5.E: The Harmonic Oscillator and the Rigid Rotor (Exercises)

Solutions to select questions can be found online.

5.7

Calculate the reduced mass of HCl molecule given that the mass of H atom is 1.0078 amu and the mass of Cl atom is 34.9688 amu. Note that 1 amu = 1.660565*10^{-27} kg.

Solution

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

$$\mu = \frac{1.0078\ amu \times 34.9688\ amu}{1.0078\ amu + 34.9688\ amu} = 0.9796\ amu$$

$$\mu = 0.9796\ amu \times \frac{1.660565 \cdot 10^{-27}\ kg}{1\ amu} = 1.627 \times 10^{-27} kg$$

5.8

Calculate the reduced mass for the Br_2, Cl_2, and I_2 diatomics.

Solution

From the periodic table, the atomic masses for Br, Cl, and I are 79.904, 35.453, and 126.904 respectively.

Covert the atomic mass to kg.

$Br = (79.904\, amu)(1.6606 \times 10^{-27}\ amu/kg) = 1.327 \times 10^{-25}\ kg$ $Cl = (35.453\, amu)(1.6606 \times 10^{-27}\ amu/kg) = 5.887 \times 10^{-26}\ kg$
$I = (126.904\, amu)(1.6606 \times 10^{-27}\ amu/kg) = 2.107 \times 10^{-25}\ kg$

$$\mu = \frac{m}{2}$$

therefore

μ_{Br2}=1.327x10^{-25} kg/2=6.635x10^{-26} kg μ_{Cl2}= 5.887x10^{-26}kg/2 = 2.9435x10^{-26}kg μ_{I2}=2.107x10^{-25}kg=1.0535x10-25kg

The equation for a reduced mass (μ) of a diatomic is

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

for a diatomic molecule with identical atoms ($m_1 = m_2 = m$) so

5.14

$^{79}Br^{79}Br$ has a force constant of 240 $N \cdot m^{-1}$. Given this information:

a. Calculate the fundamental vibrational frequency and
b. Calculate the $^{79}Br^{79}Br$ zero point energy.

Solution

We must first know which formula to use which is

$$\nu_{obs} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

calculate the reduced mass

$$\mu = \frac{(79\ amu)^2}{79\ amu + 79\ amu} = 39.5 amu$$

and convert to Kg:

$$1.66e^{-27}\ kg\bullet amu^{-1}$$

substitute the given values

$$\nu = \frac{1}{2\pi}\sqrt{\frac{240 kg\ m\ s^{-2}\ s}{39.5 amu \times 1.66 \times 10^{-27} kg\ amu^{-1}}} = 9.63 \times 10^{12} s^{-1}$$

It can also be convert to wavenumber (inverse centimeter cm^{-1}):

$$\nu_{cm^{-1}} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{9.63 \times 10^{12} s^{-1}}{3.0 \times 10^{10} cm\ s^{-1}} = 321 cm^{-1}$$

Zero Point Energy:

$$E_0 = \frac{1}{2}h\nu = \frac{1}{2}hc\nu_{cm^{-1}}$$

(formula to use)

$$E_0=1/2(6.626e^{-34}J\bullet s)(2.998e^{10}cm\bullet s^{-1})(321cm^{-1})$$

$$E_0= 3.19e^{-21}J$$

5.19

Prove that the second derivative of an even function is even and odd function is odd.

Solution

This is an example..not a proof

The following is an even function:

$$y(x) = a + bx^2 + cx^4 + dx^6$$

so

$$\frac{dy}{dx} = 2bx + 4cx^3 + 6dx^5$$

and

$$\frac{d^2y}{dx^2} = 2b + 12cx^2 + 30dx^4$$

which is an even function.

The following is an odd function:

$$f(x) = ax + bx^3 + cx^5$$

so

$$\frac{df}{dx} = a + 3bx^2 + 5cx^4$$

and

$$\frac{d^2f}{dx^2} = 6bx + 10cx^3$$

which is an odd function.

