Information theory-based code optimization of matrix elements for overall rotation angular momenta

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Abstract: - In this work we develop optimized computer codes for the calculation of angular momenta matrix elements for overall rotation. We determine the matrix elements using symmetric rotor eigenfunctions. The logic of the process is described by three decision tables. By maximizing the information entropy, we transform the decision tables in optimal computer codes. In all cases, the codes exhibit an efficiency at least of a 94% of the theoretical maximum. In addition, we show that the proposed codifications are optimal for any rotational quantum number *J*.

Key-Words: - Molecular rovibrational Hamiltonian; Angular momentum operators; Matrix elements; Decision tables; Information theory; Information entropy.

1 Introduction

The complete rovibrational molecular Hamiltonian is defined by the kinetic and potential energy operators for the nuclei motion [1-3]. For a full description the three parts of the kinetic operator are needed, namely: the pure rotational, the pure vibrational, and the rotation-vibration coupling. These three elements involve the effect of angular momentum operators. In this work, we focus in the computation of the angular momentum matrix elements for overall rotation appearing in any variational treatment of the molecular rovibrational Hamiltonian. The calculation of these matrix elements is carried out relying in the use and code conversion of decision tables. A classical Decision Table (DT) is a tabular form displaying the full decision logic of a problem [4]. Thus, the associated DT describes the existing set of conditions, as well as the set of actions to take according to these conditions. The conditions define an upper block of rows (conditions matrix), whereas the actions define a lower block (actions matrix). The columns of the DT define the combination of conditions corresponding to the different actions (decision rules). DT´s are a tool dating back to the early 60´s of the 20th century. However, in several formats, they are still used for the optimization of processes in different research areas [5-7].

DT's can be used to generate an optimized computer code for solving the problem at hand. This optimization refers to a reduction of: machine execution time, required machine memory, or number of decision rules. Along the years, several algorithms have been developed in order to reach these goals [4, 8-10]. A key work dealing with the conversion of DT's to computer code was presented by Pollack in 1965 [9]. In this work, Pollack proposed two algorithms: one for reducing computer storage, and other for reducing total computer running time. Both algorithms are based on the localization of indifferences in decision rules [9]. Although this procedure is adequate for cases where indifferent conditions do exist, it can be ambiguous for problems with only independent cases (no indifferences). Here, a more general and formally sound method was developed by Shwayder [10]. The method applies an information theory approach [11, 12] relying in the concept of information entropy. Information theory is based in the seminal work of Shannon [11], and deals with the efficient coding of messages and communicating data [12]. Here, the information entropy (H) quantifies the number of bits needed for representing the result of an uncertain event (i.e., the information contained in a message) [11, 12].

To generalize the variational treatment of rovibrational Hamiltonians, we develop in this work the optimal algorithms for computing angular momentum matrix elements. Thus, we calculate the value of the matrix elements, define the corresponding DT´s, and generate optimized codes from them. In addition, the efficiencies of the codes are quantified as proposed by Shwayder's [10].

2 Theory

The kinetic energy operator of the rovibrational molecular Hamiltonian [13] can be expressed as a function of the angular momentum for overall rotation, **J**= (∂T/ω), and for the change on vibrational coordinates, **p**= (∂T/$\dot{q}$). Thus,

$$\hat{T} = -\frac{\hbar^2}{2}\left(\mathbf{J}\,\mathbf{G}_{\mathrm{R}}\,\mathbf{J} + \mathbf{J}\,\mathbf{G}_{\mathrm{RV}}\,\mathbf{p} + \mathbf{p}\,\mathbf{G}_{\mathrm{RV}}^{\mathrm{T}}\,\mathbf{J} + \mathbf{p}\,\mathbf{G}_{\mathrm{v}}\,\mathbf{p}\right) + U \quad (1)$$

where $\mathbf{G}_{\mathrm{R}}$, $\mathbf{G}_{\mathrm{RV}}$, and $\mathbf{G}_{\mathrm{V}}$ are components of the rovibrational **G** matrix [14], for pure rotation, rovibrational coupling and pure vibration, respectively. U is the pseudopotential term usually included in the potential function.

