Grundlagen der chemischen Bindung

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Anorganische Experimentalchemie

https://x.com/HEDM_at_LMU

Bohr:

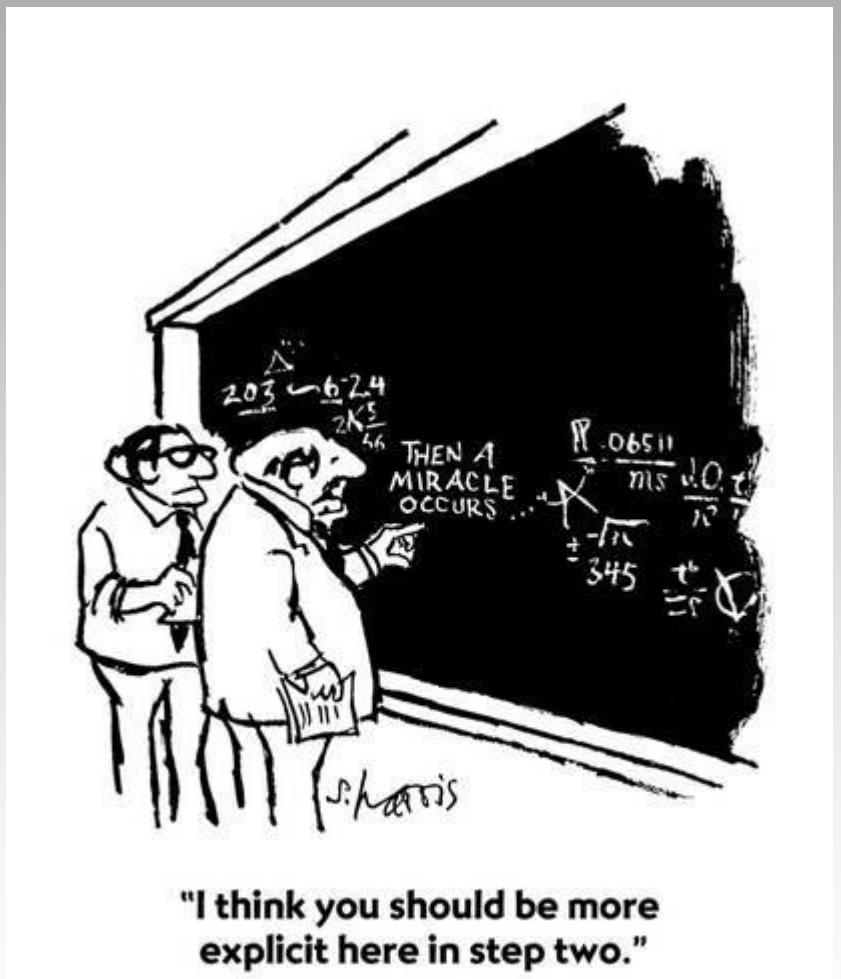
$$n\hbar = mvr$$

$$E = -\frac{e^2 Z}{8\pi\varepsilon_0 r} = -\frac{e^4 m Z^2}{8h^2 {\varepsilon_0}^2}\frac{1}{n^2}$$

1s Orbital: $$r = a_0 = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2 Z}$$

"Protons give an atom its identity, electrons its personality“

(Bill Bryson)



"I think you should be more explicit here in step two."

T. M. Klapötke, I. C. Tornieporth-Oetting, Nichtmetallchemie, VCH, Weinheim, **1994**, 13 – 37.

1927, Heisenberg

$$\Delta x * \Delta(mv_x) \geq \frac{h}{2\pi}$$

Unschärferelation

1924, de Broglie

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Welle-Teilchen-Dualismus

Kreisbahn = stehende Welle:

$$2\pi r = n\lambda$$

$$2\pi r = n\frac{h}{mv}$$

$$mvr = n\frac{h}{2\pi}$$

(vergl. Bohr)

- Welleneigenschaften des e-
- Unbestimmtheit des Ortes

} Quantenmechanik

$\int_{Raum} \Psi^* \Psi d\tau = 1$

Postulate der Quantenmechanik

I. (a) Jeder Zustand eines Systems wird so vollständig wie möglich durch eine

Wellenfunktion $\Psi(q_1, \ldots q_{3N}, t)$ beschrieben.

(b) Die Größe $\Psi^* \Psi$ ist proportional der Wahrscheinlichkeit, q_1 zwischen q_1 und dq, …

zu einer bestimmten Zeit t zu finden.

Ψ: 1. + 2. Ableitung stetig, eindeutig, quadratintegrabel, endlich, für +/- ∞ → 0

$$\int_{Raum} \Psi^* \Psi d\tau = 1$$

II. Für jede beobachtbare Eigenschaft (Observable)[#] eines Systems existiert ein entsprechender linearer, hermitescher Operator, die physikalischen Eigenschaften der Observablen können aus den mathematischen Eigenschaften des zugeordneten Operators abgeleitet werden:

$$\int_{Raum} \Psi_i^* \underline{A} \Psi_j d\tau = \int_{Raum} \Psi_j \underline{A^*} \Psi_i^* d\tau$$

$$T = \frac{1}{2} mv^2 = \frac{1}{2m} \left(p_x^2 + p_y^2 + p_z^2 \right)$$

$$p \rightarrow -i\hbar\nabla$$

$$\boldsymbol{T} = -\frac{\hbar^2}{2m} \nabla^2$$

$$\underline{H} = \underline{T} + \underline{V}$$

$$\boldsymbol{H} = -\frac{\hbar^2}{2m} \nabla^2 + \boldsymbol{V}$$

[#] alle Eigenschaften eines Syst. = dyn Variablen (z.B. r, E, p_x, …);
Beobachtbare Eigenschaften = Observable (nicht p_x,..)

III. Schrödinger-GL. Für ein Teilchen im stationären Zustand:

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

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \boldsymbol{V}\Psi = E\Psi$$

$$\frac{\hbar^2}{2m}\nabla^2\Psi + (E - \boldsymbol{V}) = 0$$

IV. Mittelwert:

$$A = \frac{\int \Psi^* \, \underline{A} \, \Psi \, d\tau}{\int |\Psi|^2 \, d\tau}$$

V. Zeitabhängigkeit:

$$i\,\hbar\,\frac{\partial\Psi}{\partial\tau} = \underline{H}\,\Psi$$

$$\Psi(q,t) = \Psi_0(q)\; e^{-(i/\hbar)At}$$

$$\psi(x,y,z,t) = \psi(x,y,z) * e^{-2\pi i\nu t}$$

Schrödinger-Gleichung

$$\psi(x,y,z,t) = \psi(x,y,z) * e^{-2\pi i \nu t}$$

$$(\underline{T} + \underline{V})\psi = \underline{H}\psi = \underline{E}\psi$$

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \qquad p \rightarrow -i\hbar\nabla$$

$$\underline{T} = \frac{\hbar^2}{2m}\nabla^2$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi = E\psi$$

ψ_s , die Lösungen der Schrödinger-Gleichung sind, sind Eigenfunktionen.

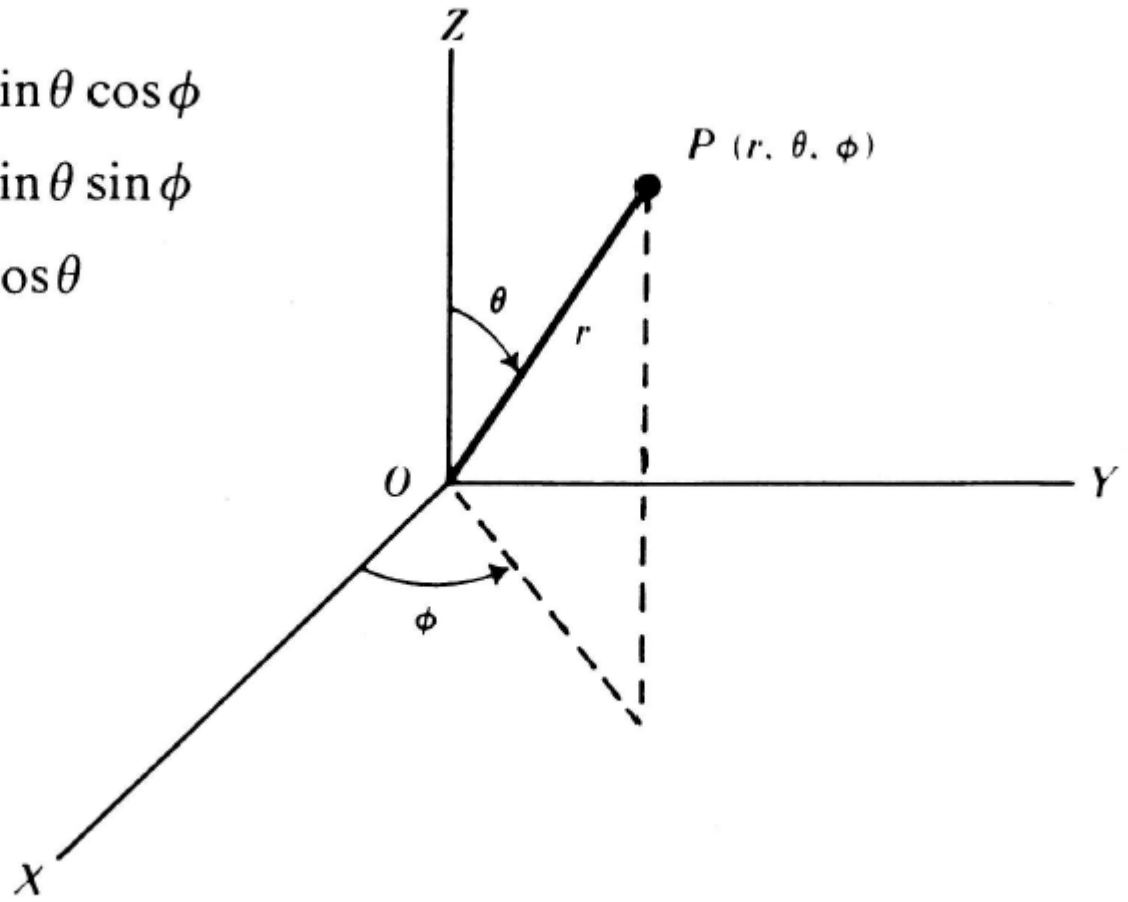
Energiewerte, die zu den Eigenfunktionen gehören, sind Eigenwerte.

$$\psi_{n,l,m_L} = NR_{n,l}(r) * X_{l,m_L}(\vartheta,\varphi) \qquad [\psi]^2 \equiv \text{Wahrscheinlichkeit}$$

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$



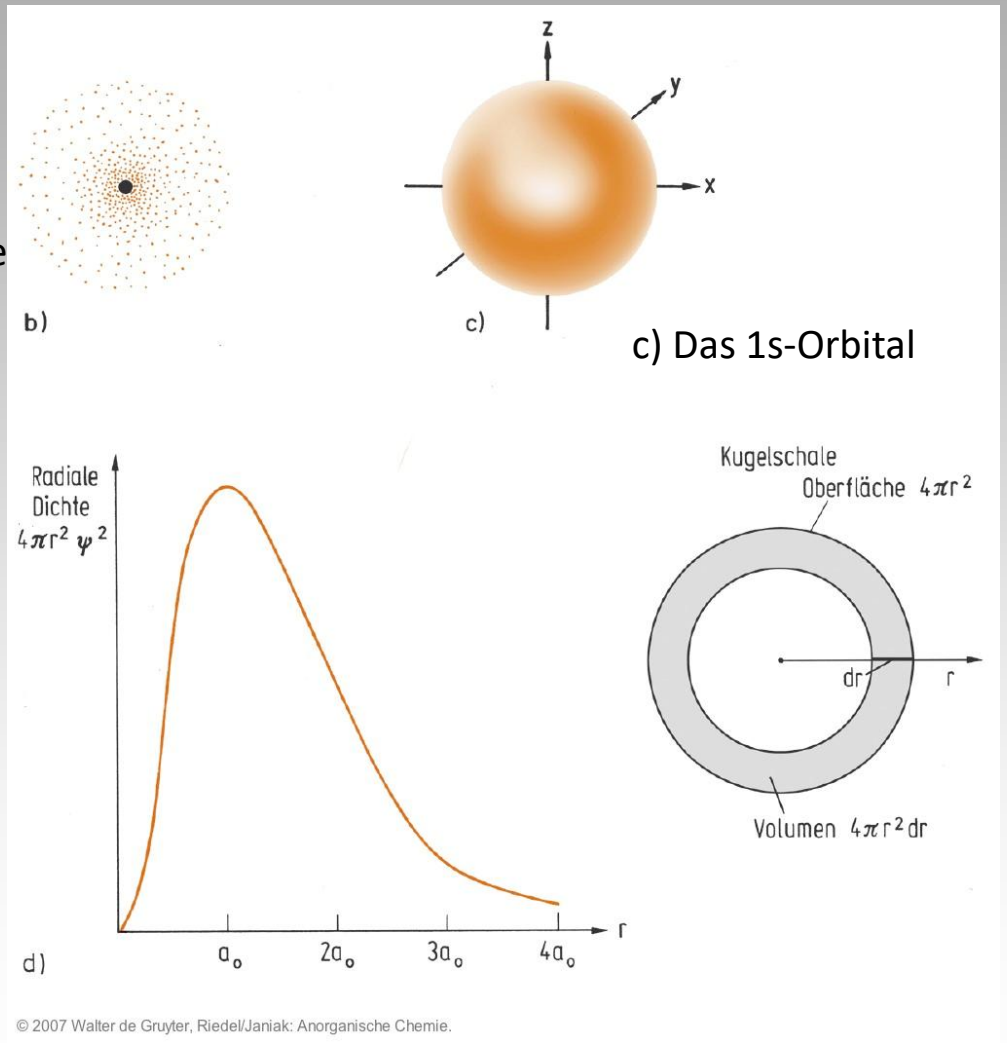
Sphärische Polarkoordinaten. Ein Punkt $P(r, \theta, \phi)$ ist durch zwei Winkel und eine Strecke definiert.

Einige Eigenfunktionen des Wasserstoffatoms

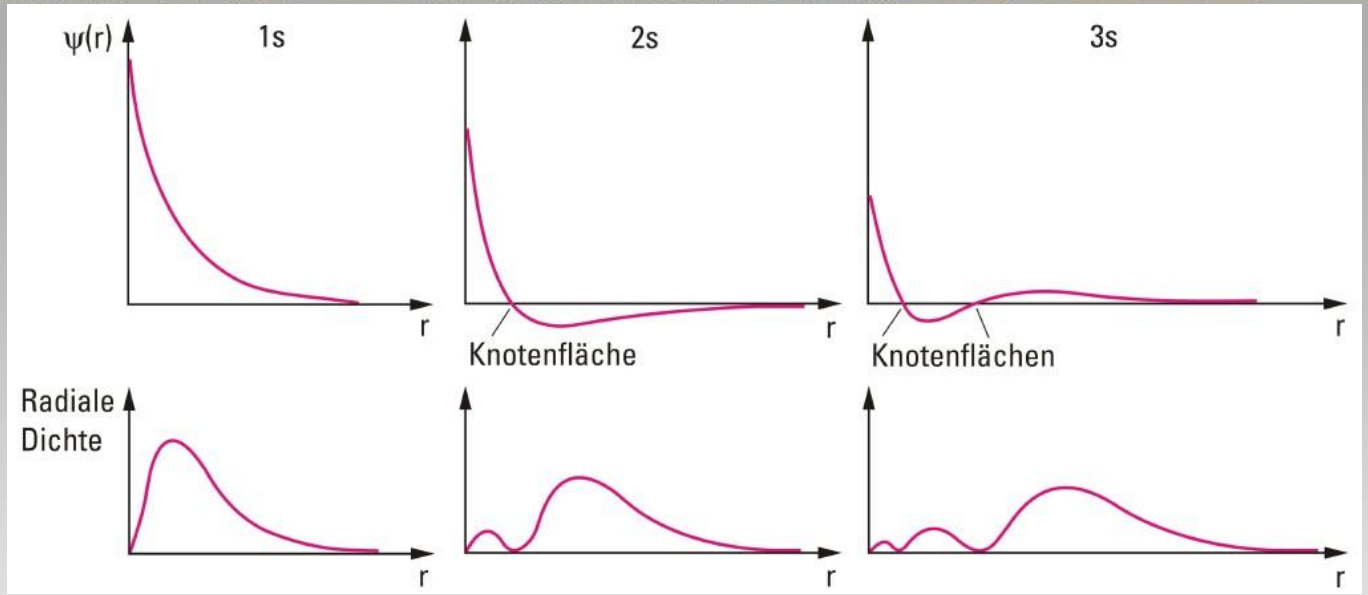
Quantenzahlen			Orbital	Eigenwert	Normierte Radialfunktion	Normierte Winkelfunktion
n	l	m_l		E_n	$R_{n,l}(r)$	$\chi_{l,m_l}(\vartheta,\varphi)$
1	0	0	1s	E_1	$\frac{2}{\sqrt{a_0^3}}\,e^{-\frac{r}{a_0}}$	$\frac{1}{2\sqrt{\pi}}$
2	0	0	2s	$E_2=\frac{E_1}{4}$	$\frac{1}{2\sqrt{2a_0^3}}\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$	$\frac{1}{2\sqrt{\pi}}$
2	1	1	$2p_x$	$E_2=\frac{E_1}{4}$	$\frac{1}{2\sqrt{6a_0^3}}\,\frac{r}{a_0}\,e^{-\frac{r}{2a_0}}$	$\frac{\sqrt{3}}{2\sqrt{\pi}}\sin\vartheta\cos\varphi$
2	1	0	$2p_z$	$E_2=\frac{E_1}{4}$	$\frac{1}{2\sqrt{6a_0^3}}\,\frac{r}{a_0}\,e^{-\frac{r}{2a_0}}$	$\frac{\sqrt{3}}{2\sqrt{\pi}}\cos\vartheta$
2	1	−1	$2p_y$	$E_2=\frac{E_1}{4}$	$\frac{1}{2\sqrt{6a_0^3}}\,\frac{r}{a_0}\,e^{-\frac{r}{2a_0}}$	$\frac{\sqrt{3}}{2\sqrt{\pi}}\sin\vartheta\sin\varphi$

a_0 ist der Bohr-Radius (vgl. Gl. 1.17). Er beträgt $a_0=\frac{h^2\varepsilon_0}{\pi m e^2}$ = 0.53 Å

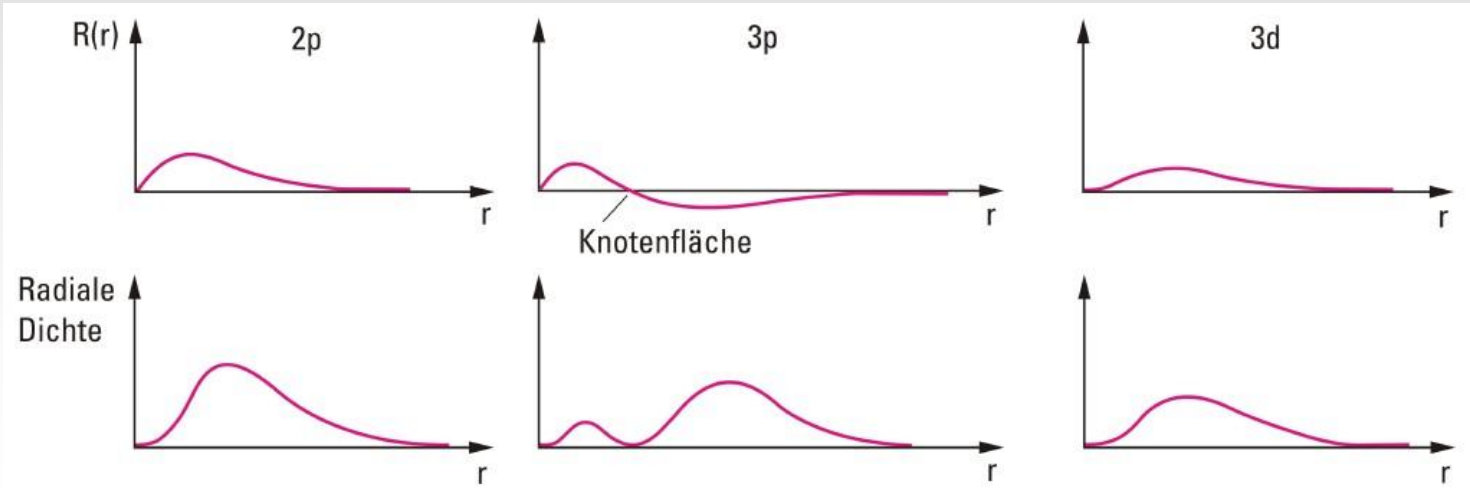
b) Schnitt durch den Atomkern.
ψ^2 wird durch eine unterschiedliche Punktdichte dargestellt.



c) Das 1s-Orbital



Darstellungen der Wellenfunktion ψ(r) und der radialen Dichte von s-Orbitalen.



Schematische Darstellung der Radialfunktion R(r) und der radialen Dichte für 2p-, 3p- und 3d-Orbitale.

Quantenzahlen

n **HQZ** n = 1,2,3, …
- Größe des Orbitals
- Energie (vgl. Bohr)
- Gesamtkontenzahl: n-1

l **NQZ** l = 0, 1, 2, …, n-1
- Gestalt des Orbitals
- Gesamtdrehimpuls
- l Knoten im Winkel (X) Teil

$$\underline{L}^2 X_{l,m_L}(\vartheta,\varphi) = l(l+1)\hbar^2 X$$

m_L **MQZ** m_L = l, l-1, …, 0, …, -l
- Orientierung des Orbitals im Raum

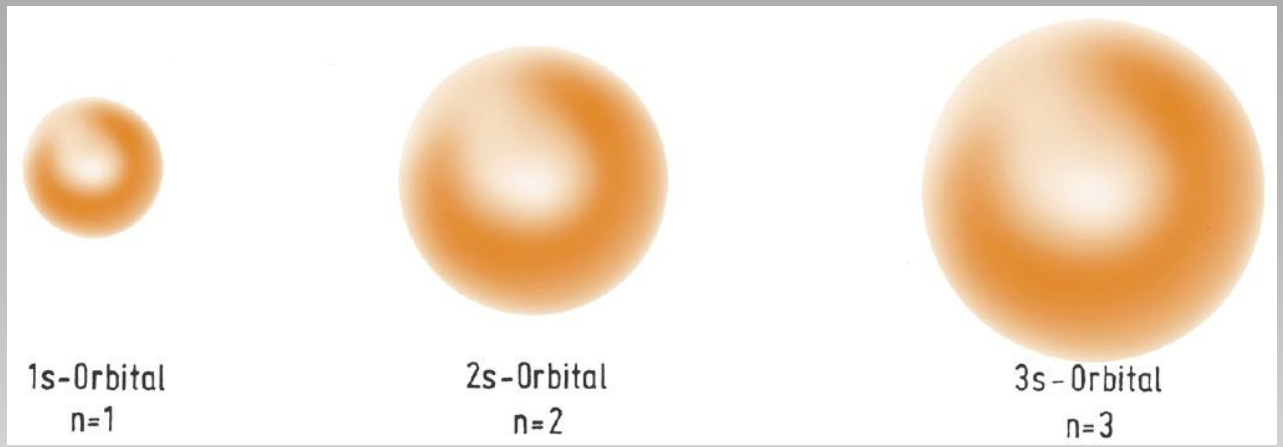
$$\underline{L}_z \Phi_{m_L}(\varphi) = m_L \hbar \Phi_z(\varphi)$$

m_s **SQZ** $m_s = \pm\frac{1}{2}$; α, β; $\uparrow, \downarrow$

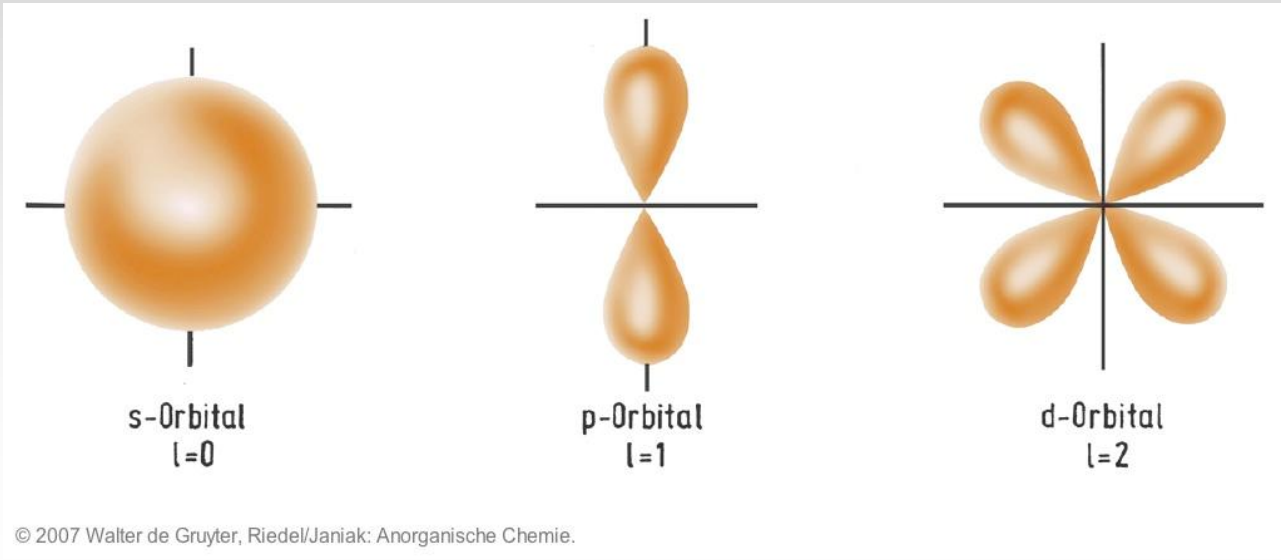
$$\underline{s}^2 \chi_s = s(s+1)\hbar^2 \chi_s$$

$$\underline{s}_z \chi_s = m_s \hbar \chi_s$$

Hauptquantenzahl (n)
Nebenquantenzahl (l)
Magnetische Quantenzahl (m_L)
Spinquantenzahl (m_s)

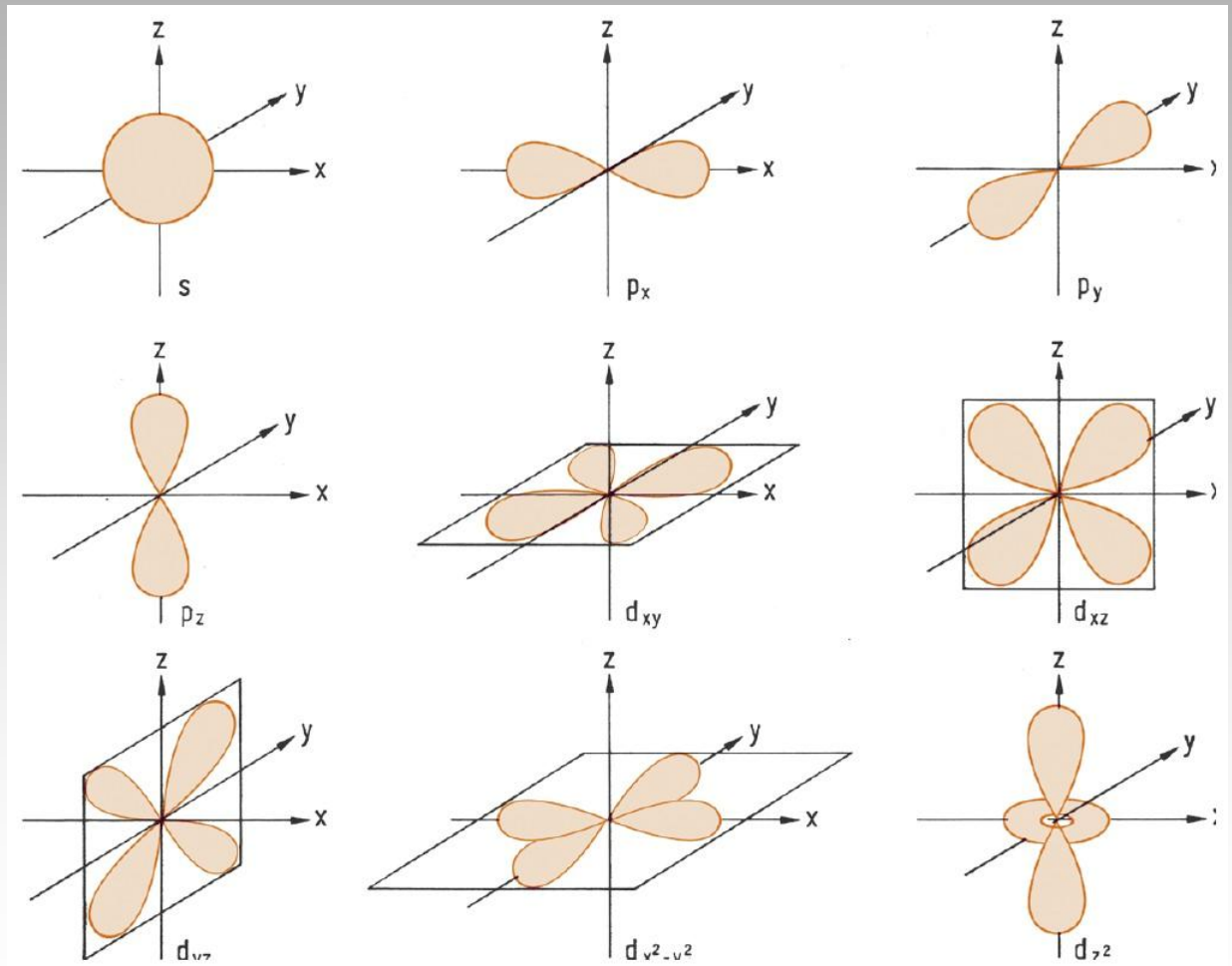


Die **Hauptquantenzahl n** bestimmt die Größe der Orbitale.



