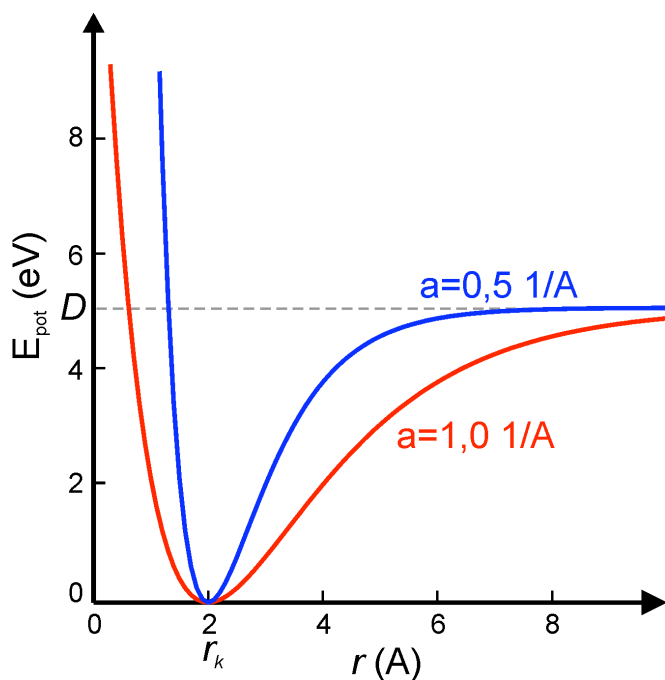


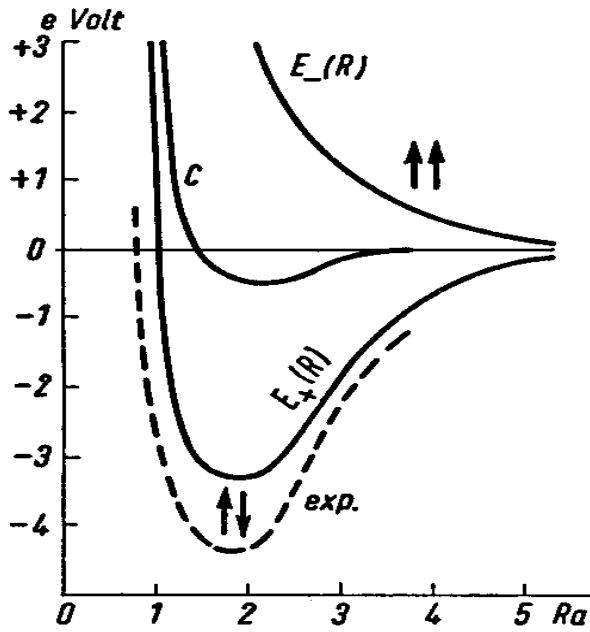
Kapitel 1

- 1.1. Das H₂ - Molekül: "Valence Bond" - Methode (Lit. 3, S. 52-61)
Einschub: Spinwellenfunktion
 - 1.2. Molekülorbitalansatz für H₂⁺ und H₂ (Lit. 3, S. 52-61)
Vergleich der Wellenfunktionen für H₂: MO- und VB-Ansatz
 - 1.3. MO-Beschreibung zweiatomiger Moleküle: Variationsansatz für homonukleare und heteronukleare Moleküle
 - 1.4. MO-Schema und Aufbauprinzip: Bindungsordnung, Bindungslänge, und Bindungsenergie
 - 1.5. Photoelektronenspektren: Beispiel N₂
 - 1.6. MO-Schema und Photoelektronenspektren der HX-(X-Halogen) Verbindungen (Hinweis auf Spin-Bahn-Kopplung)
- Computerübung: MO-Schemata aus Hartree-Fock-Berechnungen für zweiatomige Moleküle*

