"Time-Reversal Invariance, Representations for Scattering Wave Functions, Symmetry of the Scattering Matrix, and Differential Cross Sections," D. G. Truhlar, C. A. Mead, and M. A. Brandt, in *Advances in Chemical Physics*, Vol. 33, edited by I. Prigogine and S. A. Rice (John Wiley and Sons, New York, 1975), pp. 295-344.

TIME–REVERSAL INVARIANCE, REPRESENTATIONS FOR SCATTERING WAVEFUNCTIONS, SYMMETRY OF THE SCATTERING MATRIX, AND DIFFERENTIAL CROSS–SECTIONS*

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CONTENTS

*Supported in part by the National Science Foundation through grant GP-28684, by the Alfred P. Sloan Foundation through a research fellowship to one of the authors (D.G.T.), and by the Graduate School of the University of Minnesota.

Offprints from
ADVANCES IN CHEMICAL PHYSICS, VOL. 33
Edited by Prigogine/Rice
Published by John Wiley & Sons, Inc., 1975

I. INTRODUCTION

In general all the information necessary to completely describe a binary collision of two (composite or elementary) particles is contained in the scattering matrix. When it is desired to express the scattering matrix for general multichannel collision processes in the absence of external fields, a useful representation is one in which the total angular momentum and one of its components are quantum numbers.[1] Our term for this is "total-angular-momentum representation." In Section II we review some examples of descriptions of scattering processes that involve total-angular-momentum representations.

Time-reversal invariance is a fundamental symmetry property that can often be used to simplify the determination of the scattering matrix. For example, Coester[2] and others have used time-reversal invariance to prove that the scattering matrix in a total-angular-momentum representation is symmetric for certain phase conventions for the wavefunctions. In Section III we prove that all symmetry operators must be unitary or antiunitary and that time-reversal is antiunitary. We review antiunitary operators, the time-reversal operator, and some associated properties. In Section IV we prove a general theorem that provides sufficient conditions under which the scattering matrix is symmetric in a total-angular-momentum representation.

In Section V we review the formula for calculating the differential cross-section $d\sigma/d\Omega$ (where Ω specifies the scattering solid angle) from the scattering matrix, and we discuss the application of the results of Section IV to some common examples. The phase conventions used in several published expressions for calculating differential cross-sections from scattering matrices are checked for the properties of the time-reversed state.

Examples are furnished of representations that give a symmetric scattering matrix even though they do not satisfy the conditions usually stated as sufficient for this symmetry. The practical problem of consistent use of a phase convention is also discussed.

II. TOTAL-ANGULAR-MOMENTUM REPRESENTATIONS

In the usual partial-wave expansion,[1a,3-10] the scattering of an elementary particle without spin from a central potential is characterized by the good quantum numbers l, m_l, and Π. Here $\vec{l}$ is the orbital angular momentum* with quantum number l, l_z is its z-component with quantum number m_l, z is a space-fixed axis, and Π is the total parity of the system. In this case the total-angular-momentum quantum number J and the quantum number M of its z-component are identical to l and m_l. Thus the usual partial-wave expansion provides the simplest example of a total-angular-momentum representation in a scattering problem.

The hamiltonian H for an elementary particle interacting with a noncentral potential[11] is not rotationally invariant. In this chapter we are concerned only with systems whose total hamiltonian is rotationally invariant.

The scattering of an elementary particle with spin from a rotationally invariant potential (which may depend on the spin) may be characterized[1b,3a,7a,8a,10a] by the quantum numbers J, M, Π, l, and the internal angular momentum quantum number s, where

$$\vec{J}=\vec{l}+\vec{s} \tag{1}$$

Since J and M are included among the quantum numbers specifying the state, such a description is a total-angular-momentum representation. An alternative description of this system which is *not* a total-angular-momentum representation is characterized by the quantum numbers l, m_l, s, and m_s, where s_z is the component of $\vec{s}$ on the space-fixed axis and m_s is the quantum number associated with that component. For certain treatments of or approximations to the scattering problem, the latter representation may prove more useful. However, since rotational invariance implies

$$[\hat{H},\hat{J}^2]=0 \qquad \text{and} \qquad [\hat{H},\hat{J}_z]=0$$

where a hat (caret) over a symbol denotes a quantum-mechanical operator and z is the space-fixed axis, the scattering matrix is diagonal in J and M and independent of M.[1b,7b,10a] Thus generally a representation in which J

*Throughout the chapter, angular momentum is measured in units of $\hbar$.

and M are included among the quantum numbers will be most convenient. This property of a block diagonal scattering matrix is the general reason for preferring a total-angular-momentum representation.

The scattering of an elementary particle without spin by a rigid diatomic rotator without spin was treated by Arthurs and Dalgarno,[12] Micha,[13] and others[14] in terms of the quantum numbers J, M, Π, l, and s, where s for this problem is the rotational angular momentum quantum number of the diatom. The scattering of an elementary particle without spin from a diatomic rotator-vibrator may be treated[15] in terms of the quantum numbers J, M, Π, l, s, and n, where s is again the internal angular momentum of the target and n is the vibrational quantum number. These problems may also be treated in other total-angular-momentum representations[16] and in representations in which J is not a quantum number.[17] In fact, the last-named type of representation sometimes provides a simplification in approximate calculations. In this chapter we consider only the total-angular-momentum representations.

The scattering of an elementary particle whose spin is neglected from a rigid diatomic rotator with spin $\vec{f}$ and angular momentum $\vec{k}$ of rotation of the molecular framework may be treated[18] in terms of the quantum numbers J, M, Π, l, s, f, and k, where

$$\vec{s} = \vec{k} + \vec{f}$$

In this case s is again the total-internal-angular-momentum quantum number.

For electron-atom scattering by low-atomic-number atoms at nonrelativistic energies, it is common to neglect spin-orbit coupling. Then the total orbital angular momentum $\vec{L}$ and the total spin angular momentum* $\vec{S}$ are separately conserved. In this case spin may be removed from the problem except for its role in enforcing a specific permutational symmetry for the spatial part of the electronic wavefunction. Then $\vec{L}$ effectively plays the role of total angular momentum and it is most convenient[9a] to include it among the good quantum numbers labeling the representation.

Further examples of total-angular-momentum representations may be found in the theory of atom-atom collisions with transitions among hyperfine levels,[19] in other atomic collisions,[20] and in Section V.

III. TIME REVERSAL

The operation commonly called "time reversal" might more logically be named "motion reversal." It consists not in a true reversal of the direction

*Total spin $\vec{S}$ and the quantum number S and operator $\hat{\vec{S}}$ for total spin should not be confused with the scattering operator $\hat{S}$ for which we use the same capital letter.

of time (which would be unphysical), but in a reversal of all velocities and spins, with spatial coordinates being left invariant (a more precise definition is given in Section III.A). In deference to tradition, however, we use the term "time reversal" for this operation, denoting it by $\hat{T}$. Since we shall have occasion to make use of some of the properties of $\hat{T}$, and since these are not widely understood among chemists, we present in this section a self-contained treatment carrying the theory of time reversal far enough to derive the results we shall require. For more details, the reader is referred to the excellent treatment of Wigner.[21]

A. Symmetry Operators

We define a symmetry operator $\hat{N}$ as any operator that satisfies, for all $|q\rangle$, $|r\rangle$,

$$|\langle \hat{N}q|\hat{N}r\rangle| = |\langle q|r\rangle| \tag{2}$$

and the distributive law

$$\hat{N}(|q\rangle + |r\rangle) = N|q\rangle + N|r\rangle \tag{3}$$

and has an inverse $\hat{N}^{-1}$ which is also a symmetry operator. Gottfried[22] has given a discussion of how (2) corresponds to our physical ideas of a symmetry operator. Note that we cannot use any simple physical argument involving symmetry to put restrictions on the phases of the two sides of (2). This is because $|r\rangle$ and $e^{i\alpha}|r\rangle$ represent the same physical state.[22a]

The time-reversal operator $\hat{T}$ is defined as the symmetry operator that reverses the signs of all velocities and spins, while leaving spatial coordinates unaltered. In the absence of external magnetic fields, this is equivalent to the reversal of all linear and angular momenta (including spin), while leaving coordinates unchanged. We always assume in this chapter that no external magnetic field is present, which means that $\hat{T}$ may be defined as reversing momenta and spin. This does not prevent us from including the effect of magnetic fields generated by the orbital or spin motion of the particles of the system under study. In the presence of an external magnetic field, there does not appear to be a well-defined operator that reverses velocities while leaving the external field unaltered.

The rest of this subsection is a proof of Wigner's theorem:[22b,23] all symmetry operators must be unitary or antiunitary (defined below).

To explore the consequences of properties (2) and (3), let $|u\rangle$, $|v\rangle$, etc., be a complete orthonormal set of state vectors with

$$\langle u|v\rangle = \delta_{uv} \tag{4}$$

and let $\hat{N}$ be some symmetry operator. It follows immediately from (2),

plus the positive definiteness of $\langle q|q\rangle$, that $|\hat{N}u\rangle, \ldots,$ are also orthonormal:

$$\langle \hat{N}u|\hat{N}v\rangle = \delta_{uv} \tag{5}$$

The $|\hat{N}u\rangle$ are also complete. For if $|w\rangle$ is orthogonal to them all, then $|\hat{N}^{-1}w\rangle$ is orthogonal to all the $|u\rangle$, contrary to the hypothesis that the $|u\rangle$ are complete.

Now select one of the $|u\rangle$ arbitrarily, and consider the action of the symmetry operator $\hat{N}$ on the vector $(a|u\rangle)$, where a is a complex number. Because $\langle v|au\rangle = a\delta_{uv}$ and because of (2), we must have

$$|\langle \hat{N}v|\hat{N}au\rangle| = |a|\delta_{uv} \tag{6}$$

From the completeness and orthonormality of the $|\hat{N}v\rangle$, it follows that

$$\hat{N}a|u\rangle = a'|\hat{N}u\rangle \qquad \text{with} \quad |a'| = |a| \tag{7}$$

We next consider an arbitrary vector $|r\rangle$ expanded in terms of the $|u\rangle$:

$$|r\rangle = \Sigma r_u|u\rangle$$

Because of (3) and (7), we have

$$|\hat{N}r\rangle = \Sigma r'_u|\hat{N}u\rangle, \qquad |r'_u| = |r_u| \tag{8}$$

Now for arbitrary $|v\rangle$, $|w\rangle$ from the complete set, we define the vector

$$|f_{vw}\rangle = |v\rangle + |w\rangle$$

It follows from (3) that

$$|\hat{N}f_{vw}\rangle = |\hat{N}v\rangle + |\hat{N}w\rangle \tag{9}$$

Now, making use of (9), (5), (8), (2), and (4), we find

$$|\langle \hat{N}f_{vw}|\hat{N}r\rangle| = |r'_v + r'_w| = |\langle f_{vw}|r\rangle| = |r_v + r_w| \tag{10}$$

It is evident that (8) and (10) can be satisfied only if the relative phase of r'_v and r'_w is the same in absolute value as that of r_v and r_w. Furthermore, this must remain true when r_v and r_w are varied independently, and for all choices of $|v\rangle$ and $|w\rangle$. There are thus two possibilities: either the relative phase remains the same, in which case

$$r'_u = e^{i\phi}r_u \tag{11}$$

or the relative phase changes sign, leading to

$$r'_u = e^{i\phi} r_u^* \tag{12}$$

In both cases (11) and (12), the common phase factor ϕ must be the same for all $|u\rangle$. Applying (11) or (12) to the case $r_u = 1$, moreover, we find

$$\hat{N}|u\rangle \equiv |\hat{N}u\rangle = e^{i\phi}|\hat{N}u\rangle$$

from which it follows that $\phi = 0$.

We are thus left with just two possibilities. If (11) holds, we have

$$\hat{N}a|u\rangle = a|\hat{N}u\rangle$$

from which and from (3) it follows by expanding arbitrary $|q\rangle$, $|r\rangle$ in the $|u\rangle$ that

$$\hat{N}(a|q\rangle + b|r\rangle) = a|\hat{N}q\rangle + b|\hat{N}r\rangle \tag{13}$$

and

$$\langle \hat{N}q|\hat{N}r\rangle = \langle q|r\rangle \tag{14}$$

In this case, the symmetry operator $\hat{N}$ is called unitary, and, in accordance with (13), linear.

On the other hand, if (12) is obeyed, we have

$$\hat{N}a|u\rangle = a^*|\hat{N}u\rangle$$

$$\hat{N}(a|q\rangle + b|r\rangle) = a^*|\hat{N}q\rangle + b^*|\hat{N}r\rangle \tag{15}$$

$$\langle \hat{N}q|\hat{N}r\rangle = \langle q|r\rangle^* \tag{16}$$

In this case, the operator is said to be antiunitary (and antilinear). This completes the proof of Wigner's theorem.*

The familiar symmetry operations such as rotations and parity are unitary.[22b] In the Section III.B we show that $\hat{T}$ is antiunitary.

B. Antiunitary Nature of the Time-Reversal Operator

In the absence of external fields producing velocity- or spin-dependent forces (of which the only important example is the magnetic field), the

*If one does not initially assume the distributive law (3), the proof of Wigner's theorem is slightly more difficult and the result itself slightly weaker.[22b] Without assuming the distributive law, it can be shown that an appropriate and permissible phase convention leads to all our results being true, but other phase conventions are possible in which the distributive law is not obeyed and in which the phase angle ϕ in (11) or (12) is not necessarily zero.

operation of time reversal does not change the energy of chemical systems. Thus, for such a system, if

$$\hat{H}|j\rangle = \hbar w_j |j\rangle$$

then also

$$\hat{H}|\hat{T}j\rangle = \hbar w_j |\hat{T}j\rangle$$

We will say that such a system has a time-reversal-invariant hamiltonian. Since we are using $\hat{T}$ only in such cases, and since $\hat{T}$ is not necessarily well defined otherwise, we assume this property from now on.

Now consider a simple example of a system with a time-reversal-invariant hamiltonian: a classical free particle, moving in one dimension. At time zero, let the particle be at the origin, moving with velocity v, and consider the effect of two different sequences of operations. In the first sequence, we apply $\hat{T}$ (changing v to $-v$), and then let the particle travel for a (positive) time t. The result is that the particle is at the point $(-vt)$ and has velocity $-v$. In the second sequence, we go back in time to $(-t)$, and then apply $\hat{T}$. Again, the result is that the particle is at $(-vt)$ and has velocity $-v$. In other words, time reversal followed by propagation *forward* by t has the same effect as propagation *backward* by t followed by time reversal. A little reflection shows that this is a property of all time-reversal-invariant systems, i.e., of all systems with time-reversal-invariant hamiltonians.