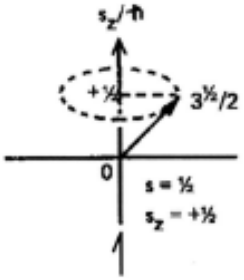
Die **Nebenquantenzahl l** bestimmt die Gestalt der Orbitale.

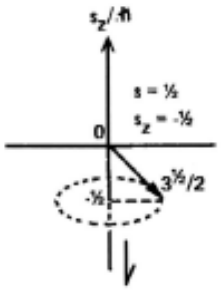
Gestalt und räumliche Orientierung der s, p- und d-Orbitale.



Orientations of spin angular momentum vectors for one and two electrons relative to an external magnetic field directed along the z-axis. $\hbar = h/2\pi$

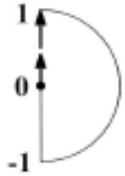
one electron



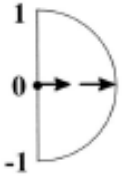


two electrons

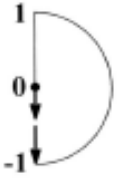
$S = 0$
$S_Z = 0$



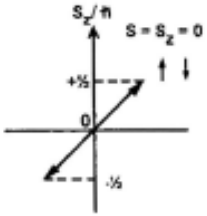
$S = 1$
$S_Z = 1$

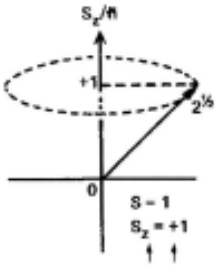


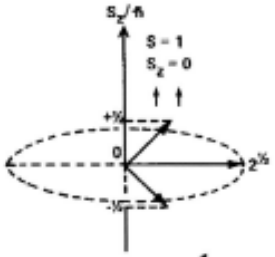
$S = 1$
$S_Z = 0$

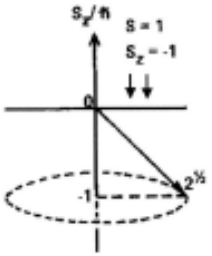


$S = 1$
$S_Z = -1$









$$(\uparrow\downarrow - \downarrow\uparrow)\frac{1}{\sqrt{2}}$$

$$\uparrow\uparrow$$

$$(\uparrow\downarrow + \downarrow\uparrow)\frac{1}{\sqrt{2}}$$

$$\downarrow\downarrow$$

$$\left((\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)\frac{1}{\sqrt{2}}$$

anti -

$$\alpha(1)\alpha(2)$$

$$\left((\alpha(1)\beta(2) + \beta(1)\alpha(2)\right)\frac{1}{\sqrt{2}}$$

$$\beta(1)\beta(2)$$

symmetric

Spinquantenzahl

$$\underline{s}^2\chi_s = s(s+1)\hbar^2\chi$$

$$s_z\chi_s = m_s\hbar\chi_s$$

$$m_s = \pm\frac{1}{2}$$

$$\underline{s}_z\alpha = \frac{1}{2}\hbar\alpha \qquad \underline{s}_z\beta = -\frac{1}{2}\hbar\beta$$

$$\underline{s}^2{}_z\alpha = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\alpha$$

$$\underline{s}^2{}_z\beta = \frac{1}{2}(\frac{1}{2}+1)\hbar^2$$

PAULI-Prinzip (1925): In einem Atom oder Molekül können keine zwei Elektronen mit den gleichen vier (n, l, m_L, m_s) existieren:

$$P(1,2)\Psi = -1\Psi$$

1. Hundsche Regel: Der Grundzustand eines Atoms hat stets die höchste Spinmultiplizität.

2. Hundsche Regel: Unter den Zuständen höchster Spinmultiplizität ist derjenige der Grundzustand, der den größten Wert von L hat:

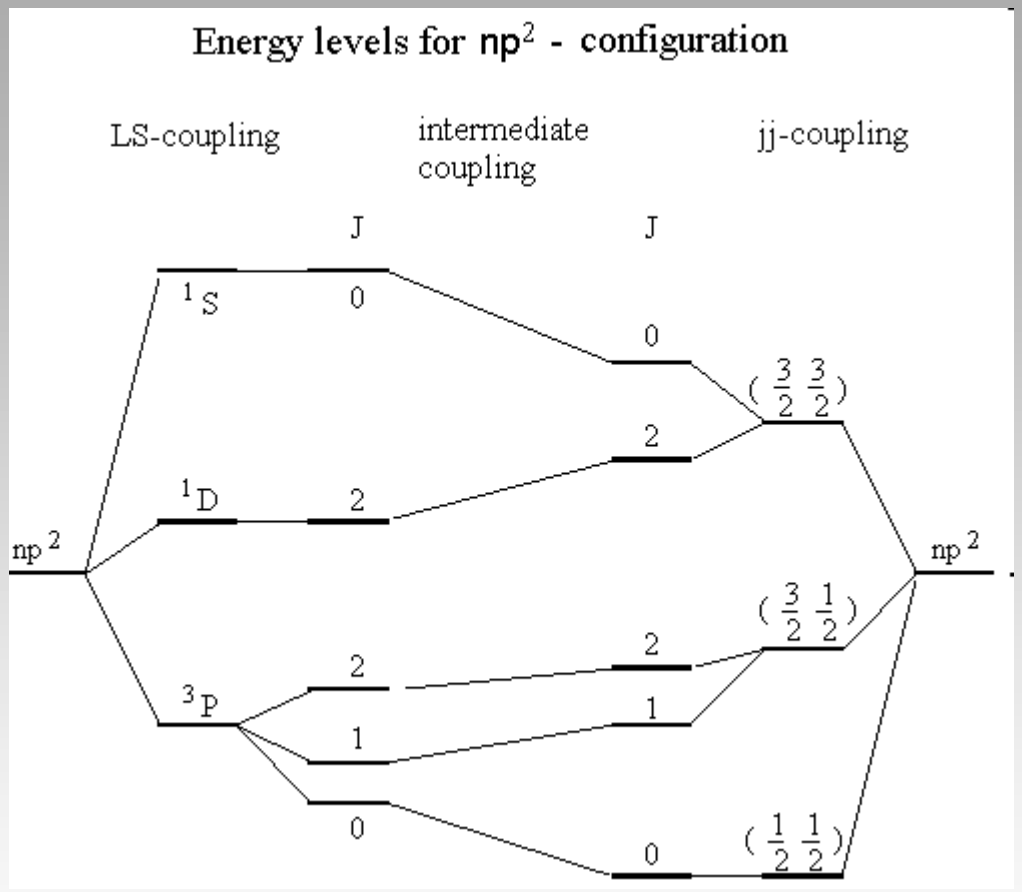
$$L = \sum_i m_{L,i}$$

3. Hundsche Regel: Die Energie eines Zustands steigt mit J an, wenn das teilweise gefüllte Niveau weniger als halbbesetzt ist. Anderenfalls fällt die Energie mit steigendem J: $J = |L+S|, |L+S|-1, \ldots, |L-S|.$

Termsymbole: $^{2S+1}L_J$

Li	Be	B	C	N	O	F	Ne
$^2S_{1/2}$	$^1S_0$	$^2P_{1/2}$	$^3P_0$	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^1S_0$

j-j-Kopplung



Achtung: schwere Atome
j-j-Kopplung,
s. VL rel. Effekte

L-S-Kopplung

$$J = L + S$$

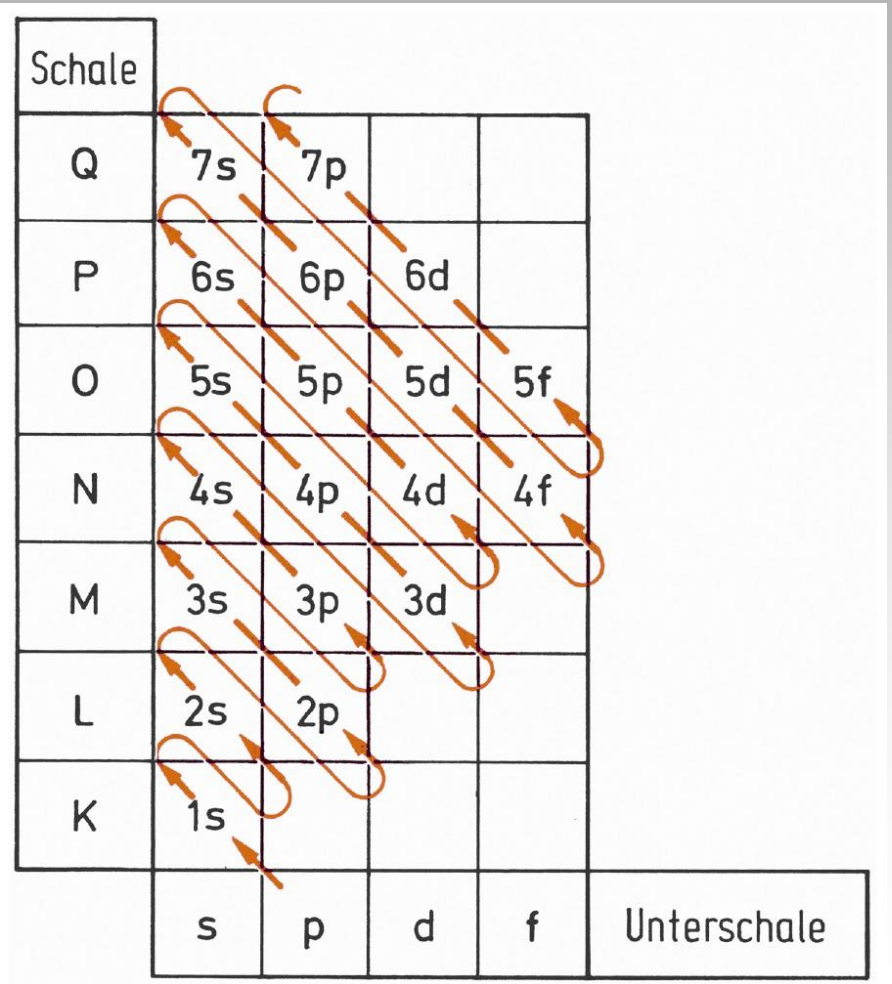
$$L = \sum_i l_i$$

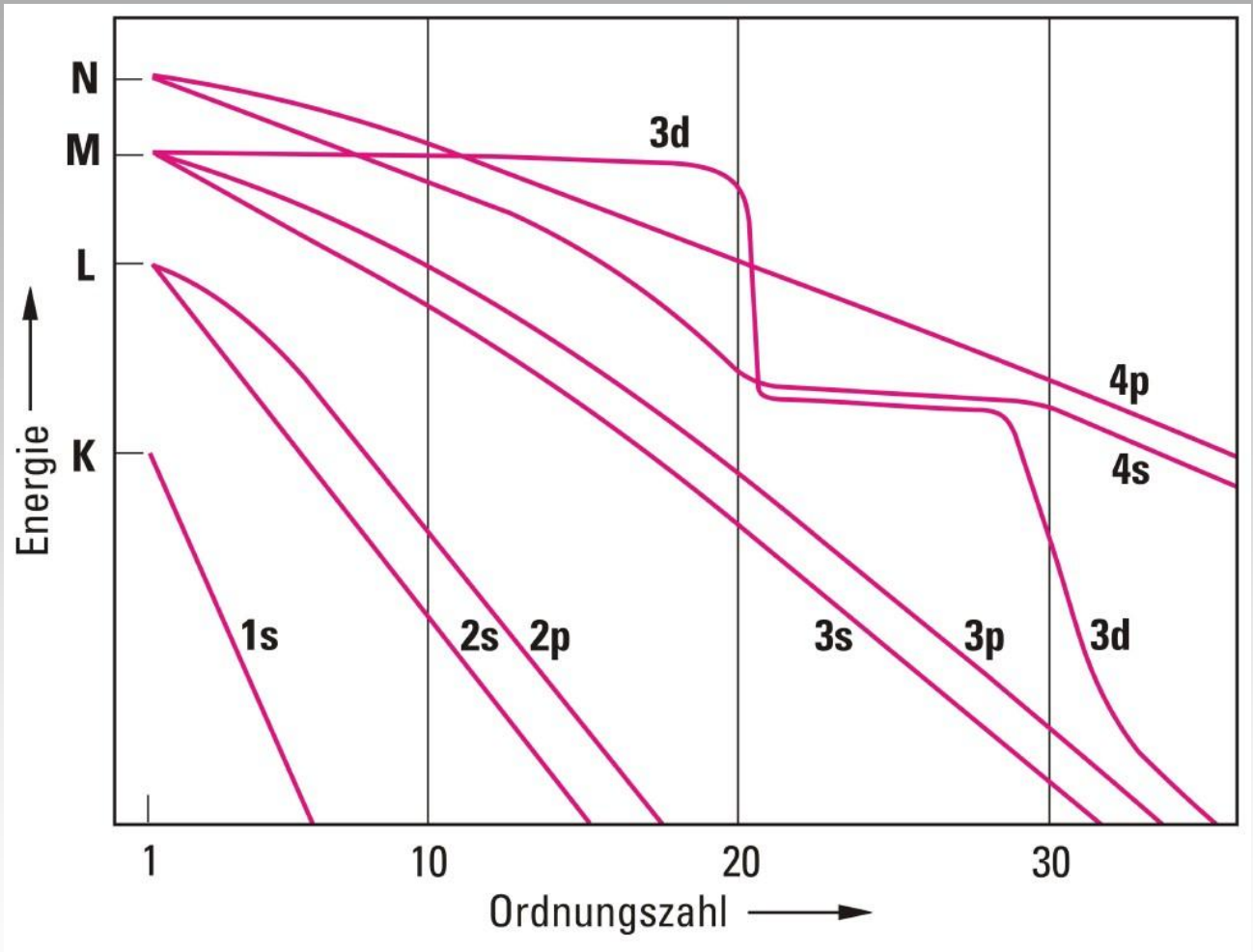
$$S = \sum_i s_i$$

j-j-Kopplung

$$J = \sum_i j_i = \sum_i (l_i + s_i)$$

Reihenfolge der Besetzung von Unterschalen





Änderung der Energie der Unterschalen mit wachsender Ordnungszahl.

Tabelle 7.1 Gauß-Funktionen (GTO)

Kennzeichnung	GTO
1s	$N \exp(-\alpha r^2)$
$2p_x$	$N\, x \exp(-\alpha r^2)$
$2p_y$	$N\, y \exp(-\alpha r^2)$
$2p_z$	$N\, z \exp(-\alpha r^2)$
$3d_{xx}$	$N\, x^2 \exp(-\alpha r^2)$
$3d_{xy}$	$N\, xy \exp(-\alpha r^2)$
$3d_{xz}$	$N\, xz \exp(-\alpha r^2)$
$3d_{yy}$	$N\, y^2 \exp(-\alpha r^2)$
$3d_{yz}$	$N\, yz \exp(-\alpha r^2)$
$3d_{zz}$	$N\, z^2 \exp(-\alpha r^2)$

Beispiel 17: Gauß-Funktionen

Wie wollen zeigen, daß die Linearkombination der Funktionen $3d_{xx}$, $3d_{yy}$ und $3d_{zz}$ eine 3s-Funktion ergibt:

$$3d_{x^2} + 3d_{y^2} + 3d_{z^2} = N(x^2 + y^2 + z^2)e^{-\alpha r^2} = Nr^2 e^{-\alpha r^2} = 3s$$

FIVE EQUIVALENT d ORBITALS

Table 1. Polar and Cartesian Representations of the Angular Part of d-Type Real Hydrogen-like Wave Functions

Orbital	Polar Representation	Cartesian Representation on a Unit Sphere ($r = 1$)
d_{xy}	$\sin^2\theta \sin 2\varphi$	$2xy$
$d_{x^2-y^2}$	$\sin^2\theta \cos 2\varphi$	$x^2 - y^2$
d_{xz}	$\cos\theta \sin\theta \cos\varphi$	xz
d_{yz}	$\cos\theta \sin\theta \sin\varphi$	yz
d_{z^2}	$3\cos^2\theta - 1$	$2z^2 - (x^2 + y^2)$

$$d_0 = c_1 d_{z^2} + c_2 d_{xz} + c_3 d_{yz} + c_4 d_{x^2-y^2} + c_5 d_{xy}$$

Table 2. Coefficients Giving the Pyramidal d Orbitals

$$\begin{bmatrix} d_0 \\ d_{1/5} \\ d_{2/5} \\ d_{3/5} \\ d_{4/5} \end{bmatrix} = \begin{bmatrix} \sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}} & 0 & \sqrt{\frac{2}{5}} & 0 \\ \sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{\pi}{5} \\ \sqrt{\frac{1}{5}} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{\pi}{5} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} \\ \sqrt{\frac{1}{5}} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{\pi}{5} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & \sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} \\ \sqrt{\frac{1}{5}} & \sqrt{\frac{2}{5}}\cos\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{2\pi}{5} & -\sqrt{\frac{2}{5}}\cos\frac{\pi}{5} & -\sqrt{\frac{2}{5}}\sin\frac{\pi}{5} \end{bmatrix} \begin{bmatrix} d_{z^2} \\ d_{xz} \\ d_{yz} \\ d_{x^2-y^2} \\ d_{xy} \end{bmatrix}$$

$$d_0 = \sqrt{1/5}\, d_{z^2} + \sqrt{2/5}\, d_{xz} + \sqrt{2/5}\, d_{x^2-y^2}$$

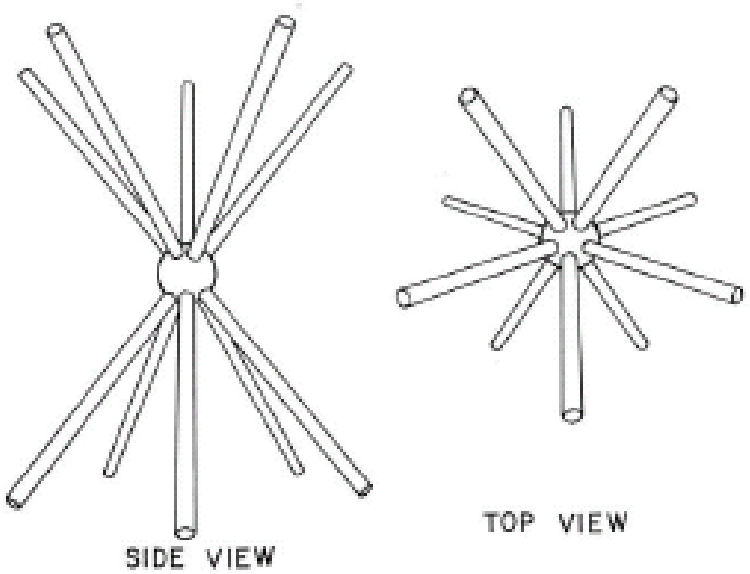


Figure 1. The directions of the five equivalent d orbitals.

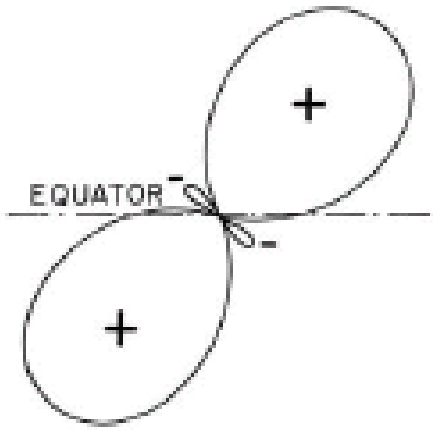


Figure 2. Angular factor of eigenfunction for a pyramidal d orbital, side view.

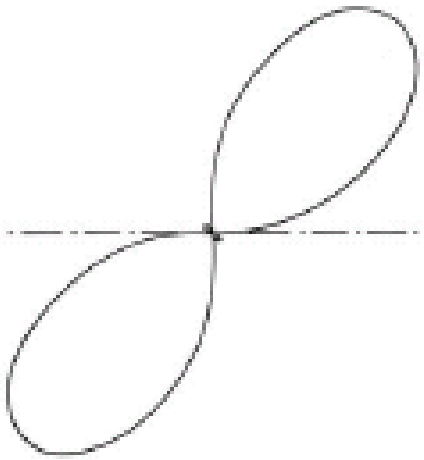


Figure 3. Square of angular factor, side view.

If the Slater-type orbitals (STO) which have a radial decay of the form of e^{-r} are replaced by Gaussian-type orbitals (GTO), originally introduced by Boys (1950), with a radial decay of the type of e^{-r^2} the general functional form of a normalized GTO in atom-centered Cartesian coordinates is:

$$\Phi\,(x, y, z: \alpha, i, j, k) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left[\frac{(8\alpha)^{i+j+k}\; i!\, j!\, k!}{(2i)!(2j)!(2k)!}\right]^{1/2} x^i\; y^j\; z^k\; e^{-\alpha(x^2+y^2+z^2)}$$

$2z^2 - x^2 - y^2$	→	d_{z^2}
$x^2 - y^2$	→	$d_{z^2-y^2}$
xy	→	d_{xy}
xz	→	d_{xz}
yz	→	d_{yz}
$x^2 + y^2 + z^2$	→	s orbital

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C J Cramer, Essentials of Computational Chemistry – Theories and Models, 2nd edn., Wiley, Chichester, 2004.

Chemische Bindung

Give us insight, not numbers.
Charles Coulson, theoretical chemist, 1960

A picture is worth a thousand words.

What are the electrons really doing in molecules ?
R S Mulliken

Born-Oppenheimer Näherung

Born und Oppenheimer zeigten (1927), daß in einer sehr guten Näherung die Bewegungen der Kerne und die des Elektrons (der Elektronen) getrennt betrachtet werden können. Nun wird die elektronische Schrödinger-Gleichung für alle möglichen Kernkonfigurationen berechnet. Man erhält einen Satz von Energien und dazugehörigen Wellenfunktionen (für jede während der Rechnung festgehaltene Kernkonfiguration) und sucht das Energieminimum. Die dazugehörige Struktur nennt man Minimumstruktur. Bezogen auf das H_2^+-Molekül wird der Abstand zwischen den beiden Kernen variiert. Somit ergibt sich die elektronische Schrödingergleichung zu

$$H^{el}\,\Psi^{el}(r) = E^{el}\,\Psi^{el}(r)$$

wobei für den elektronischen Hamilton-Operator gilt:

$$H^{el} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0(R_1 - r)} - \frac{e^2}{4\pi\varepsilon_0(R_2 - r)}$$

Und damit ist die Gesamtenergie gegeben als:

$$E_n\,(\text{gesamt}) = U_n(R_1, R_2) = E_n^{el} + \frac{e^2}{4\pi\varepsilon_0|R_1 - R_2|}$$

Für ein polyatomares Molekül aus N Elektronen und M Kernen können wir also allgemein schreiben:

$$H^{el}\,\Psi^{el}(r_1, r_2, \ldots, r_N) = E^{el}\,\Psi^{el}(r_1, r_2, \ldots r_N)$$

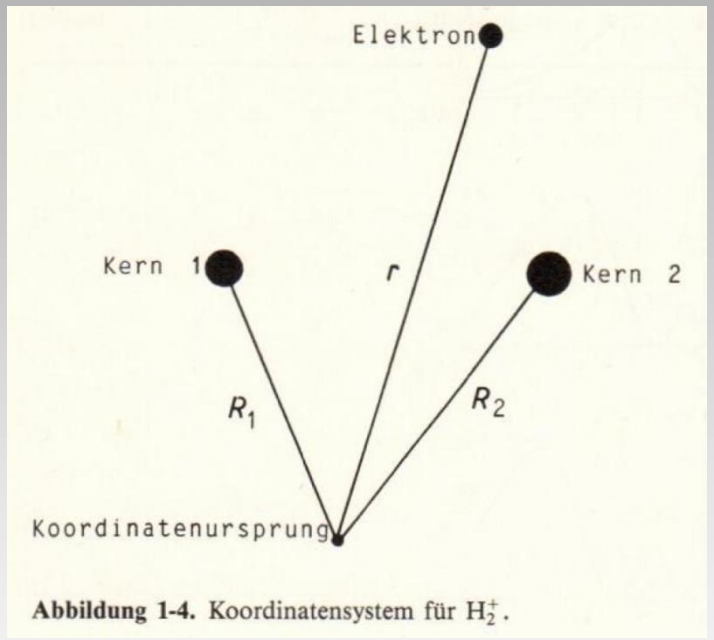


Abbildung 1-4. Koordinatensystem für H_2^+.

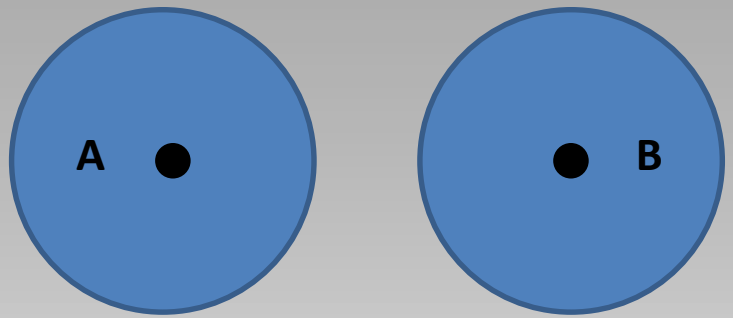
wobei wir den Hamilton-Operator wie folgt schreiben können:

$$H^{el} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 + \sum_{\substack{i,j=1\\ i<j}}^{N}\frac{e^2}{4\pi\varepsilon_0|r_i - r_j|} - \sum_{j=1}^{N}\sum_{\alpha=1}^{M}\frac{Z_\alpha e^2}{4\pi\varepsilon_0|R_\alpha - r_j|}$$

$$T(e^-) \quad + \quad V(e^- - e^-) \quad + \quad V(K - e^-)$$

H_2, H_2^+

AOs: ϕ_A, ϕ_B



MO: $\psi_{AB}^{(*)} = \varphi_A \pm \lambda\varphi_B \qquad \lambda = 1$

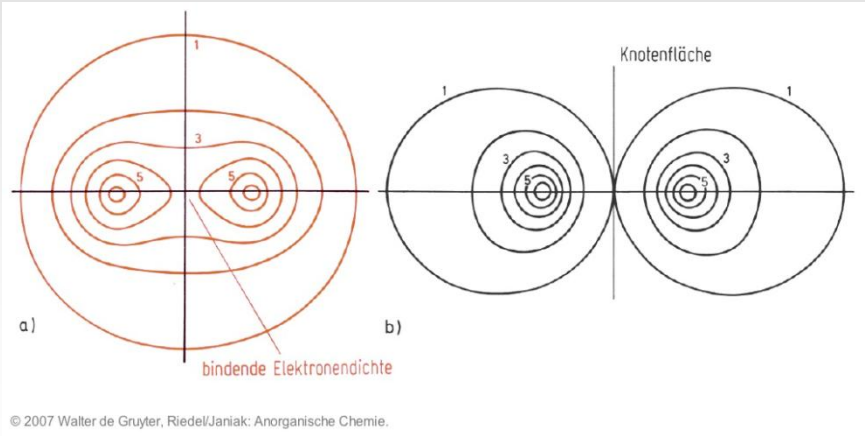
$$\psi^{MO} = \psi_{AB}(1)\psi_{AB}(2) * \chi$$

2-e⁻ Wellenfkt. als Produkt von 1-e⁻ MOs !!!

