

Alan Hinchliffe

MOLECULAR
MODELLING
for
BEGINNERS

 WILEY

Molecular Modelling for Beginners

Alan Hinchliffe

UMIST, Manchester, UK



Copyright © 2003 by John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester,
West Sussex PO19 8SQ, England

National 01243 779777
International (+44) 1243 779777

E-mail (for orders and customer service enquiries): cs-books@wiley.co.uk
Visit our Home Page on www.wileyeurope.com

or
www.wiley.com

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, electronic, mechanical, photocopying, recording, scanning or otherwise, except under the terms of the Copyright, Designs and Patents Act 1988 or under the terms of a licence issued by the Copyright Licensing Agency Ltd, 90 Tottenham Court Road, London W1P 4LP, UK, without the permission in writing of the Publisher. Requests to the Publisher should be addressed to the Permissions Department, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, or emailed to permreq@wiley.co.uk, or faxed to (+44) 1243 770620.

This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the Publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

Other Wiley Editorial Offices

John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 33 Park Road, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada M9W 1L1

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Library of Congress Cataloging-in-Publication Data

(to follow)

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0 470 84309 8 (Hardback)

0 470 84310 1 (Paperback)

Typeset in 10.5/13pt Times by Thomson Press (India) Ltd., Chennai

Printed and bound in Great Britain by TJ International Ltd., Padstow, Cornwall

This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

Molecular Modelling for Beginners

Preface

There is nothing radically new about the techniques we use in modern molecular modelling. Classical mechanics hasn't changed since the time of Newton, Hamilton and Lagrange, the great ideas of statistical mechanics and thermodynamics were discovered by Ludwig Boltzmann and J. Willard Gibbs amongst others and the basic concepts of quantum mechanics appeared in the 1920s, by which time J. C. Maxwell's famous electromagnetic equations had long since been published.

The chemically inspired idea that molecules can profitably be treated as a collection of balls joined together with springs can be traced back to the work of D. H. Andrews in 1930. The first serious molecular Monte Carlo simulation appeared in 1953, closely followed by B. J. Alder and T. E. Wainwright's classic molecular dynamics study of hard disks in 1957.

The Hartrees' 1927 work on atomic structure is the concrete reality of our everyday concept of atomic orbitals, whilst C. C. J. Roothaan's 1951 formulation of the HF-LCAO model arguably gave us the basis for much of modern molecular quantum theory.

If we move on a little, most of my colleagues would agree that the two recent major advances in molecular quantum theory have been density functional theory, and the elegant treatment of solvents using ONIOM. Ancient civilizations believed in the cyclical nature of time and they might have had a point for, as usual, nothing is new. Workers in solid-state physics and biology actually proposed these models many years ago. It took the chemists a while to catch up.

Scientists and engineers first got their hands on computers in the late 1960s. We have passed the point on the computer history curve where every 10 years gave us an order of magnitude increase in computer power, but it is no coincidence that the growth in our understanding and application of molecular modelling has run in parallel with growth in computer power. Perhaps the two greatest driving forces in recent years have been the PC and the graphical user interface. I am humbled by the fact that my lowly 1.2 GHz AMD Athlon office PC is far more powerful than the world-beating mainframes that I used as a graduate student all those years ago, and that I can build a molecule on screen and run a B3LYP/6-311++G(3d, 2p) calculation before my eyes (of which more in Chapter 20).

We have also reached a stage where tremendously powerful molecular modelling computer packages are commercially available, and the subject is routinely taught as part of undergraduate science degrees. I have made use of several such packages to

produce the screenshots; obviously they look better in colour than the greyscale of this text.

There are a number of classic (and hard) texts in the field; if I'm stuck with a basic molecular quantum mechanics problem, I usually reach for Eyring, Walter and Kimball's *Quantum Chemistry*, but the going is rarely easy. I make frequent mention of this volume throughout the book.

