

CHAPTER 3
PARTICLE IN BOX (PIB) MODELS
OUTLINE

Homework Questions Attached

SECT	TOPIC
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- | | |
|----|--|
| 1. | The Classical Particle in a Box (PIB) |
| 2. | The Quantum Mechanical PIB |
| 3. | PIB Properties |
| 4. | Other PIB Models |
| 5. | The Free Electron Molecular Orbital (FEMO) Model |
| 6. | PIB and the Color of Vegetables |
| 7. | Multidimensional Systems: The 2D PIB and 3D PIB |
| 8. | Statistical Mechanics: Translational Contributions to the Thermodynamic Properties of Gases.* <ul style="list-style-type: none">(a) The Boltzmann Distribution(b) The Partition Function (Q)(c) Thermodynamic Properties in Terms of Q(d) Partition Function for Non-Interacting Particles(e) The Molecular Partition Function (q)(f) The Total Partition Function for a System of Molecules (Q)(g) The Translational Partition Function(h) Translational Contributions to Thermodynamic Properties |

***Note:** Because this is the first chapter in which we introduce Statistical Mechanics, this section is longer than the equivalent Stat. Mech. sections in later chapters.

Chapter 3 Homework

- Solve the differential equation: $d^2y/dx^2 - 4y = 0$, subject to the Boundary Conditions, $y(0) = 2$, $y'(0) = 4$.
Hint: Assume that the solution is of the form: $y = Ae^{\alpha x} + Be^{-\alpha x}$
- Assume that a hydrogen molecule is confined to a box of length $8 \text{ \AA}$. Calculate the following:
 - the zero-point energy, in J.
 - the velocity of the H_2 molecule in the ground state.
 - the quantum number, n , corresponding to the hydrogen molecule moving at a speed of $1.5 \times 10^5 \text{ m/s}$.
- When an electron in a one-dimensional box drops from the $n = 5$ to $n = 2$ level, it emits a photon of wavelength 500 nm . Calculate the length of the box.
- The wavefunctions for the first and third energy levels of a PIB are:

$$\psi_1 = A \sin\left(\frac{1\pi x}{a}\right) \text{ and } \psi_3 = A \sin\left(\frac{3\pi x}{a}\right)$$
 Prove that these two wavefunctions are orthogonal to each other.
- An approximate wavefunction for the ground state of the PIB is:

$$\psi_{app} = Ax^2(a - x) \quad 0 \leq x \leq a$$
 :
 - A (the normalization constant)
 - The probability that the particle lies in the region, $0 \leq x \leq 0.40a$
 - $\langle x^2 \rangle$
 - $\langle E \rangle$
- Use the Free Electron Molecular Orbital (FEMO) to estimate the wavelength of the lowest $\pi \rightarrow \pi^*$ transition in 1,3,5-hexatriene. Take the CC bond length to be 0.14 nm , and the mass of the electron to be $9.11 \times 10^{-31} \text{ kg}$.
- Assume that the six π electrons in benzene can be modeled as particles in a two dimensional box of length 0.35 nm ($= 3.5 \text{ \AA}$) on a side. Calculate the wavelength, in nm , of the lowest $\pi \rightarrow \pi^*$ transition in benzene.
- Consider a particle in a Two Dimensional box of length a and b , with $b = 2a$. Calculate the energy levels (in units of h^2/ma^2) for the first 8 (eight) energy levels.
- For 3 (three) moles of $NO_2(g)$ at 100°C and 0.50 atm , calculate the translational contributions to the internal energy, constant volume heat capacity, enthalpy, entropy, Helmholtz energy and Gibbs energy.

10. In class, we showed that the molecular translational partition function of O₂ at 25 °C and 1 atm. is: $q^{\text{tran}} = 4.28 \times 10^{30}$.

- (a) What is the value of q^{tran} for Cl₂ at 25 °C and 1 atm.?
- (b) What is the value of q^{tran} for O₂ at 1000 °C and 1 atm.?
- (c) What is the value of q^{tran} for O₂ at 1000 °C and 10 atm.?

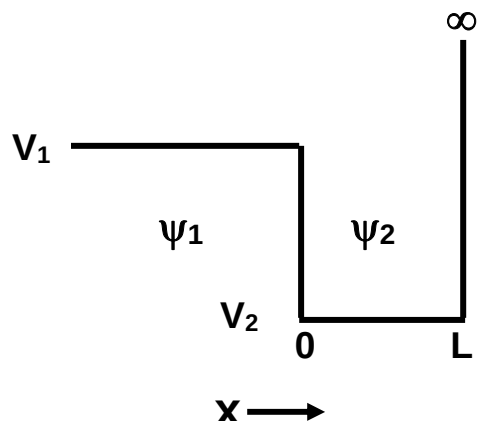
11. Consider a particle in a semi-infinite box (right) with the potential energy defined by:

$$V(x) = V_1 \quad -\infty < x \leq 0$$

$$V(x) = V_2 \quad 0 < x \leq L$$

$$V(x) \rightarrow \infty \quad x > L$$

V_1 and V_2 are constants.



For $V_2 < E < V_1$, the wave functions in the two regions are of the form:

$$\psi_1 = Ae^{+\alpha x} + Be^{-\alpha x} \quad \alpha \text{ and } \beta \text{ are real, positive constants.}$$

$$\psi_2 = C \sin[\beta(L - x)] + D \cos[\beta(L - x)]$$

- (a) Apply the appropriate boundary condition at $x \rightarrow -\infty$ to simplify ψ_1 and use your result in the Schrödinger equation to develop an equation for α as a function of E , m , V_1 and $\hbar$.
- (b) Apply the appropriate boundary condition at $x = L$ to simplify ψ_2 and use your result in the Schrödinger equation to develop an equation for β as a function of E , m , V_2 and $\hbar$.
- (c) Apply the appropriate boundary conditions at $x = 0$ to develop **two** relationships between the wavefunction parameters in the two regions.

DATA

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

$$R = 8.31 \text{ J/mol}\cdot\text{K}$$

$$R = 8.31 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg (electron mass)}$$

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$k \cdot N_A = R$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ atm.} = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$\int \sin(\alpha x) \sin(\beta x) dx = A^2 \left\{ \frac{\sin[(\alpha - \beta)x]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)x]}{2(\alpha + \beta)} \right\}$$

Some “Concept Question” Topics

Refer to the PowerPoint presentation for explanations on these topics.

- The Correspondence Principle
- Heisenberg Uncertainty Principle and PIB Zero-Point-Energy
- Tunneling
- Equipartition of translational energy and heat capacity

Chapter 3

Particle-in-Box (PIB) Models

Slide 1

Carrots are Orange.

Tomatoes are Red.

But Why?

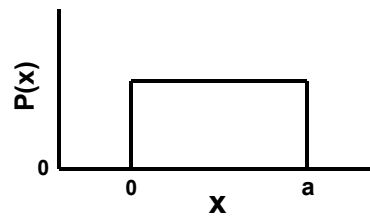
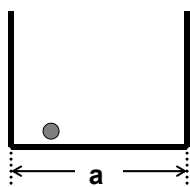
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Outline

- The Classical Particle in a Box (PIB)
- The Quantum Mechanical PIB
- PIB Properties
- Other PIB Models
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Slide 3

The Classical Particle in a Box



$$P(x) = \text{Const.} = C \quad 0 \leq x \leq a$$
$$P(x) = 0 \quad x < 0, x > a$$

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \text{any value, including } 0$$

i.e. the energy is **not** quantized
and there is no minimum.

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$$P(x) = \text{Const.} = C \quad 0 \leq x \leq a$$

$$P(x) = 0 \quad x < 0, x > a$$

Normalization

$$\int_{-\infty}^{\infty} P(x) dx = 1 \Rightarrow \int_{-\infty}^0 0 dx + \int_0^a C dx + \int_a^{\infty} 0 dx = C[x]_0^a = Ca \longrightarrow P(x) = C = \frac{1}{a}$$

$\langle x \rangle$

$$\langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = \int_0^a x \cdot \frac{1}{a} dx = \frac{1}{a} \left[\frac{x^2}{2} \right]_0^a = \frac{1}{a} \frac{a^2}{2} = \frac{a}{2}$$

$\langle x^2 \rangle$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) dx = \int_0^a x^2 \cdot \frac{1}{a} dx = \frac{1}{a} \left[\frac{x^3}{3} \right]_0^a = \frac{1}{a} \frac{a^3}{3} = \frac{a^2}{3}$$

$$\text{Note: } \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{a^2}{3} - \left(\frac{a}{2} \right)^2 = \frac{a^2}{12} > 0$$

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Quantum Mechanical Particle-in-Box

Schrödinger Equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

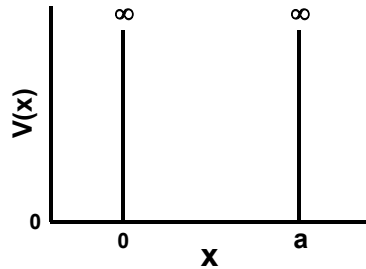
Outside the box: $x < 0, x > a$

$$P(x) = \psi^*(x)\psi(x) = 0$$

$$\psi(x) = 0$$

Inside the box: $0 \leq x \leq a$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi$$



$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) \rightarrow \infty \quad x < 0, x > a$$

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Solving the Equation

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi$$

$$-\alpha^2 \psi = -\frac{2mE}{\hbar^2} \psi$$

$$E = \frac{\alpha^2 \hbar^2}{2m}$$

Assume

$$\psi = A \sin(\alpha x) + B \cos(\alpha x)$$

$$\frac{d\psi}{dx} = \alpha A \cos(\alpha x) - \alpha B \sin(\alpha x)$$

$$\frac{d^2\psi}{dx^2} = -\alpha^2 A \sin(\alpha x) - \alpha^2 B \cos(\alpha x)$$

$$\frac{d^2\psi}{dx^2} = -\alpha^2 \psi$$

So far, there is no restriction on α and, hence none on the energy, E (other than that it cannot be negative)

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Applying Boundary Conditions (BC's)

Nature hates discontinuous behavior;
i.e. It's not really possible to stop on a dime

Because the wavefunction, ψ , is 0 outside the box, $x < 0$ and $x > a$, it must also be 0 inside the box at $x=0$ and $x=a$

$$\psi = A \sin(\alpha x) + B \cos(\alpha x)$$

$$\text{BC-1: } \psi(0) = 0 = A \sin(0) + B \cos(0) = B$$

$$\text{Therefore, } \psi(x) = A \sin(\alpha x)$$

$$\text{BC-2: } \psi(a) = 0 = A \sin(\alpha a) \quad \sin(n\pi) = 0$$

$$\text{Therefore: } \alpha a = n\pi \quad n = 1, 2, 3, \dots$$

$$\text{or: } \alpha = \frac{n\pi}{a} \quad n = 1, 2, 3, \dots$$

Why isn't $n = 0$ acceptable?

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Wavefunctions and Energy Levels

$$\alpha = \frac{n\pi}{a} \quad n = 1, 2, 3, \dots$$

$$\psi_n = A \sin(\alpha x) = A \sin\left(\frac{n\pi}{a} x\right) \quad n = 1, 2, 3, \dots$$

$$E = \frac{\alpha^2 \hbar^2}{2m} = \left(\frac{n\pi}{a}\right)^2 \frac{1}{2m} \left(\frac{h}{2\pi}\right)^2 = \frac{n^2 \pi^2}{a^2} \cdot \frac{1}{2m} \cdot \frac{h^2}{4\pi^2}$$

$$E_n = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3, \dots$$

Note that, unlike the classical particle in a box:

- (a) the allowed energies are quantized
- (b) $E = 0$ is **NOT** permissible (i.e. the particle can't stand still)

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Energy Quantization results from application of the Boundary Conditions

$$E_n = \frac{n^2 h^2}{8ma^2}$$

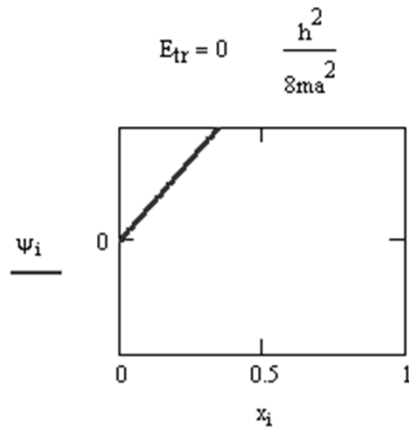
$$E_1 = 1 \frac{h^2}{8ma^2}$$

$$E_2 = 4 \frac{h^2}{8ma^2}$$

$$E_3 = 9 \frac{h^2}{8ma^2}$$

$$E_4 = 16 \frac{h^2}{8ma^2}$$

$$E_5 = 25 \frac{h^2}{8ma^2}$$



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Wavefunctions

$$\psi_3 = A \cdot \sin\left(\frac{3\pi x}{a}\right)$$

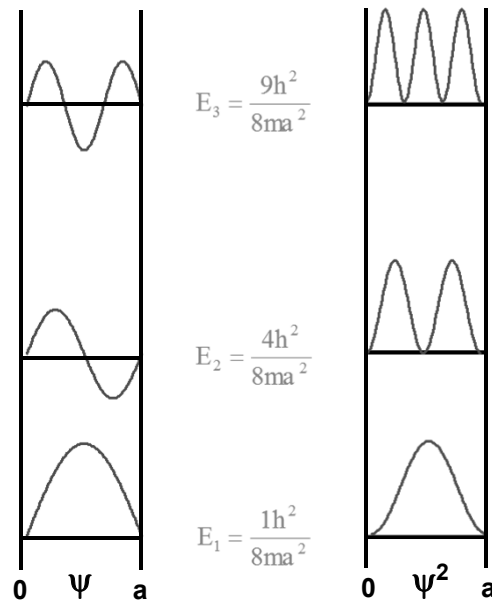
$$E_3 = \frac{9h^2}{8ma^2}$$

$$\psi_2 = A \cdot \sin\left(\frac{2\pi x}{a}\right)$$

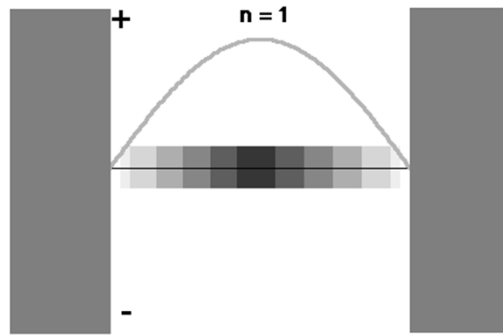
$$E_2 = \frac{4h^2}{8ma^2}$$

$$\psi_1 = A \cdot \sin\left(\frac{\pi x}{a}\right)$$

$$E_1 = \frac{1h^2}{8ma^2}$$



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Note that: (a) The Probability, ψ^2 is very different from the classical result.

