Lecture 20 (Final Exam Review)

Tuesday, November 26, 2024 11:32

Important : Final Exam Location

$\boxed{\text{Mackinnon 309}}$

cumulative, but with emphasis on second half

Practice Problems

1. For a system of two non-interacting particles of mass 9.0×10^{-26} g and 5.0×10^{-26} g in a one-dimensional box of length 1.00×10^{-8} cm, calculate the energies of the six lowest stationary states.

Solution :

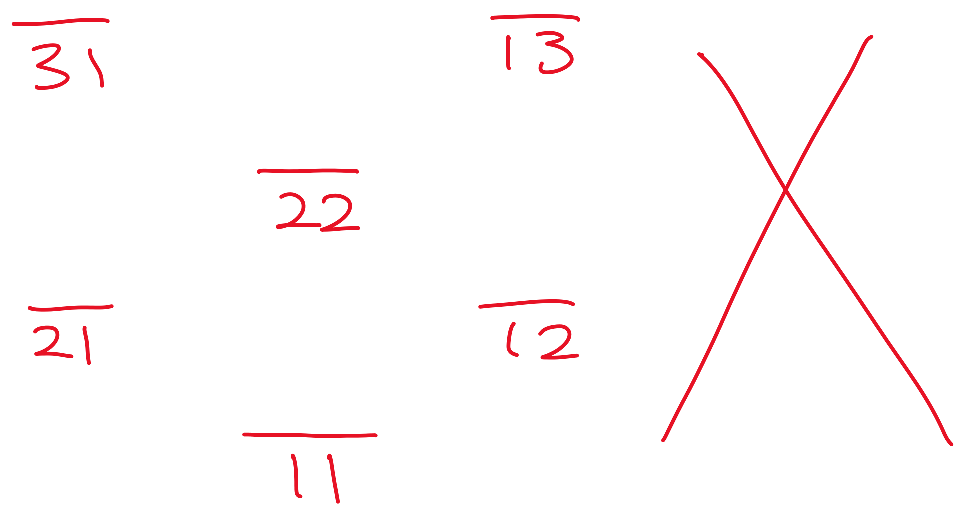
$$\Psi = \psi_1(x_1)\psi_2(x_2)$$

$$E = E_1 + E_2$$

$$E = \frac{n_1^2 h^2}{8 m_1 \ell^2} + \frac{n_2^2 h^2}{8 m_2 \ell^2}$$

$$E = \left(\frac{n_1^2}{m_1} + \frac{n_2^2}{m_2}\right)\frac{h^2}{8 \ell^2}$$

Pitfalls :



the first six states calculated are <u>not</u> the six lowest energy states

$$E_{11} = 1.71 \times 10^{-19}\ \text{J}$$

$$E_{21} = 3.54 \times 10^{-19}\ \text{J}$$

$E_{12} = 5.00 \times 10^{-19}$ J

$E_{31} = 6.59 \times 10^{-19}$ J

$E_{22} = 6.83 \times 10^{-19}$ J

$E_{32} = 9.88 \times 10^{-19}$ J

---

2. The lowest observed microwave absorption frequency of $^{12}C^{16}O$ is 115,271 MHz.

(a) Compute the bond distance in $^{12}C^{16}O$.

(b) Predict the next two lowest microwave absorption frequencies of $^{12}C^{16}O$.

(c) Calculate the ratio of the J=1 population to the J=0 population. Repeat for the J=2 to J=0 ratio. Don't forget degeneracy.

