

Chapter 2. Electronic States

Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (2005), Chap. 3, and Bunker and Jensen (1998), Chap. 9.*

2.1 The Born-Oppenheimer Approximation

Before attempting to solve the Schrödinger equation with the rovibronic Hamiltonian H_{rve} , it will be to our advantage to make a few simplifications. First is our realization that the motion of the electrons can be separated from that of the nuclei. This is to be expected because of the significantly lower mass of the electrons. We can therefore imagine that as the nuclei are moving around, the electron will be adjusting themselves on a much shorter time scale (almost instantaneously as far as the nuclei are concerned). This is the idea at the centre of the so-called **Born-Oppenheimer approximation**.

To proceed with this approximation, we introduce a new space-fixed coordinate system (ξ, η, ζ) that has its axes parallel to that of (X, Y, Z) , which was defined earlier and had its origin at the molecular centre of mass. The only difference between the two systems is that (ξ, η, ζ) has its origin at the nuclear centre of mass. This difference in the location of the origin is important as it relates the motion of the electrons to the position of the nuclei. This is an essential condition for the separation of the terms associated to the kinetic energy of the electrons in the Hamiltonian. Let us now make this change of coordinates. From their definitions, the two aforementioned sets of coordinates are related as follows

$$\begin{aligned}\xi_i &= X_i - X_N \\ \eta_i &= Y_i - Y_N \\ \zeta_i &= Z_i - Z_N,\end{aligned}\tag{2.1}$$

where X_N, Y_N , and Z_N are the coordinates of the nuclear centre of mass in the (X, Y, Z) system. If $M_N = \sum_{r=1}^N M_r$ is the total nuclear mass, and $M_N X_N \equiv \sum_{r=1}^N M_r X_r$ and so on, then we can write (taking into account the centre of mass of the molecule)

$$M_N X_N + m_e \sum_{r=N+1}^l X_r = 0,\tag{2.2}$$

with similar relations for the other directions. By insertion into the first of equations (2.1) we have

$$\begin{aligned}
\xi_i &= X_i + \frac{m_e}{M_N} \sum_{r=N+1}^l X_r \\
&= \sum_{r=2}^l \left(\delta_{ir} + \frac{m_e}{M_N} \delta_{er} \right) X_r,
\end{aligned} \tag{2.3}$$

with similar relations for η_i and ζ_i , and where δ_{er} is a Kronecker delta that will equal one only when the index r labels an electron. Using the chain rule, we can write that

$$\frac{\partial}{\partial X_r} = \sum_{i=2}^l \left(\delta_{ir} + \frac{m_e}{M_N} \delta_{er} \right) \frac{\partial}{\partial \xi_i}, \tag{2.4}$$

where $r \neq 1$, and

$$\begin{aligned}
\frac{\partial^2}{\partial X_r \partial X_s} &= \frac{\partial^2}{\partial \xi_r \partial \xi_s} + \frac{m_e}{M_N} \left[\delta_{es} \sum_{j=2}^l \frac{\partial^2}{\partial \xi_r \partial \xi_j} + \delta_{er} \sum_{i=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_s} \right] \\
&\quad + \left(\frac{m_e}{M_N} \right)^2 \delta_{es} \delta_{er} \sum_{i,j=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j},
\end{aligned} \tag{2.5}$$

where $r, s \neq 1$. From this last equation we can calculate

$$\begin{aligned}
\frac{1}{M} \sum_{r,s=2}^l \frac{\partial^2}{\partial X_r \partial X_s} &= \frac{1}{M} \sum_{i,j=2}^l \left[1 + 2 \frac{nm_e}{M_N} + \left(\frac{nm_e}{M_N} \right)^2 \right] \frac{\partial^2}{\partial \xi_i \partial \xi_j} \\
&= \frac{M}{M_N^2} \sum_{i,j=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j},
\end{aligned} \tag{2.6}$$

and

$$\sum_{r=2}^l \frac{1}{m_r} \frac{\partial^2}{\partial X_r^2} = \sum_{i=2}^l \frac{1}{m_i} \frac{\partial^2}{\partial \xi_i^2} + \frac{2}{M_N} \sum_{i=N+1}^l \sum_{j=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j} + \frac{nm_e}{M_N^2} \sum_{i,j=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j}, \tag{2.7}$$

where $n = l - N$ is the number of electrons. We already know from equation (1.119)

$$\begin{aligned}
\hat{H}_{\text{rve}} &= -\hbar^2 \sum_{r=2}^l \frac{1}{2m_r} \nabla_r^2 + \frac{\hbar^2}{2M} \sum_{r,s=2}^l \nabla_r \cdot \nabla_s + \frac{1}{4\pi\epsilon_0} \sum_{r<s=1}^l \frac{C_r C_s e^2}{R_{rs}} \\
\nabla_r &= \mathbf{e}_x \frac{\partial}{\partial X_r} + \mathbf{e}_y \frac{\partial}{\partial Y_r} + \mathbf{e}_z \frac{\partial}{\partial Z_r},
\end{aligned} \tag{2.8}$$

that the equation from the rovibronic Hamiltonian includes terms proportional to equations (2.6) and (2.7). We therefore add these two equations to find