(b) The number of “nodes” increases with increasing quantum number.

The increasing number of nodes reflects the higher kinetic energy with higher quantum number.

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The Correspondence Principle

The predictions of Quantum Mechanics cannot violate the results of classical mechanics on macroscopically sized systems.

Consider an electron in a 1 Angstrom box.

Calculate (a) the Zero Point Energy (i.e. minimum energy)

(b) the minimum speed of the electron

$$m_e = 9.1 \times 10^{-31} \text{ kg}$$

$$a = 1 \times 10^{-10} \text{ m}$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$E_1 = \frac{h^2}{8ma^2} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2}{8(9.1 \times 10^{-31} \text{ kg})(1 \times 10^{-10} \text{ m})^2} = 6.04 \times 10^{-18} \text{ J}$$

$$E_1 = \frac{mv_1^2}{2} \rightarrow v_1 = \sqrt{\frac{2E_1}{m}} = \sqrt{\frac{2(6.04 \times 10^{-18} \text{ kg}\cdot\text{m}^2/\text{s}^2)}{9.1 \times 10^{-31} \text{ kg}}}$$

$$v_1 = 3.6 \times 10^6 \text{ m/s} \ (\approx 1.7 \times 10^7 \text{ mi/hr})$$

Thus, the minimum speed of an electron confined to an atom is quite high.

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Let's perform the same calculation on a macroscopic system.

Consider a 1 gram particle in a 10 cm box.

Calculate (a) the Zero Point Energy (i.e. minimum energy)

(b) the minimum speed of the particle

$$m = 1 \times 10^{-3} \text{ kg}$$

$$a = 0.10 \text{ m}$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$E_1 = \frac{h^2}{8ma^2} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2}{8(1 \times 10^{-3} \text{ kg})(0.1 \text{ m})^2} = 5.50 \times 10^{-63} \text{ J}$$

$$E_1 = \frac{mv_1^2}{2} \rightarrow v_1 = \sqrt{\frac{2E_1}{m}} = \sqrt{\frac{2(5.50 \times 10^{-63} \text{ kg}\cdot\text{m}^2/\text{s}^2)}{1 \times 10^{-3} \text{ kg}}} = 3.3 \times 10^{-30} \text{ m/s}$$

Thus, the minimum energy and speed of a macroscopic particle are completely negligible.

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Probability Distribution of a Macroscopic Particle

Consider a 1 gram particle in a 10 cm box moving at 1 cm/s.

Calculate the quantum number, n, which represents the number of maxima in the probability, ψ^2 .

$$m = 1 \times 10^{-3} \text{ kg}$$

$$a = 0.10 \text{ m}$$

$$v = 0.01 \text{ m/s}$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$E = \frac{1}{2}mv^2 = \frac{1}{2}(1 \times 10^{-3} \text{ kg})(0.01 \text{ m/s})^2 = 5.0 \times 10^{-8} \text{ J}$$

$$E = \frac{n^2 h^2}{8ma^2} \rightarrow n^2 = \frac{8ma^2 E}{h^2} = \frac{8(1 \times 10^{-3} \text{ kg})(0.1 \text{ m})^2 (5.0 \times 10^{-8} \text{ J})}{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2}$$

$$n^2 = 9.1 \times 10^{54} \rightarrow n = 3 \times 10^{27}$$

Thus, the probability distribution is uniform throughout the box, as predicted by classical mechanics.

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Some Useful Integrals

$$\int \sin^2(\alpha x) dx = \frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x)$$

$$\int \sin(\alpha x) \sin(\beta x) dx = \frac{\sin[(\alpha - \beta)x]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)x]}{2(\alpha + \beta)}$$

$$\int \sin(\alpha x) \cos(\alpha x) dx = \frac{1}{2\alpha} \sin^2(\alpha x)$$

$$\int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

$$\int x^2 \sin^2(\alpha x) dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha x) - \frac{x \cos(2\alpha x)}{4\alpha^2}$$

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PIB Properties

Normalization of the Wavefunctions

$$\psi_n = A \sin\left(\frac{n\pi}{a} x\right) \quad 0 \leq x \leq a \quad \int \sin^2(\alpha x) dx = \frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x)$$

$$1 = \int_0^a \psi_n^2 dx = \int_0^a \left[A \sin\left(\frac{n\pi}{a} x\right) \right]^2 dx = A^2 \int_0^a \sin^2(\alpha x) dx \quad \alpha = \frac{n\pi}{a}$$

$$= A^2 \left[\frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x) \right]_0^a = A^2 \left[\left(\frac{1}{2}a - \frac{1}{4\alpha} \sin\left(2\frac{n\pi}{a}a\right) \right) - \left(0 - \frac{1}{4\alpha} \sin(0) \right) \right]$$

$$1 = A^2 \left(\frac{a}{2} \right) \longrightarrow \boxed{A = \left(\frac{2}{a} \right)^{1/2} = \sqrt{\frac{2}{a}}}$$

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Probability of finding the particle in a particular portion of the box

Calculate the probability of finding a particle with $n=1$ in the region of the box between 0 and $a/4$ $\psi_1 = A \sin\left(\frac{\pi x}{a}\right)$

$$\int \sin^2(\alpha x) dx = \frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x)$$

$$P(0 \leq x \leq a/4) = A^2 \int_0^{a/4} \sin^2(\alpha x) dx \quad \alpha = \pi/a$$

$$= A^2 \left[\frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x) \right]_0^{a/4} = A^2 \left[\left(\frac{1}{2} \cdot \frac{a}{4} - \frac{1}{4(\pi/a)} \sin\left(2\frac{\pi}{a} \cdot \frac{a}{4}\right) \right) - \left(0 - \frac{1}{4(\pi/a)} \sin(0) \right) \right]$$

$$P(0 \leq x \leq a/4) = \frac{2}{a} \left(\frac{a}{8} - \frac{a}{4\pi} \right) = \frac{1}{4} - \frac{1}{2\pi} = 0.091$$

This is significantly lower than the classical probability, 0.25.

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Orthogonality of the Wavefunctions

Two wavefunctions are orthogonal if: $\int \psi_i^* \psi_j d\tau = 0 \quad i \neq j$

We will show that the two lowest wavefunctions of the PIB

are orthogonal: $\psi_1 = A \sin\left(\frac{\pi x}{a}\right) \quad \psi_2 = A \sin\left(\frac{2\pi x}{a}\right)$

$$\int_0^a \psi_2 \psi_1 dx = \int_0^a A \sin\left(\frac{2\pi x}{a}\right) A \sin\left(\frac{\pi x}{a}\right) dx = A^2 \int_0^a \sin(\alpha x) \sin(\beta x) dx \quad \alpha = \frac{2\pi}{a} \quad \beta = \frac{\pi}{a}$$

$$\int \sin(\alpha x) \sin(\beta x) dx = \frac{\sin[(\alpha - \beta)x]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)x]}{2(\alpha + \beta)}$$

$$\int_0^a \psi_2 \psi_1 dx = A^2 \left(\frac{\sin[(\alpha - \beta)a]}{2(\alpha - \beta)} - \frac{\sin[(\alpha + \beta)a]}{2(\alpha + \beta)} \right) - A^2(0 - 0) \quad (\alpha + \beta)a = \frac{3\pi}{a}a = 3\pi$$

$$(\alpha - \beta)a = \frac{\pi}{a}a = \pi$$

$$\int_0^a \psi_2 \psi_1 dx = A^2 \left(\frac{\sin[\pi]}{2(\alpha - \beta)} - \frac{\sin[3\pi]}{2(\alpha + \beta)} \right) = 0 \quad \text{Thus, } \psi_1 \text{ and } \psi_2 \text{ are orthogonal}$$

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Using the same method as above, it can be shown that:

$$\int \psi_i^* \psi_j d\tau = 0 \quad \text{For all } i \neq j$$

Thus, the PIB wavefunctions are orthogonal.

If they have also been normalized, then the wavefunctions are **orthonormal**:

$$\int \psi_i^* \psi_j d\tau = \delta_{ij}$$

or

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

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Positional Averages

We will calculate the averages for ψ_1 and present the general result for ψ_n

$$\psi_1 = A \sin\left(\frac{\pi x}{a}\right) = A \sin(\alpha x) \quad \alpha = \frac{\pi}{a} \quad A = \sqrt{\frac{2}{a}}$$

$$\sin(\alpha a) = \sin\left(\frac{\pi}{a} a\right) = 0 \quad \sin(2\alpha a) = \sin\left(2 \frac{\pi}{a} a\right) = 0$$

$$\cos(\alpha a) = \cos\left(\frac{\pi}{a} a\right) = -1 \quad \cos(2\alpha a) = \cos\left(2 \frac{\pi}{a} a\right) = +1$$

$$\langle x \rangle$$

$$\begin{aligned} \langle x \rangle &= \langle \psi_1 | x | \psi_1 \rangle = \int_0^a \psi_1^* x \psi_1 dx = \int_0^a A \sin\left(\frac{\pi x}{a}\right) x A \sin\left(\frac{\pi x}{a}\right) dx \\ &= A^2 \int_0^a x \sin^2(\alpha x) dx \quad \alpha = \frac{\pi}{a} \end{aligned}$$

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$$\langle x \rangle = A^2 \int_0^a x \sin^2(\alpha x) dx \quad \int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

$$\langle x \rangle = \frac{2}{a} \left[\left(\frac{a^2}{4} - \frac{a \sin(2\alpha a)}{4\alpha} - \frac{\cos(2\alpha a)}{8\alpha^2} \right) - \left(0 - 0 - \frac{\cos(0)}{8\alpha^2} \right) \right]$$

$$\langle x \rangle = \frac{2}{a} \left[\left(\frac{a^2}{4} - \frac{1}{8\alpha^2} \right) - \left(-\frac{1}{8\alpha^2} \right) \right]$$

$$\langle x \rangle = \frac{a}{2}$$

General Case: $\langle x \rangle = \frac{a}{2}$

This makes sense because ψ^2 is symmetric about the center of the box.

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$$\langle x^2 \rangle$$

$$\begin{aligned}\langle x^2 \rangle &= \langle \psi_1 | x^2 | \psi_1 \rangle = \int_0^a \psi_1^* x^2 \psi_1 dx = \int_0^a A \sin\left(\frac{\pi x}{a}\right) x^2 A \sin\left(\frac{\pi x}{a}\right) dx \\ &= A^2 \int_0^a x^2 \sin^2(\alpha x) dx \quad \alpha = \frac{\pi}{a}\end{aligned}$$

$$\int x^2 \sin^2(\alpha x) dx = \frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha x) - \frac{x \cos(2\alpha x)}{4\alpha^2}$$

$$\langle x^2 \rangle = \frac{2}{a} \left[\left(\frac{a^3}{6} - \left(\frac{a^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin(2\alpha a) - \frac{a \cos(2\alpha a)}{4\alpha^2} \right) - (0 - 0 - 0) \right]$$

$$\langle x^2 \rangle = \frac{2}{a} \left(\frac{a^3}{6} - \frac{a}{4 \left(\frac{\pi}{a} \right)^2} \right) = \frac{a^2}{3} - \frac{a^2}{2\pi^2} = \left(\frac{1}{3} - \frac{1}{2\pi^2} \right) a^2 \approx 0.28a^2$$

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$$\langle x^2 \rangle = \left(\frac{1}{3} - \frac{1}{2\pi^2} \right) a^2 \approx 0.28a^2 \quad \text{compared to the classical result}$$

$$\langle x^2 \rangle = \frac{a^2}{2} \approx 0.33a^2$$

General Case: $\langle x^2 \rangle = \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} \right) a^2$

Note that the general QM value reduces to the classical result in the limit of large n, as required by the Correspondence Principle.

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Momentum Averages

Preliminary

$$\hat{p} \equiv \frac{\hbar}{i} \frac{d}{dx} \quad \hat{p}^2 \equiv -\hbar^2 \frac{d^2}{dx^2}$$

$$\psi_1 = A \sin\left(\frac{\pi}{a} x\right) = A \sin(\alpha x) \quad \alpha = \frac{\pi}{a} \quad A = \sqrt{\frac{2}{a}}$$

$$\frac{d\psi_1}{dx} = \frac{d}{dx} (A \sin(\alpha x)) = A\alpha \cos(\alpha x)$$

$$\frac{d^2\psi_1}{dx^2} = \frac{d}{dx} (A\alpha \cos(\alpha x)) = -A\alpha^2 \sin(\alpha x)$$

$$\sin(\alpha a) = \sin\left(\frac{\pi}{a} a\right) = 0 \quad \sin(2\alpha a) = \sin\left(2\frac{\pi}{a} a\right) = 0$$

$$\cos(\alpha a) = \cos\left(\frac{\pi}{a} a\right) = -1 \quad \cos(2\alpha a) = \cos\left(2\frac{\pi}{a} a\right) = 1$$

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<p>

$$\hat{p} \equiv \frac{\hbar}{i} \frac{d}{dx}$$

$$\langle p \rangle = \langle \psi_1 | \hat{p} | \psi_1 \rangle = \int_0^a \psi_1^* \frac{\hbar}{i} \frac{d\psi_1}{dx} dx = \int_0^a A \sin(\alpha x) \frac{\hbar}{i} \frac{dA \sin\left(\frac{\pi x}{a}\right)}{dx} dx \quad \alpha = \frac{\pi}{a}$$

$$= \int_0^a A \sin(\alpha x) \frac{\hbar}{i} A\alpha \cos(\alpha x) dx = A^2 \left(\frac{\hbar}{i}\right) \alpha \int_0^a \sin(\alpha x) \cos(\alpha x) dx$$

$$\int \sin(\alpha x) \cos(\alpha x) dx = \frac{1}{2\alpha} \sin^2(\alpha x)$$

$$\langle p \rangle = A^2 \left(\frac{\hbar}{i}\right) \alpha \left[\left(\frac{1}{2\alpha} \sin^2(\alpha a) \right) - \left(\frac{1}{2\alpha} \sin^2(0) \right) \right] = A^2 \left(\frac{\hbar}{i}\right) \alpha [0 - 0]$$

$$\langle p \rangle = 0 \quad (\text{General case is the same})$$

On reflection, this is not surprising.
The particle has equal probabilities of moving in the + or - x-direction,
and the momenta cancel each other.

