Tight Bonding

A single atom traps its electrons in the nuclei's Coulomb well, such that the stationary states of the electrons are localized around the atom. One way atoms can bind to form a molecule is to combine their Coulomb wells to allow de-localized stationary states that have lower energies than the sum of the atomic states. This type of bonding is known as **Tight Bonding**. In this section, we will explore the formation of such bonds for 2 atoms and then expand it to N atoms.

Covalent Bond

Consider a diatomic molecule. The Hamiltonian for the two electrons with positions \vec{x}_1 and \vec{x}_2 in this two-atom system is

$$\mathscr{H} = -\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial \vec{x}_1^2} + \frac{\partial^2}{\partial \vec{x}_2^2}\right) - k \frac{Z_1 e^2}{|\vec{x}_1 - \vec{X}_1|} - k \frac{Z_2 e^2}{|\vec{x}_2 - \vec{X}_2|} + k \frac{e^2}{|\vec{x}_1 - \vec{x}_2|}$$
(1)

where \vec{X}_1 and \vec{X}_2 , Z_1 and Z_2 are the positions and charges of the ions, which (under the Born-Oppenheimer approximation) are constants. The hamiltonian can be split into single particle hamiltonians with an interactions term

$$\mathscr{H} = h1(\vec{x}_1) + h2(\vec{x}_2) + V(\vec{x}_1, \vec{x}_2)$$
(2)

Suppose the two atoms have eigenstates $|1\rangle$, $|2\rangle$ with eigenvalues E_1 , E_2 which are orthogonal¹. Call $A = \langle 1 | V | 2 \rangle$, then in the $|1\rangle$, $|2\rangle$ basis

$$\mathscr{H} = \left(\begin{array}{cc} E_1 & A\\ A & E_2 \end{array}\right) \tag{3}$$

The eigensystem (given by Mathematica)

$$\begin{pmatrix} \frac{1}{2} \left(E_1 + E_2 - \sqrt{4A^2 + E_1^2 + E_2^2 - 2E_1E_2} \right) & \frac{1}{2} \left(E_1 + E_2 + \sqrt{4A^2 + E_1^2 + E_2^2 - 2E_1E_2} \right) \\ \left\{ -\frac{-E_1 + E_2 + \sqrt{4A^2 + E_1^2 + E_2^2 - 2E_1E_2}}{2A}, 1 \right\} & \left\{ -\frac{-E_1 + E_2 - \sqrt{4A^2 + E_1^2 + E_2^2 - 2E_1E_2}}{2A}, 1 \right\} \end{pmatrix}$$

$$(4)$$

The above form tempts the definitions of $\overline{E} = \frac{E_1 + E_2}{2}$ and $\epsilon = \frac{E_1 - E_2}{2}$, because then the eigensystem simplifies to

$$\begin{pmatrix} \bar{E} - \sqrt{A^2 + \epsilon^2} & \bar{E} + \sqrt{A^2 + \epsilon^2} \\ \left\{ \frac{\epsilon}{A} - \sqrt{1 + (\frac{\epsilon}{A})^2}, 1 \right\} & \left\{ \frac{\epsilon}{A} + \sqrt{1 + (\frac{\epsilon}{A})^2}, 1 \right\} \end{pmatrix}$$
(5)

¹In reality $\langle 1 | 2 \rangle \neq 0$, but it's not a horrible approximation and shows the right physics

Nice physical interpretation emerges when we consider identical atoms, in which case $\epsilon=0$

$$\begin{pmatrix}
\bar{E} - A & \bar{E} + A \\
\{-1, 1\} & \{1, 1\}
\end{pmatrix}$$
(6)

The two eigenstates are called the bongding and anti-bonding orbitals. This explains why hydrogens bind (both electrons occupy the bonding orbital, making the total energy of the molecule lower than the sum of the energies of the atoms), but heliums do not (bonding and anti-bonding orbitals are both occupied by two electrons).

