Kap. 6:

Chemische Bindung

6. Chemische Bindung (1)

ionische Bindung

Ionen mit abgeschlossenen Elektronenschalen
ungerichtete Bindung, 5-10 eV Bindungsenergie/Baustein

kovalente Bindung

gemeinsame Orbitale, gerichtete (Valenz-)Bindung
5-10 eV Bindungsenergie/Baustein
Halbleiter, Moleküle

Übersicht:
Allgemeiner Potentialverlauf

metallische Bindung

ungerichtete Bindung, dichte Kugelpackung
Valenzelektronen sind delokalisiert, 1 eV Bindungsenergie/Baustein

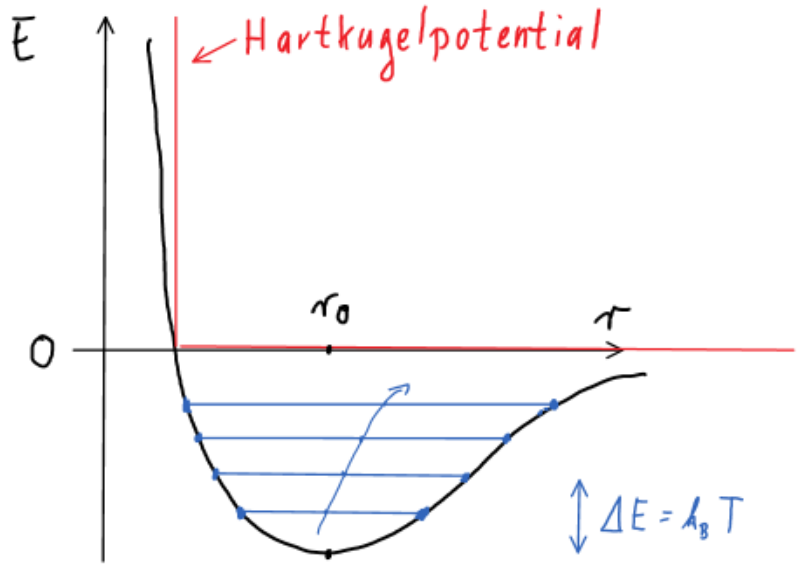
van der Waals-Bindung

Edelgase, Elektronenhülle ist polarisierbar, Dipol-Dipol-Wechselwirkung,
ungerichtete Bindung, 0,05-0,1 eV Bindungsenergie/Baustein

Wasserstoffbrücken-Bindung

Eis, DNS, starker Dipol, van der Waals-Wasserstoffbrücke,
gerichtete Bindung, 0,3 eV Bindungsenergie/Baustein

Chemische Bindung: allgemeiner Potentialverlauf



Überlagerung:

anziehende + abstoßende Kräfte

z.B. elektrostatisch

Pauli-Prinzip

thermische Ausdehnung

Ionisierungsenergie E_{Ion}: Energieaufwand, um Elektron von neutralem Atom zu lösen

(>0)

Elektronenaffinität E_{Aff}: Energiegewinn, um negatives Ion aus neutralem Atom zu erzeugen

(>0)

$$\Delta E_{A+B \to AB} = E_{Ion,A} - E_{Aff,B} - |E_{Koh,AB}| < 0$$

Bed. f. stabile ionische Bindung

$$E_{Koh} = -\sum_{i,j} \frac{Q_i Q_j}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$

Kohäsionsenergie:
elektrostatische Wechselwirkung der Ionen

6. Chemische Bindung (2)

Type of Bonding	Description	Typical of which compounds	Typical Properties
Ionic	Electron is transferred from one atom to another, and the resulting ions attract each other	Binary compounds made of constituents with very different electronegativity: Ex, group I-VII compounds such as NaCl.	• Hard, Very Brittle • High Melting Temperature • Electrical Insulator • Water Soluble
Covalent	Electron is shared equally between two atoms forming a bond. Energy lowered by delocalization of wave-function	Compounds made of constituents with similar electronegativities (ex, III-V compounds such as GaAs), or solids made of one element only such as diamond (C)	• Very Hard (Brittle) • High Melting Temperature • Electrical Insulators or Semiconductors
Metallic Bonds	Electrons delocalized throughout the solid forming a glue between positive ions.	Metals. Left and Middle of Periodic Table.	• Ductile, Maleable (due to non-directional nature of bond. Can be hardened by preventing dislocation motion with impurities) • Lower Melting Temperature • Good electrical and thermal conductors.
Molecular (van der Waals or Fluctuating Dipole)	No transfer of electrons. Dipole moments on constituents align to cause attraction. Bonding strength increases with size of molecule or polarity of constituent.	Noble Gas Solids, Solids made of Non-Polar (or slightly polar) Molecules Binding to Each Other (Wax)	• Soft, Weak • Low Melting Temperature • Electrical Insulators
Hydrogen	Involves Hydrogen ion bound to one atom but still attracted to another. Special case because H is so small.	Important in organic and biological materials	• Weak Bond (stronger than VdW though) • Important for maintaining shape of DNA and proteins

6. Chemische Bindung (3)

Ionische Bindung

Ionen mit abgeschlossenen Elektronenschalen
ungerichtete Bindungen
lokalisierte Elektronen, Isolatoren
transparent
hart, spröde

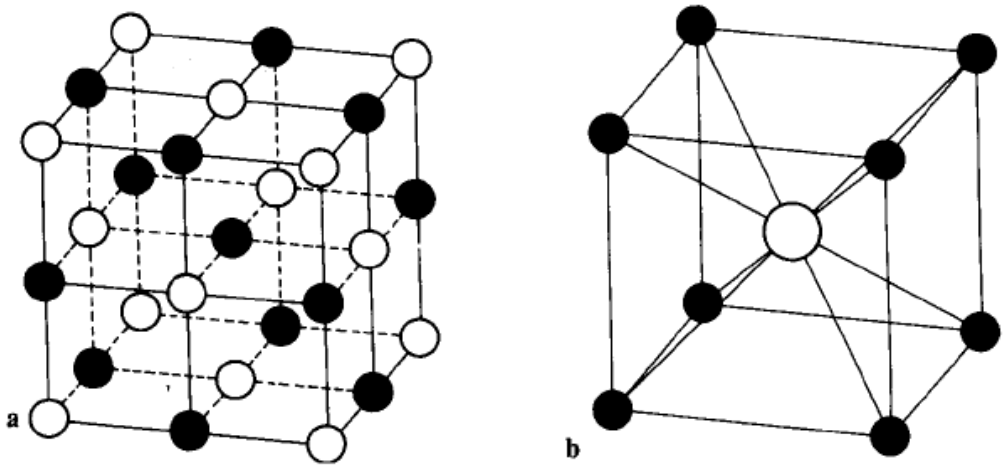


Abb. 1.6. Die beiden typischen Strukturen für Ionenbindung in Festkörpern. (**a**) NaCl-Struktur, (**b**) CsCl-Struktur

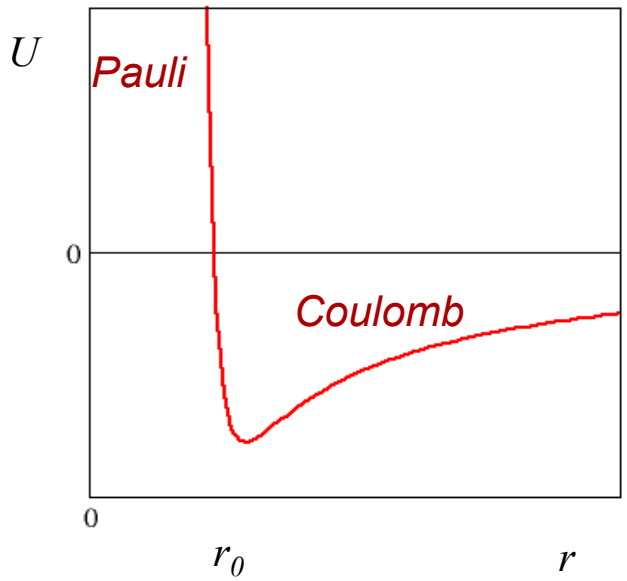
6. Chemische Bindung (4)

