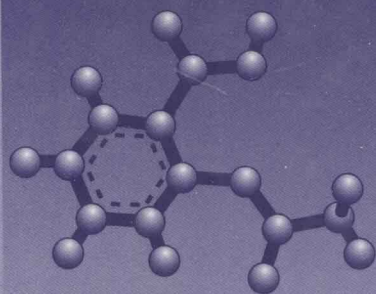


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Chemical *Modelling* APPLICATIONS AND THEORY

Volume 2

senior reporter A. HINCHLIFFE

A Specialist Periodical Report

Chemical Modelling

Applications and Theory

Volume 2

A Review of the Literature Published between
June 1999 and May 2001

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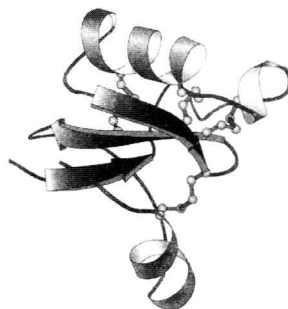
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ROYAL SOCIETY OF CHEMISTRY *Investing in Chemical Science*

Preface

I laid the foundations for this Series in Volume 1.

The ground rules are very simple: colleagues reporting on new topics are asked to give the rest of us an easily understandable historical perspective together with their own critical comments on the literature for the period under review. Colleagues reporting on continuing topics are simply expected to give a critical review of the literature for the period. The period under consideration for this volume is June 1999 to May 2001, and subsequent volumes will give biennial coverage of the literature to May 2003 + n , where $n = 0, 2, 4, 6, \dots$

Note my repeated use of the word ‘critical’. When the RSC and I market researched this new SPR title, it quickly became apparent that colleagues were not interested in a dull and uncritical compilation of literature references. Several of them remarked (rather unkindly, I thought) that they could ask their PhD students to sit at a networked PC, dial up Web of Science, and produce such a comprehensive list by the end of a single afternoon. What they wanted was critical insight into the recent literature.

That is what we are trying to give. There are still many gaps in coverage, and I’m sure you will have your own ideas as to what is good and bad with this very new title. Rather than grumbling to your colleagues and writing acidic book reviews, why not volunteer your own expertise? I am always willing to listen to constructive suggestions, and can be reached at

alan.Hinchliffe@umist.ac.uk

Volume 2 consists of eight contributions. Several are continuations from the topics treated in Volume 1, some are new. A couple of existing Reporters in Volume 1 asked to be excused for Volume 2, but will reappear in Volume 3. The contributions are not in any particular order, other than the ‘new’ topics are towards the start of the volume.

The molecular simulation of liquids is now a vast field of human endeavour, and we open with a contribution on ‘Simulation of the Liquid State’ by David Heyes. David captures the spirit of the SPR exactly when he writes ‘...The ready availability of fast computers has meant that there are many more researchers working in this ever expanding field ...[and] ...I have restricted my discussion to ... areas that have interested me’.

Several people pointed out a gap in the coverage of Volume 1, namely the field of enumeration. Nenad Trinajstić and his co-workers have written our first chapter

in this field, which strikes a nice balance between historical perspective and up-to-the-minute literature.

Michael Springborg continues to report on the growth of density functional theory.

Theodore Simos reported on the current status of atomic structure calculations in Volume 1. He has broadened the scope a little for Volume 2, and reports on progress in the solution of 1D, 2D and 3D differential equations in chemistry.

It was always my intention to include industrial applications. Much of this kind of work never reaches the primary journals because of confidentiality restrictions and commercial forces. I am very pleased to tell you that Richard Lewis has been able to give us a fascinating glimpse into the world of commercial computer-aided drug design, without apparently breaching a single one of his employer's trade secrets.

David Pugh continues his coverage of electric and magnetic properties. David also gives us a historical insight into those rare beasts magnetizability and hypermagnetizability.

Steven Wilson continues his coverage of many body perturbation theory, whilst Paul Popelier and Paul Smith continue the story of recent advances in the theory of quantum topological atoms.

