CHEM 26100 (Quantum Mechanics) Problem Sets

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1 Blackbodies and the Photoelectric Effect

10/6: 1. The intensity (or emissive power) of solar radiation at the surface of the earth is $1.4 \times 10^3\,\mathrm{W/m^2}$, the distance from the center of the sun to the sun's surface is $7 \times 10^8\,\mathrm{m}$, and the distance from the center of the sun to the earth is $1.5 \times 10^{11}\,\mathrm{m}$.

(a) Assuming that the sun is a black body, calculate the temperature at the surface of the sun in Kelvin. (Hint: The surface area of a sphere of radius r is $4\pi r^2$.)

Answer. Let

$$I = 1400\,\frac{\mathrm{W}}{\mathrm{m}^2} \qquad r_1 = 7 \times 10^8\,\mathrm{m} \qquad r_2 = 1.5 \times 10^{11}\,\mathrm{m}$$

and let $\sigma = 5.67 \times 10^{-8}\,\mathrm{W\,m^{-2}}$ be Stefan's constant. If P is the total power radiated by the sun, we have from physics that

$$\begin{aligned} I &= \frac{P}{4\pi r_2^2} \\ P &= 4\pi r_2^2 I \end{aligned}$$

and from quantum that

$$\begin{aligned} P &= R \cdot 4\pi r_1^2 \\ &= \sigma T^4 \cdot 4\pi r_1^2 \end{aligned}$$

Thus, setting these two quantities equal to each other, we obtain

$$\begin{aligned} 4\pi r_2^2 I &= \sigma T^4 \cdot 4\pi r_1^2 \\ r_2^2 I &= \sigma T^4 r_1^2 \\ T &= \sqrt[4]{\frac{r_2^2 I}{\sigma r_1^2}} \\ &\boxed{T = 5803\,\mathrm{K}} \end{aligned}$$

□

(b) Secondly, compute the wavelength at which the emissive power at the sun's surface has its maximum. In which region of the radiation spectrum does this wavelength lie, i.e., infrared (IR), visible, or ultraviolet (UV)?

Answer. If $b = 2.898 \times 10^{-3}\,\mathrm{m\,K}$ is Wien's displacement constant and we plug in the temperature value T from part (a), then Wien's first law gives us

$$\begin{aligned} \lambda_{\max} T &= b \\ \lambda_{\max} &= \frac{b}{T} \\ &\boxed{\lambda_{\max} = 4.99 \times 10^{-7}\,\mathrm{m}} \end{aligned}$$

This wavelength lies in the $\boxed{\text{visible}}$ spectrum. □

2. (a) Using Planck's formula for the energy density $\rho(\lambda, T)$, prove that the total energy density $\rho(T)$ is given by $\rho(T) = aT^4$, where $a = 8\pi^5 k^4/(15h^3c^3)$. (Hint: Use the integral $\int_0^\infty x^3/(\mathrm{e}^x - 1)\,\mathrm{d}x = \pi^4/15$.)

Proof. Planck's formula for the energy density is

$$\mathrm{d}\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5}\cdot\frac{\mathrm{d}\lambda}{\mathrm{e}^{hc/\lambda kT}-1}$$

Thus, if we use the change of variables $x = hc/(\lambda kT)$ (also implying $\lambda = hc/(xkT)$ and $\mathrm{d}\lambda = -hc/(x^2kT)\,\mathrm{d}x$), we have that

$$\begin{aligned}
\int_0^\infty \mathrm{d}\rho(\lambda,T) &= \int_{\lambda=0}^\infty \frac{8\pi hc}{\lambda^5}\cdot\frac{\mathrm{d}\lambda}{\mathrm{e}^{hc/\lambda kT}-1}\\
\int_0^\infty \rho_\lambda(T)\,\mathrm{d}\lambda &= \int_{x=\infty}^0 \frac{8\pi hc}{\left(\frac{hc}{xkt}\right)^5}\cdot\frac{1}{\mathrm{e}^x-1}\cdot-\frac{hc}{x^2kt}\,\mathrm{d}x\\
\rho(T) &= \int_{x=\infty}^0 -\frac{8\pi(hc)^2(kT)^5x^5}{(hc)^5(\mathrm{e}^x-1)(x^2)(kT)}\\
&= \int_{x=0}^\infty \frac{8\pi(kT)^4x^3}{(hc)^3(\mathrm{e}^x-1)}\\
&= \frac{8\pi(kT)^4}{(hc)^3}\int_0^\infty \frac{x^3}{\mathrm{e}^x-1}\,\mathrm{d}x\\
&= \frac{8\pi(kT)^4}{(hc)^3}\cdot\frac{\pi^4}{15}\\
&= \frac{8\pi^5k^4}{15h^3c^3}T^4\\
&= aT^4
\end{aligned}$$

as desired. □

(b) Does this agree with the Stefan-Boltzmann law for the total emissive power?

Answer. Yes — we are given the conversion factor $\rho(\lambda,T) = 4/c\cdot R(\lambda,T)$, so from the above, we should have

$$\begin{aligned}
R(T) &= \frac{c}{4}\cdot R(\lambda,T)\\
&= \frac{c}{4}\cdot\frac{8\pi^5k^4}{15h^3c^3}T^4\\
&= \frac{2\pi^5k^4}{15h^3c^2}T^4
\end{aligned}$$

But by plugging in the appropriate values, we can determine that

$$\frac{2\pi^5k^4}{15h^3c^2} = \sigma$$

where σ is Stefan's constant, giving us

$$R(T) = \sigma T^4$$

as desired. □

3. The photoelectric work function for lithium is $2.3\,\mathrm{eV}$.

(a) Find the threshold frequency ν_t and the corresponding λ_t.

Answer. From Einstein's annus mirabilis papers, we have that

$$\nu_t = \frac{W}{h} \qquad\qquad \lambda_t = \frac{c}{\nu_t} = \frac{ch}{W}$$

Plugging in $W = 3.685 \times 10^{-19}$ J and $h = 6.626 \times 10^{-34}\,\mathrm{J\,s^{-1}}$, we have that

$$\boxed{\nu_t = 5.56 \times 10^{14}\,\mathrm{Hz}} \qquad \boxed{\lambda_t = 5.39 \times 10^{-7}\,\mathrm{m}}$$

□

(b) If UV light of wavelength $\lambda = 3000\,\text{Å}$ is incident on the Li surface, calculate the maximum kinetic energy of the electrons.

Answer. From Einstein's annus mirabilis papers, we have that

$$\begin{aligned} KE_{\max} &= h\nu - W \\ &= \frac{hc}{\lambda} - W \\ \Aboxed{KE_{\max} &= 2.941 \times 10^{-19}\,\mathrm{J}} \end{aligned}$$

□

4. (a) Using the Bohr model, compute the ionization energies for He^+ and Li^{2+}.

Answer. From the Bohr model, we have that

$$\begin{aligned} IE &= E_\infty - E_1 \\ &= -\frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \cdot \frac{1}{\infty^2} + \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \cdot \frac{1}{1^2} \\ &= \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \end{aligned}$$

It follows since $Z = 2$ for He^+ and $Z = 3$ for Li^{2+} that

$$\boxed{IE(\mathrm{He}^+) = 8.72 \times 10^{-18}\,\mathrm{J}} \qquad \boxed{IE(\mathrm{Li}^{2+}) = 1.962 \times 10^{-19}\,\mathrm{J}}$$

in units of Joules per electron. □

(b) Can the Bohr model be employed to compute the first ionization energy for He and Li? Explain briefly.

Answer. No — the Bohr model is only valid for single electron systems as it does not take into account electron-electron interactions. □

5. (a) An electron is confined within a region of atomic dimensions on the order of 1×10^{-10} m. Compute the uncertainty in its momentum.

Answer. From the Heisenberg uncertainty principle, we have that

$$\begin{aligned} \Delta x \cdot \Delta p &\geq \frac{h}{4\pi} \\ \Delta p &\geq \frac{h}{4\pi \Delta x} \\ \Aboxed{\Delta p &\geq 5.273 \times 10^{-25}\,\frac{\mathrm{kg\,m}}{\mathrm{s}}} \end{aligned}$$

□

(b) Repeat the calculation for a proton confined to a region of nuclear dimensions on the order of 1×10^{-14} m.

Answer. From the Heisenberg uncertainty principle, we have that

$$\Delta p \geq \frac{h}{4\pi\Delta x}$$

$$\boxed{\Delta p \geq 5.273 \times 10^{-21}\ \frac{\text{kg m}}{\text{s}}}$$

□

6. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet "Blackbody Radiation" on Canvas and answer the following questions.

   (a) Using the interactive graph of the spectral energy density $\rho(\nu, T)$ as a function of the frequency ν and temperature T, determine the frequency in Hz at which the spectral energy density peaks at a temperature of 700 K.

   Answer.

   $$\boxed{5 \times 10^{13}\ \text{Hz}}$$

   □

   (b) The cosmic background radiation, discovered in 1964 by Penzias and Wilson, can be explained by treating the universe as a blackbody. Using the interactive plot, determine the frequency (in Hz) and wavelength (in m) at which the cosmic background radiation peaks.

   Answer.

   $$\boxed{\nu = 2 \times 10^{11}\ \text{Hz}}$$

   $$\lambda = \frac{c}{\nu}$$

   $$\boxed{\lambda = 1.5 \times 10^{-3}\ \text{m}}$$

   □

   (c) In which region of the electromagnetic spectrum does the peak cosmic background radiation lie?

   Answer. In the $\boxed{\text{microwave}}$ region. □

7. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet "Photoelectric Effect" on Canvas and answer the following questions.

   (a) Copy and complete Table 1 of the worksheet.

   Answer. □

	Au	Mg	Pb	Na	Average value of h:
Threshold frequency (ν_0)	1.084×10^{15} Hz	8.793×10^{14} Hz	1.034×10^{15} Hz	5.684×10^{14} Hz	
Planck's constant (h)	6.681×10^{-34} J s	6.553×10^{-34} J s	6.717×10^{-34} J s	6.522×10^{-34} J s	6.618×10^{-34} J s

Table 1: Photoelectric data for Au, Mg, Pb, and Na.