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$$\langle p^2 \rangle$$

$$\hat{p}^2 \equiv -\hbar^2 \frac{d^2}{dx^2}$$

$$\begin{aligned} \langle p^2 \rangle &= \langle \psi_1 | \hat{p}^2 | \psi_1 \rangle = \int_0^a \psi_1^* (-\hbar^2) \frac{d^2 \psi_1}{dx^2} dx = \int_0^a A \sin(\alpha x) (-\hbar^2) \frac{d^2 A \sin\left(\frac{\pi x}{a}\right)}{dx^2} dx \quad \alpha = \frac{\pi}{a} \\ &= \int_0^a A \sin(\alpha x) (-\hbar^2) (-A \alpha^2) \sin(\alpha x) dx = A^2 \hbar^2 \alpha^2 \int_0^a \sin^2(\alpha x) dx \\ &\quad \int \sin^2(\alpha x) dx = \frac{1}{2} x - \frac{1}{4\alpha} \sin(2\alpha x) \end{aligned}$$

$$\langle p^2 \rangle = A^2 \hbar^2 \alpha^2 \left[\left(\frac{a}{2} - \frac{1}{4\alpha} \sin(2\alpha a) \right) - \left(0 - \frac{1}{4\alpha} \sin(0) \right) \right] = \left(\frac{2}{a} \right) \hbar^2 \alpha^2 \left[\frac{a}{2} \right]$$

$$\langle p^2 \rangle = \hbar^2 \alpha^2 = \frac{\pi^2 \hbar^2}{a^2}$$

$$\text{General Case: } \langle p^2 \rangle = \frac{n^2 \pi^2 \hbar^2}{a^2}$$

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Standard Deviations and the Uncertainty Principle

$$\text{Heisenberg Uncertainty Principle: } \sigma_x \sigma_p \geq \frac{\hbar}{2}$$

$$\langle x \rangle = \frac{a}{2} = 0.50a \quad \langle p \rangle = 0$$

$$\langle x^2 \rangle \approx 0.28a^2 \quad \langle p^2 \rangle = \frac{\pi^2 \hbar^2}{a^2}$$

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{0.28a^2 - (0.50a)^2} \approx 0.17a$$

$$\sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\langle p^2 \rangle - 0} = \frac{\pi \hbar}{a} \approx 3.14 \frac{\hbar}{a}$$

$$\sigma_x \sigma_p \approx (0.17a) \left(3.14 \frac{\hbar}{a} \right) \approx 0.53\hbar$$

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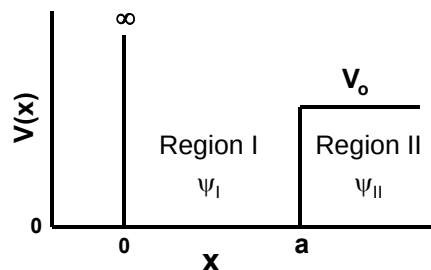
Outline

- The Classical Particle in a Box (PIB)
- The Quantum Mechanical PIB
- PIB Properties
- **Other PIB Models**
 - The Free Electron Molecular Orbital (FEMO) Model
 - PIB and the Color of Vegetables
 - Multidimensional Systems: The 2D PIB and 3D PIB
 - Statistical Thermodynamics: Translational contributions to the thermodynamic properties of gases.

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Other PIB Models

PIB with one non-infinite wall



$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

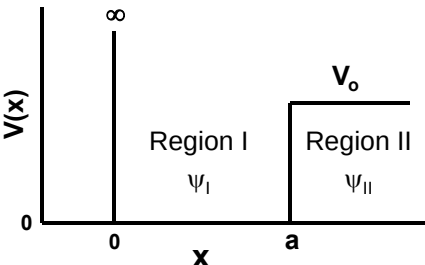
We will first consider the case where $E < V_0$.

Boundary Conditions

The wavefunction must satisfy two conditions at the boundaries ($x=0$, $x=a$, $x \rightarrow \infty$)

- 1) ψ must be continuous at all boundaries.
- 2) $d\psi/dx$ must be continuous at the boundaries **unless** $V \rightarrow \infty$ at the boundary.

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$V(x) \rightarrow \infty \quad x < 0$
 $V(x) = 0 \quad 0 \leq x \leq a$
 $V(x) = V_0 \quad x > a$

We will first consider the case where $E < V_0$.

Region I

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_I}{dx^2} + 0 = E\psi_I$$

$$\frac{d^2\psi_I}{dx^2} = -\frac{2mE}{\hbar^2} \psi_I = -\text{const} \cdot \psi_I$$

can assume

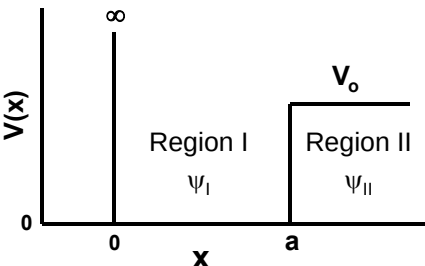
$$\psi_I = A \sin(\alpha x) + B \cos(\alpha x)$$

$$\frac{d\psi_I}{dx} = A\alpha \cos(\alpha x) - B\alpha \sin(\alpha x)$$

$$\frac{d^2\psi_I}{dx^2} = -A\alpha^2 \sin(\alpha x) - B\alpha^2 \cos(\alpha x)$$

$$\frac{d^2\psi_I}{dx^2} = -\alpha^2 \psi_I$$

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$V(x) \rightarrow \infty \quad x < 0$
 $V(x) = 0 \quad 0 \leq x \leq a$
 $V(x) = V_0 \quad x > a$

We will first consider the case where $E < V_0$.

Region I

Relation between α and E

$$\frac{d^2\psi_I}{dx^2} = -\frac{2mE}{\hbar^2} \psi_I \quad \longrightarrow \quad -\alpha^2 \psi_I = -\frac{2mE}{\hbar^2} \psi_I$$

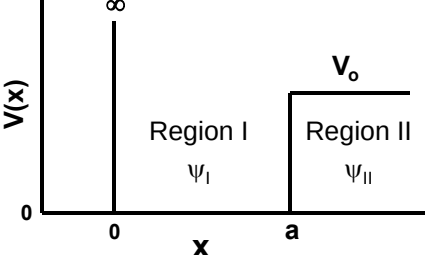
$$\psi_I = A \sin(\alpha x) + B \cos(\alpha x)$$

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi_I}{dx^2} = -\alpha^2 \psi_I$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

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$V(x) \rightarrow \infty \quad x < 0$
 $V(x) = 0 \quad 0 \leq x \leq a$
 $V(x) = V_0 \quad x > a$

We will first consider the case where $E < V_0$.

Region II

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_{II}}{dx^2} + V_0 \psi_{II} = E \psi_{II}$$

$$\frac{d^2 \psi_{II}}{dx^2} = -\frac{2m}{\hbar^2} (E - V_0) \psi_{II}$$

$$\frac{d^2 \psi_{II}}{dx^2} = +\frac{2m}{\hbar^2} (V_0 - E) \psi_{II} = +\text{const} \cdot \psi_{II}$$

can assume

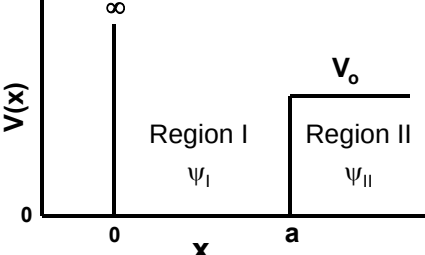
$$\psi_{II} = C e^{\beta x} + D e^{-\beta x}$$

$$\frac{d\psi_{II}}{dx} = C \beta e^{\beta x} - D \beta e^{-\beta x}$$

$$\frac{d^2 \psi_{II}}{dx^2} = C \beta^2 e^{\beta x} + D \beta^2 e^{-\beta x}$$

$$\frac{d^2 \psi_{II}}{dx^2} = \beta^2 \psi_{II}$$

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$V(x) \rightarrow \infty \quad x < 0$
 $V(x) = 0 \quad 0 \leq x \leq a$
 $V(x) = V_0 \quad x > a$

We will first consider the case where $E < V_0$.

Region II

Relation between β and E

$$\frac{d^2 \psi_{II}}{dx^2} = +\frac{2m}{\hbar^2} (V_0 - E) \psi_{II} \longrightarrow \beta^2 \psi_{II} = +\frac{2m}{\hbar^2} (V_0 - E) \psi_{II}$$

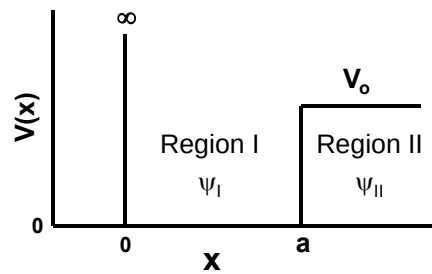
$$\psi_{II} = C e^{\beta x} + D e^{-\beta x}$$

$$\beta^2 = +\frac{2m}{\hbar^2} (V_0 - E)$$

$$\frac{d^2 \psi_{II}}{dx^2} = \beta^2 \psi_{II}$$

$$\beta = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)}$$

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$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Boundary Conditions

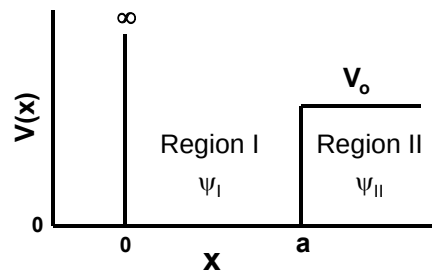
BC: $x = 0$

$$\psi_I = A \sin(\alpha x) + B \cos(\alpha x) \quad \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\psi_I(0) = 0 = A \sin(0) + B \cos(0) = B \quad \longrightarrow \quad B = 0$$

Therefore: $\psi_I = A \sin(\alpha x)$

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$$V(x) \rightarrow \infty \quad x < 0$$

$$V(x) = 0 \quad 0 \leq x \leq a$$

$$V(x) = V_0 \quad x > a$$

We will first consider the case where $E < V_0$.

Boundary Conditions

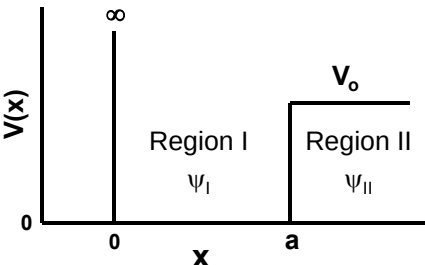
BC: $x = \infty$

$$\psi_{II} = Ce^{\beta x} + De^{-\beta x} \quad \beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

$$\psi_{II}(\infty) = 0 = Ce^{\infty} + De^{-\infty} = Ce^{\infty} \quad \longrightarrow \quad C = 0$$

Therefore: $\psi_{II} = De^{-\beta x}$

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$V(x) \rightarrow \infty \quad x < 0$
 $V(x) = 0 \quad 0 \leq x \leq a$
 $V(x) = V_0 \quad x > a$

We will first consider the case where $E < V_0$.

Boundary Conditions
BC's: $x = a$

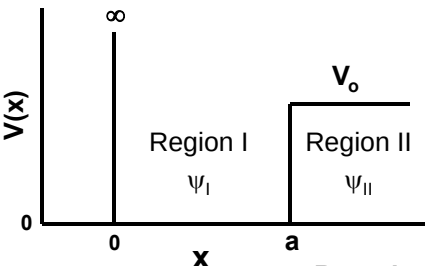
$\psi_I = A \sin(\alpha x) \quad \alpha = \sqrt{\frac{2mE}{\hbar^2}}$
 $\frac{d\psi_I}{dx} = A\alpha \cos(\alpha x)$
 $\psi_I(a) = \psi_{II}(a)$
 or

$A \sin(\alpha a) = D e^{-\beta a}$

$\psi_{II} = D e^{-\beta x} \quad \beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$
 $\frac{d\psi_{II}}{dx} = -D\beta e^{-\beta x}$
 $\left(\frac{d\psi_I}{dx}\right)_a = \left(\frac{d\psi_{II}}{dx}\right)_a$
 or

$A\alpha \cos(\alpha a) = -D\beta e^{-\beta a}$

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$V(x) \rightarrow \infty \quad x < 0$
 $V(x) = 0 \quad 0 \leq x \leq a$
 $V(x) = V_0 \quad x > a$

We will first consider the case where $E < V_0$.

Boundary Conditions
BC's: $x = a$

$\psi_I = A \sin(\alpha x) \quad \alpha = \sqrt{\frac{2mE}{\hbar^2}}$

$\psi_{II} = D e^{-\beta x} \quad \beta = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$

$A \sin(\alpha a) = D e^{-\beta a} \quad A\alpha \cos(\alpha a) = -D\beta e^{-\beta a}$

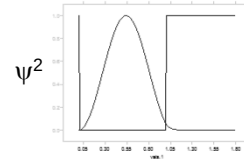
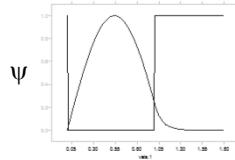
These equations can be solved analytically to obtain the allowed values of the energy, E . However, it's fairly messy.

