Summary from last time:

Atomic orbitals are a convenient basis for describing molecular orbitals.

\[ \phi \equiv c_1 |\text{left hydrogen, 1s}\rangle + c_2 |\text{right hydrogen, 1s}\rangle \]

molecular-orbital

If the on-site energies are similar, then
- \( c_1 \) & \( c_2 \) have similar magnitude
- We see interference effects where the atomic orbitals overlap
  \[ \rightarrow \text{covalent bonds} \]

**ENERGY LEVEL DIAGRAMS FOR MOLECULAR ORBITALS**

Left side shows isolated left atom
Middle represents the molecule.
Right side represents isolated right atom

Energy

2β

This line shows that the atomic orbital is part of the molecular orbital.
Example: Use a molecular orbital energy diagram to show how to Li atoms bond together (imagine two Li atoms in vacuum, no other Li atoms nearby).

\[ \Psi = c_1 |H_1s\rangle + c_2 \left( \frac{1}{\sqrt{2}} |F_2p_x\rangle + \frac{1}{\sqrt{2}} |F_2s\rangle \right) \]

Note: The 1s bonding/anti-bonding orbitals are both filled, therefore, the 1s states aren't stabilizing the molecule.

Sometimes a hybrid MAO enters the MO.

Example: S-P HYBRID ATOMIC ORBITALS

H-F

\[ \Psi = c_1 |H_1s\rangle + c_2 \left( \frac{1}{\sqrt{2}} |F_2p_x\rangle + \frac{1}{\sqrt{2}} |F_2s\rangle \right) \]

standard atomic orbital

hybrid atomic orbital.
To formally figure out whether a hybrid AO plays a role, we need to solve Eqn.

Assuming that

\[ \langle H, 1s \rangle \]
\[ \langle F, 2p_x \rangle \]
\[ \langle F, 2s \rangle \]

is a complete basis, the matrix form of the Hamiltonian is

\[
H = \begin{bmatrix}
\alpha_{H,1s} & \beta_1 & \beta_2 \\
\beta_1 & \alpha_{F,2s} & \beta_3 \\
\beta_2 & \beta_3 & \alpha_{2p_x}
\end{bmatrix}
\]

Then solving \( H | \Psi_M \rangle = E | \Psi_M \rangle \) will tell us if the lowest energy state includes a mix of 2s & 2px.

Why would the 5p hybrid lower the energy of the MO?

\[ \langle H, 1s \rangle \]
\[ \langle F, 2p_x \rangle \]
\[ \langle F, 2s \rangle \]

The 5p hybrid has the biggest overlap with the \( | H, 1s \rangle \).
A useful way to visualize s-p hybrids

\[ \psi > 0 \rightarrow \psi < 0 \]

Region of constructive interference.

FROM MOLECULES TO 1-DIMENSIONAL SOLIDS

First, a qualitative picture of where we are heading:

- H₂ molecule
- H₂ molecule

\[ \uparrow E \]

(Molecular orbitals for an "H₄ molecule" (such a molecule doesn't exist in nature, but we can still calculate molecular orbitals for this configuration of atoms: \( \uparrow \uparrow \uparrow \uparrow \uparrow \)))
8 molecular orbitals formed from the 1s AOs of the 8 hydrogen atoms.

Our goal is to show, for a chain of N hydrogen atoms, that the molecular orbitals have the following energy distribution:

\[
\begin{array}{c}
\alpha \\
E \\
\alpha
\end{array}
\]

To prove this result, we start with \( H_4 \):

\[
\hat{H} = \begin{bmatrix}
\alpha_{\text{end}} & \beta & 0 & 0 \\
\beta & \alpha_{\text{mid}} & \beta & 0 \\
0 & \beta & \alpha_{\text{mid}} & \beta \\
0 & 0 & \beta & \alpha_{\text{end}}
\end{bmatrix}
\]
This Hamiltonian assumes my basic states are 1s on atom 1, 1s on atom 2, 1s on atom 3, 1s on atom 4.

It also assumes that hopping integrals are only non-zero for neighboring atoms.

Note that onsite energy is slightly different for the end atoms because they are "special", they only have one neighbor.

The S. Eqn in matrix form is

$$
\hat{H} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix}
$$

And in linear eqn format, the S. Eqn requires

$$
c_1 \alpha_{end} + c_2 \beta = E c_1 \\
c_1 \beta + c_2 \alpha_{mid} + c_3 \beta = E c_2 \\
c_2 \beta + c_3 \alpha_{mid} + c_4 \beta = E c_3 \\
c_3 \beta + c_4 \alpha_{end} = E c_4
$$
The middle two eqns follow a nice pattern
\[ c_{n-1} \beta + c_n \alpha + c_{n+1} \beta = Ec_n \]

But the first and last eqn break the pattern.

Our overall goal is to understand very long chains of atoms where end effects are negligible.

Therefore, we will use a trick called periodic boundary conditions to make all four atoms equivalent (no ends to the chain).