   (b) What is the computed average value of Planck's constant, and how does this value compare to its experimental value?

   Answer. The computed average value of Planck's constant is $\boxed{6.618 \times 10^{-34}\ \text{J s}}$. It is $\boxed{0.12\%\ \text{off}}$ from the true value of 6.626×10^{-34} J s. □

   (c) For which element is it *least* difficult to eject an electron?

   Answer. $\boxed{\text{Sodium}}$ — lowest threshold frequency means least energy required to excite an electron to the infinite energy level. □

2 Boxes and Waves

10/13: 1. (a) Imagine the particle in the infinite square well bouncing back and forth against the walls classically. In the absence of friction, the particle will continue to bounce back and forth with a constant speed. What is the probability $P(x)$ of finding this classical particle as a function of its position in the box?

Answer. Let L be the length of the box and let v be the speed of the particle. If $0 \leq x \leq L$, the probability $P(x, x + \mathrm{d}x)$ that the particle is between x and $x + \mathrm{d}x$ is equal to the time the particle spends in the sliver of the box between x and $x + \mathrm{d}x$ per unit time divided by the total time. If we let our unit of time be the amount of time it takes the particle to cross the box from end to end once, then we have

$$\begin{aligned} P(x, x + \mathrm{d}x) &= \frac{t_{\text{between } x \text{ and } x + \mathrm{d}x}}{t_{\text{total}}} \\ &= \frac{\mathrm{d}x\,/v}{L/v} \\ \mathrm{d}P(x) &= \frac{\mathrm{d}x}{L} \end{aligned}$$

Note that as $\mathrm{d}x \to 0$, $P(x) \to 0$ as well for any x, so technically the probability of finding the particle at any exact spot is always zero. □

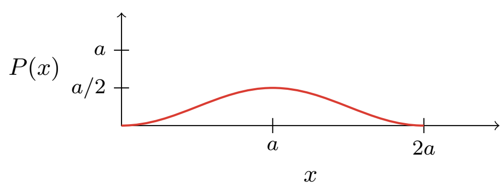
(b) Secondly, consider the particle to be in the quantum ground state. What is the probability $P(x)$ of finding this quantum particle as a function of its position in the box? Give a sketch.

Answer. If the box is of length $L = 2a$, then the probability is

$$P(x) = \psi^*(x)\psi(x)$$

$$\boxed{P(x) = \frac{1}{a}\sin^2\left(\frac{\pi x}{2a}\right)}$$

Sketch:



□

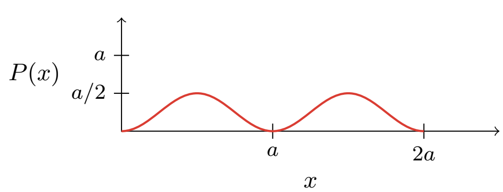
(c) Thirdly, consider the particle to be in the quantum state $n = 2$. What is the probability $P(x)$ of finding this quantum particle as a function of its position in the box? Give a sketch.

Answer. If the box is of length $L = 2a$, then the probability is

$$P(x) = \psi^*(x)\psi(x)$$

$$\boxed{P(x) = \frac{1}{a}\sin^2\left(\frac{\pi x}{a}\right)}$$

Sketch:



□

(d) As the quantum state n of the particle approaches infinity, the energy and frequency of the particle become very large. What happens to the probability $P(x)$ of finding this quantum particle as a function of its position in the box?

Answer. The probability $P(x)$ becomes more evenly distributed throughout the box, so the particle behaves more classically. □

2. The spread or uncertainty in position and momentum may be computed by a mathematical measure of the deviation from the average position

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{1}$$

and

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{2}$$

where the notation $\langle \ \rangle$ was developed by Dirac to denote the expectation value. The text evaluates these uncertainties for a particle in the ground state of an infinite square well.

(a) Do they satisfy the Heisenberg uncertainty relation?

Answer. From McQuarrie and Simon (1997), we have that

$$\Delta x = \frac{a}{2\pi}\sqrt{\frac{\pi^2}{3} - 2} \qquad\qquad \Delta p = \frac{\pi\hbar}{a}$$

These $\boxed{\text{do}}$ obey the Heisenberg uncertainty relation since

$$\Delta x \cdot \Delta p = \frac{\hbar}{2}\sqrt{\frac{\pi^2}{3} - 2} \geq \frac{\hbar}{2}$$

□

(b) Evaluate these uncertainties for a particle in the second- and fourth-excited states (the first and second even excited states) of an infinite square well. Do they satisfy the Heisenberg uncertainty relation?

Answer. From McQuarrie and Simon (1997), we have that

$$\Delta x = \frac{a}{2\pi \cdot 3}\sqrt{\frac{\pi^2 \cdot 3^2}{3} - 2} \qquad\qquad \Delta p = \frac{3 \cdot \pi\hbar}{a}$$

$$\Delta x = \frac{a}{2\pi \cdot 5}\sqrt{\frac{\pi^2 \cdot 5^2}{3} - 2} \qquad\qquad \Delta p = \frac{5 \cdot \pi\hbar}{a}$$

These $\boxed{\text{do}}$ obey the Heisenberg uncertainty relation since

$$\Delta x \cdot \Delta p = \frac{\hbar}{2}\sqrt{\frac{\pi^2 \cdot 3^2}{3} - 2} \geq \frac{\hbar}{2}$$

$$\Delta x \cdot \Delta p = \frac{\hbar}{2}\sqrt{\frac{\pi^2 \cdot 5^2}{3} - 2} \geq \frac{\hbar}{2}$$

□

(c) Compare the uncertainties in the position and momentum for the ground, second-excited, and fourth-excited states. What would you expect to happen to the uncertainties as the state n approaches infinity?

Answer. From the ground to the second-excited to the fourth-excited state, uncertainty in position increases slightly each time and uncertainty in momentum increases linearly.
As $n \to \infty$, uncertainty in position will approach the asymptotic limit of $\frac{a}{2\sqrt{3}}$, but uncertainty in momentum will diverge to ∞. ☐

3. Consider a particle in a one-dimensional infinite square well where the infinite walls are located and $-b$ and $+b$. Give the time-dependent form of the ground and the first-excited states.

Answer. We have that the time-independent forms of the ground and first-excited states are, respectively

$$\psi_1(x) = \frac{1}{\sqrt{b}} \cos\left(\frac{\pi x}{2b}\right) \qquad \psi_2(x) = \frac{1}{\sqrt{b}} \sin\left(\frac{\pi x}{b}\right)$$

Thus, the time-dependent forms are

$$\psi_1(x,t) = \frac{1}{\sqrt{b}} \cos\left(\frac{\pi x}{2b}\right) \cdot \mathrm{e}^{-iE_1 t/\hbar} \qquad \psi_2(x,t) = \frac{1}{\sqrt{b}} \sin\left(\frac{\pi x}{b}\right) \cdot \mathrm{e}^{-iE_2 t/\hbar}$$

$$\boxed{\psi_1(x,t) = \frac{1}{\sqrt{b}} \cos\left(\frac{\pi x}{2b}\right) \cdot \mathrm{e}^{-i\hbar\pi^2 t/8mb^2}} \qquad \boxed{\psi_2(x,t) = \frac{1}{\sqrt{b}} \sin\left(\frac{\pi x}{b}\right) \cdot \mathrm{e}^{-i\hbar\pi^2 t/2mb^2}}$$

☐

4. We have been examining a one-dimensional infinite square well where the infinite walls are located at $-b$ and $+b$. The energy levels in this quantum system are non-degenerate, that is, for each energy, there is only one wave function. Let us place an infinite potential step between $-b/2$ and $+b/2$.

(a) Is the particle more likely to be in the left or the right infinite square well?

Answer. Because of symmetry, the particle is $\boxed{\text{equally likely}}$ to be in the left and right side of the well. ☐

(b) What are the new energy levels and wave functions of this modified system? (Hint: How are they related to the infinite square well?)

Answer. To derive a wave function ψ pertaining to the entire system, we will modify the particle in a box procedure to derive two separate wave functions $\psi_{\mathrm{I}}, \psi_{\mathrm{II}}$ corresponding to the two sides of the infinite potential step. Let's begin.
For the negative side (corresponding to ψ_{I}, start with the Schrödinger equation in the form

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) = -k^2\psi(x)$$

where $k = \sqrt{2mE}/\hbar$. The general solution to this ODE will be of the form

$$\psi_{\mathrm{I}}(x) = A\cos(kx) + B\sin(kx)$$

Our boundary conditions are

$$\begin{aligned} 0 &= \psi_{\mathrm{I}}(-b) \\ &= A\cos(kb) - B\sin(kb) \end{aligned} \qquad \begin{aligned} 0 &= \psi_{\mathrm{II}}(-b/2) \\ &= A\cos(kb/2) - B\sin(kb/2) \end{aligned}$$

We can make both of the above equations equal to zero three different ways: We can let $A = B = 0$, we can let $\cos(kb) = \cos(kb/2) = B = 0$, and we can let $\sin(kb) = \sin(kb/2) = A = 0$. We will work through each possibility in turn, either finding a nontrivial ψ_{I} or proving that no such function exists under such conditions. Let's begin.

If $A = B = 0$, then $\psi_{\text{I}} = 0$, and we have a trivial solution.

Now suppose that $B = 0$. Then to make $\cos(kb) = 0$, we must have $kb = \pi n/2$ where n is odd. To make $\cos(kb/2) = 0$, we *also* must have $kb/2 = \pi n'/2$ where n' is odd. But there is no pair of odd numbers n, n' that satisfy both of these equations, because if there were, we would have

$$\begin{aligned} \frac{\pi n/2}{2} &= \frac{\pi n'}{2} \\ n &= 2n' \end{aligned}$$

implying that n is even, a contradiction.

