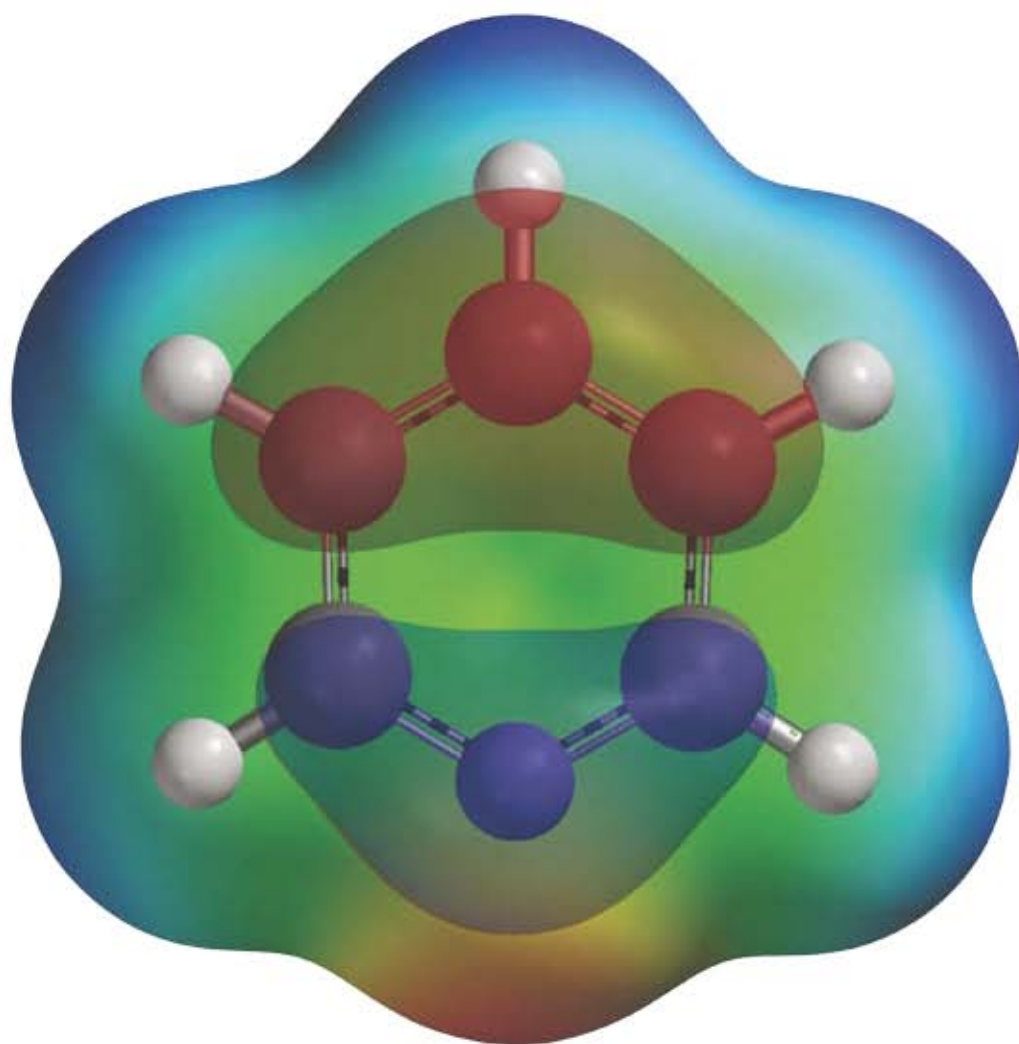


# Quanta, Matter, and Change

A molecular approach to physical chemistry



Peter Atkins, Julio de Paula, and Ronald Friedman

---

*This page intentionally left blank*

---

# Quanta, Matter, and Change

A molecular approach to physical chemistry

---

Library of Congress Control Number: 2005936591

*Quanta, Matter, and Change: A molecular approach to physical chemistry*  
© 2009 by Peter Atkins, Julio de Paula, and Ronald Friedman  
All rights reserved

ISBN: 0-7167-6117-3

Published in the United States and Canada by W. H. Freeman and Company  
This edition has been authorized by Oxford University Press for sale in the  
United States and Canada only and not for export therefrom.

First printing 2009

Typeset by Graphicraft Ltd, Hong Kong  
Printed and bound in China by C&C Offset Printing Co. Ltd

W. H. Freeman and Company  
41 Madison Avenue  
New York, NY 10010  
[www.whfreeman.com](http://www.whfreeman.com)

---

# Quanta, Matter, and Change

A molecular approach to physical chemistry

**Peter Atkins**

*Professor of Chemistry,  
University of Oxford,  
and Fellow of Lincoln College, Oxford*

**Julio de Paula**

*Professor and Dean of the College of Arts and Sciences,  
Lewis and Clark College,  
Portland, Oregon*

**Ronald Friedman**

*Professor and Chair of Chemistry,  
Indiana University Purdue University Fort Wayne,  
Fort Wayne, Indiana*



W. H. Freeman and Company  
New York



---

## About the book

---

Our *Physical Chemistry* has always started with thermodynamics, progressed on to quantum mechanics, and then brought these two great rivers together by considering statistical thermodynamics. We always took care to enrich the thermodynamics with molecular understanding, and wrote the text so that it could be used flexibly to suit the pedagogical inclinations of its users. There are many, though, who consider it more appropriate to build an understanding of the subject from a firm foundation of quantum theory and then to show how the concepts of thermodynamics emerge as the microscopic evolves into the macroscopic. This text is directed at them.

We have taken the cloth of *Physical Chemistry*, unravelled it, and woven a new cloth that begins from quantum theory, establishes the link with the macroscopic world by introducing statistical thermodynamics, and then shows how thermodynamics is used to describe bulk properties of matter. But this is no mere reordering of topics. As we planned the book and then progressed through its writing, we realized that we had to confront issues that required fundamentally new approaches even to very familiar material. In fact, we experienced a kind of intellectual liberation that comes from looking at a familiar subject from a new perspective. Therefore, although readers will see material that has appeared throughout the editions of *Physical Chemistry*, there is an abundance of new material, new approaches to familiar topics, and—we hope—a refreshing new insight into the familiar.

The text is divided into five parts and preceded by a *Fundamentals* section that reviews the material that we presume is already familiar to readers at this level but about which their memories might need a gentle prod. In *Part 1, Quantum theory*, we set out the foundations of quantum mechanics in terms of its postulates and then show how these principles are used to describe motion in one and more dimensions. We have acknowledged the present surge of interest in nanoscience, and have built our presentation around these exciting systems. In *Part 2, Atoms molecules, and assemblies*, we turn to the more traditional nanosystems of chemistry and work progressively through the building blocks of chemistry, ending with solids. We have paid particular attention to computational chemistry, which is, of course, of great practical significance throughout chemistry. We have confronted head on the sheer difficulty of presenting computational chemistry at this level by illustrating all the major techniques by focusing on an almost trivially simple system. Our aim in this important chapter was to give a sense of reality to this potentially recondite subject: we develop understanding and provide a launching platform for those who wish to specialize further. *Part 3, Molecular spectroscopy*, brings together all the major spectroscopic techniques, building on the principles of quantum mechanics introduced in Part 1.

*Part 4, Molecular thermodynamics*, was for us the most challenging—and therefore the most exciting—part to write, for here we had to make the awesome passage from the quantum theory of microscopic systems to the thermodynamic properties of bulk matter. The bridge is provided by that most extraordinary concept, the Boltzmann distribution. Once that concept has been established, it can be used to develop an understanding of the central thermodynamic properties of internal energy and entropy. We have trodden carefully through this material, trying to maintain the sense that thermodynamics is a self-contained subject dealing with phenomenological relations between properties but, at the same time, showing the illumination that comes from a molecular perspective. We hope this sensitivity to the subject is apparent and that the new insights that we ourselves have acquired in the course of developing this material will be found to be interesting and informative. There are parts of traditional thermodynamics (phase equilibria, among them), we have to admit, that are not open to this kind of elucidation or at least would be made unduly complicated, and

we have not hesitated where our judgement persuaded us to set the molecular aside and present the material from a more straightforward classical viewpoint.

In *Part 5, Chemical dynamics*, we turn to another main stream of physical chemistry, the rates of reactions. Some of this material—the setting up of rate laws, for instance—can be expressed in a purely traditional manner, but there are aspects of the dynamics of chemical reactions that draw heavily on what has gone before.

