where we have used (10.1). Thus the rotational molecular energies are smaller than the electronic energies by a factor of the order of $m/M$, and smaller than the vibrational energies by a factor of the order of $(m/M)^{12}$. The rotational motion leads to a ‘second-order’ splitting of the electronic lines, the spacing being of the order of 0.001 eV, which is very small compared with the ‘first-order’ splitting of about 0.1 eV produced by the vibrational motion. Transitions between rotational levels, belonging to the same electronic and vibrational level, are observed in the far infra-red and the microwave regions at wave numbers of 1 to $10^2$ cm$^{-1}$.

Because of the small ratio of the electronic mass to the nuclear mass ($m/M = 10^{-3}$–$10^{-5}$), and since the period of a motion is of the order of $\hbar$ divided by its energy, we see from (10.1)–(10.3) that the nuclear periods are much longer than the electronic periods. Thus the electronic and nuclear motions can essentially be treated independently, and it is a good approximation to determine the electronic states at each value of the internuclear separation by treating the nuclei as fixed. The charge distribution of the electrons is then a function of the nuclear positions and determines the nuclear motion. In the next paragraphs we shall use these qualitative ideas to develop a mathematical formalism for diatomic molecules.

### 10.2 The Born–Oppenheimer Separation for Diatomic Molecules

To see how the ideas of the previous paragraph can be implemented, we shall consider a diatomic molecule composed of nuclei A and B, of masses $M_A$ and $M_B$ together with a number $N$ of electrons. The internuclear position vector will be denoted by $\mathbf{R}$ and the position vectors of the electrons with respect to O, the centre of mass of A and B, by $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ (see Fig. 10.4). We shall write the position vectors of A and B with respect to O as $\mathbf{R}_A$ and $\mathbf{R}_B$ respectively, so that $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$.

The Hamiltonian operator

$$H = T_N + T_e + V$$

where $T_N$ is the kinetic energy operator for the nuclei with respect to the space-fixed frame, or space-fixed frame, and the reduced mass $\mu$ of the system is

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

It follows that

$$T_N = -\frac{\hbar^2}{2\mu} \nabla^2_{\mathbf{R}}$$

and

$$T_e = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m_i} \right)$$

It will be convenient to work with the coordinates $(R, \Theta, \Phi)$ of $\mathbf{R}$, or

$$T_N = -\frac{\hbar^2}{2\mu} \left[ \right.$$
The Hamiltonian operator for the complete molecule can be expressed as
\[ H = T_N + T_e + V \]  
(10.4)

where \( T_N \) is the kinetic energy operator for the nuclei, \( T_e \) is the kinetic energy operator for the electrons and \( V \) is the total potential energy of the system. We shall take \( O \) to be the origin of a coordinate system fixed in space (the laboratory or space-fixed frame), and neglect the mass of an electron \( m \) with respect to the reduced mass \( \mu \) of the nuclei \( A \) and \( B \), where
\[ \mu = \frac{M_A M_B}{M_A + M_B} \]  
(10.5)

It follows that
\[ T_N = -\frac{\hbar^2}{2\mu} \nabla^2_R \]  
(10.6)

and
\[ T_e = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} \right) \]  
(10.7)

It will be convenient to express \( T_N \) in terms of the spherical polar coordinates \((R, \Theta, \Phi)\) of \( \mathbf{R} \), so that
\[ T_N = -\frac{\hbar^2}{2\mu} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - \frac{N^2}{\hbar^2 R^2} \right] \]  
(10.8)

where \( N \) is the orbital angular momentum operator for the relative motion of the two nuclei \( A \) and \( B \), and (see (2.159))
\[ N^2 = -\hbar^2 \left[ \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left( \sin \Theta \frac{\partial}{\partial \Theta} \right) + \frac{1}{\sin^2 \Theta} \frac{\partial^2}{\partial \Phi^2} \right] \]  
(10.9)
If the small spin-dependent interactions are neglected, the potential energy consists of the sum of the Coulomb interactions between the electrons themselves, and between the two nuclei. Denoting the charges on the nuclei A and B by \( Z_A e \) and \( Z_B e \), we have

\[
V(\mathbf{R}; r_1, r_2, \ldots, r_N) = -\sum_{i=1}^{N} \left[ \frac{Z_A e^2}{(4\pi \varepsilon_0)|\mathbf{r}_i - \mathbf{R}_A|} + \frac{Z_B e^2}{(4\pi \varepsilon_0)|\mathbf{r}_i - \mathbf{R}_B|} \right] + \sum_{i<j=1}^{N} \frac{e^2}{(4\pi \varepsilon_0)|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z_A Z_B e^2}{(4\pi \varepsilon_0)R}
\]

The time-independent Schrödinger equation for the molecule is

\[
H\Psi(\mathbf{Q}_A, \mathbf{Q}_B; q_1, q_2, \ldots, q_N) = E\Psi(\mathbf{Q}_A, \mathbf{Q}_B; q_1, q_2, \ldots, q_N)
\]

where \( Q_A \) and \( Q_B \) represent the space and spin coordinates of the nuclei collectively and \( q_1, q_2, \ldots, q_N \) the space and spin coordinates of the electrons collectively. The wave function \( \Psi \) must obey the Pauli exclusion principle and be antisymmetric under the interchange of the coordinates (both space and spin) of any pair of electrons. If the nuclei A and B are identical \( \Psi \) must also be either symmetric or antisymmetric under the interchange of A and B, for nuclei having integer (including zero) or half-odd integer spin, respectively. In what follows, to simplify the notation, the dependence of \( \Psi \) on the spin variables will not be displayed and we shall write \( \Psi(\mathbf{R}; r_1, r_2, \ldots, r_N) \).

