Molecular Physics: An International Journal at the Interface Between Chemistry and Physics

An approach to the anomalous commutation relations of rotational angular momenta in molecules

J.M. Brown & B.J. Howard

a Department of Chemistry, The University, Southampton, SO9 5NH, U.K.
b Physical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ

Published online: 23 Aug 2006.

To cite this article: J.M. Brown & B.J. Howard (1976) An approach to the anomalous commutation relations of rotational angular momenta in molecules, Molecular Physics: An International Journal at the Interface Between Chemistry and Physics, 31:5, 1517-1525, DOI: 10.1080/00268977600101191

To link to this article: http://dx.doi.org/10.1080/00268977600101191

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions
An approach to the anomalous commutation relations of rotational angular momenta in molecules

by J. M. BROWN and B. J. HOWARD†
Department of Chemistry, The University, Southampton SO9 5NH, U.K.

(Received 19 November 1975)

1. INTRODUCTION

It has long been appreciated [1, 2] that the components of the rotational angular momentum of a molecule, when referred to molecule-fixed axes \((x, y, z)\), obey anomalous commutation relations

\[
[J_x, J_y] = -i J_z
\]

and cyclic permutations. In order to evaluate matrix elements of operator expressions which involve such components, Van Vleck [2] devised the method of reversed angular momentum. In this, he reversed the direction of each internal momentum \(P\) (which obey normal commutation relations) so that the components of the reversed angular momentum \(\bar{P} = -P\) obey commutation rules similar to (1). In this way he was able to exploit existing results from the coupling of angular momenta in atoms to the full since all the angular momentum operators obeyed the same (though anomalous) commutation relationships.

Over the past fifteen years, molecular spectroscopists have come to appreciate the power of the spherical tensor methods introduced by Racah [3] for dealing with coupling problems, particularly those which involve three or more angular momenta. These methods were introduced for atomic problems and are specifically based on the normal commutation relationships. An important early paper on the application of spherical tensor methods to molecular problems was that of Curl and Kinsey [4], in which they dealt with asymmetric top molecules. Subsequent papers have been concerned with angular momentum problems in diatomic molecules. The first of these, by Freed [5], was an attempt to marry existing spherical tensor algebra with the reversed momentum method, a difficult task, since each is based on different commutation relations. Carrington et al.

† Present address : Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ.
[6] introduced a slightly different approach which involved defining spherical tensor components with the sign of the $y$-component of the angular momentum reversed. More recently, Féménias and Athénour [7] have constructed a new spherical tensor algebra which is based on the anomalous commutation relations (1) rather than the normal relations.

In this paper we present an alternative approach to the calculation of matrix elements in molecular problems which we have used for several years in our laboratory (see, e.g., [8]); our approach is foreshadowed in the work of Curl and Kinsey [4]. We abandon the reversed angular momentum method and evaluate matrix elements directly in a space-fixed rather than a molecule-fixed axis system, referring components to axes mounted on the molecule only when necessary. In this way the anomalous commutation relations are completely avoided and spherical tensor methods can be applied if desired in their standard form. There is thus no necessity for introducing a cumbersome new mathematical apparatus, let alone the array of symbols which go with it. More important, we believe our approach offers greater physical insight into the various coupling schemes. Van Vleck introduced his reversed angular momentum method at a time when students of physics were familiar with atomic coupling schemes but not with those for molecules. It was therefore sensible to draw analogies with the atomic coupling schemes even though such analogies were mathematical rather than physical. Most molecular spectroscopists today have only a passing acquaintance with atomic coupling schemes and the force of Van Vleck's arguments is largely unappreciated. In this situation the concept of reversed angular momenta tends to confuse rather than to help and it is much more sensible to perform the calculation directly.

2. THE CALCULATION OF MATRIX ELEMENTS

Although we present our method using spherical tensor techniques, it should be emphasized at the outset that the general approach is equally applicable to a formulation in cartesian tensors. Furthermore, the approach is valid for both linear and non-linear molecules provided that the former are described using Hougen's isomorphic rotational hamiltonian [9].

