Bands of states in solids

Metal: highest occupied orbital is in the middle of a band.
Semiconductor/Insulator: band gap between HOMO and LUMO.

Metals: resistivity increases w/ temp.
Due to vibrations of atoms.
Semiconductors: resistivity decreases w/ temp.
Greater population of e-'s in conduction band.

Conduction Band

Egap: 1.1 for Si

Valence Band

Irrurities: Donors: N, P, As, Sb

Lowered IP to about 0.5 eV.

Donor:

N 0.14
P 0.045 0.013
As 0.054 0.014
Sb 0.043 0.010

AlP: 2.45 eV
GaAs: 1.43 eV
InSb: 0.18 eV

Remove this e- into the conduction band.
Acceptor Impurities create holes in the valence band:

\[ \text{Si} \]
\[ \text{B} \quad 0.045 \]
\[ \text{Al} \quad 0.067 \]
\[ \text{Ga} \quad 0.079 \]
\[ \text{In} \quad 0.153 \]
\[ \text{Te} \quad 0.25 \]

For H, \( \text{IP} = \frac{-Ze^2}{2R} \)

we correct with a dielectric constant for solids:

\[ \text{IP} = \frac{-Ze^2}{2Re} \quad \varepsilon = 10 \]

10 times easier to ionize a Si in a solid than in vacuum.

\( \text{IP} = 0.04 \text{ eV for Si, doped w/ P.} \)

solve for \( \bar{R} \) with this value - 16 Å

ionized electron from the donor impurity is spread out over 16 Å.

spread out over 8 neighbors in the crystal. In an s-like orbital.

Hydrogen-like spectrum can be seen for this e-.
Before the electron is ionized, the N can distort to accommodate the extra e-. Al will distort to become more planar.

what about a vacancy? Si atoms will distort to become closer to each other.

E state. Jahn-Teller distortion. Two different singlet states.

Energy cost of a vacancy? We lose 4 Si-Si bonds and gain a little bit from spin pairing. Si-Si bond in the crystal - 54 kcal/mol. 208 kcal/mol = 9 eV

In fact, it is about 5 eV.
2 vacancies: only 7 bonds are lost in a divacancy.
8 bonds are lost in 2 separated vacancies.
2 vacancies as second nearest neighbors is very bad.
One Si loses 2 bonds very bad.
Replace a Si vacancy with O.

\[
\begin{align*}
\text{Si} & \quad \text{O} \quad \text{Si} \\
\text{Si} & \quad \text{Si}
\end{align*}
\]

Ionic Bonding \quad \text{NaCl}

Covalent bond: 3s on Na, 3p on Cl

\[
\begin{align*}
\text{Na} & \quad \infty \\
\text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{Na}_2 & \quad 3.08 \text{ Å} \quad 1.75 \text{ eV} \\
\text{Cl}_2 & \quad 1.99 \text{ Å} \quad 2.48 \text{ eV}
\end{align*}
\]

\[
\begin{align*}
\text{Covalent NaCl} & \quad 2.52 \text{ Å} \quad 1.61 \text{ eV} \\
\text{Actual NaCl} & \quad 2.56 \text{ Å} \quad 4.23 \text{ eV}
\end{align*}
\]

Ionic character.
Natural overlap between 3s and 2p orbitals for covalent bond. Na⁺ Cl⁻ ionic character contributes to the formation of the bond.

Approximation:

Ionize Na⁻→Na⁺  IP = 5.11 eV
Cl⁻→Cl⁻  EA = 3.62 eV

So to make Na⁺ and Cl⁻ infinitely separated, the cost is 1.52 eV. As we bring them together, we get Coulomb attraction.

We use the bond radii of 2.36 Å. We get 6.1 eV of bonding.

\[
\text{Net bond: } 3.6 \text{ eV.}
\]

Actual bond has about 85%, ionic character based on dipole moment, some covalent character.
NaCl dimer - roughly square shape.

Crystal structure - cubic shape.

Other structures are possible for other ionic compounds.