Equally, there are a number of beautifully produced elementary texts and software reference manuals that can apparently transform you into an expert overnight. It's a two-edged sword, and we are victims of our own success. One often meets self-appointed experts in the field who have picked up much of the jargon with little of the deep understanding. It's no use (in my humble opinion) trying to hold a conversation about gradients, Hessians and density functional theory with a colleague who has just run a molecule through one package or another but hasn't the slightest clue what the phrases or the output mean.

It therefore seemed to me (and to the Reviewers who read my New Book Proposal) that the time was right for a middle course. I assume that you are a 'Beginner' in the sense of *Chambers Dictionary*—'someone who begins; a person who is in the early stages of learning or doing anything . . .'—and I want to tell you how we go about modern molecular modelling, why we do it, and most important of all, explain much of the basic theory behind the mouse clicks. This involves mathematics and physics, and the book neither pulls punches nor aims at instant enlightenment. Many of the concepts and ideas are difficult ones, and you will have to think long and hard about them; if it's any consolation, so did the pioneers in our subject. I have given many of the derivations in full, and tried to avoid the dreaded phrase 'it can be shown that'.

There are various strands to our studies, all of which eventually intertwine. We start off with molecular mechanics, a classical treatment widely used to predict molecular geometries. In Chapter 8 I give a quick guide to statistical thermodynamics (if such a thing is possible), because we need to make use of the concepts when trying to model arrays of particles at non-zero temperatures. Armed with this knowledge, we are ready for an assault on Monte Carlo and Molecular Dynamics.

Just as we have to bite the bullet of statistical mechanics, so we have to bite the equally difficult one of quantum mechanics, which occupies Chapters 11 and 12. We then turn to the quantum treatment of atoms, where many of the sums can be done on a postcard if armed with knowledge of angular momentum.

The Hartree–Fock and HF–LCAO models dominate much of the next few chapters, as they should. The Hartree–Fock model is great for predicting many molecular properties, but it can't usually cope with bond-breaking and bond-making. Chapter 19 treats electron correlation and Chapter 20 deals with the very topical density functional theory (DFT). You won't be taken seriously if you have not done a DFT calculation on your molecule.

Quantum mechanics, statistical mechanics and electromagnetism all have a certain well-deserved reputation amongst science students; they are hard subjects. Unfortunately all three feature in this new text. In electromagnetism it is mostly a matter of getting to grips with the mathematical notation (although I have spared you

Maxwell's equations), whilst in the other two subjects it is more a question of mastering hard concepts. In the case of quantum mechanics, the concepts are often in direct contradiction to everyday experience and common sense. I expect from you a certain level of mathematical competence; I have made extensive use of vectors and matrices not because I am perverse, but because such mathematical notation brings out the inherent simplicity and beauty of many of the equations. I have tried to help by giving a mathematical Appendix, which should also make the text self-contained.

I have tried to put the text into historical perspective, and in particular I have quoted directly from a number of what I call *keynote papers*. It is interesting to read at first hand how the pioneers put their ideas across, and in any case they do it far better than me. For example, I am not the only author to quote Paul Dirac's famous statement

The underlying Physical Laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact application of these laws leads to equations much too complicated to be soluble.

I hope you have a profitable time in your studies, and at the very least begin to appreciate what all those options mean next time you run a modelling package!