Considering the angular momentum operator, **J**, along the molecule-fixed axis (x, y, z), its components $\mathbf{J}_x$, $\mathbf{J}_y$, and $\mathbf{J}_z$, satisfy the following commutation relations [3]:

$$\begin{aligned} &\left[\mathrm{J}_x,\mathrm{J}_y\right] = -i\hbar\mathrm{J}_z,\left[\mathrm{J}_y,\mathrm{J}_z\right] = -i\hbar\mathrm{J}_x, \\ &\left[\mathrm{J}_x,\mathrm{J}_z\right] = -i\hbar\mathrm{J}_y,\left[\mathrm{J}_z,\mathrm{J}_{\pm}^{m}\right] = \mp\hbar\mathrm{J}_{\pm}^{m}, \end{aligned} \quad (2)$$

where:

$$\mathrm{J}_{\pm}^{m} = \mathrm{J}_x \pm i\mathrm{J}_y \quad (3)$$

are the ladder operators.

Using equations (2) and (3), and a complete set of basis functions we can obtain the matrix elements arising in the variational treatment of the rovibrational Hamiltonian. These elements have the form:

$$\left\langle J',k',m'\middle|\hat{\mathrm{O}}\middle|J,k,m\right\rangle \quad (4)$$

Here, Ô represents any angular momentum operator and J, k, and m refer to the usual rotational quantum numbers. Using symmetric rotor eigenfunctions, we can obtain the non-vanishing matrix elements as described in [3, 15, 16]. Only three different cases can appear: 1) Operators with the form $\mathbf{J}_a$, where a indicates the x, y, or z component. 2) Operators with the form $(\mathbf{J}_a)^2$. 3) Operators with the form $\mathbf{J}_a\mathbf{J}_b$. Case 1) corresponds to the rovibrational coupling, whereas cases 2) and 3) correspond to the pure rotation. The results are collected in Table 1.

Table 1. Non-vanishing (J'=J) matrix elements for angular momentum operators.

Operator (Ô)	k′	Matrix element	Label
$\mathbf{J}_x$	k–1	$\hbar/2[(J+k)(J-k+1)]^{1/2}$	x1
	k+1	$\hbar/2[(J-k)(J+k+1)]^{1/2}$	x2
$\mathbf{J}_y$	k–1	$-i\hbar/2[(J+k)(J-k+1)]^{1/2}$	y1
	k+1	$i\hbar/2[(J-k)(J+k+1)]^{1/2}$	y2
$\mathbf{J}_z$	k	$\hbar\,k$	z1
$\mathbf{J}_x^2$	k	$\hbar^2/2[J^2+J-k^2]$	xx1
	k–2	$\hbar^2/4[J^2+J-k^2-k]^{1/2}[J^2+J-k^2-3k-2]^{1/2}$	xx2
	k+2	$\hbar^2/4[J^2+J-k^2+k]^{1/2}[J^2+J-k^2+3k-2]^{1/2}$	xx3
$\mathbf{J}_y^2$	k	$\hbar^2/2[J^2+J-k^2]$	yy1
	k–2	$-\hbar^2/4[J^2+J-k^2-k]^{1/2}[J^2+J-k^2-3k-2]^{1/2}$	yy2
	k+2	$-\hbar^2/4[J^2+J-k^2+k]^{1/2}[J^2+J-k^2+3k-2]^{1/2}$	yy3
$\mathbf{J}_z^2$	k	$\hbar^2\,k^2$	zz1
$\mathbf{J}_x\mathbf{J}_y$	k	$-i\hbar^2/2\;k$	xy1
	k–2	$-i\hbar^2/4[J^2+J-k^2+k]^{1/2}[J^2+J-k^2+3k-2]^{1/2}$	xy2
	k+2	$i\hbar^2/4[J^2+J-k^2-k]^{1/2}[J^2+J-k^2-3k-2]^{1/2}$	xy3
$\mathbf{J}_y\mathbf{J}_x$	k	$i\hbar^2/2\;k$	yx1
	k–2	$-i\hbar^2/4[J^2+J-k^2+k]^{1/2}[J^2+J-k^2+3k-2]^{1/2}$	yx2
	k+2	$i\hbar^2/4[J^2+J-k^2-k]^{1/2}[J^2+J-k^2-3k-2]^{1/2}$	yx3
$\mathbf{J}_x\mathbf{J}_z$	k–1	$\hbar^2/2(k)[J^2+J-k^2+k]^{1/2}$	xz1
	k+1	$\hbar^2/2(k)[J^2+J-k^2-k]^{1/2}$	xz2
$\mathbf{J}_z\mathbf{J}_x$	k–1	$\hbar^2/2(k-1)[J^2+J-k^2+k]^{1/2}$	zx1
	k+1	$\hbar^2/2(k+1)[J^2+J-k^2-k]^{1/2}$	zx2
$\mathbf{J}_y\mathbf{J}_z$	k–1	$-i\hbar^2/2(k)[J^2+J-k^2+k]^{1/2}$	yz1
	k+1	$i\hbar^2/2(k)[J^2+J-k^2-k]^{1/2}$	yz2
$\mathbf{J}_z\mathbf{J}_y$	k–1	$-i\hbar^2/2(k-1)[J^2+J-k^2+k]^{1/2}$	zy1
	k+1	$i\hbar^2/2(k+1)[J^2+J-k^2-k]^{1/2}$	zy2