I'll just show you some results obtained by numerical solution of the Schrödinger Equation.

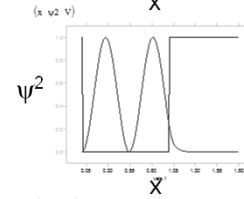
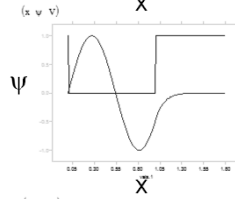
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$$V_0 = 30 \frac{h^2}{8ma^2} \quad \text{This is an arbitrary value of } V_0$$

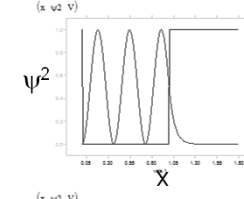
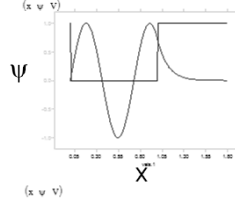
$$E_1 = 0.9 \frac{h^2}{8ma^2}$$



$$E_2 = 3.4 \frac{h^2}{8ma^2}$$



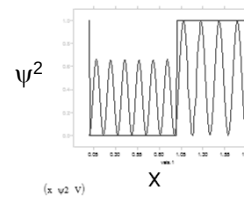
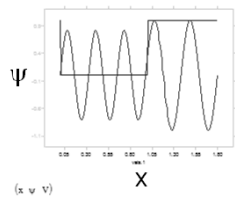
$$E_3 = 7.6 \frac{h^2}{8ma^2}$$



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$$V_0 = 30 \frac{h^2}{8ma^2}$$

$$E_6 = 38.2 \frac{h^2}{8ma^2}$$



What happened??

Why is the wavefunction so different?

The condition for the earlier solution, $E < V_0$,
is no longer valid.

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Region I
 ψ_I

Region II
 ψ_{II}

$V_0 = 30 \frac{h^2}{8ma^2}$
 $V(x) \rightarrow \infty \quad x < 0$
 $V(x) = 0 \quad 0 \leq x \leq a$
 $V(x) = V_0 \quad x > a$

$E > V_0$

$E_6 = 38.2 \frac{h^2}{8ma^2}$

Region I

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_I}{dx^2} + 0 = E\psi_I$$

$$\frac{d^2\psi_I}{dx^2} = -\frac{2mE}{\hbar^2} \psi_I = -\text{const} \cdot \psi_I$$

↓

$$\psi_I = A \sin(\alpha x) + B \cos(\alpha x)$$

Region II

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_{II}}{dx^2} + V_0\psi_{II} = E\psi_{II}$$

$$\frac{d^2\psi_{II}}{dx^2} = -\frac{2m}{\hbar^2} (E - V_0) \psi_{II} = +\cancel{\text{const}} \cdot \psi_{II}$$

↓

$$\psi_{II} = C \sin(\beta x) + D \cos(\beta x)$$

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PIB with central barrier: Tunneling

Preliminary: Potential Energy Barriers in Classical Mechanics

Bowling Ball

$m = 16 \text{ lb} = 7.3 \text{ kg}$
 $v = 30 \text{ mph} = 13.4 \text{ m/s}$

$KE = \frac{1}{2}mv^2 = 650 \text{ J}$

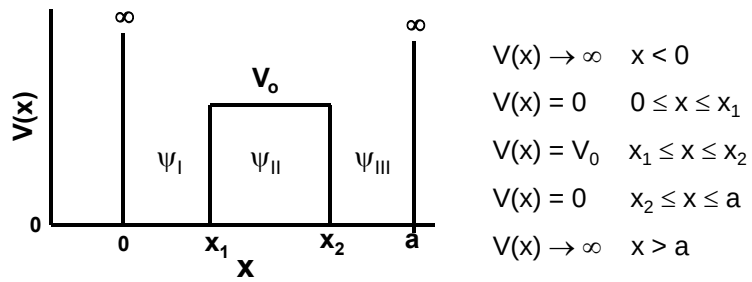
$V_0 = mgh = 1430 \text{ J}$

$h = 20 \text{ m}$

Will the bowling ball make it over the hill? Of course not!!

In classical mechanics, a particle cannot get to a position in which the potential energy is greater than the particle's total energy.

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I'll just show the Boundary Conditions and graphs of the results.

BC: $x=0$

$$\psi_I(0) = 0$$

BC's: $x=x_1$

$$\psi_I(x_1) = \psi_{II}(x_1)$$

BC's: $x=x_2$

$$\psi_{II}(x_2) = \psi_{III}(x_2)$$

BC: $x=a$

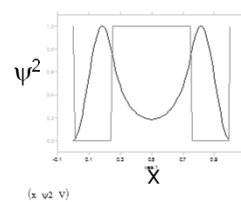
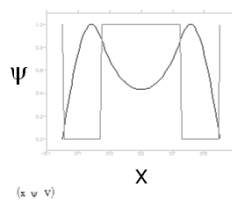
$$\psi_{III}(a) = 0$$

$$\left(\frac{d\psi_I}{dx} \right)_{x_1} = \left(\frac{d\psi_{II}}{dx} \right)_{x_1} \quad \left(\frac{d\psi_{II}}{dx} \right)_{x_2} = \left(\frac{d\psi_{III}}{dx} \right)_{x_2}$$

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$$V_0 = 20 \frac{h^2}{8ma^2}$$

$$E_1 = 7.2 \frac{h^2}{8ma^2}$$



Note that there is a significant probability of finding the particle inside the barrier, even though $V_0 > E$.

This means that the particle can get from one side of the barrier to the other by **tunneling** through the barrier.

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We have just demonstrated the quantum mechanical phenomenon called **tunneling**, in which a particle can be in a region of space where the potential energy is higher than the total energy of the particle.

This is not simply an abstract phenomenon, but is known to occur in many areas of Chemistry and Physics, including:

- Ammonia inversion (the ammonia clock)
- Kinetic rate constants
- Charge carriers in semiconductor devices
- Nuclear radioactive decay
- Scanning Tunneling Microscopy (STM)

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Outline

- The Classical Particle in a Box (PIB)
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- PIB and the Color of Vegetables
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- Statistical Thermodynamics: Translational contributions to the thermodynamic properties of gases.

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Carrots are Orange.

Tomatoes are Red.

But why??

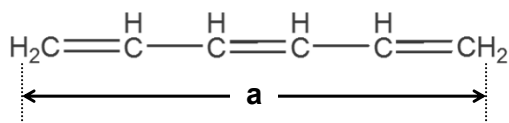
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Free Electron Molecular Orbital (FEMO) Model

So, does the solution to the quantum mechanical “particle in a box” serve any role other than to torture P. Chem. students???

Yes!!

To a good approximation, the π electrons in conjugated polyalkenes are free to move within the confines of the π orbital system.



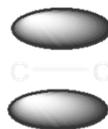
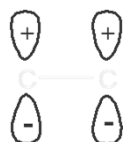
Notes: Estimation of the box length, a , will be discussed later.

Each carbon in this conjugated system contributes 1 π electron. Thus, there are 6 electrons in the π -system of 1,3,5-hexatriene (above)

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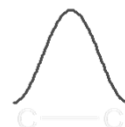
π Bonding in Ethylene

Bonding (π) Orbital



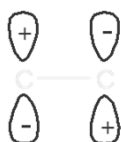
Maximum electron density between C's

PIB (ψ_1^2)



Maximum electron density between C's

Anti-bonding (π^*) Orbital



Electron density node between C's

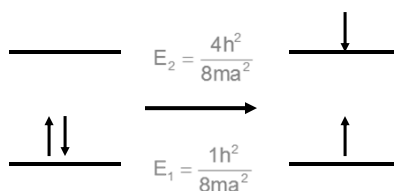
PIB (ψ_2^2)



Electron density node between C's

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$\pi \rightarrow \pi^*$ Transition in Ethylene using FEMO

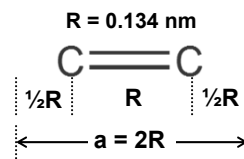


$$\Delta E = E_2 - E_1 = \frac{4h^2}{8ma^2} - \frac{1h^2}{8ma^2} = \frac{3h^2}{8ma^2}$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$m = 9.11 \times 10^{-31} \text{ kg}$$

$$a = ??? = 0.268 \text{ nm}$$



It is common (although not universal) to assume that the π electrons are free to move approximately $\frac{1}{2}$ bond length beyond each outermost carbon.

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$$\Delta E = \frac{3h^2}{8ma^2} = \frac{3(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.11 \times 10^{-31} \text{ kg})(0.268 \times 10^{-9} \text{ m})^2} = 2.52 \times 10^{-18} \text{ J}$$

$$\text{Units: } \frac{\text{J}^2 \cdot \text{s}^2}{\text{kg} \cdot \text{m}^2} = \frac{\text{J} \cdot \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} \cdot \text{s}^2}{\text{kg} \cdot \text{m}^2} = \text{J}$$

Calculation of λ_{max}

$$\Delta E = E_{\text{phot}} = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{2.52 \times 10^{-18} \text{ J}}$$

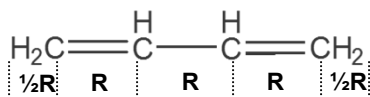
$$\lambda = 7.9 \times 10^{-8} \text{ m} \approx 80 \text{ nm}$$

$$\lambda(\text{exp}) = 190 \text{ nm}$$

The difficulty with applying FEMO to ethylene is that the result is extremely sensitive to the assumed box length, a .

Slide 53

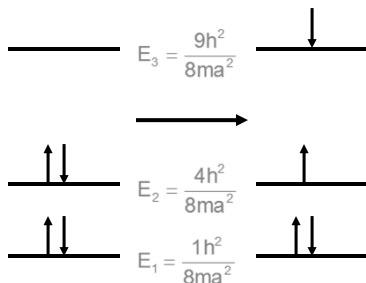
Application of FEMO to 1,3-Butadiene



It is common to use $R = 0.14 \text{ nm}$ (the C-C bond length in benzene, where the bond order is 1.5) as the average bond length in conjugated polyenes.

$$L = 3 \cdot R + 2 \cdot (\frac{1}{2}R) = 4 \cdot R$$

$$L = 4 \cdot 0.14 \text{ nm} = 0.56 \text{ nm}$$



$$\Delta E = E_3 - E_2 = \frac{9h^2}{8ma^2} - \frac{4h^2}{8ma^2} = \frac{5h^2}{8ma^2}$$

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$$\Delta E = \frac{5h^2}{8ma^2} = \frac{5(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.11 \times 10^{-31} \text{ kg})(0.56 \times 10^{-9} \text{ m})^2} = 9.62 \times 10^{-19} \text{ J}$$

Calculation of λ_{max}

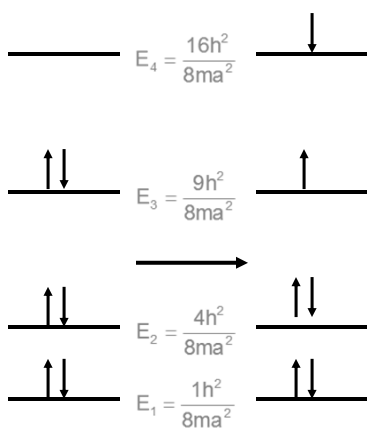
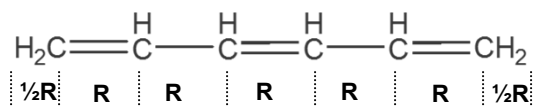
$$\Delta E = E_{\text{phot}} = \frac{hc}{\lambda} \rightarrow \lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{9.62 \times 10^{-19} \text{ J}}$$

$$\lambda = 2.07 \times 10^{-7} \text{ m} \approx 207 \text{ nm}$$

$$\lambda(\text{exp}) = 217 \text{ nm}$$

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Application of FMO to 1,3,5-Hexatriene



$$a = 5 \cdot R + 2 \cdot (\frac{1}{2}R) = 6 \cdot R$$

$$a = 6 \cdot 0.14 \text{ nm} = 0.84 \text{ nm}$$

$$\Delta E = E_4 - E_3 = \frac{16h^2}{8ma^2} - \frac{9h^2}{8ma^2} = \frac{7h^2}{8ma^2}$$

$$\Delta E = 5.98 \times 10^{-19} \text{ J}$$

$$\lambda(\text{exp}) = 258 \text{ nm}$$

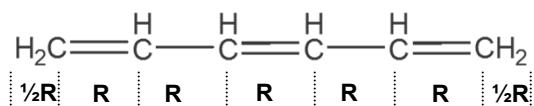
$$\lambda = 332 \text{ nm}$$

Problem worked out in detail in Chapter 3 HW

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The Box Length

Hexatriene



$$a = 5 \cdot R + 2 \cdot (\frac{1}{2}R) = 6 \cdot R$$

General: $a = nb \cdot R + 2 \cdot (\frac{1}{2}R) = (nb+1) \cdot R$ $R = 1.40 \text{ \AA} = 0.14 \text{ nm}$

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Outline

- The Classical Particle in a Box (PIB)
- The Quantum Mechanical PIB
- PIB Properties
- Other PIB Models
- The Free Electron Molecular Orbital (FEMO) Model
- **PIB and the Color of Vegetables**
- Multidimensional Systems: The 2D PIB and 3D PIB
- Statistical Thermodynamics: Translational contributions to the thermodynamic properties of gases.