Alan Hinchliffe
alan.hinchliffe@umist.ac.uk
Manchester 2003

List of Symbols

| | |
|--------------------------|---|
| $\langle \dots \rangle$ | Mean value/time average |
| a_0 | Atomic unit of length (the bohr) |
| A | Thermodynamic Helmholtz energy |
| α | GTO orbital exponent; exchange parameter in $X\alpha$ DFT |
| α_A | Hückel π -electron Coulomb integral for atom A |
| α_e | Vibration-rotation coupling constant |
| α | Electric polarizability matrix |
| B | Wilson B matrix |
| β_{AB}^0 | Bonding parameter in semi-empirical theories (e.g. CNDO) |
| β_{AB} | Hückel π -electron resonance integral for bonded pairs A, B |
| χ | Electronegativity; basis function in LCAO theories |
| C_6, C_{12} | Lennard-Jones parameters |
| C_v, C_p | Heat capacities at constant volume and pressure. |
| d | Contraction coefficient in, for example, STO-nG expansion |
| $D(\varepsilon)$ | Density of states |
| D_0 | Spectroscopic dissociation energy |
| D_e | Thermodynamic dissociation energy |
| $d\tau$ | Volume element |
| E | Electron affinity |
| E_h | Atomic unit of energy (the hartree) |
| $\mathbf{E}(\mathbf{r})$ | Electric field vector (\mathbf{r} = field point) |
| ε | Particle energy |
| F | Force (a vector quantity) |
| Φ | Total mutual potential energy |
| $\phi(\mathbf{r})$ | Electrostatic potential (\mathbf{r} = field point) |
| g | Gradient vector |
| G | Thermodynamic gibbs energy |
| H | Hessian matrix |
| H | Thermodynamic enthalpy; classical hamiltonian |
| \mathbf{h}_1 | Matrix of one-electron integrals in LCAO models |
| $H_\nu(\xi)$ | Hermite polynomial of degree ν |
| I | Ionization energy |
| ϵ_0 | Permittivity of free space |
| ϵ_r | Relative permittivity |

| | |
|---|--|
| j | Square root of -1 |
| J, K and G | Coulomb, exchange and G matrices from LCAO models |
| k_s | Force constant |
| I, L | Angular momentum vectors |
| L-J | Lennard-Jones (potential) |
| μ | Reduced mass |
| n | Amount of substance |
| p | Pressure |
| P(r) | Dielectric polarization (\mathbf{r} = field point) |
| \mathbf{p}_e | Electric dipole moment |
| q | Normal coordinate; atomic charge; molecular partition function |
| q | Quaternion |
| Q | Partition function |
| Q_A | Point charge |
| \mathbf{q}_e | Electric second moment tensor |
| Θ_e | Electric quadrupole moment tensor |
| R | Gas constant |
| R | Rotation matrix |
| $\rho(\mathbf{r})$ | Electrostatic charge distribution (\mathbf{r} = field point) |
| \mathbf{r}, \mathbf{R} | Field point vectors |
| R_∞ | Rydberg constant for one-electron atom with infinite nuclear mass. |
| $\rho_1(\mathbf{x}_1)$ | One-electron density function |
| $\rho_2(\mathbf{x}_1, \mathbf{x}_2)$ | Two-electron density function |
| R_A | Position vector |
| R_e | Equilibrium bond length |
| R_H | Rydberg constant for hydrogen |
| S | Thermodynamic entropy |
| U | Mutual potential energy |
| U, U_{th} | Thermodynamic internal energy |
| V | Volume |
| ω | Angular vibration frequency |
| $\omega_e x_e$ | Anharmonicity constant |
| $\psi(\mathbf{r})$ | Orbital (i.e. single-particle wavefunction) |
| $\Psi(\mathbf{R}, t)$ | Time-dependent wavefunction |
| $\Psi(\mathbf{R}_1, \mathbf{R}_2, \dots)$ | Many-particle wavefunction |
| Z | Atomic number |
| ζ | STO orbital exponent |

