Van Vleck Transformation as an Alternative to the Contact Transformation
Non-linear Molecules off Resonance

THORVALD PEDERSEN
Chemical Laboratory V, University of Copenhagen, The H. C. Ørsted Institute, 5, Universitetsparken, DK-2100 Copenhagen, Denmark

The projector formulation for the Van Vleck transformation has been applied to the Wilson-Howard Hamiltonian (i.e., the Hamiltonian for the vibration–rotation energy of rigid molecules). Formal expressions are obtained for γ and η constants, for the linear vibrational dependence of quartic and for the sextic centrifugal distortion constants.

1. INTRODUCTION

The problem of calculating vibration–rotation energy levels for rigid molecules (as opposed to molecules exhibiting large amplitude internal motions) was first attacked by Wilson and Howard in 1936 (1). Ordinary perturbation theory was applied to obtain corrections of various types. Already here the concept of an effective rotation/centrifugal distortion operator (matrix) was latent. This concept was to be fully exposed and exploited in the long series of papers by Amat, Nielsen, and many collaborators (cf. Ref. (2) for further references). The key concept in this development was the “contact transformation.” Later Allen and Cross (3) reformulated the original approach by Wilson and Howard in terms of the Van Vleck transformation as described by Kemble (4) and Jordahl (5). The contact transformation and the Van Vleck transformation were both formulated in terms of an exponential exp(iS). In the former transformation S was a polynomial in normal coordinates and conjugated momenta or, alternatively, creation and annihilation operators (6), while in the latter it was to be considered as a matrix.

Jørgensen and Pedersen (7,8) found that an operator version equivalent to the matrix version could be given in terms of projection operators, and in collaboration with Chedin (9) they established the connection between the two apparently different approaches.

In recent years, it has become customary to follow a suggestion by Watson, to classify terms in the Wilson–Howard operator as \( H_{m,n} \) signifying operators of the form \( (q_i, p_j)J_{ij} \) (cf. Mills (10)). The corresponding terms in the contact transformed Hamiltonian are classified similarly as \( \hat{H}_{m,n} \) and \( \hat{H}_{m,n} \) is then written symbolically in terms of \( H_{m,n} \) as shown in the recent paper by Alliev and Watson (11) on sextic centrifugal distortion, where \( \hat{H}_{0,0} \) contains \( H_{1,1}, H_{1,2}, H_{2,2} \), etc. As will be shown below, this
notation is very closely related to the expressions that one obtains using the projector formulated Van Vleck transformation of Ref. (7) rather than the contact transformation.

In Section 2 the effective Hamiltonian for the state \( \nu \) is then obtained using the projector form of the Van Vleck transformation and using \( \kappa(= \sqrt{m_{\nu}/m_{\nu}}) \) as the perturbation parameter. This requires that one includes tenth order terms in order to include sextic centrifugal distortion. Alternatively one can consider \( H - H_0 \) as a single perturbation and then go to third or fourth order of perturbation and collect the various powers of \( \kappa \). This has been done by Brown in connection with calculation of \( \gamma \)-constants (12).

One advantage of using \( \kappa \) as the perturbation parameter is that all odd order terms vanish as was shown in Ref. (9), so that one needs only \( A_{2n} \) \( n = 1 \)–5. Expressions for \( A_{2n} \) for \( n = 1, 2, 3 \) are already available (13) and in Appendix A we give also \( A_8 \) and \( A_{10} \). (\( A \) is used rather than \( \hat{H} \) (cf. Sec. 2)). It may appear to be a great disadvantage to need to apply tenth order perturbation theory, however, as long as \( m \) in \( \hat{H}_{m,n} \) is small, it is in fact quite easy to select exactly those terms which contribute, so that rather than being an obstacle, it appears to a convenient bookkeeping tool.

It is not obvious whether one approach is preferable to the other, but since the present version is closer to degenerate perturbation theory, it appears to be conceptually simpler, at least to some authors working in the field of high resolution spectroscopy (3, 10, 12, 14).

2. EFFECTIVE HAMILTONIAN FOR A VIBRATIONAL STATE

Throughout this paper it will be assumed that no state is accidentally degenerate with the state considered. The Wilson–Howard operator in Watson's formulation (15) is written in two different ways (\( U \) denoting Watson's potential \(-\frac{1}{2} \hbar^2 \text{Tr}(\mu)\)),

\[
H = H_{2,0} + \kappa H_{3,0} + \kappa^2 \{ H_{4,0} + H_{2,1} + H_{0,2} \}
+ \kappa^3 \{ H_{5,0} + H_{3,1} + H_{1,2} + U_{1,0} \} + \cdots \text{etc.} \quad (2.1)
\]

The alternative notation is defined as follows:

\[
\kappa^{m+2n-2} H_{m,n} = h_m^{(n)} \cdot J^{(n)}, \quad \kappa^{m+2} U_{m,0} = u_m^{(0)},
\]

where \( h_m^{(n)} \) and \( J^{(n)} \) are \( n \)th rank cartesian tensors, the \( n \) components of which are referred to the molecule fixed coordinate system. The dot signifies the "scalar product" and (2.2a) is then to be interpreted as

\[
h_m^{(n)} \cdot J^{(n)} = \langle h_m^{(n)} \rangle_{fg} \cdots J_f J_g J_h \cdots \quad (2.2b)
\]

