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CODABLE : 93

UNCODABLE : 86

SUBMITTED BY : OJAS SINGH

Chapter 1

Example 1.1 : Codable (Wrong Answer)

Example 1.2 : Codable (Wrong Answer)

Example 1.3 : Uncodable (Non numerical answer)

Example 1.3

If a (123) plane intersects the x axis at $6a$, what are its intercepts on the y and z axes?

The Miller indices h, k, l are proportional to reciprocals of the intercepts measured in terms of a, b , and c , respectively. Here

$$1 = f \frac{a}{OA}, \quad 2 = f \frac{b}{OB}, \quad 3 = f \frac{c}{OC},$$

with

$$OA = 6a.$$

Combining the first and fourth equations yields the constant of proportionality

$$f = 6.$$

Substituting this into rearranged forms of the second and third equations gives us

$$OB = 6 \frac{b}{2} = 3b, \quad OC = 6 \frac{c}{3} = 2c.$$

Other (123) planes are parallel to this plane at equidistant intervals.

Example 1.4 : Uncodable (Answer in ratio form)

Example 1.4

X-ray studies of a cubic crystal by the Bragg method yielded the ratios

$$d_{100} : d_{110} : d_{111} = 1.000 : 0.709 : 1.164.$$

What lattice does the crystal possess?

These numbers are very close to those in (1.6):

$$1 : \frac{\sqrt{2}}{2} : \frac{2\sqrt{3}}{3} = 1.000 : 0.707 : 1.155.$$

So the crystal has a face-centered cubic lattice.

Example 1.5 : Uncodable

Example 1.5

At what radius ratio do the anions begin to touch each other in the cesium chloride structure?

Consider an electrolyte AB in which the ions are spherical, with

$$\begin{aligned}r_{A^+} &= \text{radius of } A^+, \\r_{B^-} &= \text{radius of } B^-.\end{aligned}$$

Let r_{A^+} be large enough so that eight B^- ions can be packed around it without touching each other. Keep the oppositely charged ions in contact and decrease the radius of the cation until the anions meet each other along each edge of the unit cube. If a is the length of an edge of the cube, then

$$a = 2r_{B^-}$$

But each diagonal through the cube passes through one half of a B^- , the A^+ , and one half of another B^- ; consequently,

$$\sqrt{3}a = 2r_{A^+} + 2r_{B^-}.$$

Now, eliminate a from these two equations,

$$\sqrt{3}(2r_{B^-}) = 2r_{A^+} + 2r_{B^-},$$

rearrange

$$r_{A^+} = (\sqrt{3} - 1)r_{B^-},$$

and solve for the desired radius ratio

$$\frac{r_{A^+}}{r_{B^-}} = \sqrt{3} - 1 = 0.732.$$

Example 1.6 : Codable

Chapter 2

Example 2.1 : Codable (Final answer presented in a different form)

Example 2.2 : Uncodable (Answer in variable form)

Example 2.2

Show that for a homonuclear diatomic molecule, equation (2.34) reduces to (2.31).

For a diatomic molecule, equation (2.34) becomes

$$\bar{I}(\theta) = A_1 A_1 \frac{\sin s r_{11}}{s r_{11}} + A_1 A_2 \frac{\sin s r_{12}}{s r_{12}} + A_2 A_1 \frac{\sin s r_{21}}{s r_{21}} + A_2 A_2 \frac{\sin s r_{22}}{s r_{22}}$$

But

$$r_{11} = r_{22} = 0$$

and

$$\lim_{\alpha \rightarrow 0} \frac{\sin \alpha}{\alpha} = \lim_{\alpha \rightarrow 0} \cos \alpha = 1.$$

Also

$$r_{12} = r_{21} = r.$$

So the equation for a diatomic molecule reduces to

$$\bar{I}(\theta) = A_1^2 + A_2^2 + 2A_1 A_2 \frac{\sin s r}{s r}.$$

When the two atoms are the same, the scattering factors are equal,

$$A_1 = A_2 = A_0,$$

we obtain

$$\bar{I}(\theta) = 2A_0^2 \left(1 + \frac{\sin s r}{s r} \right).$$

Example 2.3 : Codable

Chapter 3

Example 3.1 : Uncodable (Answer in variable form)

Boyle's law, an approximate law summarizing experimental results, states that the volume of a gas varies inversely with its pressure when the temperature is fixed:

$$PV = f(T).$$

Here T is the temperature on a suitable scale. On comparing this equation with (3.15), we see that the translational energy E_{tr} is a function of T alone in the ideal gas; thus

$$E_{\text{tr}} = \frac{3}{2} f(T).$$

Example 3.2 : Codable

Example 3.3 : Codable

Example 3.4 : Codable

Example 3.5 : Codable

Example 3.6 : Codable

Example 3.7 : Codable

Example 3.8 : Codable

Example 3.9 : Codable

Example 3.10 : Uncodable (Answer in variable form)

Example 3.10

Evaluate the integral

$$\int_0^\infty x^2 e^{-ax^2} dx.$$

Carry out an integration by parts:

$$\int_0^\infty x^2 e^{-ax^2} dx = -\frac{1}{2a} \int_0^\infty xe^{-ax^2} (-2ax dx) = -\frac{1}{2a} xe^{-ax^2} \Big|_0^\infty + \frac{1}{2a} \int_0^\infty e^{-ax^2} dx = 0 + \frac{1}{4a} \left(\frac{\pi}{a} \right)^{1/2}$$

In the last step, the result from example 10.5 has been introduced. Since the integrand is even, we also have

$$\int_{-\infty}^\infty x^2 e^{-ax^2} dx = \frac{1}{2a} \left(\frac{\pi}{a} \right)^{1/2}$$

This formula was used in line (3.89).

Example 3.11 : Uncodable (Answer in variable form)

Example 3.11

Evaluate the integral

$$\int_0^\infty x^3 e^{-ax^2} dx.$$

Again, integrate by parts:

$$\begin{aligned}\int_0^\infty x^3 e^{-ax^2} dx &= -\frac{1}{2a} \int_0^\infty x^2 e^{-ax^2} (-2ax dx) = -\frac{1}{2a} x^2 e^{-ax^2} \Big|_0^\infty - \frac{1}{2a^2} \int_0^\infty e^{-ax^2} (-2ax dx) \\ &= 0 - \frac{1}{2a^2} e^{-ax^2} \Big|_0^\infty = \frac{1}{2a^2}.\end{aligned}$$

Example 3.12 : Uncodable (Answer in variable form)

Example 3.12

Calculate the most probable speed of a molecule in an ideal gas.

The most probable speed is the speed at which the probability density $f(v)$ is a maximum. But the derivative of expression (3.94),

$$\frac{df}{dv} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \left(2v - \frac{m}{kT} v^3 \right) e^{-mv^2/2kT},$$

vanishes when

$$v^2 = \frac{2kT}{m}$$

and

$$v = \left(\frac{2kT}{m} \right)^{1/2}.$$

Example 3.13 : Codable

Example 3.14 : Codable

Chapter 4

Example 4.1 : Uncodable (Answer in variable form)

Example 4.1

How much heat is absorbed by n moles of an ideal gas undergoing a reversible, isothermal process?

When an ideal gas absorbs heat, it may use the energy to do work against an external pressure and to increase the thermal agitation of its molecules. None is used to do work against intermolecular attraction as the volume increases, because this attraction is negligible.

As the temperature is kept constant, we have

$$\Delta E_T = 0$$

for the ideal gas, and

$$q_T = -w_T.$$

Substituting for w_T with (4.18) yields

$$q_T = nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_2}{P_1}.$$

Example 4.2 : Uncodable (Answer in variable form)

Example 4.2

What is the significance of the PV term in the enthalpy?

The work needed to make a hole of volume V in a fluid with a constant pressure P is

$$w = \int_0^V P dV = P \int_0^V dV = PV.$$

So when a system of volume V is immersed in such a fluid (gas or liquid), it seemingly possesses this energy.

Indeed, expanding the system by volume ΔV requires the energy $\Delta(PV)$. On contracting to the original volume, this energy is reclaimed. Thus, PV is the energy a system *appears* to possess because it fills the volume V in a surrounding fluid at pressure P .

Example 4.3 : Codable

Example 4.4 : Uncodable (Answer in variable form)

Example 4.4

Determine how C_P is related to C_V when the system is an ideal gas.

The equation of state for n moles of ideal gas is

$$PV = nRT.$$

By definition, the enthalpy is given by

$$H = E + PV.$$

Combine these two equations,

$$H = E + nRT,$$

differentiate

$$dH = dE + nR dT,$$

and introduce relations (4.43) and (4.38):

$$C_P dT = C_V dT + nR dT = (C_V + nR) dT.$$

Thus, we find that

$$C_P = C_V + nR$$

for the ideal gas.

Example 4.5 : Codable

Example 4.6 : Codable

Example 4.7 : Uncodable (Answer in variable form)

Example 4.7

Relate

$$\left(\frac{\partial E}{\partial T}\right)_P \text{ to } \left(\frac{\partial E}{\partial T}\right)_V \text{ and } \left(\frac{\partial E}{\partial P}\right)_T \text{ to } \left(\frac{\partial E}{\partial V}\right)_T$$

for a uniform thermodynamic system.

In the system, volume V is a function of temperature T and pressure P ; so

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP.$$

Since we may consider the internal energy E to be a function of either T and V or T and P , both (4.77) and (4.78) are valid. Substituting the form for dV into (4.77) gives us

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right].$$

Comparing this result with (4.78) yields

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

and

$$\left(\frac{\partial E}{\partial P}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T.$$

Chapter 5

Example 5.1 : Codable

Example 5.2 : Codable

Example 5.3 : Uncodable (Answer in statement form)

Example 5.3

How does one calculate ΔS when 1.00 mol liquid water at -10° C and 1.00 atm freezes to ice at the same temperature and pressure?

Equation (5.19) and its integral can only be applied along a reversible path. Here one would determine integral (5.22) for heating the liquid water from -10° to 0° C. Then (5.23) would be applied to the reversible freezing at 0° C. Finally, integral (5.22) would be determined for the ice cooling from 0° to -10° C. These results would be added.

Example 5.4 : Codable

Example 5.5 : Codable

Example 5.6 : Uncodable (Not calculable)

Example 5.6

Obtain $(\partial E / \partial V)_T$ for an ideal gas. An ideal gas obeys the equation

$$P = \frac{nRT}{V}.$$

Differentiate this with respect to T at constant V ,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V},$$

and substitute into formula (5.90):

$$\left(\frac{\partial E}{\partial V} \right)_T = T \frac{nR}{V} - P = 0.$$

Example 5.7 : Uncodable (Variable answer)

Example 5.7

Obtain $C_p - C_v$ for an ideal gas. Rearrange the ideal gas equation to

$$V = \frac{nRT}{P}$$

and differentiate with respect to T at constant P :

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}.$$

Substitute this result and that from example 5.6 into formula (4.81)

$$C_p - C_v = (0 + P) \frac{nR}{P} = nR.$$

Note that this agrees with the result obtained in example 4.4,

Example 5.8* (Printing mistake in book) : Codable

Example 5.9* (Printing mistake in book) : Codable

Chapter 6

Example 6.1 : Uncodable (Answer in statement form)

Example 6.1.

What does the Gibbs phase rule tell us about a one-component system?

When $c = 1$, equation (6.1) becomes

$$f = 3 - p.$$

When only one phase is present, this reduces to

$$f = 2.$$

On a pressure-temperature diagram, the region for such a phase appears as an area. When two phases are present, we have

$$f = 1.$$

On a pressure-temperature diagram, the points where the two phases coexist in equilibrium form a curved line. When three phases are present, we have

$$f = 0.$$

There is now no freedom; three phases coexist in equilibrium at a point.

