ANGULAR MOMENTUM THEORY

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I. INTRODUCTION

The best known example of an angular momentum operator is the orbital angular momentum $\boldsymbol{l}$ associated with a vector $\boldsymbol{r}$,

$$\boldsymbol{l} \equiv -i\boldsymbol{r} \times \boldsymbol{\nabla}_r, \tag{1}$$

also written as

$$l_i = -i \sum_{jk} \epsilon_{ijk} r_j \frac{\partial}{\partial r_k}, \quad \text{with} \quad i, j, k = 1, 2, 3 = x, y, z, \tag{2}$$

where ϵ_{ijk} is the Levi-Civita antisymmetric tensor,

$$\epsilon_{ijk} = \begin{cases} 0 & \text{if two or more indices are equal,} \\ 1 & \text{if } ijk \text{ is an even permutation of } 1\,2\,3, \\ -1 & \text{if } ijk \text{ is an odd permutation of } 1\,2\,3. \end{cases} \tag{3}$$

The nabla operator is: $\boldsymbol{\nabla}_r = (\nabla_1, \nabla_2, \nabla_3)$ with $\nabla_i = \partial/\partial r_i$.

It is well-known that the l_i satisfy the commutation relations

$$\boxed{[l_i, l_j] \equiv l_i l_j - l_j l_i = i \sum_k \epsilon_{ijk} l_k.} \tag{4}$$

Often one takes the latter equations as a definition. Three operators j_i that satisfy the commutation relations (4) are then by definition angular momentum operators.

The importance of angular momentum operators in quantum physics is due to the fact that they are constants of the motion (Hermitian operators that commute with the Hamiltonian) in the case of isotropic interactions and also in the case of the motion of a quantum system in isotropic space. This will be shown in the next section, where we will derive the relation between 3-dimensional rotations and angular momentum operators.

In the third section we introduce abstract angular momentum operators acting on abstract spaces, and in the fourth we consider the decomposition of tensor products of these spaces.

Then we will introduce irreducible tensor operators (angular momentum operators are an example of such operators) and discuss the celebrated Wigner-Eckart theorem.

In the sixth section we will discuss the concept of recoupling and introduce the $6j$-symbol. In the final section we will show how matrix elements, appearing in the close-coupling approach to atom-diatom scattering, may be evaluated by an extension of the

Wigner-Eckart theorem and that the algebraic (easy) part of the calculation requires the evaluation of a $6j$-symbol.

These notes form the content of a six hour lecture course for graduate students specializing in theoretical chemistry. Since obviously six hours are not enough to cover all details of the program just outlined, most of the derivations are delegated to appendices and were skipped during the lectures. Furthermore the exposition will be restricted to 3-dimensional rotations; spin or half-integer quantum numbers will not be discussed.

II. THE CONNECTION BETWEEN ROTATIONS AND ANGULAR MOMENTA

In this section we will subsequently rotate: vectors, functions, operators, and N-particle systems.

A. The rotation of vectors

A proper rotation of the real 3-dimensional Euclidean space is in one-to-one correspondence with a real orthogonal matrix $\mathbb{R}$ with unit determinant. That is, if the vector $\boldsymbol{r}'$ is obtained by rotating $\boldsymbol{r}$, then

$$\boldsymbol{r}' = \mathbb{R}\boldsymbol{r}, \quad \text{with} \quad \mathbb{R}^T = \mathbb{R}^{-1} \quad \text{and} \quad \det \mathbb{R} = 1. \tag{5}$$

A product of two proper (unit determinant) orthogonal matrices is again a proper orthogonal matrix. The inverse of such a matrix exists and is again orthogonal and has unit determinant. Matrix multiplication satisfies the associative law

$$((\mathbb{A}\mathbb{B})\mathbb{C}) = (\mathbb{A}(\mathbb{B}\mathbb{C})). \tag{6}$$

These properties show that the (infinite) set of all orthogonal matrices form a group: the special (unit determinant) orthogonal group in three dimensions $SO(3)$.

It is well-known that any rotation has a rotation axis. This fact was first proved geometrically by Leonhard Euler[1], and is therefore known as *Euler's theorem.* We will prove this fact algebraically and notice to this end that it is equivalent to the statement that every orthogonal matrix has an eigenvector with unit eigenvalue. Knowing the following rules for $n \times n$ determinants: $\det \mathbb{A}^T = \det \mathbb{A}$, $\det \mathbb{A}\mathbb{B} = \det \mathbb{A} \det \mathbb{B}$ and $\det(-\mathbb{A}) = (-1)^n \det \mathbb{A}$, we consider the secular equation of $\mathbb{R}$ with $\lambda = 1$,

$$\begin{aligned} \det\left(\mathbb{R} - \mathbb{1}\right) &= \det\Big((\mathbb{R} - \mathbb{1})^T\Big) = \det\Big(\mathbb{R}^T(\mathbb{1} - \mathbb{R})\Big) = \det \mathbb{R}^T \det\left(\mathbb{1} - \mathbb{R}\right) \\ &= \det\left(\mathbb{1} - \mathbb{R}\right) = -\det\left(\mathbb{R} - \mathbb{1}\right), \end{aligned} \tag{7}$$

so that $\det\left(\mathbb{R} - \mathbb{1}\right) = 0$ and $\lambda = 1$ is indeed a solution of the secular equation of $\mathbb{R}$. Since an orthogonal matrix is a normal matrix, see Appendix A, it has three orthonormal eigenvectors. The product of eigenvalues of $\mathbb{R}$ being equal to $\det \mathbb{R} = 1$, the degeneracy of $\lambda = 1$ is either

[1]Novi Commentarii Academiae Scientiarium Petropolitanae **20**, 189 (1776).

one or three. In the latter case $\mathbb{R} \equiv \mathbb{1}$ and the rotation is trivial (any vector is an eigenvector of $\mathbb{1}$). The former case proves Euler's theorem.

We will designate the normalized eigenvector by $\boldsymbol{n}$. Thus,

$$\mathbb{R}\boldsymbol{n} = \boldsymbol{n} \quad \text{with} \quad |\boldsymbol{n}| = 1. \tag{8}$$

In other words, any rotation of a vector $\boldsymbol{r}$ can be described as the rotation of $\boldsymbol{r}$ over an angle ψ around an axis with direction $\boldsymbol{n}$. Accordingly we write $\mathbb{R}$ as $\mathbb{R}(\boldsymbol{n}, \psi)$.

Using the components of $\boldsymbol{n}$, we define the matrix $\mathbb{N}$ by

$$\mathbb{N} \equiv \begin{pmatrix} 0 & -n_3 & n_2 \\ n_3 & 0 & -n_1 \\ -n_2 & n_1 & 0 \end{pmatrix}, \quad \text{i.e.} \quad N_{ij} = -\sum_k \epsilon_{ijk} n_k \quad \text{and} \quad \mathbb{N}\boldsymbol{r} = \boldsymbol{n} \times \boldsymbol{r}. \tag{9}$$

In Appendix B it is shown that

$$\mathbb{R}(\boldsymbol{n}, \psi) = \mathbb{1} + \sin\psi \mathbb{N} + (1 - \cos\psi)\mathbb{N}^2, \tag{10}$$

where $\mathbb{1}$ is the 3×3 unit matrix.

B. The rotation of functions

Consider an arbitrary function $f(\boldsymbol{r})$. The rotation operator $U(\boldsymbol{n}, \psi)$ is defined as follows

$$U(\boldsymbol{n}, \psi) f(\boldsymbol{r}) \equiv f(\mathbb{R}(\boldsymbol{n}, \psi)^{-1}\boldsymbol{r}). \tag{11}$$

[The inverse of the rotation matrix appears here to ensure that the map $\mathbb{R}(\boldsymbol{n}, \psi) \mapsto U(\boldsymbol{n}, \psi)$ is a homomorphism, i.e., to conserve the order in the multiplication of operators and matrices.]

Let us next consider an infinitesimal rotation over an angle $\Delta\psi$. By infinitesimal we mean that only terms linear in $\Delta\psi$ are to be retained: $\Delta\psi \gg (\Delta\psi)^2$. We will show in Appendix C that

$$U(\boldsymbol{n}, \Delta\psi) f(\boldsymbol{r}) = (1 - i\,\Delta\psi\, \boldsymbol{n} \cdot \boldsymbol{l}) f(\boldsymbol{r}), \tag{12}$$

where $\boldsymbol{l}$ is defined in Eq. (1). Because of this relation one sometimes refers to $\boldsymbol{n} \cdot \boldsymbol{l}$ as the *generator of an infinitesimal rotation.*

Functions of operators can be defined by using the Taylor series of 'normal' functions. For instance, the exponential operator is defined by

$$e^{-i\psi\, \boldsymbol{n}\cdot\boldsymbol{l}} = \sum_{k=0}^{\infty} \frac{1}{k!}(-i\psi\, \boldsymbol{n} \cdot \boldsymbol{l})^k. \tag{13}$$

Formally one must prove that this series makes sense, i.e., that it converges with respect to some criterion. We ignore these mathematical subtleties and we also assume that differential equations satisfied by these operators can be solved in the same manner as for 'normal' functions. It is easy to derive a differential equation for $U(\boldsymbol{n}, \psi)$. Since

$$U(\boldsymbol{n},\psi+\Delta\psi)f(\boldsymbol{r}) = U(\boldsymbol{n},\psi)U(\boldsymbol{n},\Delta\psi)f(\boldsymbol{r}) \tag{14}$$
$$= U(\boldsymbol{n},\psi)(1-i\,\Delta\psi\,\boldsymbol{n}\cdot\boldsymbol{l})f(x), \tag{15}$$
$$\tag{16}$$

we find

$$\frac{dU(\boldsymbol{n},\psi)}{d\psi} = -iU(\boldsymbol{n},\psi)\,\boldsymbol{n}\cdot\boldsymbol{l}, \tag{17}$$

which, since $U(\boldsymbol{n},0)=1$, has the solution

$$\boxed{U(\boldsymbol{n},\psi) = e^{-i\psi\,\boldsymbol{n}\cdot\boldsymbol{l}}.} \tag{18}$$

So, we now have an explicit expression of the rotation operator, defined in (11), which shows most succinctly the connection with the orbital angular momentum operator $\boldsymbol{l}$.

C. The rotation of an operator

We will consider the rotation of an operator $H(\boldsymbol{r})$, where $\boldsymbol{r}$ indicates that H acts on functions of $\boldsymbol{r}$. Writing $\Psi'(\boldsymbol{r}) = H(\boldsymbol{r})\Psi(\boldsymbol{r})$, we find

$$UH(\boldsymbol{r})\Psi(\boldsymbol{r}) = U\Psi'(\boldsymbol{r}) = \Psi'(\mathbb{R}^{-1}\boldsymbol{r}) = H(\mathbb{R}^{-1}\boldsymbol{r})\Psi(\mathbb{R}^{-1}\boldsymbol{r}) = H(\mathbb{R}^{-1}\boldsymbol{r})U\Psi(\boldsymbol{r}), \tag{19}$$

so that the rotated operator is given by

$$H(\mathbb{R}^{-1}\boldsymbol{r}) = UH(\boldsymbol{r})U^{-1}. \tag{20}$$

Notice the difference with the corresponding Eq. (11) defining the rotation of functions.

Suppose next that $H(\boldsymbol{r})$ is invariant under rotation: $H(\boldsymbol{r}) = H(\mathbb{R}^{-1}\boldsymbol{r})$ for all $\mathbb{R}^{-1}$, then we find from (20) that

$$UH(\boldsymbol{r})U^{-1} \equiv e^{-i\psi\,\boldsymbol{n}\cdot\boldsymbol{l}}H(\boldsymbol{r})e^{i\psi\,\boldsymbol{n}\cdot\boldsymbol{l}} = H(\boldsymbol{r}). \tag{21}$$

Upon expansion of the exponentials we find

$$e^{-i\psi\,\boldsymbol{n}\cdot\boldsymbol{l}}He^{i\psi\,\boldsymbol{n}\cdot\boldsymbol{l}} = H + i\psi[H,\boldsymbol{n}\cdot\boldsymbol{l}] + \cdots = H + i\psi\sum_i n_i[H,l_i] + \cdots = H. \tag{22}$$

Since it was assumed that Eq. (21) holds for any $\boldsymbol{n}$ and ψ, we find the very important result that $U(\boldsymbol{n},\psi)HU(\boldsymbol{n},\psi)^{-1} = H$ if and only if $[H,l_i]=0$ for $i=1,2,3$.

Suppose $H(\boldsymbol{r})$ is the Hamiltonian of a certain one-particle system, for instance a particle moving in a spherical symmetric field due to a nucleus, or a particle moving in field-free space, then $H(\boldsymbol{r})$ is rotationally invariant. The unitary operators $U(\boldsymbol{n},\psi)$ are symmetry operators (unitary operators that commute with the Hamiltonian) and the l_i are constants of the motion of such a system.

