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Article

Using Group Theory to Obtain Eigenvalues of Nonsymmetric Systems by Symmetry Averaging

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Abstract: If the Hamiltonian in the time independent Schrödinger equation, $H\Psi = E\Psi$, is invariant under a group of symmetry transformations, the theory of group representations can help obtain the eigenvalues and eigenvectors of *H*. A finite group that is not a symmetry group of *H* is nevertheless a symmetry group of an operator H_{sym} projected from *H* by the process of symmetry averaging. In this case $H = H_{sym} + H_R$ where H_R is the nonsymmetric remainder. Depending on the nature of the remainder, the solutions for the full operator may be obtained by perturbation theory. It is shown here that when *H* is represented as a matrix [*H*] over a basis symmetry adapted to the group, the reduced matrix elements of [H_{sym}] are simple averages of certain elements of [*H*], providing a substantial enhancement in computational efficiency. A series of examples are given for the smallest molecular graphs. The first is a two vertex graph corresponding to a heteronuclear diatomic molecule. The symmetrized component then corresponds to a homonuclear system. A three vertex system is symmetry averaged in the first case to C_s and in the second case to the nonabelian C_{3v}. These examples illustrate key aspects of the symmetry-averaging process.

Keywords: Hamiltonian symmetry; group theory; symmetry-adapted basis; reduced matrix elements; symmetry-averaging

1. Introduction

In the context of the time independent Schrödinger equation:

$$H\psi = E\psi \tag{1}$$

the elements of a symmetry group G commute with H [1-3]:

$$HG_a = G_a H, G_a \in \mathrm{G} \tag{2}$$

Commutativity requires that H and G do not mix each other's invariant spaces so that the eigenfunctions of H must (barring accidental degeneracy) transform according to the irreducible representations of the symmetry group. The methods of group representations can help determine the eigenvalues and eigenvectors of H.

Suppose that H does not commute with a particular finite unitary group G but that the behavior of H under the group elements is known and given by:

$$\left\{G_a H G_a^{-1}, a = 1, 2, ..., g\right\} \tag{3}$$

Then a symmetrized operator, H_{sym}, is projected from H by symmetry averaging, summing over all transformations and dividing by the order of the group:

$$H_{sym} = \tfrac{1}{g}\sum_{a=1}^{g} G_a H G_a^{-1} \tag{4}$$

The symmetrized operator commutes with all elements of G:

$$\left\{G_a H_{sym} = H_{sym} G_a, a = 1, 2, ..., g\right\} \tag{5}$$

and is Hermitian.

The original operator is the sum:

$$H = H_{sym} + H_R \tag{6}$$

where H_R is the remainder. If H_{sym} is nonzero and the remainder H_R is sufficiently small in some sense, perturbation theory may give acceptable approximations to the eigenvalues and eigenvectors of H. A number of groups may be used for any particular system, but the optimum choice for analysis would generally be the largest group yielding a nonzero H_{sym}. In general, the larger the group, the more the reduction in analytical requirements.

This approach may be compared to established perturbation methods in which the total Hamiltonian is expressed as the sum of a high-symmetry zero-order Hamiltonian plus a symmetry lowering perturbation: $H_0 + V$. Symmetry-averaging is systematic, ensures that H_R has no identity component and provides a relationship between reduced matrix elements of H_{sym} and matrix elements of H.

It is usual to have a matrix representation, [H], of the Hamiltonian over a suitable basis of a Hilbert space, either as an initial definition or as a first step in analysis. If the basis is symmetry-adapted to the group G the matrix of the symmetrized operator [H_{sym}] will be reduced although [H] will not be. By a corollary to the symmetry-generation theorem [4-6], the reduced matrix elements of [H_{sym}] are simple averages of certain elements of [H] making the construction of [H_{sym}] much more efficient than the computationally demanding projection. Therefore, even though H_{sym} may not be the Hamiltonian of a real molecule $[H_{sym}]$ is readily determined.

