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CHEMICAL EDUCATION

Rσ diagonalization

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The **Jacobi** method provides the simplest algorithm to routinely diagonalize real summetric matrices commonly encountered in chemistry courses. While more accurate and efficient procedures exist, it is particularly helpful at least for purposes of instruction. This paper introduces a modified **Jacobi** scheme, the **Rσ** diagonalization. The methods are employed in the study of the carbocyclic systems. The accuracy of the results are evaluated by comparing them with those obtained using group theory.

Key Words: Rσ diagonalization, **Jacobi** method, eigenvectors, carbocyclic systems, Huckel approximation

STUDENTS OF CHEMISTRY ARE BECOMING INCREASINGLY EXPOSED to mathematical techniques which require the use of computers for implementation (1-3). One such technique is matrix diagonalization which can hardly be dispensed with for instance in the study of molecular structure. The average student in all likelihood is familiar with the diagonalization of 2x2 or 3x3 real symmetric matrices or similar matrices of higher dimensions with easily factorable characteristic polynomials. But even in the latter case, the calculation of eigenvectors when required can be a cumbersome task if done manually.

The **Jacobi** method provides the simplest algorithm to routinely diagonalize real symmetric matrices. While more accurate and efficient procedures exist (4), it is particularly helpful at least for purposes of instruction. In this article, we intoduce a modification of the **Jacobi** method which we refer to as the **Rσ diagonalization.**

Transformation

To diagonalize a matrix **B** means to solve the eigenvalue problem ,

$$\mathbf{BU = U\lambda,\ \ U^{-1}U = I} \qquad (1)$$

where **U** is the eigenvector matrix, **λ** the eigenvalue matrix and **I** the identity matrix. We rewrite eq. 1 as a similarity transformation

$$\mathbf{U^{-1}BU = \lambda} \qquad (2)$$

The purpose of matrix diagonalization therefore is, given **B**, to find the matrix **U** which transforms it into a diagonal matrix **λ** according to eq. 2.

The solution of eq. 2 is obtained by carrying out a sequence of transformations until the resulting matrix $\mathbf{B_n}$ is diagonal, that is,

$$\begin{aligned} \mathbf{A_1^{-1}B\,A_1} &= \mathbf{B_1} \\ \mathbf{A_2^{-1}B_1\,A_2} &= \mathbf{B_2} \\ &\vdots \\ \mathbf{A_n^{-1}B_{n-1}\,A_n} &= \mathbf{B_n} \end{aligned} \qquad (3)$$

The rate of convergence and hence the efficiency of a diagonalization method may therefore be evaluated according to the number of steps necessary to complete eq 3. Combining the above equations gives the eigenvector matrix as,

$$\mathbf{U = A_1 A_2 \ldots A_n} \qquad (4)$$

A representative transformation may be written as,

$$\mathbf{B' = A^{-1}B\,A} \qquad (5)$$

To effect the diagonalization, we introduce the matrix,

$$\mathbf{A = R\sigma} \qquad (6)$$

which has the following elements,

$$a_{pp} = \sqrt{\varepsilon},\quad o \le \varepsilon \le 1$$

$$a_{qq} = -\sqrt{\varepsilon},\quad p < q$$

$$a_{pq} = a_{qp} = \sqrt{1-\varepsilon}$$

$$a_{kk} = 1,\quad a_{kl} = o,\ k \neq l$$

In the simple case of 2x2 matrices, **R** is just the rotation matrix about the z-axis while σ is the matrix representation of a reflection in the xz-plane. As defined, **A** is an orthogonal matrix, $\mathbf{A = A^T = A^{-1}}$. Its relation to the **Jacobi** rotation matrix becomes transparent if we let $\varepsilon = \cos^2\alpha$, where α is a rotation angle. It is in this sense that the **Rσ**

transformation is a variation of the **Jacobi** method. In the following discussion, we also refer to an **Rσ** transformation as a rotation.

Substituting eq. 6 into eq. 5 yields the matrix elements **B'**,

$$b'_{pp} = x^2 b_{pp} + 2xyb_{pq} + y^2 b_{qq} \quad (7)$$

$$b'_{qq} = y^2 b_{pp} - 2xyb_{pq} + x^2 b_{qq} \quad (8)$$

$$b'_{pl} = xb_{pl} + yb_{ql} \quad (9)$$

$$b'_{ql} = yb_{pl} - xb_{ql} \quad (10)$$

$$b'_{pq} = xy(b_{pp} - b_{qq}) + (y^2 - x^2)b_{pq} \quad (11)$$

$$x = \sqrt{\varepsilon},\ y = \sqrt{1-\varepsilon} \quad (12)$$

The other elements remain the same, i.e., $b'_{kk} = b_{kk}$ and $b'_{kl} = b_{kl}$. As defined, the matrix **A** is meant to annihilate b'_{pq}, that is, make it equal to zero, by an appropriate choice of ε. From eqs. 11-12, this requires solving