(Summation over repeated indices \( f, g, h \), etc). Commutators of such scalar products are "contracted" as follows:

\[
[\alpha^{(m)} \cdot J^{(m)}, \beta^{(n)} \cdot J^{(n)}] = \langle \alpha^{(m)}, \beta^{(n)} \rangle (m+n) \cdot J^{(m+n)}
+ \langle \alpha^{(m)}, \beta^{(n)} \rangle (m+n-1) \cdot J^{(m+n-1)} \quad (2.3)
\]

The first bracket denotes a tensor with rank equal to the sum of the ranks, and the second a tensor with rank equal to the sum minus one. \( \alpha \) and \( \beta \) may themselves be such brackets. The necessary commutators have been collected in Appendix B.

The \( S \)-operators which appear in the transformation operator \( W^{(s)} \) (cf. (7)):

\[
W^{(s)} = \cdots \exp(i\kappa S_3^{(s)}) \exp(i\kappa S_2^{(s)}) \exp(i\kappa S_1^{(s)})
\]

(2.4)
are written as follows (cf. (A.13)-(A.18))

\begin{align}
\kappa S_1^{(v)} &= s_1^{(0)}, \\
\kappa^2 S_2^{(v)} &= s_2^{(0)} + s_2^{(1)} \cdot J^{(1)}, \\
\kappa^n S_n^{(v)} &= s_n^{(0)} + s_n^{(1)} \cdot J^{(1)} + s_n^{(2)} \cdot J^{(2)} & n = 3, 4, \\
\kappa^4 S_5^{(v)} &= s_5^{(0)} + s_5^{(1)} \cdot J^{(1)} + s_5^{(2)} \cdot J^{(2)} + s_5^{(3)} \cdot J^{(3)}.
\end{align}

Note here, that the lower index of \( s_i^{(v)} \) goes with the \( \kappa \)-order and not with the \( (p, q) \)-power as was the case with \( h_m^{(n)} \). The index \( v \) appearing in (2.4) and (2.5) is necessary, because unlike the contact transformation, \( W^{(v)} \) is aiming at only one vibrational state \( v \). The transformed Hamiltonian \( \mathfrak{H} \) has the form

\[ \mathfrak{H}^{(v)} = \mathfrak{H} = W^{(v)} H (W^{(v)})^{-1} = p_0^{(v)} \mathfrak{H} p_0^{(v)} + q_0^{(v)} \mathfrak{H} q_0^{(v)}. \]

The projection operator \( p_0^{(v)} \) may be written

\[ p_0^{(v)} = p_0 = \sum_L | \nu, L \rangle \langle \nu, L | \]

and

\[ q_0^{(v)} = q_0 = 1 - p_0 = \sum_{L', \nu'} | \nu', L' \rangle \langle \nu', L' | \]

Hence any operator \( B \) may be written

\[ B = (p_0 + q_0) B (p_0 + q_0) = p_0 B p_0 + q_0 B q_0 + p_0 B q_0 + q_0 B p_0 = B_{even} + B_{odd}. \]

The aim of the Van Vleck transformation is that \( \mathfrak{H} \) be even cf. (2.6). Once \( \mathfrak{H} \) is even the \( q_0 \mathfrak{H} q_0 \) operator is discarded, and the remaining operator is written:

\[ A^{(v)} \equiv p_0^{(v)} \mathfrak{H} p_0^{(v)} = p_0^{(v)} W^{(v)} H (W^{(v)})^{-1} p_0^{(v)} \]

with

\[ \mathfrak{H}^{(v)} = (W^{(v)})^{-1} p_0^{(v)}. \]

\( A^{(v)} \) is expanded as follows (omitting the zero point energy from \( a_2^{(0)} \))

\begin{align}
A^{(v)} &= \sum_{n=0}^\infty \kappa^{2n} A_{2n}^{(v)}, \\
A_0^{(v)} &= a_2^{(0)} = p_0^{(v)} \sum_k \hbar \omega_k v_k \equiv p_0^{(v)} E_v, \\
\kappa^2 A_2^{(v)} &= a_4^{(0)} + a_2^{(1)} \cdot J^{(1)} + a_0^{(2)} \cdot J^{(2)}, \\
\kappa^4 A_4^{(v)} &= a_6^{(0)} + a_4^{(1)} \cdot J^{(1)} + a_2^{(2)} \cdot J^{(2)}, \\
\kappa^6 A_6^{(v)} &= \ldots + a_4^{(2)} \cdot J^{(2)} + a_2^{(3)} \cdot J^{(3)} + a_0^{(4)} \cdot J^{(4)}, \\
\kappa^8 A_8^{(v)} &= \ldots + a_2^{(4)} \cdot J^{(4)} + a_0^{(6)} \cdot J^{(6)}, \\
\kappa^{10} A_{10}^{(v)} &= \ldots + a_0^{(8)} \cdot J^{(8)},
\end{align}

