

# 1 Introduction

## 1.1 THE SCHRÖDINGER EQUATION

We are concerned in this book with the non-empirical theory of the electronic structure of molecules. By a non-empirical (or *ab initio*) calculation in molecular quantum chemistry is normally meant the solution of a time-independent Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \quad (1.1)$$

in which the Hamiltonian  $\mathcal{H}$  is that appropriate to any model of the system which does not depend, either explicitly or implicitly, on the properties of any finite number of states of the system. In the simplest and most widely used model of a molecule, the nuclei and electrons are assumed to be non-relativistic point charges interacting through electrostatic (Coulomb) forces only, the force acting between charges  $q_1$  and  $q_2$  separated by distance  $r$  being  $q_1 q_2 / 4\pi\epsilon_0 r^2$ , where  $\epsilon_0$  is the permittivity of a vacuum.

Consider a molecule containing  $\nu$  nuclei, with charges  $Z_\alpha e$  and masses  $M_\alpha$  ( $\alpha = 1, 2, \dots, \nu$ ), and  $N$  electrons, with charges  $-e$  and masses  $m_e$ . Let the position of nucleus  $\alpha$  be given by the vector  $\mathbf{R}_\alpha$ , whose components are the coordinates of the nucleus in a fixed coordinate system, and let  $\mathbf{r}_i$  be the position vector of electron  $i$  ( $i = 1, 2, \dots, N$ ). The Hamiltonian for this system of point charges is

$$\begin{aligned} \mathcal{H} = & \sum_{\alpha=1}^{\nu} \frac{-\hbar^2}{8\pi^2 M_\alpha} \nabla_\alpha^2 + \sum_{i=1}^N \frac{-\hbar^2}{8\pi^2 m_e} \nabla_i^2 \\ & - \sum_{i=1}^N \sum_{\alpha=1}^{\nu} \frac{Z_\alpha e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_{i>j=1}^N \sum \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{\alpha>\beta=1}^{\nu} \sum \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 R_{\alpha\beta}} \end{aligned} \quad (1.2)$$

where  $\hbar$  is Planck's constant and, for example,  $r_{i\alpha} = |\mathbf{R}_\alpha - \mathbf{r}_i|$  is the distance between electron  $i$  and nucleus  $\alpha$ . The corresponding Schrödinger equation for this model has been found, through many applications, to form a satisfactory basis for the description of a very wide variety of properties of molecules, and we will be concerned in this book almost wholly with the methods that have been developed for its solution and with the interpretation of the solutions. Apart from a brief discussion

### Introduction

in §4.5 of the magnitudes of the relativistic corrections to the model, we will therefore consider as outside the scope of this book all time-dependent phenomena, the effects of external fields, as well as all magnetic interactions and other relativistic effects. Inclusion of these requires modification either of the Hamiltonian or of the form of the wave equation itself, although these modifications are often treated as perturbations on the model system (§1.5).

The Hamiltonian (1.2) contains terms which describe not only the motion of the electrons about the nuclei, but also the motion of the nuclei with respect to each other and of the molecule as a whole in space. The corresponding Schrödinger equation is very difficult to solve in general, and accurate solutions have been obtained only for the simplest molecules,  $\text{H}_2^+$  and  $\text{H}_2$  (Kolos and Wolniewicz 1964). The problem is simplified considerably however by including in the model further assumptions which result in the separation of the electronic and nuclear motions. These assumptions rely on the observation that the ratio  $m_e/M_\alpha$  of the electronic to nuclear masses is a small number compared with unity, and they are therefore consistent with our definition of a non-empirical theory. The nuclear and electronic motions may be separated exactly for a one-electron atom, and to a very good approximation for other atoms (Bethe and Salpeter 1957). The resulting Hamiltonian for the internal motion of an atom, whose nucleus has charge  $Ze$  and mass  $M$ , is

$$\mathcal{H} = \frac{-\hbar^2}{8\pi^2\mu} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i>j=1}^N \sum \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (1.3)$$

where  $\mu = m_e M / (m_e + M)$  is the reduced mass of an electron in the atom, and  $\mathbf{r}_i$  is the position vector of electron  $i$  relative to the nucleus as origin. The separation for molecules is of a somewhat different kind, the Hamiltonian for electronic motion being obtained by assuming that the nuclei have infinite masses and, therefore, have fixed positions relative to a fixed coordinate system. The Hamiltonian for the motion of the electrons in this ‘fixed-nuclei’ or Born–Oppenheimer approximation is

$$\mathcal{H} = \frac{-\hbar^2}{8\pi^2 m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{\alpha=1}^{\nu} \frac{Z_\alpha e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_{i>j=1}^N \sum \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{\alpha>\beta=1}^{\nu} \sum \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 R_{\alpha\beta}} \quad (1.4)$$

