Angular momentum theory and applications

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1999. These notes are available from:
The lecture notes of another course on angular momentum, by Paul E. S. Wormer, are also on the web:
http://www.theochem.ru.nl/~pwormer
(Teaching material, Angular momentum theory). In those notes you can
find some recommendations for further reading.

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I. ROTATIONS

Angular momentum theory is the theory of rotations. We discuss the rotation of vectors in $\mathbb{R}^3$, wave functions, and
linear operators. These objects are elements of linear spaces. In angular momentum theory it is sufficient to consider
finite dimensional spaces only.

- Rotations $\hat{R}$ are linear operators acting on an $n$-dimensional linear space $\mathcal{V}$, i.e.,
  \[ \hat{R}(\vec{x} + \vec{y}) = \hat{R}\vec{x} + \hat{R}\vec{y}, \quad \hat{R}\lambda\vec{x} = \lambda\hat{R}\vec{x} \text{ for all } \vec{x}, \vec{y} \in \mathcal{V}. \]
We introduce an orthonormal basis \( \{ \vec{e}_1, \vec{e}_2, \ldots, \vec{e}_n \} \) so that we have
\[
(\vec{e}_i, \vec{e}_j) = \delta_{ij}, \quad \vec{x} = \sum_i x_i \vec{e}_i, \quad x_i = (\vec{e}_i, \vec{x}).
\] (2)
We define the column vector \( \mathbf{x} = (x_1, x_2, \ldots, x_n)^T \), so that
\[
\vec{y} = \hat{R} \vec{x}, \quad y_i = \sum_j R_{ij} x_j, \quad R_{ij} = (\vec{e}_i, \hat{R} \vec{e}_j), \quad \mathbf{y} = R \mathbf{x}.
\] (3)

Unless otherwise specified we will work in the standard basis \( \{ \mathbf{e}_i \} \). The multiplication of linear operators is associative, thus for three rotations we have \( (R_1 R_2) R_3 = R_1 (R_2 R_3) \).

- Rotations form a group:
  - The product of two rotations is again a rotation, \( R_1 R_2 = R_3 \).
  - There is one identity element \( R = I \).
  - For every rotation \( R \) there is an inverse \( R^{-1} \) such that \( R R^{-1} = R^{-1} R = I \).

- The rotation group is a three (real) parameter continuous group. This means that every element can be labeled by three parameters \( (\omega_1, \omega_2, \omega_3) \). Furthermore, if \( R(\omega_1) = R(\omega_2) R(\omega_3) \) (4)
  we can express the parameters \( \omega_1 \) as analytic functions of \( \omega_2 \) and \( \omega_3 \). This means that we are allowed to take derivatives with respect to the parameters, which is the mathematical way of saying that there is such a thing as a "small rotation". The choice of parameters is not unique for a given group.

- Rotations are unitary operators
  \[
  (R \mathbf{x}, R \mathbf{y}) = (\mathbf{x}, \mathbf{y}), \quad \text{for all } \mathbf{x} \text{ and } \mathbf{y}.
  \] (5)
  The adjoint or Hermitian conjugate \( A^\dagger \) of a linear operator \( A \) is defined by
  \[
  (A \mathbf{x}, \mathbf{y}) = (\mathbf{x}, A^\dagger \mathbf{y}), \quad \text{for all } \mathbf{x} \text{ and } \mathbf{y}.
  \] (6)
  For the matrix elements of \( A^\dagger \) we have
  \[
  (A^\dagger)_{ij} = A^*_{ji}.
  \] (7)
  Hence, for a rotation matrix we have
  \[
  (R \mathbf{x}, R \mathbf{y}) = (\mathbf{x}, R^\dagger R \mathbf{y}) = (\mathbf{x}, \mathbf{y}),
  \] (8)
i.e., \( R^\dagger R = I \), and \( R^\dagger = R^{-1} \). For the determinant we find
  \[
  \det(R^\dagger R) = \det(R) \star \det(R) = \det(I) = 1, \quad |\det(R)| = 1.
  \] (9)
  By definition rotations have a determinant of +1.

- In \( \mathbb{R}^3 \) there is exactly one such group with the above properties and it is called \( SO(3) \), the special (determinant is +1) orthogonal group of \( \mathbb{R}^3 \). In \( \mathbb{C}^2 \) (two-dimensional complex space) there is also such a group called \( SU(2) \), the special (again since the determinant is +1) unitary group of \( \mathbb{C}^2 \). There is a 2:1 mapping between \( SU(2) \) and \( SO(3) \). The group \( SU(2) \) is required to treat half-integer spin.

A. Small rotations in \( SO(3) \)

By convention let the parameters of the identity element be zero. Consider changing one of the parameters \( (\phi \in \mathcal{R}) \). Since \( R(0) = I \) we can always write
\[
R(\epsilon) = I + \epsilon N.
\] (10)
Since \( R^\dagger R = I \) we have
\[
(I + \epsilon N)^\dagger(I + \epsilon N) = I + \epsilon(N^\dagger + N) + \epsilon^2 N^\dagger N = I,
\]
(11)
thus, for small \( \epsilon \)
\[
N^\dagger + N = 0, \quad N^\dagger = -N.
\]
(12)
The matrix \( N \) is said to be antihermitian, \( N_{ij}^* = -N_{ji} \). In \( \mathbb{R}^3 \) we may write
\[
N = \begin{bmatrix}
0 & -n_3 & n_2 \\
-n_3 & 0 & -n_1 \\
-n_2 & n_1 & 0
\end{bmatrix}.
\]
(13)
The signs of the parameters are of course arbitrary, but with the above choice we have
\[
N_x = \begin{bmatrix}
n_2 x_3 - n_3 x_2 \\
n_3 x_1 - n_1 x_3 \\
n_1 x_2 - n_2 x_1
\end{bmatrix} = \mathbf{n} \times \mathbf{x}.
\]
(14)
For small rotations we thus have
\[
\mathbf{x}' = R(\mathbf{n}, \epsilon)\mathbf{x} = \mathbf{x} + \mathbf{\epsilon} \mathbf{n} \times \mathbf{x}.
\]
(15)
Clearly, the vector \( \mathbf{n} \) is invariant under this rotation
\[
R(\mathbf{n}, \epsilon)\mathbf{n} = \mathbf{n} + \epsilon \mathbf{n} \times \mathbf{n} = \mathbf{n}.
\]
(16)
For the product of two small rotations around the same vector \( \mathbf{n} \) we have
\[
R(\mathbf{n}, \epsilon_1)R(\mathbf{n}, \epsilon_2) = (I + \epsilon_1 N)(I + \epsilon_2 N) = I + (\epsilon_1 + \epsilon_2)N + \epsilon_1 \epsilon_2 N^2 \approx R(\mathbf{n}, \epsilon_1 + \epsilon_2).
\]
(17)
(18)
(19)
We now define non-infinitesimal rotations by requiring for arbitrary \( \phi_1 \) and \( \phi_2 \) that
\[
R(\mathbf{n}, \phi_1)R(\mathbf{n}, \phi_2) = R(\mathbf{n}, \phi_1 + \phi_2).
\]
(20)
We may now proceed in two ways to obtain an explicit formula for \( R(\mathbf{n}, \phi) \). First, we may observe that “many small rotations give a big one”:
\[
R(\mathbf{n}, \phi) = R(\mathbf{n}, \phi/k)^k.
\]
(21)
By taking the limit for \( k \to \infty \) and using the explicit expression for an infinitesimal rotation we get (see also Appendix A)
\[
R(\mathbf{n}, \phi) = \lim_{k \to \infty} (I + \frac{\phi}{k} N)^k = \sum_{k=0}^{\infty} \frac{1}{k!} (\phi N)^k = e^{\phi N}.
\]
(22)
Note that a function of a matrix is defined by its series expansion.
Alternatively we may start from eq. (20) and take the derivative with respect to \( \phi_1 \) at \( \phi_1 = 0 \) to obtain the differential equation
\[
\frac{d}{d\phi_1} R(\mathbf{n}, \phi_1)|_{\phi_1=0} R(\mathbf{n}, \phi_2) = \frac{d}{d\phi_1} R(\mathbf{n}, \phi_1 + \phi_2)|_{\phi_1=0} = \frac{d}{d\phi_2} R(\mathbf{n}, \phi_2),
\]
(23)
with \( \frac{d}{d\phi_1} R(\mathbf{n}, \phi_1) = N \) this gives
\[
\frac{d}{d\phi} R(\mathbf{n}, \phi) = NR(\mathbf{n}, \phi).
\]
(24)
Solving this equation with the initial condition \( R(\mathbf{n}, 0) = I \) again gives \( R(\mathbf{n}, \phi) = e^{\phi N} \).
B. Computing $e^{i\phi N}$

This problem is similar to solving the time-dependent Schrödinger equation, but it involves an antihermitian, rather than an Hermitian matrix. Therefore, we define the matrix $L_n = iN$, which is easily verified to be Hermitian

$$L^\dagger = (iN)^\dagger = -i(-N) = L. \quad (25)$$

Thus, we have

$$R(n, \phi) = e^{-i\phi L}. \quad (26)$$

The general procedure for computing functions of Hermitian matrices starts with computing the eigenvalues and eigenvectors

$$Lu_i = \lambda_i u_i. \quad (27)$$

This may be written in matrix notation

$$LU = U\Lambda, \ U = [u_1 \ldots u_n], \ \Lambda_{ij} = \lambda_i \delta_{ij}. \quad (28)$$

For Hermitian matrices the eigenvalues are real and the eigenvectors may be orthonormalized so that $U$ is unitary and we have

$$L = U\Lambda U^\dagger. \quad (29)$$

If a function $f$ is defined by its series expansion

$$f(x) = \sum_k f_k x^k \quad (30)$$

we have

$$f(L) = \sum_k f_k L^k = \sum_k f_k (U\Lambda U^\dagger)^k = \sum_k f_k U\Lambda^k U^\dagger = U (\sum_k f_k \Lambda^k) U^\dagger = U f(\Lambda) U^\dagger. \quad (31)$$

For the diagonal matrix $\Lambda$ we simply have

$$[f(\Lambda)]_{ij} = \sum_k f_k (\lambda_i \delta_{ij})^k = \sum_k f_k \lambda_i^k \delta_{ij} = f(\lambda_i) \delta_{ij}. \quad (32)$$

Thus after computing the eigenvectors $u_i$ and eigenvalues $\lambda_i$ of $L$ we have

$$R(n, \phi)x = e^{-i\phi L}x = U e^{-i\phi \Lambda}U^\dagger x = \sum_k e^{-i\phi \lambda_k} u_k (u_k, x). \quad (33)$$

Note that the eigenvalues of $R(n, \phi)$ are $e^{-i\phi \lambda_k}$. Since the $\lambda_k$’s are real, these (three) eigenvalues lie on the unit circle in the complex plane. Clearly, this must hold for any unitary matrix, since for any eigenvector $u$ of some unitary matrix $U$ with eigenvalue $\lambda$ we have

$$(Uu, Uu) = (\lambda u, \lambda u) = \lambda^* \lambda (u, u) = (u, u), \ \text{i.e., } |\lambda| = 1.. \quad (34)$$

Note that $R(n, \phi)n = n$. This does not yet prove that any $R$ can be generated by an infinitesimal rotation. Since $R$ is real for every complex eigenvalue $\lambda$ there must be an eigenvalue $\lambda^*$. The three eigenvalues lie on the unit circle in the complex plane and their product is equal to the determinant (+1), therefore $R$ must have at least one eigenvalue equal to 1. In this way, one can prove that any rotation is a rotation around some axis $n$.

