tive $\beta$ value is very small in these systems [compare $\beta$(Li$_2$) with $\beta$(H$_2$) in Table 6.2] the destabilizing effect of the repulsion between the two bonding electrons in Li$_2$ overbalances the difference between $\beta$ and $2\beta$ in going from Li$_2^+$ to Li$_2$. An examination of H$_2$ and H$_2^+$ at a distance $R \sim 2.5 \alpha_0$, where the $\beta$ values are considerably smaller in magnitude than at $R_e$, shows that the binding energy of H$_2^+$ at that distance is greater than that of H$_2$.

6.1.5 VB treatment

Application of the VB method to homonuclear diatomics is based on direct extension of the formulation given for H$_2$. Each bond is treated individually and an electron-pair function is written for it. The AO’s are categorized either as doubly occupied orbitals which do not contribute to bonding or singly occupied orbitals which do. Taking N$_2$ as an example, we have to consider the three singly occupied 2p orbitals on each atom, the 1s and 2s orbitals being doubly occupied. Using the same overlap arguments as in MO theory, we expect valence bonds to be formed between (2p$_{x\alpha}$, 2p$_{y\alpha}$), (2p$_{x\beta}$, 2p$_{y\beta}$), and (2p$_{x\alpha}$, 2p$_{y\beta}$). The resulting wave function for the N$_2$ bonds is

$$\left[2p_{x\alpha}(1) 2p_{x\beta}(2) + 2p_{y\alpha}(2) 2p_{y\beta}(1)\right]$$

$$\times \left[2p_{x\alpha}(3) 2p_{y\alpha}(4) + 2p_{x\beta}(4) 2p_{y\beta}(3)\right]$$

$$\times \left[2p_{x\alpha}(5) 2p_{y\alpha}(6) + 2p_{x\beta}(6) 2p_{y\beta}(5)\right]$$

where antisymmetrization of the overall function (including doubly occupied orbitals and spin) will be required to give a complete description satisfying the Pauli principle. The VB result agrees with the MO conclusion that there is a triple bond in N$_2$. Corresponding VB functions can be written down for other homonuclear diatomics (Problem 6.2.).

6.1.6 Spin multiplicity and term symbols

There is no ambiguity in the spin states predicted by the simple MO ground-state configurations for the molecules and ions in Table 6.2, with the exception of C$_2$ and O$_2$. For example, the molecules H$_2$, He$_2$, Li$_2$, Be$_2$, B$_2$, N$_2$, F$_2$, and Ne$_2$ all have two electrons in each occupied orbital, and since the Pauli principle requires that their spins be paired, these molecules are all predicted by the simple MO theory to be singlets. The molecule ions H$_2^+$, He$_2^+$, and O$_2^+$ have one singly occupied orbital and are doublets. In the ground-state configurations of C$_2$ and O$_2$, however, a twofold degenerate level (2p$_x$ in the case of C$_2$ and 2p$_x^*$ in the case of O$_2$) is occupied by two electrons in the simple MO theory. If both electrons were to occupy the same orbital, the spins would have to be paired and the state would be a singlet; if each of the two orbitals were singly occupied, the state could be a singlet or a triplet, depending on whether the spins are opposed or parallel. Extension of Hund’s first rule (Section 4.6.2), which was introduced for the atomic case, to MO’s suggests that both C$_2$ and O$_2$ are expected to be triplets. From our discussion of He(1s$^2$2s) in

Chapter 4, we know that both states with two singly occupied orbitals should be more stable than that with a doubly occupied orbital, since the electron repulsion is less if two electrons are in different orbitals. Of the two states with singly occupied orbitals, the triplet is more stable because the antisymmetric triplet wave function is small when the two electrons are near one another; that is, the average electron-electron repulsion energy $(e^2/ru)$ is expected to be smaller for a pair in a triplet state than in a singlet state. Since all of these arguments are equally valid for atoms and molecules, Hund’s rule of maximum spin multiplicity should hold for both.

Term symbols for homonuclear diatomic molecules are obtained by a procedure corresponding to that used for many-electron atoms. The term symbol is written $2S + 1 \Lambda$, where $2S + 1$ is the multiplicity (1 for singlet, 2 for doublet, etc.) and $\Lambda$ is the magnitude of the total electronic angular momentum about the molecular axis; that is,

$$M = m_1 + m_2 + \cdots$$

$$\Lambda = |M|$$

where $m_1$, $m_2$, . . . are the $z$-component quantum numbers of the occupied MO’s. As in the orbital designations, Greek letters are used for $\Lambda$; that is,

$$\begin{array}{ccccccc}
\lambda & 0 & 1 & 2 & 3 & \cdots \\
\Sigma & \Pi & \Delta & \Phi & \cdots \\
\end{array}$$

