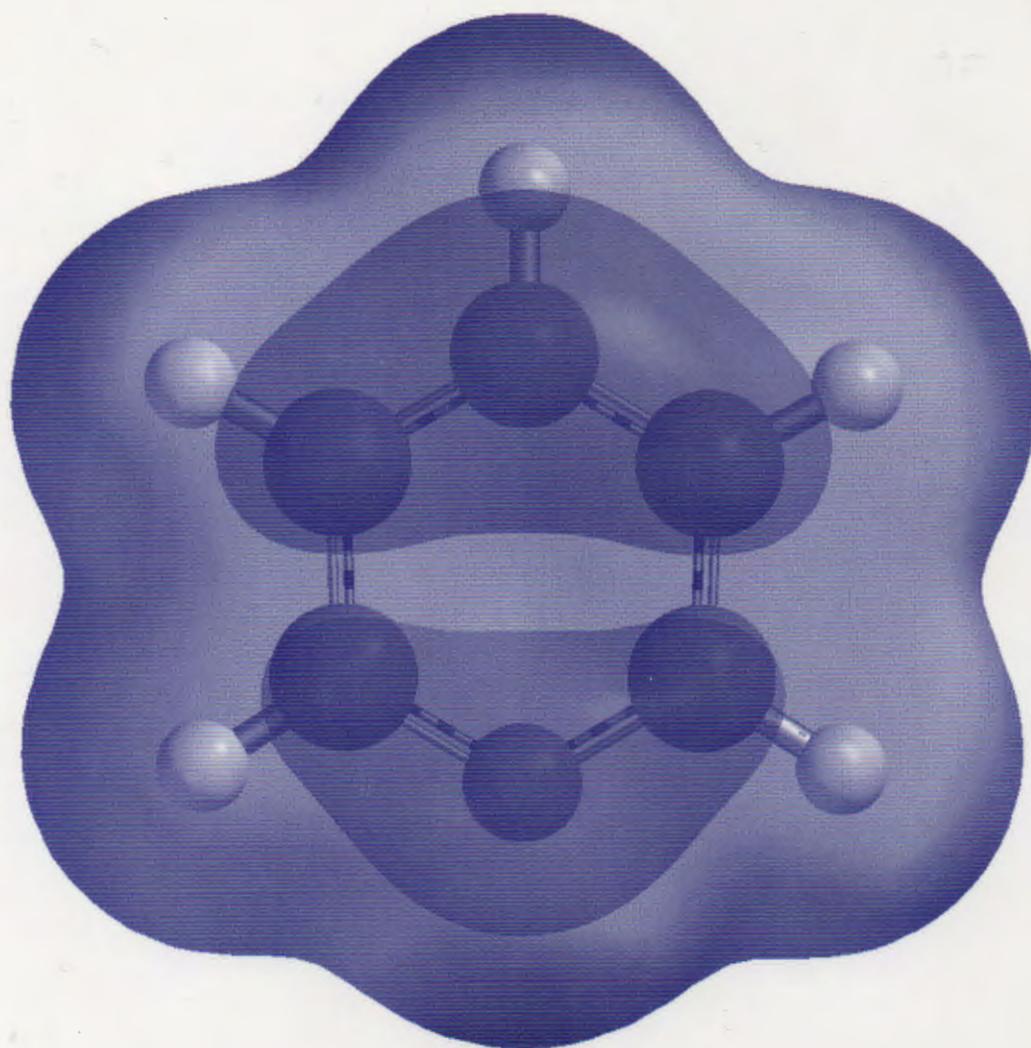


Student Solutions Manual to Accompany

# Quanta, Matter, and Change

A molecular approach to physical chemistry



Charles Trapp, Marshall Cady, Carmen Giunta

# STUDENT SOLUTIONS MANUAL FOR QUANTA, MATTER, AND CHANGE:

A MOLECULAR APPROACH TO PHYSICAL CHEMISTRY

## C. A. Trapp

Professor of Chemistry, University of Louisville,  
Louisville, Kentucky, USA

## M. P. Cady

Professor of Chemistry,  
Indiana University Southeast, New Albany Indiana, USA

## C. Giunta

Professor of Chemistry,  
Le Moyne College, Syracuse, NY, USA

**OXFORD**  
UNIVERSITY PRESS

**OXFORD**  
UNIVERSITY PRESS

Oxford University Press, Great Clarendon Street, Oxford,  
OX2 6DP, United Kingdom

Oxford is a registered trade mark of Oxford University Press  
in the UK and in certain other countries.

