Symmetry-Adapted Bases of Matrix Spaces Applied to Quantum Chemistry

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Generalized normalized irreducible tensorial matrices (GNITM) are obtained by symmetry-adapting the matrix basis of a matrix space that is invariant to reducible representations of a unitary group. Like previously defined normalized irreducible tensorial matrices (NITM), the GNITM are orthonormal under the trace and transform irreducibly under G. The GNITM are useful for constructing matrices having specific behavior under G. In particular, an Hamiltonian matrix is invariant under the symmetry group of the corresponding physical system and is expressed as a linear combination of invariant GNITM. The orbital model of ammonia is treated as an example.

I. INTRODUCTION

Quantum mechanics requires the diagonalization of a suitable Hamiltonian matrix incorporating the properties of the corresponding physical system. If the system exhibits symmetry, the Hamiltonian matrix must commute with the corresponding group of unitary operations.[1] The Hamiltonian may contain rectangular blocks—submatrices—invariant to the symmetry group.[2] The set of matrices with m rows and n columns of complex numbers is an mn-dimensional Hilbert space.

In this paper, bases of matrix spaces symmetry-adapted to unitary groups are appraised for quantum mechanical applications. These bases consist of generalized normalized irreducible tensorial matrices (GNITM). Unlike previously defined normalized irreducible tensorial matrices NITM,[3−5] the GNITM cannot generally be expressed in terms of tabulated V coefficients[6,7] or 3j symbols[8−10] but are obtained by symmetry-adaptation[11,2] of the relevant matrix basis. The GNITM can be used to construct the most general Hamiltonian matrix for a physical system having a particular symmetry group, thereby clarifying the fundamental parameterization of the problem.

The next section treats matrix spaces and group transformations on them. A general symmetry-adaptation algorithm is reviewed in the third section. In the fourth section, the GNITM are obtained by symmetry-adapting the basis of a matrix space. GNITM expansions of invariant matrices are considered in the fifth section, and the orbital model of ammonia is given as an example in the sixth section. The last section is a conclusion.

II. MATRIX SPACES

The set, M($m\times n$), of all matrices $[X]$ with m rows and n columns of complex numbers is a vector space over the field C of complex numbers. A matrix basis of M($m\times n$) is the set

$$\{[e_{ij}],\ i = 1,...,m;\ j = 1,...n\} \tag{2.1}$$

such that

$$[e_{ij}]_{kl} = \delta(i,k)\delta(j,l) \tag{2.2}$$

Then elements of M($m\times n$) are expanded on this basis according to

$$[X] = \sum_{i=1}^{m}\sum_{j=1}^{n}[X]_{ij}[e_{ij}] \tag{2.3}$$

An Hermitian inner product is given by

$$([X],[Y]) = \sum_{i=1}^{m}\sum_{j=1}^{n}[X]_{ij}^{*}[Y]_{ij}$$

$$= trace\{[X]^{\dagger}[Y]\} \tag{2.4}$$

where the dagger indicates the Hermitian adjoint—the complex conjugate transpose. The matrix basis is orthonormal with respect to this inner product

$$trace\{[e_{ij}]^{\dagger}[e_{kl}]\} = \delta(i,k)\delta(j,l) \tag{2.5}$$

For quantum mechanics, an important aspect of such a matrix space is transformation under a unitary group:

$$\mathrm{G} = \{G_1,...,G_a,...,G_g\} \tag{2.6}$$

where G_1 is taken to be the identity and g is the order for a finite group. Let Γ^{ω_1} and Γ^{ω_2} be matrix representations of G of dimension f(ω_1) and f(ω_2), respectively, then the elements of the matrix space M($\omega_1\times\omega_2$) are defined to transform under the operations of G according to

$$[G_a\circ X]^{\omega_1,\omega_2} \equiv [G_a X G_a^{-1}]^{\omega_1,\omega_2}$$

$$= [G_a]^{\omega_1}[X]^{\omega_1,\omega_2}[G_a^{-1}]^{\omega_2} \tag{2.7}$$

where $[G_a]^{\omega_1} \in \Gamma^{\omega_1}$ and $[G_a^{-1}]^{\omega_2} \in \Gamma^{\omega_2}$.

