

Linear Combination of Atomic Orbitals (LCAO)

1 Introduction

Little drops of water make a mighty ocean

We begin this study of the solid state by studying a diatomic molecule. Once this is understood we can build up to larger molecules and even bio-molecules. In fact if our cluster of atoms is sufficiently large, say a thousand, we may begin to understand nanosystems. This is still a far cry from the number of atoms one finds in a microchip. However the language and insights we gain from the diatomic molecule will stand us in good stead when in our study. You may recall that the two level system plays a seminal role in many fields of physics. The Ising model and the study of two level dynamics in lasers are good examples.

When two atoms are brought close enough their atomic orbitals overlap and the existing energy levels get modified. However, the total number of states are conserved. That is - no states disappear and none are created. If the sum of energies of occupied states decrease as the atoms are brought together, the atoms get bound and a molecule is said to be formed. The energies of the occupied electronic states in small molecules and in solids with large number of atoms can be understood at least approximately using a Linear Combination of Atomic Orbitals (LCAO).

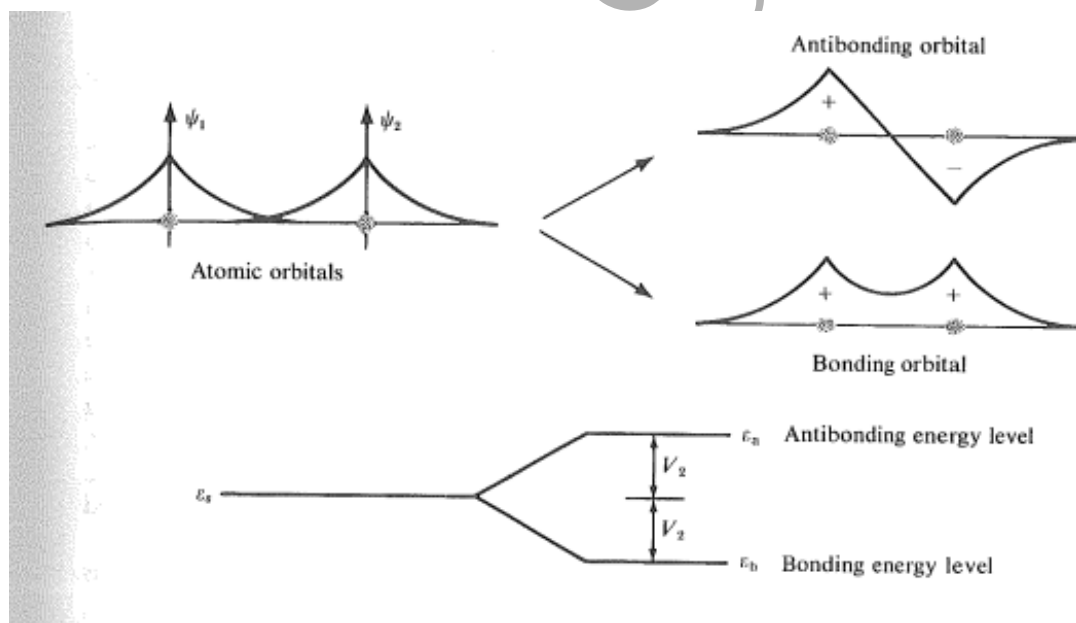


Figure 1: A Diatomic Molecule

2 Theory

The basic philosophy of the LCAO theory is that the molecular orbital $|\psi\rangle$ is formed by the linear combination of basis states of the atomic orbitals. For simplicity we take one orbital per atom and designate it by $|\alpha\rangle$ ($\alpha = 1, 2, 3, \dots, N$). Here N is the total number of orbitals (in this simplified case also the total number of atoms).

The LCAO perspective is then

$$|\psi\rangle = \sum_{\alpha} u_{\alpha} |\alpha\rangle \quad (1)$$

We then obtain,

$$\sum_{\alpha} \langle \beta | H | \alpha \rangle u_{\alpha} - E u_{\beta} = 0 \quad (2)$$

We can write it in algebraic equation form,

$$\sum_{\alpha=1}^N H_{\beta\alpha} u_{\alpha} - E u_{\beta} = 0 \quad (3)$$

where $H_{\beta\alpha} = \langle \beta | H | \alpha \rangle$ and $\beta = 1, 2, \dots, N$.

