Advanced Mathematical Methods For Chemistry

QUIZ 6 – SOLUTIONS

1. Coefficient of $x^2 = \frac{1}{2!}\left|\frac{\partial^2}{\partial x^2}\left(\frac{1}{\sqrt{1+x^2}}\right)\right|_{x=0} = 1$ (a)

2. $P(r) \propto r^6 e^{-2r/3a_0}$ $\quad \frac{d}{dR}P(r)=0$ at maximum or minimum

$$\Rightarrow r^5\left[6 - \frac{2r}{3a_0}\right]e^{-2r/3a_0} = 0$$

$$\Rightarrow \underbrace{r=0,\ r=\infty}_{\text{minima}} \quad \text{or} \quad \underbrace{\frac{r}{a_0} = 9}_{\text{maximum}} \qquad (c)$$

3. $(PV^2+a)(V-b) = \frac{4aRV^2}{27b}$ or $P = \frac{4aR}{27b(V-b)} - \frac{a}{V^2}$

$$\frac{dP}{dV} = 0 \Rightarrow \frac{-4aR}{27b(V-b)^2} + \frac{2a}{V^3} = 0$$

Cubic Equation for V

$$-\frac{4aR}{27b}V^3 + 2aV^2 - 4abV + 2ab^2 = 0$$

3 possible extrema (d)

4. At sadde point $\frac{dP}{dV} = \frac{d^2P}{dV^2} = 0$

$$\Rightarrow \frac{2R}{27b(V-b)^2} = \frac{1}{V^3}$$

$$\frac{4aR}{27b(V-b)^3} = \frac{6a}{V^4} \Rightarrow V = 3b \qquad (c)$$

5. $\sin(xy)$: Coefficient of $xy \Rightarrow \frac{\partial^2 \sin(xy)}{\partial x\,\partial y}\Big|_{(0,0)}$

$$= \frac{\partial}{\partial x}\left(x\cos xy\right)\Big|_{(0,0)} = \Big|\cos(xy) - (xy)\sin(xy)\Big|_{(0,0)} = 1 \qquad (b)$$

6. $\frac{\partial V}{\partial x} = y - 2xy^2 + 0.25(2x) + 0.125 \times 4x^3$

$$= y - 2xy^2 + 0.5x + 0.5x^3 = 0 \quad \text{at } (1,1)$$

$$\frac{\partial V}{\partial y} = x - 2yx^2 + 0.5y + 0.5y^3 = 0 \quad \text{at } (1,1)$$

$\frac{\partial^2 V}{\partial x^2} = -2y^2 + 0.5 + 1.5x^2 = 0$ at $(1,1)$

$\frac{\partial^2 V}{\partial x^2} = -2x^2 + 0.5 + 1.5y^2 = 0$ at $(1,1)$

$\Rightarrow (1,1)$ is a saddle point (c)

$\boxed{7}$ $V(x,y) = xy - 0.25x^2y^2 + 0.25(x^2+y^2)$

$V_{x} = y - 0.5xy^2 + 0.5x$ $\quad V_y = x - 0.5yx^2 + 0.5y$

$V_{xx} = -0.5y^2 + 0.5$ $\quad V_{yy} = -0.5x^2 + 0.5$

$V_{xy} = 1 - xy$ $\quad V_{yx} = 1 - xy$

At $x = y = 0$ Hessian $= (0.5)^2 - 1 = -0.75$ (a)

$\boxed{8}$ $f - \lambda g = 2x - 3y - \lambda(x^2+y^2-13)$

$\frac{\partial}{\partial x}(f - \lambda g) = 0 \Rightarrow 2 - 2\lambda x = 0$ $\quad \frac{\partial}{\partial y}(f-\lambda g) = 0 \Rightarrow -3 - 2\lambda y = 0$

$\Rightarrow \lambda = \frac{1}{x}$ $\quad -3x - 2y = 0$

$y = -\frac{3}{2}x$

$\Rightarrow 2x - 3y = 2x + \frac{9x}{2} = \cancel{+\frac{13x}{2}}\ \frac{13x}{2}$

$x^2 + y^2 = 13 \Rightarrow \frac{9}{4}x^2 + x^2 = 13 \Rightarrow \frac{x^2}{4} = 1 \quad x = \pm 2$

$x = 2,\ y = -3$

$2x - 3y = 13$ (c)

$\boxed{9}$ $\frac{\partial^2 f}{\partial x^2} = 6x \quad \frac{\partial^2 f}{\partial y^2} = 2 \quad \frac{\partial f}{\partial x} = 3x^2 - 3 \quad \frac{\partial f}{\partial y} = 2y - 3$

Extremum at $x = \pm 1 \quad y = \frac{3}{2} \quad \frac{\partial^2 f}{\partial x \partial y} = 0$

at $x = 1, y = \frac{3}{2} \quad \frac{\partial^2 f}{\partial x^2} = 6 > 0, \quad \frac{\partial^2 f}{\partial y^2} = 2 > 0 \quad \frac{\partial^2 f}{\partial x \partial y} = 0$

Saddle point

at $x = -1 \quad y = \frac{3}{2} \quad \frac{\partial^2 f}{\partial x^2} = -6 < 0 \quad \frac{\partial^2 f}{\partial y^2} = 2 > 0 \quad \frac{\partial^2 f}{\partial x \partial y} = 0$

Saddle point

2 saddle points — (c)

$\boxed{10}$

$\boxed{10}$ $A = 2(ab+bc+ca)$ $P = 4(a+b+c) = P_0$

$$A - \lambda P = 2(ab+bc+ca) - \lambda.[4(a+b+c) - P_0]$$

$$\frac{\partial}{\partial a}(A - \lambda P) = 0 \Rightarrow 2(b+c) - 4\lambda = 0$$

$$\Rightarrow b+c = 2\lambda$$

Similary $a+b = 2\lambda$, $a+c = 2\lambda \Rightarrow a=b=c=\lambda$

Shape = Cube (a)