Now suppose that $A = 0$. Then nontrivial solutions let $kb = \pi n'$ where n' is any integer *and* $kb/2 = \pi n$ where n is any integer. Solving this system gives $n' = 2n$, which does *not* break the integer condition. Thus, choosing n as our quantum number (that can take on any integer value), we have as our solution

$$\psi_{\text{I}}(x) = B \sin\left(\frac{2\pi n}{b} x\right)$$

which does indeed satisfy

$$0 = \psi(-b) = \psi(-b/2)$$

It follows by a symmetric argument that we have

$$\psi_{\text{II}}(x) = D \sin\left(\frac{2\pi n}{b} x\right)$$

This allows us to define

$$\psi(x) = \begin{cases} \psi_{\text{I}}(x) & -b \leq x \leq -\frac{b}{2} \\ \psi_{\text{II}}(x) & \frac{b}{2} \leq x \leq b \\ 0 & \text{otherwise} \end{cases}$$

Before we normalize, note that by part (a), $|B|^2 = |D|^2$. Thus, we can normalize as follows.

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} \psi^2(x)\,\mathrm{d}x \\ &= \int_{-b}^{-b/2} \psi_{\text{I}}^2(x)\,\mathrm{d}x + \int_{b/2}^{b} \psi_{\text{II}}^2(x)\,\mathrm{d}x \\ &= \int_{-b}^{-b/2} B^2 \sin^2\left(\frac{2\pi n}{b} x\right)\mathrm{d}x + \int_{b/2}^{b} B^2 \sin^2\left(\frac{2\pi n}{b} x\right)\mathrm{d}x \\ &= B^2 \left(\int_{-b}^{-b/2} \frac{1 - \cos\left(\frac{4\pi n}{b} x\right)}{2}\,\mathrm{d}x + \int_{b/2}^{b} \frac{1 - \cos\left(\frac{4\pi n}{b} x\right)}{2}\,\mathrm{d}x \right) \\ &= B^2 \left(\left[\frac{x}{2} - \frac{b}{8\pi n} \sin\left(\frac{4\pi n}{b} x\right) \right]_{-b}^{-b/2} + \left[\frac{x}{2} - \frac{b}{8\pi n} \sin\left(\frac{4\pi n}{b} x\right) \right]_{b/2}^{b} \right) \\ &= B^2 \left(\left[\frac{b}{4}\right] + \left[\frac{b}{4}\right] \right) \\ B &= \pm\sqrt{\frac{2}{b}} \end{aligned}$$

Thus, our wave function for this system is

$$\boxed{\psi(x) = \sqrt{\frac{2}{b}} \sin\left(\frac{2\pi n}{b} x\right)}$$

where $n = 1, 2, 3, \ldots$, and defined as on the piecewise domain above.

Considering that we substituted $k = 2\pi n/b$ in the above derivation, the energy levels for this system will be

$$\begin{aligned}
\frac{2\pi n}{b} &= \sqrt{\frac{2mE_n}{\hbar^2}} \\
\frac{4\pi^2 n^2}{b^2} &= \frac{2mE_n}{\hbar^2} \\
E_n &= \frac{2\pi^2 n^2 \hbar^2}{mb^2} \\
\Aboxed{E_n &= \frac{n^2 h^2}{2mb^2}}
\end{aligned}$$

□

(c) Are the energy levels degenerate, and if so, what is the degeneracy?

Answer. $\boxed{\text{Yes.}}$ We have the two linearly independent piecewise solutions

$$\psi(x) = \begin{cases} \psi_{\mathrm{I}}(x) & -b \leq x \leq -\frac{b}{2} \\ \psi_{\mathrm{II}}(x) & \frac{b}{2} \leq x \leq b \end{cases} \qquad \psi(x) = \begin{cases} \psi_{\mathrm{I}}(x) & -b \leq x \leq -\frac{b}{2} \\ -\psi_{\mathrm{II}}(x) & \frac{b}{2} \leq x \leq b \end{cases}$$

so the degeneracy is $\boxed{2}$. □

(d) Are the new energies higher or lower than the box without the infinite step?

Answer. By comparing the results from part (b) to those from the pure particle in a box, the energy levels are more spread apart by a factor of 16. Therefore, the new energies are most certainly $\boxed{\text{higher}}$ than the box without the infinite step. □

5. Consider an electron of energy E incident on the potential step where

$$V(x) = \begin{cases} 0\,\mathrm{eV} & x < 0 \\ 8\,\mathrm{eV} & x > 0 \end{cases}$$

Calculate the reflection coefficient R and the transmission coefficient T

(a) When $E = 4\,\mathrm{eV}$;

Answer. For $E < V$, we automatically have

$$\boxed{R = 1} \qquad \boxed{T = 0}$$

□

(b) When $E = 16\,\mathrm{eV}$;

Answer. We have that

$$\begin{aligned}
\alpha &= \frac{\sqrt{2m \cdot 16}}{\hbar} \\
&= \frac{4}{\hbar}\sqrt{2m}
\end{aligned} \qquad \begin{aligned}
\beta &= \frac{\sqrt{2m \cdot 8}}{\hbar} \\
&= \frac{4}{\hbar}\sqrt{m}
\end{aligned}$$

Thus, we have that

$$R = \frac{(\alpha-\beta)^2}{(\alpha+\beta)^2} = \frac{\left(\frac{4}{\hbar}\sqrt{2m} - \frac{4}{\hbar}\sqrt{m}\right)^2}{\left(\frac{4}{\hbar}\sqrt{2m} + \frac{4}{\hbar}\sqrt{m}\right)^2} = \frac{2m - 2m\sqrt{2} + m}{2m + 2m\sqrt{2} + m} = \frac{3-2\sqrt{2}}{3+2\sqrt{2}}$$
$$\boxed{R = 17 - 12\sqrt{2}}$$

$$T = \frac{4\alpha\beta}{(\alpha+\beta)^2} = \frac{4\cdot\frac{4}{\hbar}\sqrt{2m}\cdot\frac{4}{\hbar}\sqrt{m}}{\left(\frac{4}{\hbar}\sqrt{2m} + \frac{4}{\hbar}\sqrt{m}\right)^2} = \frac{4m\sqrt{2}}{2m + 2m\sqrt{2} + m} = \frac{4\sqrt{2}}{3+2\sqrt{2}}$$
$$\boxed{T = 12\sqrt{2} - 16}$$

□

(c) When $E = 8\,\text{eV}$.

Answer. We have that

$$\alpha = \frac{\sqrt{2m\cdot 8}}{\hbar} = \frac{4}{\hbar}\sqrt{m}$$

$$\beta = \frac{\sqrt{2m\cdot 0}}{\hbar} = 0$$

Thus, we have that

$$R = \frac{(\alpha-\beta)^2}{(\alpha+\beta)^2} = \frac{\left(\frac{4}{\hbar}\sqrt{m} - 0\right)^2}{\left(\frac{4}{\hbar}\sqrt{m} + 0\right)^2}$$
$$\boxed{R = 1}$$

$$T = \frac{4\alpha\beta}{(\alpha+\beta)^2} = \frac{4\cdot\frac{4}{\hbar}\sqrt{m}\cdot 0}{\left(\frac{4}{\hbar}\sqrt{m} + 0\right)^2}$$
$$\boxed{T = 0}$$

□

6. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet "Particle in a Box" on Canvas and answer the following questions.

(a) Based on the interactive plot, does the wave function become more classical as the quantum number n increases?

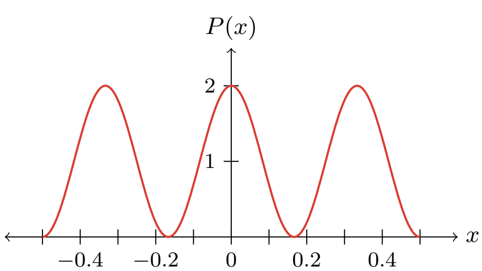
Answer. $\boxed{\text{Yes.}}$ It predicts an increasingly "continuous" probability distribution, wherein the particle is equally likely to be found anywhere. □

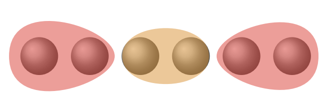
(b) Does the energy spacing between states become more or less classical as n increases?

Answer. $\boxed{\text{Less classical.}}$ Higher energy states are spaced farther apart. □

(c) Sketch the $n = 3$ state of the particle in a box and the third molecular orbital of the hydrogen chain.

Answer.





□

(d) What do you observe about the nodal patterns in part (c)?

Answer. They correspond to each other (both in terms of number and placement). □

(e) Based on parts (c) and (d), are the particle-in-a-box wave functions a good model for the wave functions of the hydrogen chain?

Answer. $\boxed{\text{Yes.}}$ □

3 Harmonic Oscillators and Diatomics

10/20: 1. Consider an electron with total energy E incident from *left to right* across a potential "drop" where

$$V(x) = \begin{cases} V_0 & x < 0 \\ 0 & x > 0 \end{cases}$$

(a) Give an expression for the wave function in each of the two regions.

Answer. If region I is $(-\infty, 0)$ and region II is $(0, \infty)$, then

$$\boxed{\psi_{\text{I}}(x) = A\mathrm{e}^{i\alpha x} + B\mathrm{e}^{-i\alpha x}} \qquad \boxed{\psi_{\text{II}}(x) = C\mathrm{e}^{i\beta x} + D\mathrm{e}^{-i\beta x}}$$

□

(b) Which coefficient in the wave functions from (a) is zero? Explain briefly why.

Answer. As written, we will have $\boxed{D = 0}$. This is because while the particle travels left to right in regions I and II (so $A, C \neq 0$) and there may be reflection back into region I at the intersection (so potentially $B \neq 0$), there is no particle in region II traveling right to left nor is there a barrier that could reflect some of the particle backwards. □

(c) Using continuity of the wave function and its derivative at $x = 0$, derive an expression for the reflection coefficient.