Ionische Bindung

Ein gutes Beispiel für ionische Bindung geben die Alkali-Halogenide wie Na^+Cl^-.
Alkali$^+$ und *Halogen*$^-$ Ionen haben Edelgaskonfiguration, sind kugelsymmetrisch und sind schwer polarisierbar.
Die Coulombwechselwirkung dominiert die attraktive Bindung:

Coulomb-Potential für Ion Nr. i:

$$U_i^C = \sum_j \frac{\pm e^2}{4\pi\varepsilon_0 r_{ij}}$$



Pauliabstoßung: Born-Mayer-Potential
→ nur für nächste Nachbarn wichtig

Die genaue Form von U^B ist nur schwer zu berechnen
(Modellierung eines stark abstoßenden Potentials)

$$U_{ij}^B \approx B \exp(-r_{ij} / \rho)$$

$$\text{mit } \rho \approx 0{,}1 \cdot r_0$$

6. Chemische Bindung (5)

Ionische Bindung

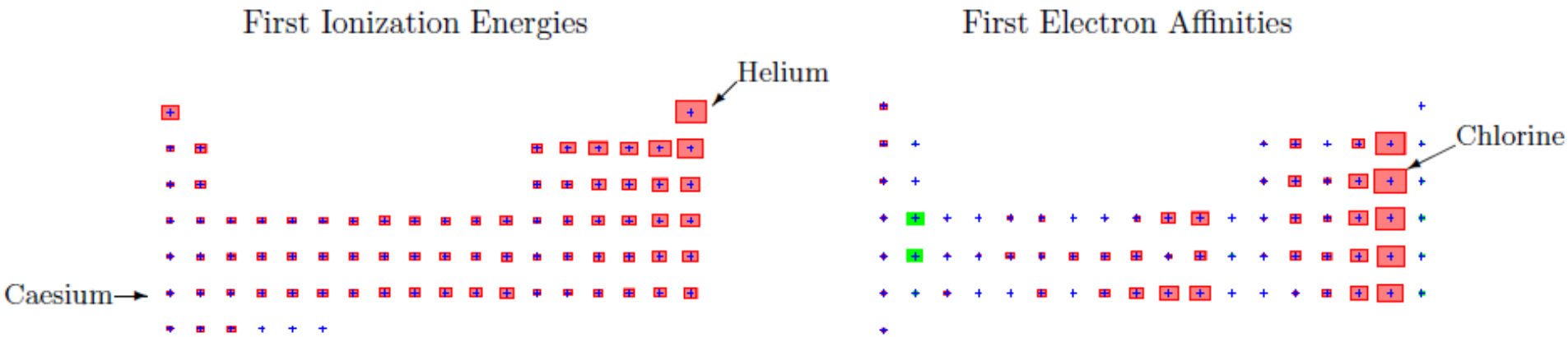


Figure 5.2: Pictorial Tables of First Ionization Energies (left) and First Electron Affinities (right). The word "First" here means that we are measuring the energy to lose or gain a first electron starting with a neutral atom. The linear size of each box represents the magnitude of the energies (scales on the two plots differ). For reference the largest ionization energy is helium, at roughly 24.58 eV per atom, the lowest is caesium at 3.89 eV. The largest electron affinity is chlorine which gains 3.62 eV when binding to an additional electron. The few light green colored boxes are atoms that have *negative* electron affinities.

6. Chemische Bindung (6)

„Elektronegativität ist ein Maß für das Attraktionsvermögen eines Atoms in einem Molekül ein Elektron zu sich zu ziehen."

Anteil des ionischen Charakters einer Bindung $= 1 - \exp(-\frac{1}{4}(x_A - x_B))$

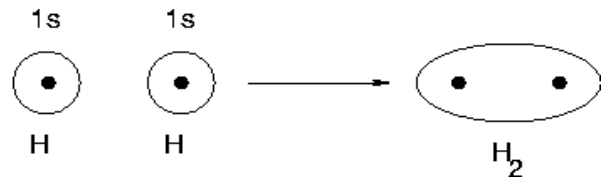
H 2.1																	
Li 1.0	Be 1.5												B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2												Al 1.2	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Sr 1.0	Sc 1.0	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6		Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Ba 0.8	Y 0.8												Sn 1.8	Sb 1.9	Te 2.1	I 2.5

6. Chemische Bindung (7)

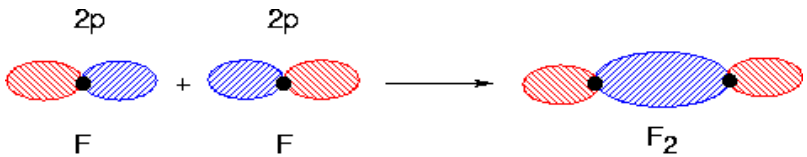
kovalente Bindung

gemeinsames bindendes Orbitale zweier Atome
ähnliche Elektronegativität
gerichtete (Valenz-)Bindung
erhöht die Elektronendichte zwischen den positiven Kernen
Diamant, Graphit, Halbleiter, Moleküle

Bsp. Moleküle:



s-Orbital:
i.d.R. keine kovalente Bindung!



Häufig:

p, d-Orbitale

(da gerichtet)

6. Chemische Bindung (8)

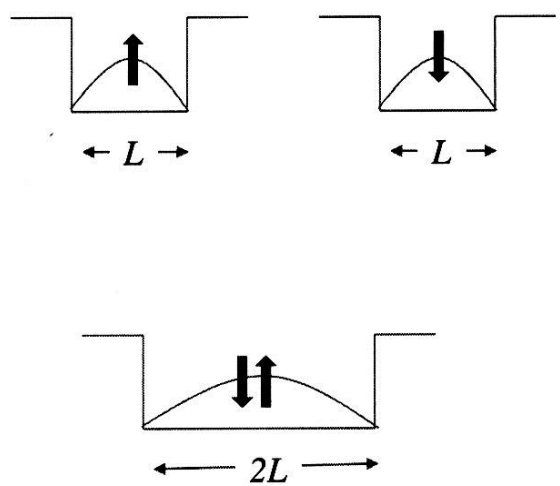
kovalente Bindung

Entstehung einer Bindung durch stärkere Delokalisierung der Elektronen in einem gemeinsamen, größeren Potentialtopf

Rechnung: Kovalente Bindung

Vereinfachtes 1D-Modell zur Veranschaulichung:
- niedrigster Energiezustand → bindendes Orbital
- nächsthöherer Energiezustand → “anti-bindendes” Orbital

Fig. 6.3 Particle in a box picture of covalent bonding. Two separated hydrogen atoms are like two different boxes each with one electron in the lowest eigenstate. When the two boxes are pushed together, one obtains a larger box—thereby lowering the energy of the lowest eigenstate—which is known as the *bonding* orbital. The two electrons can take opposite spin states and can thereby both fit in the bonding orbital. The first excited state is known as the *antibonding* orbital