3 Methods and Implementation

The results for the three cases shown in Table 1 are transformed in three different DT's as shown in Tables 2, 3 and 4. In these DT's the C's are the conditions, the A's are the actions, and the R's represent the decision rules (i.e., the matrix elements of Table 1). To convert the DT's in a computer code, optimizing the execution time, we use the Shwayder approach, which is based in Shannons's noiseless coding theorem [10]. This method establishes that the optimal code is obtained by maximizing the associated information entropy (*H*). Therefore, we start with a given DT, selecting the condition with the highest entropy. Then, for each branch of the condition, we will have two sub-DT's. One of the sub-DT's corresponds to the rules with the initial condition set to true (or 1), and the other to the rules with the condition set to false (or 0). For each sub-DT we select again the condition with the highest entropy, and the process is applied recursively until no conditions left. In this form, we obtain the optimal testing order of the conditions. Considering that we have no indifferences and that we use two coding characters (1-0 or true-false) the maximum information entropy for a given condition is obtained as [10]:

$$H = -\left(P(1) \log_2 P(1) + P(0) \log_2 P(0) \right) \quad (5)$$

In equation (5), *P(1)* represents the probability of the condition being true (or 1), and *P(0)* the probability of being false (or 0). For computing *P(0)* and *P(1)* we need the frequency of apparition (*f*) of each decision rule (columns of the DT). Therefore,

$$P(1) = \Sigma f_i \text{ (with condition equal 1)} \quad (6)$$
$$P(0) = 1 - P(1)$$

To determine the frequencies for the different decision rules in Tables 2, 3 and 4 tests for $J = 5$, 10, and 50 were carried out. All the tests provide similar results. The frequencies differ at most in the second decimal place. This fact indicates that the code resulting from the DT's is the same for the different values of *J*. Tables 2, 3, and 4 use the results for $J=50$. With this information we can apply the described procedure to transform the three DT's in the corresponding optimized code.

Case 1. The DT in Table 2 is the simplest one. Three conditions (C) are evaluated to generate the five decision rules (R). Values of $a = x$, and y are taken into account in the conditions. The $a = z$ component, is implicitly taken into account. In the same form, only a condition for k'= k+1 or k-1 is needed to generate all the remaining decision rules. Five decision rules (R) are evaluated corresponding to the the five different matrix elements (the actions, A), see Table 1. Chart1 shows the resulting code that maximizes information entropy.

Table 2. DT for the $\mathbf{J}_a$ angular momentum operators.

	$\mathbf{J}_a$	R1	R2	R3	R4	R5
C1	a=x	1	1	0	0	0
C2	a=y	0	0	1	1	0
C3	k′=k−1	1	0	1	0	0
	f (J=50)	0.199	0.199	0.199	0.199	0.201
A1	x1	X	-	-	-	-
A2	x2	-	X	-	-	-
A3	y1	-	-	X	-	-
A4	y2	-	-	-	X	-
A5	z1	-	-	-	-	X

```
if C1 then
  if C3 then
    <R1>
  else <R2>
  end_if
else
  if C2 then
    if C3 then
      <R3>
    else <R4>
    end_if
  else <R5>
  end_if
end_if
```

Chart 1. Optimal pseudocode for the DT in Table 2.

