4 Harmonic Oscillators II and the Hydrogen Atom

10/27: 1. The $J = 0$ to $J = 1$ transition for carbon monoxide ($^{12}C^{16}O$) occurs at 1.153×10^5 MHz.

(a) Calculate the value of the bond length in carbon monoxide.

Answer. Let $\nu = 1.153 \times 10^{11}$ Hz. We have from McQuarrie and Simon (1997) that

$$\nu = \frac{h}{4\pi^2 I}(0+1)$$

for the transition from $J = 0$ to $J = 1$. Thus,

$$I = \frac{h}{4\pi^2 \nu} = 1.456 \times 10^{-46}\,\mathrm{kg\,m^2}$$

This combined with the fact that the reduced mass is

$$\mu = \frac{12 \cdot 16}{12 + 16} = 1.140 \times 10^{-26}\,\mathrm{kg}$$

and that $I = \mu r^2$ tells us that

$$\boxed{r = 1.130 \times 10^{-10}\,\mathrm{m}}$$

□

(b) Predict the $J = 1$ to $J = 2$ transition for carbon monoxide.

Answer. From McQuarrie and Simon (1997), we have that the $J = 0 \to 1$ and $J = 1 \to 2$ transitions are, respectively,

$$\nu_0 = \frac{h}{4\pi^2 I}(0+1) \qquad \nu_1 = \frac{h}{4\pi^2 I}(1+1)$$

Thus, $\nu_1 = 2\nu_0$, so

$$\boxed{\nu_1 = 2.306 \times 10^{11}\,\mathrm{Hz}}$$

□

2. The harmonic oscillator has a finite zero-point energy because of the uncertainty relation. In contrast, the lowest possible energy for the 2D rigid rotor is zero.

(a) For the ground state of the 2D rigid rotor, what is the expectation value of the angular momentum, and what is the uncertainty ΔL_z in the expectation value? Recall that

$$(\Delta L_z)^2 = \langle \hat{L}_z^2 \rangle - \langle \hat{L}_z \rangle^2$$

Answer. Since this is the ground state $m = 0$, we have that

$$\begin{aligned}
\langle \hat{L}_z \rangle &= \int_0^{2\pi} \psi^*(\phi) \hat{L}_z \psi(\phi)\,\mathrm{d}\phi \\
&= \int_0^{2\pi} \left(\frac{1}{\sqrt{2\pi}} \mathrm{e}^{-i(0)\phi}\right) \left(-i\hbar \frac{\partial}{\partial \phi}\right) \left(\frac{1}{\sqrt{2\pi}} \mathrm{e}^{i(0)\phi}\right) \mathrm{d}\phi \\
&= \frac{1}{2\pi} \int_0^{2\pi} (1) \cdot -i\hbar \cdot 0\,\mathrm{d}\phi \\
\boxed{\langle \hat{L}_z \rangle = 0}
\end{aligned}$$

and that

$$\begin{aligned}
\langle \hat{L}_z^2 \rangle &= \int_0^{2\pi} \psi^*(\phi) \hat{L}_z^2 \psi(\phi) \, \mathrm{d}\phi \\
&= \int_0^{2\pi} \left(\frac{1}{\sqrt{2\pi}} \mathrm{e}^{-i(0)\phi} \right) \left(-i\hbar \frac{\partial}{\partial \phi} \right)^2 \left(\frac{1}{\sqrt{2\pi}} \mathrm{e}^{i(0)\phi} \right) \mathrm{d}\phi \\
&= \frac{1}{2\pi} \int_0^{2\pi} (1) \cdot -i\hbar \cdot 0 \, \mathrm{d}\phi \\
&= 0
\end{aligned}$$

so

$$\begin{aligned}
(\Delta L_z)^2 &= \langle \hat{L}_z^2 \rangle - \langle \hat{L}_z \rangle^2 \\
&= 0 - 0 \\
\boxed{\Delta L_z = 0}
\end{aligned}$$

□

(b) In words, describe the uncertainty in position.

Answer. Since the uncertainty in angular momentum is 0, the uncertainty in position (the Fourier transform of the uncertainty in position) is $\boxed{\text{infinite}}$. □

(c) Using your answers to (a) and (b), explain briefly why the 2D rigid rotor can have a vanishing zero-point energy and yet still remain consistent with the uncertainty relation.