Example 6.2 : Codable

Example 6.3 : Codable

Example 6.4 : Codable

Example 6.5 : Codable

Example 6.6 : Codable

Example 6.7 : Codable

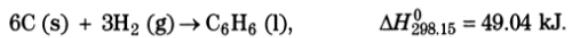
Example 6.8 : Codable

Chapter 7

Example 7.1 : Uncodable (Answer in statement form)

Example 7.1

Interpret the following:



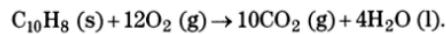
The chemical equation represents 6 moles solid carbon and 3 moles gaseous hydrogen reacting to form 1 mole liquid benzene. When each of these is in its standard state at 298.15 K, the enthalpy increase is 49.04 kilojoules.

Example 7.2 : Codable

Example 7.3 : Uncodable (Answer in variable form)

Example 7.3

Relate the isobaric reaction heat to the isochoric one for the process



In this reaction there are 10 moles of gaseous product and 12 moles of gaseous reactant. Consequently,

$$\Delta n = 10 - 12 = -2$$

and

$$\Delta H_P = \Delta E_V - 2RT$$

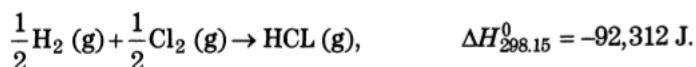
whence

$$q_P = q_V - 2RT.$$

Example 7.4 : Uncodable (Answer in variable form)

Example 7.4

Construct an expression for the temperature dependence of the standard enthalpy change in the reaction



With the empirical function

$$\Delta C_P^0 = \Delta a + \Delta bT + \Delta cT^2,$$

equation (7.20) becomes

$$\Delta H = \Delta H_0 + \int (\Delta a + \Delta bT + \Delta cT^2) dT = \Delta H_0 + \Delta aT + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3.$$

Coefficients Δa , $\Delta b/2$, and $\Delta c/3$ calculated from the pertinent numbers in table 7.1 are

$$\Delta a = -2.215 \text{ J K}^{-1}, \frac{\Delta b}{2} = -1.422 \times 10^{-3} \text{ J K}^{-2}, \frac{\Delta c}{3} = 8.533 \times 10^{-7} \text{ J K}^{-3}.$$

Then term ΔH_0 is

$$\begin{aligned} \Delta H_0 &= \Delta H_{T_1} - \Delta aT_1 - \frac{\Delta b}{2}T_1^2 - \frac{\Delta c}{3}T_1^3 \\ &= -92,312 + 2.215(298.15) + 1.422 \times 10^{-3}(298.15)^2 - 8.533 \times 10^{-7}(298.15)^3 \text{ J} = -91,548 \text{ J.} \end{aligned}$$

Inserting these parameters into the general form gives us

$$\Delta H_T^0 = -91,548 - 2.215T - 1.422 \times 10^{-3}T^2 + 8.533 \times 10^{-7}T^3 \text{ J.}$$

Example 7.5 : Codable

Example 7.6 : Codable

Example 7.7 : Codable

Example 7.8 : Codable

Example 7.9 : Codable

Example 7.10 : Uncodable (Answer in variable form)

Example 7.10

How does the fraction of dissociation α vary with pressure P for (a) reaction (7.69), (b) reaction (7.73)?

(a) Begin with 1 mole PCl_5 and 0 mole PCl_3 and Cl_2 . Then

$$n_0 = a = 1, \quad b = c = 0, \quad x = \alpha,$$

and equation (7.72) reduces to

$$K_P = \frac{\alpha^2 P}{(1-\alpha)(1+\alpha)} = \frac{\alpha^2 P}{1-\alpha^2}.$$

(b) Begin with 1 mole N_2O_4 and 0 mole NO_2 . Then

$$n_0 = a = 1, \quad b = 0, \quad x = \alpha,$$

and equation (7.75) reduces to

$$K_P = \frac{4\alpha^2 P}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 P}{1-\alpha^2}.$$

Example 7.11 : Codable

Example 7.12 : Codable

Example 7.13 : Codable

Chapter 8

Example 8.1 : Codable

Example 8.2 : Codable

Example 8.3 : Codable

Example 8.4 : Codable

Example 8.5 : Codable

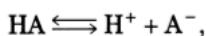
Example 8.6 : Codable

Example 8.7 : Uncodable

Example 8.7

Calculate m_{H^+} in 1.00×10^{-6} m acetic acid.

In this dilute solution we have to consider both equilibria



simultaneously. Here HA represents the acetic acid molecule, A^- the acetate ion.

The 1.00×10^{-6} mol acetic acid per 1000 g H_2O appears as HA and A^- ; there is no other contribution to m_{A^-} . So

$$1.00 \times 10^{-6} \text{ m} = m_{HA} + m_{A^-} .$$

From the electrical neutrality condition, we have

$$m_{H^+} = m_{A^-} + m_{OH^-} .$$

And governing the equilibria, we have

$$\frac{m_{H^+} m_{A^-}}{m_{HA}} = 1.754 \times 10^{-5} \text{ m},$$

$$m_{H^+} m_{OH^-} = 1.008 \times 10^{-14} \text{ m}^2 .$$

Let us rearrange these simultaneous equations in a set of type (8.37) - (8.40):

$$m_{OH^-} = \frac{1.008 \times 10^{-14}}{m_{H^+}} ,$$

$$m_{A^-} = m_{H^+} - m_{OH^-} ,$$

$$m_{HA} = \frac{m_{H^+} m_{A^-}}{1.754 \times 10^{-5}} ,$$

$$m_{H^+} = 1.00 \times 10^{-6} - m_{HA} + m_{OH^-} .$$

If the acetic acid were completely ionized and the contribution from ionization of water were negligible, we would have

$$m_{H^+} = 1.00 \times 10^{-6} \text{ m.}$$

Put this into the first equation of the set and complete the round:

$$m_{OH^-} = \frac{1.008 \times 10^{-14}}{1.00 \times 10^{-6}} = 1.008 \times 10^{-8} \text{ m,}$$

$$m_{A^-} = 1.00 \times 10^{-6} - 0.01 \times 10^{-6} = 0.99 \times 10^{-6} \text{ m,}$$

$$m_{HA} = \frac{(1.00 \times 10^{-6})(0.99 \times 10^{-6})}{1.754 \times 10^{-5}} = 0.56 \times 10^{-7} \text{ m,}$$

$$m_{H^+} = 1.00 \times 10^{-6} - 0.056 \times 10^{-6} + 0.010 \times 10^{-6} = 0.954 \times 10^{-6} \text{ m.}$$

Repeating the steps with this number gives us (in the final step)

$$m_{H^+} = 1.00 \times 10^{-6} - 0.051 \times 10^{-6} + 0.011 \times 10^{-6} = 0.960 \times 10^{-6} \text{ m.}$$

The average of these two values is

$$m_{H^+} = 0.957 \times 10^{-6} \text{ m.}$$

To illustrate use of equation (8.44), we replace the final equation in the set with

$$y = 1.00 \times 10^{-6} - m_{HA} - m_{A^-}.$$

Again, if the acetic acid were completely ionized but the contribution from ionization of water were negligible, we would have

$$x_1 = (m_{H^+})_1 = 1.00 \times 10^{-6} \text{ m.}$$

If only the water ionized, we would have

$$x_2 = (m_{H^+})_2 = 1.004 \times 10^{-7} \text{ m.}$$

With x_1 the first three equations are the same as in the first round before. So

$$m_{OH^-} = 1.008 \times 10^{-8} \text{ m,}$$

$$m_{A^-} = 0.990 \times 10^{-6} \text{ m,}$$

$$m_{HA} = 0.56 \times 10^{-7} \text{ m,}$$

and

$$y_1 = 1.00 \times 10^{-6} - 0.056 \times 10^{-6} - 0.990 \times 10^{-6} = -0.046 \times 10^{-6} \text{ m.}$$

With x_2 , we find that

$$m_{OH^-} = \frac{1.008 \times 10^{-14}}{1.004 \times 10^{-7}} = 1.004 \times 10^{-7} \text{ m,}$$

$$m_{A^-} = 0,$$

$$m_{HA} = 0,$$

$$y_2 = 1.00 \times 10^{-6} \text{ m.}$$

Substituting these into formula (8.44) yields

$$m_{H^+} = 1.00 \times 10^{-6} - \frac{-0.90 \times 10^{-6}}{1.046 \times 10^{-6}} (-0.046 \times 10^{-6}) = 1.00 \times 10^{-6} - 0.040 \times 10^{-6} = 0.960 \times 10^{-6} \text{ m.}$$

Employing this as the new x_2 , we obtain

$$y_2 = -0.002 \times 10^{-6} \text{ m.}$$

Using the same x_1 and y_1 as before, we now have

$$m_{H^+} = 1.00 \times 10^{-6} - \frac{-0.040 \times 10^{-6}}{1.044 \times 10^{-6}} (-0.046 \times 10^{-6}) = 1.00 \times 10^{-6} - 0.042 \times 10^{-6} = 0.958 \times 10^{-6} \text{ m.}$$

This checks the result found by the first method.

Example 8.8 : Codable

Example 8.9 : Codable

Example 8.10 : Codable

Example 8.11 : Codable

Example 8.12 : Codable (Answer provided in the book wrong)

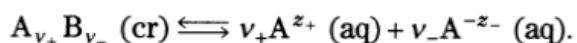
Example 8.13 : Uncodable (Answer in variable form)

Example 8.13

How may one determine the equilibrium constant for a sparingly soluble electrolyte?

The procedure involves solubility measurements in the presence of various concentrations of an inert salt. By chemical analysis, the mean ionic molality of the given electrolyte and the ionic strength in each solution are determined.

Suppose the equilibrium is



From formulas (8.110), (8.117), (8.120), the activity of the electrolyte is

$$a = a_\pm^v = \gamma_\pm^v m_\pm^v = K$$

But the logarithm of the last equality is

$$v \log \gamma_\pm + v \log m_\pm = \log K,$$

whence

$$\log m_\pm = -\log \gamma_\pm + \frac{1}{v} \log K.$$

Introducing the Debye-Hückel limiting law (8.122) then yields the formula

$$\log m_\pm = Az_+ z_- \sqrt{\mu} + \frac{1}{v} \log K.$$

In practice, the experimental $\log m_\pm$ is plotted against the experimental $\sqrt{\mu}$. A slightly curved line is obtained. This is extrapolated to zero $\sqrt{\mu}$ and the result identified as $(1/v) \log K$. From this, K itself is calculated.

Chapter 9

Example 9.1 : *Codable*

Example 9.2 : *Codable*

Example 9.3 : *Codable*

Example 9.4 : *Codable*

Example 9.5 : *Codable*

Example 9.6 : *Codable*

Example 9.7 : *Codable*

Example 9.8 : *Codable*

Chapter 10

Example 10.1 : Uncodable (Answer in variable form)

Example 10.1

In the state function for translation, find the distance between successive points at the same phase.

From equation (10.5), we have

$$\Psi = Ae^{i(kx - \omega t)} = Ae^{i\alpha}$$

with the phase angle

$$kx - \omega t = \alpha.$$

At a given time t , an increase in the phase angle appears as

$$k \Delta x = \Delta \alpha.$$

From the periodicity of the cosine and sine and from the identity

$$\exp(i\alpha) = e^{i\alpha} = \cos\alpha + i\sin\alpha,$$

we see that the exponential function goes through one cycle when α increases by 2π .

