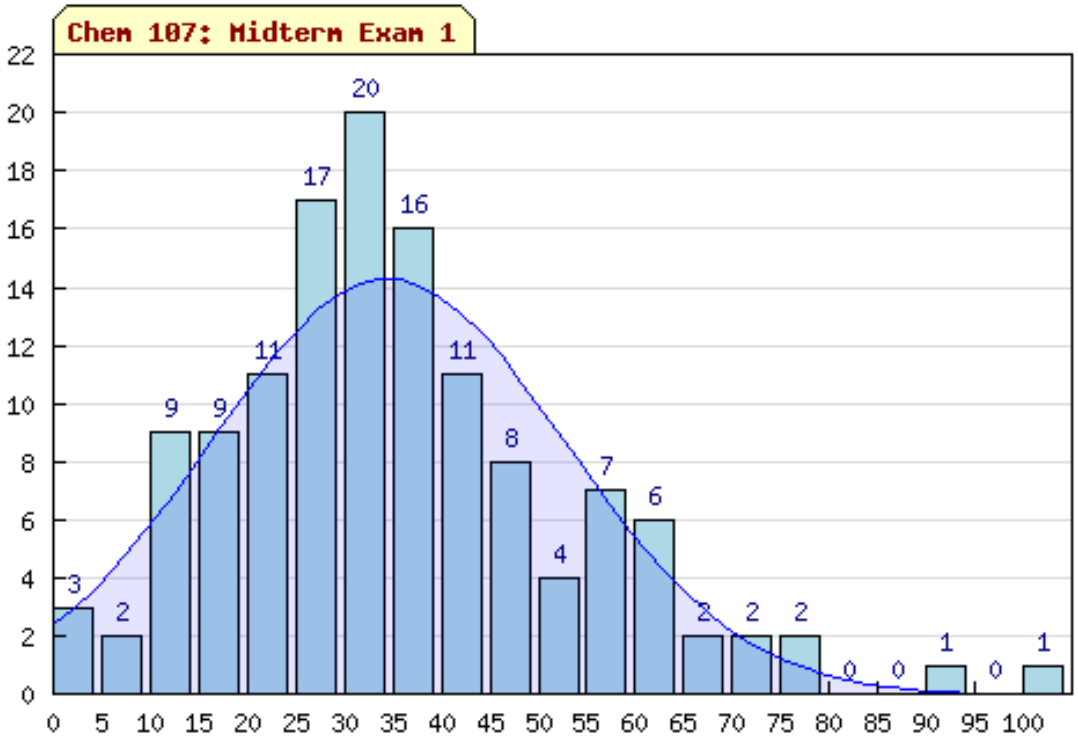
# Midterm I Results




**Mean: 35.5 (out of 100 pts)**
**Median: 33**
**Mode: 25**
**Max: 104**
**Min: 2**
**SD: 18**

**Compare to:**
**2013 Mean: 59%**
**2014 Mean: 51%**

??

# Crystal Thermodynamics and Electronic Structure

Chapter 7

Monday, October 26, 2015

# Explaining Simple Ionic Structures

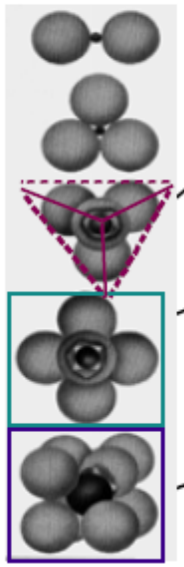
**The crystal structure adopted depends mostly on:**

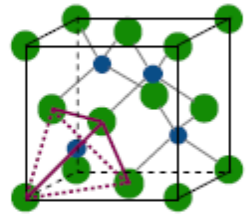
- **The relative sizes of the atoms/ions**
- **The relative number of the two types of atoms/ions**
- **The electronic structure of the atoms/ions**

**The radius ratio is typically defined as $r^+/r^-$, where $r^+$ is the radius of the cation and $r^-$ is the radius of the anion.**

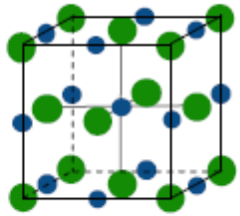
How many anions (bigger) can be arranged around a cation (smaller)?

| $\frac{r_{cation}}{r_{anion}}$ | Coord # | |
|---|---|---|
| < 0.155 | 2 | linear |
| 0.155 - 0.225 | 3 | triangular |
| 0.225 - 0.414 | 4 | $T_D$ |
| 0.414 - 0.732 | 6 | $O_H$ |
| 0.732 - 1.000 | 8 | cubic |

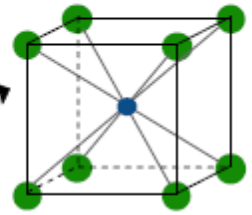




ZnS (zincblende)