VB:

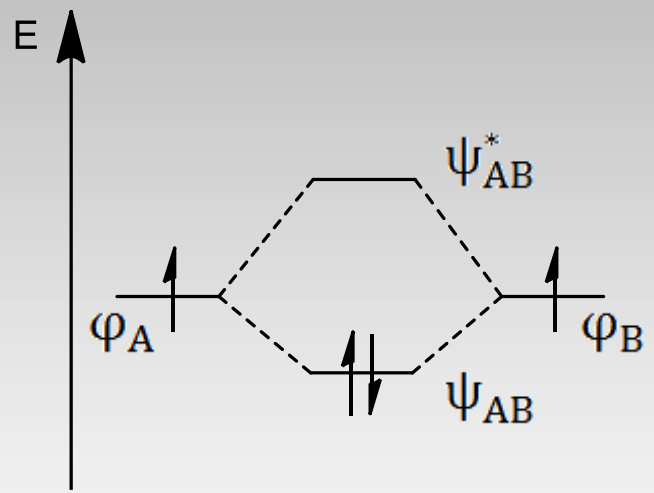
$$\psi^{VB} = \varphi_A(1)\varphi_B(2) + \varphi_A(2)\varphi_B(1) * \chi$$

2-e⁻ Wellenfkt. als Produkt von einfach besetzten AOs !!!



Elektrondichte im H_2-Molekül

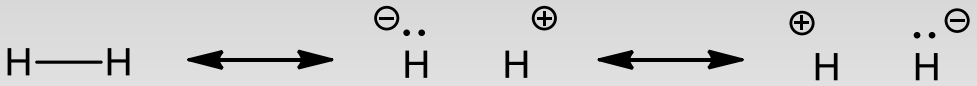
MO Diagramm



MO:

$$\psi^{MO,CI} = \psi_{AB}(1)\psi_{AB}(2) + k[\psi^{*}_{AB}(1)\psi^{*}_{AB}(2)]$$

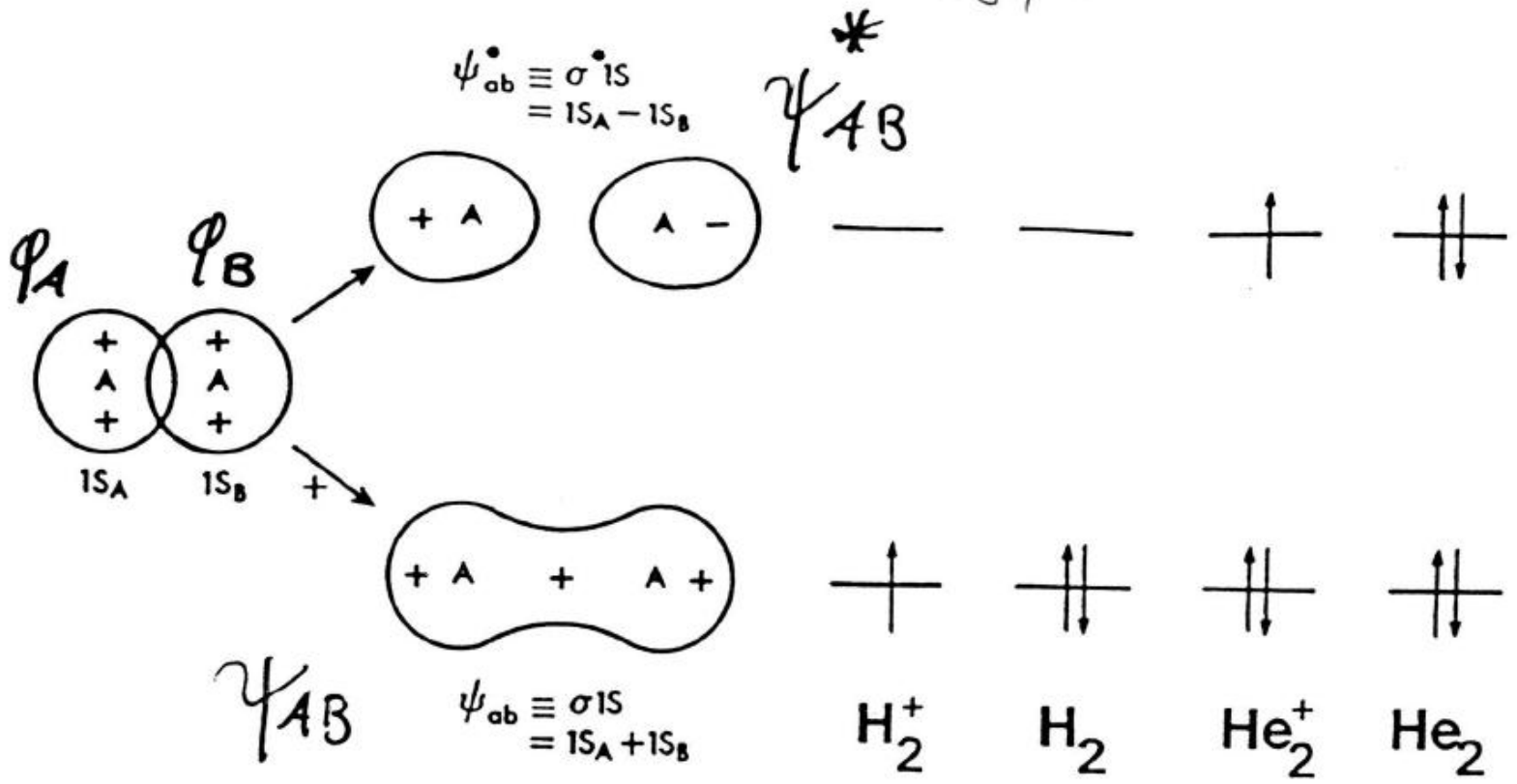
ionische Resonanz:



VB:

$$\psi^{VB,Res.} = \varphi_A(1)\varphi_B(2) + \varphi_A(2)\varphi_B(1) + \lambda[\varphi_A(1)\varphi_A(2) + \varphi_B(1)\varphi_B(2)]$$

$$\chi = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$



$\sigma 1s$ and $\sigma^* 1s$ bonding and antibonding molecular orbitals, orbital occupations for the ground-state configurations of H_2, He_2^+ and He_2.

ψ^{MO}

ψ^{VB}

$\psi^{VB,Res.}$

wave-function	parameters	D_e(eV)	$R_e(a_o)$
$\{1s_A(1) + 1s_B(1)\}\{1s_A(2) + 1s_B(2)\}$	$\zeta = 1.0$	2.695	1.61
"	$\zeta = 1.197$	3.488	1.38
$1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)$	$\zeta = 1.0$	3.156	1.64
"	$\zeta = 1.166$	3.782	1.41
$\phi_A(1)\phi_B + \phi_B(1)\phi_A(2)$ $\phi = 1s + \mu 2p_z$	$\zeta_{1s} = \zeta_{2p} = 1.19$ $\mu = 0.105$	4.04	1.416
$1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)$ $+ \lambda\{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)\}$	$\zeta = 1$ $\lambda = 0.105$	3.230	1.67
"	$\zeta = 1.194$ $\lambda = 0.265$	4.025	1.43
$\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)$ $+ \lambda\{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)\}$	$\zeta = 1.190$ $\lambda = 0.175$ $\mu = 0.07$	4.122	1.41
experimental		4.74759	1.4006

Simple wave-functions, dissociation energies and equilibrium internuclear distances for H_2 ground-state. (Adapted from Table 5-12 of "Atoms and Molecules", by M. Karplus and R.N. Porter, (Benjamin, N.Y., 1970).)

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Note

A note on some valence bond calculations for the ground-state of the hydrogen molecule

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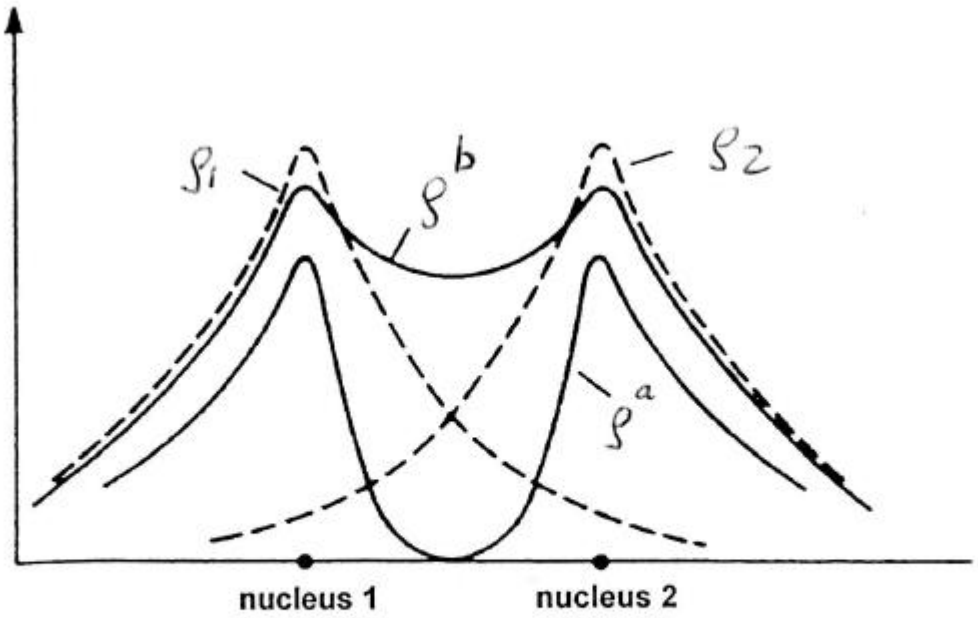
Dedicated to Professor Paul v. Ragué Schleyer on the occasion of his 75th birthday.

Abstract

The results of ab initio valence bond (VB) calculations are reported for H_2, with up to 30 nuclear centred (15 at each H atom) 1s, 2s, 2p, 3s, 3p, 3d and 4s (cc-pVTZ+4s) atomic orbitals (AOs) included in them. A 30 AO complete active space VB calculation (CASVB) with 465 $S = 0$ spin structures gives an cc-pVTZ+4s energy of −1.17245 a.u. for d(H–H) = 1.4 a.u., which is identical to the CISD/cc-pVTZ+4s estimate obtained from a molecular orbital (MO) configuration interaction (CI) calculation with all single and double (CISD) substitutions.

Aufenthaltswahrscheinlichkeit



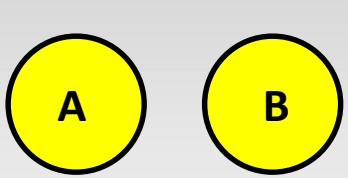
Schematic representation of the electron density (ρ) derived from $|\varphi_1|^2 = \rho_1$, $|\varphi_2|^2 = \rho_2$, $|\psi^b|^2 = \rho^b$ and $|\psi^a|^2 = \rho^a$.

Virialsatz

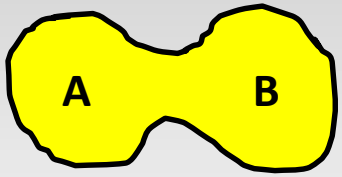
$$2\langle T\rangle = -\langle V\rangle = -2E$$

bei $\left(\frac{\delta E}{\delta R}\right) = 0$

J. C. Slater, H. Hellmann



H_2



$E_1 = 2E_A$

E_2

allg.: $E_A + E_B$

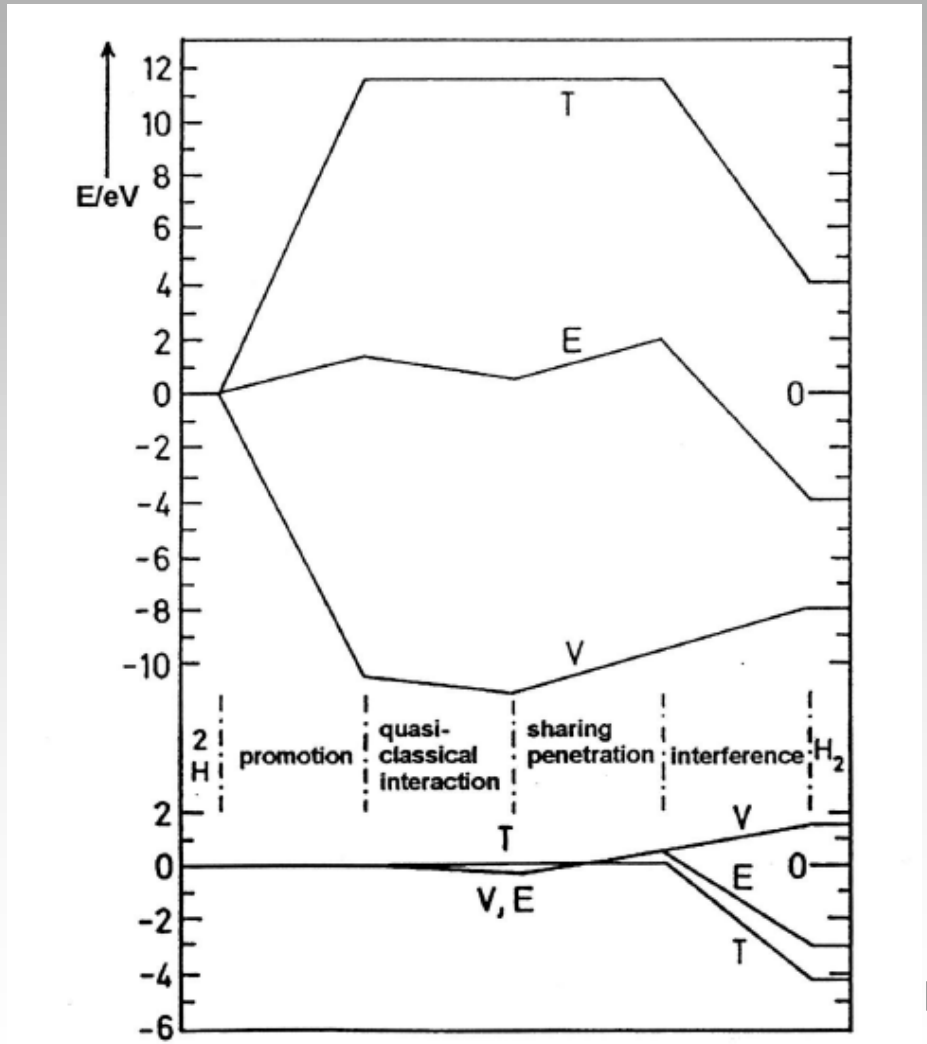
$|E_2| > |E_1|$

$-E_1 = \langle T_1\rangle$

$-E_2 = \langle T_2\rangle$

T immer >0 ⇒ $\langle T_2\rangle > \langle T_1\rangle$

Verteilung der kinetischen und potentiellen Energie in der Diwasserstoff-Bindung

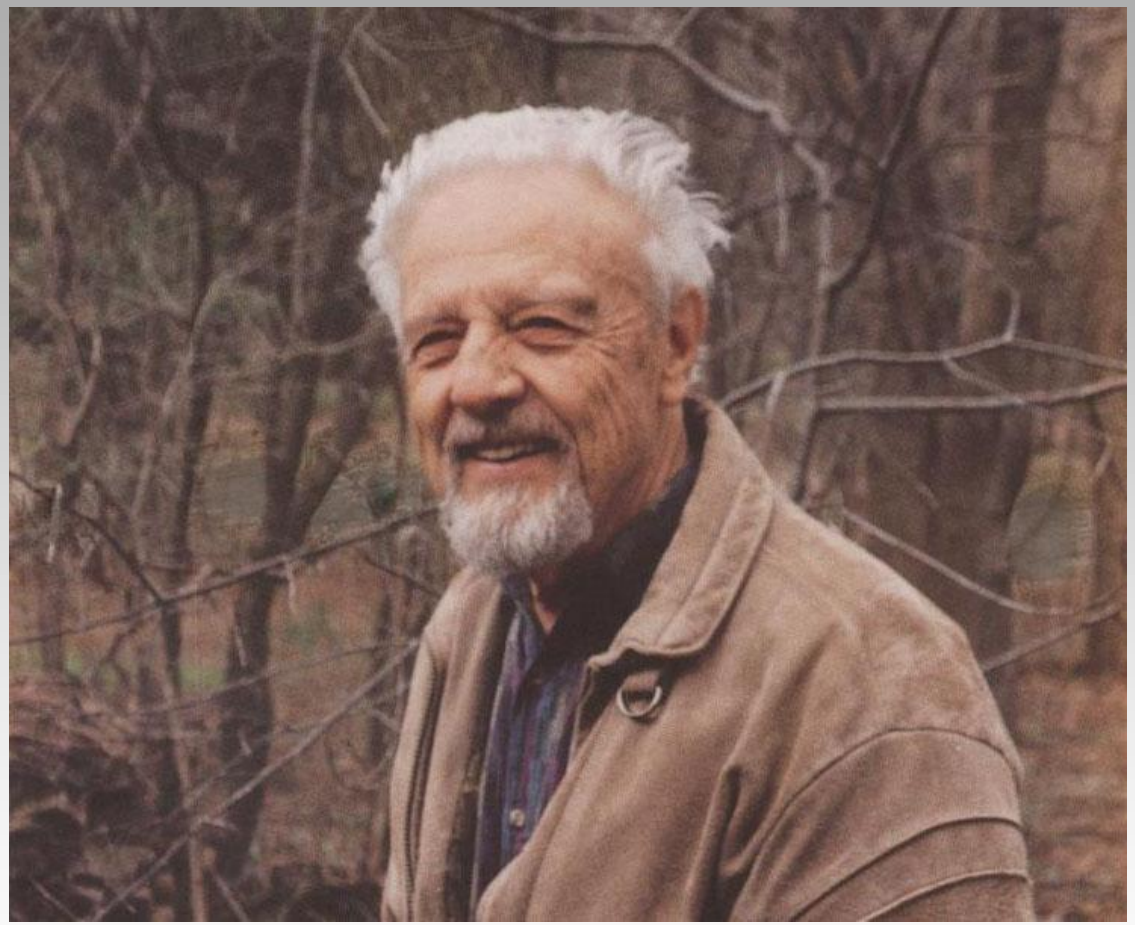


Klaus Ruedenberg, The Phys. Nature of the Chemical Bond, *Rev. Mod. Phys.* **1962**, *34*, 326 – 376.

K Ruedenberg, M W Schmidt, Physical Understanding Through variational Reasoning: Electron Sharing and Covalent Bonding, *J Phys Chem A* **2009**, *113(10)*, 1954 – 1968.

H_2^+: 0.102 a.u.

H_2: 0.174 a.u.



Klaus Ruedenberg, ursprünglich Klaus Rüdenberg, (* 25. August 1920 in Bielefeld) ist ein deutschstämmiger US-amerikanischer Chemiker (Theoretische Chemie, Quantenchemie).

$$\psi^{MO} = c_A\varphi_A \pm c_B\varphi_B \qquad \text{allg.:} \quad \psi^{MO} = \sum c_k\,\varphi_k$$

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

$$E = \frac{\int \psi^* \underline{H} \psi d\tau}{\int |\psi|^2 d\tau} \qquad \left(\frac{\delta E}{\delta c_i}\right) = 0$$

$$E = \frac{\alpha \pm \beta}{1 \pm S}$$

$\alpha = \int \varphi_A{}^* \underline{H} \varphi_A d\tau$	Coulomb-Integral
$\beta = \int \varphi_A{}^* \underline{H} \varphi_B d\tau$	Austausch-oder Resonanz- Integral
$S = \int \varphi_A{}^* \varphi_B d\tau$	Überlappungs-Integral

$$\bar{E} = \frac{\int \bar{\Psi}^* H \bar{\Psi} \, d\tau}{\int |\bar{\Psi}|^2 d\tau}$$

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

wobei wir zur Vereinfachung eingeführt haben:

$H_{11} = \alpha_1 = \int \phi_1^* H \phi_1 \, d\tau$

$H_{22} = \alpha_2 = \int \phi_2^* H \phi_2 \, d\tau$

$H_{12} = \beta = \int \phi_1^* H \phi_2 \, d\tau$

H_{11} und H_{22}: Coulomb-Integral, entspricht der Energie des Elektrons im AO

H_{12}: Austausch-Integral

$S_{11} = \int \phi_1^* \phi_1 \, d\tau$

$S_{22} = \int \phi_2^* \phi_2 \, d\tau$

$S_{12} = S = \int \phi_1^* \phi_2 \, d\tau$

S_{11} und $S_{22} = 1$, wenn ϕ_1 und ϕ_2 (AO Basis) normiert sind

S_{12}: Überlappungsintegral

Um ein Minimum für E zu finden, müssen wir nun die Ableitungen

$$\left(\frac{\partial E}{\partial c_1}\right) = 0 \qquad \text{und} \qquad \left(\frac{\partial E}{\partial c_2}\right) = 0$$

bilden und erhalten

$$c_1 (H_{11} - ES_{11}) + c_2 (H_{12} - ES_{12}) = 0 \qquad \text{und}$$

$$c_1 (H_{12} - ES_{12}) + c_2 (H_{22} - ES_{22}) = 0$$

Eine nichttriviale Lösung dieser beiden sogenannten Säkular-Gleichungen Säkular-Determinanten:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha_1 - E & \beta - ES \\ \beta - ES & \alpha_2 - E \end{vmatrix} = 0$$

Setzen wir voraus, daß für das homonucleare H_2^+ gilt: $\alpha_1 = \alpha_2 = \alpha$, Determinante:

$$(\alpha - E)^2 = (\beta - ES)^2$$

und damit

$$\alpha - E = \pm(\beta - ES) \qquad \text{bzw.} \qquad E = \frac{\alpha \pm \beta}{1 \pm S}$$

Die erste Säkulargleichung in α, β-Schreibweise lautet:

$$c_1(\alpha - E) + c_2(\beta - ES) = 0 \qquad \text{bzw.} \qquad c_1 = -\frac{\beta - ES}{\alpha - E} c_2$$

Daraus folgt, daß für $E = \dfrac{\alpha + \beta}{1 + S}$ gilt: $c_1 = c_2$

und für $E = \dfrac{\alpha - \beta}{1 - S}$ gilt: $c_1 = -c_2$

Daher können wir nun für das H_2^+ endgültig schreiben:

$$\Psi_{MO} = c_1 \phi_1 \pm c_2 \phi_2$$

Durch Normierung dieser Gleichung zu

$$\int |\psi_{MO}|^2 d\tau = 1 = c_1^2 + c_2^2$$

ergibt sich der Koeffizient c_1 zu

$$c_1 = \pm \frac{1}{\sqrt{2 \pm 2S}}$$

$$\Psi^a = \frac{1}{\sqrt{2-2S}} (\phi_1 - \phi_2)$$

$$\Psi^b = \frac{1}{\sqrt{2+2S}} (\phi_1 + \phi_2)$$

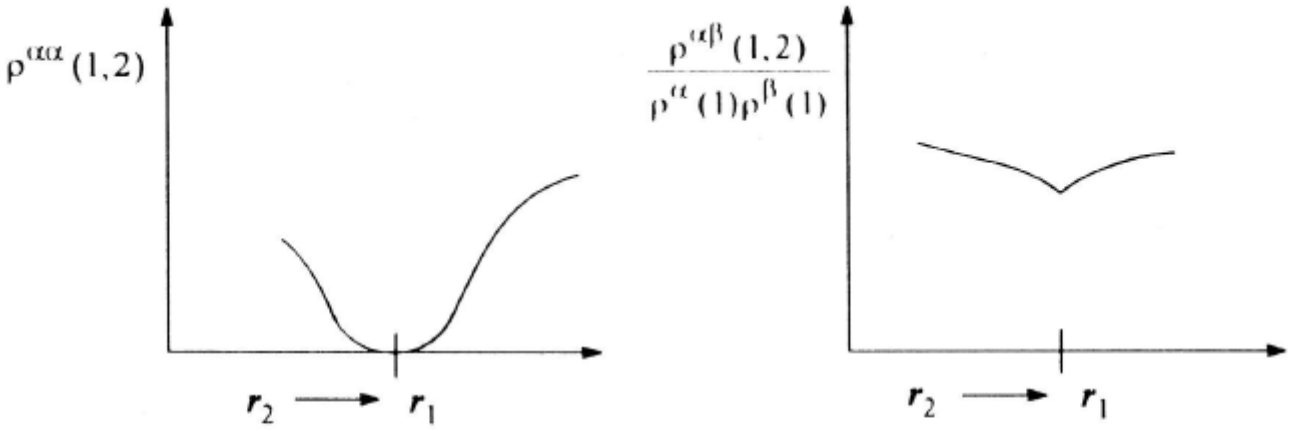
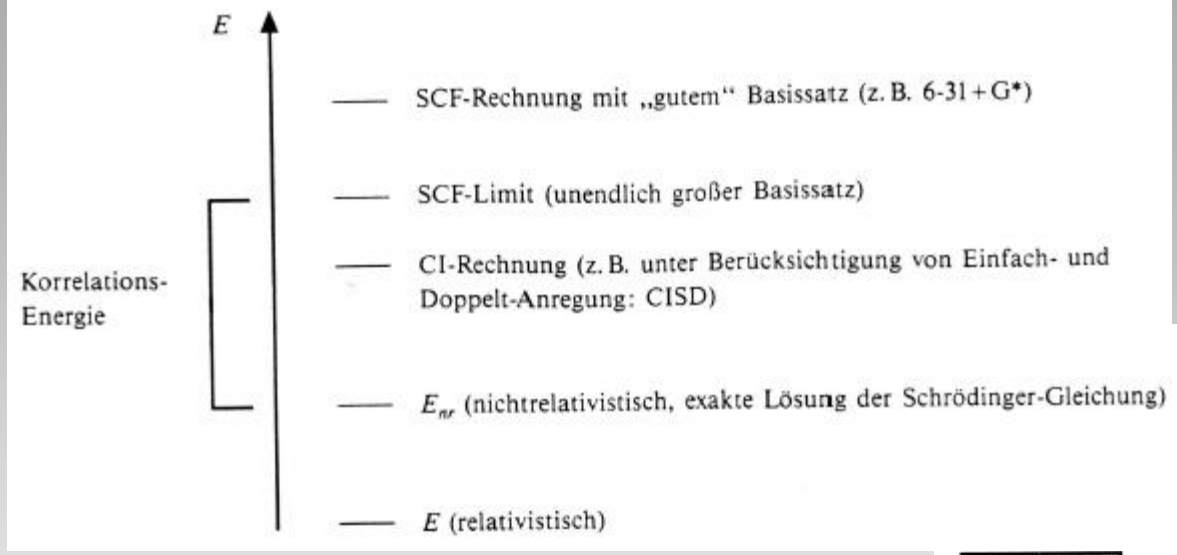
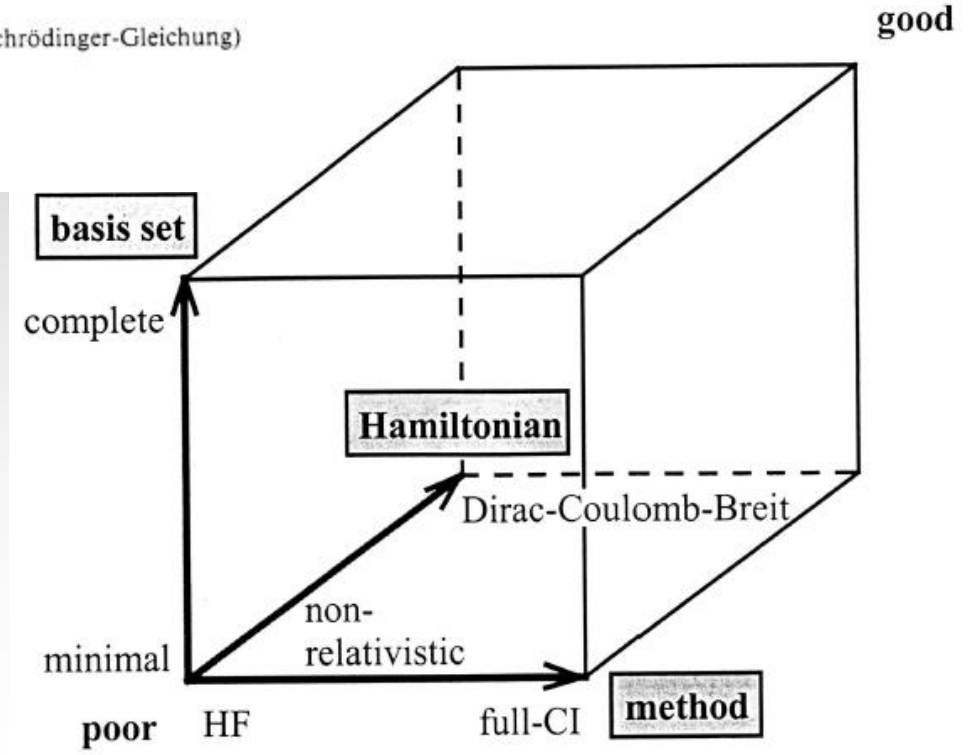


Illustration des Fermi- und Coulomb-Loches. Es ist für zwei α-Spinelektronen nicht möglich, sich gleichzeitig an einem Ort ($r_1 = r_2$) aufzuhalten (Fermi-Loch). Für ein Paar an α- und β-Spinelektronen besitzt die Paardichte hier ihren kleinsten Wert, geht jedoch nicht auf Null zurück (Coulomb-Loch).