Alan Hinchliffe
Manchester, 2001

Contents

Chapter 1 Simulation of the Liquid State	1
<i>By D.M. Heyes</i>	
1 Introduction	1
2 Simple Liquids	2
2.1 Dynamics	2
2.2 Thermodynamics	8
2.3 Mixtures	10
3 Water and its Solutions	11
3.1 Pure Water	11
3.2 Aqueous Solutions	15
4 Organic Liquids	16
4.1 Alkanes	16
4.2 Oxygen Containing Molecules	19
5 Non-equilibrium Molecular Dynamics (NEMD)	19
6 Glasses	24
6.1 Phenomenology	24
6.2 Structural Models for Supercooled Liquids	26
6.3 Ageing	32
6.4 Rheology	34
6.5 Glasses in Confined Geometries	35
7 Liquid Surfaces	36
7.1 Liquid–Vapour Interfaces	36
7.2 Liquid–Liquid Interfaces	39
7.3 Liquid–Solid Interfaces	40
7.4 Tribology	41
7.5 Two-dimensional Liquids	42
7.6 Droplets	42
8 Dissipative Particle Dynamics	43
9 Computational Techniques	45
9.1 Introduction	45
9.2 Periodic Boundary Conditions	45
9.3 Long-range Coulomb Forces	46
9.4 Integrators and Thermostatting	48

9.5	Ergodicity and Sampling of Rare Events	49
	References	50
Chapter 2	Enumeration in Chemistry	56
	<i>By D.J. Klein, D. Babić and N. Trinajstić</i>	
1	Introduction and Historical Review	56
1.1	Early History: Isomer Enumeration	56
1.2	Further Enumerations	57
1.3	Why Enumerate?	59
2	Enumeration Methods	60
2.1	Enumeration under Group Equivalences	61
2.2	Linear Recursive Methods – Kekule Structure Counting	64
2.3	Transfer Matrix Methods	67
2.4	Exhaustive Generation (Brute Force) Methods	70
2.5	Other Methods	71
3	Current Results	73
3.1	Isomers: Enumeration and Generation	73
3.2	Fullerenes and Related Objects	81
3.3	Counts of Resonance Structures and Related Items	84
3.4	Walks, Connected Subgraphs and Vertices at a Given Distance	85
3.5	Other Enumerations	86
4	Conclusion	88
	References	88
Chapter 3	Density Functional Theory	96
	<i>By Michael Springborg</i>	
1	Introduction	96
2	Basic Principles	98
3	Functionals	101
4	Semi-empirical Methods	103
5	Order- N Methods	111
6	Heterogeneous Catalysis	119
7	Descriptions of Chemical Reactions	127
8	Quantum Treatment of Other Particles	135
9	Problems with $1/r$ Potentials	140
10	Exact-exchange Methods	142
11	Time-dependent Density-functional Theory	148
12	Polarizability and Hyperpolarizability	158
13	Conclusions	164
	Acknowledgements	166
	References	166
Chapter 4	Numerical Methods for the Solution of 1D, 2D, and 3D Differential Equations Arising in Chemical Problems	170
	<i>By T.E. Simos</i>	
1	Introduction	170

