Angular momentum theory and applications

Gerrit C. Groenenboom
Theoretical Chemistry, Institute for Molecules and Materials,
Radboud University Nijmegen, Heyendaalseweg 135,
6525 ED Nijmegen, The Netherlands, e-mail: gerritg@theochem.ru.nl
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`http://www.theochem.ru.nl/cgi-bin/dbase/search.cgi?Groenenboom:99`

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.*

Contents

I. ROTATIONS

Angular momentum theory is the theory of rotations. We discuss the rotation of vectors in $\mathcal{R}^3$, 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.,

$$\hat{R}(\vec{x}+\vec{y}) = \hat{R}\vec{x} + \hat{R}\vec{y}, \quad \hat{R}\lambda\vec{x} = \lambda\hat{R}\vec{x} \;\text{ for all } \vec{x},\vec{y} \in \mathcal{V}. \tag{1}$$

We introduce an orthonormal basis $\{\vec{e}_1, \vec{e}_2, \dots, \vec{e}_n\}$ so that we have

$$(\vec{e}_i, \vec{e}_j) = \delta_{ij}, \quad \vec{x} = \sum_i x_i \vec{e}_i, \quad x_i = (\vec{e}_i, \vec{x}). \tag{2}$$

We define the column vector $\mathbf{x} = (x_1, x_2, \dots, x_n)^T$, so that

$$\vec{y} = \hat{R}\vec{x}, \quad y_i = \sum_j R_{ij} x_j, \quad R_{ij} = (\vec{e}_i, \hat{R}\vec{e}_j), \quad \mathbf{y} = R\mathbf{x}. \tag{3}$$

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 $(R_1R_2)R_3 = R_1(R_2R_3)$.

- Rotations form a group:
  - The product of two rotations is again a rotation, $R_1R_2 = R_3$.
  - There is one identity element $R = I$.
  - For every rotation R there is an inverse R^{-1} such that $RR^{-1} = R^{-1}R = I$.
- 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

$$R(\omega_1) = R(\omega_2)R(\omega_3) \tag{4}$$

  we can express the parameters ω_1 as analytic functions of ω_2 and ω_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

$$(R\mathbf{x}, R\mathbf{y}) = (\mathbf{x}, \mathbf{y}), \quad \text{for all } \mathbf{x} \text{ and } \mathbf{y}. \tag{5}$$

  The *adjoint* or Hermitian conjugate $A^\dagger$ of a linear operator A is defined by

$$(A\mathbf{x}, \mathbf{y}) = (\mathbf{x}, A^\dagger\mathbf{y}), \quad \text{for all } \mathbf{x} \text{ and } \mathbf{y}. \tag{6}$$

  For the matrix elements of $A^\dagger$ we have

$$(A^\dagger)_{ij} = A^*_{ji}. \tag{7}$$

  Hence, for a rotation matrix we have

$$(R\mathbf{x}, R\mathbf{y}) = (\mathbf{x}, R^\dagger R\mathbf{y}) = (\mathbf{x}, \mathbf{y}), \tag{8}$$

  i.e., $R^\dagger R = I$, and $R^\dagger = R^{-1}$. For the determinant we find

$$\det(R^\dagger R) = \det(R)^* \det(R) = \det(I) = 1, \quad |\det(R)| = 1. \tag{9}$$

  By definition rotations have a determinant of +1.
- In $\mathcal{R}^3$ there is exactly one such group with the above properties and it is called $SO(3)$, the special (determinant is +1) orthogonal group of $\mathcal{R}^3$. In 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 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

$$R(\epsilon) = I + \epsilon N. \tag{10}$$

Since $R^\dagger R = I$ we have

$$(I + \epsilon N)^\dagger (I + \epsilon N) = I + \epsilon(N^\dagger + N) + \epsilon^2 N^\dagger N = I, \tag{11}$$

thus, for small ϵ

$$N^\dagger + N = 0, \quad N^\dagger = -N. \tag{12}$$

The matrix N is said to be *antihermitian*, $N^*_{ij} = -N_{ji}$. In $\mathcal{R}^3$ we may write

$$N = \begin{bmatrix} 0 & -n_3 & n_2 \\ n_3 & 0 & -n_1 \\ -n_2 & n_1 & 0 \end{bmatrix}. \tag{13}$$

The signs of the parameters are of course arbitrary, but with the above choice we have

$$N\mathbf{x} = \begin{bmatrix} n_2 x_3 - n_3 x_2 \\ n_3 x_1 - n_1 x_3 \\ n_1 x_2 - n_2 x_1 \end{bmatrix} = \mathbf{n} \times \mathbf{x}. \tag{14}$$

For small rotations we thus have

$$\mathbf{x}' = R(\mathbf{n}, \epsilon)\mathbf{x} = \mathbf{x} + \epsilon \mathbf{n} \times \mathbf{x}. \tag{15}$$

Clearly, the vector $\mathbf{n}$ is invariant under this rotation

$$R(\mathbf{n}, \epsilon)\mathbf{n} = \mathbf{n} + \epsilon \mathbf{n} \times \mathbf{n} = \mathbf{n}. \tag{16}$$

For the product of two small rotations around the same vector $\mathbf{n}$ we have

$$R(\mathbf{n}, \epsilon_1) R(\mathbf{n}, \epsilon_2) = (I + \epsilon_1 N)(I + \epsilon_2 N) \tag{17}$$

$$= I + (\epsilon_1 + \epsilon_2) N + \epsilon_1 \epsilon_2 N^2 \tag{18}$$

$$\approx R(\mathbf{n}, \epsilon_1 + \epsilon_2). \tag{19}$$

We now define non-infinitesimal rotations by requiring for *arbitrary* ϕ_1 and ϕ_2 that

$$R(\mathbf{n}, \phi_1) R(\mathbf{n}, \phi_2) = R(\mathbf{n}, \phi_1 + \phi_2). \tag{20}$$

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":

$$R(\mathbf{n}, \phi) = R(\mathbf{n}, \phi/k)^k. \tag{21}$$

By taking the limit for $k \to \infty$ and using the explicit expression for an infinitesimal rotation we get (see also Appendix A)

$$R(\mathbf{n}, \phi) = \lim_{k \to \infty} (I + \frac{\phi}{k} N)^k = \sum_{k=0}^{\infty} \frac{1}{k!} (\phi N)^k = e^{\phi N}. \tag{22}$$

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 ϕ_1 at $\phi_1 = 0$ to obtain the differential equation

$$\frac{d}{d\phi_1} R(\mathbf{n}, \phi_1)|_{\phi_1 = 0} R(\mathbf{n}, \phi_2) = \frac{d}{d\phi_1} R(\mathbf{n}, \phi_1 + \phi_2)|_{\phi_1 = 0} = \frac{d}{d\phi_2} R(\mathbf{n}, \phi_2), \tag{23}$$

with $\frac{d}{d\phi_1} R(\mathbf{n}, \phi_1) = N$ this gives

$$\frac{d}{d\phi} R(\mathbf{n}, \phi) = N R(\mathbf{n}, \phi). \tag{24}$$

Solving this equation with the initial condition $R(\mathbf{n}, 0) = I$ again gives $R(\mathbf{n}, \phi) = e^{\phi N}$.