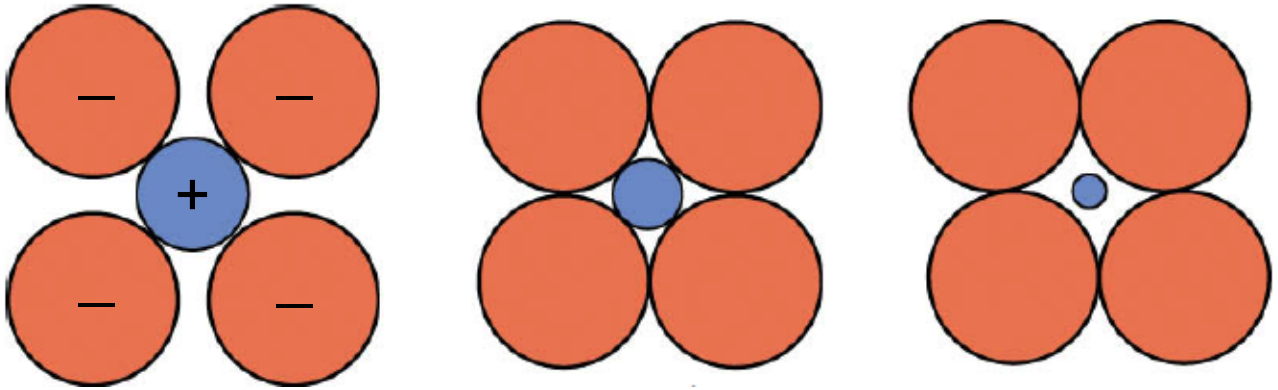
NaCl (sodium chloride)



CsCl (cesium chloride)

# Radius Ratio Rules

**In order to maximize the net electrostatic attraction between ions in a structure, the Coordination Number of the Cation will be Maximized subject to the criterion of Maintaining Cation-Anion Contact**




stable transitional unstable

Determined by comparison of the ratio of the ionic radii (r+/r-), with values derived from the **geometric contact criterion**

## Radius Ratio Rules

**The Radius Ratio Rules are correct ONLY 2/3 of the time!**

# Thermodynamics of Ionic Crystal Formation

**The energetics associated with the formation of an ionic crystal can be calculated using Hess' Law (Born-Haber cycle).**

| | |
|---|---|
| $Li(s) \longrightarrow Li(g)$ | $\Delta H_{sub}$ |
| $\frac{1}{2}F_2(g) \longrightarrow F(g)$ | **BDE** |
| $Li(g) \longrightarrow Li^+(g) + e^-$ | **IP** |
| $F(g) + e^- \longrightarrow F^-(g)$ | **EA** |
| $Li^+(g) + F^-(g) \longrightarrow LiF(s)$ | $-\Delta H_{lattice} = -\Delta U - \Delta nRT$ |
| $Li(s) + \frac{1}{2}F(g) \longrightarrow LiF(s)$ | $\Delta H_f$ |

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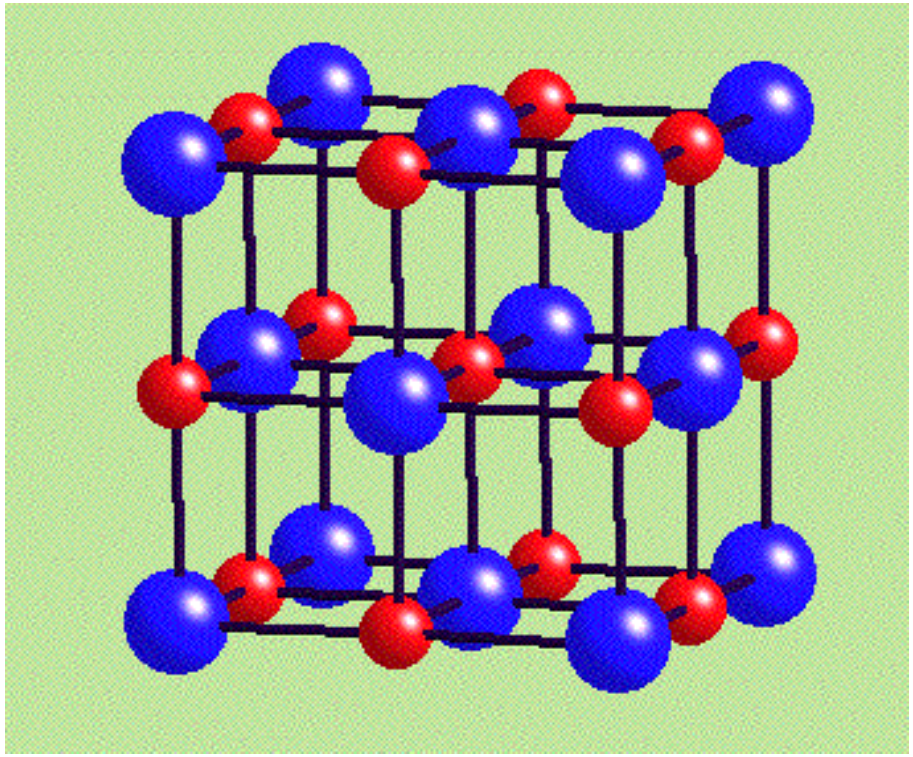
# Lattice Energy

