{g(aa)}(\rho))</td>
</tr>
<tr>
<td>Bending</td>
<td>(g^{\rho \rho})</td>
<td>(\mu_{\rho \rho})</td>
<td>(\frac{2a}{m r^3} R_{g(\rho \rho)}(\rho))</td>
</tr>
<tr>
<td>Effective a-axis rotation constant</td>
<td>(\frac{2a}{m} A(\rho))</td>
<td>(g^{\phi \rho})</td>
<td>(\mu_{\phi \rho})</td>
</tr>
<tr>
<td>Effective b-axis rotation constant</td>
<td>(\frac{2a}{m} B(\rho))</td>
<td>(g^{\phi \rho})</td>
<td>(\mu_{\phi \rho})</td>
</tr>
<tr>
<td>Effective c-axis rotation constant</td>
<td>(\frac{2a}{m} C(\rho))</td>
<td>(g^{\phi \phi})</td>
<td>(\mu_{\phi \phi})</td>
</tr>
<tr>
<td>Coriolis correction to c-axis constant</td>
<td>(\frac{2a}{m} \Delta C(\rho))</td>
<td>(g^{\phi \rho})</td>
<td>(\mu_{\phi \rho})</td>
</tr>
</tbody>
</table>

\(^a\) Refs. (8–12).
\(^b\) Ref. (J).
\(^c\) Refs. (5–7).
\(^d\) \(g^{ss}\) to \(g^{\phi \phi}\) from Ref. (J).
\(^e\) The Coriolis correction term needed to calculate the vibrational dependence of \(C(\rho)\) has been given previously by BDD (8). Its present form is that derived originally by Hoy and Bunker (J) and in its present form from Jensen et al. (7).

© 2002 Elsevier Science
TABLE 2

| Auxiliary Functions Used in Table 1: The $R_i$ Are Needed to Convert from the Instantaneous to the Reference Frame and Are Used in the Definitions of the $g^{\text{nucl}}$ and the Angle-Dependent Force Constants |
|-----------------|-----------------|-----------------|
| $R_v(r, \rho)$  | $[\cos^2(\xi) + p \sin^2(\xi)] - 2\frac{\partial}{\partial \rho}(p - 1) \sin(\xi) \cos(\xi)$ | $R_v(r, \rho)$  |
| $R_v(r, \rho)$  | $[\sin^2(\xi) + p \cos^2(\xi)] + \frac{\partial}{\partial \rho}(p - 1) \sin(\xi) \cos(\xi)$ | $R_v(r, \rho)$  |
| $R_v(r, \rho)$  | $[\cos^2(\xi) + p \sin^2(\xi)] - 2\frac{\partial}{\partial \rho}(p - 1) \sin(\xi) \cos(\xi)$ | $4\frac{\partial^2}{\partial \rho^2}(p - 1) \sin(\xi) \cos(\xi)$ |
| $R_v(r, \rho)$  | $[\sin^2(\xi) + p \cos^2(\xi)] + \frac{\partial}{\partial \rho}(p - 1) \sin(\xi) \cos(\xi)$ | $4\frac{\partial^2}{\partial \rho^2}(p - 1) \sin(\xi) \cos(\xi)$ |
| $a_{\rho}^{\text{nucl}}$ | $\frac{\rho}{2\sqrt{2}} [1 + p \cos^2(\xi) + \sin^2(\xi)] (\sin^2\xi - \cos^2\xi)^{-1/2}$ | $a_{\rho}^{\text{nucl}}$ |

**Note:** $r^{\prime\prime} = \partial r^{\prime}(\rho)/\partial \rho$ and $p = 1 + 2m_1/m_2$. The analytical form of $a_{\rho}^{\prime\prime}$ has been derived from the formulae given by Jensen et al. (7).

To simplify the notation we omitted the label specifying the potential energy surface of a particular electronic state. To simplify the notation we omitted the label specifying the electronic state. A comparison of the notation used in our present and previous papers, and those in the papers following on from the HBJ approach, in particular from Bunker and Jensen and their colleagues (6, 7), is given in Table 1. In the present paper we have tried to present a unified notation, which follows closely that which we introduced in paper (1). The functions of angle and bond length, which are necessary, are collected in Table 2, along with the new functions required when overall rotation is being considered.

