

The hydrogen molecule

The simplest function puts two electrons in the orbital $\phi = N(1s_A + 1s_B)$:

$$\Phi = \mathcal{A}\phi(1)\alpha(1)\phi(2)\beta(2) = \phi(1)\phi(2) \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)],$$

where \mathcal{A} is the antisymmetrizer. This is the **molecular orbitals** (MO) approach, which is easily extended to larger molecules.

The experimental molecular parameters are $R_e=0.74 \text{ \AA}$, $D_e=4.75 \text{ eV}$. The function above gives 0.84 \AA and 2.65 eV . Optimizing the $1s$ exponent at each R improves the results to 0.73 \AA and 3.49 eV . The Hartree-Fock function (best molecular orbitals) gives 0.73 \AA and 3.63 eV , still 1.12 eV off the experimental D_e . The remaining error is due to correlation. For molecular systems we can see that the neglect of correlation leads to other problems too. If we write the MOs explicitly, the spatial part of Φ is

$$\begin{aligned} \phi(1)\phi(2) &= \frac{1}{2(1+S)}[1s_A(1) + 1s_B(1)][1s_A(2)1s_B(2)] = \\ &= \frac{1}{2(1+S)}[1s_A1s_A + 1s_A1s_B + 1s_B1s_A + 1s_B1s_B]. \end{aligned}$$

When the molecule dissociates ($R \rightarrow \infty$), the second and third terms in this sum describe dissociation to two neutral H atoms, whereas the first and last terms correspond to dissociation to $H^+ + H^-$, with both electrons on the same nucleus. If this were true, the dissociation of H_2 would have equal probability to produce two neutral atoms or two ions. This is a very poor result: since it takes 13.6 eV to ionize the H atom, and its electron affinity is 0.75 eV , the ion pair is higher by $\sim 13 \text{ eV}$ than two

neutral atoms. The physical reason for this is neglect of correlation. The second electron “knows” only the average distribution of the first, with equal probability on each nucleus, but not its actual location. It therefore chooses the nuclei with equal probability, and has a 50% chance of ending up on the same nucleus as the first electron. This is a general phenomenon, and MO single determinant functions are thus not suitable for describing the whole potential surface. The region around the equilibrium configuration is usually described with reasonable accuracy. Hartree-Fock functions also give in most cases a good description of one-electron properties, such as dipole moments and charge distribution. On the other hand, binding energies come out 30–50% too low. The reason is that forming bonds usually involves new electron pairs with more correlation energy, so that the estimate of the binding energy of the molecule AB by the difference between its Hartree-Fock energy and that of atoms A and B is too low. A notorious example is that of the F_2 molecule, which has a rather low D_e . The difference in correlation energy between the atom and molecule is sufficient to produce a **negative** binding energy.

The Valence Bond method

This was actually the first method used (1927) to study molecular structure, predating MO by one year. It has the advantage of giving molecular descriptions close to chemical concepts, and makes better predictions than MO. Its major problem is the difficulty of application to any but the smallest molecules. The vast majority of quantum chemical application use some form of MO methods.

The simplest way to describe the H₂ molecule is by the function

$$1s_A(1)1s_B(2), \quad 1s = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-r/a_0}.$$

However, this form ignores the basic assumption that electrons are indistinguishable. To allow for this property and for the antisymmetry with respect to interchanging the electrons, we must use the form

$$\Psi = N[1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}.$$

The normalization constant N is obtained by

$$1 = \int \Psi^2 d\tau = N^2 \int [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)]^2 d\tau = 2 + 2S^2,$$

where $S = \int 1s_A(1)1s_B(1)d\tau(1)$, giving $N = \frac{1}{\sqrt{2(1+S^2)}}$. The energy is

$$E = \int \Psi H \Psi d\tau = \frac{1}{2(1+S^2)} \left\{ 2 \int 1s_A(1)1s_B(2)H1s_A(1)1s_B(2)d\tau + 2 \int 1s_A(1)1s_B(2)H1s_B(1)1s_A(2)d\tau \right\} = \frac{J' + K'}{1+S^2}.$$

J' is the Coulomb integral, which describes an interaction between two charge distributions, $1s_A^2$ and $1s_B^2$ in the present case. K' is the exchange integral, which appears here because of the indistinguishability of identical particles in quantum mechanics. It may be shown that the energy is also

$$E = 2E_H + \frac{J + K}{1+S^2},$$

where E_H is the energy of an H atom, and J and K are Coulomb and exchange integrals with the interaction ΔH , which includes

the terms in the molecular Hamiltonian which do not appear in the separate atoms,

$$\Delta H = -\frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}.$$

This form shows the energy change from separate atoms to molecule. It is interesting to note that both $J(R)$ and $K(R)$ give functions with minima and contribute to the binding energy, but the contribution of J is far smaller (in absolute value) than that of K . This may explain the fact that attempts to explain molecular binding using classical mechanics failed.