Ionic structures are held together by electrostatic forces and, therefore, are arranged so that cations are surrounded by anions, and vice versa

**Lattice Energy (U)** = energy required to completely separate one mole of a crystal into a gas of its ions.

$NaCl\ (s) \rightarrow Na^+\ (g) + Cl^-\ (g)\ ,\ \Delta H_{lattice} \approx U$



$U_{NaCl} = 778\ kJ/mol$

Electrostatic potential energy (attraction & repulsion):

$$V = -\frac{Z_+ Z_- e^2}{r}$$

Short-range Pauli repulsion:

$$V = \frac{B}{r^n}$$

B: Born constant

n: Born exponent (n = 5-12)

**Example**: NaCl structure

Start with one $Na^+$ cation.

Next neighbors: 6 $Cl^-$ at distance $r$:

$$V_1 = -6\, Z_+Z_-e^2/r$$

Next nearest neighbors:

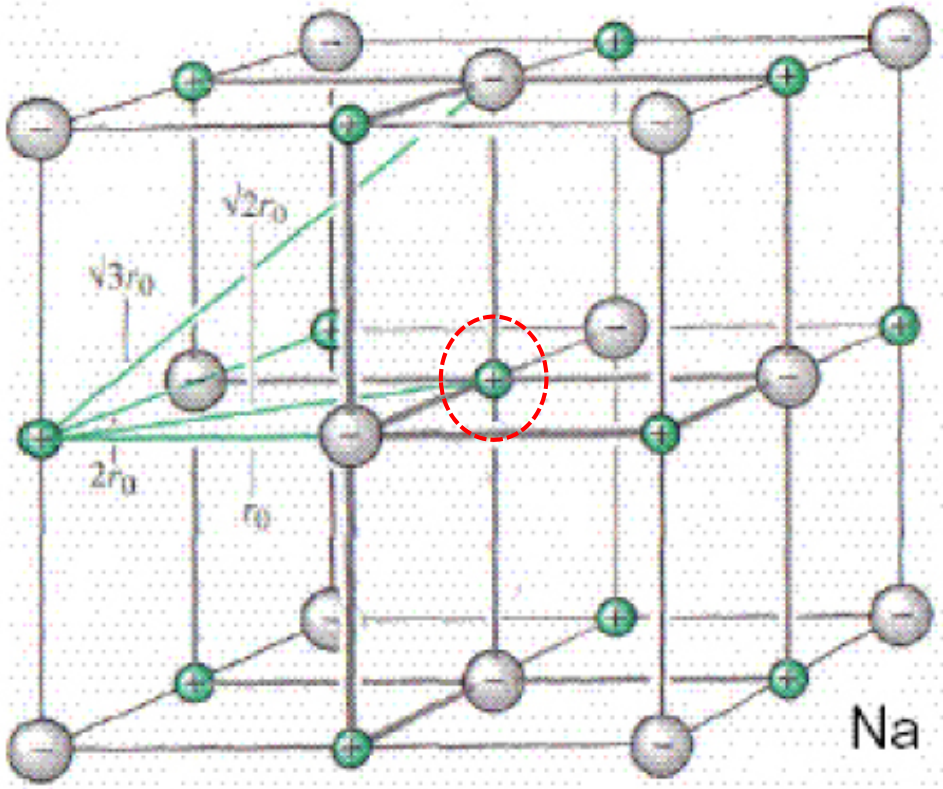
12 $Na^+$ at distance $\sqrt{2}r$:

$$V_2 = +12\, Z_+Z_-e^2/(\sqrt{2}r)$$

Next next:

8 $Cl^-$ at distance $\sqrt{3}r$:

$$V_3 = -8\, Z_+Z_-e^2/(\sqrt{3}r)$$




**Net attractive electrostatic energy between one $Na^+$ and the rest**:

$$V = V_1 + V_2 + V_3 + \ldots = -Z_+Z_-e^2/r \cdot \{6 - 12/\sqrt{2} + 8/\sqrt{3} - 6/\sqrt{4} + \ldots\}$$

**Net attractive electrostatic energy**:

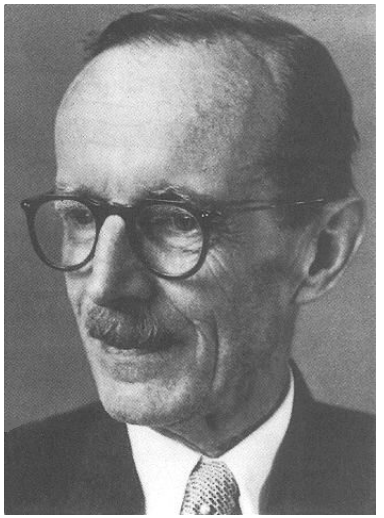
repeat summation for each ion, i.e. for $2N$ ions per mole NaCl, then divide by 2!