Answer. It follows from the continuity of the wave function *itself* at $x = 0$ that

$$A + B = A\mathrm{e}^{i\alpha(0)} + B\mathrm{e}^{-i\beta(0)} = \psi_{\text{I}}(0) = \psi_{\text{II}}(0) = C\mathrm{e}^{i\alpha(0)} = C$$

Similarly, it follows from the continuity of the *derivative* of the wave function at $x = 0$ that

$$i\alpha A - i\alpha B = \frac{\mathrm{d}}{\mathrm{d}x}\left(A\mathrm{e}^{i\alpha x} + B\mathrm{e}^{-i\alpha x}\right)_{x=0} = \left(\frac{\mathrm{d}\psi_{\text{I}}}{\mathrm{d}x}\right)_{x=0} = \left(\frac{\mathrm{d}\psi_{\text{II}}}{\mathrm{d}x}\right)_{x=0} = \frac{\mathrm{d}}{\mathrm{d}x}\left(C\mathrm{e}^{i\beta x}\right)_{x=0} = i\beta C$$

Thus, we have that

$$A = \frac{C(\alpha + \beta)}{2\alpha} \qquad B = \frac{C(\alpha - \beta)}{2\alpha}$$

We know that the probability of the particle going left to right in region I is $|A|^2$ and that the probability of the particle going from right to left in region I is $|B|^2$. Thus, since the incident/reflected flux factors in the speed c of the particle in either direction, the respective fluxes are $c|A|^2$ and $c|B|^2$. But this implies that

$$\begin{aligned} R &= \frac{c|B|^2}{c|A|^2} \\ &= \frac{|B|^2}{|A|^2} \\ \Aboxed{R &= \frac{(\alpha - \beta)^2}{(\alpha + \beta)^2}} \end{aligned}$$

□

(d) Calculate the reflection coefficient R when $V_0 = 8\,\text{eV}$ and $E = 16\,\text{eV}$.

Answer. We have that

$$\alpha = \frac{\sqrt{2m\cdot(16-8)}}{\hbar} = \frac{4}{\hbar}\sqrt{m} \qquad \beta = \frac{\sqrt{2m\cdot 16}}{\hbar} = \frac{4}{\hbar}\sqrt{2m}$$

Thus, we have that

$$\begin{aligned} R &= \frac{(\alpha-\beta)^2}{(\alpha+\beta)^2} \\ &= \frac{(\frac{4}{\hbar}\sqrt{m}-\frac{4}{\hbar}\sqrt{2m})^2}{(\frac{4}{\hbar}\sqrt{m}+\frac{4}{\hbar}\sqrt{2m})^2} \\ &= \frac{m-2m\sqrt{2}+2m}{m+2m\sqrt{2}+2m} \\ &= \frac{3-2\sqrt{2}}{3+2\sqrt{2}} \\ &\boxed{R = 17-12\sqrt{2}} \end{aligned}$$

□

(e) Compare this result with the result from problem 5b of Problem Set 2.

Answer. The answers are $\boxed{\text{identical}}$. □

(f) From your result in (e), explain whether the degree of reflection depends on both the direction (step or "drop") *and* magnitude of the potential change or only the magnitude of the change.

Answer. Since the answer in part (e) matches that of a setup with the same magnitude but opposite direction, the degree of reflection depends $\boxed{\text{solely on the magnitude of the potential change}}$, not the direction (step or drop). □

2. A good approximation to the intermolecular potential for a diatomic molecule is the Morse potential

$$V(x) = D(1-\mathrm{e}^{-\beta x})^2$$

where x is the displacement from the equilibrium bond length.

(a) Compute the Taylor series expansion of the Morse potential about $x=0$ through second order.

Answer. Since

$$V(0) = D(1-\mathrm{e}^{-\beta(0)})^2 = 0 \qquad V'(0) = 2D(1-\mathrm{e}^{-\beta(0)})\cdot\beta\mathrm{e}^{-\beta(0)} = 0$$

$$\begin{aligned} V''(0) &= -2D\beta^2\mathrm{e}^{-\beta(0)} + 4D\beta^2\mathrm{e}^{-2\beta(0)} \\ &= 2D\beta^2 \end{aligned}$$

we have that

$$\begin{aligned} \tilde{V} &= V(0) + V'(0)x + \frac{1}{2}V''(0)x^2 \\ &\boxed{\tilde{V} = D\beta^2x^2} \end{aligned}$$

□

(b) Comparing the result with the potential for the harmonic oscillator, give an expression for the harmonic force constant k in terms of D and β.

Answer. For a harmonic oscillator, we have $V(x) = kx^2/2$. Setting this equal to the above, we have that

$$\frac{1}{2}kx^2 = D\beta^2x^2$$
$$\boxed{k = 2D\beta^2}$$

□

(c) Given that $D = 7.31 \times 10^{-19}$ J/molecule and $\beta = 1.81 \times 10^{10}\,\text{m}^{-1}$ for HCl, calculate the force constant for HCl.

Answer. Plugging the given values into the equation from part (b) gives

$$\boxed{k = 479\,\text{N/m}}$$

□

3. In the infrared spectrum of $H^{79}Br$, chemists find an intense line at $2630\,\text{cm}^{-1}$. For $H^{79}Br$, calculate

(a) The force constant.

Answer. Let $m_{\text{H}} = 1.0$ and let $m_{\text{Br}} = 79.0$. Then

$$\begin{aligned}\mu &= \frac{m_{\text{H}}m_{\text{Br}}}{m_{\text{H}} + m_{\text{Br}}} \cdot \frac{1 \times 10^{-3}\,\text{kg}}{6.02 \times 10^{23}\,\text{u}} \\ &= 1.64 \times 10^{-27}\,\text{kg}\end{aligned}$$

Let $\bar{\nu}_{\text{obs}} = 2.630 \times 10^5\,\text{m}^{-1}$. Then

$$\bar{\nu}_{\text{obs}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$
$$k = (2\pi c\bar{\nu}_{\text{obs}})^2\mu$$
$$\boxed{k = 403\,\text{N/m}}$$

□

(b) The period of vibration.

Answer. We have that

$$\frac{2\pi}{T} = \omega = \sqrt{\frac{k}{\mu}}$$
$$T = 2\pi\sqrt{\frac{\mu}{k}}$$
$$\boxed{T = 1.27 \times 10^{-14}\,\text{s}}$$

□

(c) The zero-point energy.

Answer. We have that

$$\begin{aligned} E_0 &= \frac{1}{2}\hbar\omega \\ &= \frac{1}{2}\hbar\sqrt{\frac{k}{\nu}} \\ \Aboxed{E_0 &= 2.61\times 10^{-20}\text{ J}} \end{aligned}$$

□

4. Using the fact that the wave functions of the harmonic oscillator are either even or odd, show that the average values (or expectation values) of odd powers of position x and momentum p vanish, that is

$$\langle x^k\rangle = 0 \qquad\qquad \langle p^k\rangle = 0$$

when k is odd.

Answer. Since Hermite polynomials $H_v(\xi)$ are even functions if v is even and odd functions if v is odd, and ψ_v is the product of all even functions and a Hermite polynomial for all v, we know that the parity of the Hermite polynomial determines the parity of ψ_v for all v. Thus, ψ_v is even when v is even, and odd when v is odd.

Since the square of either an odd or an even function is even, ψ_v^2 is even for all v. Additionally, x^k is odd for all k. Thus, $x^k\psi_v^2$ is odd for all k, v. But this means that

$$\langle x^k\rangle = \int_{-\infty}^{\infty}\psi_v(x)x^k\psi_v(x)\,\mathrm{d}x = 0$$

as desired.

Similarly, since the derivative of an even function is odd and vice versa, we know that all odd-order derivatives of ψ_v have opposite parity to ψ_v. But this implies that the product of ψ_v and an odd-order derivative of ψ_v is always odd. It follows that

$$\langle p^k\rangle = \int_{-\infty}^{\infty}\psi_v(x)\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right)^k\psi_v(x)\,\mathrm{d}x = 0$$

as desired. □

5. For the ground state of the harmonic oscillator...

(a) Evaluate the Heisenberg uncertainty relation where the spread (or uncertainty) in position and momentum may be computed by

$$(\Delta x)^2 = \int\psi^*(x)(x-\langle x\rangle)^2\psi(x)\,\mathrm{d}x \qquad\qquad (\Delta p)^2 = \int\psi^*(x)(\hat{p}-\langle\hat{p}\rangle)^2\psi(x)\,\mathrm{d}x$$

Use the results of Exercise 5.17 in McQuarrie and Simon (1997) to evaluate the necessary integrals.

Answer. We have from McQuarrie and Simon (1997) that $\langle x\rangle = 0$. Thus,

$$\begin{aligned} (\Delta x)^2 &= \int\psi_0^*(x)(x-\langle x\rangle)^2\psi_0(x)\,\mathrm{d}x \\ &= \int_{-\infty}^{\infty}\sqrt[4]{\frac{\alpha}{\pi}}\mathrm{e}^{-\alpha x^2/2}x^2\sqrt[4]{\frac{\alpha}{\pi}}\mathrm{e}^{-\alpha x^2/2}\,\mathrm{d}x \\ &= \sqrt{\frac{\alpha}{\pi}}\int_{-\infty}^{\infty}x^2\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x \end{aligned}$$

$$\begin{aligned}
&= \sqrt{\frac{\alpha}{\pi}} \cdot \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}} \\
&= \frac{1}{2\alpha} \\
\Delta x &= \sqrt{\frac{1}{2\alpha}}
\end{aligned}$$

Additionally, we have that $\langle p \rangle = 0$. Thus,

$$\begin{aligned}
(\Delta p)^2 &= \int \psi_0^*(x)(\hat{p} - \langle \hat{p} \rangle)^2 \psi_0(x)\,\mathrm{d}x \\
&= \int_{-\infty}^{\infty} \sqrt[4]{\frac{\alpha}{\pi}} \mathrm{e}^{-\alpha x^2/2} \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x}\right)^2 \sqrt[4]{\frac{\alpha}{\pi}} \mathrm{e}^{-\alpha x^2/2}\,\mathrm{d}x \\
&= -\hbar^2 \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2/2} \frac{\mathrm{d}}{\mathrm{d}x}\left(-\alpha x \mathrm{e}^{-\alpha x^2/2}\right) \mathrm{d}x \\
&= -\hbar^2 \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2/2}(-\alpha \mathrm{e}^{-\alpha x^2/2} + \alpha^2 x^2 \mathrm{e}^{-\alpha x^2/2})\,\mathrm{d}x \\
&= \hbar^2 \sqrt{\frac{\alpha^3}{\pi}} \int_{-\infty}^{\infty} (1 - \alpha x^2) \mathrm{e}^{-\alpha x^2}\,\mathrm{d}x \\
&= \hbar^2 \sqrt{\frac{\alpha^3}{\pi}} \cdot \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \\
&= \frac{1}{2}\alpha\hbar^2 \\
\Delta p &= \hbar\sqrt{\frac{\alpha}{2}}
\end{aligned}$$

Therefore, we have

$$\Delta x \cdot \Delta p = \frac{\hbar}{2} \geq \frac{\hbar}{2}$$

□

(b) In terms of the uncertainty relation, what is special about the harmonic oscillator?