Case 2. Here, the DT for the double application of the $\mathbf{J}_a$ operator is presented. This case corresponds to the pure rotational terms appearing when using a principal axes coordinate system. As shown in Table 3, we have now four different conditions and seven different decision rules. Applying the maximization of the information entropy we obtain the code presented in Chart 2.

Case 3. This is the most complex case. Here, we have seven different conditions and fourteen decision rules, see Table 4. Now the cases $k \leftarrows k$, $k \pm 2$, and $k \pm 1$ are taken into account. After maximizing the information entropy the time optimal code shown in Chart 3 is obtained.

It can be observed in Charts 1 to 3 that the different decision rules, i.e., the matrix elements to compute, appear just once. Inefficient implementations of the problem logic would lead to codes where different decision rules appear more than once.

It is possible to quantify the efficiency of the codes as proposed by Shwayder [10]. The idea is to determine

the average information entropy per comparison in a given code.

Table 3. DT for the $(\mathbf{J}_a)^2$ angular momentum operators.

	$(\mathbf{J}_a)^2$	R1	R2	R3	R4	R5	R6	R7
C1	a=x	1	1	1	0	0	0	0
C2	a=y	0	0	0	1	1	1	0
C3	k′=k	1	0	0	1	0	0	1
C4	k′=k–2	0	1	0	0	1	0	0
	f (J=50)	0.144	0.141	0.141	0.144	0.141	0.144	0.141
A1	xx1	X	-	-	X	-	-	-
A2	xx2	-	X	-	-	-	-	-
A3	xx3	-	-	X	-	-	-	-
A4	yy2	-	-	-	-	X	-	-
A5	yy3	-	-	-	-	-	X	-
A6	zz1	-	-	-	-	-	-	X

```
if C1 then
  if C3 then
    <R1>
  else
    if C4 then
      <R2>
    else <R3>
    end_if
  end_if
else
  if C3 then
    if C2 then
      <R4>
    else <R7>
    end_if
  else
    if C4 then
      <R5>
    else <R6>
  end_if
end_if
```

Chart 2. Optimal pseudocode for the DT in Table 3.

Table 4. DT for the $\mathbf{J}_a\mathbf{J}_b$ angular momentum operators.

	$\mathbf{J}_a\mathbf{J}_b$	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14
C1	a=x	1	1	1	1	1	0	0	0	0	0	0	0	0	0
C2	a=y	0	0	0	0	0	1	1	1	1	1	0	0	0	0
C3	b=x	0	0	0	0	0	1	1	1	0	0	1	1	0	0
C4	b=y	1	1	1	0	0	0	0	0	0	0	0	0	1	1
C5	k′=k	1	0	0	0	0	1	0	0	0	0	0	0	0	0
C6	k′=k–1	0	0	0	1	0	0	0	0	1	0	1	0	1	0
C7	k′=k–2	0	1	0	0	0	0	1	0	0	0	0	0	0	0
	f(J=50)	0.072	0.070	0.070	0.071	0.071	0.072	0.070	0.070	0.071	0.071	0.071	0.071	0.071	0.071
A1	xy1	X	-	-	-	-	-	X	-	-	-	-	-	-	-
A2	xy2	-	X	-	-	-	-	-	X	-	-	-	-	-	-
A3	xy3	-	-	X	-	-	-	-	-	-	-	-	-	-	-
A4	xz1	-	-	-	X	-	-	-	-	-	-	-	-	-	-
A5	xz2	-	-	-	-	X	-	-	-	-	-	-	-	-	-
A6	yx1	-	-	-	-	-	X	-	-	-	-	-	-	-	-
A7	yz1	-	-	-	-	-	-	-	-	X	-	-	-	-	-
A8	yz2	-	-	-	-	-	-	-	-	-	X	-	-	-	-
A9	zx1	-	-	-	-	-	-	-	-	-	-	X	-	-	-
A10	zx2	-	-	-	-	-	-	-	-	-	-	-	X	-	-
A11	zy1	-	-	-	-	-	-	-	-	-	-	-	-	X	-
A12	zy2	-	-	-	-	-	-	-	-	-	-	-	-	-	X