© C. A. Trapp, M. P. Cady, and C. Giunta, 2009

The moral rights of the author have been asserted.

First printing

ISBN: 978-0-1995-5907-7

All rights reserved. No part of this publication may be reproduced,  
stored in a retrieval system, or transmitted, in any form  
or by any means, without the prior permission in writing of  
Oxford University Press, or as expressly permitted by law, or under  
terms agreed with the appropriate reprographics rights organization.  
Enquiries concerning reproduction outside those terms and in other  
countries should be sent to the Rights Department,  
Oxford University Press at the address above.

You must not circulate this book in any other binding or  
cover and you must impose the same condition on any acquirer.

Published in the United States and Canada by  
W. H. Freeman and Company  
41 Madison Avenue  
New York, NY 10010  
[www.whfreeman.com](http://www.whfreeman.com)

ISBN-10: 1-4292-2375-8 ISBN-13: 978-1-4292-2375-1

British Library Cataloguing in Publication Data  
Data available

OXFORD  
UNIVERSITY PRESS

# Contents

## Preface

This manual provides detailed solutions to all of the end-of-chapter (a) Exercises, and to the odd-numbered Discussion Questions and Problems in *Quanta, Matter, and Change*.

The solutions to some of the Exercises and many of the Problems in this manual relied heavily on the mathematical, graphical, and molecular modeling software that is now generally accessible to physical chemistry students. The availability of the software makes it possible to create and solve problems that can realistically mimic scientific research. Many of the problems specifically requested the use of such software, and, indeed, would have been almost unsolvable otherwise. We used the following software for many of the solutions in this manual: Excel™ for spreadsheet calculations and graphing, and Mathcad™ for mathematical calculations and the plotting of the results. When a quantum chemical calculation or molecular modeling process was called for, we usually provided the solution with PC Spartan™ because of its common availability. However, the majority of the Exercises and many of the Problems can still be solved with a modern hand-held scientific calculator.

In general we adhered rigorously to the rules for significant figures in displaying the final answers. However, when intermediate answers are shown, they are often given with one more figure than would be justified by the data. These excess figures are indicated with an overline.

The solutions were carefully cross-checked for errors not only by us, but very thoroughly by Valerie Walters, who also made many helpful suggestions for improving the solutions. We would be grateful to any readers who bring any remaining errors to our attention.

We warmly thank our publishers, especially Jonathan Crowe and Jessica Fiorillo, and also Samantha Calamari, for their patience in guiding this complex, detailed project to completion.

Answers to discussion questions	1	Answers to discussion questions	C. T.
Answers to exercises	1	Answers to exercises	M. C.
Answers to problems	1	Answers to problems	C. G.
Answers to numerical problems	1	Answers to numerical problems	
Answers to theoretical problems	1	Answers to theoretical problems	
Answers to applications	1	Answers to applications	
<hr/>			
<b>PART 2: LIGHT, MATTER, AND QUANTUM MECHANICS</b>			
<hr/>			
1. Atomic structure and energy levels	19	1. Atomic structure	199
Answers to discussion questions	20	Answers to discussion questions	200
Answers to exercises	20	Questions to exercises	201
Answers to problems	20	Questions to problems	202
Solutions to numerical problems	20	Solutions to numerical problems	203
Solutions to theoretical problems	20	Solutions to theoretical problems	204
Solutions to applications	20	Solutions to applications	205

