Chem 30324, Spring 2025, Homework 5

Due February 28, 2025

Q1. Real-world particle-in-a-box.

A one-dimensional particle-in-a-box is a simple but plausible model for the π electrons of a conjugated alkene, like butadiene (C_4H_6, shown here). Suppose all the C–C bonds in a polyene are 1.4 Å long and the polyenes are perfectly linear.

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1. Plot out the normalized $n = 2$ particle-in-a-box wavefunction for an electron in butadiene and the normalized $n = 2$ probability distribution. Indicate on the plots the most probable location(s) of the electron, the average location of the electron, and the positions of any nodes.

In [46]:
```python
import numpy as np
import matplotlib.pyplot as plt

# Define the length of the box (Angstroms)
L = 3 * 1.4   # Butadiene has four C atoms, so three bonds; scale is Angstrom

# Quantum number
n = 2

# Generate x values from 0 to L with 1000 points
x = np.linspace(0, L, 1000)

# Define the normalized wave function
def psi_but(x):
    return np.sqrt(2 / L) * np.sin((n * np.pi * x) / L)

# Compute the wave function values
psi = psi_but(x)

# Plot the wave function
plt.plot(x, psi, label=r'$\Psi_b(x)$')
```

```python
# Plot the probability density
plt.plot(x, psi**2, label=r'$|\Psi_b(x)|^2$', linestyle='dashed')

# Add legend
plt.legend(fontsize='small')

# Set x-axis limit
plt.xlim(0, L)

# Label axes
plt.xlabel(r'$x(\AA)$')
plt.ylabel(r'$\Psi_2(x)(\AA^{-1/2}), |\Psi_2(x)|^2(\AA^{-1})$')

# Set title
plt.title(r'n = 2 Particle-in-a-box Wavefunction and Probability Distributic

# Draw a horizontal dashed line at y=0
plt.axhline(y=0, color='k', linestyle='--')

# Add annotations for most probable locations and node
plt.annotate('the most probable \n location', xy=(L/4, 0), xytext=(1.0, 0.25
            arrowprops=dict(facecolor='black', shrink=0.05))

plt.annotate('the most probable \n location', xy=(3*L/4, 0), xytext=(2.3, 0.
            arrowprops=dict(facecolor='black', shrink=0.05))

plt.annotate('node average \n location', xy=(L/2, 0), xytext=(1.5, -0.3),
            arrowprops=dict(facecolor='red', shrink=0.05))

# Show the plot
plt.show()
```
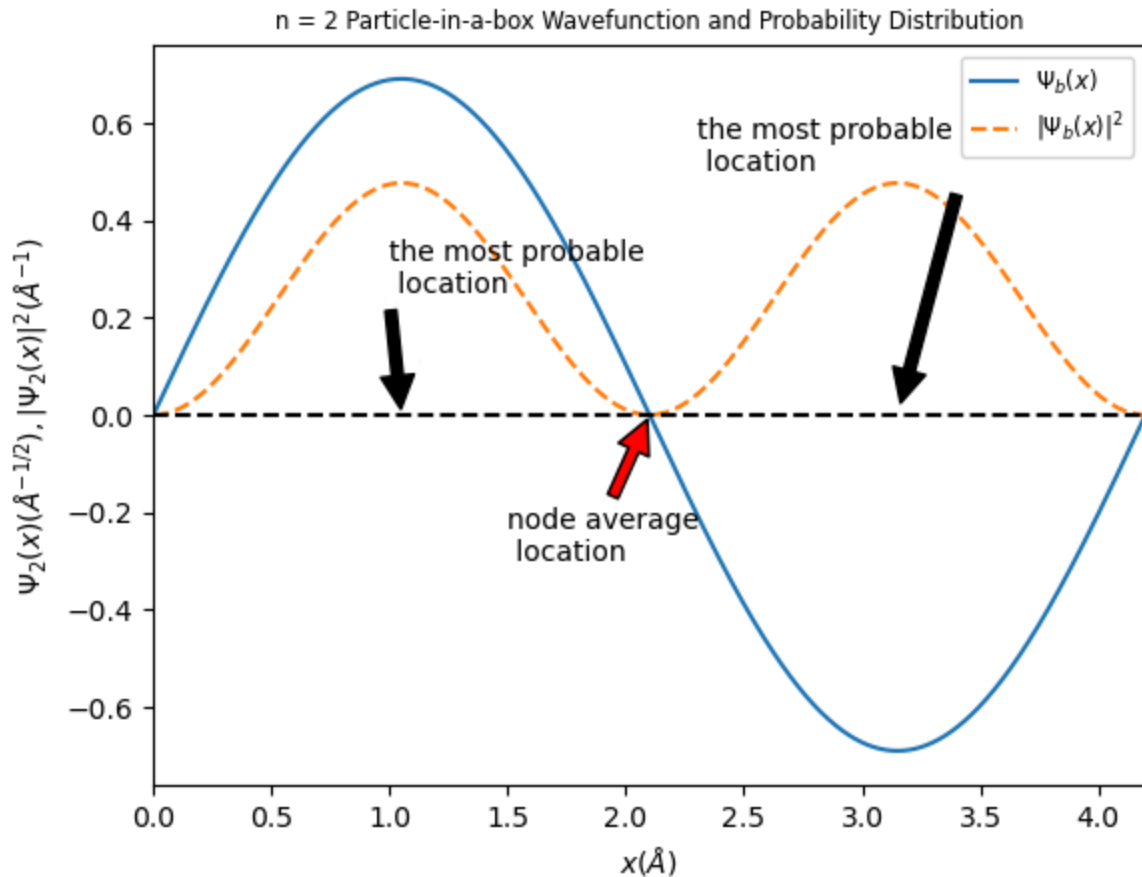
n = 2 Particle-in-a-box Wavefunction and Probability Distribution