Since the theoretical maximum is 1 bit of entropy per comparison, the average entropy directly gives how close we are to the maximum possible information entropy. This value, therefore, represents a measure of the efficiency of the code proposed. The average entropy per comparison can be determined as follows. First we identify the conditions that appear in the code, some can appear more than once. For instance, in the pseudocode of Chart 1 we test four conditions, C1, C3, C2 and C3. For each condition we determine its frequency of evaluation (*f*) by adding the probabilities of all the decision rules than can be reached from it. In addition we compute the maximum information entropy (*H*) of each condition using equation (5). The *P(1)* and *P(0)* probabilities for each condition are obtained from the frequencies of the decision rules below it using equation (6). The weighted entropies (*WH*) are defined as the product *f*H* for each condition. The efficiency is obtained from the quotient of total *WH* to total *f*. Table 5 shows the results for the codes in Charts 1 to 3. Table 5 shows that the three implementations, Charts 1, 2, and 3, have efficiencies of 97%, 98%, and 94%, respectively.

```
if C1 then
  if C4 then
    if C5 then
      <R1>
    else
      if C7 then
        <R2>
      else <R3>
      end_if
    end_if
  else
    if C6 then
      <R4>
    else <R5>
    end_if
  end_if
else
  if C2 then
    if C3 then
      if C5 then
        <R6>
      else
        if C7 then
          <R7>
        else <R8>
        end_if
      end_if
   else
     if C6 then
       <R9>
     else <R10>
     end_if
   end_if
  else
    if C4 then
      if C6 then
        <R13>
      else <R14>
    else
      if C6 then
        <R11>
      else <R12>
      end_if
    end_if
  end_if
end_if
```

Chart 3. Optimal pseudocode for the DT in Table 4.

4 Conclusions

In this paper, we obtain the most efficient algorithms for computing angular momentum matrix elements for overall rotation. Using symmetric rotor eigenfunctions we determine the matrix elements needed for the variational treatment of overall rotation and rovibrational coupling. The process logic is described using three decision tables (DT's). Then, the optimal computer code corresponding to each DT is obtained by maximizing the information entropy (H) of the resulting algorithm. The efficiency of each codification is quantified by comparison with the theoretical maximum value of H. We find efficiencies of 97%, 98% and 94% for the three considered DT's. These results show that the codifications are extremely efficient. In addition, we find that the frequency of apparition of each matrix element is almost constant for different values of the rotational quantum number J. Since this frequency is the factor determining the resulting computer code, the codifications proposed are optimal for any J.

Table 5. Efficiencies of the algorithms corresponding to the codes in Charts 1 to 3.

Case 1. DT in Table 2.				
Decision node	**Condition**	***H***	***f***	***WH***
1	C1	0.9704	1.0000	0.9704
2	C3	1.0000	0.3992	0.3992
3	C2	0.9204	0.6007	0.5528
4	C3	1.0000	0.3992	0.3992
Total			2.3992	2.3216
Efficiency= 97 %				
Case 2. DT in Table 3.				
Decision node	**Condition**	***H***	***f***	***WH***
1	C1	0.9848	1.0000	0.9848
2	C3	0.9226	0.4277	0.3946
3	C3	0.9999	0.5722	0.5722
4	C4	1.0000	0.2832	0.2832
5	C2	1.0000	0.2889	0.2889
6	C4	1.0000	0.2832	0.2832
Total			2.8555	2.8072
Efficiency= 98 %				
Case 3. DT in Table 4.				
Decision node	**Condition**	***H***	***f***	***WH***
1	C1	0.9401	1.0000	0.9401
2	C4	0.9714	0.3569	0.3467
3	C2	0.9912	0.6430	0.6374
4	C5	0.9226	0.2138	0.1973
5	C6	1.0000	0.1430	0.1430
6	C3	0.6752	0.3569	0.2410
7	C4	1.0000	0.2861	0.2861
8	C7	1.0000	0.1416	0.1416
9	C5	0.9226	0.2138	0.1973
10	C6	1.0000	0.1430	0.1430
11	C6	1.0000	0.1430	0.1430
12	C6	1.0000	0.1430	0.1430
13	C7	1.0000	0.1416	0.1416
Total			3.9263	3.7016
Efficiency= 94 %				

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