$$V = -Z_+Z_-e^2/r \cdot N \cdot A$$

$A$: Madelung constant

# Madelung Constant

$$V = -\frac{Z_+ Z_- e^2}{r}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \ldots.\right)$$



Madelung

**Madelung Constant (A):**
The numerical value of the series summation

- Depends only on the geometrical arrangements of ions (the crystal structure), not the lattice constant

| Crystal structure | Madelung constant | Coordination |
|---|---|---|
| Rock salt | 1.748 | 6 : 6 |
| CsCl | 1.763 | 8 : 8 |
| Zincblende | 1.638 | 4 : 4 |
| Fluorite | 5.039 | 8 : 4 |
| Rutile | 4.816 | 6 : 3 |

# Born-Landé Equation for Lattice Energy

U is the sum of net Coulombic attraction and Pauli repulsion:

$$U = -\frac{Z_+ Z_- e^2 NA}{r} + \frac{BN}{r^n}$$

$$\frac{dU}{dr} = \frac{Z_+ Z_- e^2 NA}{r_e^2} - \frac{nBN}{r_e^{n+1}} = 0$$

$$B = \frac{Z_+ Z_- e^2 A r_e^{n-1}}{n}$$

$$U = -\frac{Z_+ Z_- e^2 NA}{r_e}\left(1 - \frac{1}{n}\right)$$

This is the Born-Landé equation (1918)

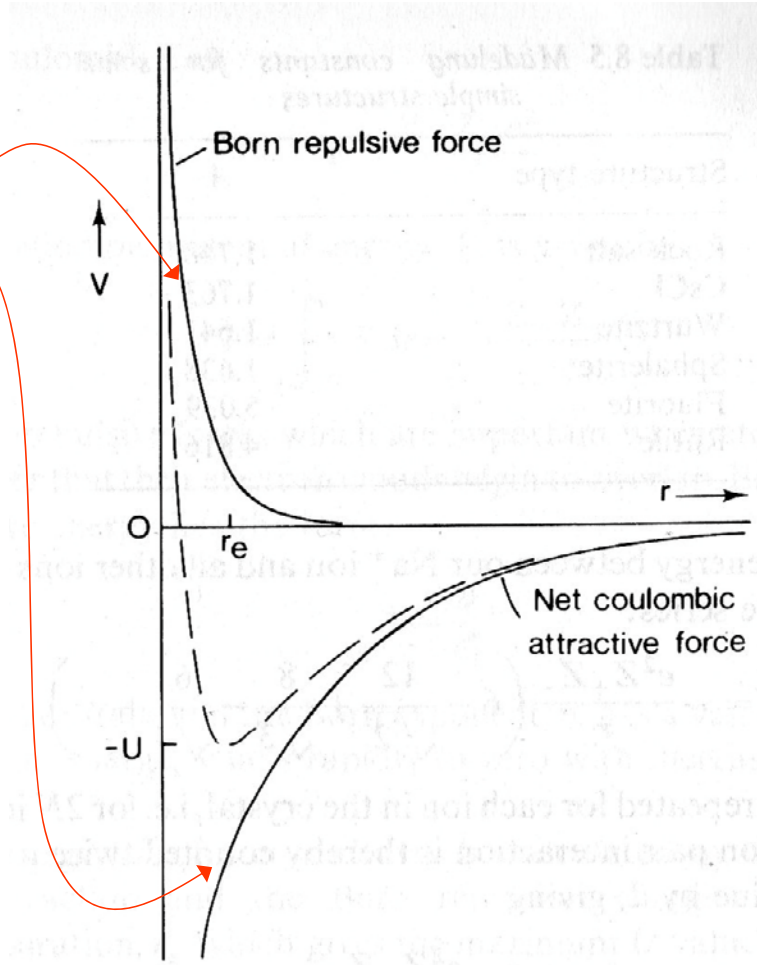



**Fig. 8.5** Lattice energy (dashed line) of ionic crystals as a function of internuclear separation

# Some Lattice Energies

- for a given crystal structure, U depends most strongly on the charge on the ions
- the internuclear separation $r_e$ has a smaller effect

Table 8.6 *Some lattice energies* ($kJ\,mol^{-1}$). (Data from Ladd and Lee, 1963)

| | | | | | |
|---|---|---|---|---|---|
| MgO | 3938 | LiF | 1024 | NaF | 911 |
| CaO | 3566 | LiCl | 861 | KF | 815 |
| SrO | 3369 | LiBr | 803 | RbF | 777 |
| BaO | 3202 | LiI | 744 | CsF | 748 |

increasing lattice constant

Melting point: MgO: 2800°C
CaO: 2572°C
BaO: 1923°C

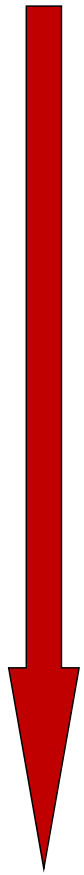
# Limits of the Ionic Model

The Born-Landé equation is a poor approximation to the lattice energy for compounds with significant non-ionic character

| | $U_{Born-Lande}$ (calculation) | $U_{Born-Haber}$ (experiment) | $\Delta U$ |
|---|---|---|---|
| AgF | 920 | 953 | 33 |
| AgCl | 832 | 903 | 71 |
| AgBr | 815 | 895 | 80 |
| AgI | 777 | 882 | 105 |