The representations Γ^{ω_1} and Γ^{ω_2} may be reducible or irreducible. Strictly irreducible representations will be indicated here by superscripts α or β. An irreducible representation that is completely reduced will be represented as $\Gamma^{\underline{\omega}}$. Thus, a nonreduced reducible representation Γ^{ω} is equivalent to a completely reduced reducible representation according to

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$$[S_1]\Gamma^{\omega}[S_1^{-1}] = \Gamma^{\underline{\omega}} = \sum_{\alpha=1}^{M} \oplus \mathrm{f}(\omega;\alpha)\Gamma^{\alpha} \tag{2.8}$$

where the frequency is given by the usual character formula[12]

$$\mathrm{f}(\omega;\alpha) = \frac{1}{g}\sum_{\rho=1}^{M} n_\rho \chi^{\alpha}_{\bar{\rho}}\chi^{\omega}_{\rho} \tag{2.9}$$

and M is the number of classes and irreducible representations of G, n_ρ is the order of the ρth class, $\chi^{\alpha}_{\bar{\rho}}$ is the irreducible representation character of the inverses of the elements in the ρth class, and χ^{ω}_{ρ} is the character of the ρth class in the reducible representation Γ^{ω}.

The matrix basis elements of $\mathrm{M}(\omega_1\times\omega_2)$ transform under G according to

$$([G_a]^{\omega_1}[e_{ij}]^{\omega_1,\omega_2}[G_a^{-1}]^{\omega_2})_{kl} = \sum_{i'=1}^{\mathrm{f}(\omega_1)}\sum_{j'=1}^{\mathrm{f}(\omega_2)} [G_a]^{\omega_1}_{ki'}[e_{ij}]^{\omega_1,\omega_2}_{i'j'}[G_a^{-1}]^{\omega_2}_{j'l}$$

$$= [G_a]^{\omega_1}_{ki}[G_a]^{\omega_2 *}_{lj} \tag{2.10}$$

$$= \sum_{i'=1}^{\mathrm{f}(\omega_1)}\sum_{j'=1}^{\mathrm{f}(\omega_2)} [e_{i'j'}]^{\omega_1,\omega_2}_{kl}[G_a]^{\omega_1}_{i'i}[G_a]^{\omega_2 *}_{j'j}$$

where the inverse matrix has been replaced by the Hermitian adjoint. Thus, the matrix basis elements transform according to the Kronecker product representation[13] $\Gamma^{\omega_1}\times\Gamma^{\hat{\omega}_2}$ where $\Gamma^{\hat{\omega}_2}$ is the representation contragredient to Γ^{ω_2}.

III. SYMMETRY-ADAPTED BASES

Let a vector space V^{ω} be invariant under a group G, and let a basis of V^{ω} be $\mathrm{B}(\omega) = \{|1\rangle,...,|\mathrm{f}(\omega)\rangle\}$. Then a representation of G is generated on $\mathrm{B}(\omega)$ by the transformation

$$G_a|i\rangle = \sum_{i'=1}^{\mathrm{f}(\omega)}[G_a]^{\omega}_{i'i}|i'\rangle \tag{3.1}$$

where the matrix $[G_a]^{\omega}$ belongs the representation Γ^{ω}. A basis $\mathrm{B}(\underline{\omega})$ is symmetry-adapted to a group G if the generated representation $\Gamma^{\underline{\omega}}$ is reduced as in eq 2.8. Then $\mathrm{B}(\underline{\omega})$ can be written

$$\mathrm{B}(\underline{\omega}) = \{|\omega;\rho\alpha r\rangle,\ \alpha = 1,...,M;\ \rho = 1,...,\mathrm{f}(\omega;\alpha);\ r = 1,...,\mathrm{f}(\alpha)\} \tag{3.2}$$

where

$$G_a|\omega;\rho\alpha r\rangle = \sum_{r'=1}^{\mathrm{f}(\alpha)}[G_a]^{\alpha}_{r'r}|\omega;\rho\alpha r'\rangle \tag{3.3}$$