In order to construct a set of basis states into which the total wave function \( \Psi \) can be expanded, let us consider the time-independent Schrödinger equation for the \( N \) electrons moving in the Coulomb potential of the nuclei A and B, where \( \mathbf{R} \) is held fixed, which is

\[
H_e \Phi_q(\mathbf{R}; r_1, r_2, \ldots, r_N) = E_q(\mathbf{R}) \Phi_q(\mathbf{R}; r_1, r_2, \ldots, r_N)
\]

where \( H_e \) is the electronic Hamiltonian

\[
H_e = T_e + V
\]

Equation (10.12) is known as the electronic wave equation. The eigenvalues \( E_q(\mathbf{R}) \) and the wave functions \( \Phi_q(\mathbf{R}; r_1, r_2, \ldots, r_N) \) for each electronic state \( q \) depend parametrically on the internuclear position vector \( \mathbf{R} \), which is held fixed when \( E_q \) and \( \Phi_q \) are calculated. Since the energies \( E_q \) cannot depend on the orientation of the internuclear line in the absence of any external fields, they depend parametrically only on the magnitude \( R \) of the vector \( \mathbf{R} \). The wave functions \( \Phi_q \), on the other hand, depend on \( R \) and on the angles \( \Theta \) and \( \Phi \) as parameters.

For each (fixed) internuclear position vector \( \mathbf{R} \), the electronic wave functions \( \Phi_q \) form a complete set, which can be taken to be orthonormal

\[
\langle \Phi_q | \Phi_p \rangle = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \ldots, d\mathbf{r}_N \, \Phi^*_q(\mathbf{R}; r_1, r_2, \ldots, r_N) \Phi_p(\mathbf{R}; r_1, r_2, \ldots, r_N)
\]

\[
= \delta_{qp}
\]
Since the set of functions $\Phi_q$ is complete, the exact wave function $\Psi$ for the molecule can be expanded as

$$\Psi(R; r_1, r_2, \ldots, r_N) = \sum_q F_q(R) \Phi_q(R; r_1, r_2, \ldots, r_N)$$  \hspace{1cm} (10.15)$$

where the expansion coefficients $F_q(R)$ are wave functions representing the nuclear motion (vibration and rotation) when the electronic system is in the state $q$.

To obtain equations satisfied by the wave functions $F_q(R)$, we first note that the Hamiltonian of the complete molecule can be written as

$$H = T_N + H_e$$  \hspace{1cm} (10.16)$$

so that the Schrödinger equation (10.11) for the molecule becomes

$$ (T_N + H_e)\Psi(R; r_1, r_2, \ldots, r_N) = E\Psi(R; r_1, r_2, \ldots, r_N)$$  \hspace{1cm} (10.17)$$

We now insert the expansion (10.15) into this equation, so that

$$ (T_N + H_e) \sum_q F_q(R) \Phi_q(R; r_1, r_2, \ldots, r_N)$$

$$ = E \sum_q F_q(R) \Phi_q(R; r_1, r_2, \ldots, r_N)$$  \hspace{1cm} (10.18)$$

On projecting equation (10.18) successively with the functions $\Phi_s$ ($s = 0, 1, 2, \ldots$), we obtain the coupled equations

$$\sum_q \langle \Phi_s | T_N + H_e - E | \Phi_q \rangle F_q(R) = 0, \hspace{1cm} s = 0, 1, 2, \ldots$$  \hspace{1cm} (10.19)$$

where

$$\langle \Phi_s | T_N + H_e - E | \Phi_q \rangle = \int dr_1, dr_2, \ldots, dr_N \Phi_s^*(R; r_1, r_2, \ldots, r_N) (T_N + H_e - E) \Phi_q(R; r_1, r_2, \ldots, r_N)$$  \hspace{1cm} (10.20)$$