2	Adapted, Exponentially Fitted and Trigonometrically Fitted Symplectic Integrators	171
2.1	Case $m = 0$	173
2.2	Case $m = 1$	173
2.3	Runge–Kutta–Nyström Method with FSAL Property	174
2.4	Trigonometrically Fitted Symplectic Intergrators	175
2.5	Exponentially Fitted Symplectic Intergrators	177
2.6	Exponentially Fitted and Trigonometrically Fitted Symplectic Linear Symmetric Multistep Methods	178
2.6.1	First Family of Methods – Case $t_0 = -2$	178
2.6.2	Second Family of Methods – Case $t_0 \neq -2$	188
2.6.3	Stability Analysis	194
2.7	Numerical Examples	196
2.7.1	Inhomogeneous Equation	196
2.7.2	Duffin's Equation	199
2.7.3	An Orbit Problem Studied by Stiefel and Bettis	201
3	Dissipative Methods	204
3.1	Phase-lag of Non-symmetric (Dissipative) Two-step Methods	206
3.2	Dissipative Methods Developed in the Literature	207
3.3	Generator of Dissipative Numerov-type Methods	215
3.4	Exponentially Fitted Dissipative Numerov-type Methods	216
3.4.1	New Exponentially Fitted Dissipative Two-step Method. Case I	219
3.4.2	New Trigonometrically Fitted Dissipative Two-step Method. Case I	220
3.4.3	New Exponentially Fitted Dissipative Two-step Method. Case II	221
3.4.4	New Trigonometrically Fitted Dissipative Two-step Method. Case II	222
4	Numerical Illustrations for Linear Multistep Methods and Dissipative Methods	224
4.1	Resonance Problem	224
4.1.1	The Woods–Saxon Potential	225
4.1.2	Modified Woods–Saxon Potential	228
4.2	The Bound-states Problem	230
4.3	Remarks and Conclusions	231
5	New Developments on Numerical Methods with Constant Coefficients and on the Methods with Coefficients Dependent on the Frequency of the Problem	231
5.1	Methods with Constant Coefficients (Generators of Numerical Methods)	231
5.2	Methods with Coefficients Dependent on the Frequency of the Problem	238
5.2.1	Exponentially Fitted Hybrid Methods	238
5.2.2	Bessel-fitted and Neumann-fitted Methods	240

5.3	Runge–Kutta Exponentially Fitted Methods	243
5.4	Modified Runge–Kutta Phase-fitted Methods	245
5.5	Modified Runge–Kutta–Nyström Phase-fitted Methods	246
6	Numerical Illustration on Variable-step Methods	247
6.1	Coupled Differential Equations	247
7	General Comments	249
	Appendix A	251
	Appendix B	262
	Appendix C	266
	References	268
Chapter 5	Computer-aided Drug Design 2000–2001	271
	<i>By Richard A. Lewis</i>	
1	Introduction	271
2	3D-QSAR	271
3	Pharmacophores	274
4	Library Design	275
5	ADME/Tox	278
6	Docking and Scoring	280
7	Cheminformatics	284
8	Structure-based Drug Design	285
9	Reviews	287
10	Conclusions	288
	References	288
Chapter 6	Electric Multipoles, Polarizabilities, Hyperpolarizabilities and Analogous Magnetic Properties	294
	<i>By David Pugh</i>	
1	Introduction	294
2	Response of Closed Shell Molecules to Magnetic Fields	294
2.1	Magnetic Susceptibility	295
2.2	Nuclear Shielding	296
2.3	Interaction of Molecules with Electromagnetic Fields: Higher Order Terms	297
2.4	Gauge Invariance	298
2.4.1	Change of Origin	299
2.4.2	Gauge Invariant Atomic Orbitals (London Atomic Orbitals) (GIAOs or LAOs)	299
2.4.3	Other Approaches to Gauge Invariance	301
2.5	<i>Ab initio</i> Calculations of Magnetic Response to 1999	301
2.6	Current Density Functional Theory (CDFT)	302
3	Review of Literature on Response of Molecules to Magnetic Fields: June 1999–May 2001	303
3.1	<i>Ab initio</i> Calculations	303
3.2	Density Functional Calculations	304

4	Review of Literature on Response of Molecules to Electric Fields: June 1999–May 2001	305
4.1	New Schemes for Calculation and Analysis of Properties	305
4.2	<i>Ab initio</i> Calculations on Atoms	307
4.3	<i>Ab initio</i> and DFT Calculations on Diatomic Molecules	307
4.4	<i>Ab initio</i> and DFT Calculations on Small and Medium-sized Molecules	308
4.4.1	Water	308
4.4.2	O ₃ , SO ₂ , SeO ₂ and TeO ₂	309
4.4.3	Other Molecules	309
4.5	Semi-empirical Calculations on Molecules	312
4.6	Vibrational Effects	315
4.7	Calculations on Complexes, Dimers, Clusters and Excited States	317
4.8	Fullerenes	318
4.9	Polymers	319
4.10	Crystals	320
	References	321