Quantum mechanically, this requirement is expressed as follows: for any initial state $|q\rangle$, we have

$$\hat{G}(t)\hat{T}|q\rangle = e^{i\Phi}\hat{T}\hat{G}(-t)|q\rangle \tag{17}$$

where ϕ is real and $\hat{G}(t) = \exp[-(i/\hbar)\hat{H}t]$ is the time-displacement operator. We now expand $|q\rangle$ in the eigenfunctions $|j\rangle$ of $\hat{H}$, $|q\rangle = \Sigma_j q_j |j\rangle$ and see what requirements (17) puts on $\hat{T}$. First, under the assumption that $\hat{T}$ is unitary, we find, using the rules of Section III.A,

$$\hat{G}(t)\hat{T}|q\rangle = \Sigma_j q_j e^{-iw_j t}|\hat{T}j\rangle$$

$$\hat{T}\hat{G}(-t)|q\rangle = \Sigma_j q_j e^{iw_j t}|\hat{T}j\rangle$$

which is evidently not compatible with (17).

On the other hand, assuming $\hat{T}$ to be antiunitary, we find

$$\hat{G}(t)\hat{T}|q\rangle = \Sigma_j q_j^* e^{-iw_j t}|\hat{T}j\rangle$$

$$\hat{T}\hat{G}(-t)|q\rangle = \Sigma_j q_j^* e^{-iw_j t}|\hat{T}j\rangle$$

which satisfies (17) and even satisfies

$$\hat{G}(t)\hat{T}|q\rangle = \hat{T}\hat{G}(-t)|q\rangle$$

We conclude, then, that $\hat{T}$ *must* be defined as an antiunitary operator.

C. PROPERTIES OF ANTIUNITARY OPERATORS

1. General

We use ψ to denote the set of (perhaps continuous) coefficients in the expansion of an arbitrary state vector in some complete set. We also define the operator $\overline{K}$, which replaces ψ by its complex conjugate: $\overline{K}\psi = \psi^*$.

We put a bar over K instead of a hat for the purpose of emphasizing that $\overline{K}$ as defined here has no invariant physical significance and produces in general different physical effects in different representations. For example, in the ordinary Schrödinger configuration space representation for a single particle, the complete set is just that of configuration space delta functions, and ψ is just the usual wavefunction $\psi(\vec{r})$. Application of $\overline{K}$ in this representation yields $\psi^*(\vec{r})$. On the other hand, if we change representations by expanding $\psi(\vec{r}) = \Sigma a_j \phi_j(\vec{r})$, where the ϕ_j are some complete orthonormal set, then application of $\overline{K}$ in the new representation gives $\Sigma a_j^* \phi_j(\vec{r})$, NOT $\Sigma a_j^* \phi_j^*(\vec{r})$. This is, of course, physically a different state unless the ϕ_j are all real. We therefore denote $\overline{K}$ with a bar, reserving the hat for operators with an invariant physical meaning.

In view of the foregoing discussion, we can give a meaning to an expression such as $|\overline{K}r\rangle$ only if we also specify the representation in which the ket $|r\rangle$ is being expanded. With this understanding, however, it is evident that the $\overline{K}$ associated with any particular representation is a symmetry operator, that it is antiunitary, and that $\overline{K}^2 = 1$.

Now, with a representation specified, let $\hat{W}$ be an arbitrary antiunitary operator, and consider the product $\hat{W}\overline{K}$. We find using (16) that

$$\langle \hat{W}\overline{K}q | \hat{W}\overline{K}r\rangle = \langle \hat{W}(\overline{K}q) | \hat{W}(\overline{K}r)\rangle = \langle \overline{K}q | \overline{K}r\rangle^* = \langle q | r\rangle$$

It follows that $\hat{W}\overline{K}$ for the given representation is unitary. We denote the matrix of $\hat{W}\overline{K}$ in the specified representation by $\boldsymbol{\beta}$ where the bold face letter denotes a matrix. Since $\overline{K}^2 = 1$, we have, in the given representation

$$\hat{W} = \tilde{\beta}\overline{K} \tag{18}$$

where $\tilde{\beta}$ is the operator in the given representation whose matrix is $\boldsymbol{\beta}$.

The matrix $\boldsymbol{\beta}$ is unitary in the sense that $\boldsymbol{\beta}\boldsymbol{\beta}^\dagger = 1$. It does not, however, possess the same transformation properties as matrices of unitary operators

such as those for rotations of coordinate systems. To investigate the transformation properties of $\boldsymbol{\beta}$, we let the state vectors undergo a unitary transformation to a new representation, denoted by a prime, with the matrix of the transformation denoted by $\mathbf{U}$:

$$\psi' = \mathbf{U}\psi$$

The transformation of $\hat{W}$ must be such that $\hat{W}'\psi' = (\hat{W}\psi)'$, which, with the aid of (18), becomes

$$\boldsymbol{\beta}'\overline{K}\mathbf{U}\psi = \mathbf{U}\boldsymbol{\beta}\overline{K}\psi$$

$$\boldsymbol{\beta}'\mathbf{U}^*\psi^* = \mathbf{U}\boldsymbol{\beta}\psi^*$$

Since this must hold for all ψ, it follows that

$$\boldsymbol{\beta}'\mathbf{U}^* = \mathbf{U}\boldsymbol{\beta}$$

$$\boldsymbol{\beta}' = \mathbf{U}\boldsymbol{\beta}\mathbf{U}^T \tag{19}$$

where $\mathbf{U}^T$ denotes the transpose of $\mathbf{U}$. Note that (19) is different from the transformation law for the matrices $\mathbf{A}$ representing physical quantities, which obey $\mathbf{A}' = \mathbf{U}\mathbf{A}\mathbf{U}^\dagger$, where $\mathbf{U}^\dagger$ denotes the hermitian conjugate. It is because $\boldsymbol{\beta}$ has these unusual transformation properties that we denote the operator for it in a given representation as $\tilde{\beta}$ rather than $\hat{\beta}$ or $\overline{\beta}$. Equations involving $\tilde{\beta}$ and $\overline{K}$ are often true only in given representations, although we do not repeat this warning before each such equation.

2. Involutional Antiunitary Operators

Following Wigner,[21] we call a symmetry operator an involution if, when applied twice successively, it reproduces the original physical situation. It is evident that $\hat{T}$ is an involutional antiunitary operator. We now proceed to investigate some properties of such operators.

Let $\hat{\Theta}$ be antiunitary and involutional. It follows from (18), and from the definition of an involution, that

$$\hat{\Theta}^2 = \tilde{\beta}\overline{K}\tilde{\beta}\overline{K} = e^{i\eta}\hat{1} \tag{20}$$

where η is a real number. Applying (20) to a state function, we find

$$\hat{\Theta}^2\psi = e^{i\eta}\psi = \tilde{\beta}\overline{K}\tilde{\beta}\overline{K}\psi = \tilde{\beta}\overline{K}\tilde{\beta}\psi^* = \tilde{\beta}\tilde{\beta}^*\psi$$

It follows that

$$\tilde{\beta}\tilde{\beta}^* = e^{i\eta}$$

$$\tilde{\beta} = e^{i\eta}\tilde{\beta}^T \tag{21}$$

The transpose of (21) is

$$\tilde{\beta}^T = e^{i\eta}\tilde{\beta} \tag{22}$$

Inserting (22) into (21), we find

$$\tilde{\beta} = e^{2i\eta}\tilde{\beta}$$

from which follows $e^{i\eta} = \pm 1$. Accordingly, there are two possibilities for the square of an involutional antiunitary operator:

$$\hat{\Theta}^2 = \tilde{\beta}\tilde{\beta}^* = \pm \hat{1} \tag{23}$$

Note that (23) is not the result of normalization, as would be the case with a unitary operator; that is, a unitary operator $\hat{U}$ may be replaced by $\hat{U}' = e^{i\phi}\hat{U}$ without changing any physical properties, and in such a case $\hat{U}^2$ is replaced by $(\hat{U}')^2 = e^{2i\phi}\hat{U}^2$. If one does the same thing with an antiunitary operator $\hat{W}$, one finds

$$(\hat{W}')^2 = e^{i\phi}\hat{W}e^{i\phi}\hat{W} = e^{i\phi}e^{-i\phi}\hat{W}^2 = \hat{W}^2$$

When an involutional antiunitary operator is applied twice, any physical quantity returns to its original value. Accordingly, the physical quantities to be considered are divided into two classes according to whether they are left unchanged [class I $(\hat{\Theta})$] or change sign [class II $(\hat{\Theta})$] on application of an involutionary antiunitary operator $\hat{\Theta}$. By symmetrizing and antisymmetrizing, a variable that is neither class I $(\hat{\Theta})$ nor class II $(\hat{\Theta})$ may be expressed as a sum of class I $(\hat{\Theta})$ and a class II $(\hat{\Theta})$ variable, and we lose no generality by confining our attention to these two classes. We now investigate the commutation properties with $\hat{\Theta}$ of variables of these two classes. If $\hat{A}$ is a physical quantity that is class I $(\hat{\Theta})$, this means the complete set of eigenvectors $|j\rangle$ of $\hat{A}$ where

$$\hat{A}|j\rangle = a_j|j\rangle$$

are such that

$$\hat{A}|\hat{\Theta}j\rangle = a_j|\hat{\Theta}j\rangle$$

Expanding an arbitrary vector $|r\rangle$ as

$$|r\rangle = \Sigma_j r_j|j\rangle$$

we find

$$\hat{\Theta}\hat{A}|r\rangle = \hat{\Theta}\Sigma_j r_j a_j|j\rangle = \Sigma_j r_j^* a_j|\hat{\Theta}j\rangle$$

$$\hat{A}\hat{\Theta}|r\rangle = \hat{A}\Sigma_j r_j^*|\hat{\Theta}j\rangle = \Sigma_j r_j^* a_j|\hat{\Theta}j\rangle$$

Since $|r\rangle$ was arbitrary, we conclude that the operator for the variable A which is class I ($\hat{\Theta}$) must satisfy

$$\hat{A}\hat{\Theta} = \hat{\Theta}\hat{A} \tag{24}$$

Note that for systems with time-reversal-invariant hamiltonians (see Section III.B), $\hat{H}$ is class I ($\hat{T}$); thus it commutes with $\hat{T}$.[1c,8b] If we write $\hat{\Theta}$ as $\tilde{\beta}\hat{K}$ [see (18)], (24) becomes

$$\hat{A}\tilde{\beta} = \tilde{\beta}\hat{A}^* \tag{25}$$

For a variable B that is class II ($\hat{\Theta}$) and has a complete set of eigenvectors $|j\rangle$ where

$$\hat{B}|j\rangle = b_j|j\rangle$$

and

$$\hat{B}|\hat{\Theta}j\rangle = -b_j|\hat{\Theta}j\rangle$$

we find, proceeding as before,

$$\hat{B}\hat{\Theta} = -\hat{\Theta}\hat{B} \tag{26}$$

$$\hat{B}\tilde{\beta} = -\tilde{\beta}\hat{B}^* \tag{27}$$

All class I ($\hat{\Theta}$) variables, then, commute with $\hat{\Theta}$ and satisfy the equivalent equations (24) and (25), whereas class II ($\hat{\Theta}$) variables anticommute with $\hat{\Theta}$ and satisfy (26) and (27).

It is quite easy to show that (24) is sufficient as well as necessary for a hermitian operator $\hat{A}$ to be class I ($\hat{\Theta}$): for if (24) holds and

$$\hat{A}|j\rangle = a_j|j\rangle$$

we have

$$\hat{A}\hat{\Theta}|j\rangle = \hat{\Theta}\hat{A}|j\rangle = \hat{\Theta}a_j|j\rangle = a_j|\hat{\Theta}j\rangle$$

where the last step follows because a_j is real. Thus the physical quantity $\hat{A}$ is unchanged on application of $\hat{\Theta}$, which is what was to be proved. An entirely analogous argument shows that (26) is sufficient as well as necessary for a hermitian operator $\hat{B}$ to be class II ($\hat{\Theta}$).

3. Eigenstates of Involutional Antiunitary Operators

We next consider whether a complete set of states $|u\rangle$ may be taken to be eigenstates of $\hat{\Theta}$ so that $|u\rangle = e^{i\phi}|\hat{\Theta}u\rangle$ i.e., $|u\rangle$ and $|\hat{\Theta}u\rangle$ are physically

the same state. There are two cases, corresponding to $\hat{\Theta}^2 = \pm 1$.

If $\hat{\Theta}^2 = +1$, define the states

$$|u_+\rangle = |u\rangle + |\hat{\Theta}u\rangle \tag{28}$$

$$|u_-\rangle = |u\rangle - |\hat{\Theta}u\rangle \tag{29}$$

Applying $\hat{\Theta}$, we find

$$\hat{\Theta}|u_+\rangle = |\hat{\Theta}u\rangle + \hat{\Theta}^2|u\rangle = |\hat{\Theta}u\rangle + |u\rangle = |u_+\rangle$$

A similar calculation gives

$$\hat{\Theta}|u_-\rangle = -|u_-\rangle$$

In this case, therefore, the states can be chosen to be eigenvectors of $\hat{\Theta}$. The foregoing construction gives the eigenvalues ± 1, but in actuality the phase of the eigenvalue turns out to be arbitrary. To see this, we first verify that the absolute value of the eigenvalue must be unity. If

$$\hat{\Theta}|u\rangle = c|u\rangle$$

then $\hat{\Theta}^2|u\rangle = |u\rangle = \hat{\Theta}c|u\rangle = c^*\hat{\Theta}|u\rangle = c^*c|u\rangle$, from which follows $c^*c = 1$. Now suppose that

$$\hat{\Theta}|r\rangle = e^{i\lambda}|r\rangle$$

with λ real; then $e^{i\eta}|r\rangle$, with η real, is an eigenvector of $\hat{\Theta}$ with eigenvalue $e^{i(\lambda - 2\eta)}$, since

$$\hat{\Theta}e^{i\eta}|r\rangle = e^{-i\eta}\hat{\Theta}|r\rangle = e^{i(\lambda-\eta)}|r\rangle = e^{i(\lambda-2\eta)}e^{i\eta}|r\rangle$$

If $\hat{\Theta}^2 = -1$, however, the situation is different. Let us try to construct an eigenvector of $\hat{\Theta}$ in this case. If we postulate the existence of an eigenvector $|q\rangle$, with

$$\hat{\Theta}|q\rangle = c|q\rangle$$

we find

$$\hat{\Theta}^2|q\rangle = -|q\rangle = \hat{\Theta}c|q\rangle = c^*\hat{\Theta}|q\rangle = c^*c|q\rangle$$

Since we can never have $c^*c = -1$, this is a contradiction, and it follows that the postulated state cannot exist. In this case, therefore, $|\hat{\Theta}u\rangle$ is always physically different from $|u\rangle$.