Rock Salt

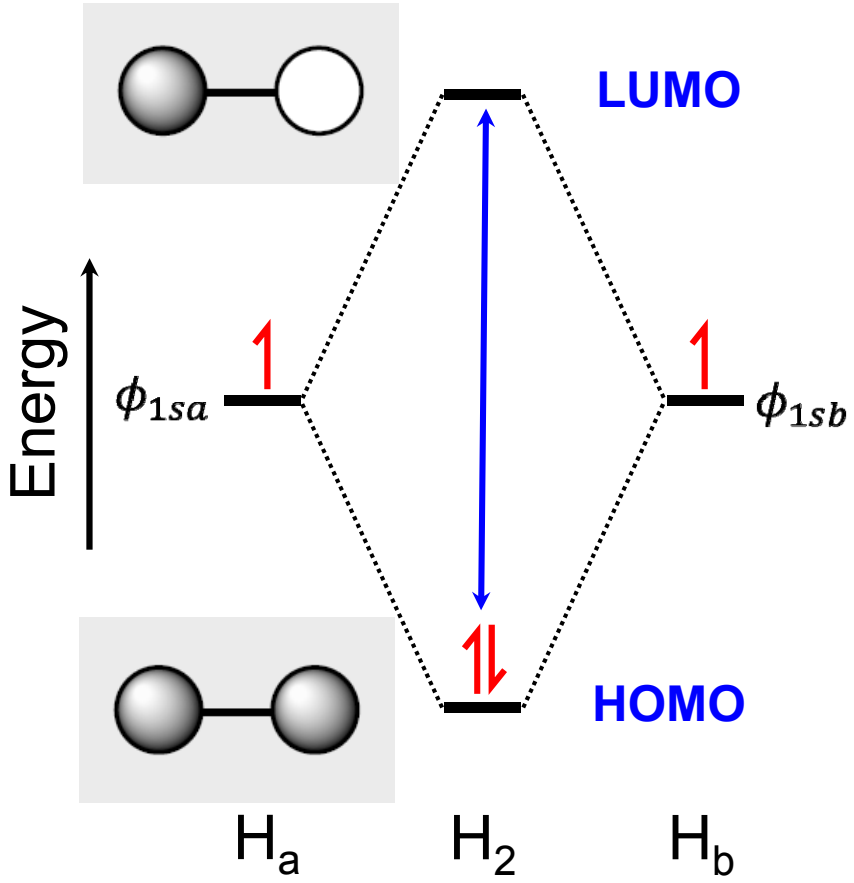
CN 4 structure



**Increasingly covalent!**

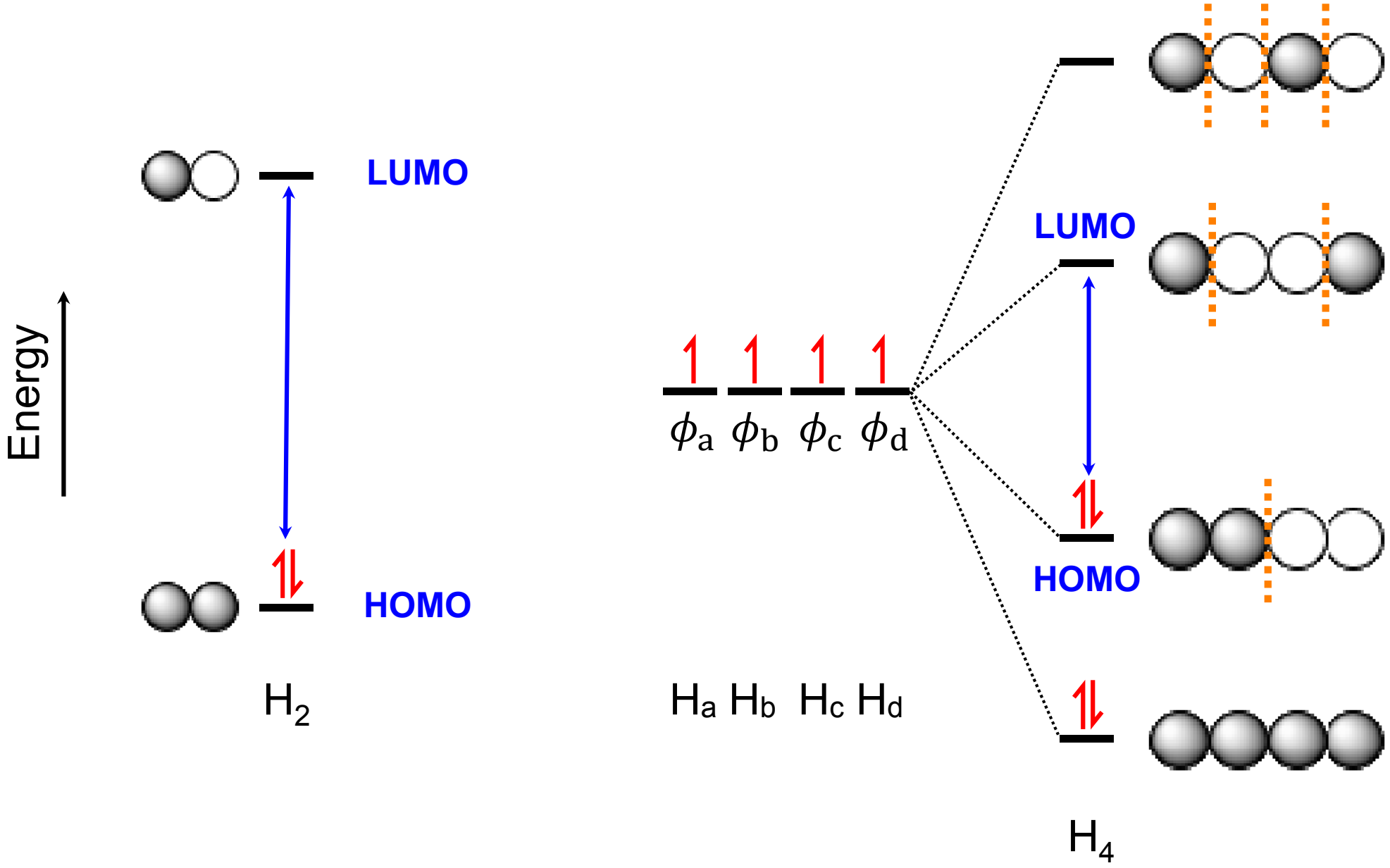
# From MOs to Band Theory

**We've seen before how AOs on atoms are combined to give MOs for molecules.**



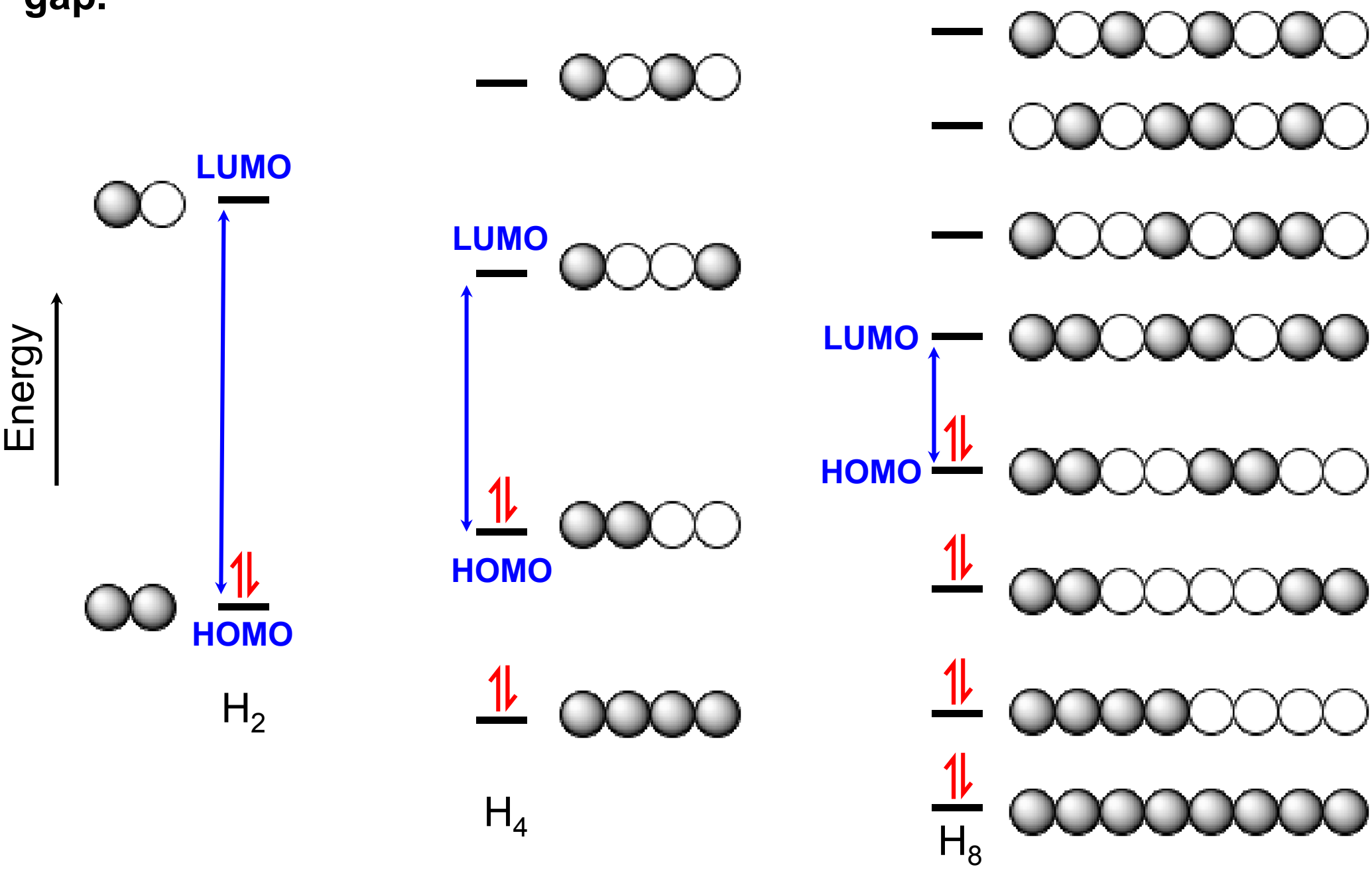