$$\sqrt{\varepsilon(1-\varepsilon)} = (2\varepsilon - 1)Q,\ Q = \frac{b_{pq}}{b_{pp} - b_{qq}} \quad (13)$$

for ε. Equivalent to this is the following equation which has the roots ε_+ and ε_-,

$$\varepsilon^2 - \varepsilon + \omega = 0,\ \omega = \frac{Q^2}{4Q^2 + 1} \quad (14)$$

$$\varepsilon_+ = \frac{2Q^2}{1 + 4Q^2 + \sqrt{1 + 4Q^2}} < \tfrac{1}{2} \quad (15)$$

$$\varepsilon_- = 1 - \varepsilon_+ > \tfrac{1}{2},\ \varepsilon_+\varepsilon_- = \omega \quad (16)$$

There are two solutions which we discuss below. Meanwhile, assuming ε is known, we rewrite eqs. 7-11 as follows,

$$b'_{pp} = b_{pp} + tb_{pq},\ t = y/x \quad (17)$$

$$b'_{qq} = b_{qq} - tb_{pq} \quad (18)$$

$$b'_{pl} = b_{pl} + yf \quad (19)$$

$$b'_{ql} = b_{ql} - (x + 1)f \quad (20)$$

$$b'_{pq} = 0 \quad (21)$$

$$f = b_{ql} - \frac{y\, b_{pl}}{x + 1} \quad (22)$$

The elements of **B'** are thus expressed in terms of the original elements of **B** with correction terms which reflect the effect of the transformation. Compared to similar equations in the **Jacobi** method (5), eqs. 19-20 are particularly noteworthy in that b'_{pl} and b'_{ql} have a common correction factor f, weighted essentially by the value of ε as determined from eq. 14. This welcome feature also appears in the calculation of the eigenvectors.

Equation 4 may be written as,

$$\begin{aligned} \mathbf{U} &= (\mathbf{U}_0\, \mathbf{A}_1)\mathbf{A}_2\, \mathbf{A}_3 \ldots \mathbf{A}_n \\ &= (\mathbf{U}_1\, \mathbf{A}_2)\mathbf{A}_3 \ldots \mathbf{A}_n \\ &= (\mathbf{U}_2\, \mathbf{A}_3) \ldots \ldots \mathbf{A}_n \end{aligned} \quad (23)$$

where $\mathbf{U}_0$ is the identity matrix. From eqs. 3 and 23, the eigenvector matrix at the kth step is

$$\mathbf{U}_k = \mathbf{U}_{k-1}\, \mathbf{A}_k$$

Dropping the subscripts, the matrix elements are thus given by the following equations,

$$u'_{kp} = u_{kp} + yg$$

$$u'_{kq} = u_{kq} - (x + 1)g$$

$$g = u_{kq} - \frac{yu_{kp}}{x + 1}$$

where the primed elements refer to those of $\mathbf{U}_k$ and the unprimed elements to those of $\mathbf{U}_{k-1}$. The other elements remain unchanged, i.e., $u'_{kl} = u_{kl}$. We note the common factor g, similar to the common factor f in eqs. 19-20.

Rσ/A Transformation

The solution of eq. 14 may be confined to values of x and y in the first quadrant of the unit circle, that is, eq. 12. This, however, leads to an algorithm that is slowly convergent when compared to the **Jacobi** method. To overcome this problem, we restrict the values of x and y to those in the first and fourth quadrants,

$$x = \sqrt{\varepsilon},\ y = \text{sign}\,(Q)\,\sqrt{1-\varepsilon} \quad (24)$$

For Q > 0, we have from eq. 13,

$$\sqrt{\varepsilon(1-\varepsilon)} = (2\varepsilon - 1)Q > 0$$

so that 2ε-1 > 0 or ε = ε_- > 1/2. Whereas, for Q < 0, we have

$$-\sqrt{\varepsilon(1-\varepsilon)} = (2\varepsilon - 1)Q < 0$$

in which case, it must be that 2ε-1 > 0 or ε = ε_- > 1/2. In both instances, therefore, we find ε = ε_-. This leads to the following results,

$$x = \sqrt{\varepsilon_-},\ y = \text{sgn}\,(Q)\,\sqrt{1 - \varepsilon_-} = \text{sgn}\,(Q)\,\sqrt{\varepsilon_+},\ t = y/x \quad (25)$$

Computationally, we generate the solution according to the following route: using eqs. 15-16 and 25, we obtain

$$t = \frac{2Q}{1 + \sqrt{1 + 4Q^2}} \quad (26)$$

We then solve for x and y as follows,

$$x = \frac{1}{\sqrt{1 + t^2}}, \; y = tx \quad (27)$$

Equations 26-27 may be used in a straightforward manner to calculate the eigenvalues and eigenvectors of matrices with only one non-zero off-diagonal element b_{pq}. This, of course, extends to similar submatrices of a block-diagonal matrix. From eqs. 17-18, the eigenvalues are

$$\lambda p = b_{pp} + tb_{pq}, \; \lambda_q = b_{qq} - tb_{pq}, \; \lambda_k = b_{kk} \quad (28)$$