2. Butadiene has 4 π electrons, and we will learn later that in its lowest energy state, two of these are in the $n = 1$ and two in the $n = 2$ levels. Compare the wavelength of light (in nm) necessary to promote ("excite") one electron from either of these levels to the empty $n = 3$ level.

In [47]:
```python
import numpy as np

# Constants
h_bar = 1.05457e-34   # Reduced Planck's constant (J·s)
m_e = 9.10938215e-31 # Electron mass (kg)
bond_length = 1.4e-10   # Bond length in meters
hc = 1230   # eV·nm (Planck's constant * speed of light in nm units)

# Define the energy function in terms of num (number of C) and n (energy lev

# Returns energy in eV
def E(n, num):
    L = (num - 1) * bond_length  # Correct length for conjugated system
    return ((n**2 * np.pi**2 * h_bar**2) / (2 * m_e * L**2)) * 6.2415e18   #

# Butadiene has 4 carbons
num = 4

# Compute energy levels
```

```
E_n1 = E(1, num)
E_n2 = E(2, num)
E_n3 = E(3, num)

# Energy gaps
E_31 = E_n3 - E_n1  # Transition from n=1 to n=3
E_32 = E_n3 - E_n2  # Transition from n=2 to n=3

# Calculate the wavelength from the energy
lamb_32 = hc / E_32
lamb_31 = hc / E_31

# Print the results
print(f'Wavelength from n=1 to n=3 is {lamb_31:.2f} nm')
print(f'Wavelength from n=2 to n=3 is {lamb_32:.2f} nm')
```

```
Wavelength from n=1 to n=3 is 72.13 nm
Wavelength from n=2 to n=3 is 115.40 nm
```

3. The probability of an electron jumping between two energy states by emitting or absorbing light is proportional to the square of the "transition dipole," given by the integral $|\langle \psi_{initial} | \hat{x} | \psi_{final} \rangle|^2$. Contrast the relative probabilities of an electron jumping from $n = 1$ to $n = 3$ and from $n = 2$ to $n = 3$ levels. Can you propose any general rules about "allowed" and "forbidden" jumps?

