Theor Chim Acta (1987) 71: 333-357

Theoretica
Chimica Acta

Fixed-nuclei and laboratory-frame formalisms for electron scattering by a spherical top, with full incorporation of symmetry

Najib Abusalbi, David W. Schwenke, C. Alden Mead, and Donald G. Truhlar

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

(Received September 24, 1986, revised and accepted January 28, 1987)

We discuss molecule-frame and laboratory-frame symmetry-adapted formalisms for electron scattering by a spherical top. The molecule-frame formalism is based on the fixed-nuclear-orientation approximation, both for electronically elastic scattering by a vibrationally rigid molecule and also for the more general case where electronic excitation and vibrational degrees of freedom are included. The laboratory-frame formalism is based on the exact symmetries of the problem, which are carefully related to the approximate symmetries of the molecule-frame treatment. We present both the forward and backward transformations between the two representations.

Key words: Electron scattering — Symmetry — Close coupling

1. Introduction

Calculations of electron scattering by molecules can be greatly facilitated by means of the fixed-nuclei approximation [1]. In this approximation, valid if the collison time is sufficiently short (incident electron energy sufficiently high), the scattering calculation is carried out in a body-fixed coordinate system, fixed with respect to the target molecule, and the incident electron's motion is decoupled from the rotational and vibrational motion of the target molecule in the calculation. Then the observable laboratory-frame scattering matrix can be calculated from the molecule-frame scattering matrix by an orthogonal transformation [2, 3].

For electronically elastic scattering by diatomic molecules, the method has been formulated by Temkin and coworkers [4] and by Burke and Sinfailam [5] with further theoretical developments and calculations by Burke and Chandra [6], Chang and Fano [7], and Shugard and Hazi [8]. Choi and Poe [9] have developed a generalization in which the projection of scattering electron angular momentum along the internuclear axis is treated as a conserved quantity, but other aspects of the fixed-nuclei approximation are relaxed.

Burke, Chandra, and Gianturco [10] have shown how to apply the method to scattering by general asymmetric top polyatomic molecules, and further developments and calculations have been carried out by Gianturco and Thompson and Jain and Thompson [11, 12]. Some interesting sum rules, valid for fixed-nuclei scattering of linear, symmetric-top, and spherical-top molecules, have been obtained by Shimamura [13–15].

The advantage of the fixed-nuclei approximation is that it accounts for the approximate channel decoupling that results under many conditions from the small ratio of electronic to nuclear masses. This small ratio means, for example, that the component $l_z (= \Lambda)$ of the scattering electron's orbital angular momentum along the internuclear axis is approximately conserved in electronically elastic electron-diatom collisions. More generally, if we neglect the kinetic energy operator associated with molecular rotation, the molecule-frame scattering matrix will be block diagonal in electronic basis functions that transform according to the irreducible representations of the molecular point group. Then, we can take advantage of the molecular symmetry quite transparently in fixed-nuclei calculations.

Although the usefulness of the fixed-nuclei approximation is beyond dispute, it does remain an approximation subject to limitations. It is expected to become invalid at energies near threshold [7,8], and recent studies [16] have indicated that, even for nonresonant scattering by the nonpolar H_2 molecule, there can be significant inaccuracies in the usual method of extracting cross sections from fixed-nuclei calculations even at energies several times threshold. Moreover, the method does not lend itself easily to systematic improvement. As it is usually formulated, there is no convenient way to bring in the nuclear kinetic energy as a correction. Thus, one might wish to use the fixed-nuclei approximation only for small electron-molecule distances or small orbital or total angular momenta, where it is most valid, transform these results to a laboratory-frame representation, and combine them with less approximate calculations for the long-range or high-angular-momentum processes [7, 17, 18]. However, for target molecules possessing symmetry, the symmetry operations that are appropriate in the fixed-nuclei formalism are only approximate symmetries for the full problem, and this complicates both the laboratory-frame treatment and the transformation formalism. In particular, the question of the correct inclusion of improper operations (reflections, inversions, rotary reflections) belonging to the molecular point group is not a trivial one. The reason for this is that the rotational wave function of the target molecule, taken as rigid, depends only on the Euler angles, for which no improper operations are defined. Nevertheless, there does exist a group of exact symmetries, isomorphic to the point group of the target molecule, which makes possible, in the exact problem as in the approximate approach, a full exploitation of the molecular symmetry. The present paper is concerned with the utilization of these symmetries from the points of view of both molecule-fixed and laboratory frames and with the relationship between them.

We are concerned with spherical-top molecules with symmetry. Since nearly all molecules of this type are of symmetry T_d or O_h, we confine ourselves to these two cases to avoid overburdening the notation. We exhibit both approximate and exact symmetries, identify appropriate quantum numbers, and show how to transform scattering amplitudes calculated in the fixed-nuclei approximation with approximate symmetries to give approximate results for the amplitudes with respect to the exact quantum numbers. We also present a few remarks on the incorporation of target symmetry into distortion potentials [19] for an approximate treatment of electron exchange in the electronically inelastic case.

A laboratory-frame calculation for scattering by methane was recently carried out by two of us together with Eades, Nam, Thirumalai, Dixon, and Dupuis [20]. In this calculation, however, the symmetry was not fully exploited. In a recent article by Natanson [21], the selection rules for electron scattering by polyatomic molecules are discussed using the formalism of the feasible permutation-inversion group, and correct results are presented, but without a full development of the quantum numbers and transformation rules. Our approach is somewhat different, though essentially equivalent; we feel that it is an appropriate and transparent approach to this problem.

The plan of the paper is as follows: Sect. 2 presents the fixed-nuclei approximation [10, 11] for elastic electron-spherical top scattering and obtains coupled-channel equations in a way which will facilitate the later transformation to the laboratory frame. One motivation for presenting this material in detail is that certain properties of the expansion of symmetry-adapted wave functions in terms of spherical harmonics need to be treated in considerable detail for our purposes. In Sect. 3, the problem is set up in the laboratory frame, and the exact symmetry operations are defined and compared with the approximate symmetries. Also, the transformation equations between the two systems are exhibited. It should be noted that this transformation is different from that used previously in the literature [10–15] in that it refers specifically to the exact quantum numbers of the system. Section 4 extends the discussion to include electronic excitation; in this section we assume that the initial electronic state is the ground state and that this is totally symmetric. Section 5 illustrates some of the results of Sects. 2–4 by specializing them to the case of T_d symmetry. Section 6 presents a brief summary.

For the convenience of the reader, all notation in this paper, including phases, is consistent with that of [20], and all angular momentum functions and coupling coefficients are defined using the convections of Edmonds [22].

2. Molecule-frame scattering theory for electronically elastic scattering

We will restrict our discussion to spherical-top molecules and assume that the molecule does not vibrate or rotate during a collision with a scattering particle. We also assume in this section that only one electronic state of the molecule is considered explicitly, i.e., charge polarization effects are included by effective potentials rather than by electronic-state close coupling [23, 24]. If the scattering particle is an electron then we assume that effects arising from exchange of the scattering particle with a bound electron are included by an effective exchange potential rather than by explicit anitsymmetrization [23, 24]. The frame transformations we present do not depend on the use of effective potentials to include charge polarization and exchange effects but the explicit form assumed for the wave function in this section [Eq. (1) below] does. The generalization to explicitly include excited electronic states of the target is considered in Sect. 5.

The total wavefunction for electronically elastic scattering of a particle by an N-electron molecular target in a totally symmetric electronic state can be expressed as

$$\Psi^{PU}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N, r, \tilde{\omega}; \boldsymbol{G}) = F^{PU}(r, \tilde{\omega}; \boldsymbol{G}')\Phi(\sigma)\phi_0^{P^0 1}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)\delta(\boldsymbol{G}-\boldsymbol{G}'), \tag{1}$$

where P stands for a particular irreducible representation of the molecular symmetry group, P^0 for the totally symmetric irreducible component of the representations (which is one-dimensional), and U for the component of the representations. The vectors $\boldsymbol{x}_i$ $(i=1, \ldots, N)$ are the space-spin coordinates of the target electrons, and $(r, \tilde{\omega}, \sigma)$ or $(\tilde{\boldsymbol{r}}, \sigma)$ denotes the space-spin coordinates $(r, \tilde{\theta}, \tilde{\phi}, \sigma)$ of the scattering particle; the tilde on $\tilde{\omega}$ or $\tilde{\boldsymbol{r}}$ denotes that angular coordinates are defined with respect to the molecule-fixed frame, and r is the distance of the particle from the center of mass of the molecule. For simplicity we use $\tilde{\omega}$ to denote $\tilde{\theta}$, $\tilde{\phi}$. $F^{PU}(r, \tilde{\omega}; \boldsymbol{G}')$ is the space wavefunction for the scattering electron, $\Phi(\sigma)$ is it spin wave-function, and $\phi_0^{P^0 1}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ is the anitsymmetrized electronic space-spin wavefunction for the target. The orientation of the target molecule with respect to laboratory-fixed axes is denoted by $\boldsymbol{G}$, which specifies the Euler angles α, β, and γ; $\boldsymbol{G}'$ denotes a particular fixed value of these angles.

The scattering function can be expanded as

$$F^{PU}(\tilde{\boldsymbol{r}}; \boldsymbol{G}') = \sum_{L=0}^{\infty} \sum_{H=1}^{H_{\max}(P,L)} r^{-1} f_{HL}^{PU}(r) X_{HL}^{PU}(\tilde{\omega}), \tag{2}$$

where $X_{HL}^{PU}(\tilde{\omega})$ are the symmetrized harmonics which define a basis for the Uth component of the Pth irreducible representation of the molecular point group, and where H distinguishes between basis functions corresponding to the same values of P, U, and orbital quantum number L. In writing this equation we have used the fact that $F^{PU}(\tilde{\boldsymbol{r}}; \boldsymbol{G}')$ is independent of $\boldsymbol{G}'$ because $\tilde{\boldsymbol{r}}$ is a molecule-fixed vector. We have denoted the maximum value of H by $H_{\max}(P, L)$. In practice, the sum over L is cut off at some maximum value $L_{\max}(P)$ for which the scattering calculations are reasonably converged. Furthermore, for a given P, U some L values are missing from Eq. (2) by symmetry.

