Übungen zur Vorlesung Aliphaten und Cycloaliphaten

-MO-Theorie-

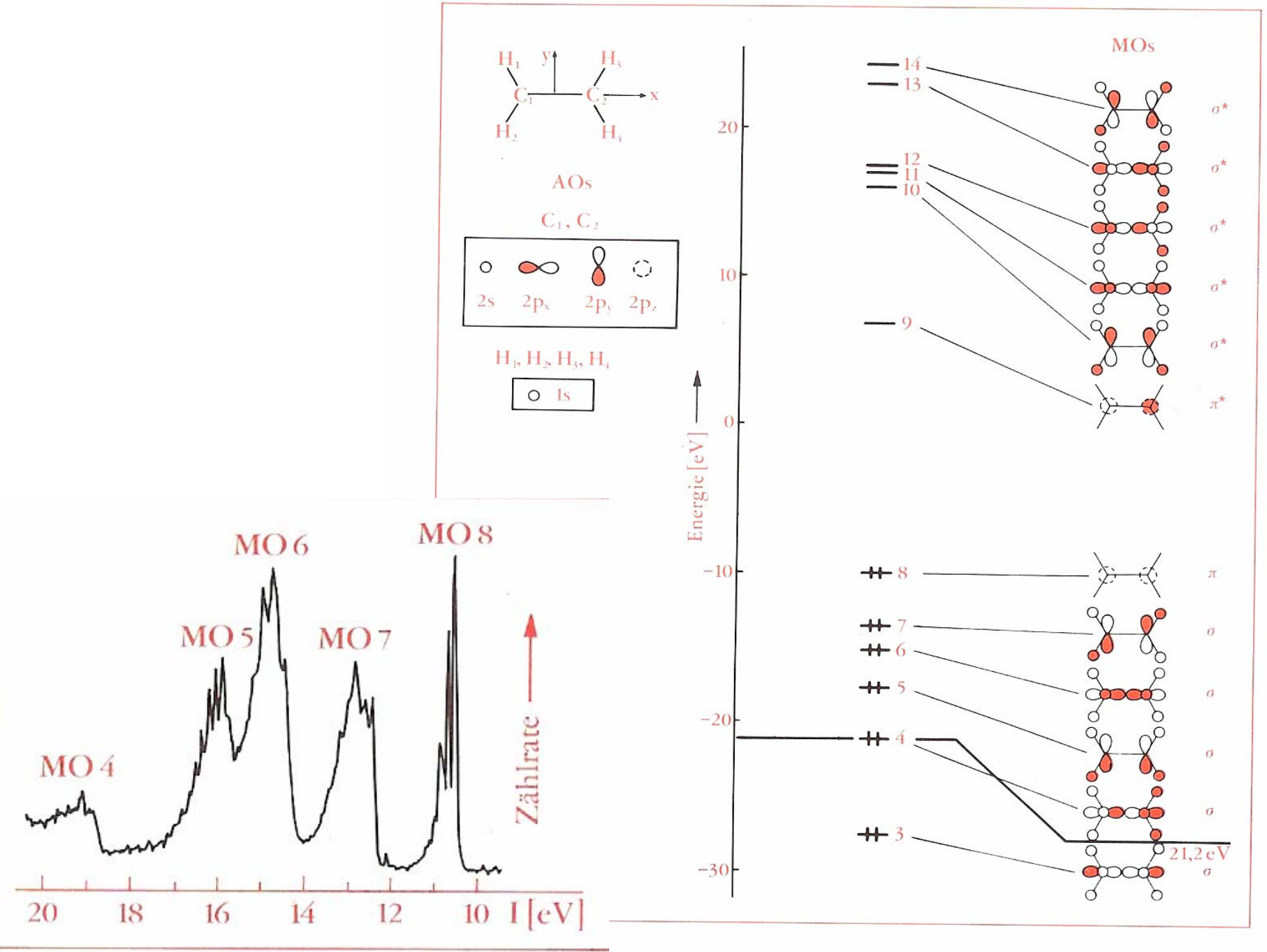
) Berechnen Sie für Butadien im Grundzustand und im 1. angeregten Zustand die π-Bindungsordnungen, die π-Ladungsdichten und die Indices der freien Valenz