$$E = \frac{\hbar^2 \pi^2}{2mL^2}$$

$$E_{bonding} = \frac{\hbar^2 \pi^2}{2m(2L)^2}$$

$$E_{anti-bonding} = \frac{\hbar^2 (2\pi)^2}{2m(2L)^2}$$

6. Chemische Bindung (9)

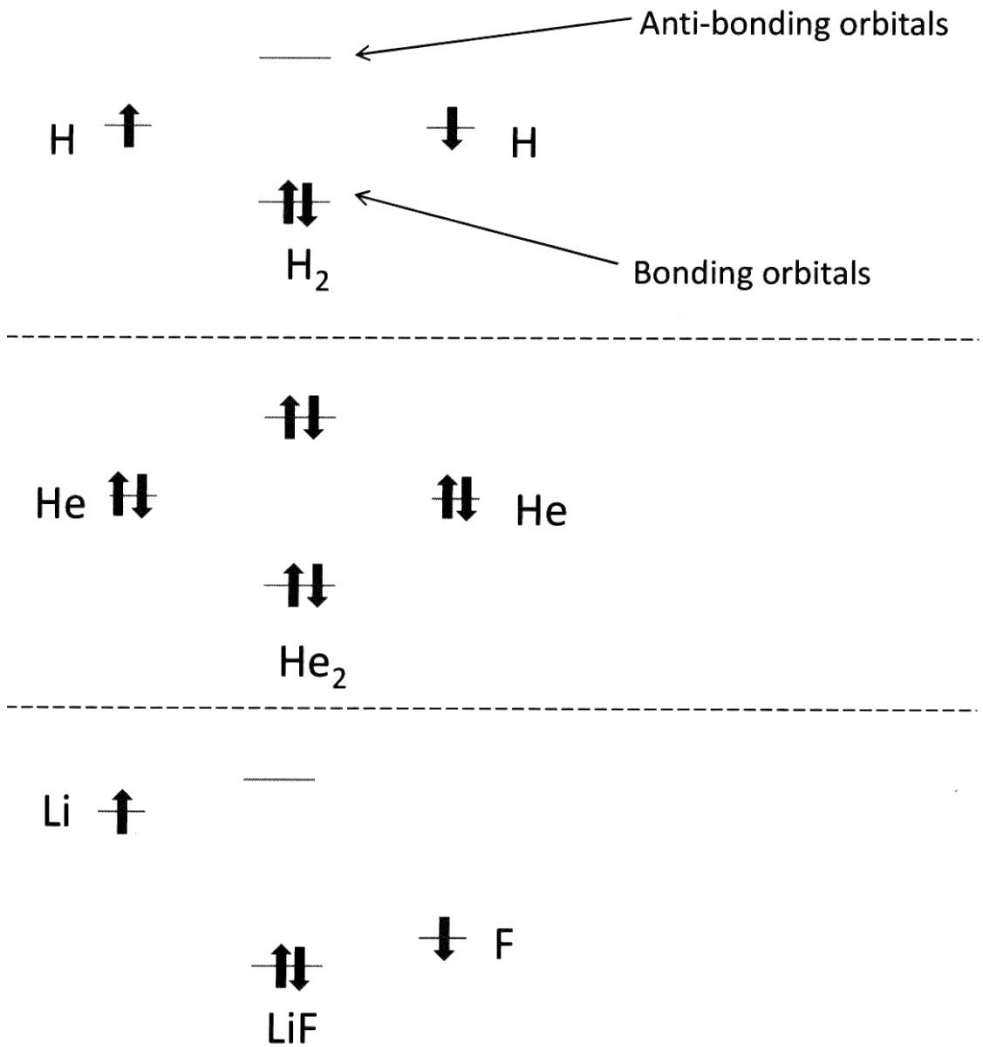


Fig. 6.4 Molecular orbital picture of bonding. In this type of picture, on the far left and far right are the orbital energies of the individual atoms well separated from each other (energy is the vertical axis). In the middle of the diagram are the orbital energies when the atoms come together to form a molecule. **Top:** Two hydrogen atoms (one having a spin-up electron and one having spin-down) come together to form a H_2 molecule. In the particle-in-a-box picture, the lowest-energy eigenstate is reduced in energy when the atoms come together and both electrons go into this bonding orbital. **Middle:** In the case of helium, since there are two electrons per atom, the bonding orbitals are filled, and the antibonding orbitals must be filled as well. The total energy is not reduced by the two helium atoms coming together (thus helium does not form He_2). **Bottom:** In the case of LiF, the energies of the lithium and the fluorine orbitals are different. As a result, the bonding orbital is mostly composed of the orbital on the F atom—meaning that the bonding electrons are mostly transferred from Li to F—forming a more ionic bond. See Exercise 6.3.

6. Chemische Bindung (10)

kovalente Bindung

Abstandsabhängigkeit der bindenden und anti-bindenden Niveaus:

ohne Pauli-Abstoßung

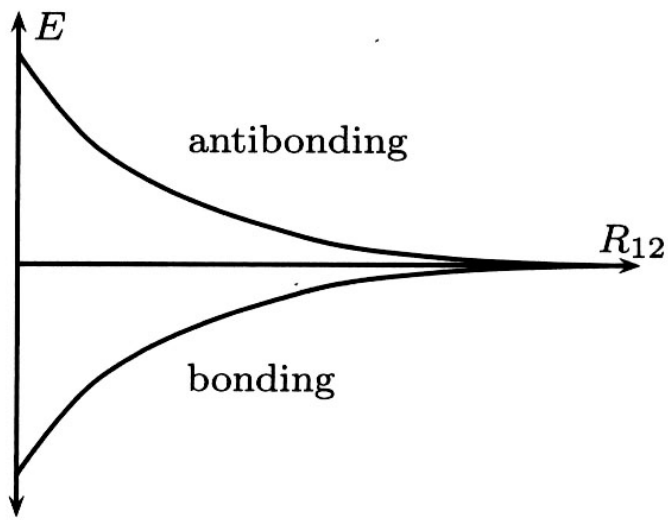


Fig. 6.5 Model tight binding energy levels as a function of distance between the nuclei of the atoms.

mit Pauli-Abstoßung

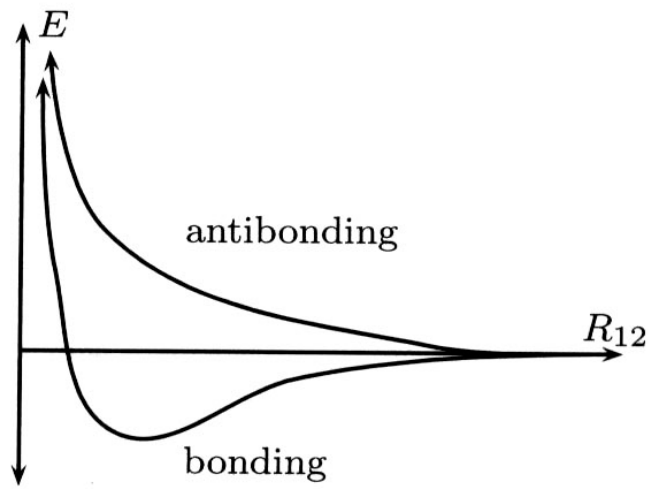


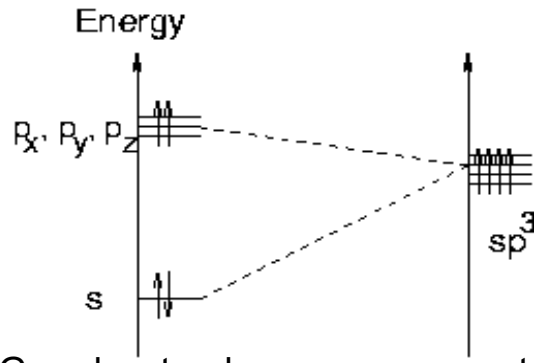
Fig. 6.6 More realistic energy levels as a function of distance between the nuclei of the atoms.

6. Chemische Bindung (11)

Ergänzung:
Hybridisierung u. LCAO-Ansatz

Kohlenstoff C

Hybridisierte Orbitale

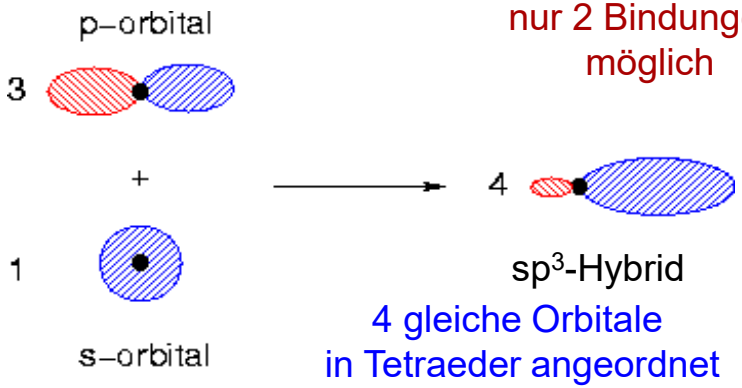


Grundzustand

nur 2 Bindungen möglich

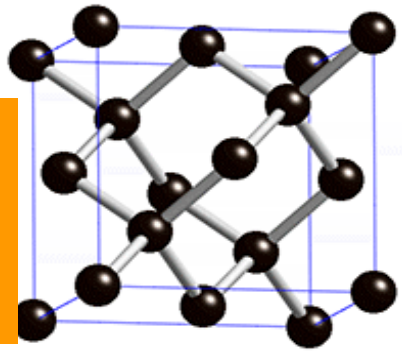
angeregter Zustand
sp^3-Hybrid

4 Bindungen möglich

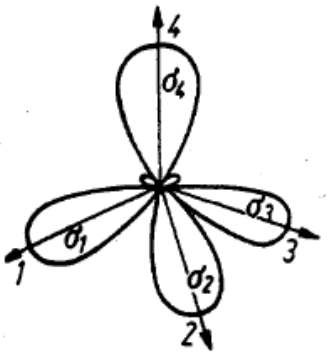


sp^3-Hybrid

4 gleiche Orbitale
in Tetraeder angeordnet



Kristalle:
Diamant-Struktur
C,Si,Ge,
…



sp^3-Hybride vierwertiger Atome:
Die Orbitale sind nach den Ecken eines Tetraeders ausgerichtet (Bindungswinkel 109 Grad).