Answer. It is consistent with the uncertainty relation because we have total certainty in one term and zero certainty in the other. □

3. For the ground state of the hydrogen atom, compute

(a) The *average* distance from the nucleus for finding the electron.

Answer. We have that

$$\begin{aligned}
\langle r \rangle &= \int_0^\infty \psi_{100}^*(r) r \psi_{100}(r) 4\pi r^2 \, \mathrm{d}r \\
&= \int_0^\infty \left(\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \mathrm{e}^{-r/a_0} \right) r \left(\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \mathrm{e}^{-r/a_0} \right) 4\pi r^2 \, \mathrm{d}r \\
&= 4a_0 \int_0^\infty \sigma^3 \mathrm{e}^{-2\sigma} \, \mathrm{d}\sigma \\
&= 4a_0 \left[-\frac{1}{2} \sigma^3 \mathrm{e}^{-2\sigma} \bigg|_0^\infty + \frac{3}{2} \int_0^\infty \sigma^2 \mathrm{e}^{-2\sigma} \, \mathrm{d}\sigma \right] \\
&= 4a_0 \left[\frac{3}{2} \cdot \frac{2}{2} \cdot \frac{1}{2} \int_0^\infty \mathrm{e}^{-2\sigma} \, \mathrm{d}\sigma \right] \\
&= 4a_0 \cdot \frac{3}{8} \\
\boxed{\langle r \rangle = \frac{3}{2} a_0}
\end{aligned}$$

□

(b) The *most probable* distance from the nucleus for finding the electron.

Answer. We have from McQuarrie and Simon (1997, p. 211) that the probability that the electron is between r and $r + \mathrm{d}r$ is

$$\mathrm{Prob}(r) = \frac{4}{a_0^3} r^2 \mathrm{e}^{-2r/a_0}$$

We want to find the point where $\mathrm{d}\,\mathrm{Prob}(r)/\mathrm{d}r = 0$, as this will be the maximum. Note that we know that $\mathrm{Prob}(r)$ takes on positive values, and we know that $\mathrm{Prob}(0) = \mathrm{Prob}(\infty) = 0$, so we need not consider the boundary points. We can do this as follows.

$$\begin{aligned}
0 &= \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{4}{a_0^3} r^2 \mathrm{e}^{-2r/a_0}\right) \\
&= \frac{4}{a_0^3}\left(2r\mathrm{e}^{-2r/a_0} - \frac{2r^2}{a_0}\mathrm{e}^{-2r/a_0}\right) \\
&= \mathrm{e}^{-2r/a_0} - \frac{r}{a_0}\mathrm{e}^{-2r/a_0} \\
\frac{r}{a_0} &= 1 \\
\boxed{r = a_0}
\end{aligned}$$

□

(c) Repeat the calculation for the second excited state ($n = 3$ and $l = 0$) and compare your results with the ground state.