C. Adding the series expansion

As an alternative approach we may start from

$$e^{i\phi N} = \sum_{k=0}^\infty \frac{1}{k!} (\phi N)^k. \quad (35)$$
From Eq. (27) it follows that
\[ N \mathbf{u}_k = -i\lambda_k \mathbf{u}_k \equiv \alpha_k \mathbf{u}_k. \] (36)

For the present discussion we will not actually need the eigenvectors and eigenvalues, we will only use the fact that they exist. We define the matrix \( A(N) \)
\[ A(N) = (N - \alpha_1 I)(N - \alpha_2 I)(N - \alpha_3 I). \] (37)

It is easily verified that for any eigenvector \( \mathbf{u}_k \) we have
\[ A(N) \mathbf{u}_k = 0. \] (38)

Since any vector may be written as a linear combination of the eigenvectors \( \mathbf{u}_k \) we actually know that \( A(N) = 0_{3 \times 3} \), the zero matrix in \( \mathbb{R}^3 \). Thus, the polynomial \( A(N) \) is referred to as a annihilating polynomial. Expanding \( A(N) \) gives
\[ A(N) = N^3 + c_2 N^2 + c_1 N + c_0 I = 0, \] (39)

where the coefficients \( c_k \) can easily be expressed as functions of the eigenvalues \( \alpha_k \). We now observe that \( N^3 \) may be expressed as a linear combination of lower powers of \( N \):
\[ N^3 = -c_2 N^2 - c_1 N - c_0 I. \] (40)

From this equation we may directly compute the coefficients \( c_k \), without knowing the eigenvalues \( \alpha_k \). By direct multiplication we construct the matrices \( N^k, k = 2, 3 \). By putting the matrix elements of these matrices in column vectors of length \( 3 \times 3 = 9 \) we can turn the matrix equation into a set of 9 equations with 3 unknowns \( c_k, k = 0, 1, 2 \).

It may be of interest to know that this procedure is quite general: for a completely arbitrary \( n \times n \) matrix \( A \) in \( \mathbb{C}^n \) there exist an annihilating polynomial of degree \( n \). It can always be found by plugging the matrix \( A \) back into the characteristic polynomial \( P(\lambda) \equiv \det(A - \lambda I) \). In this case we have (see Appendix A)
\[ N^3 = -N. \] (41)

so that
\[ N^{2k+1} = (-1)^k N \text{ for } k \geq 0 \] (42)
\[ N^{2k+2} = (-1)^k N^2 \text{ for } k \geq 1. \] (43)

As a consequence, the infinite sum simplifies to
\[ e^{\phi N} = I + \sum_{k=1}^{\infty} \frac{1}{k!} \phi^k N^k = I + \sin \phi N + (1 - \cos \phi)N^2. \] (44)

D. Basis transformations of vectors and operators

We will refer to the basis \( \{ \mathbf{e}_k \} \) used so far as the space fixed basis. We now introduce a new orthonormal basis \( \{ \mathbf{b} \} \) which we will refer to as the body fixed basis. These names are chosen with a typical application in a quantum mechanical problem in mind. If the body fixed coordinates are indicated with a prime we have
\[ \sum_k \mathbf{e}_k x_k = \sum_k \mathbf{b}_k x'_{k}, \quad \mathbf{x} = B \mathbf{x}'. \] (45)

Let a linear operator \( \hat{A} \) be represented by the matrix \( A \) in the space fixed basis. We now define a transformed or rotated operator \( \hat{A}' \), which is represented by the matrix \( A' \) in space fixed coordinates, by the requirement that it is represented by the matrix \( A \) when expressed in body fixed coordinates:
\[ (\mathbf{b}_i, A' \mathbf{b}_j) = A_{ij}, \quad B^T A' B = A. \] (46)

Using the unitarity of \( B \) we get
\[ A' = BAB^T. \] (47)
Using this definition we may also transform any function of $A$ defined by its series expansion

$$f(A) = Bf(A)B^\dagger = B(\sum_k f_k A^k)B^\dagger = \sum_k f_k (BA^k B^\dagger) = \sum_k f_k (A')^k = f(A').$$

(48)

As an example we consider the transformation of a rotation operator

$$R' = BR(n, \phi)B^\dagger = Be^{\phi N}B^\dagger = e^{\phi BN B^\dagger}.$$  

(49)

We work out the exponent by considering

$$BN B^\dagger x = B(n \times B^\dagger x)$$

(50)

For an arbitrary unitary transformation of a cross product we have the rule (see Appendix A)

$$U x \times U y = \det(U) U(x \times y)$$

(51)

so that we have

$$B(n \times B^\dagger x) = (Bn) \times (BB^\dagger x) = (Bn) \times x \equiv N_B n x$$

(52)

Thus, with the notation $N_B n x = N_B n$,

$$BN_B B^\dagger = N_B n$$

(53)

and for the transformed rotation

$$BR(n, \phi)B^\dagger = e^{\phi BN_B B^\dagger} = R(Bn, \phi).$$

(54)

### E. Vector operators

Define the three matrices $N_i \equiv N_{e_i}$. The matrix $N$ can now be expressed as a linear combination of these matrices

$$N = \begin{bmatrix} 0 & -n_3 & n_2 \\ n_3 & 0 & -n_1 \\ -n_2 & n_1 & 0 \end{bmatrix} = n_1 \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} + n_2 \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix} + n_3 \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(55)

where we introduced the vector operator $N$. The components of the vector operator transform as

$$BN_j B^\dagger = BN_{e_j} B^\dagger = N_{Be_j} = N_{b_j} = b_j \cdot N = \sum_i N_i B_{ij}.$$  

(57)

We also define the Hermitian vector operator $L = iN$ for which we also have

$$BL_j B^\dagger = \sum_i L_i B_{ij}$$

(58)

Since $B$ is an arbitrary orthonormal matrix we may take $B = R(n, \phi) = e^{-i \phi n L}$ which gives

$$e^{-i \phi n L} L_j e^{i \phi n L} = \sum_i L_i R_{ij}(n, \phi)$$

(59)

For two operators $A$ and $B$ we have a relation which is sometimes referred to as the Baker-Campbell-Hausdorff form (appendix A)

$$e^A Be^{-A} = \sum_{k=0}^{\infty} \frac{1}{k!} [A, B]_k,$$

(60)
where the repeated commutator $[A, B]_k$ is defined by
\begin{align}
[A, B]_0 &= B \\
[A, B]_1 &= [A, B] = AB - BA \\
[A, B]_k &= [A, [A, B]_{k-1}].
\end{align}
(61) (62)

The importance of this relation is that the (repeated) commutation relations fully define the exponential form. Hence, from Eq. (59) we find for arbitrary angular momentum operators
\begin{align}
\hat{R}(\mathbf{n}, \phi)\hat{j} \hat{R}^\dagger(\mathbf{n}, \phi) &= R^T(\mathbf{n}, \phi)\hat{j}.
\end{align}
(63)

The commutation relations of two arbitrary antihermitian matrices $N_a$ and $N_b$ follow from a property of the cross product (see appendix A)
\begin{align}
x \times (y \times z) + y \times (z \times x) + z \times (x \times y) = 0.
\end{align}
(64)
Using the property $x \times y = -y \times x$ we find
\begin{align}
a \times (b \times x) - b \times (a \times x) - (a \times b) \times x = 0.
\end{align}
(65)
In matrix notation this gives
\begin{align}
N_a N_b x - N_b N_a x - N_{a \times b} x = 0.
\end{align}
(66)
Since this holds for any $x$ we obtain the commutation relation
\begin{align}
[N_a, N_b] = N_{a \times b}.
\end{align}
(67)

The cross product of two basis vectors in an orthonormal basis may be written using the Levi-Civita tensor ($e_{123} = 1$, it changes sign when two indices are permuted),
\begin{align}
e_i \times e_j = \sum_k e_{ijk} e_k,
\end{align}
(68)
so that we can write the commutation relations for the components of the vector operator $\mathbf{N}$ as
\begin{align}
[N_i, N_j] = \sum_k e_{ijk} N_k.
\end{align}
(69)
From this equation we immediately find the commutation relations for the Hermitian operators $L_i$ as
\begin{align}
[L_i, L_j] = \sum_k i e_{ijk} L_k.
\end{align}
(70)
These commutation relations, together with Eq. (60) allow us to write the left hand side of Eq. (59) as a linear combination of the operators $L_i$. The right hand side is also a linear combination of the operators $L_i$. Thus, we can immediately solve for the matrix elements $R_{ij}(\mathbf{n}, \phi)$, whenever the operators $L_i$ are linearly independent (i.e., when $\sum_k a_k L_k = 0 \Rightarrow a_k = 0$).