Contents

| | |
|--|-------------|
| Preface | xiii |
| List of Symbols | xvii |
| 1 Introduction | 1 |
| 1.1 Chemical Drawing | 1 |
| 1.2 Three-Dimensional Effects | 2 |
| 1.3 Optical Activity | 3 |
| 1.4 Computer Packages | 4 |
| 1.5 Modelling | 4 |
| 1.6 Molecular Structure Databases | 6 |
| 1.7 File Formats | 7 |
| 1.8 Three-Dimensional Displays | 8 |
| 1.9 Proteins | 10 |
| 2 Electric Charges and Their Properties | 13 |
| 2.1 Point Charges | 13 |
| 2.2 Coulomb's Law | 15 |
| 2.3 Pairwise Additivity | 16 |
| 2.4 The Electric Field | 17 |
| 2.5 Work | 18 |
| 2.6 Charge Distributions | 20 |
| 2.7 The Mutual Potential Energy U | 21 |
| 2.8 Relationship Between Force and Mutual Potential Energy | 22 |
| 2.9 Electric Multipoles | 23 |
| 2.9.1 Continuous charge distributions | 26 |
| 2.9.2 The electric second moment | 26 |
| 2.9.3 Higher electric moments | 29 |
| 2.10 The Electrostatic Potential | 29 |
| 2.11 Polarization and Polarizability | 30 |
| 2.12 Dipole Polarizability | 31 |
| 2.12.1 Properties of polarizabilities | 33 |
| 2.13 Many-Body Forces | 33 |
| 3 The Forces Between Molecules | 35 |
| 3.1 The Pair Potential | 35 |
| 3.2 The Multipole Expansion | 37 |
| 3.3 The Charge–Dipole Interaction | 37 |
| 3.4 The Dipole–Dipole Interaction | 39 |

| | | |
|----------|--|-----------|
| 3.5 | Taking Account of the Temperature | 41 |
| 3.6 | The Induction Energy | 41 |
| 3.7 | Dispersion Energy | 43 |
| 3.8 | Repulsive Contributions | 44 |
| 3.9 | Combination Rules | 46 |
| 3.10 | Comparison with Experiment | 46 |
| | 3.10.1 Gas imperfections | 47 |
| | 3.10.2 Molecular beams | 47 |
| 3.11 | Improved Pair Potentials | 47 |
| 3.12 | Site–Site Potentials | 48 |
| 4 | Balls on Springs | 51 |
| 4.1 | Vibrational Motion | 52 |
| 4.2 | The Force Law | 55 |
| 4.3 | A Simple Diatomic | 56 |
| 4.4 | Three Problems | 57 |
| 4.5 | The Morse Potential | 60 |
| 4.6 | More Advanced Potentials | 61 |
| 5 | Molecular Mechanics | 63 |
| 5.1 | More About Balls on Springs | 63 |
| 5.2 | Larger Systems of Balls on Springs | 65 |
| 5.3 | Force Fields | 67 |
| 5.4 | Molecular Mechanics | 67 |
| | 5.4.1 Bond-stretching | 68 |
| | 5.4.2 Bond-bending | 69 |
| | 5.4.3 Dihedral motions | 69 |
| | 5.4.4 Out-of-plane angle potential (inversion) | 70 |
| | 5.4.5 Non-bonded interactions | 71 |
| | 5.4.6 Coulomb interactions | 72 |
| 5.5 | Modelling the Solvent | 72 |
| 5.6 | Time-and-Money-Saving Tricks | 72 |
| | 5.6.1 United atoms | 72 |
| | 5.6.2 Cut-offs | 73 |
| 5.7 | Modern Force Fields | 73 |
| | 5.7.1 Variations on a theme | 74 |
| 5.8 | Some Commercial Force Fields | 75 |
| | 5.8.1 DREIDING | 75 |
| | 5.8.2 MM1 | 75 |
| | 5.8.3 MM2 (improved hydrocarbon force field) | 76 |
| | 5.8.4 AMBER | 77 |
| | 5.8.5 OPLS (Optimized Potentials for Liquid Simulations) | 78 |
| | 5.8.6 R. A. Johnson | 78 |
| 6 | The Molecular Potential Energy Surface | 79 |
| 6.1 | Multiple Minima | 79 |
| 6.2 | Saddle Points | 80 |
| 6.3 | Characterization | 82 |
| 6.4 | Finding Minima | 82 |
| 6.5 | Multivariate Grid Search | 83 |
| | 6.5.1 Univariate search | 84 |