In closed shell molecules the total angular momentum and that of the nuclear frame are identical. However, in open shell molecules, with unpaired electron orbital ($\tilde{L}$) and electron spin ($\tilde{S}$) angular momentum, it is convenient to follow Hougou (14) in introducing $\tilde{R}$ as a vector operator for the rotation of the nuclear frame only, so that $\tilde{R}_a$, $\tilde{R}_b$, and $\tilde{R}_c$ are the operators for the internal projections of

$$\tilde{R} = \tilde{J} - \tilde{L} - \tilde{S}. \quad [7]$$

Hence in open shell molecules we have

$$\hat{H}_{\text{e}} = \hat{H}_{\text{str}} + \hat{H}_{\text{rot}} + \hat{H}_{\text{so}}, \quad [8]$$

where $\hat{H}_{\text{str}}$ and $\hat{H}_{\text{rot}}$ are given by Eqs. [4] and [6], in which $J$ is replaced by $R$, and the spin–orbit coupling operator, $\hat{H}_{\text{so}}$, is given by

$$\hat{H}_{\text{so}} = A_{\text{so}} \tilde{L}_a \tilde{S}_a. \quad [9]$$

Note that in all the above the dimensions of the Hamiltonian operators are those of energy. It is often convenient to work in units of cm$^{-1}$, which is achieved by dividing each of these operators by $hc$. The notation which we use is

$$A(\rho) = \frac{\hbar^2 A'(\rho)}{hc}, \quad B(\rho) = \frac{\hbar^2 B'(\rho)}{hc}, \quad C(\rho) = \frac{\hbar^2 C'(\rho)}{hc}; \quad [10]$$

i.e., the “primed” rotational constants are those in energy units, while the “unprimed” are in units of cm$^{-1}$. The analytical forms of these functions have been given in Table 1.

The effective Hamiltonian for spin–orbit interaction is derived by a route different from that for vibration and rotation of the nuclear frame, as $H_{\text{so}}$ is related to a microscopic Hamiltonian via the Wigner–Eckart theorem. As a result the spin–orbit coupling constant, $A_{\text{so}}$, is often given in cm$^{-1}$, with the appropriate multiplication factor to ensure that the dimensions of the Hamiltonian operators remain those of energy; i.e.,

$$A_{\text{so}}(\rho) = \frac{\hbar^2 A'_{\text{so}}(\rho)}{hc} \quad [11]$$

Owing to some differences in the approaches to treating spin–orbit interaction in triatomic molecules, the coordinate dependence of this interaction will be discussed in more detail later in this paper.

Following the adiabatic method of separating nuclear and electronic coordinates, the total wave function is expanded in terms of electronic functions $\psi_{\text{el}}^{(i)}$ that depend parametrically on the nuclear coordinates and the wavefunctions for nuclear motion, $\psi_{\text{nucl}}^{(i)}$,

$$\psi = \sum_i \psi_{\text{nucl}}^{(i)} \psi_{\text{el}}^{(i)}, \quad [12]$$

where $i = (\Sigma, |\Lambda|, \Gamma)$ represents the electronic and electron spin quantum numbers, with $\Sigma$ and $\Lambda$ the quantum numbers for the $\alpha$-axis projections of $\tilde{S}$ and $\tilde{L}$, respectively, for $R = 0$, and $\Gamma$ a symmetry index. The nuclear wave function corresponding to the electronic state $i$ is a product of bending, stretching, and rotational functions,

$$\psi_{\text{nucl}}^{(i)} = \Phi_{\nu_1 \nu_2 \Sigma \Sigma}^{\text{nucl}}(\rho) \chi_{\nu_1}^{\text{nucl}}(S_{\nu_1}; \rho) \chi_{\nu_2}^{\text{nucl}}(S_{\nu_2}; \rho) D_{\nu_1 \nu_2}^{\Sigma \Sigma}(\theta, \chi, \varphi). \quad [13]$$

While the bending functions $\Phi_{\nu_1 \nu_2 \Sigma \Sigma}^{\text{nucl}}(\rho)$ are obtained numerically for each set of quantum numbers $\nu_1, \nu_2, k, \Sigma$, the stretching functions are approximated by either harmonic oscillator or Morse functions that depend parametrically on the bending co-ordinate $\rho^{(1)}$. $D_{\nu_1 \nu_2}^{\Sigma \Sigma}(\theta, \chi, \varphi)$ are the Wigner rotational functions, with $(\theta, \chi, \varphi)$ the Euler angles describing the orientation of the molecular frame in the laboratory axis system. The $\alpha$-axis rotational part of $D_{\nu_1 \nu_2}^{\Sigma \Sigma}(\theta, \chi, \varphi)$ is $(2\pi)^{-1/2} e^{i\alpha\varphi}$. Our
electronic basis functions are
\[ \Psi_{el}^{(\Sigma, |\Lambda| \pm \pm)} = f^{(|\Lambda| \pm \pm)}(\varphi - v) \phi^{(|\Lambda|)}(r_1 \ldots r_{3n-1}; \rho, S_a, S_b)|\Sigma\rangle. \]  \[ 14 \]