# Contents

<b>Fundamentals</b>	<b>1</b>	<b>5 The chemical bond</b>	<b>102</b>
<b>PART 1 Quantum theory</b>	<b>15</b>	Answers to discussion questions	102
<b>1 The principles of quantum theory</b>	<b>17</b>	Solutions to exercises	104
Answers to discussion questions	17	Solutions to problems	110
Solutions to exercises	18	Solutions to numerical problems	110
Solutions to problems	26	Solutions to theoretical problems	124
Solutions to numerical problems	26	Solutions to applications	128
Solutions to theoretical problems	28	<b>6 Computational chemistry</b>	<b>132</b>
Solutions to applications	31	Answers to discussion questions	132
<b>2 Nanosystems 1: motion in one dimension</b>	<b>33</b>	Solutions to exercises	133
Answers to discussion questions	33	Solutions to problems	143
Solutions to exercises	34	Solutions to numerical problems	143
Solutions to problems	43	Solutions to theoretical problems	146
Solutions to numerical problems	43	Solutions to applications	154
Solutions to theoretical problems	45	<b>7 Molecular symmetry</b>	<b>156</b>
Solutions to applications	52	Answers to discussion questions	156
<b>3 Nanosystems 2: motion in several dimensions</b>	<b>55</b>	Solutions to exercises	156
Answers to discussion questions	55	Solutions to problems	162
Solutions to exercises	55	Solutions to numerical problems	162
Solutions to problems	62	Solutions to applications	173
Solutions to numerical problems	62	<b>8 Molecular assemblies</b>	<b>176</b>
Solutions to theoretical problems	66	Answers to discussion questions	176
Solutions to applications	72	Solutions to exercises	179
<b>PART 2 Atoms, molecules, and assemblies</b>	<b>77</b>	Solutions to problems	185
<b>4 Atomic structure and atomic spectra</b>	<b>79</b>	Solutions to numerical problems	185
Answers to discussion questions	79	Solutions to applications	193
Solutions to exercises	80	<b>9 Solids</b>	<b>196</b>
Solutions to problems	88	Answers to discussion questions	196
Solutions to numerical problems	88	Solutions to exercises	198
Solutions to theoretical problems	92	Solutions to problems	207
Solutions to applications	98	Solutions to numerical problems	207
		Solutions to theoretical problems	210
		Solutions to applications	221

<b>PART 3 Molecular spectroscopy</b>	<b>225</b>	<b>15 The second law of thermodynamics</b>	<b>352</b>
<b>10 Rotational and vibrational spectra</b>	<b>227</b>	Answers to discussion questions	352
Answers to discussion questions	227	Solutions to exercises	354
Solutions to exercises	228	Solutions to problems	364
Solutions to problems	236	Solutions to numerical problems	364
Solutions to numerical problems	236	Solutions to theoretical problems	374
Solutions to theoretical problems	244	Solutions to applications	382
Solutions to applications	247	<b>16 Physical equilibria</b>	<b>385</b>
<b>11 Electronic spectroscopy</b>	<b>251</b>	Answers to discussion questions	385
Answers to discussion questions	251	Solutions to exercises	386
Solutions to exercises	253	Solutions to problems	395
Solutions to problems	261	Solutions to numerical problems	395
Solutions to numerical problems	261	Solutions to theoretical problems	401
Solutions to theoretical problems	265	Solutions to applications	406
Solutions to applications	267	<b>17 Chemical equilibrium</b>	<b>411</b>
<b>12 Magnetic resonance</b>	<b>271</b>	Answers to discussion questions	411
Answers to discussion questions	271	Solutions to exercises	413
Solutions to exercises	272	Solutions to problems	422
Solutions to problems	279	Solutions to numerical problems	422
Solutions to numerical problems	279	Solutions to applications	433
Solutions to theoretical problems	284	<b>PART 5 Chemical dynamics</b>	<b>439</b>
Solutions to applications	286	<b>18 Molecular motion</b>	<b>441</b>
<b>PART 4 Molecular thermodynamics</b>	<b>289</b>	Answers to discussion questions	441
<b>13 The Boltzmann distribution</b>	<b>291</b>	Solutions to exercises	443
Answers to discussion questions	291	Solutions to problems	454
Solutions to exercises	292	Solutions to numerical problems	454
Solutions to problems	304	Solutions to theoretical problems	459
Solutions to numerical problems	304	Solutions to applications	466
Solutions to theoretical problems	308	<b>19 Chemical kinetics</b>	<b>469</b>
Solutions to applications	311	Answers to discussion questions	469
<b>14 The first law of thermodynamics</b>	<b>314</b>	Solutions to exercises	472
Answers to discussion questions	314	Solutions to problems	479
Solutions to exercises	315	Solutions to numerical problems	479
Solutions to problems	326	Solutions to theoretical problems	486
Solutions to numerical problems	326	Solutions to applications	489
Solutions to theoretical problems	335		
Solutions to applications	348		