The ‘Using the book’ section that follows gives details of the pedagogical apparatus in the book, but there is one feature that is so important that it must be mentioned in this Preface. The principal impediment to the ‘quantum first’ approach adopted by this text is the level of mathematics required, or at least the *perceived* level if not the actual level, for we have taken great pains to step carefully through derivations. The actual level of mathematics needed to understand the material is not great, but the thought that it exists can be daunting. To help overcome this barrier to understanding we have included a series of *Mathematical background* features between various chapters. These sections (there are eight) give background support to the mathematics that has been used in the preceding chapter and which will be drawn on in later chapters. We are aware that many chemists prefer the concrete to the abstract, and have illustrated the material with numerous examples.

We hope that you will enjoy using the book as much as we have enjoyed—and learned from—writing it and will appreciate that we have aimed to produce a book that illuminates physical chemistry from a new direction.

PWA  
JdeP  
RSF



# Using the book

We have paid attention to the needs of the student, and have provided a lot of pedagogical features to make the learning process more enjoyable and effective. This section reviews these features. Paramount among them, though, is something that pervades the entire text: we have tried throughout to *interpret* the mathematical expressions, for mathematics is a language, and it is crucially important to be able to recognize what it is seeking to convey. We have paid particular attention to the level at which we introduce information, the possibility of progressively deepening one's understanding, and providing background information to support the development in the text. We have also been very alert to the demands associated with problem solving, and have provided a variety of helpful procedures.

## Organizing the information

### Checklist of key ideas

We have summarized the principal concepts introduced in each chapter as a checklist at the end of the chapter. We suggest checking off the box that precedes each entry when you feel confident about the topic.

#### Checklist of key ideas

- |   |   |
|---|---|
| <input type="checkbox"/> 1. A van der Waals interaction between closed-shell molecules is inversely proportional to the sixth power of their separation.  | <input type="checkbox"/> 8. A hydrogen bond is an interaction where A and B are N, O, or F.   |
| <input type="checkbox"/> 2. The permittivity is the quantity $\epsilon$ in the Coulomb potential energy, $V = Q_1 Q_2 / 4\pi\epsilon r$ .   | <input type="checkbox"/> 9. The Lennard-Jones (12,6) potential is a model of the total intermolecular energy.   |
| <input type="checkbox"/> 3. A polar molecule is a molecule with a permanent electric dipole moment; the magnitude of a dipole moment is the product of the partial charge and the separation.   | <input type="checkbox"/> 10. In real gases, molecular interactions are modeled by the true equation of state in which the coefficients $B, C, \dots$ : $pV_m = RT + Bp + Cp^2 + \dots$                            |
| <input type="checkbox"/> 4. The potential energy of the dipole-dipole interaction between two fixed (non-rotating) molecules is proportional to $\mu_1 \mu_2 / r^3$ and that between molecules that are free to rotate is proportional to $\mu_1 \mu_2 / r^3$ . | <input type="checkbox"/> 11. The van der Waals equation of state is the true equation of state in which the parameters $a$ and $b$ are represented by a parameter $a$ and $b$ : $p = nRT / (V - nb) - a(n/V)^2$ . |

### Impact sections

Where appropriate, we have separated the principles from their applications: the principles are constant; the applications come and go as the subject progresses. The *Impact* sections show how the principles developed in the chapter are currently being applied in a variety of modern contexts, especially biology and materials science.

#### IMPACT ON BIOCHEMISTRY

##### I13.1 The helix-coil transition in polypeptides

The hydrogen bonds between amino acids of a polypeptide give rise to stable helical or sheet structures, which may collapse into a random coil when certain conditions are changed. The unwinding of a helix into a random coil is a *cooperative transition*, in which the polymer becomes increasingly more susceptible to structural changes once the process has begun. We examine here a model based on the principles of statistical thermodynamics that accounts for the cooperativity of the helix-coil transition in polypeptides.

To calculate the fraction of polypeptide molecules present as helix or coil we need to set up the partition function for the vari-

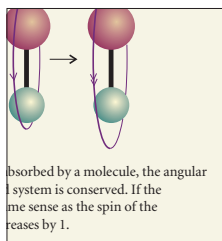
ward: we simply replace the upper li

$$\frac{q}{q_0} = \sum_{i=0}^n C(n,i) s^i$$

A cooperative transformation is moderate, and depends on building a model, conversion from  $h$  to  $c$  is all about the one undergoing the conversion. Thus, the zipper model allows a transition  $\dots \rightarrow \dots hhhcc \dots$ , but not a transition  $\dots \rightarrow \dots hchch \dots$ . The only exception is the very first conversion from  $h$  to

### Notes on good practice

Science is a precise activity and its language should be used accurately. We have used this feature to help encourage the use of the language and procedures of science in conformity to international practice (as specified by IUPAC, the International Union of Pure and Applied Chemistry) and to help avoid common mistakes.

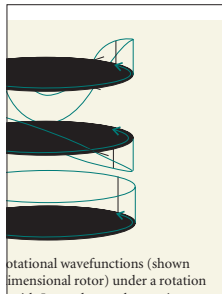


**Self-test 10.4** Repeat the problem for  $C^{35}CH_3$  (see Self-test 10.2 for details).  
[Lines of separation  $0.944 \text{ cm}^{-1}$  (28.3 GHz)]

**A note on good practice** For the discussion of spectroscopic transitions, the upper state is written first. So  $X \rightarrow Y$  is an emission and  $X \leftarrow Y$  is an absorption, where X and Y specify the states in some way (such as by giving the value of the rotational quantum number  $J$ , as we have done above).

### Justifications

On first reading it might be sufficient simply to appreciate the 'bottom line' rather than work through detailed development of a mathematical expression. However, mathematical development is an intrinsic part of physical chemistry, and to achieve full



For hydrogen,  $I = \frac{1}{2}$ , and the ratio is 3:1. For  $N_2$ , with  $I = 1$ , the ratio is 1:2.

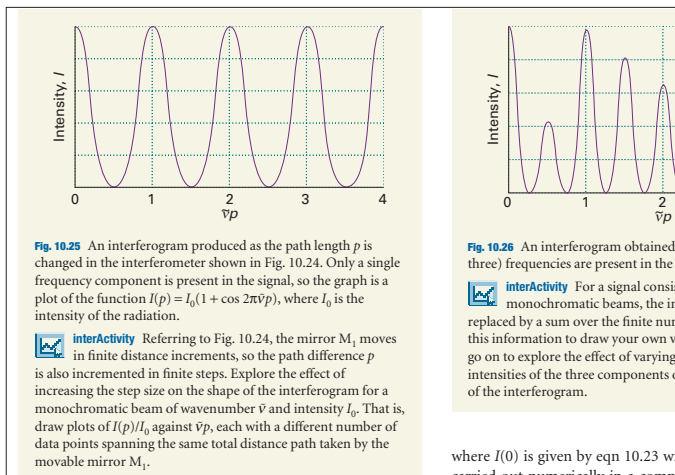
**Justification 10.1** The effect of nuclear statistics on rotational spectra

Hydrogen nuclei are fermions (particles with half-integer spin quantum number; in their case  $I = \frac{1}{2}$ ), so the Pauli principle requires the overall wavefunction to change sign under particle interchange. However, the rotation of an  $H_2$  molecule through  $180^\circ$  has a more complicated effect than merely relabelling the nuclei, because it interchanges their spin states too if the nuclear spins are paired ( $\uparrow\downarrow$ ) but not if they are parallel ( $\uparrow\uparrow$ ).  
For the overall wavefunction of the molecule to change

understanding it is important to see how a particular expression is obtained. The *Justifications* let you adjust the level of detail that you require to your current needs, and make it easier to review material.

### interActivities

You will find that many of the graphs in the text have an *interActivity* attached: this is a suggestion about how you can use the on-line-resources of the book's website to explore the consequences of changing various parameters or of carrying out a more elaborate investigation related to the material in the illustration.



### Further information

In some cases, we have judged that a derivation is too long, too detailed, or too different in level for it to be included in the text. In these cases, the derivations will be found less obtrusively at the end of the chapter.