D. The rotation of an N-particle system

The theory of this section was so far derived for the rotation of *one* vector $\boldsymbol{r}$, say the coordinate of one electron. It is easy to generalize the theory to N particles. If we simultaneously rotate all coordinate vectors $\boldsymbol{r}(\alpha)$ ($\alpha = 1, \ldots, N$) around the same axis $\boldsymbol{n}$ and over the same angle ψ, then the N-particle rotation operator still has the exponential form of Eq. (18), but the angular momentum operator is now given by

$$\boldsymbol{L} = \sum_{\alpha=1}^{N} \boldsymbol{l}(\alpha), \tag{23}$$

where $\boldsymbol{l}(\alpha) = -i\boldsymbol{r}(\alpha) \times \boldsymbol{\nabla}(\alpha)$. This is due to the fact that $[l_i(\alpha), l_j(\beta)] = 0$ (for $\alpha \neq \beta$), so that the N-particle rotation factorizes into a product of one-particle rotations,

$$e^{-i\psi\boldsymbol{n}\cdot\boldsymbol{L}} = \prod_{\alpha=1}^{N} e^{-i\psi\boldsymbol{n}\cdot\boldsymbol{l}(\alpha)}. \tag{24}$$

If the N particles do not interact, the separate rotation of any coordinate vector is a symmetry operation, and the angular momenta $\boldsymbol{l}(\alpha)$ are all constants of the motion. If, on the other hand, the particles do interact via an isotropic interaction potential $V(r_{\alpha\beta})$, with $r_{\alpha\beta} = |\boldsymbol{r}(\alpha) - \boldsymbol{r}(\beta)|$, then obviously only the *same simultaneous rotation* of *all* particles conserves the interparticle distances and commutes with the Hamiltonian. Thus, in the case of interacting particles only the rotation in Eq. (24) is a symmetry operation and only the total angular momentum $\boldsymbol{L}$ is a constant of the motion.

E. Exercises

1. We have seen that $\boldsymbol{n}$ is an eigenvector of $\mathbb{R}(\boldsymbol{n}, \psi)$ with unit eigenvalue. What are the other two eigenvalues of this matrix?

2. Given the vector $\boldsymbol{n}' = \mathbb{S}\boldsymbol{n}$ with orthogonal $\mathbb{S}$. Prove that $\mathbb{R}(\boldsymbol{n}', \psi) = \mathbb{S}\mathbb{R}(\boldsymbol{n}, \psi)\mathbb{S}^T$.

3. The tetrahedral group T consists of twelve proper (unit determinant) rotation matrices that map the four vectors

$$\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \quad \begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix}, \quad \begin{pmatrix} -1 \\ 1 \\ -1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 \\ -1 \\ -1 \end{pmatrix} \tag{25}$$

   onto each other. Give the twelve matrices. Hint: Use Eq. (10) for one 3-fold rotation, the result of the previous exercise and the fact that $\mathbb{R}^T = \mathbb{R}^{-1}$.

4. Prove that $\mathbb{R}(\boldsymbol{n}, \psi) = \exp(\psi\mathbb{N})$, where $\boldsymbol{n}$ and $\mathbb{N}$ are related by Eq. (9). Hint: use that $\mathbb{N}^3 = -\mathbb{N}$.

5. Show by expanding and considering the first few terms that $e^{\mathbb{A}}e^{\mathbb{B}} = e^{\mathbb{A}+\mathbb{B}}$ if and only if $[\mathbb{A}, \mathbb{B}] = 0$.

III. EIGENSPACES OF j^2 AND j_3

We consider an abstract Hilbert space $\mathcal{L}$ and assume that it is invariant under the Hermitian operators $j_i, i = 1, 2, 3$ that satisfy the commutation relations (4), i.e.,

$$[j_i, j_j] = i \sum_k \epsilon_{ijk} j_k.$$

In one of the first papers on quantum mechanics[1] it was already shown that $\mathcal{L}$ decomposes into a direct sum of subspaces V_α^j spanned by orthonormal kets

$$|\,\alpha, j, m\,\rangle, \qquad m = -j, \dots, j, \tag{26}$$

with

$$j^2|\,\alpha, j, m\,\rangle = j(j+1)|\,\alpha, j, m\,\rangle, \tag{27}$$

$$j_3|\,\alpha, j, m\,\rangle = m|\,\alpha, j, m\,\rangle, \tag{28}$$

$$j_\pm|\,\alpha, j, m\,\rangle = \sqrt{j(j+1) - m(m \pm 1)}|\,\alpha, j, m \pm 1\,\rangle, \tag{29}$$

where $j^2 = \sum_i j_i^2$, and $j_\pm = j_1 \pm i j_2$ are the well-known step up/down operators. It may happen that an eigenspace of j^2, characterized by a certain quantum number j, occurs more than once in $\mathcal{L}$. The index α resolves this multiplicity. Having made this point, we will from here on suppress α in our notation.

The proof of the existence of basis (26) is very well-known. Briefly, the main arguments are:

- As $[j^2, j_3] = 0$, we can find a common eigenvector $|\,a, b\,\rangle$ of j^2 and j_3 with $j^2|\,a, b\,\rangle = a^2|\,a, b\,\rangle$ and $j_3|\,a, b\,\rangle = b|\,a, b\,\rangle$. (Since it is easy to show that j^2 has only non-negative real eigenvalues, we write its eigenvalue as a squared number).

- Considering the commutation relations $[j_\pm, j_3] = \pm j_\pm$ and $[j^2, j_\pm] = 0$, we find, that $j^2 j_+|\,a, b\,\rangle = a^2 j_+|\,a, b\,\rangle$ and $j_3 j_+|\,a, b\,\rangle = (b+1) j_+|\,a, b\,\rangle$. Hence $j_+|\,a, b\,\rangle = |\,a, b+1\,\rangle$

- If we apply j_+ now $k+1$ times we obtain, using $j_+^\dagger = j_-$, the ket $|\,a, b+k+1\,\rangle$ with norm

$$\langle\, a, b+k\,|\,j_- j_+\,|\,a, b+k\,\rangle = [a^2 - (b+k)(b+k+1)]\langle\, a, b+k\,|\,a, b+k\,\rangle. \tag{30}$$

  Thus, if we let k increase, there comes a point that the norm on the left hand side would have to be negative (or zero), while the norm on the right hand side would still be positive. A negative norm is in contradiction with the fact that the ket belongs to the Hilbert space $\mathcal{L}$. Hence there must exist a value of the integer k, such that the ket $|\,a, b+k\,\rangle \neq 0$, while $|\,a, b+k+1\,\rangle = 0$. Also $a^2 = (b+k)(b+k+1)$ for that value of k.

- Similarly $l+1$ times application of j_- gives a zero ket $|\,a, b-l-1\,\rangle$ with $|\,a, b-l\,\rangle \neq 0$ and $a^2 = (b-l)(b-l-1)$.

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[1] M. Born, W. Heisenberg, and P. Jordan, Z. Phys. **35**, 557–615 (1926).

- From the fact that $a^2 = (b+k)(b+k+1) = (b-l)(b-l-1)$ follows $2b = l-k$, so that b is integer or half-integer. This quantum number is traditionally designated by m. The maximum value of m will be designated by j. Hence $a^2 = j(j+1)$.

- Requiring that $|\, j, m\,\rangle$ and $j_\pm |\, j, m\,\rangle$ are normalized and fixing phases, we obtain the well-known formula (29).

The spaces with half-integer j (and m) belong to a spin Hilbert space. In agreement with what was stated in the introduction, we will not consider half-integer j any further.

We can define a unitary rotation operator, as in Eq. (18)

$$U(\boldsymbol{n}, \psi) \equiv e^{-i\psi\, \boldsymbol{n}\cdot\boldsymbol{j}}. \tag{31}$$

An exponential operator is defined by its expansion, cf. Eq. (13). Since the eigenspace V^j of j^2 spanned by the basis (26) is invariant under j_1, j_2, and j_3, it is also invariant under $U(\boldsymbol{n}, \psi)$ and we can define its matrix with respect to that orthonormal basis

$$U(\boldsymbol{n}, \psi) |\, j, m\,\rangle = \sum_{m'=-j}^{j} |\, j, m'\,\rangle \langle\, j, m'\,|\, U(\boldsymbol{n}, \psi)\,|\, j, m\,\rangle, \quad m = -j, \ldots, j. \tag{32}$$

Often one writes

$$D^j_{m',m}(\boldsymbol{n}, \psi) \equiv \langle\, j, m'\,|\, U(\boldsymbol{n}, \psi)\,|\, j, m\,\rangle, \tag{33}$$

the so-called *Wigner D-matrix*.

The unitary D-matrices satisfy certain orthogonality relations. In order to explain this, we note that the map $\mathbb{R}(\boldsymbol{n}, \psi) \mapsto \mathbb{D}^j(\boldsymbol{n}, \psi)$ is a representation of the group $SO(3)$ carried by V^j. (Strictly speaking we must prove at this point that this map satisfies the homomorphism condition, but we forgo this proof). The space V^j is not only invariant under $SO(3)$, but also irreducible, which means that we cannot find a proper subspace of V^j that is invariant under $\{U(\boldsymbol{n}, \psi)\}$. (We omit the proof of this fact, too). Next, we recall from elementary group theory the so-called great orthogonality relations for irreducible representations

$$\sum_{g\in G} D^\lambda_{ij}(g)^{-1} D^\mu_{kl}(g) = \delta_{\lambda\mu}\delta_{jk}\delta_{il} \frac{|G|}{f^\lambda}, \tag{34}$$

where λ and μ label irreducible matrix representations of the finite group G of order $|G|$. The number f^λ is the dimension of $\mathbb{D}^\lambda$. These orthogonality relations can be generalized to certain kinds of groups of infinite order, among which $SO(3)$. In this generalization the sum over the finite group is replaced by integrals over the parameter space. Because a rotation around $\boldsymbol{n}$ over the angle $2\pi - \psi$ is the same as the rotation over ψ around $-\boldsymbol{n}$, we cover all of $SO(3)$ if we restrict ψ to run from 0 to π and $\boldsymbol{n}$ over the unit sphere. So, if θ and ϕ are the spherical polar angles of $\boldsymbol{n}$, the parameter space of $SO(3)$ is

$$0 \le \psi \le \pi, \quad 0 \le \theta \le \pi, \quad 0 \le \phi \le 2\pi. \tag{35}$$

It requires some knowledge of tensor analysis (or Lie group theory) to derive the proper volume element. Moreover, the actual derivation is tedious, so we give the result without proof:

$$d\tau = 2(1-\cos\psi)\sin\theta d\psi d\theta d\phi \quad \text{hence} \quad |SO(3)| = \int_0^\pi \int_0^\pi \int_0^{2\pi} \mathrm{d}\tau = 8\pi^2. \tag{36}$$

The Wigner D-matrices thus satisfy the orthogonality relations

$$\int_0^\pi \int_0^\pi \int_0^{2\pi} D^{j_1}_{m_1' m_1}(\boldsymbol{n},\psi)^* D^{j_2}_{m_2' m_2}(\boldsymbol{n},\psi)\, \mathrm{d}\tau = \delta_{j_1,j_2}\delta_{m_1',m_2'}\delta_{m_1,m_2}\frac{8\pi^2}{2j_1+1}, \tag{37}$$

where we have used that the D-matrix is unitary

$$D^{j_1}_{m_1' m_1}(\boldsymbol{n},\psi)^* = D^{j_1}_{m_1 m_1'}(\boldsymbol{n},\psi)^{-1}. \tag{38}$$

A. Exercises

6. Prove by only using (4) the commutation relations: $[j^2, j_i] = 0$ for $i = 1,2,3$ and $[j_\pm, j_3] = \pm j_\pm$.
7. Show that $j_- j_+ = j^2 - j_3(j_3+1)$, again by only using (4).
8. Show from (10) that $\mathbb{R}(-\boldsymbol{n}, 2\pi-\psi) = \mathbb{R}(\boldsymbol{n},\psi)$.

IV. VECTOR COUPLING

In this section we will indicate operators with a hat (as $\widehat{A}$), in order to distinguish clearly between the operators and their quantum numbers.