The solutions of the corresponding Schrödinger equation depend on the nuclear positions, and a separate calculation of any electronic state must

*The Schrödinger equation*

be performed for each assumed molecular geometry. The stable geometry (in the Born–Oppenheimer approximation) for any state is that with the lowest energy.

The eigenfunctions of the Hamiltonian, (1.3) for an atom and (1.4) for a molecule, describe the stationary electronic states of the system. They are functions of the coordinates of the electrons, and they can always be chosen to be normalized and orthogonal (orthonormal); if  $\Psi_m$  and  $\Psi_n$  are any two eigenfunctions,

$$\int \Psi_m^* \Psi_n \, d\tau = \begin{cases} 1 & \text{if } m = n, \text{ for normalization} \\ 0 & \text{if } m \neq n, \text{ for orthogonality} \end{cases}$$

where  $\Psi_m^*$  is the complex conjugate of  $\Psi_m$ , and  $\int \dots d\tau$  implies integration over all the coordinates of the electrons. An important property of the eigenfunctions is that they form a *complete set* of functions in the sense that any arbitrary wave function  $\Psi$ , which is not an eigenfunction of  $\mathcal{H}$  but which satisfies the same boundary conditions as the eigenfunctions, can be expressed as a linear combination of the eigenfunctions:

$$\Psi = \sum_n C_n \Psi_n$$

If the eigenfunctions are orthonormal, the coefficients are given by

$$C_n = \int \Psi_n^* \Psi \, d\tau$$

**1.2 ATOMIC UNITS**

The Schrödinger equation with Hamiltonian (1.4) for a Born–Oppenheimer molecule may be freed of the experimentally determined quantities  $e$ ,  $h$ ,  $\epsilon_0$  and  $m_e$  by the substitutions

$$\mathcal{H} = (m_e e^4 / 4h^2 \epsilon_0^2) \mathcal{H}', \quad E = (m_e e^4 / 4h^2 \epsilon_0^2) E'$$

and, for example,

$$r_{ij} = (\epsilon_0 h^2 / \pi m_e e^2) r'_{ij}$$

The conversion factors are often treated as units, atomic units (Shull and Hall 1959). They are the Bohr radius  $a_\infty$  (or  $a_0$ ) and the Hartree energy  $H_\infty$ :

$$\left. \begin{aligned} a_\infty &= \epsilon_0 h^2 / \pi m_e e^2 = 5.2918 \times 10^{-11} \text{ m} \\ H_\infty &= m_e e^4 / 4h^2 \epsilon_0^2 = e^2 / 4\pi \epsilon_0 a_\infty = 4.3598 \times 10^{-18} \text{ J} \end{aligned} \right\} \quad (1.5)$$

## Introduction

The resulting dimensionless Schrödinger equation and Hamiltonian are

$$\left. \begin{aligned} \mathcal{H}'\Psi' &= E'\Psi' \\ \mathcal{H}' &= -\frac{1}{2} \sum_{i=1}^N \nabla_i'^2 - \sum_{i=1}^N \sum_{\alpha=1}^v \frac{Z_\alpha}{r_{i\alpha}} + \sum_{i>j=1}^N \sum \frac{1}{r_{ij}} + \sum_{\alpha>\beta=1}^v \sum \frac{Z_\alpha Z_\beta}{R'_{\alpha\beta}} \end{aligned} \right\} \quad (1.6)$$

and the primes, which convert energies and lengths to numbers, are in practice omitted.

