16

Transformation Theory

A General

In our example of the diagonalization of the asymmetric rotator Hamiltonian in the last chapter, we encountered a very special case of a very general problem in quantum theory, the transformation from one basis in Hilbert space to another. In our example, it was a transformation from the $|JMK\rangle$ basis to the $|JME_\alpha\rangle$ basis, involving two different complete sets of commuting operators to specify the two different bases. In our specific example of the $J = 1$ energy eigenstates, the transformation was a very simple one, in a 3-D subspace of the asymmetric rotator subspace of the full Hilbert space of our problem, and thus it involved a 3×3 transformation.

For a general state vector, $|\psi\rangle$, in the asymmetric rotator subspace of the Hilbert space of the polyatomic molecule system, we could use either the representation

$$|\psi\rangle = \sum_{JMK} |JMK\rangle\langle JMK|\psi\rangle \tag{1}$$

or the representation

$$|\psi\rangle = \sum_{JM\alpha} |JM\alpha\rangle\langle JM\alpha|\psi\rangle, \tag{2}$$

where we have used the abbreviation α for E_α, and

$$\langle JM\alpha|\psi\rangle = \sum_{K} \langle JM\alpha|JMK\rangle\langle JMK|\psi\rangle, \tag{3}$$

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and

$$\langle JMK|\psi\rangle = \sum_{\alpha} \langle JMK|JM\alpha\rangle\langle JM\alpha|\psi\rangle. \tag{4}$$

Here, eqs. (1) and (2) are the analogs in Hilbert space of the relations in ordinary n-dimensional vector space that give the specification of a vector $\vec{V}$ in terms of the components along a set of axes defined by unit vectors $\vec{e}_i$, or in terms of components along a set of $\vec{e}^{\,\prime}_{\alpha}$, which are unit vectors along a set of rotated coordinate axes.

$$\vec{V} = \sum_k \vec{e}_k V_k, \tag{5}$$

$$\vec{V} = \sum_{\alpha} \vec{e}^{\,\prime}_{\alpha} V'_{\alpha}, \tag{6}$$

with

$$V'_{\alpha} = \sum_k O_{\alpha k} V_k, \qquad \text{where} \qquad O_{\alpha k} = \vec{e}^{\,\prime}_{\alpha} \cdot \vec{e}_k. \tag{7}$$

The inverse gives

$$V_k = \sum_{\alpha} (O^{-1})_{k\alpha} V'_{\alpha}, \qquad \text{with} \quad (O^{-1})_{k\alpha} = O_{\alpha k}, \tag{8}$$

showing the orthogonal character of the transformation matrix, i.e., the $O_{\alpha k}$ satisfy the orthogonality relations

$$\sum_k O_{\alpha k} O_{\beta k} = \delta_{\alpha\beta}, \qquad \sum_{\alpha} O_{\alpha k} O_{\alpha j} = \delta_{kj}. \tag{9}$$

Now, eqs. (3) and (4) are the analogs in Hilbert space of the ordinary vector relations, eqs. (7) and (8). If we name $\langle JM\alpha|\psi\rangle \equiv c'_{\alpha}$ and $\langle JMK|\psi\rangle \equiv c_K$,

$$\begin{aligned} c'_{\alpha} &= \sum_K \langle JM\alpha|JMK\rangle c_K = \sum_K U_{\alpha K} c_K, \\ c_K &= \sum_{\alpha} \langle JMK|JM\alpha\rangle c'_{\alpha} = \sum_{\alpha} (U^{-1})_{K\alpha} c'_{\alpha}, \end{aligned} \tag{10}$$

where now

$$(U^{-1})_{K\alpha} = \langle JMK|JM\alpha\rangle = \langle JM\alpha|JMK\rangle^* = U^*_{\alpha K}. \tag{11}$$

That is, the transformation is now unitary, rather than just orthogonal. The U matrix elements satisfy the unitary conditions

$$\sum_K U_{\alpha K} U^*_{\beta K} = \delta_{\alpha\beta}, \qquad \sum_{\alpha} U_{\alpha K} U^*_{\alpha K'} = \delta_{KK'}. \tag{12}$$

Now, the inverse matrix is the complex conjugate of the transposed matrix. We can also think of the U, not as a matrix, but as an operator, where

$$U = \sum_{\alpha,K} |JM\alpha\rangle\langle JM\alpha|JMK\rangle\langle JMK|. \tag{13}$$

That is, U is the operator converting a $|JMK\rangle$ into a $|JM\alpha\rangle$ and multiplying it by the complex number $U_{\alpha K}$. Similarly,

$$U^{-1} = \sum_{K,\alpha} |JMK\rangle\langle JMK|JM\alpha\rangle\langle JM\alpha|, \tag{14}$$

where now

$$U^{-1} = U^{\dagger}. \tag{15}$$

For the very specific case of the $J = 1$ states of the asymmetric rotator, using the ordering of energies of eqs. (28)–(30) of Chapter 15 for the index α, we have

$$U = \langle\alpha|K\rangle = \begin{matrix} & K=+1 & K=0 & K=-1 \\ \alpha=1 & 0 & 1 & 0 \\ \alpha=2 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \alpha=3 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{matrix}$$

and

$$U^{\dagger} = \langle K|\alpha\rangle = \begin{matrix} & \alpha=1 & \alpha=2 & \alpha=3 \\ K=+1 & 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ K=0 & 1 & 0 & 0 \\ K=-1 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{matrix}.$$