For G a finite group, the original basis $\mathrm{B}(\omega)$ can be symmetry-adapted to $\mathrm{B}(\underline{\omega})$ by means of matrix basis elements e^{α}_{rs} of the Frobenius algebra $\mathrm{A}(G)$.[2,12] An element $X\in\mathrm{A}(G)$ is expressed on the matric basis according to

$$X = \sum_{\alpha=1}^{M}\sum_{r=1}^{\mathrm{f}(\alpha)}\sum_{s=1}^{\mathrm{f}(\alpha)}[X]^{\alpha}_{rs}\, e^{\alpha}_{rs} \tag{3.4}$$

where the matric basis elements multiply according to

$$e^{\alpha}_{rs}e^{\beta}_{tu} = \delta(\alpha,\beta)\delta(s,t)e^{\alpha}_{ru} \tag{3.5}$$

The matric basis elements are expressed in terms of the group elements by

$$e^{\alpha}_{rs} = \frac{\mathrm{f}(\alpha)}{g}\sum_{a=1}^{g}[G_a^{-1}]^{\alpha}_{sr}G_a \tag{3.6}$$

which leads immediately to the familiar orthogonality relation.

Symmetry-adaptation of $\mathrm{B}(\omega)$ proceeds by generating the matrices

$$[e^{\alpha}_{r1}]^{\omega} = \frac{\mathrm{f}(\alpha)}{g}\sum_{a=1}^{g}[G_a^{-1}]^{\alpha}_{1r}[G_a]^{\omega} \tag{3.7}$$

for all α such that $\mathrm{f}(\omega;\alpha) \neq 0$. Diagonalization of the Hermitian idempotent matrix $[e^{\alpha}_{11}]^{\omega}$ yields $\mathrm{f}(\omega;\alpha)$ orthonormal eigenvectors $\{|\omega;\rho\alpha 1\rangle,\ \rho = 1,...\mathrm{f}(\omega;\alpha)\}$ such that

$$e^{\alpha}_{11}|\omega;\rho\alpha 1\rangle = |\omega;\rho\alpha 1\rangle \tag{3.8}$$

The remaining basis elements are obtained from

$$e^{\alpha}_{r1}|\omega;\rho\alpha 1\rangle = |\omega;\rho\alpha r\rangle = \sum_{i=1}^{\mathrm{f}(\omega)}|\omega i\rangle\langle\omega i|\omega;\rho\alpha r\rangle \tag{3.9}$$

with the symmetry adaptation coefficients $\langle\omega i|\omega;\rho\alpha r\rangle$ being elements of a unitary transformation. It follows that

$$[e^{\alpha}_{rs}]^{\omega}_{ij} = \frac{\mathrm{f}(\alpha)}{g}\sum_{a=1}^{g}[G_a^{-1}]^{\alpha}_{sr}[G_a]^{\omega}_{ij} = \sum_{\rho=1}^{\mathrm{f}(\omega;\alpha)}\langle\omega i|\rho\alpha r\rangle\langle\rho\alpha s|\omega j\rangle \tag{3.10}$$

If Γ^{ω} represents a Kronecker product representation, $\Gamma^{\omega_1}\times\Gamma^{\omega_2}$, then (3.10) becomes

$$\sum_{\rho=1}^{\mathrm{f}(\omega_1,\omega_2;\alpha)}\langle\omega_1 i_1,\omega_2 i_2|\rho\alpha r\rangle\langle\rho\alpha s|\omega_1 j_1,\omega_2 j_2\rangle = \frac{\mathrm{f}(\alpha)}{g}\sum_{\rho=1}^{g}[G_a^{-1}]^{\alpha}_{sr}[G_a]^{\omega_1}_{i_1 j_1}[G_a]^{\omega_2}_{i_2 j_2} \tag{3.11}$$

with the frequency given by

$$\mathrm{f}(\omega_1,\omega_2;\alpha_1) = \frac{1}{g}\sum_{\rho=1}^{M} n_\rho \chi^{\alpha_1}_{\bar{\rho}}\chi^{\omega_1}_{\rho}\chi^{\omega_2}_{\rho} \tag{3.12}$$

IV. GNITM

Constructing a symmetry-adapted basis for the matrix space $\mathrm{M}(\omega_1\times\omega_2)$ corresponds to reducing the Kronecker

product $\Gamma^{\omega_1}\times\Gamma^{\hat{\omega}_2}$ with the coefficients $\langle\omega_1 i_1,\hat{\omega}_2 i_2|\rho\alpha r\rangle$. The GNITM are therefore

$$[n_r^{\rho\alpha}]^{\omega_1,\omega_2} = \sum_{i_1=1}^{f(\omega_1)}\sum_{i_2=1}^{f(\omega_2)}[e_{i_1 i_2}]^{\omega_1,\omega_2}\langle\omega_1 i_1,\hat{\omega}_2 i_2|\rho\alpha r\rangle \quad (4.1)$$