In [48]:
```python
from sympy import * # import sympy for symbolic mathematics
#Simplified integrals with wavefunctions not normalized, l = 1
import numpy as np

l=1 # m

x = symbols('x')
# calculate integral of psi1 * x * psi3
a = integrate((sin(np.pi*(x/l))*x*sin(3*np.pi*(x/l))),(x,0,l))
print('Probability of transition from n=1 to n=3 is', a**2)
# calculate integral of psi2 * x * psi3
b = integrate((sin(2*np.pi*(x/l))*x*sin(3*np.pi*(x/l))),(x,0,l))
print('Probability of transition from n=2 to n=3 is', b**2)
```

```
Probability of transition from n=1 to n=3 is 0
Probability of transition from n=2 to n=3 is 0.00946112924591708
```

The probability of jumping from n=1 to n=3 is 0, so it is forbidden, while jumping from n=2 to n=3 is allowed because there is a non-zero number here. More generally these rules apply based on the difference between the two energy states, with an even difference ($\Delta n = 2$) being forbidden while odd differences ($\Delta n = 1$) are allowed.

$$\int_0^L sin(\frac{n\pi x}{L}) * x * sin(\frac{m\pi x}{L}) \, dx = \begin{cases} 0 & n - m = 2x \\ > 0 & n - m \neq 2x \end{cases}$$

4. Consider the reaction of two ethylene molecules to form butadiene:

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5. As a very simple estimate, you could take the energy of each molecule as the sum of the energies of its π electrons, allowing only two electrons per energy level. Again taking each C—C bond as 1.4 Å long and treating the π electrons as particles in a box, calculate the total energy of an ethylene and a butadiene molecule within this model (in kJ/mol), and from these calculate the net reaction energy. Compare your results to the experimental reaction enthalpy. How well did the model do?

In [49]:
```python
l=1.4e-10# m, length of one C-C bond

# Constants
h_bar = 1.05457e-34  # Reduced Planck's constant (J·s)
m_e = 9.10938215e-31 # Electron mass (kg)
bond_length = 1.4e-10  # Bond length in meters
hc = 1230  # eV·nm (Planck's constant * speed of light in nm units)


def E(n,num):
    return ((n**2*np.pi**2*h_bar**2)/(2*m_e*(l*(num-1))**2)*6.0221e20)# Rede

E_eth = 2*E(1,2)
E_but = 2*E(1,4) + 2*E(2,4)
E_net = E_but - 2*E_eth
print('\nInitial energy is', E_eth, 'kJ/mol','\nFinal energy is', E_but, 'kJ

# Experimental enthalpy of formation data from NIST
Ef_ethylene = 52.4 # kJ/mol
Ef_butadiene = 108.8 # kJ/mol
E_reaction = Ef_butadiene - 2*Ef_ethylene # kJ/mol
print('The experimental reaction enthalpy is {:.1f}kJ/mol.'.format(E_reactio
```

```
Initial energy is 3702.145987248957 kJ/mol
Final energy is 2056.747770693865 kJ/mol
Net energy is -5347.544203804049 kJ/mol
The experimental reaction enthalpy is 4.0kJ/mol.
```

Model does not really work for this at all. σ bonds are neglected and the infinite potential well is non-physical.

6. This particle-in-a-box model has many flaws, not the least of which is that the ends of the polyene "box" are not infinitely high potential walls. In a somewhat better model the π electrons would travel in a finite-depth potential well. State two things that would change from the infinite depth to the finite depth model.

Electrons have a finite probability of going past the ending C atoms.

Energy levels decrease in energy.

States with high enough energies leave the well completely, meaning only a finite number of energy states are bound.

Q2. Really large box with a particle.

A gas molecule rattling around in a bottle can be described as a particle in a 3-dimensional box. Consider ethylene gas in a cubic "bottle" 1 dm on a side.

7. What is the particle-in-a-box "zero point energy" of one of these ethylene molecules, in kJ/mol? Is this energy of chemical significance?