Chapter 7 Many-body Perturbation Theory and Its Application to the Molecular Electronic Structure Problem 329

By S. Wilson

1	Introduction	329
2	Many-body Perturbation Theory through Second Order	331
2.1	Rayleigh–Schrödinger Perturbation Theory through Second Order	332
2.2	Møller–Plesset Perturbation Theory	337
2.3	Partitioning and the Remainder Term	344
2.4	The Choice of Zero-order Hamiltonian	349
2.5	Scaling of the Zero-order Hamiltonian	350
2.6	Multireference Second-order Many-body Perturbation Theory, Intruder States and Brillouin–Wigner Perturbation Theory through Second Order	354
3	Some Applications of Second-order Many-body Perturbation Theory with a Møller–Plesset Reference Hamiltonian	360
3.1	Publications with the String ‘ <i>MP2</i> ’ in Their Title	361
3.2	Publications with the String ‘ <i>MP2</i> ’ in Their Title and/or Keywords	364
3.2.1	Journal of Chemical Physics	365
3.2.2	Chemical Physics Letters	367
3.2.3	Journal of Physical Chemistry A	370
3.2.4	Journal of Physical Chemistry B	376
4	Summary and Prospects	377

Acknowledgements	378
References	378
Chapter 8 Quantum Topological Atoms	391
<i>By P.L.A. Popelier and P.J. Smith</i>	
1 Introduction	391
2 Theoretical	398
2.1 Alternative Partitioning	398
2.2 Electron Correlation	399
2.3 Algorithms and Software	400
2.4 Transferability	400
2.5 Pseudopotential	401
2.6 Intermolecular Interaction	401
2.7 Transfer Probability	402
2.8 Entropy	402
2.9 General Extensions	402
2.10 Quantum Monte Carlo	403
2.11 Magnetic Coupling	403
3 Chemical Bonding	403
3.1 Theory	403
3.2 Heavy Atom Group Elements	404
3.3 Surface Science	406
3.4 Fluorides	407
3.5 Transition Metals	407
3.6 van de Waals	410
3.7 Agostic	411
3.8 Radicals	411
3.9 Alkali and Alkaline Earth Oxides and Halides	412
3.10 Organic	412
3.11 Aromaticity	414
3.12 Minerals	415
3.13 Populations	415
3.14 Bond and Valence Indices	416
3.15 Solid State	416
3.16 Organometallics	417
3.17 Chemical Shift	417
3.18 Biological	417
3.19 Noble Gases	418
3.20 Zeolites	418
3.21 Hypervalency	418
3.22 Polymers	419
4 X-Ray Diffraction	419
4.1 Organic Compounds	419
4.2 Minerals	419
4.3 Metals	420
4.4 Hydrogen Bonding	420

4.5	Comparison between Theory and Experiment	420
4.6	Transition Metals	422
4.7	Biological	422
5	Laplacian of the Electron Density	423
5.1	Surface Science	423
5.2	Theory: Electron Pair Localization	423
5.3	Transition Metals	424
5.4	Heavy Metal Group	424
5.5	Non-linear Optics	424
6	Hydrogen Bonding	425
6.1	Reviews	425
6.2	Dihydrogen Bond	425
6.3	Groups 13/15	425
6.4	C–H...X	426
6.5	Organic	426
6.6	Cooperative Effect	427
6.7	Blue-shifted	427
6.8	Biochemical	427
6.9	With Ions	427
6.10	Isotope Effects	428
6.11	Low Barrier	428
6.12	Intramolecular	428
6.13	π -Systems	429
6.14	Kinetic Energy Density	429
6.15	Organometallic	429
7	Topology of Other Functions	430
7.1	ELF	430
7.2	Electrostatic Potential	432
7.3	Intracule–Extracule	432
8	Reactions	433
8.1	Organic	433
8.2	Inorganic	436
8.3	Transition Metals	436
8.4	Mass Spectrometry	437
8.5	Rotation Barrier	437
8.6	Biological	437
9	Ionic Materials	437
9.1	Thermodynamics	437
9.2	Phase Change	437
9.3	Impurity/Doping	438
10	Spectroscopy	438
11	Opinions and Plans	438
12	Conclusion	439
13	Disclaimer	439
	References	440