5.27

The Harmonic oscillator Hamiltonian obeys the reflective property:

$$\hat{H}(x) = \hat{H}(-x)$$

What does this say about the nature of the harmonic oscillator wave function?

Solution

The harmonic oscillator switches from odd to even due to the fact that the reflective property will alternate.

5.28

If $\langle x\rangle$ is an odd function, what does that say about p_x?

Hint: use

$$\frac{d\langle p_x\rangle}{dt} = \left\langle \frac{-dV}{dx} \right\rangle$$

also known as **Ehrenfest's Theorem**, where V is the potential of a one dimensional harmonic oscillator.

Hence, $\langle p_x\rangle$ does not depend on time.

5.32

Convert ∇^2 from Cartesian coordinates to cylindrical coordinates.

Solution

We have to start with the conversion of *Cartesian coordinates* $\{x, y, z\}$ to *cylindrical coordinates* $\{r, \theta, z\}$

$x = r\cos\theta \;\; y = r\sin\theta \;\; z = z$

Now putting it all together

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} + \frac{1}{r^2}\frac{d^2}{d\theta^2} + \frac{d^2}{dz^2}$$

$$r = \sqrt{x^2 + y^2}$$

$$\cos\theta = \frac{x}{\sqrt{x^2 + y^2}}$$

$$\sin\theta = \frac{x}{\sqrt{x^2 + y^2}}$$

Now by chain rule we get

$$\frac{d}{dx} = \frac{dr}{dx}\frac{d}{dr} + \frac{d\theta}{dx}\frac{d}{d\theta}$$

$$\frac{d}{dy} = \frac{dr}{dy}\frac{d}{dr} + \frac{d\theta}{dy}\frac{d}{d\theta}$$

$$\frac{dr}{dx} = \frac{x}{r} = \cos\theta$$

$$\frac{dr}{dx} = \sin\theta$$

using **implicit differentiation** and taking the second derivatives will yield

$$\frac{d^2}{dx^2} = \left(\cos\theta\frac{d}{dr} - \frac{\sin\theta}{r}\frac{d}{d\theta}\right)\left(\cos\theta\frac{d}{dr} - \frac{\sin\theta}{r}\frac{d}{d\theta}\right)$$

$$\frac{d^2}{dy^2} = \left(\sin\theta\frac{d}{dr} + \frac{\cos\theta}{r}\frac{d}{d\theta}\right)\left(\sin\theta\frac{d}{dr} + \frac{\cos\theta}{r}\frac{d}{d\theta}\right)$$

$$\frac{d^2}{dz^2} = \frac{d^2}{dz^2}$$

5.37

Find the magnitude of angular momentum and the z component of angular momentum for electrons in a hydrogen-like species with

a. quantum numbers $n = 1, l = 0, m = 0$; and
b. $n = 2, l = 0, m = 0$.

Compare your answers and explain your results.

Solution

The wave function for this problem is given by:

$$\psi_{100} = R(r)_{10} Y(\theta, \phi)_{00} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}}$$

Using that:

$$\hat{L}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi),$$

and

$$\hat{L}_z = m\hbar$$

Then $\hat{L}^2 = 0$ and $\hat{L}_z = 0$. Given that the values for l and m are the same as above, the answers would also be the same.

The reason why both answers are the same is that the operators for angular momentum only act on the angular part of the wave function. Since only the quantum number n varied between these two states, the angular momentum eigenvalues did not change.