In [50]:
```python
import numpy as np
l = .1 #length of the box in meters
hbar = 1.05457e-34 #units in J*s
m = 28.053*1.6605e-27# mass of ethylene in kg

#our zero point energy is when nx, ny, nz, are equal to 1, so each of those
E=3*np.pi**2*hbar**2/(2*m*l**2)#these units are in J per molecule, need to c
print(f"{E * 6.022e23 / 1000:.3e} kJ/mol")
```
2.128e-19 kJ/mol

8. According to the kinetic theory of gases, the average kinetic energy of an ethylene molecule in any one direction is $k_B T/2$. What is the approximate value of n_x of a gas molecule in this box and with this kinetic energy at 298 K?

We're going to set this equal to 1D equation from the previous problem and solve for n_x:

$$E_x = \frac{k_B T}{2} = \frac{n_x^2 \pi^2 \hbar^2}{2mL^2}$$

Rearranging:

$$\sqrt{\frac{k_B T m L^2}{\pi^2 \hbar^2}} = n_x$$

Solve via code:

```
k=1.38065e-23#Boltzman constant in J/K
T=298#Temp in K
#Using m, l, and hbar variables from question 7
n=np.sqrt(k*T*m*l**2/(np.pi**2*hbar**2))
print("approximate value is ",int(n))
```

approximate value is 4178628300

9. Suppose you can measure the average kinetic energy in a direction within 1 ppm. Estimate the number of n_x within 1 ppm of $k_B T/2$ at 298 K (this is called a "density of states"). Do you have any hope of determining the exact value of n_x for a particular molecule?

We'll solve for the difference in nx between the low and range of our accuracy to give us the density of states, first looking at the value of $k_B T/2$ at 298 K:

$$E_x = \frac{k_B T}{2} = \frac{n_x^2 \pi^2 \hbar^2}{2mL^2}$$

We'll be changing the KE so we'll leave the equation in terms of E_x

$$\sqrt{\frac{2mL^2 E_x}{\pi^2 \hbar^2}} = n_x$$

We want to look at the difference between n_{low} and n_{high}

$$\sqrt{\frac{2mL^2 E_{high}}{\pi^2 \hbar^2}} - \sqrt{\frac{2mL^2 E_{low}}{\pi^2 \hbar^2}}$$

Simplify a bit just for ease of understanding

$$\sqrt{\frac{2mL}{\pi^2\hbar^2}}\sqrt{E_{high}-E_{low}}$$

In [52]:
```python
##Energy at the lowest and the highest (Any will work)
KE=k*T/2
lowE=KE-0.000001*KE
highE=KE+0.000001*KE


print(KE,lowE, highE)
# you can see that our detection limits are no where near the precision we r

dN=np.sqrt(2*m*l**2/(np.pi**2*hbar**2))*np.sqrt(highE-lowE)

print(int(dN),"different n_x between detection limits")
#No hope on determining exact value
```

```
2.0571685000000002e-21 2.0571664428315004e-21 2.0571705571685e-21
5909472 different n_x between detection limits
```

Q3. Quantum mechanics of vibrating NO.

The diatomic nitric oxide (NO) is an unusual and important molecule. It has an odd number of electrons, which is a rarity for stable molecule. It acts as a signaling molecule in the body, helping to regulate blood pressure, is a primary pollutant from combustion, and is a key constituent of smog. It exists in several isotopic forms, but the most common, $^{14}N= {}^{16}O$, has a bond length of 1.15077 Å and vibrational force constant of 1594.8 N/m.

10. Compute the **reduced mass** μ (amu), **harmonic vibrational frequency** (cm^{-1}), and **zero point vibrational energy** (kJ/mol) of $^{14}N= {}^{16}O$. Recall $1/\mu = 1/M_N + 1/M_O$.

