有關相作用軌域能階差異的影響

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爲了提供一點點數學的背景，來支持我在課堂上所說：相互作用的兩軌域能階越接近時，作用力越大，生成的鍵結軌域能階下降得愈多，反之則愈小，特節錄 Atkins, P.; Friedman, R. *Molecular Quantum Mechanics*; Oxford University Press: New York; 4th ed., 2005，一書中相關的說明供各位參考：

First, to participate significantly in bond formation, *atomic orbitals must be neither too diffuse nor too compact*. In either case, there would be only weak constructive or destructive overlap between neighbouring atoms, and only feeble bonds would result. It follows that in Period 2, (1*s*,1*s*)-overlap can be largely neglected in comparison with (2*s*,2*s*)-overlap, for 1*s*-orbitals are too compact to have significant overlap with each other. Indeed, it is generally safe, for qualitative discussions at least, to consider only overlap between orbitals of the valence shell, for only these orbitals are neither too compact nor too diffuse to have significant overlap.

Second, *the energies of the orbitals should be similar*. To see why this is so, consider the following secular determinant for the bond formed between two different atoms A and B:

alpha與beta是實驗可取得之參數，S = 0，現階段別管它，重要的E是要解的 MO 軌域能階

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0 \qquad (8.32)$$

The roots are found by solving the quadratic equation for the energy, and when $|\alpha_A - \alpha_B| \gg \beta$ and $S = 0$ they are

$$E_+ = \alpha_A - \frac{\beta^2}{\alpha_B - \alpha_A} \qquad E_- = \alpha_B + \frac{\beta^2}{\alpha_B - \alpha_A} \qquad (8.33)$$

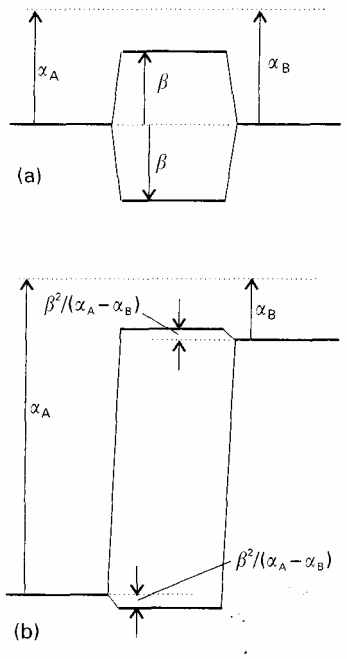

Fig. 8.17 The molecular orbital energy levels stemming from atomic orbitals of (a) the same energy, (b) different energy.

These results (which are illustrated in Fig. 8.17) show that the molecular orbital energies are shifted from the atomic orbital energies (α_A and α_B) by only a small amount when α_A and α_B are very different. The implication is that in homonuclear diatomic molecules, the atomic orbitals of identical energy dominate the bonding. The strongest bonds will therefore have compositions such as (2*s*,2*s*) and (2*p*,2*p*), and there is no need (for qualitative discussions, at least) to consider (2*s*,1*s*) and (2*p*,1*s*) contributions. There is normally insufficient energy difference between 2*s*- and 2*p*-orbitals for it to be safe to ignore (2*s*,2*p*) contributions, although in elementary accounts that is often adopted as an initial approximation.

With these rules in mind, it is quite easy to set up a plausible molecular orbital energy level diagram for the Period 2 homonuclear diatomic molecules. We consider only the valence orbitals (and, in due course, the electrons they contain). From the four atomic orbitals of Σ symmetry (the 2*s*- and $2p_z$-orbitals on each atom), we can form four linear combinations; these are the four σ-orbitals marked on the diagram. To a first approximation we can think of the 2*s*-orbitals as forming bonding and antibonding combinations and the $2p_z$-orbitals as doing the same. However, it is better to think of all four combinations as formed from the four atomic orbitals, with increasing energy from the most bonding combination ($1\sigma_g$) to the most antibonding combination ($2\sigma_u$). All four σ-orbitals have mixed 2*s*- and $2p_z$-orbital character, with the lowest energy combination predominantly 2*s*-orbital in character and the highest energy combination predominantly $2p_z$. The four orbitals with Π symmetry likewise form four combinations, but because they span the two-dimensional irreducible representation, they fall into two doubly degenerate sets, which we call $1\pi_u$ and $1\pi_g$. It is hard to predict the order of energy levels, particularly the relative ordering of the σ and π sets, but it is found experimentally and confirmed by more detailed calculations that the order shown on the left of Fig. 8.18 applies from Li_2 to N_2, whereas the order shown on the right applies to O_2 and F_2.

請讀者不要介意式 8.32，只要看由之導出的式 8.33，此式顯示生成的分子軌域中，鍵結軌域能階 E_+ 與反鍵結軌域能階 E_- 的大小，相較於組成此一分子的兩個原子軌域的能階(α_A, α_B)而言，其差異是 $\beta^2/(\alpha_A-\alpha_B)$ (請參考圖 8.17)。因此兩個原子軌域的能階差異越大$\beta^2/(\alpha_A-\alpha_B)$就越小。

另外請特別讀一下上文倒數第五行開始的文句，有助於我們對 Li_2 到 F_2 所看到的分子軌域能階變化，所該抱持的態度。

上述之說明是簡化的計算, 實際上 S 即為課堂上簡略提到的 overlap integral , 並非為零, 將之考慮進去時所得到的數學形式將顯示 E- 能階上升的幅度是較大的。