Morse-Kurve

$$E(r) = D(1 - e^{-a(r-r_k)})^2$$





$$E_{\pm} = 2E_H + \frac{C \pm A}{1 \pm S}$$

Bild 34.
Wechselwirkung zweier H-Atome

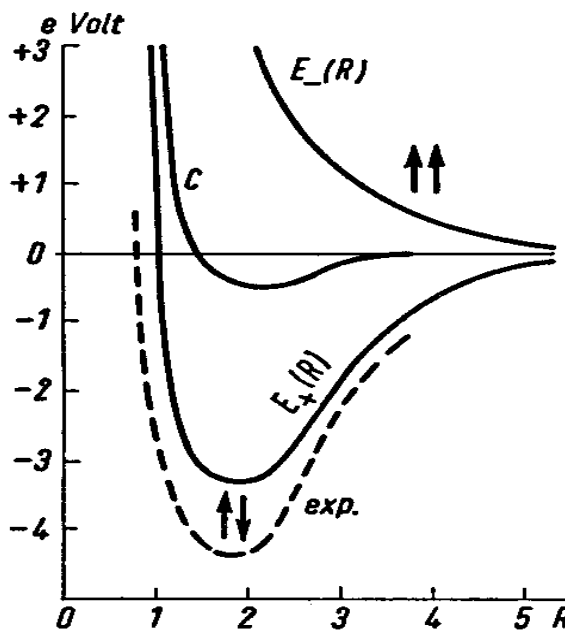
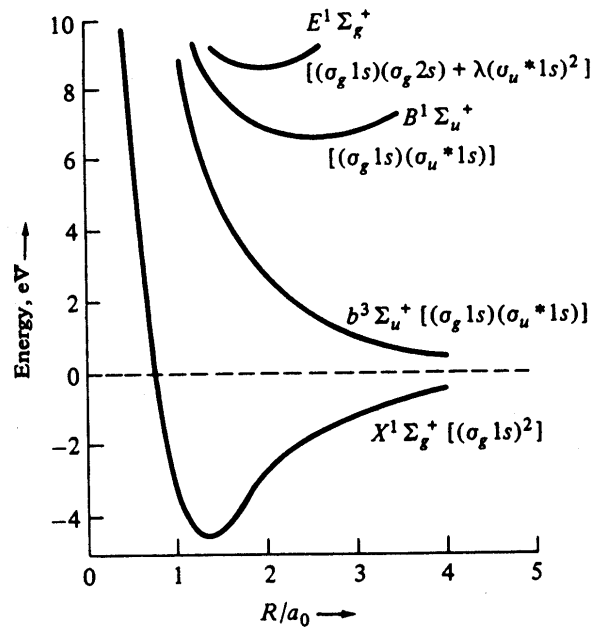
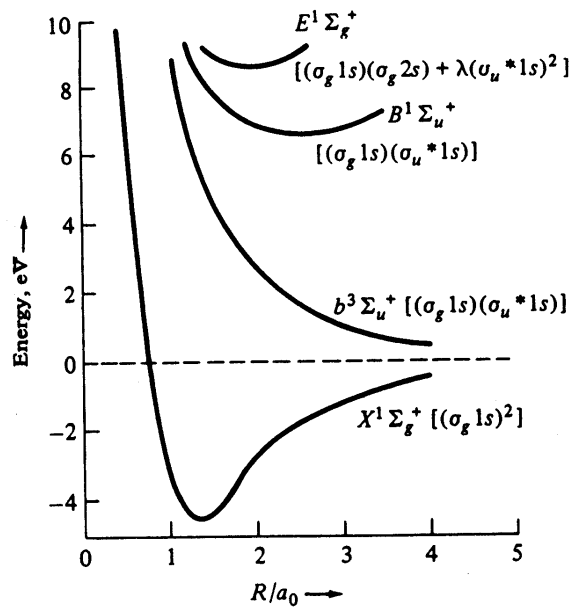
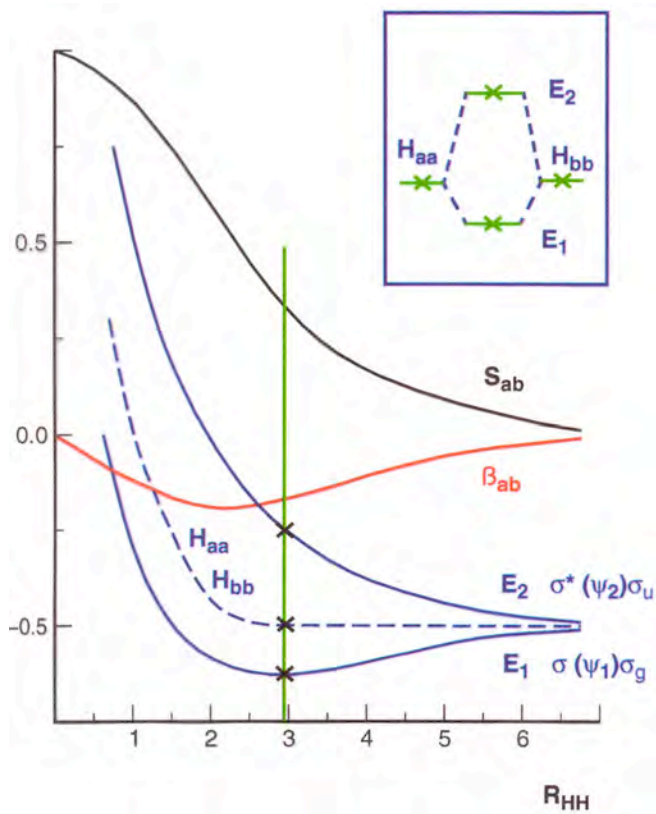