\((\varphi - v)\) is the electronic azimuthal angle with respect to the molecular plane, and \(r_1, \ldots, r_{3n-1}\) are the remaining electronic coordinates. In the linear molecule limit the functions \(f^{(|\Lambda| \pm \pm)}(\varphi - v)\) take the analytical form
\[ f^{(|\Lambda| \pm \pm)}(\varphi - v) = \frac{1}{2\sqrt{\pi}} \left( e^{i|\Lambda|(\varphi - v)} \pm e^{-i|\Lambda|(\varphi - v)} \right). \]  \[ 15 \]

If there is no electronic angular momentum, \(\Lambda = 0\), the only allowable function is
\[ f^{(0)} = \frac{1}{\sqrt{2\pi}}. \]

In the next two sections we will derive the matrix elements of \(\hat{H}_{strb} + \hat{H}_{so}\) and \(\hat{H}_{rot}\) before integration over the bending coordinate; i.e., we will derive effective bending operators. In Section 5 we will then evaluate the matrix elements of these operators between the bending functions and discuss the structure of the final interaction matrix of the Hamiltonian \(\hat{H}_{evr}\), Eq. [8]. Diagonalizing this matrix we obtain the eigenvalues and eigenfunctions of \(\hat{H}_{evr}\).

3. THE EFFECTIVE STRETCH–BEND AND SPIN–ORBIT COUPLING OPERATORS

First of all let us consider the \(a\)-axis rotation term of \(\hat{H}_{strb}\), \(\hat{H}_{rot}^a = A' \hat{R}_a^2\) and the spin–orbit operator, \(\hat{H}_{so}\). The \(a\)-axis rotation operator can be written as
\[ \hat{R}_a = A'(\hat{N}_a - \hat{L}_a)^2 = A'(\hat{N}_a - \hat{L}_a)^2 \]  \[ 16 \]

with
\[ \hat{N}_a = -i \hbar \frac{\partial}{\partial \varphi}; \quad \hat{L}_a = -i \hbar \frac{\partial}{\partial (\varphi - v)}. \]  \[ 17 \]

Since
\[ \hat{L}_a \Psi_{el}^{(\Sigma, |\Lambda| \pm \pm)} = \hbar |\Lambda\rangle \Psi_{el}^{(\Sigma, |\Lambda| \pm \pm)}, \]  \[ 18 \]
both \(\hat{H}_{rot}^a\) and \(\hat{H}_{so}\) operators have off-diagonal elements between the two symmetry components of those electronic states with \(|\Lambda| \neq 0\), Eq. [14]. They are diagonal in all other quantum numbers. To simplify the notation, \(|\Lambda|\) has been replaced by \(\Lambda\) taken as a positive quantity in subsequent equations. It should be noted here that only in the linear molecule limit is \(\Lambda\) a good quantum number taking integer values. As the molecule bends the orbital angular momentum is partially quenched and \(\Lambda\) is no longer integral. From Eqs. [9] and [16] we obtain the operators of Barrow \(et\ al.\) (9), after integrating over all coordinates except the bending coordinate, \(\rho\),
\[ \mathbf{H}_{rot}^a(\rho) = \left( \begin{array}{cc} h^2 A_1^1(\rho)(k^2 + \Lambda^2) & -2 h^2 A_2^1(\rho) k \Lambda \\ -2 h^2 A_2^1(\rho) k \Lambda & h^2 A_2^2(\rho)(k^2 + \Lambda^2) \end{array} \right). \]  \[ 19 \]

and
\[ \mathbf{H}_{so} = \left( \begin{array}{cc} 0 & h^2 A_{so}^1 \Lambda \Sigma \\ h^2 A_{so}^2 \Lambda \Sigma & 0 \end{array} \right). \]  \[ 20 \]

The off-diagonal element \(A_{12}(\rho)\) may be taken as \(A_{12}(\rho) = \frac{1}{2}(A_{11}(\rho) + A_{22}(\rho))\).