Erinnerung an Atomphysik:

LCAO-Ansatz $\quad |\psi\rangle = \sum_n \phi_n |n\rangle$

neue (hybridisierte) Wellenfunktion

Linearkombination über atomare Orbitale

Orbital in abstr. Darst., in Ortsdarstellung $\psi_n(\vec{r})$

Gewichtungskoeffizient

Dort gilt eine effektive Schrödingergleichung

$$\underline{\underline{H}}\ \underline{\phi} = E\ \underline{\phi}$$

$$\begin{pmatrix} H_{11} & \dots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \dots & H_{NN} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \vdots \\ \phi_N \end{pmatrix}$$

$\underline{\phi}$: Vektor der Koeffizienten

$\underline{\underline{H}}$: Matrix des Hamilton-Operators

$$H_{n,m} = \langle n | H | m \rangle = \int d^3r\, \psi_n^*(\vec{r})\, H(\vec{r})\, \psi_m(\vec{r})$$

$\hat{=}$ Skalarprodukt in linearer Algebra $(\dots)\begin{pmatrix} \dots \end{pmatrix}\begin{pmatrix} \vdots \end{pmatrix}$ in Ortsdarstellung

LCAO-Ansatz: $|\psi\rangle = \sum_n \phi_n |n\rangle$ mit $n = 1, \dots, N$

$$\sum_n \phi_n H |n\rangle = \underline{H|\psi\rangle = E|\psi\rangle} = E \sum_n \phi_n |n\rangle \qquad | \cdot \langle m|$$

Startpunkt Schrödingergleichung

Herausproj. der m-ten Komponente

$$\sum_n \phi_n \langle m|H|n\rangle = E \sum_n \phi_n \underbrace{\langle m|n\rangle}_{\delta_{m,n} \text{ f. orthonormierte Basis}}$$

$$\sum_n \langle m|H|n\rangle \phi_n = E\, \phi_m$$

m-te Zeile der Matrix-Gl.

$$\begin{pmatrix} H_{11} & \dots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \dots & H_{NN} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \vdots \\ \phi_N \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \vdots \\ \phi_N \end{pmatrix}$$

6. Chemische Bindung (12)

Kohlenstoff C

Auch möglich: flächige Hybridisierung + schwach bindendes, dazu senkrechtes p-Orbital

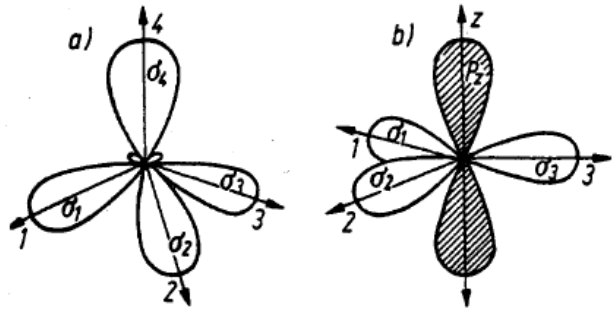
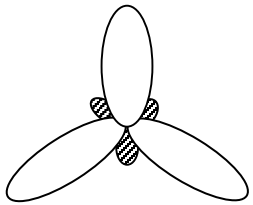
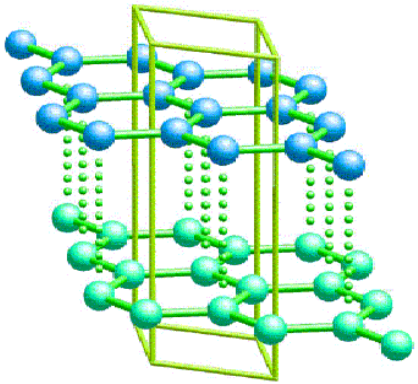


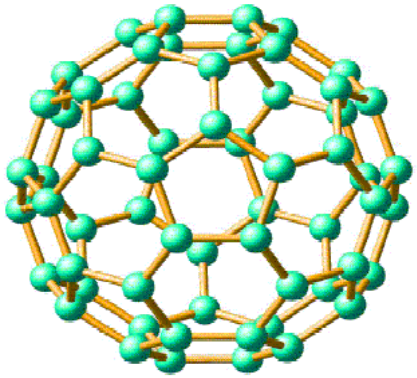
Abb. 5.30. sp^3- und sp^2-Hybride 4wertiger Atome. Die sp^3-Orbitale (a) sind nach den Ecken eines Tetraeders gerichtet, die Bindungswinkel betragen 109°. Die sp^2-Orbitale (b) bilden eine planare Anordnung mit Bindungswinkeln von 120°, auf der das p_z-Orbital senkrecht steht

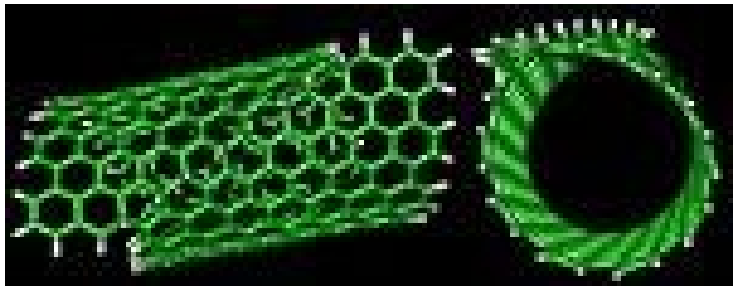


1p Orbital + sp^2-Hybrid

Graphit + neue Kohlenstoff-Materialien: Fullerene (Graphitkugel), Carbon-Nanotubes (Graphitröhre)







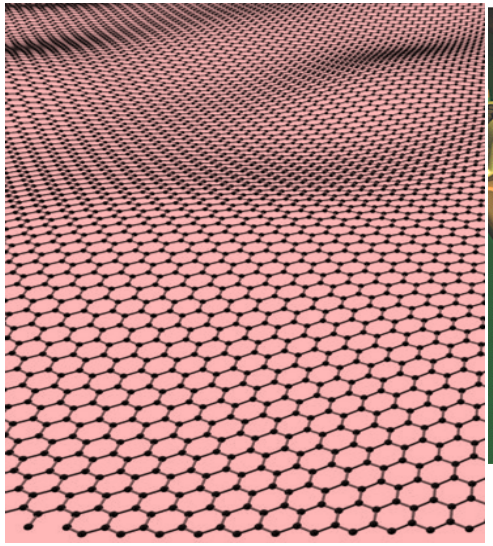
6. Chemische Bindung (13)

Übersicht Kohlenstoff-Modifikationen:

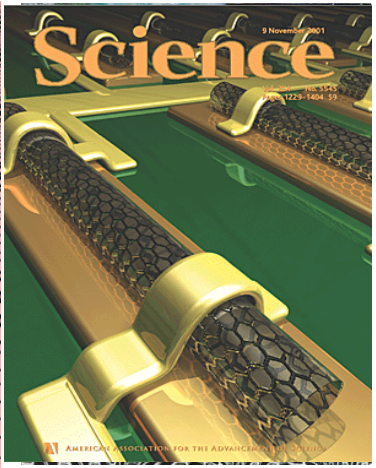
Diamant

Graphit

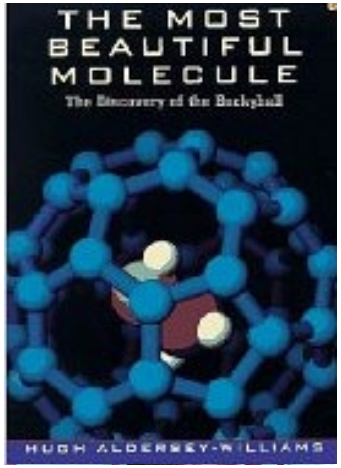
Graphen

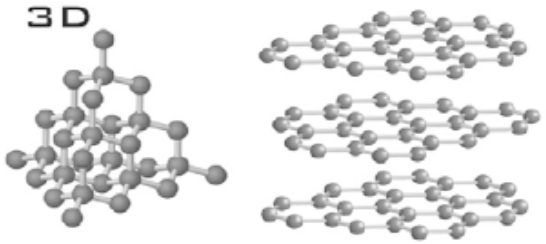


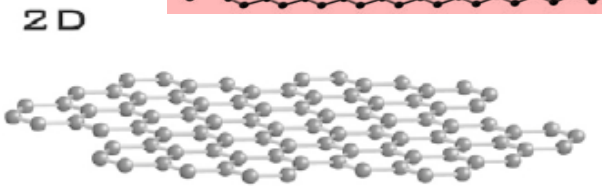
Nanoröhren

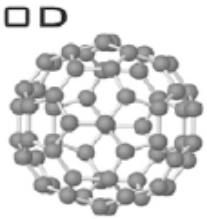


Fullerene (C_{60})



