From Atoms to Materials: Predictive Theory and Simulations

Week 2: Electronic Structure and Bonding of Molecules and Crystals

Lecture 2.3: Linear Combination of Atomic Orbitals

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Bonding: a more quantitative view

- Consider a collection of atoms far away from each other
  - Electronic states is the collection of atomic states
- Bring atoms together so wavefunctions overlap
  - The wavefunctions will change
  - The energy of the states will change

Energy goes down  \( \Rightarrow \) make a bond

- Consider a di-atomic molecule with like atoms (homopolar bond)
  - Approximate molecular orbital: a linear combination of atomic orbitals:

\[
\psi(\vec{r}) = a_L \psi_L(\vec{r}) + a_R \psi_R(\vec{r})
\]
Bonding: a more quantitative view at LCAO

\[ H\psi(\vec{r}) = E\psi(\vec{r}) \quad \text{with} \quad \psi(\vec{r}) = a_L\psi_L(\vec{r}) + a_R\psi_R(\vec{r}) \]

Multiply by \( Y_L \) from left and integrate over all space:

\[
\int \psi_L H(a_L\psi_L + a_R\psi_R) d^3r = \int \psi_L E(a_L\psi_L + a_R\psi_R) d^3r
\]

\[
a_L \int \psi_L H\psi_L d^3r + a_R \int \psi_L H\psi_R d^3r = E \left[ \int \psi_L^2 d^3r + \int \psi_L \psi_R d^3r \right]
\]

\[
a_L H_{LL} + a_R H_{LR} = E[1 + S_{LR}]
\]

Multiply by \( Y_R \) from left and integrate over all space:

\[
a_L H_{RL} + a_R H_{RR} = E[1 + S_{RL}]
\]

\[
H_{LL} = H_{RR} = h_0 \quad \text{Neglect Overlap}
\]

\[
H_{RL} = H_{LR} = -\frac{V}{2} \quad S_{RL} = S_{LR} = 0
\]
Bonding in homopolar diatomic molecule

In matrix form:

\[ a_L h_0 - a_R V_2 = E a_L \]
\[-a_L V_2 + a_R h_0 = E a_R \]

Eigenvalue Problem

\[
\begin{vmatrix}
  h_0 - E & -V_2 \\
  -V_2 & h_0 - E \\
\end{vmatrix} = 0 = (h_0 - E)^2 - V_2^2
\]

Eigenvalues (energies)

\[ E_1 = h_0 - V_2 \]
\[ E_2 = h_0 + V_2 \]

Eigenvectors (wavefunction)

\[ a_L = a_R \]
\[ a_L = -a_R \]
Bonding in homopolar diatomic molecule

We can use the $H_2^+$ solution to obtain a qualitative picture of diatomic H and He

Quantitative predictions require:
- Treating electron-electron interactions
- Exchange interactions (anti-symmetric nature of the wavefunction)
Let’s bring to Li-row atoms together

Adapted from: W. Harrison, “Electronic structure and the properties of solids”
Images from Wikipedia
Heteropolar diatomic molecule

\[
\begin{bmatrix}
  h_0^{(1)} & -V_2 \\
  -V_2 & h_0^{(2)}
\end{bmatrix}
\begin{bmatrix}
  a_L \\
  a_R
\end{bmatrix}
= E
\begin{bmatrix}
  a_L \\
  a_R
\end{bmatrix}
\]

Polar energy: \( V_3 = \frac{h_0^1 - h_0^2}{2} \)

Average energy of cation and anion: \( \bar{h} = \frac{h_0^1 + h_0^2}{2} \)

Energies:
\[
E_b = \bar{h} - \sqrt{V_2^2 + V_3^2}
\]
\[
E_a = \bar{h} + \sqrt{V_2^2 + V_3^2}
\]

See HW assignment
Additional reading

- Atoms and Molecules: An Introduction for Students of Physical Chemistry,
  M. Karplus, Richard Needham Porter

- Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond,
  Walter Harrison