The molecule-frame symmetrized harmonics are expressed as linear combinations of the spherical harmonics, i.e.

$$X^{PU}_{HL}(\tilde{\omega}) = \sum_{m_L} b^{PU}_{HLm_L} Y^{m_L}_{L}(\tilde{\omega}), \tag{3}$$

where m_L is the projection of L along the z-axis of the molecule-fixed frame. Equation (3) may be rewritten in a *bra-ket* form as

$$|LPUH\rangle = \sum_{m_L} \langle Lm_L | LPUH\rangle |Lm_L\rangle, \tag{4a}$$

where

$$b^{PU}_{HLm_L} = \langle Lm_L | LPUH\rangle. \tag{4b}$$

This form makes closures easier to see and thus will be useful in later sections of the paper. Note that in Sect. 3 we will use $|\boldsymbol{G}'LPUH\rangle$ to stand for the product basis functions $\delta(\boldsymbol{G}-\boldsymbol{G}')X^{PU}_{HL}(\tilde{\omega})$ that occur when Eq. (2) is substituted into Eq. (1). In this article we do not explicitly indicate upper and lower limits of sums over angular momentum projections since such sums always go over the usual range from minus to plus the angular momentum quantum number. In practice however some terms may be zero; for example the sum in (3) need only include values of m_L for which $b^{PU}_{HLm_L} \neq 0$ by symmetry. The expansion coefficients for the symmetrized harmonics of spherical top point groups like the tetrahedral T_d (e.g. CH_4) or the octahedral O_h (e.g. SF_6) groups as well as for other symmetry groups were derived by Altmann and Cracknell [25]. Their real coefficients, which we denote by $\bar{b}^{PUc}_{HL|m_L|}$ or $\bar{b}^{PUs}_{HL|m_L|}$, are related to those of Eq. (3) as follows

$$b^{PU}_{HLm_L} = \begin{cases} \bar{b}^{PUc}_{HL|m_L|}, & m_L = 0 \\ \dfrac{1}{\sqrt{2}} i^{m_L+|m_L|}[\bar{b}^{PUc}_{HL|m_L|} - i \operatorname{sign}(m_L)\bar{b}^{PUs}_{HL|m_L|}], & m_L \neq 0 \end{cases} \tag{5}$$

where the superscripts c and s respectively stand for the c-type and s-type harmonics, i.e. functions with $\cos m_L\phi$ and $\sin m_L\phi$ dependency [25]. Notice that although the sum in Eq. (3) in principle has $(2L+1)$ terms, in practice many of the coefficients vanish by symmetry. Also $\bar{b}^{PUc}_{HL|m_L|}$ and $\bar{b}^{PUs}_{HL|m_L|}$ are never both different from zero. It follows from this fact and from Eqs. (4) and (5) that $b^{PU}_{HLm_L}$ is always either real or pure imaginary. With these conventions, the $X^{PU}_{HL}(\tilde{\omega})$ defined by Eqs. (3) and (5) are always real functions, and they transform under the symmetry group according to real, orthogonal, irreducible representations.

The basis functions $X^{PU}_{HL}(\tilde{\omega})$ are normalized such that

$$\int d\tilde{\omega} X^{P'U'*}_{H'L}(\tilde{\omega}) X^{PU}_{HL}(\tilde{\omega}) = \delta_{PP'}\delta_{UU'}\delta_{HH'}. \tag{6}$$

The coefficients $b^{PU}_{HLm_L}$ then satisfy the orthonormality relations [10]

$$\sum_{m_L} b^{P'U'*}_{H'Lm_L} b^{PU}_{HLm_L} = \delta_{PP'}\delta_{UU'}\delta_{HH'} \tag{7}$$

and

$$\sum_{P} \sum_{U=1}^{U_{\max}(P)} \sum_{H=1}^{H_{\max}(P,L)} b^{PU*}_{HLm_L'} b^{PU}_{HLm_L} = \delta_{m_L m_L'}. \tag{8}$$

It is easier to see these orthonormality relations by using the *bra-ket* interpretation of $b^{PU}_{HLm_L}$ introduced in (4b).

For electronically elastic scattering the effective potential has the full symmetry of the molecule, and hence it can be written as [10, 26]

$$v(r, \tilde{\omega}) = \sum_{\lambda=0}^{\infty} \sum_{h_\lambda=1} V_{\lambda h_\lambda}(r) X^{P^0 1}_{h_\lambda \lambda}(\tilde{\omega}), \tag{9}$$

where the number of terms in the sum over h_λ is the number of generalized harmonics with $P = P^0$ and with λ nodes in θ. With $X^{P^0 1}_{h_\lambda \lambda}(\tilde{\omega})$ given by (3) with the phase conventions of (4a) and (4b) the potential components $V_{\lambda h_\lambda}(r)$ are real. The sum over λ in Eq. (9) is truncated for practical purposes at some maximum value $\lambda_{\max}$ for which the right hand side of (9) converges sufficiently well to $v(r, \tilde{\omega})$.

We will require matrix elements of the effective potential between two angular basis functions, i.e.,

$$\begin{aligned} V^{P'U'PU}_{H'L'HL}(r) &= \langle L'P'U'H'|v|LPUH\rangle \\ &= \int d\tilde{\omega} X^{P'U'*}_{H'L'}(\tilde{\omega}) v(r, \tilde{\omega}) X^{PU}_{HL}(\tilde{\omega}). \end{aligned} \tag{10}$$

Since $v(r, \tilde{\omega})$ is totally symmetric [i.e. it belongs to the first irreducible representation ($P = P^0$, $U = 1$) of the symmetry group] and is a scalar operator, the only nonzero integrals are those diagonal in the irreducible representations P[27] and consequently in their components U since all the partners (or components) in the same basis in a multidimensional representation are taken here as orthogonal [25, 28]. The nonzero elements will be called $V^{PU}_{HLH'L'}$ or $\langle L'PUH'|v|LPUH\rangle$, and they are independent of U. Substituting (3) and (9) into (10) yields

$$\begin{aligned} V^{PU}_{H'L'HL}(r) = \sum_{m_L} \sum_{m_L'} \sum_{\lambda=0}^{\lambda_{\max}} \sum_{h_\lambda} \sum_{m_\lambda} b^{PU*}_{H'L'm_{L'}} b^{PU}_{HLm_L} b^{P^0 1}_{h_\lambda \lambda m_\lambda} \\ \times V_{\lambda h_\lambda}(r) \int d\tilde{\omega} Y^{m_L^*}_{L'}(\tilde{\omega}) Y^{m_\lambda}_{\lambda}(\tilde{\omega}) Y^{m_L}_{L}(\tilde{\omega}). \end{aligned} \tag{11}$$

The integral in (11) can be done using Eqs. (2.5.6) and (4.6.3) of Edmonds [22]; this yields

$$V^{PU}_{H'L'HL}(r) = (4\pi)^{-1/2} V_{01}(r) \delta_{LL'} \delta_{HH'} + \sum_{\lambda>0}^{\lambda_{\max}} \sum_{h_\lambda} C^{PU}_{H'L'HL;\lambda h_\lambda} V_{\lambda h_\lambda}(r), \tag{12}$$

where

$$\begin{aligned} C^{PU}_{H'L'HL;\lambda h_\lambda} = [(2L+1)(2\lambda+1)(2L'+1)/4\pi]^{1/2} \begin{pmatrix} L' & \lambda & L \\ 0 & 0 & 0 \end{pmatrix} \\ \times \sum_{m_{L'}} b^{PU*}_{H'L'm_{L'}} (-1)^{M_{L'}} \sum_{m_L} b^{PU}_{HLm_L} \sum_{m_\lambda} b^{P^0 1}_{h_\lambda \lambda m_\lambda} \begin{pmatrix} L' & \lambda & L \\ -M_{L'} & m_\lambda & m_L \end{pmatrix}, \end{aligned} \tag{13}$$

in which $\left(\begin{smallmatrix} a & b & c \\ d & e & f \end{smallmatrix}\right)$ is a $3j$ symbol. In addition to symmetry selection rules, the $3j$ selection rules restrict the nonzero elements in (13) as follows

$$L+\lambda+L'=\text{even}, \tag{14a}$$

$$|L'-L|\leq\lambda\leq L'+L, \tag{14b}$$

and

$$m_L+m_\lambda-m_{L'}=0. \tag{14c}$$

Although, as stated above, the coefficients $b^{PU}_{HLm_L}$ are either real or pure imaginary, the selection rules given in (14) exclude the possibility of getting non-real coefficients $C^{PU}_{H'L'HL;\lambda h_\lambda}$ in (13). It is worth mentioning here that the coefficients in (13) corresponding to a multi-dimensional irreducible representation are independent of the choice of the component U of that particular representation.

To derive the close coupling equations we require that the Schrödinger equation be satisfied in the subspace spanned by the angular basis functions:

$$\int \mathrm{d}\tilde{\omega} X^{PU*}_{HL}(\tilde{\omega})[\mathscr{H}_{\text{eff}}(r,\tilde{\omega})-E]F^{PU}(r,\tilde{\omega})=0, \tag{15}$$

where

$$\mathscr{H}_{\text{eff}}(r,\tilde{\omega})=-\frac{\hbar^2}{2\mu_r}\nabla^2_r+v(r,\tilde{\omega}) \tag{16}$$

with μ_r the reduced mass and E the total energy. This yields

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{L(L+1)}{r^2}+\frac{2\mu_r}{\hbar^2}V^{PU}_{HLHL}(r)+k^2\right]f^{PU}_{HL}(r)=-\frac{2\mu_r}{\hbar^2}\sum_{H'L'}{}' V^{PU}_{HLH'L'}(r)f^{PU}_{H'L'}(r), \tag{17}$$

where $\sum'$ indicates that the sum does not include the term corresponding to $H'=H$ and $L'=L$, and where k is the scattering particle's wave number given by

$$k^2=2\mu_r E/\hbar^2. \tag{18}$$

The solution to the close coupling equations with scattering boundary conditions yields the transition matrix elements $T^{PU}_{HLH'L'}$. Section 3 gives the frame transformation from the molecule-fixed to the laboratory-frame T matrix which can be used to calculate the differential $\mathrm{d}\sigma_{jj'}/\mathrm{d}\Omega$, integral $\sigma_{jj'}$, and momentum transfer $\sigma^m_{jj'}$ state-to-state (rotationally elastic and inelastic) cross sections for initial rotational quantum number j and final rotational quantum number j'. Alternatively one can calculate the orientation-averaged cross sections directly in the molecule-fixed frame, e.g. the orientation-averaged integral cross section is given by

$$\bar{\sigma}=\frac{\pi}{k^2}\sum_{L'}\sum_{L}\sum_{H'}\sum_{H}\sum_{P}\sum_{U}|T^{PU}_{HLH'L'}|^2. \tag{19}$$

Under the assumption that the internal energy differences of the rigid rotator are negligible with respect to E, the orientation-averaged cross sections are equal to the rotationally summed state-to-state cross sections obtained by the frame transformation, i.e.

$$\bar{\sigma} = \sum_{j'} \sigma_{jj'}. \tag{20}$$

Notice that in the fixed-nuclei approximation the sum in (20) is independent of j.