It can also be shown for the case $\hat{\Theta}^2 = -1$ that $|\hat{\Theta}q\rangle$ is always orthogonal to $|q\rangle$. To show this, we presume the contrary—that is, for some $|q\rangle$,

assumed normalized to unity, we have

$$|\hat{\Theta}q\rangle = c|q\rangle + |r\rangle \tag{30}$$

where $|r\rangle$ is a ket orthogonal to $|q\rangle$. Since $|\hat{\Theta}q\rangle$ must also be normalized, we have

$$cc^* + \langle r|r\rangle = 1 \tag{31}$$

Applying $\hat{\Theta}$ to both sides of (30), we find

$$\hat{\Theta}^2|q\rangle = -|q\rangle = c^*|\hat{\Theta}q\rangle + |\hat{\Theta}r\rangle = c^*c|q\rangle + c^*|r\rangle + |\hat{\Theta}r\rangle$$

which can be solved for $|\hat{\Theta}r\rangle$ to give

$$|\hat{\Theta}r\rangle = -(1 + c^*c)|q\rangle - c^*|r\rangle$$

Taking the norms of both sides, we obtain

$$\langle \hat{\Theta}r|\hat{\Theta}r\rangle = \langle r|r\rangle = (1 + c^*c)^2 + c^*c$$

which contradicts (31) unless $c = 0$. We conclude, then, that when $\hat{\Theta}^2 = -1$, we always have $\langle q|\hat{\Theta}q\rangle = 0$.

D. Properties of the Time-Reversal Operator

1. Explicit Form

To determine explicitly the form of the time-reversal operator $\hat{T}$ for a system of particles of arbitrary spin, we proceed as follows: we classify all variables as class I ($\hat{T}$) or class II ($\hat{T}$) according to whether they are left unchanged or change sign, respectively, on application of $\hat{T}$. According to (18), the determination of the explicit form of $\hat{T}$ reduces to that of $\tilde{\beta}$; also, if $\boldsymbol{\beta}$ is determined in one representation, we can use (19) to determine it in all others. We choose the Schrödinger coordinate space representation, in which the operator for a coordinate x is simply multiplication by x, and that for p_x is $(\hbar/i)(\partial/\partial x)$.

All coordinates are class I($\hat{T}$), so, according to (25), since $\hat{x}^* = \hat{x}$, $\tilde{\beta}$ must commute with all of them. The momenta are class II($\hat{T}$), and $\hat{p}^* = -\hat{p}$, so it follows from (27) that $\tilde{\beta}$ also commutes with all the momenta. We conclude that $\tilde{\beta}$ must operate solely on the spin variables and that it is simply the unit operator if the particles are spinless. It is important to note, however, that even the unit operator is not invariant under (19); thus it does *not* follow that $\tilde{\beta} = 1$ in all representations for spinless particles.

We illustrate the transformation properties of the unitary operator $\tilde{\beta}$ by calculating its form in the momentum representation for a spinless particle (in one dimension) by two methods: by direct inspection, and by means of the transformation law (19).

In this representation, we have $\hat{p}=p=\hat{p}^*$, and $\hat{x}=i\hbar(d/dp)=-\hat{x}^*$. Since $\hat{x}$ is class I ($\hat{T}$), we must have

$$\hat{x}\tilde{\beta}=\tilde{\beta}\hat{x}^*=-\tilde{\beta}\hat{x}$$

and, since $\hat{p}$ is class II ($\hat{T}$),

$$\hat{p}\tilde{\beta}=-\tilde{\beta}\hat{p}^*=-\tilde{\beta}\hat{p}$$

Thus $\tilde{\beta}$ must anticommute with both $\hat{x}$ and $\hat{p}$. It is easily verified that these conditions are satisfied by the operator $\tilde{Q}$ defined as the operator that changes p to $-p$. For, with this assumption, we have

$$\hat{x}\tilde{\beta}\phi(p)=i\hbar\frac{d}{dp}\phi(-p)=-i\hbar\frac{d\phi}{dp}(-p)$$

$$\tilde{\beta}\hat{x}\phi(p)=\tilde{\beta}i\hbar\frac{d}{dp}\phi(p)=i\hbar\frac{d\phi}{dp}(-p)=-i\hbar\frac{d}{dp}\phi(-p)$$

$$\hat{p}\tilde{\beta}\phi(p)=\hat{p}\phi(-p)$$

$$\tilde{\beta}\hat{p}\phi(p)=-\hat{p}\phi(-p)$$

Also, if $\tilde{\alpha}$ is some other unitary operator anticommuting with both $\hat{x}$ and $\hat{p}$, we have

$$\tilde{\alpha}\tilde{\beta}\hat{x}=-\tilde{\alpha}\hat{x}\tilde{\beta}=\hat{x}\tilde{\alpha}\tilde{\beta}$$

that is, $(\tilde{\alpha}\tilde{\beta})$ commutes with $\hat{x}$ and, similarly, with $\hat{p}$ as well. It follows that $(\tilde{\alpha}\tilde{\beta})$ is just a constant times the unit operator and that $\tilde{\alpha}$ is a constant times $\tilde{\beta}^{-1}$. By (23), since the upper sign applies in the present case $\tilde{\beta}^{-1}=\tilde{\beta}^*$. Since $\tilde{\beta}$ is real in the present case, this argument shows that $\tilde{\alpha}$ is a constant times $\tilde{\beta}$. Thus our assumed form for $\tilde{\beta}$ is, apart from a constant phase factor, the only possible one.

If we denote the matrix for the $\tilde{\beta}$ operator in the Schrödinger representation by $\boldsymbol{\beta}_x=1$, then according to (19), the matrix for $\tilde{\beta}$ in the momentum representation is given by

$$\boldsymbol{\beta}_p=\mathbf{U}\mathbf{U}^T$$

where in this case

$$\langle p|\hat{U}|x\rangle=\langle x|\hat{U}^T|p\rangle=\hbar^{-1/2}e^{-ipx/\hbar}$$

We thus find

$$\langle p|\tilde{\beta}|p'\rangle = \int_{-\infty}^{\infty} \langle p|\hat{U}|x\rangle dx \langle x|\hat{U}^T|p'\rangle = \delta(p+p')$$

and thus

$$\tilde{\beta}\phi(p) = \int \langle p|\tilde{\beta}|p'\rangle \phi(p')\, dp' = \phi(-p)$$

which verifies that the two approaches give the same result, as they should.

To determine the spin part of $\tilde{\beta}$, we first consider a single spin-$\frac{1}{2}$-particle. All three components of spin are class II ($\hat{T}$), and letting $\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_y$, $\boldsymbol{\sigma}_z$ represent the usual Pauli matrices,[5a,6a,22c,23a] we have

$$\boldsymbol{\sigma}_x^* = \boldsymbol{\sigma}_x; \qquad \boldsymbol{\sigma}_y^* = -\boldsymbol{\sigma}_y; \qquad \boldsymbol{\sigma}_z^* = \boldsymbol{\sigma}_z$$

According to (27), therefore, $\boldsymbol{\beta}$ must anticommute with $\boldsymbol{\sigma}_x$ and $\boldsymbol{\sigma}_z$ and commute with $\boldsymbol{\sigma}_y$. This is satisfied by

$$\boldsymbol{\beta} = e^{i\Phi}\boldsymbol{\sigma}_y = e^{i\Phi}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

where ϕ is any real number. This equation does not single out the y direction as having special properties. The spin component s_y is a physical quantity, its representation is $\frac{1}{2}\boldsymbol{\sigma}_y$ only in the usual representation (see Section III.F.2), and it transforms according to $\mathbf{s}_y' = \mathbf{U}\mathbf{s}_y\mathbf{U}^\dagger$ when we go to another representation, whereas $\boldsymbol{\beta}$ transforms according to (19). Thus $\boldsymbol{\beta} = e^{i\Phi}(2\mathbf{s}_y)$ holds only in one particular representation. Using (19) it is easy to show that

$$\boldsymbol{\beta}' = \mathbf{U}e^{i\Phi}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\mathbf{U}^T = (\det \mathbf{U})e^{i\Phi}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Since $|\det \mathbf{U}| = 1$ for any unitary matrix $\mathbf{U}$, this yields for all representations for a spin-$\frac{1}{2}$-particle[24]

$$\boldsymbol{\beta}' = e^{i\eta}\boldsymbol{\sigma}_y$$

with η real.

If there are several spin-$\frac{1}{2}$-particles, the spin components of them all are separately class II ($\hat{T}$), and $\boldsymbol{\beta}$ becomes a direct product of the $\boldsymbol{\sigma}_y$ matrices for all the particles. If there are particles with spin greater than $\frac{1}{2}$, they may be regarded as built up from spin-$\frac{1}{2}$-particles, and $\boldsymbol{\beta}$ constructed accordingly. The treatment of Section III.F makes this more explicit.

With our explicit form of $\boldsymbol{\beta}$, we can determine the sign of $\hat{T}^2$ by using (23). The space part of $\boldsymbol{\beta}$ clearly contributes just $+1$. For each spin-$\frac{1}{2}$-

particle, the spin part, according to (23), contributes a factor

$$\boldsymbol{\beta}\boldsymbol{\beta}^* = \boldsymbol{\sigma}_y \boldsymbol{\sigma}_y^* = -\boldsymbol{\sigma}_y^2 = -\mathbf{1}$$

It follows immediately that the sign of $\hat{T}^2$ is positive or negative according to whether the total spin is integral or half-odd integral.

It is also of interest to consider the behavior of $\tilde{\beta}$ under a rotation of coordinates. The operator for an infinitesimal rotation is*

$$\hat{U} = \hat{1} + i\vec{e}\cdot\hat{\vec{J}}$$

where the direction of $\vec{e}$ gives that of the axis of rotation and its magnitude (assumed infinitesimal), the angle of rotation; $\hat{\vec{J}}$ is the vector total-angular-momentum operator, in an arbitrary coordinate system. Since $\hat{\vec{J}}$ is hermitian and $\vec{e}$ real, we have

$$\hat{U}^T = \hat{1} + i\vec{e}\cdot\hat{\vec{J}}^*$$

Also, since $\vec{J}$ is class II ($\hat{T}$), (27) yields

$$\hat{\vec{J}}\tilde{\beta} = -\tilde{\beta}\hat{\vec{J}}^*$$

The effect of the transformation on $\tilde{\beta}$, through the first order in $\vec{e}$, is given by

$$\tilde{\beta}' = \hat{U}\tilde{\beta}\hat{U}^T = \tilde{\beta} + i\vec{e}\cdot\left(\hat{\vec{J}}\tilde{\beta} + \tilde{\beta}\hat{\vec{J}}^*\right) = \tilde{\beta}$$

In other words, $\tilde{\beta}$ is not changed by a rotation of coordinates. If, therefore, the matrix form of $\tilde{\beta}$ has been worked out with respect to one Cartesian coordinate system, one can use the same form for all such coordinate systems.

Finally we note that $\boldsymbol{\beta}$ is changed by a unitary transformation which just multiplies by a phase factor: If $\mathbf{U} = e^{i\phi}\mathbf{1}$, then

$$\mathbf{U}\boldsymbol{\beta}\mathbf{U}^T = e^{2i\phi}\boldsymbol{\beta}$$

2. Kramers Degeneracy

If the hamiltonian is time-reversal-invariant (see Section III.B), it follows that each energy eigenstate $|j\rangle$ has the same energy as $|\hat{T}j\rangle$. If these eigenstates can be chosen also to be eigenstates of $\hat{T}$, so that $|j\rangle = e^{i\phi}|\hat{T}j\rangle$, (i.e., $|j\rangle$ and $|\hat{T}j\rangle$ are the same states), this does not introduce any new degeneracy. However, if $|\hat{T}j\rangle$ is necessarily physically different from $|j\rangle$,

*Compare the discussion at the beginning of Section III.F.1.

the time-reversal invariance brings about twofold degeneracy.

If $\hat{T}^2 = +1$, the result of Section III.C.3 is that the eigenstates of $\hat{H}$ can be chosen to be eigenvectors of $\hat{T}$. Thus consideration of $\hat{T}$ alone does not require degeneracy.

If $\hat{T}^2 = -1$, however, the result of Section III.C.3 is that $|\hat{T}j\rangle$ is always physically distinct from $|j\rangle$. Thus the time-reversal invariance introduces a twofold degeneracy known as "Kramers degeneracy."[5b,22d]

E. Minimization of the Number of Class II ($\hat{T}$) Variables in the Complete Set of Commuting Variables

Consider a system of particles with no external fields present, so that the energy eigenstates may be chosen to be eigenstates of total angular momentum $\vec{J}$ (quantum number J) and of its z-component J_z (quantum number M). Let d denote the set of scalar observables which, together with J and M, are sufficient to determine the state.* Since J_z is a class II ($\hat{T}$) variable and $\hat{J}^2$ is class I ($\hat{T}$), we certainly have

$$\hat{T}|d,J,M\rangle = e^{i\gamma(d,J,M)}|d_t,J,-M\rangle \tag{32}$$

where $\gamma(d,J,M)$ is real and d_t differs from d in that the signs of all class II ($\hat{T}$) variables have been reversed. The question arises of whether it is possible to choose d to consist only of class I ($\hat{T}$) variables, so that $d = d_t$ and J_z is the only class II ($\hat{T}$) variable used in the specification of a state.

To answer this question, we introduce the operator $\hat{R}_x$, a rotation through 180° about the x-axis, and $\hat{C}_x = \hat{R}_x\hat{T}$. Applying $\hat{R}_x$ to both sides of (32), we find, since the d are scalars,

$$\hat{C}_x|d,J,M\rangle = e^{i[\gamma(d,J,M)+q(d,J,-M)]}|d_t,J,M\rangle \tag{33}$$

where $q(d,J,-M)$ is real. The operator $\hat{C}_x$ is evidently antiunitary and involutional. We see from (33) that d_t can be chosen identical with d if and only if the eigenstates can be chosen to be eigenstates of $\hat{C}_x$; and this, according to the treatment of Section III.C.3, depends on whether $\hat{C}_x^2 = +1$ or -1. We now proceed to investigate this question.

The class I ($\hat{C}_x$) variables are x, p_y, p_z, s_y, s_z, but y, z, p_x, s_x are class II ($\hat{C}_x$). The space part of the $\tilde{\beta}$ operator [see (18)] for $\hat{C}_x$ in the Schrödinger coordinate space representation is just the usual 180° rotation, and contributes $+1$ to $\hat{C}_x^2$. To calculate the spin part $\tilde{\beta}_s$, we again consider a spin-$\frac{1}{2}$-particle, the usual representation of spin components in terms of the Pauli matrices, and use (27). We find this time that $\boldsymbol{\beta}_s$ must anticommute

*It is shown in Appendix A that the variables d can always be chosen to be scalars.

with σ_y and σ_x and commute with σ_z. This is satisfied by $\beta_s = \sigma_z$. Using (23) again, we find $\hat{C}_x^2 = \sigma_z \sigma_z^* = \sigma_z^2 = +1$.