B. Computing $e^{\phi N}$

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 $L_{\mathbf{n}} = iN$, which is easily verified to be Hermitian

$$L^\dagger = (iN)^\dagger = -i(-N) = L. \tag{25}$$

Thus, we have

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

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

$$L\mathbf{u}_i = \lambda_i \mathbf{u}_i. \tag{27}$$

This may be written in matrix notation

$$LU = U\Lambda, \;\; U = [\mathbf{u}_1 \mathbf{u}_2 \ldots \mathbf{u}_n], \;\; \Lambda_{ij} = \lambda_i \delta_{ij}. \tag{28}$$

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

$$L = U\Lambda U^\dagger. \tag{29}$$

If a function f is defined by its series expansion

$$f(x) = \sum_k f_k x^k \tag{30}$$

we have

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

For the diagonal matrix Λ we simply have

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

Thus after computing the eigenvectors $\mathbf{u}_i$ and eigenvalues λ_i of L we have

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

Note that the eigenvalues of $R(\mathbf{n}, \phi)$ are $e^{-i\phi\lambda_k}$. Since the λ_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 $\mathbf{u}$ of some unitary matrix U with eigenvalue λ we have

$$(U\mathbf{u}, U\mathbf{u}) = (\lambda\mathbf{u}, \lambda\mathbf{u}) = \lambda^*\lambda(\mathbf{u}, \mathbf{u}) = (\mathbf{u}, \mathbf{u}), \;\; \text{i.e., } |\lambda| = 1.. \tag{34}$$

Note that $R(\mathbf{n}, \phi)\mathbf{n} = \mathbf{n}$. This does not yet prove that any R can be generated by an infinitesimal rotation. Since R is real for every complex eigenvalue λ there must be an eigenvalue λ^*. 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 $\mathbf{n}$.

C. Adding the series expansion

As an alternative approach we may start from

$$e^{\phi N} = \sum_{k=0}^{\infty} \frac{1}{k!} (\phi N)^k. \tag{35}$$

From Eq. (27) it follows that

$$N\mathbf{u}_k = -i\lambda_k \mathbf{u}_k \equiv \alpha_k \mathbf{u}_k. \tag{36}$$

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 $A(N)$

$$A(N) = (N - \alpha_1 I)(N - \alpha_2 I)(N - \alpha_3 I). \tag{37}$$

It is easily verified that for any eigenvector $\mathbf{u}_k$ we have

$$A(N)\mathbf{u}_k = 0. \tag{38}$$

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 $\mathcal{R}^3$. Thus, the polynomial $A(N)$ is referred to as a annihilating polynomial. Expanding $A(N)$ gives

$$A(N) = N^3 + c_2 N^2 + c_1 N + c_0 I = 0, \tag{39}$$

where the coefficients c_k can easily be expressed as functions of the eigenvalues α_k. We now observe that N^3 may be expressed as a linear combination of lower powers of N:

$$N^3 = -c_2 N^2 - c_1 N - c_0 I \tag{40}$$

From this equation we may directly compute the coefficients c_k, without knowing the eigenvalues α_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 C^n there exist an annihilating polynomial of degree n. It can always be found be plugging the matrix A back into the characteristic polynomial $P(\lambda) \equiv \det(A - \lambda I)$. In this case we have (see Appendix A)

$$N^3 = -N. \tag{41}$$

so that

$$N^{2k+1} = (-1)^k N \quad \text{for } k \geq 0 \tag{42}$$

$$N^{2k+2} = (-1)^k N^2 \quad \text{for } k \geq 1. \tag{43}$$

As a consequence, the infinite sum simplifies to

$$e^{\phi N} = I + \sum_{k=1}^{\infty} \frac{1}{k!} \phi^k N^k = I + \sin\phi N + (1 - \cos\phi) N^2. \tag{44}$$

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

$$\sum_k \mathbf{e}_k x_k = \sum_k \mathbf{b}_k x'_k, \quad \mathbf{x} = B\mathbf{x}'. \tag{45}$$

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:

$$(\mathbf{b}_i, A'\mathbf{b}_j) = A_{ij}, \quad B^\dagger A' B = A. \tag{46}$$

Using the unitarity of B we get

$$A' = BAB^\dagger. \tag{47}$$

Using this definition we may also transform any function of A defined by its series expansion

$$f(A)' = Bf(A)B^\dagger = B(\sum_k f_k A^k)B^\dagger = \sum_k f_k(BA^kB^\dagger) = \sum_k f_k(A')^k = f(A'). \tag{48}$$

As an example we consider the transformation of a rotation operator

$$R' = BR(\mathbf{n},\phi)B^\dagger = Be^{\phi N}B^\dagger = e^{\phi BNB^\dagger}. \tag{49}$$

We work out the exponent by considering

$$BNB^\dagger \mathbf{x} = B(\mathbf{n} \times B^\dagger \mathbf{x}) \tag{50}$$

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

$$U\mathbf{x} \times U\mathbf{y} = \det(U)U(\mathbf{x} \times \mathbf{y}) \tag{51}$$

so that we have

$$B(\mathbf{n} \times B^\dagger \mathbf{x}) = (B\mathbf{n}) \times (BB^\dagger \mathbf{x}) = (B\mathbf{n}) \times \mathbf{x} \equiv N_{B\mathbf{n}}\mathbf{x} \tag{52}$$

Thus, with the notation $N_\mathbf{n} = N$,

$$BN_\mathbf{n}B^\dagger = N_{B\mathbf{n}} \tag{53}$$

and for the transformed rotation

$$BR(\mathbf{n},\phi)B^\dagger = e^{\phi BN_\mathbf{n}B^\dagger} = R(B\mathbf{n},\phi). \tag{54}$$

E. Vector operators

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

$$N = \begin{bmatrix} 0 & -n_3 & n_2 \\ n_3 & 0 & -n_1 \\ -n_2 & n_1 & 0 \end{bmatrix} = n_1 \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} + n_2 \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix} + n_3 \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{55}$$

$$= n_1N_1 + n_2N_2 + n_3N_3 = \mathbf{n} \cdot \underline{N}, \tag{56}$$

where we introduced the vector operator $\underline{N}$. The components of the vector operator transform as

$$BN_jB^\dagger = BN_{\mathbf{e}_j}B^\dagger = N_{B\mathbf{e}_j} = N_{\mathbf{b}_j} = \mathbf{b}_j \cdot \underline{N} = \sum_i N_i B_{ij}. \tag{57}$$

We also define the Hermitian vector operator $\underline{L} = i\underline{N}$ for which we also have

$$BL_jB^\dagger = \sum_i L_i B_{ij} \tag{58}$$

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

$$e^{-i\phi\mathbf{n}\underline{L}}L_je^{i\phi\mathbf{n}\underline{L}} = \sum_i L_i R_{ij}(\mathbf{n},\phi) \tag{59}$$

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

$$e^ABe^{-A} = \sum_{k=0}^{\infty} \frac{1}{k!}[A,B]_k, \tag{60}$$

where the repeated commutator $[A,B]_k$ is defined by

$$\begin{aligned} [A,B]_0 &= B \\ [A,B]_1 &= [A,B] = AB - BA \qquad (61) \\ [A,B]_k &= [A,[A,B]_{k-1}]. \qquad (62) \end{aligned}$$

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

$$\hat{R}(\mathbf{n},\phi)\hat{\mathbf{j}}\hat{R}^\dagger(\mathbf{n},\phi) = R^T(\mathbf{n},\phi)\hat{\mathbf{j}}. \qquad (63)$$

The commutation relations of two arbitrary antihermitian matrices $N_\mathbf{a}$ and $N_\mathbf{b}$ follow from a property of the cross product (see appendix A)

$$\mathbf{x}\times(\mathbf{y}\times\mathbf{z}) + \mathbf{y}\times(\mathbf{z}\times\mathbf{x}) + \mathbf{z}\times(\mathbf{x}\times\mathbf{y}) = 0. \qquad (64)$$

Using the property $\mathbf{x}\times\mathbf{y} = -\mathbf{y}\times\mathbf{x}$ we find

$$\mathbf{a}\times(\mathbf{b}\times\mathbf{x}) - \mathbf{b}\times(\mathbf{a}\times\mathbf{x}) - (\mathbf{a}\times\mathbf{b})\times\mathbf{x} = 0. \qquad (65)$$

In matrix notation this gives

$$N_\mathbf{a}N_\mathbf{b}\mathbf{x} - N_\mathbf{b}N_\mathbf{a}\mathbf{x} - N_{\mathbf{a}\times\mathbf{b}}\mathbf{x} = 0. \qquad (66)$$