Simulation of the Liquid State

BY D.M. HEYES

1 Introduction

The molecular simulation of liquids is a now vast field of research, and as with many others in recent years it is becoming increasingly difficult to keep abreast of all of the significant developments that are taking place. The ready availability of fast computers has meant that there are many more researchers working in this ever expanding field of applications, producing ever larger amounts of work to assimilate! This poses something of a problem when it comes to writing a review, especially one with the rather ambitious title of ‘Computer Simulation of Liquids’. I am not going to attempt to cover all the branches of this field. Rather, in my review of the developments between 1999 and 2001 I have restricted my discussion to a few areas that have interested me. The choice is inevitably somewhat subjective, but hopefully by adopting this approach I will have a better chance of producing a useful document, rather than a gallop through many topics with only the briefest of discussion about each, which I am sure would be of little use to the scientific community. There are a number of molecular simulation books that describe the standard techniques, and these are recommended as background material for the present article, *e.g.* refs. 1–7.

I am therefore not going to discuss the ‘nuts and bolts’ of molecular simulation, except to mention an often overlooked fact, which is the reason for much of the success of these approaches. Most simulations are carried out still typically for less than a thousand molecules, and if it was not for the use of periodic boundary conditions (PBC) it would not be possible to simulate bulk systems with this number of molecules. These systems would have such a high surface to volume ratio that the results would be dominated by surface effects. The PBC procedure is illustrated in Figure 1, which shows a two-dimensional square cell in which the molecules are surrounded by image cells. A molecule near the cell boundary interacts with the ‘real’ molecules in the central cell and with image cell molecules. Molecules leaving the cell re-enter through the opposite face with the same velocity.

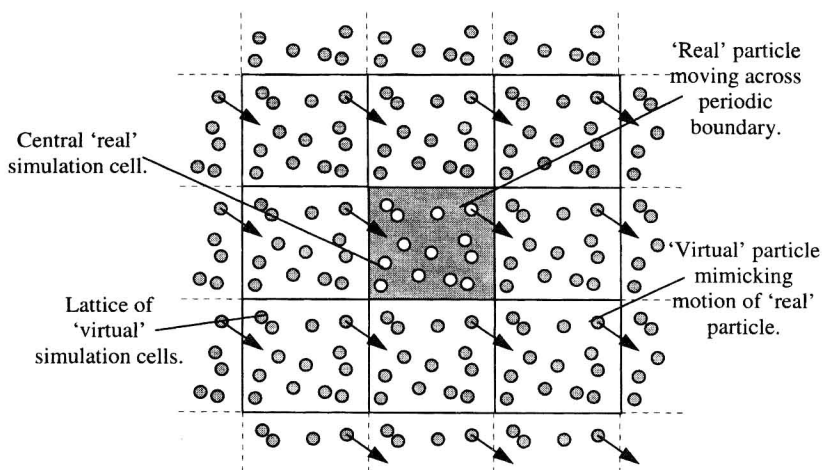


Figure 1 *Schematic representation of the Periodic Boundaries construction in two dimensions. A particle from the central cell moves across a boundary (defined by the arrow) and is replaced by an image of itself. The image then becomes a 'real' particle and the simulation continues uninterrupted*
(Courtesy of Dr. C.A. Bearehell, Department of Chemistry, University of Surrey)