| | | |
|----------|--|------------|
| 6.6 | Derivative Methods | 84 |
| 6.7 | First-Order Methods | 85 |
| 6.7.1 | Steepest descent | 85 |
| 6.7.2 | Conjugate gradients | 86 |
| 6.8 | Second-Order Methods | 87 |
| 6.8.1 | Newton–Raphson | 87 |
| 6.8.2 | Block diagonal Newton–Raphson | 90 |
| 6.8.3 | Quasi-Newton–Raphson | 90 |
| 6.8.4 | The Fletcher–Powell algorithm [17] | 91 |
| 6.9 | Choice of Method | 91 |
| 6.10 | The Z Matrix | 92 |
| 6.11 | Tricks of the Trade | 94 |
| 6.11.1 | Linear structures | 94 |
| 6.11.2 | Cyclic structures | 95 |
| 6.12 | The End of the Z Matrix | 97 |
| 6.13 | Redundant Internal Coordinates | 99 |
| 7 | A Molecular Mechanics Calculation | 101 |
| 7.1 | Geometry Optimization | 101 |
| 7.2 | Conformation Searches | 102 |
| 7.3 | QSARs | 104 |
| 7.3.1 | Atomic partial charges | 105 |
| 7.3.2 | Polarizabilities | 107 |
| 7.3.3 | Molecular volume and surface area | 109 |
| 7.3.4 | $\log(P)$ | 110 |
| 8 | Quick Guide to Statistical Thermodynamics | 113 |
| 8.1 | The Ensemble | 114 |
| 8.2 | The Internal Energy U_{th} | 116 |
| 8.3 | The Helmholtz Energy A | 117 |
| 8.4 | The Entropy S | 117 |
| 8.5 | Equation of State and Pressure | 117 |
| 8.6 | Phase Space | 118 |
| 8.7 | The Configurational Integral | 119 |
| 8.8 | The Virial of Clausius | 121 |
| 9 | Molecular Dynamics | 123 |
| 9.1 | The Radial Distribution Function | 124 |
| 9.2 | Pair Correlation Functions | 127 |
| 9.3 | Molecular Dynamics Methodology | 128 |
| 9.3.1 | The hard sphere potential | 128 |
| 9.3.2 | The finite square well | 128 |
| 9.3.3 | Lennardjonesium | 130 |
| 9.4 | The Periodic Box | 131 |
| 9.5 | Algorithms for Time Dependence | 133 |
| 9.5.1 | The leapfrog algorithm | 134 |
| 9.5.2 | The Verlet algorithm | 134 |
| 9.6 | Molten Salts | 135 |
| 9.7 | Liquid Water | 136 |
| 9.7.1 | Other water potentials | 139 |
| 9.8 | Different Types of Molecular Dynamics | 139 |
| 9.9 | Uses in Conformational Studies | 140 |