The remaining part of the operator, \(\hat{H}_{strb} - \hat{H}_{rot}^a\), is diagonal in the electronic quantum numbers, but has diagonal and off-diagonal matrix elements in \(v_1\) and \(v_3\). Integrating over the stretch coordinates we obtain for the diagonal elements
\[ \langle \chi_{v_1}^{s,i} , \chi_{v_3}^{s,i} | \hat{H}_{strb} - \hat{H}_{rot}^a | \chi_{v_1}^{s,i} , \chi_{v_3}^{s,i} \rangle = \frac{\hbar^2}{2} \left[ -g_{pp} f(\rho) + g_{pp} \frac{\partial^2}{\partial \rho^2} \right] + V_{i}^{(v_1,v_3)}(\rho). \]  \[ 21 \]

where
\[ V_{i}^{(v_1,v_3)} = \langle \chi_{v_1}^{s,i} , \chi_{v_3}^{s,i} | - \frac{\hbar^2}{2} \left[ g_{pp} \frac{\partial^2}{\partial \rho^2} + g_{aa} \frac{\partial^2}{\partial S_a^2} \right] + V_{i}^{(s,i)}(\rho, S_a, S_b) \rangle \]
\[ - \frac{\hbar^2}{2} g_{pp} \left[ \langle \chi_{v_1}^{s,i} | \frac{\partial^2 \chi_{v_1}^{s,i}}{\partial \rho^2} \rangle + \langle \chi_{v_3}^{s,i} | \frac{\partial^2 \chi_{v_3}^{s,i}}{\partial \rho^2} \rangle \right]. \]  \[ 22 \]

To describe the symmetric and antisymmetric stretch motions we introduce analytic approximations, either harmonic oscillator or Morse oscillator functions, which depend parametrically on the bending co-ordinate \(\rho\). Therefore the matrix elements between the stretching functions can be evaluated analytically. The terms in the second line of Eq. [22] are the vibrational adiabatic correction terms analogous to the more familiar electronic adiabatic corrections. In addition, there are terms off-diagonal in \(v_1\) and \(v_3\) but diagonal in the electronic quantum numbers. Such terms arise from both the potential energy (Fermi resonance coupling terms) and the kinetic energy (nonadiabatic stretch–bend and Darling–Dennison coupling terms) operators, as derived in our original article on the stretch-bender model; see Eq. (36) of Ref. (1).
The matrix elements diagonal in the symmetric and antisymmetric stretch functions define the large-amplitude bending operator

\[ H(\rho) = -\frac{\hbar^2}{2} \left[ -g^{\rho\rho} f(\rho) + g^{\rho\rho} \frac{\partial}{\partial \rho} \right] 1 + \left( \left( (V_1(\rho) + h^2 A_{11}(\rho)(k^2 + \Lambda^2) - 2h^2 A_{12}(\rho)k + h^2 A_{10}\Lambda \Sigma) - 2h^2 A_{12}(\rho)k + h^2 A_{10}\Lambda \Sigma, V_2(\rho) + h^2 A_{22}(\rho)(k^2 + \Lambda^2) \right) \right), \]

where \( 1 \) denotes the \( 2 \times 2 \) unity matrix. The term in front of this matrix is the kinetic energy operator, \( T(\rho) \). The bending basis functions \( \Phi^{b,ij}_{\nu_1\nu_2\nu_3}\rho \) are obtained numerically for each set of quantum numbers \( (\nu_1, \nu_2, \nu_3, k, \Sigma) \) as eigenfunctions of the transformed operator

\[ \hat{H}(\rho) = U^T(\rho)H(\rho)U(\rho), \]

where the transformation matrix \( U(\rho) \) is chosen to diagonalize the \( 2 \times 2 \) potential energy matrix in the last line of Eq. [23]. Owing to its \( \rho \)-dependence, \( U(\rho) \) does not commute with the kinetic energy operator, \( T(\rho) \), in Eq. [23]; hence small diagonal and slightly larger off-diagonal coupling elements are generated between the two electronic states. The transformed kinetic energy operator is

\[ \hat{T}(\rho) = T(\rho) + \left( \left( 2g^{\rho\rho}(\rho) \left( \frac{\partial \gamma(\rho)}{\partial \rho} \right)^2 \left[ T(\rho), \gamma(\rho) \right] \right) [T(\rho), \gamma(\rho)] - 2g^{\rho\rho}(\rho) \left( \frac{\partial \gamma(\rho)}{\partial \rho} \right)^2 \right). \]  