Consider two different spaces V^{j_1} and V^{j_2} spanned by $|\, j_1, m_1\,\rangle$, $m_1 = -j_1, \dots, j_1$, and $|\, j_2, m_2\,\rangle$, $m_2 = -j_2, \dots, j_2$, respectively. The tensor product space $V^{j_1} \otimes V^{j_2}$ is by definition the space spanned by the product kets $|\, j_1, m_1\,\rangle \otimes |\, j_2, m_2\,\rangle \equiv |\, j_1 m_1; j_2 m_2\,\rangle$. The product space is invariant under the operators $\widehat{J}_i \equiv \widehat{j}_i \otimes \widehat{1} + \widehat{1} \otimes \widehat{j}_i$, $i = 1,2,3$. This means that the elements of $V^{j_1} \otimes V^{j_2}$ are mapped onto elements in the space under the action of the operators, so that we can diagonalize $\widehat{J}^2 = \widehat{J}_1^2 + \widehat{J}_2^2 + \widehat{J}_3^2$ and $\widehat{J}_3$ on the product space. [The reason why we would like to do this was pointed out above: it may be that $\widehat{J}^2$ is a constant of the motion and that $\widehat{j}^2(1)$ and $\widehat{j}^2(2)$ are not]. The two-particle operators $\widehat{J}_i$ obviously satisfy the angular momentum commutation relations.

A remark on the notation is in order at this point. In quantum chemistry one usually writes a two-particle orbital product as $\psi(1)\phi(2)$. In mathematics one would write more often $\psi \otimes \phi$, i.e., the orbital product is an element of a tensor product space. Notice that $\psi\otimes\phi \neq \phi\otimes\psi$ just as $\psi(1)\phi(2) \neq \phi(1)\psi(2)$. Operators on a tensor product space may be tensor product operators themselves, written as $\widehat{A}\otimes\widehat{B}$. Their action is defined by

$$(\widehat{A}\otimes\widehat{B})\psi\otimes\phi \equiv (\widehat{A}\psi)\otimes(\widehat{B}\phi). \tag{39}$$

The matrix of this operator is a Kronecker product matrix. In quantum chemistry one would write this expression as

$$\widehat{A}(1)\widehat{B}(2)\psi(1)\phi(2) = (\widehat{A}\psi(1))(\widehat{B}\phi(2)). \tag{40}$$

Clearly the operator $\hat{j}_i \otimes \hat{1} + \hat{1} \otimes \hat{j}_i \equiv \hat{j}_i(1) + \hat{j}_i(2)$. Note that the terms commute, which was already used to arrive at Eq. (24). We will use the quantum chemical as well as tensor notation, whichever is the most convenient.

As the reasoning by which we decomposed a Hilbert space is valid for *any* angular momentum, we know that the product space must contain eigenkets $|\,(j_1 j_2)JM\,\rangle$, $M = -J, \ldots, J$ of $\hat{J}^2$ and $\hat{J}_3$. The pair $(j_1 j_2)$ indicates that the eigenket is formed as a linear combination of product kets $|\,j_1 m_1; j_2 m_2\,\rangle$.

The question now arises which eigenvalues $J(J+1)$ of $\hat{J}^2$ we may expect in the product space. This problem was solved (in a different context) by two German mathematicians: R.F.A. Clebsch[1] and P.A. Gordan[2]. The quantum number J occurs only once and it satisfies the *triangle condition*

$$|j_1 - j_2| \leq J \leq j_1 + j_2. \tag{41}$$

The proof of the triangle condition is given in Appendix D. By using the resolution of the identity on $V^{j_1} \otimes V^{j_2}$ we can write

$$|\,(j_1 j_2)JM\,\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |\,j_1 m_1; j_2 m_2\,\rangle\langle\,j_1 m_1; j_2 m_2\,|\,(j_1 j_2)JM\,\rangle. \tag{42}$$

This is the *Clebsch-Gordan series* and the coefficients $\langle\,j_1 m_1; j_2 m_2\,|\,(j_1 j_2)JM\,\rangle$ are known as Clebsch-Gordan (CG) coefficients. Since $\{|\,(j_1 j_2)JM\,\rangle\}$ is also an orthonormal basis of the product space $V^{j_1} \otimes V^{j_2}$ we can write

$$|\,j_1 m_1; j_2 m_2\,\rangle = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} |\,(j_1 j_2)JM\,\rangle\langle\,(j_1 j_2)JM\,|\,j_1 m_1; j_2 m_2\,\rangle. \tag{43}$$

In Appendix E we give an explicit expression (without proof) for the CG-coefficients, which shows that they are real numbers. Since the CG-coefficients give a transformation between orthonormal bases, they constitute a unitary matrix. Moreover, they are real so that $\langle\,j_1 m_1; j_2 m_2\,|\,(j_1 j_2)JM\,\rangle = \langle\,(j_1 j_2)JM\,|\,j_1 m_1; j_2 m_2\,\rangle$. Some more properties of the CG-coefficients are given in Appendix E. In the following we will usually drop the quantum numbers j_1 and j_2 standing next to JM in the CG-coefficients because they are superfluous.

The symmetry relations of CG-coefficients (see Appendix E) are awkward and difficult to remember. Wigner[3] introduced the following coefficients, *3j-symbols*, that have more pleasant symmetry properties:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \equiv \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} \langle\,j_1 m_1; j_2 m_2\,|\,j_3, -m_3\,\rangle. \tag{44}$$

From the results in Appendix E it follows easily that

[1] *Theorie der binären algebraische Formen*, Teubner, Leipzig, (1872).
[2] *Uber das Formensystem binärer Formen*, Teubner, Leipzig, (1875).
[3] Unpublished notes (1940) reprinted in: *Quantum Theory of Angular Momentum*, L.C. Biedenharn and H. van Dam, Academic, New York (1965).

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix}, \tag{45}$$

i.e., the $3j$-symbol is invariant under a cyclic (even) permutation of its columns and obtains the phase $(-1)^{j_1+j_2+j_3}$ upon an odd permutation (transposition) of any two of its columns. Further

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \tag{46}$$

and finally we find directly from Eq. (44) that the $3j$-symbol vanishes unless $m_1+m_2+m_3 = 0$.

It is of importance to see what happens to the matrix of the rotation operator (31), or rather to its two-particle equivalent, which describes the simultaneous rotation of two particles over the same axis and around the same angle

$$U(\boldsymbol{n},\psi) \equiv e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{J}}} = e^{-i\psi\, \boldsymbol{n}\cdot\left(\widehat{\boldsymbol{j}}(1)+\widehat{\boldsymbol{j}}(2)\right)} \equiv e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{j}}} \otimes e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{j}}}, \tag{47}$$

when we decompose the product space $V^{j_1} \otimes V^{j_2}$ into eigenspaces of $\widehat{J}^2$. The matrix $\langle\, J'M' \,|\, U(\boldsymbol{n},\psi) \,|\, JM \,\rangle$ is diagonal in J and J' because the spaces spanned by $|\, JM \,\rangle$ are invariant under $\widehat{J}_1$, $\widehat{J}_2$ and $\widehat{J}_3$. [Observe that we suppressed $(j_1 j_2)$ in $|\, JM \,\rangle$. It is understood that $|\, JM \,\rangle$ belongs to $V^{j_1} \otimes V^{j_2}$ for a *fixed* pair (j_1, j_2). The running indices describing bases are either the pair m_1, m_2, or the pair J, M]. Introducing twice the resolution of the identity, we find

$$\begin{aligned} \langle\, J'M' \,|\, e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{J}}} \,|\, JM \,\rangle = \sum_{m_1 m_2 m_1' m_2'} & \langle\, J'M' \,|\, j_1 m_1'; j_2 m_2' \,\rangle \langle\, j_1 m_1'; j_2 m_2' \,|\, e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{J}}} \,|\, j_1 m_1; j_2 m_2 \,\rangle \\ & \times \langle\, j_1 m_1; j_2 m_2 \,|\, JM \,\rangle \end{aligned} \tag{48}$$

from which follows,

$$\begin{aligned} \sum_{m_1 m_2 m_1' m_2'} & \langle\, J'M' \,|\, j_1 m_1'; j_2 m_2' \,\rangle \langle\, j_1 m_1' \,|\, e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{j}}(1)} \,|\, j_1 m_1 \,\rangle \langle\, j_2 m_2' \,|\, e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{j}}(2)} \,|\, j_2 m_2 \,\rangle \\ & \times \langle\, j_1 m_1; j_2 m_2 \,|\, JM \,\rangle = \delta_{J'J}\, \langle\, JM' \,|\, e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{J}}} \,|\, JM \,\rangle. \end{aligned} \tag{49}$$

This may be rewritten as

$$\begin{aligned} \sum_{\substack{m_1 m_2 \\ m_1' m_2'}} \langle\, J'M' \,|\, j_1 m_1'; j_2 m_2' \,\rangle \left(\mathbb{D}^{j_1}(\boldsymbol{n},\psi) \otimes \mathbb{D}^{j_2}(\boldsymbol{n},\psi)\right)_{m_1' m_2'; m_1 m_2} \langle\, j_1 m_1; j_2 m_2 \,|\, JM \,\rangle \\ = \delta_{J'J}\, D^J_{M'M}(\boldsymbol{n},\psi). \end{aligned} \tag{50}$$

Equation (50) shows that the Kronecker product matrix $\mathbb{D}^{j_1}(\boldsymbol{n},\psi) \otimes \mathbb{D}^{j_2}(\boldsymbol{n},\psi)$, which in principle is a completely filled matrix, is block-diagonalized by means of a unitary similarity transformation by CG-coefficients. The blocks on the diagonal in the matrix on the left hand side are labeled by $J = |j_1 - j_2|, \ldots, j_1 + j_2$, block J being of dimension $2J+1$. It is also easy to go the other way,

$$\langle\, j_1m_1'; j_2m_2' \,|\, e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{J}}} \,|\, j_1m_1; j_2m_2 \,\rangle = \sum_{JMM'} \langle\, j_1m_1'; j_2m_2' \,|\, JM' \,\rangle \times\langle\, JM' \,|\, e^{-i\psi\, \boldsymbol{n}\cdot\widehat{\boldsymbol{J}}} \,|\, JM \,\rangle\langle\, JM \,|\, j_1m_1; j_2m_2 \,\rangle. \tag{51}$$

This may be rewritten as

$$\Big(\mathbb{D}^{j_1}(\boldsymbol{n},\psi)\otimes\mathbb{D}^{j_2}(\boldsymbol{n},\psi)\Big)_{m_1'm_2';m_1m_2} = \sum_{JMM'} \langle\, j_1m_1'; j_2m_2' \,|\, JM' \,\rangle\; D^J_{M'M}(\boldsymbol{n},\psi) \times\langle\, JM \,|\, j_1m_1; j_2m_2 \,\rangle. \tag{52}$$

We are now in a position to show the following useful relation, which we will need in the proof of the Wigner-Eckart theorem:

$$\int D^{j_1}_{m_1'm_1}(\boldsymbol{n},\psi)^* D^{j_2}_{m_2'm_2}(\boldsymbol{n},\psi) D^{j_3}_{m_3'm_3}(\boldsymbol{n},\psi) d\tau = \frac{8\pi^2}{2j_1+1}\langle\, j_1m_1' \,|\, j_2m_2'; j_3m_3' \,\rangle \times\langle\, j_1m_1 \,|\, j_2m_2; j_3m_3 \,\rangle, \tag{53}$$

where the integral and its volume element are defined in Eq. (36). To show this relation we first use Eq. (52), so that (suppressing integration variables) we get

$$\int (D^{j_1}_{m_1'm_1})^* D^{j_2}_{m_2'm_2} D^{j_3}_{m_3'm_3} d\tau = \sum_{JM'M} \langle\, j_2m_2'; j_3m_3' \,|\, JM' \,\rangle\langle\, JM \,|\, j_2m_2; j_3m_3 \,\rangle \times \int (D^{j_1}_{m_1'm_1})^* D^J_{M'M} d\tau \tag{54}$$

By the use of (37) we find

$$\int (D^{j_1}_{m_1'm_1})^* D^J_{M'M} d\tau = \delta_{j_1 J}\delta_{m_1'M'}\delta_{m_1 M}\frac{8\pi^2}{2J+1}, \tag{55}$$

so that

$$\begin{aligned}\int (D^{j_1}_{m_1'm_1})^* D^{j_2}_{m_2'm_2} D^{j_3}_{m_3'm_3} d\tau &= \sum_{JM'M} \delta_{j_1 J}\delta_{m_1'M'}\delta_{m_1 M}\frac{8\pi^2}{2J+1} \\ &\quad\times\langle\, j_2m_2'; j_3m_3' \,|\, JM' \,\rangle\langle\, JM \,|\, j_2m_2; j_3m_3 \,\rangle \\ &= \frac{8\pi^2}{2j_1+1}\langle\, j_2m_2'; j_3m_3' \,|\, j_1m_1' \,\rangle\langle\, j_1m_1 \,|\, j_2m_2; j_3m_3 \,\rangle, \end{aligned}\tag{56}$$

which proves Eq. (53).

A. Exercises

9. Evaluate $\langle\, 20 \,|\, 11; 1-1 \,\rangle$ by the explicit expression in Appendix E.

10. Decompose explicitly the space $V^1 \otimes V^1$ by the use of step-down operators. Hint: this product space is invariant under the transposition P_{12}. This observation may be used in the required orthogonalizations.