$$\begin{aligned}
\frac{1}{M} \sum_{r,s=2}^l \frac{\partial^2}{\partial X_r \partial X_s} - \sum_{r=2}^l \frac{1}{m_r} \frac{\partial^2}{\partial X_r^2} &= \frac{M - nm_e}{M_N^2} \sum_{i,j=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j} - \sum_{i=2}^l \frac{1}{m_i} \frac{\partial^2}{\partial \xi_i^2} - \frac{2}{M_N} \sum_{i=N+1}^l \sum_{j=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j} \\
&= \frac{1}{M_N} \left(\sum_{i,j=2}^N + 2 \sum_{i=2}^N \sum_{j=N+1}^l + \sum_{i,j=N+1}^l \right) \frac{\partial^2}{\partial \xi_i \partial \xi_j} - \sum_{i=2}^l \frac{1}{m_i} \frac{\partial^2}{\partial \xi_i^2} \\
&\quad - \frac{2}{M_N} \sum_{i=N+1}^l \sum_{j=2}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j} \\
&= - \sum_{i=2}^l \frac{1}{m_i} \frac{\partial^2}{\partial \xi_i^2} + \frac{1}{M_N} \left(\sum_{i,j=2}^N \frac{\partial^2}{\partial \xi_i \partial \xi_j} + \sum_{i,j=N+1}^l \frac{\partial^2}{\partial \xi_i \partial \xi_j} \right).
\end{aligned} \tag{2.9}$$

Substituting this result into equation (2.8), we write for the Hamiltonian

$$\hat{H}_{\text{rve}} = \hat{T}_e + \hat{T}_N + V(\mathbf{R}_N, \mathbf{r}_e), \tag{2.10}$$

with

$$\begin{aligned}
\hat{T}_e &= -\frac{\hbar^2}{2m_e} \sum_{i=N+1}^l \nabla_i^2 + \frac{\hbar^2}{2M_N} \sum_{i,j=N+1}^l \nabla_i \cdot \nabla_j \\
\hat{T}_N &= -\frac{\hbar^2}{2} \sum_{i=2}^N \frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_N} \sum_{i,j=2}^N \nabla_i \cdot \nabla_j \\
V(\mathbf{R}_N, \mathbf{r}_e) &= \frac{1}{4\pi\epsilon_0} \sum_{r<s=1}^l \frac{C_r C_s e^2}{R_{rs}},
\end{aligned} \tag{2.11}$$

with this time

$$\nabla_i \equiv \mathbf{e}_\xi \frac{\partial}{\partial \xi_i} + \mathbf{e}_\eta \frac{\partial}{\partial \eta_i} + \mathbf{e}_\zeta \frac{\partial}{\partial \zeta_i}. \tag{2.12}$$

In the last of equations (2.11) \mathbf{R}_N and \mathbf{r}_e denote the sets of nuclear and electronic coordinates, respectively. We can furthermore break the potential energy into three terms such that

$$V(\mathbf{R}_N, \mathbf{r}_e) = V_{ee}(\mathbf{r}_e) + V_{NN}(\mathbf{R}_N) + V_{Ne}(\mathbf{R}_N, \mathbf{r}_e), \tag{2.13}$$

where the different terms on the right hand side are for the separate summations of electron-electron, nucleus-nucleus, and nucleus-electron electrostatic potential energies, respectively.

When applying the Born-Oppenheimer approximation, we are assuming that the electrons are unaffected by the motion of the nuclei, i.e., we consider the nuclei as being stationary. This is equivalent to setting $\hat{T}_N = 0$ in equation (2.10). It is also appropriate to neglect the nucleus-nucleus potential energy term (i.e., V_{NN}) in equation (2.13), since it will not affect the behavior of the electrons in any way. Finally, we can bring one further approximation to the rovibronic Hamiltonian. Close examination of the first of equations (2.11) concerning the electronic kinetic energy reveals that the second term on the right hand side is much smaller than the first, since it is inversely proportional to the total nuclear mass (as opposed to the electron mass). In fact, it is common to write

$$\hat{T}_e = \hat{T}_e^0 + T'_e, \quad (2.14)$$

with

$$\begin{aligned} \hat{T}_e^0 &= -\frac{\hbar^2}{2m_e} \sum_{i=N+1}^l \nabla_i^2 \\ \hat{T}'_e &= \frac{\hbar^2}{2M_N} \sum_{i,j=N+1}^l \nabla_i \cdot \nabla_j. \end{aligned} \quad (2.15)$$

As stated above, within the Born-Oppenheimer approximation we assume that $|\hat{T}'_e| \ll |\hat{T}_e^0|$, and the time-independent Schrödinger equation for the electronic states of the molecule becomes

$$\left(\hat{T}_e^0 + V_{ee} + V_{Ne} \right) \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) = \hat{H}_{\text{elec}} \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) \equiv V_{\text{elec},n} \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e), \quad (2.16)$$

where the nuclei coordinates \mathbf{R}_N are held constant, and n corresponds to the successive electronic states ($n = 1, 2, \dots$) pertaining to the nuclear configuration \mathbf{R}_N . That is to say that the both the electronic wave functions $\Phi_{\text{elec},n}$ and energies $V_{\text{elec},n}$ are dependent on the nuclear arrangement.