Then

$$k \Delta x = 2\pi$$

and

$$\Delta x = \frac{2\pi}{k} = \lambda.$$

The distance λ that is required for a sinusoidal or an exponential function to go through one cycle is called its *wavelength*. The reciprocal of the wavelength gives the number of cycles per unit length, the *wave number*. For it, we write

$$\frac{1}{\lambda} = \frac{k}{2\pi} = \bar{k}$$

Example 10.2 : Uncodable (Answer in variable form)

Example 10.2

At what speed does a given phase of the translational state function travel?

Solve the phase angle equation in example 10.1 for x :

$$x = \frac{\omega}{k}t + \frac{\alpha}{k}.$$

Then differentiate with respect to t at the given α :

$$\frac{dx}{dt} = \frac{\omega}{k} = w.$$

By convention, w is called the *phase velocity* or wave velocity, k the *wavevector*, and ω the *angular frequency* for Ψ . The entity is called a *de Broglie wave* after the man who

Example 10.3 : Uncodable (Answer in variable form)

Example 10.3

Interpret the product of the wavelength and the conventional frequency.

Wavelength λ is the distance between two successive points at the same phase along the periodic axis of a function. Furthermore, *frequency* v is the number of cycles executed per unit time at a fixed point on that axis. Multiplying these yields the distance traveled in unit time, the phase velocity. Thus

$$w = \lambda v = \frac{2\pi}{k} v = \frac{\omega}{k}.$$

In the last step, we have introduced the relation between the conventional frequency and the angular frequency:

$$v = \frac{\omega}{2\pi}.$$

Example 10.4 : Codable

Example 10.5 : Uncodable (Answer in variable form)

Example 10.5

Evaluate the integral

$$I = \int_0^\infty e^{-ax^2} dx.$$

This integral may be taken along either the x or the y axis without affecting its value; so we also have

$$I = \int_0^\infty e^{-ay^2} dy.$$

Multiplying the two forms for I yields a double integral,

$$I^2 = \int_0^\infty e^{-ax^2} dx \int_0^\infty e^{-ay^2} dy = \int_0^\infty \int_0^\infty e^{-a(x^2+y^2)} dx dy,$$

over the first quadrant of the xy plane.

In polar coordinates, the element of area is

$$dA = r d\varphi dr,$$

while the square of the radius vector locating the area is

$$r^2 = x^2 + y^2.$$

So the double integral can be rewritten as

$$I^2 = \int_0^\infty \int_0^{\pi/2} e^{-ar^2} r d\varphi dr,$$

whence

$$I^2 = \int_0^{\pi/2} d\varphi \int_0^\infty e^{-ar^2} r dr = \varphi \left(-\frac{e^{-ar^2}}{2a} \right) \Big|_0^{\pi/2} = \frac{\pi}{4a}$$

and

$$I = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}.$$

Because the given integrand is even, the integral from $-\infty$ to 1 equals that from 0 to ∞ ? and

$$\int_{-\infty}^\infty e^{-ax^2} dx = \left(\frac{\pi}{a} \right)^{1/2}.$$

This value is used in line (10.43).

When the nonzero limit is finite, one employs the definition of the *error function* (erf):

$$\int_0^u e^{-w^2} dw = \frac{(\pi)^{1/2}}{2} \operatorname{erf} u.$$

For $w = a^{1/2}x$ and $u = a^{1/2}b$, we have

$$\int_0^b e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2} \operatorname{erf} a^{1/2}b$$

and

$$\int_{-b}^b e^{-ax^2} dx = \left(\frac{\pi}{a} \right)^{1/2} \operatorname{erf} a^{1/2}b.$$

Standard tables of the error function are available.

Example 10.6 : Codable

Example 10.7 : Codable

Example 10.8 : Codable

Example 10.9 : Uncodable (Answer in variable form)

Example 10.9

How are the reflected and the transmitted waves related to an incident de Broglie wave for the potential function in figure 10.4?

To the left of the origin, the forward and the backward traveling waves superpose:

$$\psi_1 = A_1 e^{ikx} + B_1 e^{-ikx}.$$

But in the high potential region, there is no reflected wave; so

$$\psi_2 = A_2 e^{-\kappa x}.$$

The pertinent derivatives are

$$\frac{d\psi_1}{dx} = ikA_1 e^{ikx} - ikB_1 e^{-ikx}$$

and

$$\frac{d\psi_2}{dx} = -\kappa A_2 e^{-\kappa x}.$$

At the boundary, at $x = 0$, the state functions and the first derivatives are equal. And since $e^0 = 1$, we have

$$A_1 + B_1 = A_2,$$

$$ikA_1 - ikB_1 = -\kappa A_2.$$

Solving these equations for A_2 and B_1 yields

$$\begin{aligned} A_2 &= \frac{2A_1}{1+i(\kappa/k)} = \left(\frac{1+i(\kappa/k)}{1+i(\kappa/k)} + \frac{1-i(\kappa/k)}{1+i(\kappa/k)} \right) A_1 \\ &= (1+e^{-2i\alpha})A_1. \\ B_1 &= \frac{1-i(\kappa/k)}{1+i(\kappa/k)} A_1 = e^{-2i\alpha} A_1. \end{aligned}$$

Angle α is defined by the equation

$$\alpha = \tan^{-1}(\kappa/k).$$

Note that the magnitude of B_1 equals that of A_1 when κ is real. Then the reflected wave is of the same intensity as the incident one.

Substituting the expressions for A_2 and B_1 into the original forms and reducing leads to

$$\psi = 2Ae^{-i\alpha} \cos(kx + \alpha) \quad \text{for } x < 0,$$

$$\psi = 2Ae^{-i\alpha} \cos \alpha e^{-\kappa x} \quad \text{for } x > 0.$$

Here we have dropped the subscript 1 on A and have dropped the subscripts on the Ψ 's.

Example 10.10 : Uncodable (Answer in variable form)

Example 10.10

Express $\nabla^2\Psi$ in spherical coordinates.

The spherical coordinates of a point are defined with respect to a center and Cartesian axes based on the center as figure 10.7 shows. The line element traced out when only r changes is dr . When only θ increases, the line element is $r d\theta$. When only ϕ increases, it is $r \sin \theta d\phi$.

So with $q_1 = r$, $q_2 = \theta$, and $q_3 = \phi$, we have

$$\begin{array}{lll} q_1 = r, & q_2 = \theta, & \text{and } q_3 = \phi, \\ h_1 = 1, & h_2 = r, & h_3 = r \sin \theta. \end{array}$$

If we also replace C with Ψ , equation (10.146) becomes

$$\begin{aligned}\nabla^2 \psi &= \frac{1}{r^2 \sin\theta} \left[\frac{\partial}{\partial r} \left(\frac{r^2 \sin\theta}{1} \frac{\partial \psi}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\frac{r \sin\theta}{r} \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial}{\partial \varphi} \left(\frac{r}{r \sin\theta} \frac{\partial \psi}{\partial \varphi} \right) \right] \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \psi}{\partial \theta} \right) + \left(\frac{1}{r^2 \sin^2\theta} \frac{\partial^2 \psi}{\partial \varphi^2} \right).\end{aligned}$$

Example 10.11 : Uncodable (Answer in variable form)

Example 10.11

Construct a differential volume element for spherical coordinates.

From figure 10.7, we see that the line elements dr , $r d\theta$, $r \sin\theta d\varphi$ are mutually perpendicular. Furthermore, these form the edges of an infinitesimal volume element such as figure 11.6 shows. So we have

$$\begin{aligned}d^3 \mathbf{r} &= (dr)(r d\theta)(r \sin\theta d\varphi) \\ &= r^2 \sin\theta dr d\theta d\varphi.\end{aligned}$$

Introducing the element of solid angle

$$d\Omega = \sin\theta d\theta d\varphi$$

yields the alternate form

$$d^3 \mathbf{r} = r^2 d\Omega dr,$$

which can also be constructed from the description of $d\Omega$ in section 8.6.

Chapter 11

Example 11.1 : Uncodable (Answer in variable form)

Example 11.1

Show that a rigid linear rotator is represented by a single particle of mass μ traveling on a sphere at distance r from the center-of-mass position.

Consider point masses

$$m_1, m_2, \dots, m_n$$

located at fixed positions

$$r_1, r_2, \dots, r_n$$

along a straight line. Let the origin of a spherical coordinate system be located at the center of mass, as figure 11.1 indicates. We then have

$$m_1 r_1 + m_2 r_2 + \dots + m_n r_n = 0.$$

The square of an element of path traced out by point mass m_j in time dt is

$$ds_j^2 = r_j^2 d\theta^2 + r_j^2 \sin^2 \theta d\phi^2.$$

For the kinetic energy of the system, we obtain

$$T = \sum \frac{1}{2} m_j v_j^2 = \frac{1}{2} \sum m_j r_j^2 \left[\left(\frac{d\theta}{dt} \right)^2 + \sin^2 \theta \left(\frac{d\phi}{dt} \right)^2 \right] = \frac{I}{2} [\dot{\theta}^2 + (\sin^2 \theta) \dot{\phi}^2] = \frac{1}{2} I \omega^2,$$

where a dot over a symbol indicates differentiation with respect to t , the second summation is identified as the moment of inertia,

$$I = m_1 r_1^2 + m_2 r_2^2 + \dots + m_n r_n^2,$$

and ω is the net angular velocity.

Proceeding in the same way for the model in figure 11.2, we find that

$$T = \frac{1}{2} \mu v^2 = \frac{1}{2} \mu r^2 [\dot{\theta}^2 + (\sin^2 \theta) \dot{\phi}^2] = \frac{1}{2} I \omega^2$$

if we set

$$I = \mu r^2.$$

The kinetic energy T is taken as that of the linear rotator. To complete the definition of the model, we then choose the reduced mass μ by the formula

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} + \dots + \frac{1}{m_n}.$$

Example 11.2 : Uncodable (Answer in variable form)

Example 11.2

Show that for a diatomic molecule, r in figure 11.2 equals the interatomic distance.
To locate the origin at the center of mass, we set

$$m_1 r_1 = -m_2 r_2.$$

For the reciprocal of the reduced mass, we have

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2}.$$

But the moment of inertia is

$$\mu r^2 = m_1 r_1^2 + m_2 r_2^2.$$

Divide this by μ and introduce the expression for $1/\mu$:

$$r^2 = \frac{1}{\mu} \left(m_1 r_1^2 + m_2 r_2^2 \right) = \frac{m_1}{m_2} r_1^2 + r_1^2 + r_2^2 + \frac{m_2}{m_1} r_2^2.$$

The equation determining the center of mass tells us that

$$\frac{m_1 r_1^2}{m_2} = -r_1 r_2, \quad \frac{m_2 r_2^2}{m_1} = -r_1 r_2.$$

These relations reduce the preceding equation to

$$r^2 = r_1^2 - 2r_1 r_2 + r_2^2 = (r_2 - r_1)^2,$$

whence

$$r = r_2 - r_1.$$

Since r_1 is negative, this is the interatomic distance.

Example 11.3 : Uncodable (Answer in variable form)

Example 11.3

Verify formula (11.25). When $J = 1$, $\sum M^2 = 1^2 = 1$ and

$$\frac{J(J+1)(2J+1)}{6} = \frac{(1)(2)(3)}{6} = 1.$$

When $J = 2$, $\sum M^2 = 1^2 + 2^2 = 5$ and

$$\frac{J(J+1)(2J+1)}{6} = \frac{(2)(3)(5)}{6} = 5.$$

Thus, the equation is true for the two lowest values of J .

