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Rotation operator formalism for open-shell complexes

Gerrit C. Groenenboom* and Ad van der Avoird
Institute of Theoretical Chemistry, N3RIM, University of Nijmegen
Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

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I. INTRODUCTION

The study of complexes containing open shell atoms and/or open-shell diatomic molecules is an active field of research. The theoretical description of these complexes is more involved than the description of complexes containing closed shell molecules because in general the interaction between the fragments is determined by multiple, asymptotically degenerate, potential energy surfaces. Usually, the explicit inclusion of nonadiabatic couplings between the (nearly) degenerate electronic states is avoided by switching to a diabatic basis. Another source of complication in an open-shell complex is the presence of electronic orbital and/or spin angular momentum.

The derivation of the rotational kinetic energy operator and its matrix elements for, e.g., a complex consisting of an open-shell diatomic molecule and a closed shell atom is a relatively straightforward extension of the derivation for open-shell diatomic molecules. Although the final expressions are simple, the derivation involves two-angle embedded angular momentum operators that satisfy awkward commutation relations. Several rigorous derivations dealing with two-angle embedded frames that can be found in the literature[1–4] do not use the full power of angular momentum theory. In Secs. II and III we will review the rotation operator formalism that we used in recent work [5–7]. The method is rather formal, but it is rigorous and compact and it simplifies the notorious phase convention problems[8] in the definition of the parity operator, as we will show in Sec. IV.

There are certain constraints on the angular expansion of diabatic potentials. For the case of an open shell diatomic molecule with a closed shell atom the proper functional form was derived by considering the multipole expansion of

*Electronic address: gerritg@theochem.ru.nl
the interaction energy[9]. For the open-shell atom+closed shell diatom the expressions were also derived by assuming that an open shell atom in, e.g., a P-state may be treated as if it were a closed shell diatomic molecule in a \( l = 1 \) state [10-12]. We derived the same functional forms in a more formal way, by requiring the interaction operator to be invariant under rotation, inversion, and hermitian conjugation [5, 6]. Recently it was shown that in the case of two interacting open shell atoms the analogy between an open shell atom and a diatomic molecule breaks down, whereas the formal approach still applies[13], as we will explain in Sec. V. All angular momentum theory used here can be found in Ref. [14], much of which is reviewed in Ref. [15].

II. ROTRONIC WAVE FUNCTIONS FOR NONLINEAR RIGID MOLECULES

Space-fixed and body-fixed electronic coordinates are related through

\[ r^{SF} = R(\alpha, \beta, \gamma) r^{BF}, \]

where the \( 3 \times 3 \) orthogonal matrix \( R \), expressed in \( xyz \) Euler angles, defines a so-called three-angle embedded frame. Following Wigner's convention, we have, for an electronic wave function expressed in body fixed electronic coordinates,

\[ \Phi^{\text{elec}}(r^{BF}) = \Phi^{\text{elec}}(R(\alpha, \beta, \gamma)^{-1} r^{SF}) = \hat{R}(\alpha, \beta, \gamma) \Phi^{\text{elec}}(r^{SF}). \]

Since we wish to include electronic spin it is convenient to switch to Dirac notation for the electronic wave function

\[ |n\Sigma\rangle^{SF} = \hat{R}(\alpha, \beta, \gamma) |n\Sigma\rangle^{BF}, \]

where the superscript indicates to which axis (or frame) the spin-projection quantum number \( \Sigma \) and possibly other electronic quantum numbers \( n \) refer. The rotation operator \( \hat{R}(\alpha, \beta, \gamma) \), in the active rotation convention has the explicit form

\[ \hat{R}(\alpha, \beta, \gamma) = e^{-i\alpha \hat{j}_z} e^{-i\beta \hat{j}_y} e^{-i\gamma \hat{j}_x}, \]

where \( \hat{j} \) is the space-fixed total electronic angular momentum operator. Matrix elements of this operator in the standard basis \( \{|JM\rangle, M = -J, \ldots, J\} \) are the familiar Wigner D-functions

\[ D^J_{M,\Omega}(\alpha, \beta, \gamma) = \langle JM | \hat{R}(\alpha, \beta, \gamma) | J\Omega \rangle. \]

For a rigid, nonlinear molecule we may now write an (unnormalized) rotronic wave function as

\[ D^{J*}_{M,\Omega}(\alpha, \beta, \gamma) |n\Sigma \rangle^{BF} = D^{J*}_{M,\Omega}(\alpha, \beta, \gamma) \hat{R}(\alpha, \beta, \gamma) |n\Sigma \rangle^{BF}. \]
Without the rotation operator in the middle the rotronic wave function would be a direct product of a pure nuclear rotational wave function and a purely electronic wave function and all rotational properties would follow from elementary angular momentum theory. Only two fundamental relations involving the rotation operator, given below, are required to derive the rotational properties of the body-fixed wave function. Note that the body-fixed electronic function $|nS\Sigma\rangle^{BF}$ depends on the nuclear coordinates via the choice of a frame attached to the nuclei.