We could have proceeded along a different route by recognizing that the Born-Oppenheimer approximation is equivalent to saying that the (approximate) rovibronic wave function $\Phi_{\text{rve},nj}^0$ is expressed as the product of the electronic wave function $\Phi_{\text{elec},n}$ and the rotation-vibration wave function $\Phi_{\text{rv},nj}$

$$\Phi_{\text{rve},nj}^0 = \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{\text{rv},nj}(\mathbf{R}_N), \quad (2.17)$$

where the indices n and j ($n, j = 1, 2, \dots$) relate to the particular electronic and rotation-vibration states, respectively. Obviously, we must realize that although the nuclei coordinates \mathbf{R}_N are assumed constant in $\Phi_{\text{elec},n}$, they are certainly allowed to vary in $\Phi_{\text{rv},nj}$. The Schrödinger equation is then

$$\begin{aligned}
\hat{H}_{\text{rve}} \Phi_{\text{rve},nj}^0(\mathbf{R}_N, \mathbf{r}_e) &= \left[(\hat{T}_e^0 + V_{\text{ee}} + V_{\text{Ne}}) + (\hat{T}_N + V_{\text{NN}}) \right] \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{\text{rv},nj}(\mathbf{R}_N) \\
&= (\hat{T}_e^0 + V_{\text{ee}} + V_{\text{Ne}}) \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{\text{rv},nj}(\mathbf{R}_N) \\
&\quad + \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) (\hat{T}_N + V_{\text{NN}}) \Phi_{\text{rv},nj}(\mathbf{R}_N) \\
&= V_{\text{elec},n} \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{\text{rv},nj}(\mathbf{R}_N) \\
&\quad + \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) (\hat{T}_N + V_{\text{NN}}) \Phi_{\text{rv},nj}(\mathbf{R}_N) \\
&= \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) (\hat{T}_N + V_{\text{NN}} + V_{\text{elec},n}) \Phi_{\text{rv},nj}(\mathbf{R}_N),
\end{aligned} \tag{2.18}$$

or

$$\begin{aligned}
\hat{H}_{\text{rve}} \Phi_{\text{rve},nj}^0(\mathbf{R}_N, \mathbf{r}_e) &= E_{\text{rve},nj}^0 \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) \Phi_{\text{rv},nj}(\mathbf{R}_N) \\
&= E_{\text{rve},nj}^0 \Phi_{\text{rve},nj}^0(\mathbf{R}_N, \mathbf{r}_e),
\end{aligned} \tag{2.19}$$

with $E_{\text{rve},nj}^0$ the eigenvalue when the molecule is in the electronic state n and rotation-vibration state j . The last line of equation (2.18) suggests that we can define a new *rotation-vibration Schrödinger equation*, which can be written as

$$(\hat{T}_N + V_{\text{NN}} + V_{\text{elec},n}) \Phi_{\text{rv},nj}(\mathbf{R}_N) \equiv E_{\text{rve},nj}^0 \Phi_{\text{rv},nj}(\mathbf{R}_N), \tag{2.20}$$

It is therefore apparent that the potential energy for the nuclear rotation-vibration Hamiltonian is $(V_{\text{NN}} + V_{\text{elec},n})$ and includes a contribution from the electronic state through the presence of $V_{\text{elec},n}$. It is customary to rewrite things so that the *zero energy* for the rotation-vibration equation, in a given electronic state, is the minimum value of $(V_{\text{NN}} + V_{\text{elec},n})$, which is usually called the *electronic energy* $E_{\text{elec},n}$. Our molecular problem is then rewritten with two Schrödinger equations: one determining the electronic states and another the nuclear (rotation-vibration) states

$$\boxed{
\begin{aligned}
(\hat{T}_e^0 + V_{\text{ee}} + V_{\text{Ne}}) \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) &= V_{\text{elec},n} \Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) \\
(\hat{T}_N + V_{\text{N},n}) \Phi_{\text{rv},nj}(\mathbf{R}_N) &= E_{\text{rv},nj} \Phi_{\text{rv},nj}(\mathbf{R}_N)
\end{aligned}
} \tag{2.21}$$

with

$$\begin{aligned}
V_{\text{N},n} &= V_{\text{NN}} + V_{\text{elec},n} - E_{\text{elec},n} \\
E_{\text{rv},nj} &= E_{\text{rve},nj}^0 - E_{\text{elec},n}.
\end{aligned} \tag{2.22}$$

2.2 Molecular Structure

Although our goal is to use the *a priori* known structure of a molecule to explain its spectroscopy, it is important to have a basic understanding of how and why it acquired its configuration. This will also be important for determining the symmetry of the electronic wave functions later on. In what follows, we therefore introduce elementary concepts concerning molecular structure in general. Our treatment will, however, stay at a rudimentary level, as this aspect of molecular quantum mechanics is a field of its own and a thorough study would bring us well beyond the scope of this course.

2.2.1 Spin and the Pauli Exclusion Principle

Every elementary particle has associated to it an intrinsic angular momentum called **spin**. For an electron, the spin operator and its projection on the space-fixed Z -axis are denoted by \hat{s} and \hat{s}_z . For a nucleus we use \hat{i} and \hat{i}_z . The total electronic and nuclei spins for a molecule are expressed using the capitalized operators \hat{S} and \hat{S}_z and \hat{I} and \hat{I}_z , respectively. Particles with half-integer and integer spins (including zero) are correspondingly called **fermions** and **bosons**. The electron, which has a one-half spin, is a fermion, whereas nuclei can be either fermions or bosons. It is important to realize that there is no classical analog to the quantum mechanical spin, and it can only be explained through the unification of quantum mechanics and special relativity.