Or in matrix form,

$$\begin{bmatrix} H_{11} - E & H_{12} & \cdot & \cdot & \cdot & H_{1N} \\ H_{21} & H_{22} - E & \cdot & \cdot & \cdot & H_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ H_{N1} & H_{N2} & \cdot & \cdot & \cdot & H_{NN} - E \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ \cdot \\ \cdot \\ \cdot \\ u_N \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{bmatrix}$$

A solution exists provided the corresponding determinant is zero.

$$\text{Det}[H_{\beta\alpha} - E\delta_{\alpha\beta}] = 0 \quad (4)$$

3 Examples

Let us now apply LCAO formalism to few examples.

3.1 Diatomic Homopolar Molecule (Orthogonal Case)

We first apply this to diatomic molecule (say hydrogen-like) with two electrons. For this molecule we use two orbitals $|1\rangle$ and $|2\rangle$.

So $|\alpha\rangle : 1, 2$

.

We define $H_{\alpha\alpha} = \langle 1 | H | 1 \rangle = \langle 2 | H | 2 \rangle = \epsilon_s$

and $H_{21} = H_{12} = -V_2$.

The matrix element $-V_2$ is called covalent energy. Note V_2 is positive.

Equation (6) when applied to this example yields,

$$\begin{aligned}(\epsilon_s - E)u_1 - V_2u_2 &= 0 \\ -V_2u_1 + (\epsilon_s - E)u_2 &= 0\end{aligned}$$

We pause to note that this may also be expressed in terms of the Pauli matrices and the Identity matrix as

$$((\epsilon_s - E)\hat{I} - V_2\hat{\sigma}_x)\bar{u} = 0.$$

Then,

$$\text{Det} \begin{pmatrix} \epsilon_s - E & -V_2 \\ -V_2 & \epsilon_s - E \end{pmatrix} = 0$$

$$\implies E = \epsilon_s \pm V_2$$

We define the state with the lower energy $\epsilon_b = \epsilon_s - V_2$ as the bonding state. For this value of E , $u_1 = u_2 = 1/\sqrt{2}$

The state with the higher value of energy $\epsilon_a = \epsilon_s + V_2$ is termed the anti-bonding state. Corresponding to this value of E , we can show that $u_1 = -u_2 = 1/\sqrt{2}$.