Let us suppose that the equation has been verified for numbers up to and including $J - 1$. Then for number J , we have

$$\begin{aligned} \sum_{M=1}^J M^2 &= \sum_{M=1}^{J-1} M^2 + J^2 = \frac{(J-1)(J)(2J-1)}{6} + J^2 = \frac{1}{6}(2J^3 - 3J^2 + J + 6J^2) = \frac{1}{6}(2J^3 + 3J^2 + J) \\ &= \frac{1}{6}J(J+1)(2J+1). \end{aligned}$$

Thus, the equation is true when the sum goes to J . By iteration, one can proceed from the two lowest values, where we know that the formula holds, to any desired finite value of J , by unit steps.

Example 11.4 : Codable

Example 11.5 : Codable

Example 11.6 : Codable

Example 11.7 : Codable

Example 11.8 : Uncodable (Answer in variable form)

Example 11.8

Show that $1/r$ is a solution of the Laplace equation.

When Ψ depends only on r , the angular terms in the representation of $\nabla^2\Psi$ from example 10.10 drop out. Equation (11.70) then reduces to

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Psi}{dr} \right) = 0.$$

But when

$$\Psi = \frac{1}{r},$$

we have

$$\frac{d\Psi}{dr} = -\frac{1}{r^2}$$

and

$$\frac{d}{dr} \left(r^2 \frac{d\Psi}{dr} \right) = \frac{d}{dr} (-1) = 0.$$

So $1/r$ satisfies the Laplace equation.

Example 11.9 : Uncodable (Answer in variable form)

Example 11.9

Let $\partial x/\partial s = a$, $\partial y/\partial s = b$, $\partial z/\partial s = c$, with a , b , and c constant. Then show that whenever Ψ is a solution to the Laplace equation, then $\partial\Psi/\partial s$ is also.

Here a , b , and c are the direction cosines for a straight line passing through the origin, while s is the distance to a point on this line. We have

$$\frac{\partial}{\partial s} = \frac{\partial x}{\partial s} \frac{\partial}{\partial x} + \frac{\partial y}{\partial s} \frac{\partial}{\partial y} + \frac{\partial z}{\partial s} \frac{\partial}{\partial z} = a \frac{\partial}{\partial x} + b \frac{\partial}{\partial y} + c \frac{\partial}{\partial z}.$$

Let this operator act on equation (11.70) with a , b and c fixed:

$$\begin{aligned} \frac{\partial}{\partial s} \nabla^2 \Psi &= \left(a \frac{\partial}{\partial x} + b \frac{\partial}{\partial y} + c \frac{\partial}{\partial z} \right) \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) = \frac{\partial^2}{\partial x^2} \left(a \frac{\partial \Psi}{\partial x} + b \frac{\partial \Psi}{\partial y} + c \frac{\partial \Psi}{\partial z} \right) \\ &+ \frac{\partial^2}{\partial y^2} \left(a \frac{\partial \Psi}{\partial x} + b \frac{\partial \Psi}{\partial y} + c \frac{\partial \Psi}{\partial z} \right) + \frac{\partial^2}{\partial z^2} \left(a \frac{\partial \Psi}{\partial x} + b \frac{\partial \Psi}{\partial y} + c \frac{\partial \Psi}{\partial z} \right) = \nabla^2 \left(\frac{\partial \Psi}{\partial s} \right) = 0. \end{aligned}$$

We see that the spatial derivative $\partial\Psi/\partial s$ is a solution whenever Ψ is.

Chapter 12

Example 12.1 : Uncodable (Answer in variable form)

Example 12.1

Construct a one particle model for the oscillation of a diatomic molecule.

The electron mass associated with an atom in a molecule is very small with respect to the nuclear mass. So even if the center of its electron mass is displaced considerably from the nucleus, the center of the atom's mass is practically at the nuclear center. So in our discussions we will consider the mass of each atom to reside at the center of its nucleus.

Consider the diatomic molecule depicted in figure 12.1. Suppose that the masses of the two atoms, m_1 and m_2 , are at positions r_1 and r_2 along an axis at time t . Let us locate the origin at the center of mass, so

$$m_1 r_1 + m_2 r_2 = 0$$

whence

$$r_1 = -\frac{m_2}{m_1} r_2.$$

Since the masses are constant, the derivative of r_1 with respect to time t is given by

$$\dot{r}_1 = -\frac{m_2}{m_1} \dot{r}_2$$

Note that a dot over a symbol represents differentiation with respect to t . With this notation, the vibrational kinetic energy is

$$T = \frac{1}{2} m_1 \dot{r}_1^2 + \frac{1}{2} m_2 \dot{r}_2^2 = \frac{1}{2} m_1 \frac{m_2^2}{m_1^2} \dot{r}_2^2 + \frac{1}{2} m_2 \dot{r}_2^2 = \frac{1}{2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) m_2^2 \dot{r}_2^2 = \frac{1}{2} \mu \frac{m_2^2}{\mu^2} \dot{r}_2^2.$$

In the last step, the reduced mass μ has been introduced by the equation

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}.$$

The internuclear distance is given by

$$r = r_2 - r_1 = r_2 + \frac{m_2}{m_1} r_2 = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) m_2 r_2 = \frac{m_2 r_2}{\mu},$$

whence

$$\dot{r} = \frac{m_2 \dot{r}_2}{\mu}.$$

Substituting this into the expression for T yields

$$T = \frac{1}{2} \mu \dot{r}^2.$$

But differentiating equation (12.3),

$$\dot{x} = \dot{r},$$

and inserting the result into the kinetic energy form leads to

$$T = \frac{1}{2} \mu \dot{x}^2.$$

Thus, a particle of mass μ in the potential

$$V = V(x) = V(r - r_e)$$

has the same kinetic energy and potential energy as the diatomic molecule. As a model for the vibrational motion, it represents these properties faithfully.

Example 12.2 : Uncodable (Answer in variable form)

Example 12.2

If the two atom system in figure 12.1 obeyed Newtonian mechanics, what would its frequency of oscillation be?

The internuclear distance in the system is

$$r = r_2 - r_1.$$

So differentiating (12.3) yields

$$dx = dr = dr_2 - dr_1.$$

In the harmonic approximation, equation (12.2) holds. Differentiating it and inserting the above relationship yields

$$dV = fx \, dx = fxdx_2 - fxdx_1.$$

But we have

$$dV = \frac{\partial V}{\partial r_2} dr_2 + \frac{\partial V}{\partial r_1} dr_1 = -F_2 dr_2 - F_1 dr_1,$$

where F_2 and F_1 are the forces acting on masses m_2 and m_1

Applying Newton's second law to each mass yields

$$m_2 \frac{d^2 r_2}{dt^2} = F_2 = -fx, \quad m_1 \frac{d^2 r_1}{dt^2} = F_1 = fx.$$

These equations combine to give

$$\frac{d^2 x}{dt^2} = \frac{d^2 r_2}{dt^2} - \frac{d^2 r_1}{dt^2} = -\left(\frac{f}{m_2} + \frac{f}{m_1}\right)x = -\frac{f}{\mu}x$$

or

$$\frac{d^2 x}{dt^2} + \frac{f}{\mu}x = 0.$$

Integrating this equation leads to the result

$$x = A \cos \left[\left(\frac{f}{\mu} \right)^{1/2} t + \alpha \right] = A \cos(\omega t + \alpha)$$

whence

$$\omega = \left(\frac{f}{\mu} \right)^{1/2} \quad \text{and} \quad v = \frac{\omega}{2\pi} = \frac{1}{2\pi} \left(\frac{f}{\mu} \right)^{1/2}.$$

We call ω the angular frequency and v the conventional frequency.

Example 12.3 : Uncodable (Answer in variable form)

Example 12.3

Evaluate (a) $(D - w)(D + w)\psi$, (b) $(D + w)(D - w)\psi$.

Since D is the differentiating operator (12.10), it has transforming as well as algebraic properties. Employing the rule for differentiating a product, we find that

$$(D - w)(D + w)\psi = (D - w)(D\psi + w\psi) = D^2\psi + wD\psi + \psi - wD\psi - w^2\psi = (D^2 - w^2 + 1)\psi$$

and

$$(D + w)(D - w)\psi = (D + w)(D\psi - w\psi) = D^2\psi - wD\psi - \psi + wD\psi - w^2\psi = (D^2 - w^2 - 1)\psi.$$

Example 12.4 : Uncodable (Answer in variable form)

Example 12.4

Normalize function (12.36).

This solution yields the probability density

$$\rho = \psi^* \psi = \left(A^* e^{-w^2/2} \right) \left(A e^{-w^2/2} \right) = A^* A e^{-w^2} = A^* A e^{-ax^2}$$

Let us take A to be real and set the total probability equal to 1:

$$\int_{-\infty}^{\infty} \rho dx = A^2 \int_{-\infty}^{\infty} e^{-ax^2} dx = 1.$$

Inserting the value of the integral from example 10.5 leads to

$$A = \left(\frac{a}{\pi} \right)^{\frac{1}{4}}.$$

Example 12.5 : Uncodable (Answer in variable form)

Example 12.5

Show that a sum of the two nodeless solutions satisfies the Schrödinger equation asymptotically at any energy E . Construct the form

$$\psi = A e^{-w^2/2} + B e^{w^2/2}.$$

Differentiate twice

$$\begin{aligned} \frac{d\psi}{dw} &= -A w e^{-w^2/2} + B w e^{w^2/2}, \\ \frac{d^2\psi}{dw^2} &= A w^2 e^{-w^2/2} + B w^2 e^{w^2/2} - A e^{-w^2/2} + B e^{w^2/2}. \end{aligned}$$

As $w \rightarrow \pm\infty$, the last two terms can be neglected and

$$\frac{d^2\psi}{dw^2} \approx w^2 \psi.$$

Furthermore, b can be neglected with respect to w^2 in equation (12.9). Thus, it reduces to

$$\frac{d^2\psi}{dw^2} \approx w^2 \psi,$$

the same as the preceding approximate equation. Since the ψ above contains two arbitrary constants A and B and since the differential equation is only second order, this is the most general asymptotic solution for either $w = \infty$ or $w = -\infty$.

Example 12.6 : Codable

Example 12.7 : Codable

Example 12.8 : Uncodable (Answer in variable form)

Example 12.8

What would the wave number for a given mode be if the reduced mass for its model were 1 u and the force constant $10^2 \text{ N m}^{-1} = 10^2 \text{ kg s}^{-2}$?

Since each atomic mas unit (u) contributes 1 g to the mass of a mole of pure substance and 1 mol contains Avogadro's number N of particles, the mass in grams of a particle of mass μ' u is

$$\mu = \frac{\mu'}{N}.$$

But from equation (12.32) and the final equation in example 12.2, we have

$$k_0 = \frac{v_{\text{vib}}}{c} = \frac{1}{2\pi c} \left(\frac{f}{\mu} \right)^{1/2} = \frac{1}{2\pi c} \left(\frac{fN}{\mu'} \right)^{1/2}$$

Substitute in the given numbers to obtain:

$$k_0 = \frac{\left[(10^5 \text{ g s}^{-2}) (6.02214 \times 10^{23} \text{ g}^{-1}) \right]^{1/2}}{2\pi (2.99792 \times 10^{10} \text{ cm s}^{-1})} = 1302.79 \text{ cm}^{-1}.$$

So from

$$f = \frac{\mu'}{N} (2\pi ck_0)^2,$$

we can write

$$f = \mu' \left(\frac{k_0}{1302.79 \text{ cm}^{-1}} \right)^2 \times 10^2 \text{ N m}^{-1}.$$

Example 12.9 : Codable

Example 12.10 : Codable

Example 12.11 : Codable

Example 12.12 : Uncodable (Answer in variable form)

Example 12.12

How does the electronic energy in a hydrogenlike system vary with the pertinent quantum numbers?