11. Prove Eqs. (45) and (46) from the relations in Appendix E.

V. THE WIGNER-ECKART THEOREM

The Wigner-Eckart theorem[1] is a tool to evaluate matrix elements of tensor operators, and so we start this section with the introduction of such operators. Let us first consider a simple example, namely a tensor operator of rank one, also known as a vector operator. We have seen in Eq. (20) that an arbitrary one-particle operator $Q(\boldsymbol{x})$ rotates as follows

$$Q(\mathbb{R}(\boldsymbol{n},\psi)^{-1}\boldsymbol{x}) = U(\boldsymbol{n},\psi)Q(\boldsymbol{x})U(\boldsymbol{n},\psi)^{\dagger}. \tag{57}$$

Thus, each component of the coordinate operator transforms in this way, and we can write

$$\mathbb{R}(\boldsymbol{n},\psi)^{-1}\boldsymbol{x} = U(\boldsymbol{n},\psi)\boldsymbol{x}U(\boldsymbol{n},\psi)^{\dagger}, \tag{58}$$

or

$$U(\boldsymbol{n},\psi)x_iU(\boldsymbol{n},\psi)^{\dagger} = \sum_{j=1}^{3} x_j R_{ji}(\boldsymbol{n},\psi). \tag{59}$$

This equation serves as the definition of a vector operator: a vector operator consists of three components that upon rotation of the system transform among themselves as in Eq. (59). Another example is $\boldsymbol{\nabla}_r = (\nabla_1, \nabla_2, \nabla_3)$. Recall that a vector product $\boldsymbol{x}\times\boldsymbol{y}$ rotates as a vector

$$(\mathbb{R}\boldsymbol{x})\times(\mathbb{R}\boldsymbol{y}) = (\det\mathbb{R})\,\mathbb{R}(\boldsymbol{x}\times\boldsymbol{y}) \tag{60}$$

and for a proper rotation $\det\mathbb{R} = 1$. It is then evident that the angular momentum defined as a vector product in Eq. (1) is another example of a vector operator.

It is often convenient to work with spherical vectors, defined by

$$(x_1, x_0, x_{-1}) \equiv (x, y, z)\,\mathbb{S} \quad \text{with} \quad \mathbb{S} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & 0 & 1 \\ -i & 0 & -i \\ 0 & \sqrt{2} & 0 \end{pmatrix}. \tag{61}$$

Observe that this is the same transformation as between real and complex atomic p-orbitals, and indeed, the spherical components of a vector are proportional to $r\,Y^1_m(\theta,\phi)$, where $Y^1_m(\theta,\phi)$ is a spherical harmonic function and $m = 1, 0, -1$. Recall that spherical harmonic functions satisfy the relations (27), (28), and (29), where the angular momentum is the orbital angular momentum of Eq. (1).

If we compute the matrix of $U(\boldsymbol{n},\psi)$ on basis of $Y^1_m(\theta,\phi)$, with $m = 1, 0, -1$, we obtain the matrix $\mathbb{D}^1(\boldsymbol{n},\psi)$. If we perform the transformation (61) on this matrix, we get $\mathbb{R}(\boldsymbol{n},\psi)$, i.e.,

$$\mathbb{S}\,\mathbb{D}^1(\boldsymbol{n},\psi)\,\mathbb{S}^{\dagger} = \mathbb{R}(\boldsymbol{n},\psi) \tag{62}$$

[1] C. Eckart, Rev. Mod. Phys. **2**, 305 (1930); E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren*, Vieweg, Braunschweig, 1931. Translated by J.J. Griffin as: *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra*, Academic, New York (1959).

and so,

$$\left(\mathbb{S}^\dagger\, \mathbb{R}(\boldsymbol{n},\psi)\, \mathbb{S}\right)_{m'm} = D^1_{m'm}(\boldsymbol{n},\psi). \tag{63}$$

Using this equation and Eq. (61), we can rewrite Eq. (59) in terms of spherical components,

$$U(\boldsymbol{n},\psi)\, x_m\, U(\boldsymbol{n},\psi)^\dagger = \sum_{m=-1}^{1} x_{m'} D^1_{m'm}(\boldsymbol{n},\psi). \tag{64}$$

We now come to the definition of a spherical tensor operator, which is defined with respect to a set of axes attached to a quantum mechanical system (an atom, a molecule, etc.). If the $2j+1$ operators T^j_m transform among themselves as

$$U(\boldsymbol{n},\psi) T^j_m U(\boldsymbol{n},\psi)^\dagger = \sum_{m=-j}^{j} T^j_{m'} D^j_{m'm}(\boldsymbol{n},\psi). \tag{65}$$

upon rotation of the system, then the set $\{T^j_m | m = -j, \dots, j\}$ is called an *irreducible spherical tensor operator*. The adjective 'irreducible' refers to the fact that the D-matrices constitute an irreducible matrix representation of $SO(3)$.

A very well-known example of a tensor operator is the electric multipole operator

$$M^l_m \equiv \sqrt{\frac{4\pi}{2l+1}} \sum_{\alpha=1}^{N} Z_\alpha r^l_\alpha Y^l_m(\theta_\alpha, \phi_\alpha), \tag{66}$$

where r_α, θ_α and ϕ_α are the spherical polar coordinates of particle α and Z_α is its charge. From the fact that spherical harmonics are eigenfunctions of l^2 and l_3 follows

$$U(\boldsymbol{n},\psi) |\, Y^l_m \,\rangle = \sum_{m'=-l}^{l} |\, Y^l_{m'} \,\rangle D^l_{m'm}(\boldsymbol{n},\psi), \tag{67}$$

and considered as a one-particle multiplicative (local) operator a spherical harmonic satisfies therefore (65). Hence the multipole operator is a tensor operator, provided we rotate all N particles simultaneously.

A rank-zero tensor operator has by definition $j = 0$. Since $\mathbb{D}^0$ is unity, we see that its definition (65) coincides with Eq. (21), where a rotationally invariant operator was defined. One also refers to rank-zero operators as scalar operators in analogy to rank-one operators, which are vector operators.

The following is the famous Wigner-Eckart theorem:

$$\langle\, \gamma' j' m' \,|\, T^k_q \,|\, \gamma j m \,\rangle = \langle\, j' m' \,|\, kq; jm \,\rangle \langle\, \gamma' j' \,||T^k||\, \gamma j \,\rangle, \tag{68}$$

which states that the $(2j'+1)(2k+1)(2j+1)$ different matrix elements are all given by a CG-coefficient (the algebraic part) times a so-called *reduced matrix element* $\langle\, \gamma' j' \,||T^j||\, \gamma j \,\rangle$, which contains the dynamics of the problem and hence is the difficult part. We introduced the extra quantum numbers γ and γ' to remind us of the fact that in general j and m are not sufficient to label a state.

The proof of the Wigner-Eckart theorem is simple. Since $U(\boldsymbol{n},\psi)$ is unitary, we have

$$C \equiv \langle \gamma' j' m' \,|\, T^k_q \,|\, \gamma j m \rangle = \langle U(\boldsymbol{n},\psi)\gamma' j' m' \,|\, U(\boldsymbol{n},\psi) T^k_q U(\boldsymbol{n},\psi)^\dagger \,|\, U(\boldsymbol{n},\psi)\gamma j m \rangle. \tag{69}$$

We may integrate both sides of this equation over $SO(3)$. On the left hand side this gives simply $8\pi^2 C$. In the matrix element on the right hand side we first let $U(\boldsymbol{n},\psi)$ act in bra, ket, and on the operator and obtain

$$8\pi^2 C = \sum_{\mu' q' \mu} \langle \gamma' j' \mu' \,|\, T^k_{q'} \,|\, \gamma j \mu \rangle \int D^{j'}_{\mu' m'}(\boldsymbol{n},\psi)^* D^k_{q' q}(\boldsymbol{n},\psi) D^j_{\mu m}(\boldsymbol{n},\psi) d\tau. \tag{70}$$

When we substitute Eq. (53) into Eq. (70) and define the following quantity

$$\langle \gamma' j' \,|\,|T^k|\,|\, \gamma j \rangle \equiv \frac{1}{2j'+1} \sum_{\mu' q' \mu} \langle j' \mu' \,|\, k q'; j \mu \rangle \langle \gamma' j' \mu' \,|\, T^k_{q'} \,|\, \gamma j \mu \rangle, \tag{71}$$

which obviously does not depend on μ', q' or μ, we get

$$C = \langle j' m' \,|\, k q; j m \rangle \langle \gamma' j' \,|\,|T^k|\,|\, \gamma j \rangle. \tag{72}$$

This proves the Wigner-Eckart theorem.

The Clebsch-Gordan coefficient arising in the case of a scalar operator is,

$$\langle j' m' \,|\, 00; j m \rangle = \delta_{j' j} \delta_{m' m}. \tag{73}$$

So, we see that only states of the same j and m quantum numbers mix under a scalar operator. An example of such an operator is the Hamiltonian H of an atom,

$$\langle \gamma' j' m' \,|\, H \,|\, \gamma j m \rangle = \delta_{j' j} \delta_{m' m} \langle \gamma' j \,|\,|H|\,|\, \gamma j \rangle \tag{74}$$

and we see here a confirmation of the fact that j^2 is a constant of the motion of an atom, as the Hamiltonian matrix on basis of $|\, \gamma j m \rangle$ is obviously block diagonal. The blocks are labeled by j and the quantum numbers γ' and γ label the rows and columns of the blocks. Notice also that the matrix element of a scalar operator is independent of m.

As another application of the Wigner-Eckart theorem (68) we discuss the Gaunt series[1]. This series expresses a coupled product of two spherical harmonics depending on the *same* angles as a spherical harmonic,

$$\sum_{m_1 m_2} Y^{l_1}_{m_1}(\theta,\phi) Y^{l_2}_{m_2}(\theta,\phi) \langle l_1 m_1; l_2 m_2 \,|\, L M \rangle = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)} \right]^{\frac{1}{2}} \langle l_1 0; l_2 0 \,|\, L 0 \rangle Y^L_M(\theta,\phi). \tag{75}$$

The Gaunt series resembles the CG-series, but differs in the fact that the CG-series pertains to different coordinates, for instance the coordinate vectors of two *different* particles. To prove Eq. (75), we observe that $Y^\lambda_\mu(\theta,\phi)$ is complete, hence we may write

$$\sum_{m_1 m_2} Y^{l_1}_{m_1}(\theta,\phi) Y^{l_2}_{m_2}(\theta,\phi) \langle l_1 m_1; l_2 m_2 \,|\, L M \rangle = \sum_{\lambda\mu} C^{LM}_{\lambda\mu} \; Y^\lambda_\mu(\theta\phi), \tag{76}$$

[1]J.A. Gaunt, Trans. Roy. Soc. **A228**, 151 (1929).

where $C^{LM}_{\lambda\mu}$ is an expansion coefficient. Project both sides with $\langle\, Y^{l_3}_{m_3}\,|$ and we get by the orthonormality of the spherical harmonics

$$\sum_{m_1 m_2} \langle\, Y^{l_3}_{m_3}\,|\, Y^{l_1}_{m_1}\,|\, Y^{l_2}_{m_2}\,\rangle \langle\, l_1 m_1; l_2 m_2\,|\, LM\,\rangle = C^{LM}_{l_3 m_3}. \tag{77}$$

Apply the Wigner-Eckart theorem:

$$\langle\, Y^{l_3}_{m_3}\,|\, Y^{l_1}_{m_1}\,|\, Y^{l_2}_{m_2}\,\rangle = \langle\, l_3\,|\,|l_1|\,|\, l_2\,\rangle\; \langle\, l_3 m_3\,|\, l_1 m_1; l_2 m_2\,\rangle \tag{78}$$

and use

$$\sum_{m_1 m_2} \langle\, l_3 m_3\,|\, l_1 m_1; l_2 m_2\,\rangle \langle\, l_1 m_1; l_2 m_2\,|\, LM\,\rangle = \delta_{l_3 L}\delta_{m_3 M}. \tag{79}$$

Then from Eq. (77)

$$C^{LM}_{l_3 m_3} = \langle\, L\,|\,|l_1|\,|\, l_2\,\rangle \delta_{l_3 L}\delta_{m_3 M}, \tag{80}$$

which substituted into (76) gives

$$\sum_{m_1 m_2} Y^{l_1}_{m_1}(\theta,\phi) Y^{l_2}_{m_2}(\theta,\phi) \langle\, l_1 m_1; l_2 m_2\,|\, LM\,\rangle = \langle\, L\,|\,|l_1|\,|\, l_2\,\rangle Y^L_M(\theta,\phi). \tag{81}$$

In order to determine the reduced matrix element we use the fact that

$$Y^l_m(0,0) = \left[\frac{2l+1}{4\pi}\right]^{\frac{1}{2}} \delta_{m0}, \tag{82}$$

and insert this into the left and the right hand side of (81). Thus

$$\left[\frac{(2l_1+1)(2l_2+1)}{16\pi^2}\right]^{\frac{1}{2}} \langle\, l_1 0; l_2 0\,|\, L0\,\rangle = \langle\, L\,|\,|l_1|\,|\, l_2\,\rangle \left[\frac{2L+1}{4\pi}\right]^{\frac{1}{2}}, \tag{83}$$

and so

$$\langle\, L\,|\,|l_1|\,|\, l_2\,\rangle = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}\right]^{\frac{1}{2}} \langle\, L0\,|\, l_1 0; l_2 0\,\rangle, \tag{84}$$

which, after substitution into (81), proves Eq. (75).