We note that for calculations the number of coupled Eqs. (17) is made finite by imposing an upper limit $L_{\max}$ on the orbital angular momentum L for every irreducible representation. One can use the same $L_{\max}$ for every P (following the procedure suggested by Burke et al. [10] in their discussion of low-energy e^- scattering by the C_{2v} asymmetric-top H_2O for which they used $L_{\max}=6$ as an example) or by choosing a different $L_{\max}$ for every P (following the procedure used by Gianturco and Thompson [11] for T_d spherical-top CH_4). For accurate results the cross section s of interest should be converged with respect to increasing $L_{\max}(P)$ for all P.

3. Exact symmetries in laboratory frame; transformation between molecule-fixed and laboratory-fixed frames

3.1. Definition of laboratory-frame symmetry-adapted basis functions

In this subsection we define laboratory-frame symmetry-adapted basis functions in a way that is convenient for our purposes. In a laboratory-fixed frame, the target molecule is no longer treated as fixed in orientation, but as a spherical top capable of rotation relative to the laboratory. We will continue though to treat the target as rigid, i.e. non-vibrating. A convenient basis set from which to start is that made up of simple products of angular momentum eigenfunctions for the top and the scattering particle:

$$\chi^{jl}_{k_j m_j m_l}(\boldsymbol{G}, \omega) = D^{j}_{k_j m_j}(\boldsymbol{G})\, Y_l^{m_l}(\omega), \tag{21}$$

where $D^{j}_{k_j m_j}(\boldsymbol{G})$ is a spherical top wave function, $\boldsymbol{G}=(\alpha, \beta, \gamma)$ denotes the Euler angles fixing the orientation of the molecule relative to the laboratory-fixed axes, and $\omega=(\theta, \phi)$ stands for the angular coordinates of the electron, again relative to the laboratory. The quantum numbers referring to the electron in (21) are l, its orbital angular momentum quantum number in the laboratory frame, and m_l, the projection of l on the laboratory-fixed z-axis. Those for the target molecule are j for rotational angular momentum, k_j for the projection on the molecule-fixed z-axis, and m_j for the projection on the laboratory-fixed z-axis. It is known [22] that the spherical top wave functions in (21) can be expressed as

$$D^{j}_{k_j m_j}(\boldsymbol{G}) = N_j \mathscr{D}^{(j)}_{k_j m_j}(\boldsymbol{G}), \tag{22}$$

where

$$N_j = [(2j+1)/8\pi^2]^{1/2}, \tag{23}$$

and $\mathscr{D}^{(j)}_{k_j m_j}(\boldsymbol{G})$ is a finite-rotation matrix element for rotation of the coordinate system through the angles (α, β, γ) while holding the physical system fixed (or, equivalently, the inverse rotation applied to the system).

The basis functions that we will actually use in this section will be linear combinations of the functions (21) chosen in such a way that they (a) have definite values for the total angular momentum, J, and its projection on the laboratory-fixed z-axis, M, and (b) also exploit to the fullest the T_d or O_h symmetry of the target molecule. Property (a) is easily achieved using Clebsch-Gordan coefficients. To achieve property (b), it is necessary to investigate in some detail the consequences of the target symmetry for problems of this type.

The usefulness of T_d or O_h symmetry for our problem lies in the fact that certain orientations of the scattering particle relative to the target are symmetry-related and hence equivalent. The operations of T_d or O_h for our system are proper and improper rotations. These operations are to be formulated as operations on the wave functions of target and/or projectile which bring about the desired change in the relative configuration. One possible formulation for a proper rotation is to think of a group operation as a rotation of the scattering particle's wave function about a molecule-fixed axis. Similarly an improper group operation can be formulated as a proper rotation combined with inversion of the scattering particle's wave function through the origin at the center of the molecule. These operations, however, are only approximate symmetries of the system, since they fail to commute with the rotational kinetic energy of the target. In the case of a proper rotation, the same change in relative configuration can be brought about by applying the rotation in the opposite sense to the target wave function, leaving the wave function of the scattering particle unchanged. This operation affects only the quantum number k_j in (21). The inversion, however, cannot be applied to the target wave function, which is a function only of the orientational Euler angles. Since any set of Euler angles describes simply a sequence of *rotations* starting from some reference orientation, it is clear that no change in the Euler angles can be consistently interpreted as representing an inversion. Nevertheless, we can achieve the change in *relative* configuration defined by an improper group operation if we apply the rotational part in the reverse sense to the target wave function, followed by inversion of the *scattering particle* wave function. For basis functions in terms of spherical harmonics, like those of (21), this inversion simply results in multiplication by $(-1)^l$. Moreover, the group operations construed in this way are *exact* symmetries of the system. The impossibility of defining the inversion operator for the Euler angles is equivalent to the fact that inversion of a rigid molecule like methane is "unfeasible" since it would convert a right-handed molecule into a left-handed one [29]; however, we shall not require the concept of unfeasible operations for the work presented here.

Projections of the basis functions (21) onto irreducible representations of this group are thus obtained by taking linear combinations of target wave functions with various k_j, sometimes accompanied by multiplication by $(-1)^l$. We thus form linear combinations of the basis functions (21) which still have well-defined quantum numbers j, l, m_j, and m_l, and which belong to occurrence h, component μ of irreducible representation p:

$$\bar{\chi}^{al}_{jm_jm_l}(\boldsymbol{G}, \omega) = \bar{\chi}^{p\mu hl}_{jm_jm_l}(\boldsymbol{G}, \omega) = q_{ja} \sum_{k_j} B^{p\mu l}_{hjk_j} \chi^{jl}_{k_jm_jm_l}(\boldsymbol{G}, \omega), \tag{24}$$

where the $B^{p\mu l}_{hjk_j}$ are coefficients to be determined, q_{ja} is a phase factor chosen for convenience, and a is used as a shorthand notation for $(p\mu h)$. The coefficients $B^{p\mu l}_{hjk_j}$ are clearly related to the $b^{p\mu}_{hjk_j}$ as defined in (3), since both transform functions of definite angular momentum projection into ones belonging to irreducible representations. There are two differences, however. First, the rotational symmetry operations are applied to Eq. (24) in the opposite sense to that understood in Eq. (3), and to spherical top wave functions, not ordinary spherical harmonics. As the detailed analysis given in the appendix shows, this replaces each coefficient $b^{p\mu}_{hjk_j}$ by its complex conjugate. Secondly, the inversion operator applied to Eq. (3), with l and m_l replaced by j and k_j would correspond to multiplication by $(-1)^j$, whereas in our case, as we have seen, inversion results in multiplication by $(-1)^l$. This makes no difference if $(j-l)$ is an even number; if $(j-l)$ is odd, however, the behavior under improper operations of the resulting functions differs by a factor of (-1) from what it would be if $(j-l)$ were even. Thus, the coefficients $b^{p\mu}_{hjk_j}$ that give functions belonging to representation p and component μ in the molecule-frame symmetry-adapted basis will produce functions belonging to representation p and component μ in the laboratory-frame symmetry-adapted basis when $(j-l)$ is even but will produce functions belonging to representation $\bar{p}$ and component $\bar{\mu}$ in the laboratory-frame symmetry-adapted basis when $(j-l)$ is odd, where $(\bar{p}\bar{\mu})$ is the representation and component "conjugate" to $(p\mu)$ in the sense that it has the same behavior under proper rotations but differs in sign in its behavior under improper operations. In the case of O_h, the conjugate representation is obtained by interchanging the subscripts g and u. For T_d, A_1 and A_2 are conjugate as are T_1 and T_2. The representation E of T_d is its own conjugate; however, if the components s, t of E are chosen so as to be respectively odd and even under some arbitrarily chosen reflection operation, we have $\bar{s} = t$, $\bar{t} = -s$. We thus have

$$B^{p\mu l}_{hjk_j} = b^{p\mu *}_{hjk_j}, \quad \text{if } (j-l) \text{ is even;} \tag{25a}$$

and

$$B^{\bar{p}\bar{\mu}l}_{hjk_j} = b^{p\mu *}_{hjk_j}, \quad \text{if } (j-l) \text{ is odd.} \tag{25b}$$

This implies, for example, for T_d symmetry, that states with $p = A_1$ and $j \leq 5$ will always have $(j-l)$ even since there are no nonzero $b^{A_21}_{hjk_j}$ coefficients for $j \leq 5$. In addition, an initial state with $j = 0$ which belongs to A_1 for total angular momentum 0 (when $j = l$) will belong to representation A_2 for odd values of the total angular momentum. For another example, we note that for $j = 12$ there are two A_1 sets and only one A_2 set. More precisely, let $H_{\max}(p, j)$ be the number of occurrences of irreducible representation p in the decomposition of spherical harmonics of order j according to Eq. (3), and let $h_{\max}(p, j, l)$ be the number of occurrences of representation p in the decomposition (24) of the top-projectile product functions with fixed j, l, m_j, and m_l. We then have

$$h_{\max}(p, j, l) = H_{\max}(p, j), \quad \text{if } (j-l) \text{ is even;} \tag{25c}$$

$$h_{\max}(p, j, l) = H_{\max}(\bar{p}, k), \quad \text{if } (j-l) \text{ is odd.} \tag{25d}$$

Thus, the index h runs over the same range on both sides of Eqs. (25a) and (25b), but for a given p, μ, and j, there may be more or fewer nonzero $b^{p\mu}_{hjk_j}$ than $b^{\bar{p}\bar{\mu}}_{hjk_j}$.

The basis functions (24) can now be further transformed so as to have well-defined values of total angular momentum J and its projection M on the laboratory-fixed z-axis. The resulting functions are

$$\mathcal{Y}^{JM}_{jal}(\boldsymbol{G}, \omega) = \sum_{m_l} \sum_{m_j} (l m_l j m_j \,|\, l j J M) \bar{\chi}^{al}_{j m_j m_l}(\boldsymbol{G}, \omega), \tag{26}$$

where $(l m_l j m_j \,|\, l j J M)$ is a Clebsch-Gordan coefficient. We now consider the transformation between the laboratory-frame symmetry-adapted basis functions (26) and the molecule-frame ones used in the previous section.

