

Structure of Solids - Bonding in solids

Lecture 9

CHM 637

Chemistry & Physics of Materials

Varadharajan Srinivasan
Dept. Of Chemistry
IISER Bhopal

Lecture Plan

- General expectations
- Bonding in elemental solids
- Bonding in compound crystals

General Expectations

Cohesive Energy: Energy required to overcome the bonding forces in a solid and break it up into its constituent atoms.

$$E_{coh} = (nE_A(g) - E_{A_n}(s)) / n$$

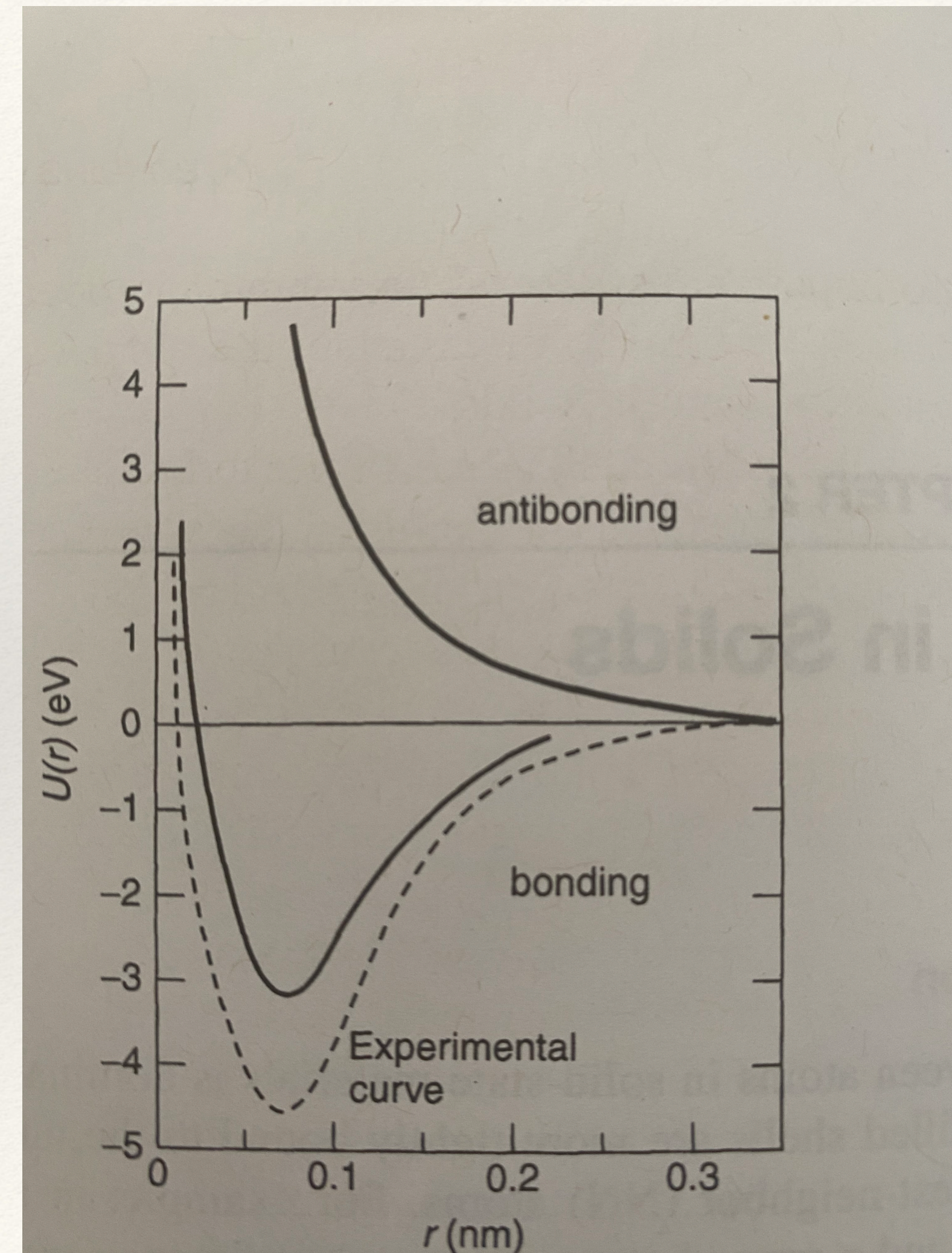
where A_n is assumed to be the formula unit of an elemental solid.