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PIB and the Color of Vegetables

Introduction

The FEMO model predicts that the $\pi \rightarrow \pi^*$ absorption wavelength, λ , increases with the number of double bonds, #DB

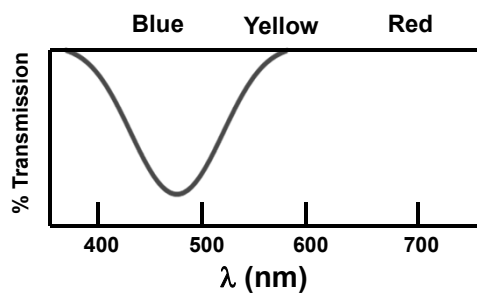
Compound	#DB	$\lambda(\text{FEMO})$
Ethylene	1	80 nm
Butadiene	2	207
Hexatriene	3	333

This is because: $\Delta E \propto \frac{(N+1)^2 - N^2}{a^2} \overset{\text{roughly}}{\propto} \frac{nb}{(nb)^2} \propto \frac{1}{nb}$ N = # of electron pairs

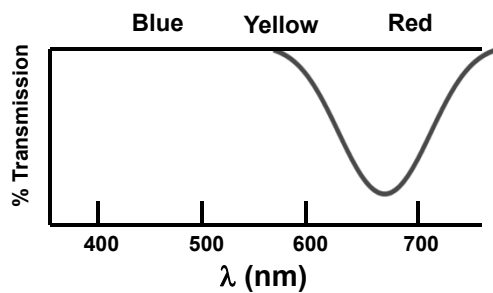
and: $\lambda \propto \frac{1}{\Delta E} \propto nb$

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Light Absorption and Color



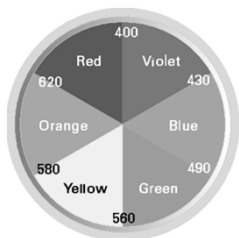
If a substance absorbs light in the blue region of the visible spectrum, the color of the transmitted (or reflected) light will be red.



If a substance absorbs light in the red region of the visible spectrum, the color of the transmitted (or reflected) light will be blue.

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Conjugated π Systems and the Color of Substances



White light contains all wavelengths of visible radiation ($\lambda = 400 - 700 \text{ nm}$)

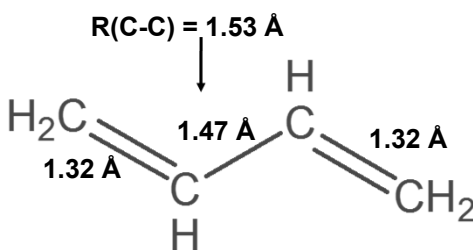
If a substance absorbs certain wavelengths, then the remaining light is reflected, giving the appearance of the complementary color.

e.g. a substance absorbing violet light appears to be yellow in color.

Molecule	No. of Conj. Doub. Bonds	λ_{max}	Region
Ethylene	1	190 nm	UV
1,3-Butadiene	2	217	UV
1,3,5-Hexatriene	3	258	UV
β -Carotene	11	~ 450	Vis. Carrots
Lycopene	13	~ 500	Vis. Tomatoes

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Structure of Ground State Butadiene

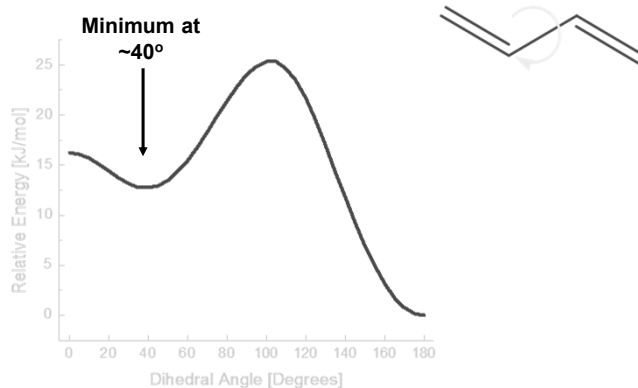


As well known, there is a degree of electron delocalization between the conjugated double bonds, giving some double bond character to the central bond.

Calculation: HF/6-31G(d) – 1 minute

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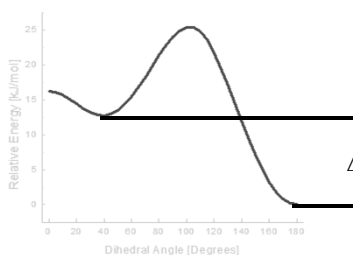
Potential Energy Surface (PES) of Ground State Butadiene



Calculation: HF/6-31G(d) – 37 optimizations – 25 minutes

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Energy Difference Between Trans and “Cis”-Butadiene



$$\Delta E(\text{cal}) = E_{\text{cis}} - E_{\text{trans}} = 12.7 \text{ kJ/mol}$$

Experiment

At room temperature (298 K), butadiene is a mixture with approximately 97% of the molecules in the trans conformation (and 3% “cis”).

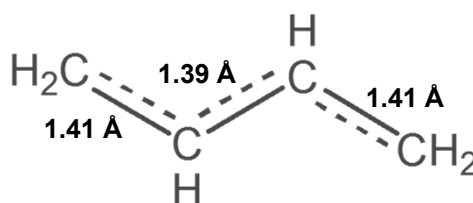
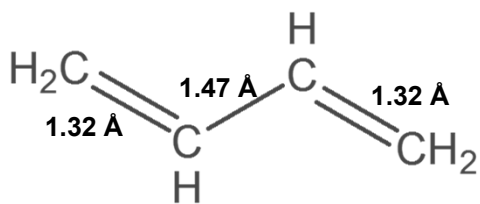
$$\frac{N_{\text{cis}}}{N_{\text{trans}}} = e^{\frac{-\Delta E(\text{exp})}{RT}} \longrightarrow \Delta E(\text{exp}) = -RT \ln \left(\frac{N_{\text{cis}}}{N_{\text{trans}}} \right)$$

$$\Delta E(\text{exp}) = -(8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K})(298 \text{ K}) \ln \left(\frac{0.03}{0.97} \right) = 8.6 \text{ kJ/mol}$$

We could get very close to experiment by using a higher level of theory.

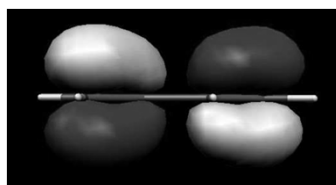
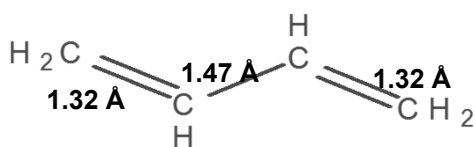
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Structure of Excited State Butadiene



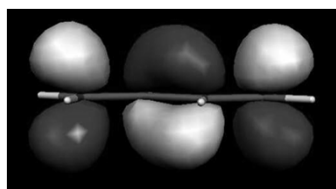
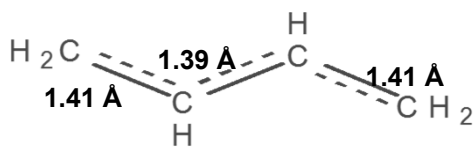
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Structure of Excited State Butadiene



HOMO

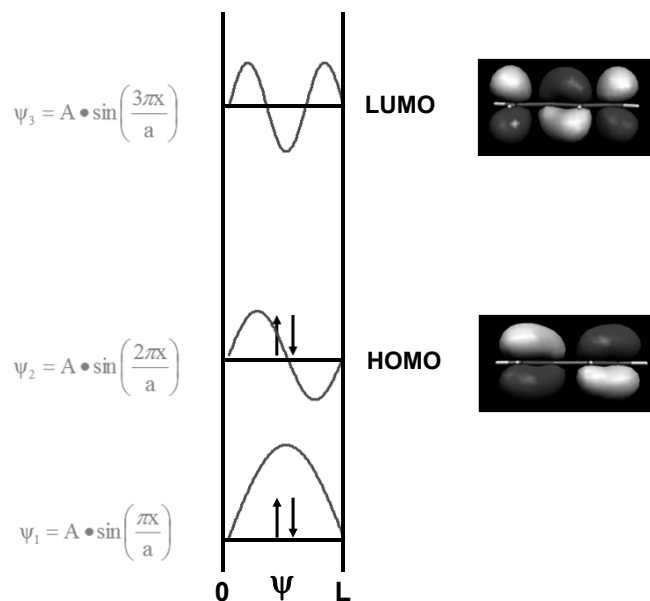
$\pi \rightarrow \pi^*$ Transition



LUMO

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Comparison of FEMO and QM Wavefunctions



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Outline

- The Classical Particle in a Box (PIB)
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- Statistical Thermodynamics: Translational contributions to the thermodynamic properties of gases.

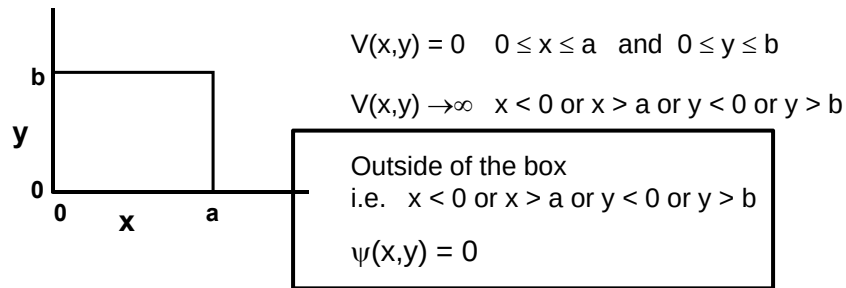
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Multidimensional Systems: The 2D PIB

The 2D Hamiltonian: $H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + V(x,y)$

The 2D Schr. Eqn.: $-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x,y) + V(x,y)\psi(x,y) = E\psi(x,y)$

The Potential Energy



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Solution: Separation of Variables

The 2D Schr. Eqn.: $-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x,y) + V(x,y)\psi(x,y) = E\psi(x,y)$

Inside the box: $V(x,y) = 0 \quad 0 \leq x \leq a \quad \text{and} \quad 0 \leq y \leq b$

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} = H_x + H_y$$

Note: On following slides, I will show how this two dimensional differential equation can be solved by the method of **Separation of Variables**.

You are **NOT** responsible for the details of the solution, but only the assumptions and results.

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Solution: Separation of Variables

Inside the box: $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} = H_x + H_y$

$\uparrow$ $\uparrow$
 H_x H_y

$$H_x \psi(x, y) + H_y \psi(x, y) = E \psi(x, y)$$

Assume: $\psi(x, y) = X(x)Y(y)$

$$H_x X(x)Y(y) + H_y X(x)Y(y) = EX(x)Y(y)$$

$$Y(y)H_x X(x) + X(x)H_y Y(y) = EX(x)Y(y)$$

$$\frac{1}{X(x)} H_x X(x) + \frac{1}{Y(y)} H_y Y(y) = E$$

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Solution: Separation of Variables

Inside the box: $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} = H_x + H_y$

$$\frac{1}{X(x)} H_x X(x) + \frac{1}{Y(y)} H_y Y(y) = E$$

$\uparrow$ $\uparrow$ $\uparrow$
 $f(x)$ $g(y)$ C

If: $f(x) + g(y) = C$

then: $f(x) = C_1$ and $g(y) = C_2$

$$C_1 + C_2 = C$$

$$-\frac{\hbar^2}{2m} \frac{1}{X} \frac{d^2 X}{dx^2} - \frac{\hbar^2}{2m} \frac{1}{Y} \frac{d^2 Y}{dy^2} = E$$

$\parallel$ $\parallel$
 E_x E_y

$E = E_x + E_y$

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$$\begin{array}{ccc}
 -\frac{\hbar^2}{2m} \frac{1}{X} \frac{d^2 X}{dx^2} - \frac{\hbar^2}{2m} \frac{1}{Y} \frac{d^2 Y}{dy^2} = E & & \\
 \downarrow \quad \quad \quad \parallel \quad \quad \quad \parallel & & \\
 -\frac{\hbar^2}{2m} \frac{1}{X} \frac{d^2 X}{dx^2} = E_x & & -\frac{\hbar^2}{2m} \frac{1}{Y} \frac{d^2 Y}{dy^2} = E_y \\
 \downarrow & & \downarrow \\
 -\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X & \text{Range } 0 \leq x \leq a & -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y & \text{Range } 0 \leq y \leq b \\
 \downarrow & & \downarrow \\
 E_x = \frac{n_x^2 \hbar^2}{8ma^2} \quad n_x = 1, 2, 3, \dots & & E_y = \frac{n_y^2 \hbar^2}{8mb^2} \quad n_y = 1, 2, 3, \dots \\
 X(x) = A_x \sin\left(\frac{n_x \pi x}{a}\right) \quad A_x = \sqrt{\frac{2}{a}} & & Y(y) = A_y \sin\left(\frac{n_y \pi y}{b}\right) \quad A_y = \sqrt{\frac{2}{b}} \\
 \\
 \boxed{\psi(x, y) = X(x)Y(y) \quad E = E_x + E_y} & &
 \end{array}$$

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Two Dimensional PIB: Summary

Inside the box: $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} = H_x + H_y$

Assume: $\psi(x, y) = X(x)Y(y)$

$$\begin{array}{ccc}
 -\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X & \text{Range } 0 \leq x \leq a & -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y & \text{Range } 0 \leq y \leq b \\
 \downarrow & & \downarrow & \\
 \boxed{E_x = \frac{n_x^2 \hbar^2}{8ma^2} \quad n_x = 1, 2, 3, \dots} & & \boxed{E_y = \frac{n_y^2 \hbar^2}{8mb^2} \quad n_y = 1, 2, 3, \dots} & \\
 \boxed{X(x) = A_x \sin\left(\frac{n_x \pi x}{a}\right) \quad A_x = \sqrt{\frac{2}{a}}} & & \boxed{Y(y) = A_y \sin\left(\frac{n_y \pi y}{b}\right) \quad A_y = \sqrt{\frac{2}{b}}} & \\
 \\
 \boxed{\psi(x, y) = X(x)Y(y) \quad E = E_x + E_y} & & &
 \end{array}$$

