Chem 1410 HW #3 Answers

1. Orthogonality of $e^{in\phi}$ and $e^{im\phi}$?

$$\int_0^{2\pi} e^{-in\phi} e^{im\phi} d\phi = \left.\frac{e^{i(m-n)\phi}}{i(m-n)}\right|_0^{2\pi} = 0, \text{ if } m, n \text{ integers}, m \neq n$$

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2. $Y_1^0 \sim 1$, $Y_2^0 \sim \cos\theta$, $z \sim \cos\theta$

$$\int_0^{\pi} 1 \cdot \cos^2\theta \sin\theta \, d\theta = \frac{\cos^3\theta}{3} = 0.667 \text{ ; allowed}$$

$Y_1^0 \sim 1$, $Y_2^{\pm 1} \sim \sin\theta \begin{cases} \sin\phi \\ \cos\phi \end{cases}$, $z = \cos\theta$

$$\int_0^{\pi} 1 \cdot \sin\theta \sin\theta \cos\theta \, d\theta \int_0^{2\pi} \sin\phi \, d\phi = 0 \text{ due to } \phi \text{ integral}$$

ditto for $\cos\phi$

what if the operator is $x \sim \sin\theta\cos\phi$

$$\int_0^{2\pi}\int_0^{\pi} 1 \cdot \sin\theta\cos\phi \sin\theta \sin\theta \sin\phi \, d\theta \, d\phi = \int_0^{\pi} \sin^3\theta \, d\theta \underbrace{\int_0^{2\pi} \cos\phi \sin\phi \, d\phi}$$

$Y_0^0 \to Y_2^0$: $\int_0^{\pi} (3\cos^2\theta - 1)\cos\theta \sin\theta \, d\theta = \left. \frac{3}{4}\cos^3\theta - \frac{1}{2}\cos^2\theta \right|_0^{\pi}$

operator z $= 0$

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4. $T = 300K \to 200 \text{ cm}^{-1} \sim 0.00092 \text{ a.u}$

$$2\mu r_0^2 kT = 2(2)^2 5000 (0.00092) = 36.8$$

$P_0 = 1 \, e^{-0/36.8} = 1$

$P_1 = 3 \, e^{-2/36.8} = 2.84$

$P_2 = 5 \, e^{-6/36.8} = 4.23$

$P_3 = 7 \, e^{-12/36.8} = 5.05$

$P_4 = 9 \, e^{-20/36.8} = 5.22$

$P_5 = 11 \, e^{-30/36.8} = 4.81$

Actually these are #'s in each level, not probabilities. So they should be labeled $n_0, n_1, n_2, n_3, n_4, n_5$ — The probabilities are then

$P_0 = 1/(1 + 2.84 + 4.23 + 5.05 + \ldots)$

$P_1 = 2.84/(1 + 2.84 + 4.23 + 5.05 + \ldots)$

$P_3 = 5.05/(1 + 2.84 + 4.23 + 5.05 + \ldots)$

etc.