The use of the symbols  $a_\infty$  and  $H_\infty$  for the atomic units of length and energy requires a few words of explanation. The most commonly used symbol for the Bohr radius is  $a_0$ , but no generally accepted symbol exists for the Hartree energy, and many authors avoid the use of special symbols by denoting the atomic unit of every physical quantity by the abbreviation a.u. The symbols  $a_\infty$  and  $H_\infty$  proposed here have been chosen to be consistent with the SI-recommended symbol  $R_\infty$  for the Rydberg constant, which is related to the Hartree energy by  $H_\infty = 2hcR_\infty$ , where  $c$  is the speed of light. In the case of an atom whose Hamiltonian (1.3) involves the reduced mass  $\mu$  instead of the electronic mass  $m_e$ , the Schrödinger equation is reduced to the dimensionless form (1.6), not involving  $\mu$ , by the conversion factors obtained from  $a_\infty$  and  $H_\infty$  by replacing  $m_e$  by  $\mu$ . The new conversion factors can be distinguished from  $a_\infty$  and  $H_\infty$  by a change of subscript to specify the nature of the nucleus. Thus the Rydberg constant for the normal (<sup>1</sup>H) hydrogen atom is

$$R_{\text{H}} = R_\infty m_{\text{p}} / (m_{\text{p}} + m_{\text{e}})$$

where  $m_{\text{p}}$  is the mass of the proton, and the corresponding symbols for the length and energy are  $a_{\text{H}}$  and  $H_{\text{H}}$ . In general for any subscript X,

$$H_{\text{X}} = 2hcR_{\text{X}} \quad \text{and} \quad a_{\text{X}}H_{\text{X}} = e^2/4\pi\epsilon_0$$

In this book we shall ignore, for simplicity, the small difference in value between  $m_e$  and the reduced mass  $\mu$  of an electron in an atom; this corresponds to the Born–Oppenheimer assumption of infinite nuclear mass.

Any four of the five quantities  $m_e$ ,  $e$ ,  $\hbar = h/2\pi$ ,  $a_\infty$  and  $H_\infty$  may be regarded as base atomic units for the construction of the atomic units of all those other physical quantities which, in SI, involve only the units of length mass, time and electric current. A list of some of the more important quantities is given in table 1.1. Other quantities used as units in this book include the ångström  $\text{Å} = 10^{-10} \text{m} = 1.8897a_\infty$ ; the debye  $\text{D} = 3.3356 \times 10^{-30} \text{Cm}$ , which is related to the atomic unit of electric dipole moment by  $ea_\infty = 2.5418 \text{D}$ ; the electron volt

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Excerpt

[More information](#)*Atomic units*TABLE I.1 *Atomic units*

Physical quantity	Atomic unit	Value in SI units
Mass	$m_e$	$9.1096 \times 10^{-31}$ kg
Charge	$e$	$1.6022 \times 10^{-19}$ C
Angular momentum	$\hbar = h/2\pi$	$1.0546 \times 10^{-34}$ J s
Length	$a_\infty = 4\pi\epsilon_0\hbar^2/m_e e^2$	$5.2918 \times 10^{-11}$ m
Energy	$H_\infty = m_e e^4/16\pi^2\epsilon_0^2\hbar^2$	$4.3598 \times 10^{-18}$ J
Time	$\hbar/H_\infty$	$2.4189 \times 10^{-17}$ s
Linear momentum	$\hbar/a_\infty$	$1.9928 \times 10^{-24}$ kg m s <sup>-2</sup>
Electric current	$eH_\infty/\hbar$	$6.6237 \times 10^{-3}$ A
Electric potential	$H_\infty/e$	$2.7211 \times 10^1$ V
Electric dipole moment	$ea_\infty$	$8.4784 \times 10^{-30}$ C m
Electric charge density	$e/a_\infty^3$	$1.0812 \times 10^{12}$ C m <sup>-3</sup>

eV =  $1.6022 \times 10^{-19}$  J, with  $H_\infty = 27.211$  eV; and the molar energy  $LH_\infty = 2.6255 \times 10^6$  J mol<sup>-1</sup>, where  $L$  is the Avogadro constant.

**1.3 THE VARIATION PRINCIPLE**

In a non-empirical calculation one attempts to find eigenfunctions and eigenvalues of the 'exact' model Hamiltonian (1.6). Except for the simplest systems however, a complete solution of the Schrödinger equation is still an intractable problem, and it is therefore always necessary to resort to methods of finding approximate solutions. Almost all of these methods are based on the variation principle.