#### Further information 13.2 The partition functions of polyatomic rotors

The energies of a symmetric rotor are

$$E_{J,K,M_J} = hcB(J+1) + hc(A-B)K^2$$

with  $J = 0, 1, 2, \dots, K = J, J-1, \dots, -J$ , and  $M_J = J, J-1, \dots, -J$ . Instead of considering these ranges, we can cover the same values by allowing  $K$  to range from  $-\infty$  to  $\infty$ , with  $J$  confined to  $|K|, |K|+1, \dots, \infty$  for each value of  $K$  (Fig. 13.23). Because the energy is independent of  $M_J$ , and there are  $2J+1$  values of  $M_J$  for each value of  $J$ , each value of  $J$  is  $(2J+1)$ -fold degenerate. It follows that the partition function

$$q = \sum_{J=0}^{\infty} \sum_{K=-J}^J \sum_{M_J=-J}^J e^{-E_{J,K,M_J}/kT}$$

can be written equivalently as

$$q = \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-E_{J,K,M_J}/kT}$$

$$= \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-hc[B(J+1) + (A-B)K^2]/kT} \quad (13.59)$$

Now we assume that the temperature is so high that the sums may be approximated by integrals:

$$q = \int_{-\infty}^{\infty} e^{-[hc(A-B)/kT]K^2} \int_{|K|}^{\infty} (2J+1) e^{-hcBJ/kT} dJ$$

As before, the integral over  $J$  can be recognized as the derivative of a function, which is the function

$$\int_{|K|}^{\infty} (2J+1) e^{-hcB(J+1)/kT} dJ = \int_{|K|}^{\infty} \left( -\frac{kT}{hcB} \right) e^{-hcB(J+1)/kT} dJ$$

$$= \left( -\frac{kT}{hcB} \right) e^{-hcB(J+1)/kT}$$

$$= \left( \frac{kT}{hcB} \right) e^{-hcB(J+1)/kT}$$

$$= \left( \frac{kT}{hcB} \right) e^{-hcB(J+1)/kT}$$

### Synoptic tables and the Resource section

Long tables of data are helpful for assembling and solving exercises and problems, but can break up the flow of the text. The *Resource section* at the end of the text consists of a *Data section* with a lot of useful numerical information and a collection of other useful tables. Short extracts in the *Synoptic tables* in the text itself give an idea of the typical values of the physical quantities we are introducing.

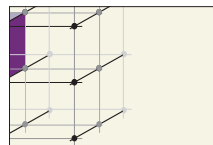
#### Part 1 Data section

Physical properties of selected materials					
Elements	$\rho/(\text{g cm}^{-3})$ at 293 K†	$T_f/\text{K}$	$T_b/\text{K}$	$\rho/(\text{g cm}^{-3})$ at 293 K†	
Aluminium(s)	2.698	933.5	2740	Inorganic compounds	
Argon(g)	1.381	83.8	87.3	CaCO <sub>3</sub> (s, calcite)	2.71
Boron(s)	2.340	2573	3931	CuSO <sub>4</sub> ·5H <sub>2</sub> O(s)	2.284
Bromine(l)	3.123	265.9	331.9	HBr(g)	2.77
Carbon(s, gr)	2.260	3700s		HCl(g)	1.187
Carbon(s, d)	3.513			HI(g)	2.85
Chlorine(g)	1.507	172.2	239.2	H <sub>2</sub> O(l)	0.997
Copper(s)	8.960	1357	2840	D <sub>2</sub> O(l)	1.104
Fluorine(g)	1.108	53.5	85.0	NH <sub>3</sub> (g)	0.817
Gold(s)	19.320	1338	3080	KBr(s)	2.750
Helium(g)	0.125		4.22	KCl(s)	1.984
Hydrogen(g)	0.071	14.0	20.3	NaCl(s)	2.165
Iodine(s)	4.930	386.7	457.5	H <sub>2</sub> SO <sub>4</sub> (l)	1.841
Iron(s)	7.874	1808	3023	Organic compounds	
Krypton(g)	2.413	116.6	120.8	Acetaldehyde, CH <sub>3</sub> CHO(l)	0.788
Lead(s)	11.350	600.6	2013	Acetic acid, CH <sub>3</sub> COOH(l)	1.049

### Mathematics support

#### A brief comment

A topic often needs to draw on a mathematical procedure or a concept of physics; A *brief comment* is a quick reminder of the procedure or concept.



sided (but not necessarily the entire crystal structure can be symmetrized (not reflections, rotations,

**A brief comment** A *symmetry operation* is an action (such as a rotation, reflection, or inversion) that leaves an object looking the same after it has been carried out. There is a corresponding *symmetry element* for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed. For instance, an *n-fold rotation* (the symmetry operation) about an *n-fold axis of symmetry* (the corresponding symmetry element) is a rotation through  $360^\circ/n$ . See Chapter 7 for a more detailed discussion of symmetry.

## Mathematical background

It is often the case that you need a more full-bodied account of a mathematical concept, either because it is important to understand the procedure more fully or because you need to use a series of tools to develop an equation. The eight *Mathematical background* sections are located between chapters, primarily where they are first needed, and include many illustrations of how each concept is used.

MATHEMATICAL BACKGROUND 8: MULTIVARIATE CALCULUS

**MATHEMATICAL BACKGROUND 8**  
**Multivariate calculus**

A property of a system typically depends on a number of variables, such as the pressure depending on the amount, volume, and temperature according to an equation of state,  $p = f(n, T, V)$ . To understand how these properties vary with the conditions we need to understand how to manipulate their derivatives. This is the field of **multivariate calculus**, the calculus of several variables.

**MB8.1 Partial derivatives**

A **partial derivative** of a function of more than one variable, such as  $f(x, y)$ , is the slope of the function with respect to one of the variables, all the other variables being held constant (Fig. MB8.1). Although a partial derivative shows how a function changes when one variable changes, it may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if  $f$  is a function of  $x$  and  $y$  then, when  $x$  and  $y$  change by  $dx$  and  $dy$ , respectively,  $f$  changes by

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \quad (\text{MB8.1})$$

**Self test MB8.1** Evaluate  $df$  for verify that the order of taking the is irrelevant. [ $df = 4x^2y dx + 2xy^2 dy$ ]

## Problem solving

### A brief illustration

A *brief illustration* is a short example of how to use an equation that has just been introduced in the text. In particular, we show how to use data and how to manipulate units correctly.

**• A BRIEF ILLUSTRATION**

Consider a complex salt with three unpaired electrons per complex cation at 298 K, of mass density  $3.24 \text{ g cm}^{-3}$ , and molar mass  $200 \text{ g mol}^{-1}$ . First note that

$$\frac{N_A g^2 \mu_B^2}{3k} = 6.3001 \times 10^{-6} \text{ m}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

Consequently,

$$\chi_m = 6.3001 \times 10^{-6} \times \frac{S(S+1)}{T/K} \text{ m}^3 \text{ mol}^{-1}$$

Substitution of the data with  $S = \frac{3}{2}$  gives  $\chi_m = 7.9 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$ . Note that the density is not needed at this stage. To obtain the volume magnetic susceptibility, the molar susceptibility is divided by the molar volume  $V_m = M/\rho$ , where  $\rho$  is the mass density. In this illustration,  $V_m = 61.7 \text{ cm}^3 \text{ mol}^{-1}$ , so  $\chi = 1.3 \times 10^{-3}$ . ●

**(c) Induced magnetic moments**

An applied magnetic field induces the currents. These currents give rise to a magnetic field that opposes the applied field, so the substance is diamagnetic. In a few cases the induced field augments the substance is then paramagnetic.

The great majority of molecules with unpaired electrons are diamagnetic. In these cases, the electrons occur within the orbitals of the molecule in its ground state. In the few cases in which a molecule is paramagnetic despite having no unpaired electrons, the paramagnetism can make use of unoccupied orbitals that are higher in energy. This orbital paramagnetism is called **temperature-independent paramagnetism (TIP)**.

We can summarize these remarks as

## Worked examples

Each *Worked example* has a *Method* section to suggest how to set up the problem (another way might seem more natural: setting up problems is a highly personal business) and use or find the necessary data. Then there is the worked-out *Answer*, where we emphasize the importance of using units correctly.

**Example 13.5** Evaluating the rotational partition function explicitly

Evaluate the rotational partition function of  $^1\text{H}^{35}\text{Cl}$  at  $25^\circ\text{C}$ , given that  $B = 10.591 \text{ cm}^{-1}$ .

**Method** We use eqn 13.19 and evaluate it term by term. Once again, we use  $kT/hc = 207.224 \text{ cm}^{-1}$  at  $298.15 \text{ K}$ . The sum is readily evaluated by using mathematical software.

**Answer** To show how successive terms contribute, we draw up the following table by using  $hcB/kT = 0.05111$  (Fig. 13.8):

$J$	0	1	2	3	4	...	10
$(2J+1)e^{-0.05111J(J+1)}$	1	2.71	3.68	3.79	3.24	...	0.08

The sum required by eqn 13.19 (the sum of the numbers in the second row of the table) is 19.9, hence  $q^R = 19.9$  at this temperature. Taking  $J$  up to 50 gives  $q^R = 19.902$ . Notice that about ten  $J$ -levels are significantly populated but the number of populated states is larger on account of the  $(2J+1)$ -fold degeneracy of each level. We shall shortly encounter the approximation that  $q^R \approx kT/hcB$ , which in the present case gives  $q^R = 19.6$ , in good agreement with the exact value and with much less work.