Combining (12.110) and (12.109) leads to

$$b = \frac{\mu Z^2 e^4}{2(4\pi\epsilon)^2 \hbar^2} = \frac{1}{2} \mu \left(\frac{e^2 \times 10^{-7} e^2}{\hbar} \right)^2 Z^2.$$

Then substituting in accepted values of the fundamental constants, letting μ_r be μ/m_e , yields

$$\begin{aligned} b &= \frac{1}{2} (9.10939 \times 10^{-31} \text{ kg}) \left(\frac{(2.99792 \times 10^8)^2 (10^{-7} \text{ C}^{-2} \text{ J m}) (1.60218 \times 10^{-19} \text{ C})^2}{1.05457 \times 10^{-34}} \right) \mu_r Z^2 \\ &= 2.1799 \times 10^{-18} \mu_r Z^2 \text{ J} = \frac{2.1799 \times 10^{-18} \mu_r Z^2}{1.60218 \times 10^{-19} \text{ J (eV)}^{-1}} = 13.606 \mu_r Z^2 \text{ eV}. \end{aligned}$$

Formula (12.117) becomes

$$E = -13.606 \frac{Z^2}{n^2} \mu_r \text{ eV}.$$

The energy of an electron in the field of a single particle carrying positive charge is independent of the azimuthal and magnetic quantum numbers (l and m_l).

Example 12.13 : Codable**Example 12.14 : Uncodable (Answer in variable form)****Example 12.14**

How do two 1s orbitals and a 2s orbital combine to form a ground state for Li?

Let $1s(i)$, $2s(i)$, $\alpha(i)$, and $\beta(i)$ represent the i th electron in the appropriate 1s orbital, 2s orbital, $+1/2\hbar$ spin state, and $-1/2\hbar$ spin state, respectively. Then Slater determinant (12.127) may be either

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} = \frac{1}{\sqrt{6}} [1s(1)\alpha(1)1s(2)\beta(2)2s(3)\alpha(3) \\ +1s(2)\alpha(2)1s(3)\beta(3)2s(1)\alpha(1)+1s(3)\alpha(3)1s(1)\beta(1)2s(2)\alpha(2)-1s(3)\alpha(3)1s(2)\beta(2)2s(1)\alpha(1) \\ -1s(2)\alpha(2)1s(1)\beta(1)2s(3)\alpha(3)-1s(1)\alpha(1)1s(3)\beta(3)2s(2)\alpha(2)]$$

or

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\beta(3) \end{vmatrix} = \frac{1}{\sqrt{6}} [1s(1)\alpha(1)1s(2)\beta(2)2s(3)\beta(3) \\ +1s(2)\alpha(2)1s(3)\beta(3)2s(1)\beta(1)+1s(3)\alpha(3)1s(1)\beta(1)2s(2)\beta(2)-1s(3)\alpha(3)1s(2)\beta(2)2s(1)\beta(1) \\ -1s(2)\alpha(2)1s(1)\beta(1)2s(3)\beta(3)-1s(1)\alpha(1)1s(3)\beta(3)2s(2)\beta(2)].$$

Since two disjoint forms for ψ exist, the ground state of Li is doubly degenerate. This degeneracy is associated with the two orthogonal choices for the last column in the determinant. These correspond to the net spin S_z equal to $+1/2\hbar$; and to $-1/2\hbar$.

A zeroth order approximation would employ hydrogenlike atomic orbitals in the Slater determinant. Then for the first order approximation, one could argue that the average electron cloud in which a given electron moves has the result of reducing the effective charge on the nucleus. The other electrons are said to screen part of the nuclear charge.

To allow for this effect, one can replace the Z for each 1s orbital with a variable Z_1 . For the 2s orbital, one can replace Z with a variable Z_2 . One finds the lowest energy, -201.2 eV, for $Z_1 = 2.69$ and $Z_2 = 1.78$. But the experimental energy is -203.48 eV.

Actually, the screening should vary with r . Thus, the hydrogenlike radial function with altered Z is not adequate.

Example 12.15 : Uncodable (Answer in variable form)

Example 12.15

What terms arise when the electrons outside closed shells and subshells have the configuration (a) 3d4d, (b) 2p3p4p?

Sequence (12.136) is employed to find the possible L 's, sequence (12.137) for the possible S 's, and sequence (12.138) for the possible J 's, for successive couplings, until the configuration outside the closed shells and subshells is covered.

(a) Here $l_1 = 2$ and $l_2 = 2$. With sequence (12.135), we obtain

$$L = 4, 3, 2, 1, 0.$$

With sequence (12.137), we find that

$$S = 1, 0 \quad \text{and} \quad 2S + 1 = 3, 1.$$

The corresponding terms are

$$^3G, ^3F, ^3D, ^3P, ^3S, ^1G, ^1F, ^1D, ^1P, ^1S.$$

For each of these, the possible J 's can be readily determined and added as subscripts. Thus for the first term, we obtain

$$^3G_5, ^3G_4, ^3G_3$$

while for the sixth term, we have only

$$^1G_4.$$

(b) Here $l_1 = 1$, $l_2 = 1$, $l_3 = 1$. From l_1 and l_2 , we obtain

$$L' = 2, 1, 0 \quad \text{and} \quad S' = 1, 0.$$

Combining these results with l_3 , we find that

$$L = 3, 2, 1, 2, 1, 0, 1 \quad \text{and} \quad S = 3/2, \frac{1}{2}, \frac{1}{2}.$$

These yield the terms

$$^4F, ^4D, ^4P, ^2F, ^2D, ^2P, ^2P, ^4D, ^4P, ^4S, ^2D, ^2D, ^2P, ^2P, ^2S, ^2S, ^4P, ^2P, ^2P.$$

Again, the J 's could be added when needed in a detailed analysis.

Example 12.16 : Uncodable (Answer in variable form)

Example 12.16

Derive the terms for an np^2 configuration.

From the results for L' and S' in the (b) part of example 12.15, we see that if the Pauli exclusion principle did not intervene, the terms would be

$$^3D, ^3P, ^3S, ^1D, ^1P, ^1S.$$

But half of these are forbidden on ruling out doubly occupied states.

For a p electron, l is 1 and m_l may be +1, 0, or -1. Furthermore, s is 1/2 and m_s may be +1/2 or -1/2. Let us list the possibilities with \uparrow representing an electron with $m_s = 1/2$, \downarrow an electron with $m_s = -1/2$. The Pauli exclusion principle then allows the states appearing in the first three columns of table 12.3.

These yield the sums appearing in the fourth and fifth columns. There is only one state with $M_L = 2$, only one with $M_L = -2$. So the 3D term is ruled out. Going with the extreme states are one with $M_L = 1$, one with $M_L = 0$, one with $M_L = -1$, for term 1D . That leaves three states with $M_L = 1$, three with $M_L = -1$. These belong to the 3P term. Also with these are three states with $M_L = 0$. Left is a $M_L = 0, M_S = 0$ state. This forms the S term.

Thus, the allowed terms are

$$^1D, ^3P, ^1S.$$

Chapter 13

Example 13.1 : Uncodable (Answer in variable form)

Example 13.1

Derive the identities employed in equations (13.14) and (13.15).

First construct figure 13.2. Then employ the definitions of cosine and sine to obtain

$$x' = a \cos(\phi + \alpha) = b \cos \alpha - c \sin \alpha = a \cos \phi \cos \alpha - a \sin \phi \sin \alpha \quad \text{and}$$

and

$$y' = a \sin(\phi + \alpha) = b \sin \alpha + c \cos \alpha = a \cos \phi \sin \alpha + a \sin \phi \cos \alpha$$

whence

$$\cos(\alpha + \phi) = \cos \alpha \cos \phi - \sin \alpha \sin \phi,$$

$$\sin(\alpha + \phi) = \cos \alpha \sin \phi + \sin \alpha \cos \phi.$$

Example 13.2 : Uncodable (Answer in variable form)

Example 13.2

Determine the symmetry number for benzene.

Perpendicular to the plane of figure 13.4 through the center is a sixfold axis. The operations $I, C_6, C_3, C_2, C_3^{-1}, C_6^{-1}$ about it yield 6 permutations from the initial orientation. Perpendicular to the sixfold axis are three twofold axes passing through opposite vertices of the hexagon. These yield 3 additional permutations. Also perpendicular to the sixfold axis are three twofold axes passing through the middles of opposite edges of the hexagon. These yield 3 more permutations. So we have

$$\sigma = 6 + 3 + 3 = 12.$$

Example 13.3 : Uncodable (Answer in variable form)

Example 13.3

Subject figure 13.5 to the C_2, S_4 , and σ_d operations indicated and determine how the base vectors on the carbon atom transform.

Under the operation C_2 , we have

$$\mathbf{i}' = C_2 \mathbf{i} = -\mathbf{i}, \quad \mathbf{j}' = C_2 \mathbf{j} = -\mathbf{j}, \quad \mathbf{k}' = C_2 \mathbf{k} = \mathbf{k}, \quad \text{and}$$

and

$$(\mathbf{i}' \mathbf{j}' \mathbf{k}') = (\mathbf{i} \mathbf{j} \mathbf{k}) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The sum of the elements on the principal diagonal is -1.

Under the operation S_4 , we have

$$\mathbf{i}' = S_4 \mathbf{i} = \mathbf{j}, \quad \mathbf{j}' = S_4 \mathbf{j} = -\mathbf{i}, \quad \mathbf{k}' = S_4 \mathbf{k} = -\mathbf{k}, \quad \text{and}$$

and

$$(\mathbf{i}' \mathbf{j}' \mathbf{k}') = (\mathbf{i} \mathbf{j} \mathbf{k}) \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

The sum of elements on the principal diagonal is -1.

Under the operation σ_d , we have

$$\mathbf{i}' = \sigma_d \mathbf{i} = \mathbf{j}, \quad \mathbf{j}' = \sigma_d \mathbf{j} = \mathbf{i}, \quad \mathbf{k}' = \sigma_d \mathbf{k} = \mathbf{k}, \quad \text{and}$$

and

$$(\mathbf{i}' \mathbf{j}' \mathbf{k}') = (\mathbf{i} \mathbf{j} \mathbf{k}) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Example 13.4 : Uncodable (Answer in variable form)

Example 13.4

Subject figure 13.6 to the C_2 , S_4 , and σ_d operations indicated and determine the elements on the principal diagonal of the representation matrix.

Under the C_2 and S_4 operations, all the base vectors are permuted and we have all zeros on the principal diagonal.

Under the σ_d operation, we find that

$$\mathbf{k}_1' = \sigma_d \mathbf{k}_1 = \mathbf{k}_1, \quad \mathbf{k}_2' = \sigma_d \mathbf{k}_2 = \mathbf{k}_2,$$

while all other base vectors are permuted. We are left with two ones on the principal diagonal of the representation matrix. These add to give 2.

Example 13.5 : Uncodable (Answer in variable form)

Example 13.5

Subject figure 13.7 to the C_3 and σ_d operations indicated and determine how the stretching vectors transform.