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The Wavefunctions

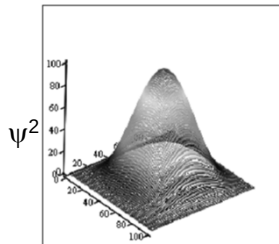
$$\psi(x, y) = X(x) \cdot Y(y) = \left[A_x \sin\left(\frac{n_x \pi x}{a}\right) \right] \cdot \left[A_y \sin\left(\frac{n_y \pi y}{b}\right) \right] \quad A_x = \sqrt{\frac{2}{a}} \quad A_y = \sqrt{\frac{2}{b}}$$

$$\psi(x, y) = \sqrt{\frac{4}{ab}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \quad \begin{array}{ll} n_x = 1, 2, 3, \dots & 0 \leq x \leq a \\ n_y = 1, 2, 3, \dots & 0 \leq y \leq b \end{array}$$

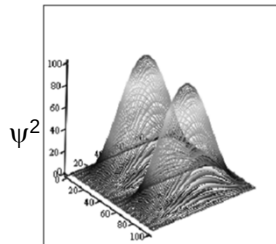
Range

$$0 \leq x \leq a$$

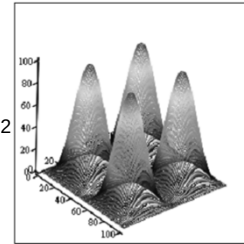
$$0 \leq y \leq b$$



ψ^2
 $n_x = 1 \quad n_y = 1$



ψ^2
 $n_x = 2 \quad n_y = 1$



ψ^2
 $n_x = 2 \quad n_y = 2$

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The Energies: Wavefunction Degeneracy

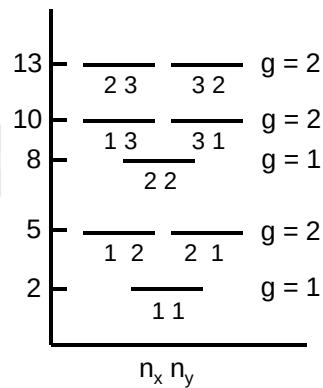
$$E = E_x + E_y = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right) \quad \begin{array}{l} n_x = 1, 2, 3, \dots \\ n_y = 1, 2, 3, \dots \end{array}$$

Square Box

$$a = b$$

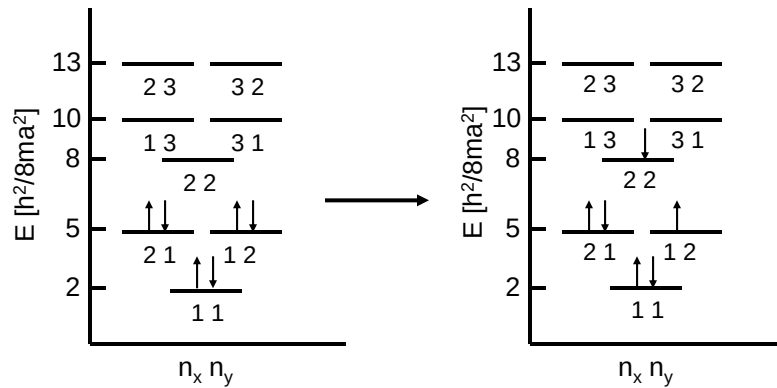
$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2)$$

$$E \left[\frac{h^2}{8ma^2} \right]$$



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Application: $\pi \rightarrow \pi^*$ Absorption in Benzene



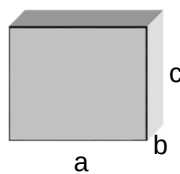
The six π electrons in benzene can be approximated as particles in a square box.

One can estimate the wavelength of the lowest energy $\pi \rightarrow \pi^*$ from the 2D-PIB model (See HW problem)

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Three Dimensional PIB

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) + V(x, y, z) \psi(x, y, z) = E \psi(x, y, z)$$



$$V(x, y, z) = 0 \quad \begin{aligned} 0 &\leq x \leq a \\ 0 &\leq y \leq b \\ 0 &\leq z \leq c \end{aligned}$$

$$V(x, y, z) \rightarrow \infty \quad \text{Outside the box}$$

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

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$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = (H_x + H_y + H_z) \psi = E \psi$$

Assume: $\psi(x, y, z) = X(x) \cdot Y(y) \cdot Z(z)$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 X}{\partial x^2} = E_x X$$



$$E_x = \frac{n_x^2 \hbar^2}{8ma^2} \quad n_x = 1, 2, 3, \dots$$

$$X(x) = A_x \sin\left(\frac{n_x \pi x}{a}\right)$$

$$A_x = \sqrt{\frac{2}{a}}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 Y}{\partial y^2} = E_y Y$$



$$E_y = \frac{n_y^2 \hbar^2}{8mb^2} \quad n_y = 1, 2, 3, \dots$$

$$Y(y) = A_y \sin\left(\frac{n_y \pi y}{b}\right)$$

$$A_y = \sqrt{\frac{2}{b}}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 Z}{\partial z^2} = E_z Z$$



$$E_z = \frac{n_z^2 \hbar^2}{8mc^2} \quad n_z = 1, 2, 3, \dots$$

$$Z(z) = A_z \sin\left(\frac{n_z \pi z}{c}\right)$$

$$A_z = \sqrt{\frac{2}{c}}$$

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$$\psi(x, y, z) = X(x) \cdot Y(y) \cdot Z(z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$n_x = 1, 2, 3, \dots$$

$$n_y = 1, 2, 3, \dots$$

$$n_z = 1, 2, 3, \dots$$

$$E = E_x + E_y + E_z = \frac{n_x^2 \hbar^2}{8ma^2} + \frac{n_y^2 \hbar^2}{8mb^2} + \frac{n_z^2 \hbar^2}{8mc^2} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Cubical Box **Note:** You should be able to determine the energy levels and degeneracies for a cubical box and for various ratios of a:b:c

$$a = b = c$$

$$E = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

Slide 80

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Slide 81

Introduction to Statistical Thermodynamics

Statistical Thermodynamics is the application of Statistical Mechanics to predict thermodynamic properties of molecules.

But this is a Quantum Mechanics course.

Why discuss thermodynamics??

1. The Statistical Thermodynamic formulas used to predict the properties come from the Quantum Mechanical energies for systems such as the PIB, Rigid Rotor (Chap. 4) and Harmonic Oscillator (Chap. 5).
2. Various properties of the molecules, including moments of inertia, vibrational frequencies, and electronic energy levels are required to calculate the thermodynamic properties

Often, these properties are not available experimentally, and must be obtained from QM calculations.

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Some Applications of QM/Stat. Thermo.

- Molecular Heat Capacities [$C_v(T)$ and $C_p(T)$]
- Molecular Enthalpies of Formation [ΔH_f]
- Bond Dissociation Enthalpies [aka Bond Strengths]
- Reaction Enthalpy Changes [ΔH_{rxn}]
- Reaction Entropy Changes [ΔS_{rxn}]
- Reaction Gibbs Energy Changes [ΔG_{rxn}]
and Equilibrium Constants [K_{eq}]
- Kinetics: Activation Enthalpies [$\Delta H^\ddagger$] and Entropies [$\Delta S^\ddagger$]
- Kinetics: Rate Constants

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Output from G-98 geom. opt. and frequency calculation on O₂ (at 298 K)

Frequencies -- 1661.9057

QCISD/6-311G(d)

- Thermochemistry -

Temperature 298.150 Kelvin, Pressure 1.00000 Atm.
Thermochemistry will use frequencies scaled by 0.9540.
Atom 1 has atomic number 8 and mass 15.99491
Atom 2 has atomic number 8 and mass 15.99491
Molecular mass: 31.98983 amu.
Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	0.00000	41.27885	41.27885
X	0.00000	0.90352	0.42854
Y	0.00000	-0.42854	0.90352
Z	1.00000	0.00000	0.00000

THIS MOLECULE IS A PROLATE SYMMETRIC TOP.
ROTATIONAL SYMMETRY NUMBER 2.
ROTATIONAL TEMPERATURE (KELVIN) 2.09825
ROTATIONAL CONSTANT (GHZ) 43.720719
Zero-point vibrational energy 9483.1 (Joules/Mol)

2.26653 (Kcal/Mol)
VIBRATIONAL TEMPERATURES: 2281.11 (KELVIN)
Zero-point correction= 0.003612 (Hartree/Particle)
Thermal correction to Energy= 0.005976
Thermal correction to Enthalpy= 0.006920
Thermal correction to Gibbs Free Energy= -0.016348
Sum of electronic and zero-point Energies= -150.022558
Sum of electronic and thermal Energies= -150.020195
Sum of electronic and thermal Enthalpies= -150.019250
Sum of electronic and thermal Free Energies= -150.042518

	E (Thermal) KCAL/MOL	CV CAL/MOL-K	S CAL/MOL-K
TOTAL	3.750	5.023	48.972
ELECTRONIC	0.000	0.000	2.183
TRANSLATIONAL	0.889	2.981	36.321
ROTATIONAL	0.592	1.987	10.459
VIBRATIONAL	2.269	0.055	0.008

	Q	LOG10(Q)	LN(Q)
TOTAL BOT	0.330741D+08	7.519488	17.314260
TOTAL V=0	0.151654D+10	9.180853	21.139696
VIB (BOT)	0.218193D-01	-1.661159	-3.824960
VIB (V=0)	0.100048D+01	0.000207	0.000476
ELECTRONIC	0.300000D+01	0.477121	1.098612
TRANSLATIONAL	0.711178D+07	6.851978	15.777263
ROTATIONAL	0.710472D+02	1.851547	4.263345

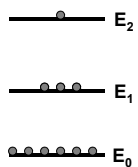
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Mini-Outline for Stat. Thermo. Development

- The Boltzmann Distribution
- The Partition Function (Q)
- Thermodynamic properties in terms of Q
- Partition function for non-interacting molecules
- The molecular partition function (q)
- The total partition function for a system of molecules (Q)
- The translational partition function
- Translational contributions to thermodynamic properties

Slide 85

The Boltzmann Distribution



$$p(E_i) \propto e^{-\frac{E_i}{kT}} \quad k = \frac{R}{N_A} = 1.3806 \times 10^{-23} \text{ J/K}$$

$$\approx 1.38 \times 10^{-23} \text{ J/K}$$

$$p(E_i) = A e^{-\frac{E_i}{kT}}$$

Normalization

$$\sum_i p(E_i) = 1 = A \sum_i e^{-\frac{E_i}{kT}} \longrightarrow A = \left(\sum_i e^{-\frac{E_i}{kT}} \right)^{-1}$$

Therefore:

$$p(E_i) = \frac{e^{-\frac{E_i}{kT}}}{\sum_i e^{-\frac{E_i}{kT}}} = \frac{e^{-\frac{E_i}{kT}}}{Q}$$

Boltzmann Distribution

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The Partition Function

$$p(E_i) = \frac{e^{-\frac{E_i}{kT}}}{Q} \quad \text{where} \quad Q = \sum_i e^{-\frac{E_i}{kT}}$$

Q is called the "Partition Function". Thermodynamic properties, including, U, C_v, H, S, A, G, can be calculated from Q.

Alternative Form

One can sum over energy "levels" rather than individual energy states.

$$p(E_j) = \frac{g_j e^{-\frac{E_j}{kT}}}{Q} \quad \text{where} \quad Q = \sum_{j(\text{level})} g_j e^{-\frac{E_j}{kT}}$$

g_j is the degeneracy of the j'th energy level, E_j

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Thermodynamic Properties from Q: Internal Energy (U)

$$U = \langle E \rangle = \sum_i E_i p(E_i) = \frac{\sum_i E_i e^{-\frac{E_i}{kT}}}{Q} \quad Q = \sum_i e^{-\frac{E_i}{kT}}$$

$$\left(\frac{\partial \ln(Q)}{\partial T} \right)_{V,N} = \frac{1}{Q} \left(\frac{\partial Q}{\partial T} \right)_{V,N} = \frac{1}{Q} \left(\frac{\partial \sum_i e^{-\frac{E_i}{kT}}}{\partial T} \right)_{V,N}$$

Derivative at constant V,N because energy depends on volume and No. of Molecules

$$= \frac{1}{Q} \sum_i \left(\frac{\partial e^{-\frac{E_i}{kT}}}{\partial T} \right)_{V,N} = \frac{1}{Q} \sum_i \left(\frac{E_i}{kT^2} \right) e^{-\frac{E_i}{kT}}$$

$$U = \langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} = \sum_i E_i \frac{e^{-\frac{E_i}{kT}}}{Q} = \sum_i E_i p(E_i)$$

NOTE: On an exam, you will be provided with any required SM formula for a thermodynamic property (e.g. the above expression for U)

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Thermodynamic Properties from Q: Other Properties

Constant Volume Heat Capacity: $C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N}$

The math involved in relating other thermodynamic properties to Q is a bit more involved.

It can be found in standard P. Chem. texts; e.g. *Physical Chemistry*, by R. A. Alberty and R. J. Silbey, Chap. 17

I'll just give the results.

Pressure: $P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_T$

Entropy: $S = k \ln Q + \frac{U}{T}$

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Thermodynamic Properties from Q: Other Properties

Enthalpy: $H = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} + kT \left(\frac{\partial \ln Q}{\partial \ln V} \right)_{T,N}$

Note: If $Q \neq f(V)$, then $H = U$

Constant Pressure Heat Capacity: $C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N}$

Helmholtz Energy: $A = U - TS = -kT \ln Q$

Gibbs Energy: $G = H - TS = -kT \ln Q + kT \left(\frac{\partial \ln Q}{\partial \ln V} \right)_{T,N}$

Note: If $Q \neq f(V)$, then $G = A$

NOTE: On an exam, you will be provided with any required SM formula for a thermodynamic property.