Substituting (2.2) into (4.1) gives for the elements of this matrix

$$[n_r^{\rho\alpha}]^{\omega_1,\omega_2}_{i_1 i_2} = \langle\omega_1 i_1,\hat{\omega}_2 i_2|\rho\alpha r\rangle \quad (4.2)$$

The irreducible tensorial basis is then

$$\{[n_r^{\rho\alpha}]^{\omega_1,\omega_2};\ \rho = 1,...f(\omega_1,\omega_2;\alpha);\ \alpha = 1,...,M;\ r = 1,...,f(\alpha)\} \quad (4.3)$$

This basis is orthonormal under the trace

$$trace\{[n_r^{\rho\alpha}]^{\omega_1,\omega_2\dagger}[n_{r'}^{\rho'\alpha'}]^{\omega_1,\omega_2}]\} = \delta(\rho,\rho')\delta(\alpha,\alpha')\delta(r,r') \quad (4.4)$$

so that matrices of $M(\omega_1\times\omega_2)$ are expressed as

$$[X]^{\omega_1,\omega_2} = \sum_{\alpha=1}^{M}\sum_{\rho=1}^{f(\omega_1,\omega_2;\alpha)}\sum_{r=1}^{f(\alpha)}(X)_r^{\omega_1,\omega_2;\rho\alpha}[n_r^{\rho\alpha}]^{\omega_1,\omega_2} \quad (4.5)$$

where the coefficients are given by

$$(X)_r^{\omega_1,\omega_2;\rho\alpha} = trace\{[n_r^{\rho\alpha}]^{\omega_1,\omega_2\dagger}[X]^{\omega_1,\omega_2}\} \quad (4.6)$$

Each of these GNITM transforms irreducibly under the operations of G

$$G_a\circ[n_r^{\rho\alpha}]^{\omega_1,\omega_2} = [G_a]^{\omega_1}[n_r^{\rho\alpha}]^{\omega_1,\omega_2}[G_a^{-1}]^{\omega_2} = \sum_{r'=1}^{f(\alpha)}[G_a]^{\alpha}_{r'r}[n_{r'}^{\rho\alpha}]^{\omega_1,\omega_2} \quad (4.7)$$

Three cases respecting the nature of the representations Γ^{ω_1} and $\Gamma^{\hat{\omega}_2}$ are considered here: 1. Both representations are irreducible. 2. At least one of the representations is reducible and both representations are completely reduced. 3. At least one of the representations is reducible and is not completely reduced.

1. When both representations are irreducible, (4.3) is a simple basis of $M(\omega_1\times\omega_2)$ discussed previously.[3,2] Using (3.12) for semisimple groups with coupling frequencies of zero or one, elements of the NITM are given by

$$[n_r^{\alpha}]^{\alpha_1;\alpha_2}_{r_1 r_2} = \langle\alpha_1 r_1,\hat{\alpha}_2 r_2|\alpha r\rangle = \frac{\sqrt{f(\alpha)}}{\sqrt{f(\alpha_1)}}\langle\alpha_1 r_1|\alpha r\alpha_2 r_2\rangle = \phi\sqrt{f(\alpha)}\,V\begin{pmatrix}\alpha_1 & \alpha & \alpha_2\\ \hat{r}_1 & r & r_2\end{pmatrix} \quad (4.8)$$

where ϕ is an appropriate phase factor, V is Griffith's V coefficient for finite groups or a 3-j symbol for SU(2), and $\hat{r}_1$ is an appropriate contragredient index.