The space-fixed total angular momentum operator $\hat{J}$ is given by

$$\hat{J} = \hat{\mathcal{L}} + \hat{j},$$  \hspace{1cm} (7)

with the nuclear angular momentum operator $\hat{\mathcal{L}}$ given by

$$\hat{L}_x = i \cos \alpha \cot \beta \frac{\partial}{\partial \alpha} + i \sin \alpha \frac{\partial}{\partial \beta} - i \frac{\cos \alpha}{\sin \beta} \frac{\partial}{\partial \gamma},$$ \hspace{1cm} (8)

$$\hat{L}_y = i \sin \alpha \cot \beta \frac{\partial}{\partial \alpha} - i \cos \alpha \frac{\partial}{\partial \beta} - i \frac{\sin \alpha}{\sin \beta} \frac{\partial}{\partial \gamma},$$ \hspace{1cm} (9)

$$\hat{L}_z = -i \frac{\partial}{\partial \alpha}.$$ \hspace{1cm} (10)

Body fixed components of this angular momentum operator are defined by

$$\hat{\mathcal{L}}^{BF} \equiv \Re(\alpha, \beta, \gamma)^T \hat{\mathcal{L}}$$ \hspace{1cm} (11)

and similarly for $\hat{j}^{BF}$ and $\mathcal{J}^{BF}$. The action of $\hat{\mathcal{L}}$ and $\hat{\mathcal{L}}^{BF}$ on the rigid rotor functions $D_{M,\Omega}^{J}$ is known from elementary angular momentum theory. The two fundamental relations involving the rotation operator are the defining property of a vector operator

$$\hat{R}(\alpha, \beta, \gamma) \hat{j} \hat{R}(\alpha, \beta, \gamma)^\dagger = \Re(\alpha, \beta, \gamma)^T \hat{j}$$ \hspace{1cm} (12)

and

$$\hat{L} \hat{R}(\alpha, \beta, \gamma) = -\hat{j} \hat{R}(\alpha, \beta, \gamma).$$ \hspace{1cm} (13)

This last relation may not be as familiar. For the $z$ component it is easily verified by applying $\hat{L}_z$ [see Eq. (10)] to the rotation operator defined in Eq. (4). The proof for the other components involves repeated use of Eq. (12). Actually, taking the complex conjugate of a matrix element $\langle J M | \ldots | J \Omega \rangle$ to the left and the right of Eq. (13) gives the familiar action of $\hat{\mathcal{L}}$ on $D_{M,\Omega}^{J*}(\alpha, \beta, \gamma)$. Eq. (12) may be rewritten as

$$\Re^T \hat{j} \hat{R} = \hat{R} \hat{j},$$ \hspace{1cm} (14)
where we omitted the Euler angles for clarity, and together with Eq. (13) this gives
\[
\mathbb{R}^T \hat{L} \hat{R} = -\mathbb{R}^T \hat{j} \hat{R} = -\hat{R} \hat{j}.
\] (15)

Adding Eqs. (14) and (15) gives
\[
\mathbb{R}^T \hat{j} \hat{R} = 0 \quad \text{and hence} \quad \hat{j} \hat{R} = 0.
\] (16)

This proves that
\[
\hat{j} |nS\Sigma\rangle_{\text{BF}} = \hat{j}^\text{BF} |nS\Sigma\rangle_{\text{BF}} = 0,
\] (17)
i.e., the body fixed electronic wave function is invariant under simultaneous rotation of the electrons and the nuclei. Furthermore, since the electronic angular momentum operator \( \hat{j} \) does not act on \( D_L^n(a,b) \) we find that applying \( \hat{j} \) or \( \hat{j}^\text{BF} \) to the rotronic wave function of Eq. (6) amounts to acting with \( \hat{L} \), respectively \( \hat{L}^\text{BF} \) on \( D_L^n(a,b) \).