One other example of Hermitian operators satisfying the commutation relations Eq. (70) are the generators of $SU(2)$,
\begin{align}
\sigma_1 = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\end{align}
(71)
Note that $e^{-i(\phi+2\pi)}\sigma_k = -e^{-i\phi}\sigma_k$. This is in agreement with the 2 : 1 mapping between $SU(2)$ and $SO(3)$ mentioned earlier.
F. Euler parameters

So far we have used the \((n, \phi)\) parameterization of \(SO(3)\). Since Euler parameters are used widely we describe them here. A linear operator in \(R^3\) is defined by its action on the three basis vectors. Let us assume that a rotation operator \(R\) maps the basis vector \(e_3\) onto \(e'_3\). We can then write the matrix \(R\) as

\[
R = R(e_3', \gamma)R_1,
\]  

(72)

where \(R_1\) may be any rotation for which \(e'_3 = R_1e_3\). If the polar angles of \(e'_3\) are \((\beta, \alpha)\) we can take

\[
R_1 = R(e_3, \alpha)R(e_2, \beta).
\]

(73)

Thus, any rotation \(R\) can be written as

\[
R(\alpha, \beta, \gamma) = R(R_1e_3, \gamma)R_1 = R_1R(e_3, \gamma)R_1^†R_1,
\]

(74)

so that and

\[
R(\alpha, \beta, \gamma) = R(e_3, \alpha)R(e_2, \beta)R(e_3, \gamma)
\]

(75)

From this derivation we see that the ranges of the parameters required to span \(SO(3)\) are

\[
0 \leq \alpha < 2\pi, \quad 0 \leq \beta < \pi, \quad 0 \leq \gamma < 2\pi.
\]

(76)

For the inverse we have

\[
R(\alpha, \beta, \gamma)^{-1} = R(e_3, -\gamma)R(e_2, -\beta)R(e_3, -\alpha).
\]

(77)

We may bring \(-\beta\) back into the range \([0, \pi]\) by inserting \(R(e_3, \pi)R(e_3, -\pi)\) at both sides of \(R(e_2, -\beta)\) twice and by using the relation

\[
R(e_3, -\pi)R(e_2, -\beta)R(e_3, \pi) = R(-e_2, -\beta) = R(e_2, \beta),
\]

(78)

which gives

\[
R(\alpha, \beta, \gamma)^{-1} = R(e_3, -\gamma + \pi)R(e_2, \beta)R(e_3, -\alpha - \pi).
\]

(79)

We may also define a volume element for integration

\[
d\tau = d\alpha \sin \beta d\beta d\gamma,
\]

(80)

which has the important property that for any function \(f(\alpha, \beta, \gamma)\) the integral is invariant under rotation of the function \(f\). The definition of a “rotated function” is given in the next section.

G. Rotating wave functions

We may extend the definition of rotations in \(R^3\) to the rotation of one particle wave functions \((\Psi(x))\) by Wigner’s convention

\[
(\hat{R}\Psi)(x) \equiv \Psi(R^{-1}x).
\]

(81)

Usually, \(\Psi\) will be an element of some Hilbert space. For our purposes it is sufficient to think of \(\Psi\) as an element of some finite dimensional linear space \(\mathcal{V}\). Of course, we must assume that \(\hat{R}\Psi\) is also an element of \(\mathcal{V}\), whenever \(\Psi \in \mathcal{V}\). We use the hat (\(^\hat{\cdot}\)) to distinguish the operators on \(\mathcal{V}\) from the corresponding operators in \(R^3\).

The inverse in the definition is important since it gives

\[
\hat{R}_1(\hat{R}_2\Psi) = (\hat{R}_1\hat{R}_2)\Psi.
\]

(82)

This is readily verified:

\[
[\hat{R}_1(\hat{R}_2\Psi)](x) = (\hat{R}_2\Psi)(\hat{R}_1^{-1}x) = \Psi(\hat{R}_2^{-1}\hat{R}_1^{-1}x) = \Psi[(\hat{R}_1\hat{R}_2)^{-1}x] = [(\hat{R}_1\hat{R}_2)\Psi](x).
\]

(83)
Note that Wigner’s convention is consistent with Dirac notation
\[
\Psi(x) = \langle x|\Psi \rangle, \quad \langle x|R\Psi \rangle = \langle R^\dagger x|\Psi \rangle = \langle R^{-1}x|\Psi \rangle.
\]
(84)

For small rotations we have
\[
\hat{R}(n, \epsilon)\Psi(x) = \Psi(x - \epsilon n \times x).
\]
(85)

To first order in \(\epsilon\) we have in general
\[
f(x + \epsilon y) = f(x) + \sum_k \epsilon y_k \frac{\partial}{\partial x_k} f(x) \equiv f(x) + \epsilon y \cdot \nabla f(x),
\]
(86)

so that we may write
\[
f(x - \epsilon n \times x) = [1 - \epsilon(n \times x) \cdot \nabla] f(x).
\]
(87)

Using \(n \times x \cdot \nabla = e_{ijk} n_i x_j \nabla_k = n \cdot x \times \nabla\) we find
\[
\hat{R}(n, \epsilon) = 1 - \epsilon n \cdot x \times \nabla = 1 - i\epsilon n \cdot \mathbf{\hat{L}},
\]
(88)

where we defined
\[
p \equiv -i\nabla
\]
(89)
\[
\mathbf{\hat{L}} \equiv x \times p.
\]
(90)

Using integration by parts, and assuming that the surface term vanishes, it is easy to show that the operators \(\nabla_k\) are antihermitian, i.e. \((\nabla_k f, g) = (f, -\nabla_k g)\). The multiplicative operators \(x_k\) are Hermitian and it is also straightforward to evaluate the commutator \([\nabla_i, x_j] = \delta_{ij}\). It is left as an exercise for the reader to verify that the operators \(\mathbf{\hat{L}}_k\) are Hermitian and that they satisfy the commutation relations
\[
[\mathbf{\hat{L}}_i, \mathbf{\hat{L}}_j] = i \sum_k e_{ijk} \mathbf{\hat{L}}_k.
\]
(91)

We may now follow the same procedure as before to find the expression for a non-infinitesimal rotation
\[
\hat{R}(n, \phi) = e^{-i\phi n \cdot \mathbf{\hat{L}}}.
\]
(92)

If we choose a \(n\) dimensional (orthonormal) basis \(\{ |i\rangle, i = 1, \ldots, n \}\) in the space \(V\) we may represent the operators \(\hat{R}\) and \(\mathbf{\hat{L}}_k\) by \(n\) dimensional matrices. For rotations we will denote these matrices as \(D(\hat{R})\). By definition
\[
D_{ij}(\hat{R}) = \langle i|\hat{R}|j \rangle.
\]
(93)

We also use the notation \(D(n, \phi) = D[\hat{R}(n, \phi)]\). The unitary matrices \(D(\hat{R})\) are a representation of \(SO(3)\), since
\[
R(n_1, \phi_1)R(n_2, \phi_2) = R(n_3, \phi_3)
\]
(94)

implies
\[
D(n_1, \phi_1)D(n_2, \phi_2) = D(n_3, \phi_3).
\]
(95)

This representation may be reducible. That is, it may be possible to find a unitary transformation of the basis that will simultaneously block diagonalize the matrices \(D(\hat{R})\) for all \(\hat{R}\).

**II. IRREDUCIBLE REPRESENTATIONS**

Suppose we can divide the space \(V\) into a subspace \(S\) and its orthogonal complement \(T\), i.e. \(S \oplus T = V\), such that for all \(\Psi \in S\) and for all \(\hat{R}(n, \phi)\) we have \(\hat{R}\Psi \in S\). In this case \(S\) is called an invariant subspace. Since the operators \(\hat{R}\) are unitary \(T\) must also be an invariant subspace. If not, we could find some \(f \in T\) and \(g \in S\) such that for some \(\hat{R}\) we would have \((g, \hat{R}f) \neq 0\). However, that would mean that \((\hat{R}^{-1}g, f) \neq 0\), which is in contradiction with \(S\) being
an invariant subspace. Thus, if we construct a basis \( \{ |i\rangle, i = 1, \ldots, n \} \) where the first \( m \) vectors \( \{ |i\rangle, i = 1, \ldots, m \} \) span the space \( S \) and the vectors \( \{ |i\rangle, i = m+1, \ldots, n \} \) span the space \( T \) we find that all matrices \( D(\hat{R}) \) have a block structure.

Suppose some Hermitian operator \( \hat{A} \) commutes with all operators \( \hat{R}(n, \phi) \)
\[
[\hat{A}, \hat{R}(n, \phi)] = 0.
\] (96)

Let \( S_\lambda \) be the space spanned by all eigenvectors \( f_i \) with eigenvalue \( \lambda \)
\[
\hat{A} f_i = \lambda f_i.
\] (97)

For each each \( f \in S_\lambda \) we find that \( g = \hat{R} f \) also has eigenvalue \( \lambda \)
\[
\hat{A} g = \hat{A}\hat{R} f = \hat{R}\hat{A} f = \lambda g,
\] (98)
i.e., \( g \in S_\lambda \), which shows that \( S_\lambda \) is an invariant subspace. In order to find an operator \( \hat{A} \) that commutes with each \( \hat{R} \) it is sufficient to find an operator that commutes with \( \hat{L}_1, \hat{L}_2, \) and \( \hat{L}_3 \).

From the commutation relations of \( \hat{L}_k \) we can show that the Hermitian operator
\[
\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2
\] (99)
commutes with \( \hat{L}_1, \hat{L}_2, \) and \( \hat{L}_3 \). It turns out that the commutation relations also allow us to derive the possible eigenvalues of \( \hat{L}^2 \) and the dimensions of the subspaces. Furthermore, within each eigenspace of \( \hat{L}^2 \) we can construct a basis of eigenfunctions of the \( \hat{L}_3 \) operator and we can even derive the matrix elements of all operators \( \hat{L}_k \) in this basis. We summarize this general result:

A linear (or Hilbert) space \( \mathcal{V} \) which is invariant under the Hermitian operators \( \hat{j}_i, i = 1, 2, 3 \) that satisfy the commutation relations
\[
[\hat{j}_i, \hat{j}_j] = i \sum_k \epsilon_{ijk} \hat{j}_k
\] (100)
decomposes into invariant subspaces \( \mathcal{V}^j \) of \( \hat{j}^2 = \hat{j}_1^2 + \hat{j}_2^2 + \hat{j}_3^2 \). The spaces \( \mathcal{V}^j \) are spanned by orthonormal kets
\[
|j, m\rangle, \ m = -j, \ldots, j,
\] (101)
with
\[
\hat{j}^2 |j, m\rangle = j(j+1)|j, m\rangle,
\] (102)
\[
\hat{j}_3 |j, m\rangle = m|j, m\rangle,
\] (103)
\[
\hat{j}_\pm |j, m\rangle = C_\pm (j, m)|j, m \pm 1\rangle,
\] (104)
with
\[
\hat{j}_\pm = \hat{j}_1 \pm i\hat{j}_2,
\] (105)
\[
C_\pm (j, m) = \sqrt{j(j+1) - m(m+1)}.
\] (106)
The \( \hat{j}_\pm \) are the so called step up/down operators.