Answer. The product of the uncertainties is *exactly* $\hbar/2$, as opposed to some number greater than it. In other words, it can be described as precisely as any quantum system. □

6. Using the expectation values from the previous problem, show for the ground state of the harmonic oscillator that the average values of the kinetic and the potential energies are equal to one half of the total energy, i.e.,

$$\langle T \rangle = \langle V \rangle = \frac{E_0}{2}$$

This relation, known as the **virial theorem**, is true for all states of the harmonic oscillator.

Answer. Invoking the definitions of $\langle T \rangle$ and $\langle V \rangle$ and substituting from Problem 5a, we have that

$$\begin{aligned}
\langle T \rangle &= \int \psi_0^*(x)\hat{H}\psi_0(x)\,\mathrm{d}x \\
&= \frac{1}{2\mu}\int \psi_0^*(x)\hat{p}^2\psi_0(x)\,\mathrm{d}x \\
&= \frac{1}{2\mu} \cdot \frac{1}{2}\alpha\hbar^2 \\
&= \frac{\hbar^2}{4\mu} \cdot \frac{\sqrt{k\mu}}{\hbar}
\end{aligned}
\qquad
\begin{aligned}
\langle V \rangle &= \int \psi_0^*(x)\hat{V}\psi_0(x)\,\mathrm{d}x \\
&= \frac{1}{2}k\int \psi_0^*(x)x^2\psi_0(x)\,\mathrm{d}x \\
&= \frac{1}{2}k \cdot \frac{1}{2\alpha} \\
&= \frac{k}{4} \cdot \frac{\hbar}{\sqrt{k\mu}}
\end{aligned}$$

$$= \frac{\hbar}{4}\sqrt{\frac{k}{\mu}} \qquad\qquad = \frac{\hbar}{4}\sqrt{\frac{k}{\mu}}$$

Thus, we have shown that $\langle T \rangle = \langle V \rangle$. To complete the proof, we have that

$$\langle T \rangle = \langle V \rangle = \frac{\hbar}{4}\sqrt{\frac{k}{\mu}} = \frac{\frac{\hbar\omega}{2}}{2} = \frac{\hbar\omega\left(0+\frac{1}{2}\right)}{2} = \frac{E_0}{2}$$

as desired. □

7. Use the Quantum Chemistry Toolbox in Maple to answer the lettered questions in the worksheet "Harmonic Oscillator" on Canvas.

Answer.

Molecule	**Reduced Mass (μ)**	**Spring Constant (k)**	**Angular Frequency (ω)**	**Energy Spacing (ΔE)**
HF	1.59×10^{-27} kg	1110 J/m^2	8.36×10^{14} Hz	8.81×10^{-20} J
N_2	1.16×10^{-26} kg	3130 J/m^2	5.19×10^{14} Hz	5.47×10^{-20} J
CO	1.14×10^{-26} kg	2390 J/m^2	4.58×10^{14} Hz	4.83×10^{-20} J

□

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

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

$$\boxed{\langle \hat{L}_z \rangle = 0}$$

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

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

□

(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

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

□

(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

$$\begin{aligned}
\sigma &= 13.074 \\
&\boxed{r = 13.074a_0}
\end{aligned}$$

□

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

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

Therefore, we have that

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

□

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. □

5 Exact and Approximate Solutions to the Schrödinger Equation

11/3: 1. In the book *Flatland*, Edwin Abbott explores the amazement of the inhabitants of a two-dimensional world when they are visited by a three-dimensional sphere. In class, we developed the Schrödinger equation for an atom in three dimensions. Consider how a two-dimensional atom would differ from a three-dimensional atom.

(a) Express the Schrödinger equation in the Cartesian coordinates x and y.

Answer. Since the mass of the proton is far greater than the mass of the electron, we approximate it as fixed at the origin. Thus, we need only account for the kinetic and potential energy of the electron. Naturally, the kinetic energy of the electron will be given by

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$$

where m is the mass of the electron and ∇^2 is the Laplacian in two-dimensional Cartesian coordinates. Similarly, since the electron and proton have the same charge e, they will interact through a potential field given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0\sqrt{x^2+y^2}}$$

where $\sqrt{x^2+y^2}$ is the distance of the electron from the proton (fixed at the origin). It follows that the complete Hamiltonian is given by

$$\hat{H} = \hat{T} + V$$

so our Schrödinger equation is

$$\hat{H}\psi = E\psi$$

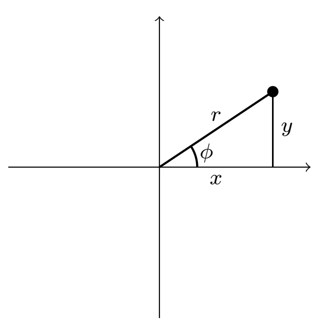
$$\boxed{\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right) - \frac{e^2}{4\pi\epsilon_0\sqrt{x^2+y^2}}\right]\psi(x,y) = E\psi(x,y)}$$

□

(b) Re-express the Schrödinger equation in the polar coordinates r and ϕ.

Answer. We will construct this expression from the ground up without motivating our steps. The motivation should be clear by the end when everything comes together. Let's begin.

Consider the following picture.



Then $r = \sqrt{x^2+y^2}$ and $\phi = \tan^{-1}(y/x)$ ($x = r\cos\phi$ and $y = r\sin\phi$ will also be useful). It follows that

$$\begin{aligned}\frac{\partial r}{\partial x} &= \frac{\partial}{\partial x}\left(\sqrt{x^2+y^2}\right)\\ &= \frac{\partial}{\partial u}\left(\sqrt{u}\right)\cdot\frac{\partial}{\partial x}\left(x^2+y^2\right)\\ &= \frac{1}{2\sqrt{u}}\cdot 2x\\ &= \frac{x}{\sqrt{x^2+y^2}}\\ &= \frac{x}{r}\\ &= \cos\phi\end{aligned}$$

$$\begin{aligned}\frac{\partial r}{\partial y} &= \frac{\partial}{\partial y}\left(\sqrt{x^2+y^2}\right)\\ &= \frac{\partial}{\partial u}\left(\sqrt{u}\right)\cdot\frac{\partial}{\partial y}\left(x^2+y^2\right)\\ &= \frac{1}{2\sqrt{u}}\cdot 2y\\ &= \frac{y}{\sqrt{x^2+y^2}}\\ &= \frac{y}{r}\\ &= \sin\phi\end{aligned}$$

and

$$\begin{aligned}\frac{\partial\phi}{\partial x} &= \frac{\partial}{\partial x}\left(\tan^{-1}\left(\frac{y}{x}\right)\right)\\ &= \frac{1}{1+(y/x)^2}\cdot -\frac{y}{x^2}\\ &= -\frac{y}{x^2+y^2}\\ &= -\frac{r\sin\phi}{r^2}\\ &= -\frac{\sin\phi}{r}\end{aligned}$$

$$\begin{aligned}\frac{\partial\phi}{\partial y} &= \frac{\partial}{\partial y}\left(\tan^{-1}\left(\frac{y}{x}\right)\right)\\ &= \frac{1}{1+(y/x)^2}\cdot\frac{1}{x}\\ &= \frac{x}{x^2+y^2}\\ &= -\frac{r\cos\phi}{r^2}\\ &= \frac{\cos\phi}{r}\end{aligned}$$

Let ψ be a function of r and ϕ. Then by the chain rule for partial differentiation,

$$\begin{aligned}\frac{\partial\psi}{\partial x} &= \frac{\partial\psi}{\partial r}\frac{\partial r}{\partial x}+\frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial x}\\ &= \frac{\partial\psi}{\partial r}\cdot\cos\phi+\frac{\partial\psi}{\partial\phi}\cdot -\frac{\sin\phi}{r}\\ &= \cos\phi\frac{\partial\psi}{\partial r}-\frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi}\end{aligned}$$

$$\begin{aligned}\frac{\partial\psi}{\partial y} &= \frac{\partial\psi}{\partial r}\frac{\partial r}{\partial y}+\frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial y}\\ &= \frac{\partial\psi}{\partial r}\cdot\sin\phi+\frac{\partial\psi}{\partial\phi}\cdot\frac{\cos\phi}{r}\\ &= \sin\phi\frac{\partial\psi}{\partial r}+\frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi}\end{aligned}$$

