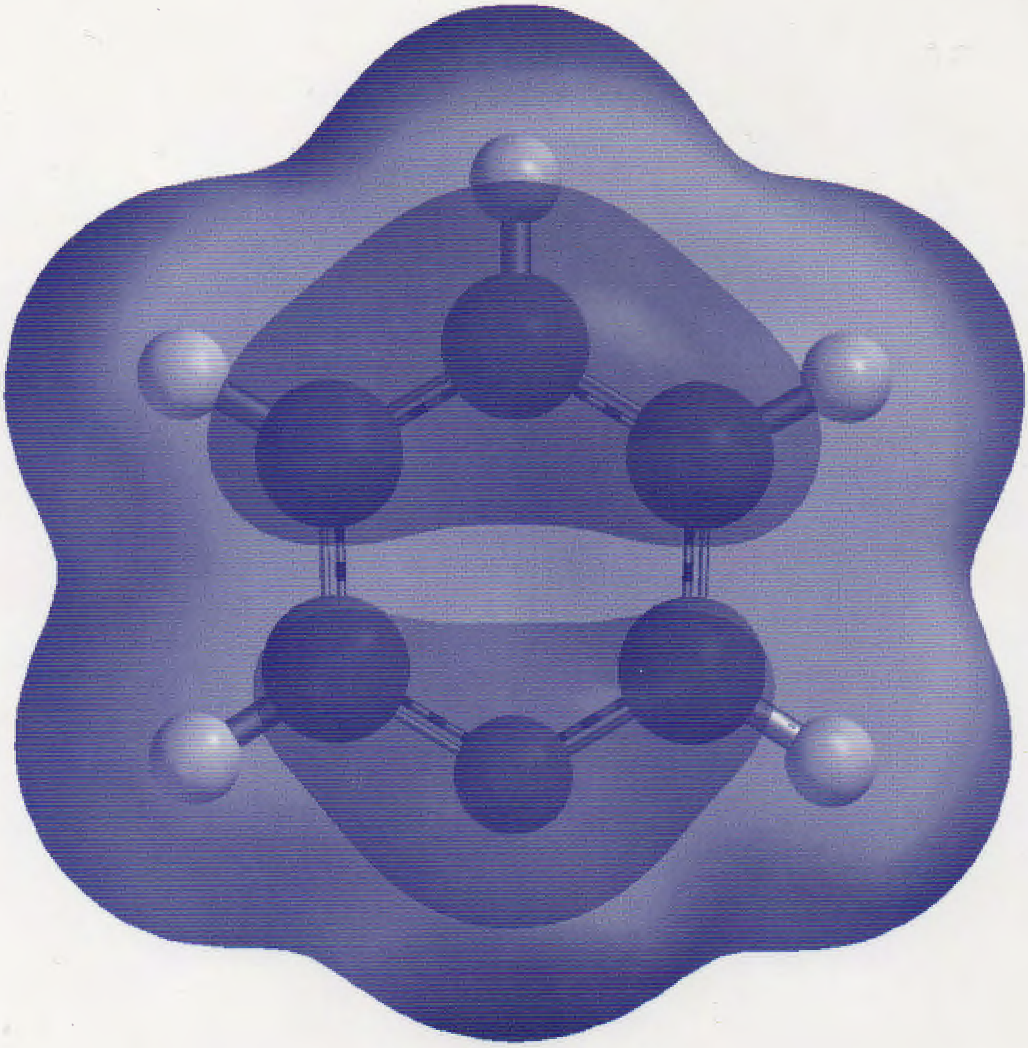
Student Solutions Manual to Accompany

Quanta, Matter, and Change

A molecular approach to physical chemistry



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STUDENT SOLUTIONS MANUAL FOR QUANTA, MATTER, AND CHANGE:

A MOLECULAR APPROACH TO PHYSICAL CHEMISTRY

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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.

C. T.
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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,** $n = 1, 2, 3, 4....$ 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	$[Ar]4s^2$
(b)	Group 7	Mn, manganese	$[Ar]3d^54s^2$
(c)	Group 15	As, arsenic	$[Ar]3d^{10}4s^24p^3$

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, mercury(I) 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.