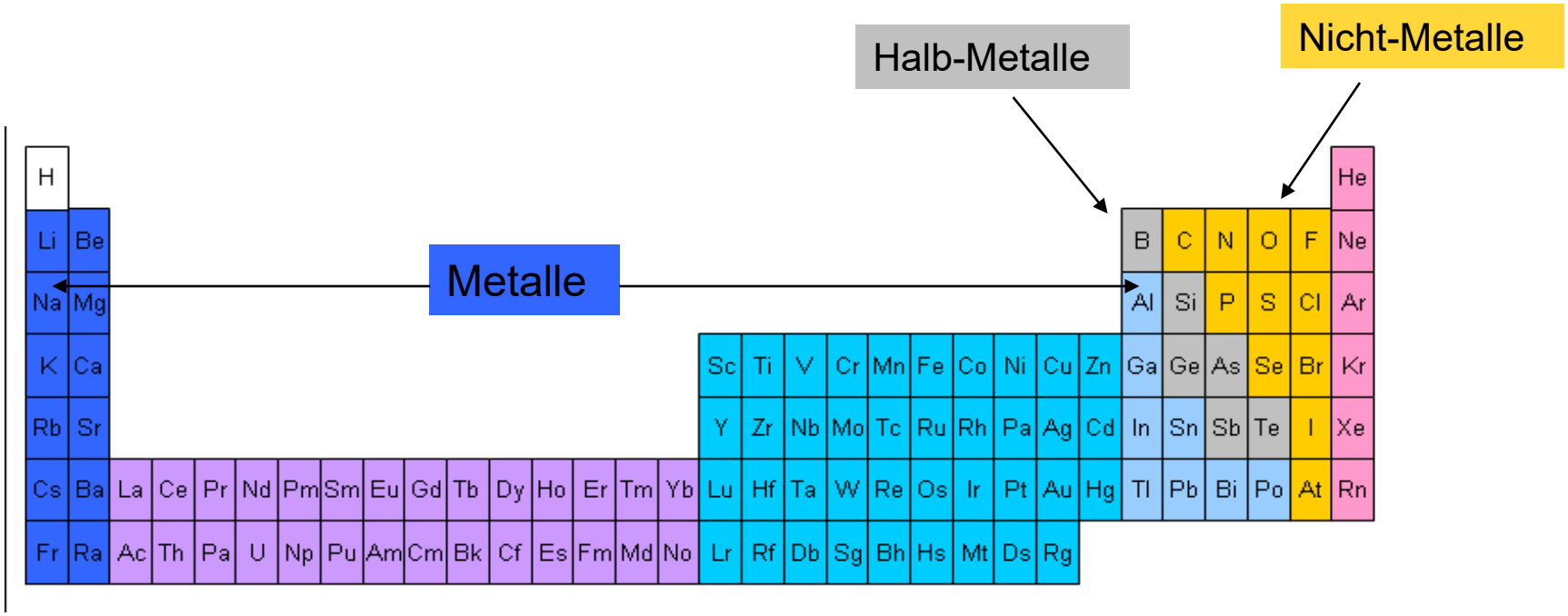






6. Chemische Bindung (14)

metallische Bindung
s-Elektronen
ungerichtete Bindung, dichte Kugelpackungen
Valenzelektronen sind delokalisiert und werden zu Leitungselektronen
hohe elektrische und thermische Leitfähigkeit
mechanische Verformbarkeit (Duktilität)

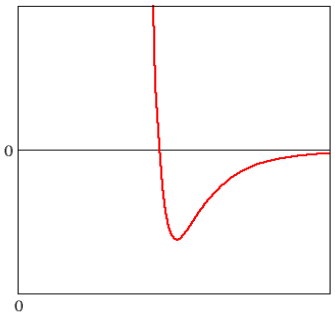


6. Chemische Bindung (15)

van der Waals-Wechselwirkung:

schwache Bindung zwischen Edelgasen sowie inerten Molekülen (z.B. N_2)
beruht auf der Polarisierbarkeit der Elektronenhüllen → induziertes Dipolmoment
attraktive Dipol-Dipol-Wechselwirkung $\sim R^{-6}$
starke Pauli-Abstoßung für kleine R $\sim R^{-12}$

Modelliert durch sogenanntes Lennard-Jones-Potential:



$$U = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

für ein Atompaar

Nur zwei empirische Parameter: σ aus Gleichgewichtsabstand R_0
ε aus Bindungsenergie

Motivation und Rechnung: Lennard-Jones-Potential

Edelgaskristall	R_0/Å	ε/eV	σ_0/Å	T(Siedepunkt)/K
He	?	$8.4*10^{-4}$	2.56	4.2
Ne	3.13	$3*10^{-3}$	2.78	27
Ar	3.76	0.010	3.40	87
Kr	4.01	0.015	3.60	120
Xe	4.35	0.019	4.10	165

Lennard-Jones-Potential

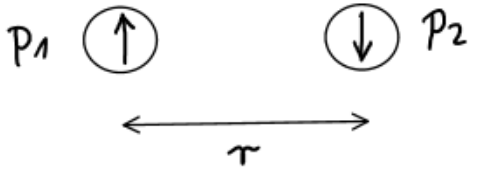
$$U = 4\varepsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right]$$

$$\frac{dU}{dR} = 0 \longrightarrow \text{Gleichgewichtsabstand } R_0 = \sqrt[6]{2}\,\sigma$$

Motivation des attraktiven r^6-Terms: Wechselwirkung fluktuierender Dipole

$$\downarrow$$

$$\langle p \rangle = 0, \quad \text{aber} \quad \langle p^2 \rangle \neq 0$$



p_1 bewirkt

$$E = \frac{p_1}{4\pi\varepsilon_0 r^3} \xrightarrow[\text{induziert}]{} p_2 = \alpha E$$

mit $E_{WW} = U = -\vec{p}\cdot\vec{E} = -\dfrac{|p_1|^2 \alpha}{(4\pi\varepsilon_0 r^3)^2} < 0$