2. When both representations Γ^{ω_1} and $\Gamma^{\hat{\omega}_2}$ are completely reduced, the NITM basis is a compound basis[2]

$$\{[n_r^{\rho\alpha}]^{\omega_1;\rho_1\alpha_1,\omega_2;\rho_2\alpha_2};\ \alpha,\alpha_1,\alpha_2 = 1,...,M;\ \rho = 1,...f(\alpha_1,\alpha_2;\alpha);\ \rho_1 = 1,...,f(\omega_1;\alpha_1);\ \rho_2 = 1,...,f(\omega_2;\alpha_2);\ r = 1,...,f(\alpha);\} \quad (4.9)$$

Elements of the NITM$[n_r^{\rho\alpha}]^{\omega_1;\rho_1\alpha_1,\omega_2;\rho_2\alpha_2}$ are zero except in the block identified by $\rho_1\alpha_1\rho_2\alpha_2$ which is identical to $[n_r^{\rho\alpha}]^{\alpha_1,\alpha_2}$. If the group is semisimple the index ρ is dropped. On this basis matrices of $M(\omega_1\times\omega_2)$ are expressed as

$$[X]^{\omega_1,\omega_2} = \sum_{\alpha,\alpha_1,\alpha_2=1}^{M}\sum_{\rho=1}^{f(\omega_1,\omega_2;\alpha)}\sum_{\rho_1=1}^{f(\omega_1;\alpha_1)}\sum_{\rho_2=1}^{f(\omega_2;\alpha_2)}\sum_{r=1}^{f(\alpha)}(X)_r^{\omega_1;\rho_1\alpha_1,\omega_2;\rho_2\alpha_2;\rho\alpha}[n_r^{\rho\alpha}]^{\omega_1;\rho_1\alpha_1,\omega_2;\rho_2\alpha_2} \quad (4.10)$$

where the coefficients are again given by the appropriate trace.

3. When at least one of the representations is not completely reduced, the GNITM cannot be expressed in terms of previously tabulated quantities but must be obtained by symmetry-adapting the matrix basis of $M(\omega_1\times\omega_2)$.

V. INVARIANT MATRICES

The Hamiltonian for a physical system with symmetry group G must be invariant to the elements of G; that is, it transforms according to the invariant or symmetric irreducible representation Γ^S: $\{[G_a]^S = [1],\ \forall\ G_a\}$

$$[G_a]^{\omega_1}[H]^{\omega_1,\omega_2}[G_a^{-1}]^{\omega_2} = [H]^{\omega_1,\omega_2} \quad (5.1)$$

Here $[H]^{\omega_1,\omega_2}$ is a possibly rectangular submatrix of the Hermitian full Hamiltonian matrix, $[H]^{\omega,\omega}$.

Invariant matrices are linear combinations of invariant GNITM

$$[H]^{\omega_1,\omega_2} = \sum_{\rho=1}^{f(\omega_1,\omega_2;S)}(H)_1^{\rho S}\,[n_1^{\rho S}]^{\omega_1,\omega_2} \quad (5.2)$$

where the frequency is given by the character formula

$$f(\omega_1,\omega_2;S) = \frac{1}{g}\sum_{\sigma=1}^{M}n_\sigma\chi^S_{\bar{\sigma}}\chi^{\omega_1}_\sigma\chi^{\hat{\omega}_2}_\sigma = \frac{1}{g}\sum_{\sigma=1}^{M}n_\sigma\chi^{\omega_1}_\sigma\chi^{\omega_2 *}_\sigma \quad (5.3)$$

using $\chi^S_{\bar{\sigma}} = 1$ and $\chi^{\hat{\omega}_2}_\sigma = \chi^{\omega_2 *}_\sigma$.

Invariant GNITM result from symmetry-adaptation and reduction of $\Gamma^{\omega_1}\times\Gamma^{\hat{\omega}_2}$ which requires in turn construction of the Hermitian idempotent matrix from (3.11)

$$[e^S_{11}]^{\omega_1,\hat{\omega}_2}_{i_1 j_1,i_2 j_2} = \frac{1}{g}\sum_{a=1}^{g}[G_a]^{\omega_1}_{i_1 j_1}[G_a]^{\omega_2 *}_{i_2 j_2} \quad (5.4)$$

This matrix can be diagonalized by any method.