Since this holds for any $\mathbf{x}$ we obtain the commutation relation

$$[N_\mathbf{a}, N_\mathbf{b}] = N_{\mathbf{a}\times\mathbf{b}}. \qquad (67)$$

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),

$$\mathbf{e}_i \times \mathbf{e}_j = \sum_k e_{ijk}\mathbf{e}_k, \qquad (68)$$

so that we can write the commutation relations for the components of the vector operator $\underline{N}$ as

$$[N_i, N_j] = \sum_k e_{ijk} N_k. \qquad (69)$$

From this equation we immediately find the commutation relations for the Hermitian operators L_i as

$$[L_i, L_j] = \sum_k i e_{ijk} L_k. \qquad (70)$$

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 $SU(2)$,

$$\sigma_1 = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_2 = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_3 = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \qquad (71)$$

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

$$R = R(\mathbf{e}_3', \gamma) R_1, \tag{72}$$

where R_1 may be *any* rotation for which $\mathbf{e}_3' = R_1 \mathbf{e}_3$. If the polar angles of $\mathbf{e}_3'$ are (β, α) we can take

$$R_1 = R(\mathbf{e}_3, \alpha) R(\mathbf{e}_2, \beta). \tag{73}$$

Thus, any rotation R can be written as

$$R(\alpha, \beta, \gamma) = R(R_1 \mathbf{e}_3, \gamma) R_1 = R_1 R(\mathbf{e}_3, \gamma) R_1^\dagger R_1, \tag{74}$$

so that and

$$R(\alpha, \beta, \gamma) = R(\mathbf{e}_3, \alpha) R(\mathbf{e}_2, \beta) R(\mathbf{e}_3, \gamma) \tag{75}$$

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

$$0 \leq \alpha < 2\pi, \; 0 \leq \beta < \pi, \; 0 \leq \gamma < 2\pi. \tag{76}$$

For the inverse we have

$$R(\alpha, \beta, \gamma)^{-1} = R(\mathbf{e}_3, -\gamma) R(\mathbf{e}_2, -\beta) R(\mathbf{e}_3, -\alpha). \tag{77}$$

We may bring $-\beta$ back into the range $[0, \pi]$ by inserting $R(\mathbf{e}_3, \pi) R(\mathbf{e}_3, -\pi)$ at both sides of $R(\mathbf{e}_2, -\beta)$twice and by using the relation

$$R(\mathbf{e}_3, -\pi) R(\mathbf{e}_2, -\beta) R(\mathbf{e}_3, \pi) = R(-\mathbf{e}_2, -\beta) = R(\mathbf{e}_2, \beta), \tag{78}$$

which gives

$$R(\alpha, \beta, \gamma)^{-1} = R(\mathbf{e}_3, -\gamma + \pi) R(\mathbf{e}_2, \beta) R(\mathbf{e}_3, -\alpha - \pi). \tag{79}$$

We may also define a volume element for integration

$$d\tau = d\alpha \, \sin\beta d\beta \, d\gamma, \tag{80}$$

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 $\mathcal{R}^3$ to the rotation of one particle wave functions $(\Psi(\mathbf{x}))$ by Wigner's convention

$$(\hat{R}\Psi)(\mathbf{x}) \equiv \Psi(R^{-1}\mathbf{x}). \tag{81}$$

Usually, Ψ will be an element of some Hilbert space. For our purposes it is sufficient to think of Ψ 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 $(\hat{\ })$ to distinguish the operators on $\mathcal{V}$ from the corresponding operators in $\mathcal{R}^3$.

The inverse in the definition is important since it gives

$$\hat{R}_1(\hat{R}_2\Psi) = (\hat{R}_1\hat{R}_2)\Psi. \tag{82}$$

This is readily verified:

$$[\hat{R}_1(\hat{R}_2\Psi)](\mathbf{x}) = (\hat{R}_2\Psi)(\hat{R}_1^{-1}\mathbf{x}) = \Psi(\hat{R}_2^{-1}\hat{R}_1^{-1}\mathbf{x}) = \Psi[(\hat{R}_1\hat{R}_2)^{-1}\mathbf{x}] = [(\hat{R}_1\hat{R}_2)\Psi](\mathbf{x}). \tag{83}$$

Note that Wigner's convention is consistent with Dirac notation

$$\Psi(\mathbf{x}) = \langle \mathbf{x}|\Psi\rangle, \;\; \langle \mathbf{x}|R\Psi\rangle = \langle R^{\dagger}\mathbf{x}|\Psi\rangle = \langle R^{-1}\mathbf{x}|\Psi\rangle. \tag{84}$$

For small rotations we have

$$\hat{R}(\mathbf{n},\epsilon)\Psi(\mathbf{x}) = \Psi(\mathbf{x} - \epsilon\mathbf{n}\times\mathbf{x}). \tag{85}$$

To first order in ϵ we have in general

$$f(\mathbf{x}+\epsilon\mathbf{y}) = f(\mathbf{x}) + \sum_k \epsilon y_k \frac{\partial}{\partial x_k} f(\mathbf{x}) \equiv f(\mathbf{x}) + \epsilon\mathbf{y}\cdot\nabla f(\mathbf{x}), \tag{86}$$

so that we may write

$$f(\mathbf{x}-\epsilon\mathbf{n}\times\mathbf{x}) = [1-\epsilon(\mathbf{n}\times\mathbf{x})\cdot\nabla]f(\mathbf{x}). \tag{87}$$

Using $\mathbf{n}\times\mathbf{x}\cdot\nabla = e_{ijk}n_i x_j \nabla_k = \mathbf{n}\cdot\mathbf{x}\times\nabla$ we find

$$\hat{R}(\mathbf{n},\epsilon) = 1 - \epsilon\mathbf{n}\cdot\mathbf{x}\times\nabla = 1 - i\epsilon\mathbf{n}\cdot\underline{\hat{L}}, \tag{88}$$

where we defined

$$\mathbf{p} \;\equiv\; -i\nabla \tag{89}$$

$$\underline{\hat{L}} \;\equiv\; \mathbf{x}\times\mathbf{p}. \tag{90}$$

Using integration by parts, and assuming that the surface term vanishes, it is easy to show that the operators ∇_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 $\hat{L}_k$ are Hermitian and that they satisfy the commutation relations

$$[\hat{L}_i, \hat{L}_j] = i\sum_k e_{ijk}\hat{L}_k. \tag{91}$$

We may now follow the same procedure as before to find the expression for a non-infinitesimal rotation

$$\hat{R}(\mathbf{n},\phi) = e^{-i\phi\mathbf{n}\cdot\underline{\hat{L}}}. \tag{92}$$

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

$$D_{ij}(\hat{R}) = \langle i|\hat{R}|j\rangle. \tag{93}$$

We also use the notation $D(\mathbf{n},\phi) = D[\hat{R}(\mathbf{n},\phi)]$. The unitary matrices $D(\hat{R})$ are a representation of $SO(3)$, since

$$R(\mathbf{n}_1,\phi_1)R(\mathbf{n}_2,\phi_2) = R(\mathbf{n}_3,\phi_3) \tag{94}$$

implies

$$D(\mathbf{n}_1,\phi_1)D(\mathbf{n}_2,\phi_2) = D(\mathbf{n}_3,\phi_3). \tag{95}$$