Answer. Average distance from the nucleus: We have that

$$\begin{aligned}
\langle r \rangle &= \int_0^\infty \psi_{300}^*(r) r \psi_{300}(r) 4\pi r^2 \,\mathrm{d}r \\
&= \int_0^\infty \left(\frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^2\right]\mathrm{e}^{-r/3a_0}\right) r \\
&\quad \cdot \left(\frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^2\right]\mathrm{e}^{-r/3a_0}\right) 4\pi r^2 \,\mathrm{d}r \\
&= \frac{1}{3^9\pi}\left(\frac{1}{a_0}\right)^3 \int_0^\infty \left([27 - 18\sigma + 2\sigma^2]\mathrm{e}^{-\sigma/3}\right) \sigma a_0 \left([27 - 18\sigma + 2\sigma^2]\mathrm{e}^{-\sigma/3}\right) 4\pi(\sigma a_0)^2 a_0 \,\mathrm{d}\sigma \\
&= \frac{4a_0}{3^9}\int_0^\infty ([27 - 18\sigma + 2\sigma^2]\mathrm{e}^{-\sigma/3})\sigma^3([27 - 18\sigma + 2\sigma^2]\mathrm{e}^{-\sigma/3}) \,\mathrm{d}\sigma \\
&= \frac{4a_0}{3^9}\int_0^\infty (27 - 18\sigma + 2\sigma^2)^2\sigma^3\mathrm{e}^{-2\sigma/3} \,\mathrm{d}\sigma \\
&= \frac{4a_0}{3^9}\int_0^\infty (4\sigma^7 - 72\sigma^6 + 432\sigma^5 - 972\sigma^4 + 729\sigma^3)\mathrm{e}^{-2\sigma/3} \,\mathrm{d}\sigma \\
&= \frac{4a_0}{3^9}\left[4\int_0^\infty \sigma^7\mathrm{e}^{-2\sigma/3}\,\mathrm{d}\sigma - 72\int_0^\infty \sigma^6\mathrm{e}^{-2\sigma/3}\,\mathrm{d}\sigma + 432\int_0^\infty \sigma^5\mathrm{e}^{-2\sigma/3}\,\mathrm{d}\sigma\right. \\
&\quad \left. -972\int_0^\infty \sigma^4\mathrm{e}^{-2\sigma/3}\,\mathrm{d}\sigma + 729\int_0^\infty \sigma^3\mathrm{e}^{-2\sigma/3}\,\mathrm{d}\sigma\right] \\
&= \frac{4a_0}{3^9}\left[4\cdot\frac{7!}{(2/3)^7}\cdot\frac{3}{2} - 72\cdot\frac{6!}{(2/3)^6}\cdot\frac{3}{2} + 432\cdot\frac{5!}{(2/3)^5}\cdot\frac{3}{2} - 972\cdot\frac{4!}{(2/3)^4}\cdot\frac{3}{2} + 729\cdot\frac{3!}{(2/3)^3}\cdot\frac{3}{2}\right] \\
\boxed{\langle r \rangle = 13.5a_0}
\end{aligned}$$

Most probable distance from the nucleus: We have from McQuarrie and Simon (1997) that

$$\begin{aligned}
R_{30}(r) &= -\sqrt{\frac{(3-0-1)!}{2\cdot 3[(3+0)!]^3}}\left(\frac{2}{3a_0}\right)^{0+3/2} r^0 \mathrm{e}^{-r/3a_0} L_{3+0}^{2\cdot 0+1}\left(\frac{2r}{3a_0}\right) \\
&= -\sqrt{\frac{2}{6^4}}\left(\frac{2}{3a_0}\right)^{3/2} \mathrm{e}^{-\sigma/3} L_3^1\left(\frac{2\sigma}{3}\right) \\
&= -\frac{1}{27\sqrt{3}a_0^{3/2}}\mathrm{e}^{-\sigma/3}\left[-3!\left(3-3\left(\frac{2\sigma}{3}\right)+\frac{1}{2}\left(\frac{2\sigma}{3}\right)^2\right)\right] \\
&= -\frac{1}{27\sqrt{3}a_0^{3/2}}\mathrm{e}^{-\sigma/3}\left[-\frac{4}{3}\sigma^2+12\sigma-18\right] \\
&= \frac{1}{81\sqrt{3}a_0^{3/2}}(4\sigma^2-36\sigma+54)\mathrm{e}^{-\sigma/3}
\end{aligned}$$

Thus,

$$\begin{aligned}
\mathrm{Prob}(r) &= [R_{30}(r)]^2 r^2 \\
&= \left[\frac{1}{3^9 a_0^3}(16\sigma^4-288\sigma^3+1728\sigma^2-3888\sigma+2916)\mathrm{e}^{-2\sigma/3}\right](a_0\sigma)^2 \\
&= \frac{1}{3^9 a_0}(16\sigma^6-288\sigma^5+1728\sigma^4-3888\sigma^3+2916\sigma^2)\mathrm{e}^{-2\sigma/3}
\end{aligned}$$

so

$$\begin{aligned}
0 &= \frac{\mathrm{d}\,\mathrm{Prob}(r)}{\mathrm{d}r} \\
&= \frac{1}{3^9 a_0}(96\sigma^5-1440\sigma^4+6912\sigma^3-11664\sigma^2+5832\sigma)\mathrm{e}^{-2\sigma/3} \\
&\quad -\frac{2}{3^{10}a_0}(16\sigma^6-288\sigma^5+1728\sigma^4-3888\sigma^3+2916\sigma^2)\mathrm{e}^{-2\sigma/3} \\
&= \frac{8}{3^{10}a_0}x(-4\sigma^5+108\sigma^4-972\sigma^3+3564\sigma^2-5103\sigma+2187)\mathrm{e}^{-2\sigma/3} \\
&= -4\sigma^5+108\sigma^4-972\sigma^3+3564\sigma^2-5103\sigma+2187
\end{aligned}$$