Since $\hat{C}_x^2 = +1$, we can choose the eigenstates of $\hat{H}$ to also be eigenstates of $\hat{C}_x$, with any eigenvalues of magnitudes unity (see Section III.C.3). By (33) this means d includes no class II ($\hat{T}$) variables and a d that is specified not to include any class II ($\hat{T}$) variables will be called D. If we choose the eigenvalues to be $+1$, we have

$$\hat{C}_x|D,J,M\rangle = \hat{R}_x\hat{T}|D,J,M\rangle = |D,J,M\rangle \tag{34}$$

The choice of phase which ensures that (34) is satisfied is derived in Section III.F.4. Applying $\hat{R}_x^{-1}$ to both sides of (34), we find

$$\hat{T}|D,J,M\rangle = \hat{R}_x^{-1}|D,J,M\rangle = e^{i\tau(D,J,M)}|D,J,-M\rangle$$

where $\tau(D,J,M)$ is real and is determined by the phase convention used in defining the states.

The conclusion of this subsection is that in the absence of external fields in systems with rotational invariance, it is always possible to choose one's quantum numbers in such a way that J_z is the only class II ($\hat{T}$) variable used. If this is done, the Kramers degeneracy in energy introduces no *new* degeneracy, since degeneracy between states with different quantum numbers M is already required by the rotational invariance. There may, of course, be a near-degeneracy such as Kramers degeneracy of the electronic state with fixed nuclei, which is only split by the interaction between electronic and nuclear motion.

It is also easily seen that the set of scalar quantum numbers D may be chosen to include the parity of the system. From the explicit form of $\hat{T}$ derived in Section III.D.1, it is evident that $\hat{T}$ does not change the parity [i.e., that parity is class I ($\hat{T}$)]. Being a rotation, $\hat{R}_x$ also leaves the parity unchanged. Thus $\hat{C}_x$ leaves the parity unchanged. Hence if the eigenstates of $\hat{C}_x$ are constructed according to the prescription of Section III.C.3, we only have to choose the state $|u\rangle$ in (28) and (29) to be an eigenstate of parity to ensure that the eigenstates of $\hat{C}_x$ are eigenstates of parity also.

It will be useful for later purposes to *summarize* the properties of $\hat{C}_x$ that we have established: $\hat{C}_x$ is involutional and antiunitary, and $\hat{C}_x^2 = +1$ always; $\hat{C}_x$ commutes with $\hat{J}^2$, $\hat{J}_z$, and the parity operator $\hat{P}$, as well as with the hamiltonian $\hat{H}$ in problems we will be considering. Hence we can always choose our complete set of states to be simultaneous eigenstates of $\hat{J}^2$, $\hat{J}_z$, $\hat{P}$, and $\hat{C}_x$. If this is done, the time-reversal operator $\hat{T}$ reverses the eigenvalue of $\hat{J}_z$, leaving all other quantum numbers unchanged. Conversely, if the only class II ($\hat{T}$) variable in our complete set of commuting

variables is $\hat{J}_z$, our states are eigenstates of $\hat{C}_x$. It is also evident that all these properties hold equally well for the analogously defined operator $\hat{C}_y = \hat{R}_y \hat{T}$, in which the role of the x-axis in $\hat{C}_x$ is assumed by the y-axis. The utility of $\hat{C}_x$ and $\hat{C}_y$ in subsequent discussions is attributable to two conditions. First, since $\hat{C}_x^2 = +1$ and $\hat{C}_y^2 = +1$, we can always choose our complete set of states to be eigenstates of $\hat{C}_x$ or $\hat{C}_y$; but since $\hat{T}^2$ is sometimes -1, we cannot always choose our states as eigenstates of $\hat{T}$. Second, $\hat{C}_x$, $\hat{C}_y$, and $\hat{P}$ commute with $\hat{J}_z$ as compared, for example, with $\hat{R}_x$, $\hat{R}_y$, and $\hat{T}\hat{P}$, which each anticommute with $\hat{J}_z$.

F. Phase Conventions in Total-Angular-Momentum Representations

1. Preliminaries

The work of Section III.E, together with that of Appendix A, shows that it is always possible to choose a representation in which the states are characterized by the total-angular-momentum quantum numbers J and M, with the other quantum numbers being class I ($\hat{T}$) scalars. In such a representation, the $(2J+1)$-dimensional manifold spanned by the states $|D,J,M\rangle$ (D and J fixed, $M = -J, -J+1, \ldots, J$) is invariant under time reversal as well as under rotation, and in particular angular momentum, operators. It follows that the properties of these operators may be studied within such a subspace without reference to the rest of the Hilbert space. We now take up the question of the properties of the operators $\hat{T}$, $\hat{R}_x$, $\hat{C}_x$, the analogous operators $\hat{R}_y$ and $\hat{C}_y$, and the angular momentum operators themselves within such a manifold, as well as their relation to one another and to the phase convention used in defining the states. The states $|D,J,M\rangle$ are assumed to be normalized and, by definition, to be eigenstates of $\hat{J}^2$ and $\hat{J}_z$. This determines each state function only up to a multiplicative phase factor $e^{i\phi}$, where ϕ is real and may be chosen arbitrarily for each state. We want to concentrate on determining the effect of this choice of phase on the properties of $\hat{T}$, $\hat{C}_x$, and so on.

We begin with a brief remark on the phasing of the rotation operators themselves. The rotation of a physical system about a given axis through an angle Θ may be expressed quantum mechanically by means of the unitary operator[8c,22e,23b]

$$\hat{U}(\vec{\Theta}) = e^{-i\vec{\Theta}\cdot\hat{J}}$$

where $\vec{\Theta}$ is a vector of magnitude Θ directed along the axis of rotation in the right-handed sense, and $\hat{J}$ is the total-angular-momentum operator. As

mentioned in the discussion following (23), however, the unitary operator $\hat{U}(\vec{\Theta})$ may be multiplied by an arbitrary phase factor $e^{i\phi(\vec{\Theta})}$, causing the $\hat{U}(\vec{\Theta})$ to be replaced by

$$\hat{U}_\phi(\vec{\Theta}) = e^{i\phi(\vec{\Theta})} e^{-i\vec{\Theta}\cdot\hat{\vec{J}}}$$

The physical effect of the $\hat{U}_\phi$ operators is the same as that of the $\hat{U}$; it is desirable, however, to choose the phases in such a way that the $\hat{U}_\phi(\vec{\Theta})$ form a representation (perhaps double-valued) of the three-dimensional rotation group. Since the $\hat{U}(\vec{\Theta})$ form a representation, the $\hat{U}_\phi$ will do so only if the phase factors $e^{i\phi(\vec{\Theta})}$ form a one-dimensional representation of the rotation group. Since the only such one-dimensional representation is the unit representation, we must set all phase factors equal to unity [i.e., represent all rotations by $\hat{U}(\vec{\Theta})$]. In conformity with universal usage, this is done throughout the chapter. Another desirable property of this convention is that the rotation of the *physical system* through an angle Θ is mathematically identical (including its effect on phases) to a rotation of the *coordinate system* about the same axis through $(-\Theta)$. The infinitesimal rotation of coordinates discussed in Section III.D.1 is thus carried out in the right-handed sense about the axis $\vec{e}$.

In the work to follow, we need certain commutation relations between $\hat{T}$, $\hat{C}_x$, etc. and the raising and lowering operators $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$. Since all components of angular momentum are class II ($\hat{T}$), we have, according to (26),

$$\hat{T}\hat{\vec{J}} = -\hat{\vec{J}}\hat{T} \tag{35}$$

Thus $\hat{T}$ anticommutes with all components of $\hat{\vec{J}}$, and, since it is antiunitary, also with the factor i. We therefore find

$$\hat{T}\hat{J}_\pm = \hat{T}\hat{J}_x \pm \hat{T}i\hat{J}_y = \hat{T}\hat{J}_x \mp i\hat{T}\hat{J}_y = -\hat{J}_x\hat{T} \pm i\hat{J}_y\hat{T} = -\hat{J}_\mp\hat{T} \tag{36}$$

The operator $\hat{C}_x$ is antiunitary (hence anticommutes with i) and reverses only J_x, leaving J_y and J_z invariant. According to (24) and (26), therefore, it commutes with $\hat{J}_y$ and anticommutes with $\hat{J}_x$. Hence we find

$$\hat{C}_x\hat{J}_\pm = \hat{C}_x\hat{J}_x \pm \hat{C}_x i\hat{J}_y = \hat{C}_x\hat{J}_x \mp i\hat{C}_x\hat{J}_y = -\hat{J}_x\hat{C}_x \mp i\hat{J}_y\hat{C}_x = -\hat{J}_\pm\hat{C}_x \tag{37}$$

The analogous operator $\hat{C}_y$ is defined as $\hat{C}_y = \hat{R}_y\hat{T}$, where $\hat{R}_y$ is a rotation through 180° about the y-axis. The operator $\hat{C}_y$ reverses J_y, leaves J_x and J_z invariant, and is antiunitary. It therefore commutes with $\hat{J}_x$ and anticom-

mutes with i and $\hat{J}_y$. We find for $\hat{C}_y$, analogously to (37)

$$\hat{C}_y \hat{J}_\pm = \hat{J}_\pm \hat{C}_y \tag{38}$$

We also need the analogous relations for the unitary rotation operators $\hat{R}_x$ and $\hat{R}_y$. To obtain these, we first note that the derivation of (24) and (26) does not depend on the antiunitary nature of the operator concerned; thus the results hold for unitary involutional operators as well. It follows that $\hat{R}_x$, which reverses J_z and J_y, leaving J_x invariant, must anticommute with $\hat{J}_z$, $\hat{J}_y$ and commute with $\hat{J}_x$ and (since it is unitary, not antiunitary), with numerical factors such as i. Accordingly, we obtain

$$\hat{R}_x \hat{J}_\pm = \hat{R}_x \hat{J}_x \pm \hat{R}_x i\hat{J}_y = \hat{J}_x \hat{R}_x \mp i\hat{J}_y \hat{R}_x = \hat{J}_\mp \hat{R}_x \tag{39}$$

The analogous calculation for $\hat{R}_y$ yields

$$\hat{R}_y \hat{J}_\pm = -\hat{J}_\mp \hat{R}_y \tag{40}$$

2. Normal Phase Conventions

It follows from the general theory of angular momentum that[6b,25]

$$|D,J,M+1\rangle = N_{JM} e^{i\phi(D,J,M)} \hat{J}_+ |D,J,M\rangle \tag{41}$$

and

$$|D,J,M\rangle = N_{JM} e^{-i\phi(D,J,M)} \hat{J}_- |D,J,M+1\rangle \tag{42}$$

where $N_{JM} = [(J-M)(J+M+1)]^{-1/2}$ is a real positive normalizing factor, and $\phi(D,J,M)$ is a (real) phase angle that may be chosen arbitrarily. [The identity of the phase angles in (41) and (42) follows because $|D,J,M\rangle$ is an eigenstate of $\hat{J}_-\hat{J}_+$ with a real, nonnegative eigenvalue.] We define a *normal* (n) phase convention as one in which all the $\phi(D,J,M)$ in (41) and (42) are zero. This determines the *relative* phases of the $|D,J,M\rangle$ with common D and J, leaving only a common phase factor free. In this subsection, we study the properties of the various operators under normal phase conventions, including several special cases.

Since the matrix representation of a *linear* operator depends only on the *relative* phases of the state vectors, the form of the angular momentum operators, and of all operators constructed from them, will be completely determined when one specifies a normal phase convention. For example, it is easily verified in the case of spin-$\frac{1}{2}$ that the components of spin angular momentum have their usual Pauli form $\vec{s} = \frac{1}{2}\vec{\sigma}$ if the phase convention is

normal. The form of the time-reversal and other antiunitary operators will depend on the common phase factor still left unspecified.

If the phase convention is normal, we have

$$|D,J,M+1\rangle_n = N_{JM}\hat{J}_+|D,J,M\rangle_n$$

where the subscript n simply reminds us of the normality of the phase convention. The rotation $\hat{R}_x$ reverses J_z, hence we have

$$\hat{R}_x|D,J,M\rangle_n = e^{i\rho_M}|D,J,-M\rangle_n$$

where ρ_M is a real number to be determined. From (39) and (42) with $\phi(D,J,M)=0$, from the definition of N_{JM}, and from the last two equations, it follows that

$$\begin{aligned}\hat{R}_x|D,J,M+1\rangle_n &= N_{JM}\hat{R}_x\hat{J}_+|D,J,M\rangle_n \\ &= N_{JM}\hat{J}_-\hat{R}_x|D,J,M\rangle_n = N_{JM}\hat{J}_- e^{i\rho_M}|D,J,-M\rangle_n \\ &= N_{JM}N^{-1}_{J,-M-1}e^{i\rho_M}|D,J,-M-1\rangle_n = e^{i\rho_M}|D,J,-M-1\rangle_n\end{aligned}$$

It follows that all the ρ_M are equal, which means that we can drop the subscript M.

To determine ρ, we first specify $\hat{R}_x$ as a rotation through π in the right-handed sense, that is,

$$\hat{R}_x = e^{-i\pi\hat{J}_x}$$

Since the form of the operators $\hat{J}$ is determined by the quantum number J plus the normal phase convention, this choice will completely determine $\hat{R}_x$. It suffices, therefore, to determine ρ for any special case with total-angular-momentum quantum number J and normal phase convention. We choose the case in which a state of total angular momentum J is built up by combining $2J$ spin-$\frac{1}{2}$-particles. For each particle, we have

$$\hat{R}_x = e^{-i\pi s_x} = e^{-i(\pi/2)\sigma_x} = -i\sigma_x \sin\frac{\pi}{2} = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$$

The state $|D,J,J\rangle$ is simply a direct product of states $|\frac{1}{2}, \frac{1}{2}\rangle$, and $|D,J,-J\rangle$ is the same direct product of $|\frac{1}{2}, -\frac{1}{2}\rangle$ states.

For each single spin, we evidently have

$$\hat{R}_x|\tfrac{1}{2},\tfrac{1}{2}\rangle = -i|\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

Therefore the effect of $\hat{R}_x$ applied to the direct product $|D,J,J\rangle$ is

$$\hat{R}_x|D,J,J\rangle=(-i)^{2J}|D,J,-J\rangle$$

We conclude that

$$e^{i\rho}=(-i)^{2J}$$

Our result is therefore

$$\hat{R}_x|D,J,M\rangle_n=(-i)^{2J}|D,J,-M\rangle_n \tag{43}$$

From (43) follows the well-known result[22c]

$$\hat{R}_x^2=(-1)^{2J} \tag{44}$$

Note that for integer J, the result would have been the same if we had defined $\hat{R}_x$ as a rotation in the left-handed sense. For half-odd integer J, the two choices yield $e^{i\rho}$ phase factors that differ by a factor of (-1), corresponding to a rotation through 2π.