Note that another combination with the proper symmetry is

$$N[1s_A(1)1s_B(2) - 1s_B(1)1s_A(2)].$$

This function is antisymmetric under electron exchange, and the spin part must therefore be symmetric. There are three such functions:

$$\alpha(1)\alpha(2), \quad \alpha(1)\beta(2) + \beta(1)\alpha(2), \quad \beta(1)\beta(2),$$

which correspond to a **triplet** state. The energy of the state is

$$E_T = \frac{J' - K'}{1 - S^2} = 2E_H + \frac{J - K}{1 - S^2}.$$

The potential curve is repulsive, and the state is not bound.

The parameters given by the ground state function are $R_e=0.80 \text{ \AA}$, $D_e=3.20 \text{ eV}$. Comparing with experiment (0.74 \AA and 4.75 eV), we see that the VB values are better than MO at the same level. Here again we can improve the function by optimizing the exponent of the $1s$ orbital and adding more functions. A few results are shown in the table:

	$R_e(\text{\AA})$	$D_e(\text{eV})$
exp	0.74	4.75
MO: e^{-r/a_0}	0.84	2.65
$e^{-\alpha r/a_0}$	0.73	3.49
HF	0.73	3.63
VB: e^{-r/a_0}	0.80	3.20
$e^{-\alpha r/a_0}$	0.74	3.78
$+2p_z$	0.74	4.04

Since H_2 is a very small molecule, it is possible to get highly accurate results. James and Coolidge proposed in 1933 a function written in the elliptical coordinates

$$\xi = \frac{r_A + r_B}{R}, \quad \eta = \frac{r_A - r_B}{R}, \quad \varphi.$$

The function is an exponential multiplied by a polynomial in these coordinates,

$$\Psi = \sum_{pqrst} c_{pqrst} (\xi_1^p \eta_1^q \xi_2^r \eta_2^s + \xi_1^r \eta_1^s \xi_2^p \eta_2^q) r_{12}^t e^{-\alpha(\xi_1 + \xi_2)}.$$

The function is less frightening than it looks. The 1st term in the parentheses is a monomial in ξ and η (p, q, r, s, t are small non-negative integers), the second term is needed to make the function symmetric to electron interchange, r_{12} is the interelectron separation, the inclusion of which is the most straightforward way to take care of correlation, and the exponential is known to determine the behavior of the electrons. 13 terms of this type were chosen carefully and the linear coefficients c were optimized. The dissociation energy obtained was 4.72 eV. The function was extended to 40 terms in 1960, giving accuracy equal to or better than experiment.

Like in the He case, the goal is not so much to match experimental accuracy as to make sure we know everything about the forces and effects in the system. An added benefit in the molecular case is the treatment of excited states with similar methods and accuracy. Excited states cannot be studied directly by experiment. What one measures is spectroscopic transitions of various types (electronic, vibrational, rotational), and interprets them to extract structure information. For these states, James-Coolidge-type functions provide more and better information than experiment.

Diatomic molecules

The terms (energy levels) of diatomic molecules are built in a similar manner to atoms. They are classified and named by the value of L_z , denoted Λ : $\Lambda=0,1,2$ give Σ, Π, Δ states, respectively. Closed shells always give $^1\Sigma$ levels. If we look at the open shell π^2 configuration, it has 4 spinorbitals ($\pi_{\pm 1}$, with spins α and β), therefore $\frac{4 \cdot 3}{2} = 6$ determinants. Λ is simply the sum over electrons $\sum_i \lambda_i$.

M_S	$\Lambda = 2$	0	-2
1		$\pi_1\alpha\pi_{-1}\alpha$	
0	$\pi_1\alpha\pi_1\beta$	$\pi_1\alpha\pi_{-1}\beta$ $\pi_{-1}\alpha\pi_1\beta$	$\pi_{-1}\alpha\pi_{-1}\beta$
-1		$\pi_1\beta\pi_{-1}\beta$	

Note that L_z is **not** an angular momentum. As a result, Λ does not have to change in steps of 1. We follow the same scheme as for atoms. The extreme function $\pi_1\alpha\pi_{-1}\alpha$ represents a $^3\Sigma$ state, which has 3 components, with $\Lambda=1$ and $M_S=1,0,-1$. Another extreme state, $\pi_1\alpha\pi_1\beta$ gives a $^1\Delta$ state, with components having $\Lambda = \pm 2$ and $M_S=0$. After the corresponding functions are deleted, there remains one function with $\Lambda = 0, M_S = 0$, which gives a $^1\Sigma$ state. The explicit form of this function may be found as follows: applying the S^- operator to the $^3\Sigma(M_S = 1)$ state $\pi_1\alpha\pi_{-1}\alpha$, in the way we did for atoms, gives

$$^3\Sigma(M_S = 0) = \sqrt{\frac{1}{2}}(\pi_1\beta\pi_{-1}\alpha + \pi_1\alpha\pi_{-1}\beta).$$