Symmetry-averaging as a projection is presented in the next section and the use of the symmetry-adapted basis for symmetry-averaging is described in the third section. In the fourth section, the simplest example of a heteronuclear diatomic molecule corresponding to a two-vertex graph with one edge is presented. In the fifth section, symmetry-averaging of a three vertex system to two different groups is described. The sixth section is the conclusion.

2. Symmetry-averaging

Using the methods of finite group algebra, the identity for a finite group is given in terms of simple projectors as:

$$I = \sum_{\alpha}^{M} e^{\alpha} \tag{7}$$

where the sum is over the M irreducible representations of the group and the projectors e^{α} are commuting orthogonal idempotents:

$$e^{\alpha} e^{\beta} = e^{\beta} e^{\alpha} = \delta(\alpha, \beta) e^{\alpha} \tag{8}$$

This is the notation of Littlewood [7] and Weyl [8] in which irreducible representations are indexed by lower case Greek letters. It is convenient to take the lead term, $\alpha = 1$ to correspond to the totally symmetric irreducible representation occurring in every group. Then the corresponding projector is the symmetrizer:

$$e^{1} = \tfrac{1}{g} \sum_{a=1}^{g} G_a \tag{9}$$

where the sum is over all g elements of the group. The effect of the symmetrizer on an arbitrary operator is to project out the totally symmetric component:

$$H_{sym} = e^{1} \circ H \equiv \tfrac{1}{g} \sum_{a}^{g} G_a H G_a^{-1} \tag{10}$$

where the "∘" operation is defined as shown to be the appropriate linear combination of equivalence transformations. Then H_{sym} commutes with all elements of the group. The original operator is expressed as the sum of H_{sym} and a remainder:

$$\begin{aligned} H &= I \circ H = e^{1} \circ H + \sum_{\alpha=2}^{M} e^{\alpha} \circ H \\ &= H_{sym} + H_R \end{aligned}$$

Since the right hand side of Equation 10 is the average of all the system orientations produced by the group transformations, the term symmetry-averaging is appropriate.

3. Symmetry-adapted basis

The elements of a basis symmetry-adapted to a group G transform irreducibly under the elements of the group according to:

$$G_a \left| \omega; \rho\alpha r \right\rangle = \sum_{r'=1}^{f(\alpha)} \left[G_a \right]_{r'r}^{\alpha} \left| \omega; \rho\alpha r' \right\rangle \tag{11}$$

where α denotes an irreducible representation of G, r' and r index the rows and columns of the $f(\alpha) \times f(\alpha)$ matrix $[G_a]^{\alpha}$, ρ distinguishes repeated irreducible representations, and ω identifies the complete space. The representation of the group on a symmetry-adapted basis is completely reduced. A symmetry-adapted basis is suitably-conditioned if all of the $|\omega;\rho\alpha r\rangle$, $\rho = 1,\ldots, f(\omega;\alpha)$, transform according to identical matrices $[G_a]^{\alpha}$. Here, $f(\omega;\alpha)$ is the number of times the α irreducible representation occurs, given by the usual character formula. Matrix elements of an operator H are expressed on this basis as:

$$\left\langle \omega; \rho\alpha r \right| H \left| \omega; \rho'\alpha' r' \right\rangle \tag{12}$$

If the operator is defined as a matrix $[H]^{\omega}$ on some defining basis: $\{|\omega i\rangle,\ i = 1,\ldots,f(\omega)\}$, it is necessary to perform the transformation to the symmetry-adapted basis:

$$\left| \omega; \rho\alpha r \right\rangle = \sum_{i=1}^{f(\omega)} \left| \omega i \right\rangle \left\langle \omega i \right| \rho\alpha r \left. \right\rangle \tag{13}$$