somit $U \sim 1/r^6$

6. Chemische Bindung (16)

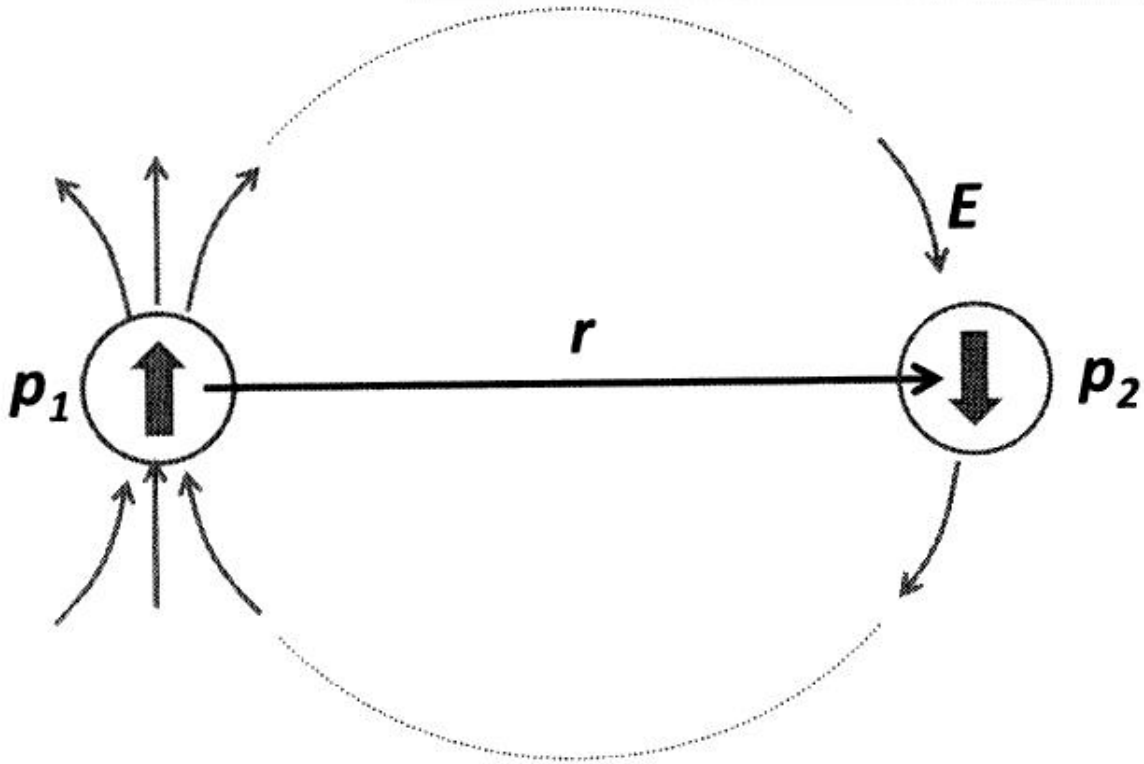


Fig. 6.7 An atom with a polarization p_1 induces a polarization p_2 in a second atom.

6. Chemische Bindung (17)

Wasserstoff-Brückenbindung

Eis-Struktur, DNS-Helix Struktur, Clathrate (Einschlussverbindungen)
schwache Bindung, gerichtete Dipol-Wechselwirkung unter Wasserstoff-Beteiligung

H = e^- + sehr kleines Proton = unabgeschirmte positive Ladung auf Oberfl. des Bindungspartners = starker elektrischer Dipol (permanent!)

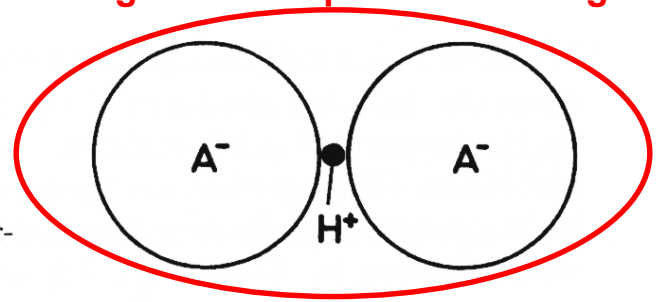
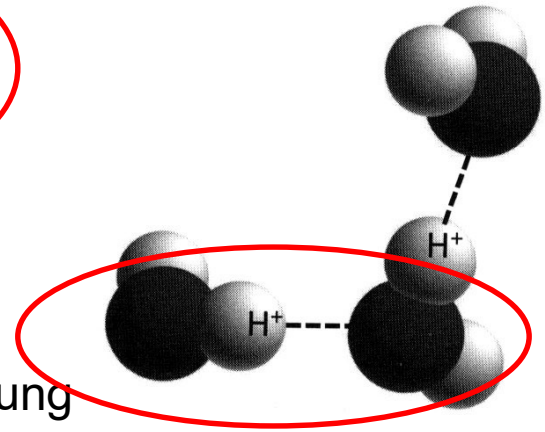


Fig. 1.28
Bindung zweier Atome über eine Wasserstoffbrücke



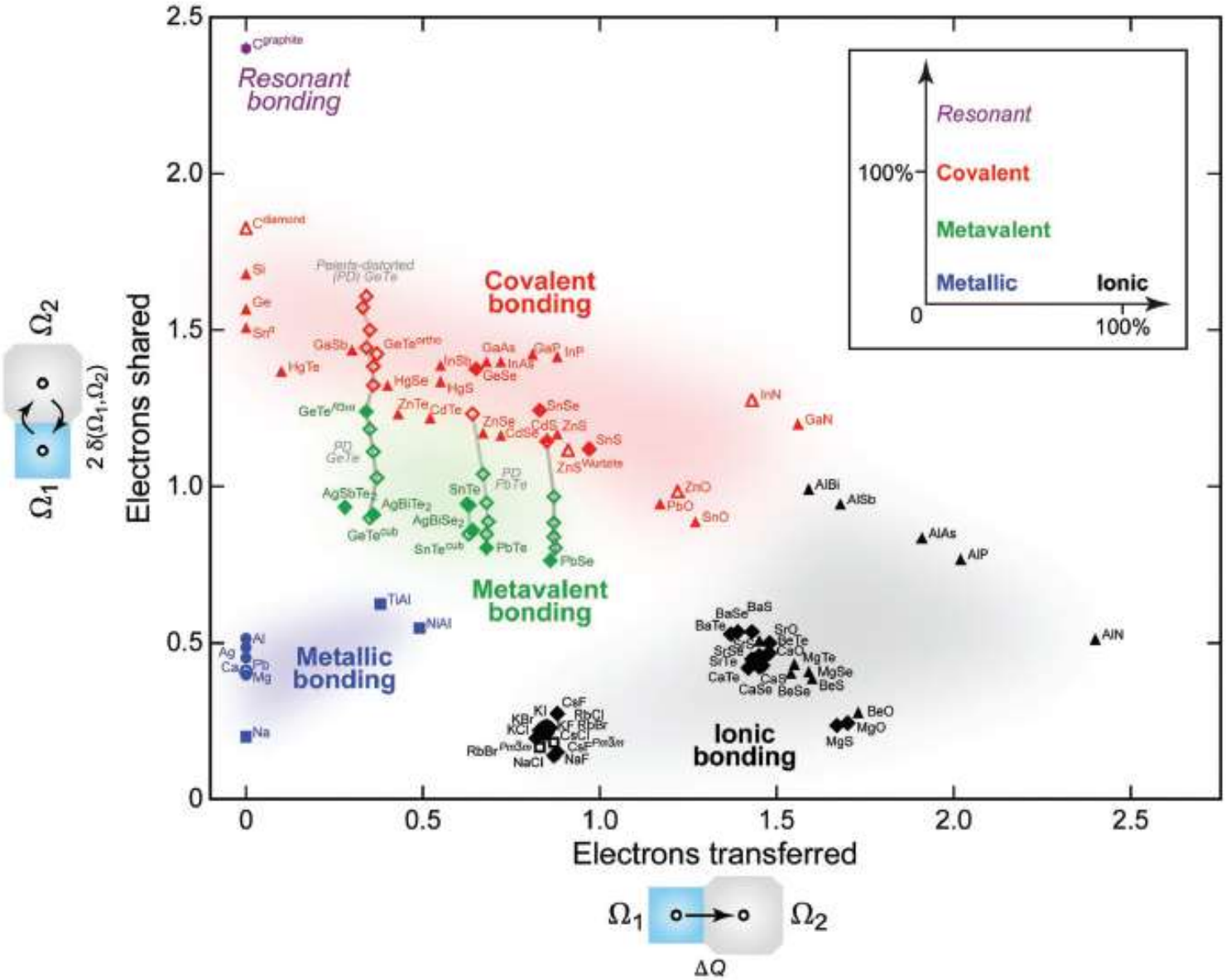
Tetraedrische Koordination in Eis bedingt durch H^+-Brückenbindung
Bindungsenergie ~ 25 meV pro H_2O ~ k_BT bei Zimmertemperatur

Fig. 6.8 Hydrogen bonds in H_2O. A hydrogen on one water molecule is attracted to an oxygen on another molecule forming a weak hydrogen bond. These bonds are strong enough to form ice below the 273.15 K.

Bsp. Lebenswiss.: H-Brückenbindung in der Doppelhelix der DNS

Bsp. Chemie: Vernetzung der Stränge von Nylon über H-Brücke

Exkurs: Ein sechster fundamentaler Bindungstyp?