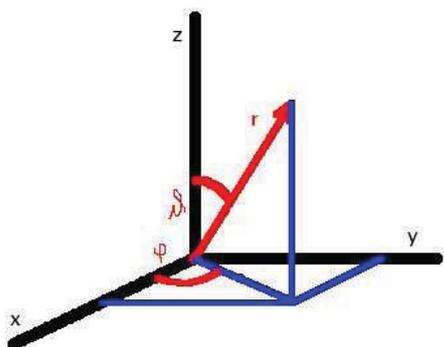
The $^1\Sigma$ state must be orthogonal to that, therefore

$$^1\Sigma(M_S = 0) = \sqrt{\frac{1}{2}}(\pi_1\beta\pi_{-1}\alpha - \pi_1\alpha\pi_{-1}\beta).$$

Σ functions have an additional symmetry. It is related to reflection in the xz plane which includes the molecular (z) axis. The angle φ is transformed by such reflection to $-\varphi$ (see graph below), and the π orbitals therefore transform by

$$\pi_1 = R(r, \theta) e^{i\varphi} \xrightarrow{\sigma(xz)} R(r, \theta) e^{-i\varphi} = \pi_{-1}.$$

R is the factor of the π orbital which depends on the r, θ coordinates.



The equation above gives

$$\sigma(xz)^1\Sigma = \sqrt{\frac{1}{2}}(\pi_{-1}\beta\pi_1\alpha - \pi_{-1}\alpha\pi_1\beta) = {}^1\Sigma,$$

where it should be remembered that each term in the parenthesis is actually a determinant, so that changing orbital order involves a minus sign. The triplet functions, on the other hand, go to minus themselves under the reflection. The states are therefore denoted by ${}^1\Sigma^+$ and ${}^3\Sigma^-$. States with higher Λ do not have this symmetry, because they are always doubly degenerate. The two components may be denoted $+$ and $-$, but they mix freely and this distinction is meaningless.

Non-equivalent electrons

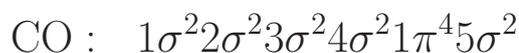
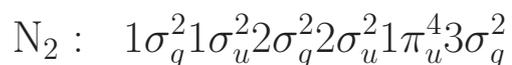
Here we can simply combine the λ values, adding and subtracting them. Remember that λ does not represent angular momentum, so no vector addition is done. Taking the $\pi\delta$ configuration, with λ_i values of ± 1 and ± 2 , the total Λ can be

± 1 and ± 3 , giving Π and Φ states. The spins of the two electrons are added vectorially to $S = 0, 1$, so that the levels of the system will be ${}^1, {}^3\Pi$ and ${}^1, {}^3\Phi$.

$\pi\pi'$ is also a configuration with nonequivalent electrons. The addition and subtraction of the λ_i values, both of which are ± 1 , gives $\Lambda = \pm 2, 0, 0$, and the resulting terms are ${}^1, {}^3\Delta$ and two sets of ${}^1, {}^3\Sigma$. Further analysis shows that the Σ states are ${}^1, {}^3\Sigma^+$ and ${}^1, {}^3\Sigma^-$.

Heteronuclear diatomic molecules

Here it is not possible to give a scheme applicable to all molecules of this type. The two atoms may be close to each other, as in CO, or far away, as in HCl. The structure of CO is not very different than that of N_2 , except that there is no inversion symmetry and the g, u classification disappears. Compare the configurations:



For HCl, the $1s^2 2s^2 2p^6 3s^2$ electrons of the Cl atom have considerably lower energies than the $1s$ on H, so they do not change much when HCl is formed. They are **inner shell** orbitals. The bond is formed between the $H1s$ and $Cl3p_z$. The $Cl 3p_x$ and $3p_y$ are in the valence shell, but there are no hydrogen orbitals of the right symmetry and energy to combine with them, so they remain largely atomic. Such orbitals are **non-bonding**, and the electrons in them form **lone pairs**. The configuration of the HCl ground state is thus



Note that the bonding orbital $3p_{zCl} + k1s_H$ is not an equal

mix of the two AOs. We know that Cl is more electronegative than H, and expect k to be smaller than 1. There is also an antibonding orbital, $3p_{zCl} - k'1s_H$, which is not occupied in the ground state.