| | |
|--|------------|
| 10 Monte Carlo | 143 |
| 10.1 Introduction | 143 |
| 10.2 MC Simulation of Rigid Molecules | 148 |
| 10.3 Flexible Molecules | 150 |
| 11 Introduction to Quantum Modelling | 151 |
| 11.1 <i>The Schrödinger Equation</i> | 151 |
| 11.2 The Time-Independent Schrödinger Equation | 153 |
| 11.3 Particles in Potential Wells | 154 |
| 11.3.1 The one-dimensional infinite well | 154 |
| 11.4 The Correspondence Principle | 157 |
| 11.5 The Two-Dimensional Infinite Well | 158 |
| 11.6 The Three-Dimensional Infinite Well | 160 |
| 11.7 Two Non-Interacting Particles | 161 |
| 11.8 The Finite Well | 163 |
| 11.9 Unbound States | 164 |
| 11.10 Free Particles | 165 |
| 11.11 Vibrational Motion | 166 |
| 12 Quantum Gases | 171 |
| 12.1 Sharing Out the Energy | 172 |
| 12.2 Rayleigh Counting | 174 |
| 12.3 The Maxwell Boltzmann Distribution of Atomic Kinetic Energies | 176 |
| 12.4 Black Body Radiation | 177 |
| 12.5 Modelling Metals | 180 |
| 12.5.1 The Drude model | 180 |
| 12.5.2 The Pauli treatment | 183 |
| 12.6 The Boltzmann Probability | 184 |
| 12.7 Indistinguishability | 188 |
| 12.8 Spin | 192 |
| 12.9 Fermions and Bosons | 194 |
| 12.10 The Pauli Exclusion Principle | 194 |
| 12.11 Boltzmann's Counting Rule | 195 |
| 13 One-Electron Atoms | 197 |
| 13.1 Atomic Spectra | 197 |
| 13.1.1 Bohr's theory | 198 |
| 13.2 The Correspondence Principle | 200 |
| 13.3 The Infinite Nucleus Approximation | 200 |
| 13.4 Hartree's Atomic Units | 201 |
| 13.5 Schrödinger Treatment of the H Atom | 202 |
| 13.6 The Radial Solutions | 204 |
| 13.7 The Atomic Orbitals | 206 |
| 13.7.1 $l = 0$ (<i>s</i> orbitals) | 207 |
| 13.7.2 The <i>p</i> orbitals | 210 |
| 13.7.3 The <i>d</i> orbitals | 211 |
| 13.8 The Stern–Gerlach Experiment | 212 |
| 13.9 Electron Spin | 215 |
| 13.10 Total Angular Momentum | 216 |
| 13.11 Dirac Theory of the Electron | 217 |
| 13.12 Measurement in the Quantum World | 219 |

| | |
|--|------------|
| 14 The Orbital Model | 221 |
| 14.1 One- and Two-Electron Operators | 221 |
| 14.2 The Many-Body Problem | 222 |
| 14.3 The Orbital Model | 223 |
| 14.4 Perturbation Theory | 225 |
| 14.5 The Variation Method | 227 |
| 14.6 The Linear Variation Method | 230 |
| 14.7 Slater Determinants | 233 |
| 14.8 The Slater–Condon–Shortley Rules | 235 |
| 14.9 The Hartree Model | 236 |
| 14.10 The Hartree–Fock Model | 238 |
| 14.11 Atomic Shielding Constants | 239 |
| 14.11.1 Zener’s wavefunctions | 240 |
| 14.11.2 Slater’s rules | 241 |
| 14.12 Koopmans’ Theorem | 242 |
| | |
| 15 Simple Molecules | 245 |
| 15.1 The Hydrogen Molecule Ion H_2^+ | 246 |
| 15.2 The LCAO Model | 248 |
| 15.3 Elliptic Orbitals | 251 |
| 15.4 The Heitler–London Treatment of Dihydrogen | 252 |
| 15.5 The Dihydrogen MO Treatment | 254 |
| 15.6 The James and Coolidge Treatment | 256 |
| 15.7 Population Analysis | 256 |
| 15.7.1 Extension to many-electron systems | 258 |
| | |
| 16 The HF–LCAO Model | 261 |
| 16.1 Roothaan’s Landmark Paper | 262 |
| 16.2 The J and K Operators | 264 |
| 16.3 The HF–LCAO Equations | 264 |
| 16.3.1 The HF–LCAO equations | 267 |
| 16.4 The Electronic Energy | 268 |
| 16.5 Koopmans’ Theorem | 269 |
| 16.6 Open Shell Systems | 269 |
| 16.7 The Unrestricted Hartree–Fock Model | 271 |
| 16.7.1 Three technical points | 273 |
| 16.8 Basis Sets | 273 |
| 16.8.1 Clementi and Raimondi | 274 |
| 16.8.2 Extension to second-row atoms | 275 |
| 16.8.3 Polarization functions | 276 |
| 16.9 Gaussian Orbitals | 276 |
| 16.9.1 STO/ nG | 280 |
| 16.9.2 STO/4–31G | 282 |
| 16.9.3 Gaussian polarization and diffuse functions | 283 |
| 16.9.4 Extended basis sets | 283 |
| | |
| 17 HF–LCAO Examples | 287 |
| 17.1 Output | 289 |
| 17.2 Visualization | 293 |
| 17.3 Properties | 294 |
| 17.3.1 The electrostatic potential | 295 |