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 $\mathcal{V}$ into a subspace $\mathcal{S}$ and its orthogonal complement $\mathcal{T}$, i.e. $\mathcal{S}\oplus\mathcal{T} = \mathcal{V}$, such that for all $\Psi\in S$ and for all $\hat{R}(\mathbf{n},\phi)$ 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 $\hat{R}(\mathbf{n}, \phi)$

$$[\hat{A}, \hat{R}(\mathbf{n}, \phi)] = 0. \tag{96}$$

Let S_λ be the space spanned by all eigenvectors f_i with eigenvalue λ

$$\hat{A} f_i = \lambda f_i. \tag{97}$$

For each each $f \in S_\lambda$ we find that $g = \hat{R} f$ also has eigenvalue λ

$$\hat{A} g = \hat{A}\hat{R} f = \hat{R}\hat{A} f = \lambda g, \tag{98}$$

i.e., $g \in S_\lambda$, which shows that S_λ 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

$$\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2 \tag{99}$$

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

$$[\hat{j}_i, \hat{j}_j] = i \sum_k \epsilon_{ijk} \hat{j}_k \tag{100}$$

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

$$|j, m\rangle, \quad m = -j, \ldots, j, \tag{101}$$

with

$$\hat{j}^2 |j, m\rangle = j(j+1) |j, m\rangle, \tag{102}$$

$$\hat{j}_3 |j, m\rangle = m |j, m\rangle, \tag{103}$$

$$\hat{j}_\pm |j, m\rangle = C_\pm(j, m) |j, m \pm 1\rangle, \tag{104}$$

with

$$\hat{j}_\pm = \hat{j}_1 \pm i \hat{j}_2 \tag{105}$$

$$C_\pm(j, m) = \sqrt{j(j+1) - m(m \pm 1)}. \tag{106}$$

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 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 $\hat{j}_+^\dagger = \hat{j}_-$, the ket $|a, b+k+1\rangle$ with norm

$$\langle a, b+k | \hat{j}_- \hat{j}_+ | a, b+k\rangle = [a^2 - (b+k)(b+k+1)] \langle a, b+k | a, b+k\rangle. \tag{107}$$

  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 $2b = l-k$, 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 $\hat{j}_\pm|j,m\rangle$ 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

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

$$\langle jm'|\hat{j}_1|jm\rangle = \frac{1}{2}\left[C_+(j,m)\delta_{m',m+1} + C_-(j,m)\delta_{m',m-1}\right] \tag{109}$$

$$\langle jm'|\hat{j}_2|jm\rangle = -i\frac{1}{2}\left[C_+(j,m)\delta_{m',m+1} - C_-(j,m)\delta_{m',m-1}\right] \tag{110}$$

$$\langle jm'|\hat{j}_3|jm\rangle = m\delta_{m'm}. \tag{111}$$

A. Rotation matrices

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

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

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

$$D^j_{k,m}(\mathbf{n},\phi) \equiv \langle jk|\hat{R}(\mathbf{n},\phi)|jm\rangle. \tag{113}$$

Thus, for a rotated vector we have

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

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:

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

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 $D^j_{m,k}(\hat{R})$ 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:

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

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 I B it is straightforward to derive

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

To find $D^j(\mathbf{e}_2,\beta)$ we must exponentiate $-i\beta\hat{j}_2^{(j)}$, where $\hat{j}_2^{(j)}$ is the matrix representation of $\hat{j}_2$ 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^j_{jj} element in the upper left corner we find

$$\begin{aligned} d^0(\beta) &= 1 & (120)\\ d^{\frac{1}{2}}(\beta) &= \begin{pmatrix} \cos\frac{\beta}{2} & -\sin\frac{\beta}{2} \\ \sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix} & (121)\\ d^1(\beta) &= \begin{pmatrix} \frac{1+\cos\beta}{2} & -\frac{\sin\beta}{\sqrt{2}} & \frac{1-\cos\beta}{2} \\ \frac{\sin\beta}{\sqrt{2}} & \cos\beta & -\frac{\sin\beta}{\sqrt{2}} \\ \frac{1-\cos\beta}{2} & \frac{\sin\beta}{\sqrt{2}} & \frac{1+\cos\beta}{2} \end{pmatrix}. & (122) \end{aligned}$$

There is also a general formula:

$$d^j_{km}(\beta) = [(j+k)!(j-k)!(j+m)!(j-m)!]^{\frac{1}{2}} \sum_s \frac{(-1)^{k-m+s}(\cos\frac{\beta}{2})^{2j+m-k-2s}(\sin\frac{\beta}{2})^{k-m+2s}}{(j+m-s)!s!(k-m+s)!(j-k-s)!}, \tag{123}$$

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

$$D(-\gamma, -\beta, -\alpha) = D(-\gamma+\pi, \beta, -\alpha-\pi). \tag{124}$$

For $\alpha = \gamma = 0$ this gives

$$d^j_{mk}(-\beta) = e^{-im\pi} d^j_{mk}(\beta) e^{ik\pi} = (-1)^{m-k} d^j_{mk}(\beta). \tag{125}$$

Note that $m-k$ must be integer, hence $(-1)^{-m+k} = (-1)^{m-k}$. Since d^j is real

$$d^j_{mk}(-\beta) = d^j_{km}(\beta) = (-1)^{m-k} d^j_{mk}(\beta). \tag{126}$$

From the explicit formula for the d^j matrix we see

$$d^j_{km}(\beta) = d^j_{-m,-k}(\beta). \tag{127}$$

From the last two equation we derive

$$D^{j,*}_{km}(\hat{R}) = (-1)^{k-m} D^j_{-k,-m}(\hat{R}). \tag{128}$$

If j and j' are both either integer or half integer, the D matrices satisfy the following orthogonality relations

$$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma\, D^{j,*}_{mk}(\alpha,\beta,\gamma) D^{j'}_{m'k'}(\alpha,\beta,\gamma) = \frac{8\pi^2}{2j+1}\delta_{mm'}\delta_{kk'}\delta_{jj'}. \tag{129}$$

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 α and γ.

From Eq. (116) we know that $D^{j,*}_{mk}(\alpha, \beta\,\gamma)$ transforms as $|jm\rangle$. For $k = 0$ (and thus, necessarily $j = l$ is integer) we define

$$C_{lm}(\theta,\phi) = D^{l,*}_{m0}(\phi,\theta,0), \tag{130}$$

which are spherical harmonics in Racah normalization. From Eq. (129) we find

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta C^*_{lm}(\theta,\phi) C_{l'm'}(\theta,\phi) = \frac{4\pi}{2l+1}\delta_{mm'}\delta_{ll'}. \tag{131}$$

Thus, the relation with spherical harmonics in the standard normalization is

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}} C_{lm}(\theta,\phi). \tag{132}$$

Also setting m to zero gives us Legendre polynomials

$$P_l(\cos\theta) = d^l_{00}(\theta) = C_{l0}(\theta,\phi). \tag{133}$$

We also define the regular harmonics,

$$R_{lm}(\mathbf{r}) = r^l C_{lm}(\hat{r}), \tag{134}$$

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

$$R_{0,0}(\mathbf{r}) = 1 \tag{135}$$
$$R_{1,1}(\mathbf{r}) = -\frac{1}{\sqrt{2}}(x+iy) \equiv r_{+1} \tag{136}$$
$$R_{1,0}(\mathbf{r}) = z \equiv r_0 \tag{137}$$
$$R_{1,-1}(\mathbf{r}) = \frac{1}{\sqrt{2}}(x-iy) \equiv r_{-1}. \tag{138}$$

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

$$\tilde{\mathbf{r}} \equiv \begin{bmatrix} r_+ \\ r_0 \\ r_- \end{bmatrix} = \sqrt{\frac{1}{2}} \begin{bmatrix} -1 & -i & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & -i & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \equiv S^T\mathbf{r}. \tag{139}$$

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

$$\mathbf{r} \equiv R(\mathbf{n},\phi)\mathbf{r}', \ \Rightarrow \mathbf{r}'^T = \mathbf{r}^T R(\mathbf{n},\phi) \tag{140}$$

and for the spherical components we find

$$\hat{R}(\mathbf{n},\phi) R_{lm}(\mathbf{r}) = R_{lm}[R(\mathbf{n},\phi)^{-1}\mathbf{r}] = R_{lm}(\mathbf{r}') = \sum_k R_{lk}(\mathbf{r}) D^l_{km}(\mathbf{n},\phi). \tag{141}$$