On a symmetry-adapted basis, the elements of an operator, H_{sym}, that commutes with G satisfy the relation [9]:

$$\left\langle \omega; \rho\alpha r \right| H_{sym} \left| \omega; \rho'\alpha' r' \right\rangle = \delta(\alpha, \alpha')\delta(r, r') \left\langle \omega; \rho\alpha \right\| H_{sym} \left\| \omega; \rho'\alpha \right\rangle \tag{14}$$

where the far right factor is a reduced matrix element. Since these elements are zero unless α equals α' and r equals r', and the reduced matrix elements are independent of r, the matrix is partitioned into scalar submatrices on the symmetry-adapted basis. Reordering the basis to group together elements with the same α and r gives a partition with $f(\alpha)$ identical $f(\omega;\alpha) \times f(\omega;\alpha)$ blocks down the diagonal resulting in a factored secular polynomial. These blocks are the reduced matrices. Suppose, for example, that a basis symmetry-adapted to the point group C_{3v} contains one A_1 and two E irreducible representations:

$$\left\{ \left| A_1 1 \right\rangle, \left| 1E1 \right\rangle, \left| 1E2 \right\rangle, \left| 2E1 \right\rangle, \left| 2E2 \right\rangle \right\} \tag{15}$$

then the corresponding representation of the group element G_a is:

$$\begin{bmatrix} [G_a]_{11}^{A_1} & 0 & 0 & 0 & 0 \\ 0 & [G_a]_{11}^{E} & [G_a]_{12}^{E} & 0 & 0 \\ 0 & [G_a]_{21}^{E} & [G_a]_{22}^{E} & 0 & 0 \\ 0 & 0 & 0 & [G_a]_{11}^{E} & [G_a]_{12}^{E} \\ 0 & 0 & 0 & [G_a]_{21}^{E} & [G_a]_{22}^{E} \end{bmatrix} \tag{16}$$

The matrix of an operator that commutes with the group has the form:

$$\begin{bmatrix} \langle 1A_1 \| H_{sym} \| 1A_1 \rangle & 0 & 0 & 0 & 0 \\ 0 & \langle 1E \| H_{sym} \| 1E \rangle & 0 & \langle 1E \| H_{sym} \| 2E \rangle & 0 \\ 0 & 0 & \langle 1E \| H_{sym} \| 1E \rangle & 0 & \langle 1E \| H_{sym} \| 2E \rangle \\ 0 & \langle 2E \| H_{sym} \| 1E \rangle & 0 & \langle 2E \| H_{sym} \| 2E \rangle & 0 \\ 0 & 0 & \langle 2E \| H_{sym} \| 1E \rangle & 0 & \langle 2E \| H_{sym} \| 2E \rangle \end{bmatrix} \tag{17}$$

A reordering of the basis to group together elements with the same *r*:

$$\{ |A_1 1\rangle, |1E1\rangle, |2E1\rangle, |1E2\rangle, |2E2\rangle \} \tag{18}$$

results in further reduction to block diagonal form:

$$\begin{bmatrix} \langle 1A_1 \| H_{sym} \| 1A_1 \rangle & 0 & 0 & 0 & 0 \\ 0 & \langle 1E \| H_{sym} \| 1E \rangle & \langle 1E \| H_{sym} \| 2E \rangle & 0 & 0 \\ 0 & \langle 2E \| H_{sym} \| 1E \rangle & \langle 2E \| H_{sym} \| 2E \rangle & 0 & 0 \\ 0 & 0 & 0 & \langle 1E \| H_{sym} \| 1E \rangle & \langle 1E \| H_{sym} \| 2E \rangle \\ 0 & 0 & 0 & \langle 2E \| H_{sym} \| 1E \rangle & \langle 2E \| H_{sym} \| 2E \rangle \end{bmatrix} \tag{19}$$

illustrating the power of group theory.