Combining this with the matrix, $H_{KK'}$ of Chapter 15, we can see by straightforward matrix multiplication that

$$\sum_{K,K'} \langle\alpha'|K'\rangle\langle K'|H|K\rangle\langle K|\alpha\rangle = \langle\alpha'|H|\alpha\rangle, \tag{16}$$

or, in matrix form,

$$\sum_{K,K'} U_{\alpha'K'} H_{K'K} (U^{\dagger})_{K\alpha} = H_{\alpha'\alpha} = E_{\alpha}\delta_{\alpha'\alpha}. \tag{17}$$

B Note on Generators of Unitary Operators and the Transformation $UHU^{\dagger} = H'$

A unitary operator, U, can be generated by a hermitian operator, $G = G^{\dagger}$, by exponentiation

$$U = e^{i\epsilon G}, \tag{18}$$

where ϵ is a real finite number and the operator G is called the generator of the unitary transformation. To prove the unitary character of U, consider first an infinitesimal transformation, with $\epsilon = \epsilon_0 \ll 1$, so

$$U = 1 + i\epsilon_0 G, \qquad U^{\dagger} = 1 - i\epsilon_0 G, \tag{19}$$

so

$$UU^{\dagger} = (1 + i\epsilon_0 G)(1 - i\epsilon_0 G) = 1 + \text{Order}(\epsilon_0^2) = 1. \tag{20}$$

To convert this to a transformation with a finite ϵ, write the exponential in the limiting form

$$\begin{aligned} e^{i\epsilon G} &= \lim_{N\to\infty}\left(1 + i\frac{\epsilon}{N}G\right)^N \\ &= \lim_{N\to\infty}\sum_k \frac{(i\epsilon)^k}{N^k}\frac{G^k}{k!}\frac{N!}{(N-k)!} = \sum_k \frac{(i\epsilon)^k}{k!}G^k. \end{aligned} \tag{21}$$

To prove the product of N factors $(1 + i\frac{\epsilon}{N}G)$ is unitary, we still need to show the product of two unitary operators is unitary

$$\begin{aligned} (U_1U_2)^{\dagger} &= U_2^{\dagger}U_1^{\dagger} \\ &= (U_1U_2)^{-1} = U_2^{-1}U_1^{-1} = U_2^{\dagger}U_1^{\dagger} \end{aligned} \tag{22}$$

if $U_1^{-1} = U_1^{\dagger}$ and $U_2^{-1} = U_2^{\dagger}$. Finally, it will be very useful to have a series expansion in powers of ϵ of the transformed Hamiltonian, $H' = UHU^{\dagger}$,

$$\begin{aligned} H' = e^{i\epsilon G}He^{-i\epsilon G} &= \left(1 + i\epsilon G + \frac{(i\epsilon)^2}{2!}G^2 + \cdots\right)H\left(1 - i\epsilon G + \frac{(-i\epsilon)^2}{2!}G^2 + \cdots\right) \\ &= H + i\epsilon[G,H] + \frac{(i\epsilon)^2}{2!}[G,[G,H]] \\ &\quad + \cdots + \frac{(i\epsilon)^n}{n!}[G,[G,[G,\ldots[G,H]]]]_n + \cdots \end{aligned} \tag{23}$$

where we have used $(G^2H - 2GHG + HG^2) = [G,[G,H]]$ for the second term. The n^{th} term, involving n commutators, can be seen to follow from the $(n-1)^{th}$ term from the Taylor expansion in ϵ,

$$f(\epsilon) = e^{i\epsilon G}He^{-i\epsilon G} = \sum_n \frac{\epsilon^n}{n!}\left(\frac{d^n f(\epsilon)}{d\epsilon^n}\right)_{\epsilon=0}, \tag{24}$$

where

$$\frac{df(\epsilon)}{d\epsilon} = e^{i\epsilon G}i[G,H]e^{-i\epsilon G},$$

and with

$$\begin{aligned} \frac{d^{(n-1)}f(\epsilon)}{d\epsilon^{(n-1)}} &= e^{i\epsilon G}i^{n-1}[G,[G,\cdots[G,H]]]_{n-1}e^{-i\epsilon G}, \\ \frac{d^n f(\epsilon)}{d\epsilon^n} &= iG\frac{d^{(n-1)}f(\epsilon)}{d\epsilon^{(n-1)}} - i\frac{d^{(n-1)}f(\epsilon)}{d\epsilon^{(n-1)}}G = i[G, \frac{d^{(n-1)}f(\epsilon)}{d\epsilon^{(n-1)}}]. \end{aligned} \tag{25}$$

This expansion in multiple commutators of G with H is particularly useful, if (1) the n^{th} commutator is zero for a relatively small n; (2) if H and H' differ only by a small term (perturbation theory), so the infinite series can, in good approximation, be terminated after a few terms; or (3) if the n^{th} commutator is so simple the series can be summed.