For $l = 1$ this gives $\tilde{\mathbf{r}}'^T = \tilde{\mathbf{r}}^T D^1(\mathbf{n},\phi)$, so that

$$\tilde{\mathbf{r}}'^T = \mathbf{r}'^T S = \mathbf{r}^T R S = \mathbf{r}^T S D^1, \tag{142}$$

which gives

$$R = S D^1 S^\dagger. \tag{143}$$

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 $\hat{J}^{(1)}_\mu = \sum_i \hat{J}_i S_{i\mu}$, with $\mu = +1, 0, -1$, i.e.,

$$\hat{J}^{(1)}_{+1} = -\sqrt{\frac{1}{2}}(\hat{J}_1 + i\hat{J}_2) \tag{144}$$
$$\hat{J}^{(1)}_0 = \hat{J}_3 \tag{145}$$
$$\hat{J}^{(1)}_{-1} = \sqrt{\frac{1}{2}}(\hat{J}_1 - i\hat{J}_2) \tag{146}$$

we obtain

$$\hat{R}(\mathbf{n},\phi)\hat{J}^{(1)}_m \hat{R}(\mathbf{n},\phi)^\dagger = \sum_k \hat{J}^{(1)}_k D^1_{km}(\mathbf{n},\phi). \tag{147}$$

III. VECTOR COUPLING

In quantum chemistry one usually writes a two electron wave function as, e.g., $\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)-\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$. 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 $\mathcal{V}_1$ and $\mathcal{V}_2$ with dimensions n_1, n_2, the tensor product space $\mathcal{V}_1\otimes\mathcal{V}_2$ is a $n_1\times n_2$ dimensional linear space which contains the tensor products $f\otimes g$, with $f\in\mathcal{V}_1$ and $g\in\mathcal{V}_2$. For a complete definition me must point out when two elements of $\mathcal{V}_1\otimes\mathcal{V}_2$ are the same:

$$(\lambda f)\otimes g = f\otimes(\lambda g)=\lambda(f\otimes g) \tag{148}$$
$$(f+g)\otimes h = f\otimes h+g\otimes h \tag{149}$$
$$f\otimes(g+h) = f\otimes g+f\otimes h. \tag{150}$$

For linear operators $\hat{A}$ and $\hat{B}$ defined on $\mathcal{V}_1$ and $\mathcal{V}_2$, respectively, we define

$$(\hat{A}\otimes\hat{B})(f\otimes g)=(\hat{A}f)\otimes(\hat{B}g). \tag{151}$$

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 $\mathcal{V}_1$ and $\mathcal{V}_2$ by

$$(f_1\otimes g_1, f_2\otimes g_2)=(f_1,f_2)(g_1,g_2). \tag{152}$$

If we have an orthonormal basis $\{\mathbf{e}_i, i=1,\ldots,n_1\}$ on $\mathcal{V}_1$ and an orthonormal basis $\{\mathbf{f}_i, i=1,\ldots,n_2\}$ then $\mathbf{e}_i\otimes\mathbf{f}_j, i=1,\ldots,n_1; j=1,\ldots,n_2\}$ forms an orthonormal basis for $\mathcal{V}_1\otimes\mathcal{V}_2$. Clearly, we have

$$(\mathbf{e}_i\otimes\mathbf{f}_j,\mathbf{e}_{i'}\otimes\mathbf{f}_{j'})=(\mathbf{e}_i,\mathbf{e}_{i'})(\mathbf{f}_j,\mathbf{f}_{j'})=\delta_{ii'}\delta_{jj'}. \tag{153}$$

If the matrix elements $A_{ij}=(\mathbf{e}_i,\hat{A}\mathbf{e}_j)$ and $B_{ij}=(\mathbf{f}_i,\hat{B}\mathbf{f}_j)$ are known, we can easily compute the matrix elements of the tensor product $\hat{A}\otimes\hat{B}$ in the tensor product basis

$$(\mathbf{e}_i\otimes\mathbf{f}_j,[\hat{A}\otimes\hat{B}]\mathbf{e}_{i'}\otimes\mathbf{f}_{j'})=(\mathbf{e}_i\otimes\mathbf{f}_j,\hat{A}\mathbf{e}_{i'}\otimes\hat{B}\mathbf{f}_{j'})=(\mathbf{e}_i,\hat{A}\mathbf{e}_{i'})(\mathbf{f}_j,\hat{B}\mathbf{f}_{j'})=A_{ii'}B_{jj'}. \tag{154}$$

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

$$(\hat{A}\otimes\hat{I}+\hat{I}\otimes\hat{B})(f_i\otimes g_j)=\hat{A}f_i\otimes\hat{I}g_j+\hat{I}f_i\otimes\hat{B}g_j=\lambda_i f_i\otimes g_j+\mu_j f_i\otimes g_j=(\lambda_i+\mu_j)f_i\otimes g_j, \tag{155}$$

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

$$[\hat{A}\otimes\hat{I},\hat{I}\otimes\hat{B}]=0 \tag{156}$$

and so we have

$$e^{\hat{A}\otimes\hat{I}+\hat{I}\otimes\hat{B}}=e^{\hat{A}}\otimes e^{\hat{B}}. \tag{157}$$

A. An irreducible basis for the tensor product space

Let us assume that $\mathcal{V}^{j_1}$ and $\mathcal{V}^{j_2}$ are spaces spanned by the bases $\{|j_1,m_1\rangle, m_1=-j_1,\ldots,j_1\}$ and $\{|j_2,m_2\rangle, m_2=-j_2,\ldots,j_2\}$, 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

$$\hat{J}_i\equiv\hat{j}_i\otimes\hat{1}+\hat{1}\otimes\hat{j}_i,\ \ i=1,2,3 \tag{158}$$

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

$$|j_1m_1j_2m_2\rangle\equiv|j_1m_1\rangle\otimes|j_2m_2\rangle,\ m_1=-j_1,\ldots,j_1;\ m_2=-j_2,\ldots,j_2. \tag{159}$$

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 $|(j_1 j_2)JM\rangle, M = -J, \ldots, J$, 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

$$|(j_1 j_2)JM\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 m_1 j_2 m_2\rangle C^{JM}_{m_1 m_2}(j_1 j_2). \tag{160}$$

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 $\langle j_1 m_1 j_2 m_2 | (j_1 j_2)JM\rangle$ which is usually simplified to $\langle j_1 m_1 j_2 m_2 | JM\rangle$.

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 $|(j_1 j_2)JJ-1\rangle$, 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

$$|(j_1 j_2)JM\rangle, J = |j_1 - j_2|, \ldots, j_1 + j_2, \quad M = -J, \ldots, J. \tag{161}$$

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

$$\sum_{m1,m2} \langle JM | j_1 m_1 j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | J'M'\rangle = \delta_{JJ'}\delta_{MM'} \tag{162}$$

$$\sum_{J,M} \langle j_1 m_1 j_2 m_2 | JM\rangle \langle JM | j_1 m_1' j_2 m_2'\rangle = \delta_{m_1 m_1'}\delta_{m_2 m_2'} \tag{163}$$

and we may invert Eq. (160)

$$|j_1 m_1 j_2 m_2\rangle = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} |(j_1 j_2)JM\rangle \langle JM | j_1 m_1 j_2 m_2\rangle. \tag{164}$$

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

$$\hat{J}_\pm |(j_1 j_2)JM\rangle = |(j_1 j_2)JM \pm 1\rangle C^\pm_{JM} \tag{165}$$

$$= \sum_{m_1 m_2} |j_1 m_1\rangle |j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | JM \pm 1\rangle C^\pm_{JM} \tag{166}$$

and on the right hand side

$$\sum_{m_1 m_2} \hat{J}_\pm |j_1 m_1\rangle |j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | JM\rangle \tag{167}$$

$$= \sum_{m_1 m_2} \left[|j_1 m_1 \pm 1\rangle |j_2 m_2\rangle C^\pm_{j_1 m_1} + |j_1 m_1\rangle |j_2 m_2 \pm 1\rangle C^\pm_{j_2 m_2} \right] \langle j_1 m_1 j_2 m_2 | JM\rangle \tag{168}$$

$$= \sum_{m_1 m_2} |j_1 m_1\rangle |j_2 m_2\rangle \left[C^\pm_{j_1 m_1 \mp 1} \langle j_1 m_1 \mp 1 j_2 m_2 | JM\rangle + C^\pm_{j_2 m_2 \mp 1} \langle j_1 m_1 j_2 m_2 \mp 1 | JM\rangle \right]. \tag{169}$$