E
SCF-Rechnung mit „gutem" Basissatz (z. B. 6-31+G*)
SCF-Limit (unendlich großer Basissatz)
CI-Rechnung (z. B. unter Berücksichtigung von Einfach- und Doppelt-Anregung: CISD)
Korrelations-Energie
E_{nr} (nichtrelativistisch, exakte Lösung der Schrödinger-Gleichung)
E (relativistisch)


good
basis set
complete
Hamiltonian
Dirac-Coulomb-Breit
non-
relativistic
minimal
poor
HF
full-CI
method

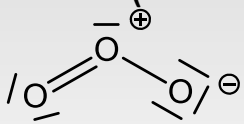
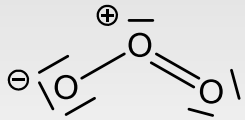
Linearkombinationen:

1) ψ_1, ψ_2 sind Atomorbitale

- an verschiedenen Atomen → ψ^b, ψ^a **MO**
- am gleichen Atom: $\int \psi_1 \, \psi_2 = 0$

  keine Linearkomb. mit niedrigerer Energie kann konstruiert werden: **HOs** $\mathrm{sp}: h_{1,2} = \frac{1}{\sqrt{2}} (s \pm p)$

2) ψ_1, ψ_2 sind $2e^-$ (oder mehr e^-) Konfig,

- VB falls  und  die Eigenfkt. Ψ_1 und Ψ haben,

→ $\psi = \psi_1 \pm k\psi_2$ Resonanz

- MO falls Ψ_1 doppelt besetztes bind. MO und Ψ_2 doppelt besetztes antibindendes MO (mit gleichem s und s_z) → $\psi^{MO,CI} = \psi_1 \pm \lambda\psi_2$

sp

$$h_1 = \frac{1}{\sqrt{2}}(s + p)$$

$$h_1 = \frac{1}{\sqrt{2}}(s - p)$$

sp²

$$h_1 = \frac{1}{\sqrt{3}}(s + \sqrt{2}p_x)$$

$$h_2 = \frac{1}{\sqrt{6}}(\sqrt{2}s - p_x + \sqrt{3}p_y)$$

$$h_3 = \frac{1}{\sqrt{6}}(\sqrt{2}s - p_x - \sqrt{3}p_y)$$

sp³

$$h_1 = \frac{1}{2}(\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z})$$

$$h_2 = \frac{1}{2}(\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z})$$

$$h_3 = \frac{1}{2}(\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z})$$

$$h_4 = \frac{1}{2}(\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z})$$

$$\Psi = \begin{array}{c|} \\ 1 \\ 2 \\ 3 \\ \uparrow \\ \text{Orbitalnummer} \end{array} \begin{array}{|ccc|} 1 & 2 & 3 \leftarrow \text{Elektronnummer} \\ \chi_1(1) & \chi_1(2) & \chi_1(3) \\ \chi_2(1) & \chi_2(2) & \chi_3(3) \\ \chi_3(1) & \chi_3(2) & \chi_2(3) \end{array} \frac{1}{(3!)^{\frac{1}{2}}}$$

$$A_N\phi_1(1)\phi_2(2)\ldots\phi_N(N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \ldots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \ldots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \ldots & \phi_N(N) \end{vmatrix} = |\phi_1\phi_2\ldots\phi_N|$$

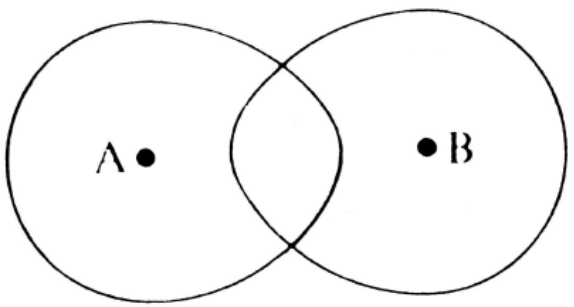
He-Atom:

$$\Psi^{SD} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 1s(1)\beta(1) & 1s(2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left[1s(1)\alpha(1)\, 1s(2)\beta(2) - 1s(2)\alpha(2)\, 1s(1)\beta(1)\right]$$

Coulsen, Fischer (1949)

Goddard (1973) → GVB



$$A = a + \mu b \qquad B = b + \mu a$$

$$a = b + \varphi_{1s}$$

$$\psi^{VB} = A(1)B(2) + A(2)B(1)$$

$$= (1 + \mu^2)\,(a(1)b(2) + b(1)a(2)) + 2\mu(a(1)a(2) + b(1)b(2))$$

$$\Rightarrow \psi^{CF} = N(a(1)b(2) + b(1)a(2)) + \lambda(a(1)a(2) + b(1)b(2))$$

The Physical Nature of the Chemical Bond

Chemical bond theory is discussed in many textbooks and any person would agree that H_2 is more stable than two isolated H atoms. Furthermore, any first year chemistry student would give as a reason for this that when AO overlap occurs between the two 1s AOs (φ_1 and φ_2) of the two hydrogen atoms H_1 and H_2 the electrons occupy the bonding MO (ψ^b) which results from positive interference of the atomic orbitals whereas the antibonding MO (ψ^a) (negative interference) remains empty (Fig. 1):

$$\psi^b = [\ 1 / (2 + 2S)^{0.5}\ ]\ (\varphi_1 + \varphi_2) \qquad \psi^a = [\ 1 / (2 - 2S)^{0.5}\ ]\ (\varphi_1 - \varphi_2)$$

with S being the overlap integral: $S = \int \varphi_1^*\ \varphi_2\ d\tau$.

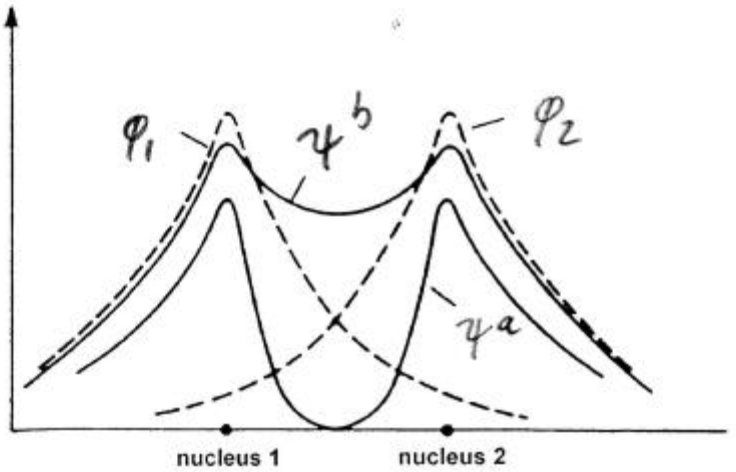


Fig. 1 Schematic representation of the electron density (ρ) derived from $|\varphi_1|^2 = \rho_1$, $|\varphi_2|^2 = \rho_2$, $|\psi^b|^2 = \rho^b$ and $|\psi^a|^2 = \rho^a$.

However, now comes the critical question. What physical mechanism is responsible for the fact that the positive interference of the AOs leads to a decrease in energy and hence to bond formation? Many textbooks give an incorrect answer to this question.

It is claimed that the accumulation of charge in the bonding region causes a decrease in the potential energy, since the electron is then situated preferentially in a region in which it is attracted simultaneously by both nuclei. This corresponds to saying that the interference produces additional electron density (the electron must be taken from somewhere else, since the total number of electrons remains constant). One actually finds that the electron density is removed from places that are much more favourable to the potential energy, particularly in the immediate vicinity of the nucleus. The (positive) interference actually leads to a slight increase in the potential energy, and not to a decrease! In other words, if the potential energy is not responsible for bonding, it can only be the kinetic energy.

The kinetic energy (T) is considerably reduced by interference. As early as in 1933 Hellmann recognized this fact which is still often ignored in general textbooks and teaching. In a very simplified but essentially correct explanation Hellmann argues that the transition from the separate H atoms to the H_2 molecule increases the space available to the electrons, *i.e.* the positional uncertainty (Δx) increases. However, an increase in the positional uncertainty implies a decrease in the uncertainty of the momentum (Δp) because according to Heisenberg's uncertainty principle we can write: $\Delta p_x \cdot \Delta x > \frac{1}{2} (h/2\pi)$. Since the average momentum is zero, smaller momenta become more probable overall, i.e. (positive) interference causes (i) the kinetic energy to become smaller and (ii) the potential energy to rise (see above).

According to the virial theorem $2\langle T\rangle = -2E = -\langle V\rangle$ which is applicable only for the exact wave function (!) the following argument is straightforward. The occurrence of bonding means that the energy of the molecule is greater in magnitude (more negative) than the sum of the energies of the separate atoms:

$$|E_{\text{molecule}}| > |E_{\text{separate atoms}}|$$

Since the virial theorem is valid for both, the molecule and the separate atoms and since $\langle T\rangle$ is always positive, the kinetic energy of the H_2 molecule must be greater than that of the separate H atoms:

$$\langle T\rangle_{\text{molecule}} > \langle T\rangle_{\text{separate atoms}}$$

This result is not a contradiction to the above finding that interference causes the kinetic energy to become smaller because interference is – the most important - but only one out of several steps (here we want to consider four) which describe the stabilization which accounts for the formation of the chemical bond in the H_2 molecule (Fig. 2):

(1) Promotion of the AOs is generally a change in the AOs on molecular formation. The AOs adapted to the molecule are more localized in the vicinity of the nuclei, i.e. this is essentially a contraction in the case of H_2 which leads to a change in the balance of the intra-atomic potential and kinetic energies. (*E.g.* $\varphi(1s,\text{H atom}) = e^{-1.00\,r}$, $\varphi(1s,\text{H in } H_2) = e^{-1.25\,r}$).

(2) Quasi-classical interactions between atoms furnish a slight energy lowering for the neutral H_2 molecule (and a slight increase in energy for the H_2^+ cation). By quasi-classical we mean that we simply add the electron densities of the atoms participating in a bond, without taking into account any change in the electron density as a result of bonding.

(3) Sharing penetration stems from the fact that the bonding MO in H_2 is doubly occupied and that the two electrons with opposite spin come very close together, even with large distances between the nuclei (see also BH_3/B_2H_6). Therefore, from the standpoint of electron correlation it would be energetically more favourable if the electrons can avoid each other.

This is illustrated by the fact that the bond energy in H_2^+ (one-electron bond) is 0.102 eV which is more than half of the bond energy in H_2 with 0.174 eV.

(4) Interference of AOs yields the large energy lowering which is crucial for formation of covalent bonds (see above).

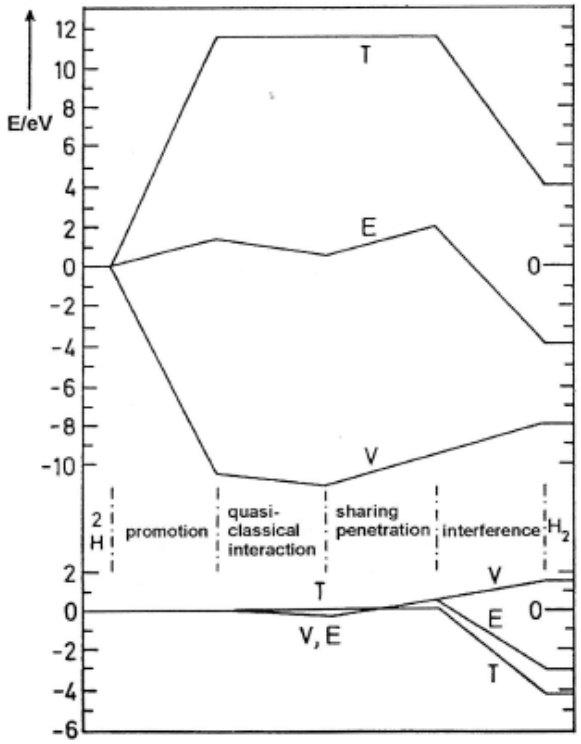


Fig. 2 Kinetic and potential energy contribution to the binding energy in H_2.

The preceding discussion has led to an interesting paradox. On the one hand, it is a fact that the molecular energy is lower than the atomic energy because the molecular potential energy is lower than the atomic potential energy, whereas the molecular kinetic energy is higher than the atomic kinetic energy, in agreement with the virial theorem. But on the other hand, it is nevertheless also true that this energy lowering comes about because under scale variations, the kinetic-energy integral behaves characteristically differently in the molecule than in the atom.

It may be helpful to realize that a similar paradox is well known in the piloting of orbiting space craft. Consider such a craft circling the earth in a stable orbit of radius r. The classical mechanical virial theorem requires

$$2\langle T\rangle = mv_2 = gmM/r = -\langle V\rangle$$

where m and v are the mass and velocity of the craft, M the mass of the Earth and g the gravitational constant. In order to reduce the time for circling the earth, the craft has to drop into a lower orbit which has a higher kinetic energy. This leads to the following maneuver: In order to achieve such acceleration, a retrorocket is fired which slows down the craft momentarily. The kinetic energy is then below the value required by the virial theorem and the centrifugal force is too weak to counteract the gravitational potential of the earth. The craft is pulled towards the earth , its potential energy decreases and its kinetic energy increases in the process. The craft can then be stabilized in a smaller circular orbit for which the virial theorem is again fulfilled. This orbit has a lower potential energy, a higher kinetic energy and a lower total energy than the initial orbit. Thus, the energy lowering which is initially introduced through a kinetic-energy decrease, is converted into a potential energy lowering, with a concomitant kinetic energy increase, by virtue of the orbital contraction in accordance with the virial theorem.

The state of the electron in the wavefunction can be compared with that of the space craft after the firing of the retrorocket: The total energy has been lowered through a lowering of the kinetic energy, arising in this case from electron sharing. The subsequent readjustment of the kinetic and potential energies through orbital contraction is similar in the two systems.

Feinberg, M. J., and Ruedenberg, K. (1971). Paradoxical Role of the Kinetic-Energy Operator in the Formation of the Covalent Bond. *J. Chem. Phys.* **54,** 1495 - 1511.

Kutzelnigg, W. (1973). The Physical Mechanism of the Chemical Bond. *Angew. Chem., Int. Ed. Engl.* **12**, 546 – 562.

Kutzelnigg, W. (1984). Chemical Bonding in Higher Main Group Elements. *Angew. Chem., Int. Ed. Engl.* **23,** 272 – 295.

Ruedenberg, K. (1962). The Physical Nature of the Chemical Bond. *Rev. Modern Phys.* **34,** 326 – 376.

$$E = \frac{\int \psi^* \underline{H} \psi d\tau}{\int |\psi|^2 d\tau}$$

$$\psi^{VB} = \varphi_A(1)\,\varphi_B(2) + \varphi_B(1)\,\varphi_A(2) + \lambda\,\overbrace{[\varphi_A(1)\,\varphi_A(2) + \varphi_B(1)\,\varphi_B(2)]}^{\text{ionische Resonanz}}$$

$$\psi^{MO} = (\varphi_A + \varphi_B)^1 \bullet (\varphi_A + \varphi_B)^1 \qquad \text{ohne CI}$$

$$= \varphi_A\,\varphi_B + \varphi_B\,\varphi_A + \underbrace{\varphi_A\,\varphi_A + \varphi_B\,\varphi_B}$$

berücksichtigt nicht genügend e^- – Korrelation
$\Rightarrow$ "falsche Dissoziation"
VB überschätzt e^- – Korrelation

$$\psi^{MO,\,CI} = (\varphi_A + \varphi_B)^1\,(\varphi_A + \varphi_B)^1 + k\,[(\varphi_A - \varphi_B)^1 \bullet (\varphi_A - \varphi_B)^1]$$

$$= \psi^b{}_{AB}(1) \bullet \psi^b{}_{AB}(2) + k\,[\psi^a{}_{AB}(1) \bullet \psi^a{}_{AB}(2)]$$

$$= (\psi^b{}_{AB})^2 + k\,(\psi^a{}_{AB})^2$$

B. Hellmann–Feynman Theorem and Berlin Analysis

The Hellmann–Feynman theorem states that the forces acting between the nuclei in a molecule are identical with the forces which would arise from the nuclear point charges and the electronic space charge according to classical electrostatics.[19] In addition, Berlin has shown[20] that within the Hellmann–Feynman force expression the electron charge in a certain "binding" region between the nuclei yields attractive force contributions, whereas the electronic density in the outlying region yields repulsive force contributions. If $dE/dR=0$, the latter, together with the nuclear repulsions, are balanced by the former. It is understandable that the simplicity of such an electrostatic picture has a very seductive appeal.

s. W. Kutzelnigg, Einf. in die Theoret. Chemie, Bd. 2, VCH, Weinheim, 1993, S. 37 ff

3.6. Das Hellmann-Feynman-Theorem

Nach diesen Bemerkungen zu einer Theorie der chemischen Bindung unter Beschränkung auf eine Diskussion der kinetischen Energie ist es angebracht, auch einen völlig entgegengesetzten Standpunkt zu Wort kommen zu lassen, bei dem die kinetische

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* K. Ruedenberg, Rev. Mod. Phys. *34*, 326 (1962); M. J. Feinberg, K. Ruedenberg, E. L. Mehler, Adv. Quant. Chem. *5*, 27 (1970); M.J. Feinberg, K. Ruedenberg, J. Chem. Phys. *59*, 1495 (1971).

Energie scheinbar völlig unberücksichtigt bleibt. Grundlage dieser Diskussion ist das sog. Hellmann-Feynman-Theorem. Dieses Theorem wurde zuerst von Hellmann in seinem Lehrbuch*) 1937 formuliert, obwohl man es als Spezialfall eines allgemeinen Theorems ansehen muß, das so alt ist wie die Quantenmechanik und das sich bereits in Paulis Handbuchartikel**) von 1933 findet. Feynman hat als sehr junger Mann das Theorem in Unkenntnis der Literatur neu entdeckt***).

Sei $\Psi_R(\vec{r}_1 \ldots \vec{r}_n)$ die auf 1 normierte exakte Wellenfunktion eines Moleküls in einer bestimmten festen Anordnung der Kerne, d.h. erfülle Ψ_R die Schrödinger-Gleichung

$$\mathbf{H}_R \Psi_R = E_R \Psi_R \qquad (3.6\text{–}1)$$

Wir können die Kraft, die auf einen Kern wirkt, durch Differenzieren der Potentialfläche E_R nach den Koordinaten des Kernes berechnen. Nehmen wir der Einfachheit halber ein zweiatomiges Molekül an und habe ein Kern die Koordinaten (0, 0, 0) und der andere (0, 0, Z) mit $Z = R$, so ist

$$-F_z = \frac{\partial <\mathbf{H}_R>}{\partial z} = \frac{\partial (\Psi_R, \mathbf{H}_R \Psi_R)}{\partial z} =$$

$$= \left(\frac{\partial \Psi_R}{\partial z}, \mathbf{H}_R \Psi_R\right) + \left(\Psi_R, \frac{\partial \mathbf{H}_R}{\partial z} \Psi_R\right) + \left(\Psi_R, \mathbf{H}_R \frac{\partial \Psi_R}{\partial z}\right) \qquad (3.6\text{–}2)$$

Benutzung der Eigenwertgleichung für Ψ_R und der Hermitizität von $\mathbf{H}_R$ erlaubt eine Umformung des ersten und dritten Terms zu

$$E_R \frac{\partial}{\partial z} (\Psi_R, \Psi_R) = E_R \frac{\partial}{\partial z} 1 = 0 \qquad (3.6\text{–}3)$$

so daß verbleibt

$$-F_z = \left(\Psi_R, \frac{\partial \mathbf{H}_R}{\partial z} \Psi_R\right) = \left(\Psi_R, \left[\frac{\partial \mathbf{T}}{\partial z} + \frac{\partial \mathbf{V}}{\partial z}\right] \Psi_R\right) = \left(\Psi_R, \frac{\partial \mathbf{V}}{\partial z} \Psi_R\right)$$

(3.6–4)

weil der Operator $\mathbf{T}$ der kinetischen Energie der Elektronen von den Kernkoordinaten nicht abhängt.

Der Operator $\mathbf{V}$ der potentiellen Energie besteht aus drei Beiträgen: $\mathbf{V}_{ee}$ der Elektronenabstoßung, $\mathbf{V}_{ke}$ der Kern-Elektronen-Anziehung und $\mathbf{V}_{kk}$ der Kernabstoßung.

* H. Hellmann: Einführung in die Quantenchemie. Deuticke, Leipzig–Wien 1937.
** W. Pauli: Die allgemeinen Prinzipien der Wellenmechanik, in Handbuch der Physik (Hrsg. H. Geiger, K. Scheel) XXIV/1, S. 83. Springer, Berlin 1933 (fast unverändert nachgedruckt in Handbuch der Physik (Hrsg. S. Flügge) *V*/1, S. 1. Springer, Berlin 1958).
*** R.P. Feynman, Phys. Rev. *56*, 340 (1939).

Da $\mathbf{V}_{ee}$ von den Kern-Koordinaten unabhängig ist, besteht $\frac{\partial \mathbf{V}}{\partial z}$ nur aus zwei Anteilen, nämlich $\frac{\partial \mathbf{V}_{ke}}{\partial z}$ und $\frac{\partial \mathbf{V}_{kk}}{\partial z}$. Der erste von beiden ist ein multiplikativer Einelektronenoperator, wir können seinen Erwartungswert bilden, indem wir mit der Elektronendichte $\rho(\vec{r})$ multiplizieren und über den Raum eines Teilchens integrieren. Der zweite Anteil, nämlich

$$\frac{\partial \mathbf{V}_{kk}}{\partial z} = \frac{\partial}{\partial R}\left(\frac{Z_A \cdot Z_B}{R}\right) = -\frac{Z_A \cdot Z_B}{R^2} \qquad (3.6\text{–}5)$$

ist von den Elektronenkoordinaten unabhängig, d.h. eine Konstante. Somit ergibt sich für $-F_z$

$$-F_z = \int \frac{\partial \mathbf{V}_{ke}}{\partial z} \rho(\vec{r})\, d\tau - \frac{Z_A Z_B}{R^2} \qquad (3.6\text{–}6)$$

(Man beachte, daß ρ hier die Elektronendichte bedeutet, und nicht wie an anderer Stelle in diesem Kapitel einen reduzierten Abstand.) Gl. (3.6–6) stellt aber nichts anderes als die Kraft dar, die die übrigen Kerne sowie die Ladungsverteilung der Elektronen rein elektrostatisch auf den betrachteten Kern ausüben. Ein in der Tat verblüffendes Ergebnis! Kennen wir die Ladungsverteilung der Elektronen, können wir alle im Molekül auftretenden Kräfte berechnen. Stabilitätsfragen kann man einfach nach den Regeln der klassischen Elektrostatik berechnen.

So schön dieses Theorem zur Abrundung der Theorie ist, so unbrauchbar ist es für die Praxis. Das liegt daran, daß wir bei seiner Ableitung davon Gebrauch machen mußten, daß die Wellenfunktion Ψ_R die Schrödinger-Gleichung exakt löst. Solche Wellenfunktionen kennt man in der Regel aber gar nicht, und es tritt die Frage auf, ob das Hellmann-Feynman-Theorem auch für Näherungslösungen der Schrödinger-Gleichung gilt. Die Antwort ist generell: nein. Man kann völlig falsche Ergebnisse erhalten, wenn man ausgehend von genäherten Ladungsdichten die Kräfte nach dem Hellmann-Feynman-Theorem berechnen will. Man kann zwar, ähnlich wie beim Virialsatz, durch einen speziellen Typ von Variationsansatz die Gültigkeit des Hellmann-Feynman-Theorems erzwingen, aber viel ist damit nicht gewonnen; denn wenn man ohnehin eine quantenmechanische Rechnung durchführt, kann man die Kräfte auch durch Differenzieren der Potentialkurve erhalten oder von einem Variationsprinzip für die Kräfte ausgehen und man ist auf das Hellmann-Feynman-Theorem nicht angewiesen. Die Hoffnung, man könne von einer nicht quantenmechanisch berechneten Ladungsverteilung ausgehen und dann das Hellmann-Feynman-Theorem anwenden, erweist sich als trügerisch. Damit ist auch die Eliminierung der kinetischen Energie nur scheinbar. Man braucht diese, um die Ladungsverteilungen zu berechnen. Ohne den Term der kinetischen Energie, nur dem Gesetz der Elektrostatik überlassen, würde übrigens jede statische Ladungsverteilung in sich zusammenfallen.

Ein Beispiel zur Warnung vor einer unkritischen Anwendung des Hellmann-Feynman-Theorems möge genügen:

Die Wechselwirkung zwischen einem H-Atom und einem Proton bei großen Entfernungen, wo Überlappungseffekte vernachlässigt werden können, beruht im wesentlichen auf einer Polarisierung des H-Atoms durch das Proton. Die Wechselwirkungsenergie ist, wie in Abschn. 15.4 gezeigt wird, für große R gleich $-\frac{9}{4R^4}$ a.u., die auf eines der beiden Protonen wirkende Kraft daher gleich $\frac{9}{R^5}$ a.u.

Berechnen wir andererseits die Kräfte auf die beiden Kerne nach dem Hellmann-Feynman-Theorem!

Auf das Proton des H-Atoms wirkt die Kraft $-\frac{1}{R^2}$ des anderen Protons, da ein Elektron im 1s-Orbital auf dessen Zentrum keine Kraft ausübt. Auf das isolierte Proton wirkt dagegen überhaupt keine Kraft, da die Beiträge des anderen Kerns und seines Elektrons wie $\frac{1}{R^2}$ gehen und sich genau kompensieren. Offensichtlich beruht dieses sicher falsche Ergebnis darauf, daß wir die ungestörte Ladungsverteilung – $1s^2$ – für das H-Atom genommen haben. Unter dem Einfluß des anderen Protons ändert sich aber die Ladungsverteilung. Aber selbst, wenn wir die Änderung der Ladung in 1. störungstheoretischer Näherung berücksichtigt hätten – was genügt, um die Wechselwirkungsenergie richtig auszurechnen – wären die Kräfte nach dem Hellmann-Feynman-Theorem immer noch falsch. Erst mit der 3. störungstheoretischen Ordnung für die Ladungsverteilung erhält man die richtigen Hellmann-Feynman-Kräfte*).