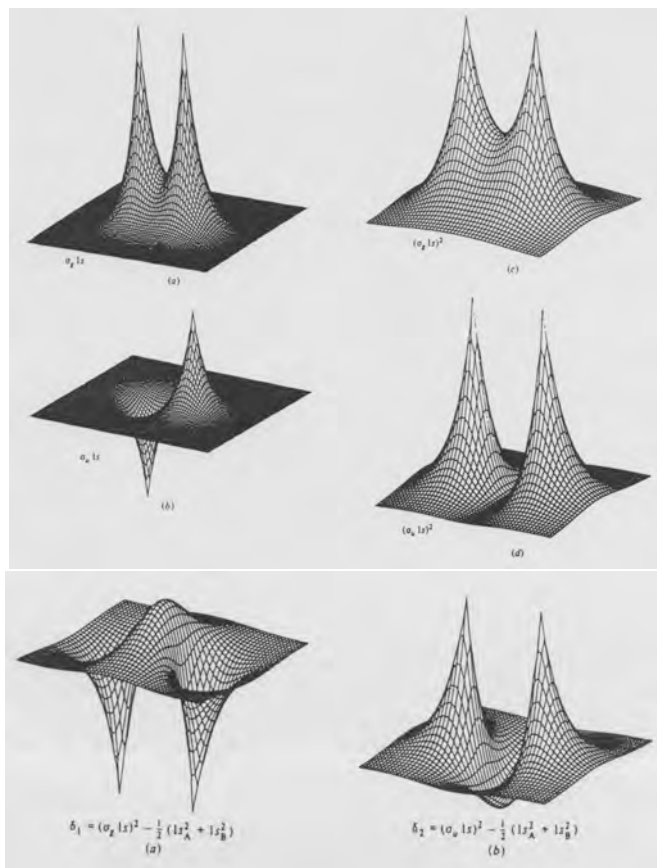
Bild 34.
Wechselwirkung zweier H-Atome

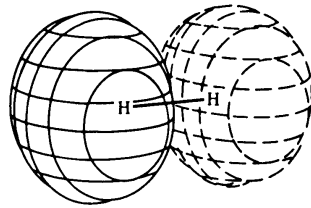


W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. 32:227 (1960).

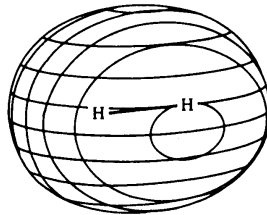


W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. 32:227 (1960).



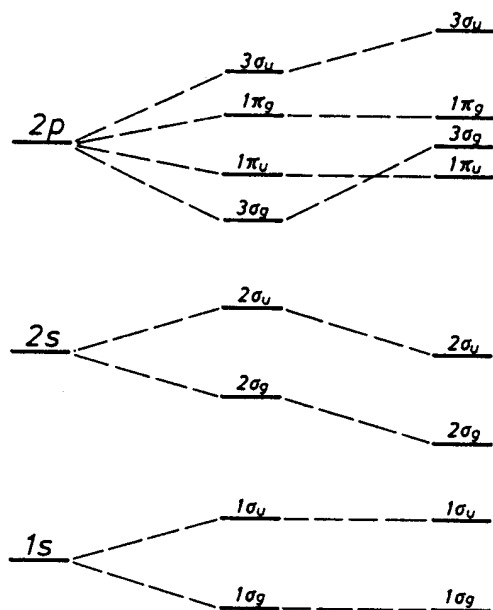


$$\epsilon_{1\sigma_u} = 0.2656 E_h$$



$$\epsilon_{1\sigma_g} = -0.5944 E_h$$

MO Energieniveaus



Tab. 4. Konfigurationen, Terme, Bindungsgrade (p), Gleichgewichtsabstände (r_e) und Bindungsenergien (D_e , = experimentell, sowie in Hartree-Fock-Näherung) homonuclearer zweiatomiger Moleküle im Grundzustand.