The most important implications of the presence of spin for the states and behavior of atoms and molecules are embodied in the so-called **Pauli Principle**. Although Pauli initially intended it for electrons, it can be given a more general form as follows

The total wave function (including spins) of a quantum mechanical system must be antisymmetric under the interchange of any pair of identical fermions and symmetric under the interchange of any pair of identical bosons.

The concept of the symmetry of a wave function can be explained by considering the case of a system composed of two electrons.

Example

As mentioned above, the electron is a one-half spin particle, and its spin operator has two eigenvalues and eigenvectors. That is, if we denote these eigenvectors by $|\alpha\rangle$ and $|\beta\rangle$ then

$$\begin{aligned}\hat{s}^2|\alpha\rangle &= s(s+1)\hbar^2|\alpha\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2|\alpha\rangle = \frac{3}{4}\hbar^2|\alpha\rangle \\ \hat{s}_z|\alpha\rangle &= m_z\hbar|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle,\end{aligned}\tag{2.23}$$

and

$$\begin{aligned}
\hat{s}^2 |\beta\rangle &= \frac{3}{4} \hbar^2 |\beta\rangle \\
\hat{s}_z |\beta\rangle &= -\frac{\hbar}{2} |\beta\rangle.
\end{aligned}
\tag{2.24}$$

Note that we have the usual relation $m_s = s - 1, \dots, s + 1$, with $s = 1/2$ in this case.

If we are dealing with two electrons, then we write the corresponding eigenvectors as $|\alpha(i)\rangle$ and $|\beta(i)\rangle$, with $i = 1, 2$ depending on the electron. When combining the spin states of the electrons, it is possible to build the following four new states

$$\begin{aligned}
|\alpha(1)\alpha(2)\rangle &\equiv |\alpha(1)\rangle|\alpha(2)\rangle \\
|\alpha(1)\beta(2)\rangle &\equiv |\alpha(1)\rangle|\beta(2)\rangle \\
|\beta(1)\alpha(2)\rangle &\equiv |\beta(1)\rangle|\alpha(2)\rangle \\
|\beta(1)\beta(2)\rangle &\equiv |\beta(1)\rangle|\beta(2)\rangle.
\end{aligned}
\tag{2.25}$$

Alternatively, we could express these same states using the total spin of the system $\hat{S} = \hat{s}_1 + \hat{s}_2$ and \hat{S}_z (defined in the same way). Since \hat{S}_z can have the set of eigenvalues $m_s = -1, 0, 1$ because of the possible orientations of the electrons, the total spin must therefore be allowed to take the values $S = 0$ and 1 , and we can write

$$\begin{aligned}
|0,0\rangle &\equiv |S = 0, m_s = 0\rangle \\
|1,-1\rangle &\equiv |S = 1, m_s = -1\rangle \\
|1,0\rangle &\equiv |S = 1, m_s = 0\rangle \\
|1,1\rangle &\equiv |S = 1, m_s = 1\rangle.
\end{aligned}
\tag{2.26}$$

It is a general quantum mechanical result that the combination of two angular momenta (not just spins) operators of values, say, j_1 and j_2 will yield a total angular momentum J that can take the values $J = |j_1 - j_2|, \dots, |j_1 + j_2|$. But since equations (2.25) and (2.26) are both complete sets of eigenvectors, then they must be linearly related. Because the set $\{|S, m_s\rangle\}$ must obey relations similar to equations (2.23), it can be shown that

$$\begin{aligned}
|\sigma_-(1,2)\rangle &\equiv |0,0\rangle = \frac{1}{\sqrt{2}} [|\alpha(1)\beta(2)\rangle - |\beta(1)\alpha(2)\rangle] \\
|\sigma_+^{(-)}(1,2)\rangle &\equiv |1,-1\rangle = |\beta(1)\beta(2)\rangle \\
|\sigma_+^{(0)}(1,2)\rangle &\equiv |1,0\rangle = \frac{1}{\sqrt{2}} [|\alpha(1)\beta(2)\rangle + |\beta(1)\alpha(2)\rangle] \\
|\sigma_+^{(+)}(1,2)\rangle &\equiv |1,1\rangle = |\alpha(1)\alpha(2)\rangle.
\end{aligned}
\tag{2.27}$$

If we now interchange the spins of the electrons, which has the same effect as exchanging the labels 1 and 2 in equations (2.27), we find that

$$\begin{aligned}
|\sigma_-(2,1)\rangle &= -|\sigma_-(1,2)\rangle \\
|\sigma_+^{(-)}(2,1)\rangle &= |\sigma_+^{(-)}(1,2)\rangle \\
|\sigma_+^{(0)}(2,1)\rangle &= |\sigma_+^{(0)}(1,2)\rangle \\
|\sigma_+^{(+)}(2,1)\rangle &= |\sigma_+^{(+)}(1,2)\rangle.
\end{aligned} \tag{2.28}$$

From this result, we say that $|\sigma_-\rangle$ and $|\sigma_+^{(ms)}\rangle$ are respectively *antisymmetric* and *symmetric* with respect to the interchange of the electrons (hence their corresponding subscripts). It is commonly said that $|\sigma_-\rangle$ is a **singlet state**, while $\{|\sigma_+^{(ms)}\rangle\}$ form a set of **triplet states**.