The partitioning of matrix (17) into scalar blocks illustrates the invariances that give rise to the symmetry-generation theorem [6]. If H_{sym} is obtained by symmetry-averaging of *H*, as in equation (10), and if the basis is suitably conditioned, then the trace of a block in matrix (17) is the sum of traces of corresponding transformed bocks of the matrix of H : $\left[G_a\right]^{\alpha}\left[H\right]^{\rho\alpha,\rho'\alpha}\left[G_a^{-1}\right]^{\alpha}$. Then as a corollary to the symmetry-generation theorem the reduced matrix elements of H_{sym} on a suitably conditioned symmetry-adapted basis are given by:

$$\left\langle \omega;\rho\alpha \left\| H_{sym} \right\| \omega;\rho'\alpha \right\rangle = \tfrac{1}{f(\alpha)} \sum_{r=1}^{f(\alpha)} \left\langle \omega;\rho\alpha r \left| H \right| \omega;\rho'\alpha r \right\rangle \tag{20}$$

That is, the reduced matrix elements of the symmetry-averaged operator are simple averages of particular matrix elements of the original operator over the symmetry-adapted basis.

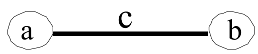
4. Two dimensional matrix

The simplest case is a two vertex graph corresponding to a two dimensional Hermitian matrix:

$$[H] = \begin{bmatrix} a & c \\ c & b \end{bmatrix} \tag{21}$$

The weighted graph is:

Figure 1



The symmetry group to be used is of order two and consists of the identity and the transposition (12):

$$\{E, (12)\}$$

The effect of the transposition on the matrix is:

$$(12)\begin{bmatrix} a & c \\ c & b \end{bmatrix}(12) = \begin{bmatrix} b & c \\ c & a \end{bmatrix} \quad (22)$$

so that symmetry averaging yields:

$$\frac{1}{2}\left\{ I\begin{bmatrix} a & c \\ c & b \end{bmatrix} I + (12)\begin{bmatrix} a & c \\ c & b \end{bmatrix}(12) \right\} = \begin{bmatrix} (a+b)/2 & c \\ c & (a+b)/2 \end{bmatrix} \quad (23)$$

Let

$$s = (a + b)/2 \qquad \text{and} \qquad d = (a - b)/2 \quad (24)$$

then:

$$\begin{bmatrix} a & c \\ c & b \end{bmatrix} = \begin{bmatrix} s & c \\ c & s \end{bmatrix} + \begin{bmatrix} d & 0 \\ 0 & -d \end{bmatrix} \quad (25)$$

as in Equation 6. Clearly, the smaller the value of d the closer [H] is to [H_{sym}] and the more appropriate this choice of symmetry. A symmetry-adapted basis is:

$$\begin{aligned} |+\rangle &= \tfrac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right) \\ |-\rangle &= \tfrac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right) \end{aligned} \quad (26)$$

where $\{|1\rangle, |2\rangle\}$ is the defining basis. The matrix of H_{sym} on this basis is:

$$\left[H_{sym}\right] = \begin{bmatrix} s+c & 0 \\ 0 & s-c \end{bmatrix} \quad (27)$$

and for the difference, H_R:

$$\left[H_R\right] = \begin{bmatrix} 0 & d \\ d & 0 \end{bmatrix} \quad (28)$$

Evidently, as a perturbation [H_R] makes only a second order correction.

Consider the numerical case $a = -40.0$, $b = -30.0$ and $c = -5.00$. The exact eigenvalues to three significant figures are:

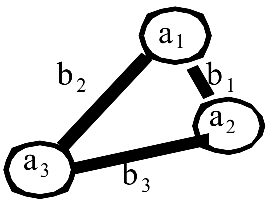
$$\lambda_1 = -42.1$$
$$\lambda_2 = -27.9 \tag{29}$$

From $[H_{sym}]$ the zero-order eigenvalues are −40.0 and −30.0. With the second order correction, these become −42.5 and −27.5.

