

Computational Quantum Mechanics

Dr M.I.J. Probert

Contents

1 Time Independent Schrödinger Equation	7
1.1 Revision of the Schrödinger equation	7
1.2 Revision of solving ordinary differential equations numerically	12
1.2.1 The Runge-Kutta method	13
1.2.2 The Numerov method	15
1.2.3 Singularities	16
1.2.4 Other methods of solution	16
1.2.5 Errors	17
1.3 Application to the Schrödinger equation	17
1.4 Final comments	18
1.5 Further reading	18
2 Scattering	19
2.1 Solving the Schrödinger equation for unbound states . .	19
2.2 The phase shift	21
2.3 Final comments	22
2.4 Further reading	23
3 Time Dependent Schrödinger Equation	25
3.1 Revision of solution of partial differential equations . .	25
3.1.1 Forward-Time Centred-Space algorithm	26
3.1.2 von Neumann stability analysis	27
3.1.3 Courant condition	28
3.1.4 Other errors	28
3.1.5 Higher order methods	29
3.1.6 Implicit schemes	29
3.2 Application to the Schrödinger equation	31
3.2.1 Constraints	32
3.3 Final comments	33
3.4 Further reading	33

4 The Variational Method	35
4.1 Introduction	35
4.2 The eigenvalue problem	35
4.2.1 Aside - a different view of the Schrödinger equation	36
4.3 Rayleigh-Ritz method	38
4.3.1 Simple Harmonic Oscillator example	38
4.4 Linear (Matrix) method	39
4.4.1 Incomplete basis sets	40
4.4.2 Efficiency	42
4.5 Final comments	43
5 Total Energies	45
5.1 Why study total energies?	45
5.1.1 Forces	46
5.1.2 Stresses	48
5.1.3 Charge Density	48
5.2 Applications	49
5.3 Final comments	49
5.4 Further reading	49
6 Basis Sets	51
6.1 Introduction	51
6.2 Revision of variational method	51
6.3 Atomic-style basis functions	52
6.3.1 Aside - Solving the generalized eigenvalue problem	55
6.4 Solid-style basis functions	56
6.4.1 Pseudo-potentials	56
6.4.2 Supercells	57
6.5 Final comments	58
6.6 Further reading	59
7 The Hartree-Fock Method	61
7.1 Introduction	61
7.2 Born-Oppenheimer approximation	62
7.3 Many-electron Hamiltonian	62
7.4 Independent particle approximation	63
7.5 Hartree method	63
7.6 Hartree-Fock method	64
7.7 Approximate Hartree-Fock	66
7.8 Improving the Hartree-Fock approach	67
7.9 Results	68
7.10 Final comments	69

CONTENTS	5
7.11 Further reading	69
8 Density Functional Theory	71
8.1 Introduction	71
8.2 A fundamental theorem	71
8.3 The search for a universal functional	72
8.4 The Exchange-Correlation functional	74
8.5 Solving the Kohn-Sham equations	75
8.5.1 Car-Parrinello approach	76
8.5.2 Conjugate-gradients approach	76
8.6 Alternatives to Kohn-Sham	77
8.7 Results	77
8.8 Final comments	79
8.9 Further reading	79
9 Quantum Monte Carlo Methods	81
9.1 Revision of numerical integration	82
9.1.1 Uniform quadrature	82
9.1.2 Gaussian quadrature	83
9.1.3 Higher dimensions	84
9.2 Monte Carlo integration	84
9.2.1 Revision of probability	84
9.2.2 Evaluating integrals	85
9.2.3 Boundary conditions	86
9.2.4 Importance sampling	86
9.3 Variational Monte Carlo	86
9.3.1 Evaluating the energy	86
9.3.2 Improving the wavefunction	88
9.4 Diffusion Monte Carlo	90
9.5 Results	92
9.6 Final comments	93
9.7 Further reading	94
A Overview	95
A.1 Direct methods of solving the Schrödinger equation	95
A.1.1 Numerical integration	95
A.1.2 Grid-based methods	96
A.1.3 Boundary conditions	96
A.2 Indirect methods of solving the Schrödinger equation	96
A.2.1 Variational principle	96
A.2.2 Many-Electron methods	97
A.2.3 Quantum Monte Carlo	97