Using the electronic wave equation (10.12) together with (10.8) and (10.14), the coupled equations (10.19) can be rewritten in the form

$$\sum_q \left\langle \Phi_s \right| \frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{N^2}{2\mu R^2} \left| \Phi_q \right\rangle F_q(R) + [E_s(R) - E] F_s(R) = 0,$$

$$s = 0, 1, 2, \ldots$$  \hspace{1cm} (10.21)$$

In (10.21), since $\Phi_q$ depends on $R$ as well as on $r_1, r_2, \ldots, r_N$, the derivatives $\partial/\partial R$ and $\partial/\partial \Phi, \partial/\partial \Phi$ (contained in $N$) operate on the product $\Phi_q F_q$. The set of coupled equations (10.21) is exact and equivalent to the full Schrödinger equation (10.17). The Born–Oppenheimer or adiabatic approximation
will now be introduced, which makes use of the fact that the nuclear motion is very slow compared with the electronic motion. As a consequence, the electronic wave functions $\Phi_s$ vary very slowly with respect to $R$, $\Theta$ and $\Phi$. This fact allows $|\partial \Phi_s / \partial R|$ to be neglected with respect to $|\partial F_s / \partial R|$ and in addition it is sufficient to retain only the diagonal term $\langle \Phi_s | N^2 | \Phi_s \rangle$.

Making these approximations, the coupled equations (10.21) reduce to the set of uncoupled equations

$$
\left[ -\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{\langle \Phi_s | N^2 | \Phi_s \rangle}{2\mu R^2} + E_s(R) - E \right] F_s(R) = 0,
$$

where $s = 0, 1, 2, \ldots$

(10.22)

Each of these equations, which describes the vibrational and rotational motion of the molecule when the electronic system is in the state $s$, is called a nuclear wave equation. The uncoupled set of equations (10.22) constitutes the Born–Oppenheimer approximation in which the total wave function reduces to the single term for a given $s$,

$$
\Psi_s = F_s(R) \Phi_s(R; r_1, r_2, \ldots, r_N)
$$

(10.23)

In the Born–Oppenheimer approximation the electronic wave equation (10.12) is first solved at different values of $R$ to obtain $E_s(R)$, and subsequently the nuclear wave equation (10.22) can be solved in which $E_s(R)$ plays the role of a potential. The general form of $E_s(R)$ for a bound state is shown in Fig. 10.5. As $R \to 0$, $E_s(R)$

---

**Figure 10.5** The general form of the electronic energy $E_s(R)$ for a bound state of a diatomic molecule. The quantity $D_s$ is the electronic (or spectroscopic) dissociation energy of the molecule in the electronic state $s$. 
10.3 Electronic structure of diatomic molecules

is dominated by the Coulomb repulsion between the two nuclei A and B, while as
\( R \to \infty \), \( E_s(R) \) tends to a constant energy \( E_s(\infty) \) which is the sum of the energies of
the two isolated atoms from which the molecule is composed. If there is a stable
bound state, \( E_s(R) \) exhibits a minimum at some internuclear separation \( R = R_0 \)
and the nuclear wave function is confined to a limited region near \( R = R_0 \). The
quantity
\[
D_s = E_s(\infty) - E_s(R_0)
\]
is often called the electronic (or spectroscopic) dissociation energy of the molecule
in the electronic state \( s \). As we shall see in Section 10.4, the quantity \( D_s \) differs
slightly from the true (also called chemical) dissociation energy \( D_0 \) of the molecule,
which takes into account the zero-point energy of the vibrational motion of the
nuclei in the electronic state \( s \) under consideration (see (10.112)).

The accuracy of the Born–Oppenheimer approximation can be estimated in
any particular case by treating the omitted terms as small perturbations and
checking that their effect is small by using first-order perturbation theory.
An important case in which the Born–Oppenheimer approximation must be
improved is when the energy \( E_s(R) \) is degenerate, because the coupling between
degenerate states cannot be ignored. When the relative motion of the nuclei is not
very slow, as in atom–atom collisions, the terms that are omitted in the Born–
Oppenheimer approximation become important and are responsible for inelastic
transitions between different electronic states. Finally, we note that for Rydberg
molecules, in which an electron is in a highly excited electronic state (Rydberg
state), the motion of this electron is slow, and the Born–Oppenheimer approxi-
mation fails.

10.3 Electronic structure of diatomic molecules

In this section we shall discuss the electronic wave functions of the simplest
diatomic molecules. Our discussion will be based on the electronic wave equation
\( \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{Ze^2}{\hbar} \psi = E \psi \) which is fixed with
respect to the molecule, taking the \( \hat{Z} \) axis along the internuclear axis from B to A
and choosing that the \( \hat{X} \) axis lies in the space-fixed \( XY \) plane. This frame of refer-
ce is called the body-fixed (or molecular) frame (see Appendix 9). The position-
vector \( \mathbf{r}_e \) of an electron is the same in the space-fixed (or laboratory) and body-
fixed frames, but the components of \( \mathbf{r}_e \) are different in each frame. In the space-
fixed frames, the components of \( \mathbf{r}_e \) along the \( X, Y \) and \( Z \) axes will be denoted by \( x_e, y_e, z_e \),
y and in the body-fixed frame along the \( \hat{X}, \hat{Y}, \hat{Z} \) axes by \( \hat{x}_e, \hat{y}_e, \hat{z}_e \).

As we have already noted the eigenvalues \( E_s(R) \) are independent of the frame
of reference, and can be calculated in the body-fixed frame for convenience. The
electronic wave function is required to be expressed in terms of the space-fixed