What is the origin of cohesion in a solid?

General Expectations

Consider the familiar bonding curve for a H_2 molecule

- For isolated atoms $U(r) \rightarrow 0$ as $r \rightarrow$ infinity.
- The bonding (lower energy) state is occupied as a singlet by 2 electrons.
- If the anti bonding state is occupied we expect the bond to break or be weakened.
- Minimum in $U(r)$ indicates a stable equilibrium geometry where molecule would be most likely found.



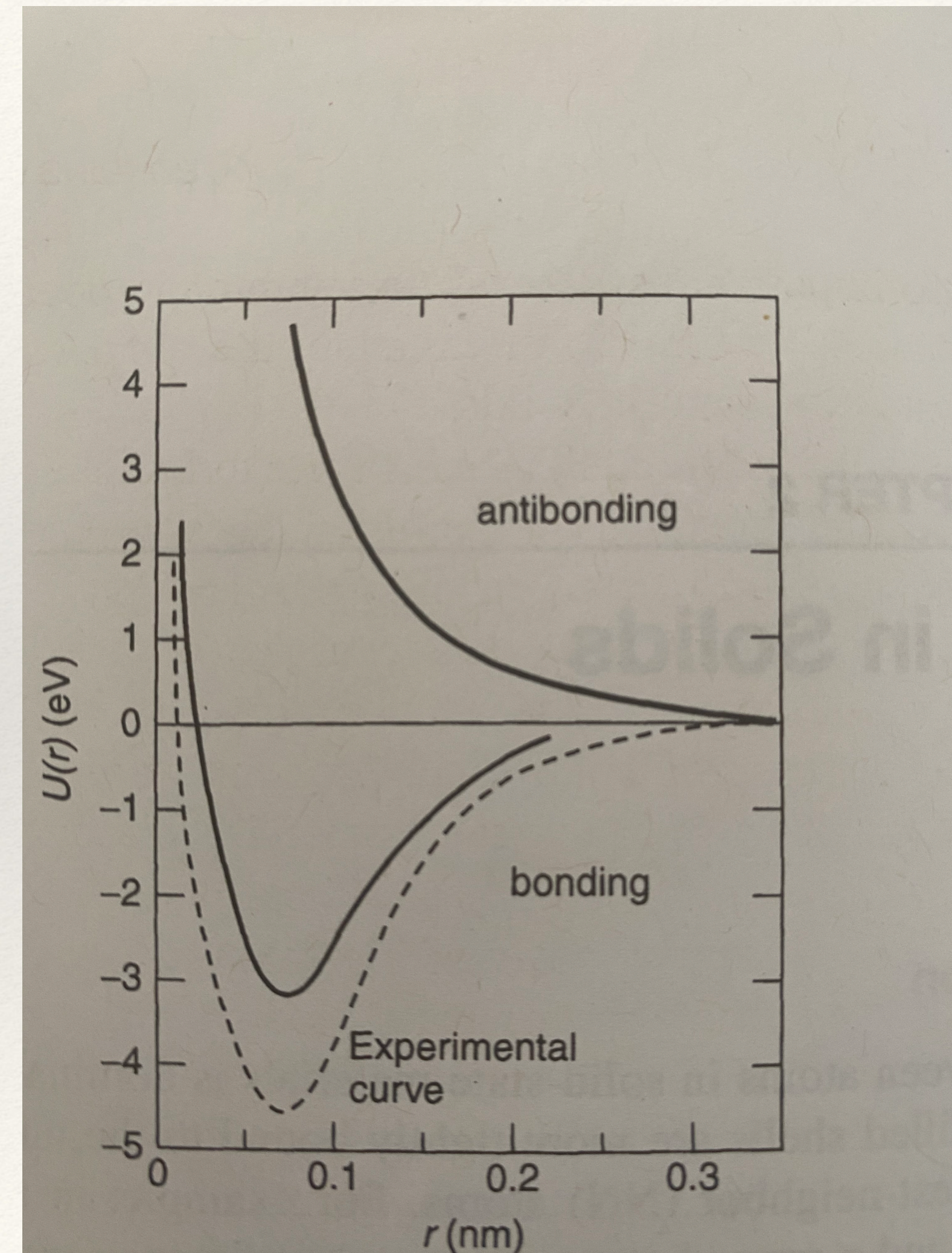
General Expectations

Consider the familiar bonding curve for a H_2 molecule

- For H_2 $r_{min}=0.07$ nm and dissociation energy is 4.52 eV.
- At shorter distances energy rises rapidly due to internuclear repulsion and Pauli Exclusion Principle.

For solids we expect similar curves with respect to lattice parameters.