In [53]:
```python
import math
from scipy.constants import hbar, h, pi, N_A

M_O = 15.995  # Oxygen atomic mass in amu
M_N = 14.003  # Nitrogen atomic mass in amu
k = 1594.8  # Vibrational force constant in N/m
c = 3e10  # Speed of light in cm/s

# Convert to atomic mass unit (amu) -> kg
```

```
mu = (1/M_O + 1/M_N) ** -1  # Reduced mass in amu
mu_kg = mu * 1.66054e-27  # Convert amu to kg
print(f"Reduced mass μ: {mu:.3e} amu")

# Calculate vibrational frequency
nu = (1 / (2 * pi)) * (k / mu_kg) ** 0.5  # Frequency in Hz
freq = nu / c  # Frequency in cm^-1
print(f"Harmonic vibrational frequency: {freq:.1f} cm^-1")

# Calculate zero-point energy (ZPE)
E_0 = 0.5 * h * nu  # Energy in J
E_0_kJmol = E_0 * N_A / 1000  # Convert to kJ/mol
print(f"Zero point vibrational energy: {E_0:.3e} J")
print(f"Zero point vibrational energy: {E_0_kJmol:.3f} kJ/mol")
```

```
Reduced mass μ: 7.466e+00 amu
Harmonic vibrational frequency: 1902.7 cm^-1
Zero point vibrational energy: 1.891e-20 J
Zero point vibrational energy: 11.389 kJ/mol
```

11. Calculate the classical minimum and maximum values of the $^{14}N={}^{16}O$ bond length for a molecule in the ground vibrational state. Hint: Calculate the classical limits on x, the value of x at which the kinetic energy is 0 and thus the total energy equals the potential energy.

In [54]:
```
# Hint: Total E = V (potential E)
# Harmonic Oscillator: V = kx**2/2 for vibration
x = math.sqrt(E_0*2/k) * 10**10 #[=]A
# calculate bond length
R_min = 1.15077-x # 1.15077A is the most common bond length
print(f'minimum value of bond length: {R_min:.3f}A')
R_max = 1.15077+x
print(f'maximum value of bond length: {R_max:.3f}A')
```

```
minimum value of bond length: 1.102A
maximum value of bond length: 1.199A
```

12. The normalized ground vibrational wavefunction of N=O can be written

$$\Psi_{v=0}(x) = \left(\frac{1}{\alpha\sqrt{\pi}}\right)^{1/2} e^{-x^2/2\alpha^2}, \quad x = R - R_{eq}, \quad \alpha = \left(\frac{\hbar^2}{\mu k}\right)^{1/4}$$