Solving this polynomial for its zeroes, and knowing that the most probable distance is going to be the zero of greatest magnitude (orbital penetration peaks will necessarily be smaller than the farthest one out), we have that the the most probable distance is

$$\sigma = 13.074$$
$$\boxed{r = 13.074a_0}$$

□

4. Using non-relativistic quantum mechanics, compute the ratio of the ground-state energy of hydrogen to that of atomic tritium.

Answer. We have from class that

$$\begin{aligned}
E_1 &= -\frac{\mu}{2\hbar^2}\left(\frac{(1e)e}{4\pi\epsilon_0}\right)^2\frac{1}{1^2} \\
&= -\frac{\mu e^4}{8h^2\epsilon_0^2}
\end{aligned}$$

Thus, since

$$\mu_{\mathrm{H}} = \frac{m_e m_p}{m_e + m_p} = 9.11 \times 10^{-31}\,\mathrm{kg} \qquad \mu_{\mathrm{T}} = \frac{m_e(3m_p)}{m_3 + 3m_p} = 9.12 \times 10^{-31}\,\mathrm{kg}$$

Therefore, we have that

$$\begin{aligned}\frac{E_{1_{\mathrm{H}}}}{E_{1_{\mathrm{T}}}} &= \frac{-\frac{\mu_{\mathrm{H}} e^4}{8h^2\epsilon_0^2}}{-\frac{\mu_{\mathrm{T}} e^4}{8h^2\epsilon_0^2}}\\ &= \frac{\mu_{\mathrm{H}}}{\mu_{\mathrm{T}}}\\ \Aboxed{E_{1_{\mathrm{H}}} : E_{1_{\mathrm{T}}} &= 0.999}\end{aligned}$$

□

5. The Hamiltonian operator for a hydrogen atom in a magnetic field where the field is in the z-direction is given by

$$\hat{H} = \hat{H}_0 + \frac{\beta_B B_z}{\hbar}\hat{L}_z$$

where $\hat{H}_0$ is the Hamiltonian operator in the absence of the magnetic field, B_z is the z-component of the magnetic field, and β_B is a constant called the Bohr magneton.

(a) Show that the wave functions of the Schrödinger equation for a hydrogen atom in a magnetic field are the same as those for the hydrogen atom in the absence of the field.

Answer. We have from McQuarrie and Simon (1997, p. 201) that $\hat{L}_z = m\hbar$ for $m = 0, \pm 1, \pm 2, \dots$. Thus, the solutions to $\hat{H}\psi = E\psi$ will be the solutions to

$$\begin{aligned}\left(\hat{H}_0 + \frac{\beta_B B_z}{\hbar}\hat{L}_z\right)\psi &= E\psi\\ \hat{H}_0\psi + \beta_B B_z m\psi &= E\psi\\ \hat{H}_0\psi &= (E - \beta_B B_z m)\psi\end{aligned}$$

i.e., the original wave functions but with a different constant (which will lead to a different energy). □

(b) Show that the energy associated with the wave function $\psi_{n,l,m}$ is

$$E = E_n^{(0)} + \beta_B B_z m$$

where $E_n^{(0)}$ is the energy in the absence of the field and m is the magnetic quantum number.

Answer. Since we have $\hat{H}_0\psi = E_n^{(0)}\psi$ originally and $\hat{H}_0\psi = (E - \beta_B B_z m)\psi$ from part (a), it follows that

$$\begin{aligned}E - \beta_B B_z m &= E_n^{(0)}\\ E &= E_n^{(0)} + \beta_B B_z m\end{aligned}$$

as desired. □