Boundary surface plots, Figure 4.3

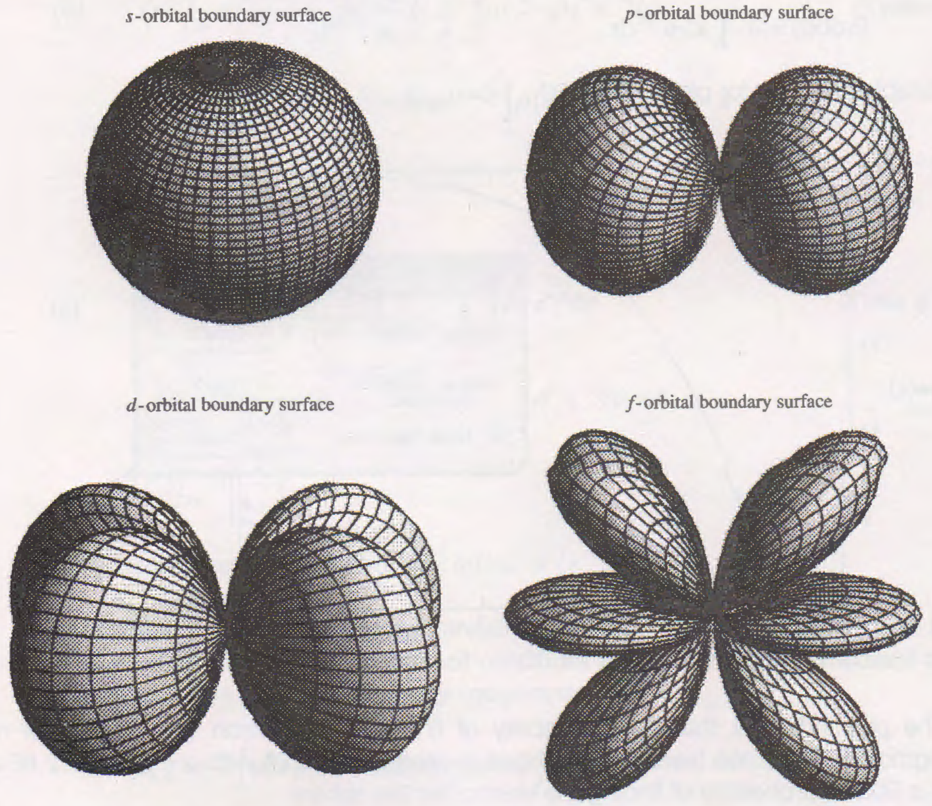

Figure 4.3

P4.19 $\psi_{1s} = \left(\dfrac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$ [4.14]

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

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

We set this equal to 0.90 and solve for r'. The integral over θ and ϕ gives a factor of 4π; 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

$$-\frac{a_0 r^2 e^{-2r/a_0}}{2}\Bigg|_0^{r'} + a_0\left[-\frac{a_0 r e^{-2r/a_0}}{2}\Bigg|_0^{r'} + \frac{a_0}{2}\left(-\frac{a_0 e^{-2r/a_0}}{2}\right)\Bigg|_0^{r'}\right]$$

$$= -\frac{a_0 (r')^2 e^{-2r'/a_0}}{2} - \frac{a_0^2 r'}{2}e^{-2r'/a_0} - \frac{a_0^3}{4}e^{-2r'/a_0} + \frac{a_0^3}{4}$$

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

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

It is easiest to solve this numerically. It is seen that $\boxed{r' = 2.66a_0}$ 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 ϕ and ψ 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 $-180° < \phi < 180°$ and $\psi = 90°$. To characterize the energy surface, one would carry out similar calculations for several values of ψ.

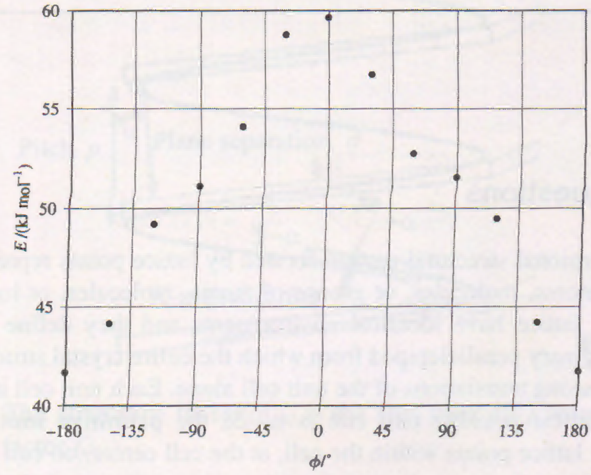

Figure 8.15

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

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

The reorganization energy, λ, appears in two of these factors:

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

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

depending on whether the energies are expressed in molar units or molecular units. The only unknown in this equation is λ. Isolating λ 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 λ at which the two lines cross. Before we put in numbers, we must make sure to use compatible units. We recognize that $H_{DA}(r)$ 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:

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

$$H_{DA}(r) = 8\times10^{-25} \text{ J}$$

$$\frac{H_{DA}{}^2}{h}\left(\frac{\pi^3}{kT}\right)^{1/2} = \frac{(8\times10^{-25} \text{ J})^2}{6.626\times10^{-34} \text{ J s}}\left(\frac{\pi^3}{1.381\times10^{-23} \text{ J K}^{-1}\times298 \text{ K}}\right)^{1/2} = 8\times10^{-5} \text{ J}^{0.5} \text{ s}^{-1}$$

$$\Delta_r G^{\ominus} = -0.185 \text{ eV} \times 1.602\times10^{-19} \text{ J eV}^{-1} = -2.96\times10^{-20} \text{ J}$$

and $4kT = 4 \times (1.381\times10^{-23} \text{ J K}^{-1}) \times (298 \text{ K}) = 1.65\times10^{-20} \text{ J}$

Thus
$$37.5 = 8\times10^{-5}\left(\frac{\text{J}}{\lambda}\right)^{1/2} \exp\left(\frac{-(-2.96\times10^{-20} \text{ J} + \lambda)^2}{\lambda\times1.65\times10^{-20} \text{ J}}\right)$$

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

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

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

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

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{\ln k_{et,2} - \ln k_{et,1}}{r_2 - r_1} = -\beta = \frac{\ln 4.51\times10^4 - \ln 2.02\times10^5}{(1.23 - 1.11) \text{ nm}}$$

so $\beta = \boxed{12.\bar{5} \text{ nm}^{-1}}$

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.