<b>20 Molecular reaction dynamics</b>	<b>492</b>	<b>21 Catalysis</b>	<b>512</b>
Answers to discussion questions	492	Answers to discussion questions	512
Solutions to exercises	493	Solutions to exercises	514
Solutions to problems	500	Solutions to problems	519
Solutions to numerical problems	500	Solutions to numerical problems	519
Solutions to theoretical problems	506	Solutions to theoretical problems	526
Solutions to applications	510	Solutions to applications	533

# STUDENT SOLUTIONS MANUAL FOR QUANTA, MATTER, AND CHANGE:

A MOLECULAR APPROACH TO PHYSICAL CHEMISTRY

## Exercises

### F1. Atoms

**F1.1(a)** The nuclear atomic model consists of a central nucleus of protons and neutrons along with all other nucleons within the nucleus, all of which are in a very small central region of the atom. Electrons occupy outside orbitals, which are voluminous regions of the atom that describe where electrons are likely to be found, with no more than two electrons in any orbital. The electrostatic attraction binds the negatively charged electrons to the positively charged nucleus, and the so-called strong interaction binds the protons and neutrons within the nucleus.

The orbitals within are grouped in shells around the nucleus, each shell being characterized by a principal quantum number,  $n = 1, 2, 3, \dots$ . A shell consists of  $n^2$  individual orbitals which are grouped together into  $n$  subshells. The subshells, and the orbitals they contain, are denoted as  $s, p, d, f, \dots$ . For all neutral atoms other than hydrogen, the electrons of a given shell have slightly different energies.

**F1.2(a)**

	Group	Element	Ground-state Electronic Configuration
(a)	Group 2	Ca, calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
(b)	Group 7	Mn, manganese	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
(c)	Group 15	As, arsenic	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

**F1.3(a)**

(a) chemical formula and name:  $MgCl_2$ , magnesium chloride  
ions:  $Mg^{2+}$  and  $Cl^-$

oxidation numbers of the elements: magnesium, +2; chlorine, -1

(b) chemical formula and name:  $FeO$ , iron(II) oxide

ions:  $Fe^{2+}$  and  $O^{2-}$

oxidation numbers of the elements: iron, +2; oxygen, -2

(c) chemical formula and name:  $Hg_2Cl_2$ , mercuric chloride

ions:  $Cl^-$  and  $Hg_2^{2+}$  (a polyatomic ion)

oxidation numbers of the elements: mercury, +1; chlorine, -1

**F1.4(a)**

Metals conduct electricity, have luster, and are malleable and ductile.
Nonmetals do not conduct electricity and are neither malleable nor ductile.
Metalloids typically have the appearance of metals but behave chemically like nonmetals.

# Fundamentals

## Exercises

### F.1 Atoms

- F1.1(a)** The **nuclear atomic model** consists of atomic number  $Z$  protons concentrated along with all atomic neutrons within the nucleus, an extremely small central region of the atom.  $Z$  electrons occupy **atomic orbitals**, which are voluminous regions of the atom that describe where electrons are likely to be found with no more than two electrons in any orbital. The electrostatic attraction binds the negatively charged electrons to the positively charged nucleus, and the so-called strong interaction binds the protons and neutrons within the nucleus.