3.2. *Transformation between basis sets*

In *ket* form, we can denote the laboratory-frame symmetry-adapted basis functions (26) by $|jalJM\rangle$. As explained below Eq. (4b), the molecule-frame symmetry-adapted basis functions with the molecule held rigidly at orientation $\boldsymbol{G}$ will be similarly denoted by $|\boldsymbol{G}LPUH\rangle$. Using Eqs. (3), (21), (22), (24), (26), we find for the basis transformation:

$$\begin{aligned}\langle \boldsymbol{G}LPUH \,|\, jalJM\rangle = N_j q_{ja} \sum_{m_L} \sum_{m_j} \sum_{m_l} \sum_{k_j} b^{PU*}_{HLm_L} B^{p\mu l}_{hjk_j} (l m_l j m_j \,|\, l j J M) \\ \times \int \mathrm{d}\boldsymbol{G}'\, \delta(\boldsymbol{G}-\boldsymbol{G}') \mathcal{D}^{(j)}_{k_j m_j}(\boldsymbol{G}') \int \mathrm{d}\tilde{\omega}'\, Y^{m_L^*}_{L}(\tilde{\omega}') Y^{m_l}_{l}(\omega').\end{aligned} \tag{27}$$

According to the conventions of Edmonds [22] (Chap. 4), the spherical harmonics transform from the molecule-fixed to the laboratory-fixed frame as follows

$$Y^{m_l}_{l}(\omega) = \sum_{m_l'} \mathcal{D}^{(l)}_{m_l' m_l}(\boldsymbol{G}) Y^{m_l'}_{l}(\tilde{\omega}). \tag{28}$$

Substituting (28) into (27) and integrating over $\tilde{\omega}$ yields

$$\begin{aligned}\langle \boldsymbol{G}LPUH \,|\, jalJM\rangle = \delta_{Ll} N_j q_{ja} \sum_{m_L} \sum_{m_l} \sum_{m_l'} \sum_{m_j} \sum_{k_j} b^{PU*}_{HLm_L} B^{p\mu l}_{hjk_j} (l m_l j m_j \,|\, l j J M) \\ \times \mathcal{D}^{(j)}_{k_j m_j}(\boldsymbol{G}) \mathcal{D}^{(l)}_{m_l' m_l}(\boldsymbol{G}) \delta_{m_L m_l'},\end{aligned} \tag{29}$$

which explicitly shows that the transformation is diagonal in the orbital quantum number, i.e. $l = L$. Summing over m_l' in (29) yields

$$\begin{aligned}\langle \boldsymbol{G}lPUH \,|\, jalJM\rangle = N_j q_{ja} \sum_{m_L} \sum_{m_l} \sum_{m_j} \sum_{k_j} b^{PU*}_{Hlm_L} B^{p\mu l}_{hjk_j} (l m_l j m_j \,|\, l j J M) \\ \times [\mathcal{D}^{(j)}_{k_j m_j}(\boldsymbol{G}) \mathcal{D}^{(l)}_{m_L m_l}(\boldsymbol{G})].\end{aligned} \tag{30}$$

Using Eq. (4.3.1) of Edmonds, the quantity in brackets may be expanded as follows

$$\begin{aligned}\mathcal{D}^{(j)}_{k_j m_j}(\mathbf{G}) \mathcal{D}^{(l)}_{m_L m_l}(\boldsymbol{G}) = \sum_{K=0}^{\infty} (j k_j l m_L \,|\, j l K, k_j + m_L) \mathcal{D}^{(K)}_{k_j + m_L, m_j + m_l}(\boldsymbol{G}) \\ \times (j l K, m_j + m_l \,|\, j m_j l m_l),\end{aligned} \tag{31}$$

where the second Clebsch-Gordan coefficient is written in Edmonds' complex conjugate notation introduced in his Eq. (3.5.2). Substituting (31) into (30) and summing over m_l and m_j gives $\delta_{JK}\delta_{M,m_j+m_l}$ by closure, and finally summing over K yields

$$\langle \boldsymbol{G}lPUH\,|\,jalJM\rangle = N_j q_{ja} \sum_{m_L}\sum_{k_j} b_{hjk_j}^{PU*} B_{hjk_j}^{p\mu l}(jk_j l m_L\,|\,jlJ, k_j+m_L)\mathscr{D}_{k_j+m_L,M}^{(J)}(\boldsymbol{G}) \tag{32}$$

3.3. *Transformation of matrices*

We now discuss the transformation of a matrix, for example the scattering matrix, transition matrix, or potential matrix. Without loss of generality we consider the transformation of the potential matrix.

In order to avoid any ambiguity, we will denote the $\tilde{\alpha}$th basis function in the molecule-fixed frame by $\Theta_{\tilde{\alpha}}(\tilde{\omega})$, where $\tilde{\alpha}$ denotes the collection P, U, H, and L, i.e.

$$\Theta_{\tilde{\alpha}}(\tilde{\omega}) = |\tilde{\alpha}\rangle = |\boldsymbol{G}LPUH\rangle. \tag{33}$$

We will denote the αth basis function in the laboratory-fixed frame by $\Phi_\alpha(\boldsymbol{G}, \omega)$ where α denotes the collection j, a, l, J, and M and where a denotes the collection p, μ, and h, i.e.

$$\Phi_\alpha(\omega, \boldsymbol{G}) = |\alpha\rangle = |jalJM\rangle. \tag{34}$$

The matrix elements in the molecule-fixed frame are then defined by

$$V_{\tilde{\alpha}'\tilde{\alpha}}(r) = \int \mathrm{d}\tilde{\omega}\; \Theta_{\tilde{\alpha}'}^{*}(\tilde{\omega}) v(r, \tilde{\omega}) \Theta_{\tilde{\alpha}}(\tilde{\omega}) \tag{35a}$$

$$= \langle \tilde{\alpha}'|v|\tilde{\alpha}\rangle \tag{35b}$$

$$= \delta(\boldsymbol{G}' - \boldsymbol{G})\langle L'P'U'H'|v|LPUH\rangle, \tag{35c}$$

and those in the laboratory-fixed frame are defined by

$$V_{\alpha'\alpha}(r) = \int \mathrm{d}\boldsymbol{G} \int \mathrm{d}\omega\; \Phi_{\alpha'}^{*}(\omega, \boldsymbol{G}) V(r, \omega, \boldsymbol{G}) \Phi_\alpha(\omega, \boldsymbol{G}) \tag{36a}$$

$$= \langle \alpha'|V|\alpha\rangle. \tag{36b}$$

Introducing two unit projection operators of the molecule-fixed frame in (36b), we get

$$V_{\alpha'\alpha}(r) = \langle \alpha'|\sum_{\tilde{\alpha}'} |\tilde{\alpha}'\rangle\langle\tilde{\alpha}'|V \sum_{\tilde{\alpha}} |\tilde{\alpha}\rangle\langle\tilde{\alpha}\,|\,\alpha\rangle. \tag{37}$$

Interchanging the sums and the integrations in (37) and using (35b) yields

$$V_{\alpha'\alpha}(r) = \sum_{\tilde{\alpha}'}\sum_{\tilde{\alpha}} \langle \alpha'\,|\,\tilde{\alpha}'\rangle V_{\tilde{\alpha}'\tilde{\alpha}}(r)\langle\tilde{\alpha}\,|\,\alpha\rangle. \tag{38}$$

Using the basis transformations given in Eq. (32), Eq. (38) may be explicitly written as

$$
\begin{aligned}
V_{\alpha'\alpha}(r) &= \langle j'a'l'J'M'|V|jalJM\rangle \\
&= N_{j'}N_j q^*_{j'a} q_{ja} \sum_{P'}\sum_{U'}\sum_{L'=0}^{\infty}\sum_{H=1}^{H_{\max}(P',L')}\sum_{P}\sum_{U}\sum_{L=0}^{\infty} \\
&\quad\times \sum_{H=1}^{H_{\max}(P,L)} \delta_{L'l'}\delta_{Ll} V_{\tilde{\alpha}'\tilde{\alpha}}(r) \sum_{m_{L'}}\sum_{k_{j'}} b^{P'U'}_{H'L'm_{L'}} \\
&\quad\times B^{p'\mu'l'*}_{h'j'k_{j'}}(j'L'J', k_{j'}+m_{L'}|j'k_{j'}L'm_{L'}) \\
&\quad\times \sum_{m_L}\sum_{k_j} b^{PU*}_{HLm_L} B^{p\mu l}_{hjk_j}(jk_jLm_L|jLJ, k_j+m_L) \\
&\quad\times \int \mathrm{d}\boldsymbol{G}\, \mathscr{D}^{(J')*}_{k_{j'}+m_{L'},M'}(\boldsymbol{G}) \mathscr{D}^{(J)}_{k_j+m_L,M}(\boldsymbol{G}).
\end{aligned}
\tag{39}
$$

Since the $\mathscr{D}^{(J)}_{MN}(\boldsymbol{G})$ functions are orthogonal in all three indices, $V_{\alpha'\alpha}(r)$ is diagonal in J and M. The diagonal elements are obtained by using Eq. (4.6.1) of Edmonds to do the integral and substituting the values of the normalization constants as given in (23). This yields

$$
\begin{aligned}
V^{JM}_{j'a'l'jal}(r) &= \langle j'a'l'JM|V|jalJM\rangle \\
&= q^*_{j'a'} q_{ja} (2j'+1)^{1/2}(2j+1)^{1/2}(2J+1)^{-1} \\
&\quad\times \sum_{P'}\sum_{U'}\sum_{H'=1}^{H_{\max}(P',l')}\sum_{P}\sum_{U}\sum_{H=1}^{H_{\max}(P,l)} V^{P'U'PU}_{H'l'Hl}(r) \\
&\quad\times \sum_{m_{L'}}\sum_{k_{j'}} b^{P'U'}_{H'l'm_{L'}} B^{p'\mu'l'*}_{h'j'k_{j'}} \sum_{m_L}\sum_{k_j} b^{PU*}_{Hlm_l} B^{p\mu l}_{hjk_j} \\
&\quad\times \delta_{k_{j'}+m_{L'},k_j+m_L}(j'l'J, k_{j'}+m_{L'}|j'k_{j'}l'm_{L'}) \\
&\quad\times (jk_jlm_L|jlJ, k_j+m_L).
\end{aligned}
\tag{40}
$$

The transformation given in Eq. (40) simplifies in the case that $V^{JM}_{j'a'l'jal}(r)$ and consequently $V^{P'U'PU}_{H'l'HL}(r)$ are matrix elements of a totally symmetric operator, such as the $v(r, \tilde{\omega})$ of Eq. (9) or the scattering operator. In such a case symmetry selection rules require that the matrix be block diagonal in the irreducible representations of the molecular point groups, and in their components. The nonzero elements in (40) will then be denoted $V^{JMp\mu}_{j'h'l'jhl}(r)$ and $V^{PU}_{H'l'HL}(r)$, and the equation may be rewritten as

$$
\begin{aligned}
V^{JMp\mu}_{j'h'l'jhl}(r) &= \langle j'p\mu h'l'JM|V|jp\mu hlJM\rangle \\
&= q^{p\mu *}_{j'h'} q^{p\mu}_{jh} (2j'+1)^{1/2}(2j+1)^{1/2}(2J+1)^{-1} \\
&\quad\times \sum_{P}\sum_{U}\sum_{H'=1}^{H_{\max}(P,l')}\sum_{H=1}^{H_{\max}(P,l)} V^{PU}_{H'l'Hl}(r) \\
&\quad\times \sum_{m_{L'}}\sum_{k_{j'}} b^{PU}_{H'l'm_{L'}} B^{p\mu l*}_{h'j'k_{j'}} \sum_{m_L}\sum_{k_j} b^{PU*}_{Hlm_L} B^{p\mu l}_{hjk_j} \\
&\quad\times \delta_{k_{j'}+m_{L'},k_j+m_L}(j'l'J, k_{j'}+m_{L'}|j'k_{j'}l'm_{L'}) \\
&\quad\times (jk_jlm_L|jlJ, k_j+m_L),
\end{aligned}
\tag{41}
$$

where

$$V_{H'l'Hl}^{PU}(r) = \langle l'PUH'|v|lPUH\rangle \delta(\boldsymbol{G}' - \boldsymbol{G}), \tag{42}$$

and where we have now denoted q_{ja} more explicitly as $q_{jh}^{p\mu}$.