The terms which involve rotational angular momenta in the molecular hamiltonian are first expressed in a space-fixed axis system $(X, Y, Z)$, that is an axis system which translates but does not rotate with the molecule. In this coordinate system all angular momentum components commute with the normal sign of $i$:

$$[J_x, J_y] = iJ_z, \text{ etc.}$$  \hspace{1cm} (2)$$

Spherical tensor methods [10, 11] are thus directly applicable since they are based on such normal commutation relations. Indeed, the definition of a spherical tensor $T^{k}_{\mu}(J)$ of rank $k$ and component $\mu$ can be taken as

$$[J_z, T^{k}_{\mu}(J)] = \mu T^{k}_{\mu}(J),$$  \hspace{1cm} (3 a)$$

$$[J_z, T^{k}_{\mu}(J)] = [k(k+1) - \mu(\mu+1)]^{1/2} T^{k}_{\mu\pm 1}(J),$$  \hspace{1cm} (3 b)$$

where $J_z = J_x + iJ_y$. Internal angular momentum operators (e.g. $L$, $S$) whose components obey (2) in either a space- or molecule-fixed axis system, present no problem and all the standard relationships can be invoked in evaluating their
matrix elements. It is only those operators which describe the rotation of the molecule-fixed axis system in space (J or N) which call for special attention; this is reasonable since such angular momenta are non-existent in atomic problems. These operators have simultaneous components referred to both space- and molecule-fixed axis systems and both components can be quantized. Nevertheless, such an operator is to be regarded as a space-fixed operator. It is related to infinitesimal rotations measured in a laboratory-fixed frame and its components measured in this frame are obviously meaningful; by contrast the significance of its components referred to the molecule-fixed axis system is much harder to grasp.

Suppose we have the scalar product of a rotation operator J and an internal angular momentum operator P which is quantized in the molecule-fixed axis system. Although it might appear sensible to evaluate J . P in a molecule-fixed axis system where both angular momenta operate, our method requires the tensor product to be expanded in the space-fixed axis system and then to refer the components of P to the molecular axis system using a rotation matrix D p q (1)(ω) [11], explicitly

\[ J \cdot P = \sum_p (-)^p T_p \lambda(J) T_{-p} \lambda(P) \]  

and

\[ T_p \lambda(P) = \sum_q D_{pq} (1)(\omega)^* T_q \lambda(P), \]

where the suffixes p and q refer to space- and molecule-fixed-components respectively† and ω stands for the three Eulerian angles (α, β, γ) which relate the two axis systems. From (4) and (5)

\[ J \cdot P = \sum_{p, q} (-)^p T_p \lambda(J) \mathcal{D}_{p q \lambda} (1)(\omega) \mathcal{D}_{-p q \lambda} (1)(\omega)^* T_q \lambda(P). \]  

The right-hand side of (6) may appear to be non-hermitian since \( T_p \lambda(J) \) does not commute with \( \mathcal{D}_{pq \lambda}(\omega)^* \), but the summation over p removes all non-commuting terms.

In order to sharpen the argument, let us consider \( P = S \), the electron spin angular momentum, for a diatomic molecule in the Hund's case a limit. Using standard nomenclature [12], we have

\[ \langle \eta' \Lambda' ; J'M'\Omega' ; S'\Sigma' | J . S | \eta \Lambda ; J M \Omega ; S \Sigma \rangle = \sum_{p, q} (-)^p \langle J'M'\Omega' | T_p \lambda(J) \mathcal{D}_{pq \lambda}(\omega)^* | J M \Omega \rangle \langle \eta' \Lambda' S'\Sigma' | T_q \lambda(S) | \eta \Lambda S \Sigma \rangle. \]  

The spin term is straightforward but the rotational term requires further consideration. It is most easily evaluated by introducing the projection operator onto the complete set of rotational functions between \( T_p \lambda(J) \) and \( \mathcal{D}_{pq \lambda}(\omega)^* \) (the closure relationship):

\[ \sum_p (-)^p \langle J'M'\Omega' | T_p \lambda(J) \mathcal{D}_{pq \lambda}(\omega)^* | J M \Omega \rangle \]

\[ = \sum_p \sum_{J'M'\Omega'} (-)^p \langle J'M'\Omega' | T_p \lambda(J) | J'M'\Omega'' \rangle \langle J'M'\Omega'' | \mathcal{D}_{pq \lambda}(\omega)^* | J M \Omega \rangle. \]  