5.38

Apply the angular momentum operator in the x direction to the following functions ($Y(\theta, \phi)$).

a. $\frac{5\pi}{4} + 7\exp(\pi^2)$
b. $3\pi\sin(\theta)$
c. $\frac{3}{2}\cos(\theta)\exp(i\phi)$

Solution

Let us begin by stating the angular momentum operator in terms of θ and ϕ.

$$\hat{L_x} = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\Big)$$

a) $Y(\theta, \phi) = \frac{5\pi}{4} + 7exp(\pi^2)$

$$\hat{L_x}(\frac{5\pi}{4} + 7exp(\pi^2)) = i\hbar\Big(\sin(\phi)\frac{\partial\frac{5\pi}{4} + 7exp(\pi^2)}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial\frac{5\pi}{4} + 7exp(\pi^2)}{\partial\phi}\Big)$$
$$= 0$$

The function does not depend on θ or ϕ so when the angular momentum operator is applied to the function, it equals 0.

b) $Y(\theta, \phi) = 3\pi\sin(\theta)$

$$\hat{L_x}(3\pi\sin(\theta)) = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta}3\pi\sin(\theta) + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}3\pi\sin(\theta)\Big)$$
$$= 3i\pi\hbar\sin(\phi)\cos(\theta)$$

c) $Y(\theta, \phi) = \frac{3}{2}\cos(\theta)exp(i\phi)$

$$\hat{L_x}(3\pi\sin(\theta)) = i\hbar\Big(\sin(\phi)\frac{\partial}{\partial\theta}\frac{3}{2}\cos(\theta)exp(i\phi) + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\frac{3}{2}\cos(\theta)exp(i\phi)\Big)$$
$$= i\hbar\Big(\frac{-3}{2}\sin(\phi)\sin(\theta)exp(i\phi) + \frac{3i}{2}\cot(\theta)\cos(\phi)\cos(\theta)exp(i\phi)\Big)$$
$$= \frac{3i\hbar exp(i\phi)}{2}(i\cot(\theta)\cos(\phi)\cos(\theta) - \sin(\phi)\sin(\theta))$$

5.41

Use the fact that $\hat{x}$ and $\hat{p}$ are Hermitian in the number operator

$$\hat{a}_- = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{p})$$
$$\hat{a}_+ = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{p})$$

and

$$\hat{H} = \frac{\hbar w}{2}(\hat{a}_-\hat{a}_+ + \hat{a}_+\hat{a}_-)$$

Show that

$$\int \psi_v^* \hat{v}\psi dx \geq 0$$

5.43

Determine the unnormalized wave function $\psi_\circ(x)$ given that $\hat{a}_- = 2^{-1/2}(\hat{x} + i\hat{p})$ and that $\hat{a_-}\psi_\circ = 0$ Then find the unnormalized wave function for $\psi_1(x)$ using $\hat{a}_+$.

Solution

It was given that $\hat{a}_-\psi_\circ = 0$, so substituting in $\hat{a}_-$ so we know

$$\hat{a_-} = 2^{-1/2}(\hat{x} + i\hat{p})\psi_\circ = 0$$

We can expand and simplify this expression to a first order partial differential equation

$$x\psi_\circ + \frac{d\psi_\circ}{dx} = 0$$

Solve by separating like terms

$$\frac{d\psi_\circ}{\psi_\circ} = -x dx$$

Solving this equation for $\psi_\circ(x)$ we find that

$$\psi_\circ = e^{\frac{-x^2}{2}}$$

To solve for ψ_1 we understand that $\psi_1 \backsim \hat{a_+}\psi_\circ \backsim \hat{x} - i\hat{p}\psi_\circ$, as well as that

$$\hat{x} - i\hat{p}\psi_\circ = x\psi_\circ - \frac{d\psi_\circ}{dx} = 2xe^{\frac{-x^2}{2}} = 2x\psi_\circ$$

So then we can say

$$\boxed{\psi_1 \backsim xe^{\frac{-x^2}{2}}}$$

5.46

Find the reduced mass of an electron in a Tritium atom. Set the mass of the Tritium to be $5.008267 \times 10^{-27}\,kg$. Then find the value of the Rydberg constant for the Tritium atom.

Solution

To solve, use the reduced mass equation, and for mass 1 enter the mass of the electron, and for mass 2 enter the mass of the Tritium atom:

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

For which one attains a value of $\mu = 9.1077x10^{-31}kg$

5.46

The mass of a deuterium atom is $3.343586 \times 10^{-27}\ kg$. First calculate the reduce mass of the deuterium atom. Then using the reduced mass calculated find the Rydberg constant for a deuterium atom.