Proceeding analogously for $\hat{R}_y$, we find with the aid of (40)

$$\hat{R}_y|D,J,M\rangle_n=e^{i\sigma_M}|D,J,-M\rangle_n$$

with $e^{i\sigma_{M+1}}=-e^{i\sigma_M}$. We thus have

$$\hat{R}_y|D,J,M\rangle_n=e^{i\sigma}(-1)^{J+M}|D,J,-M\rangle_n$$

(We have defined $\sigma=\sigma_{-J}$ so that $J+M$ rather than simply M appears in the exponent; this is convenient because the former is always an integer whereas the latter is not.) The choice

$$\hat{R}_y=e^{-i\pi\hat{J}_y}$$

corresponds to $e^{i\sigma}=(-1)^{2J}$. Our result is therefore

$$\hat{R}_y|D,J,M\rangle_n=(-1)^{3J+M}|D,J,-M\rangle_n=(-1)^{J-M}|D,J,-M\rangle_n \tag{45}$$

from which follows

$$\hat{R}_y^2=(-1)^{2J} \tag{46}$$

which is analogous to (44).

The time-reversal operator $\hat{T}$ reverses J_z, and D contains no class II ($\hat{T}$)

variables; thus we have

$$\hat{T}|D,J,M\rangle_n = e^{i\tau_M}|D,J,-M\rangle_n$$

where τ_M is real. Using (36), we find

$$\hat{T}|D,J,M+1\rangle_n = N_{JM}\hat{T}\hat{J}_+|D,J,M\rangle_n = -N_{JM}\hat{J}_-\hat{T}|D,J,M\rangle_n$$

$$= -N_{JM}\hat{J}_- e^{i\tau_M}|D,J,-M\rangle_n = -e^{i\tau_M}|D,J,-M-1\rangle_n$$

Successive values of $e^{i\tau_M}$ thus differ by a factor of (-1), and we can summarize the result as

$$\hat{T}|D,J,M\rangle_n = e^{i\tau}(-1)^{J+M}|D,J,-M\rangle_n \tag{47}$$

where τ is defined as τ_{-J}. The phase angle τ depends on the common phase factor that is still left unspecified in the definition of a normal phase convention. For if we change to a new, primed normal representation by means of

$$|D,J,M\rangle_{n'} = e^{i\eta}|D,J,M\rangle_n \tag{48}$$

we find

$$\hat{T}|D,J,M\rangle_{n'} = \hat{T}e^{i\eta}|D,J,M\rangle_n = e^{-i\eta}\hat{T}|D,J,M\rangle_n$$

$$= e^{-i\eta}e^{i\tau}(-1)^{J+M}|D,J,-M\rangle_n$$

$$= e^{-2i\eta}e^{i\tau}(-1)^{J+M}|D,J,-M\rangle_{n'}$$

Thus when the common phase is changed by the transformation (48), the phase factor $e^{i\tau}$ of (47) is replaced by

$$e^{i\tau'} = e^{i\tau}e^{-2i\eta} \tag{49}$$

In particular, notice that the $e^{i\tau}$ phase factor is unchanged if $e^{i\eta} = -1$. Thus a choice of a phase convention for the $e^{i\tau}$ phase factor still leaves the absolute sign of the wavefunction undefined. (All the phase conventions named below are phase conventions for the $e^{i\tau}$ phase factor; thus they leave the absolute sign of the wavefunction undefined.)

The matrix $\boldsymbol{\beta}$ associated with the time-reversal operator by (18) in a normal representation of this type has the elements

$$\langle D,J,-M|\tilde{\beta}|D,J,M\rangle_n = e^{i\tau}(-1)^{J+M} \tag{50}$$

with all other elements being zero. Thus specifying the $e^{i\tau}$ phase factor is equivalent to specifying $\boldsymbol{\beta}$, and vice versa.

It is now useful to work out the eigenvalues of the antiunitary operators $\hat{C}_x$ and $\hat{C}_y$. For $\hat{C}_x$ we find, with the help of (43) and (47):

$$\hat{C}_x|D,J,M\rangle_n = \hat{R}_x\hat{T}|D,J,M\rangle_n = \hat{R}_x e^{i\tau}(-1)^{J+M}|D,J,-M\rangle_n$$

$$= e^{i\tau}(-i)^{2J}(-1)^{J+M}|D,J,M\rangle_n \tag{51}$$

Proceeding in the same way for $\hat{C}_y$, and using (45) and (47), we find

$$\hat{C}_y|D,J,M\rangle_n = e^{i\tau}|D,J,M\rangle_n \tag{52}$$

We next examine a few special cases of normal phase conventions, which, as we see presently, correspond to phase conventions that have been used in the literature. First, the spherical harmonics as defined by Condon and Shortley[26] and Messiah[23c] span a normal representation for integer J, with the common phase being fixed by the requirement that $|D,J,0\rangle$ is the real Legendre polynomial[4a] P_J and is thus left invariant under $\hat{T}$. Referring to (47), we see that this is achieved by setting $e^{i\tau} = (-1)^J$ for integer J. A normal phase convention satisfying this relation for integer J will be called a *normal Legendre* (nL) phase convention. This still leaves the choice of τ for half-odd integer J free, but the most natural generalization is to set $e^{i\tau} = (\pm i)^{2J}$ for all J. Of these, we see from (50) that the lower sign gives $\boldsymbol{\beta} = \boldsymbol{\sigma}_y$ for $J = \frac{1}{2}$. Accordingly, we define the *generalized normal Legendre* (gnL) phase convention as one in which

$$e^{i\tau} = (-i)^{2J}$$

For such a convention, (47), (51), and (52) become

$$\hat{T}|D,J,M\rangle_{\text{gnL}} = (-i)^{2J}(-1)^{J+M}|D,J,-M\rangle_{\text{gnL}} \tag{53}$$

$$\hat{C}_x|D,J,M\rangle_{\text{gnl}} = (-i)^{4J}(-1)^{J+M}|D,J,M\rangle_{\text{gnL}} = (-1)^{J-M}|D,J,M\rangle_{\text{gnL}} \tag{54}$$

$$\hat{C}_y|D,J,M\rangle_{\text{gnL}} = (-i)^{2J}|D,J,M\rangle_{\text{gnL}} \tag{55}$$

Another choice that is sometimes convenient is $e^{i\tau} = 1$, which we call a

normal positive (+) phase convention. For this choice we find

$$\hat{T}|D,J,M\rangle_+ = (-1)^{J+M}|D,J,-M\rangle_+ \tag{56}$$

$$\hat{C}_x|D,J,M\rangle_+ = (-i)^{2J}(-1)^{J+M}|D,J,M\rangle_+ \tag{57}$$

$$\hat{C}_y|D,J,M\rangle_+ = |D,J,M\rangle_+ \tag{58}$$

Another choice frequently used is $e^{i\tau} = (-1)^{2J}$, which we call a normal negative (−) phase convention. In this case we obtain

$$\hat{T}|D,J,M\rangle_- = (-1)^{J-M}|D,J,-M\rangle_- \tag{59}$$

$$\hat{C}_x|D,J,M\rangle_- = (-i)^{2J}(-1)^{J-M}|D,J,M\rangle_- \tag{60}$$

$$\hat{C}_y|D,J,M\rangle_- = (-1)^{2J}|D,J,M\rangle_- \tag{61}$$

Note that the positive and negative phase conventions are identical to each other for integer angular momenta but differ for half-integer angular momenta. For spin-$\frac{1}{2}$, the positive and negative phase conventions yield $\beta = i\sigma_y$ and $\beta = -i\sigma_y$, respectively. See also Appendix C.

We see that the phase factors $e^{i\tau}$ for the ± phase convections differ from that for the gnL phase convention by $(\pm i)^{2J}$. Referring to (49), we conclude from this that

$$|D,J,M\rangle_\pm = (\mp i)^J|D,J,M\rangle_{\text{gnL}} \tag{62}$$

For integer total angular momenta, this means that the state vectors transform like Condon-Shortley spherical harmonics multiplied by $(\mp i)^J$. Since, however, all phase conventions based on the $e^{i\tau}$ phase factor leave an overall sign of the wavefunction undefined (as discussed earlier in this subsection), we see that the positive and negative normal phase conventions are the same for integer angular momenta.

3. Angular Momentum Addition Using Normal Phase Conventions and Real Clebsch-Gordan Coefficients

The typical case considered in angular momentum addition theory is that of a system consisting of two kinematically independent parts, with total-angular-momentum quantum numbers j_1 and j_2. The state of the

combined system, with total-angular-momentum quantum numbers J, M (with $J = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2|$) is expressed

$$|j_1, j_2, J, M\rangle = \sum_{m_1, m_2} |j_1, m_1\rangle |j_2, m_2\rangle \langle j_1, j_2, m_1, m_2 | j_1, j_2, J, M\rangle \qquad (63)$$

where D is (j_1, j_2) and the coefficients $\langle j_1, j_2, m_1, m_2 | j_1, j_2, J, M\rangle$ are Clebsch-Gordan (CG) coefficients. In general, there is no necessary connection between the phase conventions used for the partial systems and that for the full system, since the CG coefficients themselves contain arbitrary phase factors. It is customary, however, to adopt normal phase conventions for both partial systems, as well as for the full system, and to choose all the CG coefficients real.[8a,25,25a,26,27] If the addition is done in this customary way, the phase conventions for the two parts and for the combined system are not independent. We now investigate the connection between them.

Since all phase conventions used in this case are normal, the only thing to be determined in this relation between the overall phase angle τ for the combined system and the phase angles τ_1 and τ_2 of the partial systems defined by*

$$\hat{T}|j_1, m_1\rangle = e^{i\tau_1}(-1)^{j_1 + m_1}|j_1, -m_1\rangle$$

$$\hat{T}|j_2, m_2\rangle = e^{i\tau_2}(-1)^{j_2 + m_2}|j_2, -m_2\rangle$$

This is determined immediately from (52), which says that the phase factor is also the eigenvalue of $\hat{C}_y$. Since each term in the sum (63) is a direct product and since all coefficients are real, it follows from (52) that the overall eigenvalue is just the product of the partial ones. In other words,

$$e^{i\tau} = e^{i\tau_1} e^{i\tau_2} \qquad (64)$$

Note that because of the antiunitary nature of $\hat{C}_y$, (64) would not hold if the CG coefficients were allowed to be complex.

With the aid of (64), we see immediately that if both partial systems are phased according to the generalized normal Legendre phase convention, the overall phase factor $e^{i\tau}$ is $(-i)^{2(j_1 + j_2)}$. Since this is not always equal to $(-i)^{2J}$, it follows that the combined system must be rephased if it is to behave according to the (gnL) convention. On the other hand, if both systems follow the normal positive phase convention, or both the normal negative convention, the overall phase factor is $(\pm 1)^{2(j_1 + j_2)} = (\pm 1)^{2J}$. It

*All the names for $e^{i\tau}$ phase conventions for total-angular-momentum representations may be applied by analogy to phase conventions for these partial-angular-momenta state vectors.

follows that these two phase conventions have the useful property of "invariance under customary angular momentum addition": if both partial systems are phased according to the designated convention, the combined system will automatically also be so phased if the customary form of the CG coefficients is used. This result was given previously for the normal negative phase convention by Huby[28] and for the normal positive phase convention by Edmonds.[25b]

Equation (64) also enables us to define other types of normal phase conventions in which different types of partial angular momenta (e.g., orbital and spin) are phased differently. An example is the Alder-Winther[29] convention, in which each spin is given an $e^{i\tau}$ phase factor of unity, and each single-particle orbital angular momentum (l_i) one of $(-1)^{l_i}$. When all these are combined according to (64), the overall $e^{i\tau}$ phase factor is $(-1)^{\Sigma l_i} = \Pi$, the parity of the state. It is evident that this convention also is invariant under customary angular momentum addition.

It is sometimes convenient to write the parity as $(-1)^p$. For the Alder-Winther (AW) phase convention, we then have, using (47), (51), and (52)

$$\hat{T}|D,J,M\rangle_{\mathrm{AW}} = (-1)^{p+J+M}|D,J,-M\rangle_{\mathrm{AW}} \tag{65}$$

$$\hat{C}_x|D,J,M\rangle_{\mathrm{AW}} = (-i)^{2J}(-1)^{p+J+M}|D,J,M\rangle_{\mathrm{AW}} \tag{66}$$

$$\hat{C}_y|D,J,M\rangle_{\mathrm{AW}} = (-1)^{p}|D,J,M\rangle_{\mathrm{AW}} \tag{67}$$

Since the phase factor $e^{i\tau}$ for the Alder-Winther phase convention differs from that for the normal positive phase convention by Π, (49) and (62) show that for integer total angular momenta, the state vectors of Alder and Winther transform like Condon-Shortley spherical harmonics multiplied by $\Pi^{1/2}(-i)^J = \pm i^{p-J}$. We note that for a single spinless particle, the AW phase convention is identical with the gnL convention. For more general situations, of course, the two are not necessarily equivalent. If each of two state vectors $|j_1,m_1\rangle$ and $|j_2,m_2\rangle$ for integer spatial orbital angular momenta are phased to satisfy the gnL phase convention, they will also each satisfy the AW phase convention. The state vector $|j_1,j_2,J,M\rangle$ obtained by customary angular momentum addition will not necessarily satisfy (53) but will satisfy (65). This is the advantage of using parity to define the $e^{i\tau}$ phase convention.

Notice that (58) is equivalent to

$$\hat{C}_y\hat{P}|D,J,M\rangle_{\mathrm{AW}} = |D,J,M\rangle_{\mathrm{AW}} \tag{68}$$

The freedom to choose our set of states to be simultaneous eigenfunctions of $\hat{J}^2, \hat{J}_z, \hat{C}_y$, and $\hat{P}$ when D contains no class II ($\hat{T}$) variables was established in Section III.E. The freedom to choose the eigenvalues of involutional antiunitary operators $\hat{\Theta}$ for which $\hat{\Theta}^2 = +1$ to be $+1$ was established in Section III.C.3. But $(\hat{C}_y\hat{P})^2 = +1$, since $\hat{C}_y^2 = +1$, $\hat{P}^2 = +1$, and $\hat{C}_y$ and $\hat{P}$ commute (see Section III.E). This verifies that we always have the freedom to choose the set of states and phases to satisfy (68) as recommended for certain purposes by Alder and Winther.

Still another example is the class of phase conventions which may be called Kramers[30] phase conventions, in which each spin of $\frac{1}{2}$ is given an $e^{i\tau}$ phase factor of $(-i)$. This means that the matrix $\boldsymbol{\beta}$ in the spin space is just the direct product of $\boldsymbol{\sigma}_y$ for each spin. The spins thus contribute a factor $(-i)^n$ to the overall $e^{i\tau}$ phase factor, where n is the number of spin-$\frac{1}{2}$ particles in the system. The Kramers phase convention leaves open the phasing of the orbital contribution. For example, Wigner[21] defines a Kramers phase convention in which the orbital angular momentum follows the negative phase convention [cf. his eqs. (26.15) and (26.43)]. The overall $e^{i\tau}$ phase factor in Wigner's phase convention is thus $(-i)^{2n}(-1)^{2L} = (-i)^{2n}$.