† This association can be remembered with the help of the mnemonic, space and molecule.
For non-zero results, the first matrix element requires \( J' = J'' \), \( M' = p + M'' \) and \( \Omega' = \Omega'' \). Thus
\[
\text{RHS} = \sum_p (-)^p \langle J'M'\Omega' | T_p^{-1}(J) | J'M' - p\Omega' \rangle \langle J'M' - p\Omega' | \mathcal{D}_{-pq}^{(1)}(\omega)^\ast | JM\Omega \rangle 
\]
\[
= \sum_p (-)^p(-)^{J' - M'} \begin{pmatrix} J' & 1 & J' \\ -M' & p & M' - p \end{pmatrix} [J'(J' + 1)(2J' + 1)]^{1/2} (-)^{\Omega' - M' + p} 
\times \begin{pmatrix} J' & 1 & J \\ -\Omega' & q & \Omega \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -M' + p & -p & M \end{pmatrix} [(2J' + 1)(2J + 1)]^{1/2}.
\]
(9)

The orthogonality property of 3-j symbols
\[
\sum_p \begin{pmatrix} J & 1 & J \\ -M & p & M' - p \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -M' + p & -p & M \end{pmatrix} = (2J + 1)^{-1} \delta_{JJ'} \delta_{MM'}.
\]
(10)
can be invoked to simplify this expression, yielding the final result
\[
\sum_p (-)^p \langle J'M'\Omega' | T_p^{-1}(J) \mathcal{D}_{-pq}^{(1)}(\omega)^\ast | JM\Omega \rangle 
\]
\[
= (-)^{J' - \Omega'} \begin{pmatrix} J & 1 & J \\ -\Omega' & q & \Omega \end{pmatrix} [J(J + 1)(2J + 1)]^{1/2} \delta_{JJ'} \delta_{MM'}.
\]
(11)

In this way it can be seen that, given a phase choice implicit in equation (9) and discussed in more detail in the next section, all the equipment required for the evaluation of matrix elements in molecular angular momentum coupling problems exists in standard spherical tensor theory, irrespective of complexity. It may appear rather laborious to evaluate the matrix elements of rotational angular momentum operators in this way but it should be appreciated that equation (11) need only be derived once; thereafter it is only the result which is required. There is thus some point in defining a symbol for the operator combination on the left-hand side of equation (11), such as
\[
J_q = \sum_p (-)^p T_p^{-1}(J) \mathcal{D}_{-pq}^{(1)}(\omega)^\ast.
\]
(12)

Although \( J_q \) behaves rather like a tensor operator in the molecule-fixed axis system, it must be stressed that it is not a tensor operator since it does not satisfy the conditions given in (3 a) and (3 b). The definition in equation (12) provides the justification for the method given by Carrington et al. [6]. They expand \( J \cdot P \) as
\[
J \cdot P = \sum_q J_q T_q^{-1}(P)
\]
and then use equation (11) for the matrix elements of \( J_q \).

If the problem is formulated using cartesian rather than spherical tensors, the complication associated with reversed angular momentum can be avoided in exactly the same way. In this case the scalar product is expanded in terms of the cartesian components
Anomalous commutation of angular momenta

\[ \mathbf{J} \cdot \mathbf{P} = \sum_i J_i P_i \]

\[ = \sum_{i, \alpha} J_i \lambda_{i\alpha} P_\alpha, \quad (13) \]

where \( i \) runs over \( X, Y \) and \( Z \), \( \alpha \) runs over \( x, y \) and \( z \) and \( \lambda_{i\alpha} \) is a direction cosine, which is used to relate the space-fixed components of \( \mathbf{P} \) to its molecule-fixed components. The product \( J_i \lambda_{i\alpha} \) acts on the rotational basis functions and its matrix elements can be evaluated by using the closure relationship, as in equation (8). The matrix elements of the space-fixed components of \( \mathbf{J} \) are given by Condon and Shortley [13] and those of the direction cosines by Townes and Schawlow [14]. Using these results it is easy to show