where $x = R - R_{eq}$. Plot the normalized probability of x vs x. Indicate on your plot the classical limits on x. Do the probabilities vanish beyond those classical limits? What do we call this behavior?

```python
import matplotlib.pyplot as plt

alpha = (hbar**2 / (mu* 1.66054e-27 * k))**0.25
x_classical = x*10**-10 # x from the previous question

def P(x):
    return (1 / (alpha * np.sqrt(pi))) * np.exp(-x**2 / alpha**2)

x_vals = np.linspace(-3 * alpha, 3 * alpha, 500)
P_vals = P(x_vals)

plt.figure(figsize=(8,5))
plt.plot(x_vals * 1e10, P_vals, label=r'$P(x) = |\Psi_{v=0}(x)|^2$')  # Conv
plt.axvline(x_classical * 1e10, color='r', linestyle='--', label='Classical
plt.axvline(-x_classical * 1e10, color='r', linestyle='--')
plt.xlabel(r'Bond displacement $x$ (Å)')
plt.ylabel(r'Probability Density $P(x)$')
plt.title(r'Normalized Probability Distribution of Vibrating NO')
plt.legend()
plt.show()
print("beyond the classical limits, it will behave Quantum Mechanics")
```
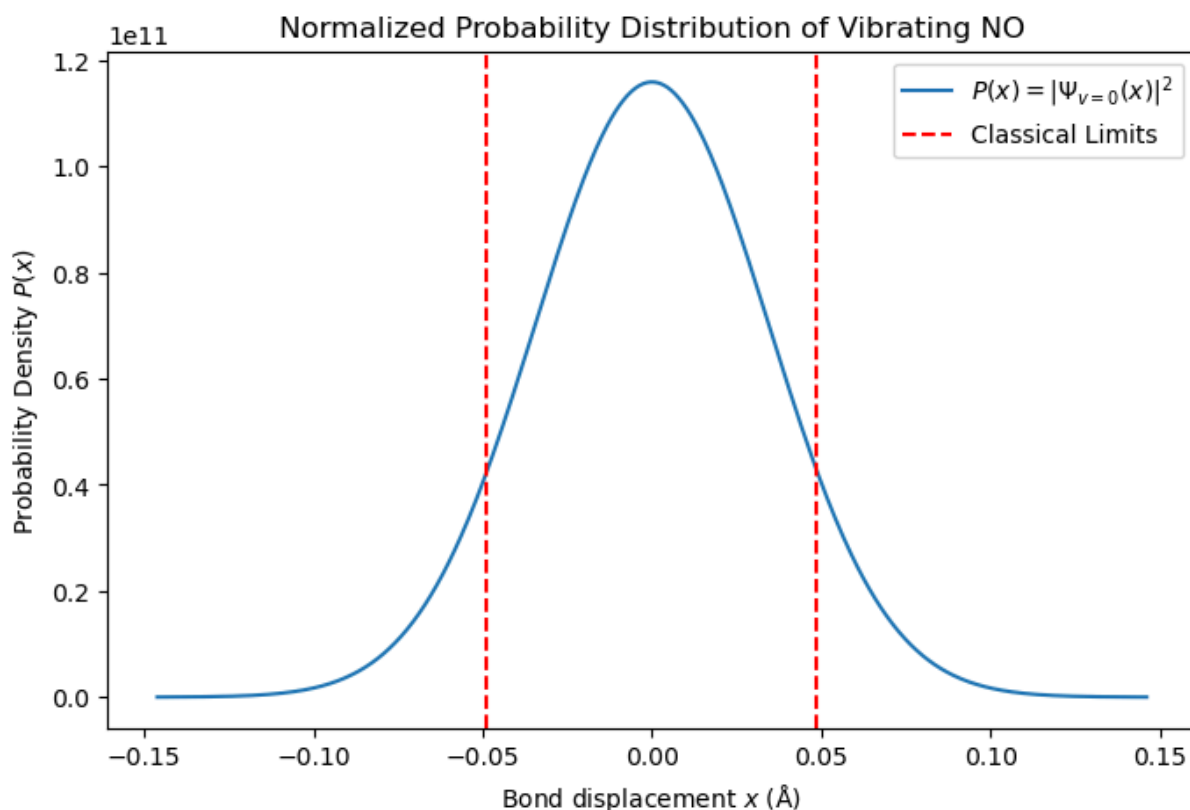

beyond the classical limits, it will behave Quantum Mechanics

13. The *general selection rule* for whether light can excite a vibration of a molecule is that the dipole moment of the molecule must change as it vibrates. Based on this criterion, do you expect NO to exhibit an absorption vibrational spectrum?

Yes, I expect to see absorption specturm because molecule has dipole that ch
anges w/ vibration. It is IR active

14. The *specific selection rule* for whether light can excite a vibration of a molecule is that $\Delta v = \pm 1$. At ambient temperature, what initial and final vibrational states would contribute most significantly to an NO vibrational spectrum? Justify your answer. (*Hint:* What does the Boltzmann distribution say about the probability to be in each v state?)

At ambient temperature, the probability ratio between the ground state (0) and the first excited state is given by

$$\frac{P(v = 1)}{P(v = 0)} = \frac{\exp\left(-\frac{hv \cdot 3}{2kT}\right)}{\exp\left(-\frac{hv \cdot 1}{2kT}\right)}$$

which is nearly zero. This implies that the denominator is significantly larger than the numerator, indicating that the majority of the probability is concentrated in the ground state.

15. Based on your answers to questions 13 and 14, what do you expect the vibrational spectrum of an $^{14}N = {}^{16}O$ molecule to look like? If it has a spectrum, in what region of the spectrum does it absorb (e.g., ultraviolet, x-ray, ...)?