CO <sub>2</sub>	v <sub>1</sub>
	v <sub>2</sub>
	v <sub>3</sub>

\* For more values, see Table 10.1 and use  $hc/k = 1.439 \text{ K cm}$ .

At room temperature  $kT/hc = 207 \text{ cm}^{-1}$  and often smaller (though the rotational levels are populated at  $n$  this is the case, the partition function is  $q^R = \frac{kT}{hcB}$  for linear rotors and  $q^R = \left(\frac{kT}{hc}\right)^3$  for non-linear rotors, where  $\bar{A}$ ,  $\bar{B}$ , and  $\bar{C}$  are the rotational constants expressed as wavenumbers. However, read on (to eqns 13.21 and 13.22).

## Self-tests

Each *Worked example* has a *Self-test* with the answer provided as a check that the procedure has been mastered. There are also a number of free-standing *Self-tests* that are located where we thought it a good idea to provide a question to check your understanding. Think of *Self-tests* as in-chapter exercises designed to help you monitor your progress.

## Discussion questions

The end-of-chapter material starts with a short set of questions that are intended to encourage reflection on the material and to view it in a broader context than is obtained by solving numerical problems.

**Discussion questions**

<p><b>17.1</b> Explain how the mixing of reactants and products affects the position of chemical equilibrium.</p> <p><b>17.2</b> Explain how a reaction that is not spontaneous may be driven forward by coupling to a spontaneous reaction.</p> <p><b>17.3</b> Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.</p> <p><b>17.4</b> Suggest how the thermodynamic equilibrium constant may respond differently to changes in pressure and temperature from the equilibrium constant expressed in terms of partial pressures.</p> <p><b>17.5</b> Account for Le Chatelier's principle in terms of thermodynamic quantities. Can you think of a reason why the principle might fail?</p>	<p><b>17.6</b> State the limits to the generality of the equation in eqn 17.28.</p> <p><b>17.7</b> Distinguish between galvanic, electrochemical, and concentration cells.</p> <p><b>17.8</b> Explain why salt bridges are routine measurements.</p> <p><b>17.9</b> Discuss how the electrochemical series can be used to predict the spontaneity of a redox reaction.</p> <p><b>17.10</b> Describe a method for the determination of a standard reaction enthalpy.</p> <p><b>17.11</b> Describe at least one non-calorimetric method for determining a standard reaction enthalpy.</p>
--	---

## Exercises and Problems

The core of testing understanding is the collection of end-of-chapter *Exercises* and *Problems*. The *Exercises* are straightforward numerical tests that give practice with manipulating numerical data. The *Problems* are more searching. They are divided into ‘numerical’, where the emphasis is on the manipulation of data, and ‘theoretical’, where the emphasis is on the manipulation of equations before (in some cases) using numerical data. At the end of the *Problems* are collections of problems that focus on practical applications of various kinds, including the material covered in the *Impact* sections. Although this text includes many of the hundreds of *Exercises* and *Problems* that are present in the 8th edition of *Physical chemistry*, well more than half of them are entirely new or have been modified.

## Exercises

**17.1(a)** Write the expressions for the equilibrium constants of the following reactions in terms of (i) activities and (ii) where appropriate, the ratios  $p/p^\circ$  and the products  $\gamma b/lb^\circ$ :

- $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{COCl}_2\text{(g)} + \text{Cl(g)}$
- $2 \text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{SO}_3\text{(g)}$
- $\text{Fe(s)} + \text{PbSO}_4\text{(aq)} \rightleftharpoons \text{FeSO}_4\text{(aq)} + \text{Pb(s)}$
- $\text{Hg}_2\text{Cl}_2\text{(s)} + \text{H}_2\text{(g)} \rightleftharpoons 2 \text{HCl(aq)} + 2 \text{Hg(l)}$
- $2 \text{CuCl(aq)} \rightleftharpoons \text{Cu(s)} + \text{CuCl}_2\text{(aq)}$

**17.1(b)** Write the expressions for the equilibrium constants of the following reactions in terms of (i) activities and (ii) where appropriate, the ratios  $p/p^\circ$  and the products  $\gamma b/lb^\circ$ :

- $\text{H}_2\text{(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2 \text{HBr(g)}$
- $2 \text{O}_3\text{(g)} \rightleftharpoons 3 \text{O}_2\text{(g)}$
- $2 \text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{H}_2\text{O(l)}$
- $\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons \text{H}_2\text{O}_2\text{(aq)}$
- $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2 \text{HI(aq)}$

**17.2(a)** Identify the stoichiometric numbers in the reaction  $\text{Hg}_2\text{Cl}_2\text{(s)} + \text{H}_2\text{(g)} \rightarrow 2 \text{HCl(aq)} + 2 \text{Hg(l)}$ .

**17.2(b)** Identify the stoichiometric numbers in the reaction  $\text{CH}_4\text{(g)} + 2 \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{H}_2\text{O(l)}$ .

**17.4(b)** The equilibrium pressure of  $\text{H}_2$ , or hydride,  $\text{UH}_3$ , at 500 K is 139 Pa. Calculate formation of  $\text{UH}_3\text{(s)}$  at 500 K.

**17.5(a)** From information in the *Data sec* Gibbs energy and the equilibrium constant for the reaction  $\text{PbO(s)} + \text{CO(g)} \rightleftharpoons \text{Pb(s)}$  reaction enthalpy is independent of temp

**17.5(b)** From information in the *Data sec* Gibbs energy and the equilibrium constant for the reaction  $\text{CH}_4\text{(g)} + 3 \text{Cl}_2\text{(g)} \rightleftharpoons \text{CHCl}_3\text{(l)}$  reaction enthalpy is independent of temp

**17.6(a)** For  $\text{CaF}_2\text{(s)} \rightleftharpoons \text{Ca}^{2+}\text{(aq)} + 2 \text{F}^-\text{(aq)}$  the standard Gibbs energy of formation of

**17.6(b)** For  $\text{PbI}_2\text{(s)} \rightleftharpoons \text{Pb}^{2+}\text{(aq)} + 2 \text{I}^-\text{(aq)}$  the standard Gibbs energy of formation of

**17.7(a)** In the gas-phase reaction  $2 \text{A} + \text{B} \rightleftharpoons 3 \text{C}$  when 1.00 mol A, 2.00 mol B, and 1.00 mol C come to equilibrium at 25°C, the resulting total pressure is 1.00 bar. Calculate  $\Delta_r G^\circ$

---

# The Book Companion Site

---

The Book Companion Site to accompany *Quanta, Matter, and Change* provides teaching and learning resources to augment the printed book. It is free of charge, and provides additional material for download, which can be incorporated into a virtual learning environment.

The book companion site can be accessed by visiting [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem).

Note that instructor resources are available only to registered adopters of the textbook. To register, simply visit [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem) and follow the appropriate links. You will be given the opportunity to select your own username and password, which will be activated once your adoption has been verified.

Student resources are openly available to all, without registration.

The materials on the book companion site include:

## Living graphs

A *Living graph* can be used to explore how a property changes as a variety of parameters are changed. To encourage the use of this resource (and the more extensive *Explorations in physical chemistry*; see below), we have included a suggested *interActivity* to many of the illustrations in the text.

## Artwork

An instructor may wish to use the figures from this text in a lecture. Almost all the figures are available in PowerPoint® format and can be used for lectures without charge (but not for commercial purposes without specific permission).

## Tables of data

All the tables of data that appear in the chapter text are available and may be used under the same conditions as the artwork.

## Group theory tables

Comprehensive group theory tables are available for downloading.

## Weblinks

There is a huge network of information available about physical chemistry, and it can be bewildering to find your way to it. Also, a piece of information may be needed that we have not included in the text. The website might suggest where to find the specific data or indicate where additional data can be found.

## Other resources

**Explorations in Physical Chemistry** by Valerie Walters, Julio de Paula, and Peter Atkins

*Explorations in Physical Chemistry* consists of interactive Mathcad® worksheets and interactive Excel® workbooks, complete with thought-stimulating exercises. They motivate students to simulate physical, chemical, and biochemical phenomena with their personal computers. Harnessing the computational power of Mathcad® by Mathsoft, Inc. and Excel® by Microsoft Corporation, students can manipulate over 75 graphics, alter simulation parameters, and solve equations to gain deeper insight into physical chemistry.

*Explorations in Physical Chemistry* can be purchased at [www.whfreeman.com/explorations](http://www.whfreeman.com/explorations); ISBN 0-7167-0841-8.