Konfiguration	Term	N_{bind}	N_{ant}	p	$r_e(\text{\AA})$	$D_e(\text{ev})$ exp.	$D_e(\text{eV})$ Hartree-Fock
$\text{H}_2^+ 1\sigma_g$	$2\Sigma_g^+$	1	—	0.5	1.06	2.7	
$\text{H}_2(1\sigma_g)^2$	$1\Sigma_g^+$	2	—	1	0.74	4.7	
$\text{He}_2^+(1\sigma_g)^2 1\sigma_u$	$2\Sigma_u^+$	2	1	0.5	1.08	2.5	
$\text{He}_2(1\sigma_g)^2(1\sigma_u)^2$	$(1\Sigma_g^+)$	2	2	0	—	—	
$\text{Li}_2^+[\text{He}_2]2\sigma_g$	$2\Sigma_g^+$	3	2	0.5	3.14	1.3	
$\text{Li}_2[\text{He}_2](2\sigma_g)^2$	$1\Sigma_g^+$	4	2	1	2.67	1.05	0.17
$\text{Be}_2[\text{He}_2](2\sigma_g)^2(2\sigma_u)^2$	$(1\Sigma_g^+)$	4	4	0	—	—	—
$\text{B}_2[\text{Be}_2](1\pi_u)^2$	$3\Sigma_g^-$	6	4	1	1.59	3 ± 0.5	0.89
$\text{C}_2[\text{Be}_2](1\pi_u)^4$	$1\Sigma_g^+$	8	4	2	1.24	6.36	0.79
$\text{N}_2^+[\text{Be}_2](1\pi_u)^4 3\sigma_g$	$2\Sigma_g^+$	9	4	2.5	1.12	8.86	3.13
$\text{N}_2[\text{Be}_2](1\pi_u)^4(3\sigma_g)^2$	$1\Sigma_g^+$	10	4	3	1.10	9.90	5.18
$\text{O}_2^+[\text{Be}_2](1\pi_u)^4(3\sigma_g)^2 1\pi_g$	$4\Pi_g$	10	5	2.5	1.12	6.55	3
$\text{O}_2[\text{Be}_2](1\pi_u)^4(3\sigma_g)^2(1\pi_g)^2$	$3\Sigma_g^-$	10	6	2	1.21	5.21	+1.28
$\text{F}_2[\text{Be}_2](2\pi_u)^4(3\sigma_g)^2(1\pi_g)^4$	$1\Sigma_g^+$	10	8	1	1.44	1.68	-1.37
$\text{Ne}_2[\text{Be}_2](1\pi_u)^4(3\sigma_g)^2(1\pi_g)^4(3\sigma_u)$	$(1\Sigma_g^+)$	10	10	0	—	—	—

W. Kutzelnigg, Einführung in die Theoretische Chemie, Bd. 2, Chem. Bindg, Verlag Chemie 1978

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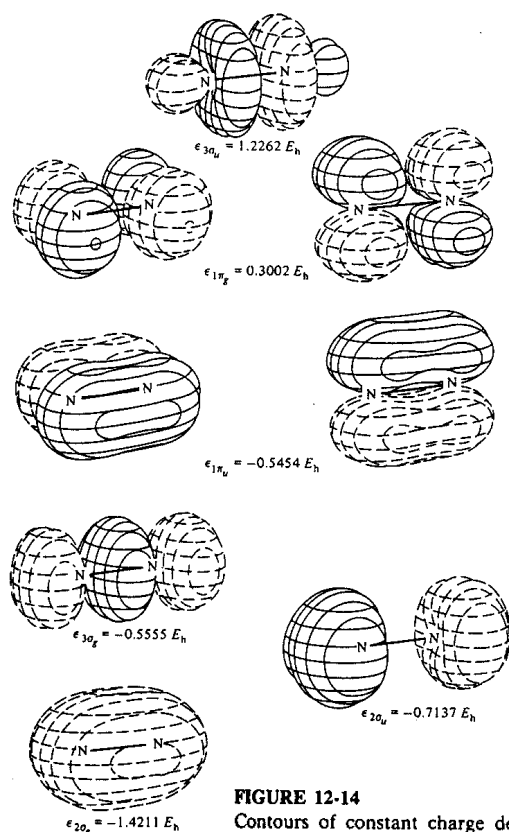


FIGURE 12-14

Contours of constant charge density for the MOs of dinitrogen based on calculations by B. J. Ransil. (Reprinted, by permission, from W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973.)

