Question

The following matrices occur in the π-molecular orbital theory of conjugated hydrocarbons. The eigenvalues of the matrices determine the energies of the molecular orbitals (this theory will be met in the second year physical chemistry course).

(a) Find the eigenvalues and eigenvectors of the following matrices: (i) Allyl radical $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$; (ii) Cyclopropenyl $\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$;

(b) Find the eigenvalues of the following matrices:

$$\text{(i) Cyclobutadiene} \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}; \text{ (ii) Butadiene} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}.$$

(c) Show that the vectors

$$\begin{pmatrix} 2 \\ -1 \\ -1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix}, \begin{pmatrix} 1 \\ 1 \\ 1 \\ \sqrt{3} \end{pmatrix}, \begin{pmatrix} 1 \\ 1 \\ 1 \\ -\sqrt{3} \end{pmatrix},$$

are all eigenvectors of the matrix

$$Trimethylenemethane \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix}$$

Find the eigenvalues corresponding to these eigenvectors. Does the matrix have any other eigenvectors?

Answer

(a) (i) $\begin{vmatrix} -\lambda & 1 & 0 \\ 1 & -\lambda & 1 \\ 0 & 1 & -\lambda \end{vmatrix} = -\lambda(\lambda^2 - 1) - (-\lambda) + 0 = -\lambda(\lambda^2 - 2) = 0$

so $\lambda = 0, \pm\sqrt{2}$.

$\underline{\lambda = 0}$ Solve $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

$$\text{or} \quad \left.\begin{array}{rcl} y & = & 0 \\ x+z & = & 0 \\ y & = & 0 \end{array}\right\} y = 0, \text{ let } x = \alpha \text{ so } z = -\alpha.$$

Suitable eigenvector: $\begin{pmatrix} \alpha \\ 0 \\ -\alpha \end{pmatrix}$.

$\underline{\lambda = \sqrt{2}}$ Solve $\begin{pmatrix} -\sqrt{2} & 1 & 0 \\ 1 & -\sqrt{2} & 1 \\ 0 & 1 & -\sqrt{2} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

$$\text{or} \quad \left.\begin{array}{rcl} -\sqrt{2}x + y & = & 0 \\ x - \sqrt{2}y + z & = & 0 \\ y - \sqrt{2}z & = & 0 \end{array}\right\} \text{let } x = \beta,\ \ y = \sqrt{2}\beta, z = \beta.$$

Suitable eigenvector: $\begin{pmatrix} \beta \\ \sqrt{2}\beta \\ \beta \end{pmatrix}$.

$\underline{\lambda = -\sqrt{2}}$ Solve $\begin{pmatrix} \sqrt{2} & 1 & 0 \\ 1 & \sqrt{2} & 1 \\ 0 & 1 & \sqrt{2} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

$$\text{or} \quad \left.\begin{array}{rcl} \sqrt{2}x + y & = & 0 \\ x + \sqrt{2}y + z & = & 0 \\ y + \sqrt{2}z & = & 0 \end{array}\right\} \text{let } x = \gamma,\ \ y = -\sqrt{2}\gamma, z = \gamma.$$

Suitable eigenvector: $\begin{pmatrix} \gamma \\ -\sqrt{2}\gamma \\ \gamma \end{pmatrix}$.

(ii)

$$\begin{aligned} \begin{vmatrix} -\lambda & 1 & 1 \\ 1 & -\lambda & 1 \\ 1 & 1 & -\lambda \end{vmatrix} &= \begin{vmatrix} -(\lambda+1) & 0 & (\lambda+1) \\ 1 & -\lambda & 1 \\ 1 & 1 & -\lambda \end{vmatrix} (R_1' = R_1 - R_3) \\ &= (1+\lambda) \begin{vmatrix} -1 & 0 & 1 \\ 1 & -\lambda & 1 \\ 1 & 1 & -\lambda \end{vmatrix} \\ &= (1+\lambda)(-\lambda^2 + \lambda + 2) \\ &= (1+\lambda)(2-\lambda)(1+\lambda) = 0 \end{aligned}$$

So $\lambda = 2,\ -1,\ -1$.

$\underline{\lambda = 2}$ Solve $\begin{pmatrix} -2 & 1 & 1 \\ 1 & -2 & 1 \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

or $\left.\begin{array}{rrcl} (1) & -2x + y + z & = & 0 \\ (2) & x - 2y + z & = & 0 \\ (3) & x + y - 2z & = & 0 \end{array}\right\}$ $(2) + 2(3) \Rightarrow 3x - 3z = 0$. Let $x = \alpha$ so that $z = \alpha$. Substitute $x = \alpha = z$ into (1) to get $y = 2x - z = 2\alpha - \alpha = \alpha$.

Suitable eigenvector: $\begin{pmatrix} \alpha \\ \alpha \\ \alpha \end{pmatrix}$

$\underline{\lambda = -1}$ (Repeated eigenvalue)

Solve $\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

So $x + y + z = 0$. If $x = \beta$ then $y + z = -\beta$ (thus we have a 2 parameter family of eigenvectors). Let $z = \gamma$ so that $y = -(\beta + \gamma)$.