## Solutions manuals

Two solutions manuals accompany this book; both are written by Charles Trapp, Marshall Cady, and Carmen Giunta.

A *Student's Solutions Manual* (ISBN 1-4292-2375-8) provides full solutions to the 'a' exercises, and the odd-numbered problems.

An *Instructor's Solutions Manual* (1-4292-2374-x) provides full solutions to the 'b' exercises, and the even-numbered problems.

---

## About the authors

---

Peter Atkins is a fellow of Lincoln College in the University of Oxford and the author of more than sixty books for students and a general audience. His texts are market leaders around the globe. A frequent lecturer in the United States and throughout the world, he has held visiting professorships in France, Israel, Japan, China, and New Zealand. He was the founding chairman of the Committee on Chemistry Education of the International Union of Pure and Applied Chemistry and was a member of IUPAC's Physical and Biophysical Chemistry Division.



Julio de Paula is Professor of Chemistry and Dean of the College of Arts & Sciences at Lewis & Clark College. A native of Brazil, Professor de Paula received a B.A. degree in chemistry from Rutgers, The State University of New Jersey, and a Ph.D. in biophysical chemistry from Yale University. His research activities encompass the areas of molecular spectroscopy, biophysical chemistry, and nanoscience. He has taught courses in general chemistry, physical chemistry, biophysical chemistry, instrumental analysis, and writing.



Ronald Friedman is Professor and Chair of the Chemistry Department at Indiana University Purdue University Fort Wayne. He received a B.S. in chemistry from the University of Virginia, a Ph.D. in chemistry from Harvard University, and did postdoctoral work at the University of Minnesota. He teaches general chemistry and physical chemistry at IPFW and has also taught at the University of Michigan and at the Technion (Israel). His research interests are theories of reaction dynamics.



---

# Acknowledgements

---

The authors have received a great deal of help during the preparation and production of this text and wish to thank all their colleagues who have made such thought-provoking and useful suggestions. In particular, we wish to record publicly our thanks to:

Temer S. Ahmadi, Villanova University  
David L. Andrews, University of East Anglia  
Martin Bates, University of York  
Warren Beck, Michigan State University  
Nikos Benteenitis, Southwestern University  
Holly Bevsek, The Citadel  
D. Neal Boehnke, Jacksonville University  
Dale J. Brugh, Ohio Wesleyan University  
William A. Burns, Arizona State University  
Colleen Byron, Ripon College  
Rosemarie C. Chinni, Alvernia College  
Stephen Davis, University of Mississippi  
Peter Derrick, University of Warwick  
Paul A. DiMilla, Northeastern University  
Robert A. Donnell, Auburn University  
Michael Dorko, The Citadel  
Mel Dutton, California State University-Bakersfield  
Matthew Elrod, Oberlin College  
James M. Farrar, University of Rochester  
Stephen Fletcher, Loughborough University  
Krishna L. Foster, California State University-Los Angeles  
James Gimzewski, UCLA  
Robert Glinski, Tennessee Tech University  
Rebecca Goyan, Simon Fraser University  
Alexander Grushow, Rider University  
Dorothy A. Hanna, Kansas Wesleyan University  
Gerard S. Harbison, University of Nebraska at Lincoln  
Shizuka Hsieh, Smith College  
Markus M. Hoffmann, SUNY-Brockport  
William Hollingsworth, Carleton College  
Karl James Jalkanen, Technical University of Denmark  
Evguenii I. Kozliak, University of North Dakota  
Jeffrey E. Lacy, Shippensburg College

Daniel B. Lawson, University Of Michigan-Dearborn  
John W. Logan, San Jose State University  
Arthur A. Low, Tarleton State University  
Michael Lyons, Trinity College Dublin  
Charles McCallum, Pacific College  
Preston MacDougall, Middle Tennessee College  
Roderick M. Macrae, Marian College  
Jeffrey D. Madura, Duquesne University  
Clyde Metz, College of Charleston  
David A. Micha, University of Florida  
Brian G. Moore, Augustana College  
Dale Moore, Mercer University  
Stephan P. A. Sauer, University of Copenhagen  
Richard Schwenz, University of Northern Colorado-Greeley  
Olle Soderman, Lund University  
Jie Song, University of Michigan-Flint  
David Smith, University of Bristol  
Julian Talbot, Duquesne University  
Earle Waghorne, University College Dublin  
Michael Wedlock, Gettysburg College  
Benjamin Whitaker, University of Leeds  
Kurt Winkelmann, Florida Institute of Technology  
Dawn C. Wisner, Lake Forest College

The publication of a book does not cease when the authors lay down their (these days, virtual) pens. We are particularly grateful to our copy editor Claire Eisenhandler and equally to Valerie Walters, who read through the proofs with meticulous attention to detail and caught in private what might have been a public grief. We are particularly grateful to Charles Trapp, Carmen Giunta, and Marshall Cady for their critical reading of the end of chapter Exercises and Problems and their recommendations for modifications.

Last, but by no means least, we wish to acknowledge the wholehearted and unstinting support of our two commissioning editors, Jonathan Crowe of Oxford University Press and Jessica Fiorillo of W.H. Freeman & Co., who—in other projects as well as this—have helped the authors to realize their vision and have done so in such an agreeable and professional a manner.

---

# Summary of contents

---

Fundamentals	1
Mathematical background 1: Differentiation and integration	18
<b>PART 1 Quantum theory</b>	<b>23</b>
1 The principles of quantum theory	25
Mathematical background 2: Differential equations	50
2 Nanosystems 1: motion in one dimension	52
Mathematical background 3: Complex numbers	76
3 Nanosystems 2: motion in several dimensions	78
<b>PART 2 Atoms, molecules, and assemblies</b>	<b>97</b>
4 Atomic structure and spectra	99
Mathematical background 4: Vectors	134
5 The chemical bond	137
Mathematical background 5: Matrices	168
6 Computational chemistry	172
7 Molecular symmetry	196
8 Molecular assemblies	220
9 Solids	254
Mathematical background 6: Fourier series and Fourier transforms	293
<b>PART 3 Molecular spectroscopy</b>	<b>297</b>
10 Rotational and vibrational spectra	297
11 Electronic spectroscopy	338
12 Magnetic resonance	371
<b>PART 4 Molecular thermodynamics</b>	<b>409</b>
13 The Boltzmann distribution	411
Mathematical background 7: Probability theory	438
14 The First Law of thermodynamics	442
Mathematical background 8: Multivariate calculus	479
15 The Second Law of thermodynamics	482
16 Physical equilibria	518
17 Chemical equilibrium	558
<b>PART 5 Chemical dynamics</b>	<b>589</b>
18 Molecular motion	591
19 Chemical kinetics	623



<b>20</b> Molecular reaction dynamics	658
<b>21</b> Catalysis	693
Resource section	723
Solutions to a) exercises	758
Solutions to odd-numbered problems	765
Index	770