Hellmann-Feynman Theorem

Sei $\Psi_R(\vec{r}_1 \ldots \vec{r}_n)$ die auf 1 normierte exakte Wellenfunktion eines Moleküls in einer bestimmten festen Anordnung der Kerne, d.h. erfülle Ψ_R die Schrödinger-Gleichung

$$\mathbf{H}_R \Psi_R = E_R \Psi_R \qquad (3.6-1)$$

Wir können die Kraft, die auf einen Kern wirkt, durch Differenzieren der Potentialfläche E_R nach den Koordinaten des Kernes berechnen. Nehmen wir der Einfachheit halber ein zweiatomiges Molekül an und habe ein Kern die Koordinaten (0, 0, 0) und der andere (0, 0, Z) mit $Z = R$, so ist

$$-F_z = \frac{\partial \langle \mathbf{H}_R \rangle}{\partial z} = \frac{\partial (\Psi_R, \mathbf{H}_R \Psi_R)}{\partial z} =$$

$$= \left(\frac{\partial \Psi_R}{\partial z}, \mathbf{H}_R \Psi_R \right) + \left(\Psi_R, \frac{\partial \mathbf{H}_R}{\partial z} \Psi_R \right) + \left(\Psi_R, \mathbf{H}_R \frac{\partial \Psi_R}{\partial z} \right) \qquad (3.6-2)$$

Benutzung der Eigenwertgleichung für Ψ_R und der Hermitizität von $\mathbf{H}_R$ erlaubt eine Umformung des ersten und dritten Terms zu

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$$(\psi, \underline{H}\psi) = \langle \psi, \underline{H}\psi \rangle = \int \psi^* \underline{H} \psi d\tau$$

Hermitesch: $$\int \Psi_i^* \underline{A} \Psi_j \, d\tau = \int \Psi_j \, \underline{A}^* \, \Psi_i^* \, d\tau$$

Linear: $$\underline{H}(f+g) = \underline{H}(f) + \underline{H}(g)$$ (in QM immer)

$$\underline{H} a f = a \underline{H} f$$

Da V_{ee} von den Kern-Koordinaten unabhängig ist, besteht $\frac{\partial V}{\partial z}$ nur aus zwei Anteilen, nämlich $\frac{\partial V_{ke}}{\partial z}$ und $\frac{\partial V_{kk}}{\partial z}$. Der erste von beiden ist ein multiplikativer Einelektronenoperator, wir können seinen Erwartungswert bilden, indem wir mit der Elektronendichte $\rho(\vec{r})$ multiplizieren und über den Raum eines Teilchens integrieren. Der zweite Anteil, nämlich

$$\frac{\partial V_{kk}}{\partial z} = \frac{\partial}{\partial R}\left(\frac{Z_A \cdot Z_B}{R}\right) = -\frac{Z_A \cdot Z_B}{R^2} \qquad (3.6-5)$$

ist von den Elektronenkoordinaten unabhängig, d.h. eine Konstante. Somit ergibt sich für $-F_z$

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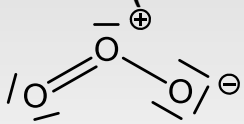
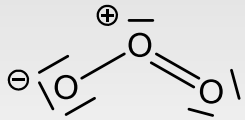
Linearkombinationen:

1) ψ_1, ψ_2 sind Atomorbitale

- an verschiedenen Atomen → ψ^b, ψ^a **MO**
- am gleichen Atom: $\int \psi_1 \, \psi_2 = 0$

  keine Linearkomb. mit niedrigerer Energie kann konstruiert werden: **HOs** $\mathrm{sp}: h_{1,2} = \frac{1}{\sqrt{2}} (s \pm p)$

2) ψ_1, ψ_2 sind $2e^-$ (oder mehr e^-) Konfig,

- VB falls  und 

  die Eigenfkt. Ψ_1 und Ψ haben,

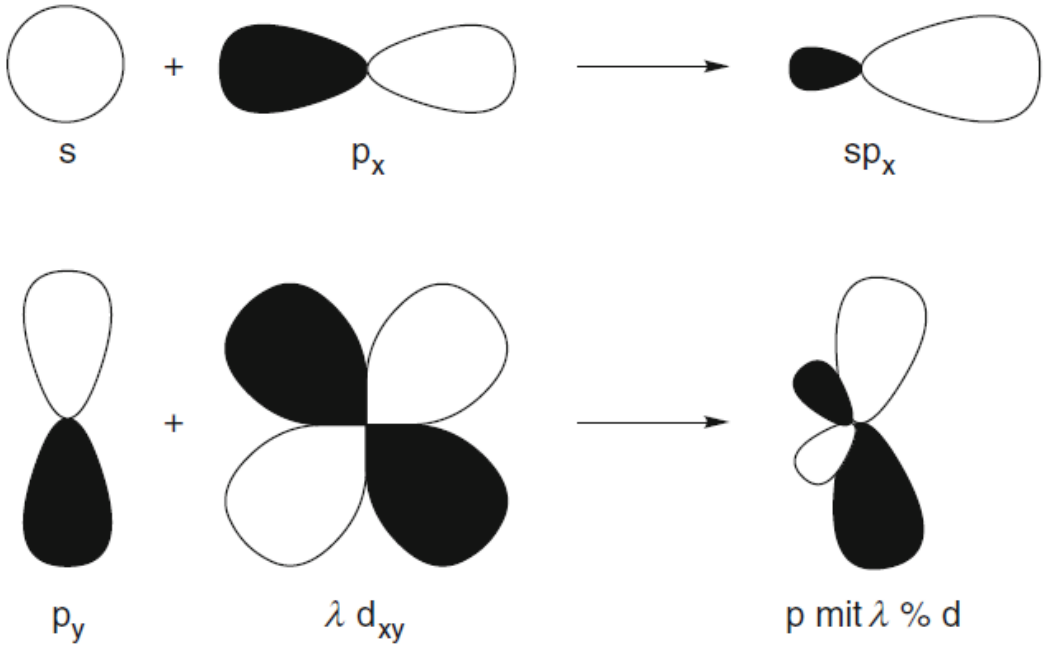
→ $\psi = \psi_1 \pm k\psi_2$ Resonanz

- MO falls Ψ_1 doppelt besetztes bind. MO und

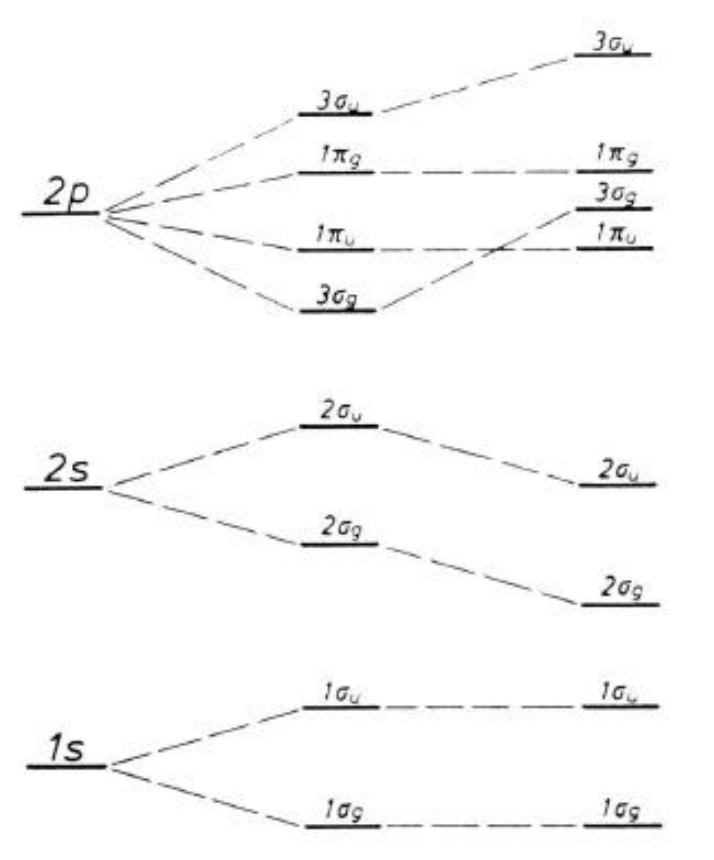
  Ψ_2 doppelt besetztes antibindendes MO

  (mit gleichem s und s_z) → $\psi^{MO,CI} = \psi_1 \pm \lambda\psi_2$

Abb. 19.8 Unterschied zwischen Hybridisierung und Polarisierung



MO-Energie-Niveaus in zweiatomigen homonuklearen Molekülen.



	$\sigma 2s$	$\sigma^* 2s$	π_x	π_y	$\sigma 2p$	π_x^*	π_y^*	$\sigma^* 2p$	n	
Li_2	2								1	Li——Li
Be_2	2	2							0	:Be Be:
B_2	2	2	1	1					1	:B × × B:
C_2	2	2	2	2					2	:C≡C:
N_2	2	2	2	2	2				3	:N≡N:
O_2	2	2	2	2	2	1	1		2	:O(×)(×)—O(○)(○):(×)(×)
$O_2^{\ddagger}$	2	2	2	2	2	2			2	:O::O:
O_2^{2-}, F_2	2	2	2	2	2	2	2		1	(-)(-) :O——O: , :F——F:
O_2^+	2	2	2	2	2	1			2.5	(+½)(+½) :O(×)(×)=O(○):(×)
O_2^-	2	2	2	2	2	2	1		1.5	(-½)(-½) :O(×)—O(○):(×)

Table 4-1 Molecular orbital configurations and valence-bond structures for diatomic molecule ground-states, and an O_2 excited state (O_2^*). (For O_2^*, O_2^+ and O_2^-, degenerate configurations are not reported here. See also Fig. 4-3).

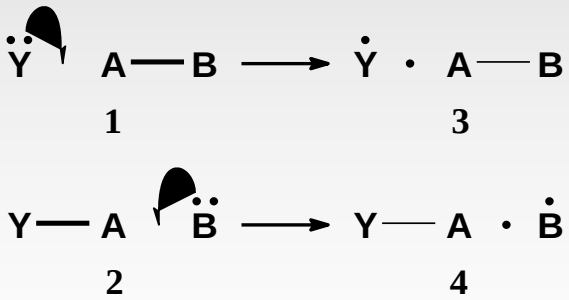
† Bond-lengths for diatomic species are taken from Ref. 2.

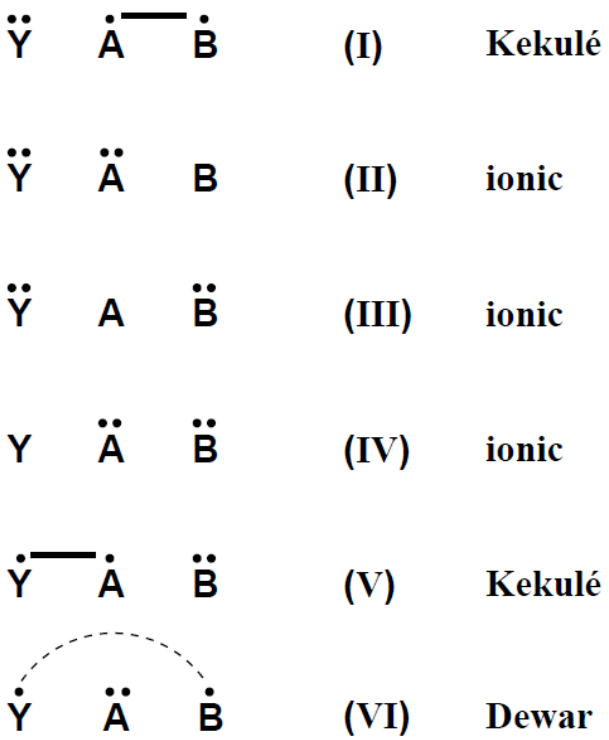
Increased valence Strukturen

3c-4e-Bindung:

$$\Psi_1(HL)=|y^{\alpha}y^{\beta}a^{\alpha}b^{\beta}|+|y^{\alpha}y^{\beta}b^{\alpha}a^{\beta}|$$

$$\Psi_2(HL)=|y^{\alpha}a^{\beta}b^{\alpha}b^{\beta}|+|a^{\alpha}y^{\beta}b^{\alpha}b^{\beta}|$$



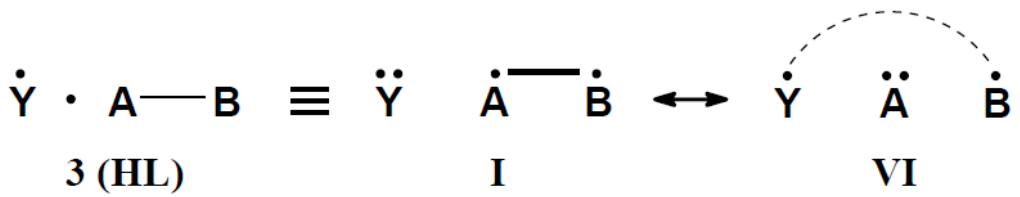


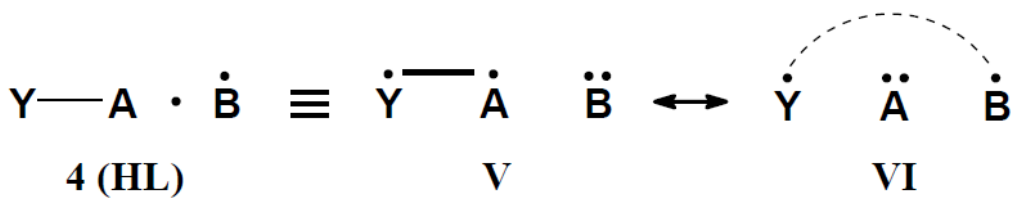
$$\Psi_{I} = |y^{\alpha}y^{\beta}a^{\alpha}b^{\beta}| + |y^{\alpha}y^{\beta}b^{\alpha}a^{\beta}|,$$
$$\Psi_{II} = |y^{\alpha}y^{\beta}a^{\alpha}a^{\beta}|,$$
$$\Psi_{III} = |y^{\alpha}y^{\beta}b^{\alpha}b^{\beta}|,$$
$$\Psi_{IV} = |a^{\alpha}a^{\beta}b^{\alpha}b^{\beta}|,$$
$$\Psi_{V} = |y^{\alpha}a^{\beta}b^{\alpha}b^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}b^{\beta}|,$$
$$\Psi_{VI} = |y^{\alpha}a^{\beta}a^{\alpha}b^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}a^{\beta}|$$

$$\Psi_3(HL) = |y^{\alpha}\psi_{ya}{}^{\beta}a^{\alpha}b^{\beta}| + |\psi_{ya}{}^{\alpha}y^{\beta}b^{\alpha}a^{\beta}|$$

$$\Psi_3(HL) = \Psi_I + l\,\Psi_{VI}$$

$$\Psi_4(HL) = |y^{\alpha}a^{\beta}\psi_{ab}^{\alpha}b^{\beta}| + |a^{\alpha}\psi_{ab}^{\beta}b^{\alpha}y^{\beta}| = k\Psi_V + \Psi_{VI}$$





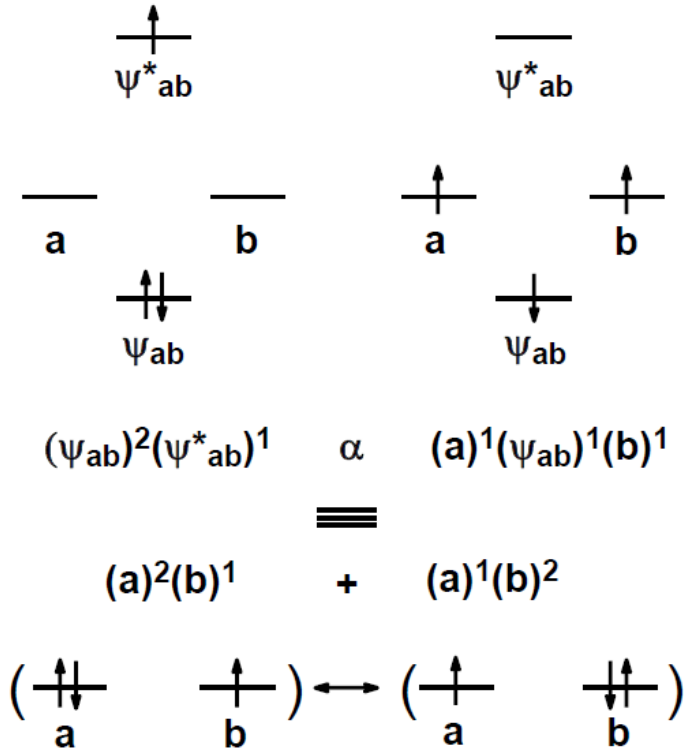
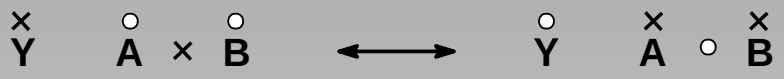
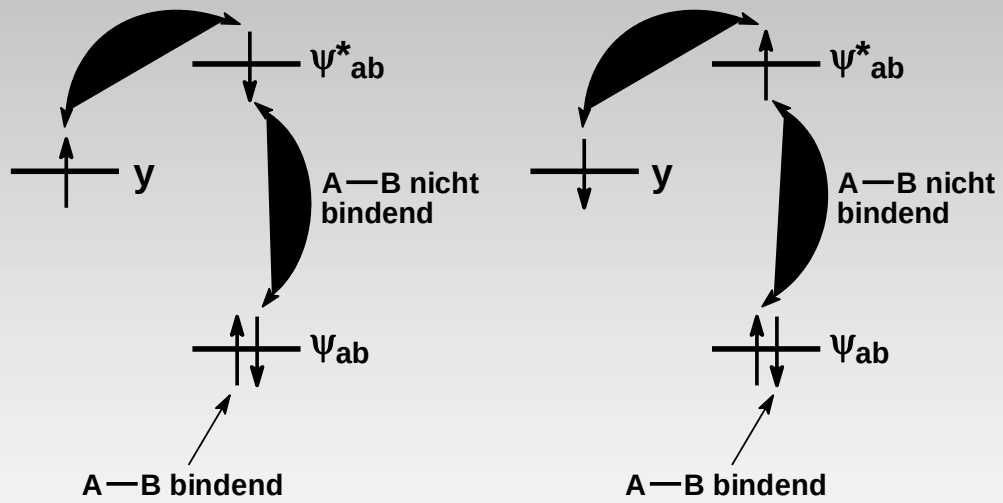
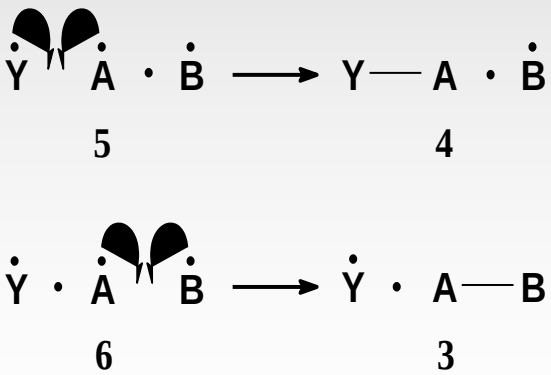


Abb. 1.17 Orbital-Diagramm für
$|\Psi_{ab}{}^{\alpha}\Psi_{ab}{}^{\beta}\Psi^{*}{}_{ab}{}^{\alpha}| \propto |a^{\alpha}\Psi_{ab}{}^{\beta}b^{\alpha}| = |a^{\alpha}a^{\beta}b^{\alpha}| + k|a^{\alpha}b^{\beta}b^{\alpha}|$ (mit $k = 1$)



Spinpaarung für eine fraktionelle Y — A und Y — B Bindung





Zusammenfassend können wir sagen, dass zwei Techniken geeignet sind, um increased-valence Strukturen zu erzeugen (dies gilt sowohl für HL- als auch für LMO-Wellenfunktionen):

•Die Delokalisierung eines nicht bindenden Elektrons einer Kekulé-Typ-Lewis-Struktur in ein bindendes LMO, wie z.B. in den Fällen **1** → **3** und **2** → **4**.

•Die Spin-Paarung eines antibindenden Elektrons einer 3-Elektronen-Bindung mit einem ungepaarten Elektron an einem weiteren Atom, wie z.B. in den Fällen **5** → **4** und **6** → **3**.

The following table shows a comparison between the main features of qualitative valence bond (VB) and molecular orbital (MO) theory. It should be emphasized, however, that both theories use different language. For example, the terms “bonding”, “nonbonding” and “antibonding orbitals” only occur in MO theory whereas the term “resonance” is only used in VB theory. Therefore, it is often difficult to compare certain aspects of each theory.

Comparison between the main features of qualitative valence bond (VB) and molecular orbital (MO) theory.

	classical VB	**MO**
Orbital type	Pure atomic orbitals (AOs) used directly	Uses AOs to form canonical molecular orbitals (MOs) which are a linear combination (+ or -) of AOs (LCAO approach). There may be bonding (+), antibonding (-) or nonbonding MOs
Hybridization	Sometimes advantageous, not essential: Linear combination of AOs to form hybrid atomic orbitals (HAOs)	Usually not used (but possible, cf. N_2, CH_4)

Is energetically advantageous because…….	Electron 1 can be at center A and electron 2 at center B or vice versa which gives a higher degree of variational freedom. This is normally described as the VB approach of a covalent bond. Sometimes ionic resonance structures are also taken into account.	Bonding MOs are lower in energy than AOs (the occupancy of the bonding MOs ought to be higher than the occupancy of the antibonding MOs)
Orbital overlap picture	AOs remain unchanged	AOs that overlap are used to form delocalized non-overlapping MOs with σ or π symmetry (σ = rotational symmetry with respect to internuclear axis, π = mirror plane in internuclear axis)
orthogonal ?	AOs are not orthogonal, they overlap	MOs are orthogonal, they do not overlap
Localised orbitals ?	strictly localized at atoms	de-localized, canonical orbitals
Do orbitals change going from atoms to molecules ?	No, but they can (AOs may, however, change “size” = promotion of orbitals)	Yes
Bonding, antibonding (sometimes non-bonding) orbitals formed ?	No	Yes

Octet rule obeyed ?	Yes, if only s and p orbitals are used for bonding in main-group molecules	Yes, if only s and p orbitals are used for construction of MOs and d orbitals for polarization only in main-group molecules
"Bonds" (= spin pairing) between non-neighbouring atoms possible ?	Yes, long bonds or Dewar bonds	No
Ionic resonance structures	Yes, if pure AOs are used	No
What happens when the electrons are not fully localized in bonds (e.g. C_6H_6, $B_3N_3H_6$, NO_3^- etc.)	Resonance between various mesomeric resonance structures, resonance stabilization energy	No, MOs are delocalized over the entire molecule, delocalozation energy, (equivalence to resonance would be configuration interaction – CI – MO theory)
Fundamental difference between theories	Resulting wavefunction is the product of singly (or doubly) occupied AOs	Resulting wavefunction is the product of singly (or doubly) occupied MOs

Wavefunctions for " 4-Electron, 3-Centre " Bonding Units

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As can be seen in tables 4 and 5, $\Psi_{ivbo,A}$ generates energies and overlaps that are very close to those of $\Psi_{bo,A}$ (which, as we have discussed above, is equivalent to both Ψ_{moci} and to $\frac{1}{2}(1-\kappa)\Psi_{npso}+\frac{1}{2}(1+\kappa)\Psi_{vbbo}$). This is not surprising since we have

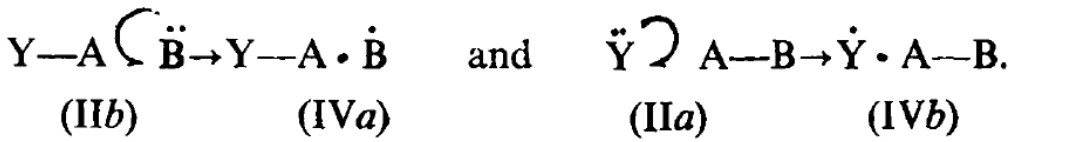
$$\Psi_{ivbo,A}(l, l', l) = (2l+l')\psi_1+2l^2\psi_2+4\psi_3+2l'l\psi_4 \qquad (29)$$

and

$$2\Psi_{bo,A}(l, \tfrac{1}{2}l') = (2l+l')\psi_1+(2l^2+\tfrac{1}{2}l'^2)\psi_2+4\psi_3+2l'l\psi_4 \qquad (30)$$

that is, the wavefunctions differ only in the coefficient of ψ_2. For the systems studied. l' is usually small relative to l, and hence the similarity of the functions is explained. This similarity is carried over to their bond parameters which are reported in table 7.

One of us has shown [11] that increased-valence formulae (IV*a*) and (IV*b*) can be generated very easily from the standard valence-bond formulae (II*a*) and (II*b*). Perhaps the simplest (but *not* the only) way to do this is to delocalize a non-bonding electron into a bonding orbital, as in [11c-11f, 22]



(II*b*) (IV*a*) and (II*a*) (IV*b*)

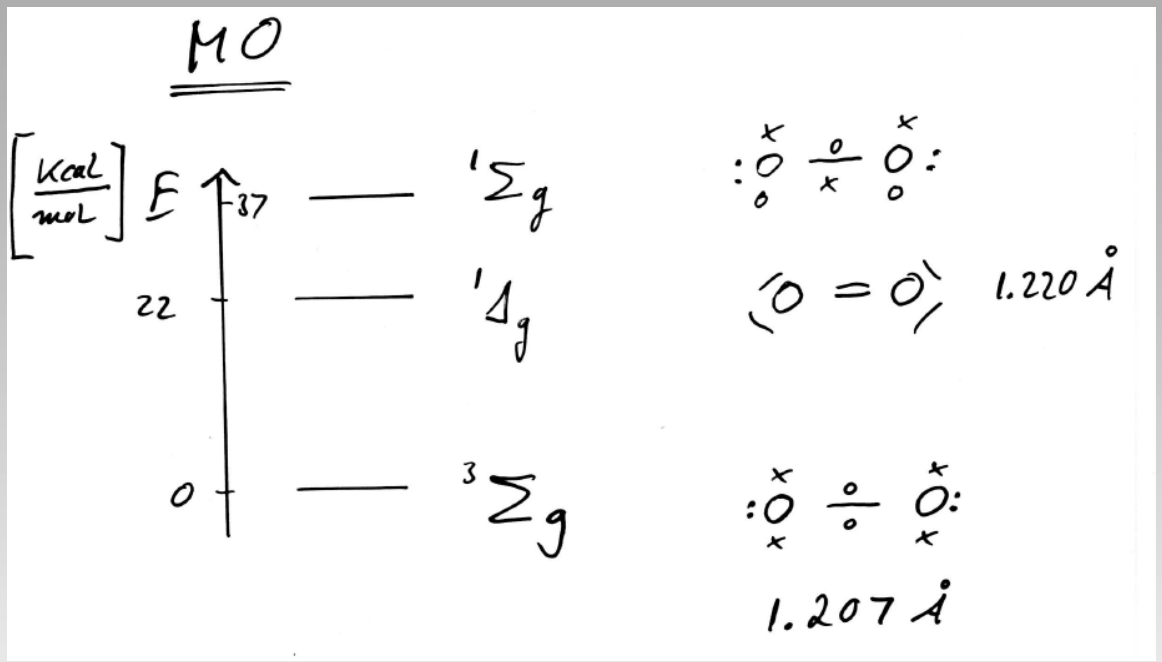
This type of delocalization stabilizes the standard valence-bond structures by allowing them to participate in resonance with the long-bond structure.

CONCLUSIONS

For a number of symmetrical electron-excess systems, we have provided evidence that the long-bond valence structure Y $\overset{\frown}{\text{A}}$ B can participate appreciably in resonance with the standard valence-bond structures Y—A $\ddot{\text{B}}$ and $\ddot{\text{Y}}$ A—B. A similar conclusion has also been obtained from semiempirical studies [22] of N_3^-, N_2O, CO_2, NO_2^+ and [25] N_2O_4, and from non-empirical valence-bond calculations [26] for systems which have one or more non-symmetrical bonding units such as FNO_2, FO_2 and CH_2N_2. This type of resonance-stabilization seems to be of particular importance for 1,3-dipolar molecules and ions, but it can also be important for systems such as H_3^-, HCO_2^-, NO_2^- and $C_3H_5^-$ with other types of formal charge arrangements.

Both the increased-valence and the non-paired spatial orbital structures summarize resonance between the standard and the long-bond valence structures. Therefore, for the purpose of providing simple localized representations of electronic structure, they should be preferred to using the standard valence-bond structures alone. Numerous examples of chemical insights which may be obtained by constructing increased-valence and non-paired spatial orbital formulae have been discussed elsewhere.[11, 13] It is our opinion that these new valence formulae should constitute an important component of elementary valence theory.

Zeigen, dass die Dewar Struktur kein Artefakt der VB-Theorie ist



$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$K_3Cr(O_2)_4 \rightarrow K_3CrO_4 + 2\ {}^1O_2$

Exp.

