

# Contents

<b>1</b>	<b>An Outline of What Computational Chemistry Is All About</b>	1
1.1	What You Can Do with Computational Chemistry	1
1.2	The Tools of Computational Chemistry	2
1.3	Putting It All Together	3
1.4	The Philosophy of Computational Chemistry	4
1.5	Summary	5
	References	5
	Easier Questions	6
	Harder Questions	7
<b>2</b>	<b>The Concept of the Potential Energy Surface</b>	9
2.1	Perspective	9
2.2	Stationary Points	13
2.3	The Born–Oppenheimer Approximation	21
2.4	Geometry Optimization	23
2.5	Stationary Points and Normal-Mode Vibrations – Zero Point Energy	30
2.6	Symmetry	36
2.7	Summary	39
	References	40
	Easier Questions	42
	Harder Questions	42
<b>3</b>	<b>Molecular Mechanics</b>	45
3.1	Perspective	45
3.2	The Basic Principles of Molecular Mechanics	48
3.2.1	Developing a Forcefield	48
3.2.2	Parameterizing a Forcefield	53
3.2.3	A Calculation Using Our Forcefield	57

3.3	Examples of the Use of Molecular Mechanics .....	60
3.3.1	To Obtain Reasonable Input Geometries for Lengthier (Ab Initio, Semiempirical or Density Functional) Kinds of Calculations .....	61
3.3.2	To Obtain Good Geometries (and Perhaps Energies) for Small- to Medium-Sized Molecules .....	64
3.3.3	To Calculate the Geometries and Energies of Very Large Molecules, Usually Polymeric Biomolecules (Proteins and Nucleic Acids).....	65
3.3.4	To Generate the Potential Energy Function Under Which Molecules Move, for Molecular Dynamics or Monte Carlo Calculations .....	65
3.3.5	As a (Usually Quick) Guide to the Feasibility of, or Likely Outcome of, Reactions in Organic Synthesis.....	66
3.4	Geometries Calculated by MM .....	67
3.5	Frequencies and Vibrational Spectra Calculated by MM .....	72
3.6	Strengths and Weaknesses of Molecular Mechanics .....	73
3.6.1	Strengths.....	73
3.6.2	Weaknesses.....	74
3.7	Summary .....	78
	References.....	79
	Easier Questions .....	82
	Harder Questions.....	82
<b>4</b>	<b>Introduction to Quantum Mechanics in Computational Chemistry ....</b>	<b>85</b>
4.1	Perspective .....	85
4.2	The Development of Quantum Mechanics. The Schrödinger Equation .....	87
4.2.1	The Origins of Quantum Theory: Blackbody Radiation and the Photoelectric Effect.....	87
4.2.2	Radioactivity .....	91
4.2.3	Relativity .....	91
4.2.4	The Nuclear Atom.....	92
4.2.5	The Bohr Atom.....	94
4.2.6	The Wave Mechanical Atom and the Schrödinger Equation.....	96
4.3	The Application of the Schrödinger Equation to Chemistry by Hückel.....	102
4.3.1	Introduction.....	102
4.3.2	Hybridization .....	103
4.3.3	Matrices and Determinants.....	108
4.3.4	The Simple Hückel Method – Theory .....	118
4.3.5	The Simple Hückel Method – Applications .....	133
4.3.6	Strengths and Weaknesses of the Simple Hückel Method.....	144

4.3.7 The Determinant Method of Calculating the Hückel $c$ 's and Energy Levels.....	146
4.4 The Extended Hückel Method .....	152
4.4.1 Theory .....	152
4.4.2 An Illustration of the EHM: the Protonated Helium Molecule..	160
4.4.3 The Extended Hückel Method – Applications .....	163
4.4.4 Strengths and Weaknesses of the Extended Hückel Method ....	164
4.5 Summary .....	165
References.....	168
Easier Questions .....	172
Harder Questions.....	172
<b>5 Ab initio Calculations .....</b>	<b>175</b>
5.1 Perspective .....	175
5.2 The Basic Principles of the Ab initio Method .....	176
5.2.1 Preliminaries.....	176
5.2.2 The Hartree SCF Method .....	177
5.2.3 The Hartree–Fock Equations.....	181
5.3 Basis Sets .....	232
5.3.1 Introduction.....	232
5.3.2 Gaussian Functions; Basis Set Preliminaries; Direct SCF.....	233
5.3.3 Types of Basis Sets and Their Uses.....	238
5.4 Post-Hartree–Fock Calculations: Electron Correlation .....	255
5.4.1 Electron Correlation.....	255
5.4.2 The Møller–Plesset Approach to Electron Correlation .....	261
5.4.3 The Configuration Interaction Approach To Electron Correlation – The Coupled Cluster Method .....	269
5.5 Applications of the Ab initio Method.....	281
5.5.1 Geometries .....	281
5.5.2 Energies .....	291
5.5.3 Frequencies and Vibrational Spectra.....	332
5.5.4 Properties Arising from Electron Distribution: Dipole Moments, Charges, Bond Orders, Electrostatic Potentials, Atoms-in-Molecules (AIM) .....	337
5.5.5 Miscellaneous Properties – UV and NMR Spectra, Ionization Energies, and Electron Affinities.....	359
5.5.6 Visualization.....	364
5.6 Strengths and Weaknesses of Ab initio Calculations.....	372
5.6.1 Strengths.....	372
5.6.2 Weaknesses.....	372
5.7 Summary .....	373
References.....	373
Easier Questions .....	388
Harder Questions.....	389