# From MOs to Band Theory

**Look at what happens when we move from two hydrogens to four hydrogens in a chain (look familiar?).**



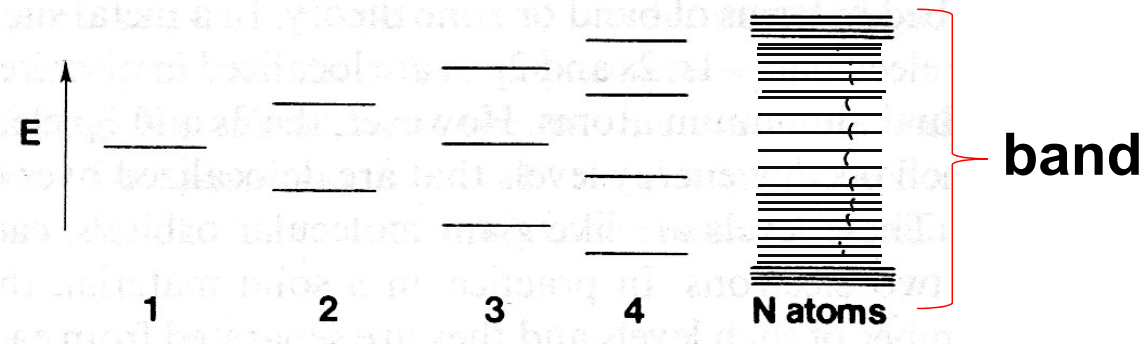
# From MOs to Band Theory

**Eight hydrogens gives eight MOs and an even smaller HOMO-LUMO gap.**



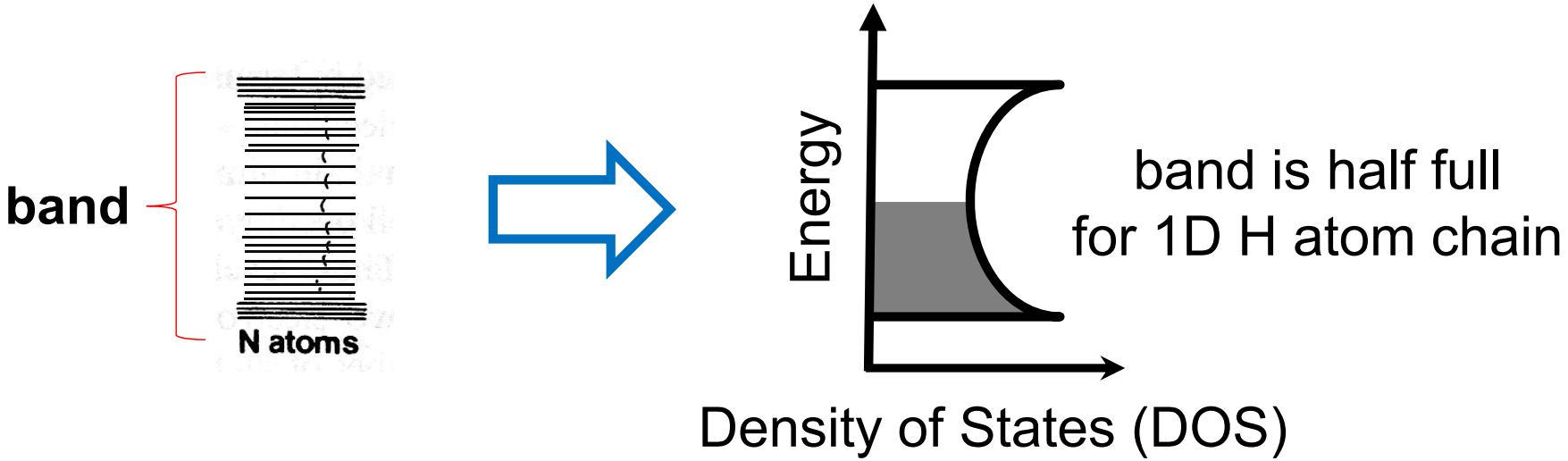