5. Three-vertex examples

The next two illustrations refer to a weighted three-edge, three-vertex graph:

Figure 2



corresponding to the matrix:

$$[H] = \begin{bmatrix} a_1 & b_1 & b_2 \\ b_1 & a_2 & b_3 \\ b_2 & b_3 & a_3 \end{bmatrix} \tag{30}$$

This graph could be embedded in Euclidean three-space so that the groups considered would be point groups such as Cs , D3 or C3v. If the effect of these operations is to permute the vertices of the graph, the Hamiltonian matrix will be permuted. These are the examples considered here. If the weights associated with two of the vertices, say numbers one and two, are closer to each other than to the third, then it would be appropriate to consider a reflection plane through vertex three and bisecting the edge between vertex one and two. The effect on the Hamiltonian matrix would be exchange of index one with two. On the other hand, if the weights associated with all three vertices are similar, then the point group C3v would be suitable, transforming the Hamiltonian matrix by the permutation group S3.

S_2 Averaging

First consider the choice of G as the two-fold symmetry group $S_2 = \{E,(12)\}$. Using symmetry averaging on the original the invariant matrix is:

$$[H_{sym}] = \begin{bmatrix} u & v & v' \\ v & u & v' \\ v' & v' & a_3 \end{bmatrix} \tag{31}$$

where

$$
\begin{aligned}
&u \equiv \tfrac{1}{2}\left(a_1 + a_2\right) \\
&v \equiv b_1 \\
&v' \equiv \tfrac{1}{2}\left(b_2 + b_3\right)
\end{aligned}
\tag{32}
$$

Using a symmetry adapted basis will give the reduced matrix directly. This basis is:

$$
\begin{aligned}
&\left|\omega;1A\right\rangle = \tfrac{1}{\sqrt{2}}\left(\left|1\right\rangle + \left|2\right\rangle\right) \\
&\left|\omega;2A\right\rangle = \left|3\right\rangle \\
&\left|\omega;A'\right\rangle = \tfrac{1}{\sqrt{2}}\left(\left|1\right\rangle - \left|2\right\rangle\right)
\end{aligned}
\tag{33}
$$

and the matrix on this basis is:

$$
\left[H\right]^{\omega} = \begin{bmatrix} \tfrac{1}{2}\left(a_1 + a_2 + 2b_1\right) & \tfrac{1}{\sqrt{2}}\left(b_2 + b_3\right) & \tfrac{1}{\sqrt{2}}\left(a_1 - a_2\right) \\ \tfrac{1}{\sqrt{2}}\left(b_2 + b_3\right) & a_3 & \tfrac{1}{\sqrt{2}}\left(b_2 - b_3\right) \\ \tfrac{1}{\sqrt{2}}\left(a_1 - a_2\right) & \tfrac{1}{\sqrt{2}}\left(b_2 - b_3\right) & \tfrac{1}{2}\left(a_1 + a_2 - 2b_1\right) \end{bmatrix}
\tag{34}
$$

The reduced matrix elements of $\left[H_{sym}\right]^{\omega}$ are then:

$$
\begin{aligned}
&\left\langle \omega;1A \left\| H_{sym} \right\| \omega;1A \right\rangle = \left\langle \omega;1A \left| H \right| \omega;1A \right\rangle = u + v \\
&\left\langle \omega;2A \left\| H_{sym} \right\| \omega;2A \right\rangle = \left\langle \omega;2A \left| H \right| \omega;2A \right\rangle = a_3 \\
&\left\langle \omega;1A \left\| H_{sym} \right\| \omega;2A \right\rangle = \left\langle \omega;1A \left| H \right| \omega;2A \right\rangle = \sqrt{2}v' \\
&\left\langle \omega;A' \left\| H_{sym} \right\| \omega;A' \right\rangle = \left\langle \omega;A' \left| H \right| \omega;A' \right\rangle = u - v
\end{aligned}
\tag{35}
$$

so that the invariant matrix on this basis is:

$$
\left[H_{sym}\right]^{\omega} = \begin{bmatrix} u + v & \sqrt{2}v' & 0 \\ \sqrt{2}v' & a_3 & 0 \\ 0 & 0 & u - v \end{bmatrix}
\tag{36}
$$

The repetition of the A irreducible representation gives rise to a 2×2 block that must be diagonalized while the non-repeated A' eigenvalue can simply be read off the diagonal.