Also, a subscript $g$ or $u$ is often included to indicate the symmetry of the total wave function with respect to inversion through the origin, chosen at the center of symmetry (i.e., midpoint) of the molecule. By inversion we mean that a point $P$ (see Fig. 6.7) is replaced by its inverse $\bar{P}$; that is, if the

![Fig. 6.7](image_url)

Fig. 6.7. The inversion operation in Cartesian and polar coordinates. The point $P$ is obtained by inversion of the point $P$. .
coordinates of \( P \) are \( x, y, z \), those of \( P' \) are \(-x, -y, -z\). From Fig. 6.7 we see that in polar coordinates inversion replaces the wave function \( \chi(r, \theta, \phi) \) by \( \chi(r, \pi - \theta, \pi + \phi) \). Each MO either does or does not change sign under inversion; if it does change sign, it is given the symbol \( u \) (ungerade) and if it does not, it is given the symbol \( g \) (gerade). The \( u, g \) symmetries of the MO's are shown in Figs. 6.8 and 6.9. All \( \sigma \) bonding orbitals are \( g \) and \( \sigma \) antibonding orbitals are \( u \). However, the \( \pi \) orbitals behave oppositely; that is, the \( \pi \) bonding orbitals are \( u \) and the \( \pi \) antibonding orbitals are \( g \), as is evident from Fig. 6.9. If there are any number of electrons in orbitals of \( g \) symmetry and an even number of electrons with \( u \) symmetry, the over-all wave function is \( g \) (i.e., does not change sign if all \( x, y, z \) are replaced by \(-x, -y, -z\)), while if there are an odd number of electrons in orbitals of \( u \) symmetry the over-all wave function is \( u \) (does change sign if all \( x, y, z \) are replaced by \(-x, -y, -z\)).

As examples of the determination of term symbols for homonuclear diatomics, we consider the ground state of \( \text{O}_2^+ \) and several states of \( \text{O}_2 \). The ground-state term symbol for \( \text{O}_2^+ \) requires consideration only of \( 2p\pi^* \) (\( 2p\pi^* \)) since all lower-energy electrons are in closed shells or subshells. The bonding \( 2p\pi \) orbitals are doubly occupied so that the electron spins are paired, and the unpaired electron in the antibonding orbital gives rise to a doublet because \( 2S + 1 = 2 \) for \( S = \frac{1}{2} \). According to Fig. 6.9 the \( 2p\pi \) orbital is ungerade \((u)\) and the \( 2p\pi^* \) orbital is gerade \((g)\); since there are an even number of electrons in the ungerade orbitals, the over-all symmetry is gerade. Only the \( \pi \) electrons can contribute to the angular momentum about the \( z \) axis. In the filled \( 2p\pi \) level, two electrons have \( m = -1 \) and two have \( m = +1 \); thus the contribution from the \( 2p\pi \) electrons is zero. The unpaired \( 2p\pi^* \) electron therefore determines the orbital electronic angular momentum of the molecule; that is, \( \Delta = |m| = 1 \). The resulting term symbol for \( \text{O}_2^+ \) is \( ^1\Pi \).

The lowest \( \text{O}_2 \) electron configuration is \( (2p\sigma)^4 (2p\pi^*)^2 \). According to Hund’s rules, in the ground state the additional electron (relative to \( \text{O}_2^+ \)) goes in the other of the two degenerate \( 2p\pi^* \) orbitals with its spin parallel to that of the first electron. Consequently, \( S = 1 \) and the state is a triplet. Since there are still an even number of electrons in \( \pi \) orbitals, the over-all symmetry is \( g \). The quantum number \( \Delta = 0 \), so one \( 2p\pi^* \) electrons
has \( m = 1 \) and the other \( m = -1 \). The term symbol is \( \Sigma_2^- \). There is, however, an additional symmetry property that must be considered to completely specify \( \Sigma \) states of linear molecules, namely, whether the wave function changes sign (\(-\)) or does not change sign (\(+\)) upon reflection in a plane through the nuclei (e.g., a vertical plane such as that shown in Fig. 6.10). To find out whether the over-all wave function is \(+\) or \(-\), consider the effect of such a reflection upon each orbital. If there is a nonzero angular momentum about the \( z \) axis associated with an orbital (e.g., \( \pi, \delta \ldots \)), reflection in a plane through the \( z \) axis converts the orbital into its degenerate partner (see Fig. 6.10). In the case of a \( \sigma \) orbital, the reflection leaves the orbital unchanged. The ground-state \( \Omega_2 \) triplet wave function must, of course, be antisymmetric with respect to exchange of the coordinates of any pair of electrons; moreover, the \emph{spatial} part of the wave function must be antisymmetric, since for a triplet state the \emph{spin} part is symmetric (see Section 4.3). Since reflection in a vertical plane interchanges the orbitals \( (2p\pi^*)_{+1} \) and \( (2p\pi^*)_{-1} \), where the subscript indicates the \( m \) quantum number, the effect is the same as an exchange of the labels of the two electrons occupying these orbitals, and the over-all antisymmetrized wave function changes sign. Thus, the complete ground-state term symbol for \( \Omega_2 \) is \( \Sigma_2^- \). Note that the \( \pm \) symmetry need be considered only for \( \Sigma \) states, since for states with \( \Lambda \neq 0 \), reflection of the wave function in a plane through the nuclei changes the sign of \( M \); that is, one member of the degenerate pair of states is transformed into the other.