\[ \langle JM\Omega \pm 1 | J_x \pm i J_y | JM\Omega \rangle = [J(J+1) - \Omega(\Omega \pm 1)]^{1/2}, \quad (14) \]

where \( J_x \) is the component of \( \mathbf{J} \) referred to the molecule-fixed axis system

\[ J_x = J_x \lambda_{Xx} + J_y \lambda_{Yx} + J_z \lambda_{Zx} \quad (15) \]

and similarly for \( J_y \).

3. Phase conventions

Some confusion has arisen in the past over the use of different phase conventions in the calculation of matrix elements. Once the relationship between the reversed angular momentum and the direct method has been clearly established, it is possible to set up a standard phase convention.

For molecular problems two phase choices must be made. The first is the well-established convention of Condon and Shortley [13] which takes the matrix elements of the space-fixed component \( J_x \) to be real and positive. This convention leads directly to the result

\[ \langle JM \pm 1 \Omega | J_x \pm i J_y | JM\Omega \rangle = [J(J+1) - M(M \pm 1)]^{1/2}. \quad (16) \]

In addition, for molecular problems, a second phase convention is required since there is an \( \Omega \)-dependent phase factor in the rotational wave function. The choice which we prefer and which is more widely used [11, 6] amounts to

\[ |JM\Omega \rangle = \left[ \frac{2J+1}{8\pi^2} \right]^{1/2} D_M^{JM}(\omega)^{*}. \quad (17) \]

We have used this result in the derivation of equation (9) in the previous section. The choice of phase factor implicit in (17) is equivalent to defining the matrix elements of \( J_x \), the component referred to the molecule-fixed axis system, as real and positive, that is to the result given in equation (14). The choice of phase factor has thus been made in the same spirit as that of Condon and Shortley for \( J_x \). Furthermore, it is consistent with that adopted in Hougen's monograph [12] and in the work of Féménias and Athénour [7]. Regrettably, it is the opposite choice to that adopted by Van Vleck in his pioneering work [2]; nevertheless we consider that there is a strong case for its universal adoption. For

† The phase convention used in this paper requires the matrix elements of the internal angular momentum component \( P_z \) to be real and positive, consistent with Condon and Shortley [13], whereas Van Vleck chose the matrix elements of the reversed angular momentum, \( \bar{P}_z \), to be real and positive.

M.P.

56
comparison with previous work, the matrix element for the spin-uncoupling
term in the rotational hamiltonian in a case a basis set has a negative sign:

\[
\langle J\Omega \pm 1; \Sigma \Sigma | \mathcal{H}_{\text{rot}} | J\Omega; \Sigma \Sigma \rangle = -B[J(J+1) - \Omega(\Omega \pm 1)]^{1/2}[S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}. \tag{18}
\]

Alternatively, matrix elements for a molecular hamiltonian in a case b basis set
with AN = ± 1 have the opposite sign to those derived in Van Vleck’s paper [2];
those with ΔN = 0, ± 2 have the same sign [8].

It should be realized that once the choice of phase factor has been made, the
transformation of basis function from one coupling scheme to another is no longer
arbitrary. For example, let us consider the coupling of the rotational and spin
angular momenta N and S to form the total angular momentum J:

\[
N + S = J. \tag{19}
\]

The space-fixed components of N and S commute and give representations in
different spaces. They also obey normal commutation relations, as do the
space-fixed components of J, from equation (19). The results of standard
angular momentum coupling theory [13] can thus be used to express the case b
function in terms of the decoupled space-fixed functions

\[
|\eta \Lambda; NKSJM\rangle = \sum_{M_N, M_S} (-1)^{N-S+M}[2J+1]^{1/2}
\begin{pmatrix}
N & S & J \\
M_N & M_S & -M
\end{pmatrix}

