CHEM 482, sec 0102. Homework #4-5

Solutions

Problem 1. (20 points)

The state of a system is given by the (unnormalized) wavefunction $\Psi = e^{ia\phi - bx^2}$. The available space covers the range from $-\infty$ to ∞ in x and from 0 to 2π in ϕ.

(a) Normalize the wavefunction.

Answer: Ψ → NΨ, where the normalization factor N is defined as $N^2 \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} |\Psi|^2 \, dx = 1$.

Because $|\Psi|^2 = e^{-2bx^2}$, integration over ϕ gives 2π, and the remaining integral is $\int_{-\infty}^{\infty} |\Psi|^2 \, dx = \int_{-\infty}^{\infty} e^{-2bx^2} dx = 2\int_0^{\infty} e^{-2bx^2} dx = \sqrt{\frac{\pi}{2b}}$. Bringing all integrals together, we get $N^2 \sqrt{\frac{2\pi^3}{b}} = 1$, hence $N = \left(\frac{b}{2\pi^3}\right)^{1/4}$.

(b) Find the expectation values for the following operators.

Answers:

$\hat{x}^2$, the expectation value is

$$\langle x^2 \rangle = \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} \Psi^* x^2 \Psi dx = N^2 2\pi \int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx = N^2 2\pi \frac{1}{2}\sqrt{\frac{\pi}{8b^3}} = \frac{1}{4b}$$

$\hat{p}_x{}^2$ (x-component of the linear momentum operator)

the expectation value is

$$\langle p_x{}^2 \rangle = -\hbar^2 \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} \Psi^* \frac{\partial^2}{\partial x^2} \Psi dx = -\hbar^2 N^2 2\pi \int_{-\infty}^{\infty} e^{-bx^2} \left(\frac{\partial^2}{\partial x^2} e^{-bx^2} \right) dx = N^2 4\pi\hbar^2 b \int_{-\infty}^{\infty} e^{-2bx^2} \left(1 - 2bx^2\right) dx$$

$$= \hbar^2 b$$

$\hat{l}_z$ (z-component of the angular momentum operator)

the expectation value is

$$\langle l_z \rangle = -i\hbar \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} \Psi^* \frac{\partial}{\partial \phi} \Psi dx = -i\hbar N^2 \int_0^{2\pi} e^{-ia\phi} \left(\frac{\partial}{\partial \phi} e^{ia\phi} \right) d\phi \int_{-\infty}^{\infty} e^{-2bx^2} dx = \hbar a$$

Problem 2. (20 points)

Consider rotational states of a diatomic molecule, e.g. H_2. The energy difference between the energy levels with l = 1 and l = 2 of the molecule is E(2) – E(1) = 243.3 cm^{-1}.

(a) From these data determine the bond length in H_2.

Answer:

From the solution to the 3D rigid-rotor problem:

$\Delta E = E(2) - E(1) = \frac{\hbar^2}{2\mu r^2}[2\times 3 - 1\times 2] = \frac{2\hbar^2}{\mu r^2}$, where $\mu = m_p/2$ is the reduced mass, m_p= 1.67261 10^{-27} kg is the proton's mass, and r is the bond length. This allows us to determine the bond length: $r = \sqrt{\frac{2\hbar^2}{\mu \Delta E}}$. Substituting $\Delta E = hc \bullet 243.3$ cm^{-1} = 4.836 10^{-21} J, we get r = 0.742 10^{-10} m = 0.742 Å.

(b) What will be the energy difference between the same rotational levels for a half-deutrated (HD) and fully deuterated (D_2) molecule. Assume that the bond length does not change upon deuteration.

Answers:

The reduced mass for HD is $\mu_{HD} = m_D{*}m_p/(m_D+m_p) = (2/3)\, m_p$ while for D_2 it is $\mu_{DD} = m_p$ (recall that $m_D = 2m_p$). Because ΔE is inversely proportional to μ, $\Delta E_{HD} = \Delta E_{HH}{*}\mu_{HH}/\mu_{HD} = \Delta E_{HH}{*}3/4$ = 182.5 cm^{-1} (or 3.628 10^{-21} J), and $\Delta E_{DD} = \Delta E_{HH}{*}\mu_{HH}/\mu_{DD} = \Delta E_{HH}/2$ = 121.7 cm^{-1} (or 2.42 10^{-21} J).