Now that we have the Hamiltonian diagonalized in the atomic basis $|1\rangle, |2\rangle$ (eigenvectors $\psi_{\pm} = \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$, eigenvalues $\epsilon_{\pm} = \bar{E} \pm A$) we can calculate exactly how a single electron state evolves with time. Suppose an electron is initially localized on atom 1

$$|\psi(0)\rangle = |1\rangle = \frac{1}{\sqrt{2}}(|\psi_{+}\rangle + |\psi_{-}\rangle)$$
(7)

and we let it evolve in time

$$|\psi(t)\rangle = e^{-i\frac{\mathscr{H}}{\hbar}t} |\psi(0)\rangle = \frac{1}{\sqrt{2}} \left(e^{-i\frac{A}{\hbar}t} |\psi_{+}\rangle + e^{i\frac{A}{\hbar}t} |\psi_{-}\rangle \right)$$
(8)

The probability of it still being localized on atom 1

$$P_1 = |\langle 1 | \psi(t) \rangle|^2 = \cos^2(\frac{A}{\hbar}t)$$
(9)

On average $\langle P_1 \rangle = \frac{1}{2}$, that is the electron is equally likely to be localized around either atom.

1D Lattice

Consider a 1D lattice of identical atoms with atomic orbitals $|1\rangle$, $|2\rangle$, \cdots , $|N\rangle$. To see the physics without tedious math, make 3 not-so-terrible assumptions

- 1. atomic orbitals are orthonormal: $\langle i | j \rangle = \delta_{ij}$
- 2. only neighbors interact: $\langle i | \mathcal{H} | j \rangle = 0, \forall |i j| > 1$
- 3. the lattice is period: $\langle 1 | \mathscr{H} | N \rangle = \langle N | \mathscr{H} | 1 \rangle \neq 0$

The Hamiltonian in the atomic basis then looks like

$$\mathscr{H} = \begin{pmatrix} E_o & A & 0 & 0 & A \\ A & E_o & A & 0 & 0 \\ 0 & A & E_o & A & 0 \\ 0 & 0 & A & E_o & A \\ A & 0 & 0 & A & E_o \end{pmatrix}$$
(10)

The more compact notation is $\mathscr{H}_{i,j} = E_o \delta_{i,j} + A(\delta_{i+1,j} + \delta_{i-1,j})$. Of course the actual matrix is $N \times N$, and diagonalizing such a matrix would be extremely difficult. Further, in the limit of an infinite lattice, diagonalization is not possible. Therefore, we need a better way to find the eigenvalues and eigenvectors of the Hamiltonian operator.

To do so, we shall express all states in the atomic basis set and use Schrödinger's equation to find the expansion coefficients. That is, suppose an arbitrary state $|\psi\rangle = \sum_{i} c_i(t) |i\rangle$, we have

$$\mathscr{H} |\psi\rangle = i\hbar \frac{d}{dt} |\psi\rangle \Rightarrow$$

$$\sum_{i} c_{i} \langle j | \mathscr{H} | i \rangle = i\hbar \sum_{i} \left\langle j \left| \frac{d}{dt} c_{i} \right| i \right\rangle \Rightarrow$$

$$E_{o}c_{j} + A(c_{j-1} + c_{j+1}) = i\hbar\dot{c}_{j} \qquad (11)$$

If $|\psi\rangle$ is an eigenstate

$$E_o c_j + A(c_{j-1} + c_{j+1}) = E c_j$$
(12)

???? Magically $c_j = e^{ikaj}$ solves the above difference equation, and we have the eigenvalues

$$E = E_o + 2A\cos(ka) \tag{13}$$

as well as the eigenvectors

$$|\psi\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{ikaj} |j\rangle \tag{14}$$

which are plane waves that are equally likely to be localized around ANY atom in the lattice. In essence, the electron behaves as if it were free! To quantify this "free" behavior, consider the dispersion relation given by equation (13) for slow-moving electrons $k \to 0$

$$E = E_o + 2A\cos(ka) \approx E_o + 2A - Ak^2a^2 \tag{15}$$

that is, the electron has "some rest energy" $E_o + 2A$ and "kinetic energy" $-Ak^2a^2$. Normally A < 0, thus consider

$$K.E. = \frac{\hbar^2 k^2}{2m^*} = |A|k^2 a^2 \Rightarrow$$
$$m^* = \frac{\hbar^2}{2|A|a^2}$$
(16)

In other words, electrons in a tight bonding chain behaves like a free electron with conjugated mass. As |A| becomes smaller, m^* becomes bigger. Recall $A = \langle i | V | i \pm 1 \rangle$ describes how "coupled" neighbouring atoms are, so the smaller |A| is, the bigger the resistance there is for electrons to move around