\times |\eta \Lambda\rangle |NM_NK\rangle |SM_SM_S\rangle \tag{20}
\]

with the restriction \( \Lambda = K \) for linear molecules [9]. Molecular interactions can
produce a decoupling of N and S in the function of the left hand side of (20) so
that the molecule-fixed components of these two angular momenta are quantized.
This is called the case a coupling scheme, although strictly speaking it refers to a
situation in which N and S are decoupled. However, we cannot express the case
b function in terms of case a functions using the standard angular momentum
coupling result because of the anomalous commutation relations of the molecule-
fixed components of J and because the molecule-fixed components of N and S
do not commute with each other†. A consistent coupling scheme is obtained by
re-writing (19) as

\[
J - S = N \tag{21}
\]

from which it can be seen that, since the molecule-fixed components of J and \(-S\)
commute with the anomalous sign, so also do those of \(N\). The correct
decomposition of the case b function into case a functions, with molecule-fixed
components quantized, is easily established from equation (20) using our
approach. The rotational wave-function |NM_NK\rangle is expressed in terms of the
rotation matrix element by equation (17) and the space-fixed spin function |SM_SM_S\rangle

† The two rotational angular momenta J and N have essentially the same operator forms
in terms of the Euler angles except that for N, the operations are performed with all space-
fixed spin coordinates held fixed, whereas for J the molecule-fixed spin coordinates are held
fixed [15, 6]. Thus the molecule-fixed components of J and S commute whereas those of
N and S do not.
Anomalous commutation of angular momenta

Anomalous commutation of angular momenta can be related to $|S \Sigma \rangle$ in a consistent manner by

$$|SM_S \rangle = \sum_\Sigma \Theta_{M \Sigma} |S \Sigma \rangle.$$  \hspace{1cm} (22)

These equations are substituted into the right-hand side of (20), the two rotation matrix elements are coupled together [11] and after some simplification we arrive at the final result

$$|\eta \Lambda ; NKSJM \rangle = \sum_\Sigma \Omega \left( \begin{array}{ccc} J & S & N \\ \Omega & -\Sigma & -K \end{array} \right) \times |\eta \Lambda ; S \Sigma ; J M \Omega \rangle.$$  \hspace{1cm} (23 a)

or alternatively, in terms of Clebsch–Gordan coefficients,

$$|\eta \Lambda ; NKSJM \rangle = \sum_\Sigma \Omega \left( \begin{array}{ccc} - \Sigma^{J+1} |JSNK| \right) |\eta \Lambda ; S \Sigma ; J M \Omega \rangle.$$  \hspace{1cm} (23 b)

This transformation is the same as that which is obtained by blindly applying the standard equation, such as (20) to the coupling of $J$ and $-S$, except for the important phase factor. As expected, the transformation in (23) has a different phase factor from that implied in Van Vleck’s work (see Hougen [16]).

An exactly analogous problem arises in the description of the coupling between rotational and vibrational angular momenta in spherical top molecules. For example, the vibrational angular momentum $j$ in an $F_1$ or $F_2$ vibrational level can be written

$$j = \zeta \mathbf{L},$$  \hspace{1cm} (24)

where $\zeta$ is a constant and $\mathbf{L}$ is a vector which has the properties of an angular momentum operator of unit magnitude and with components which obey normal commutation relations [17]. The vibrational wave-functions can be conveniently classified by their transformation properties under $\mathbf{L}$. Coriolis interactions in such a vibrational state cause the $3(2J+1)$-fold degeneracy of a rotational level $J$ to be lifted. The vibration-rotation wave-functions can then be labelled by a quantum number $R$ associated with the operator

$$R = J - L.$$  \hspace{1cm} (25)