In the last step we used

$$\sum_{m_1} |j_1 m_1 \pm 1\rangle C^{\pm}_{j_1,m_1} = \sum_{m_1} |j_1 m_1\rangle C^{\pm}_{j_1,m_1\mp 1}, \tag{170}$$

which is correct, assuming the range of summation is alway chosen to include all allowed m_1 values. Combining Eqs. 166 and 169 we obtain the recursion relations

$$C^{\pm}_{JM}\langle j_1 m_1 j_2 m_2|JM \pm 1\rangle = C^{\pm}_{j_1 m_1 \mp 1}\langle j_1 m_1 \mp 1 j_2 m_2|JM\rangle + C^{\pm}_{j_2 m_2 \mp 1}\langle j_1 m_1 j_2 m_2 \mp 1|JM\rangle. \tag{171}$$

For the upper sign with $M = J$ we get

$$0 = C^{+}_{j_1 m_1 - 1}\langle j_1 m_1 - 1 j_2 m_2|JJ\rangle + C^{+}_{j_2 m_2 - 1}\langle j_1 m_1 j_2 m_2 - 1|JJ\rangle. \tag{172}$$

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 $|JM\rangle$ elements are obtained by using the lower sign. For $J = M = 0$ this procedure gives

$$\langle j_1 m_1 j_2 m_2|00\rangle = \frac{(-1)^{j_1 - m_1}}{\sqrt{2j_1 + 1}}\delta_{j_1 j_2}\delta_{m_1,-m_2}. \tag{173}$$

It is straightforward to construct an irreducible basis in a higher dimensional tensor product space. E.g., in $\mathcal{V}^{j_1} \otimes \mathcal{V}^{j_2} \otimes \mathcal{V}^{j_3}$

$$|[(j_1 j_2)j_3]JM\rangle \equiv \sum_{m_1 m_2 m_3 m_4} |j_1 m_1\rangle|j_2 m_2\rangle|j_3 m_3\rangle\langle j_1 m_1 j_2 m_2|j_4 m_4\rangle\langle j_4 m_4 j_3 m_3|JM\rangle. \tag{174}$$

transforms like $|JM\rangle$. For $|JM\rangle = |00\rangle$ and substituting Eq. (173) we construct a so called *invariant* function

$$\sum_{m_1 m_2 m_3} |j_1 m_1\rangle|j_2 m_2\rangle|j_3 m_3\rangle\langle j_1 m_1 j_2 m_2|j_3 {-m_3}\rangle\frac{(-1)^{j_3 + m_3}}{\sqrt{2j_3 + 1}}. \tag{175}$$

This motivates the definition of the $3jm-$symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \equiv \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2j_3 + 1}}\langle j_1 m_1 j_2 m_2|j_3 - m_3\rangle. \tag{176}$$

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.

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \tag{177}$$

etc. From the inverse relation

$$\langle j_1 m_1 j_2 m_2|j_3 m_3\rangle = (-1)^{j_1 - j_2 + m_3}\sqrt{2j_3 + 1}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} \tag{178}$$

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 $\mathcal{V}^{j_1} \otimes \mathcal{V}^{j_2}$ is given by

$$\hat{R}(\mathbf{n}, \phi) = e^{-i\phi\mathbf{n}\underline{\hat{J}}} \tag{179}$$

and when operating on the coupled basis functions it gives

$$\begin{aligned} \hat{R}|(j_1 j_2)JM\rangle &= \sum_K |(j_1 j_2)JK\rangle D^J_{KM}(\hat{R}) && (180)\\ &= \sum_{k_1 k_2} |j_1 k_1\rangle|j_2 k_2\rangle\sum_K\langle j_1 k_1 j_2 k_2|JK\rangle D^J_{KM}(\hat{R}). && (181) \end{aligned}$$

Using the rules for manipulating tensor products of operators derived above we find

$$e^{-i\phi\mathbf{n}\cdot\underline{\hat{J}}} = e^{-i\phi\mathbf{n}\cdot\underline{\hat{j}_1}} \otimes e^{-i\phi\mathbf{n}\cdot\underline{\hat{j}_2}}, \tag{182}$$

which we may write symbolically as $\hat{R} = \hat{R} \otimes \hat{R}$. Thus, the uncoupled basis functions rotate as

$$(\hat{R} \otimes \hat{R})|j_1 m_1\rangle|j_2 m_2\rangle = \sum_{k_1 k_2} |j_1 k_1\rangle|j_2 k_2\rangle D^{j_1}_{k_1 m_1}(\hat{R}) D^{j_2}_{k_2 m_2}(\hat{R}). \tag{183}$$

Together with Eq. (164) this gives

$$D^{j_1}_{k_1 m_1}(\hat{R}) D^{j_2}_{k_2 m_2}(\hat{R}) = \sum_{JKM} \langle j_1 k_1 j_2 k_2|JK\rangle\langle j_1 m_1 j_2 m_2|JM\rangle D^J_{KM}(\hat{R}). \tag{184}$$

This is a remarkable useful equation. E.g., it allows us to verify the orthogonality relations Eq. (129) and to find

$$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma\, D^{J,*}_{MK}(\alpha,\beta,\gamma) D^{j_1}_{m_1 k_1}(\alpha,\beta,\gamma) D^{j_2}_{m_2 k_2}(\alpha,\beta,\gamma) = \frac{8\pi^2}{2J+1}\langle j_1 m_1 j_2 m_2|JM\rangle\langle j_1 k_1 j_2 k_2|JK\rangle. \tag{185}$$

If we take the complex conjugate, set $K = k_1 = k_2 = 0$, and eliminate the integral over the third Euler angle, we find

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta C^*_{LM}(\phi,\theta) C_{l_1 m_1}(\theta,\phi) C_{l_2 m_2}(\theta,\phi) = \frac{4\pi}{2L+1}\langle l_1 m_1 l_2 m_2|LM\rangle\langle l_1 0 l_2 0|L0\rangle. \tag{186}$$

We also may derive the recursion relation for Legendre polynomials from the explicit expressions for d^j with $z \equiv \cos\beta$

$$P_0(z) = 1 \tag{187}$$

$$P_1(z) = z. \tag{188}$$

From Eq. (184) with $m = k = 0$ and $j_1 = 1$ and $j_2 = l$ we derive a recursion relation for the Legendre polynomials

$$P_1(z)P_l(z) = \sum_L \langle 10l0|L0\rangle^2 P_L(z) \tag{189}$$

$$= \langle 10l0|l+1,0\rangle^2 P_{l+1}(z) + \langle 10l0|l-1,0\rangle^2 P_{l-1}(z) \tag{190}$$

$$= \frac{l+1}{2l+1}P_{l+1}(z) + \frac{l}{2l+1}P_{l-1}(z), \tag{191}$$

i.e.,

$$P_{l+1}(z) = \frac{z(2l+1)P_l(z) - lP_{l-1}(z)}{l+1} \tag{192}$$

$$P_2(z) = \frac{3z^2-1}{2}. \tag{193}$$

Suppose the angular part of a wave function is given by

$$\Psi(\theta,\phi) = \sum_{lm} a_{lm} C_{lm}(\theta,\phi) \tag{194}$$

and we are interested in the spatial distribution

$$P(\theta,\phi) = |\Psi(\theta,\phi))|^2 = \sum_{l_1 m_1 l_2 m_2} a^*_{l_1 m_1} a_{l_2 m_2} C^*_{l_1 m_1}(\theta,\phi) C_{l_2 m_2}(\theta,\phi). \tag{195}$$