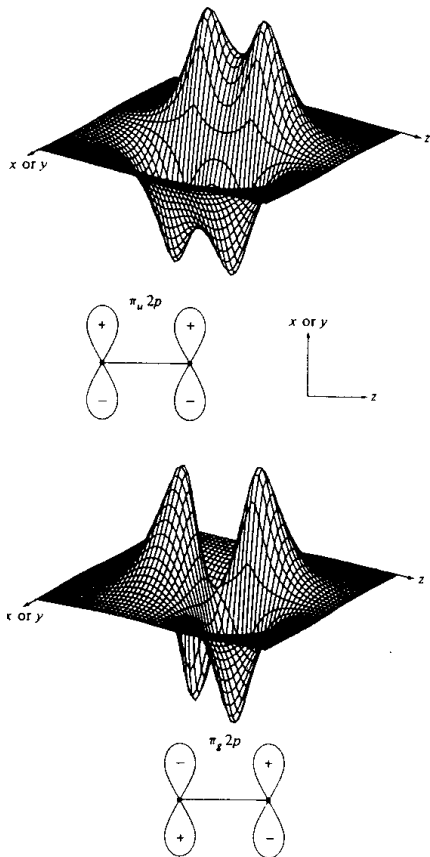


FIGURE 12-15

The $\pi_u 2p$ (bonding) and $\pi_g 2p$ (antibonding) symmetry-adapted functions. The squares (probability densities) associated with these are not shown, but both would look like four peaks above the nuclear planes indicated. However, $(\pi_u 2p)^2$ would exhibit internuclear buildup, and $(\pi_g 2p)^2$ would exhibit the opposite. The former is an example of a pi bond; such a bond has zero probability along the internuclear axis itself but has a non-zero density about this axis. Since a homonuclear diatomic molecule has cylindrical symmetry about the bond axis, the probability density $(\pi_u 2p)^2$ also has this cylindrical symmetry. The diagrams below the surface plots indicate the orientation of the $2p$ AOs which overlap to form the corresponding surface plots.

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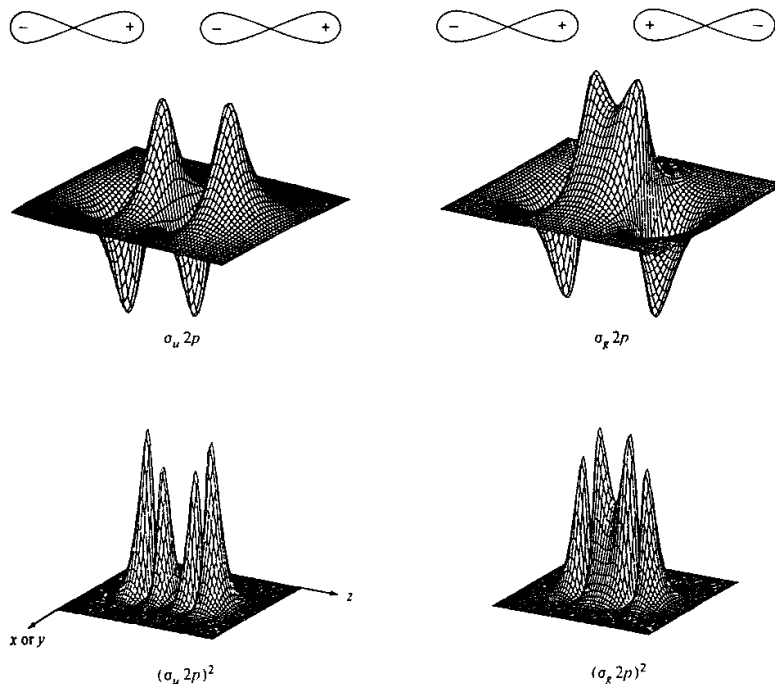


FIGURE 12-16

Surface plots of $\sigma_g 2p$ and $\sigma_u 2p$ symmetry-adapted functions and their squares for a diatomic molecule. The small diagrams at the top indicate how the $2p$ AOs making up these functions are overlapped. Note that the $\sigma_u 2p$ function shows an increase of probability density outside the internuclear region and a decrease of probability density (antibonding) inside the internuclear region whereas the $\sigma_g 2p$ function shows the opposite (bonding) effect.