Additionally, we have that

$$\begin{aligned}\frac{\partial}{\partial r}\left(\frac{\partial\psi}{\partial x}\right) &= \frac{\partial}{\partial r}\left(\cos\phi\frac{\partial\psi}{\partial r}-\frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi}\right)\\ &= \frac{\partial}{\partial r}\left(\cos\phi\frac{\partial\psi}{\partial r}\right)-\frac{\partial}{\partial r}\left(\frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi}\right)\\ &= \left[0\cdot\frac{\partial\psi}{\partial r}+\cos\phi\frac{\partial^2\psi}{\partial r^2}\right]-\left[-\frac{\sin\phi}{r^2}\frac{\partial\psi}{\partial\phi}+\frac{\sin\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\right]\\ &= \cos\phi\frac{\partial^2\psi}{\partial r^2}+\frac{\sin\phi}{r^2}\frac{\partial\psi}{\partial\phi}-\frac{\sin\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial}{\partial\phi}\left(\frac{\partial\psi}{\partial x}\right) &= \frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial\psi}{\partial r}-\frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi}\right)\\ &= \frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial\psi}{\partial r}\right)-\frac{\partial}{\partial\phi}\left(\frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi}\right)\\ &= \left[-\sin\phi\frac{\partial\psi}{\partial r}+\cos\phi\frac{\partial^2\psi}{\partial\phi\partial r}\right]-\left[\frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi}+\frac{\sin\phi}{r}\frac{\partial^2\psi}{\partial\phi^2}\right]\\ &= -\sin\phi\frac{\partial\psi}{\partial r}+\cos\phi\frac{\partial^2\psi}{\partial\phi\partial r}-\frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi}-\frac{\sin\phi}{r}\frac{\partial^2\psi}{\partial\phi^2}\end{aligned}$$

so

$$\begin{aligned}\frac{\partial}{\partial r}\left(\frac{\partial \psi}{\partial x}\right)\frac{\partial r}{\partial x} &= \left[\cos\phi\frac{\partial^2\psi}{\partial r^2} + \frac{\sin\phi}{r^2}\frac{\partial\psi}{\partial\phi} - \frac{\sin\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\right]\cdot\cos\phi \\ &= \cos^2\phi\frac{\partial^2\psi}{\partial r^2} + \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} - \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial}{\partial \phi}\left(\frac{\partial \psi}{\partial x}\right)\frac{\partial \phi}{\partial x} &= \left[-\sin\phi\frac{\partial\psi}{\partial r} + \cos\phi\frac{\partial^2\psi}{\partial\phi\partial r} - \frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi} - \frac{\sin\phi}{r}\frac{\partial^2\psi}{\partial\phi^2}\right]\cdot -\frac{\sin\phi}{r} \\ &= \frac{\sin^2\phi}{r}\frac{\partial\psi}{\partial r} - \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial\phi\partial r} + \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\sin^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\end{aligned}$$

Thus,

$$\begin{aligned}\frac{\partial^2\psi}{\partial x^2} &= \frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\right) \\ &= \frac{\partial}{\partial r}\left(\frac{\partial \psi}{\partial x}\right)\frac{\partial r}{\partial x} + \frac{\partial}{\partial \phi}\left(\frac{\partial \psi}{\partial x}\right)\frac{\partial \phi}{\partial x} \\ &= \left[\cos^2\phi\frac{\partial^2\psi}{\partial r^2} + \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} - \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\right] \\ &\quad + \left[\frac{\sin^2\phi}{r}\frac{\partial\psi}{\partial r} - \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial\phi\partial r} + \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\sin^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\right] \\ &= \cos^2\phi\frac{\partial^2\psi}{\partial r^2} + \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} - \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi} + \frac{\sin^2\phi}{r}\frac{\partial\psi}{\partial r} + \frac{\sin^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\end{aligned}$$

Furthermore, we have that

$$\begin{aligned}\frac{\partial}{\partial r}\left(\frac{\partial \psi}{\partial y}\right) &= \frac{\partial}{\partial r}\left(\sin\phi\frac{\partial\psi}{\partial r} + \frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi}\right) \\ &= \frac{\partial}{\partial r}\left(\sin\phi\frac{\partial\psi}{\partial r}\right) + \frac{\partial}{\partial r}\left(\frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi}\right) \\ &= \left[0\cdot\frac{\partial\psi}{\partial r} + \sin\phi\frac{\partial^2\psi}{\partial r^2}\right] + \left[-\frac{\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\right] \\ &= \sin\phi\frac{\partial^2\psi}{\partial r^2} - \frac{\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial}{\partial \phi}\left(\frac{\partial \psi}{\partial y}\right) &= \frac{\partial}{\partial \phi}\left(\sin\phi\frac{\partial\psi}{\partial r} + \frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi}\right) \\ &= \frac{\partial}{\partial \phi}\left(\sin\phi\frac{\partial\psi}{\partial r}\right) + \frac{\partial}{\partial \phi}\left(\frac{\cos\phi}{r}\frac{\partial\psi}{\partial\phi}\right) \\ &= \left[\cos\phi\frac{\partial\psi}{\partial r} + \sin\phi\frac{\partial^2\psi}{\partial\phi\partial r}\right] + \left[-\frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi} + \frac{\cos\phi}{r}\frac{\partial^2\psi}{\partial\phi^2}\right] \\ &= \cos\phi\frac{\partial\psi}{\partial r} + \sin\phi\frac{\partial^2\psi}{\partial\phi\partial r} - \frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi} + \frac{\cos\phi}{r}\frac{\partial^2\psi}{\partial\phi^2}\end{aligned}$$

so

$$\begin{aligned}\frac{\partial}{\partial r}\left(\frac{\partial \psi}{\partial y}\right)\frac{\partial r}{\partial y} &= \left[\sin\phi\frac{\partial^2\psi}{\partial r^2} - \frac{\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\right]\cdot\sin\phi \\ &= \sin^2\phi\frac{\partial^2\psi}{\partial r^2} - \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\end{aligned}$$

and

$$\frac{\partial}{\partial\phi}\left(\frac{\partial\psi}{\partial y}\right)\frac{\partial\phi}{\partial y} = \left[\cos\phi\frac{\partial\psi}{\partial r} + \sin\phi\frac{\partial^2\psi}{\partial\phi\partial r} - \frac{\sin\phi}{r}\frac{\partial\psi}{\partial\phi} + \frac{\cos\phi}{r}\frac{\partial^2\psi}{\partial\phi^2}\right]\cdot\frac{\cos\phi}{r}$$
$$= \frac{\cos^2\phi}{r}\frac{\partial\psi}{\partial r} + \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial\phi\partial r} - \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\cos^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}$$

Thus,

$$\begin{aligned}
\frac{\partial^2\psi}{\partial y^2} &= \frac{\partial}{\partial y}\left(\frac{\partial\psi}{\partial y}\right)\\
&= \frac{\partial}{\partial r}\left(\frac{\partial\psi}{\partial y}\right)\frac{\partial r}{\partial y} + \frac{\partial}{\partial\phi}\left(\frac{\partial\psi}{\partial y}\right)\frac{\partial\phi}{\partial y}\\
&= \left[\sin^2\phi\frac{\partial^2\psi}{\partial r^2} - \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi}\right]\\
&\quad + \left[\frac{\cos^2\phi}{r}\frac{\partial\psi}{\partial r} + \frac{\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial\phi\partial r} - \frac{\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{\cos^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\right]\\
&= \sin^2\phi\frac{\partial^2\psi}{\partial r^2} - \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi} + \frac{\cos^2\phi}{r}\frac{\partial\psi}{\partial r} + \frac{\cos^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}
\end{aligned}$$

It follows by combining the last two results that

$$\begin{aligned}
\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} &= \left[\cos^2\phi\frac{\partial^2\psi}{\partial r^2} + \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} - \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi} + \frac{\sin^2\phi}{r}\frac{\partial\psi}{\partial r} + \frac{\sin^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\right]\\
&\quad + \left[\sin^2\phi\frac{\partial^2\psi}{\partial r^2} - \frac{2\sin\phi\cos\phi}{r^2}\frac{\partial\psi}{\partial\phi} + \frac{2\sin\phi\cos\phi}{r}\frac{\partial^2\psi}{\partial r\partial\phi} + \frac{\cos^2\phi}{r}\frac{\partial\psi}{\partial r} + \frac{\cos^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\right]\\
&= (\cos^2\phi + \sin^2\phi)\frac{\partial^2\psi}{\partial r^2} + \frac{\sin^2\phi + \cos^2\phi}{r}\frac{\partial\psi}{\partial r} + \frac{\sin^2\phi + \cos^2\phi}{r^2}\frac{\partial^2\psi}{\partial\phi^2}\\
&= \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\phi^2}
\end{aligned}$$

Therefore, from the above and one of our substitutions from the picture, we have that

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{e^2}{4\pi\epsilon_0\sqrt{x^2+y^2}}\right]\psi(x,y) = E\psi(x,y)$$
$$\boxed{\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right]\psi(r,\phi) = E\psi(r,\phi)}$$

□

(c) Factoring the wave function $\psi(r,\phi)$ as $R(r)Q(\phi)$, separate the Schrödinger equation into a Schrödinger equation for $R(r)$ with quantum numbers n and m and a Schrödinger equation for $Q(\phi)$ with quantum number m.

Answer. We have from part (b) that

$$\begin{aligned}
0 &= \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right)\psi(r,\phi) + \frac{2m}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E\right]\psi(r,\phi)\\
&= \frac{\partial^2}{\partial r^2}(R(r)Q(\phi)) + \frac{1}{r}\frac{\partial}{\partial r}(R(r)Q(\phi)) + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}(R(r)Q(\phi)) + \frac{2m}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E\right]R(r)Q(\phi)\\
&= Q(\phi)\frac{\partial^2 R}{\partial r^2} + \frac{Q(\phi)}{r}\frac{\partial R}{\partial r} + \frac{R(r)}{r^2}\frac{\partial^2 Q}{\partial\phi^2} + \frac{2m}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E\right]R(r)Q(\phi)\\
&= \frac{r^2}{R(r)}\frac{\partial^2 R}{\partial r^2} + \frac{r}{R(r)}\frac{\partial R}{\partial r} + \frac{1}{Q(\phi)}\frac{\partial^2 Q}{\partial\phi^2} + \frac{2mr^2}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E\right]
\end{aligned}$$

Since r and ϕ are independent variables, it follows that we may let

$$\boxed{m^2 = \frac{r^2}{R(r)}\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{r}{R(r)}\frac{\mathrm{d}R}{\mathrm{d}r} + \frac{2mr^2}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E_n\right]} \qquad \boxed{-m^2 = \frac{1}{Q(\phi)}\frac{\mathrm{d}^2Q}{\mathrm{d}\phi^2}}$$

□

(d) Solve the Schrödinger equation for $Q(\phi)$ and explain its connection with the two-dimensional rigid rotor.