The atomic orbitals are arranged in shells around the nucleus, each shell being characterized by a **principal quantum number**,  $n = 1, 2, 3, 4, \dots$ . A shell consists of  $n^2$  individual orbitals, which are grouped together into  $n$  subshells. The **subshells**, and the orbitals they contain, are denoted s, p, d, and f. For all neutral atoms other than hydrogen, the subshells of a given shell have slightly different energies.

**F1.2(a)**

	Example	Element	Ground-state Electronic Configuration
(a)	Group 2	Ca, calcium	[Ar]4s <sup>2</sup>
(b)	Group 7	Mn, manganese	[Ar]3d <sup>5</sup> 4s <sup>2</sup>
(c)	Group 15	As, arsenic	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>

**F1.3(a)**

- (a) chemical formula and name: MgCl<sub>2</sub>, magnesium chloride  
ions: Mg<sup>2+</sup> and Cl<sup>-</sup>  
oxidation numbers of the elements: magnesium, +2; chlorine, -1
- (b) chemical formula and name: FeO, iron(II) oxide  
ions: Fe<sup>2+</sup> and O<sup>2-</sup>  
oxidation numbers of the elements: iron, +2; oxygen, -2
- (c) chemical formula and name: Hg<sub>2</sub>Cl<sub>2</sub>, mercury(I) chloride  
ions: Cl<sup>-</sup> and Hg<sub>2</sub><sup>2+</sup> (a polyatomic ion)  
oxidation numbers of the elements: mercury, +1; chlorine, -1

**F1.4(a)**

	Metals conduct electricity, have luster, and are malleable and ductile.
	Nonmetals do not conduct electricity and are neither malleable nor ductile.
	Metalloids typically have the appearance of metals but behave chemically like nonmetals.