Repulsion at short distances is consistent with low compressibility of solids in general.



General Expectations

In solids the valence electrons are primarily responsible for bonding.

The actual cohesive energies and nature of bonding can, in principle, be obtained by quantum mechanical calculations considering the electrons and the atoms/ions in the crystal.

However, this is complicated by mainly two factors:

- (1) The number of atoms (and hence electrons) in a solid is typically $\sim 10^{23}$.
- (2) The many-electron problem has no general exact analytical solutions available.

Thus we often resort to simple approximations as we shall do in this course as well.

General Expectations

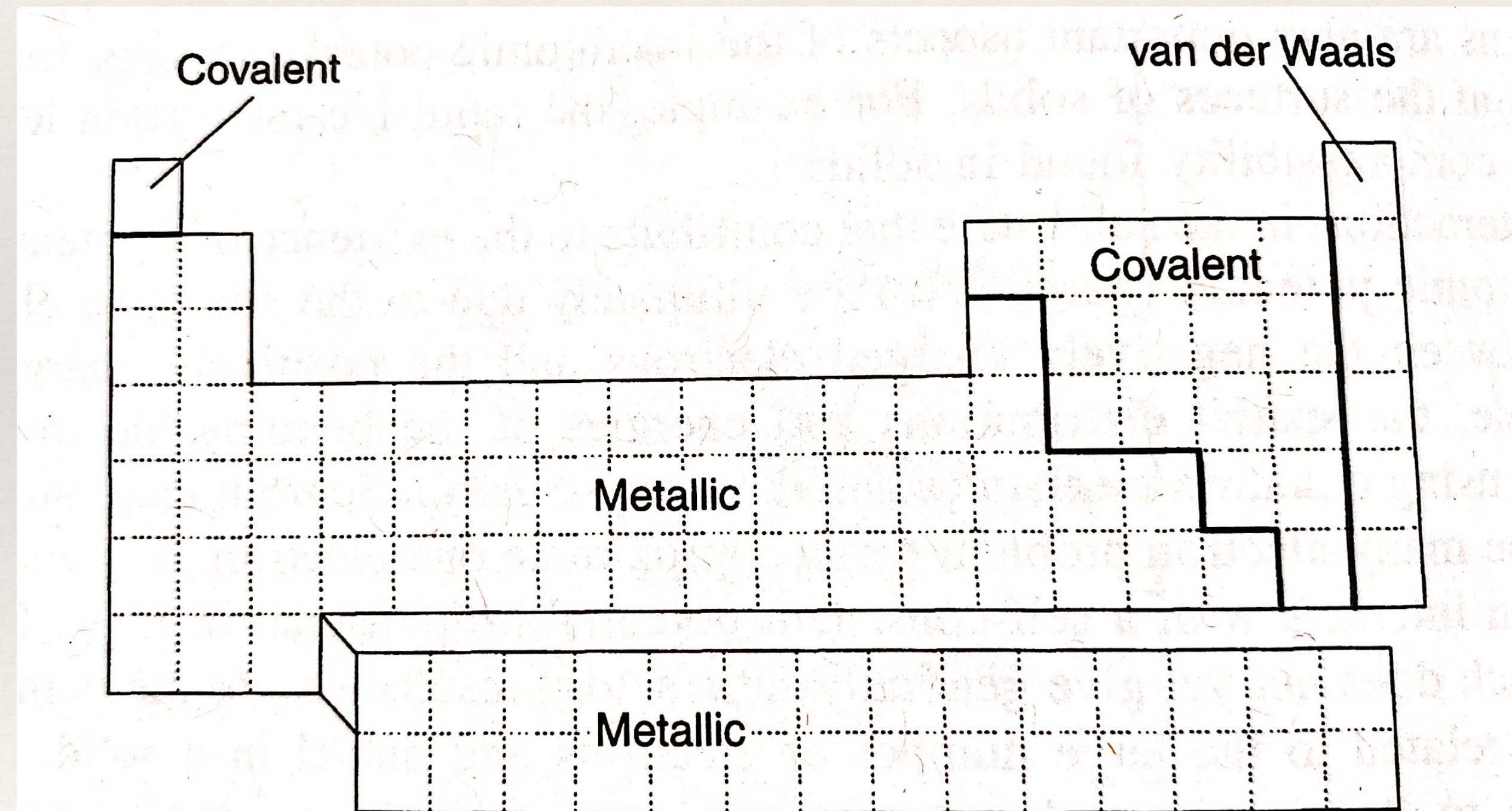
Based on the nature and the strengths of the binding we can classify bonding in solids into