# Contents

<b>Fundamentals</b>	<b>1</b>		
<b>F.1</b> Atoms	1		
<b>F.2</b> Molecules	2		
<b>F.3</b> Bulk matter	3		
<b>F.4</b> Thermodynamic properties	5		
<b>F.5</b> The relation between molecular and bulk properties	5		
<b>F.6</b> Particles	7		
<b>F.7</b> Waves	11		
<b>F.8</b> Units	13		
Exercises	14		
<b>Mathematical background 1: Differentiation and integration</b>	<b>18</b>		
<b>MB1.1</b> Differentiation: definitions	18		
<b>MB1.2</b> Differentiation: manipulations	18		
<b>MB1.3</b> Partial derivatives	18		
<b>MB1.4</b> Series expansions	19		
<b>MB1.5</b> Integration: definitions	19		
<b>MB1.6</b> Integration: manipulations	20		
<b>MB1.7</b> Multiple integrals	21		
<b>PART 1 Quantum theory</b>	<b>23</b>		
<b>1 The principles of quantum theory</b>	<b>25</b>		
<b>Three crucial experiments</b>	<b>25</b>		
<b>1.1</b> Quantization of energy	26		
<b>1.2</b> The particle character of electromagnetic radiation	26		
<b>1.3</b> The wave character of particles	28		
<b>I1.1</b> Impact on biology: Electron microscopy	29		
<b>The postulates</b>	<b>30</b>		
<b>1.4</b> Postulate I: the wavefunction	30		
<b>1.5</b> Postulate II: the Born interpretation	30		
<b>1.6</b> Postulate III: quantum mechanical operators	33		
<b>1.7</b> Postulate IV: eigenvalues and eigenfunctions	35		
<b>1.8</b> Postulate V: superpositions and expectation values	37		
<b>Complementary observables</b>	<b>41</b>		
<b>1.9</b> The Heisenberg uncertainty principle	41		
<b>1.10</b> The general form of the uncertainty principle	43		
Checklist of key ideas	45		
Further information 1.1: Dirac notation	45		
Discussion questions		46	
Exercises		46	
Problems		48	
<b>Mathematical background 2: Differential equations</b>	<b>50</b>		
<b>MB2.1</b> The structure of differential equations	50		
<b>MB2.2</b> The solution of ordinary differential equations	50		
<b>MB2.3</b> The solution of partial differential equations	51		
<b>2 Nanosystems 1: motion in one dimension</b>	<b>52</b>		
<b>Translational motion</b>	<b>53</b>		
<b>2.1</b> Free motion	53		
<b>2.2</b> A particle in a box	53		
<b>2.3</b> Tunnelling	57		
<b>I2.1</b> Impact on nanoscience: Scanning probe microscopy	59		
<b>Vibrational motion</b>	<b>61</b>		
<b>2.4</b> The energy levels	61		
<b>2.5</b> The wavefunctions	63		
<b>Techniques of approximation</b>	<b>67</b>		
<b>2.6</b> An overview of approximation techniques	67		
<b>2.7</b> Time-independent perturbation theory	67		
Checklist of key ideas		69	
Further information 2.1: Time-independent perturbation theory		69	
Discussion questions		71	
Exercises		71	
Problems		72	
<b>Mathematical background 3: Complex numbers</b>	<b>76</b>		
<b>MB3.1</b> Definitions	76		
<b>MB3.2</b> Polar representation	76		
<b>MB3.3</b> Operations	77		
<b>3 Nanosystems 2: motion in several dimensions</b>	<b>78</b>		
<b>Translational motion</b>	<b>78</b>		
<b>3.1</b> Motion in two dimensions	79		
<b>3.2</b> Motion in three dimensions	80		
<b>I3.1</b> Impact on nanoscience: Quantum dots	81		
<b>Rotational motion</b>	<b>82</b>		
<b>3.3</b> Rotation in two dimensions: a particle on a ring	82		
<b>3.4</b> Rotation in three dimensions: the particle on a sphere	86		
<b>3.5</b> Spin	91		

Checklist of key ideas	93	<b>5.8</b> Butadiene and $\pi$ -electron binding energy	159
Discussion questions	93	<b>5.9</b> Benzene and aromatic stability	160
Exercises	93	Checklist of key ideas	161
Problems	95	Discussion questions	162
		Exercises	162
		Problems	164
<b>PART 2 Atoms, molecules, and assemblies</b>	<b>97</b>	<b>Mathematical background 5: Matrices</b>	<b>168</b>
<b>4 Atomic structure and spectra</b>	<b>99</b>	<b>MB5.1</b> Definitions	168
<b>Hydrogenic atoms</b>	<b>99</b>	<b>MB5.2</b> Matrix addition and multiplication	168
<b>4.1</b> The structure of hydrogenic atoms	100	<b>MB5.3</b> Eigenvalue equations	169
<b>4.2</b> Atomic orbitals and their energies	103	<b>6 Computational chemistry</b>	<b>172</b>
<b>4.3</b> Spectroscopic transitions	111	<b>The central challenge</b>	<b>172</b>
<b>Many-electron atoms</b>	<b>114</b>	<b>6.1</b> The Hartree–Fock formalism	173
<b>I4.1</b> Impact on astrophysics: The spectroscopy of stars	115	<b>6.2</b> The Roothaan equations	175
<b>4.4</b> The orbital approximation	115	<b>6.3</b> Basis sets	178
<b>4.5</b> Term symbols	122	<b>The first approach: semiempirical methods</b>	<b>180</b>
Checklist of key ideas	127	<b>6.4</b> The Hückel method revisited	180
Further information 4.1: The separation of internal and external motion	128	<b>6.5</b> Differential overlap	181
Further information 4.2: Time-dependent perturbation theory	128	<b>The second approach: <i>ab initio</i> methods</b>	<b>181</b>
Discussion questions	129	<b>6.6</b> Configuration interaction	181
Exercises	129	<b>6.7</b> Many-body perturbation theory	183
Problems	131	<b>The third approach: density functional theory</b>	<b>184</b>
<b>Mathematical background 4: Vectors</b>	<b>134</b>	<b>6.8</b> The Kohn–Sham equations	184
<b>MB4.1</b> Definitions	134	<b>6.9</b> The exchange–correlation energy	184
<b>MB4.2</b> Operations	134	<b>Current achievements</b>	<b>186</b>
<b>MB4.3</b> The graphical representation of vector operations	135	<b>6.10</b> Comparison of calculations and experiments	186
<b>MB4.4</b> Vector differentiation	136	<b>6.11</b> Applications to larger molecules	187
<b>5 The chemical bond</b>	<b>137</b>	<b>I6.1</b> Impact on nanoscience: The structure of nanoparticles	188
<b>The Born–Oppenheimer approximation</b>	<b>138</b>	<b>I6.2</b> Impact on medicine: Molecular recognition and drug design	189
<b>Valence-bond theory</b>	<b>138</b>	Checklist of key ideas	191
<b>5.1</b> Homonuclear diatomic molecules	138	Discussion questions	192
<b>5.2</b> Polyatomic molecules	140	Exercises	192
<b>Molecular orbital theory</b>	<b>142</b>	Problems	193
<b>5.3</b> The hydrogen molecule-ion	142	<b>7 Molecular symmetry</b>	<b>196</b>
<b>5.4</b> Homonuclear diatomic molecules	146	<b>The symmetry elements of objects</b>	<b>197</b>
<b>5.5</b> Heteronuclear diatomic molecules	152	<b>7.1</b> Operations and symmetry elements	197
<b>I5.1</b> Impact on biochemistry: The biochemical reactivity of O <sub>2</sub> , N <sub>2</sub> , and NO	156	<b>7.2</b> The symmetry classification of molecules	199
<b>Polyatomic molecules: the Hückel approximation</b>	<b>157</b>	<b>7.3</b> Some immediate consequences of symmetry	203
<b>5.6</b> Ethene	157	<b>Applications</b>	<b>204</b>
<b>5.7</b> The matrix formulation of the Hückel method	158	<b>7.4</b> Character tables and symmetry labels	204
		<b>7.5</b> Vanishing integrals and orbital overlap	210
		<b>7.6</b> Vanishing integrals and selection rules	214

