Bandgap Formation and Atomic Origin: Summary Notes

Compiled for Semiconductor Physics Review

1. From Atoms to Bands

In isolated atoms, electrons occupy discrete energy levels (orbitals). When many atoms come together to form a solid, those discrete levels **split into bands** due to the Pauli exclusion principle.

- The **valence band** arises from the bonding combinations of the outer (valence) orbitals.
- The **conduction band** arises from the antibonding combinations of those same orbitals.
- The **bandgap** (E_g) is the energy separation between these two bands.

2. Which Orbitals Form the Bands

Only the **outermost (valence) electrons** contribute meaningfully to bonding and band formation.

- Inner (core) electrons form deep, narrow "core bands" that remain inert and do not affect conduction.
- Example materials:
  - Silicon: valence orbitals $3s$, $3p \rightarrow sp^3$ hybrids $\Rightarrow E_g \approx 1.1\,\text{eV}$.
  - Germanium: valence orbitals $4s$, $4p \rightarrow sp^3$ hybrids $\Rightarrow E_g \approx 0.67\,\text{eV}$.

3. Why Bandgaps Differ Between Materials

Different elements have valence electrons in different shells (different principal quantum numbers n).

- Higher $n \Rightarrow$ orbitals are **larger and more diffuse**, lying farther from the nucleus.
- Larger orbitals $\Rightarrow$ **weaker overlap** between neighboring atoms.
- Weaker overlap $\Rightarrow$ smaller bonding–antibonding energy splitting $\Rightarrow$ smaller bandgap.

Trend Example (Group IV Semiconductors)

$$\text{C (diamond)} \rightarrow \text{Si} \rightarrow \text{Ge} \rightarrow \text{Sn}$$

$$E_g: \ 5.5 \text{ eV} \ \rightarrow \ 1.1 \text{ eV} \ \rightarrow \ 0.67 \text{ eV} \ \rightarrow \approx 0 \text{ eV}$$

4. About the Principal Quantum Number (n)

The principal quantum number n labels how far an orbital generally sits from the nucleus (its spatial extent).

- Larger $n \Rightarrow$ electrons are farther out, more weakly bound, and have higher energy.
- Within a given n, subshells (s, p, d) differ in energy due to penetration and shielding effects.
- In semiconductor physics, n mainly identifies which orbitals form the **outermost, bonding-active shell**.

5. Higher Energy vs. Weaker Overlap

- Orbitals with higher atomic energy (e.g., $4s$ vs. $3s$) are farther from the nucleus and more diffuse.
- Diffuse orbitals overlap less effectively between neighboring atoms.
- Less overlap $\Rightarrow$ weaker bonding interaction $\Rightarrow$ smaller bonding–antibonding splitting $\Rightarrow$ smaller bandgap.

Thus, "higher atomic energy" and "bonding strength" trend in opposite directions.

6. Key Takeaway

The valence and conduction bands in a semiconductor come from the bonding and antibonding combinations of the **outermost valence-shell orbitals**. Higher-n orbitals are larger and overlap less strongly, so the bonding–antibonding energy splitting—and therefore the bandgap—**decreases** as you move down the periodic table.