The proof of the existence of basis (101) is well-known. Briefly, the main arguments are:

- As \([\hat{j}^2, \hat{j}_3] = 0\), we can find a common eigenvector \(|a, b\rangle\) of \( \hat{j}^2 \) and \( \hat{j}_3 \) with \( \hat{j}^2|a, b\rangle = a^2|a, b\rangle \) and \( \hat{j}_3|a, b\rangle = b|a, b\rangle \). Since it is easy to show that \( \hat{j}^2 \) has only non-negative real eigenvalues, we write its eigenvalue as a squared number.

- Considering the commutation relations \([\hat{j}_3, \hat{j}_\pm] = \pm \hat{j}_\pm \) and \([\hat{j}^2, \hat{j}_\pm] = 0\), we find, that \( \hat{j}^2 \hat{j}_+ |a, b\rangle = a^2 \hat{j}_+ |a, b\rangle \) and \( \hat{j}_3 \hat{j}_+ |a, b\rangle = (b+1) \hat{j}_+ |a, b\rangle \). Hence \( \hat{j}_+ |a, b\rangle = |a, b+1\rangle \)

- If we apply \( \hat{j}_+ \) now \( k+1 \) times we obtain, using \( \hat{j}_+^k = \hat{j}_- \), the ket \(|a, b+k+1\rangle\) with norm
\[
\langle a, b+k | \hat{j}_- \hat{j}_+ |a, b+k\rangle = |a^2 - (b+k)(b+k+1)||a, b+k\rangle |a, b+k\rangle.
\] (107)

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 a Hilbert space. 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 \( \hat{j}_- \) gives a zero ket \(|a, b - l - 1\rangle \) with \(|a, b - l\rangle \neq 0 \) and \( a^2 = (b - l)(b - l - 1) \).

• From the fact that \( a^2 = (b + k)(b + k + 1) = (b - l)(b - l - 1) \) follows \( 2h = l - k \), 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 \( \hat{j}_\pm |j, m\rangle \) are normalized and fixing phases, we obtain the well-known formula (105).

Summarizing, in \( \mathcal{V} \) we have the basis \{\(|j, m\rangle, j = 0, \frac{1}{2}, 1, \ldots; m = -j, \ldots, j\} \). Not all values of \( j \) need to occur in a given space \( \mathcal{V} \). The angular momentum operators are diagonal in \( j \), and their matrix elements are

\[
\langle jm'|\hat{j}^2 jm\rangle = j(j + 1)\delta_{m'm} \tag{108}
\]

\[
\langle jm'|\hat{j}_+ jm\rangle = \frac{1}{2} [C_+(j, m)\delta_{m',m+1} + C_-(j, m)\delta_{m',m-1}] \tag{109}
\]

\[
\langle jm'|\hat{j}_- jm\rangle = -i\frac{1}{2} [C_+(j, m)\delta_{m',m+1} - C_-(j, m)\delta_{m',m-1}] \tag{110}
\]

\[
\langle jm'|\hat{j}_\mp jm\rangle = m\delta_{m'm}. \tag{111}
\]

### A. Rotation matrices

The rotation operators in \( \mathcal{V} \) are, by definition

\[
\hat{R}(n, \phi) = e^{-i\hat{n} \cdot \mathbf{n}}. \tag{112}
\]

The matrix representation \( D(\hat{R}) \) is block diagonal in \( j \). The matrix elements of the diagonal blocks \( D^j \) are

\[
D^j_{km}(n, \phi) \equiv \langle jk|\hat{R}(n, \phi)|jm\rangle. \tag{113}
\]

Thus, for a rotated vector we have

\[
|\hat{R}|jm\rangle = \sum_k |jk\rangle \langle jm| \hat{R} \rangle = \sum_k |jk\rangle D^j_{km}(\hat{R}). \tag{114}
\]

The matrix elements of the rotation operator themselves can act as functions on which we may define the action of a rotation operator according to Wigner’s convention:

\[
\hat{R}_1 D^j_{mk}(\hat{R}_2) = D^j_{mk}(\hat{R}_1^{-1} \hat{R}_2) = \sum_{m'} D^j_{m'm} \delta_{m'm} \hat{R}_1 D^j_{m'k}(\hat{R}_2). \tag{115}
\]

Here we used the general property of representations that \( D(\hat{R}_1 \hat{R}_2) = D(\hat{R}_1)D(\hat{R}_2) \). When we compare this result with Eq. (114) we find that the function \( D^j_{mk}(\hat{R}) \) almost behaves as a ket \(|jm\rangle \), except that the inverse of \( \hat{R}_1 \) appears. This can be remedied by starting with the complex conjugate of a \( D \)-matrix element:

\[
\hat{R}_1 D^j_{mk}*(\hat{R}_2) = \sum_{m'} D^{j*}_{m'm}(\hat{R}_1^{-1}) D^j_{m'k}(\hat{R}_2) = \sum_{m'} D^{j*}_{m'k}(\hat{R}_2) D^j_{m'm}(\hat{R}_1). \tag{116}
\]

where we used another property of representations: \( D(\hat{R}^{-1}) = D(\hat{R})^{-1} \).

Many properties of \( D \)-matrices are independent of the parameterization that we choose. However, if we do need a parameterization, the Euler parameters are very useful, since they allow us to factorize any \( D \)-matrix in \( D \)-matrices depending on a single parameter:

\[
D[\hat{R}(\alpha, \beta, \gamma)] = D[\hat{R}(\mathbf{e}_3, \alpha)] D[\hat{R}(\mathbf{e}_2, \beta)] D[\hat{R}(\mathbf{e}_3, \gamma)] \equiv D(\mathbf{e}_3, \alpha) D(\mathbf{e}_2, \beta) D(\mathbf{e}_3, \gamma). \tag{117}
\]

With the procedure for exponentiating an operator described in Section 1B it is straightforward to derive

\[
D^j_{km}(\mathbf{e}_3, \gamma) = \langle jm|e^{-i\hat{e}_3 \cdot \mathbf{e}_3}|jm\rangle = e^{-im\gamma} \delta_{km}. \tag{118}
\]

To find \( D^j(\mathbf{e}_2, \beta) \) we must exponentiate \(-i\beta \hat{e}_2^{(j)}\), where \( \hat{e}_2^{(j)} \) is the matrix representation of \( \hat{e}_2 \) in \( \mathcal{V}^j \). Note that this matrix is real. Usually it is denoted by \( d^j(\beta) \equiv D^j(\mathbf{e}_2, \beta) \) so that we have

\[
D^j_{mk}(\alpha, \beta, \gamma) = e^{-im\alpha} d^j_{mk}(\beta) e^{-ik\gamma}. \tag{119}
\]
For \( j = 0, \frac{1}{2}, 1 \) it is not too difficult to carry out the exponentiation. For \( m = j, j - 1, \ldots, -j \), i.e., the \( d_{jj}^j \) element in the upper left corner we find
\[
d^0(\beta) = 1
\]
\[
d^2(\beta) = \left( \begin{array}{cc}
\cos \frac{\beta}{2} & -\sin \frac{\beta}{2} \\
\sin \frac{\beta}{2} & \cos \frac{\beta}{2}
\end{array} \right)
\]
\[
d^1(\beta) = \left( \begin{array}{cc}
\frac{1 + \cos \beta}{\sqrt{2}} & -\frac{\sin \beta}{\sqrt{2}} \\
\frac{-\sin \beta}{\sqrt{2}} & \frac{1 - \cos \beta}{\sqrt{2}}
\end{array} \right).
\]

There is also a general formula:
\[
d_{km}^j(\beta) = [(j + k)!(j - k)!(j + m)!(j - m)!]^{\frac{1}{2}} \sum_s (-1)^{k-m+s}(\cos \frac{\beta}{2})^{2j+m-k-2s}(\sin \frac{\beta}{2})^{k-m+2s} (j + m - s)!(j - k - s)!s! - k - s),
\]
where \( s \) takes all integer values that do not lead to a negative factorial.

Several symmetry relations can be derived for \( D \) matrices. From the Euler angles of the inverse of a rotation Eq. (79) we have
\[
D(-\gamma, -\beta, -\alpha) = D(-\gamma + \pi, \beta, -\alpha - \pi).
\]

For \( \alpha = \gamma = 0 \) this gives
\[
d_{mk}^j(-\beta) = e^{-im\pi}d_{mk}^j(\beta)e^{ik\pi} = (-1)^{m-k}d_{mk}^j(\beta).
\]

Note that \( m - k \) must be integer, hence \((-1)^{m+k} = (-1)^{m-k}. \) Since \( d^j \) is real
\[
d_{mk}^j(-\beta) = d_{km}^j(\beta) = (-1)^{m-k}d_{mk}^j(\beta).
\]

From the explicit formula for the \( d^j \) matrix we see
\[
d_{km}^j(\beta) = d_{-m,-k}(\beta).
\]

From the last two equation we derive
\[
D_{km}^{j*}(\hat{R}) = (-1)^{k-m}D_{k,-m}^{j*}(\hat{R}).
\]

If \( j \) and \( j' \) are both either integer or half integer, the \( D \) matrices satisfy the following orthogonality relations
\[
\int_0^{2\pi} d\alpha \int_0^\pi \sin \beta d\beta \int_0^{2\pi} d\gamma D_{mk}^{j*}(\alpha, \beta, \gamma)D_{m'k'}^{j'}(\alpha, \beta, \gamma) = \frac{8\pi^2}{2j+1}\delta_{mm'}\delta_{kk'}\delta_{jj'}.
\]

This follows from a generalization of the great orthogonality theorem for irreducible representations in finite groups. The integrals can also be evaluated without knowledge of group theory. Here, we just point out that the \( \delta_{mm'} \) and \( \delta_{kk'} \) follows directly from integration over the angles \( \alpha \) and \( \gamma. \)

From Eq. (116) we know that \( D_{mk}^{j*}(\alpha, \beta, \gamma) \) transforms as \([jm] \). For \( k = 0 \) (and thus, necessarily \( j = l \) is integer) we define
\[
C_{lm}(\theta, \phi) = D_{ml}^{l*}(\phi, \theta, 0),
\]
which are spherical harmonics in Racah normalization. From Eq. (129) we find
\[
\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta C_{lm}^{*}(\theta, \phi)C_{l'm'}(\theta, \phi) = \frac{4\pi}{2l+1}\delta_{lm}\delta_{l'm'}
\]