The integral in Eq. (78) is often written in terms of $3j$-symbols

$$\langle\, Y^{l_1}_{m_1}\,|\, Y^{l_2}_{m_2}\,|\, Y^{l_3}_{m_3}\,\rangle = (-)^{m_1} \left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}\right]^{\frac{1}{2}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix}. \tag{85}$$

This integral is known as a *Gaunt coefficient*. From the symmetry relation (46) follows immediately that the matrix element vanishes if $l_1 + l_2 + l_3$ is odd. Here we see that the Wigner-Eckart theorem furnishes a selection rule, and, indeed, the providing of selection rules is one of the important applications of the theorem.

A. Exercise

12. Given that

$$\begin{pmatrix} 1 & j & j \\ 0 & -j & j \end{pmatrix} = -\sqrt{\frac{j}{(2j+1)(j+1)}} \quad \text{compute} \quad \begin{pmatrix} 1 & j & j \\ 1 & -j & j-1 \end{pmatrix}. \tag{86}$$

Hints:
(i) From Eq.(61) follows that

$$j^1_1 \equiv -\frac{1}{\sqrt{2}}(j_1 + ij_2), \quad j^1_0 \equiv j_3, \quad \text{and} \quad j^1_{-1} \equiv \frac{1}{\sqrt{2}}(j_1 - ij_2) \tag{87}$$

are the components of a vector operator.
(ii) Compute the reduced matrix element $\langle\, j \,||j^1||\, j\,\rangle$ from $\langle\, jj \,|\, j^1_0 \,|\, jj\,\rangle$ and the given $3j$-symbol.
(iii) Use Eq. (29) and the Wigner-Eckart theorem to compute $\langle\, j, j-1 \,|\, j^1_{-1} \,|\, j, j\,\rangle$.

VI. RECOUPLING AND $6j$-SYMBOLS

Consider the tensor product space $V^{j_1} \otimes V^{j_2} \otimes V^{j_3}$ spanned by

$$|\, j_1 m_1; j_2 m_2; j_3 m_3 \,\rangle \equiv |\, j_1 m_1 \,\rangle \otimes |\, j_2 m_2 \,\rangle \otimes |\, j_3 m_3 \,\rangle,$$

where the kets satisfy Eqs. (27), (28), and (29). This space is invariant under

$$J_i = j_i(1) + j_i(2) + j_i(3) \equiv j_i \otimes 1 \otimes 1 + 1 \otimes j_i \otimes 1 + 1 \otimes 1 \otimes j_i \;\text{ with }\; i = 1, 2, 3 = x, y, z.$$

We may diagonalize J^2 and J_3 on this space, which can be done most easily by repeated Clebsch-Gordan coupling.

There are three essentially different bases of the total space that may be obtained this way. We can couple first j_1 and j_2 to angular momentum j_{12} and then couple this with j_3 to J. The basis so obtained consists of kets $|\, ((j_1 j_2) j_{12} j_3) JM \,\rangle$. We can also couple first j_2 and j_3 and then j_1, which leads to $|\, (j_1 (j_2 j_3) j_{23}) JM \,\rangle$ and finally we may couple first j_1 and j_3 to j_{13} and then j_2. If the order within one pair-coupling is permuted, we do not obtain an essentially new basis, but one which has only a different phase (cf. the third symmetry relation of CG-coefficients in Appendix E). The three different bases of $V^{j_1} \otimes V^{j_2} \otimes V^{j_3}$ are orthonormal, and all three give a resolution of the identity. Thus, for instance,

$$|\, ((j_1 j_2) j_{12} j_3) JM \,\rangle = \sum_{j_{23}} |\, (j_1 (j_2 j_3) j_{23}) JM \,\rangle \langle\, (j_1 (j_2 j_3) j_{23}) JM \,|\, ((j_1 j_2) j_{12} j_3) JM \,\rangle. \tag{88}$$

The Fourier coefficient (overlap matrix element) in Eq. (88) is a *recoupling coefficient*. We can look upon this coefficient as a matrix element of the unit operator, which is a scalar operator, so that by the Wigner-Eckart theorem the recoupling coefficient is diagonal in J and M and does not depend on M; therefore we will drop M in the recoupling coefficient.

By inserting the definition of the coupled kets into the left and right hand side of Eq. (88) we can relate the recoupling coefficient to CG-coefficients,

$$\sum_{m_1m_2m_3m_{12}} |\, j_1m_1; j_2m_2; j_3m_3 \,\rangle\langle\, j_1m_1; j_2m_2 \,|\, j_{12}m_{12} \,\rangle\langle\, j_{12}m_{12}; j_3m_3 \,|\, JM \,\rangle$$
$$= \sum_{j_{23}} \langle\, (j_1(j_2j_3)j_{23})J \,|\, ((j_1j_2)j_{12}j_3)J \,\rangle \sum_{m_1m_2m_3m_{23}} |\, j_1m_1; j_2m_2; j_3m_3 \,\rangle$$
$$\times \langle\, j_2m_2; j_3m_3 \,|\, j_{23}m_{23} \,\rangle\langle\, j_1m_1; j_{23}m_{23} \,|\, JM \,\rangle. \tag{89}$$

Equating the coefficients of the product kets gives

$$\sum_{m_{12}} \langle\, j_1m_1; j_2m_2 \,|\, j_{12}m_{12} \,\rangle\langle\, j_{12}m_{12}; j_3m_3 \,|\, JM \,\rangle = \sum_{j_{23}m_{23}} \langle\, (j_1(j_2j_3)j_{23})J \,|\, ((j_1j_2)j_{12}j_3)J \,\rangle$$
$$\times \langle\, j_2m_2; j_3m_3 \,|\, j_{23}m_{23} \,\rangle\langle\, j_1m_1; j_{23}m_{23} \,|\, JM \,\rangle. \tag{90}$$

Multiply both sides with $\langle\, j'_{23}m'_{23} \,|\, j_2m_2; j_3m_3 \,\rangle$ and sum over m_2 and m_3, use the unitarity of CG-coefficients, i.e.,

$$\sum_{m_2m_3} \langle\, j'_{23}m'_{23} \,|\, j_2m_2; j_3m_3 \,\rangle\langle\, j_2m_2; j_3m_3 \,|\, j_{23}m_{23} \,\rangle = \delta_{j'_{23}j_{23}}\delta_{m'_{23}m_{23}}, \tag{91}$$

then multiply both sides by $\langle\, J'M' \,|\, j_1m_1; j'_{23}m'_{23} \,\rangle$ sum over m_1 and m'_{23} and use again the unitarity, we then find (dropping primes)

$$\langle\, (j_1(j_2j_3)j_{23})J \,|\, ((j_1j_2)j_{12}j_3)J \,\rangle = \sum_{m_1m_2m_3m_{12}m_{23}} \langle\, JM \,|\, j_1m_1; j_{23}m_{23} \,\rangle\langle\, j_{23}m_{23} \,|\, j_2m_2; j_3m_3 \,\rangle$$
$$\times \langle\, j_1m_1; j_2m_2 \,|\, j_{12}m_{12} \,\rangle\langle\, j_{12}m_{12}; j_3m_3 \,|\, JM \,\rangle. \tag{92}$$

Since the recoupling coefficient is independent of M, we may sum the right hand side over M, provided we divide by $2J+1$. A *6j-symbol* is proportional to the recoupling coefficient, but somewhat more symmetric:

$$\begin{Bmatrix} j_3 & j_{12} & J \\ j_1 & j_{23} & j_2 \end{Bmatrix} = (-1)^{j_1+j_2+j_3+J}[(2j_{12}+1)(2j_{23}+1)]^{-\frac{1}{2}} \langle\, (j_1(j_2j_3)j_{23})J \,|\, ((j_1j_2)j_{12}j_3)J \,\rangle. \tag{93}$$

An alternative notation that is often used, is the W-coefficient of Racah:

$$W(j_1j_2j_3j_4; j_5j_6) \equiv (-1)^{j_1+j_2+j_3+j_4} \begin{Bmatrix} j_1 & j_2 & j_5 \\ j_4 & j_3 & j_6 \end{Bmatrix} \tag{94}$$

By Eq. (92) a $6j$-symbol is given as a sum of products of four CG-coefficients, or alternatively, as a sum of products of four $3j$-symbols. Since the m quantum numbers in Eq. (92) satisfy linear relations, e.g. $m_{12} = m_1 + m_2$, this equation contains in fact only a double sum. Each CG-coefficient is given by a single summation (cf. Appendix E) and hence a $6j$-symbol is defined as a six-fold summation. Racah[1] was able to reduce this six-fold sum to a single sum by a series of substitutions that were so incredibly ingenious that no-one tried to explain this ever since. We will not make an attempt either, and simply give Racah's formula in Appendix F.

[1]G. Racah, Phys. Rev. **62**, 438 (1942).

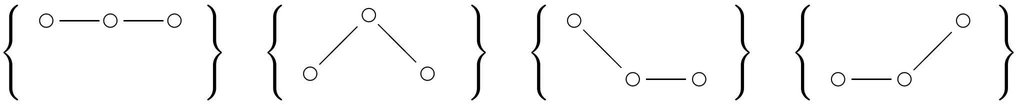
The $6j$-symbol satisfies two sets of symmetry relations that are easily derived by the use of Jucys's angular momentum diagrams. Because of time limitations we will not give the derivation, but simply state the results. First, any of the six possible permutations of its columns leaves a $6j$-symbol invariant, thus

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_2 & j_1 & j_3 \\ j_5 & j_4 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_2 & j_3 & j_1 \\ j_5 & j_6 & j_4 \end{Bmatrix}, \quad \text{etc.}\,. \tag{95}$$

Second, any two elements in the upper row may be interchanged with the elements underneath them:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_4 & j_5 & j_3 \\ j_1 & j_2 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_4 & j_2 & j_6 \\ j_1 & j_5 & j_3 \end{Bmatrix} = \begin{Bmatrix} j_1 & j_5 & j_6 \\ j_4 & j_2 & j_3 \end{Bmatrix}. \tag{96}$$

The four triangular conditions which must be satisfied by the six angular momenta in the $6j$-symbol may be illustrated in the following way:



(97)

At the same time these diagrams illustrate the second set of symmetry relations obeyed by the $6j$-symbol.

VII. ATOM-DIATOM SCATTERING

As discussed above, one often meets the case of two subsystems with different configuration spaces, that are in eigenstates of $j^2(1)$ and $j^2(2)$ and that are coupled

$$|\,(j_1 j_2) j_{12} m_{12}\,\rangle \equiv \sum_{m_1 m_2} |\,j_1 m_1\,\rangle |\,j_2 m_2\,\rangle \langle\, j_1 m_2; j_2 m_2\,|\,j_{12} m_{12}\,\rangle \quad \text{with} \quad m_{12} = m_1 + m_2, \tag{98}$$

cf. Eq. (42). An obvious (for the quantum chemist) example is formed by two atomic electrons in orbitals with quantum numbers l_1 and l_2, which are Russell-Saunders coupled to a total angular momentum L.

A somewhat less obvious example is offered by a scattering complex consisting of a diatom and an atom. In this section we will discuss the use of the Wigner-Eckart theorem to compute the angular matrix elements that arise in the coupled channel (close coupling) approach to scattering. In Fig. 1 we have drawn the coordinates of this complex, the so-called *Jacobi coordinates.*

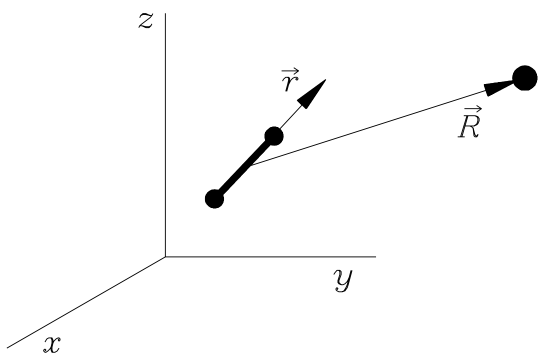


Fig. 1

The coordinates relevant in atom-diatom scattering. The vector $\vec{r}$ is along the diatom and has a length equal to the bondlength. It has the coordinate vector $\boldsymbol{r}$ with respect to space-fixed axes, labeled by x, y and z. The vector $\vec{R}$ points from the center of mass of the diatom to the atom. Its length is the intersystem distance. This vector has coordinate vector $\boldsymbol{R}$.