\ldots indicates terms which have been omitted, because they are judged to be too far
TABLE I
S-Operators

\[ s_{1}^{(0)} = s(n_{3}^{(0)}) \]

\[ s_{2}^{(0)} = s([i\alpha_{1}^{(0)}, n_{3}^{(0)}] + n_{4}^{(0)}) \]

\[ s_{2}^{(1)} = s(n_{2}^{(1)}) \]

\[ s_{3}^{(0)} = s([i\alpha_{2}^{(0)}, n_{3}^{(0)}] + \frac{1}{3} [i\alpha_{2}^{(0)}, i\alpha_{2}^{(0)}, n_{3}^{(0)}]) + \alpha_{4}^{(0)} + \mu_{4}^{(0)} \]

\[ s_{3}^{(1)} = s([i\alpha_{2}^{(1)}, n_{3}^{(0)}] + [i\alpha_{2}^{(1)}, n_{2}^{(1)}] + n_{3}^{(2)}) \]

\[ s_{4}^{(0)} = s([i\alpha_{3}^{(0)}, n_{3}^{(0)}] + [i\alpha_{3}^{(0)}, n_{3}^{(2)}]) + \alpha_{4}^{(2)} \]

\[ s_{4}^{(2)} = s([i\alpha_{3}^{(2)}, n_{3}^{(0)}] + [i\alpha_{3}^{(1)}, n_{3}^{(2)}] + [i\alpha_{3}^{(0)}, n_{2}^{(2)}]) \]

\[ s_{5}^{(0)} = s([i\alpha_{3}^{(0)}, n_{3}^{(3)}] + [i\alpha_{3}^{(2)}, n_{0}^{(2)}, n_{1}^{(3)}]) \]

\[ s_{5}^{(3)} = s([i\alpha_{3}^{(0)}, n_{3}^{(3)}] + [i\alpha_{3}^{(2)}, n_{0}^{(2)}, n_{1}^{(3)}]) \]

beyond current spectroscopic interest. Again the lower index of \( a_{m}^{(n)} \) indicates \((p, q)^{m} \).

Tables I and II contain \( S_{1} - S_{6}, S(\cdot) \) and other symbols are explained in Appendix A. In \( S_{4} \) and \( S_{5} \) only those terms which contribute to the subsequent \( a_{m}^{(n)} \) operators have been retained.

Table III lists those \( a_{m}^{(n)} \) which appear in (2.12). In Table IV the simpler of these operators are more fully expanded, again in terms of symbols defined in Appendix A.

3. DISCUSSION

It is well known that the Born–Oppenheimer approximation in the adiabatic formulation (16) is valid to \( \kappa^{6} \). (In the absolute sense, i.e., five orders smaller than a typical electronic transition. Throughout this paper a term of order \( \kappa^{6} \) is \( n \) orders smaller than a typical vibrational transition and hence \( \kappa^{n+2} \) times smaller than an electronic transition).

The \( \kappa^{6} \)-term consists of the \( \kappa^{6}H_{6,0} \) term of (2.1) and a contribution which is linear in \( Q_{k} \). The linear contribution is not explicitly accounted for in (2.1), but if the definition of \( u_{1}^{(0)} \) is relaxed, it is implicitly there. \( a_{4}^{(2)} \) is the only operator of those listed, in which \( u_{1}^{(0)} \) appears. There is one further electronic contribution of this order of magnitude.

This has been used by Morino et al. (17) in the discussion of inertial defects of planar molecules. Since it is of the same order of magnitude as \( a_{4}^{(2)} \), it is hardly meaningful to make such electronic corrections unless \( a_{4}^{(2)} \) is fully accounted for.

In order to illuminate the rather compact notation of Tables III and IV a few terms will now be considered in some detail.

1 There are a few exceptions originating from commutations according to (2.3) or from the \( u_{m}^{(0)} \) operators. Mills has commented on this situation (10).

It has the form: \[ \sum_{n} \langle 0 | L_{n} | n \rangle \langle n | L_{n} | 0 \rangle / E_{0} - E_{n} \] and originates from a second order treatment of the operator \( J_{x}L_{x} \) of the total Hamiltonian, \( L \) is the electronic angular momentum \( |0\rangle \) and \( |n\rangle \) are electronic states.
First consider $a_2^{(1)}$ which becomes (using (A.20), (2.7), and the definition $h^{(1)}_q = -\hat{\mu} \pi$)

$$\langle a_2^{(1)} \rangle_f = \langle h_2^{(1)} \rangle_f - \sum_{L, L'} \langle v, L | \langle v, L | \mu_{ij} \pi_j | v, L' \rangle \langle v, L' | \rangle_v, L'. \tag{3.1}$$

If no degenerate vibrations are excited, then (3.1) vanishes, since $\pi$ has no diagonal matrix elements. Now assume that $v$ describes a degenerate fundamental state in a prolate symmetric top ($v_u = 1$, $v_{\nu} \neq 0$, $t, t'$ are indices for degenerate modes) $L$ now assumes two "values": $l = \pm 1$; $l_{t, t'} = 0$, $a_2^{(1)}$ is hence a vector operator in the two-dimensional space spanned by $\{ |v, 1\rangle, |v, -1\rangle \} = \{ |+\rangle, |-\rangle \}$. Any operator $b$ in a two-dimensional space may be written:

$$b = |+\rangle \langle + | b^{++} | + \rangle + | \rangle \langle - | b^{-+} | - \rangle - | \langle + | b^{--} | + \rangle - | \rangle - | b^{--} \rangle \tag{3.2}$$