4. *Nonnormal Phase Conventions*

It is convenient to define an arbitrary phase convention by referring it to $|D,J,M\rangle_+$ of (56) to (58). Accordingly, let

$$|D,J,M\rangle = e^{i\xi(M)}|D,J,M\rangle_+$$

We find, using (43), (45), (56) to (58), plus the unitary nature of the $\hat{R}$ operators, and the antiunitary character of $\hat{C}_x$, $\hat{C}_y$, and $\hat{T}$:

$$\hat{R}_x|D,J,M\rangle = (-i)^{2J}e^{i[\xi(M)-\xi(-M)]}|D,J,-M\rangle \tag{69}$$

$$\hat{R}_y|D,J,M\rangle = (-1)^{J-M}e^{i[\xi(M)-\xi(-M)]}|D,J,-M\rangle \tag{70}$$

$$\hat{T}|D,J,M\rangle = (-1)^{J+M}e^{-i[\xi(M)+\xi(-M)]}|D,J,-M\rangle \tag{71}$$

$$\hat{C}_x|D,J,M\rangle = (-i)^{2J}(-1)^{J+M}e^{-2i\xi(M)}|D,J,M\rangle \tag{72}$$

$$\hat{C}_y|D,J,M\rangle = e^{-2i\xi(M)}|D,J,M\rangle \tag{73}$$

In particular, we see from (72) that (34) is satisfied if we choose $e^{i\xi(M)} = e^{i(\pi/2)M}$.

IV. SCATTERING THEORY

A. Symmetry of the S Matrix

Time-reversal invariance means (see Section III.C.2)

$$\hat{T}\hat{H} = \hat{H}\hat{T} \tag{74}$$

where $\hat{H}$ is the hamiltonian for the system. As stated in Section III.B, we only consider processes for which (74) holds. This is generally assumed to include all processes in chemical physics.[31]

Let $\hat{S}$ be the unitary scattering operator[1d,6c,7b,8d,10b] which takes the system from the state u to the state u'. We show in Appendix B that, as a consequence of (74), regardless of representation and phase convention*

$$\langle u|\hat{S}|u'\rangle = \langle \hat{T}u'|\hat{S}|\hat{T}u\rangle \tag{B-25}$$

If our representation is characterized by the quantum numbers J, M, and D, where the D are scalars and class I ($\hat{T}$) (which, we have shown in Section III.E and Appendix A, is always possible), then (B-25) becomes

$$\langle D,J,M|\hat{S}|D',J,M\rangle = \langle \hat{T}(D',J,M)|\hat{S}|\hat{T}(D,J,M)\rangle \tag{75}$$

Now, using (46) and (73), plus the definition $\hat{C}_y = \hat{R}_y\hat{T}$, we see that

$$\hat{T}|D,J,M\rangle = (-1)^{2J}\hat{R}_y\hat{C}_y|D,J,M\rangle = (-1)^{2J}\hat{R}_y e^{-2i\xi(M)}|D,J,M\rangle \tag{76}$$

Application of (76) to both the primed and unprimed states and insertion into (75) gives the result

$$\langle D,J,M|\hat{S}|D',J,M\rangle = e^{2i[\xi'(M)-\xi(M)]}\langle D',J,M|\hat{R}_y^{\dagger}\hat{S}\hat{R}_y|D,J,M\rangle \tag{77}$$

However, $\hat{R}_y$ commutes with the hamiltonian, hence also with $\hat{S}$, and is unitary; thus (77) becomes

$$\langle D,J,M|\hat{S}|D',J,M\rangle = e^{2i[\xi'(M)-\xi(M)]}\langle D',J,M|\hat{S}|D,J,M\rangle \tag{78}$$

In particular, if the same phase convention is used in both the primed and unprimed manifolds, the S matrix is symmetric. If $|D,J,M\rangle$ and $|D',J,M\rangle$ are formed by customary addition of partial angular momenta, the symmetry of **S** will be assured if for each angular momentum we use a normal

*The proof of (B-25) does, however, depend on $\hat{T}$ being antiunitary, which, as explained in Sections III.A and III.B, requires that $\hat{T}$ obey (2) and (3).

phase convection that is invariant under customary angular momentum addition.

B. Reciprocity Theorem and Discussion

The question of symmetry of the scattering matrix is usually asked and answered in specific representations with specific phase conventions.[1c] Although the proof of the previous section is more general, in this section we rederive the symmetry of the scattering matrix in a more specific representation for various phase conventions. We also prove some related results.

The quantities used to describe the scattering of A by B are defined as follows (we use the notation of Blatt and Biedenharn[32] as much as possible):

$\vec{I}, I$ the angular momentum and the angular momentum quantum number, respectively, of the target B in the channel specified by α. All angular momenta are given in the usual way "in units of $\hbar$." Unprimed and primed quantum numbers refer to the initial state and the final state, respectively.

$\vec{i}, i$ the angular momentum and the angular momentum quantum number, respectively, of A in the channel specified by α.

$\vec{s}, s$ the angular momentum and the angular momentum quantum number, respectively, of AB, excluding the angular momentum associated with the relative motion of A and B, in the channel specified by α.

$$\vec{s} = \vec{I} + \vec{i} \tag{79}$$

We call s the internal angular momentum in a given channel.

$\vec{l}, l$ the orbital angular momentum and the orbital angular momentum quantum number, respectively, for the relative motion of A and B in the channel specified by (J,s).

$\vec{J}, J$ the total angular momentum and the total-angular-momentum quantum number, respectively; $\vec{J}$ is given by (1) or by

$$\vec{J} = \vec{L} + \vec{S} \tag{80}$$

where $\vec{L}$ and $\vec{S}$ are defined in Section II.

Π the parity [i.e., eigenvalue (± 1) of the total system parity operator $\hat{P}$].

α the channel index denoting all quantum numbers, except (s,l,J,M,Π), necessary to specify the quantum state. Ap-

pendix A shows that there is no loss of generaltiy in assuming α to contain only scalars and we shall do so.

A the group of quantum numbers (α,s,l), except the energy E.

d the group of quantum numbers (α,s,l,Π).

$Z(abcd;ef)$ the Z coefficient of Blatt and Biedenharn[32] defined as $Z(abcd;\ ef)=i^{f-a+c}\bar{Z}(abcd;\ ef)$.

$\bar{Z}(abcd;\ ef)$ the $\bar{Z}$ coefficient of A. M. Lane and Thomas[33] defined as

$$\bar{Z}(abcd;\ ef)=[(2a+1)(2b+1)(2c+1)(2d+1)]^{1/2}W(abcd;\ ef)\langle ac00|acf0\rangle \tag{81}$$

where $W(abcd;\ ef)$ is the Racah coefficient defined[34] by (12) of Ref. 34 and $\langle ac00|acf0\rangle$ is the Clebsch-Gordan coefficient defined in (63) and given by (5) of Ref. 34.

M the projection quantum number of total angular momentum $\vec{J}$ on an arbitrary space-fixed axis z.

m the projection quantum number of a general angular momentum $\vec{j}$ on an arbitrary space-fixed axis z.

Y_{jm} the spherical harmonic of Condon and Shortley[26] and Messiah[23c] defined by (3.4.5), (3.4.12), and (3.4.15) of Condon and Shortley, that is,

$$Y_{jm}=(-1)^m\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}P_j^{|m|}(\cos\Theta)e^{im\phi}$$

$$P_j^{|m|}(\cos\Theta)=(\sin\Theta)^{|m|}\left[\frac{d}{d(\cos\Theta)}\right]^{|m|}P_j(\cos\Theta)$$

where $P_j(\cos\Theta)$ is a Legendre polynomial[4a] and Θ and ϕ are the colatitude and the longitude, respectively.

A solution in the total-angular-momentum representation in the asymptotic (separated-subsystem) region of the time-independent Schrödinger equation in the barycentric coordinate system corresponding to given values of the conserved quantum numbers J, M, and Π is called $u(\alpha slJM\Pi)$. This choice of quantum numbers simplifies the scattering calculations; examples have been given in Section II. The asymptotic form of $u(\alpha slJM\Pi)$ determines the subblock $\mathbf{S}^{JM\Pi}$ of the scattering matrix $\mathbf{S}$.

It is proved in Appendix B that[10c]

$$S^{JM\Pi}_{\alpha's'l';\,\alpha sl} = \langle \hat{T}u(\alpha slJM\Pi)|\hat{S}|\hat{T}u(\alpha's'l'JM\Pi) \tag{82}$$

Using (32) in (82) yields

$$S^{JM\Pi}_{\alpha's'l';\,\alpha sl} = e^{-i\gamma(\alpha slJM\Pi)} e^{i\gamma(\alpha's'l'JM\Pi)} \times \langle u(\alpha_t slJ - M\Pi)|\hat{S}|u(\alpha_t's'l'J - M\Pi)\rangle \tag{83}$$

where α_t represents the same set of quantum numbers as α but with the signs of all class II ($\hat{T}$) variables changed, and the phase angle $\gamma(\alpha slJM\Pi)$ depends on the phase conventions used in defining $u(\alpha slJM\Pi)$. For simplicity we assume that M is not negative. Using (41), (42), and the invariance of $\hat{S}$ under rotations in the form $[\hat{S},\hat{J}_-]=0$, we can show from (83) that

$$S^{JM\Pi}_{\alpha's'l';\,\alpha sl} = e^{-i\gamma(\alpha slJM\Pi)} e^{i\gamma(\alpha's'l'JM\Pi)} \times \left[\prod_{M'=-M}^{M-1}{}' e^{-i\phi(\alpha slJM'\Pi)} e^{i\phi(\alpha's'l'JM'\Pi)} \right] \times \langle u(\alpha_t slJM\Pi)|\hat{S}|u(\alpha_t's'l'JM\Pi)\rangle \tag{84}$$

where the prime in $\prod'^{M-1}_{M'=-M}$ means the product is deleted if $M=0$. Equation (84) yields immediately

$$|S^{JM\Pi}_{\alpha's'l';\,\alpha sl}| = |S^{JM\Pi}_{\alpha_t sl;\,\alpha_t's'l'}| \tag{85}$$

which is the reciprocity theorem (also called the reciprocity relation).[1c,6c,7b,8b]

Notice that our proof of (85) is entirely independent of phase conventions. Stronger results may be derived by making various assumptions about the phase conventions. For example, if we assume

1. $\gamma(AJM\Pi E)=\gamma(A_cJM\Pi E)$, where A_c and E are the subset of (α,s,l) which is conserved
2. $M=0$, or $\phi(AJM'\Pi E)=\phi(A_cJM'\Pi E)$ for $-M \leqslant M' \leqslant M-1$
3. α contains no nonneglectable* class II ($\hat{T}$) variables

*Variables that are conserved and of which the scattering matrix is independent are called *neglectable*.

then (84) becomes

$$S^{JM\Pi}_{\alpha' s' l';\, \alpha s l} = S^{JM\Pi}_{\alpha s l;\, \alpha' s' l'} \tag{86}$$

and S is symmetric. Although we have given a much more general derivation of (86) in Section IV.A, the present derivation is interesting for comparison with discussions in the literature.[1b,2,7c,8b,10b,28]

Particular phase conventions designed to ensure condition (1) have played an important role in previous discussions of symmetry of the scattering matrix. It is easily seen from Section III that condition (1) is satisfied by the generalized normal Legendre, normal positive, normal negative, and Alder-Winther phase conventions [see (32), (53), (56), (59), (65)]. Furthermore, the normal positive, normal negative, and Alder-Winther phase conventions have the property of invariance under customary angular momentum addition. Thus a particularly convenient way to ensure condition (1) is to phase each of the angular momentum states $|jm\rangle$ according to *one* of these conventions and to form $u(\alpha s l J M \Pi)$ using customary angular momentum addition. Thus the symmetry of the scattering matrix has often been discussed only for the case of a normal positive[1,1b,7c,8b] or a normal negative[10b,28] phase convention. Three of the articles[13,28,33] discussed in Section V use a normal negative phase convention (note: for integer angular momenta, the normal negative and positive phases conventions are the same, see Section III.F.2) and also satisfy conditions (2) and (3). Thus both our proofs of (86) are applicable to these articles. Some previous workers,[12,32,35–38] however, used Condon-Shortley spherical harmonics Y_{jm} as their states $|jm\rangle$ for integer angular momenta j, and the usual proof in terms of customary angular momentum addition of states all phased with either the normal positive or negative phase convention does not ensure that the scattering matrix so obtained is symmetric. However, we show in Section V that condition (1) is satisfied and our two proofs are still applicable. In Section V we discuss the changes that must be made in the formulas of these workers if $i^j Y_{jm}$ is substituted for Y_{jm} in their formulas, a procedure originally suggested by Huby.[28]

Condition (2) may easily be satisfied by taking $\phi(\alpha s l J M \Pi) = 0$. This is called a normal phase convention in Section III.F. If we take $\phi(jm) = 0$ for all $|jm\rangle$ and obtain $u(\alpha s l J M \Pi)$ by customary angular momentum addition (defined in Section III.F.3), it can be shown that $\phi(\alpha s l J M \Pi)$ will equal zero.[25a] However, condition (2) is less restrictive than this particularly convenient choice of phase conventions.

Condition (3) has apparently not received general discussion in the past. We proved in Section III.E that it is always possible to satisfy condition (3).

The proof of (86) is much easier for systems involving no spatial or spin angular momenta, and simple proofs have been given elsewhere[3b,39] for those cases. The complications come from the angular momenta as discussed previously.

Note that condition (2) alone suffices for the scattering matrix to be independent of M [this is easily seen by comparing (83) to (84) under the assumption of condition (2)].[8c] Condition (2) holds in all cases treated in Section V, which means that M is neglectable there, and the superscript M will be suppressed.

C. Detailed Balance

We have discussed the reciprocity theorem (85) and the symmetry of the S matrix [(78) or (86)] for total-angular-momentum representations. A similar result, detailed balancing[6c,8b,40]

$$|S^{JM\Pi}_{\alpha' s' l';\, \alpha s l}| = |S^{JM\Pi}_{\alpha s l;\, \alpha' s' l'}|$$

may be derived from (85) by invoking condition (3) of Section IV.B, or in particular, that α contain no nonneglectable class II ($\hat{T}$) variables. Although we have shown in Section III.E that it is always possible to satisfy condition (3) it may sometimes be convenient to characterize a system using a class II ($\hat{T}$) variable in α (but it is hard to give an example). The reciprocity theorem, symmetry of **S**, and detailed balance can sometimes be proved in nontotal-angular-momentum representations. In some such cases it may be convenient to characterize the states using a nonconserved component of angular momentum, usually spin, as one of the quantum numbers. Then detailed balancing does not hold in general, but a weaker result, semidetailed balancing, in which probabilities are averaged over spin directions in the initial and final states, does hold.[6c,40]

The reader should be cautioned that the labels "time-reversal invariance," "the reciprocity theorem," "the principle of detailed balancing," and "the principle of microscopic reversibility"[41] are often used interchangeably in the literature. For example, Landau and Lifshitz[5c] use "the principle of detailed balancing" to designate what is here called the "reciprocity theorem." Some chemists use "detailed balance" to refer to a relationship between rates at equilibrium and use "the principle of microscopic reversibility" to label what is here called semidetailed balancing.[41]

V. APPLICATIONS

In this section we discuss the symmetry of the S matrix and proper equations for calculating the differential cross-section for several standard scattering problems of chemical physics and also in general.