Thus, the relation with spherical harmonics in the standard normalization is
\[
Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} C_{lm}(\theta, \phi).
\]
Also setting \( m \) to zero gives us Legendre polynomials

\[
P_l(\cos \theta) = d^l_{00}(\theta) = C_{l0}(\theta, \phi).
\]  

We also define the regular harmonics,

\[
R_{lm}(\mathbf{r}) = r^l C_{lm}(\hat{r}),
\]

where \( r^T = (x, y, z) = r(\cos \phi \sin \theta, \sin \phi \sin \theta, \cos \theta) \), and \( \hat{r} = (\theta, \phi) \). From the explicit formulas for \( D^0 \) and \( D^1 \) we find

\[
R_{00}(\mathbf{r}) = 1
\]

\[
R_{11}(\mathbf{r}) = -\frac{1}{\sqrt{2}}(x + iy) \equiv r_{+1}
\]

\[
R_{10}(\mathbf{r}) = z \equiv r_0
\]

\[
R_{1-1}(\mathbf{r}) = \frac{1}{\sqrt{2}}(x - iy) \equiv r_{-1}
\]

The \( r_{+1}, r_0, \) and \( r_{-1} \) are the so-called spherical components of the vector \( \mathbf{r} \). They are related to the Cartesian components via the unitary transformation

\[
\tilde{\mathbf{r}} \equiv \begin{bmatrix} r_+ \\ r_0 \\ r_- \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} -1 & -i & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & -i & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \equiv S^T \mathbf{r}.
\]

We put in the transpose so that for row vectors we get \( \tilde{\mathbf{r}}^T = \mathbf{r}^T S \). We now compare the rotation of the Cartesian and the spherical components of a vector. In Cartesian coordinates we define

\[
\mathbf{r} \equiv R(\mathbf{n}, \phi) \mathbf{r}', \Rightarrow \tilde{\mathbf{r}}^T = \mathbf{r}^T R(\mathbf{n}, \phi)
\]

and for the spherical components we find

\[
\hat{R}(\mathbf{n}, \phi) R_{lm}(\mathbf{r}) = R_{lm}[R(\mathbf{n}, \phi)]^{-1} \mathbf{r} = R_{lm}(\mathbf{r}') = \sum_k R_{lk}(\mathbf{r}) D^l_{km}(\mathbf{n}, \phi).
\]

For \( l = 1 \) this gives

\[
\tilde{\mathbf{r}}^T = \mathbf{r}^T D^1(\mathbf{n}, \phi), \text{ so that}
\]

\[
\tilde{\mathbf{r}}^T = \mathbf{r}^T S = \mathbf{r}^T RS = \mathbf{r}^T SD^1,
\]

which gives

\[
R = SD^1 S^T.
\]

We recall that the components of an angular momentum operator transform as the Cartesian components of a row vector [see Eq. (59)]. Thus, if we define \( \hat{J}_\mu^{(1)} = \sum \hat{J}_\mu S_\mu \), with \( \mu = +1, 0, -1 \), i.e.,

\[
\hat{J}_+^{(1)} = -\frac{\sqrt{3}}{2}(\hat{J}_1 + i\hat{J}_2)
\]

\[
\hat{J}_0^{(1)} = \hat{J}_3
\]

\[
\hat{J}_-^{(1)} = \frac{\sqrt{3}}{2}(\hat{J}_1 - i\hat{J}_2)
\]

we obtain

\[
\hat{R}(\mathbf{n}, \phi) \hat{J}_m^{(1)} \hat{R}(\mathbf{n}, \phi) \hat{J}_m^{(1)} = \sum_k \hat{J}_k^{(1)} D^l_{km}(\mathbf{n}, \phi).
\]
III. VECTOR COUPLING

In quantum chemistry one usually writes a two electron wave function as, e.g., \( \psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1) \). Whenever convenient, we will use tensor product notation where, by definition, we keep the order of the arguments fixed, so that we can drop them, and we write \( \psi_a \otimes \psi_b - \psi_b \otimes \psi_a \). For two linear spaces \( V_1 \) and \( V_2 \) with dimensions \( n_1, n_2 \), the tensor product space \( V_1 \otimes V_2 \) is a \( n_1 \times n_2 \) dimensional linear space which contains the tensor products \( f \otimes g \), with \( f \in V_1 \) and \( g \in V_2 \). For a complete definition we must point out when two elements of \( V_1 \otimes V_2 \) are the same:

\[
(\lambda f) \otimes g = f \otimes (\lambda g) = \lambda (f \otimes g)
\]

\[
(f + g) \otimes h = f \otimes h + g \otimes h
\]

\[
f \otimes (g + h) = f \otimes g + f \otimes h.
\]

For linear operators \( \hat{A} \) and \( \hat{B} \) defined on \( V_1 \) and \( V_2 \), respectively, we define

\[
(\hat{A} \otimes \hat{B})(f \otimes g) = (\hat{A}f) \otimes (\hat{B}g).
\]

Thus, \( (\nabla_x + \nabla_y)f(x)g(y) \) written in tensor notation becomes \( (\nabla \otimes I + I \otimes \nabla)f \otimes g \).

The scalar product in the tensor product space is defined in terms of the scalar products on \( V_1 \) and \( V_2 \) by

\[
(f_1 \otimes g_1, f_2 \otimes g_2) = (f_1, f_2)(g_1, g_2).
\]

If we have an orthonormal basis \( \{e_i, i = 1, \ldots, n_1\} \) on \( V_1 \) and an orthonormal basis \( \{f_i, i = 1, \ldots, n_2\} \) then \( e_i \otimes f_i, i = 1, \ldots, n_1; j = 1, \ldots, n_2 \) forms an orthonormal basis for \( V_1 \otimes V_2 \). Clearly, we have

\[
(e_i \otimes f_i, e_{i'} \otimes f_{i'}) = \delta_{ii'} \delta_{jj'}.
\]

If the matrix elements \( A_{ij} = (e_i, \hat{A}e_j) \) and \( B_{ij} = (f_i, \hat{B}f_j) \) are known, we can easily compute the matrix elements of the tensor product \( \hat{A} \otimes \hat{B} \) in the tensor product basis

\[
(A \otimes B)_{ij} = (e_i \otimes f_j, \hat{A} \otimes \hat{B})|e_{i'} \otimes f_{j'}\rangle = \delta_{ii'} \delta_{jj'}.
\]

Let \( \hat{A}f_i = \lambda_i f_i \) and \( \hat{B}g_j = \mu_j g_j \), then

\[
(\hat{A} \otimes \hat{I} + \hat{I} \otimes \hat{B})(f_i \otimes g_j) = \lambda_i f_i \otimes g_j + \hat{I}f_i \otimes \hat{B}g_j = \lambda_i f_i \otimes g_j + \mu_j f_i \otimes g_j = (\lambda_i + \mu_j) f_i \otimes g_j,
\]

i.e., the functions \( f_i \otimes g_j \) are eigenfunctions of the operator \( (\hat{A} \otimes \hat{I} + \hat{I} \otimes \hat{B}) \) with eigenvalues \( (\lambda_i + \mu_j) \).

From the Taylor expansion of an exponential one can prove that, for scalars, \( e^{a+b} = e^a e^b \). Since functions of operators are defined by the series expansion this relation also holds for operators that commute. It is readily verified that the commutator

\[
[\hat{A} \otimes \hat{I}, \hat{I} \otimes \hat{B}] = 0
\]

and so we have

\[
e^{\hat{A} \otimes \hat{I} + \hat{I} \otimes \hat{B}} = e^{\hat{A} \otimes \hat{B}}.
\]

A. An irreducible basis for the tensor product space

Let us assume that \( V^{j_1} \) and \( V^{j_2} \) are spaces spanned by the bases \( \{|j_1, m_1\}, m_1 = -j_1, \ldots, j_1\} \) and \( \{|j_2, m_2\}, m_2 = -j_2, \ldots, j_2\} \), respectively. All that we need to construct an irreducible basis for the tensor product space is a set of three Hermitian operators that satisfy the angular momentum commutation relations. It is not hard to verify that the operators

\[
\hat{J}_i = \hat{j}_i \otimes \hat{1} + \hat{1} \otimes \hat{j}_i, \quad i = 1, 2, 3
\]

satisfy these conditions. Since we have explicit expressions for the matrix elements of \( \hat{j}_i \) in the bases of \( V^{j_1} \) and \( V^{j_2} \) we can easily calculate the matrix elements of the operators \( \hat{J}_i \) in the so called uncoupled basis

\[
|j_1 m_1 j_2 m_2\rangle \equiv |j_1 m_1\rangle \otimes |j_2 m_2\rangle, \quad m_1 = -j_1, \ldots, j_1; \quad m_2 = -j_2, \ldots, j_2.
\]
We could then proceed by (e.g., numerically) diagonalizing the operator $\hat{J}^2 = \hat{J}_1^2 + \hat{J}_2^2 + \hat{J}_3^2$ to find the $(2J + 1)$ dimensional eigenspaces $S_J$ of $\hat{J}^2$. Within each space $S_J$ it should be possible to find an eigenfunction of $\hat{J}_3$ with eigenvalue $M = J$. With the step down operator $\hat{J}_- = \hat{J}_1 - i \hat{J}_2$ we could then find the other eigenfunctions of $\hat{J}_3$. We denote these simultaneous functions of $\hat{J}^2$ and $\hat{J}_3$ by $| (j_1 j_2) J M \rangle$, $M = -J, \ldots, J$, where the $(j_1 j_2)$ indicate that it is a vector in the tensor product space.

We may expand these functions in the uncoupled basis

$$
| (j_1 j_2) J M \rangle = \sum_{m_1 = -j_1}^{j_1} \sum_{m_2 = -j_2}^{j_2} |j_1 m_1 j_2 m_2 \rangle C_{m_1 m_2}^{JM} (j_1 j_2).
$$

With the proper phase conventions the expansion coefficients are real and they are known as Clebsch-Gordan (CG) coefficients. In Dirac notation they can be written as a scalar product $| (j_1 m_1 j_2 m_2) (j_1 j_2) J M \rangle$ which is usually simplified to $| (j_1 m_1 j_2 m_2) J M \rangle$.