(or, alternatively, as the matrix $B$ with matrix elements $b^{++} = \langle + | b | + \rangle$ etc.). The case considered is the well-known first-order Coriolis coupling case, where $(a_2^{(1)})_b$
\( (a_2^{(1)})_e = 0 \), and

\[
(a_2^{(1)})_a = \frac{-2\hbar c}{\hbar^2} A \xi_i (|+\rangle \langle +| - |\rangle \langle -|)
\]

\[
(-\mu_{ab} \pi_a) = -\hbar \sum_{k \geq 1} \frac{\xi_{ka} a^a}{I_{a}^{\ast}} \left( \sqrt{\frac{\omega_1}{\omega_k}} q_k p_1 - \sqrt{\frac{\omega_k}{\omega_1}} q_1 p_k \right).
\] (3.3)

In the case considered, all terms vanish except

\[
-\hbar \frac{\xi_i}{I_{a}^{\ast}} (q_1 p_2 - q_2 p_1) \quad (q_1 = q_2 \text{ etc.}).
\]

The matrix elements of \( b = q_1 p_2 - q_2 p_1 \) are \( b^+ = b^- = 0; \ b^{+\dagger} = -b^- = 1 \).

\( a_2^{(1)} \cdot J^{(1)} \) then becomes

\[
a_2^{(1)} \cdot J^{(1)} = -2\hbar c A \xi_i (|+\rangle \langle +| - |\rangle \langle -|)
\]

\[
\mathcal{g}_a = J_a / \hbar \quad \text{and} \quad A^e = \frac{\hbar^2}{2\hbar c I_{a}^{\ast}} \text{[cm}^{-1}\text{]}.
\] (3.4)

There is no off-diagonal part in (3.4), i.e., no couplings of the type \(|+\rangle \langle -| b^{++} \)

\( \text{and} \ |\rangle \langle +| b^{-+} \). Such couplings will however appear when \( a_4^{(1)} \) is included in the

Coriolis coupling operator. The diagonal part of \( a_4^{(1)} \) leads to the so-called \( \alpha^B \)-constants (Mills (10)).

In orthorhombic molecules \( a_2^{(2)} \) reduces to the well-known \( \alpha^B \)-constants multiplied

by the projection operator \(|v\rangle \langle v|\) (which may then be omitted). Using Mills' notation

(10) one finds

\[
\{x(h_2^{(1)})_b \cdot (h_2^{(1)})_b x\} = \sum_{v^\prime \neq v} \langle v| v\rangle \langle v| \mu_{bb}^\ast p_{b} \frac{|v^\prime\rangle \langle v^\prime|}{E_v - E_{v^\prime}} \mu_{bb} p_{b} |v\rangle |v\rangle
\]

\[
- \frac{\hbar c}{\hbar^2} \sum_{s} \frac{2B^2}{\omega_r} \sum_{s} (\xi_{rs} b_{r})^2 \frac{3\omega_r^2 + \omega_s^2}{\omega_r^2 - \omega_s^2} (\nu_r + \frac{1}{2}) |v\rangle \langle v|, \quad (3.4a)
\]

\[
2\{xh_4^{(0)} : (h_1^{(2)})_b b x\} = 2 \sum_{v^\prime} \langle v| v\rangle \left\{ \frac{\hbar c}{6} \sum_{s} \frac{\phi_{rst} q_{t} \phi_{s} q_{t}}{E_v - E_{v^\prime}} \mu_{bb}^{\ast} b_{b} \right\} |v\rangle \langle v|
\]

\[
- \frac{\hbar c}{\hbar^2} \sqrt{h} \sum_{r} \frac{2B^2}{\omega_r} \sum_{s} \phi_{rst} a_{s}^{\ast} b_{b} \left( \frac{\omega_r}{\omega_s^2} \right) (\nu_r + \frac{1}{2}) |v\rangle \langle v|, \quad (3.4b)
\]

\[
xh_2^{(2)} x = |v\rangle \langle v| \mu_{bb}^{\ast} |v\rangle \langle v| = - \frac{\hbar c}{\hbar^2} \sum_{r} \frac{2B^2}{\omega_r} \sum_{s} \frac{(a_{s}^{\ast} b_{s})^2}{I_{t}^{\ast}} (\nu_r + \frac{1}{2}) |v\rangle \langle v|, \quad (3.4c)
\]

For degenerate fundamental states of a \( C_{3v} \) molecule \( a_2^{2} \) gives rise to \( \alpha^B \)-constants

(diagonal contributions) as well as \( l \)-doubling effects (18) (off-diagonal contributions).