- Covalent
- Metallic
- Ionic
- Van der Waals
- Hydrogen-bonding

Bonding in elemental solids

Elemental solids generally have only three mechanisms of bonding

- Covalent
- Metallic
- Van der Waals



Source: Gersten and Smith

Bonding in elemental solids

Covalent Bonding

Results from overlap of atomic orbital wave functions.

Sharing of valence electrons in a bond.

More dominant when available valence electrons/atom \geq coordination number in solid.

This criterion is satisfied generally by p-block.

Satisfactory description of the electronic structure will require band theory to be discussed later.

Bonding in elemental solids

Covalent Bonding

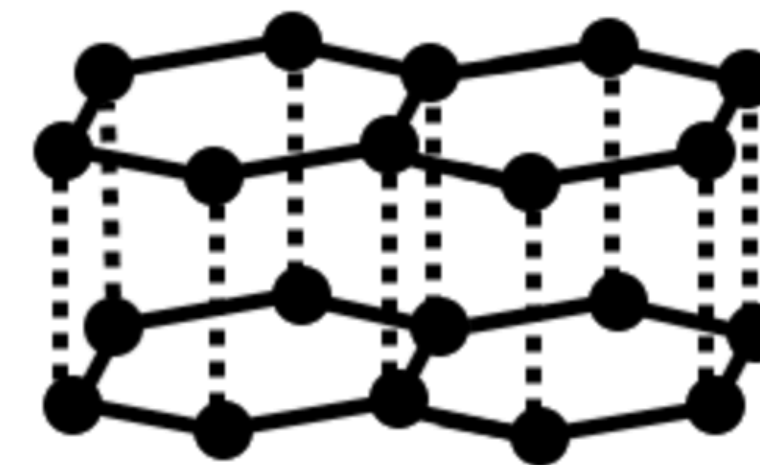
E.g. C has e.c. $2s^2 2p^2$

In diamond it undergoes sp^3 hybridisation to yield 4 bonding orbitals.