Blatt and Biedenharn[32] presented a general expression, free of all sums over angular-momentum-projection quantum numbers, for calculating from the scattering matrix **S** the differential cross-section for the scattering of unpolarized beams.[42] Their expression is particularly useful because it gives the differential cross-section as an expansion in Legendre polynomials[4a] with real coefficients. Their derivation was based in part on a paper by Wigner and Eisenbud.[43] Huby[28] remarked that the representations and phase conventions used by Wigner and Eisenbud and Blatt and Biedenharn do not always lead to a symmetric scattering matrix. The scattering matrix in the representation of Blatt and Biedenharn and corresponding to their phase conventions is designated ${}^{\mathrm{BB}}\mathbf{S}$. The assumption that **S** is symmetric is not required in the derivation of Blatt and Biedenharn's differential cross-section formula, and Huby correctly pointed out that their formula is correct if ${}^{\mathrm{BB}}\mathbf{S}$ is used. Huby gave another representation in which the normal negative phase convention of Section III.F.2 is used for all partial and total angular momentum state vectors. The scattering matrix in this representation is denoted by ${}^{\mathrm{H}}\mathbf{S}$. Huby explained how to calculate the differential cross-section in terms of ${}^{\mathrm{H}}\mathbf{S}$ instead of ${}^{\mathrm{BB}}\mathbf{S}$. The discussion of the symmetry of the scattering matrix given in Section IV shows that the phase conventions used by Huby do lead to a symmetric scattering matrix if α contains no nonneglectable class II ($\hat{T}$) variables. However, the application of these general considerations to particular cases is still often complicated. We now discuss in detail a few such applications, with emphasis on problems in chemical physics.

A. Blatt and Biedenharn; Huby

In deriving their general expression [their (3.16), (4.5), and (4.6)] for the differential cross-section, Blatt and Biedenharn[32] obtained the following intermediate expression [see their eq. (4.1)]:

$$\begin{aligned} d\sigma_{\alpha' s';\,\alpha s} = [k_\alpha{}^2(2s+1)]^{-1} \sum_{J_1} \sum_{l_1} \sum_{l_1'} \sum_{J_2} \sum_{l_2} \sum_{l_2'} i^{-l_1+l_1'+l_2-l_2'} \\ \times \left(\delta_{\alpha'\alpha}\delta_{s's}\delta_{l_1'l_1} - {}^{\mathrm{BB}}S^{J_1\Pi}_{\alpha' s' l_1';\,\alpha s l_1}\right)^* \\ \times \left(\delta_{\alpha'\alpha}\delta_{s's}\delta_{l_2'l_2} - {}^{\mathrm{BB}}S^{J_2\Pi}_{\alpha' s' l_2';\,\alpha s l_2}\right) K(J_1 l_1' l_1;\, J_2 l_2' l_2;\, s' s;\, \Theta)\, d\Omega \end{aligned} \tag{87}$$

where $\hbar k_\alpha$ is the momentum in the channel specified by α and Θ is the center-of-mass scattering angle. The factor K contains all the sums over projection quantum numbers, and Blatt and Biedernharn showed that K could be replaced by a sum over λ containing the product of two Z coefficients, a Legendre polynomial, and a weighted phase factor. That

result can be combined with the definition of the $\bar{Z}$ coefficients [see(81)] and with (87) to yield

$$d\sigma_{\alpha's';\,\alpha s} = (-1)^{s'-s}[4k_\alpha^2(2s+1)]^{-1}\sum_{\lambda}\sum_{J_1}\sum_{l_1}\sum_{l_1'}\sum_{J_2}\sum_{l_2}\sum_{l_2'} i^{-l_1+l_1'+l_2-l_2'}$$

$$\times\left(\delta_{\alpha'\alpha}\delta_{s's}\delta_{l_1'l_1} - {}^{BB}S^{J_1\Pi}_{\alpha's'l_1';\,\alpha sl_1}\right)^*$$

$$\times\left(\delta_{\alpha'\alpha}\delta_{s's}\delta_{l_2'l_2} - {}^{BB}S^{J_2\Pi}_{\alpha's'l_2';\,\alpha sl_2}\right)\bar{Z}(l_1J_1l_2J_2;\,s\lambda)$$

$$\times\,\bar{Z}(l_1'J_1l_2'J_2;\,s'\lambda)P_\lambda(\cos\Theta)\,d\Omega \tag{88}$$

Note that the derivation requires using the fact that $(l_1'l_2'00|l_1'l_2'\lambda 0)$ is zero unless $(\lambda - l_1 + l_2)$ is even.[34]

The phase factor $i^{-l_1+l_1'+l_2-l_2'}$ in (88) results from Blatt and Biedenharn's use of Y_{lm_l} instead of $i^lY_{lm_l}$ in their wavefunction. Since Y_{lm_l} was used, and the phase convention to be used for other partial-angular-momentum state vectors was not specified, the representation of Blatt and Biedenharn does not necessarily satisfy condition (1); ${}^{BB}\mathbf{S}$ cannot be proved to be symmetric by the proofs of Section IV or by the special cases of the proof of Section IV.B which have been published elsewhere. Blatt and Biedenharn do use the reciprocity theorem after their eq. (4.6) but their formula for the differential cross-section does not depend on the scattering matrix being symmetric. If $i^lY_{lm_l}$ is used instead of Y_{lm_l} as Huby suggested, a scattering matrix ${}^{H}\mathbf{S}$ is defined whose elements are related to the elements of ${}^{BB}\mathbf{S}$ by Huby's eq. (6), that is, by

$${}^{BB}S^{J\Pi}_{\alpha's'l';\,\alpha sl} = i^{l'-l}\,{}^{H}S^{J\Pi}_{\alpha's'l';\,\alpha sl} \tag{89}$$

If we substitute this into (88), the phase factor cancels out and the $\bar{Z}$ coefficients alone should be used with ${}^{H}\mathbf{S}$. Since the remaining angular momentum eigenstates χ_{sm_s} in the representation of Huby are chosen to satisfy a normal negative phase convention, conditions (1) and (2) will be satisfied and ${}^{H}\mathbf{S}$ will satisfy

$${}^{H}S^{J\Pi}_{\alpha's'l';\,\alpha sl} = {}^{H}S^{J\Pi}_{\alpha_i sl;\,\alpha_i's'l'} \tag{90}$$

If α contains no nonneglectable class II ($\hat{T}$) variables, ${}^{H}\mathbf{S}$ is symmetric.

Our statements concerning the symmetry of $\mathbf{S}$ apply as well to the reactance matrix $\mathbf{R}$ related to $\mathbf{S}$ by

$$\mathbf{S} = (\mathbf{1} - i\mathbf{R})^{-1}(\mathbf{1} + i\mathbf{R}) \tag{91}$$

The formulas of Blatt and Biedenharn have been used to calculate the differential cross-sections for the scattering of structureless particles (or particles assumed to be structureless) from rotator-vibrators by Henry[44] (e–H_2). Sums of such differential cross-sections have been calculated by Wagner and McKoy[15d] (Ar–H_2, He–0_2, He–I_2). Differential cross-sections for a transition among the $3p\ ^2P$ states of Na induced by collisions with He have been calculated by Reid.[19] Additional examples are cited in Sections V.B and V.D. Wolken et al.[15b] and McGuire and Micha[15c] have calculated differential cross-sections for the scattering of atoms (assumed structureless) from rotator-vibrators using a total-angular-momentum representation different from that used by Blatt and Biedenharn. They used the helicity representation[1b,7d,16a,45] in which $\vec{s}$ is quantized along $\vec{k}_\alpha$ and $\vec{s}'$ is quantized along $\vec{k}_{\alpha'}$.

B. Percival and Seaton; Smith

Percival and Seaton[35] have derived an expression for the differential cross-section for scattering of electrons by atomic hydrogen under the assumption (see Section II) that $\vec{L}$ and $\vec{S}$ are separately conserved. The quantum numbers used by Percival and Seaton in labeling their representation are a, l, s, L, M_L, and Π, where the set a contains the principal quantum number of the hydrogen atom, the total energy, the quantum number S[see Section II and (80)], and the quantum number M_S associated with the component S_z of $\vec{S}$ on a space-fixed axis, and s is the orbital-angular-momentum quantum number of the bound electron. Using the ideas presented by Percival and Seaton, K. Smith[37] has derived an expression for the differential cross-section for the scattering of positrons by atomic hydrogen. These expressions have been discussed elsewhere.[46] Here we summarize that discussion and relate it to the present chapter.

For all their angular momentum eigenstates $|jm\rangle$, Percival and Seaton and K. Smith chose the spherical harmonics Y_{jm} that do not satisfy normal positive or normal negative phase conventions but do satisfy condition (2). Furthermore, using the fact[8e] that Π is $(-1)^{l+s}$ for this system and the identity [eq. (3.5.17) of Ref. 25a]

$$(acef|abcd) \equiv (-1)^{e-a-c}(ace-f|a-bc-d) \tag{92}$$

we can show that condition (1) is satisfied with

$$e^{i\gamma(aslLM_L\Pi)} = \Pi(-1)^{L+M_L} \tag{93}$$

Also, since $\hat{H}$ is rotationally invariant and L and S are good quantum numbers in this approximation, $^{PS}\mathbf{S}$ is diagonal in L, M_L, S, and M_S and

independent of both M_L and M_S by a theorem[7b,8c] used in Section IV.B. Thus even though a contains the class II ($\hat{T}$) variable S_z and the Percival-Seaton representation is not a total-angular-momentum representation, S_z is a neglectable variable, and the proof of Section IV.B may be modified with L and M_L replacing J and M to show that ${}^{PS}\mathbf{S}$ is symmetric. This is an example of something pointed out in Section IV and Ref. 46—namely, that the usual rule[1b,7c,8b,28] requiring normal positive or normal negative phase conventions is not a *necessary* condition for a symmetric scattering matrix.

Since Percival and Seaton and K. Smith chose the same $|lm_l\rangle$ as did Blatt and Biedenharn, the correct expressions for the differential cross-section in terms of their scattering matrices ${}^{PS}\mathbf{S}$ are identical to the one given by Blatt and Biedenharn. Burke and co-workers[47-49] have used the phase conventions of Percival and Seaton to calculate the reactance matrix for electron–hydrogen-atom collisions in a series of successively improved approximations. Equation (91) and the formulas of Blatt and Biedenharn have been used to calculate the differential cross-sections from these reactance matrices; the results are published elsewhere.[46,50] The equations of Blatt and Biedenharn have also been used to calculate differential cross-sections for electron scattering from larger atoms.[51]

If we apply the Huby phase convention to these problems–that is, if we use $i^j Y_{jm}$ for all $|jm\rangle$, except those for spin—we find that the new representation satisfies conditions (1) and (2) [with (J,M) replaced by (L,M_L)], and the scattering matrix in this representation ${}^{H}\mathbf{S}$ can be shown to be symmetric. The correct formula to use in calculating the differential cross-section from ${}^{H}\mathbf{S}$ in these cases is Huby's formula.

If $\mathbf{X}$ represents one of the matrices $\mathbf{S}$, $\mathbf{R}$, or $\mathbf{V}$, where V is the interaction potential, the elements of ${}^{H}\mathbf{X}$ are related to the elements of ${}^{PS}\mathbf{X}$ by [46]

$$ {}^{H}X^{L\Pi}_{a's'l';\,asl} = i^{l-l'+s-s'}\,{}^{PS}X^{L\Pi}_{a's'l';\,asl} \tag{94}$$

Note that $i^{l-l'+s-s'}$ is real by conservation of total system parity;[46] thus applying the Huby phase convention does not affect the reality of the matrix elements.

C. Lane and Thomas

A. M. Lane and Thomas[33] have derived an expression for the differential cross-section for nuclear reactions. They correctly phased their representation to satisfy conditions (1) and (2) by using a normal negative phase convention and the scattering matrix ${}^{LT}\mathbf{S}$ defined by them is symmetric for systems for which α does not contain any nonneglectable class II ($\hat{T}$) variables. Since their representation used $i^l Y_{lm_l}$ for $|lm_l\rangle$, their differential cross-section formula is identical to Huby's formula and correctly uses the $\bar{Z}$ coefficients with ${}^{LT}\mathbf{S}$.

D. Arthurs and Dalgarno; Micha

Arthurs and Dalgarno[12] have derived an expression for the differential cross-section for the scattering of particles by rigid rotators with rotational angular momentum quantum number s. In this case the set of quantum numbers α includes only the total energy. Like Percival and Seaton, they chose Y_{jm} for all $|jm\rangle$, therefore their representation does satisfy condition (1), with J, M replacing L, M_L in (93). Thus $^{AD}\mathbf{S}$ is symmetric by the proof given in Section IV.B, as well as by the more general proof of Section IV.A. Their formula for the differential cross-section in terms of their $^{AD}\mathbf{S}$ is identical to the one given by Blatt and Biedenharn. By arguments similar to those used in discussing the formulas of Percival and Seaton, it can be seen that their formula is correct for this problem. Micha[13] applied Huby's phase convention to this problem (i.e., he used $i^j Y_{jm}$ for $|jm\rangle$), and his scattering matrix $^{M}\mathbf{S}$ is symmetric by the proof given by Huby, as well as by the more general proofs of Sections IV.A and IV.B. His differential cross-section formula is identical to Huby's and uses the $\bar{Z}$ coefficients with his $^{M}\mathbf{S}$; $^{M}\mathbf{X}$ is related to $^{AD}\mathbf{X}$ by (94), with L replaced by J just as $^{H}\mathbf{X}$ is related to $^{PS}\mathbf{X}$ in Section V.B.