We illustrate this only by \( xxH_{2,3} xx \) (rather than \( xh_2^{(2)} x \), since it is convenient to use
TABLE III

\( a_m^{(n)} \) Operators in Terms of Commutators and Brackets (see text)

<table>
<thead>
<tr>
<th>( m )</th>
<th>( a_m^{(0)} )</th>
<th>( a_m^{(1)} )</th>
<th>( a_m^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( a_4^{(0)} = P_0^2 \left( \frac{1}{2} i a_1^{(0)}, a_2^{(0)} \right) + a_5^{(0)} \left( \frac{1}{2} i a_1^{(0)}, a_2^{(0)} \right) )</td>
<td>( a_4^{(1)} = P_0^2 \left( \frac{1}{2} i a_1^{(1)}, a_2^{(1)} \right) + a_5^{(1)} \left( \frac{1}{2} i a_1^{(1)}, a_2^{(1)} \right) )</td>
<td>( a_4^{(2)} = P_0^2 \left( \frac{1}{2} i a_1^{(2)}, a_2^{(2)} \right) + a_5^{(2)} \left( \frac{1}{2} i a_1^{(2)}, a_2^{(2)} \right) )</td>
</tr>
<tr>
<td>4</td>
<td>( a_6^{(0)} = P_0^4 \left( \frac{1}{2} i a_1^{(0)}, a_2^{(0)}, a_3^{(0)} \right) + a_5^{(0)} \left( \frac{1}{2} i a_1^{(0)}, a_2^{(0)}, a_3^{(0)} \right) )</td>
<td>( a_6^{(1)} = P_0^4 \left( \frac{1}{2} i a_1^{(1)}, a_2^{(1)}, a_3^{(1)} \right) + a_5^{(1)} \left( \frac{1}{2} i a_1^{(1)}, a_2^{(1)}, a_3^{(1)} \right) )</td>
<td>( a_6^{(2)} = P_0^4 \left( \frac{1}{2} i a_1^{(2)}, a_2^{(2)}, a_3^{(2)} \right) + a_5^{(2)} \left( \frac{1}{2} i a_1^{(2)}, a_2^{(2)}, a_3^{(2)} \right) )</td>
</tr>
</tbody>
</table>
\[ a_0^{(4)} = p_0 \left( \frac{1}{2} a_3^{(2)}, h_2^{(1)} \right) \]
TABLE III—Continued

<table>
<thead>
<tr>
<th>(a_{0}^{(6)})</th>
<th>(\nu_{0}^{(1)}(\chi_{x}^{(2), 2})^{2}, \chi_{x}^{(1), 2}, \chi_{x}^{(2), 3}(1, 2)<em>{\alpha</em>{1}}, \gamma_{x}^{(3), 1}, \gamma_{x}^{(4), 3}, \gamma_{x}^{(4), 6})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\frac{1}{2} \chi_{x}^{(2), 2}, \chi_{x}^{(1), 2}, \chi_{x}^{(2), 3}(1, 2)<em>{\alpha</em>{1}}, \gamma_{x}^{(3), 1}, \gamma_{x}^{(4), 3}, \gamma_{x}^{(4), 6})</td>
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<td></td>
<td>(\frac{1}{2} \chi_{x}^{(2), 2}, \chi_{x}^{(1), 2}, \chi_{x}^{(2), 3}(1, 2)<em>{\alpha</em>{1}}, \gamma_{x}^{(3), 1}, \gamma_{x}^{(4), 3}, \gamma_{x}^{(4), 6})</td>
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</tr>
</tbody>
</table>

cylindrical tensor notation. In Appendix B only cartesian tensor components have been listed. \(g_{\pm}\) are defined as done by Oka (14) as \(g_{\pm} = \epsilon g_{\pm}\) (\(g\) again dimensionless angular momentum) and \(q_{\pm} = q_{11} \pm i q_{22}\). \(t = \) degenerate vibration

\[
\frac{1}{2} \hbar^2 \frac{\partial^2 \mu_j}{\partial q_+^2} x(q_+ g_{+}^2 + q_+ g_{-}^2) x = \frac{\hbar^2}{2} \frac{\partial^2 \mu_j}{\partial q_+^2} \{ |+\rangle \langle + | - |\pm\rangle \langle \pm | \} (3.5a)
\]

In (3.5) we have used

\[
x q_{\pm}^2 x = (|+\rangle \langle + | + |+\rangle \langle + | - |\pm\rangle \langle \pm | (3.5b)
\]

Next consider \(a_{0}^{(4)}\), which in the nondegenerate case gives the centrifugal distortion constants:

\[
\{ x(h_{1}^{(2)})_{f_{g}}: (h_{1}^{(2)}))_{f_{g}} x \} = \frac{1}{8} \sum_{v'v} \left| v' \right\rangle \langle v \left| \right. \frac{\mu_{f_{g}} \left| v' \right\rangle \langle v \left|}{E_{v'} - E_{v}} \mu_{h_{j}} \left| v' \right\rangle \langle v \left| \right. + \mu_{h_{j}} \left| v' \right\rangle \langle v \left| \right. \frac{\mu_{f_{g}} \left| v' \right\rangle \langle v \left|}{E_{v'} - E_{v}} \right| v \right\rangle \langle v \right| = \frac{\hbar c}{4\hbar^4} \tau_{f_{g}h_{j}} \left| v \right\rangle \langle v \right| (3.6)
\]