It is important to realize that the Pauli principle applies to the *total wave function* of this two-electron system, not only the spin functions specified in equations (2.27). More precisely, there is also a set of symmetric/antisymmetric vectors $\{|\psi_\pm\rangle\}$ specifying the orbital part of the total wave function, which must be combined to the spin states to completely define the system (for example, $\psi_\pm(\mathbf{r}) = \langle \mathbf{r} | \psi_\pm \rangle$ would specify the spatial state of the system). That is, if we write the total vector of the system as

$$|\chi_\pm\rangle \equiv |\psi_\mp\rangle |\sigma_\pm\rangle, \tag{2.29}$$

then it is to this vector that the Pauli principle applies to, not to $|\psi_\mp\rangle$ or $|\sigma_\pm\rangle$ taken separately. According to the Pauli principle, the vector $|\chi_\pm\rangle$ is therefore antisymmetric. Let us now focus on one particular vector, say

$$|\chi_-^{(+)}(1,2)\rangle = |\psi_-(1,2)\rangle |\sigma_+^{(+)}(1,2)\rangle, \tag{2.30}$$

where $|\psi_-(1,2)\rangle$ must be antisymmetric since $|\sigma_+^{(+)}(1,2)\rangle$ is symmetric. Just as was done for the definition of $|\sigma_-(1,2)\rangle$ in equations (2.27), the orbital vector $|\psi_-(1,2)\rangle$ could also be expressed with

$$|\psi_-(1,2)\rangle = \frac{1}{\sqrt{2}} [|a(1)\rangle |b(2)\rangle - |b(1)\rangle |a(2)\rangle], \tag{2.31}$$

with $|a\rangle$ and $|b\rangle$ two orbital wave vectors. We see from equations (2.27) that the two electrons have exactly the same spin state (i.e., $|\alpha\rangle$), and if we further assume that

$|a\rangle = |b\rangle$ (i.e., the electrons share the same orbital), then $|\chi_-^{(+)}(1,2)\rangle = |\psi_-(1,2)\rangle = 0$. That is, we cannot have two electrons with the same spins in the same orbital. This leads to the more general **Pauli Exclusion Principle**

Two identical fermions cannot occupy the same state.

One can easily verify that if the electrons have different spins, then the spin state is specified by $|\sigma_-(1,2)\rangle = -|\sigma_-(2,1)\rangle$. It follows that the orbital vector must be symmetric (by the Pauli principle), and we can allow for the two electrons to share the exact same orbital.

2.2.2 The Slater Determinant

One simple prescription to ensure that the electronic wave vectors of a system composed of n electrons are antisymmetric is to use the so-called **Slater determinant** defined as

$$|\Phi^{(n)}\rangle = \frac{1}{\sqrt{n!}} \begin{vmatrix} |\chi_i(1)\rangle & |\chi_j(1)\rangle & \cdots & |\chi_k(1)\rangle \\ |\chi_i(2)\rangle & |\chi_j(2)\rangle & \cdots & |\chi_k(2)\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |\chi_i(n)\rangle & |\chi_j(n)\rangle & \cdots & |\chi_k(n)\rangle \end{vmatrix}, \quad (2.32)$$

where a row determines a given electron and a column a specific spin-orbital vector $|\chi_i\rangle$. For example, the Slater determinant for the previous example of a two-electron system sharing the same orbital $|a\rangle$ is

$$\begin{aligned} |\Phi^{(2)}\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} |a(1)\alpha(1)\rangle & |a(1)\beta(1)\rangle \\ |a(2)\alpha(2)\rangle & |a(2)\beta(2)\rangle \end{vmatrix} \\ &= \frac{|a(1)a(2)\rangle}{\sqrt{2}} [|\alpha(1)\beta(2)\rangle - |\beta(1)\alpha(2)\rangle] \\ &= \frac{1}{\sqrt{2}} |a(1)a(2)\rangle |\sigma_-(1,2)\rangle. \end{aligned} \quad (2.33)$$

It should be clear that this wave vector is antisymmetric, and that if two electrons share the same orbital, then they must have opposite spins.

2.2.3 Bonding and Anti-bonding Orbitals

The determination of a complete set of orthonormal orbitals for an arbitrary molecule is a very complicated problem that cannot be solved analytically (except for some simple cases such as the H_2^+ ion). It is therefore often the custom to use atomic orbitals (AO) and their linear combinations (LCAO) as a starting point for, or as an approximation to, true

molecular orbitals (MO). Consider for example the case of the hydrogen molecule in its electronic ground state. The Hamiltonian for this system is

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R}, \quad (2.34)$$

with the one-electron Hamiltonian defined with

$$\hat{h}_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0 R_{i1}} - \frac{e^2}{4\pi\epsilon_0 R_{i2}}, \quad (2.35)$$

and $R_{i\alpha}$ the distance from electron i and proton α , r_{12} the distance between the electrons, and R the distance between the two protons. In accordance with the Born-Oppenheimer approximation we do not consider the last (proton-proton interaction) term on the right hand side of equation (2.34) when determining the electronic state on the system. Moreover, we will deliberately neglect the third term of the same equation in order to simplify the analysis as much as possible. With these approximations, we can deal with the electrons independently.