<b>6</b>	<b>Semiempirical Calculations</b>	391
6.1	Perspective	391
6.2	The Basic Principles of SCF Semiempirical Methods	393
6.2.1	Preliminaries	393
6.2.2	The Pariser-Parr-Pople (PPP) Method	396
6.2.3	The Complete Neglect of Differential Overlap (CNDO) Method	398
6.2.4	The Intermediate Neglect of Differential Overlap (INDO) Method	399
6.2.5	The Neglect of Diatomic Differential Overlap (NDDO) Methods	400
6.3	Applications of Semiempirical Methods	412
6.3.1	Geometries	412
6.3.2	Energies	419
6.3.3	Frequencies and Vibrational Spectra	423
6.3.4	Properties Arising from Electron Distribution: Dipole Moments, Charges, Bond Orders	426
6.3.5	Miscellaneous Properties – UV Spectra, Ionization Energies, and Electron Affinities	431
6.3.6	Visualization	434
6.3.7	Some General Remarks	435
6.4	Strengths and Weaknesses of Semiempirical Methods	436
6.4.1	Strengths	436
6.4.2	Weaknesses	436
6.5	Summary	437
	References	438
	Easier Questions	443
	Harder Questions	443
<b>7</b>	<b>Density Functional Calculations</b>	445
7.1	Perspective	445
7.2	The Basic Principles of Density Functional Theory	447
7.2.1	Preliminaries	447
7.2.2	Forerunners to Current DFT Methods	448
7.2.3	Current DFT Methods: The Kohn–Sham Approach	449
7.3	Applications of Density Functional Theory	467
7.3.1	Geometries	468
7.3.2	Energies	477
7.3.3	Frequencies and Vibrational Spectra	484
7.3.4	Properties Arising from Electron Distribution – Dipole Moments, Charges, Bond Orders, Atoms-in-Molecules	487
7.3.5	Miscellaneous Properties – UV and NMR Spectra, Ionization Energies and Electron Affinities, Electronegativity, Hardness, Softness and the Fukui Function	491
7.3.6	Visualization	509

7.4 Strengths and Weaknesses of DFT.....	509
7.4.1 Strengths.....	509
7.4.2 Weaknesses.....	510
7.5 Summary .....	510
References.....	512
Easier Questions .....	518
Harder Questions.....	518
<b>8 Some “Special” Topics: Solvation, Singlet Diradicals, A Note on Heavy Atoms and Transition Metals .....</b>	<b>521</b>
8.1 Solvation.....	521
8.1.1 Perspective .....	522
8.1.2 Ways of Treating Solvation .....	522
8.2 Singlet Diradicals.....	535
8.2.1 Perspective .....	535
8.2.2 Problems with Singlet Diradicals and Model Chemistries .....	535
8.2.3 (1) Singlet Diradicals: Beyond Model Chemistries. (2) Complete Active Space Calculations (CAS).....	537
8.3 A Note on Heavy Atoms and Transition Metals.....	547
8.3.1 Perspective .....	547
8.3.2 Heavy Atoms and Relativistic Corrections .....	548
8.3.3 Some Heavy Atom Calculations .....	549
8.3.4 Transition Metals.....	550
8.4 Summary .....	552
References.....	553
Solvation .....	558
Easier Questions .....	558
Harder Questions .....	558
Singlet Diradicals .....	558
Easier Questions .....	558
Harder Questions .....	559
Heavy Atoms and Transition Metals .....	559
Easier Questions .....	559
Harder Questions .....	560
<b>9 Selected Literature Highlights, Books, Websites, Software and Hardware .....</b>	<b>561</b>
9.1 From the Literature.....	561
9.1.1 Molecules.....	561
9.1.2 Mechanisms .....	566
9.1.3 Concepts.....	568
9.2 To the Literature.....	572
9.2.1 Books .....	572
9.2.2 Websites for Computational Chemistry in General.....	576

- 9.3 Software and Hardware ..... 577
  - 9.3.1 Software ..... 577
  - 9.3.2 Hardware ..... 581
  - 9.3.3 Postscript ..... 582
- References..... 582
  
- Answers** ..... 585
  
- Index** ..... 655



<http://www.springer.com/978-90-481-3860-9>

Computational Chemistry

Introduction to the Theory and Applications of Molecular and  
Quantum Mechanics

Lewars, E.G.

2011, XVI, 664 p., Hardcover

ISBN: 978-90-481-3860-9