It may not come as a surprise that we do not need a numeric diagonalization to find the eigenvalues of $\hat{J}^2$ and the CG coefficients. First we point out that the uncoupled basis functions are already eigenfunctions of $\hat{J}_3$, with eigenvalues $M = m_1 + m_2$. The largest eigenvalue that occurs is $M = j_1 + j_2$, corresponding to the eigenvector $| (j_1 j_1 j_2 j_2) \rangle$. Thus, there must be an invariant subspace $S_J$ with $J = j_1 + j_2$. This must be the largest possible value of $J$, since otherwise a larger eigenvalue of $\hat{J}_3$ would occur. For $M = J - 1$ there is a two-dimensional space of eigenfunctions of $\hat{J}_3$, spanned by the functions $| (j_1 j_1 j_2 j_2 - 1) \rangle$ and $| (j_1 j_1 - 1 j_2 j_2) \rangle$. We know that the space $S_J$ contains precisely one eigenfunction $| (j_1 j_2) J J - 1 \rangle$, so the other component of the two-dimensional space must necessarily be an element of $S_{J-1}$. If we carefully continue this procedure we find that each space $S_J$ must occur exactly once and that $J = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2|$. It is left as an exercise for the reader to verify that if we add up the dimensions of the spaces $S_J$ we get $(2j_1 + 1)(2j_2 + 1)$, i.e., the dimension of $\mathcal{V}^{j_1} \otimes \mathcal{V}^{j_2}$. Thus, the coupled basis for $\mathcal{V}^{j_1} \otimes \mathcal{V}^{j_2}$ consists of the functions

$$
| (j_1 j_2) J M \rangle, J = |j_1 - j_2|, \ldots, j_1 + j_2, \quad M = -J, \ldots, J.
$$

The CG coefficients are the matrix elements of the orthogonal matrix that transforms between the uncoupled and the coupled basis, thus we have the following orthogonality relations

$$
\sum_{m_1, m_2} \langle J M | j_1 m_1 j_2 m_2 \rangle \langle j_1 m_1 j_2 m_2 | J' M' \rangle = \delta_{J J'} \delta_{M M'}
$$

and we may invert Eq. (160)

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

Recursion relations for the CG coefficients can be obtained by applying the step up/down operators to Eq. (160). On the left hand side we get

$$
\hat{J}_\pm | (j_1 j_2) J M \rangle = | (j_1 j_2) J M \pm 1 \rangle C_\pm^{JM}
$$

and on the right hand side

$$
\sum_{m_1, m_2} \hat{J}_\pm | j_1 m_1 \rangle | j_2 m_2 \rangle \langle j_1 m_1 j_2 m_2 | J M \rangle
$$

$$
= \sum_{m_1, m_2} \left[ |j_1 m_1 \pm 1 \rangle |j_2 m_2 \rangle C_\pm^{jm_1 m_2} + |j_1 m_1 \rangle |j_2 m_2 \pm 1 \rangle C_\pm^{jm_2 m_2} \right] \langle j_1 m_1 j_2 m_2 | J M \rangle
$$

$$
= \sum_{m_1, m_2} |j_1 m_1 \rangle |j_2 m_2 \rangle \left[ C_\pm^{jm_1 m_2} \langle j_1 m_1 \pm 1 | j_2 m_2 | J M \rangle + C_\pm^{jm_2 m_2} \langle j_1 m_1 | j_2 m_2 \pm 1 | J M \rangle \right].
$$
In the last step we used
\[ \sum_{m_1} |j_1 m_1 \pm 1\rangle C_{j_1 m_1}^{\mp} = \sum_{m_1} |j_1 m_1\rangle C_{j_1 m_1, \mp 1}, \] (170)
which is correct, assuming the range of summation is always chosen to include all allowed \(m_1\) values. Combining Eqs. 166 and 169 we obtain the recursion relations
\[ C_{j_1 m_1}^{\mp}(j_1 m_1 j_2 m_2 |JM \pm 1\rangle = C_{j_1 m_1}^{\mp}(j_1 m_1 \mp 1 j_2 m_2 |JM) + C_{j_2 m_2}^{\mp}(j_1 m_1 j_2 m_2 \mp 1 |JM). \] (171)
For the upper sign with \(M = J\) we get
\[ 0 = C_{j_1 m_1 - 1}^{\mp}(j_1 m_1 - 1 j_2 m_2 |JJ) + C_{j_2 m_2 - 1}^{\mp}(j_1 m_1 j_2 m_2 - 1 |JJ). \] (172)
By convention we take \(\langle j_1, j_1, j_2, J - j_1 |J, J \rangle\) real and positive. After normalization according to Eq. (162) this fixes \(\langle j_1 m_1 j_2 m_2 |JJ \rangle\). The other values \(\langle JM \rangle\) elements are obtained by using the lower sign. For \(J = M = 0\) this procedure gives
\[ \langle j_1 m_1 j_2 m_2 |00 \rangle = \frac{(-1)^{j_1 - m_1}}{\sqrt{2J_1 + 1}} \delta_{j_1 j_2} \delta_{m_1, -m_2}. \] (173)
It is straightforward to construct an irreducible basis in a higher dimensional tensor product space. E.g., in \(V^{j_1} \otimes V^{j_2} \otimes V^{j_3}\)
\[ |(j_1 j_2 j_3 |JM \rangle \equiv \sum_{m_1 m_2 m_3} |j_1 m_1\rangle |j_2 m_2\rangle |j_3 m_3\rangle \langle j_1 m_1 j_2 m_2 j_3 m_3 |JM \rangle. \] (174)
transforms like \(|JM \rangle\). For \(|JM \rangle = |00 \rangle\) and substituting Eq. (173) we construct a so called invariant function
\[ \sum_{m_1 m_2 m_3} |j_1 m_1\rangle |j_2 m_2\rangle |j_3 m_3\rangle \langle j_1 m_1 j_2 m_2 j_3 m_3 |1 - m_3 \rangle \frac{(-1)^{j_3 + m_3}}{\sqrt{2J_3 + 1}}. \] (175)
This motivates the definition of the 3j–symbol
\[ \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2J_3 + 1}} (j_1 j_2 m_1, j_3 m_3). \] (176)
The phase convention makes the symmetry properties of the 3j symbol particularly simple: permuting two columns or changing all the \(m_i\) to \(-m_i\) gives an extra factor \((-1)^{j_1 + j_2 + j_3}\). Thus, cyclic permutations of the columns leave the 3j unchanged.
\[ \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 + j_2 + j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 + j_2 + j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \] (177)
eq \text{etc. From the inverse relation}
\[ \langle j_1 m_1 j_2 m_2 |j_3 m_3 \rangle = (-1)^{j_1 - j_2 + m_3} \sqrt{2J_3 + 1} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \] (178)
one can find how awkward the corresponding symmetry relations for CG coefficients are. Of course, a rigorous derivation of these symmetry relations must start from the recursion relations of the CG coefficients.

B. The rotation operator in the tensor product space

The rotation operator in \(V^{j_1} \otimes V^{j_2}\) is given by
\[ \hat{R}(n, \phi) = e^{-i\phi n_1} \] (179)
and when operating on the coupled basis functions it gives
\[ \hat{R}|(j_1 j_2)JM\rangle = \sum_k |(j_1 j_2)JK\rangle D_{KM}^J(\hat{R}) \] (180)
\[ \sum_{k_1 k_2} |j_1 k_1\rangle |j_2 k_2\rangle \sum_k |(j_1 k_1 j_2 k_2)JK\rangle D_{KM}^J(\hat{R}). \] (181)
Using the rules for manipulating tensor products of operators derived above we find
\[ e^{-i\phi\hat{1}} = e^{-i\phi\hat{\mathbf{j}}} \otimes e^{-i\phi\hat{\mathbf{z}}}, \]
which we may write symbolically as \( \hat{R} = \hat{\mathbf{j}} \otimes \hat{\mathbf{R}} \). Thus, the uncoupled basis functions rotate as
\[ (\hat{R} \otimes \hat{\mathbf{R}})|j_1m_1\rangle|j_2m_2\rangle = \sum_{k_1k_2} |j_1k_1\rangle|j_2k_2\rangle D_{j_1}^{k_1}(\hat{R})D_{j_2}^{k_2}(\hat{R}). \]
Together with Eq. (164) this gives
\[ D_{1j_1}^{j_1}(\hat{R})D_{2m_2}^{j_2}(\hat{R}) = \sum_{JLM} (j_1k_1j_2k_2|JK)(j_1m_1j_2m_2|JM)D_{LM}^{j_2j_1}(\hat{R}). \]
This is a remarkable useful equation. E.g., it allows us to verify the orthogonality relations Eq. (129) and to find
\[ \int_0^{2\pi} d\alpha \int_0^{2\pi} d\beta \int_0^{2\pi} d\gamma D_{MK}^{j_1j_1}(\alpha, \beta, \gamma)D_{m_1k_1}^{j_1j_1}(\alpha, \beta, \gamma)D_{m_2k_2}^{j_2j_2}(\alpha, \beta, \gamma) = \frac{8\pi^2}{2J+1} (j_1m_1j_2m_2|JM)(j_1k_1j_2k_2|JK). \]
If we take the complex conjugate, set \( K = k_1 = k_2 = 0 \), and eliminate the integral over the third Euler angle, we find
\[ \int_0^{2\pi} d\phi \int_0^{\pi} \sin \beta d\beta \int_0^{2\pi} d\theta D_{LM}^{j_1j_1}(\phi, \theta)C_{l_1m_1}(\theta, \phi)C_{l_2m_2}(\theta, \phi) = \frac{4\pi}{2L+1} (l_1m_1l_2m_2|LM)(l_10l_20|L0). \]
We also may derive the recursion relation for Legendre polynomials from the explicit expressions for \( d^j \) with \( z \equiv \cos \beta \)
\[ P_0(z) = 1 \]
\[ P_1(z) = z. \]
From Eq. (184) with \( m = k = 0 \) and \( j_1 = 1 \) and \( j_2 = l \) we derive a recursion relation for the Legendre polynomials
\[ P_1(z)P_1(z) = \sum_L (100|L0)^2 P_L(z) \]
\[ = (100|l + 1, 0)^2 P_{l+1}(z) + (100|l - 1, 0)^2 P_{l-1}(z) \]
\[ = \frac{l+1}{2l+1} P_{l+1}(z) + \frac{l}{2l+1} P_{l-1}(z), \]
i.e.,
\[ P_{l+1}(z) = \frac{z(2l+1)P(z) - lP_{l-1}(z)}{l+1} \]
\[ P_2(z) = \frac{3z^2 - 1}{2}. \]
Suppose the angular part of a wave function is given by
\[ \Psi(\theta, \phi) = \sum_{lm} a_{lm} C_{lm}(\theta, \phi) \]
and we are interested in the spatial distribution
\[ P(\theta, \phi) = |\Psi(\theta, \phi)|^2 = \sum_{l_1m_1l_2m_2} a_{l_1m_1}^* a_{l_2m_2} C_{l_1m_1}^*(\theta, \phi)C_{l_2m_2}(\theta, \phi). \]
First, from Eqs. (128) and (130) we find
\[ C_{lm}^*(\theta, \phi) = (-1)^m C_{l,-m}(\theta, \phi). \]
From Eq. (184) we have
\[ (-1)^{m_1} C_{l_1,-m_1}(\theta, \phi)C_{l_2m_2}(\theta, \phi) = (-1)^m \sum_{LM} (l_1, -m_1, l_2, m_2|LM)(l_10l_20|L0)C_{LM}(\theta, \phi). \]
thus,