A simple expression of the variation principle is that, given any trial  $N$ -electron wave function  $\Psi'$  which satisfies the necessary boundary conditions for the system, an upper bound to the exact ground-state energy  $E_0$  is

$$E = \frac{\int \Psi'^* \mathcal{H} \Psi' d\tau}{\int \Psi'^* \Psi' d\tau} \geq E_0 \quad (1.7)$$

Analogous inequalities exist for excited states. A consequence of the principle is that if a trial wave function depends on a number of arbitrary parameters,  $\lambda_1, \lambda_2, \dots, \lambda_n$ ,

$$\Psi' = \Psi(\mathbf{r}; \lambda_1, \lambda_2, \dots, \lambda_n)$$

where  $\mathbf{r}$  represents the dependence of  $\Psi'$  on the coordinates of the electrons, then the values of these parameters can be chosen to give the lowest possible, and hence the most accurate, value of the energy. The energy is a

## Introduction

function of the parameters, and the values of the parameters which give the lowest value of the energy are obtained by solving the equations

$$\frac{\partial E}{\partial \lambda_i} = 0 \quad (i = 1, 2, \dots, n)$$

The most general type of approximate wave function commonly used has the form

$$\Psi = C_1 \Phi_1 + C_2 \Phi_2 + \dots + C_n \Phi_n = \sum_{j=1}^n C_j \Phi_j \quad (1.8)$$

where the coefficients  $C_j$  are parameters, and the  $\Phi_j$  are given  $N$ -electron functions which satisfy the same boundary conditions as  $\Psi$  and which may or may not depend on further parameters. The corresponding energy (1.7) is

$$E = \frac{\sum_{i,j=1}^n C_i^* C_j H_{ij}}{\sum_{i,j=1}^n C_i^* C_j S_{ij}} \quad (1.9)$$

where

$$H_{ij} = \int \Phi_i^* \mathcal{H} \Phi_j d\tau, \quad S_{ij} = \int \Phi_i^* \Phi_j d\tau \quad (1.10)$$

and the minimization of  $E$  with respect to the  $n$  coefficients gives a set of  $n$  'secular' equations

$$\sum_{j=1}^n (H_{ij} - ES_{ij}) C_j = 0 \quad (i = 1, 2, \dots, n) \quad (1.11)$$

One (trivial) solution of the equations is obtained by setting all the coefficients equal to zero. Non-trivial solutions are obtained only if the energy  $E$  is chosen such that the secular determinant, whose elements are  $(H_{ij} - ES_{ij})$ , vanishes:

$$\det(H_{ij} - ES_{ij}) = 0$$

or

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \quad (1.12)$$

The secular determinant is a polynomial of degree  $n$  in the energy, and it has  $n$  roots, not necessarily all different,

$$E_1 \leq E_2 \leq E_3 \leq \dots \leq E_n$$

Corresponding to each energy  $E_i$ , a wave function

$$\Psi_i = \sum_{j=1}^n \Phi_j C_{ji} \quad (1.13)$$

*The variation principle*

may now be obtained by solving the secular equations and normalization. The resulting wave functions are orthonormal:

$$\int \Psi_i^* \Psi_j d\tau = \sum_{k,l=1}^n C_{ki}^* C_{lj} S_{kl} = \delta_{ij} = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases}$$

The lowest root  $E_1$  is an approximate ground-state energy, and the corresponding function  $\Psi_1$  is an approximate wave function for the ground state. In fact, the set of  $n$  solutions are approximations for the first  $n$  states of the system. If  $E_i^{(e)}$  is the exact energy of the  $i$ th state, then  $E_i \geq E_i^{(e)}$  as shown in fig 1.1, and  $E_i = E_i^{(e)}$  only if  $\Psi_i$  is the exact wave function for the  $i$ th state. The magnitudes of the separations  $(E_i - E_i^{(e)})$  depend on the functions  $\Phi_j$  included in the wave function (1.8). If the functions depend on further parameters,

$$\Phi_j = \Phi_j(\mathbf{r}; \lambda_1, \lambda_2, \dots)$$

then the parameters can be chosen to minimize one of the roots  $E_i$  of the secular problem.