III. ROTRONIC WAVE FUNCTIONS FOR DIATOMIC MOLECULES

For a diatomic molecule we take \( \beta \) and \( \alpha \) in Eq. (1) to be the polar angles defining the body-fixed z-axis of the molecule and we set \( \gamma \) to zero, which results in a two-angle embedded frame. The end-over-end angular momentum operator \( \hat{l} \) is obtained from the operators \( \hat{L} \) by dropping the terms involving \( \frac{\partial}{\partial \gamma} \). The expression equivalent to Eq. (14) for the \( \hat{l} \) operator, however, is more complicated [see Eq. (A28) in [7]] and it would seem that the derivation of the rotational properties of the (unnormalized) two-angle embedded rotronic functions
\[
D_{M\Omega}^L(a,\beta,0)\hat{R}(a,\beta,0)|n\Lambda\Sigma\rangle_{\text{SF}}^\text{SF},
\] (18)
where we explicitly included the electronic orbital angular momentum projection quantum number \( \Lambda \) is also more complicated. For this reason the two-angle embedded case is usually treated separately [1–4]. We observe, however, that for \( \Omega = \Lambda + \Sigma \) we have
\[
\hat{R}(a,\beta,0)|n\Lambda\Sigma\rangle_{\text{SF}}^\text{SF} = \hat{R}(a,\beta,\gamma)|n\Lambda\Sigma\rangle_{\text{SF}}^\text{SF} e^{\text{i} \alpha \gamma}
\] (19)
and with \( D_{M\Omega}^L(a,\beta,0)e^{\text{i} \alpha \gamma} = D_{M\Omega}^L(a,\beta,\gamma) \) we find
\[
\hat{L} D_{M\Omega}^L(a,\beta,0)|n\Lambda\Sigma\rangle_{\text{SF}}^\text{SF} = \hat{L} D_{M\Omega}^L(a,\beta,\gamma)\hat{R}(a,\beta,\gamma)|n\Lambda\Sigma\rangle_{\text{SF}}^\text{SF}
\] (20)
To evaluate the matrix elements of the \( \hat{l}^2 \) operator one commonly substitutes
\[
\hat{l}^2 = \hat{j}^2 - 2\hat{j}^\text{BF} \cdot \hat{j}^\text{BF} + \hat{j}^2,
\] (21)
where for a linear molecule $J \equiv j + l$. A previous derivation of this relation was cumbersome because of the complicated commutation relations between $j^{BF}$ and $J^{BF}$ [1]. However, the corresponding expression for space-fixed operators is easily derived by observing that $[\hat{J}_i, \hat{J}_j] = 0$. Next, switching to the body-fixed expression requires $[\hat{j}_i^{BF}, \hat{j}_j^{BF}(\alpha, \beta, \gamma)] = 0$, which is trivial, since the electronic operator $j^{BF}$ does not act on the rotation matrix. One should be aware, however, that sometimes the body-fixed operators are defined by a rotation from the right, in which case the order of $j^{BF}$ and $J^{BF}$ should be reversed. Finally, note that we do not have to rewrite $\hat{J}^2$ in body-fixed operators to compute the matrix elements, as was shown in the previous section.

IV. PARITY

The spatial inversion operator $\hat{i}$ inverts the space-fixed electronic and nuclear coordinates and leaves the space-fixed spin functions invariant. Since the body-fixed frame is attached to the nuclear coordinates, $\hat{i}$ also acts on the Euler angles. One axis of the body-fixed frame should be defined as the cross-product of the other two, in order to keep a right-handed frame. As a result, $\hat{i}$ maps a right-handed frame onto another right-handed frame and the action of $\hat{i}$ on the Euler angles follows from

$$\hat{i}R(\alpha, \beta, \gamma)\hat{i}^\dagger = R(\alpha', \beta', \gamma').$$

(22)

For example, in the case of the two-angle embedded frame define above we find

$$\alpha' = \hat{i}\alpha\hat{i}^\dagger = \alpha + \pi,$$

(23)

$$\beta' = \hat{i}\beta\hat{i}^\dagger = \pi - \beta.$$  

(24)

When evaluating the effect of this transformation on the rotation operator in the case of half-integer spin we should be aware that rotations over $2\pi$ radians do not correspond to the identity operator and we should use the relations for the rotation operator in function space

$$\hat{R}(\alpha, \beta, \gamma)\hat{R}(\hat{n}, \phi)\hat{R}^\dagger(\alpha, \beta, \gamma) = \hat{R}(R(\alpha, \beta, \gamma)\hat{n}, \phi),$$