First, from Eqs. (128) and (130) we find

$$C^*_{lm}(\theta,\phi) = (-1)^m C_{l,-m}(\theta,\phi). \tag{196}$$

From Eq. (184) we have

$$(-1)^{m_1} C_{l_1 -m_1}(\hat{r}) C_{l_2 m_2}(\theta,\phi) = (-1)^m \sum_{LM} \langle l_1, -m_1, l_2, m_2|LM\rangle\langle l_1 0 l_2 0|L0\rangle C_{LM}(\theta,\phi) \tag{197}$$

thus,

$$P(\theta,\phi) = \sum_{l_1 l_2 m_1 m_2 LM} a^*_{l_1 m_1} a_{l_2,m_2} (-1)^m \langle l_1, -m_1, l_2, m_2 | LM\rangle \langle l_1 0 l_2 0 | L0\rangle C_{LM}(\theta,\phi). \tag{198}$$

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

$$P(\theta,\phi) = \sum_{LM} |a_{lm}|^2 (-1)^m \langle l, -m, l, m|LM\rangle \langle l0l0|L0\rangle C_{LM}(\theta,\phi) \tag{199}$$

$$= \sum_{L} |a_{lm}|^2 (-1)^m \langle l, -m, l, m|L0\rangle \langle l0l0|L0\rangle P_L(\cos\theta). \tag{200}$$

It follows from the triangular conditions for $\langle l0l0|L0\rangle$ that L runs from 0 to $2l$. 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 $3jm$ 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 μ is the dipole operator. A scalar product can be written in spherical coordinates

$$\mathbf{e}\cdot\mu = \sum_m (-1)^m e^{(1)}_{-m} \mu^{(1)}_m = -\sqrt{3}\sum_m e^{(1)}_{-m}\mu^{(1)}_m . \langle 1{-m}1m|00\rangle \tag{201}$$

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

$$\mu^{(1)}_m(\mathbf{r}) = qR_{1m}(\mathbf{r}) = qrC_{1m}(\hat{r}). \tag{202}$$

The matrix elements of $\hat{T}$ in the basis $\Psi_{nlm}(\mathbf{r}) = f_{nl}(r)C_{lm}(\hat{r})$ are

$$\langle \Psi_{n_1 l_1 m_1}|\hat{T}|\Psi_{n_2 l_2 m_2}\rangle = \sum_m (-1)^m e^{(1)}_{-m} \int d\hat{r} C^*_{l_1 m_1}(\hat{r}) C_{1m}(\hat{r}) C_{l_2 m_2}(\hat{r}) \int r^2 dr f^*_{n_1 l_1}(r) qr f_{n_2 l_2}(r) \tag{203}$$

$$= \sum_m (-1)^m e_{-m} A_{n_1 l_1 n_2 l_2} \langle l_1 m_1 1 m | l_2 m_2\rangle \langle l_1 010|l_2 0\rangle. \tag{204}$$

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 $\langle l_1 010|l_2 0\rangle$ into $A_{l_1 l_2}$, so that we get

$$\langle l_1 m_1|\hat{T}|l_2 m_2\rangle = A_{l_1 l_2}\langle l_1 m_1 1 m|l_2 m_2\rangle. \tag{205}$$

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

$$\hat{T} = \sum_{l_1 m_1 l_2 m_2} A_{l_1 l_2} |l_1 m_1\rangle\langle l_2 m_2| \langle l_1 m_1 1 m|l_2 m_2\rangle. \tag{206}$$

D. Density matrix formalism

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

$$\hat{\rho} = \sum_i |\Psi_i\rangle p_i \langle\Psi_i|, \tag{207}$$

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

$$\langle\hat{A}\rangle \equiv \mathrm{Tr}(\hat{\rho}\hat{A}) = \sum_{ji}\langle j|\Psi_i\rangle p_i \langle\Psi_i|\hat{A}|j\rangle = \sum_{ji} p_i \langle\Psi_i|\hat{A}|j\rangle\langle j|\Psi_i\rangle = \sum_i p_i\langle\Psi_i|\hat{A}|\Psi_i\rangle. \tag{208}$$

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

$$A(\hat{r}) = \sum p_i \langle\Psi_i|\hat{r}\rangle\langle\hat{r}|\Psi_i\rangle = \sum_i p_i |\Psi_i(\hat{r})|^2. \tag{209}$$

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

$$A = \sum p_i \langle\Psi_i| \sum_f \hat{T}|\Psi_f\rangle\langle\Psi_f|\hat{T}|\Psi_i\rangle = \sum_{i,f} p_i |\langle\Psi_f|\hat{T}|\Psi_i\rangle|^2. \tag{210}$$

To determine an angular distribution after photo-excitation we take

$$\hat{A}(\hat{r}) = \hat{T}\hat{P}|\hat{r}\rangle\langle\hat{r}|\hat{P}\hat{T} \text{ with } \hat{P} = \sum_f |\Psi_f\rangle\langle\Psi_f|, \tag{211}$$

which gives

$$A(\hat{r}) = \sum_{i,f} p_i |\Psi_f(\hat{r})|^2 |\langle\Psi_f|\hat{T}|\Psi\rangle_i|^2. \tag{212}$$

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

E. The space of linear operators

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

$$\hat{A} = \sum_{ij} A_{ij} |i\rangle\langle j|. \tag{213}$$

Indeed, for the matrix elements we get

$$\langle k|\hat{A}|l\rangle = \langle k| \sum_{ij} A_{ij}|i\rangle\langle j|l\rangle = A_{kl}. \tag{214}$$

Thus we may think of

$$\hat{T}_{ij} \equiv |i\rangle\langle j| \tag{215}$$

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 $\hat{A}^\dagger\hat{B}$, since that gives

$$\mathrm{Tr}(\hat{A}^\dagger\hat{B}) = \sum_{ij} \langle j|\hat{A}^\dagger|i\rangle\langle i|\hat{B}|j\rangle = \sum_{ij} A^*_{ij} B_{ij}, \tag{216}$$

completely analogous to $(\mathbf{x}, \mathbf{y}) = \sum_i x_i^* y_i$. We also have

$$A_{ij} = \mathrm{Tr}(\hat{T}^\dagger_{ij}\hat{A}) \tag{217}$$

and

$$\mathrm{Tr}(\hat{T}^\dagger_{ij}\hat{T}_{i'j'}) = \delta_{ii'}\delta_{jj'}. \tag{218}$$

Furthermore

$$\mathrm{Tr}(\hat{A}^\dagger\hat{B}) = \mathrm{Tr}(\hat{B}^\dagger\hat{A})^*. \tag{219}$$

and

$$\hat{T}^\dagger_{ij} = |j\rangle\langle i| = \hat{T}_{ji}. \tag{220}$$

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

$$\hat{T}'_{ij} \equiv |i\rangle'{}'\langle j| = \hat{R}\hat{T}_{ij}\hat{R}^\dagger. \tag{221}$$

One can easily verify that if $\hat{R}$ is a unitary transformation on $\mathcal{V}$, then $\hat{T}'_{ij}$ is again an orthonormal basis, i.e., $\mathrm{Tr}(\hat{T'}^\dagger_{ij}\hat{T'}_{i'j'}) = \delta_{ij}\delta_{i'j'}$. Note that one may also think of $\hat{T}_{ij}$ as an element of $\mathcal{V} \otimes \mathcal{V}^*$.

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 $\mathcal{R}$ or 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 $\{\langle jm|, m=-j,\ldots,j\}$ is a basis in $\mathcal{V}^*$, which we call the *dual* basis. Hermitian conjugation takes us back and forth between $\mathcal{V}$ and $\mathcal{V}^*$, $|jm\rangle^\dagger = \langle jm|$, $\langle j_1m_1|j_2m_2\rangle \equiv \delta_{j_1j_2}\delta_{m_1m_2}$, hence $(|jm\rangle c)^\dagger = \langle jm|c^*$.