2 Simple Liquids

The study of simple liquids can be said to be the beginning of Molecular Dynamics and Monte Carlo in the 1950s and 60s. Although the scope of molecular simulation, as a field or discipline, has widened dramatically since then, there is nevertheless a continual interest in simple liquids. In fact, this is partly due to the fact that the so-called 'simple' liquids are far from simple! One of the motivations for the continual interest in the simple liquids is that, because of the basic nature of the interparticle interactions, an improved understanding of these systems should lead to better theoretical models, which can be extended to more complex molecular liquids. Also, the rapid growth of interest in colloids and polymers (so-called 'complex' liquids) in recent years has provided new areas where the theories of simple liquids can be applied, especially those associated with local structure and thermodynamics. In the latter case, phase equilibria and the location of phase boundaries feature prominently. In this section, some of the recent advances in our understanding of simple liquids are covered.

2.1 Dynamics. – Of course, within the category of 'simple liquids' studied by statistical mechanics and molecular simulation, there are model liquids that are, strictly speaking, not found in nature. For example, the ubiquitous hard sphere fluid, where the pair potential has the form

$$\begin{aligned}\phi(r) &= \infty, & r &\leq \sigma \\ &= 0, & r &> \sigma\end{aligned}\quad (2.1)$$

is a case in point. The energy is infinite on contact of the spheres (at σ) and zero for larger separations. This is the energy of interaction which would approximate that of two macroscopically sized elastic spheres with high elastic modulus, say two snooker or billiard balls. In these cases the length-scale of the particle interactions is many orders of magnitude smaller than the particle diameter. One of the main features of hard spheres is the co-ordination number. It has been shown recently that for spheres at random close packing, the mean number of particle contacts is 4.8, which is somewhat lower than has often been assumed before (6, and even 12, have been used).⁸ Interestingly these authors also performed a computer ‘simulation’ in which they took a random test sphere, and placed immobile point contacts on its surface. They determined the mean number of points required on the surface of the sphere to eradicate the possibility of translation of the test particle, which was found to be $2D + 1$, where D is the space dimension. Therefore, in 3D this ‘co-ordination number’ is 7, which is lower than the value of 4.8, indicating that in states where the contacts are ‘correlated’ (*i.e.* in a dense liquid or glassy state) translational diffusion can be removed by fewer contacts. The procedure for carrying out Metropolis Monte Carlo of hard spheres is particularly simple, as the Boltzmann factor does not require specific evaluation – just overlap detection. Jater proposed an improved Metropolis Monte Carlo algorithm to simulate hard core systems, in which they replaced the usual sequence of single particle trial displacements by a collective trial ‘move’ of a chain of particles.⁹

The hard-sphere system is widely used in statistical mechanics as a reference state in theories of liquids and solids. Its uses have traditionally been quite broad, extending from equations of state, the structure of molecular liquids and dynamical properties. As mentioned already, it has also found a new lease of life as a model reference system for some colloids and granular materials. Simple molecules (*e.g.* water) interact with an appreciable attractive tail extending beyond the hard core, and which usually has more or less the same range as the core. It is not possible to find a simple molecule that does not have an appreciable attractive or van der Waals region as well as a hard repulsive core. In contrast, on the micron and larger scale, for these systems, the hard-sphere can be an even more realistic representation of the effective pair potential, which can be steeply repulsive and have a negligible attractive component. It must be borne in mind, however, that the hard-sphere particle potential is fundamentally unrealistic in that its pair potential is discontinuous and non-differentiable unlike those for *all* real systems. Considerable care is therefore required in extrapolating from any steeply repulsive potential, made progressively steeper, to the hard-sphere potential. This is because many quantities diverge either to zero or infinity according to the order in which the limit is made, of potential steepness and number of particles *etc.*, any of which factors may be significant. Non-physical results such as purely exponential and delta function time correlation functions may be generated. These