Answer. We have from part (c) that

$$\frac{\mathrm{d}^2Q}{\mathrm{d}\phi^2} + m^2Q(\phi) = 0$$

Taking an operator perspective, we can factor this differential equation to

$$\left(\frac{\mathrm{d}}{\mathrm{d}\phi} + im\right)\left(\frac{\mathrm{d}}{\mathrm{d}\phi} - im\right)Q = 0$$

Thus, a solution Q to this differential equation will be in the null space of $\mathrm{d}/\mathrm{d}\phi - im$ or, since the operators commute, in the null space of $\mathrm{d}/\mathrm{d}\phi + im$. Solving the differential equation corresponding to each operator independently yields

$$\begin{aligned} \frac{\mathrm{d}Q}{\mathrm{d}\phi} &= imQ & \frac{\mathrm{d}Q}{\mathrm{d}\phi} &= -im\phi \\ \ln Q &= im\phi + C_1 & \ln Q &= -im\phi + C_2 \\ Q(\phi) &= A_1\mathrm{e}^{im\phi} & Q(\phi) &= A_2\mathrm{e}^{-im\phi} \end{aligned}$$

Clearly, any linear combination of these solutions will be a solution as well, so the complete general solution is

$$Q(\phi) = A_1\mathrm{e}^{im\phi} + A_2\mathrm{e}^{-im\phi}$$

Furthermore, since Q must be single-valued, we must have that $Q(\phi+2\pi) = Q(\phi)$. Thus, it must be that

$$\begin{aligned} A_1\mathrm{e}^{im(\phi+2\pi)} + A_2\mathrm{e}^{-im(\phi+2\pi)} &= A_1\mathrm{e}^{im\phi} + A_2\mathrm{e}^{-im\phi} \\ A_1\mathrm{e}^{im\phi}\mathrm{e}^{i2\pi m} + A_2\mathrm{e}^{-im\phi}\mathrm{e}^{-i2\pi m} &= A_1\mathrm{e}^{im\phi} + A_2\mathrm{e}^{-im\phi} \end{aligned}$$

Since A_1 and A_2 are independent variables, we must have that

$$\begin{aligned} A_1\mathrm{e}^{im\phi}\mathrm{e}^{i2\pi m} &= A_1\mathrm{e}^{im\phi} & A_2\mathrm{e}^{-im\phi}\mathrm{e}^{-i2\pi m} &= A_2\mathrm{e}^{-im\phi} \\ \mathrm{e}^{i2\pi m} &= 1 & \mathrm{e}^{-i2\pi m} &= 1 \\ \cos(2\pi m) + i\sin(2\pi m) &= 1 + 0i & \cos(2\pi m) - i\sin(2\pi m) &= 1 + 0i \\ m &= 0, \pm 1, \pm 2, \dots & m &= 0, \pm 1, \pm 2, \dots \end{aligned}$$

i.e., that overall,

$$\boxed{m = 0, \pm 1, \pm 2, \dots}$$

Thus, the general solution can be written as one equation

$$\boxed{Q(\phi) = A\mathrm{e}^{im\phi}}$$

Indeed, these results show that the angular wave functions of this system are identical to those of the rigid rotor, as we would expect considering that both systems describe a quantum particle at some invariant distance from the nucleus. □

(e) For *only* $n = 1$ and $m = 0$, solve the Schrödinger equation for the ground-state energy and wave function.

Answer. Let $m = 0$. Then the radial equation from part (c) can be written in the form

$$\frac{r^2}{R(r)}\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{r}{R(r)}\frac{\mathrm{d}R}{\mathrm{d}r} + \frac{2mr^2}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E_1\right] = 0$$

which after multiplying through by $R(r)/r^2$ becomes

$$\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \frac{2m}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E_1\right]R(r) = 0$$

Performing an asymptotic analysis (i.e., taking the limit as $r \to \infty$) causes all terms with r in the denominator to go to zero, leaving us with

$$\frac{\mathrm{d}^2}{\mathrm{d}R^2}(r) + \frac{2mE_1}{\hbar^2}R(r) = 0$$

Solving this equation by the method of part (d) gives

$$R(r) = B\mathrm{e}^{ir\sqrt{2mE_1}/\hbar}$$

as the $n = 1$ solution. Thus, since

$$\frac{\mathrm{d}R}{\mathrm{d}r} = \frac{Bi\sqrt{2mE_1}}{\hbar}\mathrm{e}^{ir\sqrt{2mE_1}/\hbar} \qquad\qquad \frac{\mathrm{d}^2R}{\mathrm{d}r^2} = -\frac{2mE_1B}{\hbar^2}\mathrm{e}^{ir\sqrt{2mE_1}/\hbar}$$

plugging our solution back into the original differential equation yields

$$\begin{aligned}
0 &= r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + r\frac{\mathrm{d}R}{\mathrm{d}r} + \frac{2mr^2}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E_1\right]R(r) \\
&= r^2\left(-\frac{2mE_1B}{\hbar^2}\mathrm{e}^{ir\sqrt{2mE_1}/\hbar}\right) + r\left(\frac{Bi\sqrt{2mE_1}}{\hbar}\mathrm{e}^{ir\sqrt{2mE_1}/\hbar}\right) + \frac{2mr^2}{\hbar^2}\left[\frac{e^2}{4\pi\epsilon_0 r} + E_1\right]B\mathrm{e}^{ir\sqrt{2mE_1}/\hbar} \\
&= \frac{Bir\sqrt{2mE_1}}{\hbar}\mathrm{e}^{ir\sqrt{2mE_1}/\hbar} + \frac{2Bmre^2}{4\pi\epsilon_0\hbar^2}\mathrm{e}^{ir\sqrt{2mE_1}/\hbar}
\end{aligned}$$

Cancelling terms from the above, we have

$$\begin{aligned}
i\sqrt{2mE_1} &= -\frac{me^2}{2\pi\epsilon_0\hbar} \\
-2mE_1 &= \frac{m^2e^4}{4\pi^2\epsilon_0^2\hbar^2} \\
&= -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2} \\
&\boxed{E_1 = -\frac{e^2}{2\pi\epsilon_0 a_0}}
\end{aligned}$$

where $a_0 = 4\pi\epsilon_0\hbar^2/me^2$ is the Bohr radius.
It follows that the ground-state wave function is

$$\begin{aligned}
\psi(r,\phi) &= B\mathrm{e}^{ir\sqrt{2m\cdot -me^4/8\pi^2\epsilon_0^2\hbar^2}/\hbar}A\mathrm{e}^{i(0)\phi} \\
&= C\mathrm{e}^{-rme^2/2\pi\epsilon_0\hbar^2} \\
&= C\mathrm{e}^{-2r/a_0}
\end{aligned}$$

where we bundle the two constants A, B into the constant $C = AB$. We can determine the value of C by normalizing as follows.

$$\begin{aligned}
1 &= \int_0^{2\pi} \mathrm{d}\phi \int_0^{\infty} \mathrm{d}r\, rC^2 \mathrm{e}^{-4r/a_0} \\
&= C^2 \int_0^{2\pi} \mathrm{d}\phi \left[-\frac{ra_0}{4}\mathrm{e}^{-4r/a_0}\bigg|_0^{\infty} + \frac{a_0}{4}\int_0^{\infty} \mathrm{e}^{-4r/a_0}\,\mathrm{d}r \right] \\
&= C^2 \int_0^{2\pi} \mathrm{d}\phi \left[-\frac{ra_0}{4}\mathrm{e}^{-4r/a_0} - \frac{a_0^2}{16}\mathrm{e}^{-4r/a_0} \right]_0^{\infty} \\
&= \frac{C^2 a_0^2}{16} \cdot 2\pi \\
C &= \sqrt{\frac{2}{\pi}}\frac{2}{a_0}
\end{aligned}$$

It follows that

$$\boxed{\psi(r,\phi) = \sqrt{\frac{2}{\pi}}\frac{2}{a_0}\mathrm{e}^{-2r/a_0}}$$

□

(f) What is the ratio of the ground-state energy of the two-dimensional hydrogen atom to the ground-state energy of the three-dimensional hydrogen atom?

Answer. From part (e) and class,

$$\begin{aligned}
\frac{E_{\text{2D}}}{E_{\text{3D}}} &= \frac{-\frac{e^2}{2\pi\epsilon_0 a_0}}{-\frac{e^2}{8\pi\epsilon_0 a_0 (1)^2}} \\
\Aboxed{E_{\text{2D}} : E_{\text{3D}} &= 4}
\end{aligned}$$

□

(g) On the same figure, draw (or graph electronically) as a function of r the probability for finding the electron in the ground state of the 3D hydrogen atom as well as the probability for finding the electron in the ground state of the 2D hydrogen atom. Briefly compare and contrast these two probability distributions.

Answer. It follows from part (e) that

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

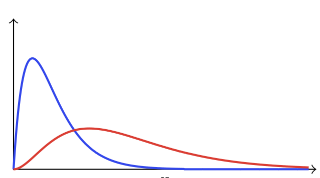
We also know that

$$R_{1s}(r) = \frac{2}{a_0^{3/2}}\mathrm{e}^{-r/a_0}$$

Thus, the radial probability densities are

$$[R(r)]^2 r = \frac{16r}{a_0^2}\mathrm{e}^{-4r/a_0} \qquad\qquad [R_{1s}(r)]^2 r^2 = \frac{4r^2}{a_0^3}\mathrm{e}^{-2r/a_0}$$

Therefore, we have that



where the blue line corresponds to $R(r)$ and the red line corresponds to $R_{1s}(r)$. The probability densities follow the same general trend, but are normalized differently and peak at different places, meaning the electrons differ in terms of their most probable distance from the nucleus. In fact, the most probable distance from the nucleus for the planar atom is one-fourth the Bohr radius. □

2. Using your lecture notes and Problem 7-1 as a guide, give a proof of the variational theorem, i.e., that...

   (a) The energy from a trial wave function will always be greater than or equal to the exact ground-state energy.