Checklist of key ideas	215	Checklist of key ideas	286
Discussion questions	216	Discussion questions	287
Exercises	216	Exercises	287
Problems	217	Problems	289
<b>8 Molecular assemblies</b>	<b>220</b>	<b>Mathematical background 6: Fourier series and Fourier transforms</b>	<b>293</b>
<b>Interactions between molecules</b>	<b>220</b>	<b>MB6.1</b> Fourier series	293
<b>8.1</b> Interactions between partial charges	220	<b>MB6.2</b> Finite approximations and Parseval's theorem	294
<b>8.2</b> Electric dipole moments	221	<b>MB6.3</b> Fourier transforms	295
<b>8.3</b> Interactions between dipoles	223	<b>MB6.4</b> The convolution theorem	296
<b>8.4</b> Induced dipole moments	226		
<b>8.5</b> Hydrogen bonding	229	<b>PART 3 Molecular spectroscopy</b>	<b>297</b>
<b>I8.1</b> Impact on biochemistry: Proteins and nucleic acids	229	<b>10 Rotational and vibrational spectra</b>	<b>299</b>
<b>8.6</b> The total interaction	233		
<b>I8.2</b> Impact on nanoscience: Colloidal nanoparticles	235	<b>Pure rotational spectra</b>	<b>299</b>
<b>Gases and liquids</b>	<b>237</b>	<b>10.1</b> Moments of inertia	300
<b>8.7</b> Molecular interactions in gases	238	<b>10.2</b> Rotational energy levels	302
<b>8.8</b> Molecular interactions in liquids	244	<b>10.3</b> Rotational transitions	305
<b>I8.3</b> Impact on materials science: Liquid crystals	246	<b>10.4</b> Rotational Raman spectra	308
Checklist of key ideas	247	<b>10.5</b> Nuclear statistics and rotational states	310
Further information 8.1: The dipole–dipole interaction	247	<b>I10.1</b> Impact on astrophysics: Rotational spectroscopy of interstellar molecules	312
Further information 8.2: The basic principles of molecular beams	248	<b>The vibrations of diatomic molecules</b>	<b>313</b>
Discussion questions	249	<b>10.6</b> Techniques	313
Exercises	249	<b>10.7</b> Molecular vibrations	315
Problems	250	<b>10.8</b> Selection rules	316
<b>9 Solids</b>	<b>254</b>	<b>10.9</b> Anharmonicity	317
<b>Crystal lattices</b>	<b>254</b>	<b>10.10</b> Vibration–rotation spectra	318
<b>9.1</b> Lattices and unit cells	254	<b>10.11</b> Vibrational Raman spectra of diatomic molecules	319
<b>9.2</b> The identification of lattice planes	256	<b>The vibrations of polyatomic molecules</b>	<b>320</b>
<b>9.3</b> The investigation of structure	259	<b>10.12</b> Normal modes	321
<b>I9.1</b> Impact on biochemistry: X-ray crystallography of biological macromolecules	266	<b>10.13</b> Infrared absorption spectra of polyatomic molecules	322
<b>9.4</b> Neutron and electron diffraction	267	<b>I10.2</b> Impact on environmental science: Climate change	323
<b>Crystal structure</b>	<b>268</b>	<b>10.14</b> Vibrational Raman spectra of polyatomic molecules	324
<b>9.5</b> Metallic solids	268	<b>I10.3</b> Impact on biochemistry: Vibrational microscopy	326
<b>9.6</b> Ionic solids	270	<b>10.15</b> Symmetry aspects of molecular vibrations	327
<b>9.7</b> Molecular solids and covalent networks	273	Checklist of key ideas	328
<b>The properties of solids</b>	<b>274</b>	Further information 10.1: The Einstein coefficients	329
<b>9.8</b> Mechanical properties	274	Further information 10.2: Selection rules for rotational and vibrational spectroscopy	330
<b>9.9</b> Electrical properties	276	Discussion questions	332
<b>I9.2</b> Impact on technology: Conducting polymers	280	Exercises	332
<b>I9.3</b> Impact on nanoscience: Nanowires	280	Problems	334
<b>9.10</b> Optical properties	280	<b>11 Electronic spectroscopy</b>	<b>338</b>
<b>9.11</b> Magnetic properties	282	<b>Experimental techniques</b>	<b>338</b>
<b>9.12</b> Superconductors	284	<b>11.1</b> Spectrometers	338
		<b>11.2</b> The Beer–Lambert law	339

<b>The characteristics of electronic transitions</b>	<b>341</b>	<b>13.2</b> The molecular partition function	414
<b>11.3</b> The electronic spectra of diatomic molecules	341	<b>13.3</b> Contributions to the molecular partition function	417
<b>11.4</b> The electronic spectra of polyatomic molecules	346	<b>I13.1</b> Impact on biochemistry: The helix–coil transition in polypeptides	424
<b>I11.1</b> Impact on biochemistry: Vision	349	<b>13.4</b> The mean energy	425
<b>The fates of electronically excited states</b>	<b>350</b>	<b>The canonical partition function</b>	<b>428</b>
<b>11.5</b> Fluorescence and phosphorescence	351	<b>13.5</b> The canonical ensemble	428
<b>I11.2</b> Impact on nanoscience: Single-molecule spectroscopy	352	<b>13.6</b> The mean energy of a system	429
<b>11.6</b> Dissociation and predissociation	354	<b>13.7</b> Independent molecules	430
<b>11.7</b> General principles of laser action	355	Checklist of key ideas	431
<b>11.8</b> Examples of practical lasers	360	Further information 13.1: The derivation of the Boltzmann distribution	431
Checklist of key ideas	363	Further information 13.2: The partition functions of polyatomic rotors	433
Discussion questions	364	Discussion questions	433
Exercises	364	Exercises	434
Problems	367	Problems	436
<b>12 Magnetic resonance</b>	<b>371</b>	<b>Mathematical background 7: Probability theory</b>	<b>438</b>
<b>The effect of magnetic fields on electrons and nuclei</b>	<b>371</b>	<b>MB7.1</b> Discrete distributions	438
<b>12.1</b> The energies of electrons in magnetic fields	372	<b>MB7.2</b> Continuous distributions	440
<b>12.2</b> The energies of nuclei in magnetic fields	372	<b>14 The First Law of thermodynamics</b>	<b>442</b>
<b>12.3</b> Magnetic resonance spectroscopy	373	<b>The internal energy</b>	<b>442</b>
<b>Nuclear magnetic resonance</b>	<b>374</b>	<b>14.1</b> Work, heat, and energy	443
<b>12.4</b> The NMR spectrometer	374	<b>14.2</b> The First Law	444
<b>12.5</b> The chemical shift	375	<b>14.3</b> Expansion work	445
<b>12.6</b> The fine structure	379	<b>14.4</b> Heat transactions	448
<b>12.7</b> Conformational conversion and exchange processes	386	<b>14.5</b> Enthalpy	454
<b>Pulse techniques in NMR</b>	<b>387</b>	<b>I14.1</b> Impact on biochemistry: Differential scanning calorimetry	457
<b>12.8</b> The magnetization vector	387	<b>14.6</b> Adiabatic changes	458
<b>12.9</b> Spin relaxation	390	<b>Thermochemistry</b>	<b>460</b>
<b>I12.1</b> Impact on medicine: Magnetic resonance imaging	393	<b>14.7</b> Standard enthalpy changes	460
<b>12.10</b> Spin decoupling	394	<b>14.8</b> Standard enthalpies of formation	462
<b>12.11</b> The nuclear Overhauser effect	395	<b>14.9</b> The temperature dependence of reaction enthalpies	463
<b>12.12</b> Two-dimensional NMR	396	<b>Properties of the internal energy and the enthalpy</b>	<b>464</b>
<b>12.13</b> Solid-state NMR	397	<b>14.10</b> Changes in internal energy	464
<b>Electron paramagnetic resonance</b>	<b>398</b>	<b>14.11</b> The Joule–Thomson effect	467
<b>12.14</b> The EPR spectrometer	399	Checklist of key ideas	470
<b>12.15</b> The <i>g</i> -value	399	Further information 14.1: Adiabatic processes	471
<b>12.16</b> Hyperfine structure	400	Discussion questions	472
<b>I12.2</b> Impact on biochemistry: Spin probes	403	Exercises	472
Checklist of key ideas	403	Problems	474
Discussion questions	404	<b>Mathematical background 8: Multivariate calculus</b>	<b>479</b>
Exercises	404	<b>MB8.1</b> Partial derivatives	479
Problems	406	<b>MB8.2</b> Exact differentials	479
<b>PART 4 Molecular thermodynamics</b>	<b>409</b>		
<b>13 The Boltzmann distribution</b>	<b>411</b>		
<b>The distribution of molecular states</b>	<b>412</b>		
<b>13.1</b> Configurations and weights	412		