Under the operation C_3 , we have

$$\mathbf{r}_1' = \mathbf{r}_1, \quad \mathbf{r}_2' = \mathbf{r}_3, \quad \mathbf{r}_3' = \mathbf{r}_4, \quad \mathbf{r}_4' = \mathbf{r}_2,$$

and

$$\begin{pmatrix} \mathbf{r}_1' & \mathbf{r}_2' & \mathbf{r}_3' & \mathbf{r}_4' \end{pmatrix} = \begin{pmatrix} \mathbf{r}_1 & \mathbf{r}_2 & \mathbf{r}_3 & \mathbf{r}_4 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}.$$

The sum of the elements on the principal diagonal is 1.

Under the operation σ_d , we have

$$\mathbf{r}_1' = \mathbf{r}_1, \quad \mathbf{r}_2' = \mathbf{r}_2, \quad \mathbf{r}_3' = \mathbf{r}_4, \quad \mathbf{r}_4' = \mathbf{r}_3,$$

Example 13.6 : Uncodable (Answer in variable form)

Example 13.6

Subject figure 13.8 to the C_2 and σ_d operations indicated and determine how the bond angles transform.

Under the C_2 operation, atom 1 moves to the 2 position, atom 2 to the 1 position, atom 3 to the 4 position, and atom 4 to the 3 position. So the angles between these transform as follows:

$$\alpha_{12}' = \alpha_{12}, \quad \alpha_{13}' = \alpha_{24}, \quad \alpha_{14}' = \alpha_{23}, \quad \alpha_{23}' = \alpha_{14}, \quad \alpha_{24}' = \alpha_{13}, \quad \alpha_{34}' = \alpha_{34},$$

whence

$$\begin{pmatrix} \alpha_{12}' & \alpha_{13}' & \alpha_{14}' & \alpha_{23}' & \alpha_{24}' & \alpha_{34}' \end{pmatrix} = \begin{pmatrix} \alpha_{12} & \alpha_{13} & \alpha_{14} & \alpha_{23} & \alpha_{24} & \alpha_{34} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The sum of the elements on the principal diagonal is 2.

Under the σ_d operation, only atoms 3 and 4 are interchanged. So we have

$$\begin{pmatrix} \alpha_{12}' & \alpha_{13}' & \alpha_{14}' & \alpha_{23}' & \alpha_{24}' & \alpha_{34}' \end{pmatrix} = \begin{pmatrix} \alpha_{12} & \alpha_{13} & \alpha_{14} & \alpha_{23} & \alpha_{24} & \alpha_{34} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The sum of the elements on the principal diagonal is 2.

Example

13.7 : Uncodable (Answer in variable form)

Example 13.7

Show that C_3 and C_3^{-1} belong to the same class when σ_v is also a symmetry operation.

Consider a molecule whose symmetry operations belong to the C_{3v} group. Break it down into three equivalent members and label these as in the left triangle of figure 13.10. Note the positions of the C_3 axis and the σ_v plane. Then apply operations σ_v^{-1} , C_3 , and σ_v in succession. The resulting configuration is the same as that obtained on applying C_3^{-1} alone. We thus find that

$$\sigma_v C_3 \sigma_v^{-1} = C_3^{-1}.$$

Example 13.8 : Uncodable (Answer in variable form)

Example 13.9 : Uncodable (Answer in variable form)

Example 13.10 : Uncodable (Answer in variable form)

Example 13.8

Determine the components of the character vector for the representation based on the Cartesian atomic displacements in tetrahedral methane and in similar molecules.

The unit displacement vectors are described by figures 13.5 and 13.6. For the identity operation, the number of vectors left unchanged is $3 \times 5 = 15$. So the entry under I in the character table is 15. With each C_3 , all the vectors are permuted; the entry under $8C_3$ is 0. With each C_2 and S_4 , the vectors on the central atom yield -1, as example 13.3 indicated, while those on the attached atoms yield 0, as example 13.4 concluded. The sum equals -1. With each σ_d , the vectors on the central atom yield 1 and those on the attached atoms yield 2, for a total of 3. The results are collected in table 13.3.

Example 13.9

Determine the components of the character vector for the representation based on the bond stretchings in tetrahedral methane and in similar molecules.

The radial unit displacement vectors are described in figure 13.7. For the identity operation, the number of vectors left unchanged is 4. So the entry under I is 4. From example 13.5, the component for the C_3 class is 1; the component for the σ_d class is 2. In the C_2 and S_4 operations, all the \mathbf{r}_j 's are permuted; so the corresponding components are 0. The results appear in table 13.3.

Example 13.10

Determine the components of the character vector for the representation based on the bond angle variations in tetrahedral methane and in similar molecules.

There are 6 bond angles. In the identity operation, the number left unchanged is 6. So the entry under I is 6. In the C_3 and S_4 operations, all 6 are permuted; so the corresponding components are 0. From example 13.6, the component for the C_2 class is 2; the component for the σ_d class is also 2. The results are listed in table 13.3.

Example 13.11 : Uncodable (Answer in variable form)

Example 13.12 : Uncodable (Answer in variable form)

Example 13.11

Determine the primitive symmetry species that contribute to motions of the atoms in tetrahedral AB_4 .

The first row in table 13.3 lists the components of the character vector for these motions. We see that these are obtained by adding the components for A_1 , E , F_1 , and $3F_2$ from table 13.2. Thus

$$\chi(\mathbf{i}_i, \mathbf{j}_i, \mathbf{k}_i) = A_1 + E + F_1 + 3F_2.$$

Now the translation of the center of mass behaves as (x, y, z) ; the rotation about this center, as (R_x, R_y, R_z) . Subtracting out the corresponding characters leaves

$$\chi(\text{vibration}) = A_1 + E + 2F_2.$$

Tetrahedral AB_4 thus has only four fundamental vibrational frequencies, one nondegenerate, one doubly degenerate, and two triply degenerate.

The vibrational F_2 modes involve the central atom moving oppositely to the center of mass of the attached atoms, so that the center of mass of the whole molecule does not move. This central atom motion is neglected in some of the following discussion. Taking it into account mixes some bond bending motion into the bond stretching motion and vice versa.

Example 13.12

Determine the primitive symmetry species that contribute to (a) the radial motions and (b) the angular motions in tetrahedral AB_4 .

The components in the second row of table 13.3 are obtained on adding the components for A_1 and F_2 . Thus

$$\chi(\mathbf{r}_i) = A_1 + F_2.$$

The components in the third row of table 13.3 are obtained on adding the components for A_1 , E , and F_2 . Thus

$$\chi(\alpha_{ij}) = A_1 + E + F_2.$$

From example 13.11, only one A_1 vibration exists. Since it involves the molecule expanding and contracting radially (a breathing motion), it does not involve any change in the angles. Only the E and the second F_2 motions are legitimate angular motions.

Example 13.13 : Uncodable (Answer in variable form)

Example 13.13

For tetrahedral AB_4 , how many fundamental transitions are active (a) in infrared absorption and emission, (b) in Raman interaction?

From example 13.11, the vibrations belong to A_1 , E , and two F_2 primitive symmetry types. But according to table 13.2, only an F_2 array behaves as a Cartesian coordinate. So there are two active infrared (IR) transitions. From example 13.12, one of these involves stretching of the bonds, the other bending of the bonds.

Also according to table 13.2, the rotational arrays generate the F_1 representation. So there is one triply degenerate rotationsl band.

The molecule here has a center of symmetry. So the F_2 transitions do not appear in Raman spectra. However, the A_1 and E arrays also behave as homogeneous quadratic functions of the Cartesian coordinates. The corresponding transitions are active in Raman transitions.

Example 13.14 : Uncodable (Answer in variable form)

Example 13.15 : Uncodable (Answer in variable form)

Example 13.14

In the absorption spectra of methane, two intense bands centered at 1306.2 and 3020.3 cm^{-1} appear. Assign these.

The force constant for stretching a bond is about ten times as large as that for bending it. So the higher wave number (and frequency) vibration involves this stretching. We assign the 3020.3 cm^{-1} band to the F_2 stretching mode, the 1306.2 cm^{-1} band to the F_2 bending mode.

Strictly, the former frequency has been altered somewhat by the mixing in of some bending motion; the latter frequency, by the mixing in of some stretching motion. Recall the comments in example 13.11.

Example 13.15

How do spectral studies support the tetrahedral structure for methane?

The tetrahedral structure for AB_4 is the most symmetric possible. Reducing the symmetry splits primitive symmetry species and so increases the number of fundamentals. In the problem set, group theoretical calculations on square pyramidal and square planar AB_4 are introduced. The results are summarized in table 13.4 Since methane has only two intense absorption bands, spectral measurements support the tetrahedral structure.

Example 13.16 : Codable

Example 13.17 : Uncodable (Answer in variable form)

Example 13.17

Consider a square molecule with unit displacement vectors arranged on nuclear equilibrium positions as figure 13.11 shows. Combine these to make up bases for pure modes of motion. Each of these modes must belong to a row of a primitive symmetry species.

Under operations of the C_4 group, unit vectors \mathbf{u}_1 , \mathbf{u}_5 , and \mathbf{u}_9 transform as table 13.5 shows. In table 13.6, the components of the character vectors are listed. Let us combine entries as formula (13.44) indicates.

For the A symmetry species, we find that

$$\mathbf{f}_1 = \mathbf{u}_1 + \mathbf{u}_2 + \mathbf{u}_3 + \mathbf{u}_4 \text{ for the breathing motion,}$$

$$\mathbf{f}_2 = \mathbf{u}_5 + \mathbf{u}_6 + \mathbf{u}_7 + \mathbf{u}_8 \text{ for rotation about the } z \text{ axis,}$$

$$\mathbf{f}_3 = \mathbf{u}_9 + \mathbf{u}_{10} + \mathbf{u}_{11} + \mathbf{u}_{12} \text{ for the translation in the } z \text{ direction.}$$

Chapter 14

Example 14.1 : Uncodable (Answer in variable form)

Example 14.1

To the approximation that the atomic orbitals and parameter α do not change in the process, what is the energy increment on forming a single symmetric covalent bond?

Applying formula (14.11) to the separated atoms gives

$$E = h_{AA} + h_{BB} = 2\alpha.$$

But formula (14.18) applies to each electron in the final state. We have

$$\Delta E = \frac{2\alpha + 2\beta}{1+S} - 2\alpha = \frac{2\beta - 2\alpha S}{1+S}$$

In the approximation that S is small, we find that

$$\Delta E \approx 2\beta.$$

This form explains why β is called the bond integral.

Example 14.2 : Uncodable (Answer in variable form)

Example 14.2

How much stability is gained in the formation of a three-center bond from a two-center bond and an empty orbital on the third center?

As a rough approximation, employ formulas (14.18) and (14.33) with α and β constant. Then we have

$$\Delta E = \frac{2\alpha + 4\beta}{1+2S} - \frac{2\alpha + 2\beta}{1+S} = \frac{2\beta - 2\alpha S}{(1+2S)(1+S)}.$$

If $S \approx 0$, then we find that

$$\Delta E \approx 2\beta.$$

Example 14.3 : Codable**Example 14.4 : Uncodable (Answer in variable form)****Example 14.4**

Construct the molecular orbital for the $\alpha + 0.61803\beta$ level in fulvene.

The simultaneous equations behind equation (14.124) are

$$\begin{aligned} (\alpha - E)a_1 + \beta a_2 &= 0, \\ \beta a_1 + (\alpha - \beta - E)a_2 &= 0. \end{aligned}$$

Here a_1 is the coefficient multiplying expression (14.115), a_2 the coefficient multiplying expression (14.116), in the molecular orbital.