The formulas of Blatt and Biedenharn and Arthurs and Dalgarno have been used to calculate the differential cross-section $d\sigma_{s';s}/d\Omega$ for a transition from rotational state s to rotational state s' ($s \to s'$) many times. For scattering of an atom or molecule (assumed structureless) from a rigid rotator they have been used by Roberts[52] ($0 \to 2$), Allison and Dalgarno[53] ($0 \to 2$), Munn and Monchick[54] ($1 \to 1$), Erlewein et al.[55] ($0 \to 2$), Johnson and Secrest[56] ($0 \to 2, 1 \to 3$), Miller[16a] ($0 \to 2$), Hayes et al.[57] ($0 \to 0, 0 \to 2$), Heukels and van de Ree[58] ($0 \to 0, 1 \to 1, 2 \to 2$, $0 \to 1, 1 \to 2, 0 \to 2$), and two of the present authors and R. L. Smith[50] ($0 \to 2, 2 \to 2$). For scattering of an electron by a rigid rotator, they have been used by Henry and N. F. Lane[59] ("elastic," $1 \to 3, 2 \to 4, 3 \to 5$), N. F. Lane and Geltman[60] ($1 \to 1, 1 \to 3$), Itikawa[61] ($0 \to 0, 0 \to 1$), Crawford and Dalgarno[62] ($0 \to 0, 0 \to 1, 0 \to 2$), and Sams et al.[63] ($1 \to 1, 1 \to 3$). Sums of such differential cross-sections have been calculated by Burke and Chandra.[64]

E. Davison

Davison[38] has derived an expression for the differential cross-section for the scattering of two rigid rotators, one with rotational angular momentum quantum number I and the other with rotational angular momentum quantum number i. In this case the set of quantum numbers α is (I, i, E), where E is the total energy. Davison also used Y_{jm} for the angular momentum eigenfunctions. Since Davison used the same $|lm_l\rangle$ chosen by Blatt and Biedenharn, his expression for the differential cross-section correctly involves the Z coefficients with his scattering matrix $^{D}\mathbf{S}$. Also the total system parity, which is $(-1)^{l+I+i}$ for this system is again conserved.

Once more both conditions (1) and (2) are satisfied, as they were in the Sections V.B and V.D. Since α contains no class II ($\hat{T}$) variables, both our proofs may be used to show $^{D}\mathbf{S}$ is symmetric. By arguments similar to those given previously in this section, if we apply the Huby phase convention to this problem, we get another symmetric $^{H}\mathbf{S}$ to be used with Huby's formula for the differential cross-section: $^{H}\mathbf{X}$ is related to $^{D}\mathbf{X}$ by (94) but with $i^{s-s'}$ and L replaced by $i^{l+i-l'-i'}$ and J, respectively.

Davison's formulas were used to compute differential cross-sections for inelastic scattering by Roberts.[52]

F. Alder and Winther Phase Conventions

Alder and Winther[29] have given a phase convention for angular momentum eigenfunctions that may be very convenient because it will make all the single-particle matrix elements of the electromagnetic multipole operators[65] real. Using (65) it is clear that $u(\alpha slJM\Pi)$ obtained with these phase conventions satisfies (93), with J, M replacing L, M_L in (93). Thus condition (1) is satisfied. Condition (2) is also satisfied. Thus if α contains no nonneglectable class II ($\hat{T}$) variables, both proofs of Section IV show that $\mathbf{S}$ is symmetric for this phase convention.

Two examples of the Alder-Winther phase convention for $|lm_l\rangle$ are Y_{lm_l} and $(-1)^l Y_{lm_l}$. If either of these phase conventions is used in defining $\mathbf{S}$, the Z coefficient of Blatt and Biedenharn[32] should again be used in the differential cross-section formula.

G. Summary

In general, the answer to whether to use the differential cross-section formula of Blatt and Biedenharn[32] (involving Z coefficients[32]) or that of Huby[28] and A. M. Lane and Thomas[33] (involving $\bar{Z}$ coefficients[33]) is strictly a function of which of the choices Y_{lm_l}, $(-1)^l Y_{lm_l}$, or $i^l Y_{lm_l}$ is made for the angular basis function for relative motion. The first choice implies that the formula of Blatt and Biedenharn[32] should be used. The second choice is also consistent with the formula of Blatt and Biedenharn. The third choice is consistent with the formula of Huby[28] or the identical formula of A. M. Lane and Thomas.[33] Specific choices of representation and phase convention for χ_{sm_s} and $\chi_{s'm'_s}$ (the wavefunctions for the separated reagents and products, respectively, in the notation of Blatt and Biedenharn[32]) will determine whether (86) and (90) are valid, as discussed earlier, but will not determine whether to use the Z or $\bar{Z}$ coefficients.

APPENDIX A

Proof that the Nontotal-Angular-Momentum Quantum Numbers in a Total-Angular-Momentum Representation may be Taken to Consist Entirely of Scalar Variables.

That the quantum numbers d (defined near the beginning of Section III.E) can be chosen to be scalars is simply shown as follows:

We choose our states to have quantum numbers J, M, Π, E, and enough other quantum numbers to completely specify the states where J, M, and Π have the meaning indicated in Section III and near the beginning of Section IV, and E is the eigenvalue of some hamiltonian (either exact or approximate) that is invariant under rotations. If there are no two states with the same values of all four of these quantum numbers, our task of specifying our states by J, M, Π, and scalar quantum numbers is complete (since E is of course a scalar).

Suppose, however, that there are two or more states with the same J, M, Π, and E. Choose one of them (with $M = M_0$, say), and arbitrarily denote it by $|A_1, J, M_0, \Pi, E\rangle$. By applying angular momentum raising and lowering operators to this state, we generate $(2J+1)$ states all with the same J, Π, and E, which we denote by $|A_1, J, M, \Pi, E\rangle$, with $M = -J, -J+1, \ldots, J$. Now let $|A_2, J, M_0, \Pi, E\rangle$ be a state with the quantum numbers J, M_0, Π, and E but orthogonal to $|A_1, J, M_0, \Pi, E\rangle$. By hypothesis, such a state exists. Again applying raising and lowering operators, we generate the states $|A_2, J, M, \Pi, E\rangle$, which are orthogonal to the $|A_1, J, M, \Pi, E\rangle$. We continue this process until all the states with quantum numbers J, M_0, Π, and E are used up. If we think of A_1, A_2, and so on, as different values of some quantity A, we can say that a state is completely specified by specifying J, M, Π, E, and A. The quantity A is a physical property of the system, since different values of A correspond in general to physically different states. Moreover, by construction it is invariant under rotations about the z-axis (since it is diagonal simultaneously with J_z) as well as those about the x- and y-axes (since it is left unaltered by the raising and lowering operators $\hat{J}_x \pm i\hat{J}_y$, hence commutes with them). It also commutes with parity, since it is simultaneously diagonal with it. It follows that A is a scalar, which is what was to be proved.

This result is a special case of a more general group theoretic result.[66] Using this more general result, we may show that any vector components included in the complete commuting set of variables in addition to J_z must be a scalar times J_z. Thus we can use the scalar as the additional dynamical variable.

APPENDIX B

The Time-Reversal-Invariance Property of the Scattering Matrix

In this appendix, we use the following known properties of the time-reversal operator $\hat{T}$ (see ref. 21 and Section III):

1. $\hat{T}$ is antilinear. That is, for any state functions ϕ_1 and ϕ_2 and complex numbers a_1 and a_2, we have

$$\hat{T}(a_1\phi_1 + a_2\phi_2) = a_1^* \hat{T}\phi_1 + a_2^* \hat{T}\phi_2 \tag{B-1}$$

2. If the total spin of the system is integral, $S = n$, then

$$\hat{T}^2\phi = \phi \qquad \text{for} \quad \text{all state functions } \phi \tag{B-2}$$

In this case, if the hamiltonian $\hat{H}$ is time-reversal invariant, the arguments of Section III.C.3 show that its eigenfunctions ϕ_j may be chosen to be also eigenfunctions of $\hat{T}$ with eigenvalues ± 1:

$$\hat{T}\phi_j = k_j\phi_j, \qquad k_j = \pm 1 \tag{B-3}$$

Actually Section III.C.3 shows that we could always choose $k_j = +1$, but we shall not need to do so.

3. If the total spin is half-odd integral $S = n + \frac{1}{2}$, we have

$$\hat{T}^2\phi = -\phi \qquad \text{for} \quad \text{all } \phi \tag{B-4}$$

In this case, the eigenfunctions of $\hat{H}$ cannot be eigenfunctions of $\hat{T}$, but they can be grouped into degenerate pairs ϕ_j and $\bar{\phi}_j$ with the properties

$$\hat{T}\phi_j = \bar{\phi}_j \tag{B-5}$$

$$\hat{T}\bar{\phi}_j = -\phi_j \tag{B-6}$$

Notice that the phase conventions of (53), (56), and (59) yield

$$\hat{T}^2|jm\rangle = (-1)^{2j}|jm\rangle \tag{B-7}$$

which is compatible with (B-2) and (B-4).

We now consider the matrix element of the time-displacement operator $\hat{G}(t) = \exp(-i\hat{H}t/\hbar)$ between an initial state u and a final state u', which we compare with the matrix element of the same operator between $\hat{T}u'$ and $\hat{T}u$.

First, in the case $S = n$, we can expand u and u' in the simultaneous eigenfunctions of $\hat{H}$ and $\hat{T}$:

$$u = \Sigma_j a_j \phi_j \tag{B-8}$$

and

$$u' = \Sigma_j b_j \phi_j \tag{B-9}$$

Obviously,

$$\hat{G}(t)u = \Sigma_j a_j e^{(-iw_j t)} \phi_j \tag{B-10}$$

where $\hbar w_j$ is the jth eigenvalue of $\hat{H}$. Using orthonormality of the $\{\phi_j\}$ (see Section III.C.3), we find

$$\langle u' | \hat{G}(t) | u \rangle = \Sigma_j b_j^* a_j e^{(-iw_j t)} \tag{B-11}$$

To study the time-reversed situation, we use (B-1) and (B-3) to obtain

$$\hat{T}u = \Sigma_j a_j^* k_j \phi_j \tag{B-12}$$

and

$$\hat{T}u' = \Sigma_j b_j^* k_j \phi_j \tag{B-13}$$

Applying $\hat{G}(t)$ to (B-13) yields

$$\hat{G}(t)\hat{T}u' = \Sigma_j b_j^* k_j e^{(-iw_j t)} \phi_j$$

and we obtain

$$\langle \hat{T}u | \hat{G}(t) | \hat{T}u' \rangle = \Sigma_j a_j b_j^* e^{(-iw_j t)} \tag{B-14}$$

Comparing (B-11) and (B-14) yields

$$\langle \hat{T}u | \hat{G}(t) | \hat{T}u' \rangle = \langle u' | \hat{G}(t) | u \rangle \tag{B-15}$$

To prove that (B-15) also holds for $S = n + \frac{1}{2}$, we proceed analogously. We expand u and u' in eigenfunctions of $\hat{H}$ chosen to satisfy (B-5) and (B-6):

$$u = \Sigma_j \left(a_j \phi_j + \bar{a}_j \bar{\phi}_j \right) \tag{B-16}$$

$$u' = \Sigma_j \left(b_j \phi_j + \bar{b}_j \bar{\phi}_j \right) \tag{B-17}$$

Using these expansions and the degeneracy of the states ϕ_j, $\bar{\phi}_j$, we im-

mediately obtain

$$\hat{G}(t)u = \Sigma_j\left(a_j\phi_j + \bar{a}_j\bar{\phi}_j\right)e^{(-iw_jt)} \tag{B-18}$$

and

$$\langle u'|\hat{G}(t)|u\rangle = \Sigma_j\left(b_j^*a_j + \bar{b}_j^*\bar{a}_j\right)e^{(-iw_jt)} \tag{B-19}$$

For the time-reversed situation, (B-1), (B-5), and (B-6) give

$$\hat{T}u = \Sigma_j\left(a_j^*\bar{\phi}_j - \bar{a}_j^*\phi_j\right) \tag{B-20}$$

$$\hat{T}u' = \Sigma_j\left(b_j^*\bar{\phi}_j - \bar{b}_j^*\phi_j\right) \tag{B-21}$$

Equation (B-21) yields

$$\hat{G}(t)(\hat{T}u') = \Sigma_j\left(b_j^*\bar{\phi}_j - \bar{b}_j^*\phi_j\right)e^{(-iw_jt)} \tag{B-22}$$

and

$$\langle\hat{T}u|\hat{G}(t)|\hat{T}u'\rangle = \Sigma_j\left(a_jb_j^* + \bar{a}_j\bar{b}_j^*\right)e^{(-iw_jt)} \tag{B-23}$$

Comparing (B-19) and (B-23) yields (B-15) again.

Equation (B-15) shows that the time-displacement operator $\hat{G}(t)$ possesses the symmetry claimed for the scattering operator $\hat{S}$ in Section IV.A. But[1d]

$$\hat{S} = \lim_{\substack{t_1\to\infty \\ t_2\to-\infty}} \exp\left(i\frac{\hat{H}_0}{\hbar}t_1\right)\hat{G}(t_1 - t_2)\exp\left(-i\frac{\hat{H}_0}{\hbar}t_2\right)$$

Thus, if u, u' are eigenfunctions of the zero-order hamiltonian $\hat{H}_0$ with eigenvalues $\hbar w, \hbar w'$, respectively, we have

$$\langle u'|\hat{S}|u\rangle = \lim_{\substack{t_1\to\infty \\ t_2\to-\infty}} \exp[i(w't_1 - wt_2)]\langle u'|\hat{G}(t_1 - t_2)|u\rangle \tag{B-24}$$

The passage to infinite time causes the matrix element (B-24) to vanish unless u, u' are "on the energy shell" (i.e., unless $w = w'$). In this case, however, the phase factor on the right-hand side of (B-24) becomes

$$\exp[iw(t_1 - t_2)]$$

Because of the degeneracy between $u, \hat{T}u$, as well as between $u', \hat{T}u'$, it

follows that this phase factor will be the same for $\langle \hat{T}u|\hat{S}|\hat{T}u'\rangle$, from which we conclude that [10c]

$$\langle \hat{T}u|\hat{S}|\hat{T}u'\rangle = \langle u'|\hat{S}|u\rangle \tag{B-25}$$

This result is independent of representation. In particular total-angular-momentum representations (B-25) becomes (75) and (82). It is important to point out that our proofs of (B-25), (75), and (82) are independent of phase convention, except that the representation must be compatible with

$$\hat{T}(|q\rangle + |r\rangle) = \hat{T}|q\rangle + \hat{T}|r\rangle$$

[see (3)].

APPENDIX C

For fixed D, J an arbitrary state $|\Phi\rangle$ may be expanded as

$$|\Phi\rangle = \sum_M \phi_M |D,J,M\rangle_+$$

Applying (56) we find

$$\hat{T}|\Phi\rangle = \sum_M (-1)^{J+M} \phi_M^* |D,J,-M\rangle_+$$

and

$$\phi_M^T \equiv {}_+\langle D,J,M|\hat{T}|\Phi\rangle = (-1)^{J-M} \phi^*_{-M} \tag{C-1}$$

Although (C-1) looks similar to (59), they really correspond to different phase conventions (for half-odd-integral spin). Possible ambiguity in the sign of β for spin $\frac{1}{2}$ can be caused by failure to be explicit as to whether (59) or (C-1) is meant[67] or by changing from one to the other without warning.[68]

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