Solution: microwave absorption →

rotational degrees of freedom

rigid rotor model:

$$E = \frac{J(J+1)\hbar^2}{2\mu d^2}, \quad J = 0, 1, 2, \ldots$$

$$m_{^{12}C} = 12.000 \text{ g}\cdot\text{mol}^{-1}$$

$$m_{^{16}O} = 15.995 \text{ g}\cdot\text{mol}^{-1}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

(a) Lowest frequency transition:

J=0 to J=1

$$\Delta E = \frac{(1)(2)\hbar^2}{2\mu d^2} - \cancel{\frac{(0)(1)\hbar^2}{2\mu d^2}}$$

$$\Delta E = \frac{\cancel{2}\hbar^2}{\cancel{2}\mu d^2}$$

$$d = \left(\frac{\hbar^2}{\mu \Delta E}\right)^{\frac{1}{2}}$$

$$d = \left(\frac{\hbar^2}{\mu h \nu}\right)^{\frac{1}{2}} \qquad \hbar = \frac{h}{2\pi}$$

$$\hbar^2 = \frac{h^2}{4\pi^2}$$

$$d = \left(\frac{h^{\cancel{2}}}{4\pi^2 \mu \cancel{h} \nu}\right)^{\frac{1}{2}}$$

$$d = \left(\frac{h}{4\pi^2 \mu \nu}\right)^{\frac{1}{2}}$$

$$d = 1.13 \times 10^{-10}\ m$$

$$\boxed{d = 1.13\ \text{Å}}$$

(b) $$\Delta E_{21} = \frac{(2)(3)\hbar^2}{2\mu d^2} - \frac{(1)(2)\hbar^2}{2\mu d^2}$$

$$\Delta E_{21} = \frac{2\hbar^2}{\mu d^2}$$

$$\Delta E_{32} = \frac{(3)(4)\hbar^2}{2\mu d^2} - \frac{(2)(3)\hbar^2}{2\mu d^2}$$

$$\Delta E_{32} = \frac{3\hbar^2}{\mu d^2}$$

$$\boxed{\begin{aligned} \nu_{21} &= \frac{h}{2\pi^2 \mu d^2} = 2.305 \times 10^{11}\ Hz \\ \nu_{32} &= \frac{3h}{4\pi^2 \mu d^2} = 3.458 \times 10^{11}\ Hz \end{aligned}}$$

(c) $p = g_i e^{-E_i/k_BT}$

Boltzmann population

(2J+1)-fold degenerate

$$\frac{P_1}{P_0} = \frac{[2(1)+1]\, e^{-7.64\times10^{-23}\,J/k_BT}}{[(2)(0)+1]\, e^0}$$

$$\boxed{\frac{P_1}{P_0} = 2.94}$$

$$\frac{P_2}{P_0} = \frac{[(2)(2)+1]\, e^{-2.29\times10^{-22}\,J/k_BT}}{1}$$

$$\boxed{\frac{P_2}{P_0} = 4.73}$$

3. (a) Explain why the degree of degeneracy of an H-atom energy level is given by $\sum_{l=0}^{n-1}(2l+1)$.

(b) Break this sum into two sums. Evaluate the first sum using the fact that $\sum_{j=1}^{k} j = \frac{1}{2}k(k+1)$. Show that the degree of degeneracy of the H-atom levels is n^2 with spin omitted.

(c) Prove that $\sum_{j=1}^{k} j = \frac{1}{2}k(k+1)$.

Solution: (a) For a given quantum number n in the H-atom, l ranges from 0 to $n-1$.

e.g. $n=1$, $l=0$ 1s

$n=2$, $l=0,1$ 2s, 2p

$n=3, \ell=0,1,2$ 3s, 3p, 3d

Then, for each ℓ, m ranges from $-\ell$ to $+\ell$, including 0

$(2\ell+1)$ m values for each ℓ

e.g. $\ell=0 \rightarrow m=0$

$\ell=1 \rightarrow m=-1,0,+1$

p_x, p_y, p_z

$\ell=2 \rightarrow m=-2,-1,0,+1,+2$

$d_{xy}, d_{yz}, d_{xz},$

$d_{x^2-y^2}, d_{z^2}$

H-atom energies depend on n only.

Thus, the degeneracy is given by $\sum_{\ell=0}^{n-1} 2\ell+1$.