Suitable eigenvector: $\begin{pmatrix} \beta \\ -(\beta + \gamma) \\ \gamma \end{pmatrix}$.

(b) (i)

$$\begin{vmatrix} -\lambda & 1 & 0 & 1 \\ 1 & -\lambda & 1 & 0 \\ 0 & 1 & -\lambda & 1 \\ 1 & 0 & 1 & -\lambda \end{vmatrix} = \begin{vmatrix} -\lambda & 0 & \lambda & 0 \\ 1 & -\lambda & 1 & 0 \\ 0 & 1 & -\lambda & 1 \\ 1 & 0 & 1 & -\lambda \end{vmatrix} (R_1' = R_1 - R_3)$$

(Expand determinant along first row)

$$\begin{aligned} &= (-\lambda)(-1)^{1+1} \begin{vmatrix} -\lambda & 1 & 0 \\ 1 & -\lambda & 1 \\ 0 & 1 & -\lambda \end{vmatrix} + 0 + (\lambda)(-1)^{1+3} \begin{vmatrix} 1 & -\lambda & 0 \\ 0 & 1 & 1 \\ 1 & 0 & -\lambda \end{vmatrix} + 0 \\ &= -\lambda[-\lambda(\lambda^2 - 1) - (-\lambda)] + \lambda[-\lambda + \lambda(-1)] \\ &= \lambda^2(\lambda^2 - 4) \end{aligned}$$

So $\lambda = 0,\ 0,\ 2,\ -2$.

(ii)

$$\begin{vmatrix} -\lambda & 1 & 0 & 0 \\ 1 & -\lambda & 1 & 0 \\ 0 & 1 & -\lambda & 1 \\ 0 & 0 & 1 & -\lambda \end{vmatrix} = (-\lambda)(-1)^{1+1} \begin{vmatrix} -\lambda & 1 & 0 \\ 1 & -\lambda & 1 \\ 0 & 1 & -\lambda \end{vmatrix} + (-1)^{1+2} \begin{vmatrix} 1 & 1 & 0 \\ 0 & -\lambda & 1 \\ 0 & 1 & -\lambda \end{vmatrix} + 0 + 0$$

(Expand determinant along first row)

$$\begin{aligned} &= -\lambda[-\lambda(\lambda^2 - 1) - (-\lambda)] - [\lambda^2 - 1] \\ &= \lambda^4 - 3\lambda^2 + 1 = 0 \end{aligned}$$

Think of this as a quadratic in λ^2, so that

$$\lambda^2 = \frac{3 \pm \sqrt{9-4}}{2} = \frac{3 \pm \sqrt{5}}{2}.$$

Hence $\lambda = \pm\sqrt{\dfrac{3 \pm \sqrt{5}}{2}} = \pm\left(\dfrac{1 \pm \sqrt{5}}{2}\right)$

$\left(\text{You should check that } \left(\dfrac{1+\sqrt{5}}{2}\right)^2 = \dfrac{3+\sqrt{5}}{2}\right)$

(c)

$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 2 \\ -1 \\ -1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 0 \begin{pmatrix} 2 \\ -1 \\ -1 \\ 0 \end{pmatrix} \quad \text{eigenvalue} = 0$$

$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 0 \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} \quad \text{eigenvalue} = 0$$

$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ 1 \\ \sqrt{3} \end{pmatrix} = \begin{pmatrix} \sqrt{3} \\ \sqrt{3} \\ \sqrt{3} \\ 3 \end{pmatrix} = \sqrt{3} \begin{pmatrix} 1 \\ 1 \\ 1 \\ \sqrt{3} \end{pmatrix} \quad \text{eigenvalue} = \sqrt{3}$$

$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ 1 \\ -\sqrt{3} \end{pmatrix} = \begin{pmatrix} -\sqrt{3} \\ -\sqrt{3} \\ -\sqrt{3} \\ 3 \end{pmatrix} = -\sqrt{3} \begin{pmatrix} 1 \\ 1 \\ 1 \\ -\sqrt{3} \end{pmatrix} \quad \text{eigenvalue} = -\sqrt{3}$$

An n x n matrix has at most n orthogonal eigenvectors.

The eigenvectors of this 4x4 matrix are mutually orthogonal (you should check this!) and there are four of them - the maximum number possible. Hence any other eigenvector of the matrix will be a linear combination of these four orthogonal vectors:

$$r \begin{pmatrix} 2 \\ -1 \\ -1 \\ 0 \end{pmatrix} + s \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} + t \begin{pmatrix} 1 \\ 1 \\ 1 \\ \sqrt{3} \end{pmatrix} + u \begin{pmatrix} 1 \\ 1 \\ 1 \\ -\sqrt{3} \end{pmatrix}$$

for any scalars $r,\ s,\ t,\ u$.