Consider now \(a_{0}^{(4)}\) in the case \(v_{1} = 1 \ v_{2} = 0\) in a \(C_{2s}\) symmetric top. Again we consider \(\epsilon^2 x H_{1,2} x: H_{1,2} x\) rather than \(x h_{1}^{(2)}: h_{1}^{(2)} x\) because we want to use cylindrical tensor notation:

\[
\hbar^4 \left( \frac{\partial \mu_{f_{g}}}{\partial q_{+}} \right)^2 x(q_+ g_{+}^2 + q_+ g_{-}^2) x = -2\hbar^4 \left( \frac{\partial \mu_{f_{g}}}{\partial q_{+}} \right)^2 \frac{1}{\hbar c \omega_{i}} \{ |+\rangle \langle + | g_{+}^2 g_{-}^2 - |+\rangle \langle + | g_{+}^2 g_{-}^2 \} (3.7a)
\]

where we have used

\[
\langle + | q_{-} x | + \rangle = -\langle - | q_{+} x | - \rangle = \frac{-2}{\hbar c \omega_{i}} (3.7b)
\]

\[
\langle - | q_{-} x | - \rangle = \langle + | q_{+} x | + \rangle = 0 \text{ etc.} (3.7c)
\]
TABLE IV  
Expanded Commutators and Brackets

<table>
<thead>
<tr>
<th>$a_4^{(1)}$</th>
<th>$a_4^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}(x(h_1^{(1)}, h_3^{(0)})_f - x(h_3^{(0)}; h_1^{(0)})_x)$</td>
<td>$\frac{1}{2}(x(h_1^{(1)}, h_3^{(0)})_f - x(h_3^{(0)}; h_1^{(0)})_x)$</td>
</tr>
<tr>
<td>$\frac{1}{2}(x(h_1^{(1)}, h_3^{(0)})_f - x(h_3^{(0)}; h_1^{(0)})_x)$</td>
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<tr>
<td>$\frac{1}{2}(x(h_1^{(1)}, h_3^{(0)})_f - x(h_3^{(0)}; h_1^{(0)})_x)$</td>
<td>$\frac{1}{2}(x(h_1^{(1)}, h_3^{(0)})_f - x(h_3^{(0)}; h_1^{(0)})_x)$</td>
</tr>
<tr>
<td>$\frac{1}{2}(x(h_1^{(1)}, h_3^{(0)})_f - x(h_3^{(0)}; h_1^{(0)})_x)$</td>
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<td>$\frac{1}{2}(x(h_1^{(1)}, h_3^{(0)})_f - x(h_3^{(0)}; h_1^{(0)})_x)$</td>
</tr>
</tbody>
</table>

$a_4^{(1)}$ gives the linear (in the vibrational quantum numbers) corrections to the $\tau$ constants and $a_4^{(2)}$ the sextic centrifugal distortion constants. All the types of terms found in Ref. (11) may be verified by insertion of the $S$ operators of Table II.

$a_4^{(1)}$, $a_4^{(2)}$, and $a_0^{(0)}$ are active in degenerate states only. They have not so far been used in spectroscopy to the authors’ knowledge.

In order to have a complete alternative to the contact transformation it remains to treat resonance cases and the transition operators. Research continues in these directions.
APPENDIX A

The operators $A_{2n}$ mentioned in Sec. 2 are given for $n = 0, 1, 2$ in terms of multi-commutators as follows:

\[ A_0 = E_0 P_0, \]  
\[ A_2 = P_0 \{ \frac{1}{2} T_1(V_1) + V_2 \} P_0, \]  
\[ A_4 = P_0 \{ \frac{1}{2} T_{11}(V_1) + \frac{1}{2} T_{10}(V_1) + \frac{1}{2} T_{10}(V_2) + T_3(V_2) + T_4(V_2) + V_1 \} P_0. \]

Here the symbol $T_r(V_i)$ means:

\[ T_r(V_i) = \frac{1}{r!} [iS_1, [iS_1, \ldots V_i]] \ldots \equiv \frac{1}{r!} [iS_1, V_i]^{(r)}, \]

$T_{sr}(V_i)$ means

\[ T_{sr}(V_i) = \frac{1}{s!} [iS_2, T_r(V_i)]^{(s)} \]

e tc.

We give $A_6 - A_{10}$ in terms of the operator $J$, the twice transformed Hamiltonian:

\[ J = \sum_{n=0}^{\infty} \lambda^n J_n = \exp(i\lambda^2 S_2) \exp(i\lambda S_1) H \exp(-i\lambda S_1) \exp(-i\lambda^2 S_2) \]

for which closed expressions are available (7).

\[ A_6 = P_0 \{ J_6 + \frac{1}{2} T_{160}(J_6) \} P_0, \]  
\[ A_8 = P_0 \{ J_8 + T_{100}(J_6) + \frac{1}{2} T_{1400}(J_4) + T_{200}(J_4) + \frac{1}{2} T_{1100}(J_3) \} P_0, \]  
\[ A_{10} = P_0 \{ J_{10} + T_{100}(J_8) + T_{1000}(J_6) + \frac{1}{2} T_{10000}(J_6) + T_{200}(J_4) + T_{1100}(J_3) + T_{2000}(J_2) + \frac{1}{2} T_{10100}(J_2) + T_{11000}(J_3) \} P_0. \]

