Advanced Mathematical Methods for Chemistry

Quiz 2: SOLUTIONS

1. Determinant of any rotation matrix = 1

If $A^T = A^{-1}$ (for any orthogonal matrix)

$$\text{Det}\left(AA^T\right) = \text{Det}(I) = 1$$

$$\text{Det}\left(AA^T\right) = \text{Det}(A) \cdot \text{Det}(A^T)$$

But $\text{Det}(A^T) = \text{Det}(A)$

So, $\left(\text{Det}\, A\right)^2 = 1 \qquad \text{Det}\, A = \pm 1$

For Rotation Matrices, $\text{Det}\, A = +1$

(Note that product of Rotation matrices is also a rotation matrix)

2. $R_x(\theta)$ and $R_y(\theta)$

$R_x(\theta)$ and $R_y(\theta)$ have one eigenvalue = 1

Ex.

$$R_x(\theta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = 1 \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

Similarly for $R_y(\phi)$

3.

$$\begin{bmatrix} \sqrt{3}/2 & 0 & 1/2 \\ 0 & 1 & 0 \\ -1/2 & 0 & \sqrt{3}/2 \end{bmatrix} \begin{bmatrix} 2 \\ 4 \\ 1 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} + \sqrt{3} \\ 4 \\ -1 + \frac{\sqrt{3}}{2} \end{bmatrix},$$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \frac{1}{2} + \sqrt{3} \\ 4 \\ -1 + \frac{\sqrt{3}}{2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} - \sqrt{3} \\ -4 \\ 1 - \frac{\sqrt{3}}{2} \end{bmatrix} = \begin{bmatrix} -2.23 \\ -4 \\ 0.13 \end{bmatrix}$$

(d) has an extra -ve sign.

However, the correct answer is still (d) since it is closest.

4.
$$\det\begin{vmatrix} a-\lambda & b & 0 & b \\ b & a-\lambda & b & 0 \\ 0 & b & a-\lambda & b \\ b & 0 & b & a-\lambda \end{vmatrix} = 0$$

$$\Rightarrow \quad 0 = (a-\lambda)\begin{vmatrix} a-\lambda & b & 0 \\ b & a-\lambda & b \\ 0 & b & a-\lambda \end{vmatrix} - b\begin{vmatrix} b & 0 & b \\ a-\lambda & b & 0 \\ b & a-\lambda & b \end{vmatrix} - b\begin{vmatrix} b & a-\lambda & b \\ 0 & b & a-\lambda \\ b & 0 & b \end{vmatrix}$$

$$0 = (a-\lambda)\left[(a-\lambda)^3 - b^2(a-\lambda) - b^2(a-\lambda)\right]$$
$$- b^4 - b^2(a-\lambda)^2 + b^4 \quad - b^4 - b(a-\lambda)^2 b + b^4$$

$$\Rightarrow \quad (a-\lambda)^2\left[(a-\lambda)^2 - 4b^2\right] = 0$$

$$(a-\lambda)^2 (a-\lambda+2b)(a-\lambda-2b) = 0$$

$\lambda = a$, $\lambda = a+2b$, $\lambda = a-2b$

$\lambda = a$

Answer (c) : NB: This appears in Hückel theory for conjugated π-electrons.

5.
$$\det\begin{vmatrix} a-\lambda & b & 0 & 0 & 0 & b \\ b & a-\lambda & b & 0 & 0 & 0 \\ 0 & b & a-\lambda & b & 0 & 0 \\ 0 & 0 & b & a-\lambda & b & 0 \\ 0 & 0 & 0 & b & a-\lambda & b \\ b & 0 & 0 & 0 & b & a-\lambda \end{vmatrix} = 0$$

Though this determinant looks big, we can use some tricks to calculate eigenvalues, since Row and column operations leave determinant unchanged.

Do: $C_1 = C_1 + C_2 + C_3 + C_4 + C_5 + C_6$ to get

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

Clearly $a+2b$ is an eigenvalue

Now do $R_2 - R_1$, $R_3 - R_1$, $R_4 - R_1$, $R_5 - R_1$, $R_6 - R_1$ to get

$$(a+2b-\lambda)\begin{vmatrix} a-\lambda-b & b & 0 & 0 & -b \\ 0 & a-\lambda & b & 0 & -b \\ -b & b & a-\lambda & b & -b \\ -b & 0 & b & a-\lambda & 0 \\ -b & 0 & 0 & b & a-b-\lambda \end{vmatrix}$$

Notice, this is a 5×5 determinant

Now, we can do $R_3 + \frac{b}{a-\lambda-b}R_1$, $R_5 + \frac{b}{a-\lambda-b}$, so we can identify two more eigenvalues

$(a+2b-\lambda)(a-\lambda-b)(a-\lambda)$,

Thus $\lambda = a+2b$, $\lambda = a-b$, $\lambda = a$

By symmetry we can find 3 other eigenvalues

$\lambda = a-2b$ $\quad \lambda = a+b$ $\quad \lambda = a$

Thus, we have largest eigenvalue $\underline{a+2b}$

6. Clearly, matrix is symmetric about diagonal

Not Hermitian since $(A^T)^* \neq A$

7. Not Hermitian, since $(A^T)^* \neq A$

Hermitian matrix must have off diagonal elements be complex conjugates of their transpose element and diagonal elements must be REAL

$$A^{+} A = \frac{1}{3}\begin{bmatrix} 1 & 1 & 1 \\ 1 & \frac{-1+i\sqrt{3}}{2} & \frac{-1-i\sqrt{3}}{2} \\ 1 & \frac{-1-i\sqrt{3}}{2} & \frac{-1+i\sqrt{3}}{2} \end{bmatrix} \begin{bmatrix} 1 & 1 & 1 \\ 1 & \frac{-1-i\sqrt{3}}{2} & \frac{-1+i\sqrt{3}}{2} \\ 1 & \frac{-1+i\sqrt{3}}{2} & \frac{-1-i\sqrt{3}}{2} \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Unitary but not Hermitian

8. For Hermitian matrix, ALL eigenvalues MUST be real. Eigenvectors are orthogonal but can have complex coefficients.

9. $\begin{bmatrix} a & c \\ c & b \end{bmatrix}$ Arbitrary symmetric 2x2 matrix

$(a-\lambda)(b-\lambda) - c^2 = 0$ gives eigenvalues

$\lambda^2 - (a+b)\lambda + (ab-c^2) = 0$

$$\lambda = \frac{(a+b) \pm \sqrt{a^2+2ab+b^2 - 4ab + 4c^2}}{2}$$

$$= \frac{(a+b) \pm \sqrt{(a-b)^2 + (2c)^2}}{2}$$

If $a, b,$ ~~can~~ and c are real then eigenvalues ~~f~~ are real because $(a-b)^2 + (2c)^2 \geq 0$

But a, b, c can be complex, so λ can be complex.

Solution is (d)

10. $$\text{Det} \begin{vmatrix} 1 & 4 & 3 \\ 4 & 2 & 1 \\ -5 & 8 & 8 \end{vmatrix} = 1(16-8) + 4(-5-32) + 3(32+10)$$

$$= 8 - 148 + 126$$

$$= -14$$

Inverse exists. A^{-1}_{11} (1st element) $= -\frac{8}{14}$

Solution is (d) – None of above