Boundary surface plots, Figure 4.3

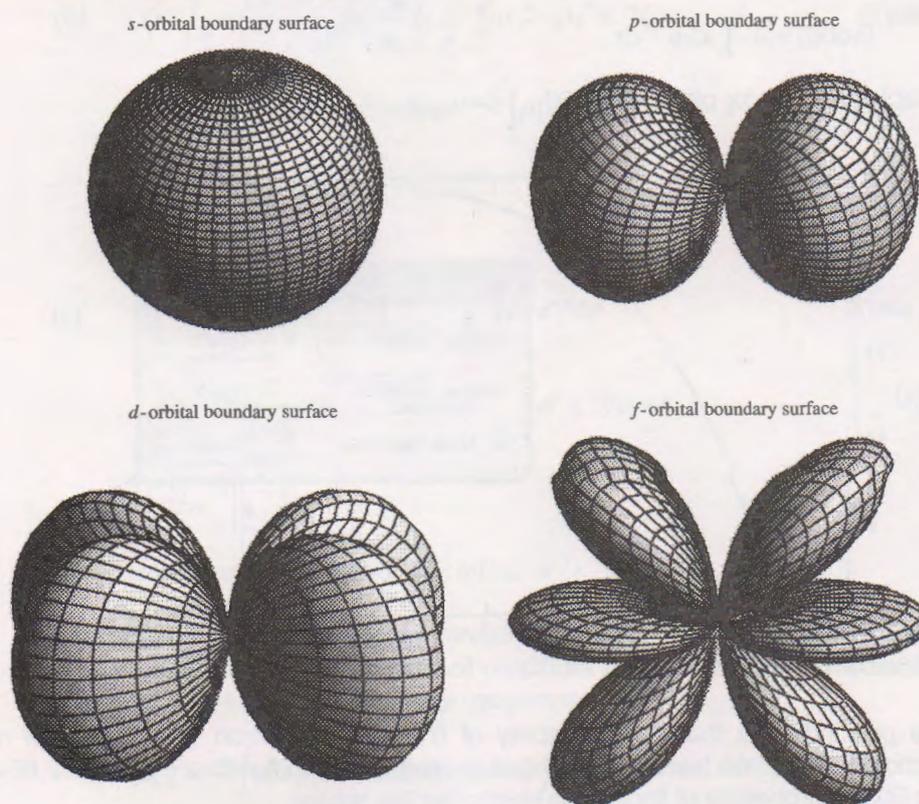


Figure 4.3

P4.19

$$\psi_{1s} = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \quad [4.14]$$

The probability of the electron being within a sphere of radius  $r'$  is

$$\int_0^{r'} \int_0^\pi \int_0^{2\pi} \psi_{1s}^2 r^2 \sin\theta \, d\theta \, d\phi \, dr$$

We set this equal to 0.90 and solve for  $r'$ . The integral over  $\theta$  and  $\phi$  gives a factor of  $4\pi$ ; thus

$$0.90 = \frac{4}{a_0^3} \int_0^{r'} r^2 e^{-2r/a_0} \, dr$$

$\int_0^{r'} r^2 e^{-2r/a_0} \, dr$  is integrated by parts to yield

$$\begin{aligned} & -\frac{a_0 r^2 e^{-2r/a_0}}{2} \Big|_0^{r'} + a_0 \left[ -\frac{a_0 r e^{-2r/a_0}}{2} \Big|_0^{r'} + \frac{a_0}{2} \left( -\frac{a_0 e^{-2r/a_0}}{2} \right) \Big|_0^{r'} \right] \\ & = -\frac{a_0 (r')^2 e^{-2r'/a_0}}{2} - \frac{a_0^2 r' e^{-2r'/a_0}}{2} - \frac{a_0^3 e^{-2r'/a_0}}{4} + \frac{a_0^3}{4} \end{aligned}$$

Multiplying by  $\frac{4}{a_0^3}$  and factoring  $e^{-2r'/a_0}$ ,

$$0.90 = \left[ -2 \left( \frac{r'}{a_0} \right)^2 - 2 \left( \frac{r'}{a_0} \right) - 1 \right] e^{-2r'/a_0} + 1 \quad \text{or} \quad 2 \left( \frac{r'}{a_0} \right)^2 + 2 \left( \frac{r'}{a_0} \right) + 1 = 0.10 e^{2r'/a_0}$$

It is easiest to solve this numerically. It is seen that  $r' = 2.66 a_0$  satisfies the above equation. Mathematical software has powerful features for handling this type of problem. Plots are very convenient to both make and use. Solve blocks can be used as functions. Both features are demonstrated below using Mathcad®.

An alternative method for studying the energy dependence on  $\phi$  and  $\psi$  involves a method like that specified above but with the AMBER computation performed at fixed values of both angles. Figure 8.15 summarizes a set of computations with  $-180^\circ < \phi < 180^\circ$  and  $\psi = 90^\circ$ . To characterize the energy surface, one would carry out similar calculations for several values of  $\psi$ .

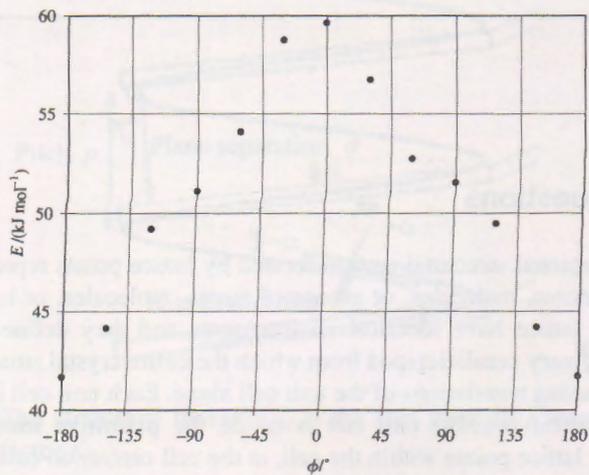


Figure 8.15

**E20.19(a)** The rate constant for electron transfer is

$$k_{\text{et}} = C \{H_{\text{DA}}(r)\}^2 e^{-\Delta^\ddagger G/RT} \quad [20.58]$$