| | | |
|-----------|---|------------|
| 17.4 | Geometry Optimization | 297 |
| 17.4.1 | The Hellmann–Feynman Theorem | 297 |
| 17.4.2 | Energy minimization | 298 |
| 17.5 | Vibrational Analysis | 300 |
| 17.6 | Thermodynamic Properties | 303 |
| 17.6.1 | The ideal monatomic gas | 304 |
| 17.6.2 | The ideal diatomic gas | 306 |
| 17.6.3 | q_{rot} | 306 |
| 17.6.4 | q_{vib} | 307 |
| 17.7 | Back to L-phenylalanine | 308 |
| 17.8 | Excited States | 309 |
| 17.9 | Consequences of the Brillouin Theorem | 313 |
| 17.10 | Electric Field Gradients | 315 |
| 18 | Semi-empirical Models | 319 |
| 18.1 | Hückel π -Electron Theory | 319 |
| 18.2 | Extended Hückel Theory | 322 |
| 18.2.1 | Roald Hoffman | 323 |
| 18.3 | Pariser, Parr and Pople | 324 |
| 18.4 | Zero Differential Overlap | 325 |
| 18.5 | Which Basis Functions Are They? | 327 |
| 18.6 | All Valence Electron ZDO Models | 328 |
| 18.7 | Complete Neglect of Differential Overlap | 328 |
| 18.8 | CNDO/2 | 329 |
| 18.9 | CNDO/S | 330 |
| 18.10 | Intermediate Neglect of Differential Overlap | 330 |
| 18.11 | Neglect of Diatomic Differential Overlap | 331 |
| 18.12 | The Modified INDO Family | 331 |
| 18.12.1 | MINDO/3 | 332 |
| 18.13 | Modified Neglect of Overlap | 333 |
| 18.14 | Austin Model 1 | 333 |
| 18.15 | PM3 | 333 |
| 18.16 | SAM1 | 334 |
| 18.17 | ZINDO/1 and ZINDO/S | 334 |
| 18.18 | Effective Core Potentials | 334 |
| 19 | Electron Correlation | 337 |
| 19.1 | Electron Density Functions | 337 |
| 19.1.1 | Fermi correlation | 339 |
| 19.2 | Configuration Interaction | 339 |
| 19.3 | The Coupled Cluster Method | 340 |
| 19.4 | Møller–Plesset Perturbation Theory | 341 |
| 19.5 | Multiconfiguration SCF | 346 |
| 20 | Density Functional Theory and the Kohn–Sham LCAO Equations | 347 |
| 20.1 | The Thomas–Fermi and X_{α} Models | 348 |
| 20.2 | The Hohenberg–Kohn Theorems | 350 |
| 20.3 | The Kohn–Sham (KS–LCAO) Equations | 352 |
| 20.4 | Numerical Integration (Quadrature) | 353 |
| 20.5 | Practical Details | 354 |