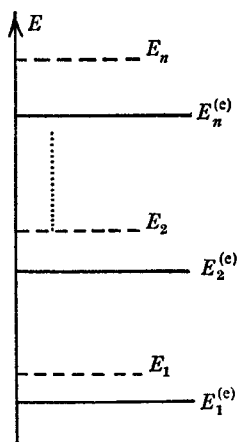


Fig. 1.1

It is generally true that increasing the number of variational parameters in a wave function results in improved accuracy of the corresponding energy. If the wave function has a general enough form, the exact solution is approached as the number of parameters is increased indefinitely. In particular, the 'method of linear combinations' outlined above provides better approximations to more and more states as the number  $n$  increases. In practice however the form of the wave function is often

## Introduction

constrained, and cannot lead to an exact solution of the Schrödinger equation. An example is the orbital approximation, discussed in some detail in chapter 3, in which the wave function and energy approach definite (Hartree–Fock) limiting values as the number of variational parameters increases, but these limits do not represent an exact solution of the Schrödinger equation. As we shall see, the wave function obtained in this way is an eigenfunction not of the Hamiltonian (1.6) but of a different Hamiltonian, the Hartree–Fock Hamiltonian. In this way a new model based on the *form* of the wave function is obtained as an approximation to the original ‘exact’ model, to which it reduces when the constraints imposed on the form of the wave function are relaxed.

### 1.4 MATRIX REPRESENTATION OF THE SCHRÖDINGER EQUATION

The Schrödinger equation for an  $N$ -electron system is a partial differential equation in  $3N$  variables, but the method of linear combinations discussed in the previous section shows how it may be transformed into an equivalent matrix equation. The secular equations (1.11) can be written in the matrix form

$$\mathbf{HC} = E\mathbf{SC} \quad (1.14)$$

where  $\mathbf{H}$  and  $\mathbf{S}$  are square ( $n \times n$ ) matrices whose elements are  $H_{ij}$  and  $S_{ij}$  defined by (1.10), and  $\mathbf{C}$  is a column matrix (vector) whose elements are the coefficients  $C_j$  of the expansion (1.8); written out in full, (1.14) is

$$\begin{pmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \dots \\ C_n \end{pmatrix} = E \begin{pmatrix} S_{11} & S_{12} & \dots & S_{1n} \\ S_{21} & S_{22} & \dots & S_{2n} \\ \dots & \dots & \dots & \dots \\ S_{n1} & S_{n2} & \dots & S_{nn} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \dots \\ C_n \end{pmatrix}$$

The matrix  $\mathbf{H}$  is a representation of the Hamiltonian  $\mathcal{H}$  in terms of the *basis* of  $n$  functions  $\Phi_j$ . As has already been remarked, the solutions of the matrix equation are approximations for  $n$  states of the system, and increasing the number of basis functions leads to better approximations for more and more states. When  $n$  becomes infinitely large and the basis becomes complete,† the matrix equation (1.14) becomes entirely equiva-

† The definition of a complete set given on p. 3 is sufficient for our purposes. Given a set of functions  $\Phi_n$  ( $n = 1, 2, \dots, M$ ) satisfying certain boundary conditions, the set is said to be complete if any arbitrary function  $\Phi$ , which satisfies the same boundary



*Matrix representation of Schrödinger equation*

lent to the differential Schrödinger equation, having the same set of eigenvalues and eigenfunctions, the latter being expressed in the form (1.13) as linear combinations of the basis functions.

Given a basis therefore, the problem of solving the Schrödinger equation is reduced to the evaluation of the matrix elements  $H_{ij}$  and  $S_{ij}$ , and to the solution of the corresponding matrix equation. The only serious problem is concerned with the choice of basis functions. Ideally, we would like to be able to use a basis which gives both easily evaluated matrix elements and a rapid convergence (small  $n$ ) of the expansion (1.13) of the wave function. This is not always possible, particularly for polyatomic molecules.