The rotational wave function of a diatomic molecule is $Y^l_m(\hat{r})$, where $\hat{r}$ is a unit vector along $\vec{r}$. Notice that there is a one-to-one correspondence between $\hat{r}$ and the spherical polar angles θ and ϕ of $\boldsymbol{r}$, which explains the notation $Y^l_m(\hat{r})$. The relative motion of the atom and the diatom is described by spherical waves depending on $\hat{R}$, i.e., by the functions $Y^L_M(\hat{R})$. The total angular momentum of the complex is $\vec{J} = \vec{l} + \vec{L}$, where $\vec{l}$ is a vector operator with components $-i\boldsymbol{r} \times \boldsymbol{\nabla}_r$ with respect to the space-fixed frame and the vector operator $\vec{L}$, depending on $\boldsymbol{R}$, is defined similarly. Remember that $\vec{J}$ is a constant of the motion if and only if the Hamiltonian is invariant under a simultaneous rotation of $\vec{r}$ and $\vec{R}$, that is, under a rotation of the total collision complex. Because we assume the complex to move in an isotropic space (no external fields), this is the case. Notice that a rotation of only $\vec{r}$, (or $\vec{R}$) changes the interaction energy, and hence $\vec{l}$ and $\vec{L}$ are *not* constants of the motion, at least at distances where the interaction is appreciable.[1]

The atom-diatom interaction can be expanded in terms of Legendre functions $P_\lambda(\cos\gamma)$ depending on the angle γ between $\vec{r}$ and $\vec{R}$. The famous spherical harmonic addition theorem relates $P_\lambda(\cos\gamma)$ to spherical harmonics depending on the space-fixed coordinates θ, ϕ and Θ, Φ of $\vec{r}$ and $\vec{R}$, respectively:

$$P_\lambda(\cos\gamma) = \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} (-1)^\mu Y^\lambda_{-\mu}(\theta,\phi) Y^\lambda_\mu(\Theta,\Phi). \tag{99}$$

To prove Eq. (99), we first note that the right hand side of this equation is a rotational invariant. Indeed, since in the usual Condon & Shortley phase convention $(-1)^\mu Y^\lambda_{-\mu} = (Y^\lambda_\mu)^*$ and because the Wigner D-matrices are unitary, the quantity $\sum_\mu |Y^\lambda_\mu|^2$ is an invariant. Alternatively, one can look upon the right hand side of Eq. (99) as being proportional to a CG coupling of two spherical harmonics to total $L = 0$, because $\langle\, \lambda\mu; \lambda\mu' \,|\, 00 \,\rangle = \delta_{\mu,-\mu'}(-1)^{\lambda-\mu}[2\lambda+1]^{-1/2}$. Since the right hand side of Eq. (99) is invariant under rotation of the collision complex, the spherical harmonic addition theorem follows easily by rotating the whole complex, such that $\vec{r}\,'$ is along the space-fixed z-axis, i.e., $\boldsymbol{r}' = (0, 0, r)$. Inserting (82) we get, using the rotational invariance,

$$\frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} (-1)^\mu Y^\lambda_{-\mu}(\theta,\phi) Y^\lambda_\mu(\Theta,\Phi) = \left[\frac{4\pi}{2\lambda+1}\right]^{\frac{1}{2}} Y^\lambda_0(\Theta',\Phi') = P_\lambda(\cos\Theta'). \tag{100}$$

The angle Θ' is the angle that the rotated vector $\vec{R}'$ makes with the z-axis and hence is equal to γ.

In the coupled channel approach one projects the Schrödinger equation by a coupled set of spherical harmonics

[1] The attentive reader may note that the interaction is invariant under any rotation of $\vec{R}$ around $\vec{r}$. However, some Coriolis terms arising in the kinetic energy operator are not invariant under this rotation, and hence $\vec{r} \cdot \vec{L}$ is not a constant of the motion. When we neglect these small Coriolis terms, as one does in the coupled state approximation in scattering theory, we obtain axial rotation symmetry with infinitesimal generator $\vec{r} \cdot \vec{L}$. In the coupled channel approximation the Coriolis terms are not neglected.

$$| \, (lL)JM \, \rangle = \sum_{mM} Y^l_m(\theta,\phi) Y^L_M(\Theta,\Phi) \langle \, lm; LM \, | \, JM \, \rangle, \tag{101}$$

and since J and M are good quantum numbers we meet only matrix elements diagonal in J and M

$$\langle \, (l'L')J \; M \, | \sum_\mu (-1)^\mu Y^\lambda_{-\mu}(\hat{r}) \; Y^\lambda_\mu(\hat{R}) \, | \, (lL)J \; M \, \rangle = \langle \, JM \, | \, 00; JM \, \rangle \langle \, (l'L')J \, | \, |P_\lambda| \, | \, (lL)J \, \rangle. \tag{102}$$

As $\langle \, JM \, | \, 00; JM \, \rangle = 1$, the matrix elements are independent of M. The reduced matrix element can be evaluated by the Wigner-Eckart theorem. In doing so one meets algebraic coefficients: the $6j$-symbols.

Before evaluating the matrix element (102), we will treat general tensor operators and consider

$$C \equiv \langle \, (j_1'j_2')J'M' \, | \sum_\mu (-1)^\mu T^\lambda_{-\mu} S^\lambda_\mu \, | \, (j_1 j_2)JM \, \rangle. \tag{103}$$

Remember that the scalar operator is diagonal in J and M. The tensor operator T^λ_μ acts on the first subsystem and S^λ_μ on the second. We use Eq. (42) in bra and ket and the Wigner-Eckart theorem [Eq. (68)] to write C,

$$\begin{aligned} C = \sum_{\mu m_1' m_2' m_1 m_2} & (-1)^\mu \langle \, JM \, | \, j_1 m_1; j_2 m_2 \, \rangle \langle \, j_2' m_2' \, | \, \lambda\mu; j_2 m_2 \, \rangle \langle \, j_1' m_1' \, | \, \lambda, -\mu; j_1 m_1 \, \rangle \\ & \times \langle \, j_1' m_1'; j_2' m_2' \, | \, JM \, \rangle \langle \, j_1' \, | \, |T^\lambda| \, | \, j_1 \, \rangle \langle \, j_2' \, | \, |S^\lambda| \, | \, j_2 \, \rangle. \end{aligned} \tag{104}$$

Substitute

$$\langle \, j_2' m_2' \, | \, \lambda\mu; j_2 m_2 \, \rangle = (-1)^{j_2 - j_2' - \mu} \left[\frac{2j_2' + 1}{2j_2 + 1} \right]^{\frac{1}{2}} \langle \, j_2 m_2 \, | \, \lambda, -\mu; j_2' m_2' \, \rangle, \tag{105}$$

and

$$\langle \, j_1' m_1' \, | \, \lambda, -\mu; j_1 m_1 \, \rangle = (-)^{j_1 + \lambda - j_1'} \langle \, j_1 m_1; \lambda, -\mu \, | \, j_1' m_1' \, \rangle \tag{106}$$

then we find, while replacing μ by $-\mu$,

$$\begin{aligned} C = & \left[\frac{2j_2' + 1}{2j_2 + 1} \right]^{\frac{1}{2}} \langle \, j_1' \, | \, |T^\lambda| \, | \, j_1 \, \rangle \langle \, j_2' \, | \, |S^\lambda| \, | \, j_2 \, \rangle (-1)^{j_1 + j_2 - j_2' - j_1' + \lambda} \\ & \times \sum_{\substack{\mu m_1' m_2' \\ m_1 m_2}} \langle \, JM \, | \, j_1 m_1; j_2 m_2 \, \rangle \langle \, j_2 m_2 \, | \, \lambda\mu; j_2' m_2' \, \rangle \langle \, j_1 m_1; \lambda\mu \, | \, j_1' m_1' \, \rangle \langle \, j_1' m_1'; j_2' m_2' \, | \, JM \, \rangle \\ = & (-1)^{j_1 + j_2 - j_2' - j_1' + \lambda} \left[\frac{2j_2' + 1}{2j_2 + 1} \right]^{\frac{1}{2}} \langle \, j_1' \, | \, |T^\lambda| \, | \, j_1 \, \rangle \langle \, j_2' \, | \, |S^\lambda| \, | \, j_2 \, \rangle \\ & \times \langle \, (j_1(\lambda j_2')j_2)J \, | \, ((j_1\lambda)j_1'j_2')J \, \rangle, \end{aligned} \tag{107}$$

where we used Eq. (92) for the recoupling coefficient. Introducing the $6j$-symbol [Eq. (93)] we finally find for the matrix element (103)

$$C = (-1)^{j_2-j_1'-J}\,[(2j_1'+1)(2j_2'+1)]^{\frac{1}{2}}\,\langle\, j_1'\,|\,|T^\lambda|\,|\,j_1\,\rangle\langle\, j_2'\,|\,|S^\lambda|\,|\,j_2\,\rangle \begin{Bmatrix} j_2' & j_1' & J \\ j_1 & j_2 & \lambda \end{Bmatrix}. \tag{108}$$

In the case of atom-diatom scattering we have the tensor operators $T^\lambda_\mu = Y^\lambda_\mu(\theta,\phi)$ and $S^\lambda_\mu = Y^\lambda_\mu(\Theta,\Phi)$, cf. Eq. (99). The reduced matrix elements are given by (84), so that in total Eq. (102) becomes

$$\begin{aligned}\langle\,(l'L')J'\;M'\,|\,\sum_\mu(-1)^\mu Y^\lambda_{-\mu}(\hat{r})\;Y^\lambda_\mu(\hat{R})\,|\,(lL)J\;M\,\rangle &= \delta_{J'J}\delta_{M'M}(-1)^{L-l'-J}\frac{2\lambda+1}{4\pi} \\ &\times[(2l+1)(2L+1)]^{\frac{1}{2}}\langle\,\lambda 0; l0\,|\,l'0\,\rangle\langle\,\lambda 0; L0\,|\,L'0\,\rangle \begin{Bmatrix} L' & l' & J \\ l & L & \lambda \end{Bmatrix}.\end{aligned} \tag{109}$$

The right hand side of this equation is known as a Percival-Seaton coefficient[1].

A. Exercise

13. Prove the spherical expansion of a plane wave:

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = 4\pi\sum_{l=0}^{\infty} i^l j_l(kr)\sum_{m=-l}^{l}(-1)^m Y^l_m(\hat{r})\,Y^l_{-m}(\hat{k}), \tag{110}$$

where $j_l(kr)$ is a spherical Bessel function of the first kind defined by

$$j_l(\rho) \equiv (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{\sin\rho}{\rho}. \tag{111}$$

Hints:
(i) Use that Legendre functions $P_l(x)$ are complete on the interval $(-1,1)$.
(ii) Use that $\int_{-1}^{1} P_{l'}(x)P_l(x)dx = \delta_{ll'}2/(2l+1)$.
(iii) Use the integral representation of the Bessel function:

$$j_l(kr) = \frac{1}{2}i^l\int_0^\pi e^{ikr\cos\theta}P_l(\cos\theta)\sin\theta d\theta. \tag{112}$$

(iv) Use the spherical harmonic addition theorem.

[1]I.C. Percival and M.J. Seaton, Proc. Camb. Phil. Soc. **53**, 654 (1957).

APPENDIX A: EULER'S THEOREM

Basically Euler's theorem states that any rotation is around a certain axis. We will generalize this statement to unitary matrices. Remember from linear algebra that an $n \times n$ matrix $\mathbb{A}$ can be unitarily diagonalized, (has n orthonormal eigenvectors) if and only if it is *normal*, that is, if $\mathbb{A}$ satisfies

$$\mathbb{A}^\dagger \mathbb{A} = \mathbb{A}\mathbb{A}^\dagger. \tag{A1}$$

The most important examples of normal matrices are Hermitian matrices: $\mathbb{A}^\dagger = \mathbb{A}$ and unitary matrices: $\mathbb{A}^\dagger = \mathbb{A}^{-1}$. Recall that a real unitary matrix is usually referred to as 'orthogonal matrix'.