| | | |
|-----------|--|------------|
| 20.6 | Custom and Hybrid Functionals | 355 |
| 20.7 | An Example | 356 |
| 20.8 | Applications | 358 |
| 21 | Miscellany | 361 |
| 21.1 | Modelling Polymers | 361 |
| 21.2 | The End-to-End Distance | 363 |
| 21.3 | Early Models of Polymer Structure | 364 |
| | 21.3.1 The freely jointed chain | 366 |
| | 21.3.2 The freely rotating chain | 366 |
| 21.4 | Accurate Thermodynamic Properties; The G1, G2 and G3 Models | 367 |
| | 21.4.1 G1 theory | 367 |
| | 21.4.2 G2 theory | 369 |
| | 21.4.3 G3 theory | 369 |
| 21.5 | Transition States | 370 |
| 21.6 | Dealing with the Solvent | 372 |
| 21.7 | Langevin Dynamics | 373 |
| 21.8 | The Solvent Box | 375 |
| 21.9 | ONIOM or Hybrid Models | 376 |
| | Appendix: A Mathematical Aide-Mémoire | 379 |
| A.1 | Scalars and Vectors | 379 |
| A.2 | Vector Algebra | 380 |
| | A.2.1 Vector addition and scalar multiplication | 380 |
| | A.2.2 Cartesian coordinates | 381 |
| | A.2.3 Cartesian components of a vector | 381 |
| | A.2.4 Vector products | 382 |
| A.3 | Scalar and Vector Fields | 384 |
| A.4 | Vector Calculus | 384 |
| | A.4.1 Differentiation of fields | 385 |
| | A.4.2 The gradient | 386 |
| | A.4.3 Volume integrals of scalar fields | 387 |
| | A.4.4 Line integrals | 388 |
| A.5 | Determinants | 389 |
| | A.5.1 Properties of determinants | 390 |
| A.6 | Matrices | 391 |
| | A.6.1 The transpose of a matrix | 391 |
| | A.6.2 The trace of a square matrix | 392 |
| | A.6.3 Algebra of matrices | 392 |
| | A.6.4 The inverse matrix | 393 |
| | A.6.5 Matrix eigenvalues and eigenvectors | 393 |
| A.7 | Angular Momentum | 394 |
| A.8 | Linear Operators | 396 |
| A.9 | Angular Momentum Operators | 399 |
| | References | 403 |
| | Index | 407 |

1 Introduction

1.1 Chemical Drawing

A vast number of organic molecules are known. In order to distinguish one from another, chemists give them names. There are two kinds of names: *trivial* and *systematic*. Trivial names are often brand names (such as aspirin, and the amino acid phenylalanine shown in Figure 1.1). Trivial names don't give any real clue as to the structure of a molecule, unless you are the recipient of divine inspiration. The IUPAC systematic name for phenylalanine is 2-amino-3-phenyl-propionic acid. Any professional scientist with a training in chemistry would be able to translate the systematic name into Figure 1.1 or write down the systematic name, given Figure 1.1. When chemists meet to talk about their work, they draw structures. If I wanted to discuss the structure and reactivity of phenylalanine with you over a cup of coffee, I would draw a sketch, such as those shown in Figure 1.1, on a piece of paper. There are various conventions that we can follow when drawing chemical structures, but the conventions are well understood amongst professionals. First of all, I haven't shown the hydrogen atoms attached to the benzene ring (or indeed the carbon atoms within), and I have taken for granted that you understand that the normal valence of carbon is four. Everyone understands that hydrogens are present, and so we needn't clutter up an already complicated drawing.

The right-hand sketch is completely equivalent to the left-hand one; it's just that I have been less explicit with the CH₂ and the CH groups. Again, everyone knows what the symbols mean.

I have drawn the benzene ring as alternate single and double bonds, yet we understand that the C—C bonds in benzene are all the same. This may not be the case in the molecule shown; some of the bonds may well have more double bond character than others and so have different lengths, but once again it is a well-understood convention. Sometimes a benzene ring is given its own symbol Ph or ϕ . Then again, I have drawn the NH₂ and the OH groups as 'composites' rather than showing the individual O—H and N—H bonds, and so on. I have followed to some extent the convention that all atoms are carbon atoms unless otherwise stated.

Much of this is personal preference, but the important point is that no one with a professional qualification in chemistry would mistake my drawing for another molecule. Equally, given the systematic name, no one could possibly write down an incorrect molecule.