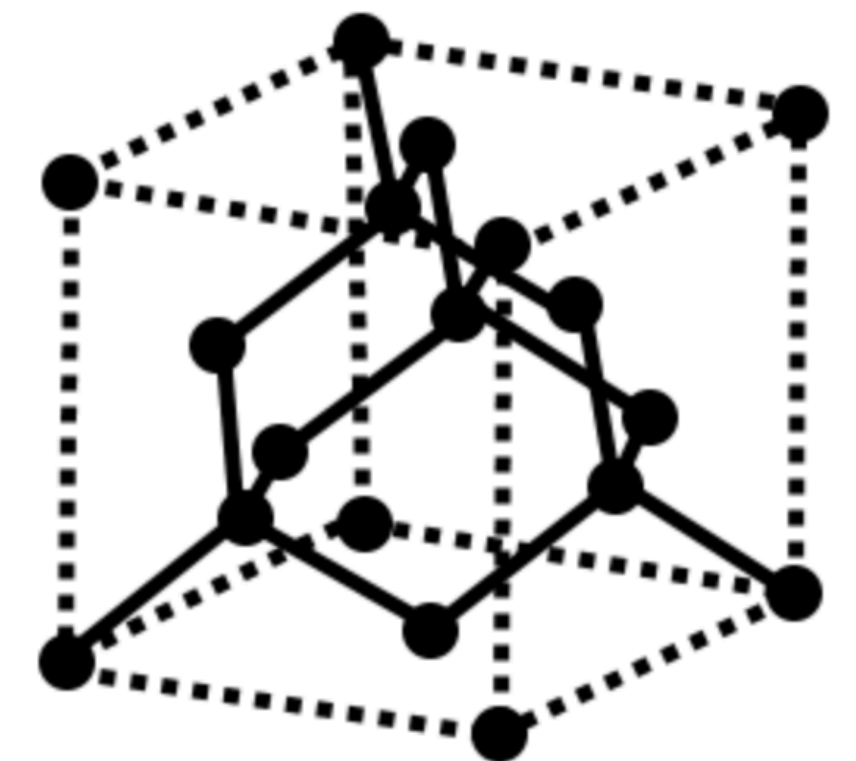
This is to accommodate the 4 nearest-neighbours (NN) in the diamond structure yielding a covalent solid.

On the other hand, in graphite there are 3 NNs and only 3 electrons/atom needed for bonding.

This results in sp^2 hybridisation and 2-D structure. Extra electrons form π orbitals.



Graphite Structure



Diamond Structure

Bonding in elemental solids

Covalent Bonding

Diamond structures are formed by Si, Ge and α -Sn.

Sn and Pb also form metallic bonding structure as 5s and 6s levels are more tightly bound by the nucleus and are less available for covalent bonding.

Similar arguments hold for other *p*-block solids.

Halogens usually form molecular solids with no extended covalent bonding.