(b) $$\sum_{l=0}^{n-1} 2l+1 = \sum_{l=0}^{n-1} 2l + \sum_{l=0}^{n-1} 1$$

first term is zero

$$= \sum_{l=1}^{n-1} 2l + \underbrace{\sum_{l=1}^{n} 1}_{\text{add 1 n times}}$$

formula: $\sum_{j=1}^{k} j = \frac{1}{2} k(k+1)$

$$= 2\sum_{l=1}^{n-1} l + n$$

$$= 2 \cdot \frac{1}{2}(n-1)(n) + n$$

$$= n^2 - n + n$$

$$= n^2$$ QED

k k

(c) $\sum_{j=1}^{k} j + \sum_{j=1}^{k} j$

$= (1 + 2 + 3 + \cdots + k)$

$+ [k + (k-1) + (k-2) + \cdots + 1]$

$= (k+1) + (k-1+2) + (k-2+3) + \cdots$

$= \underbrace{(k+1) + (k+1) + (k+1) + \cdots}_{k \text{ terms}}$

$= k(k+1)$

$$\boxed{\therefore \sum_{j=1}^{k} j = \frac{1}{2} k(k+1)}$$

---

4. A stationary-state wavefunction is an eigenfunction of the Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$. It may be tempting to state that Ψ is an

tempting to ...

eigenfunction of $\hat{T}$ and $\hat{V}$, but this is not correct. For the ground state of the hydrogen atom, verify directly that ψ is not an eigenfunction of $\hat{T}$ or of $\hat{V}$, but is an eigenfunction of $\hat{T}+\hat{V}$.

$$\psi_{100} = \frac{1}{a^{3/2}\pi^{1/2}} e^{-r/a}$$

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2}_{\hat{T}} \underbrace{-\frac{e^2}{4\pi\varepsilon_0 r}}_{\hat{V}}$$

Solution: for the Laplacian in spherical coordinates, we need $\frac{\partial}{\partial r}$ and $\frac{\partial^2}{\partial r^2}$.

$$\frac{\partial}{\partial r}\psi_{100} = -\frac{1}{a}\frac{1}{\pi^{1/2}a^{3/2}} e^{-r/a}$$

$$\frac{\partial^2}{\partial r^2}\psi_{100} = \frac{1}{a^2}\frac{1}{\pi^{\frac{1}{2}} a^{3/2}} e^{-r/a}$$

$$\hat{T} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \cancel{\frac{1}{2\mu r^2}\hat{L}^2}\right)$$

$$\hat{L}^2 = -\hbar\left(\underbrace{\frac{\partial^2}{\partial \theta^2}}_{0} + \underbrace{\cot\theta\frac{\partial}{\partial \theta}}_{0} + \underbrace{\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}}_{0}\right)$$

$$\hat{T}\psi_{100} = -\frac{\hbar^2}{2\mu}\left(\frac{1}{a^2}\psi_{100} - \frac{2}{ar}\psi_{100}\right)$$

ψ_{100} is not an eigenfunction of $\hat{T}$.

$$\hat{V}\psi_{100} = -\frac{e^2}{4\pi\varepsilon_0 r}\psi_{100}$$

ψ_{100} is not an eigenfunction of $\hat{V}$.

$$a \equiv \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

$$(\hat{T}+\hat{V})\psi_{100} = -\frac{\hbar^2}{2\mu a^2}\psi_{100}$$

$$+\frac{2\hbar^2}{2\mu a r}\psi_{100} - \frac{e^2}{4\pi\varepsilon_0 r}\psi_{100}$$

$$= -\frac{\hbar^2}{2\mu a^2}\psi_{100} + \underbrace{\frac{\cancel{2}\cancel{\hbar^2}\cancel{\mu} e^2\psi_{100}}{4\pi\varepsilon_0\cancel{\hbar^2}\cancel{2\mu} r} - \frac{e^2}{4\pi\varepsilon_0 r}\psi_{100}}_{\text{these will cancel}}$$

$$\hat{H}\psi_{100} = -\frac{\hbar^2}{2\mu a^2}\psi_{100}$$

$$\boxed{\therefore\ \psi_{100} \text{ is an eigenfunction of } \hat{T}+\hat{V}.}$$