S_3 Averaging

The S_3 symmetry averaged matrix is:

$$
\left[H_{sym}\right] = \begin{bmatrix} x & y & y \\ y & x & y \\ y & y & x \end{bmatrix}
\tag{37}
$$

where

$$
x \equiv \left(a_1 + a_2 + a_3\right)/3
\tag{38}
$$

and

$$y \equiv (b_1 + b_2 + b_3)/3 \tag{39}$$

It is unnecessary, however, to obtain this matrix, since [*H*] can be directly transformed to a symmetry-adapted basis. Assuming that the elements of the defining basis are centered at the vertices and transform in the same way, a symmetry-adapted basis is:

$$\begin{aligned} |\omega; A_1\rangle &= \tfrac{1}{\sqrt{3}}\left(|1\rangle + |2\rangle + |3\rangle\right) \\ |\omega; E1\rangle &= \tfrac{1}{\sqrt{2}}\left(|2\rangle - |3\rangle\right) \\ |\omega; E2\rangle &= \tfrac{1}{\sqrt{6}}\left(2|1\rangle - |2\rangle - |3\rangle\right) \end{aligned} \tag{40}$$

where the C_{3v} names of the irreducible representations of have been used. On this basis, the matrix is:

$$[H]^{\omega} = \begin{bmatrix} \tfrac{1}{3}(a_1 + a_2 + a_3) + \tfrac{2}{3}(b_1 + b_2 + b_3) & \tfrac{1}{\sqrt{6}}(a_2 - a_3 + b_1 - b_2) & \left(\tfrac{1}{\sqrt{12}}\right)(2a_1 - a_2 - a_3 + b_1 + b_2 - 2b_3) \\ \tfrac{1}{\sqrt{6}}(a_2 - a_3 + b_1 - b_2) & \tfrac{1}{2}(a_2 + a_3 - 2b_3) & \tfrac{1}{\sqrt{6}}(-a_2 + a_3 + 2b_1 - 2b_2) \\ \left(\tfrac{1}{\sqrt{12}}\right)(2a_1 - a_2 - a_3 + b_1 + b_2 - 2b_3) & \tfrac{1}{\sqrt{6}}(-a_2 + a_3 + 2b_1 - 2b_2) & \tfrac{1}{6}(4a_1 + a_2 + a_3 - 4b_1 - 4b_2 + 2b_3) \end{bmatrix} \tag{41}$$

From equation 20 the reduced matrix elements of $[H_{sym}]^{\omega}$ are then:

$$\begin{aligned} \left\langle \omega; 1A_1 \middle\| H_{sym} \middle\| \omega; 1A_1 \right\rangle &= \left\langle \omega; 1A_1 1 \middle| H \middle| \omega; 1A_1 1 \right\rangle = x + 2y \\ \left\langle \omega; 1E \middle\| H_{sym} \middle\| \omega; 1E \right\rangle &= \tfrac{1}{2}\left(\left\langle \omega; 1E1 \middle| H \middle| \omega; 1E1 \right\rangle + \left\langle \omega; 1E2 \middle| H \middle| \omega; 1E2 \right\rangle\right) = a - b \end{aligned} \tag{42}$$

so that the invariant matrix is:

$$\left[H_{sym}\right]^{\omega} = \begin{bmatrix} x + 2y & 0 & 0 \\ 0 & x - y & 0 \\ 0 & 0 & x - y \end{bmatrix} \tag{43}$$

and the difference matrix is:

$$[H_1]^{\omega} = \begin{bmatrix} 0 & \tfrac{1}{\sqrt{6}}(a_2 - a_3 + b_1 - b_2) & \left(\tfrac{1}{\sqrt{12}}\right)(2a_1 - a_2 - a_3 + b_1 + b_2 - 2b_3) \\ \tfrac{1}{\sqrt{6}}(a_2 - a_3 + b_1 - b_2) & -\tfrac{1}{6}(2a_1 - a_2 - a_3 - 2b_1 - 2b_2 + 4b_3) & \tfrac{1}{\sqrt{6}}(-a_2 + a_3 + 2b_1 - 2b_2) \\ \left(\tfrac{1}{\sqrt{12}}\right)(2a_1 - a_2 - a_3 + b_1 + b_2 - 2b_3) & \tfrac{1}{\sqrt{6}}(-a_2 + a_3 + 2b_1 - 2b_2) & \tfrac{1}{6}(2a_1 - a_2 - a_3 - 2b_1 - 2b_2 + 4b_3) \end{bmatrix} \tag{44}$$

It is instructive to consider some numerical values. The first case appears to have little symmetry.

$$[H] = \begin{bmatrix} -10.0 & -4.00 & -5.00 \\ -4.00 & -20.0 & -6.00 \\ -5.00 & -6.00 & -30.0 \end{bmatrix}$$

The symmetry averaged component on the symmetry adapted basis is:

$$\left[H_{sym}\right]^{\omega} = \begin{bmatrix} -30.0 & 0 & 0 \\ 0 & -15.00 & \\ 0 & 0 & -15.00 \end{bmatrix}$$

with the difference matrix:

$$\left[H_1\right]^{\omega} = \begin{bmatrix} 0 & 4.49 & 9.53 \\ 4.49 & -4.00 & -3.27 \\ 9.53 & -3.27 & 4.00 \end{bmatrix}$$

The first order solutions are −30.0, −19.0, and −11.0. The exact solutions to three significant figures are −34.4, −17.4, −8.18.

A second example may be considered more symmetrical since the elements of the difference matrix are smaller.

$$\left[H\right] = \begin{bmatrix} -19.0 & -4.90 & -5.00 \\ -4.90 & -20.0 & -5.10 \\ -5.00 & -5.10 & -21.0 \end{bmatrix}$$

which gives the same symmetrized component as before on the symmetry adapted basis:

$$\left[H_{sym}\right]^{\omega} = \begin{bmatrix} -30.0 & 0 & 0 \\ 0 & -15.0 & 0 \\ 0 & 0 & -15.0 \end{bmatrix}$$

with a difference matrix of:

$$\left[H_R\right]^{\omega} = \begin{bmatrix} 0 & 0.449 & 0.953 \\ 0.449 & -0.400 & -0.327 \\ 0.953 & -0.327 & 0.400 \end{bmatrix}$$

The first order solutions are −30.0, −15.4, and −14.6, close to the exact eigenvalues to three significant figures of −30.1, −15.4, −14.5. The elements of the difference matrix are smaller by a factor of ten then in the previous case.

6. Conclusion

Since symmetry-averaging by projection requires a sum of triple matrix products it becomes computationally impractical as the sizes of basis and symmetry group increase. As shown here this calculation is unnecessary on a suitably conditioned symmetry-adapted basis so that symmetry-averaging is practical even for large systems.

The examples given here are purposely extremely small and simple; nevertheless, important properties of symmetry averaging can be determined from them. First, even if the system seems to have no symmetry, symmetry-averaging can be useful. For the two-vertex example the symmetry determined eigenvalues are good to second order. In the S_2 treatment of the three vertex example the exact eigenvalues separate into two groups similar to the approximate result. In the second S_3 treatment, the smaller difference term gives an indication of how symmetry averaging can be useful. In this case, the approximate eigenvalues are within 1% or less of the exact values.

It is anticipated that *ab initio* and DFT calculations can profit from this theory. Fock and Kohn-Sham matrices would be reduced on a suitably-conditioned symmetry-adapted basis and the matrix elements determined by the method described here.

A more general extended approach is to project out all the different irreducible symmetry components of the parent H. The noninvariant remainder H_R would then be the sum of several irreducible tensorial operators. The Wigner-Eckart theorem can then be used to evaluate the matrix elements of these operators. This approach is being developed.

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