\[ P(\theta, \phi) = \sum_{l_1 l_2 m_1 m_2} a^*_l m_1 a_{l_2 m_2} (-1)^m \langle l_1, -m_1, l_2, m_2 | L M \rangle \langle l_1 0 | l_2 0 \rangle C_{LM}(\theta, \phi). \]  

(198)

For a pure state, \( \Psi(\theta, \phi) = C_{lm}(\theta, \phi) \)

\[ P(\theta, \phi) = \sum_{LM} |a_{lm}|^2 (-1)^m \langle l, -m, l, m | L M \rangle \langle 0 0 | L 0 \rangle C_{LM}(\theta, \phi) \]

(199)

\[ = \sum_L |a_{lm}|^2 (-1)^m \langle l, -m, l, m | 0 0 \rangle \langle 0 0 | L 0 \rangle P_L(\cos \theta). \]  

(200)

It follows from the triangular conditions for \( \langle 0 0 | L 0 \rangle \) that \( L \) runs from 0 to 2\( l \). Furthermore, a CG coefficient is zero if all the \( m \)'s are zero and the sum of the \( l \)'s is odd (prove this using Eq. (176) and the symmetry properties of \( 3j \)m symbols) so \( L \) must be even.

C. Application to photo-absorption and photo-dissociation

The transition amplitude in a one-photon electric dipole transition between two states is proportional to the matrix elements of the operator \( \hat{T} = \mathbf{e} \cdot \mu \), where \( \mathbf{e} \) is the polarization vector of the photon and \( \mu \) is the dipole operator. A scalar product can be written in spherical coordinates

\[ \mathbf{e} \cdot \mu = \sum_m (-1)^m e_j^{(1)} m H_m^{(1)} = -\sqrt{3} \sum_m e_j^{(1)} m H_m^{(1)} \langle 1 - m | m | 0 0 \rangle \]

(201)

The spherical components of the dipole operator for a one-particle system are

\[ \mu_{lm}^{(1)}(r) = q R_{lm}(r) = qr C_{lm}(r). \]

(202)

The matrix elements of \( \hat{T} \) in the basis \( \Psi_{n_l m_1 m_2} \) are

\[ \langle \Psi_{n_1 l_1 m_1} | \hat{T} | \Psi_{n_2 l_2 m_2} \rangle = \sum_m (-1)^m e_j^{(1)} m \int d\mathbf{r} \hat{C}_{l_1 m_1}^* (\mathbf{r}) C_{l_2 m_2} (\mathbf{r}) \int d^2 r f^*_{n_1 l_1} (r) q r f_{n_2 l_2} (r) \]

(203)

\[ = \sum_m (-1)^m e_j^{(1)} m A_{n_1 l_1 m_1 m_2} \langle l_1 m_1 1 m | l_2 m_2 \rangle \langle l_1 0 0 | l_2 0 \rangle. \]

(204)

For simplicity we assume that one component of \( \mathbf{e} \) is 1, and the others 0. Since we want to focus on the angular part of the problem, we drop the \( n \) quantum numbers and also we absorb the factor \( \langle l_1 0 0 | l_2 0 \rangle \) into \( A_{l_1 l_2} \), so that we get

\[ \langle l_1 m_1 | \hat{T} | l_2 m_2 \rangle = A_{l_1 l_2} \langle l_1 m_1 1 m | l_2 m_2 \rangle. \]

(205)

Thus, we can write the (angular part of) the operator \( \hat{T} \) as

\[ \hat{T} = \sum_{l_1 m_1 l_2 m_2} A_{l_1 l_2} \langle l_1 m_1 | l_2 m_2 \rangle \langle l_1 0 0 | l_2 0 \rangle. \]

(206)

D. Density matrix formalism

A quantum mechanical system can be completely described by its density operator

\[ \hat{\rho} = \sum_i |\Psi_i\rangle p_i \langle \Psi_i|, \]

(207)

where the \( p_i \) are the probabilities of the system being in the state \( |\Psi_i\rangle \). To every observable some Hermitian operator \( \hat{A} \) corresponds and the mean result of a measurement of this quantity is given by

\[ \langle \hat{A} \rangle \equiv \text{Tr}(\hat{\rho} \hat{A}) = \sum_{ij} \langle j | \Psi_i \rangle p_i \langle \Psi_i | \hat{A} | j \rangle = \sum_{ij} p_i \langle \Psi_i | \hat{A} | j \rangle \langle j | \Psi_i \rangle = \sum_i p_i \langle \Psi_i | \hat{A} | \Psi_i \rangle. \]

(208)
For example, measuring an angular probability distribution, as in the example above, corresponds to taking $\hat{A} = |\vec{r}\rangle\langle\vec{r}|$, which gives

$$A(\vec{r}) = \sum_i p_i |\Psi_i(\vec{r})|^2.$$  

(209)

A photoabsorption experiment is described by $\hat{A} = \sum_f \hat{T} |\Psi_f\rangle\langle\Psi_f|\hat{T}$ which gives

$$A = \sum_i p_i |\Psi_i(\vec{r})|^2.$$  

(210)

To determine an angular distribution after photo-excitation we take

$$\hat{A}(\vec{r}) = \hat{T} \hat{P} |\vec{r}\rangle\langle\vec{r}| \hat{T} \hat{P}$$  

with $\hat{P} = \sum_f |\Psi_f\rangle\langle\Psi_f|$, which gives

$$A(\vec{r}) = \sum_{i,f} p_i |\Psi_f(\vec{r})|^2 |\langle\Psi_f|\hat{T}|\Psi_i\rangle|^2.$$  

(212)

Thus, in any case we need to evaluate $\text{Tr}(\hat{\rho} \hat{A}) = \text{Tr}(\hat{A} \hat{\rho}^\dagger)$, since $\hat{\rho}$ is Hermitian.

E. The space of linear operators

Let $|i\rangle$ be an orthonormal basis in $V$, i.e., $\langle i|j\rangle = \delta_{ij}$. In Dirac notation, any linear operator can be written as

$$\hat{A} = \sum_{ij} A_{ij} |i\rangle\langle j|.$$  

(213)

Indeed, for the matrix elements we get

$$\langle k|\hat{A}|l\rangle = \langle k| \sum_{ij} A_{ij} |i\rangle\langle j| |l\rangle = A_{kl}.$$  

(214)

Thus we may think of $\hat{T}_{ij} \equiv |i\rangle\langle j|$ as a “basis function” for the space of linear of operators, and of the matrix element $A_{ij}$ as an expansion coefficient.

We define the “scalar product” between operators $\hat{A}$ and $\hat{B}$ as the trace of $\hat{A} \hat{B}^\dagger$, since that gives

$$\text{Tr}(\hat{A} \hat{B}^\dagger) = \sum_{ij} \langle j|\hat{A}|i\rangle \langle i|\hat{B}^\dagger|j\rangle = \sum_{ij} A^*_{ij} B_{ij},$$  

(216)

completely analogous to $(x,y) = \sum_i x_i y_i$. We also have

$$A_{ij} = \text{Tr}(\hat{T}_{ij}^\dagger \hat{A})$$  

(217)

and

$$\text{Tr}(\hat{T}_{ij}^\dagger \hat{T}_{i'j'}) = \delta_{ii'} \delta_{jj'}.$$  

(218)

Furthermore

$$\text{Tr}(\hat{A} \hat{B}^\dagger) = \text{Tr}(\hat{B}^\dagger \hat{A}).$$  

(219)

and

$$\hat{T}_{ij}^\dagger = |j\rangle\langle i| = \hat{T}_{ji}.$$  

(220)

A basis transformation $|i\rangle' = \hat{R}|i\rangle$ gives

$$\hat{T}_{ij}' \equiv |i\rangle'|\langle j'| = \hat{R} \hat{T}_{ij} \hat{R}^\dagger.$$  

(221)

One can easily verify that if $\hat{R}$ is a unitary transformation on $V$, then $\hat{T}_{ij}'$ is again an orthonormal basis, i.e.,

$$\text{Tr}(\hat{T}_{ij}' \hat{T}_{i'j'}) = \delta_{ij} \delta_{i'j'}.$$  

Note that one may also think of $\hat{T}_{ij}$ as an element of $V \otimes V^\ast$. 
IV. ROTATING IN THE DUAL SPACE

The dual space $\mathcal{V}^*$ associated with the vector space $\mathcal{V}$ is the linear space of linear functionals on $\mathcal{V}$. A linear functional is a linear mapping of $\mathcal{V}$ onto $\mathbb{R}$ or $\mathbb{C}$. Every linear functional can be defined as “taking the scalar product with some vector”. The dimension of $\mathcal{V}^*$ is the same as the dimension of $\mathcal{V}$ and the dual of $\mathcal{V}^*$ is $\mathcal{V}$. In other words, the dual space is simply the space where the Dirac bra’s live. If we have a basis $\{ |jm\rangle, m = -j, \ldots, j \}$ in $\mathcal{V}$, then $\{ |jm\rangle, m = -j, \ldots, j \}$ is a basis in $\mathcal{V}^*$, which we call the dual basis. Hermitian conjugation takes us back and forth between $\mathcal{V}$ and $\mathcal{V}^*$: $\langle jm | = \langle jm |^\dagger = \langle jm |^\ast |c\rangle$. Hence $\langle jm |$ is also well defined if $j$ is half integer (for $(-1)^{j}$ one could take $i$ as well as $-i$). In any case, we can now define an alternative basis for the dual space

$$\langle jm | \equiv (jm)^\dagger = \sum_k |jk\rangle D^j_{km}(\hat{R}),$$

(222)