**1.5 PERTURBATION THEORY**

It is often the case that the Hamiltonian  $\mathcal{H}$  for the system of interest differs only slightly from the Hamiltonian  $\mathcal{H}_0$  of a related system. One example is a molecule in a weak external electric field for which the Hamiltonian can be written as

$$\mathcal{H} = \mathcal{H}_0 + \lambda V \quad (1.15)$$

where  $\mathcal{H}_0$  describes the unperturbed system which is the molecule in the absence of the field, and  $\lambda V$  is a 'small' perturbation term which describes the interaction of the molecule with the field.  $\lambda$  is a parameter, called the perturbation parameter (for example, the field strength), which is a measure of the strength of the perturbation.

It is generally assumed in perturbation theory that the eigenfunctions and eigenvalues of  $\mathcal{H}_0$  are known,

$$\mathcal{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)} \quad (1.16)$$

or, since in practice only a few eigenfunctions may be known, that at least the unperturbed wave function  $\Psi_n^{(0)}$  for the state of interest is known. We shall also assume, for simplicity, that the state of interest is one for which the energy  $E_n^{(0)}$  is non-degenerate. Then, if  $\Psi_n$  and  $E_n$  are the

conditions, can be expressed as a linear combination  $\Phi = \sum_{n=1}^M C_n \Phi_n$ . If the basis functions are orthonormal,  $\int \Phi_m^* \Phi_n \, d\tau = \delta_{mn}$ , the coefficients are given by

$$C_n = \int \Phi_n^* \Phi \, d\tau,$$

Such complete sets of functions are almost always infinite, notable exceptions being the sets of  $N$ -electron spin functions containing  $2^N$  members (§2.7).

### Introduction

(unknown) eigenfunction and eigenvalue of  $\mathcal{H}$  for this state,

$$\mathcal{H}\Psi_n = E_n \Psi_n \quad (1.17)$$

it follows that in the limit  $\lambda \rightarrow 0$ ,

$$\mathcal{H} \rightarrow \mathcal{H}_0, \quad E_n \rightarrow E_n^{(0)}, \quad \Psi_n \rightarrow \Psi_n^{(0)}$$

The basic assumption of perturbation theory is that the energy and wave function for the perturbed state may be expanded as power series in  $\lambda$  about the corresponding energy and wave function of the unperturbed state,

$$\left. \begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \\ \Psi_n &= \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots \end{aligned} \right\} \quad (1.18)$$

and that these expansions are valid for the whole range of values of  $\lambda$  between zero and the value of interest. The quantity  $E_n^{(i)}$  is called the  $i$ th-order energy and  $\Psi_n^{(i)}$  is the  $i$ th-order wave function. Substitution of the expansions for the energy and wave function in the Schrödinger equation (1.17) gives

$$\begin{aligned} (\mathcal{H}_0 + \lambda V)(\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots) \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots) \end{aligned}$$

or

$$\begin{aligned} (\mathcal{H}_0 - E_n^{(0)})\Psi_n^{(0)} + \lambda[(\mathcal{H}_0 - E_n^{(0)})\Psi_n^{(1)} + (V - E_n^{(1)})\Psi_n^{(0)}] \\ + \lambda^2[(\mathcal{H}_0 - E_n^{(0)})\Psi_n^{(2)} + (V - E_n^{(1)})\Psi_n^{(1)} - E_n^{(2)}\Psi_n^{(0)}] + \dots = 0 \end{aligned} \quad (1.19)$$

In order that the equation be satisfied for arbitrary values of  $\lambda$ , it is necessary that the coefficient of each power of  $\lambda$  be separately zero. The zeroth-order equation is

$$(\mathcal{H}_0 - E_n^{(0)})\Psi_n^{(0)} = 0$$

which is simply the original Schrödinger equation for the unperturbed state. The first- and second-order equations are

$$(\mathcal{H}_0 - E_n^{(0)})\Psi_n^{(1)} + (V - E_n^{(1)})\Psi_n^{(0)} = 0 \quad (1.20)$$

$$(\mathcal{H}_0 - E_n^{(0)})\Psi_n^{(2)} + (V - E_n^{(1)})\Psi_n^{(1)} = E_n^{(2)}\Psi_n^{(0)} \quad (1.21)$$

We therefore obtain, if the perturbation  $\lambda V$  is small enough, a set of equations which can be solved in sequence to give progressively more accurate solutions of the Schrödinger equation for the perturbed state. In many applications it is not necessary to go beyond the first-order wave function as this determines the energy to third order.

The solution of the perturbation equations is discussed in standard