The specified solution of the secular equation is

$$\alpha - E = -0.61803\beta.$$

Substituting this into the first equation yields

$$-0.61803\beta a_1 + \beta a_2 = 0$$

whence

$$a_2 = 0.61803 a_1.$$

Parameterize the normalization relation

$$a_1^2 + a_2^2 = 1$$

by setting

$$a_1 = \cos \alpha, \quad a_2 = \sin \alpha.$$

Then we find that

$$\alpha = \tan^{-1} 0.61803 = 31.72^\circ$$

and

$$a_1 = \cos 31.72^\circ = 0.85065,$$

$$a_2 = \sin 31.72^\circ = 0.52573.$$

But since

$$c_1 = \frac{a_1}{\sqrt{2}} = -c_4,$$

$$c_2 = \frac{a_2}{\sqrt{2}} = -c_3,$$

the molecular orbital is

$$\psi_{\text{III}} = 0.6015\psi_1 + 0.3718\psi_2 - 0.3718\psi_3 - 0.6015\psi_4.$$

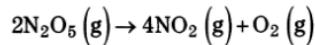
Chapter 15

Example 15.1 : Uncodable (Answer in variable form)

Example 15.2 : Uncodable (Answer in variable form)

Example 15.1

How does the total pressure in the reaction



vary with the degree of dissociation at a given temperature?

In the approximation that the constituents behave as ideal gases, we have

$$P = \frac{n}{V} RT = \frac{n}{n_0} \frac{n_0}{V} RT = \frac{n}{n_0} P_0.$$

Consider that we start with n_0 moles of pure gaseous reactant. Also let v be the number of moles of product gases produced from one mole of reactant. Then if α is the fraction dissociating in time t , we have

$$n = [1 + (v - 1)\alpha]n_0.$$

Combining these two equations yields

$$P = [1 + (v - 1)\alpha]P_0.$$

For the decomposition of N_2O_5 , parameter $v = 5/2$ and

$$P = \left(1 + \frac{3}{2}\alpha\right)P_0.$$

Example 15.2

How is the partial pressure of N_2O_5 related to the total pressure in the system described in example 15.1?

For the reaction



the degree of dissociation α satisfies the equation

$$1 - \alpha = \frac{n_{\text{A}}}{n_{\text{A}0}}.$$

When the reactant behaves as an ideal gas, we also have

$$P_{\text{A}} = \frac{n_{\text{A}}}{V} RT = \frac{n_{\text{A}}}{n_{\text{A}0}} \frac{n_{\text{A}0}}{V} RT = (1 - \alpha)P_0.$$

But from the penultimate equation in example 15.1, we obtain

$$(v - 1)\alpha = \frac{P}{P_0} - 1.$$

Thus from pressure measurements and knowledge of v , a person can determine P_{A} .

For the N_2O_5 decomposition, we find that

$$\frac{P_{\text{A}}}{P_0} = \left[1 - \frac{2}{3}\left(\frac{P}{P_0} - 1\right)\right] = \frac{5}{3} - \frac{2}{3}\frac{P}{P_0},$$

where A is N_2O_5 .

Example 15.3 : Codable

Example 15.4 : Codable

Example 15.5 : Uncodable (Answer in variable form)

Example 15.5

How does formula (15.65) reduce when the reaction is second order and the fraction reacted is 1/2?

First solve for $t_{1-\alpha}$,

$$t_{1-\alpha} = \frac{\alpha^{1-n} - 1}{(n-1)ka^{n-1}}.$$

Then consider that n is 2 and set $1 - \alpha$ equal to 1/2. We obtain

$$t_{1/2} = \frac{(1/2)^{-1} - 1}{(1)ka^1} = \frac{1}{k} \frac{1}{a}.$$

When a reaction is second order, a plot of the half life $t_{1/2}$ against the reciprocal of the chosen initial values should be a straight line with the slope $1/k$.

Example 15.6 : Uncodable (Answer in variable form)

Example 15.6

Repeat the calculation in example 15.5 for a fraction reacted of 1/4.

Now α is 3/4. So substituting into the rearranged formula (15.65) leads to

$$t_{1/4} = \frac{(3/4)^{-1} - 1}{(1)ka^1} = \frac{1}{3k} \frac{1}{a}.$$

When a reaction is second order, a plot of the quarter life $t_{1/4}$ against the reciprocal of the chosen initial values should be a straight line with the slope $1/(3k)$. Alternatively, one may divide $1/a$ by $t_{1/4}$ for the chosen intervals. Approximate constancy would indicate that the reaction is second order. One would then proceed to average the results and divide by 3 to get k .

Example 15.7 : Codable

Example 15.8 : Codable

Example 15.9 : Codable

Example 15.10 : Codable

Chapter 16

Example 16.1 : Uncodable (Answer in variable form)

Example 16.1

In 1919, Perrin proposed that reactant molecules acquire their activation energy by absorbing electromagnetic radiation from the surrounding walls. What is wrong with this hypothesis?

The radiation hypothesis requires the confining walls to do work on the reacting system by inducing chemical change in the mixture. But both the walls and the mixture are at the same temperature T . To produce appreciable net chemical work, the source needs to be at a much higher temperature than the reaction mixture, according to the second law of thermodynamics.

On the other hand, radiation with a non-Maxwellian distribution of frequencies may contain considerable work. The energy in radiation limited to a very narrow band is practically pure work. As an example, we have the radiation produced by an infrared laser.

Such a laser operating at or near the frequency of a vibrational mode of a reactant can be very effective in exciting the reactant and causing unimolecular reaction.

Example 16.2 : Codable

Chapter 17

Example 17.1 : Uncodable (Answer in variable form)

Example 17.1

Reduce equation (10.47) to a convenient form for calculating molecular translational partition functions.

Factor out the molecular mass, the absolute temperature, and the volume. Then introduce accepted values of the fundamental constants and carry out the indicated operations:

$$z_{\text{tr}} = \left(\frac{2\pi m_u k}{h^2} \right)^{3/2} M^{3/2} T^{3/2} V = \left[\frac{2\pi (1.660540 \times 10^{-27} \text{ kg u}^{-1}) (1.380658 \times 10^{-23} \text{ J K}^{-1})}{(6.626076 \times 10^{-34})^2 (\text{J s})(\text{kg m}^2 \text{ s}^{-1})} \right]^{3/2} M^{3/2} T^{3/2} V \\ = (1.879333 \times 10^{26} \text{ u}^{-3/2} \text{ K}^{-3/2} \text{ m}^{-3}) M^{3/2} T^{3/2} V.$$

Example 17.2 : Uncodable (Answer in variable form)

Example 17.3 : Uncodable (Answer in variable form)

Example 17.4 : Uncodable (Answer in variable form)

Example 17.2

For a linear molecule, the rotational partition function is given by equation (11.54), Reduce this to a convenient form for calculations from spectroscopic data.

From the separations between successive maxima in the rotational spectrum, or in the vibration- rotation spectrum, one obtains the parameter $2B$ in reciprocal centimeters. So we employ (11.54) in the form

$$z_{\text{rot}} = \frac{kT}{\sigma B} = \frac{0.69504 \text{ cm}^{-1} \text{ K}^{-1}}{\sigma} \frac{T}{B},$$

in which the result from example 11.7 has been introduced.

Example 17.3

For a nonlinear molecule, the rotational partition function is given by equation (11.57), Reduce this to a convenient form for calculations from spectroscopic data,

The rotational parts of the vibration-rotation spectrum of the given molecule are fitted to the calculated levels as approximated in table 11.1, Thus, parameters A , B , and C are obtained in reciprocal centimeters. So we employ (11.57) in the form

$$z_{\text{rot}} = \frac{\pi^{1/2} k^{3/2}}{\sigma(ABC)^{1/2}} T^{3/2} = \frac{\pi^{1/2} (0.69504 \text{ cm}^{-1} \text{ K}^{-1})^{3/2}}{\sigma(ABC)^{1/2}} T^{3/2} = \frac{(1.02704 \text{ cm}^{-3/2} \text{ K}^{-3/2}) T^{3/2}}{\sigma(ABC)^{1/2}}.$$

As before, σ is the symmetry number while A , B , and C are the rotational constants.

Example 17.4

For a vibrational mode, one form of the partition function appears in equation (12.53). Rewrite this employing the lowest energy level as the zero for energy. Also consider the Q line to be in reciprocal centimeters.

From the Q line in the vibrational and/or Raman spectra, one obtains the vibrational spacing $\hbar\omega$ for the mode in reciprocal centimeters. So referred to the lowest energy level as zero, we have

$$z_{\text{vib}} = \frac{1}{1 - e^{-\hbar\omega/kT}} = \frac{1}{1 - e^{-\hbar\omega/(0.69504 \text{ cm}^{-1} \text{ K}^{-1})T}}.$$

Example 17.5 : Uncodable (Answer in variable form)**Example 17.5**

Evaluate the *gamma function*

$$\Gamma(N+1) = \int_0^\infty t^N e^{-t} dt$$

for $N = 0$ and $N = 1$

Carrying out the integration for $N = 0$ yields

$$\Gamma(1) = \int_0^\infty e^{-t} dt = -e^{-t} \Big|_0^\infty = 1.$$

Similarly for $N = 1$,

$$\Gamma(2) = \int_0^\infty te^{-t} dt = -te^{-t} \Big|_0^\infty + \int_0^\infty e^{-t} dt = 0 + 1 = 1.$$

Example 17.6 : Uncodable (Answer in variable form)**Example 17.6**

Construct a recurrence formula for the gamma function.

Integrate the defining integral by parts with $N > 0$:

$$\Gamma(N+1) = \int_0^\infty t^N e^{-t} dt = -t^N e^{-t} \Big|_0^\infty + N \int_0^\infty t^{N-1} e^{-t} dt = 0 + N \Gamma(N) = N \Gamma(N).$$

For factorial N , we similarly have

$$N! = N(N-1)!$$

But from example 17.5, one can set

$$\Gamma(1) = 0! \quad \text{and} \quad \Gamma(2) = 1!$$

So when N is a positive integer, we find that

$$N! = \int_0^\infty t^N e^{-t} dt.$$

Example 17.7 : Uncodable (Answer in variable form)

Example 17.7

Construct a closed form approximation for $N!$.

In the gamma function integral, set

$$t^N e^{-t} = e^{g(t)},$$

so

$$g = N \ln t - t$$

and

$$\frac{dg}{dt} = \frac{N}{t} - 1,$$

$$\frac{d^2 g}{dt^2} = -\frac{N}{t^2}.$$

Then expand $g(t)$ about the point to $t_0 = N$, where

$$g = N \ln N - N, \quad \frac{dg}{dt} = 0, \quad \frac{d^2 g}{dt^2} = -\frac{1}{N},$$

in the Taylor series

$$g(t) = N \ln N - N - \frac{1}{2N} (t - t_0)^2 + \dots$$

Neglect higher terms and substitute into the integral:

$$N! \cong e^{N \ln N - N} \int_0^\infty e^{-(t-t_0)^2/2N} dt \cong \sqrt{2N} e^{N \ln N - N} \int_{-\infty}^\infty e^{-x^2} dx = \sqrt{2\pi N} \left(\frac{N}{e}\right)^N.$$

This result is known as the *Stirling approximation*. Its logarithm has the form

$$\ln N! \cong N \ln N - N + \frac{1}{2} \ln(2\pi N).$$

When N is large, the last term may be neglected.

Example 17.8 : Uncodable (Answer in variable form)

Example 17.9 : Uncodable (Answer in variable form)

Example 17.8

Construct a formula for the ideal rotational entropy of a system of identical linear molecules.