For the first electron (i.e., $i = 1$), the first two terms on the right hand side of equation (2.35) correspond to the Hamiltonian of the hydrogen atom. We can therefore write

$$\hat{h}_1 |\psi_{1s}(H_1)\rangle = E_1 |\psi_{1s}(H_1)\rangle - \frac{e^2}{4\pi\epsilon_0 R_{12}} |\psi_{1s}(H_1)\rangle, \quad (2.36)$$

where $|\psi_{1s}(H_1)\rangle$ is the ket associated with the 1s orbital (i.e., the ground state) for the electron of the equivalent hydrogen atom centered at the position of the first proton (H_1), and the energy is

$$E_1 = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} < 0. \quad (2.37)$$

A similar equation can be written for the same electron with an orbital $|\psi_{1s}(H_2)\rangle$ centered on the second proton (if we consider instead the first and last terms on the right hand side of equation (2.35)). If we use these two AOs as the basis for our molecule, then the one-electron Hamiltonian matrix can be written as

$$\hat{h}_1 = \begin{bmatrix} W & -Q \\ -Q & W \end{bmatrix}, \quad (2.38)$$

with

$$\begin{aligned}
W &= \langle \psi_{1s}(\mathbf{H}_1) | \hat{h}_1 | \psi_{1s}(\mathbf{H}_1) \rangle = \langle \psi_{1s}(\mathbf{H}_2) | \hat{h}_1 | \psi_{1s}(\mathbf{H}_2) \rangle \\
Q &= -\langle \psi_{1s}(\mathbf{H}_2) | \hat{h}_1 | \psi_{1s}(\mathbf{H}_1) \rangle = -\langle \psi_{1s}(\mathbf{H}_1) | \hat{h}_1 | \psi_{1s}(\mathbf{H}_2) \rangle > 0,
\end{aligned}
\tag{2.39}$$

since $\langle \mathbf{r} | \psi_{1s}(\mathbf{H}_1) \rangle$ and $\langle \mathbf{r} | \psi_{1s}(\mathbf{H}_2) \rangle$ are both real and positive (in fact, these wave functions only have a radial dependency). Diagonalizing matrix (2.38), as was shown in section 1.4, we find that the eigenvectors are

$$\begin{aligned}
|\psi\rangle &= \frac{1}{\sqrt{2}} [|\psi_{1s}(\mathbf{H}_1)\rangle + |\psi_{1s}(\mathbf{H}_2)\rangle] \\
|\psi^*\rangle &= \frac{1}{\sqrt{2}} [|\psi_{1s}(\mathbf{H}_1)\rangle - |\psi_{1s}(\mathbf{H}_2)\rangle],
\end{aligned}
\tag{2.40}$$

with associated energies

$$\begin{aligned}
E &= W - Q \\
E^* &= W + Q > E.
\end{aligned}
\tag{2.41}$$

The vectors (2.40) are the MOs associated with the first electron. Obviously, they are also valid for the second electron, since both electrons have similar one-electron Hamiltonians. The lowest energy configuration is found to be at $2(W - Q)$ when both electrons are in the $|\psi\rangle$ state. Since this value for the energy is less than that for two non-interacting hydrogen atoms (i.e., $2W \rightarrow 2E_1$), then the two atoms will have a strong tendency to join and form a molecule with each electron occupying this MO (with one in the spin state $|\alpha\rangle$ and the other in the spin state $|\beta\rangle$, as dictated by the Pauli exclusion principle). The $|\psi\rangle$ MO is thus called a **bonding orbital**. On the other hand, the highest energy configuration (i.e., $2(W + Q)$) is obtained if both electrons are in the $|\psi^*\rangle$ state (again with opposite spins). But since this energy level is higher than that for two non-interacting hydrogen atoms, then such atoms will be less likely to form a bond. The $|\psi^*\rangle$ MO is thus called an **anti-bonding orbital**. In spite of their name, one should not assume that anti-bonding orbitals couldn't be occupied for a given molecule; they can.

It must be emphasized that our treatment was highly simplified. One should (and usually does) find a way to take into account the electron-electron interaction term present in the Hamiltonian (i.e., equation (2.34)). This is usually accomplished using the so-called **Hartree-Fock approximation** (see Bunker and Jensen (2005) sections 3.3.2 to 3.3.4). Nevertheless, this example demonstrates how molecular bonds can be established between atoms. Although we started with AOs of equal energies, the same result applies in general, as long as the AOs are *i)* not too diffuse nor too compact and *ii)* their energies are not too far apart. Condition *i)* implies that it is usually sufficient to restrict oneself to the valence electrons when qualitatively investigating the approximate electronic configuration of a molecule in its ground state.