Consider the $n \times n$ unitary or orthogonal matrix $\mathbb{A}$ and its unitary eigenvector matrix $\mathbb{U}$:

$$\mathbb{U}^\dagger \, \mathbb{A} \, \mathbb{U} = \mathbb{D} \;\text{ with }\; \mathbb{D} = \mathrm{diag}(\lambda_1, \ldots, \lambda_n). \tag{A2}$$

Since

$$\mathbb{U}^\dagger \, \mathbb{A} \, \mathbb{U} \left(\mathbb{U}^\dagger \, \mathbb{A} \, \mathbb{U}\right)^\dagger = \mathbb{D} \, \mathbb{D}^\dagger = \mathbb{D} \, \mathbb{D}^* = \mathbb{1}, \tag{A3}$$

we find that $\lambda_i \lambda_i^* = 1$ for $i = 1, \ldots, n$. *All eigenvalues of unitary and orthogonal matrices lie on the unit circle in the complex plane.*

Recall further the fundamental theorem of algebra: a polynomial $P_n(x)$ of degree n in the variable x has n roots z_i. These roots may be real or complex. Suppose that the coefficients of $P_n(x)$ are all real. If z_i is a root, that is $P_n(z_i) = 0$, then obviously $P_n(z_i)^* = P_n(z_i^*) = 0$ and z_i^* is also a root. Thus, the fundamental theorem of algebra has as a corollary that the roots of a polynomial with real coefficients are either real or appear in complex conjugate pairs.

Consider now the secular problem of an orthogonal matrix $\mathbb{O}$: $\det(\mathbb{O} - \lambda \mathbb{1}) = 0$. This equation has n complex roots which, since the elements of $\mathbb{O}$ are real, appear in complex conjugate pairs and lie on the unit circle in the complex plane. Obviously, $\det \mathbb{O} = \prod_i \lambda_i$ is real and hence is ± 1. We find that there are two possibilities for a proper ($\det = +1$) orthogonal matrix:

(i) The dimension n is even, then the eigenvalues 1 are degenerate of even degree and there is no *single* invariant vector. (Since zero is even, zero degeneracy is not excluded and the matrix may not have a unit eigenvalue at all in this case).

(ii) The dimension n is odd, then the eigenvalues 1 are degenerate of odd degree, so there is at least one invariant vector.

If we return to the case $n = 3$ then we see that the eigenvalue 1 of $\mathbb{R}$ either occurs with multiplicity 3, and $\mathbb{R} \equiv \mathbb{1}$, or with multiplicity 1 and then the corresponding eigenvector $\boldsymbol{n}$ is uniquely determined. This proves Euler's theorem.

APPENDIX B: PROOF OF EQUATION (10)

Decompose $\boldsymbol{r}$ into a component parallel to the invariant unit vector $\boldsymbol{n}$ and a component $\boldsymbol{x}_\perp$ perpendicular to it:

$$\boldsymbol{r} = (\boldsymbol{r}\cdot\boldsymbol{n})\,\boldsymbol{n} + \boldsymbol{x}_\perp \quad \text{with} \quad \boldsymbol{x}_\perp = \boldsymbol{r} - (\boldsymbol{r}\cdot\boldsymbol{n})\,\boldsymbol{n}. \tag{B1}$$

The vectors $\boldsymbol{x}_\perp$, $\boldsymbol{y}_\perp \equiv \boldsymbol{n}\times\boldsymbol{r}$, and $\boldsymbol{n}$ form a right-handed frame. The vector $\boldsymbol{n}$ has unit length by definition and the vectors $\boldsymbol{x}_\perp$ and $\boldsymbol{y}_\perp$ both have the length $|\boldsymbol{r}|^2 - (\boldsymbol{n}\cdot\boldsymbol{r})^2$ (which is not necessarily unity). When we rotate $\boldsymbol{r}$ around $\boldsymbol{n}$ its component along $\boldsymbol{n}$ is unaffected and its perpendicular component transforms as

$$\boldsymbol{x}_\perp \rightarrow \cos\psi\boldsymbol{x}_\perp + \sin\psi\boldsymbol{y}_\perp. \tag{B2}$$

Hence,

$$\mathbb{R}(\boldsymbol{n},\psi)\boldsymbol{r} = \cos\psi[\boldsymbol{r} - (\boldsymbol{r}\cdot\boldsymbol{n})\,\boldsymbol{n}] + \sin\psi\,\boldsymbol{n}\times\boldsymbol{r} + (\boldsymbol{r}\cdot\boldsymbol{n})\,\boldsymbol{n}. \tag{B3}$$

We have already seen that

$$\boldsymbol{n}\times\boldsymbol{r} = \mathbb{N}\,\boldsymbol{r}, \tag{B4}$$

where $\mathbb{N}$ is given in Eq. (9). The dyadic product $\boldsymbol{n}\otimes\boldsymbol{n}$ is a matrix with i,j element equal to $n_i n_j$. Evidently,

$$(\boldsymbol{r}\cdot\boldsymbol{n})\,\boldsymbol{n} = \boldsymbol{n}\otimes\boldsymbol{n}\,\boldsymbol{r}. \tag{B5}$$

By direct calculation one shows that

$$\mathbb{N}^2 = \boldsymbol{n}\otimes\boldsymbol{n} - \mathbb{1}. \tag{B6}$$

By substituting (B4), (B5) and (B6) into (B3) we obtain finally

$$\mathbb{R}(\boldsymbol{n},\psi)\boldsymbol{r} = [\mathbb{1} + \sin\psi\mathbb{N} + (1-\cos\psi)\mathbb{N}^2]\boldsymbol{r}, \tag{B7}$$

from which Eq. (10) follows, because $\boldsymbol{r}$ is arbitrary.

APPENDIX C: PROOF OF EQUATION (12)

Let us write the infinitesimally rotated function as follows

$$\tilde{f}(\boldsymbol{r};\Delta\psi) \equiv U(\boldsymbol{n},\Delta\psi)f(\boldsymbol{r}) = f(\boldsymbol{r}'), \tag{C1}$$

where $\boldsymbol{r}' \equiv \mathbb{R}(\boldsymbol{n},\Delta\psi)^{-1}\boldsymbol{r}$. Since $\Delta\psi$ is infinitesimal, $\tilde{f}(\boldsymbol{r};\Delta\psi)$ can be written in the following two-term Taylor series

$$\tilde{f}(\boldsymbol{r};\Delta\psi) = \tilde{f}(\boldsymbol{r};0) + \Delta\psi\left(\frac{d\tilde{f}(\boldsymbol{r};\psi)}{d\psi}\right)_{\psi=0}. \tag{C2}$$

Because of (C1) we have $\tilde{f}(\boldsymbol{r};0) = f(\boldsymbol{r})$. In order to evaluate the derivative in Eq. (C2) we apply the chain rule to the rightmost term of Eq. (C1)

$$\left(\frac{d\tilde{f}(\boldsymbol{r};\psi)}{d\psi}\right)_{\psi=0} = \left(\frac{df(\boldsymbol{r}')}{d\psi}\right)_{\psi=0} = \sum_i \left(\frac{\partial f}{\partial r'_i}\right)_{\psi=0} \left(\frac{dr'_i}{d\psi}\right)_{\psi=0}. \tag{C3}$$

Obviously, $(\partial f/\partial r'_i)_{\psi=0} = \partial f/\partial r_i$. Using Eq. (10) we find

$$\left(\frac{d\boldsymbol{r}'}{d\psi}\right)_{\psi=0} = \left(\frac{d\,\mathbb{R}(\boldsymbol{n},\psi)^{-1}}{d\psi}\right)_{\psi=0} \boldsymbol{r} = -\mathbb{N}\,\boldsymbol{r}. \tag{C4}$$

Invoking Eq. (9), we now find

$$\left(\frac{d\tilde{f}(\boldsymbol{r};\psi)}{d\psi}\right)_{\psi=0} = -\sum_{ij} N_{ij} r_j \frac{\partial f}{\partial r_i} = \sum_{ijk} \epsilon_{ijk} n_k r_j \frac{\partial}{\partial r_i} f(\boldsymbol{r}). \tag{C5}$$

Because of Eq. (2) this equation can be rewritten in terms of the l_k,

$$\left(\frac{d\tilde{f}(\boldsymbol{r};\psi)}{d\psi}\right)_{\psi=0} = -i \sum_k n_k l_k f(\boldsymbol{r}), \tag{C6}$$

and substitution of this result into (C2) finally gives

$$\tilde{f}(\boldsymbol{r};\Delta\psi) = f(\boldsymbol{r}) - i\Delta\psi\, \boldsymbol{n}\cdot\boldsymbol{l} f(\boldsymbol{r}), \tag{C7}$$

which is the required result.

APPENDIX D: PROOF OF THE TRIANGULAR CONDITION

We shall show that

$$|j_1 - j_2| \leq J \leq j_1 + j_2. \tag{D1}$$

As stated in the main text, the $(2j_1+1)(2j_2+1)$ dimensional product space $V^{j_1} \otimes V^{j_2}$ spanned by $|\, j_1, m_1; j_2, m_2\,\rangle$, ($m_1 = -j_1, \ldots, j_1$, and $m_2 = -j_2, \ldots, j_2$), is invariant under J^2 and J_3. This means that both operators can be diagonalized simultaneously on this space. Product kets are automatically eigenkets of J_3 with eigenvalue $M = m_1 + m_2$, so that it suffices to diagonalize J^2 on the eigensubspaces of J_3 contained in $V^{j_1} \otimes V^{j_2}$. We will discuss how, in principle, bases of the eigenspaces of J^2 can be constructed.

In order to see which subspaces occur we consider Fig. 2, where we give an example for $j_1 = 3$ and $j_2 = 2$.

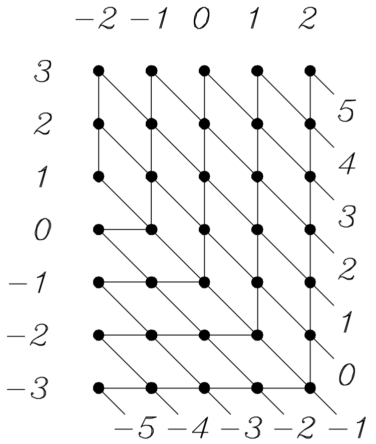


Fig. 2

Schematic representation of the basis of the product space with $j_1 = 3$ and $j_2 = 2$. Each dot represents a product ket $|\,3, m_1; 2, m_2\,\rangle$. The quantum numbers m_1 and m_2 are given on the lefthand side and on the top of the diagram, respectively. On the righthand side and at the bottom of the diagram we find $M = m_1 + m_2$.

The hooks represent eigenspaces of J^2, see text for details.

Evidently, there is only one product ket $|\,j_1, j_1; j_2, j_2\,\rangle$ of maximum M, $M_{\mathrm{max}} = j_1 + j_2$, i.e., this eigenspace of J_3 is one dimensional and the eigenproblem of J^2 on this space is also one-dimensional. In other words, $|\,j_1, j_1; j_2, j_2\,\rangle$ is automatically an eigenvector of J^2. In Fig. 2 this is the ket in the upper righthand corner with $M_{\mathrm{max}} = 5$. Acting with $J_+ \equiv j_+(1) + j_+(2)$ onto this ket, we generate zero, and hence $|\,j_1, j_1; j_2, j_2\,\rangle$ is indeed an upper rung. The J quantum number of a ladder being equal to its highest M quantum number, this ladder is characterized by the quantum number $J = M_{\mathrm{max}} = j_1 + j_2$, [i.e., all rungs are eigenkets of J^2 with eigenvalue $(j_1 + j_2)(j_1 + j_2 + 1)$]. The lower rungs may be generated by repeated action of J_-.

In Fig. 2 we see that the second highest eigenvalue of J_3 ($M = 4$) occurs twice, so that the corresponding eigenproblem of J^2 is of dimension two. However, we already found one eigenvector, namely $|\,j_1 + j_2, j_1 + j_2 - 1\,\rangle \equiv J_-|\,j_1 + j_2, j_1 + j_2\,\rangle$, so that a diagonalization of J^2 is unnecessary. (Notice parenthetically that we use the notation $|\,JM\,\rangle$ for the coupled ket, suppressing j_1 and j_2). We only have to find a ket in the two-dimensional space that is orthogonal to $|\,j_1 + j_2, j_1 + j_2 - 1\,\rangle$; this will be an eigenfunction of J^2.

It is easy to see that this orthogonalized function will again be the highest M state of a ladder of eigenkets of J^2. Indeed, write briefly $|\,\psi\,\rangle = |\,j_1 + j_2, j_1 + j_2 - 1\,\rangle$ and the orthogonalized function as $|\,\phi\,\rangle$, then action of J_+ onto $|\,\phi\,\rangle$ must give an eigenfunction of J_3 with eigenvalue M_{max}, i.e., a function proportional to $J_+|\,\psi\,\rangle$, or zero. The former case is excluded because

$$\langle\, J_+\phi \,|\, J_+\psi \,\rangle = \langle\, \phi \,|\, J_-J_+ \,|\, \psi \,\rangle = \langle\, \phi \,|\, J^2 - J_3(J_3 + 1) \,|\, \psi \,\rangle = 0, \tag{D2}$$

which follows from $|\,\psi\,\rangle$ being an eigenfunction of J^2 and J_3, together with the orthogonality $\langle\, \phi \,|\, \psi \,\rangle = 0$. Hence $J_+|\,\phi\,\rangle = 0$ does not have a non-zero component along $J_+|\,\psi\,\rangle$. The highest rung $|\,\phi\,\rangle$ having $M = j_1 + j_2 - 1$, the whole ladder generated by acting with J_- is characterized by $J = j_1 + j_2 - 1$. Since the eigenspace of J_3 with $M_{\mathrm{max}} - 1$ is two-dimensional, the eigenvalue $j_1 + j_2 - 1$ occurs only once in the product space.