VI. AMMONIA

The orbital model of ammonia provides a simple example illustrating the use of GNITM. The symmetry group of NH_3 is C_{3v}, the smallest nonabelian point group.[11] The valence orbital basis is

$$B = \{|1s_{H1}\rangle, |1s_{H2}\rangle, |1s_{H3}\rangle, |2s_N\rangle, |2p_{zN}\rangle, |2p_{xN}\rangle, |2p_{yN}\rangle\} \tag{6.1}$$

which divides into two subsets invariant under C_{3v}: hydrogen orbitals

$$B(H) = \{|1s_{H1}\rangle, |1s_{H2}\rangle, |1s_{H3}\rangle\} \tag{6.2}$$

and nitrogen orbitals

$$B(N) = \{|2s_N\rangle, |2p_{zN}\rangle, |2p_{xN}\rangle, |2p_{yN}\rangle\} \tag{6.3}$$

Each of $|2s_N\rangle$ and $|2p_{zN}\rangle$ is also invariant to C_{3v}, but for convenience they will be included here in B(N). Nitrogen is assumed to be at the origin of the molecular coordinate system. Hydrogen 1 is in the xz plane at $\phi = 0°$, hydrogen 2 is at $\phi = 120°$, and hydrogen 3 is at $\phi = 240°$, all with the same θ. The representations Γ^H and Γ^N of C_{3v} generated on these two bases are displayed in Tables 1 and 2. The representation Γ^H is reducible and not reduced, while Γ^N is reducible and completely reduced. It follows that B(N) is symmetry-adapted, and its elements can be classified according to the irreducible representations of C_{3v}

$$|2s_N\rangle = |2s;a_1\rangle, \quad |2p_{zN}\rangle = |2p;a_1\rangle$$
$$|2p_{xN}\rangle = |2p;e1\rangle, \quad |2p_{yN}\rangle = |2p;e2\rangle \tag{6.3}$$

The GNITM for the matrix spaces M($H\times H$), M($N\times N$), and M($H\times N$) are obtained by symmetry-adapting the Kronecker product representations $\Gamma^H\times\Gamma^H$, $\Gamma^N\times\Gamma^N$, and $\Gamma^H\times\Gamma^N$ with the method describe in section III. Note that all the representations of C_{3v} considered here are real so that the contragredient representation $\Gamma^{\hat{\omega}}$ is identical to Γ^{ω} in each case. The characters of Γ^H and Γ^N are given together with a character table of C_{3v} in Table 3. From (3.12) the invariant coupling frequencies are

$$f(H,H;A_1) = 2$$
$$f(N,N;A_1) = 5 \tag{6.4}$$
$$f(H,N;A_1) = 3$$

where A_1 represents the invariant irreducible representation of C_{3v}. Symmetry-adaptation proceeds by first constructing the representations of two generators, say $[\sigma_{v1}]^{H,N} = [\sigma_{v1}]^H\times[\sigma_{v1}]^N$ and $[\sigma_{v2}]^{H,N} = [\sigma_{v2}]^H\times[\sigma_{v2}]^N$, and generating the remaining representations. Generally, the matrices $[e^{\alpha}_{r1}]^{H,N}$ are obtained from relation (3.7), but for the present purpose only the invariant matrix $[e^{A_1}_{11}]^{H,N}$ need be constructed. Diagonalization of $[e^{A_1}_{11}]^{H,N}$ gives f($H,N;A_1$) orthonormal eigenvectors

$$\{|H,N;\rho A_1\ 1\rangle, \rho = 1,...,f(H,N;A_1)\} \tag{6.5}$$

where

$$|H,N;\rho A_1\ 1\rangle = \sum_{i=1}^{3}\sum_{j=1}^{4}|Hi,Nj\rangle\langle Hi,Nj|\rho A_1\ 1\rangle \tag{6.6}$$

By (4.2) elements of the invariant GNITM are then

$$[n_1^{\rho A_1}]^{H,N}_{ij} = \langle Hi,Nj|\rho A_1\ 1\rangle \tag{6.7}$$

Table 1. Representation Γ^H of C_{3v} on Ammonia Hydrogen Basis, B(H)

I	σ_{v1}	σ_{v2}	σ_{v3}	C_3	C_3^2
$\begin{bmatrix}1&\cdot&\cdot\\ \cdot&1&\cdot\\ \cdot&\cdot&1\end{bmatrix}$	$\begin{bmatrix}1&\cdot&\cdot\\ \cdot&\cdot&1\\ \cdot&1&\cdot\end{bmatrix}$	$\begin{bmatrix}\cdot&\cdot&1\\ \cdot&1&\cdot\\ 1&\cdot&\cdot\end{bmatrix}$	$\begin{bmatrix}\cdot&1&\cdot\\ 1&\cdot&\cdot\\ \cdot&\cdot&1\end{bmatrix}$	$\begin{bmatrix}\cdot&\cdot&1\\ 1&\cdot&\cdot\\ \cdot&1&\cdot\end{bmatrix}$	$\begin{bmatrix}\cdot&1&\cdot\\ \cdot&\cdot&1\\ 1&\cdot&\cdot\end{bmatrix}$