In the above equation \( \gamma(\rho) \) is the transformation angle to eliminate the potential coupling for a particular value of \( \rho \) and \( [T, \gamma] \) denotes the commutator. Details may be found in Ref. (8). All off diagonal terms, i.e., those off-diagonal in the electronic basis and also those off-diagonal in the symmetric and antisymmetric stretch basis, which are neglected at this stage, will be considered when the final interaction matrix is set up; See Section 5.

4. THE EFFECTIVE OVERALL ROTATION OPERATOR

The operator for overall rotation, Eq. [6], can be rearranged to give

\[ \hat{H}_{\text{rot}}^{b,c} = \frac{1}{2}(B' + C')(\hat{R}_b^2 + \hat{R}_c^2) + \frac{1}{2}(B' - C')(\hat{R}_b^2 - \hat{R}_c^2). \]  

Inserting Eq. [7] into the expression for \( \hat{H}_{\text{rot}}^{b,c} \) will give rise to terms which are diagonal in the angular momenta involved, which we will write as \( \hat{J}_b^2 + \hat{J}_c^2 = \hat{J}^2 - \hat{J}_a^2 \), etc., and various cross terms which we express in terms of the shift operators

\[ \hat{J}_\pm = \hat{J}_b \pm i\hat{J}_c, \]
\[ L_\pm = L_b \pm iL_c, \]
\[ \hat{S}_\pm = \hat{S}_b \pm i\hat{S}_c. \]  

The effect of the shift operators acting on a suitable ket is

\[ \hat{L}_\pm |L\Lambda\rangle = f_\pm(L, \Lambda)|L\Lambda \pm 1\rangle \]
\[ \hat{S}_\pm |S\Sigma\rangle = f_\pm(S, \Sigma)|S\Sigma \pm 1\rangle \]

but

\[ J^\pm |J\rho\rangle = f_\pm(J, \rho)|J\rho \mp 1\rangle, \]

where

\[ f_\pm(j, m) = h\sqrt{j(j + 1) - m(m \pm 1)}. \]

and

\[ p = k + \Sigma. \]

The superscript \( \pm \) on \( \hat{J} \) indicates the “reversed” angular momentum rules obeyed by \( \hat{J} \) attached to the rotating molecular frame. To obtain a more convenient expression we set

\[ \hat{J}_\pm = \hat{J}_\mp, \]

where \( \hat{J}_\pm \) obeys the normal angular momentum rules. Standard angular momentum techniques are then applied to yield the following expression for \( \hat{H}_{\text{rot}}^{b,c} \):

\[ \hat{H}_{\text{rot}}^{b,c} = \frac{1}{2}(B' + C')(\hat{J}_b^2 - \hat{J}_a^2 + \hat{S}_b^2 - \hat{S}_a^2) - \frac{1}{2}(B' + C') \times [\hat{J}_+\hat{S}_+ + \hat{J}_-\hat{S}_- + \hat{J}_a^2 + \hat{J}_b^2 + \hat{S}_+^2 + \hat{S}_-^2] - \frac{1}{2}(B' - C')(\hat{J}_-\hat{S}_+ + \hat{J}_+\hat{S}_-). \]

Note that in the above no terms involving the electronic angular momentum \( \hat{L} \) are retained. The diagonal terms contribute to the electronic energy only, and can be included in the definition of the potential energy surface, while the off-diagonal terms, which couple different electronic states, are neglected.

The matrix representation of the operator [33] is diagonal in the electronic quantum numbers \( i = (\Sigma, |L|\Gamma) \). It is also diagonal in the quantum numbers \( \nu_1 \) and \( \nu_2 \), since in our model \( A', B' \), and \( C' \) do not depend explicitly on the symmetric and antisymmetric stretching coordinates, the stretching amplitudes being assumed small with respect to the \( \rho \)-dependent reference configuration. However, it is not diagonal in \( \nu_3 \), nor in the quantum numbers \( k \) and \( \Sigma \). The explicit expressions for the matrix elements will now be given. Integrating over all coordinates except that for bending, and suppressing some of the diagonal quantum
numbers, the matrix elements may be derived to be