When B/kT is small, equation (11.51) or (11.52) holds. The corresponding internal energy is given by formula (11.60). For molecules, we have

$$[E - E(0)]_{\text{rot}} = NkT$$

and

$$Z_{\text{rot}} = z_{\text{rot}}^N = \left(\frac{kT}{\sigma B}\right)^N = \left(\frac{0.69504 \text{ cm}^{-1} \text{ K}^{-1}}{\sigma} \frac{T}{B}\right)^N.$$

Substituting into equation (17.19) and letting N be the Avogadro number yields

$$S_{\text{rot}} = Nk \ln z_{\text{rot}} + Nk = R(1 + \ln 0.69504 + \ln T - \ln \sigma B) = R(0.63621 + \ln T - \ln \sigma B).$$

Here T is in kelvins, B in reciprocal centimeters, while σ is the symmetry number.

Example 17.9

Construct a formula for the ideal rotational entropy of a system of identical nonlinear molecules.

When $ABC/(kT)^3$ is small, equation (11.57) or (11.58) holds. The corresponding internal energy is given by formula (11.62). For N molecules, we have

$$[E - E(0)]_{\text{rot}} = \frac{3}{2} N k T$$

and

$$Z_{\text{rot}} = z_{\text{rot}}^N = \left(\frac{\pi^{1/2} k^{3/2} T^{3/2}}{\sigma(ABC)^{1/2}} \right)^N = \left[\frac{(1.02704 \text{ cm}^{-3/2} \text{ K}^{-3/2}) T^{3/2}}{\sigma(ABC)^{1/2}} \right]^N.$$

Substituting into equation (17.19) and letting N be the Avogadro number yields

$$\begin{aligned} S_{\text{rot}} &= Nk \ln z_{\text{rot}} + \frac{3}{2} Nk = R \left[\left(\frac{3}{2} \right) + \ln 1.02704 + \left(\frac{3}{2} \right) \ln T - \ln \sigma(ABC)^{1/2} \right] \\ &= R \left[1.52668 + \left(\frac{3}{2} \right) \ln T - \ln \sigma(ABC)^{1/2} \right]. \end{aligned}$$

Here T is in kelvins, A, B, C are in reciprocal centimeters, while σ is the symmetry number.

Example 17.10 : Uncodable (Answer in variable form)

Example 17.11 : Uncodable (Answer in variable form)

Example 17.10

Construct a formula for the partition function of Na (g). The molecular mass M is 22.990 u, while the lowest electronic state is a doublet.

We consider that practically all the atoms are in their ground electronic state. Since this is a doublet, we have

$$z_{\text{el}} = 2.$$

Since there are no rotational or vibrational modes, we take

$$z_{\text{rot}} = z_{\text{vib}} = 1.$$

From the formula in example 17.1, we obtain

$$z_{\text{tr}} = \left(1.8793 \times 10^{26} \right) \left(22.990 \right)^{3/2} T^{3/2} V \text{ K}^{-3/2} \text{ m}^{-3} = \left(2.0716 \times 10^{28} \right) T^{3/2} V \text{ K}^{-3/2} \text{ m}^{-3}.$$

Multiplying these factors yields

$$z_{\text{Na}} = z_{\text{tr}} z_{\text{rot}} z_{\text{vib}} z_{\text{el}} = \left(4.1432 \times 10^{28} \right) T^{3/2} V \text{ K}^{-3/2} \text{ m}^{-3}.$$

Example 17.11

Construct a formula for the partition function of Na_2 (g). The parameters for the molecule are $B = 0.1547 \text{ cm}^{-1}$, $k_0 = 159.2 \text{ cm}^{-1}$, $D = 70.4 \text{ kJ mol}^{-1}$.

Since all electrons are paired in the ground state, we have

$$z_{\text{el}} = 1.$$

Since the molecule is linear, the rotational formula in example 17.2 applies:

$$z_{\text{rot}} = \frac{kT}{\sigma B} = \frac{0.69504}{2} \frac{T \text{ K}^{-1}}{0.1547} = 2.24641 T \text{ K}^{-1}.$$

For the one vibrational mode, the formula in example 17.4 is employed:

$$z_{\text{vib}} = \frac{1}{1 - e^{-k_0/kT}} = \frac{1}{1 - e^{-(229.05 \text{ K})/T}}.$$

For the three translational modes, we have

$$z_{\text{tr}} = \left(1.8793 \times 10^{26} \right) \left(45.98 \right)^{3/2} T^{3/2} V \text{ K}^{-3/2} \text{ m}^{-3} = \left(5.8594 \times 10^{28} \right) T^{3/2} V \text{ K}^{-3/2} \text{ m}^{-3}.$$

Multiplying these four factors gives us z_{Na_2} . Also note that

$$\frac{D}{RT} = \frac{70.4 \times 10^4 \text{ K}}{8.31451 T} = \frac{8.46713 \times 10^3}{T} \text{ K}.$$

Example 17.12 : *Codable*

Example 17.13 : *Codable*

Example 17.14 : *Codable*

Example 17.15 : *Codable*

Chapter 18

Example 18.1 : Uncodable (Answer in variable form)

Example 18.1

Evaluate the integral

$$\int_0^\infty ve^{-av^2} dv.$$

Rearrange and identify the resulting integral as follows:

$$\int_0^\infty ve^{-av^2} dv = -\frac{1}{2a} \int_0^\infty e^{-av^2} (-2av dv) = -\frac{1}{2a} e^{-av^2} \Big|_0^\infty = \frac{1}{2a}.$$

Example 18.2 : Uncodable (Answer in variable form)

Example 18.2

Evaluate

$$\int_0^\infty e^{-av^2} dv.$$

From example 10.5, this integral equals

$$\frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}.$$

Example 18.3 : Uncodable (Answer in variable form)

Example 18.3

Estimate the frequency factor A for a unimolecular reaction at 25° C.

The pre-exponential factor from formula (18.11) has the form

$$A = \frac{kT}{h} \frac{z^*}{z_A},$$

in which z_A is the partition function per unit volume for the reactant and z^* is the residual partition function per unit volume for the transition state. The translational factors for z_A and z^* are equal; in the ratio they cancel. The moment(s) of inertia in the transition state is(are) somewhat larger than in the initial state. We neglect this change and let the rotational factors in z_A and z cancel. There is one less vibrational factor in z , that along the reaction coordinate. However, the vibrational factors are not much greater than 1 and the increase in the remaining ones may partially compensate for the one lost in z .

So we reach the approximation

$$A \approx \frac{kT}{h}$$

for the unimolecular reaction. At 25° C, we have

$$A = \frac{(1.3807 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}{6.6261 \times 10^{-34} \text{ Js}} = 6.21 \times 10^{12} \text{ s}^{-1}.$$

If the Boltzmann distribution is disturbed significantly by the reaction, the reaction may be abnormally slow. On the other hand, if the process is complex, the reaction may be abnormally fast.

Example 18.4 : Uncodable (Answer in variable form)

Example 18.4

Formulate the specific reaction rate for atom A striking atom B as in section 3.15. Consider the electronic partition functions to equal 1.

From formula (10.47), the partition functions per unit volume for A and B are

$$z_A = \frac{(2\pi m_A kT)^{3/2}}{h^3}, \quad z_B = \frac{(2\pi m_B kT)^{3/2}}{h^3}.$$

Similarly, the three-dimensional partition function per unit volume for the complex is

$$z_{tr} = \frac{[2\pi(m_A + m_B)kT]^{3/2}}{h^3}.$$

From formula (11.54), the rotational partition function for the complex is

$$z_{rot} = \frac{8\pi^2 \mu r^2 kT}{h^2}$$

where

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad \text{and} \quad r = r_A + r_B.$$

Substituting into the coefficient of [AB] in (18.11) yields

$$k_c = \frac{kT}{h} K^* = \frac{kT}{h} \frac{\left\{ [2\pi(m_A + m_B)kT]^{3/2} / h^3 \right\} (8\pi^2 \mu r^2 kT / h^2)}{\left[(2\pi m_A kT)^{3/2} / h^3 \right] \left[(2\pi m_B kT)^{3/2} / h^3 \right]} e^{-\Delta E_0 / RT} = \pi r^2 \left(\frac{8kT}{\pi \mu} \right)^{1/2} e^{-\Delta E_0 / RT}.$$

Note that this agrees with the coefficient in formula (3.101) when the energy barrier ΔE_0 vanishes,

Example 18.5 : Uncodable (Answer in variable form)

Example 18.5

Atom A approaches a linear molecule B along its axis. A bond is formed with the struck atom while the atom at the other end of B is set free. Formulate the specific reaction rate. The translational partition functions per unit volume for A, B, and AB appear as in example 18.4. They introduce the factor

$$\frac{[2\pi(m_A + m_B)kT]^{3/2} / h^3}{\left[(2\pi m_A kT)^{3/2} / h^3 \right] \left[(2\pi m_B kT)^{3/2} / h^3 \right]} = \frac{h^3}{(2\pi \mu kT)^{3/2}}$$

into K^\ddagger . For the ratio of the rotational partition functions in K^\ddagger , we have

$$[8\pi^2 I^\ddagger kT/\hbar^3] / [8\pi^2 I_B kT/\sigma_B \hbar^3] = \sigma_B I^\ddagger / I_B$$

On forming the complex AB, two low frequency bending vibrational modes appear. They introduce the factor

$$z_{\text{vib}}^\ddagger = \frac{1}{(1 - e^{-\beta \hbar \omega_0})^2}$$

into K^\ddagger . For the coefficient of [AB] in the rate expression, we obtain

$$\frac{kT}{h} K^\ddagger = \frac{kT}{h} \frac{\hbar^3}{(2\pi\mu kT)^{3/2}} \frac{\sigma_B I^\ddagger}{I_B} z_{\text{vib}}^\ddagger e^{-\Delta E_0/RT} = \frac{\hbar^2}{(2\pi\mu)^{3/2} (kT)^{1/2}} \frac{\sigma_B I^\ddagger}{I_B} z_{\text{vib}}^\ddagger e^{-\Delta E_0/RT}$$

Note how the additional structure in B has altered the expression k_c in the preceding example. Since the new expression contains geometric constraints on how A must approach B, it generally yields a smaller specific reaction rate.

One might multiply k_c by a steric factor p that varies with the temperature T and thus get agreement.

Example 18.6 : Codable

Example 18.7 : Uncodable (Answer in variable form)

Example 18.7

When the friction coefficient $\mu\beta$ is large, movement to the transition state may be described as a diffusion process. Relate the Kramers coefficient κ^{KR} to the pertinent diffusion coefficient.

From the Stokes law, equation (5.106), the retarding force on the average reacting complex is

$$f = -6\pi\eta r\dot{x}.$$

Set the coefficient of x in (18.42) equal to the coefficient here and introduce relationship (5.113) to construct

$$\mu\beta = 6\pi\eta r = \frac{k_B T}{D}.$$

Then substitute the resulting β into formula (18.57) to get

$$\kappa^{KR} = \frac{\mu\omega_0 D}{k_B T}.$$

Example 18.8 : Codable

Chapter 19

Example 19.1 : Codable

Example 19.2 : Uncodable

Example 19.2

Let a photon be absorbed by a particle of mass M initially at rest and determine what fraction of the photon energy appears as recoil kinetic energy.

Here the momentum p of the photon ends up as momentum of the excited particle. Let E_{re} be the recoil energy while E is the photon energy.

From formula (19.9), we have

$$p = \frac{E}{c}.$$

But the recoil energy is

$$E_{\text{re}} = \frac{p^2}{2M} = \frac{E^2}{2Mc^2}$$

whence

$$\frac{E_{\text{re}}}{E} = \frac{E}{2Mc^2}.$$

Example 19.3 : Codable

Example 19.4 : Codable

Example 19.5 : Codable

Example 19.6 : Codable