Solution

μ = reduced mass

$$\mu_{deuterium} = \frac{(9.109390 \times 10^{-31}kg)(3.343586 \times 10^{-27}kg)}{(9.109390 \times 10^{-31}kg + 3.343586 \times 10^{-27}kg)}$$

$$\mu_{deuterium} = 9.106909 \times 10^{-31}kg = 0.9997277m_e$$

R_H = Rydberg constant

$$R_H = (109,737.2cm^{-1})(0.9997277m_e) = 109,707.3cm^{-1}$$

5.47

What is the ratio of the frequency of spectral lines of C-14 that has been ionized 5 times and C-12 that has been ionized 5 times?

Solution

Carbon that has been ionized 5 times is a hydrogen like ion, so we can use the Bohr model to find the desired ratio.

$$E = \frac{uZ^2e^4n^2}{8\varepsilon_0^2h^3c}$$

gives the placement of spectral lines. The coefficient of n^2 is proportional to the frequency of these lines, so the ratio of $E_{C\text{-}14}/E_{c\text{-}12}$ will give the ratio of frequency of the lines. The only difference between these two isotopes is the reduced mass u. So the problem reduces to $\mathbf{u_{C\text{-}14}/\ u_{C\text{-}12}}$. Mass in amu is used below. m_e = mass of electron = 5.4858*10^{-4} amu.

$$\mu_{C-14} = \frac{m_e m_{c-14}}{m_e + m_{c-14}} = \frac{(14.003)(5.4858 \times 10^{-4})}{14.003 + 5.4858 \times 10^{-4}} = 5.485585 \times 10^{-4}$$

$$\mu_{C-12} = \frac{m_e m_{c-12}}{m_e + m_{c-12}} = \frac{(12)(5.4858 \times 10^{-4})}{12 + 5.4858 \times 10^{-4}} = 5.485549 \times 10^{-4}$$

$$\frac{\mu_{C-14}}{\mu_{C-12}} = 1.0000065$$

5.47

Calculate the Rydberg constant for a deuterium atom and atomic hydrogen given the reduced mass of a deuterium atom is $9.106909 \times 10^{-31} kg$ and the reduced mass of hydrogen is $9.104431 \times 10^{-31} kg$. Compare both of these answers with the experimental result ($109677.6 cm^{-1}$). Then determine the ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium.

Solution

The Rydberg constant is found using

$$R_H = \frac{me^4}{8\epsilon_o^2 ch^3}$$

For a deuterium atom

$$R_H = \frac{(9.104431 \times 10^{-31} kg)(1.602 \times 10^{-19} C)^4}{8(8.854 \times 10^{-12} \frac{F}{m})^2 (2.998 \times 10^8 \frac{m}{s})(6.626 \times 10^{-34} J \cdot s)^3}$$

$$R_H = 109707.3 cm^{-1}$$

This is different by $2.7 \times 10^{-2}\%$.

The ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium is equivalent to the ratio of the Rydberg constants we just found.

$$\frac{109707.3\ cm^{-1}}{109677.5\ cm^{-1}} = 1.000272$$

$$R_H = \frac{(9.106909 \times 10^{-31} kg)(1.602 \times 10^{-19} C)^4}{8(8.854 \times 10^{-12} \frac{F}{m})^2 (2.998 \times 10^8 \frac{m}{s})(6.626 \times 10^{-34} J \cdot s)^3}$$

$$R_H = 109677.5 cm^{-1}$$

This is different by $9.1 \times 10^{-5}\%$.

For a hydrogen atom

5.46

Find the reduced mass of HCl where the mass of hydrogen in 1 amu and the mass of chloride is 35 amu.

Solution

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

$$\mu = \frac{(1.00)(35.00)}{36.00} 1.603 \times 10^{-27} kg = 1.558 \times 10^{-27} kg$$