In contrast to those of $\mathbf{L}$, the molecule-fixed components of $J$ and hence $R$, obey anomalous commutation relations. The analogy between equations (21) and (25) allows the expression for the vibration-rotation basis functions in terms of the decoupled basis functions to be written down immediately:

$$|JLRk_R M \rangle = \sum_{k_J, k_L} (-)^{R-L+k_J[2R+1]} \left( \begin{array}{ccc} J & L & R \\ k_J & -k_L & -k_R \end{array} \right) \times |JMk_J \rangle |Lk_L \rangle.$$  \hspace{1cm} (26 a)

or

$$|JLRk_R M \rangle = \sum_{k_J, k_L} (-)^{R-J+k_L(Jk_J L - k_L)} |JLRk_R \rangle |JMk_J \rangle |Lk_L \rangle.$$  \hspace{1cm} (26 b)

\* The vibrational wavefunctions cannot be classified in a simple way by their transformations under $j$ since the components of $j$ do not obey simple angular momentum commutation relations, see equation (24).
In these equations the functions $|Lk_L\rangle$ are the spherical tensor components of the three vibrational wave-functions [17]; the decoupled basis diagonalizes $\mathbf{J}, \mathbf{L}, J_z$ and $L_z$ while the coupled basis diagonalizes $\mathbf{J}, \mathbf{L}, \mathbf{R}$ and $R_z$. The quantum numbers $k_R$, $k_J$, and $k_L$ are associated with the operators $R_z$, $J_z$ and $L_z$ respectively. The phase choice in (26 a) or (26 b) differs from that used by Hecht [17].

4. ADDITIONAL REMARKS ON REVERSED ANGULAR MOMENTA

In this paper we have presented an alternative approach to the calculation of some matrix elements and transformation coefficients for molecular problems. We believe that our method is both easier to understand and to use than previous methods, principally because it avoids reference to reversed angular momenta. We emphasize that we intend no adverse criticism of Van Vleck's paper [2] (indeed, quite the opposite) but suggest that it has perhaps been put to some uses for which it was not really intended.

In an attempt to redress the balance, it should be pointed out that the concept of reversed angular momenta is extremely useful in a qualitative sense since it provides the key to understanding the symmetry classification of molecular wave-functions. Consider again the coupling of $\mathbf{N}$ and $\mathbf{S}$ to give the total angular momentum $\mathbf{J}$. As far as space-fixed components are concerned, each operator obeys normal commutation relations and those of $\mathbf{N}$ and $\mathbf{S}$ commute with each other. Thus the appropriate form of the vector coupling equation is (19) and $J$ and $M_J$ are the good quantum numbers as far as the space-fixed axes are concerned. For the molecule-fixed components, $\mathbf{J}$ and $\mathbf{N}$ obey the anomalous relations and $\mathbf{J}$ and $\mathbf{S}$ commute so that the vector coupling equation must be cast in the form (21) if the results of angular momentum theory are to be exploited. As a result, it is the molecule-fixed component of $\mathbf{N}$, that is $K$ or $\Omega - \Sigma$, which is useful for classifying states subject to the spin-uncoupling perturbation $-2BJ \cdot S$ rather than the component of $\mathbf{J}$. In the same way it is the quantum number $k_R = k_J - k_L$ rather than $k_J$ which is useful for classifying the vibration-rotation levels of a spherical top molecule under the influence of a Coriolis interaction. Similar arguments can be advanced to justify Hougen's quantum number $G$ which is used for classifying the ro-vibronic levels of symmetric top molecules [18]. In all these examples the resultant angular momentum quantum number (e.g. $N$ or $R$) has a formal rather than a physical significance since the associated operator has been chosen simply so that the form of the vector coupling equations is satisfied. The representations of these operators in the manifold of states to which they refer display angular momentum properties; when states outside this manifold are included, the quantum numbers lose their validity. Thus $R$ is a good quantum number for classifying the Coriolis-split levels of an isolated vibrational state of a spherical top molecule but ceases to be so when the state in question is perturbed by other vibrational levels.

We are very grateful to Professor I. M. Mills and Dr. A. G. Robiette for pointing out the relevance of our work to spherical top problems, to Dr. J. K. G. Watson for several edifying discussions and to Dr. F. D. Wayne for a critical reading of the manuscript. B.J.H. thanks the Royal Society for a Pickering Research Fellowship.
Anomalous commutation of angular momenta

REFERENCES