$Cl_2 + 2\ OH^- \rightarrow ClO^- + Cl^- + H_2O$

$ClO^- + H_2O_2 \rightarrow ClOOH + OH^-$ slow

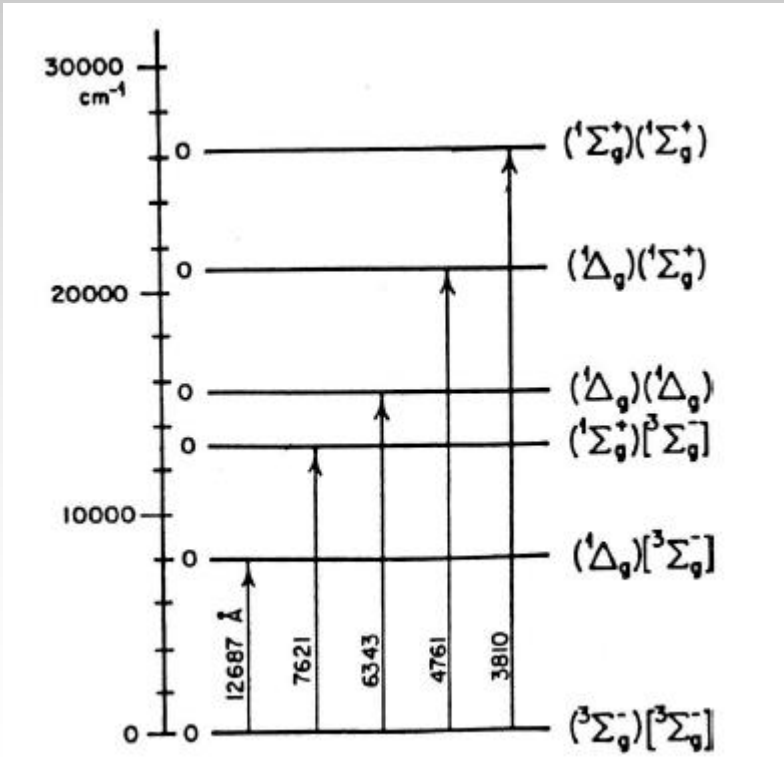
$ClOOH \rightarrow HCl + {}^1O_2$ fast

$$2\ {}^1O_2({}^1\Delta_g) \rightarrow 2\ {}^3O_2({}^3\Sigma_g^-)$$

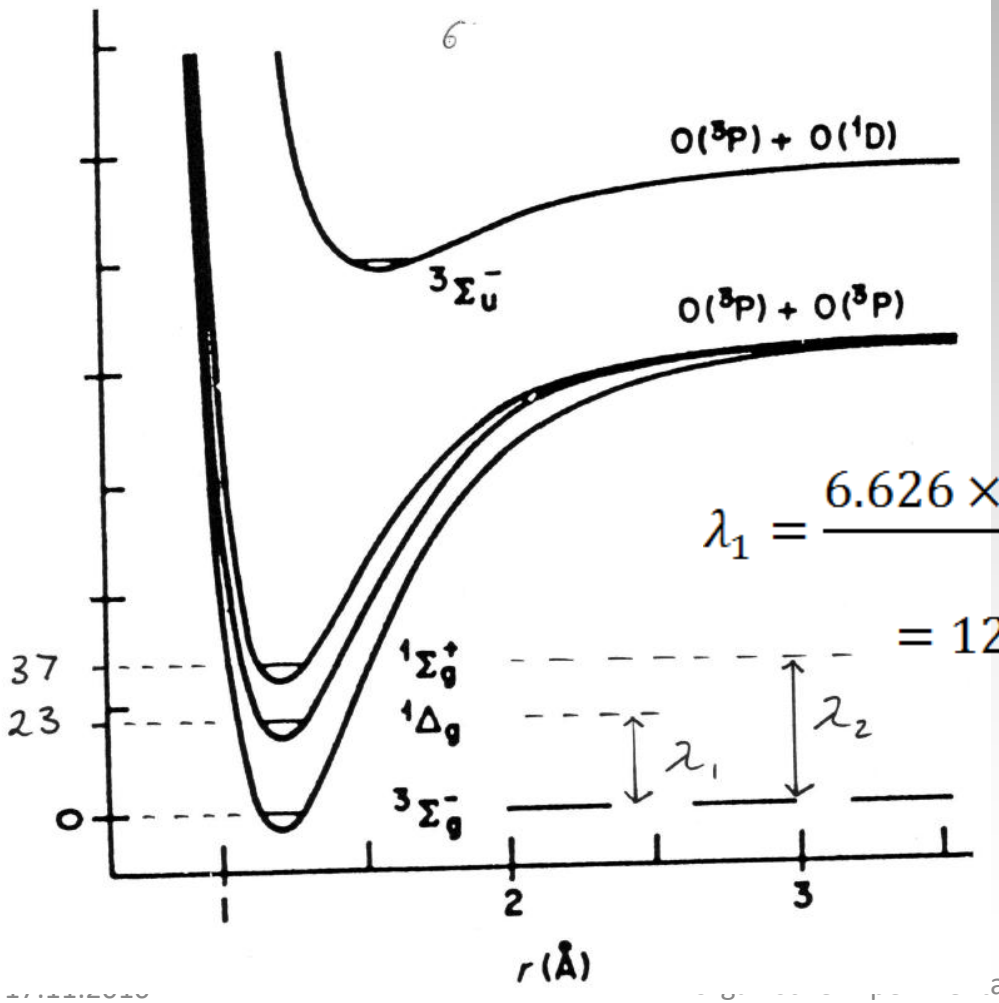
$$-\Delta E = 2x23\ \text{kcal mol}^{-1}$$

$$O_2({}^1\Sigma_g^+) \rightarrow {}^3O_2({}^3\Sigma_g^-)$$

$$-\Delta E = 37\ \text{kcal mol}^{-1}$$



Potentialkurven von molekularem Sauerstoff



$$\Delta E = h\nu = \frac{hc}{\lambda}$$

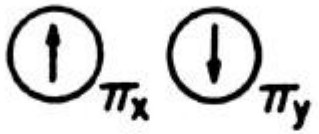
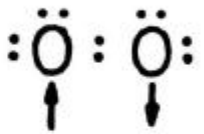
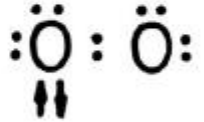
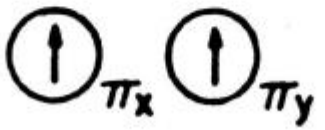
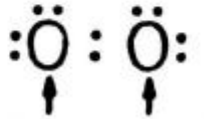
$$\lambda = \frac{hc}{E}$$

$$\lambda_1 = \frac{6.626 \times 10^{-34}\,\text{Js} \times 3 \times 10^{8}\,\text{m} \times 6.022 \times 10^{23}}{96 \times 1000\,\text{J mol}^{-1}\ \text{s}\ \ \text{mol}}$$

$$= 1247\ \text{nm}$$

$$2 \times \lambda_1 = 623\ \text{nm}$$

$$\lambda_2 = 477\ \text{nm}$$

STATE	ORBITAL ASSIGNMENT	LEWIS STRUCTURE	WAVE FUNCTION
$^1\Sigma_g^+$			$\pi_x(1)\ \alpha(1)\ \pi_y(2)\ \beta(2)$
$^1\Delta_g$			$\pi_x(1)\ \alpha(1)\ \pi_x(2)\ \beta(2)$
$^3\Sigma_g^-$			$\pi_x(1)\ \alpha(1)\ \pi_y(2)\ \alpha(2)$

Primitive representations of molecular oxygen lowest singlet and triplet states.

- fail to take into account e^- indistinguishability (interchanges of indices 1 and 2)
- are not anti-symmetric ➔ P = has to be -1; $\underline{\mathbf{P}}(1,2)\ \Psi = P\ \Psi$

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(\mathbf{1\pi_g})^2$$

$$\pi_g^+ \equiv X \qquad \pi_g^- \equiv Y$$

		$L_z(M_L)$	$S_z(M_S)$		
↑↓	—	−2	0	$\Psi_1 = \lvert x\alpha x\beta \rvert$	$^1\Delta_g$
↑	↑	0	1	$\Psi_2 = \lvert x\alpha y\alpha \rvert$	$^3\Sigma_g^-$
↑	↓	0	0	$\Psi_3 = \lvert x\alpha y\beta \rvert$	$^3\Sigma_g^-$
↓	↑	0	0	$\Psi_4 = \lvert y\alpha x\beta \rvert$	$^1\Sigma_g^+$
↓	↓	0	−1	$\Psi_5 = \lvert x\beta y\beta \rvert$	$^3\Sigma_g^-$
—	↑↓	2	0	$\Psi_6 = \lvert y\alpha y\beta \rvert$	$^1\Delta_g$

$$\psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} x(1)\alpha(1) & x(2)\alpha(2) \\ x(1)\beta(1) & x(2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left[x(1)\alpha(1)x(2)\beta(2) - x(1)\beta(1)x(2)\alpha(2) \right]$$

$$\psi_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} x(1)\alpha(1) & x(2)\alpha(2) \\ y(1)\beta(1) & y(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \ldots$$

$$\psi_4 = \ldots = \frac{1}{\sqrt{2}} \left[x(1)\beta(1)y(2)\alpha(2) - y(1)\alpha(1)x(2)\beta(2) \right]$$

$$\psi_3 = \frac{1}{\sqrt{2}} \left(\Psi_3 + \Psi_4 \right) \qquad \psi_4 = \frac{1}{\sqrt{2}} \left(\Psi_3 - \Psi_4 \right)$$

$$\psi_3 = \frac{1}{2} \left[x(1)\alpha(1)y(2)\beta(2) - x(2)\alpha(2)y(1)\beta(1) + x(1)\beta(1)y(2)\alpha(2) - x(2)\beta(2)y(1)\alpha(1) \right]$$

$$= \frac{1}{2} \left[x(1)y(2) - x(2)y(1) \right] \left[\alpha(1)\beta(2) + \alpha(2)\beta(1) \right]$$

$$\psi_4 = \frac{1}{2} [\quad + \quad][\quad - \quad]$$

$\psi_3 \Rightarrow {}^3\Sigma_g^-$ $\qquad$ $\psi_4 \Rightarrow {}^1\Sigma_g^+$

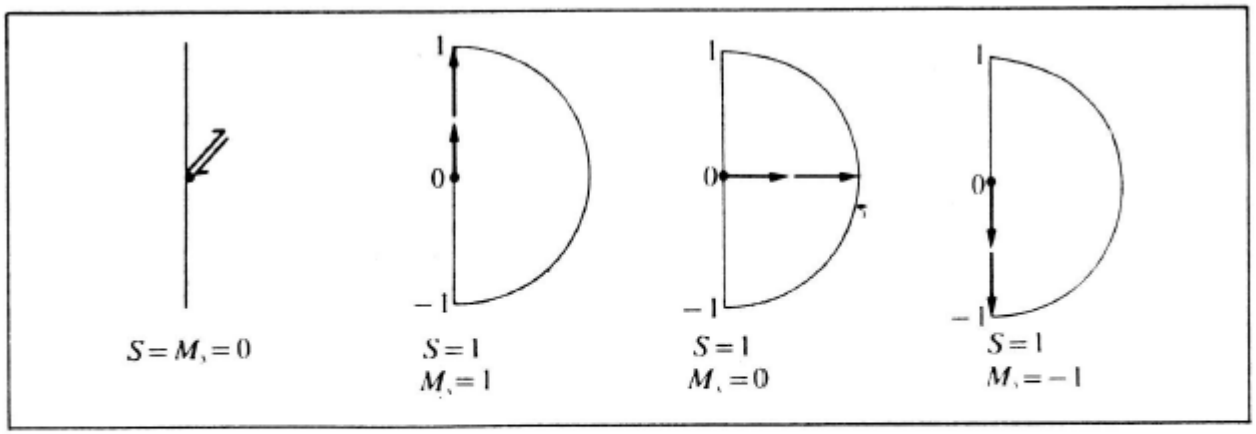


Fig. 5.5. Vektordiagramm für die Spinzusammensetzung. Antiparallele Kopplung („Paarung") ergibt nur einen Zustand ($S = 0$). Parallele Kopplung ergibt den Gesamtspin $S = 1$; durch Anlegen eines Magnetfeldes (vertikale Richtung) nimmt die quantisierte Komponente in Feldrichtung die drei möglichen Werte $M_s = 1, 0, -1$ an. Der Triplett-Zustand wird durch ein Feld in drei Zustände mit etwas unterschiedlichen Energiewerten aufgespalten.

MO-Energie-Niveaus in zweiatomigen homonuklearen Molekülen.

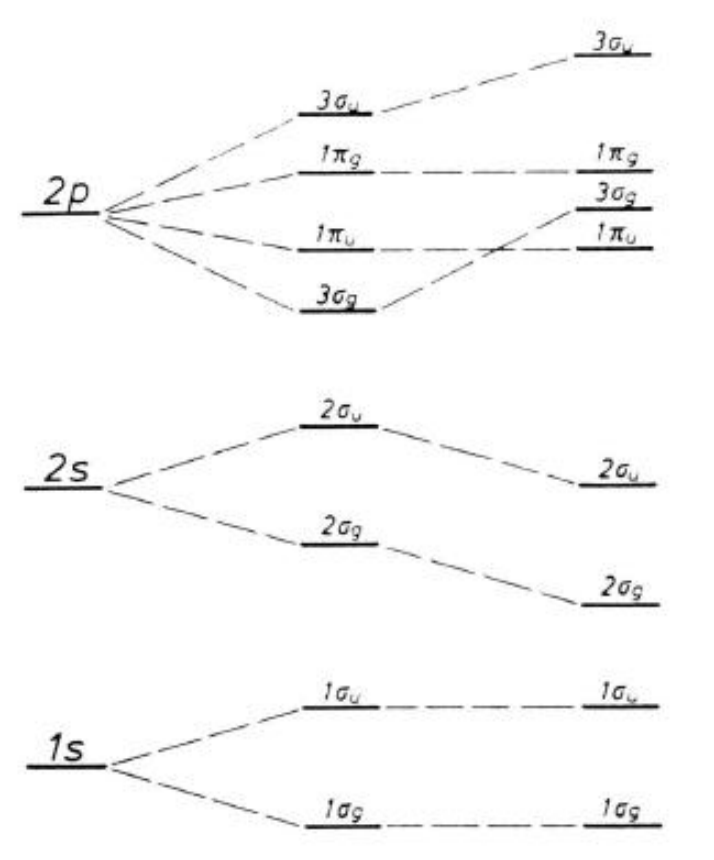


Abb. 19.5 MO-Schema und VB-Repräsentation für den Triplett-Grundzustand von O_2

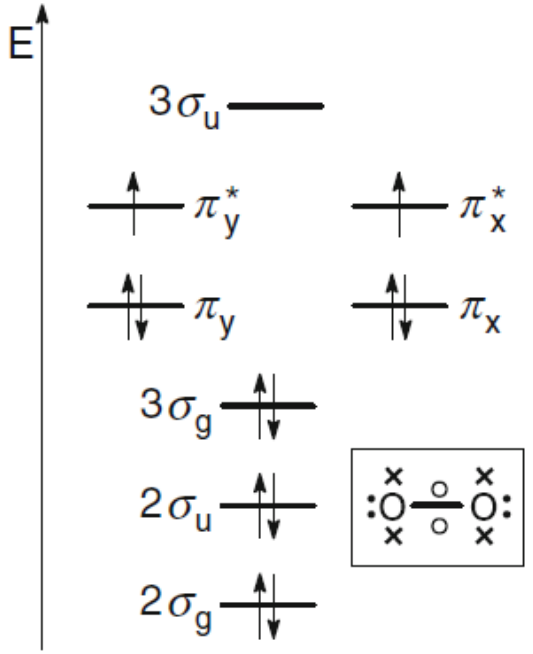


Abb. 19.6 Einfachste MO- und VB-Beschreibungen für den Triplett-Grundzustand ($^3\Sigma$) und die beiden ersten angeregten Singulett-Zustände ($^1\Delta$ und $^1\Sigma$) im O_2-Molekül

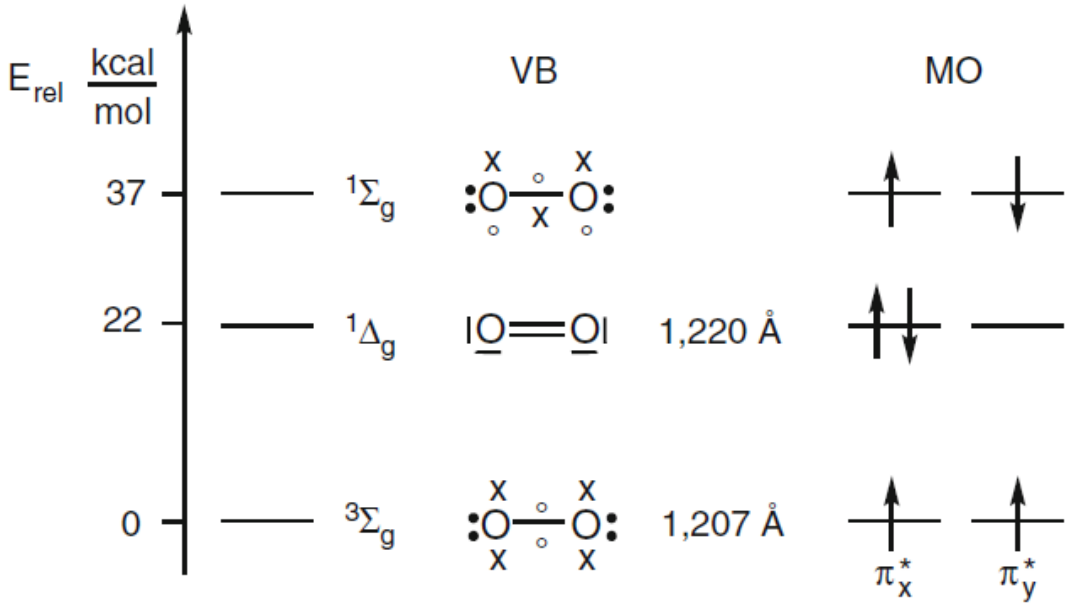
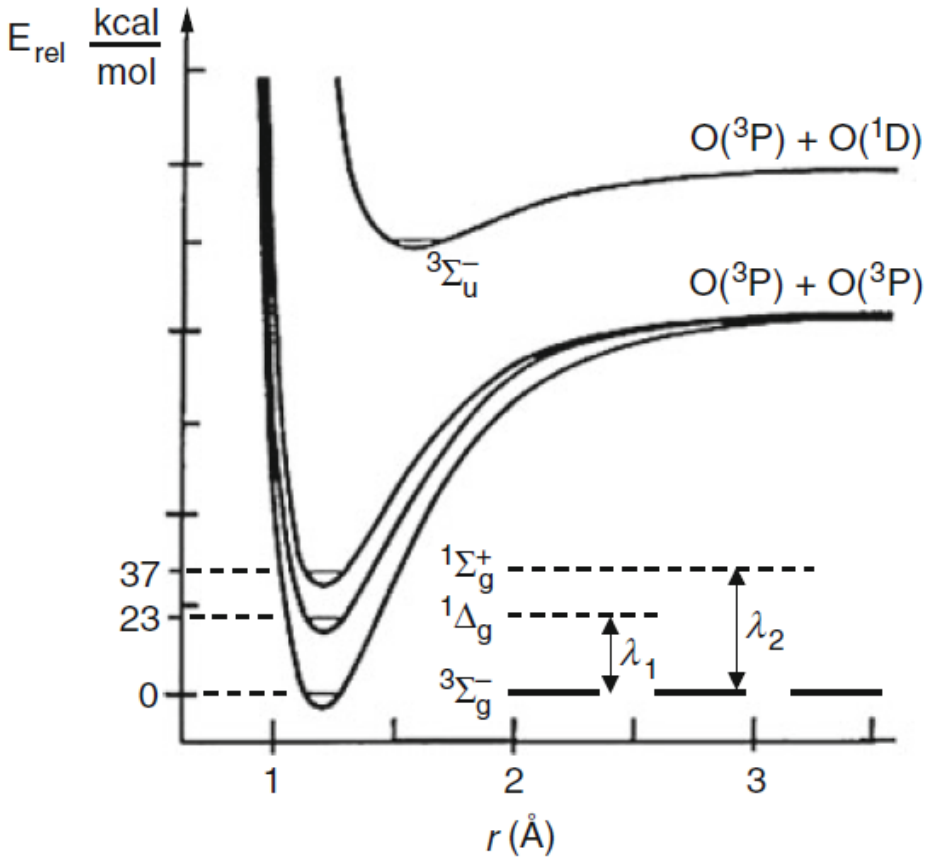
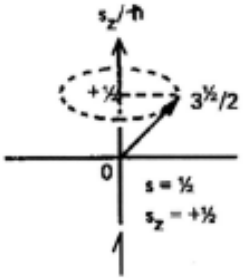


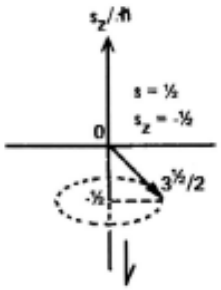
Abb. 19.7 Potential/Energie-Kurve für das O_2-Molekül in den niedrigsten elektronischen Zuständen



Orientations of spin angular momentum vectors for one and two electrons relative to an external magnetic field directed along the z-axis. $\hbar = h/2\pi$

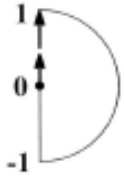
one electron



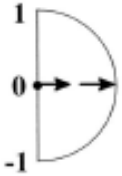


two electrons

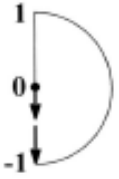
$S = 0$
$S_Z = 0$



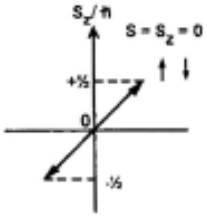
$S = 1$
$S_Z = 1$

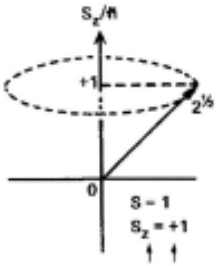


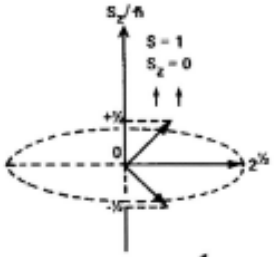
$S = 1$
$S_Z = 0$

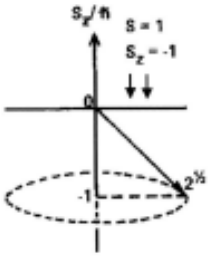


$S = 1$
$S_Z = -1$









$$(\uparrow\downarrow - \downarrow\uparrow)\frac{1}{\sqrt{2}} \qquad \uparrow\uparrow \qquad (\uparrow\downarrow + \downarrow\uparrow)\frac{1}{\sqrt{2}} \qquad \downarrow\downarrow$$

$$\big((\alpha(1)\beta(2) - \beta(1)\alpha(2)\big)\frac{1}{\sqrt{2}} \qquad \alpha(1)\alpha(2) \qquad \big((\alpha(1)\beta(2) + \beta(1)\alpha(2)\big)\frac{1}{\sqrt{2}} \qquad \beta(1)\beta(2)$$

anti - symmetric

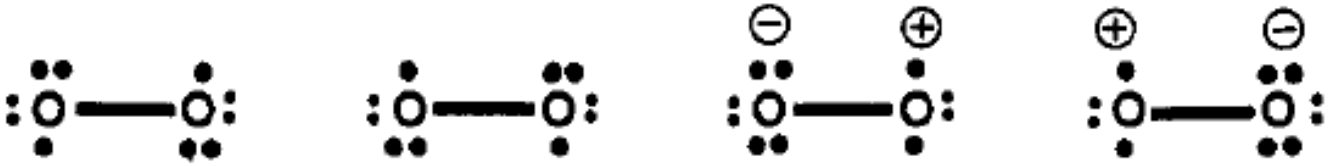
STATE	COMPLEX WAVE FUNCTION	SPIN–ORBITAL DIAGRAM
$^1\Sigma_g^+$	$\frac{1}{2}\{\lvert\pi_+\,\bar{\pi}_-\rvert - \lvert\bar{\pi}_+\,\pi_-\rvert\}$	$[\uparrow_+\downarrow_-] - [\downarrow_+\uparrow_-]$
$^1\Delta_g$	$\frac{1}{\sqrt{2}}\lvert\pi_+\,\bar{\pi}_+\rvert$ $\frac{1}{\sqrt{2}}\lvert\pi_-\,\bar{\pi}_-\rvert$	$[\uparrow\downarrow_+\,\bigcirc_-]$ $[\bigcirc_+\,\uparrow\downarrow_-]$
$^3\Sigma_g^-$	$\frac{1}{\sqrt{2}}\lvert\pi_+\,\pi_-\rvert$ $\frac{1}{2}\{\lvert\pi_+\,\bar{\pi}_-\rvert + \lvert\bar{\pi}_+\,\pi_-\rvert\}$ $\frac{1}{\sqrt{2}}\lvert\bar{\pi}_+\,\bar{\pi}_-\rvert$	$[\uparrow_+\uparrow_-]$ $[\uparrow_+\downarrow_-] + [\downarrow_+\uparrow_-]$ $[\downarrow_+\downarrow_-]$

Complex wave functions for the lowest electronic states of molecular oxygen.

STATE	REAL WAVE FUNCTION	SPIN-ORBITAL DIAGRAM
$^1\Sigma_g^+$	$\frac{1}{2}\{\lvert\pi_x\,\bar{\pi}_x\rvert + \lvert\pi_y\,\bar{\pi}_y\rvert\}$	$[\uparrow\downarrow_x\,\bigcirc_y] + [\bigcirc_x\,\uparrow\downarrow_y]$
$^1\Delta_g$	$\frac{1}{2}\{\lvert\pi_x\,\bar{\pi}_x\rvert - \lvert\pi_y\,\bar{\pi}_y\rvert\}$ $\frac{1}{2}\{\lvert\pi_x\,\bar{\pi}_y\rvert - \lvert\bar{\pi}_x\,\pi_y\rvert\}$	$[\uparrow\downarrow_x\,\bigcirc_y] - [\bigcirc_x\,\uparrow\downarrow_y]$ $[\uparrow_x\,\uparrow_y] - [\downarrow_x\,\uparrow_y]$
$^3\Sigma_g^-$	$\frac{1}{\sqrt{2}}\lvert\pi_x\,\pi_y\rvert$ $\frac{1}{2}\{\lvert\pi_x\,\bar{\pi}_y\rvert + \lvert\bar{\pi}_x\,\pi_y\rvert\}$ $\frac{1}{\sqrt{2}}\lvert\bar{\pi}_x\,\bar{\pi}_y\rvert$	$[\uparrow_x\,\uparrow_y]$ $[\uparrow_x\,\downarrow_y] + [\downarrow_x\,\uparrow_y]$ $[\downarrow_x\,\downarrow_y]$

Real wave functions for the lowest electronic states of molecular oxygen.

The results of recent ab initio valence bond (VB) calculations for the $^3\Sigma_g^-$ ground state of O_2[1,2] show that the dominant Lewis-type VB structures are (**1**–**4**) when the equilibrium bond length



(1) (2) (3) (4)

of 1.21 Å is assumed in the calculations. Each of these structures has three $2p\pi_x$ and three $2p\pi_y$ electrons, with parallel spins for the two odd electrons. McWeeny[1,2] has calculated the ground-state linear combination of eq 1, for which structures **1′**, **1″**, **2′**, and

$$\Psi = 0.58675(\Psi_1 + \Psi_2) - 0.22508(\Psi_3 + \Psi_4) +$$

J. Phys. Chem. **1992**, *96*, 7616–7619

1. Electronic Structure and Sensitization

O_2 $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^2$

ORBITAL ASSIGNMENT	EIGENVALUE UNDER $h/2\pi$ $\hat{L}_z$	$\hat{S}_z$	COMPONENTS OF STATE
$\pi_g^+ \ \bar{\pi}_g^+$	2	0	$^1\Delta_g$
$\pi_g^+ \ \pi_g^-$	0	1	$^3\Sigma_g^-$
$\pi_g^+ \ \bar{\pi}_g^-$	0	0	$^3\Sigma_g^-, {}^1\Sigma_g^+$
$\bar{\pi}_g^+ \ \pi_g^-$	0	0	$^3\Sigma_g^-, {}^1\Sigma_g^+$
$\bar{\pi}_g^+ \ \bar{\pi}_g^-$	0	-1	$^3\Sigma_g^-$
$\pi_g^- \ \bar{\pi}_g^-$	-2	0	$^1\Delta_g$

Fig. 5. Molecular oxygen configuration components.

STATE	COMPLEX WAVE FUNCTION	SPIN–ORBITAL DIAGRAM
$^1\Sigma_g^+$	$\frac{1}{2}\{\lvert\pi_+\,\bar{\pi}_-\rvert - \lvert\bar{\pi}_+\,\pi_-\rvert\}$	$[\uparrow_+\downarrow_-] - [\downarrow_+\uparrow_-]$
$^1\Delta_g$	$\frac{1}{\sqrt{2}}\lvert\pi_+\,\bar{\pi}_+\rvert$ $\frac{1}{\sqrt{2}}\lvert\pi_-\,\bar{\pi}_-\rvert$	$[\uparrow\downarrow_+\ \bigcirc_-]$ $[\bigcirc_+\ \uparrow\downarrow_-]$
$^3\Sigma_g^-$	$\frac{1}{\sqrt{2}}\lvert\pi_+\,\pi_-\rvert$ $\frac{1}{2}\{\lvert\pi_+\,\bar{\pi}_-\rvert + \lvert\bar{\pi}_+\,\pi_-\rvert\}$ $\frac{1}{\sqrt{2}}\lvert\bar{\pi}_+\,\bar{\pi}_-\rvert$	$[\uparrow_+\uparrow_-]$ $[\uparrow_+\downarrow_-] + [\downarrow_+\uparrow_-]$ $[\downarrow_+\downarrow_-]$

Fig. 6. Complex wave functions for the lowest electronic states of molecular oxygen.