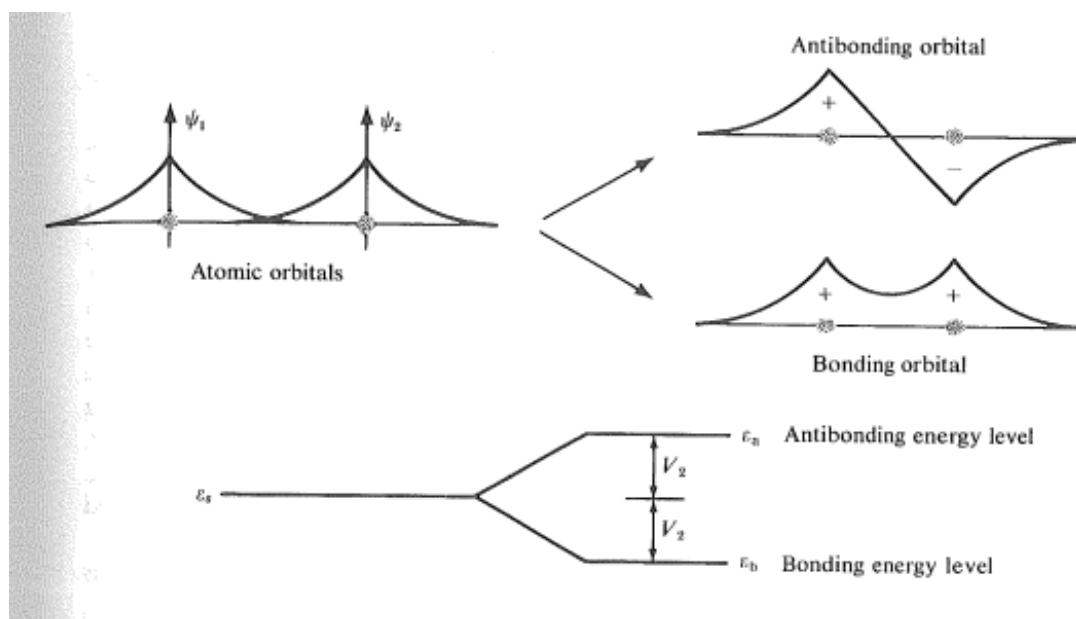


Figure 2: Homopolar Diatomic Molecule

Figure 2 suggests that for the bonding state the electron population is evenly divided between the two atoms. The anti-bonding state is orthogonal to the bonding state. Please note that we have used orthogonal eigenfunctions for the two atomic states, i.e., the overlap $\langle 1|2 \rangle = 0$.

3.2 Homopolar diatomic molecule (Non-orthogonal Case)

The atomic orbitals are usually of the exponential type (recall hydrogenic orbitals) and are called Slater type orbitals (STO). They are normalized but not orthogonal. We consider the homopolar case where the overlap between the atomic orbitals on the two atoms is given by S where $0 < S < 1$, e.g.

$$\langle 1|2\rangle = S = \langle 2|1\rangle$$

$$\langle 1|1\rangle = \langle 2|2\rangle = 1$$

For the homopolar case, the wavefunction

$$|\psi\rangle = u_1 |1\rangle + u_2 |2\rangle$$

The equations for the non zero overlap case are

$$\begin{pmatrix} \epsilon_s & -V_2 \\ -V_2 & \epsilon_s \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$

Without loss of generality we can take $\epsilon_s = 0$, then

$$\begin{pmatrix} -E & -V_2 - ES \\ -V_2 - ES & -E \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = 0$$

Then the determinantal condition yields

$$E^2 - (V_2 + ES)^2 = 0$$

$$E^2(1 - S^2) - 2V_2ES - V_2^2 = 0 \quad (5)$$

Solving this equation to find E , we get

$$\begin{aligned} E &= \frac{2V_2S \pm \sqrt{(2V_2S)^2 + 4(1 - S^2)V_2^2}}{2(1 - S^2)} \\ &= \frac{V_2S \pm V_2}{(1 - S^2)} \\ &= \frac{V_2(S \pm 1)}{(1 - S^2)} \end{aligned}$$

That is,

$$E = \frac{V_2}{(1 - S)}, \quad -\frac{V_2}{(1 + S)} \quad (6)$$

Assigning these values respectively to antibonding and bonding levels, we get

$$E_a = \frac{V_2}{(1 - S)} \text{ and } E_b = -\frac{V_2}{(1 + S)} \quad (7)$$

therefore the energy difference is

$$\Delta E = E_a - E_b = \frac{V_2}{(1 - S)} + \frac{V_2}{(1 + S)} \quad (8)$$

$$= \frac{2V_2}{1 - S^2} \quad (9)$$

The energy difference, when compared to the simple orthogonal case is enhanced.

When S is small, S^2 is smaller. In that case

$$\Delta E \simeq 2V_2(1 + S^2)$$
 (lowest correction is of order S^2)

If $S = 0.5$ then the gap is enhanced by 25%. If we set $S = 0$ we regain the orthogonal result.

Some References

- 1) R. S. Mulliken *Rev. Mod. Phys.* **2** 506 (1930); **3** (1931); **4** (1932).
- 2) John P. Lowe *Quantum Chemistry* Academic Press Inc. London (1978).
- 3) Walter A. Harrison *Electronic Structure and the Properties of Solids* W. H. Freeman and Company, San Francisco (1980).
- 4) R. P. Messmer (*Phys. Rev. B* **15** 1881, 1976 where the non-orthogonal case $S = \alpha I + \beta H$ is worked out in the Appendix.
- 5) Vijay A. Singh, C. Weigel, J. W. Corbett and L. M. Roth *Phys. Stat. Sol. (b)* **81** 637 (1977). Here the equations of LCAO for silicon clusters with defects along with the inputs for the Hamiltonian matrix elements and the overlaps are clearly spelled out and sample calculations presented in detail.