

# Appendix A

## Overview

### A.1 Direct methods of solving the Schrödinger equation

#### A.1.1 Numerical integration

We may choose to use a variety of standard or specialised techniques for solving the time-independent Schrödinger equation, considering it as an ordinary differential equation.

#### **Runge-Kutta method**

The advantage of this method is that it is a single-step method which has the advantage of being self-starting and of coping with discontinuities in the potential. It can also be simply used in a variable step-size manner, where the step-size is automatically adjusted to keep some measure of the numerical error in the solution within some prescribed limit. The disadvantage of this method is that it requires many function evaluations per step - the most commonly used fourth-order Runge-Kutta requires four function evaluations per step.

#### **Numerov method**

The advantage of this method is that it is of higher-order than the standard fourth-order Runge-Kutta method and yet only requires two function evaluations per step. The disadvantage of this method is that it is a multi-step method which means that it cannot be self-starting, and so another method has to be used for the first step. This also makes it much less stable when there are discontinuities in the potential.

### A.1.2 Grid-based methods

If we consider the time-dependent Schrödinger equation as an initial-value partial differential equation, then there are many standard techniques that at first sight appear applicable to its solution. However, an error analysis shows that many of these methods are unstable for the Schrödinger equation, and do not preserve the normalisation of the wavefunction.

#### Crank-Nicholson method

This is the method of choice for a direct solution of the time-dependent Schrödinger equation, as it is unconditionally stable and is also guaranteed to preserve the normalisation of the wavefunction.

### A.1.3 Boundary conditions

Most often, the boundary conditions are specified as initial-value conditions, in which case the above methods are best. However, boundary conditions can also be boundary-value type, in which case a different approach is required. In the finite-difference approach, we apply a spatial grid to the problem and replace differentials by lattice sums and iterate around all grid points to self-consistency. Various types of grid may be used giving rise to a hierarchy of methods.

## A.2 Indirect methods of solving the Schrödinger equation

### A.2.1 Variational principle

We can also exploit the eigenvalue properties of the Schrödinger equation to derive a variational principle, which can be used to derive the ground state wavefunction and energy without directly solving the equation.

#### Rayleigh-Ritz method

In this method, an analytic approximation to the wavefunction is derived from minimising the energy according to the variational principle. It can give good insight into the true behaviour of the system, but is limited by the quality of the guessed functional form.

#### Linear Variational method

This is a very powerful, general-purpose method that can be used to derive approximate energies and wavefunctions for much more complex systems without requiring a good initial guess.

### A.2.2 Many-Electron methods

Most methods of solving the many-electron problem rely on the variational principle rather than a direct solution approach. The three major approaches considered in this course were Hartree-Fock, Density Functional Theory and Quantum Monte Carlo method.

#### Hartree-Fock theory

This is a variational method based upon a wavefunction approach. It is assumed that the many-electron wavefunction can be written as a Slater determinant of single-electron functions, whereupon the Hartree-Fock equations can be derived. This method is capable of treating both ground state, and excited states if the theory is appropriately extended and multiple determinants containing excited single-electron states are included. Such extensions are very expensive. This method has the advantage of treating the electrons as fermions and has an exact treatment of the effects of exchanging electrons as required by the Pauli exclusion principle. However, any further effect of electron correlation is ignored except in the multi-determinant extensions.

#### Density Functional Theory

This is a variational method based upon a charge density approach. The charge density is a much simpler quantity than the many-electron wavefunction. As such, this method is capable of treating much larger systems than Hartree-Fock methods. However, whilst in principle an exact theory, in practice there is an unknown component to the equation which has to be approximated. This unknown term is known as the exchange-correlation potential, and the quality of the results is dependent upon the accuracy of the approximation used here. This approximation includes treating the effects of the Pauli principle and also dynamical electron correlation, and can sometimes perform significantly better than the Hartree-Fock method. However, there is no way of systematically improving this approximation, unlike the (considerably more computational expensive) Hartree-Fock extensions.

### A.2.3 Quantum Monte Carlo

The only computational technique that can accurately treat all the subtle features of electron correlation at the moment is Quantum Monte Carlo. This comes in various flavours, of which the two most popular are:

#### Variational Monte Carlo

In the variational Monte Carlo approach, an attempt is made to improve the single-particle wavefunction input (which must come from a previous

Hartree-Fock or Density Functional Theory calculation) by adding a Jastrow factor to incorporate the effects of electron correlation. This is the key difference between a single-particle and a many-body wavefunction. The variational technique is then used to optimise the coefficients of the Jastrow factor, and Monte Carlo integration is used to evaluate the many-dimensional integrals that result.

### **Diffusion Monte Carlo**

This takes a totally different viewpoint to the time-dependent Schrödinger equation. By writing it in imaginary time, it is transformed into a diffusion equation. This is then solved by randomly moving walkers around an energy landscape to build up a Monte Carlo sampling picture of the true wavefunction. However, electrons are fermions and so there is a problem with interpreting the sign change in wavefunction upon crossing a node. Therefore, the nodes of the wavefunction are fixed in space (they must come from a previous Hartree-Fock or Density Functional Theory or variational Monte Carlo calculation) and the rest of the wavefunction is allowed to evolve. In this way, a true many-body wavefunction is derived, with a full treatment of electron correlation. This improves upon the variational Monte Carlo calculation with its prescribed form for correlation and is the most accurate method for solving the Schrödinger equation. The only approximation left in this method is that the nodes of the input wavefunction are correct - hence the use of a variational Monte Carlo wavefunction as input.