The same procedure is followed for the remaining two matrix spaces, and the results are displayed in Table 4. In this case, none of the GNITM have overlapping matrix elements. Since B(N) is completely reduced, the corresponding GNITM constitute a compound NITM basis which can be indexed as

$$[n_1^{1A_1}]^{N,N} = [n_1^{A_1}]^{2sA_1,2sA_1}$$
$$[n_1^{2A_1}]^{N,N} = [n_1^{A_1}]^{2sA_1,2p_zA_1}$$
$$[n_1^{3A_1}]^{N,N} = [n_1^{A_1}]^{2p_zA_1,2sA_1} \tag{6.8}$$
$$[n_1^{4A_1}]^{N,N} = [n_1^{A_1}]^{2p_zA_1,2p_zA_1}$$
$$[n_1^{5A_1}]^{N,N} = [n_1^{A_1}]^{2pE,2pE}$$

The hydrogen block $[H]^{H,H}$ is expressed in terms of the two invariant GNITM according to

$$[H]^{H,H} = \begin{bmatrix}a&b&b\\ b&a&b\\ b&b&a\end{bmatrix} = a\sqrt{3}[n_1^{1A_1}]^{H,H} + b\sqrt{6}[n_1^{2A_1}]^{H,H} \tag{6.9}$$

The nitrogen block $[H]^{N,N}$ is expressed in terms of the five GNITM according to

$$[H]^{N,N} = \begin{bmatrix}c&d&\cdot&\cdot\\ d^*&e&\cdot&\cdot\\ \cdot&\cdot&f&\cdot\\ \cdot&\cdot&\cdot&f\end{bmatrix} = c[n_1^{1A_1}]^{N,N} + d[n_1^{2A_1}]^{N,N} + d^*[n_1^{3A_1}]^{N,N} + e[n_1^{4A_1}]^{N,N} + f\sqrt{2}[n_1^{5A_2}]^{N,N} \tag{6.10}$$

The Hermitian condition requires that the coefficient of $[n_1^{3A_1}]^{N,N}$ be the complex conjugate of the coefficient of $[n_1^{2A_1}]^{N,N}$. Therefore, four independent parameters are sufficient to define $[H]^{N,N}$. The interaction block $[H]^{H,N}$ is given by

$$[H]^{H,N} = \begin{bmatrix}p&q&2r&\cdot\\ p&q&-r&r\sqrt{3}\\ p&q&-r&-r\sqrt{3}\end{bmatrix} = p\sqrt{3}[n_1^{1A_1}]^{H,N} + q\sqrt{3}[n_1^{2A_1}]^{H,N} + 2r\sqrt{3}[n_1^{3A_1}]^{H,N} \tag{6.11}$$

Again, the Hermitian condition requires that $[H]^{N,H} = [H]^{H,N\dagger}$ so that these parameters are sufficient. The total Hamiltonian matrix is displayed in Table 5.

The extended Hückel treatment of ammonia is formally consistent with this result, which may explain any successes of that simplistic model. A notable exception is the mixing of the $|2s_N\rangle$ and $|2p_{zN}\rangle$ orbitals, absent in the overlap

Table 2. Representation Γ^N of C_{3v} on Ammonia Nitrogen Orbital Basis, B(N)

I	σ_{v1}	σ_{v2}	σ_{v3}	C_3	C_3^2
$\begin{bmatrix} 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & -1 \end{bmatrix}$	$\begin{bmatrix} 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & -a & -b \\ \cdot & \cdot & -b & a \end{bmatrix}$	$\begin{bmatrix} 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & -a & b \\ \cdot & \cdot & b & a \end{bmatrix}$	$\begin{bmatrix} 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & -a & -b \\ \cdot & \cdot & -b & a \end{bmatrix}$	$\begin{bmatrix} 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & -a & b \\ \cdot & \cdot & -b & -a \end{bmatrix}$

[a] $a = {}^1/_2$, $b = \sqrt{3}/2$.