The corresponding eigenvector matrix has the following elements,

$$a_{pp} = x, \; a_{qq} = -x, \; a_{pq} = a_{qp} = y$$

$$a_{kk} = 1, \; a_{kl} = 0, \; k \neq l \quad (29)$$

There are two special cases to consider:

Case 1. $b_{pp} = b_{qq}$, $|b_{pq}| \neq 0$. From eqs. 11, 21 and 24, $\varepsilon = 1/2$ so that $x = y = \sqrt{1/2}$ and $t = 1$. This is a particularly simple solution which permits diagonalization by inspection when only one rotation, as in the immediately preceding discussion, is required. The eigenvalues and eigenvectors are given by eqs. 28-29 using the appropriate values of x, y and t.

Case 2. $Q << 1$, $Q^2 \sim 0$. Under this condition, we let $\varepsilon = \omega$ in eq. 14. Since $\omega < 1/2$, we have $\varepsilon = \varepsilon_+ = \omega$. Using $\varepsilon_+ = \omega/\varepsilon_-$, eq. 14 may be written as

$$\frac{Q^4}{(4Q^2 + 1)} \left(\frac{1}{\varepsilon_-}\right)^2 - Q^2 \left(\frac{1}{\varepsilon_-}\right) + Q^2 = 0 \quad (30)$$

We therefore choose $\varepsilon_- = 1$ if eq. 30 is to hold. From eq. 25, this gives the solution

$$x = \sqrt{\varepsilon_-} = 1, \; y = \text{sgn}(Q)\sqrt{\varepsilon_+} = \frac{Q}{\sqrt{1 + 4Q^2}}, \; t = y$$

Rσ/B Transformation

An alternative procedure is to solve the equation,

$$t^2 + 2\theta t - 1 = 0, \; t = y/x, \; 2\theta = \frac{1}{Q}$$

which is obtained by setting $b'_{pq} = 0$ in eq. 11. We use the root

$$t = \frac{\text{sgn}(\theta)}{|\theta| + \sqrt{1 + \theta^2}}$$

which is identical with eq. 26. When $|b_{pq}| << |b_{pp} - b_{qq}|$ we let

$$t = \frac{1}{2\theta} = Q$$

It is here where **Rσ/B** differs from the earlier transformation. The values of x and y are calculated as in eq. 27.

The above solution closely parallels that of Press, et al (6). Our definition of θ, however, differs by a minus sign. In addition, the computational aspects discussed in the same reference are incorporated in the computer programs to implement the **Rσ** and **Jacobi** algorithms. These include the sweep procedure, threshold calculation, and bypassing of rotations under certain conditions.

Discussion

We employed the **Rσ** and **Jacobi** methods to study the carbocyclic systems C_nH_n, n = 1, 12 within the Huckel approximation. The accuracy of the eigenvalues and eigenvectors were evaluated by comparing them with those obtained using group theory. Moreover, the three algorithms yield numerical results which agree to six decimal places.

The number of rotations required to complete the diagonalization as a function of the dimension **n** of the hamiltonian matrix is shown in Table 1.

It is clear that the **Rσ** methods compare very well with the **Jacobi** algorithm and are even more rapidly convergent in several cases.

We also used the three methods to diagonalize matrices with elements $b_{kl} = b_{lk} = k/10$, k = 1, n, l = k, n, n = 1-12, 16, 19. The number of rotations as a function of matrix dimension is the same for all three methods, ranging from 9 rotations for n = 3, 289 for n = 12, to 827 for n = 19.

Table 1. Number of rotations to diagonalize hamiltonian matrix of dimension **n**

n	3	4	5	6	7	8	9	10	11	12	16	19
Rσ/A	2	19	30	51	76	131	142	203	235	318	647	908
Rσ/B	2	19	30	51	75	130	142	202	237	318	657	911
Jacobi	2	19	33	51	99	131	189	200	281	319	645	929

As above, the eigenvalues and eigenvectors agree to six decimal places. Unlike the C_nH_n systems where numerous degeneracies (doubly) occur, these test matrices yield non-degenerate eigenvalues.

The **Rσ** methods have a distinct advantage over the **Jacobi** procedure which consists in having common correction factors f and g, weighted essentially by the quantities $\sqrt{\varepsilon}$ and $\sqrt{1 - \varepsilon}$. Quite clearly, they are more indicative of the effect of the transformation at each step of eq. 3. Perhaps, more importantly, the corrections to the elements of **B'** and $\mathbf{U}_k$ are incorporated in a more balanced manner than they are in the **Jacobi** method.

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