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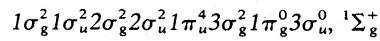


Table 3.3. Bands Observed in the He II PE Spectrum of N₂^a

Ionization Energy (eV)	Relative Intensity of Band	Ionized Orbital or Ionization Process
15.58	1	3σ _g
16.98	1.53	1π _u
18.75	0.40	2σ _u
25.3	0.03	CI ^b
28.8	0.10	CI ^b
32.8	0.02	CI ^b
36.6	0.07	2σ _g

^a From Ref. 22.

^b Configuration interaction processes.

Table 3.4. Ionic States Produced in Photoionization to Various Electronic Configurations of N₂⁺.

Number of Electrons in MOs						Final States
2σ _g	2σ _u	1π _u	3σ _g	1π _g	3σ _u	
2	2	4	1	0	0	2Σ _g ⁺
2	2	3	2	0	0	2Π _u ⁺
2	1	4	2	0	0	2Σ _u ⁺
1	2	4	2	0	0	2Σ _g ⁺
2	2	4	0	0	1	2Σ _u ⁺
2	2	3	1	1	0	2 ² Σ _u ⁺ , 4Σ _u ⁺ , 2 ² Σ _u ⁻ , 4Σ _u ⁻ , 2 ² Δ _u , 4Δ _u
2	1	3	2	1	0	2 ² Σ _g ⁺ , 4Σ _g ⁺ , 2 ² Σ _g ⁻ , 4Σ _g ⁻ , 2 ² Δ _g , 4Δ _g
2	2	4	0	1	0	2Π _g
2	2	2	2	1	0	4 ² Π _g , 2 ⁴ Π _g , 2 ² Φ _g , 4Φ _g