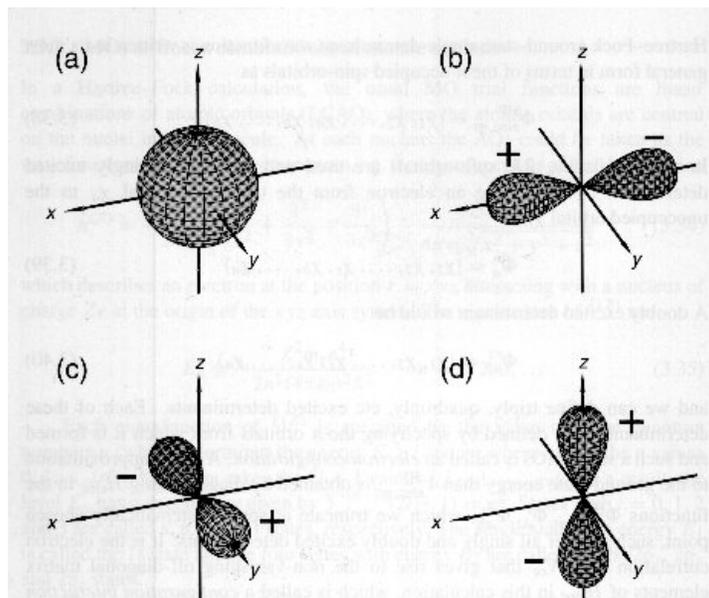


Figure 2-1 – The shapes of s , p_x , p_y , and p_z orbitals in (a), (b), (c), and (d), respectively.

2.2.4 Hybridization

In the previous example for the hydrogen molecule, we used two $1s$ orbitals to form the MOs. We are not restricted to these however. For example, the carbon atom in its ground state can be thought of as having four valence electrons that can occupy the $2s$, $2p_x$, $2p_y$, or $2p_z$ orbitals (shown in Figure 2-1). Since these four orbitals form a basis (they are also of the same energy level), any set of four other orbitals obtained from their linear combinations could also be used as bases. LCAOs obtained from these four AOs (or any other) are called **hybrid orbitals**. Here are three sets of LCAOs obtained this way.

2.2.4.1 sp^3 Hybridization

Consider the initial set of wave function ψ_{2s} , ψ_{2p_x} , ψ_{2p_y} , and ψ_{2p_z} from which we build a new basis of sp^3 orbitals as follows

$$\begin{pmatrix} \phi_1^{(sp^3)} \\ \phi_2^{(sp^3)} \\ \phi_3^{(sp^3)} \\ \phi_4^{(sp^3)} \end{pmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{bmatrix} \begin{pmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_y} \\ \psi_{2p_z} \end{pmatrix}. \quad (2.42)$$

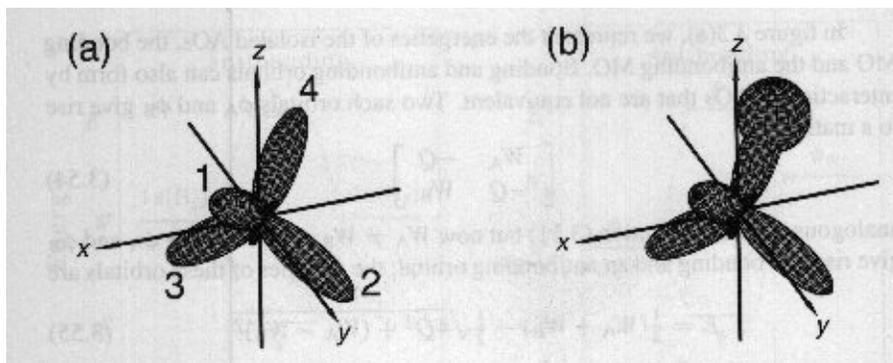


Figure 2-2 - sp^3 hybridization in (a), and the bonding of one $\phi_j^{(sp^3)}$ orbital from a carbon atom with a 1s orbital from a hydrogen atom in (b).

The resulting wave functions (shown in Figure 2-2(a)) have cylindrical symmetry and, taken together can be thought of as tracing the structure of a tetrahedron. These orbitals can be used to explain the structure of the methane molecule (CH_4). To do this, we imagine that the four hydrogen atoms each connect to the end of one $\phi_j^{(sp^3)}$ orbital through a 1s orbital, as shown in Figure 2-2(b). The combination of these two orbitals (i.e., one hydrogen 1s and one carbon sp^3) will generate a pair of bonding and anti-bonding MOs. Each bonding MO will be filled with two electrons of opposite spins; one from a hydrogen atom and another from the valence shell of the carbon atom. All of the available electrons are accounted this way.

2.2.4.2 sp^2 Hybridization

For this type of hybridization we keep the ψ_{2p_z} carbon orbital untouched, but we form a set of so-called sp^2 orbitals as follows

$$\begin{pmatrix} \phi_1^{(sp^2)} \\ \phi_2^{(sp^2)} \\ \phi_3^{(sp^2)} \end{pmatrix} = \begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \\ 1/\sqrt{3} & -1/6 & -1/\sqrt{2} \end{bmatrix} \begin{pmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_y} \end{pmatrix}. \quad (2.43)$$

The resulting wave functions are shown in Figure 2-3(a), with the three $\phi_j^{(sp^2)}$ orbitals occupying a single plane and the ψ_{2p_z} orbital unchanged. This set is well suited to explain the configuration of the ethylene molecule (C_2H_4). To do so, we imagine that each carbon atom bonds with a hydrogen atom along two of its $\phi_j^{(sp^2)}$ orbitals (exactly as was the case for the methane molecule above), while the two remaining sp^2 orbitals (one for each carbon atom) will couple to give a pair of bonding and anti-bonding MOs called σ -orbitals