In order to derive the backward (laboratory-fixed to molecule-fixed) transformation, consider

$$V_{\tilde{\alpha}'\tilde{\alpha}}(r) = \sum_{\alpha'}\sum_{\alpha} \langle \tilde{\alpha}\,|\,\alpha'\rangle\langle\alpha'|\,V|\alpha\rangle\langle\alpha\,|\,\tilde{\alpha}\rangle, \tag{43}$$

which, using Eqs. (32)–(36b), may be written explicitly as

$$\begin{aligned} V_{\tilde{\alpha}'\tilde{\alpha}}(r) = {} & \sum_{p'\mu'h'}\sum_{p\mu h}\sum_{j'l'}\sum_{jl}\sum_{J'M'}\sum_{JM} N_{j'}N_j q_{j'a'}^{*} q_{ja} \\ & \times \sum_{m_{L'}}\sum_{k_{j'}} \delta_{L'l'} b_{H'l'm_{L'}}^{P'U'*} B_{h'j'k_{j'}}^{p'\mu'l'} (j'k_{j'}l'm_{L'}\,|\,j'l'J', k_{j'}+m_{L'}) \\ & \times \mathscr{D}_{k_{j'}+m_{L'},M'}^{(J')*}(\boldsymbol{G}')\, V_{\alpha'\alpha}(r) \sum_{m_L}\sum_{k_j} \delta_{Ll} b_{Hlm_L}^{PU} B_{hjk_j}^{p\mu l*} \\ & \times (jlJ, k_j+m_L\,|\,jk_jlm_L)\, \mathscr{D}_{k_j+m_L,M}^{(J)}(\boldsymbol{G}). \end{aligned} \tag{44}$$

On the other hand, $V_{\tilde{\alpha}'\tilde{\alpha}}(r)$ may be expressed as in (35c), and we now integrate both (35c) and (44) over $\boldsymbol{G}$. Integrating (35c) yields $\langle l'P'U'H'|v|lPUH\rangle$, but when (44) is integrated over $\boldsymbol{G}'$ all terms except those containing $\mathscr{D}_{0,0}^{(0)*}(\boldsymbol{G}')$ yield zero. Furthermore, since the integral of (35c) is independent of $\boldsymbol{G}$, only those terms containing $\mathscr{D}_{0,0}^{(0)}(\boldsymbol{G})$ may survive integration of (44). Hence, $\langle l'P'U'H'|v|lPUH\rangle$ can be written as a sum over only terms with

$$J = J' = 0 \tag{45a}$$

$$M = M' = 0 \tag{45b}$$

and

$$k_j + m_L = k_{j'} + m_{L'} = 0. \tag{45c}$$

(45a) implies

$$j = 1 \quad \text{and} \quad j' = l' \tag{45d}$$

and (45b) implies

$$m_j + m_l = m_{j'} + m_{l'} = 0. \tag{45e}$$

Since

$$\int \mathrm{d}\boldsymbol{G}'\, \mathscr{D}_{00}^{(0)}(\boldsymbol{G}') = 8\pi^2, \tag{46}$$

we conclude that

$$\begin{aligned} V_{\tilde{\alpha}'\tilde{\alpha}}(r) & = \langle l'P'U'H'|v|lPUH\rangle \\ & = 8\pi^2 \sum_{p'\mu'h'}\sum_{p\mu h}\sum_{l'}\sum_{l} N_{l'}N_l q_{l'a'}^{*} q_{la} \sum_{m_{L'}} \delta_{L'l} b_{H'l'm_{L'}}^{P'U'*} \\ & \quad \times B_{h'l',-m_{L'}}^{p'\mu'l'} (l', -m_{L'}, l'm_{L'}\,|\,l'l'00)\, V_{l'a'l'lal}^{00}(r) \\ & \quad \times \sum_{m_L} \delta_{Ll} b_{Hlm_L}^{PU} B_{hl,-m_L}^{p\mu l*} (1100\,|\,l, -m_L, lm_L), \end{aligned} \tag{17}$$

where

$$V^{00}_{l'a'l'lal}(r) = \langle j' = l', p'\mu' h' l', J' = 0, M' = 0 | V | j = l, p\mu hl, J = 0, M = 0\rangle. \tag{48}$$

Summing over l and l' and substituting for N_l and $N_{L'}$ their values given by (23), (47) reduces to

$$\begin{aligned} V^{P'U'PU}_{H'l'Hl}(r) = {} & \sum_{p'\mu'h'} \sum_{p\mu h} q^*_{l'a'} q_{la} (2l+1)^{1/2} (2l'+1)^{1/2} \\ & \times \sum_{m_{L'}} \sum_{m_L} b^{P'U'*}_{H'l'm_{L'}} B^{p'\mu' l'}_{h'l',-m_{L'}} (l', -m_{L'}, l'm_{L'} | l'l'00) \\ & \times V^{00}_{l'a'l'lal}(r) b^{PU}_{Hlm_L} B^{p\mu l*}_{hl,-m_L} (ll00 | l, -m_L, lm_L). \end{aligned} \tag{49}$$

According to Eq. (3.5.13) of Edmonds

$$(l, -m_L, lm_L | 1100) = (-1)^{l+m_L} (2l+1)^{-1/2}. \tag{50}$$

Equation (49) then reduces to

$$\begin{aligned} V^{P'U'PU}_{H'l'Hl}(r) = {} & \sum_{p'\mu'h'} \sum_{p\mu h} q^*_{l'a'} q_{la} (-1)^{l+l'} \sum_{m_L} \sum_{m_{L'}} (-1)^{m_L + m_{L'}} \\ & \times b^{P'U'*}_{H'l'm_{L'}} B^{p'\mu' l'}_{h'l',-m_{L'}} b^{PU}_{Hlm_L} B^{p\mu l*}_{hl,-m_L} V^{00}_{l'a'l'lal}(r). \end{aligned} \tag{51}$$

For the special case of a totally symmetric operator, the matrix is diagonal in P and U or p and μ, and the diagonal elements become

$$\begin{aligned} V^{PU}_{H'l'HL}(r) = {} & \sum_p \sum_\mu \sum_{h'} \sum_h q^{p\mu *}_{l'h'} q^{p\mu}_{lh} (-1)^{l+l'} \sum_{m_L} \sum_{m_{L'}} (-1)^{m_L + m_{L'}} \\ & \times b^{PU*}_{H'l'm_{L'}} B^{p\mu l'}_{h'l',-m_{L'}} b^{PU}_{Hlm_L} B^{p\mu l*}_{hl,-m_L} V^{00p\mu}_{l'h'l'lhl}(r). \end{aligned} \tag{52}$$

Using the properties of the coefficients $b^{p\mu}_{hlm_l}$, namely those given in (5), (7), and (25) and summing over all indices, Eq. (51) reduces to

$$\begin{aligned} \langle lP'U'H' | V | lPUH \rangle = {} & q^{P'U'*}_{l'H'} q^{PU}_{lH} \langle j' = l', p' = P', \mu' = U', h' = H', l', J' = 0, \\ & M' = 0 | V | j = l, p = P, \mu = U, h = H, l, J = 0, M = 0 \rangle, \end{aligned} \tag{53}$$

and Eq. (52) becomes

$$\begin{aligned} \langle lPUH' | V | lPUH \rangle = {} & q^{PU*}_{l'H'} q^{PU}_{lH} \langle j' = l', p' = P, \mu' = U, h' = H', l', J' = 0, \\ & M' = 0 | V | j = l, p = P, \mu = U, h = H, l, J = 0, M = 0 \rangle. \end{aligned} \tag{54}$$

The last equation states that in the fixed-nuclei approximation the potential (or scattering) matrix in the molecule-fixed frame and in any irreducible representation of the molecular point group is equivalent, up to a phase factor, to the potential (or scattering) matrix in the laboratory-fixed frame also in the same irreducible representation with a zero total angular momentum.

4. Electronic excitation of a nondegenerate electronic state

We now consider electronically inelastic scattering of an electron by an N-electron spherical top molecule. A scattering channel $\tilde{\alpha}$ of definite symmetry properties is totally defined by specifiying the set of quantum numbers pertaining to the internal state of the molecule, the scattering electron's wave number $k_{\tilde{\alpha}}$, and the quantum numbers associated with the scattering electron, particularly its orbital angular momentum.