\[ \langle Jp\Sigma | \hat{H}_{\text{rot}}^{b,c} | Jp'\Sigma' \rangle \]

\[ = \frac{1}{2} (B' + C') \langle Jp\Sigma | [\hat{J}^2 - \hat{J}_z^2 + \hat{S}^2 - \hat{S}_z^2] | Jp\Sigma \rangle \]

\[ - \frac{1}{2} (B' + C') \langle Jp\Sigma | \hat{J} \cdot \hat{S} - Jp - 1 \Sigma - 1 \rangle + \frac{1}{4} (B' - C') \]

\[ \times \left[ \langle Jp\Sigma | \hat{J} \cdot \hat{S} - Jp + 1 \Sigma + 1 \rangle + \frac{1}{4} (B' - C') \right] \]

\[ + \langle Jp\Sigma | \hat{J} \cdot \hat{S} - Jp + 1 \Sigma + 1 \rangle + \frac{1}{4} (B' - C') \]

\[ \times \left[ \langle Jp\Sigma | \hat{J} \cdot \hat{S} - Jp - 2 \Sigma + 1 \rangle + \langle Jp\Sigma | \hat{J} \cdot \hat{S} - Jp - 2 \Sigma + 1 \rangle \right] \]

\[ - \frac{1}{2} (B' - C') \langle Jp\Sigma | \hat{J} \cdot \hat{S} - Jp + 1 \Sigma + 1 \rangle \]

\[ + \langle Jp\Sigma | \hat{J} \cdot \hat{S} - Jp + 1 \Sigma + 1 \rangle \]. [34]

Using Eqs. [27]–[32] for the shift operators, we finally arrive at the desired expressions,

\[ \langle Jp\Sigma | \hat{H}_{\text{rot}}^{b,c} | Jp'\Sigma' \rangle / \hbar^2 \]

\[ = \frac{1}{2} (B' + C') \left[ J(J + 1) - p^2 + S(S + 1) - \Sigma^2 \right] \delta_{p, p'} \delta_{\Sigma, \Sigma'} \delta_{k, k'} \]

\[ - \frac{1}{2} (B' + C') \left[ f_+(J, p - 1) f_+(S, \Sigma - \Sigma') \delta_{p - 1, p'} \delta_{\Sigma - 1, \Sigma'} \delta_{k, k'} \right] \]

5. SOLVING THE EIGENVALUE PROBLEM

The full matrix representation of \( \hat{H}_{\text{rov}} \), Eq. [8], is obtained by integrating over the bending coordinate, using the numerical

\[
\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
(v_1, v_2) & (0,0) & (1,0) & (2,0) & (0,2) & (1,2) & (2,2) & \ldots \\
\hline
(0,0) & \text{1}^A_b & \text{2}^B_1 & \text{FR} & 0 & \text{FR} & \text{NA} & 0 & 0 & 0 & 0 & \text{DD} & 0 & \ldots \\
\hline
(1,0) & \text{2}^A_1 & \text{2}^B_2 & \text{FR} & 0 & \text{FR} & \text{NA} & 0 & 0 & 0 & 0 & \text{DD} & 0 & \ldots \\
\hline
(2,0) & \text{2}^A_1 & \text{2}^B_2 & \text{DD} & 0 & \text{DD} & \text{NA} & 0 & 0 & 0 & 0 & \ldots \\
\hline
(0,2) & \text{2}^A_1 & \text{2}^B_2 & \text{FR} & 0 & \text{FR} & \text{NA} & 0 & 0 & 0 & \ldots \\
\hline
(1,2) & \text{2}^A_1 & \text{2}^B_2 & \text{FR} & 0 & \text{FR} & \text{NA} & 0 & 0 & 0 & \ldots \\
\hline
(2,2) & \text{2}^A_1 & \text{2}^B_2 & \text{FR} & 0 & \text{FR} & \text{NA} & 0 & 0 & 0 & \ldots \\
\hline
\end{array}
\]

\( ^2A_1/2^B_1 \), diagonal blocks containing the \( v_2 \) bending levels.

RT, Renner-Teller coupling terms.

FR, Fermi resonance terms.

NA, Non-adiabatic (\( \Delta v = \pm 2 \)) terms.

DD, Darling-Dennison (\( \Delta v = \pm 2 \)) terms.