Table 3. Characters for Irreducible and Reducible Representations of C_{3v}

	I	σ_{1v}, σ_{2v}, σ_{3v}	C_3,C_3^2
A_1	1	1	1
A_2	1	−1	1
E	2	0	−1
H	3	1	0
N	4	2	1

Table 4. GNITM for Ammonia

$$[n_1^{1A_1}]^{H,H} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \cdot & \cdot \\ \cdot & \frac{1}{\sqrt{3}} & \cdot \\ \cdot & \cdot & \frac{1}{\sqrt{3}} \end{bmatrix} \quad [n_1^{2A_1}]^{H,H} = \begin{bmatrix} \cdot & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{6}} & \cdot & \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \cdot \end{bmatrix} \quad [n_1^{5A_1}]^{N,N} = \begin{bmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \frac{1}{\sqrt{2}} & \cdot \\ \cdot & \cdot & \cdot & \frac{1}{\sqrt{2}} \end{bmatrix}$$

$$[n_1^{1A_1}]^{N,N} = \begin{bmatrix} 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix} \quad [n_1^{2A_1}]^{N,N} = \begin{bmatrix} \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix} \quad [n_1^{3A_1}]^{N,N} = \begin{bmatrix} \cdot & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix} \quad [n_1^{4A_1}]^{N,N} = \begin{bmatrix} \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

$$[n_1^{1A_1}]^{H,N} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \cdot & \cdot \\ \frac{1}{\sqrt{3}} & \cdot & \cdot \\ \frac{1}{\sqrt{3}} & \cdot & \cdot \end{bmatrix} \quad [n_1^{2A_1}]^{H,N} = \begin{bmatrix} \cdot & \frac{1}{\sqrt{3}} & \cdot \\ \cdot & \frac{1}{\sqrt{3}} & \cdot \\ \cdot & \frac{1}{\sqrt{3}} & \cdot \end{bmatrix} \quad [n_1^{3A_1}]^{H,N} = \begin{bmatrix} \cdot & \cdot & \frac{1}{\sqrt{3}} & \cdot \\ \cdot & \cdot & \frac{-\sqrt{3}}{6} & \frac{1}{2} \\ \cdot & \cdot & \frac{-\sqrt{3}}{6} & \frac{1}{2} \end{bmatrix}$$

Table 5. Total Hamiltonian Matrix for Ammonia

	$1s_{H1}$	$1s_{H2}$	$1s_{H3}$	$2s_N$	$2p_{zN}$	$2p_{xN}$	$2p_{yN}$
$1s_{H1}$	a	b	b	p	q	$2r$	·
$1s_{H2}$	b	a	b	p	q	$-r$	$r\sqrt{3}$
$1s_{H3}$	b	b	a	p	q	$-r$	$-r\sqrt{3}$
$2s_N$	p^*	p^*	p^*	c	d	·	·
$2p_{zN}$	q^*	q^*	q^*	d^*	e	·	·
$2p_{xN}$	$2r^*$	$-r^*$	$-r^*$	·	·	f	·
$2p_{yN}$	·	$r^*\sqrt{3}$	$-r^*\sqrt{3}$	·	·	·	f

paradigm. With this term included $[H]^{N,N}$ fits the superposition model.[2,3]

VII. CONCLUSION

The systematic nature of this approach lends itself to computer methods. For any finite group all that is required is a set of generating relations and the various representation matrices for the generators. In simple cases the matrix $[e_{11}^{\alpha}]^{\omega_1,\omega_2}$ may be diagonalized by inspection, but the larger problems require an advanced algorithm. For the frequency $f(\omega_1,\omega_2;\alpha)$ greater than one, the eigenvectors of $[e_{11}^{\alpha}]^{\omega_1,\omega_2}$, and the resulting GNITM, are not unique. Some study may be required to select the most useful set.

For a system with symmetry, the most general form of a Hamiltonian matrix over any basis—not just symmetry-adapted ones—can be efficiently constructed. The nature of various parameterizations and interactions can then be analyzed directly. If a Hamiltonian matrix is already available, the expansion coefficients are easily computed from the trace expression (5.3). It is intended to apply these techniques to Fock matrices.

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