First we present the theory for a vibrationally rigid molecule; the generalization to include vibrational degrees of freedom will be presented in the last paragraph of this section. The total wavefunction of the $(N+1)$-electron system for some initial scattering channel α can be written as

$$\Psi^{PU}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N, r, \tilde{\omega}, \sigma) = \sum_i \sum_{P_i} \sum_{U_i} F_i^{P(i)U(i)}(r, \tilde{\omega})\phi_i(\sigma)\phi_i^{P_iU_i}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N), \quad (55)$$

where $\sum_i$ stands for a sum over the discrete electronic states of the molecule. We have again assumed that we need not explicitly antisymmetrize the wavefunction with respect to $(r, \tilde{\omega}, \sigma)$ and the coordinates of the bound electrons; this means that exchange effects are included by effective exchange potentials [19, 30-32]. In the close coupling approximation the sum over electronic states is truncated to include the initial state i_0 and one or more other states. For this paper, to simplify the sums, we will assume that the molecule is initialy in a nondegenerate state, but, following previous work on electron-atom scattering [19], we will show how to implement effective exchange potentials with no restrictions on the final state or any other state included in the expansion. The scattering function $F_i^{P(i)U(i)}(r, \tilde{\omega})$ in (55) belongs to the $U(i)$th component of the $P(i)$th irreducible representation, where $P(i)$ is one of the symmetries contained in the direct product of P_i, the internal-state irreducible representation of the target in electronic state i, and P, the irreducible representation to which the total wavefunction belongs:

$$P(i) = P \times P_i. \quad (56)$$

The scattering function can then be expanded in the basis of the symmetrized harmonics as follows

$$F_i^{P(i)U(i)}(r, \tilde{\omega}) = \sum_{l=0}^{\infty} \sum_{H=1}^{H_{\max}(P(i),l)} r^{-1} f_{iHl}^{P(i)U(i)}(r) X_{Hl}^{P(i)U(i)}(\tilde{\omega}). \quad (57)$$

We now consider the complete Schrödinger equation and require that it is satisfied in the subspace spanned by the basis functions defined by coupling the electron angular basis functions with the wavefunctions representing the target internal states, i.e.,

$$\int \mathrm{d}\boldsymbol{x}_1 \cdots \mathrm{d}\boldsymbol{x}_N \, \mathrm{d}\tilde{\omega} \, \mathrm{d}\sigma \, \phi_{i'}^{P_{i'}U_{i'}}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)^* X_{H'l'}^{P(i')U(i')}(\tilde{\omega})^* \Phi_{i'}^*(\sigma)$$
$$\times (\mathscr{H} - E)\Psi^{PU}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N, r, \tilde{\omega}, \sigma) = 0. \quad (58)$$

Substituting (55) and (57) into (58) and integrating over all variables yields the close coupling equations

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{l(l+1)}{r^2}-k_i^2\right)f_{iHl}^{P(i)U(i)}(r)$$

$$=-\frac{2\mu_r}{\hbar^2}\sum_{i'}\sum_{P(i')}\sum_{U(i')}$$

$$\times\sum_{l'=0}^{\infty}\sum_{H'=1}^{H_{\max}(P(i'),\,l')} V_{i'H'l'iHl}^{P(i')U(i')P(i)U(i)}(r)f_{i'H'l'}^{P(i')U(i')}(r), \tag{59}$$

where k_i^2 is the channel energy given by

$$k_i^2=\frac{2\mu_r}{\hbar^2}(E-\varepsilon_i), \tag{60}$$

in which ε_i is the internal excitation energy of the ith electronic state. The potential matrix elements in (59) are defined by

$$V_{i'H'l'iHl}^{P(i')U(i')P(i)U(i)}(r)=\langle l'P(i')U(i')H'|v_{i'i}|lP(i)U(i)H\rangle$$

$$=\int d\tilde{\omega}\,X_{H'l'}^{P(i')U(i')}(\tilde{\omega})^*v_{i'i}(r,\tilde{\omega})X_{Hl}^{P(i)U)i)}(\tilde{\omega}), \tag{61}$$

where $v_{i'i}(r,\tilde{\omega})$ is the effective transition potential for the $i\rightarrow i'$ transition, i.e.

$$v_{i'i}(r,\tilde{\omega})=\int \mathrm{d}\boldsymbol{x}_1\cdots\mathrm{d}\boldsymbol{x}_N\,\mathrm{d}\sigma\,\phi_{i'}^{P_{i'}U_{i'}}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)^*\Phi_{i'}^*(\sigma)v(\boldsymbol{x}_1,\ldots\boldsymbol{x}_N,r,\tilde{\omega})$$

$$\times\phi_i^{P_iU_i}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)\Phi_i(\sigma). \tag{62}$$

The effective transition potential belongs to one of the irreducible representations $P_{i'i}$ obtained from the direct product $P_{i'}\times P_i$. Hence, the only nonzero potential matrix elements in (61) are those for which the direct product $P(i')\times P(i)$ also contains one of the $P_{i'i}$. The potential matrix elements are explicitly given by the analogues of Eqs. (12) and (13), derived earlier for elastic scattering, i.e.

$$\langle l'P(i')U(i')H'|V_{i'i}|lP(i)U(i)H\rangle$$

$$=(4\pi)^{-1/2}v_{01}^{i'i}(r)\delta_{P(i')P(i)}\delta_{U(i')U(i)}\delta_{l'l}\delta_{H'H}+\sum_{\lambda>0}^{\lambda_{\max}}\sum_{h_\lambda}C_{H'l'Hl;\lambda h_\lambda}^{P(i')U(i')P(i)U(i)}v_{\lambda h_\lambda}^{i'i}(r), \tag{63}$$

where

$$C_{H'l'Hl;\lambda h_\lambda}^{P(i')U(i')P(i)U(i)}=[(2l+1)(2\lambda+1)(2l'+1)/4\pi]^{1/2}\begin{pmatrix} l' & \lambda & l \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times\sum_{m_l'}(-1)^{m_l'}b_{H'l'm_l'}^{P(i')U(i')*}\sum_{m_l}b_{Hlm_l}^{P(i)U(i)}$$

$$\times\sum_{m_\lambda}\sum_{P_{i'i}}\sum_{U_{i'i}}b_{h_\lambda\lambda m_\lambda}^{P_{i'i}U_{i'i}}\begin{pmatrix} l & \lambda & l \\ -m_l' & m_\lambda & m_l \end{pmatrix}, \tag{64}$$

in which $U_{i'i}$ is the component of $P_{i'i}$.

The transformation of these and other matrix elements to the laboratory-fixed frame is given by Eq. (40) and the inverse transformation by (51).

Finally we consider the local approximation for the exchange term. The exact exchange operators, although nonlocal, have the same transformation properties as the local potentials. The variational two-electron exchange term coupling electronic states i' and i for an antisymmetrized trial function is

$$\hat{v}^E_{i'i}F_i^{P(i)U(i)}(r,\boldsymbol{\omega}) = -\int \mathrm{d}\boldsymbol{x}_1\cdots\mathrm{d}\boldsymbol{x}_N\,\mathrm{d}\sigma\,\phi_{i'}^{P_{i'}U_{i'}^*}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)\Phi^*_{i'}(\sigma)$$

$$\times\sum_{\eta=1}^{N}\frac{1}{|\boldsymbol{r}_m-\boldsymbol{r}_\eta|}\hat{\tau}_\eta\phi_i^{P_iU_i}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)F_i^{P(i)U(i)}(\boldsymbol{r})\Phi_i(\sigma) \tag{65}$$

$$= -N\int \mathrm{d}\boldsymbol{x}_1\cdots\mathrm{d}\boldsymbol{x}_N\,\mathrm{d}\sigma\,\phi_{i'}^{P_{i'}U_{i'}^*}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)\Phi^*_{i'}(\sigma)$$

$$\times\frac{1}{|\boldsymbol{r}_m-\boldsymbol{r}_N|}\hat{\tau}_N\phi_i^{P_iU_i}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)F_i^{P(i)U(i)}(\boldsymbol{r})\Phi_i(\sigma), \tag{66}$$

where $\hat{\tau}_\eta$ is a permutation operator that permutes the molecule-frame space-spin coordinates $\boldsymbol{x}_\eta$ and $\boldsymbol{x}=(\boldsymbol{r}_m,\sigma)=(r,\boldsymbol{\omega},\sigma)$ and we have employed hartree atomic units. Following Refs. [30] and [31], the operator $\hat{v}^E_{i'i}$ as given in (66) may be approximated by the local coupling potential

$$v^E_{i'i}(\boldsymbol{r}) = -\frac{4\pi N}{\kappa_i^2(\boldsymbol{r},i',i)}\int \mathrm{d}\boldsymbol{x}_1\cdots\mathrm{d}\boldsymbol{x}_{N-1}\,\mathrm{d}\sigma_N\,\mathrm{d}\sigma\,\phi_{i'}^{P_{i'}U_{i'}^*}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_{N-1},\boldsymbol{r},\sigma_N)$$

$$\times\Phi^*_{i'}(\sigma)\phi_i^{P_iU_i}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_{N-1},\boldsymbol{r},\sigma)\Phi_i(\sigma_N), \tag{67}$$

where $\frac{1}{2}\kappa_i^2(\boldsymbol{r},i'i)$ is the local kinetic energy corresponding to the translational wavefunction $F_i^{P(i)U(i)}(\boldsymbol{r})$ as approximated for the coupling potential $V^E_{i'i}(\boldsymbol{r})$. In order for the coupled equations satisfied by the $F_j^{P(j)U(j)}(\boldsymbol{r})$ to be self-adjoint, we require

$$\kappa_i^2(\boldsymbol{r},i',i)=\kappa_{i'}^2(\boldsymbol{r},i,i'). \tag{68}$$

Furthermore, in order for $v^E_{i'i}(\boldsymbol{r})$ to transform the same as $\hat{v}^E_{i'i}$ under the symmetry operations of the molecular point group we require $\kappa_i^2(\boldsymbol{r},i',i)$ to transform according to be the ground state, only functions transforming according to the totally symmetric representation. We assume therefore that $\kappa_i^2(\boldsymbol{r},i',i)$ is approximated by some physical model, e.g. the self-consistent models previously applied to electron-atom scattering [19], that satisfies both of these requirements. Then $v^E_{i'i}(\boldsymbol{r})$ transforms as the direct product $P_{i'}\times P_i$ and we may treat it the same as $v_{i'i}(\boldsymbol{r})$ or Eq. (62).

So far this section has been explicitly concerned with electronic excitation of a vibrationally rigid molecule, but it is easily generalized to the case of vibrational or vibrational-plus-electronic excitation. This simply involves replacing the $\phi_i^{P_iU_i}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)$ by vibronic functions $\sigma_i^{P_iU_i}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N,Q_1,\ldots,Q_{3N_A-6})$, where N_A is the number of atoms in the molecule, $\{Q_i\}_{i=1}^{3N_A-6}$ are the vibrational coordinates, and P_iU_i now denote vibronic (rather than electronic) symmetry species.