Slide 90

Partition Function for Non-interacting Molecules (aka IDG)

Case A: Distinguishable Molecules

The microstate of molecule 'a' is given by j, of molecule 'b' by k...

$$E_i = \epsilon_{a,j} + \epsilon_{b,k} + \epsilon_{c,l} + \dots$$

a, b, c, ... designates the molecule

i, j, k, ... designates the molecule's set of energies (e.g. trans., rot., vib., ...)

$$Q = \sum_i e^{-\frac{E_i}{kT}} = \sum_{j,k,l,\dots} e^{-\frac{\epsilon_{a,j} + \epsilon_{b,k} + \epsilon_{c,l} + \dots}{kT}} = \sum_{j,k,l,\dots} e^{-\frac{\epsilon_{a,j}}{kT}} \cdot e^{-\frac{\epsilon_{b,k}}{kT}} \cdot e^{-\frac{\epsilon_{c,l}}{kT}} \dots$$

$$Q = \sum_j e^{-\frac{\epsilon_{a,j}}{kT}} \cdot \sum_k e^{-\frac{\epsilon_{b,k}}{kT}} \cdot \sum_l e^{-\frac{\epsilon_{c,l}}{kT}} \dots$$

$$Q = q_a \cdot q_b \cdot q_c \dots \quad \text{where} \quad q_a = \sum_j e^{-\frac{\epsilon_{a,j}}{kT}}, \text{etc.}$$

If the molecules are the same, $q_a = q_b = q_c = \dots = q$

Therefore, for N molecules we have: $Q = q^N$

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Partition Function for Non-interacting Molecules (aka IDG)

Case B: Indistinguishable Molecules

Distinguishable Molecules: $Q = q^N$

In actuality, one cannot distinguish between different molecules in a gas.

Let's say that there is one state in which the quantum numbers for molecule 'a' are $m_1, n_1, \dots$ and for molecule 'b' are $m_2, n_2, \dots$

This state is the same as one in which the quantum numbers for molecule 'a' are $m_2, n_2, \dots$ and for molecule 'b' are $m_1, n_1, \dots$

However, the two sets of quantum numbers above would give two terms in the above equation for Q. i.e. we've overcounted the number of terms.

It can be shown that the overcounting can be eliminated by dividing Q by N! (the number of ways of permuting N particles). Therefore,

Indistinguishable Molecules:

$$Q = \frac{q^N}{N!}$$

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The Molecular Partition Function (q)

To a good approximation, the Hamiltonian for a molecule can be written as the sum of translational, rotational, vibrational and electronic Hamiltonians:

$$H = H^{tran} + H^{rot} + H^{vib} + H^{elect}$$

Therefore, the molecule's total energy (ϵ_i) is the sum of individual energies:

$$\epsilon_i = \epsilon_j^{tran} + \epsilon_k^{rot} + \epsilon_l^{vib} + \epsilon_m^{elect}$$

The partition function is:

$$q = \sum_i e^{-\frac{\epsilon_i}{kT}} = \sum_j \sum_k \sum_l \sum_m e^{-\frac{\epsilon_j^{tran} + \epsilon_k^{rot} + \epsilon_l^{vib} + \epsilon_m^{elect}}{kT}} = \sum_j \sum_k \sum_l \sum_m e^{-\frac{\epsilon_j^{tran}}{kT}} \cdot e^{-\frac{\epsilon_k^{rot}}{kT}} \cdot e^{-\frac{\epsilon_l^{vib}}{kT}} \cdot e^{-\frac{\epsilon_m^{elect}}{kT}}$$

$$q = \sum_j e^{-\frac{\epsilon_j^{tran}}{kT}} \cdot \sum_k e^{-\frac{\epsilon_k^{rot}}{kT}} \cdot \sum_l e^{-\frac{\epsilon_l^{vib}}{kT}} \cdot \sum_m e^{-\frac{\epsilon_m^{elect}}{kT}}$$

$$q = q^{tran} \cdot q^{rot} \cdot q^{vib} \cdot q^{elect} \quad \text{where } q^{tran} = \sum_j e^{-\frac{\epsilon_j^{tran}}{kT}}, \text{ etc.}$$

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The Total Partition Function (Q)

$$Q = \frac{q^N}{N!} \quad q = q^{tran} \cdot q^{rot} \cdot q^{vib} \cdot q^{elect}$$



$$Q = \frac{(q^{tran} \cdot q^{rot} \cdot q^{vib} \cdot q^{elect})^N}{N!}$$

$$Q = \frac{(q^{tran})^N}{N!} \cdot (q^{rot})^N \cdot (q^{vib})^N \cdot (q^{elect})^N = Q^{tran} \cdot Q^{rot} \cdot Q^{vib} \cdot Q^{elect}$$

$$Q^{tran} = \frac{(q^{tran})^N}{N!}$$

It can be shown that the term, $1/N!$ belongs to Q^{tran}

$$Q^{rot} = (q^{rot})^N$$

$$Q^{vib} = (q^{vib})^N$$

$$Q^{elect} = (q^{elect})^N$$

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Thermodynamic Properties of Molecules

$$Q = Q^{tran} \cdot Q^{rot} \cdot Q^{vib} \cdot Q^{elect}$$

The expressions for the thermodynamic properties all involve $\ln Q$; e.g.

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} = kT^2 \left(\frac{\partial \ln [Q^{tran} \cdot Q^{rot} \cdot Q^{vib} \cdot Q^{elect}]}{\partial T} \right)_{V,N}$$

$$U = kT^2 \left(\frac{\partial \ln Q^{tran}}{\partial T} \right)_{V,N} + kT^2 \left(\frac{\partial \ln Q^{rot}}{\partial T} \right)_{V,N} + kT^2 \left(\frac{\partial \ln Q^{vib}}{\partial T} \right)_{V,N} + kT^2 \left(\frac{\partial \ln Q^{elect}}{\partial T} \right)_{V,N}$$

$$U = U^{tran} + U^{rot} + U^{vib} + U^{elect}$$

where $U^{tran} = kT^2 \left(\frac{\partial \ln Q^{tran}}{\partial T} \right)_{V,N}$, etc.

Similarly $C_V = C_V^{tran} + C_V^{rot} + C_V^{vib} + C_V^{elect}$
etc.

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The Translational Partition Function for an Ideal Gas

Consider that the molecules of a gas are confined in a cubical box of length 'a' on each side.*

The energy levels are given by: $E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$

The molecular translational partition function is:

$$q^{tran} = \sum_i e^{-\frac{E_i^{tran}}{kT}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\alpha n_x^2} e^{-\alpha n_y^2} e^{-\alpha n_z^2}, \quad \alpha = \frac{h^2}{8ma^2 kT}$$

$$q^{tran} = \sum_{n_x=1}^{\infty} e^{-\alpha n_x^2} \cdot \sum_{n_y=1}^{\infty} e^{-\alpha n_y^2} \cdot \sum_{n_z=1}^{\infty} e^{-\alpha n_z^2} = \left(\sum_{n=1}^{\infty} e^{-\alpha n^2} \right)^3$$

*One gets the same result if the box is not assumed to be cubical, with a bit more algebra.

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$$q^{tran} = \left(\sum_{n=1}^{\infty} e^{-\alpha n^2} \right)^3 \quad \alpha = \frac{h^2}{8ma^2kT}$$

One can show that the summand (term in summation) is an extremely slowly varying function of n.

For example, for O₂ [M = 32x10⁻³ kg/mol] in a 10 cm (0.1 m) box at 298 K:

$$\alpha = \frac{h^2}{8ma^2kT} \approx 2.5 \times 10^{-20} \quad \Delta[Expon] = \alpha(n+1)^2 - \alpha n^2 = \alpha(2n+1)$$

n	$\Delta[Expon]$
1	8×10^{-20}
10 ⁶	5×10^{-14}
10 ¹²	5×10^{-8}

The extremely slowly changing exponent results from the fact that:

$$\frac{\Delta \varepsilon}{kT} \ll 1 \quad \text{or} \quad \Delta \varepsilon \ll kT$$

$\Delta \varepsilon$ is the change in energy between successive quantum levels.

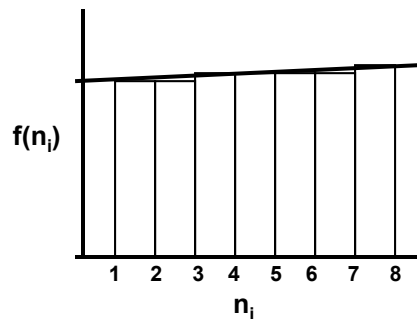
This leads to an important simplification in the expression for q^{tran} .

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Relation between sum and integral for slowly varying functions

If $f(n_i)$ is a slowly varying function of n_i , then one may replace the sum by the integral:

$$\sum_{i=n_1}^{n_2} f(n_i) = \int_{n_1}^{n_2} f(n) dn$$



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$$q^{tran} = \left(\sum_{n=1}^{\infty} e^{-\alpha n^2} \right)^3 = \left(\int_0^{\infty} e^{-\alpha n^2} dn \right)^3 \quad \alpha = \frac{h^2}{8ma^2kT}$$

$$\downarrow \int_0^{\infty} e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = \left(\frac{\pi}{4\alpha} \right)^{1/2}$$

$$q^{tran} = \left[\left(\frac{\pi}{4\alpha} \right)^{1/2} \right]^3 = \left(\frac{\pi}{4 \left(\frac{h^2}{8ma^2kT} \right)} \right)^{3/2} = \left(\frac{2\pi ma^2kT}{h^2} \right)^{3/2} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} a^3$$

$$q^{tran} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

V is the volume of the box

Note: The translation partition function is the only one which depends upon the system's volume.

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$$q^{tran} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \quad \text{This is the translational partition function for a single molecule.}$$

A note on the calculation of V (in SI Units)

One is normally given the temperature and pressure, from which one can calculate V from the IDG law.

$$V = \frac{nRT}{P} \quad R = 8.31 \text{ J/mol-K} = 8.31 \text{ Pa-m}^3/\text{mol-K}$$

One should use the pressure in Pa [1 atm. = 1.013x10⁵ Pa], in which case V is given in m³ [SI Units]

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$$q^{tran} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

Calculate q^{tran} for one mole of O_2 at 298 K and 1 atm.

$$m = \frac{M}{N_A} = \frac{32 \times 10^{-3} \text{ kg/mol}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 5.32 \times 10^{-26} \text{ kg}$$

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(8.31 \text{ Pa} \cdot \text{m}^3 / \text{mol} \cdot \text{K})(298 \text{ K})}{1.013 \times 10^5 \text{ Pa}}$$

$$V = 2.45 \times 10^{-2} \text{ m}^3$$

$$q^{tran} = \left[\frac{2(3.14)(5.32 \times 10^{-26} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \cdot (2.45 \times 10^{-2} \text{ m}^3)$$

$$q^{tran} = [3.13 \times 10^{21} \text{ m}^{-2}]^{3/2} \cdot (2.45 \times 10^{-2} \text{ m}^3) = 4.28 \times 10^{30}$$

$$\begin{aligned} N_A &= 6.02 \times 10^{23} \text{ mol}^{-1} \\ h &= 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \\ k &= 1.38 \times 10^{-23} \text{ J/K} \\ R &= 8.31 \text{ Pa} \cdot \text{m}^3 / \text{mol} \cdot \text{K} \\ M &= 32 \text{ g/mol} \\ 1 \text{ J} &= 1 \text{ kg} \cdot \text{m}^2 / \text{s}^2 \\ 1 \text{ atm.} &= 1.013 \times 10^5 \text{ Pa} \end{aligned}$$

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$$q^{tran} = \left[\frac{2(3.14)(5.32 \times 10^{-26} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \cdot (2.45 \times 10^{-2} \text{ m}^3) = 4.28 \times 10^{30}$$

$$\begin{aligned} \text{Units: } q^{tran} &= \left[\frac{\text{kg} \cdot (\text{J/K}) \cdot \text{K}}{\text{J}^2 \cdot \text{s}^2} \right] \cdot \text{m}^3 = \left[\frac{\text{kg}}{\text{J} \cdot \text{s}^2} \right]^{3/2} \cdot \text{m}^3 = \left[\frac{\text{kg}}{(\text{kg} \cdot \text{m}^2 / \text{s}^2)(\text{s}^2)} \right]^{3/2} \cdot \text{m}^3 \\ &= [\text{m}^{-2}]^{3/2} \cdot \text{m}^3 = 1 \text{ (Unitless)} \end{aligned}$$

G-98 Output

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

	Q	LOG10(Q)	LN(Q)
TOTAL BOT	0.330741D+08	7.519488	17.314260
TOTAL V=0	0.151654D+10	9.180853	21.139696
VIB (BOT)	0.218193D-01	-1.661159	-3.824960
VIB (V=0)	0.100048D+01	0.000207	0.000476
ELECTRONIC	0.300000D+01	0.477121	1.098612
TRANSLATIONAL	0.711178D+07	6.851978	15.777263
ROTATIONAL	0.710472D+02	1.851547	4.263345

Their output is actually

q^{tran} / N_A

$$\frac{q^{tran}}{N_A} = \frac{4.28 \times 10^{30}}{6.02 \times 10^{23}} = 7.13 \times 10^6$$

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$$q^{tran} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \quad \text{This is the translational partition function for a single molecule.}$$

Partition Function for a system with $N (=nN_A)$ molecules

$$Q^{tran} = \frac{(q^{tran})^N}{N!} = (q^{tran})^N \frac{e^N}{N^N} = \left[\frac{q^{tran} \cdot e}{N} \right]^N$$

$$\uparrow$$

$$N! = N^N / e^N$$

Stirling's Approximation

$$Q^{tran} = \left[\frac{q^{tran} \cdot e}{N} \right]^N = \left[\frac{\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V \cdot e}{N} \right]^N$$

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Calculate $\ln(Q^{tran})$ for one mole of O_2 at 298 K and 1 atm.

$$q^{tran} = 4.28 \times 10^{30}$$

$$Q^{tran} = \left[\frac{q^{tran} \cdot e}{N} \right]^N = \left[\frac{\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V \cdot e}{N} \right]^N$$

$$\ln(Q^{tran}) = \ln \left[\frac{q^{tran} \cdot e}{N} \right]^N = nN_A \ln \left[\frac{q^{tran} \cdot e}{N} \right]$$

$$= (1 \text{ mol}) (6.02 \times 10^{23} \text{ mol}^{-1}) \ln \left[\frac{(4.28 \times 10^{30})(2.72)}{(1 \text{ mol})(6.02 \times 10^{23} \text{ mol}^{-1})} \right] = 1.01 \times 10^{25}$$

This is an extremely large number.