FIG. 1. Block structure of the interaction matrix (upper triangle) for given \( K \) and \( \Sigma \), without “overall rotation.”
RENNER–TELLER AND SPIN–ORBIT INTERACTIONS IN NH2

<table>
<thead>
<tr>
<th>$p$</th>
<th>$(k, \Sigma)$</th>
<th>$p = -\frac{1}{2}$</th>
<th>$p = -\frac{1}{2}$</th>
<th>$p = \frac{1}{2}$</th>
<th>$p = \frac{1}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\frac{3}{2}$</td>
<td>$(-2, \frac{1}{2})$</td>
<td>CR</td>
<td>OR</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$-\frac{1}{2}$</td>
<td>$(0, -\frac{1}{2})$</td>
<td>CR</td>
<td>SU</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>$(0, \frac{1}{2})$</td>
<td>OR</td>
<td>SU</td>
<td>CR</td>
<td>CR</td>
</tr>
<tr>
<td>$\frac{3}{2}$</td>
<td>$(2, -\frac{1}{2})$</td>
<td>0</td>
<td>0</td>
<td>CR</td>
<td>CR</td>
</tr>
</tbody>
</table>

**FIG. 2.** Block structure of the full interaction matrix for $J = \frac{3}{2}$, $S = \frac{1}{2}$, and $K$ even. The diagonal elements of the matrices are as shown in Fig. 1 with the diagonal rotation terms added.

bending functions and the effective operators, Eqs. [25], including its off-diagonal terms in the bend and stretch functions, and [34]. The matrix of $\hat{H}_{\text{orb}}$ is diagonal in $k$ and $\Sigma$. As described in detail in (1), each $(k, \Sigma)$-block has the structure shown in Fig. 1 for the particular example of the $^2A_1/^2B_1$ Renner–Teller pair of electronic states of NH$_2$.

When overall rotation is included, $k$-blocks are coupled in increments of 2, owing to the $\hat{J}_z^2$ and $\hat{J}_z^2$ operators in Eq. [33], while the spin components, $\Sigma$, are coupled in increments of 1, owing to the spin-uncoupling operators $\hat{J}_x^2\hat{S}_x$ and $\hat{J}_y^2\hat{S}_y$ in the second line of Eq. [33]. There is also a cross term arising from the operators in the last line of Eq. [33] with matrix elements $\langle \Sigma, k \parallel \Sigma \pm 1, k \mp 2 \rangle$. These coupling terms are diagonal in the vibrational quantum numbers $v_1$ and $v_3$. In the final interaction matrix diagonal blocks of the kind shown in Fig. 1 are connected through the various rotational coupling terms just discussed. Since the parity of $K = |k|$ is conserved in our model, the final interaction matrix comprises two separate blocks. Their structures are shown in Figs. 2 and 3 for even and odd values of $K$ respectively, and with $J = \frac{3}{2}$.

In our numerical implementation of the theory outlined above, we have chosen to calculate explicitly the expectation value of $L_z$, since we have found this a very useful way of checking for the effects of vibronic mixing, in particular for helping the identification of the parentage of the vibronic levels. The main program codes contain a number of switches, which enable us to turn off many of the interactions, such as Fermi resonance or spin–orbit coupling, as well as overall rotation. We have found this facility invaluable in differentiating between the many complex couplings which can occur in these molecules. At present the least squares refinement of the parameters of the stretch-bender is restricted to the vibronic calculation. However, we hope to extend this to the rovibronic calculation.

6. QUENCHING OF ORBITAL ANGULAR MOMENTUM AND SPIN–ORBIT COUPLING Owing to the LARGE-AMPLITUDE BENDING MOTION

As we noted in Section 3, since the nuclear geometry of triatomic dihydrides may vary from linear to very strongly
bent, both the orbital angular momentum and the spin–orbit coupling parameter may in principle be dependent upon the bending angle. The quenching of the orbital angular momentum can arise from the admixture of highly excited states of the same symmetries as either the ground or the excited state, and becomes possible once the degeneracy of the parent linear molecular $^2Π_g$ electronic state is broken by the bending of the nuclear framework. This type of interaction was first considered by Jungen and Merer (9), who introduced the notation

$$\hbar^{-1} \langle A_1 | L_z | B_1 \rangle = \xi_{k}^{(1)}(\rho) \equiv \Lambda(\rho) = \Lambda - u(\rho). \quad [36]$$

They then defined a function $g_{k}(\rho)$ as

$$g_{k}(\rho) = 2A(\rho)u(\rho) = g_{k}^{0} + g_{k}^{2} \rho^{2} + \cdots. \quad [37]$$

Hence although $u(\rho)$ is isotopically independent the value of $g_{k}$ will be isotopically dependent, since the value of $A(\rho)$ for ND$_2$ will be smaller than that for NH$_2$ by a factor of $\sim 0.56$. Since $A(\rho) \sim 1/\rho^{2}$ and $u(\rho) \sim \rho^{2}$ for $\rho$ small, in the simplest approximation we may set $g_{k} = g_{k}^{0}$.