5. Specialization to a molecule with symmetry T_d

In the special case of elastic scattering by a closed-shell molecule with symmetry T_d in its ground electronic state, assumed totally symmetric as in CH_4, the effective potential has the full symmetry of the molecule, i.e. it transforms under the symmetry group operations according to the A_1 irreducible representation, hence the potential matrix, and consequently the scattering matrix, is block diagonal in P and U. The potential matrix elements are then given by Eqs. (12) and (13). Furthermore, the potential (or scattering) matrix elements transform from one reference frame to the other according to Eqs. (41) and (52). It is convenient to choose the phase factor q_{ja} in (24) as

$$q_{ja} = q_{jh}^{p\mu} = \exp\{\mathrm{i}[k_{\max}^{p\mu}(j, h)\pi/4]\}, \tag{69}$$

where $k_{\max}^{p\mu}(j, h)$ is the maximum value of k_j for which $b_{hjk_j}^{p\mu}$ is nonzero. This choice ensures the reality of the potential matrix elements in the laboratory frame, and it is consistent with the choice made in Ref. [12], where electronically elastic scattering by CH_4 in the laboratory-fixed frame was discussed. In that reference, for which the initial rotational state was restricted to be the ground state, only functions transforming according to the totally symmetric irreducible representation A_1 were retained in the expansion of the rotor functions given in Eq. (24) [20]. We need then consider only $p = P^0$ and $\mu = 1$ in (41). In the molecule-fixed frame, however, even to compute cross sections involving the ground rotational state, we must consider all five symmetries. Table 1 gives the number $H_{\max}(P, l)$ of symmetry functions with given P, U, and l for the case of a spherical top with T_d symmetry for the first thirteen values of l. A numerical application to electronically and vibrationally elastic scattering of electrons by the ground rotational state of CH_4 at 10 eV will be considered in the next paper [35].

As an example of electronically inelastic scattering we note that electron scattering by CH_4 involving the excitation of the T_2 electronic state from the ground state

Table 1. The values of $H_{\max}(P, l)$ for the first few l's retained in the expansion of continuum functions for a T_d point group

	P				
l	A_1	A_2	E	T_1	T_2
0	1	0	0	0	0
1	0	0	0	0	1
2	0	0	1	0	1
3	1	0	0	1	1
4	1	0	1	1	1
5	0	0	1	1	2
6	1	1	1	1	2
7	1	0	1	2	2
8	1	0	2	2	2
9	1	1	1	2	3
10	1	1	2	2	3
11	1	0	2	3	3
12	2	1	2	3	3

has been studied experimentally [33]. The possible irreducible representations $P(i)$ to which the scattering electron wavefunctions belong in this case are listed in Table 2 for all possible symmetries P of the total wavefunction and P_i of the molecule.

6. Summary

We have shown how electron scattering by a spherical top of T_d symmetry may be treated in a laboratory-frame formalism with full inclusion of molecular symmetry. The treatment requires an especially careful consideration of the meaning of improper rotations. We have also presented an explicit transformation relating the laboratory-frame results to a molecule-frame treatment in which the approximate symmetries appropriate to that frame are also fully incorporated.

Acknowledgment. The authors are grateful to Grigory Natanson for comments on the original manuscript. This work was supported in part by the National Science Foundation under grant nos. CHE83-17944 and CHE83-11450.

Appendix: Proof of Eqs. (25a)–(25b)

The purpose of this appendix is to derive the relations betweens between the coefficients $B^{pul}_{hjk_j}$ and $b^{pu}_{hjk_j}$ used in the text. Before beginning the derivation proper, some matters of notation must be discussed.

According to the conventions of Edmonds used in this paper, the matrices $\mathscr{D}^{(l)}(\boldsymbol{G})$ with elements $\mathscr{D}^{(l)}_{m'm}(\boldsymbol{G})$ refer to transformations of spherical harmonics $Y_l^m(\omega)$ under rotations of the coordinate system through the Euler angles $\boldsymbol{G}=(\alpha, \beta, \gamma)$, while holding the physical system fixed. For studying the consequences of symmetry, however, it is more convenient to think in terms of rotations applied to the physical system while keeping the coordinate system fixed. This is especially true in view of the fact that we need to apply rotations to *part* of our system, either projectile or target, while keeping the other part fixed. Accordingly, we

Table 2. A_1 and T_2 close coupling scheme for a T_d spherical top

P	P_i	$P(i)$
A_1	A_1	A_1
	T_2	T_2
A_2	A_1	A_2
	T_2	T_1
E	A_1	E
	T_2	T_1, T_2
T_1	A_1	T_1
	T_2	A_2, E, T_1, T_2
T_2	A_1	T_2
	T_2	A_1, E, T_1, T_2

introduce matrices $\mathbf{\Delta}^{(1)}(\boldsymbol{G})$, with elements $\Delta^{(l)}_{m'm}(\boldsymbol{G})$ which describe rotations of the physical system (wave functions) through the Euler angles $\boldsymbol{G}$ without changing the coordinate system. Because these matrices are unitary, and because a rotation applied to the physical system has formally the same effect as the inverse rotation applied to the coordinate system, we have:

$$\Delta^{(l)}_{m'm}(\boldsymbol{G}) = \mathscr{D}^{(l)*}_{mm'}(\boldsymbol{G}). \tag{A1}$$

We must also distinguish between rotations applied to the projectile (electron), and to the target (molecule), and between rotations referred to lab-fixed or molecule-fixed axes. Accordingly, for each set of Euler angles $\boldsymbol{G}$, we denote the operation of rotating the projectile through angles $\boldsymbol{G}$ with respect to a lab-fixed axis by $U(\boldsymbol{G})$, and the same rotation appplied to the target by a script $\mathscr{U}(\boldsymbol{G})$. A tilde ($\sim$) above a U or U indicates that the rotation is with respect to molecule-fixed coordinates: thus, $\tilde{U}(\boldsymbol{G})$ and $\tilde{\mathscr{U}}(\boldsymbol{G})$ denote rotation of projectile and target, respectively, through angles $\boldsymbol{G}$ with respect to a molecule-fixed coordinate system.

For projectile wave functions whose angular part consists of either lab-fixed spherical harmonics $Y_1^{m_1}(\omega)$ or molecule-fixed spherical harmonics $Y_L^{m_L}(\tilde{\omega})$, we have

$$\langle lm_l'|U(\boldsymbol{G})|lm_l\rangle = \Delta^{(1)}_{m_l'm_l}(\boldsymbol{G}); \quad \text{and}$$
$$\langle LM_L'|\tilde{U}(\boldsymbol{G})|Lm_L\rangle = \Delta^{(L)}_{m_L'm_L}(\boldsymbol{G}). \tag{A2}$$

An element A of the abstract symmetry group (T_d) consists of a rotation through Euler angles $\boldsymbol{G}_A$, followed by the inversion i if A is an improper operation. Such a group element has two realizations of interest to us, depending on whether the rotational part of A is applied to the projectile or to the target.

In the first realization, appropriate in the fixed-nuclei approximation, the rotation and the inversion if present are both applied to the projectile wave function, with respect to a molecule-fixed axis. We denote this realization by A_p. Defining

$$\begin{aligned} &\varepsilon(A) = 1 \quad \text{if } A \text{ is a proper rotation;} \\ &\varepsilon(A) = \imath \quad \text{if } A \text{ is an improper operation,} \end{aligned} \tag{A3}$$

where $\imath$ denotes the inversion operator, we find that the operator for A_p can be expressed as $\varepsilon(A)\tilde{U}(\boldsymbol{G}_A)$. In a representation in terms of molecule-fixed spherical harmonics, the matrix representing A_p is block diagonal with a submatrix $\mathbf{\Delta}^{(L)}(A_p)$ for each L. The effect of the inversion $\imath$ on the spherical harmonics is just multiplication by $(-1)^L$. Accordingly, we define

$$\begin{aligned} &\varepsilon_L(A) = 1 \quad \text{if } A \text{ is a proper rotation;} \\ &\varepsilon_L(A) = (-1)^L \quad \text{if } A \text{ is an improper operation,} \end{aligned} \tag{A4}$$

and obtain

$$\mathbf{\Delta}^{(L)}(A_p) = \varepsilon_L(A)\mathbf{\Delta}^{(L)}(\boldsymbol{G}_A). \tag{A4a}$$

In the second realization, which corresponds to an exact symmetry of the system, the rotational part of A is applied in the inverse sense to the target wave function, still with respect to molecule-fixed axes. The inversion, if present, must still be applied to the projectile wave function. This realization, which we denote by A_t, effects the same change of projectile coordinates relative to the target as A_p. Using again the definition (A3), and with the understanding that $\imath$ is *always* applied to the projectile wave function, we have $\varepsilon(A)\tilde{U}(\bar{\boldsymbol{G}}_A)$ for the operator representing A_t, where $\bar{\boldsymbol{G}}$ denotes the Euler angles for the rotation inverse to $\boldsymbol{G}$: if $\boldsymbol{G}=(\alpha, \beta, \gamma)$, then $\bar{\boldsymbol{G}}=(-\gamma, -\beta, -\alpha)$.

We must now determine the effect of the rotational part of A_t on the target wave functions with definite total angular momentum quantum number j, and molecule- and lab-fixed projections k_j and m_j respectively. We will define a new set of basis functions by

$$\langle \boldsymbol{G}|jk_jm_j\rangle = N_h\Delta^{(j)}_{k_jm_j}(\bar{\boldsymbol{G}}), \tag{A5}$$

with N_j as defined in Eq. (23). Applying $\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)$ to (A5), we find:

$$\langle \boldsymbol{G}|\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)|jk_jm_j\rangle = \int \langle \boldsymbol{G}|\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)|\boldsymbol{G}'\rangle\,\mathrm{d}\boldsymbol{G}'\,\langle \boldsymbol{G}'|jk_jm_j\rangle. \tag{A6}$$

the matrix element $\langle \boldsymbol{G}|\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)|\boldsymbol{G}'\rangle$ is evidently a delta function at the orientation $\boldsymbol{G}'$ which is taken into $\boldsymbol{G}$ by $\mathscr{U}(\bar{\boldsymbol{G}}_A)$. We thus have

$$\langle \boldsymbol{G}|\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)|jk_jm_j\rangle = \langle \boldsymbol{G}'|jk_jm_j\rangle = N_j\Delta^{(j)}_{k_jm_j}(\bar{\boldsymbol{G}}'), \tag{A7}$$

with $\boldsymbol{G}'$ determined by

$$\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)\mathscr{U}(\boldsymbol{G}') = [\mathscr{U}(\boldsymbol{G}')\mathscr{U}(\bar{\boldsymbol{G}}_A)\mathscr{U}(\bar{\boldsymbol{G}}')]\mathscr{U}(\boldsymbol{G}') = \mathscr{U}(\bar{\boldsymbol{G}}')\mathscr{U}(\bar{\boldsymbol{G}}_A) = \mathscr{U}(\boldsymbol{G}), \tag{A8}$$

which has the solution

$$\mathscr{U}(\boldsymbol{G}') = \mathscr{U}(\boldsymbol{G})\mathscr{U}(\boldsymbol{G}_A), \tag{A9}$$

$$\mathscr{U}(\bar{\boldsymbol{G}}') = \mathscr{U}(\bar{\boldsymbol{G}}_A)\mathscr{U}(\bar{\boldsymbol{G}}). \tag{A10}$$