TABLE 2.1 Structures of the Covalently Bonded Elemental Solids

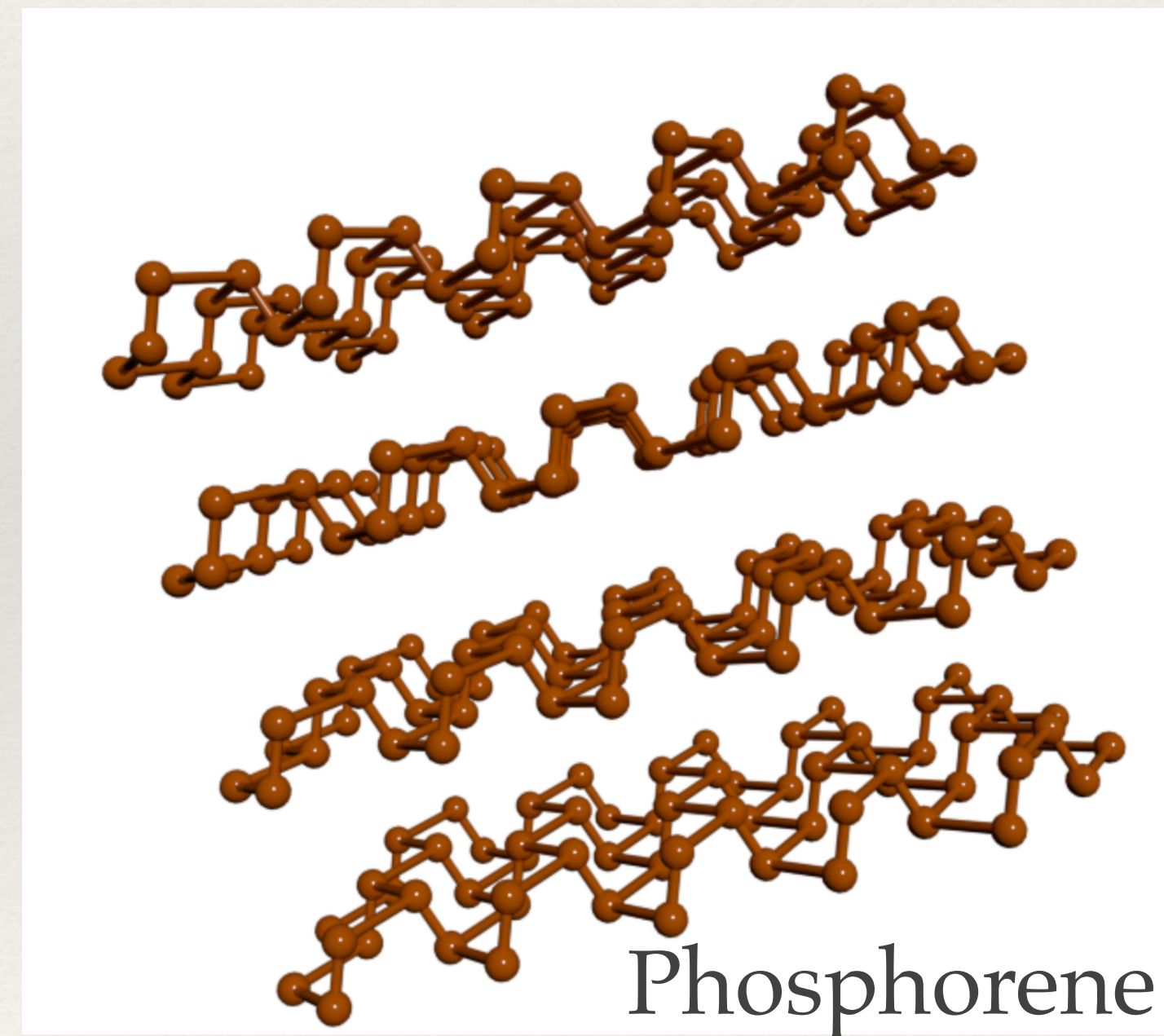
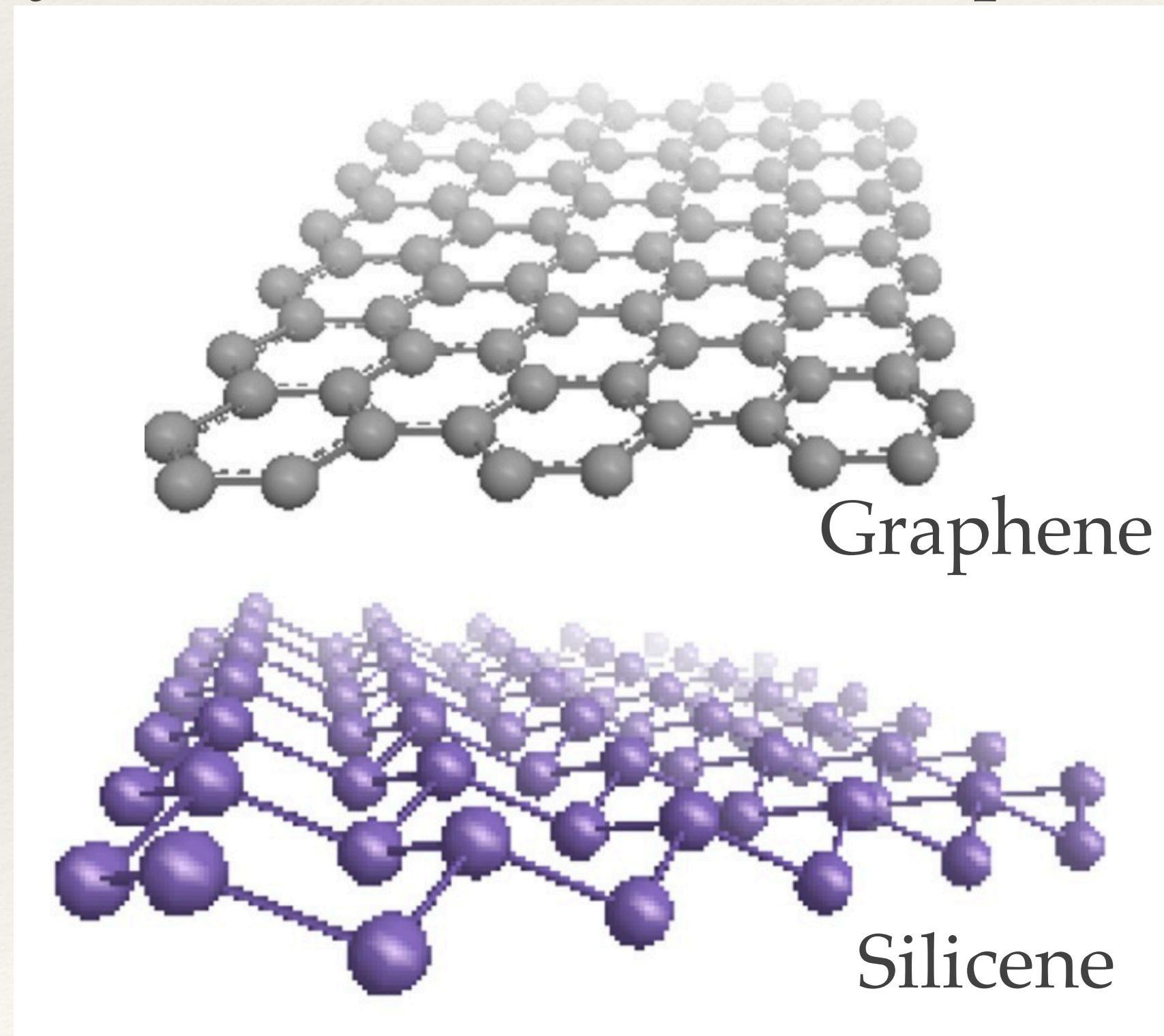
Elements	Group Number ^a	Coordination Number CN	Local Atomic Bonding Unit	Resulting Local Structures
B	III	5	B-B ₅	Icosahedra
C (diamond), Si, Ge, gray Sn	IV	4	A-A ₄	Tetrahedra (three-dimensional)
C (graphite)	IV	3	A-A ₃	Planar hexagons
P (black), As, Sb, Bi	V	3	A-A ₃	Nonplanar hexagons
S, Se, Te	VI	2	A-A ₂	A ₈ rings, spiral chains
F, Cl, Br, I	VII	1	A-A	A ₂ , diatomic molecules