The third highest eigenspace of J_3 ($M = 3$ in the example) is of dimension three. In this space we already found two eigenvectors of J^2 by the laddering technique. Orthogonalizing an arbitrary product ket in this space onto both these functions, we will find another eigenfunction of J^2. It is easily shown that this function is the highest rung of a ladder with $J = M_{\mathrm{max}} - 2$, so that this quantum number also occurs once only.

We may continue this way and thus prove the triangular conditions. Graphically we may easily convince ourselves that these relations hold by reinterpreting the dots in Fig. 2. The number of product kets is the same as the number coupled states (eigenstates of J^2 and J_3),

$$\dim(V^{j_1} \otimes V^{j_2}) = (2j_1+1)(2j_2+1) = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} 1 = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} 1 = \sum_{J=|j_1-j_2|}^{j_1+j_2} (2J+1). \tag{D3}$$

[This equation is easily proved by realizing that $\sum_J (2J+1)$ is the sum of an arithmetic series and by using the well-known sum formula for such a series]. Thus, we may let a dot stand for a coupled state, for instance the dot with coordinates $m_1 = 2, m_2 = 2$, will represent the coupled state $J_-|\,3,3;2,2\,\rangle \equiv |\,5,4\,\rangle$ and the dot with $m_1 = 3, m_2 = 1$ the state $|\,4,4\,\rangle$ orthogonal to it. Repeatedly acting with J_- onto the highest M ket we generate the border of the diagram, i.e., a hook consisting of the rightmost column and the bottom row. Acting with J_- onto coupled state with coordinates $m_1 = 3, m_2 = 1$ we again generate a hook: the ladder with $J = j_1 + j_2 - 1$, and so on. Only the last eigenvalue $J = |j_1 - j_2| = 1$ is not a hook, but the topmost part of the leftmost column. Alternatively, one can look now at equation (D3) as a change of summation variables. The sum over m_1 and m_2 covers the grid of Fig. 2 row after row, whereas the sum over J runs over the hooks and the sum over M is within hook J. The latter double sum also covers the grid exactly once.

APPENDIX E: CLEBSCH-GORDAN COEFFICIENTS

The expression below for the CG-coefficients, due to Van der Waerden[1] is the most symmetric one of the various existing forms. Since its derivation is highly non-trivial, it will not be presented.

$$\begin{aligned} \langle\, jm\,|\,j_1m_1; j_2m_2\,\rangle &= \delta_{m,m_1+m_2}\Delta(j_1,j_2,j) \qquad\qquad (\mathrm{E1})\\ &\times \sum_t (-1)^t \quad \frac{[(2j+1)(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!]^{\frac{1}{2}}}{t!(j_1+j_2-j-t)!(j_1-m_1-t)!(j_2+m_2-t)!}\\ &\qquad \times \frac{1}{(j-j_2+m_1+t)!(j-j_1-m_2+t)!}, \end{aligned}$$

where

$$\Delta(j_1,j_2,j) = \left[\frac{(j_1+j_2-j)!(j_1-j_2+j)!(-j_1+j_2+j)!}{(j_1+j_2+j+1)!}\right]^{\frac{1}{2}}, \tag{E2}$$

and the sum runs over all values of t which do not lead to negative factorials. This expression and all relations in this appendix are valid for integer and half-integer indices.

This expression immediately implies that the CG-coefficients satisfy the following symmetry properties

[1] B.L. van der Waerden, *Die Gruppentheoretische Methode in der Quantenmechanik*, Springer, Berlin (1932).

1. $\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle = \langle\, j_1m_1; j_2m_2 \,|\, jm \,\rangle,$

2. $\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle = (-1)^{j_1+j_2-j}\langle\, j, -m \,|\, j_1, -m_1; j_2, -m_2 \,\rangle,$

3. $\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle = (-1)^{j_1+j_2-j}\langle\, jm \,|\, j_2m_2; j_1m_1 \,\rangle,$

4. $\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle = \left[\dfrac{(2j+1)}{(2j_2+1)}\right]^{\frac{1}{2}} \langle\, j_2m_2 \,|\, jm; \vartheta(j_1m_1) \,\rangle,$

   where the time-reversal operator ϑ acts as follows:

   $$|\, \vartheta(j_1m_1) \,\rangle \equiv \vartheta|\, j_1m_1 \,\rangle = (-1)^{j_1-m_1}|\, j_1, -m_1 \,\rangle.$$

5. For the special case when $j = m = 0$ the CG-coefficients are equal to

   $$\langle\, 0\,0 \,|\, j_1m_1; j_2m_2 \,\rangle = \delta_{j_1j_2}\delta_{m_1,-m_2}\, (-1)^{j_1-m_1}\, (2j_1+1)^{-\frac{1}{2}}.$$

Proof:

1. The CG-coefficients are defined as an inner product; their explicit form shows that they are real. Hence

   $$\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle = \langle\, j_1m_1; j_2m_2 \,|\, jm \,\rangle^* = \langle\, j_1m_1; j_2m_2 \,|\, jm \,\rangle.$$

2. From the unitarity of the time reversal operator ϑ and the realness of CG-coefficients follows that

   $$\begin{aligned}\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle &= \langle\, jm \,|\vartheta^\dagger\vartheta|\, j_1m_1; j_2m_2 \,\rangle = \langle\, \vartheta(jm) \,|\, \vartheta(j_1m_1); \vartheta(j_2m_2) \,\rangle \\ &= (-1)^{j+j_1+j_2}(-1)^{-(m+m_1+m_2)}\langle\, j, -m \,|\, j_1, -m_1; j_2, -m_2 \,\rangle. \end{aligned} \tag{E3}$$

   Since $m = m_1 + m_2$ and m is a half-integer if and only if j is a half-integer, we find that

   $$(-1)^{-(m+m_1+m_2)} = (-1)^{-2m} = (-1)^{-2j}.$$

3. The explicit form for CG-coefficients, (E1), is invariant with respect to a simultaneous interchange $j_1 \leftrightarrow j_2$ and $m_1 \leftrightarrow -m_2$, which implies that $m = m_1 + m_2 \to -m$ and thus

   $$\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle = \langle\, j, -m \,|\, j_2, -m_2; j_1, -m_1 \,\rangle = (-1)^{j_1+j_2-j}\langle\, jm \,|\, j_2m_2; j_1m_1 \,\rangle. \tag{E4}$$

4. Make simultaneous replacements $j \leftrightarrow j_2$ and $m \leftrightarrow -m_2$ in the explicit expression for CG-coefficients, Eq. (E1), and change the summation variable t to $j_1 - m_1 - t$. Observe that except for the first factor $(2j+1)^{\frac{1}{2}}$ and the phase $(-1)^t$ they leave the expression (E1) invariant. Thus

$$
\begin{aligned}
\langle\, jm \,|\, j_1m_1; j_2m_2 \,\rangle &= \left[\frac{(2j+1)}{(2j_2+1)}\right]^{\frac{1}{2}} (-1)^{j_1-m_1}\langle\, j_2, -m_2 \,|\, j_1m_1; j, -m \,\rangle \\
&= \left[\frac{(2j+1)}{(2j_2+1)}\right]^{\frac{1}{2}} (-1)^{j_1-m_1}\langle\, j_2m_2 \,|\, jm; j_1, -m_1 \,\rangle \\
&= \left[\frac{(2j+1)}{(2j_2+1)}\right]^{\frac{1}{2}} \langle\, j_2m_2 \,|\, jm; \vartheta(j_1m_1) \,\rangle. \qquad \text{(E5)}
\end{aligned}
$$

5. Follows by applying the previous rule to the identity

$$\langle\, j_1m_1 \,|\, j_2m_2; 00 \,\rangle = \delta_{j_1j_2}\, \delta_{m_1m_2}.$$

APPENDIX F: THE 6J-SYMBOL

The following relation is due to Racah:

$$
\begin{aligned}
\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_1' & j_2' & j_3' \end{Bmatrix} &= \Delta(j_1j_2j_3)\Delta(j_1j_2'j_3')\Delta(j_1'j_2j_3')\Delta(j_1'j_2'j_3) \sum_t (-1)^t (t+1)! \\
&\times\Big[(t-j_1-j_2-j_3)!(t-j_1-j_2'-j_3')!(t-j_1'-j_2-j_3')! \\
&\times(t-j_1'-j_2'-j_3)!(j_1+j_2+j_1'+j_2'-t)! \\
&\times(j_1+j_3+j_1'+j_3'-t)!(j_2+j_3+j_2'+j_3'-t)!\Big]^{-1}, \qquad \text{(F1)}
\end{aligned}
$$

where $\Delta(abc)$ is defined in Eq. (E2). The sum over t is restricted by the requirement that the factorials occurring in (F1) are non-negative.

APPENDIX G: FURTHER READING

The first (1931) book on the subject is still highly recommendable: E. Wigner, *loc. cit.*. It gives also an introduction to group and representation theory.

Around 1960 the following books appeared, several of which saw new editions in the meantime :

1. A.R. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton U.P., Princeton, N.J. (1957). A good introduction, but errs on the distinction between active and passive rotations.

2. M.E. Rose, *Elementary Theory of Angular Momentum*, Wiley, New York, 1957. Does not follow Wigner's convention, Eq. (11), but has an antihomomorphic definition.

3. U. Fano and G. Racah, *Irreducible Tensorial Sets*, Academic, New York, (1959). G. Racah, together with E. Wigner, created the subject. Short readable book with emphasis on the distinction between standard and contrastandard sets, (also known as co- and contravariant tensors).

4. D.M. Brink and G.R. Satchler, *Angular Momentum*, Oxford U.P. London, 1962. A concise short work, very nice as a reference once one understands the material. Has also a chapter on Jucys diagrams.

5. A.P. Jucys, I.B. Levinson, and V.V. Vanagas, *Mathematical Apparatus of the Theory of Angular Momentum*. Translated from the Russian by A. Sen and A.R. Sen, Israel Program for Scientific Translations, Jerusalem, (1962). Jucys was a Lithuanian and did not spell his name in Cyrillic characters, nevertheless his name is often transcribed as Yutsis. This book is noteworthy for (i) introduction of angular momentum diagrams, which are inspired by, but not the same as, Feynman/Goldstone/Hugenholtz diagrams. And (ii) discussion of high $3n$-j symbols (recoupling coefficients).

6. L.C. Biedenharn and H. van Dam, *Quantum Theory of Angular Momentum*, Academic, New York (1965). A collection of reprints, with the most important ones being the beautiful 1940 paper by Wigner on the representations of simply reducible groups and the 1953 paper by J. Schwinger, in which he introduces into group theory boson creation and annihilation operators as a computational tool. Both papers are otherwise unpublished.

In 1981 the definitive book on the subject appeared: L.C. Biedenharn and J.D. Louck *Angular Momentum in Quantum Physics*, Addison-Wesley, Reading, (1981). This is a very complete and authoritative work, not very easy, but worth studying carefully. Since it is so complete, it is easy to overlook some of the basic material in it, such as the Wigner-Eckart theorem for coupled tensor operators, etc.

A reference work is D.A. Varshalovich, A.N. Moskalev, and V.K. Khershonskii, *Quantum Theory of Angular Momentum*, translated from the Russian, World Scientific, Singapore (1988). This book has no text, only 508 pages of formulas, all pertaining to angular momentum theory. Be careful, though, we did find some errors.

Also the book by Zare must be mentioned, R.N. Zare, *Angular Momentum*, Wiley, New York (1988), since it is very popular among beginners. However, at some places the presentation is wrong. Consider Eqs. (1.67) and (3.58), which give for instance for $J = 1$ and $M = 0$ the erroneous result $|\,1,0\,\rangle = \alpha\beta$. In contrast, the spinfunctions on p. 114 correctly read $|\,1,0\,\rangle = \big(\alpha(1)\beta(2) + \beta(1)\alpha(2)\big)/\sqrt{2}$. Equations (1.67) and (3.58) are correct only for commuting variables, such as complex numbers or boson second-quantized operators; one-electron spinfunctions do not belong to this class.

Finally, it must be pointed out that A. Messiah, *Quantum Mechanics*, Vol. II, North Holland, Amsterdam, (1965) has a very good introduction in Chapter XIII and a good summary in Appendix C. All sorts of arbitrary conventions enter the quantum theory of angular momentum, but if you follow Messiah on this you cannot go wrong.