By taking the Hermitian conjugate we find for the transformation of the dual basis

$$\langle jm | \equiv \langle jm |^\dagger = \sum_k |jk\rangle D^j_{km}(\hat{R}) = \sum_k \langle jk|(-1)^{k+m} D^j_{-k,-m}(\hat{R})$$

(223)

where we used Eq. (128). We notice two things. First, if we rotate the basis in $\mathcal{V}$ with $\hat{R}$ then the dual basis rotates with $\hat{R}^\dagger$. Second, the complex conjugate of the $D$ matrix appears. We now try to find an alternative basis in the dual space that we can rotate with the $D$-matrix, instead of its complex conjugate. First we by multiply both sides of the equation with $(-1)^{j+m}$

$$(-1)^{j+m} \langle jm | \hat{R}^\dagger = \sum_k (-1)^{j+k} |jk\rangle D^j_{-k,-m}(\hat{R})$$

(224)

and then we change the signs of $m$ and $k$

$$(-1)^{j-m} (j,-m) \hat{R}^\dagger = \sum_k (-1)^{-k} |j-k\rangle D^j_{km}(\hat{R}).$$

(225)

The reason that we multiply with $(-1)^{j,-m}$, rather than simply $(-1)^{m}$ is that the former is also well defined if $j$ is half integer (for $(-1)^{j}$ one could take $i$ as well as $-i$). In any case, we can now define an alternative basis for the dual space

$$\langle jm | \equiv (jm)^\dagger = \sum_k |jk\rangle D^j_{km}(\hat{R})$$

(226)

that rotates as

$$\langle jm | \hat{R}^\dagger = \sum_k |j\rangle D^j_{km}(\hat{R}).$$

(227)

We also introduce

$$|jm\rangle = (-1)^{-m} |j,-m\rangle,$$

(228)

which is a function in $\mathcal{V}$ that rotates like $|jm\rangle$

$$\hat{R} |jm\rangle = \sum_k |j\rangle D^j_{km}(\hat{R}).$$

(229)

We may use the $\bar{m}$ notation whenever convenient, e.g.

$$(j_1m_1j_2m_2|JM) = (-1)^{j_2-m_2} (j_1, m_1, j_2, -m_2|JM).$$

(230)

We note that the so called time reversal operator $\hat{\Theta}$ is defined as

$$\hat{\Theta} |jm\rangle = |jm\rangle.$$

(231)

We will not use this operator, but we just point out that it is defined to be anti linear

$$\hat{\Theta} \lambda |\Psi\rangle \equiv \lambda^* \hat{\Theta} |\Psi\rangle.$$
A. Tensor operators

We recall Eq. (180), where we inserted the resolution of identity,

\[
(\hat{R} \otimes \hat{R}) \sum_{m_1m_2} |j_1m_1 \rangle |j_2m_2 \rangle \langle j_1m_1 | j_2m_2 \rangle = \sum_{m_1m_2k_1k_2} |j_1k_1 \rangle |j_2k_2 \rangle D^0_{k_1m_1} (\hat{R}) D^0_{k_2m_2} (\hat{R}) \langle j_1m_1 | j_2m_2 \rangle \langle j_1k_1 | j_2k_2 \rangle \]

(233)

\[
= \sum_k \left[ \sum_{k_1k_2} |j_1k_1 \rangle |j_2k_2 \rangle \langle j_1k_1 | j_2k_2 \rangle \langle j_1k_1 | j_2k_2 \rangle \right] D^k_{KM} (\hat{R}) .
\]

(234)

This suggests the definition of the operator

\[
\hat{T}_{JM} (j_1j_2) = \sum_{m_1m_2} |j_1m_1 \rangle |j_2m_2 \rangle \langle j_1m_1 | j_2m_2 \rangle ,
\]

(235)

which rotates exactly like a \(|JM\rangle\). Completely analogous to Eq. (233) we find

\[
\hat{T}^{BF}_{JM} (j_1j_2) = \sum_{m_1m_2} |j_1m_1 \rangle |j_2m_2 \rangle \langle j_1m_1 | j_2m_2 \rangle \hat{R}^\dagger
\]

(236)

\[
= \sum_{m_1m_2} \hat{R} |j_1m_1 \rangle |j_2m_2 \rangle \hat{R}^\dagger (j_1m_1j_2m_2 | JM \rangle)
\]

(237)

\[
= \sum_{m_1m_2k_1k_2} |j_1k_1 \rangle |j_2k_2 \rangle D^0_{k_1m_1} (\hat{R}) D^0_{k_2m_2} (\hat{R}) (j_1m_1j_2m_2 | JM \rangle)
\]

(238)

\[
= \sum_{K} \sum_{k_1k_2} (j_1k_1 \rangle |j_2k_2 \rangle (j_1k_1j_2k_2 | JK \rangle D^k_{KM} (\hat{R})
\]

(239)

\[
= \sum_{K} \hat{T}_{JK} (j_1j_2) D^k_{KM} (\hat{R}).
\]

(240)

The operators \(|j_1m_1 \rangle |j_2m_2 \rangle\) constitute an orthonormal operator basis since

\[
\text{Tr}([|j_1m_1 \rangle |j_2m_2 \rangle]^{\dagger} [|j'_1m'_1 \rangle |j'_2m'_2 \rangle]) = \delta_{j_1j'_1} \delta_{j_2j'_2} \delta_{m_1m'_1} \delta_{m_2m'_2}
\]

(241)

and from the orthogonality relations of the CG coefficients we find

\[
\text{Tr}(\hat{T}_{JM} (j_1j_2) \hat{T}^{JM'} (j'_1j'_2)) = \sum_{m_1m_2} \langle j_1m_1j_2m_2 | JM \rangle \langle j_1m_1j_2m_2 | JM' \rangle = \delta_{JJ'} \delta_{MM'} \delta_{j_1j'_1} \delta_{j_2j'_2}.
\]

(242)

Thus, if we expand the operators \(\hat{A}\) and \(\hat{B}\) as

\[
\hat{A} = \sum_{JMj_1j_2} A_{JM} (j_1j_2) \hat{T}_{JM} (j_1j_2)
\]

(243)

\[
\hat{B} = \sum_{JMj_1j_2} B_{JM} (j_1j_2) \hat{T}_{JM} (j_1j_2)
\]

(244)

we find for the scalar product

\[
\text{Tr}(\hat{A}^{\dagger} \hat{B}) = \sum_{JMj_1j_2} A^*_{JM} (j_1j_2) B_{JM} (j_1j_2).
\]

(245)

This is our main result. The outcome of any experiment can be written as

\[
\text{Tr}(\hat{p}^{\dagger} \hat{T}) = \sum_{JMj_1j_2} \rho^*_{JM} (j_1j_2) T_{JM} (j_1j_2)
\]

(246)

Since the components of \(T\) are known for a given experiment, this equation shows immediately what information about the system, i.e., the density matrix \(\rho\) we can obtain.

Any operator that can be written as

\[
\hat{A}_{JM} = \sum_{j_1j_2} a_{j_1j_2} \hat{T}_{JM} (j_1j_2)
\]

(247)
is called an irreducible tensor operator. It rotates like
\[ \hat{R} \hat{A}_{JM} \hat{R}^\dagger = \sum_K \hat{A}_{JK} D^J_K(\hat{R}) \] (248)
and its matrix elements are
\[ \langle jm | \hat{A}_{JM} | jm' \rangle = a_{jj'}(\sqrt{2J+1})(-1)^{j-m} \left( \begin{array}{cccc} j & J & j' \\ -m & M & m' \end{array} \right) \] (249)
This result is known as the Wigner-Eckart theorem. The coefficient \( a_{jj'} \) is called the reduced matrix element and it is often written as \( \langle j || \hat{A} || j' \rangle \).

Gerrit C. Groenenboom, Nijmegen, November 1999

Appendix A: exercises

1. Derive the second equality sign in Eq. (22).
2. Show that \( N^3 = -N \) (Eq. 41).
3. Do the summation in Eq. (44).
4. Show that \( e^{-i\alpha \hat{p}} |x\rangle \), is an eigenfunction of \( \hat{x} \), using only the definition \( \hat{x} |x\rangle = x |x\rangle \) and the assumption that \( \hat{x} \) and \( \hat{p} \) are Hermitian operators with the commutation relation \([\hat{x}, \hat{p}] = i\). What is the eigenvalue?
5. Derive the following relations for the Levi-Civita tensor (Eq. 68)
\[
\begin{align*}
e_{ijk} e_{ij'k'} &= \delta_{jj'} \delta_{kk'} - \delta_{jk} \delta_{k'j'} \\
e_{ijk} e_{ij'k'} &= 2 \delta_{kk'} \\
e_{ijk} e_{ij'} &= 6,
\end{align*}
\] (250) (251) (252)
where we used Einstein summation convention: summation over repeated indices is implicit.
6. Show that
\[ \mathbf{x} \times (\mathbf{y} \times \mathbf{z}) = (\mathbf{x} \cdot \mathbf{z})\mathbf{y} - (\mathbf{x} \cdot \mathbf{y})\mathbf{z}. \] (253)
7. Using the last equation verify Eq. (64).
8. Derive Eq. (51). Hint: work out \( \det(U[xyz]) \) in two ways, or use the Levi-Civita tensor.
9. Show that
\[ B(t) = e^{tA} Be^{-tA} \] (254)
satisfies the equation
\[ B(0) = B, \quad \frac{d}{dt} B(t) = [A, B(t)] \] (255)
and therefore
\[ B(t) = B + \int_0^t d\tau [A, B(\tau)]. \] (256)
Solve the last equation by iteration to derive Eq. (60)
10. Show that \( \sum_{J_{1}+J_{2}=J_{1}^{+}+J_{2}^{+}}(2J+1) = (2j_{1} + 1)(2j_{2} + 1) \). Hint: draw a grid of points \((m_1, m_2)\) with \( m_1 = -j_1 \ldots j_1 \).
11. Compute the \( d^{2}(\beta) \) matrix [Eq. (121)].