<b>15 The Second Law of thermodynamics</b>	<b>482</b>		
<b>The direction of spontaneous change</b>	<b>483</b>		
15.1 The dispersal of energy	483		
15.2 Entropy	484		
I15.1 Impact on technology: Refrigeration	492		
15.3 Entropy changes accompanying specific processes	493		
15.4 The Third Law of thermodynamics	497		
<b>Concentrating on the system</b>	<b>499</b>		
15.5 The Helmholtz and Gibbs energies	499		
15.6 Standard molar Gibbs energies	503		
<b>Combining the First and Second Laws</b>	<b>505</b>		
15.7 The fundamental equation	505		
15.8 Properties of the internal energy	505		
15.9 Properties of the Gibbs energy	506		
Checklist of key ideas	510		
Further information 15.1: The Born equation	511		
Discussion questions	511		
Exercises	512		
Problems	514		
<b>16 Physical equilibria</b>	<b>518</b>		
<b>Phase diagrams</b>	<b>518</b>		
16.1 One-component systems	519		
16.2 Two-component systems	522		
I16.1 Impact on biochemistry: Biological membranes	525		
<b>Thermodynamic interpretation</b>	<b>528</b>		
16.3 Properties of the chemical potential	528		
16.4 The structure of one-component phase diagrams	530		
16.5 The structure of two-component phase diagrams	532		
I16.2 Impact on biochemistry: Osmosis and the structure of biological cells	540		
16.6 Real solutions	540		
Checklist of key ideas	547		
Further information 16.1: The phase rule	548		
Further information 16.2: The Ehrenfest classification	548		
Further information 16.3: The Debye–Hückel theory of ionic solutions	549		
Discussion questions	551		
Exercises	551		
Problems	554		
<b>17 Chemical equilibrium</b>	<b>558</b>		
<b>Spontaneous chemical reactions</b>	<b>558</b>		
17.1 The Gibbs energy minimum and the reaction Gibbs energy	559		
17.2 The thermodynamic description of equilibrium	559		
I17.1 Impact on biology: Energy conversion in biological cells	563		
17.3 The statistical description of equilibrium	564		
<b>The response of equilibria to the conditions</b>	<b>567</b>		
17.4 How equilibria respond to pressure	567		
17.5 The response of equilibria to temperature	569		
<b>Electrochemistry</b>	<b>571</b>		
17.6 Half-reactions and electrodes	571		
17.7 Varieties of cells	572		
17.8 The cell potential	573		
I17.2 Impact on engineering: Fuel cells	575		
17.9 Standard electrode potentials	576		
17.10 Applications of standard potentials	578		
I17.3 Impact on biology: The respiratory chain	580		
Checklist of key ideas	581		
Discussion questions	582		
Exercises	582		
Problems	584		
<b>PART 5 Chemical dynamics</b>	<b>589</b>		
<b>18 Molecular motion</b>	<b>591</b>		
<b>Motion in gases</b>	<b>591</b>		
18.1 The kinetic model of gases	592		
18.2 Collisions with walls and surfaces	597		
18.3 The rate of effusion	598		
18.4 Transport properties of a perfect gas	598		
<b>Motion in liquids</b>	<b>601</b>		
18.5 Experimental results	601		
18.6 The conductivities of electrolyte solutions	601		
18.7 The mobilities of ions	602		
I18.1 Impact on biochemistry: Gel electrophoresis in genomics and proteomics	605		
<b>Diffusion</b>	<b>606</b>		
18.8 The thermodynamic view	606		
18.9 The diffusion equation	608		
18.10 Diffusion probabilities	610		
18.11 The statistical view	611		
I18.2 Impact on biochemistry: Transport across membranes	612		
Checklist of key ideas	614		
Further information 18.1: The transport characteristics of a perfect gas	615		
Further information 18.2: Random coils	616		
Discussion questions	617		
Exercises	618		
Problems	620		

<b>19 Chemical kinetics</b>	<b>623</b>	<b>The dynamics of molecular collisions</b>	<b>679</b>
<b>Empirical chemical kinetics</b>	<b>623</b>	<b>20.9</b> Reactive collisions	679
<b>19.1</b> Experimental techniques	624	<b>20.10</b> Potential energy surfaces	680
<b>19.2</b> The rates of reactions	625	<b>20.11</b> Some results from experiments and calculations	682
<b>19.3</b> Integrated rate laws	628	Checklist of key ideas	685
<b>19.4</b> Reactions approaching equilibrium	631	Further information 20.1: The RRK model of unimolecular reactions	686
<b>Accounting for the rate laws</b>	<b>634</b>	Further information 20.2: The Gibbs energy of activation of electron transfer	686
<b>19.5</b> Elementary reactions	634	Discussion questions	687
<b>19.6</b> Consecutive elementary reactions	635	Exercises	687
<b>The kinetics of complex reactions</b>	<b>639</b>	Problems	689
<b>19.7</b> The Lindemann–Hinshelwood mechanism of unimolecular reactions	639	<b>21 Catalysis</b>	<b>693</b>
<b>19.8</b> Polymerization kinetics	640	<b>Homogeneous catalysis</b>	<b>694</b>
<b>19.9</b> Photochemistry	643	<b>21.1</b> Acid and base catalysis	694
<b>I19.1</b> Impact on biochemistry: Harvesting of light during plant photosynthesis	648	<b>21.2</b> Enzymes	694
Checklist of key ideas	651	<b>Heterogeneous catalysis</b>	<b>699</b>
Further information 19.1: Förster theory of resonance energy transfer	652	<b>21.3</b> The growth and structure of surfaces	699
Discussion questions	652	<b>21.4</b> The extent of adsorption	702
Exercises	653	<b>21.5</b> The rates of surface processes	707
Problems	654	<b>I21.1</b> Impact on biochemistry: Biosensor analysis	710
<b>20 Molecular reaction dynamics</b>	<b>658</b>	<b>21.6</b> Mechanisms of heterogeneous catalysis	711
<b>The temperature dependence of reaction rates</b>	<b>658</b>	<b>21.7</b> Catalytic activity at surfaces	712
<b>20.1</b> The Arrhenius equation	659	<b>I21.2</b> Impact on technology: Catalysis in the chemical industry	713
<b>20.2</b> The activation energy of a composite reaction	660	Checklist of key ideas	715
<b>Reactive encounters</b>	<b>661</b>	Further information 21.1: The BET isotherm	716
<b>20.3</b> Collision theory	661	Discussion questions	717
<b>20.4</b> Diffusion-controlled reactions	666	Exercises	717
<b>20.5</b> The material balance equation	668	Problems	719
<b>Transition state theory</b>	<b>669</b>	Resource section	723
<b>20.6</b> The Eyring equation	670	Solutions to a) exercises	758
<b>20.7</b> Thermodynamic aspects	673	Solutions to odd-numbered problems	765
<b>20.8</b> Electron transfer in homogeneous systems	675	Index	770

---

# List of Impact sections

---

<b>I1.1</b>	Impact on biology : Electron microscopy	29
<b>I2.1</b>	Impact on nanoscience: Scanning probe microscopy	59
<b>I3.1</b>	Impact on nanoscience: Quantum dots	81
<b>I4.1</b>	Impact on astrophysics: The spectroscopy of stars	115
<b>I5.1</b>	Impact on biochemistry: The biochemical reactivity of O <sub>2</sub> , N <sub>2</sub> , and NO	156
<b>I6.1</b>	Impact on nanoscience: The structure of nanoparticles	188
<b>I6.2</b>	Impact on medicine: Molecular recognition and drug design	189
<b>I8.1</b>	Impact on biochemistry: Proteins and nucleic acids	229
<b>I8.2</b>	Impact on nanoscience: Colloidal nanoparticles	235
<b>I8.3</b>	Impact on materials science: Liquid crystals	246
<b>I9.1</b>	Impact on biochemistry: X-ray crystallography of biological macromolecules	266
<b>I9.2</b>	Impact on technology: Conducting polymers	280
<b>I9.3</b>	Impact on nanoscience: Nanowires	280
<b>I10.1</b>	Impact on astrophysics: Rotational spectroscopy of interstellar molecules	312
<b>I10.2</b>	Impact on environmental science: Climate change	323
<b>I10.3</b>	Impact on biochemistry: Vibrational microscopy	326
<b>I11.1</b>	Impact on biochemistry: Vision	349
<b>I11.2</b>	Impact on nanoscience: Single-molecule spectroscopy	352
<b>I12.1</b>	Impact on medicine: Magnetic resonance imaging	393
<b>I12.2</b>	Impact on biochemistry: Spin probes	403
<b>I13.1</b>	Impact on biochemistry: The helix–coil transition in polypeptides	424
<b>I14.1</b>	Impact on biochemistry: Differential scanning calorimetry	457
<b>I15.1</b>	Impact on technology: Refrigeration	492
<b>I16.1</b>	Impact on biochemistry: Biological membranes	525
<b>I16.2</b>	Impact on biochemistry: Osmosis and the structure of biological cells	540
<b>I17.1</b>	Impact on biology: Energy conversion in biological cells	563
<b>I17.2</b>	Impact on engineering: Fuel cells	575
<b>I17.3</b>	Impact on biology: The respiratory chain	580
<b>I18.1</b>	Impact on biochemistry: Gel electrophoresis in genomics and proteomics	605
<b>I18.2</b>	Impact on biochemistry: Transport across membranes	612
<b>I19.1</b>	Impact on biochemistry: Harvesting of light during plant photosynthesis	648
<b>I21.1</b>	Impact on biochemistry: Biosensor analysis	710
<b>I21.2</b>	Impact on technology: Catalysis in the chemical industry	713



- [click Gargoyles: Stories for free](#)
- [Pathfinder Chronicles: Faction Guide book](#)
- [download online The Accumulation of Freedom: Writings on Anarchist Economics](#)
- [The Man Who Collected Machen and Other Weird Tales pdf](#)
- [download Whisky: The Manual for free](#)
  
- <http://korplast.gr/lib/The-Rose-at-Twilight.pdf>
- <http://aseasonedman.com/ebooks/Pathfinder-Chronicles--Faction-Guide.pdf>
- <http://monkeybubblemedia.com/lib/The-Accumulation-of-Freedom--Writings-on-Anarchist-Economics.pdf>
- <http://pittiger.com/lib/The-Man-Who-Collected-Machen-and-Other-Weird-Tales.pdf>
- <http://thermco.pl/library/l--Lucifer--Finally--the-Other-Side-of-the-Story.pdf>