ORBITAL ASSIGNMENT	$h/2\pi$ EIGENVALUE UNDER $\hat{L}_z$	$\hat{S}_z$	COMPONENTS OF STATE
$\pi_g^+ \ \bar{\pi}_g^+$	2	0	$^1\Delta_g$
$\pi_g^+ \ \pi_g^-$	0	1	$^3\Sigma_g^-$
$\pi_g^+ \ \bar{\pi}_g^-$	0	0	$^3\Sigma_g^-, {}^1\Sigma_g^+$
$\bar{\pi}_g^+ \ \pi_g^-$	0	0	$^3\Sigma_g^-, {}^1\Sigma_g^+$
$\bar{\pi}_g^+ \ \bar{\pi}_g^-$	0	-1	$^3\Sigma_g^-$
$\pi_g^- \ \bar{\pi}_g^-$	-2	0	$^1\Delta_g$

Fig. 5. Molecular oxygen configuration components.

STATE	COMPLEX WAVE FUNCTION	SPIN–ORBITAL DIAGRAM
$^1\Sigma_g^+$	$\frac{1}{2}\{\lvert\pi_+ \bar{\pi}_-\rvert - \lvert\bar{\pi}_+ \pi_-\rvert\}$	$[\uparrow_+\downarrow_-] - [\downarrow_+\uparrow_-]$
$^1\Delta_g$	$\frac{1}{\sqrt{2}}\lvert\pi_+ \bar{\pi}_+\rvert$	$[\uparrow\downarrow_+ \ \ \_]$
	$\frac{1}{\sqrt{2}}\lvert\pi_- \bar{\pi}_-\rvert$	$[\_ \ \ \uparrow\downarrow_-]$
$^3\Sigma_g^-$	$\frac{1}{\sqrt{2}}\lvert\pi_+ \pi_-\rvert$	$[\uparrow_+\uparrow_-]$
	$\frac{1}{2}\{\lvert\pi_+ \bar{\pi}_-\rvert + \lvert\bar{\pi}_+ \pi_-\rvert\}$	$[\uparrow_+\downarrow_-] + [\downarrow_+\uparrow_-]$
	$\frac{1}{\sqrt{2}}\lvert\bar{\pi}_+ \bar{\pi}_-\rvert$	$[\downarrow_+\downarrow_-]$

Fig. 6. Complex wave functions for the lowest electronic states of molecular oxygen.

Using the linear combination of $(\pi_g^+ \bar{\pi}_g^- - \bar{\pi}_g^+ \pi_g^-)$ of Fig. 5, column 1, written in determinantal form for electron indistinguishability, we obtain the unique wave function for the $^1\Sigma_g^+$ state

$$\Psi(^1\Sigma_g^+) = \tfrac{1}{2}(\lvert\pi_+ \bar{\pi}_-\rvert - \lvert\bar{\pi}_+ \pi_-\rvert)$$

which factors after expansion of the determinants into

$$\Psi(^1\Sigma_g^+) = \tfrac{1}{2}\{[\pi_+(1)\pi_-(2)] + [\pi_-(1)\pi_+(2)]\}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

again revealing a singlet spin function, with a symmetric orbital function under electron interchange.

Finally, as a last example we resolve the $^3\Sigma_g^-$ $(M_S = 0)$ component, for which Fig. 6 indicates the determinantal form of the linear combination $(\pi_g^+ \bar{\pi}_g^- + \bar{\pi}_g^+ \pi_g^-)$ of Fig. 5, column 1

$$\Psi(^3\Sigma_g^-, M_S = 0) = \tfrac{1}{2}(\lvert\pi_+ \bar{\pi}_-\rvert + \lvert\bar{\pi}_+ \pi_-\rvert)$$

which factors upon expansion of the determinants into

$$\Psi(^3\Sigma_g^-, M_S = 0) = \tfrac{1}{2}\{[\pi_+(1)\pi_-(2)] - [\pi_-(1)\pi_+(2)]\}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

revealing a *symmetric* or *triplet* spin function and an antisymmetric orbital function, under electron interchange. This last represents an electronic state with zero component of spin angular momentum with respect to the z axis. The remaining state functions of Fig. 6 are formulated analogously from the components of Fig. 5, column 1.

Thus, the compactness of the determinantal form as displayed in Fig. 6 for the lowest electronic states of molecular oxygen permits a full resolution into electronic state components and at the same time reveals their distinctive differences as well as features in common. We may summarize as follows.

From the single molecular orbital configuration $\ldots(1\pi_g)^2$ we have generated six different electronic states with distinctive electronic distribution patterns, energies, and magnetic characteristics. There is a unique $^1\Sigma_g^+$ state; there are in zeroth approximation two equal energy $^1\Delta_g$ states and three equal energy $^3\Sigma_g^-$ states. Arising as they do from a single molecular orbital configuration, we could anticipate the potential curve (Fig. 1) common features for the cluster of $^1\Sigma_g^+$, $^1\Delta_g$, and $^3\Sigma_g^-$ states: they have nearly coincident potential minima, indicating almost identical binding energies, and the states dissociate to a common limit.

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The following table shows a comparison between the main features of qualitative valence bond (VB) and molecular orbital (MO) theory. It should be emphasized, however, that both theories use different language. For example, the terms “bonding”, “nonbonding” and “antibonding orbitals” only occur in MO theory whereas the term “resonance” is only used in VB theory. Therefore, it is often difficult to compare certain aspects of each theory.

Comparison between the main features of qualitative valence bond (VB) and molecular orbital (MO) theory.

	classical VB	**MO**
Orbital type	Pure atomic orbitals (AOs) used directly	Uses AOs to form canonical molecular orbitals (MOs) which are a linear combination (+ or -) of AOs (LCAO approach). There may be bonding (+), antibonding (-) or nonbonding MOs
Hybridization	Sometimes advantageous, not essential: Linear combination of AOs to form hybrid atomic orbitals (HAOs)	Usually not used (but possible, cf. N_2, CH_4)

Is energetically advantageous because…….	Electron 1 can be at center A and electron 2 at center B or vice versa which gives a higher degree of variational freedom. This is normally described as the VB approach of a covalent bond. Sometimes ionic resonance structures are also taken into account.	Bonding MOs are lower in energy than AOs (the occupancy of the bonding MOs ought to be higher than the occupancy of the antibonding MOs)
Orbital overlap picture	AOs remain unchanged	AOs that overlap are used to form delocalized non-overlapping MOs with σ or π symmetry (σ = rotational symmetry with respect to internuclear axis, π = mirror plane in internuclear axis)
orthogonal ?	AOs are not orthogonal, they overlap	MOs are orthogonal, they do not overlap
Localised orbitals ?	strictly localized at atoms	de-localized, canonical orbitals
Do orbitals change going from atoms to molecules ?	No, but they can (AOs may, however, change “size” = promotion of orbitals)	Yes
Bonding, antibonding (sometimes non-bonding) orbitals formed ?	No	Yes

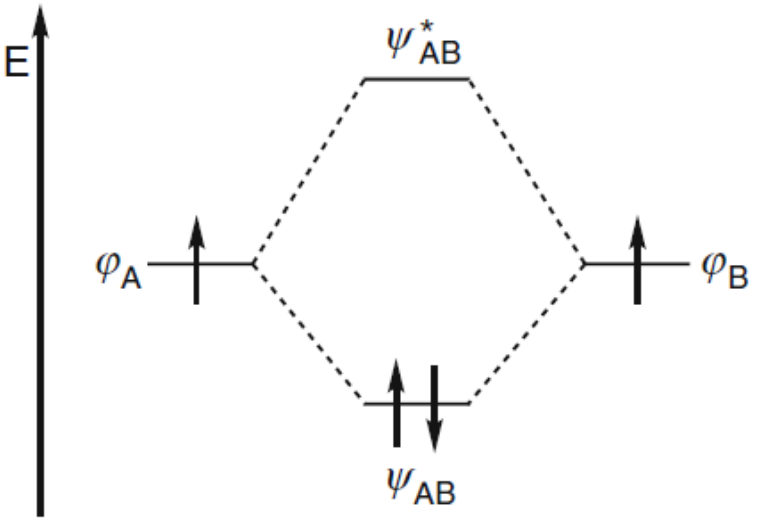
Octet rule obeyed ?	Yes, if only s and p orbitals are used for bonding in main-group molecules	Yes, if only s and p orbitals are used for construction of MOs and d orbitals for polarization only in main-group molecules
"Bonds" (= spin pairing) between non-neighbouring atoms possible ?	Yes, long bonds or Dewar bonds	No
Ionic resonance structures	Yes, if pure AOs are used	No
What happens when the electrons are not fully localized in bonds (e.g. C_6H_6, $B_3N_3H_6$, NO_3^- etc.)	Resonance between various mesomeric resonance structures, resonance stabilization energy	No, MOs are delocalized over the entire molecule, delocalozation energy, (equivalence to resonance would be configuration interaction – CI – MO theory)
Fundamental difference between theories	Resulting wavefunction is the product of singly (or doubly) occupied AOs	Resulting wavefunction is the product of singly (or doubly) occupied MOs

$$\underline{S}_z\alpha = \frac{1}{2}\hbar\alpha \qquad \underline{S}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\,\alpha$$

$$\underline{S}_z\beta = -\frac{1}{2}\hbar\beta \qquad \underline{S}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\,\beta$$

$$m_s = \pm\frac{1}{2}\,;\ \alpha,\beta;\ \uparrow,\downarrow$$

Abb. 19.1 Qualitatives MO-Schema für das H_2-Molekül. (Beachte: Das antibindende MO ist im Vergleich zu den AOs immer etwas mehr destabilisiert als das bindende MO energetisch stabilisiert ist.)



(φ_A und φ_B) können wir die folgenden beiden Linearkombinationen anschreiben (aus n AOs werden immer n MOs):

$$\Psi_{AB} = \varphi_A + \varphi_B \quad \text{und} \quad \Psi_{AB}{}^* = \varphi_A - \varphi_B$$

Abb. 19.2 a Verteilung der Elektronendichte in den isolierten H-Atomen und im H_2-Molekül, b Beiträge der kinetischen (T) und potentiellen Energie (V) zur Bindungsbildung im H_2-Molekül. (Abbildung gezeichnet nach Rev. of Modern Phys. 1962, 34, 326.)

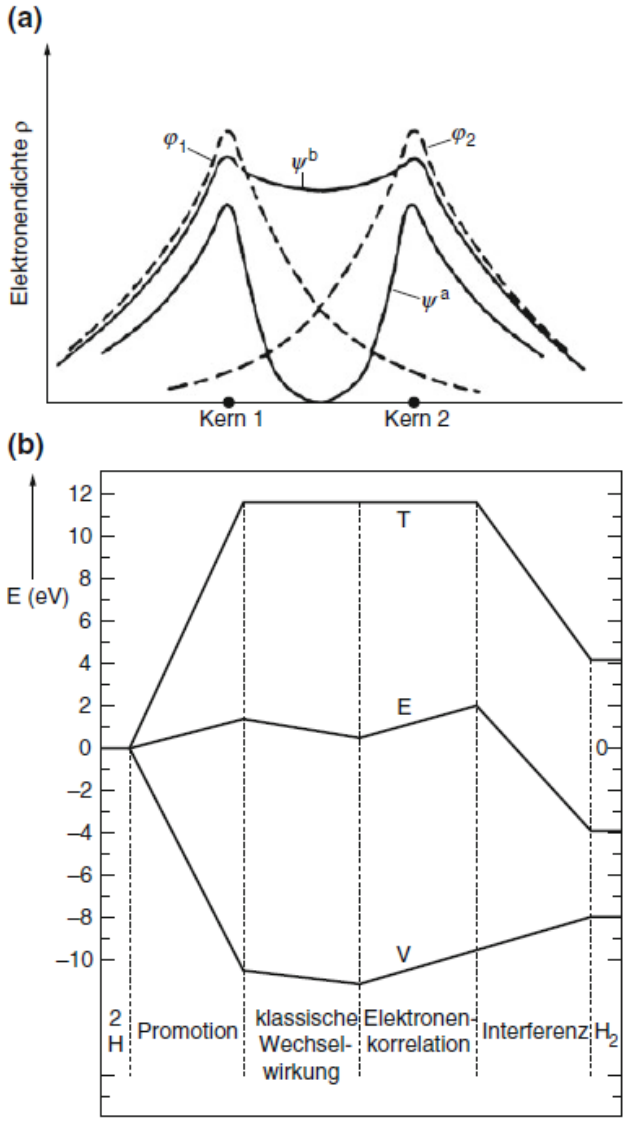


Abb. 19.3 Mögliche Ψ_{AB}- und Ψ_{AB}^*-Orbitalbesetzungen

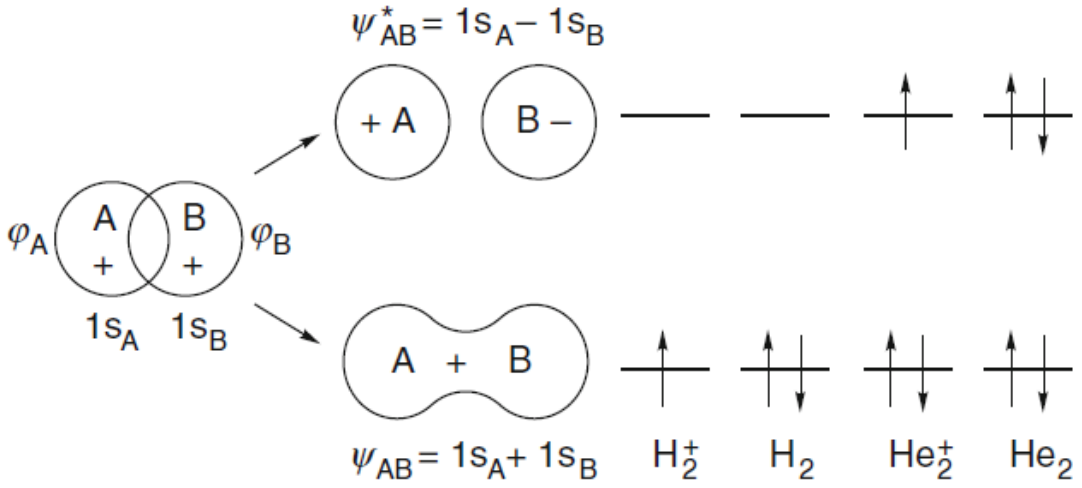
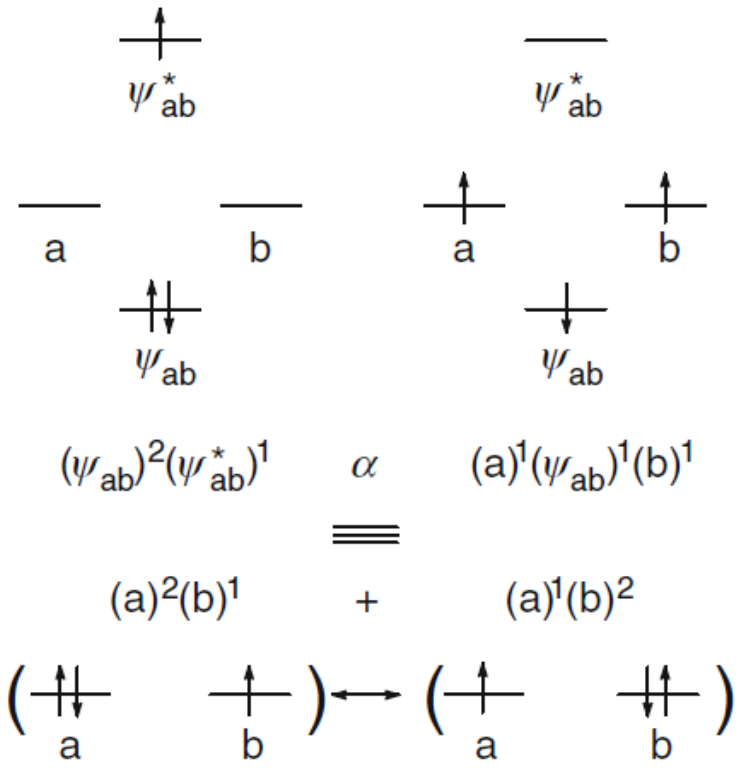


Abb. 19.4 Die Pauling'sche Dreielektronenbindung



$$\Psi^{MO} = [\Psi_{AB}(1)\,\Psi_{AB}{}^{*}(2)] - [\Psi_{AB}{}^{*}(1)\,\Psi_{AB}(2)]$$
$$= -2\{[\varphi_A(1)\,\varphi_B(2)] - [\varphi_B(1)\,\varphi_A(2)]\}$$

Abb. 19.8 Unterschied zwischen Hybridisierung und Polarisierung

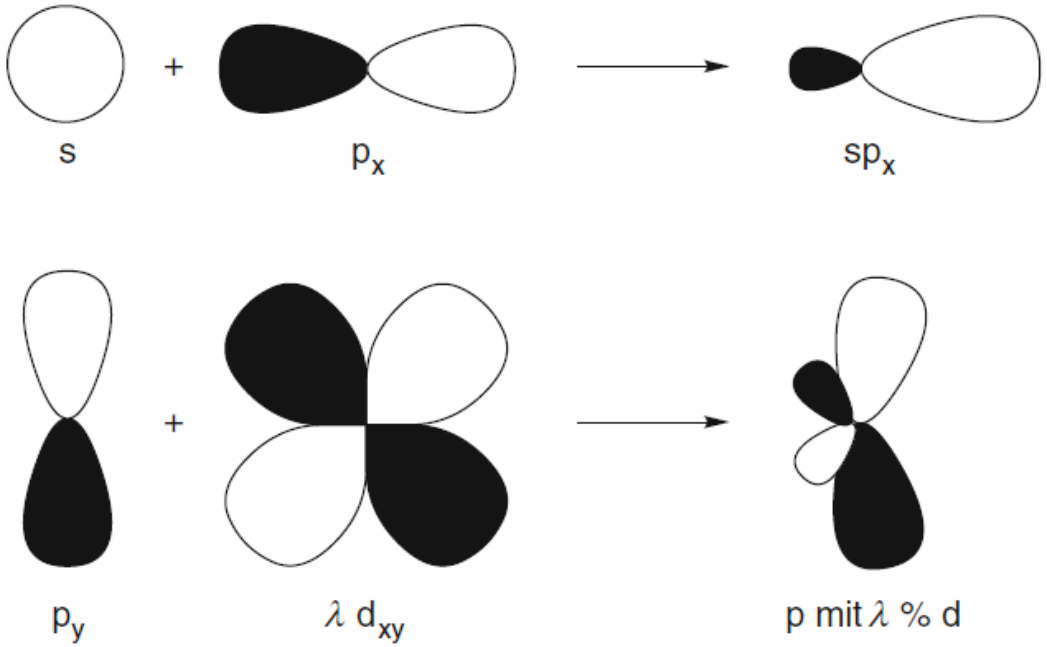
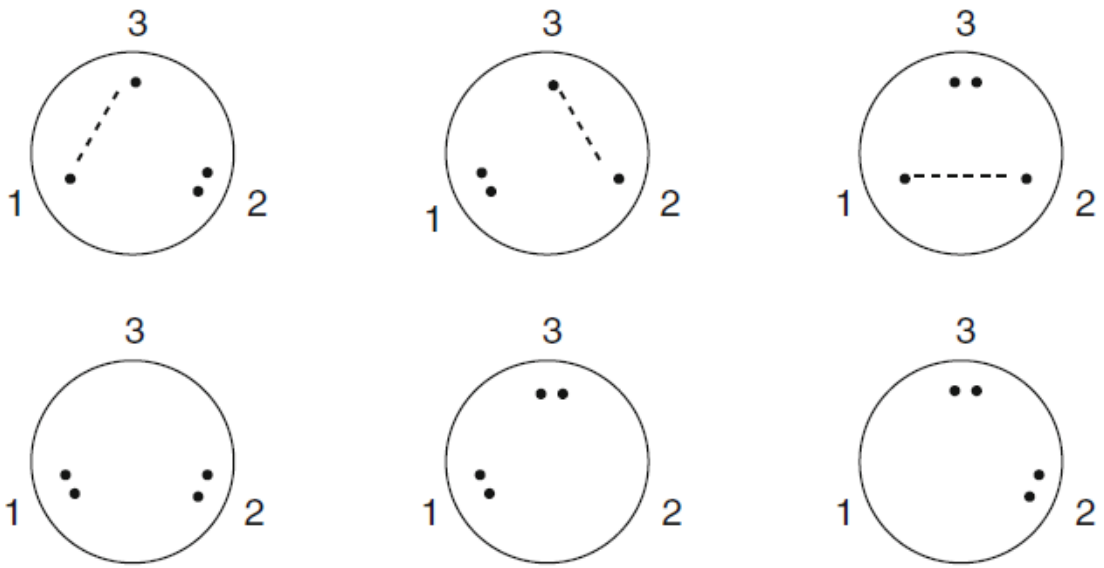


Abb. 19.9 Rumer-Diagramm für die π-Elektronenverteilung im O_3-Molekül



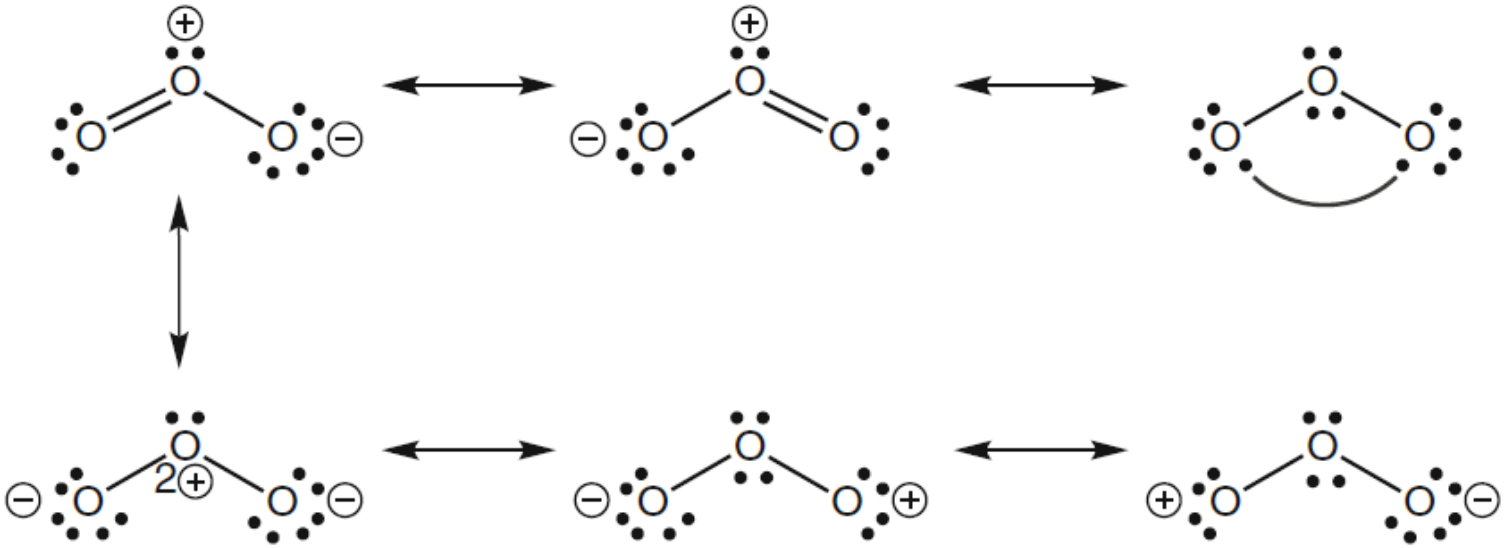


Abb. 19.10 Lewis-π-Resonanzstrukturen für das O_3-Molekül

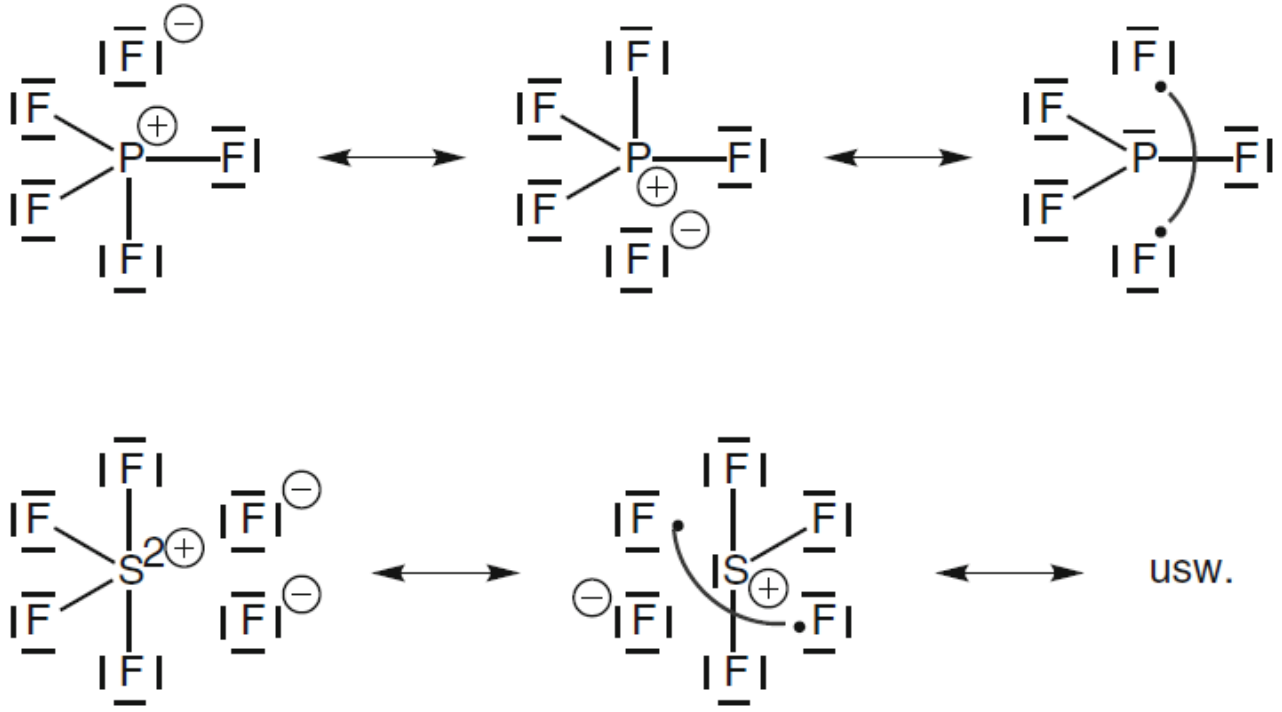


Abb. 19.11 Bindungsverhältnisse in den Molekülen PF_5 und SF_6 (Der besseren Übersichtlichkeit halber, sind die freien Elektronenpaare der an den „normalen" Zweizentren-Zweielektronen-Bindungen beteiligten F-Atomen nicht eingezeichnet, sondern nur für die an den Dreizentren-Vierelektronen beteiligten F-Atome.)