^aThe group number in the periodic table is also the number of valence electrons per atom.

Bonding in elemental solids

Covalent Bonding

Layered structures of Group IV and V elements



Layers are held together by VW forces.

They display really interesting optical, electronic and mechanical properties.

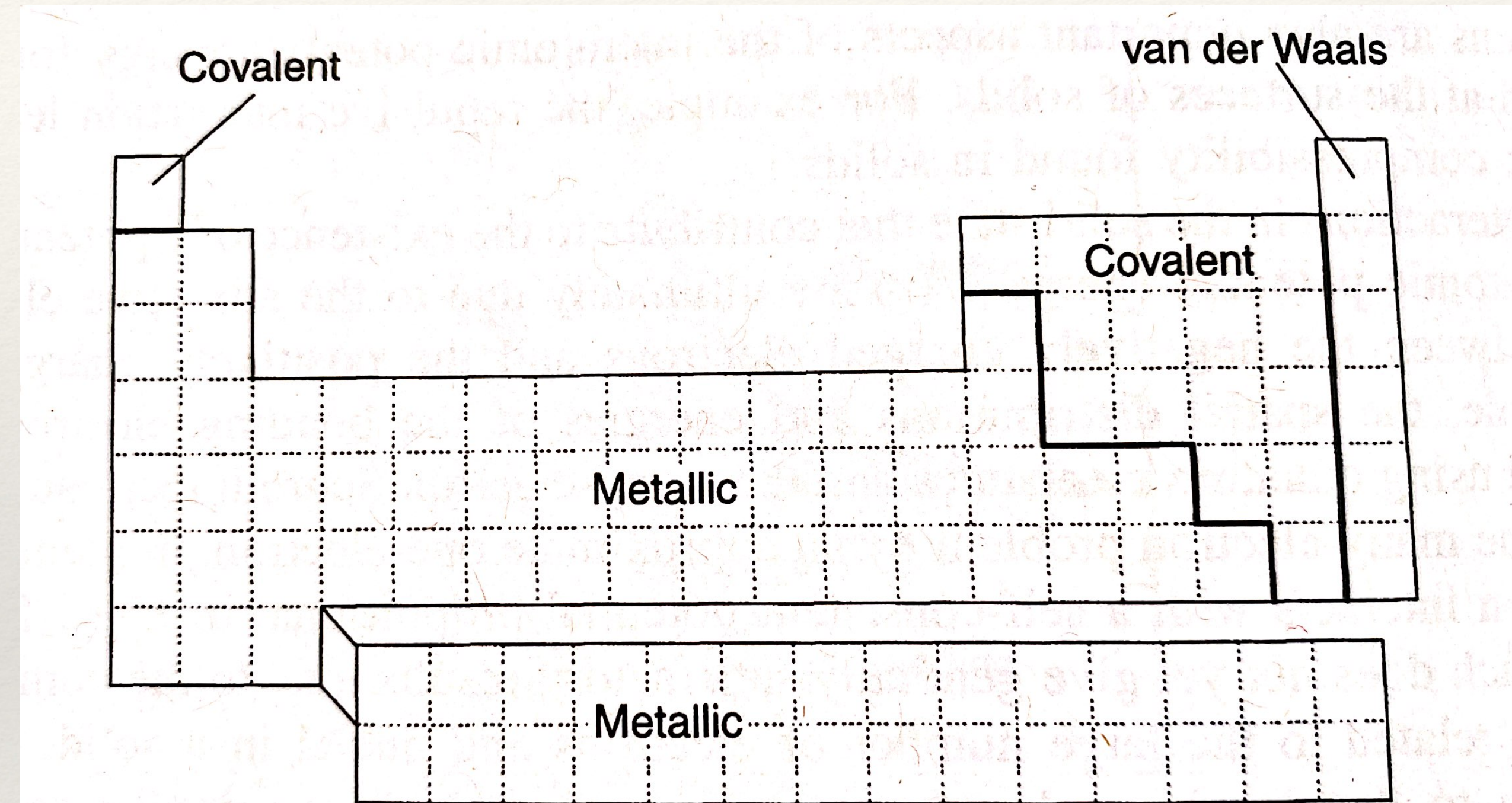
Bonding in elemental solids

Metallic Bonding

Structures where metallic bonding dominates originate in elements in the left and bottom of the periodic table.

Groups IA, IIA, IIIA involve s and p orbitals only are termed *simple* metals.

d -block generates *transition* metals where the bonding involves d electrons in the valence as well.



Similarly f -block gives rise to the so-called *rare earth* metals.

Bonding in elemental solids

Metallic Bonding

Common to all these metallic bonded structures is the occurrence of very high coordination numbers (8-12) unlike in the covalent solids.

Since the no. of valence electrons/atom is much less than this number the electrons are shared through delocalisation over the entire solid and not in specific bonding orbitals. *i.e.* their wave functions are spread out throughout the crystal.

As a result metallic bonding is non-directional (at least in the simple metals).

Bonding in elemental solids

Metallic Bonding

A chemical description of the stability of metallic solids can be illustrated by the case of Na.

The atomisation energy increases from 0.39 eV/atom for Na₂ to 1.13 eV/atom for solids Na (b.c.c.). The latter corresponds to ~ 0.28 eV per Na-Na pair in the solid.

But valence electrons are less strongly bound in solid than in clusters:

I.P. (Na₂) = 4.93 eV while average binding energy of electrons in Na solid = 4.0 eV.

=> Enhanced stability of metals like Na in the solid state compared to clusters is due to stronger bonding of the Na⁺ ions by delocalised valence electrons and not due to stronger binding of electrons.

Bonding in elemental solids

Metallic Bonding

Alternatively, we could view the metal as a sea of free electrons.

In this picture, the kinetic energy of the electrons is lowered by delocalisation over the solid.

The screening of nuclear attraction by other valence electrons weakens it so much so that delocalizations becomes energetically favourable.

This point of view will also justify the use of free-electron theory for describing properties of metals.