A multicommutator expression for $A_6$ may be found in Ref. (13). In this reference $S_1 - S_5$ is also given, see below. They are expressed as $S(A)$, ($A$ is an arbitrary, hermitean operator) defined by

\[ iS(A) = S_+(A) - S_-(A), \]

\[ S_+ = -(S_-)^* = P_0 A \frac{Q_0}{a^n}, \]

where $Q_0/a$ is defined by

\[ \frac{Q_0}{a^n} = Q_0 (E_0 - H_0)^{-n} Q_0 \quad n = 1, 2, \ldots \]

which is well-defined because $H_0$ does not have the eigenvalue $E_0$ in the space $\Omega_0^+$ projected by $Q_0$. In the present context $Q_0/a^n$ may be expressed as

\[ \frac{q_0}{a^n} \equiv \frac{q_0^n}{a^n} = \sum_{L'} \frac{|\psi' L' \rangle \langle \psi' L' |}{(E_\psi - E_{\psi'})^n}. \]
We now quote $S_1$--$S_6$: from Ref. (13).

\[ S_1 = S(V_1), \]  
\[ S_2 = S(T_1(V_1) + V_2), \]  
\[ S_3 = S(T_{10}(V_1) + \frac{2}{3}T_2(V_1) + T_1(V_2) + V_3), \]  
\[ S_4 = S(T_{100}(V_1) + \frac{1}{2}T_{11}(V_1) + T_3(V_1) + T_{10}(V_2) + T_2(V_2) + T_1(V_3) + V_4), \]  
\[ S_5 = S(T_{1000}(V_1) + \frac{1}{6}T_{101}(V_1) + T_{12}(V_1) + \frac{3}{2}T_4(V_1) + T_{100}(V_2) + T_{11}(V_2) + T_5(V_2) + T_{10}(V_3) + T_3(V_3) + T_1(V_4) + V_5). \]

Since $V_1$ is equal to $h_8^{(0)}$, $S(V_1)$ is of rank zero (cf. (2.2) and (2.5)). It follows that $S_2$ contains terms of rank 0 and 1 since $V_2$ contains $h_8^{(1)}, J^{(1)}$ and $h_8^{(2)}, J^{(2)}$, of which the latter commutes with $p_0$ and therefore vanishes:

\[ S_+(h_0^{(2)}, J^{(2)}) = p_0h_0^{(2)}J^{(2)}q_0 \]
\[ = h_0^{(2)}J^{(2)}p_0q_0 a = 0 \]

because in general $P_0Q_0 = Q_0P_0 = 0$ (see (A.11) and (A.25)). Now the ranks involved in $S_3$ are easily surveyed, because $V_n$ contains terms of rank 0, 1, 2 for $n > 2$. Thus $S(T_{10}(V_1))$ has terms of rank 0 and 1, $S(T_{10}(V_3))$ of rank zero, $T_1(V_2)$ of rank 1, and $S(V_3)$ of rank 2 and so on. Explicit expressions have been collected in Table I. Using (2.5) one can now easily survey the ranks of any multicommutator. The following occurring in $A_8$ are the ones that give terms of rank 4:

\[ \frac{1}{2}T_{201}(V_1), \frac{1}{3}T_{1100}(V_1), \frac{3}{2}T_{30}(V_2), T_{111}(V_2), T_{200}(V_2), \frac{1}{2}T_{1010}(V_2), T_{21}(V_2), T_{102}(V_3), T_{110}(V_3), \frac{1}{2}T_{1001}(V_3), T_{20}(V_3), T_{101}(V_3), \frac{1}{2}T_{1000}(V_4), T_{100}(V_5) \]

and the terms $T_{200}(V_2)$ and $T_{110}(V_3)$ give the fifth rank terms.

The multicommutators of $A_{10}$ which contribute terms of rank 6 are easily localized by the same procedure and are found to be:

\[ \frac{1}{2}T_{210}(V_2), \frac{1}{3}T_{1610}(V_2), T_{120}(V_3), \frac{1}{2}T_{10010}(V_3), T_{201}(V_3), T_{1100}(V_3), T_{200}(V_4). \]

A stenographic notation which greatly simplifies the explicit terms of Tables II and IV is defined by

\[ x = p_0^v, \]
\[ : = \frac{q_0^v}{a^v}, \]
\[ :: = \frac{q_0^v}{a^v^2} \text{ etc.} \]

By "rank" is meant $n$ in $J^{(n)}$ in this connection.
In evaluating the commutators we use the following notation valid under the conditions in the parentheses
\[ [a, b] = 2\{ab\}_H, \quad (a = -a^1; b = b^1), \] (A.21)
\[ [a, [b, c]] = 2\{abc - acb\}_H, \quad (a = -a^1; b = -b^1; c = c^1), \] (A.22)
\[ [a, [b, [c, d]]] = 2\{abcd - abde - cdeb + adeb\}_H, \quad (a = -a^1; b = -b^1; c = -c^1; d = d^1), \] (A.23)
\[ \{[a, [b, cd]]\}_H = \{abed - ucclb - bcdu + cdub\}_H, \quad (a = -a^1; b = -b^1; c = c^1; d = d^1) \] (A.24)
where \(\{A\}_H = \frac{1}{2}(A + A^\dagger)\).