# Infinite 1D Chain of H Atoms

**Interaction of many atoms:**



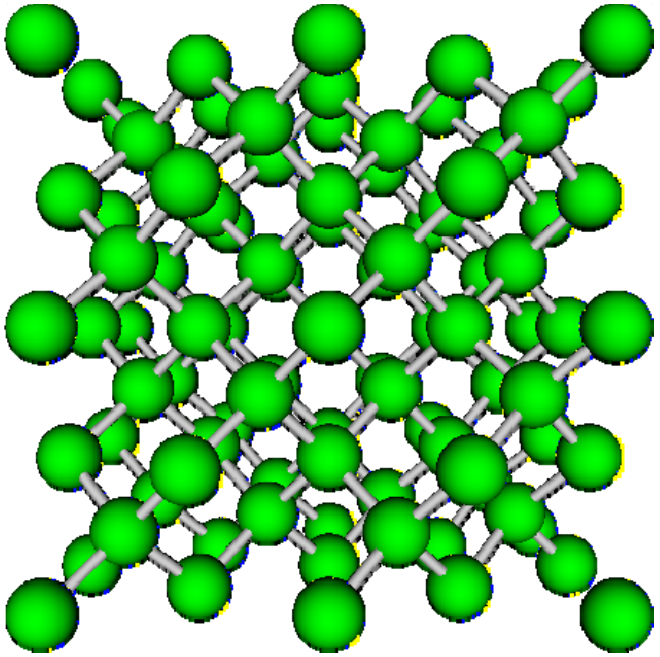

**N atomic orbitals always give N molecular orbitals.**

**when N is enormous, the MOs form continuous *bands*** ($\Delta E << kT$)

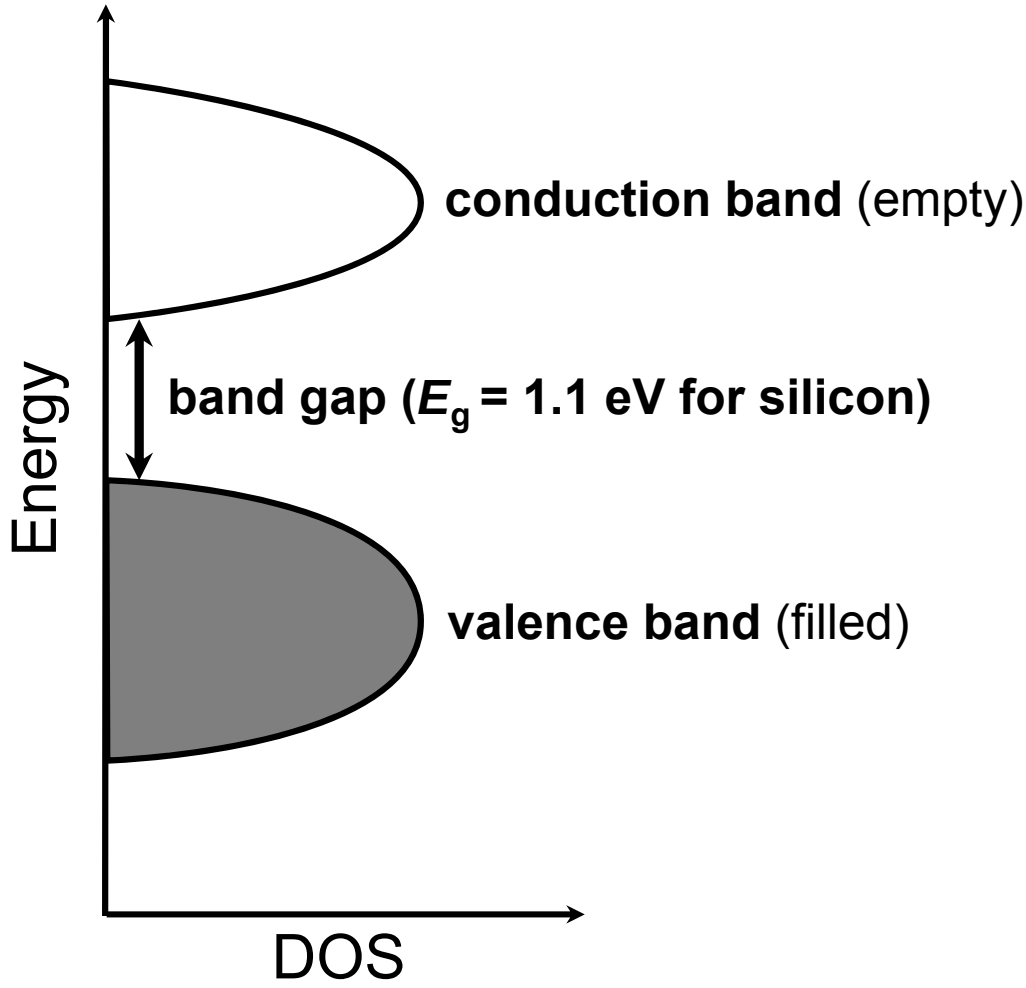


# Band Theory of 3D Solids

**Now consider what happens in a three-dimensional solid with many, many atoms within bonding distance...**



**crystalline silicon**




Instead of a discrete MOs, we get a ***band*** of filled orbitals (***valence band***) and a band of empty orbitals (***conduction band***).