

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.

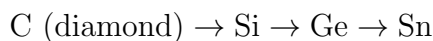
- Inner (core) electrons form deep, narrow “core bands” that remain inert and do not affect conduction.
- Example materials:
 - Silicon: valence orbitals $3s, 3p \rightarrow sp^3$ hybrids $\Rightarrow E_g \approx 1.1$ eV.
 - Germanium: valence orbitals $4s, 4p \rightarrow sp^3$ hybrids $\Rightarrow E_g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



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

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.