Aktuelle Diskussion:

Existenz eines eigenständigen sechsten Bindungstyps “Metavalente Bindung”? (Wuttig et al.)

Abb. aus
J. Raty et al.,
Adv. Mat. 31, 1806280 (2018)

Exkurs: Metavalente Bindung?

ADVANCED MATERIALS

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The Myth of "Metavalency" in Phase-Change Materials

Robert O. Jones, Stephen R. Elliott, Richard Dronskowski

First published: 10 May 2023 | https://doi.org/10.1002/adma.202300836 | Citations: 27

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Abstract

Phase-change memory materials (PCMs) have unusual properties and important applications, and recent efforts to find improved materials have focused on their bonding mechanisms. "Metavalent bonding" or "metavalency," intermediate between "metallic" and "covalent" bonding and comprising single-electron bonds, has been proposed as a fundamentally new mechanism that is relevant both here and for halide perovskite materials. However, it is shown that PCMs, which violate the octet rule, have two types of covalent bond: two-center, two-electron (2c-2e) bonds, and electron-rich, multicenter bonds (3c-4e bonds, hyperbonds) involving lone-pair electrons. The latter have bond orders less than one and are examples of the century-old concept of "partial" bonds.

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First published: 07 December 2023 | https://doi.org/10.1002/advs.202308578 | Citations: 2

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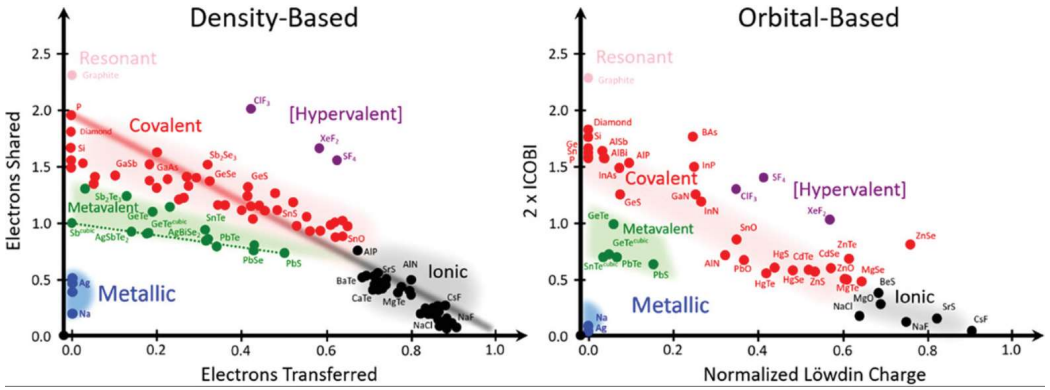
Abstract

A family of solids including crystalline phase change materials such as GeTe and Sb_2Te_3, topological insulators like Bi_2Se_3, and halide perovskites such as $CsPbI_3$ possesses an unconventional property portfolio that seems incompatible with ionic, metallic, or



6. Reale Bindungen: Mischtypen ionisch/kovalent (18)

8-N-Regel *Grimm-Sommerfeld*

$A^N B^{8-N}$

ionisch

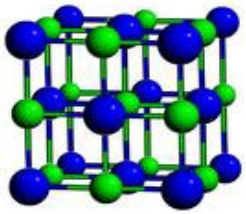
1-7 Verbindungen Alkali-Halogenide *LiF, NaCl, …*

2-6 " Erdalkali-Chalkogenide *CaO*, …

3-5 " *BN*, Halbleiter *GaAs, InSb*

4-4 " *C, Si, Ge, SiC*

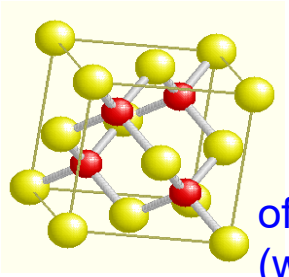
kovalent



NaCl

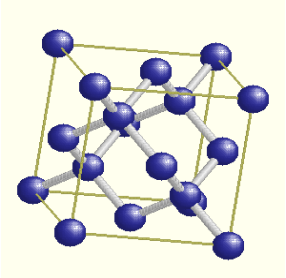
kompakt

offene Strukturen (wg. gerichteter Bindung)



Wurtzite

starke Kovalenz
sehr hart



Diamant

ionischer/kovalenter Bindungsanteil bestimmt durch Elektronegativität!

- Schlussfolgerung: reale Bindung = Mix von idealisierten Grenzfällen
- Zusätzlich: sehr starke Bindung durch Mehrfachbindungen (z.B: N_2 mit Dreifachbindung)

6. Reale Bindungen: Mischtypen metallisch/kovalent (19)

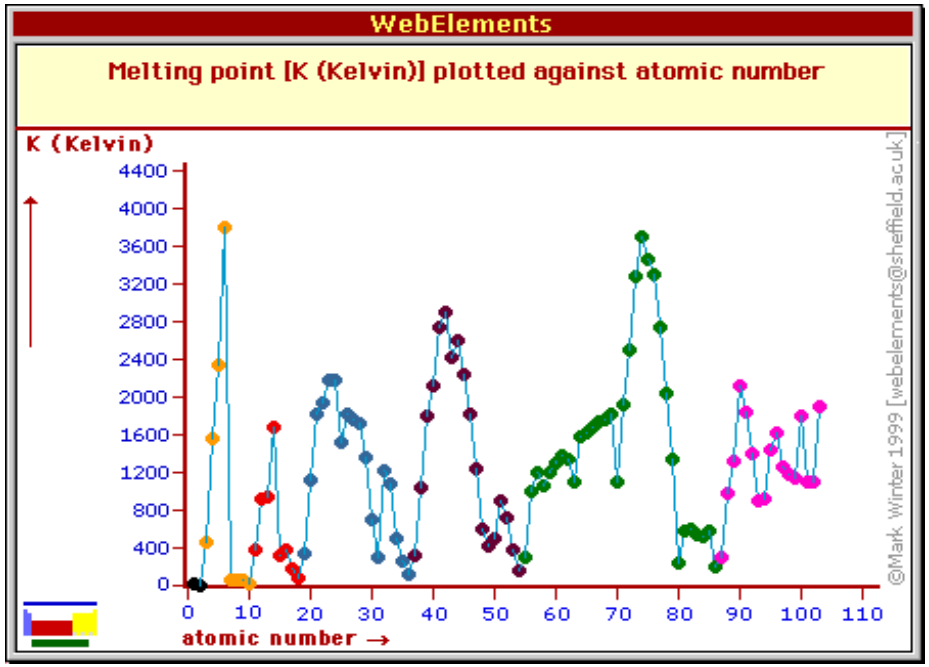
d-Übergangsmetalle

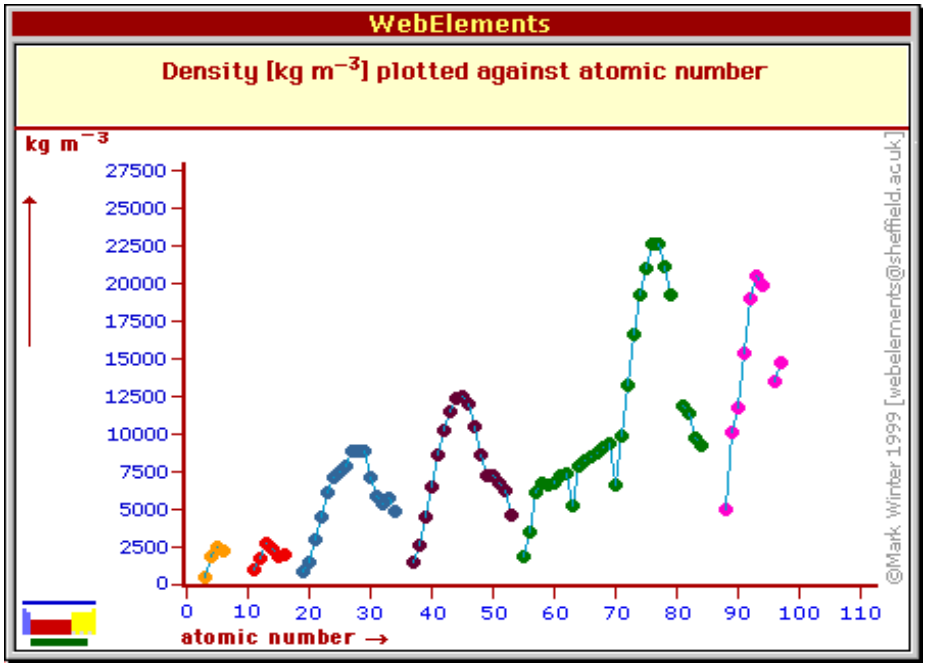
d-Orbitale sind ein Reservoir für zusätzliche kovalente Bindungen

hohe Schmelzpunkte und Dichten in Mitte der d-Reihen,

3d-Metalle: $T_{Schmelz}$ bis ~ 2000 K, W: 3695 K

Ergänzung: Hochtemperatur-Werkstoffe





Hochtemperatur-Werkstoffe

Idee: Erhöhung des Wirkungsgrades thermodynamischer Maschinen (Gasturbine, Flugzeugtriebwerk etc.)