Because of (A10), we have

$$\boldsymbol{\Delta}^{(j)}(\bar{\boldsymbol{G}}') = \boldsymbol{\Delta}^{(j)}(\bar{\boldsymbol{G}}_A)\Delta^{(j)}(\bar{\boldsymbol{G}}). \tag{A11}$$

Inserting (A11) into (A7), we find

$$\begin{aligned}\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)\langle \boldsymbol{G}|jk_jm_j\rangle &= N_j\sum_{k_j'}\Delta^{(j)}_{k_jk_j'}(\bar{\boldsymbol{G}}_A)\Delta^{(j)}_{k'm_j}(\bar{\boldsymbol{G}})\\ &= \sum_{k_j'}\Delta^{(j)}_{kk_j'}(\bar{\boldsymbol{G}}_A)\langle \boldsymbol{G}|jk_jm_j\rangle,\end{aligned} \tag{A12}$$

so that

$$\langle j'k_j'm_j'|\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)|jk_jm_j\rangle = \delta_{jj'}\delta_{mm'}\Delta^{(j)}_{k_jk_j'}(\bar{\boldsymbol{G}}_A), \tag{A13}$$

which because of unitarity is equivalent to

$$\langle j'k_j'm_j'|\tilde{\mathscr{U}}(\bar{\boldsymbol{G}}_A)|jk_jm_j\rangle = \delta_{jj'}\delta_{m_jm_j'}\Delta^{(j)*}_{k_j'k_j}(\boldsymbol{G}_A). \tag{A14}$$

The rotational part of A_t is thus given by (A14); it is diagonal in j and m_j, and it couples different values of k_j via the complex conjugate of a $\Delta^{(j)}$ matrix. The inversion, if present, still acts only on the projectile wave function. A matrix representation for A_t can thus be defined with respect to a basis made up of products $\langle \boldsymbol{G} | jk_j m_j \rangle Y^l_{m_l}(\tilde{\omega})$ of projectile and target wave functions. Because of (A14), and because ε_A just results in multiplication by $(-1)^l$, such a representation will be block-diagonal in j, k, m_j, and m_l, and independent of m_j and m_l. The block referring to given j and l [repeated $(2j+1)(2l+1)$ times as m_j and m_l run over their allowed values] will be denoted by $\boldsymbol{\Delta}^{(jl)}(A_j)$. Using (A4), (A4a), and (A14), we find:

$$\boldsymbol{\Delta}^{(lj)}(A_t) = \varepsilon_1(A)\boldsymbol{\Delta}^{(j)*}(\boldsymbol{G}_A). \tag{A15}$$

Computing $\boldsymbol{\Delta}^{(j)*}(\boldsymbol{G}_A)$ from Eqs. (4) and (4a) we obtain

$$\boldsymbol{\Delta}^{(lj)}(A_t) = \varepsilon_{(l-j)}(A)\boldsymbol{\Delta}^{(j)*}(A_p). \tag{A16}$$

Now suppose that we have succeeded in block-diagonalizing the matrices $\boldsymbol{\Delta}^{(j)}(A_p)$ into direct sums of irreducible representations $\boldsymbol{\Delta}^{(p)}(A)$:

$$\boldsymbol{S}^{-1}\boldsymbol{\Delta}^{(j)}(A_p)\boldsymbol{S} = \sum_p \sum_h \boldsymbol{\Delta}^{(p)}(A), \tag{A17}$$

where the summation sign denotes the block-diagonal direct sum; the index p is for irreducible representations, and multiple occurrences of the same irreducible representation are accounted for by the sum over h. The indices labelling rows and columns of the transformed matrices in (A17) are now puh, and the matrix elements of $\boldsymbol{S}$ are given by

$$\langle jk_j | S | puh \rangle = b^{pu}_{hjk_j}. \tag{A18}$$

Taking the complex conjugates on both sides of (A17), using (A16), and recalling that the $\Delta^{(p)}(A)$ are real, we find

$$\boldsymbol{S}^{*-1}\boldsymbol{\Delta}^{(lj)}(A_t)\boldsymbol{S}^* = \varepsilon_{(1-j)}(A) \sum_p \sum_h \boldsymbol{\Delta}^{(p)}(A). \tag{A19}$$

Because of (A18) and the definitions given in Sect. 3, (A19) is equivalent to (25a) and (25b). This completes the derivation.

We finish by discussing two of the practical aspects of these considerations. First consider the effect of complex conjugation in Eq. (25b). Since, as noted below Eq. (5), $b^{p\mu}_{hjk_j}$ is always pure real or pure imaginary, the complex conjugations just correspond to a change in phase. Furthermore, the replacement of $p\mu$ by $\bar{p}\bar{\mu}$ is just a relabelling. Since one may always make a change of phase, provided it is done consistently, one may simply replace each B_{hjk_j} by the corresponding b_{hjk_j} and one will still obtain correct results. This does correspond to relabelling states with $(j-l)$ odd, though, so if one is calculating matrix elements connecting states with $(j-l)$ even to those with $(j-l)$ odd, one will have to include coupling between A_1 states and those relabelled A_2. When laboratory-frame symmetry is treated by the formalism of Sect. 3 though, A_1 and A_2 are rigorous symmetries and are completely uncoupled.

Secondly we consider another aspect of the symmetry conjugation of Eq. (25b). If this subtlety were ignored, the transformation to the laboratory frame would still yield correct results, within a phase factor, for scattering matrix elements with $(-1)^{j+l} = (-1)^{j'+l'}$, but one might incorrectly conclude that those with $(-1)^{j+l} \neq (-1)^{j'+l'}$, are zero. When $j = 0$, nonzero scattering matrix elements with $(-1)^{j'+l'} \neq (-1)^{l}$ occur only for $j' \leq 6$ in the correct calculation, so the quantitive effect of the conjugation is small for the results in [35]. It could, however, be expected to be very important for some excited-state-to-state cross sections.

References and notes

1. See, e.g., the reviews by (a) Lane NF (1980) Rev Mod Phys 52:29 (b) Burke PG (1980) In: Woolley RG (ed) Quantum dynamics of molecules. Plenum, New York, p 483, and (c) Gianturco FA, Thompson DG (1983) In: Hinze J (ed) Electron-atom and electron-molecule collisions. Plenum, New York, p 231
2. Chase DM (1956) Phys Rev 104:838
3. Bottcher C (1969) Chem Phys Lett 4:320
4. Temkin A, Vasuvada KV (1967) Phys Rev 160:109; Temkin A, Vasuvada KV, Chang ES, Silver A (1969) Phys Rev 186:57; Chang ES, Temkin A (1969) Phys Rev Lett 23:399
5. Burke PG, Sinfailam AL (1970) J Phys B 3:641
6. Burke, PG, Chandra N (1973) J Phys B 5:1696
7. Chang ES, Fano U (1972) Phys Rev A 6:173
8. Shugard M, Hazi AU (1975) Phys Rev A 12:1895
9. Choi BH, Poe RT (1977) Phys. Rev A 16:1821, 1831
10. Burke PG, Chandra N, Gianturco FA (1972) J Phys B 5:2212
11. Gianturco FA, Thompson DG (1976) J Phys B 9:L383; (1980) 13:613
12. Jain A, Thompson DG (1983) J Phys B 16:3077. See also Jain A, Thompson DG (1982) J Phys B 15:L631 and (1984) Phys Rev A 30:1098 and Jain A (1984) J Chem Phys 81:724
13. Shimamura I (1982) J Phys B 15:93
14. Shimamura I (1982) Z Phys A 309:107
15. Shimamura I (1983) Phys Rev A 28:1357
16. Morrison MA, Feldt AN, Austin D (1984) Phys Rev A 29:2518; Morrison MA, Feldt AN, Saha BC (1984) Phys Rev A 30:2811
17. LeDourneuf M, Lan Vo Ky, Schneider BI, work discussed in [1b]
18. Collins LA, Norcross DW (1978) Phys Rev A 18:467
19. Schwenke DW, Staszewska G, Truhlar DG (1983) J Chem Phys 78:275
20. Abusalbi N, Eades RA, Nam T, Thirumalai D, Dixon DA, Truhlar DG, Dupuis M (1983) J Chem Phys 78:1213
21. Natanson GA (1985) J Phys B 18:4481
22. Edmonds AR (1960) Angular momentum in quantum mechanics, 2nd edn. Princeton University Press, Princeton
23. Truhlar DG (1977) In Segal GA (ed) Semiempirical methods of electronic structure calculation. Part B, Plenum, New York, p 247
24. Truhlar DG (1981) In: Politzer P, Truhlar DG (eds) Chemical applications of atomic and molecular electrostatic potentials. Plenum, New York, p 123
25. Altmann SJ, Cracknell AP (1965) Rev Mod Phys 37:19. For E symmetry, we used the coefficients corresponding to both components and obtained the same answers either way; for production runs we used the second. For T_1 and T_2 there apparently are errors in the tabulated coefficients for the first two components, so we used the third component for our calculations. As examples of our phase conventions, we note that $b^{A_1 1}_{132} = -i/\sqrt{2}$ and $b^{E2}_{12-2} = 1/\sqrt{2}$. A related treatment, not used here but of possible interest to the reader, is Champion JP, Pierre G, Michelot F, Moret-Bailly J (1977) Can J Phys 55:512
26. Gianturco FA, Thompson DG (1976) Chem Phys 14:111
27. Landau LD, Lifshitz EM (1965) Quantum Mechanics, 2nd edn. Pergamon, Oxford
28. Altmann SL, Bradley CJ (1963) Philos Trans R Soc London A 255:199

29. Bunker PR (1979) Molecular symmetry and spectroscopy. Academic Press, New York, p 208
30. Riley ME, Truhlar DG (1975) J Chem Phys 63:2182
31. Truhlar DG, Mullaney NA (1978) J Chem Phys 68:1574
32. Bransden BH, Crocker M, McCarthy IE, McDowell MRC, Morgan LA (1978) J Phys. B 11:3411; Morgan LA, McDowell MRC (1979) J Phys B 12:L739
33. Johnson KE, Kim K, Johnston DB, Lipsky S (1979) J Chem Phys 70:2189 and references therein
34. Valone SM, Truhlar DG, Thirumalai D (1982) Phys Rev A 25:3003
35. Abusalbi N, Schwcuke DW, Mead CA, Truhlar DG (1987) Theor Chim Acta 71:359-374