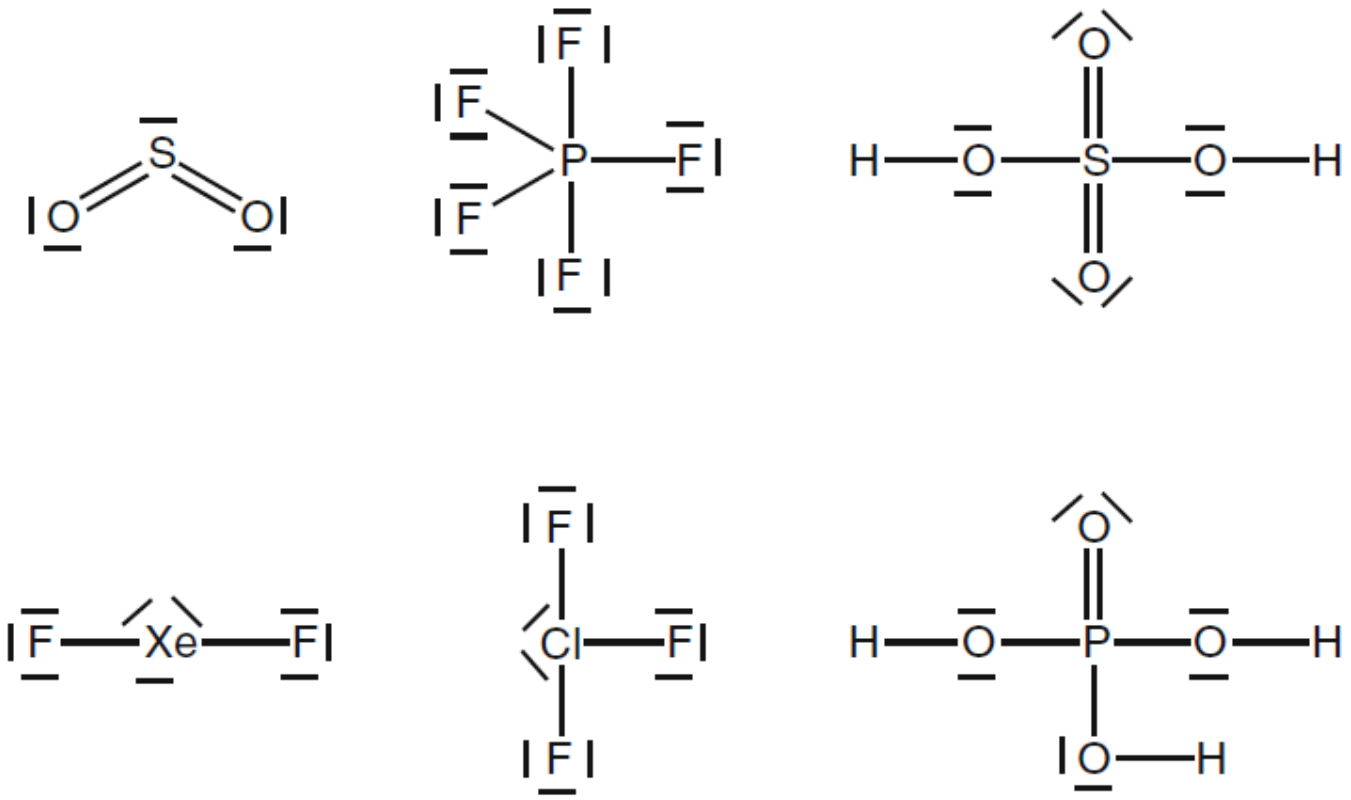
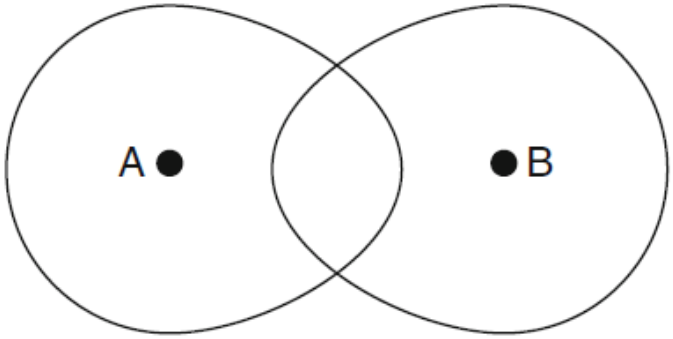


Abb. 19.12 Beispiele für hypervalente Lewis-Strukturen geringer physikalischer Relevanz

Abb. 19.13 Die Beschreibung des H_2-Moleküls mit Coulsen-Fischer-Orbitalen



1. Hybrid Atomic Orbitals (HOs) for Methane, CH_4?

In order to construct the MO scheme of methane, CH_4, we could either start from AOs and derive two sets of filled (with 8 electrons) orbitals, one low lying σ_s^b (a_1) and three degenerate orbitals also with σ symmetry (σ_x^b, σ_y^b, σ_z^b) (t_2) (**Fig. 1**).

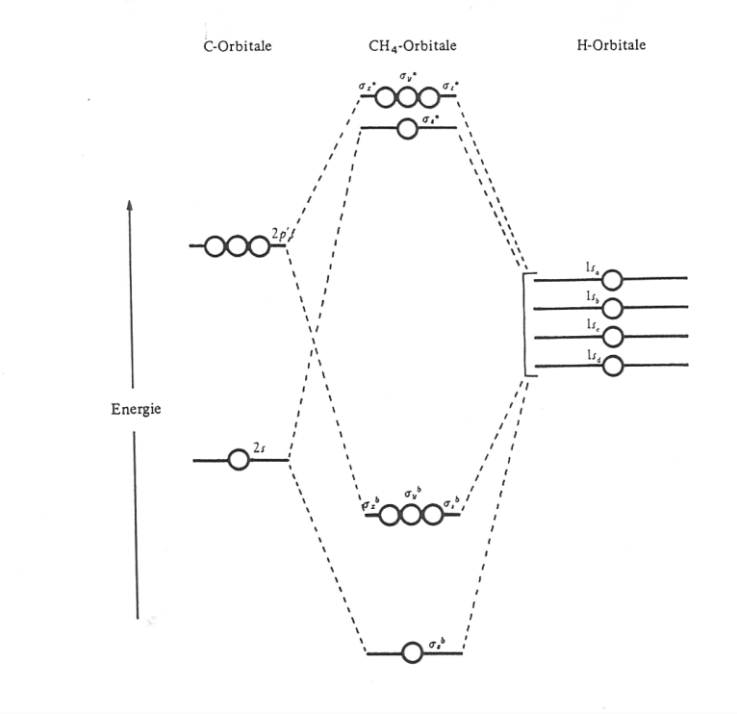


Fig. 1. MO scheme of CH_4 using only AOs to construct the MOs.

Alternatively, we could first generate four degenerate hybrid orbitals and construct the MO scheme as shown in **Fig. 2**.

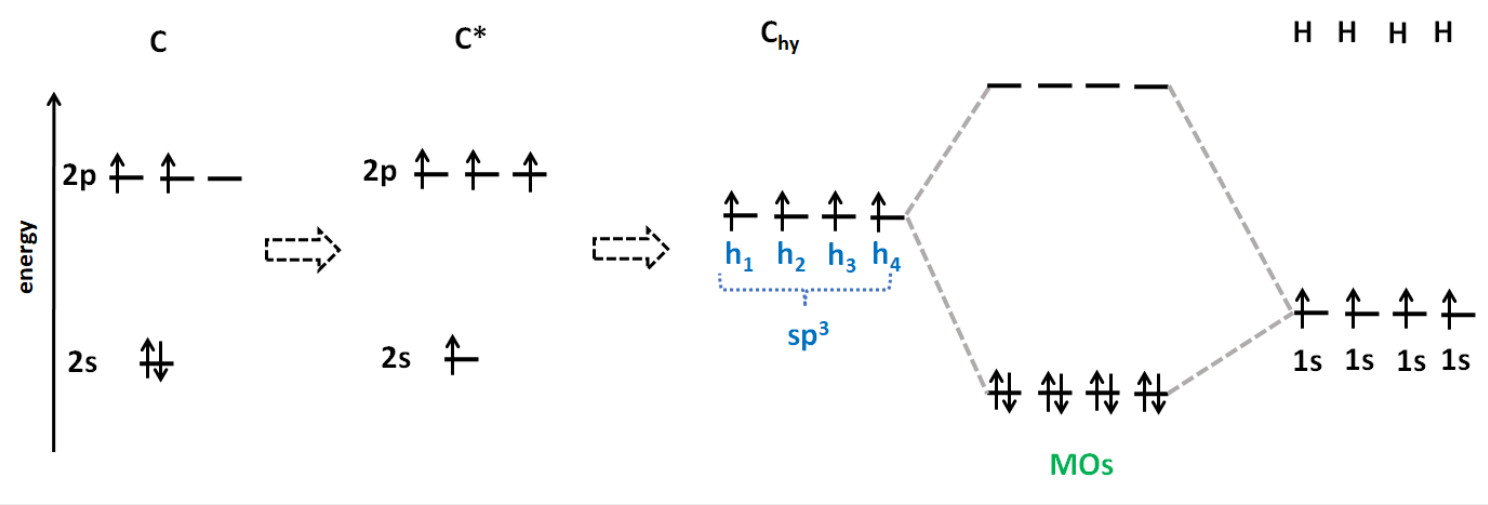


Fig. 2. MO scheme of CH_4 using hybrid orbitals (HOs (h_1, h_2, h_3, h_4)) to construct the MOs.

The hybrid atomic orbital model is often criticized with the main argument being that HOs do not appropriately describe molecular bonding. A classic piece of evidence which is used to criticize the hybridization approach and which is used to support the statement that HOs don't describe properly molecular bonding is the photoelectron spectrum of methane (**Fig. 3**). The commonly-used argument is that two peaks are observed in the PES of methane which correspond to different energies. Therefore, it is argued that the MO scheme generated using HOs must be wrong, since all four MOs of methane have the same energy and would therefore not result in the observation of two peaks in the PES. However, a detailed examination of the photoelectron spectrum performed recently reveals that this argument is incorrect and in fact, the use of HOs does in fact result in the MO scheme which is consistent with the PES spectrum.

A closer look at the PES of CH_4. Obviously, the four C-H bonds of methane are equivalent. Whereas the MOs have two distinct symmetries and energies (**Fig. 1**) (one nondegenerate a_1 and three triply degenerate t_2), all of the HOs (**Fig. 2**) have the same shape and energy, only differing in their spatial orientation. So why does excitation of the valence electrons of CH_4 results in two distinct bands (in the intensity ratio of 1:3) in the PES?

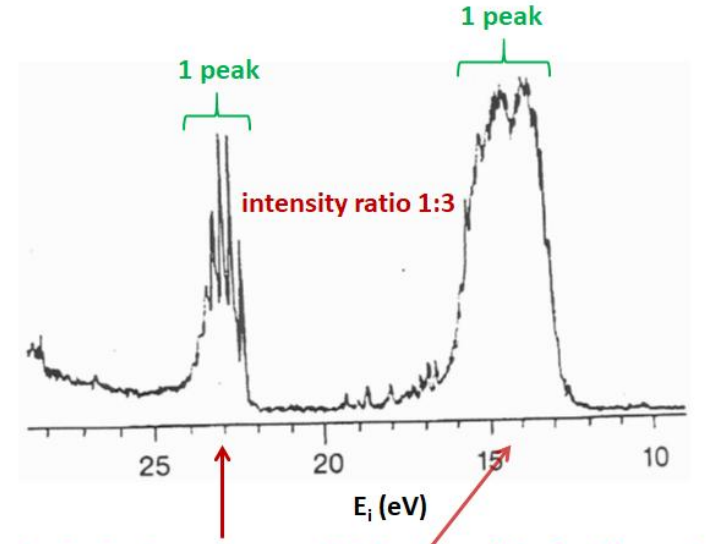


Fig. 3. The Photo Electron Spectrum (PES) of CH_4. The signal 13 – 16 eV (intensity 3) corresponds to a loss of an electron from the t_{2g} level (HOMO), while the signal at 22 – 24 eV (intensity 1) corresponds to a loss of an electron from an a_1 level. The fine structure observed for the signal at 22 – 24 eV can be ignored in this discussion.

In fact, peaks in the PES correspond to the energy differences between the ground state of the neutral molecule and the ground and excited states of the ionized molecule. Thus, we need to consider the orbital structure of both, the neutral and ionized molecules to describe the PES.

In the hybridization model, we promote one 2s electron from the ground configuration at the C atom ($2s^2$, $2p^2$) to obtain the configuration $2s^1$, $2p^3$. Hybridization of this configuration yields the h_1^1, h_2^1, h_3^1, h_4^1 configuration (**Fig. 2**) in which h_x represent the sp^3 hybrid orbitals. The initial state has the configuration in which each of the four sp^3 HOs contains 1 electron. This initial state was derived from the ground state configuration according to **Fig. 2**, by hybridization of the $2s^1$ $2p^3$ (C*). In the process of photoionization during which 1 electron is removed, if only the C orbitals are considered, we start with four, singly-occupied sp^3 HOs and due to photoionization end up with either:

(i) hybridization of configuration s^1p^2 or

(ii) hybridization of configuration s^0p^3

This would mean that there would be two peaks observed in the PES spectrum in which the one with lower energy corresponds to ionization having occurred from the C 2p orbital (i) or in which ionization occurred from the C 2s orbital which requires more energy (ii). Since there is only 1 electron in the C 2s orbital but 3 electrons in the C 2p orbitals, then the ratio observed is 1:3. On ionization of CH_4, two different CH_4^+ cations would result: one with essentially sp^2 hybridization (close to planar structure) and another with essentially p^3 hybridization (essentially pyramidal). Therefore, it is incorrect to state that the hybridization approach can be proven to be in error based on the PES of CH_4.

C. R. Landis* and F. Weinhold

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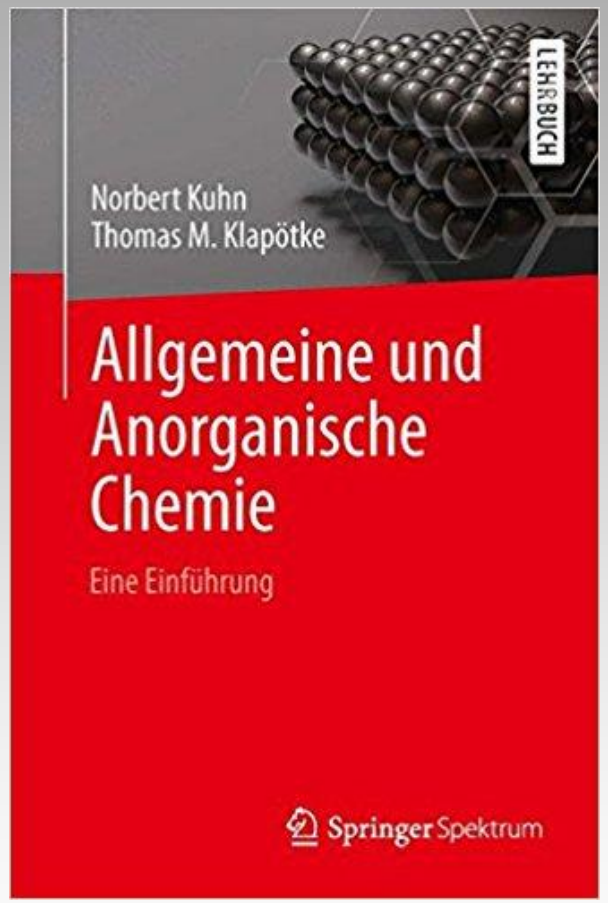

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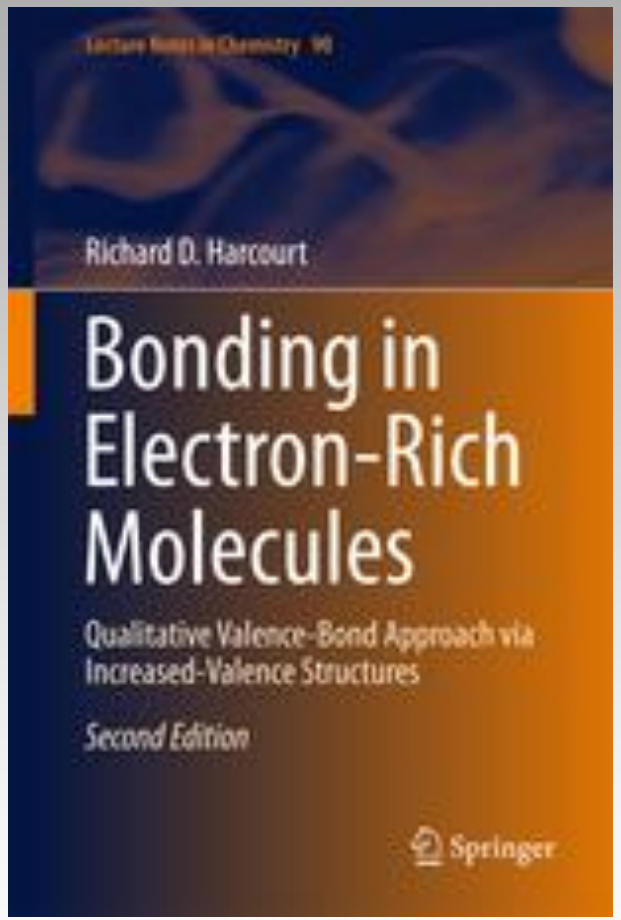

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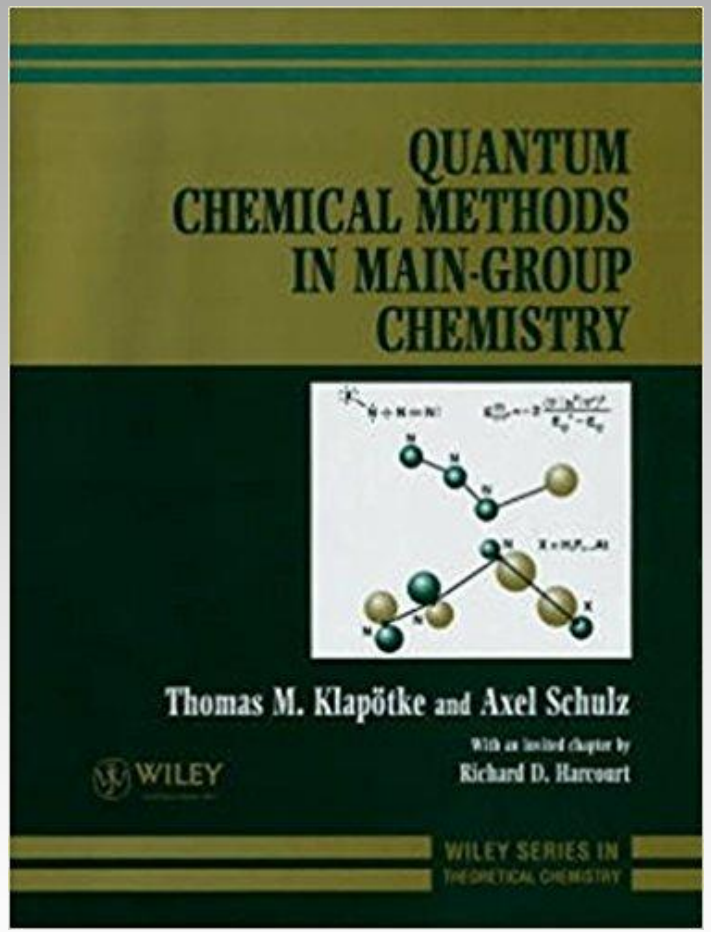
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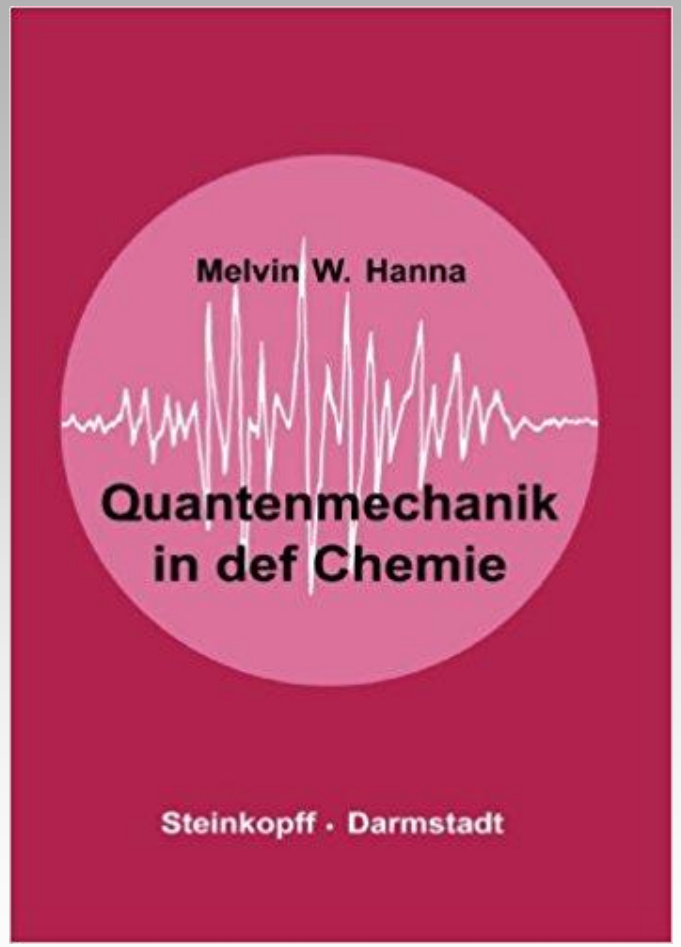
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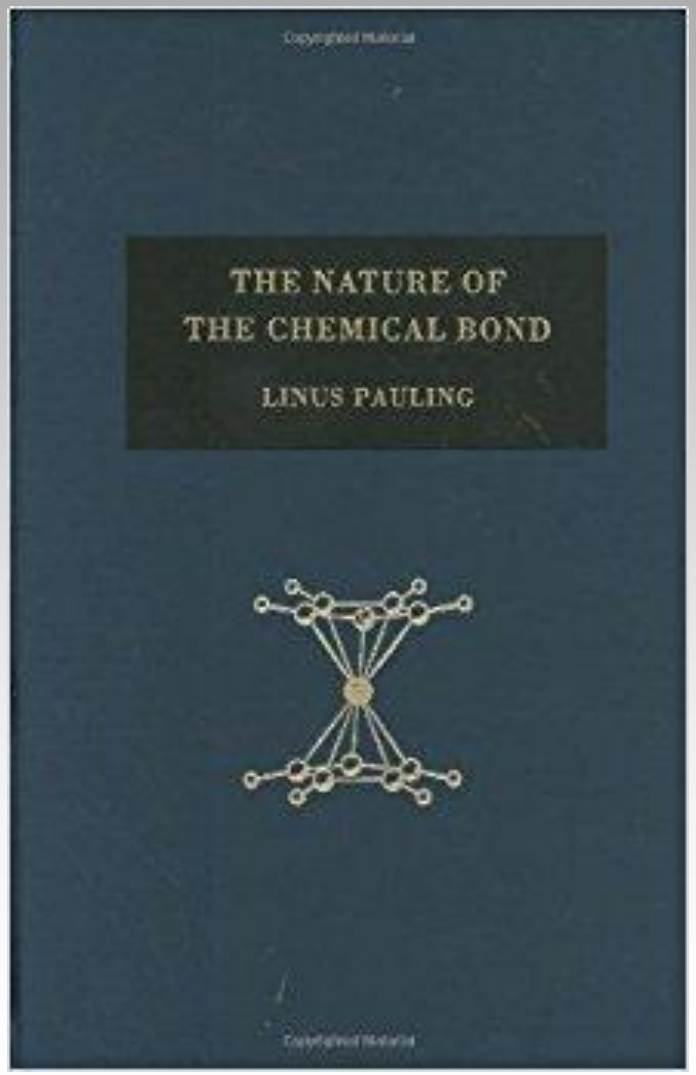
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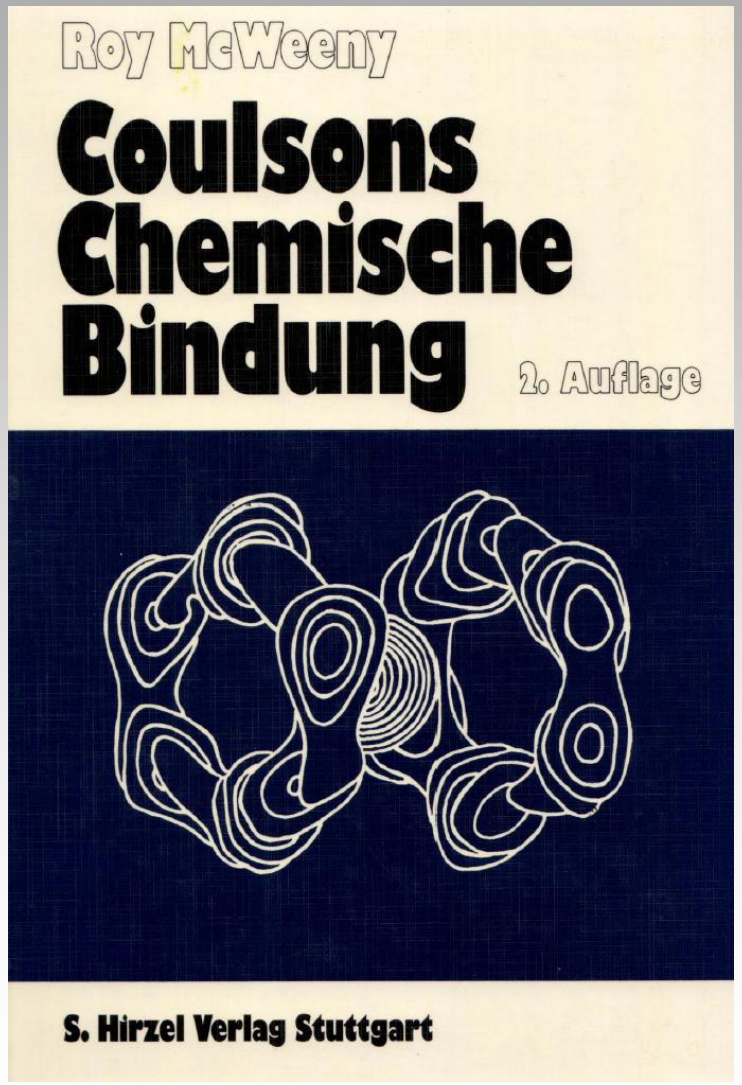
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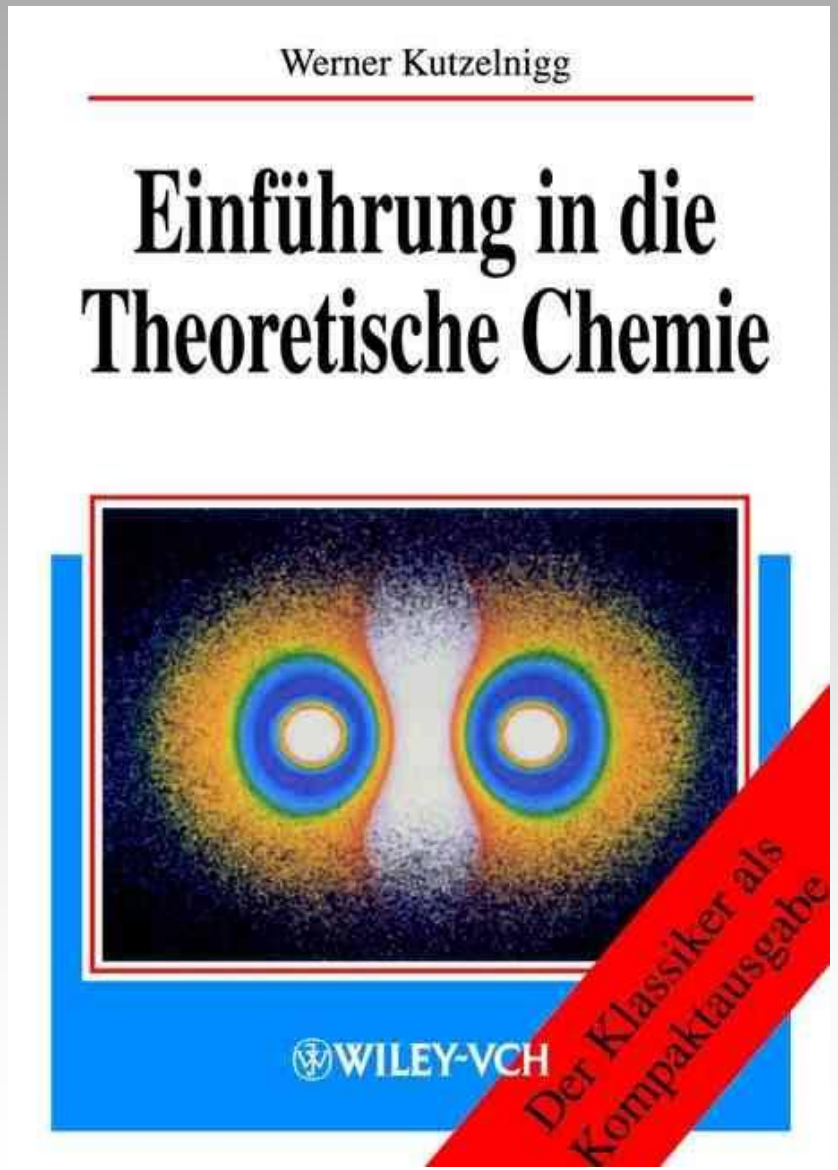
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