Carnot-Wirkungsgrad für eine zyklisch zwischen zwei Temperaturniveaus arbeitende Maschine

$$\eta = 1 - \frac{T_{niedrig}}{T_{hoch}}$$ Idealfall, $\Delta S = 0$

$$\eta = 1 - \sqrt{\frac{T_{niedrig}}{T_{hoch}}}$$ mit Dissipation, $\Delta S > 0$

In jedem Fall kann der Wirkungsgrad erhöht werden durch

$T_{niedrig} \searrow$ aber: Kühlung unpraktisch u. mit Energieaufwand verbunden

$T_{hoch} \nearrow$ aber: Schmelztemperatur setzt Grenze nach oben

$\downarrow$

Praktische Umsetzung durch Hochtemperatur-Werkstoffe

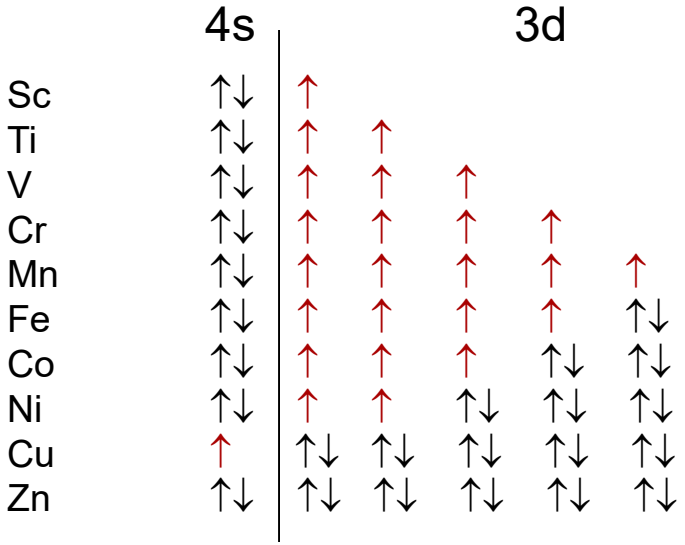
i.d.R. realisiert durch Legierungen mit hohem Anteil an Übergangselementen

typ. Vertreter: $Ni_x Al_{1-x}$ $x \approx 0{,}5$

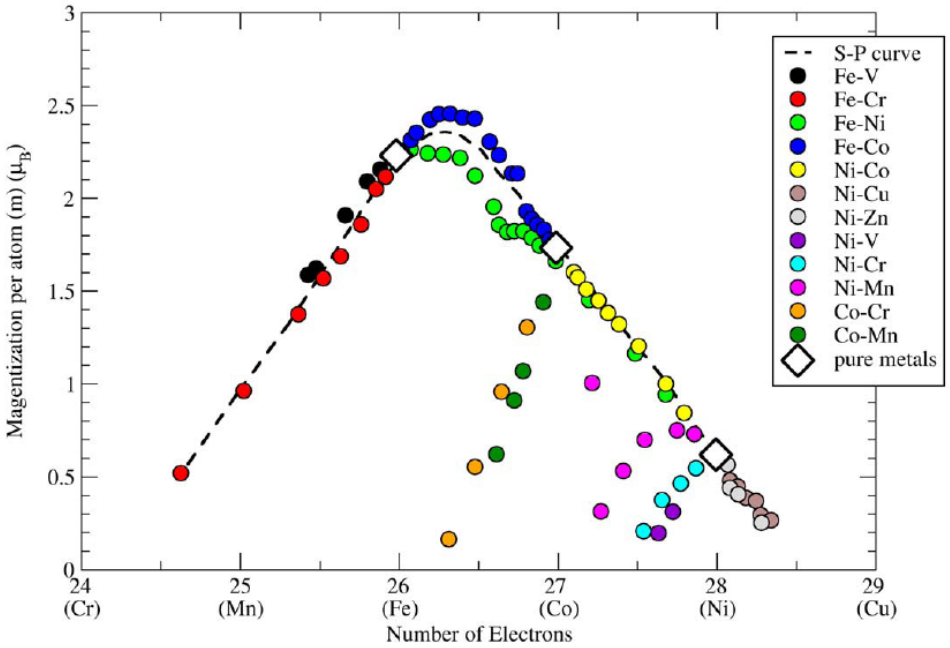
6. Elektronenstruktur und magnetisches Moment (20)

Hier: Elektronenstruktur der d-Übergangsmetalle

- Auffüllen der d-Orbitale → magnetische Eigenschaften durch ungepaarte Spins
- Beachte: Magnetische Momente für Einzelatome die Regel, kollektiver Magnetismus im Festkörper jedoch die Ausnahme (nur Fe, Co, Ni + zugehörige Legierungen).

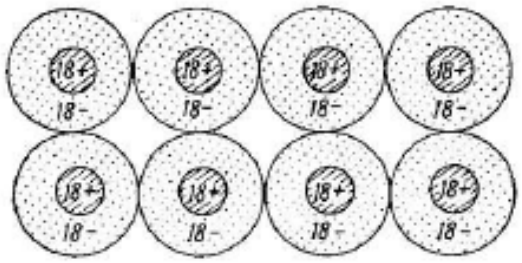


Bsp.: Slater-Pauling-Kurve

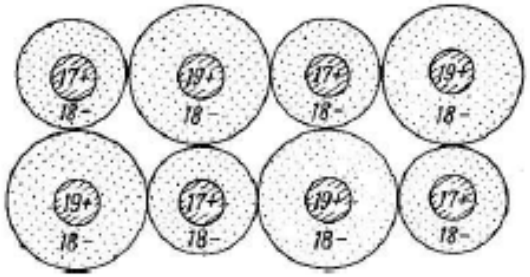


6. Chemische Bindung (21)

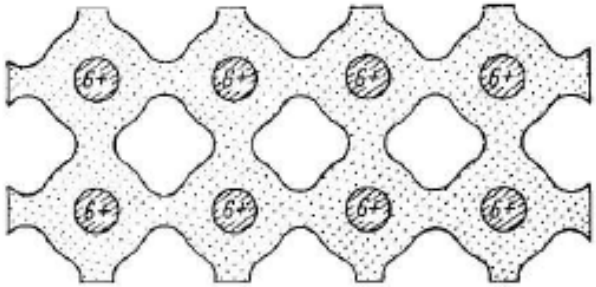
Grafische Zusammenfassung:



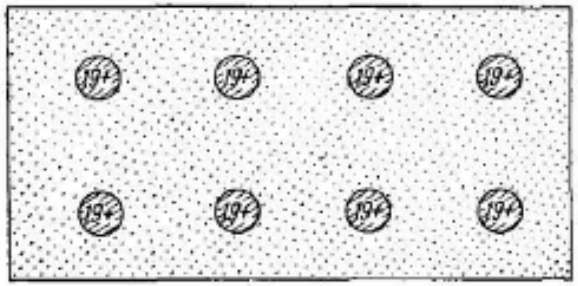
Argon Crystal. Molecular (Flucuating dipole) Bonds. No transfer of charge.



Potassium Chloride (KCl). Ionic Crystal. An electron is transferred from the K to the Cl to make K+ and Cl- which then attract each other



Carbon Crystal (Covalent Bonds). Each Atom shares electrons with its neighbors.



Metallic bonding in Potassium. Electrons are completely delocalized into an electron gas which holds together the ions.

Figure 5.8: Cartoons of Bonding Types