(25)

where a rotation over an angle $\phi$ around the rotation axis $\hat{n}$ is written as $\hat{R}(\alpha, \phi) = e^{-i\phi\hat{n}^\dagger \hat{n}}$, and

$$\hat{R}_x(\pi)\hat{R}_y(\pi) = \hat{R}_z(\pi).$$

(26)

This procedure is shown in some detail in Ref. [7]. One can prove Eq. (26) using Eq. (25).
V. FUNCTIONAL FORM OF DIABATIC POTENTIALS

As a first example we consider the interaction between a closed shell molecule and an atom in a P-state. In this case the interaction potential can be modeled by treating the atom in the P-state as if it were a diatomic molecule in a \( l = 1 \) state [11]. The potential is then expanded just as in the diatom-diatom case. The same expansion can be found by a more formal approach[6]. Denoting the degenerate electronic states by \( |\lambda, \mu\rangle, \mu = -\lambda, \ldots, \lambda \), we introduce the electronic projection operator \( \hat{P} = \sum_{\mu} |\lambda, \mu\rangle \langle \lambda, \mu| \) and we define the potential operator by

\[
\hat{P} \hat{V} \hat{P} = \sum_{\mu', \mu} |\lambda, \mu'\rangle V_{\mu', \mu}(R, r) \langle \lambda, \mu|,
\]

where \( R, r \) are the usual atom-diatom Jacobi coordinates. The proper expansion for \( V_{\mu', \mu}(R, r) \) can now be found by requiring the operator \( \hat{V} \) to be invariant under rotation, inversion, hermitian conjugation, and time reversal

\[
\hat{R} \hat{V} \hat{R}^\dagger = \hat{V}, \quad \hat{i} \hat{V} \hat{i}^\dagger = \hat{V}, \quad \hat{\theta} \hat{V} \hat{\theta}^\dagger = \hat{V}, \quad \text{and} \quad \hat{\theta} \hat{V} \hat{\theta}^\dagger = \hat{V}.
\]

The potentials obtained in this way are called diabatic. The eigenvalues of the matrix with the elements \( V_{\mu', \mu}(R, r) \) correspond to the adiabatic potentials that can be obtained in quantum chemistry calculations. In a dynamical calculation the diabatic basis is preferred because the diabatic electronic states may be assumed (approximately) independent of the nuclear geometry. This procedure has also been applied to the case of open-shell diatom+closed shell atom[5].

To perform the rotation in Eq. (28) it is convenient to express the electronic operators \( |\lambda, \mu\rangle \langle \lambda, \mu| \) in irreducible tensor operators defined by

\[
\hat{T}^L_{Q}(\lambda) = \sum_{\mu' \mu} |\lambda, \mu'\rangle \langle \lambda, \mu| (-1)^{\lambda - \mu'} \begin{pmatrix} \lambda & L & \lambda \\ -\mu' & Q & -\mu \end{pmatrix} \sqrt{2L + 1}.
\]

When the electronic functions \( |\lambda, \mu\rangle \) are modeled as spherical harmonics \( Y_{\lambda, \mu}(\theta, \phi) \) we find that the tensor \( \hat{T}^L_{Q}(\lambda) \) is simply proportional to a spherical harmonic multiplicative operator \( Y_{LQ}(\theta, \phi) \) in the space spanned by \( \{Y_{\lambda, \mu}(\theta, \phi), \mu = -\lambda, \ldots, \lambda\} \),

\[
Y_{LQ}(\theta, \phi) = \hat{T}^L_{Q}(\lambda)c_{L}(\lambda),
\]

with

\[
c_{L}(\lambda) = (-1)^{\lambda} \frac{2L + 1}{\sqrt{4\pi}} \begin{pmatrix} \lambda & L & \lambda \\ 0 & 0 & 0 \end{pmatrix}.
\]

This coefficient is only non-zero when \( L \) is even. When the complex contains a single open-shell atom only terms with even \( L \) appear in the expansion of
the potential. Hence, in that case, the formal expansion of the potential in irreducible tensor operators and the expansion where the open-shell atom is treated as an effective diatomic molecule are equivalent.

In the case of two open-shell atoms it has been shown[13] that direct products of tensor operators of odd rank appear in the expansion. In this case the formal expansion does not correspond to an effective diatom-diatom model. In a long range expansion of the potentials the odd-rank terms actually do not contribute in first order. However, when these terms are not included, the number of degrees of freedom in the diabatic model is not equal to the number of adiabatic states, which makes it impossible to construct a diabatic model consistent with the adiabats for the full range of interatomic separations.

In recent work on the OH(2II) + HCl complex it was found that also the time-reversal invariance condition in Eq. (28) is essential[16].