In addition to the ground-state term \( \Sigma_2^- \), the configuration \( (2p\pi^*)^3 \) gives rise to two others. If both electrons occupy the same degenerate orbitals, the value of \( \Lambda \) is 2 and the state is \( \Delta_2 \). If the electrons occupy different degenerate orbitals and have the antisymmetric singlet spin function \( \{a(1)\beta(2) - \beta(1)a(2)\} \), the coordinate wave function is symmetric with respect to exchange of electrons between the two orbitals (see Section 4.3) and the term symbol is \( \Sigma_2^+ \).

Application of the rules given above to the homonuclear diatomics yields the term symbols listed in Table 6.3. From a comparison between the predicted and observed term symbols, we see that the simple MO's appear to be appropriate for most of the diatomic species (i.e., \( H_2^+, \ H_2^-, \ He_2^+, \ Li_2, \ N_2, \ O_2, \ O_2^+, \ F_2 \)) but not all (i.e., the predicted term symbols are wrong for the ground states of \( B_2, \ C_2, \) and \( N_2^+ \)). To find the source of these discrepancies, we recall that in the homonuclear diatomic molecule correlation diagram (Fig. 6.5) there is an uncertainty about the relative energies of the bonding MO's formed from the \( 2p\sigma \) and \( 2p\pi \) AO's; that is, although in the large distance limit \( (R \to \infty) \), \( 2p\pi \) is lower than \( 2p\sigma \), the energies are expected to cross at a smaller distance. In determining the molecular configurations on which the term symbols are based, we have assumed that \( 2p\sigma \) is more stable than \( 2p\pi \) in all cases (Table 6.2). If we reverse the order, we obtain the configurations listed in Table 6.3, where the orbitals are identified by their \( g \) and \( u \) symmetry rather than by their bonding and antibonding character. The term symbols resulting from these configurations agree with the observed values given in Table 6.3. For ground-state \( N_2, \ O_2^+, \) and \( O_2 \), both \( 2p\pi_a \) and \( 2p\pi_e \) are completely filled, so that the configuration in the ground state is \( \Omega_2 \) independent of the level ordering. Experimental data for excited states suggest that in \( N_2 \) the \( 2p\pi_a \) orbital is more stable than \( 2p\pi_e \), while in \( O_2^+ \) and \( O_2 \) the reverse order holds. This behavior appears reasonable in terms of the correlation diagram since the \( \Delta_2^+ \) and \( \Omega_2 \) equilibrium internuclear distances are larger than that of \( N_2 \).

A quantitative understanding of the factors determining the energy-level ordering requires a more detailed consideration of MO theory. We present an introductory discussion in the following subsection.

6.1.7 Self-consistent-field orbitals In formulating the MO's for homonuclear diatomic molecules, we have so far assumed that only the same orbitals on the two atoms interact (only \( 2s_A \) with \( 2s_B \), \( 2p_{\alpha_A} \) with \( 2p_{\alpha_B} \), etc.) To obtain a more accurate description, we have to combine these orbitals with other AO's whose overlap with them is nonzero and which can thus contribute to the MO. This turns out that for homonuclear diatomic molecules, all AO's with a given \( m \) quantum number should be included. The resulting MO then is identified by the quantum number \( \lambda = |m| \) (\( \sigma, \pi, \delta \), etc.). For example, the \( \sigma \)-type MO's (\( \lambda = 0 \)) are constructed from the "occupied" \( \sigma \) orbitals \( 1s_A, 1s_B, 2s_A, 2s_B, \) and \( 2p_{\sigma_A}, \) and \( 2p_{\sigma_B} \), and even the "unoccupied" orbitals such as \( 3s_A, 3s_B, 3p_{\sigma_A}, 3p_{\sigma_B}, 3d_{\sigma_A}, 3d_{\sigma_B} \ldots \). Since in