Finally, use is made of the rules which follow immediately from (A.10):
\[ P_0iS = isQ_0 = S_+, \] (A.25a)
\[ Q_0iS = iSP_0 = -S_-, \] (A.25b)
\[ Q_0S_+ = S_+P_0 = P_0S_- = S_-Q_0 = S_+S_+ = S_-S_- \]
\[ = P_0Q_0 = Q_0P_0 = P_0 - \frac{Q_0}{a^n} = \frac{Q_0}{a^n} \]
(A.25c)

APPENDIX B

Commutators of Scalar Products

Using the notation of (2.3) and well-known commutation rules, we obtain the following expressions for the final tensor components. \(\epsilon_{rijk}\) is the permutation symbol originating from the angular momentum commutation rules. The usual summation convention is assumed. \(a\) is antihermitean \((iS)\) and \(b\) hermitean \(\text{or vice versa}\). \(\{x\}_H\) means \(\frac{1}{2}(x + x^\dagger)\). \(\{x\}_H\) defined below indicates symmetrization with respect to the indices
\[ \langle a_{(1)}, b_{(1)} \rangle_{(2)}^{(2)}_{fgh} = \{[a_f, b_g]\}^S = \frac{1}{2}([a_f, b_g] + [a_g, b_f]), \] (B.1)
\[ \langle a_{(1)}, b_{(1)} \rangle_{(1)}^{(1)}_{f} = h\{-i\epsilon_{jkh}a_jb_k\}_H, \] (B.2)
\[ \langle a_{(1)}, b_{(2)} \rangle_{(3)}^{(3)}_{fgh} = \{[a_f, b_{gh}]\}^S = \frac{1}{2}([a_f, b_{gh}] + [a_{gh}, b_f]), \] (B.3)
\[ \langle a_{(1)}, b_{(2)} \rangle_{(2)}^{(2)}_{fgh} = h\{-i\epsilon_{jkh}a_jb_{fh}\}_H^S = h\{-i\epsilon_{jkh}a_jb_{fh} - i\epsilon_{ijk}a_kb_{gj}\}_H, \] (B.4)
\[ \langle a_{(1)}, b_{(3)} \rangle_{(4)}^{(4)}_{fgh} = \{[a_f, b_{gh}]\}^S = \frac{1}{2}([a_f, b_{gh}] + [a_{gh}, b_f]), \] (B.5)
\[ \langle a_{(1)}, b_{(3)} \rangle_{(3)}^{(3)}_{fgh} = h\{-i\epsilon_{jkh}a_jb_{gh}\}_H^S = h\{-i\epsilon_{jkh}a_jb_{gh} - i\epsilon_{ijk}a_kb_{hj} - i\epsilon_{ijk}a_kb_{gh}\}_H, \] (B.6)
\[ \langle a_{(2)}, b_{(2)} \rangle_{(4)}^{(4)}_{fgh} = \{[a_{fg}, b_{hij}]\}^S = \frac{1}{2}([a_{fg}, b_{hij}] + [a_{hij}, b_{fg}]), \] (B.7)
\[ \langle a_{(2)}, b_{(2)} \rangle_{(3)}^{(3)}_{fgh} = h\{-i\epsilon_{jkh}a_jb_{fh}\}_H^S = h\{-i\epsilon_{jkh}a_jb_{fh} - i\epsilon_{jkh}a_jb_{fh}\}_H \]
\[ - i\epsilon_{jkh}a_jb_{fh} + i\epsilon_{jkh}a_jb_{fh} \] (B.8)
\[ \langle a_{(2)}, b_{(3)} \rangle_{(5)}^{(5)}_{fghij} = \{[a_{fg}, b_{hij}]\}^S = \frac{1}{2}([a_{fg}, b_{hij}] + [a_{hij}, b_{fg}]), \] (B.9)
\[ \langle a_{(2)}, b_{(3)} \rangle_{(4)}^{(4)}_{fgh} = h\{-i\epsilon_{jkh}a_jb_{hij}\}_H^S \]
\[ = h\{-i\epsilon_{jkh}a_jb_{hij} - i\epsilon_{jkh}a_jb_{hij} - i\epsilon_{jkh}a_jb_{hij} \]
\[ - i\epsilon_{jkh}a_jb_{hij} - i\epsilon_{jkh}a_jb_{hij} - i\epsilon_{jkh}a_jb_{hij}\}_H, \] (B.10)
\[
\langle a^{(2)} b^{(4)} \rangle_{fghijk}^{(6)} = \{ [a_{fgh}, b_{ijk}] \} = \frac{1}{2} \{ [a_{fgh}, b_{ijk}] + \{ a_{ijk}, b_{fgh} \} \},
\]

\[
\langle a^{(3)} b^{(3)} \rangle_{fghijk}^{(6)} = \{ [a_{fgh}, b_{ijk}] \} = \frac{1}{2} \{ [a_{fgh}, b_{ijk}] + \{ a_{ijk}, b_{fgh} \} \}.
\]

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