However, as we'll see shortly, $\ln(Q)$ is multiplied by the very small number (k) in the thermodynamics formulas.

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Translational Contributions to the Thermodynamic Properties of Ideal Gases

Preliminary

$$Q^{tran} = \left[\frac{q^{tran} \cdot e}{N} \right]^N = \left[\frac{\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V \cdot e}{N} \right]^N$$

$$\ln(Q^{tran}) = \frac{3}{2}N \cdot \ln(2\pi mk / h^2) + \frac{3}{2}N \cdot \ln(T) + N \ln(V) + N - N \ln(N)$$

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$$\ln(Q^{tran}) = \frac{3}{2}N \cdot \ln(2\pi mk / h^2) + \frac{3}{2}N \cdot \ln(T) + N \ln(V) + N - N \ln(N)$$

The Ideal Gas Equation

$$P^{tran} = P = kT \left(\frac{\partial \ln Q^{tran}}{\partial V} \right)_T$$

$$P = kT \cdot \frac{N}{V} = kT \cdot \frac{nN_A}{V} = \frac{nRT}{V} \quad (\text{because } R = kN_A)$$

$$\boxed{PV = nRT}$$

Notes: (1) Because none of the other partition functions (rotational, vibrational, or electronic) depend on V, they do not contribute to the pressure.

(2) We end up with the IDG equation because we assumed that the molecules don't interact when we assumed that the total energy is the sum of individual molecules' energies.

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$$\ln(Q^{tran}) = \frac{3}{2}N \cdot \ln(2\pi mk / h^2) + \frac{3}{2}N \cdot \ln(T) + N \ln(V) + N - N \ln(N)$$

Internal Energy

$$U^{tran} = kT^2 \left(\frac{\partial \ln Q^{tran}}{\partial T} \right)_{V,N} = kT^2 \cdot \frac{3N}{2T} = \frac{3}{2}nN_A kT$$

$$U^{tran} = \frac{3}{2}nRT \quad \text{or} \quad \bar{U}^{tran} = \frac{U^{tran}}{n} = \frac{3}{2}RT$$

Molar Internal Energy

This demonstrates the Principle of Equipartition of Translational Internal Energy (1/2RT per translation)

It arose from the assumption that the change in the exponent is very small and the sum can be replaced by an integral.

This is **always** true for translational motions of gases.

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$$\ln(Q^{tran}) = \frac{3}{2}N \cdot \ln(2\pi mk / h^2) + \frac{3}{2}N \cdot \ln(T) + N \ln(V) + N - N \ln(N)$$

Enthalpy

$$H^{tran} = kT^2 \left(\frac{\partial \ln Q^{tran}}{\partial T} \right)_{V,N} + kT \left(\frac{\partial \ln Q^{tran}}{\partial \ln V} \right)_{T,N} = U^{tran} + kT \left(\frac{\partial \ln Q^{tran}}{\partial \ln V} \right)_{T,N}$$

$$H^{tran} = \frac{3}{2}nRT + kTN = \frac{3}{2}nRT + kTnN_A = \frac{3}{2}nRT + nRT$$

$$H^{tran} = \frac{5}{2}nRT \quad \text{or} \quad \bar{H}^{tran} = \frac{H^{tran}}{n} = \frac{5}{2}RT$$

Molar Enthalpy

Note: As noted earlier, if Q is independent of V, then H = U.

This is the case for all partition functions

except Q^{tran}

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$$\bar{U}^{tran} = \frac{3}{2}RT \quad \bar{H}^{tran} = \frac{5}{2}RT$$

Heat Capacities

$$\bar{C}_V^{tran} = \frac{C_V^{tran}}{n} = \left(\frac{\partial \bar{U}^{tran}}{\partial T} \right)_{V,N} = \frac{3}{2}R = 12.47 \text{ J/mol} \cdot \text{K}$$

$$\bar{C}_P^{tran} = \frac{C_P^{tran}}{n} = \left(\frac{\partial \bar{H}^{tran}}{\partial T} \right)_{P,N} = \frac{5}{2}R = 20.79 \text{ J/mol} \cdot \text{K}$$

Experimental Heat Capacities at 298.15 K

Compd. C_P (exp)

Ar 20.79 J/mol-K

O₂ 29.36

SO₃ 50.67

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Output from G-98 geom. opt. and frequency calculation on O₂ (at 298 K)
QCISD/6-311G(d)

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-K	CAL/MOL-K
TOTAL	3.750	5.023	48.972
ELECTRONIC	0.000	0.000	2.183
TRANSLATIONAL 0.889	2.981		36.321
ROTATIONAL	0.592	1.987	10.459
VIBRATIONAL	2.269	0.055	0.008
	Q	LOG10(Q)	LN(Q)
TOTAL BOT	0.330741D+08	7.519488	17.314260
TOTAL V=0	0.151654D+10	9.180853	21.139696
VIB (BOT)	0.218193D-01	-1.661159	-3.824960
VIB (V=0)	0.100048D+01	0.000207	0.000476
ELECTRONIC	0.300000D+01	0.477121	1.098612
TRANSLATIONAL	0.711178D+07	6.851978	15.777263
ROTATIONAL	0.710472D+02	1.851547	4.263345

$$U^{tran}(\text{mol}) = 3/2RT = 3.72 \text{ kJ/mol} = 0.889 \text{ kcal/mol}$$

$$C_V^{tran}(\text{mol}) = 3/2R = 12.47 \text{ J/mol-K} = 2.98 \text{ cal/mol-K}$$

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Entropy

$$S^{tran} = k \ln Q^{tran} + \frac{U^{tran}}{T}$$

$$Q^{tran} = \left[\frac{q^{tran} \cdot e}{N} \right]^N = \left[\frac{\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V \cdot e}{N} \right]^N$$

Earlier, we showed that for one mole of O₂ at 298 K and 1 atm.,

$$\ln(Q^{tran}) = 1.01 \times 10^{25} \text{ mol}^{-1}$$

$$\bar{S}^{tran} = (1.38 \times 10^{-23} \text{ J/K}) (1.01 \times 10^{25} \text{ mol}^{-1}) + \frac{\frac{3}{2} \cdot (8.31 \text{ J/mol} \cdot \text{K}) \cdot T}{T}$$

$$\bar{S}^{tran} = 139.38 + 12.47 = 151.85 \text{ J/mol} \cdot \text{K}$$

$$\text{O}_2: S_{\text{mol}}(\text{exp}) = 205.14 \text{ J/mol} \cdot \text{K at } 298.15 \text{ K}$$

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Output from G-98 geom. opt. and frequency calculation on O₂ (at 298 K)
QCISD/6-311G(d)

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-K	CAL/MOL-K
TOTAL	3.750	5.023	48.972
ELECTRONIC	0.000	0.000	2.183
TRANSLATIONAL	0.889	2.981	36.321
ROTATIONAL	0.592	1.987	10.459
VIBRATIONAL	2.269	0.055	0.008
	Q	LOG10(Q)	LN(Q)
TOTAL BOT	0.330741D+08	7.519488	17.314260
TOTAL V=0	0.151654D+10	9.180853	21.139696
VIB (BOT)	0.218193D-01	-1.661159	-3.824960
VIB (V=0)	0.100048D+01	0.000207	0.000476
ELECTRONIC	0.300000D+01	0.477121	1.098612
TRANSLATIONAL	0.711178D+07	6.851978	15.777263
ROTATIONAL	0.710472D+02	1.851547	4.263345

$$\text{G-98: } S_{\text{mol}}^{tran} = 36.321 \text{ cal/mol} \cdot \text{K} = 151.97 \text{ J/mol} \cdot \text{K}$$

$$\text{Our Calculation (above): } S_{\text{mol}}^{tran} = 151.85 \text{ J/mol} \cdot \text{K}$$

Difference is round-off error and less Sig. Figs. in our calculation.

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Helmholtz Energy

$$\ln(Q^{\text{tran}}) = 1.01 \times 10^{25} \text{ mol}^{-1}$$

For O₂ at 298 K
(one mol):

$$A^{\text{tran}} = U^{\text{tran}} - TS^{\text{tran}} = -kT \ln(Q^{\text{tran}})$$

$$A^{\text{tran}} = -(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})(1.01 \times 10^{25} \text{ mol}^{-1})$$

$$A^{\text{tran}} = -4.154 \times 10^4 \text{ J/mol} = -41.54 \text{ kJ/mol}$$

Gibbs Energy

$$G^{\text{tran}} = H^{\text{tran}} - TS^{\text{tran}} = -kT \ln Q^{\text{tran}} + kT \left(\frac{\partial \ln Q^{\text{tran}}}{\partial \ln V} \right)_{T,N}$$

For O₂ at 298 K
(one mol):

$$= -kT \ln Q^{\text{tran}} + NkT = A + nRT$$

$$G^{\text{tran}} = -4.154 \times 10^4 \text{ J/mol} + (8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K})$$

$$= -3.906 \times 10^4 \text{ J/mol} = -39.06 \text{ kJ/mol}$$

Note: As noted before, if Q is independent of V, then
G = A.

This is the case for all partition functions

except Q^{tran}

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Output from G-98 geom. opt. and frequency calculation on O₂ (at 298 K)

Frequencies -- 1661.9057

QCISD/6-311G(d)

- Thermochemistry -

Temperature 298.150 Kelvin, Pressure 1.00000 Atm.
Thermochemistry will use frequencies scaled by 0.9540.
Atom 1 has atomic number 8 and mass 15.99491
Atom 2 has atomic number 8 and mass 15.99491
Molecular mass: 31.98983 amu.
Principal axes and moments of inertia in atomic units:

	1	2	3
EIGENVALUES --	0.00000	41.27885	41.27885
X	0.00000	0.90352	0.42854
Y	0.00000	-0.42854	0.90352
Z	1.00000	0.00000	0.00000

THIS MOLECULE IS A PROLATE SYMMETRIC TOP.
ROTATIONAL SYMMETRY NUMBER 2.
ROTATIONAL TEMPERATURE (KELVIN) 2.09825
ROTATIONAL CONSTANT (GHZ) 43.720719
Zero-point vibrational energy 9483.1 (Joules/Mol)
2.26653 (Kcal/Mol)

VIBRATIONAL TEMPERATURES: 2281.11 (KELVIN)
Zero-point correction= 0.003612 (Hartree/Particle)
Thermal correction to Energy= 0.005976
Thermal correction to Enthalpy= 0.006920
Thermal correction to Gibbs Free Energy= -0.016348
Sum of electronic and zero-point Energies= -150.022558
Sum of electronic and thermal Energies= -150.020195
Sum of electronic and thermal Enthalpies= -150.019250
Sum of electronic and thermal Free Energies= -150.042518

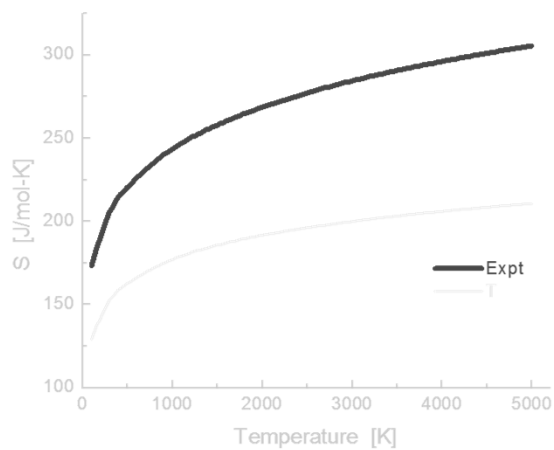
These are thermal contributions
to U, H and G.

They represent the sum of the
translational, rotational, vibrational
and (in some cases) electronic
contributions.

They are given in atomic units (au).
1 au = 2625.5 kJ/mol

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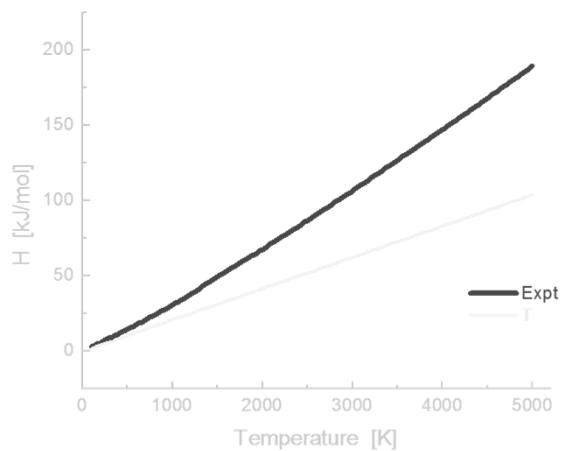
Translational Contributions to O₂ Entropy



Obviously, there are significant additional contributions (future chapters)

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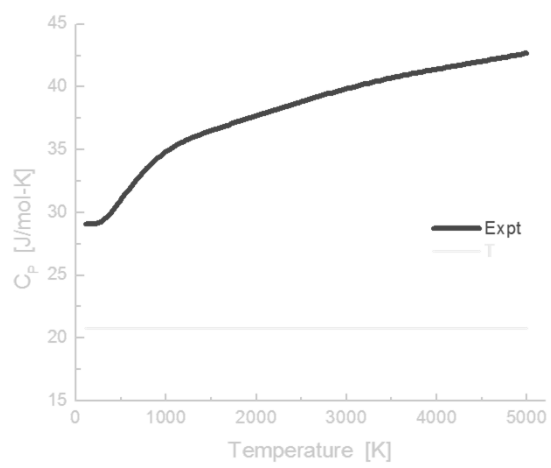
Translational Contributions to O₂ Enthalpy



Obviously, there are significant additional contributions (future chapters)

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Translational Contributions to O₂ Heat Capacity



Obviously, there are significant additional contributions (future chapters)

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