The reorganization energy,  $\lambda$ , appears in two of these factors:

$$\Delta^\ddagger G = \frac{(\Delta_r G^\ominus + \lambda)^2}{4\lambda} \quad [20.59] \quad \text{and} \quad C = \frac{1}{h} \left( \frac{\pi^3}{\lambda RT} \right)^{1/2} \quad [20.60]$$

$$\text{So} \quad k_{\text{et}} = \frac{H_{\text{DA}}^2}{h} \left( \frac{\pi^3}{\lambda RT} \right)^{1/2} \exp\left( \frac{-(\Delta_r G^\ominus + \lambda)^2}{4\lambda RT} \right) = \frac{H_{\text{DA}}^2}{h} \left( \frac{\pi^3}{\lambda kT} \right)^{1/2} \exp\left( \frac{-(\Delta_r G^\ominus + \lambda)^2}{4\lambda kT} \right)$$

depending on whether the energies are expressed in molar units or molecular units. The only unknown in this equation is  $\lambda$ . Isolating  $\lambda$  analytically is not possible; however, one can solve for it numerically using the root-finding command of a symbolic mathematics package, or graphically by plotting the right-hand side versus the (constant) left-hand side and finding the value of  $\lambda$  at which the two lines cross. Before we put in numbers, we must make sure to use compatible units. We recognize that  $H_{\text{DA}}(r)$  and  $\Delta_r G^\ominus$  are both given in molecular units, but that the former is really a wavenumber rather than an energy. So we choose to express all energies in molecular units, namely, joules:

$$H_{\text{DA}}(r) = hc \times 0.04 \text{ cm}^{-1} = (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (0.04 \text{ cm}^{-1})$$

$$H_{\text{DA}}(r) = 8 \times 10^{-25} \text{ J}$$

$$\frac{H_{\text{DA}}^2}{h} \left( \frac{\pi^3}{kT} \right)^{1/2} = \frac{(8 \times 10^{-25} \text{ J})^2}{6.626 \times 10^{-34} \text{ J s}} \left( \frac{\pi^3}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} \right)^{1/2} = 8 \times 10^{-5} \text{ J}^{0.5} \text{ s}^{-1}$$

$$\Delta_r G^\ominus = -0.185 \text{ eV} \times 1.602 \times 10^{-19} \text{ J eV}^{-1} = -2.96 \times 10^{-20} \text{ J}$$

$$\text{and} \quad 4kT = 4 \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}) = 1.65 \times 10^{-20} \text{ J}$$

$$\text{Thus} \quad 37.5 = 8 \times 10^{-5} \left( \frac{\text{J}}{\lambda} \right)^{1/2} \exp\left( \frac{-(-2.96 \times 10^{-20} \text{ J} + \lambda)^2}{\lambda \times 1.65 \times 10^{-20} \text{ J}} \right)$$

$$\text{where} \quad \lambda = \boxed{4 \times 10^{-21} \text{ J}} \quad \text{or} \quad \boxed{2 \text{ kJ mol}^{-1}}$$

**E20.20(a)** For the same donor and acceptor at different distances, eqn. 20.61 applies:

$$\ln k_{\text{et}} = -\beta r + \text{constant}$$

The slope of a plot of  $k_{\text{et}}$  versus  $r$  is  $-\beta$ . The slope of a line defined by two points is

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{\ln k_{\text{et},2} - \ln k_{\text{et},1}}{r_2 - r_1} = -\beta = \frac{\ln 4.51 \times 10^4 - \ln 2.02 \times 10^5}{(1.23 - 1.11) \text{ nm}}$$

$$\text{so} \quad \beta = \boxed{12.5 \text{ nm}^{-1}}$$

## Solutions to problems

### Solutions to numerical problems

**P20.1** If the rate constant obeys the Arrhenius equation (eqn. 20.1a), a plot of  $\ln k_r$  against  $1/T$  should yield a straight line with slope  $-E_a/R$  (eqn. 20.1b). Construct a table as follows.