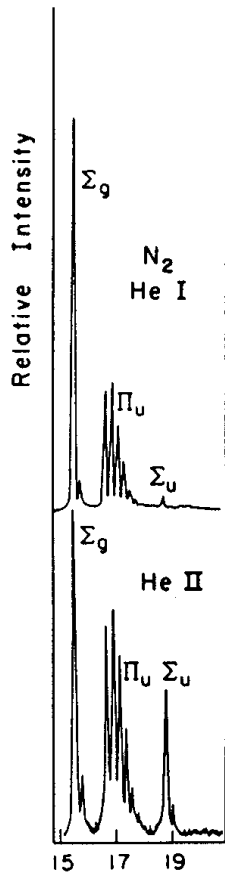


Fig. 7.1. He I and He II photoelectron spectra of N_2

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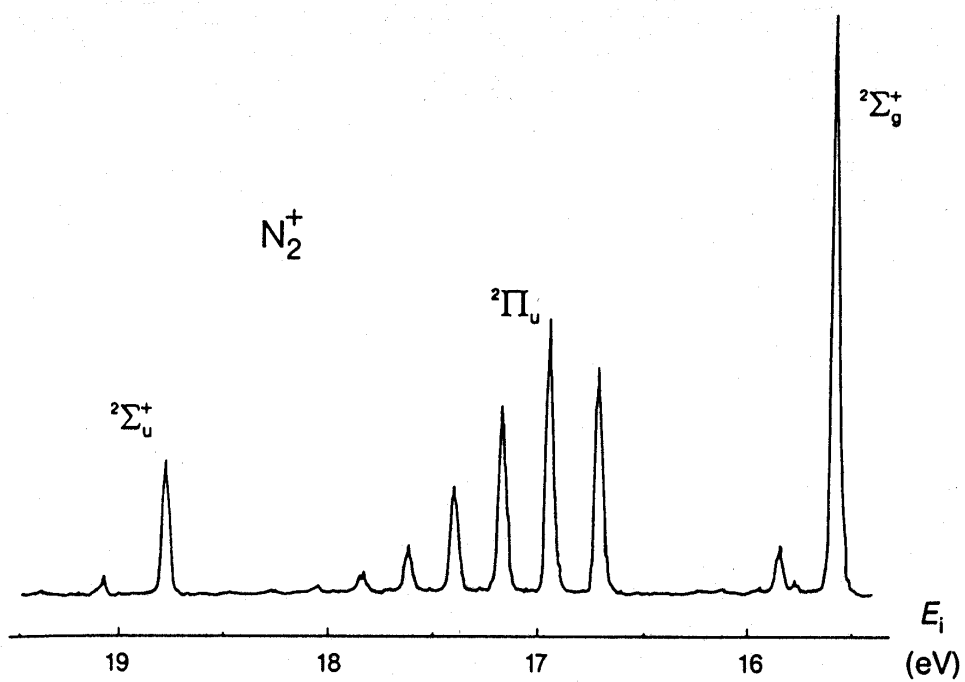
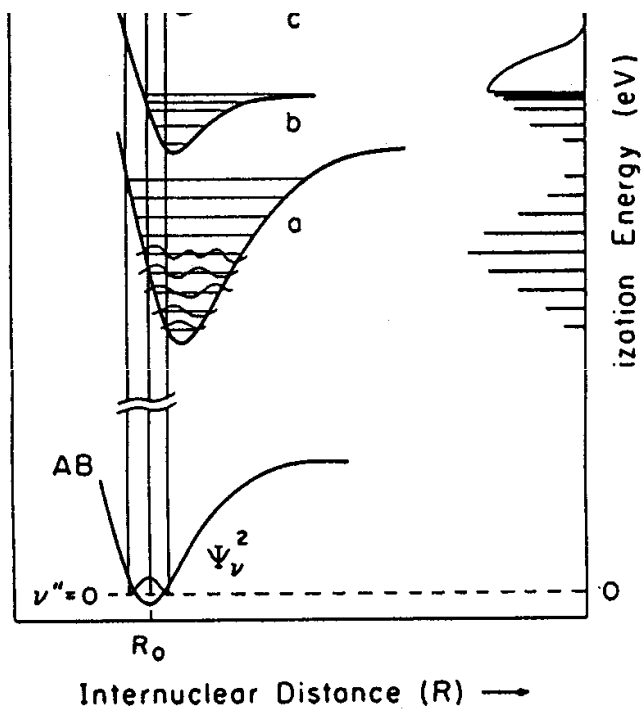


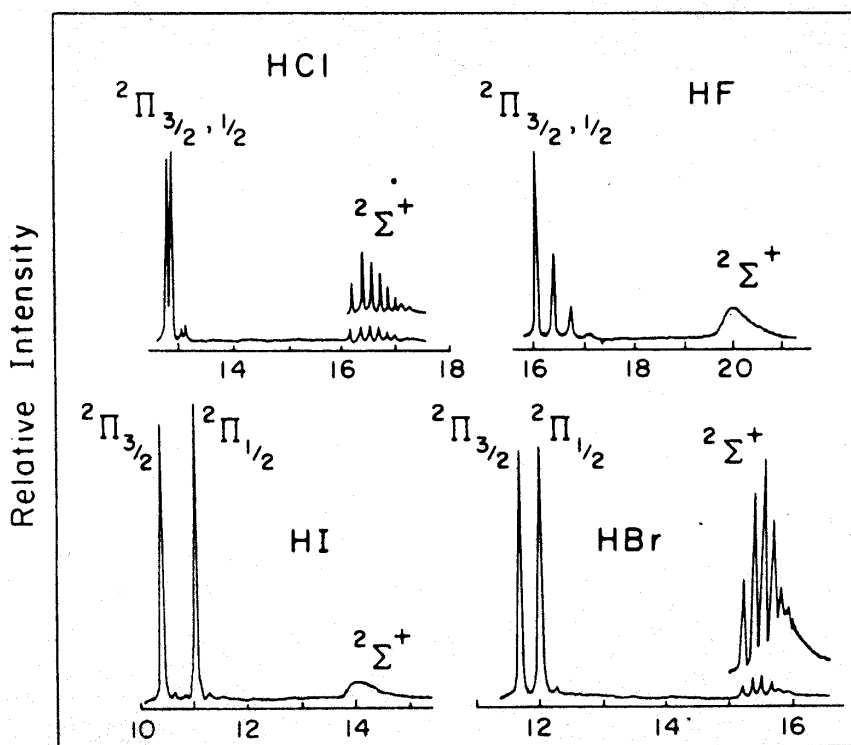
Abb. 5.28 Photoelektronenspektrum von N_2^+ im Bereich der Valenzelektronen. Die drei Liniengruppen entsprechen der Abspaltung eines Elektrons aus den drei oberste besetzten Molekülorbitalen.

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Herkunft der Schwingungsstruktur von PES



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