Rotating the basis functions in $\mathcal{V}$ gives

$$|jm\rangle' \equiv \hat{R}|jm\rangle = \sum_k |jk\rangle D^j_{km}(\hat{R}), \tag{222}$$

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

$${}'\langle jm| \equiv \langle jm|\hat{R}^\dagger = \sum_k \langle jk|\, D^{j,*}_{km}(\hat{R}) = \sum_k \langle jk|(-1)^{k-m} D^j_{-k,-m}(\hat{R}) \tag{223}$$

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 $(-1)^{j+m}$

$$(-1)^{j+m}\langle jm|\hat{R}^\dagger = \sum_k (-1)^{j+k}\langle jk|\, D^j_{-k,-m}(\hat{R}) \tag{224}$$

and then we change the signs of m and k

$$(-1)^{j-m}\langle j,-m|\hat{R}^\dagger = \sum_k (-1)^{j-k}\langle j{-k}|\, D^j_{km}(\hat{R}). \tag{225}$$

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 $(-1)^{\frac{1}{2}}$ one could take i as well as $-i$). In any case, we can now define an alternative basis for the dual space

$$\langle j\overline{m}| \equiv (-1)^{j-m}\langle j,-m| \tag{226}$$

that rotates as

$$\langle j\overline{m}|\hat{R}^\dagger = \sum_k \langle j\overline{k}|\, D^j_{km}(\hat{R}). \tag{227}$$

We also introduce

$$|j\overline{m}\rangle = (-1)^{j-m}|j,-m\rangle, \tag{228}$$

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

$$\hat{R}|j\overline{m}\rangle = \sum_k |j\overline{k}\rangle D^j_{km}(\hat{R}). \tag{229}$$

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

$$\langle j_1m_1j_2\overline{m}_2|JM\rangle \;=\; (-1)^{j_2-m_2}\langle j_1,m_1,j_2,-m_2|JM\rangle. \tag{230}$$

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

$$\hat{\Theta}|jm\rangle = |j\overline{m}\rangle. \tag{231}$$

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

$$\hat{\Theta}\lambda|\Psi\rangle \equiv \lambda^*\hat{\Theta}|\Psi\rangle. \tag{232}$$

A. Tensor operators

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

$$(\hat{R}\otimes\hat{R})\sum_{m_1m_2}|j_1m_1\rangle|j_2m_2\rangle\langle j_1m_1j_2m_2|JM\rangle = \sum_{m_1m_2k_1k_2}|j_1k_1\rangle|j_2k_2\rangle D^{j_1}_{k_1m_1}(\hat{R})D^{j_2}_{k_2m_2}(\hat{R})\langle j_1m_1j_2m_2|JM\rangle \quad (233)$$

$$= \sum_K\left[\sum_{k_1k_2}|j_1k_1\rangle|j_2k_2\rangle\langle j_1k_1j_2k_2|JK\rangle\right]D^J_{KM}(\hat{R}). \quad (234)$$

This suggest the definition of the operator

$$\hat{T}_{JM}(j_1j_2) = \sum_{m_1m_2}|j_1m_1\rangle\langle j_2\overline{m}_2|\langle j_1m_1j_2m_2|JM\rangle, \quad (235)$$

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

$$\hat{T}^{BF}_{JM}(j_1j_2) \equiv \hat{R}\hat{T}_{JM}(j_1j_2)\hat{R}^\dagger \quad (236)$$

$$= \sum_{m_1m_2}\hat{R}|j_1m_1\rangle\langle j_2\overline{m}_2|\hat{R}^\dagger\langle j_1m_1j_2m_2|JM\rangle \quad (237)$$

$$= \sum_{m_1m_2k_1k_2}|j_1k_1\rangle\langle j_2\overline{k}_2|D^{j_1}_{k_1m_1}(\hat{R})D^{j_2}_{k_2m_2}(\hat{R})\langle j_1m_1j_2m_2|JM\rangle \quad (238)$$

$$= \sum_K\sum_{k_1k_2}|j_1k_1\rangle\langle j_2\overline{k}_2|\langle j_1k_1j_2k_2|JK\rangle D^J_{KM}(\hat{R}) \quad (239)$$

$$= \sum_K\hat{T}_{JK}(j_1j_2)D^J_{KM}(\hat{R}). \quad (240)$$

The operators $|j_1m_1\rangle\langle j_2\overline{m}_2|$ constitute an orthonormal operator basis since

$$\mathrm{Tr}([|j_1m_1\rangle\langle j_2\overline{m}_2|]^\dagger\,|j_1'm_1'\rangle\langle j_2'\overline{m'}_2|) = \delta_{j_1j_1'}\delta_{j_2j_2'}\delta_{m_1m_1'}\delta_{m_2m_2'} \quad (241)$$

and from the orthogonality relations of the CG coefficients we find

$$\mathrm{Tr}(\hat{T}_{JM}(j_1j_2)^\dagger\hat{T}_{J'M'}(j_1'j_2') = \sum_{m_1m_2}\langle j_1m_1j_2m_2|JM\rangle\langle j_1m_1j_2m_2|J'M'\rangle = \delta_{JJ'}\delta_{MM'}\delta_{j_1j_1'}\delta_{j_2j_2'}. \quad (242)$$

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

$$\hat{A} = \sum_{JMj_1j_2}A_{JM}(j_1j_2)\hat{T}_{JM}(j_1j_2) \quad (243)$$

$$\hat{B} = \sum_{JMj_1j_2}B_{JM}(j_1j_2)\hat{T}_{JM}(j_1j_2) \quad (244)$$

we find for the scalar product

$$\mathrm{Tr}(\hat{A}^\dagger\hat{B}) = \sum_{JMj_1j_2}A^*_{JM}(j_1j_2)B_{JM}(j_1j_2). \quad (245)$$

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

$$\mathrm{Tr}(\hat{\rho}^\dagger\hat{T}) = \sum_{JMj_1j_2}\rho^*_{JM}(j_1j_2)T_{JM}(j_1j_2) \quad (246)$$

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 $\hat{\rho}$ we can obtain.

Any operator that can be written as

$$\hat{A}_{JM} = \sum_{j_1j_2}a_{j_1j_2}\hat{T}_{JM}(j_1j_2) \quad (247)$$

is called an irreducible tensor operator. It rotates like

$$\hat{R}\hat{A}_{JM}\hat{R}^\dagger = \sum_K \hat{A}_{JK} D^J_{KM}(\hat{R}) \tag{248}$$

and its matrix elements are

$$\langle jm|\hat{A}_{JM}|jm'\rangle = a_{jj'}(\sqrt{2J+1})(-1)^{j-m} \begin{pmatrix} j & J & j' \\ -m & M & m' \end{pmatrix} \tag{249}$$

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)

$$e_{ijk}e_{ij'k'} = \delta_{jj'}\delta_{kk'} - \delta_{jk'}\delta_{kj'} \tag{250}$$
$$e_{ijk}e_{ijk'} = 2\delta_{kk'} \tag{251}$$
$$e_{ijk}e_{ijk} = 6, \tag{252}$$

   where we used Einstein summation convention: summation over repeated indices is implicit.

6. Show that

$$\mathbf{x} \times (\mathbf{y} \times \mathbf{z}) = (\mathbf{x}, \mathbf{z})\mathbf{y} - (\mathbf{x}, \mathbf{y})\mathbf{z}. \tag{253}$$

7. Using the last equation verify Eq. (64).
8. Derive Eq. (51). Hint: work out $\det(U[\mathbf{xyz}])$ in two ways, or use the Levi-Civita tensor.
9. Show that

$$B(t) = e^{tA}Be^{-tA} \tag{254}$$

   satisfies the equation

$$B(0) = B, \quad \frac{d}{dt}B(t) = [A, B(t)] \tag{255}$$

   and therefore

$$B(t) = B + \int_0^t d\tau [A, B(\tau)]. \tag{256}$$

   Solve the last equation by iteration to derive Eq. (60)

10. Show that $\sum_{J=|j_1-j_2|}^{j_1+j_2}(2J+1) = (2j_1+1)(2j_2+1)$. Hint: draw a grid of points (m_1, m_2) with $m_i = -j_i \dots j_i$.
11. Compute the $d^{\frac{1}{2}}(\beta)$ matrix [Eq. (121)].