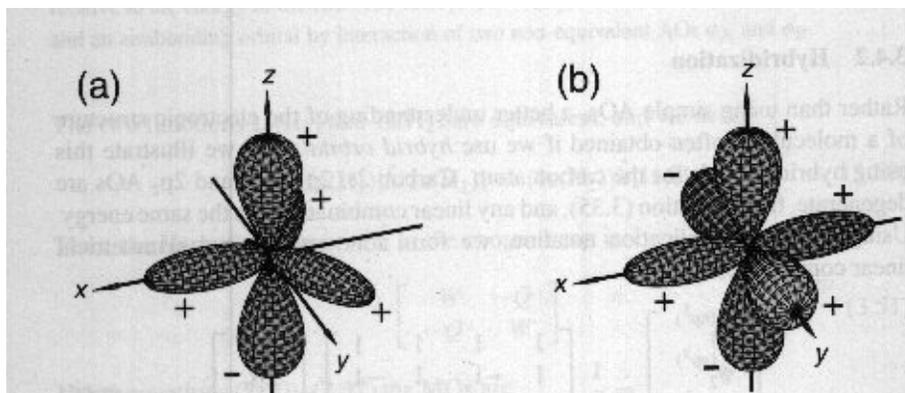


Figure 2-3 – sp^2 and sp hybridizations on (a) and (b), respectively.

$$\begin{aligned}\sigma &= \frac{1}{\sqrt{2}} \left[\phi^{(sp^2)}(C_1) + \phi^{(sp^2)}(C_2) \right] \\ \sigma^* &= \frac{1}{\sqrt{2}} \left[\phi^{(sp^2)}(C_1) - \phi^{(sp^2)}(C_2) \right],\end{aligned}\tag{2.44}$$

and the two ψ_{2p_z} orbitals form a further pair of bonding and anti-bonding MOs called π -orbitals

$$\begin{aligned}\pi &= \frac{1}{\sqrt{2}} \left[\psi_{2p_z}(C_1) + \psi_{2p_z}(C_2) \right] \\ \pi^* &= \frac{1}{\sqrt{2}} \left[\psi_{2p_z}(C_1) - \psi_{2p_z}(C_2) \right].\end{aligned}\tag{2.45}$$

The four remaining carbon electrons (two for each atom) will fill the bonding σ and π orbitals. We again account for all available electrons with this configuration (see Figure 2-4). The combination of the σ and π bonds form what is called a **double bond**. Because of this double bond the sp^2 hybridization is favorable to planar molecular configurations.

2.2.4.3 sp Hybridization

In this case we keep both the ψ_{2p_y} and ψ_{2p_z} orbitals untouched and form the remaining two AOs with

$$\begin{pmatrix} \phi_1^{(sp)} \\ \phi_2^{(sp)} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{pmatrix} \psi_{2s} \\ \psi_{2p_x} \end{pmatrix}.\tag{2.46}$$

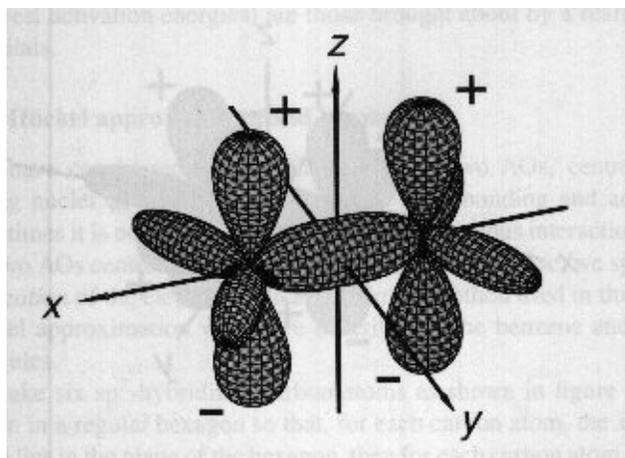


Figure 2-4 – The bonding of two sp^2 hybrids to form a structure consistent with that of the ethylene molecule.

The resulting basis is shown in Figure 2-3(b). This set of orbitals is well suited for linear molecular structures. Consider for example the acetylene molecule (C_2H_2). In this case, the two carbon atoms connect through a **triple bond**: one σ -bond, as in the first of equations (2.44), and two π -bonds, as in the first of equations (2.45). One π -bond arises from the two ψ_{2p_y} orbitals and the other from the ψ_{2p_z} orbitals. The hydrogen atoms then bond to the remaining $\phi_j^{(sp)}$ orbitals in the usual way, yielding the linear structure of acetylene (see Figure 2-5).

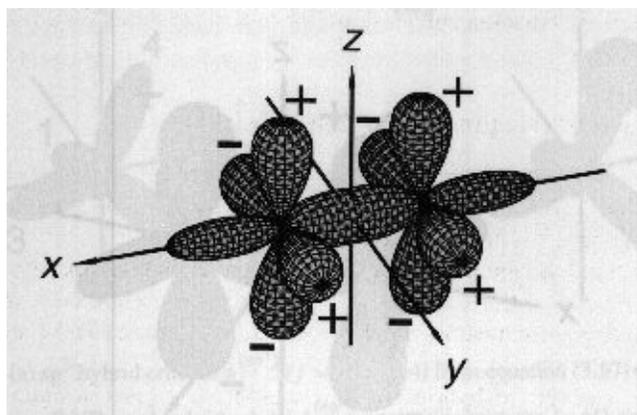


Figure 2-5 - The bonding of two sp hybrids to form a structure consistent to that of the acetylene molecule.