This quenching will affect not only the value of the electronic Coriolis coupling term $2\hbar^{2}A_{21}^{(2)}(\rho)k\Lambda(\rho)$ in Eq. [23], but also the spin–orbit coupling $\hbar^{2}A_{21}^{(0)}(\rho)\Lambda(\rho)\Sigma$, where $A_{21}^{(0)}(\rho)$ is defined in Eq. [11]. In most of our work on Renner–Teller coupling we have chosen to ignore the angular dependence of $A_{21}^{(0)}(\rho)$, and have used a value equivalent to that of the cylindrically symmetric linear configuration. In the Renner–Teller coupled $\tilde{a}^{1}A_1$ and $\tilde{b}^{1}B_1$ states of CH$_2$ only the electronic Coriolis coupling occurs, which we have interpreted using the expectation value of the quenched orbital angular momentum, $\langle L_z \rangle \equiv \langle L_{\phi} \rangle$, for a particular vibronic state. However, in NH$_2$ the effective spin–orbit interaction occurring in a vibronic state can be written as $\langle A_\rho^{(\nu)} | L_z \rangle$, and hence both terms may exhibit an angular dependence as described above. If the angular dependence of $\langle A_\rho^{(\nu)} \rangle$ may be neglected, the effective spin–orbit coupling parameter for a particular vibronic state can be set to $A_{\nu}^{(\rho)}(\rho)$ as discussed by Jungen et al. (10, 11). However, if the spin–orbit coupling has a rapid angular variation, it may be necessary to include the angular variation of $A_{\nu}^{(\rho)}$ explicitly, as has been discussed in some detail by Jensen and co-workers (15, 16).

In Table 3 the various notations for the geometry dependence of the electronic angular momentum and spin–orbit coupling are given.

### TABLE 3

<table>
<thead>
<tr>
<th>STRB (1)</th>
<th>MORBID (7, 15, 16)</th>
<th>JHM (9) (DJR) (12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective spin–orbit coupling constant (cm$^{-1}$)</td>
<td>$A_{\infty}$</td>
<td>$A_{\infty}$</td>
</tr>
<tr>
<td>Geometry dependence of electronic angular momentum</td>
<td>$\hbar^{-1} \langle A_1</td>
<td>L_z</td>
</tr>
<tr>
<td>Geometry dependence of spin–orbit coupling</td>
<td>$A_{\infty} \left( \Delta \tau_{12}, \Delta \tau_{12}^{(s)}, \rho \right)$</td>
<td>$\Lambda(\rho) = \Lambda - u(\rho) \equiv \Lambda - u(\rho)$</td>
</tr>
</tbody>
</table>

7. CONCLUSION

In this paper we have described the extension of the stretch-bender model to include both spin–orbit coupling and also overall rotation. We have also compared the method with the MORBID method of Jensen, Bunker, and their collaborators. A variational approach to the calculation of spin–vibronic levels has been previously described by Carter et al. (17), using a full three-dimensional treatment without the use of an angle-dependent reference configuration. In their calculations they assumed that the orbital angular momentum, $\Lambda$, could be treated as an integer, and that the spin–orbit coupling constant had no angular dependence. However, in the present work we have found it necessary to account for the quenching of $\Lambda$ and the angular variation of $A_{\infty}$.

In the following papers we apply our method to the calculation of the spin–rovibronic structure of the free radical NH$_2$, in highly excited vibrational levels of the electronic ground state, $\tilde{X}^{2}B_1$ only, paper 2, and in the highly perturbed region where the levels of the $\tilde{X}^{2}B_1$ state and $\tilde{A}^{2}A_1$ interact strongly, paper 3.
ACKNOWLEDGMENTS

We are indebted to the University of Bielefeld for their support of this research program. We are also very grateful to the Engineering and Physical Science Research Council for a grant from the Computational Science initiative for the provision of the workstation with which many of the initial calculations were carried out.

REFERENCES