   Answer. Let $\hat{H}\psi_0 = E_0\psi_0$ where ψ_0 is the ground-state wave function and E_0 is the ground-state energy, and let ϕ be a trial wave function meant to approximate ψ_0. Since the ψ_n are orthonormal, $\phi = \sum_i c_i\psi_i$ where each c_i is a constant. It follows since the ψ_n are orthonormal that for each n,

$$\begin{aligned}\int \psi_n^*\phi \,\mathrm{d}\tau &= \int \sum_i c_i\psi_n^*\psi_i \,\mathrm{d}\tau \\ &= \sum_i \int c_i\psi_n^*\psi_i \,\mathrm{d}\tau \\ &= c_n \int \psi_n^*\psi_n \,\mathrm{d}\tau \\ &= c_n \cdot 1 \\ &= c_n\end{aligned}$$

   Thus,

$$\begin{aligned}E_\phi &= \frac{\int \phi^*\hat{H}\phi \,\mathrm{d}\tau}{\int \phi^*\phi \,\mathrm{d}\tau} \\ &= \frac{\int \sum_i c_i^*\psi_i^*\hat{H}\sum_i c_i\psi_i \,\mathrm{d}\tau}{\int \sum_n c_n^*\psi_n^*\phi \,\mathrm{d}\tau} \\ &= \frac{\int \sum_i c_i^*\psi_i^*\sum_j c_jE_j\psi_j \,\mathrm{d}\tau}{\sum_n c_n^*\int \psi_n^*\phi \,\mathrm{d}\tau} \\ &= \frac{\sum_i\sum_j c_i^*c_jE_j\int \psi_i^*\psi_j \,\mathrm{d}\tau}{\sum_n c_n^*c_n} \\ &= \frac{\sum_n c_n^*c_nE_n}{\sum_n c_n^*c_n}\end{aligned}$$

   It follows that

$$E_\phi - E_0 = \frac{\sum_n c_n^*c_nE_n}{\sum_n c_n^*c_n} - E_0\frac{\sum_n c_n^*c_n}{\sum_n c_n^*c_n} = \frac{\sum_n c_n^*c_n(E_n - E_0)}{\sum_n c_n^*c_n}$$

   where each $c_n^*c_n = |c_n|^2$ is nonnegative and $E_n - E_0$ is nonnegative because no energy can be lower than the ground-state energy, implying that the entire right term of the above equation is nonnegative. Thus, $E_\phi \geq E_0$, as desired. □

   (b) The energy from a trial wave function, constrained to be orthogonal to the exact ground-state wave function, will always be greater than or equal to the exact energy of the first excited state.

   Answer. Let $\hat{H}\psi_n = E_n\psi_n$ be a system of interest, and let ϕ be a trial wave function such that

$$\int \psi_0^*\phi \,\mathrm{d}\tau = 0$$

Thus, if $\phi = \sum_i c_i\psi_i$, then by part (a),

$$c_0 = \int \psi_0^* \phi \,\mathrm{d}\tau = 0$$

It follows that

$$E_\phi = \frac{\sum_{i=1}^n c_i^* c_i E_i}{\sum_{i=1}^n c_i^* c_i}$$

so that

$$E_\phi - E_1 = \frac{\sum_{i=1}^n c_i^* c_i (E_i - E_1)}{\sum_{i=1}^n c_i^* c_i} \geq 0$$

as desired. □

3. Consider a particle in a box in the interval $[-a, a]$.

   (a) Use the trial wave function

   $$\psi_t = x(a^2 - x^2)$$

   to obtain an approximate energy for the first excited state of the box as a function of a.

   Answer. We have that

   $$\begin{aligned}\int \psi_t^* \hat{H} \psi_t \,\mathrm{d}\tau &= \int_{-a}^{a} (a^2x - x^3) \left(-\frac{1}{2}\frac{\partial^2}{\partial x^2}\right)(a^2x - x^3)\,\mathrm{d}x \\ &= \int_{-a}^{a} (a^2x - x^3)(3x)\,\mathrm{d}x \\ &= \int_{-a}^{a} (3a^2x^2 - 3x^4)\,\mathrm{d}x \\ &= \frac{4a^5}{5}\end{aligned}$$

   and that

   $$\begin{aligned}\int \psi_t^* \psi_t \,\mathrm{d}\tau &= \int_{-a}^{a} x(a^2 - x^2)x(a^2 - x^2)\,\mathrm{d}x \\ &= \int_{-a}^{a} (a^4x^2 - 2a^2x^4 + x^6)\,\mathrm{d}x \\ &= \frac{16}{105}a^7\end{aligned}$$

   so

   $$\begin{aligned}E_{\psi_t} &= \frac{\int \psi_t^* \hat{H} \psi_t \,\mathrm{d}\tau}{\int \psi_t^* \psi_t \,\mathrm{d}\tau} \\ &= \frac{4a^5/5}{16a^7/105}\end{aligned}$$

   $$\boxed{E_{\psi_t} = \frac{21}{4a^2}\text{ a.u.}}$$

   □

   (b) Why does this function give an approximation to the first excited state rather than the ground state?

   Answer. It is an odd function, like the first excited state, while the ground state is even. □

(c) Use the more accurate trial wave function

$$\psi_t = c_1 x(a^2 - x^2) + c_2 x^3(a^2 - x^2)$$

to obtain an approximate energy for the first excited state of the box as a function of a.

Answer. We have the following matrix entries, calculated in the same manner as H_{11} above. Note that we only perform three explicit calculations per matrix since our operators are Hermitian.

$$\begin{aligned} H_{11} &= \int_{-a}^{a} x(a^2-x^2)\hat{H}x(a^2-x^2)\,\mathrm{d}x \\ &= \frac{4a^5}{5} \end{aligned} \qquad \begin{aligned} H_{12} &= \int_{-a}^{a} x(a^2-x^2)\hat{H}x^3(a^2-x^2)\,\mathrm{d}x \\ &= \frac{12a^7}{35} \end{aligned}$$

$$\begin{aligned} H_{21} &= H_{12} \\ &= \frac{12a^7}{35} \end{aligned} \qquad \begin{aligned} H_{22} &= \int_{-a}^{a} x^3(a^2-x^2)\hat{H}x^3(a^2-x^2)\,\mathrm{d}x \\ &= \frac{92a^9}{315} \end{aligned}$$

$$\begin{aligned} S_{11} &= \int_{-a}^{a} x(a^2-x^2)x(a^2-x^2)\,\mathrm{d}x \\ &= \frac{16a^7}{105} \end{aligned} \qquad \begin{aligned} S_{12} &= \int_{-a}^{a} x(a^2-x^2)x^3(a^2-x^2)\,\mathrm{d}x \\ &= \frac{16a^9}{315} \end{aligned}$$

$$\begin{aligned} S_{21} &= S_{12} \\ &= \frac{16a^9}{315} \end{aligned} \qquad \begin{aligned} S_{22} &= \int_{-a}^{a} x^3(a^2-x^2)x^3(a^2-x^2)\,\mathrm{d}x \\ &= \frac{16a^{11}}{693} \end{aligned}$$

Thus, we are looking to solve the secular determinant/equation

$$\begin{aligned} 0 &= \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} \\ &= \begin{vmatrix} \frac{4a^5}{5} - E\frac{16a^7}{105} & \frac{12a^7}{35} - E\frac{16a^9}{315} \\ \frac{12a^7}{35} - E\frac{16a^9}{315} & \frac{92a^9}{315} - E\frac{16a^{11}}{693} \end{vmatrix} \\ &= \left(\frac{4a^5}{5} - E\frac{16a^7}{105}\right)\left(\frac{92a^9}{315} - E\frac{16a^{11}}{693}\right) - \left(\frac{12a^7}{35} - E\frac{16a^9}{315}\right)^2 \\ &= \frac{1024a^{18}}{1091475}E^2 - \frac{2048a^{16}}{72765}E + \frac{256a^{14}}{2205} \\ &= 4a^4E^2 - 120a^2E + 495 \end{aligned}$$

which we can do with the quadratic formula, getting

$$E = \frac{30 + 9\sqrt{5}}{2a^2} \qquad E = \frac{30 - 9\sqrt{5}}{2a^2}$$

It follows that the energy of the first excited state (the smaller of the two values above) is approximately

$$\boxed{E = \frac{4.94}{a^2}\text{ a.u.}}$$

□

(d) Compare the approximate energies with the exact energy (including their dependence on a) and the approximate wave functions with the exact wave functions. (Hint: In comparing the wave functions, you may want to select $a = 1$.)

Answer. We have from class that the exact energy is

$$E_1 = \frac{\pi^2(2)^2}{8a^2} = \frac{4.934\,802}{a^2} \text{ a.u.}$$

Thus, the dependence on a is identical between the approximations and the exact solution and the first and second approximations have percent error 6.39 % and 0.105 %, respectively.

As to the wave functions, the exact wave functions are sinusoidal while the approximate wave functions are third- and fifth-order polynomials, respectively, that very closely follow (especially in the optimized second case) the trajectory of the exact wave functions. ☐

4. Use the Quantum Chemistry Toolbox in Maple to answer the lettered questions in the worksheet "Variational Methods" on Canvas.

(a) Now what happens as you increase N? Do you get better approximations to the ground and first excited state, consistent with the Variational Theorem? To answer this, set $N = 5$ in the Maple input and recalculate the approximate energies.

Answer. The $\boxed{\text{approximations get much better}}$. For $N = 5$, we have percent errors 0.004 % and 0.225 % for E_0 and E_1, respectively, compared with 0.523 % and 6.948 %, respectively, for $N = 2$. ☐

(b) Is the spacing between adjacent energy levels evenly spaced, as seen in the harmonic oscillator? What happens to this spacing as energy increases?

Answer. $\boxed{\text{No}}$. As the energy increases, the $\boxed{\text{spacing decreases}}$. ☐

(c) Are there an infinite number of "bound" vibrational energy levels, as seen in the harmonic oscillator? If not, how many bounds states does HCl have?

Answer. $\boxed{\text{No}}$. As we can see from the second plot, only $\boxed{12}$ energy levels exist with $E < 0$. ☐

(d) For each series, does the energy decrease variationally as the size of the basis increases? Which series of basis sets gave rise to better energies? What did you notice regarding the time required to carry out each calculation as the size of the basis set increased?

Answer. $\boxed{\text{Yes}}$, the energy does decrease variationally as the size of the basis increases. The $\boxed{\text{second}}$ series gave rise to better energies. The time required to carry out the calculations with longer basis sets was $\boxed{\text{greater}}$. ☐

References

McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach.* University Science Books.