The light emmitted from the first excited state to the ground state is hv, which is 1401.75cm^-1, and this is in the IR region

Q4. Two-dimensional harmonic oscillator

Imagine an H atom embedded in a two-dimensional sheet of MoS_2. The H atom vibrates like a two-dimensional harmonic oscillator with mass 1 amu and force constants k_x and k_y in the two directions.

16. Write down the Schrödinger equation for the vibrating H atom. Remember to include any boundary

conditions on the solutions.

Equation:

$$-\frac{\hbar^2}{2m}\left(\frac{\delta^2\psi(x)}{\delta x^2} + \frac{\delta^2\psi(y)}{\delta y^2}\right) + \left(\frac{K_x x^2}{2} + \frac{K_y y^2}{2}\right)\psi(x,y) = E\psi(x,y)$$

Boundary Conditions:

$$\lim_{x \to \pm\infty} \psi(x,y) = 0$$

$$\lim_{y \to \pm\infty} \psi(x,y) = 0$$

17. The Schrödinger equation is *seperable*, so the wavefunctions are products of one-dimensional wavefunctions and the eigenenergies are sums of corresponding one-dimensional energies. Derive an expression for the H atom vibrational energy states, assuming $k_x = k_y/4 = k$.

The solutions to the 1D Harmonic oscillator are given in Lecture 7: v represents the vibrational quantum state and v is the frequency

$$v_i = \frac{1}{2\pi}\sqrt{\frac{k_i}{m}}$$

$$E_v = (v + \frac{1}{2})hv$$

First solve v_x and v_y and put the answer in terms of k and see how they relate to each other

$$v_x = \frac{1}{2\pi}\sqrt{\frac{k_x}{m}} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} = v$$

$$v_y = \frac{1}{2\pi}\sqrt{\frac{k_y}{m}} = \frac{1}{2\pi}\sqrt{\frac{4k}{m}} = \frac{1}{\pi}\sqrt{\frac{k}{m}} = 2v$$

$$E_{tot} = E_x + E_y = (v_x + \frac{1}{2})hv_x + (v_y + \frac{1}{2})hv_y = (v_x + \frac{1}{2})hv + (v_y + \frac{1}{2})h2v$$

$$E_{tot} = hvv_x + \frac{hv}{2} + 2hvv_y + hv = \frac{3hv}{2} + hv(v_x + 2v_y)$$

where v_x and v_y are positive integers

18. A spectroscopic experiment reveals that the spacing between the first and second energy levels is 0.05 eV. What is k, in N/m?

So the first step is figuring out that the first two energy levels are (0,0) and (1,0) since (0,1) is higher in energy

$$E_{0,0} = \frac{3h\nu}{2}$$

$$E_{1,0} = \frac{5h\nu}{2}$$

Plug in our equation for ν and solve the difference for k

$$dE = E_{1,0} - E_{0,0} = h\nu = h\frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Make sure your units make sense when you initialize variables

$$(\frac{2\pi(dE)m^{1/2}}{h})^2 = k$$

In [57]:
```python
#We're converting everyhing to SI base on initialization
dE = 0.05*1.60218e-19# difference in energy in Joules
print(dE)
m = 1.66054e-27 #mass in kg
h = 6.6260715e-34 #J s
k=((2*np.pi*dE*np.sqrt(m))/(h))**2
print(f"{k:.2f} N/m")
```

8.0109e-21
9.58 N/m

19. What are the *energies* and *degeneracies* of the four lowest-energy vibrational levels of the H atom?

We've already stated that (0,0) and (1,0) are the lowest:

$$E_{0,0} = \frac{3h\nu}{2}$$

$$E_{1,0} = \frac{5h\nu}{2}$$

We can check (0,1), (2,0), and (1,1)

$$E_{0,1} = \frac{7h\nu}{2}$$

$$E_{2,0} = \frac{7h\nu}{2}$$

$$E_{1,1} = \frac{9h\nu}{2}$$

(0,0) and (1,0) are singly degenerate/unique while (0,1) and (2,0) are doubly degenerate