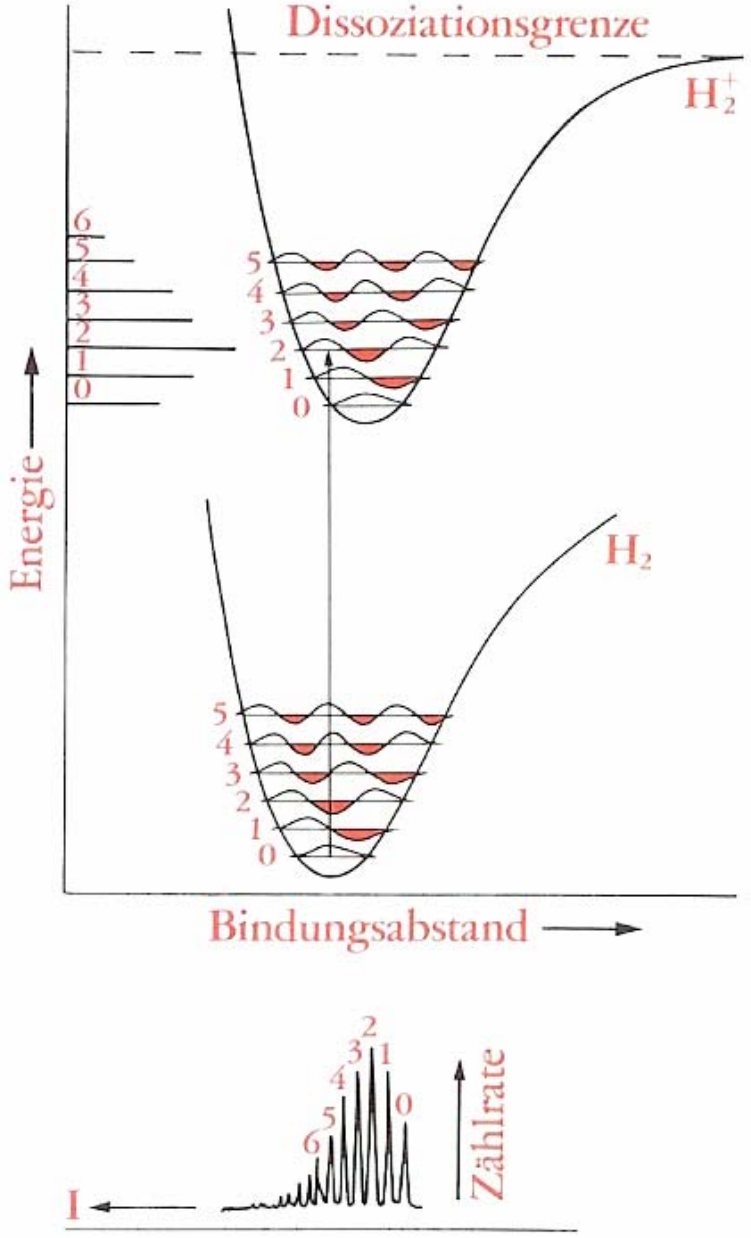
) Zeichnen Sie qualitativ die Orbitale und die schematisierten Slater-funktionen des Pentatrienyls

) Gibt es einen einfachen Zusammenhang zwischen der allgemeinen Formel zur Berechnung von π-Systemen und dem Weg über die Ausmultiplikation von Determinanten?

) Gesetzt den – hypothetischen - Fall, Ihr PES-Spektrum gäbe Ihnen Banden bei 14 eV, bei 12 eV und bei 9 eV mit einer Aufspaltung von 0,211 eV. Wie sieht das Energiediagramm aus, worauf könnte die Aufspaltung basieren (Molekularer Mechanismus)?

) Wie könnte man die energetischen Lagen unbesetzter Niveaus bestimmen (Eine Möglichkeit: Die Idee der PES aufgreifen)


H1
y
H3
C1
C2
x
H2
H4
AOs
C1, C2
2s
2px
2py
2pz
H1, H2, H3, H4
1s
MOs
14
13
12
11
10
9
8
7
6
5
4
3
σ*
σ*
σ*
σ*
σ*
π*
π
σ
σ
σ
σ
σ
20
10
0
−10
−20
−30
Energie [eV]
21,2 eV
MO 4
MO 5
MO 6
MO 7
MO 8
Zählrate
20
18
16
14
12
10
I [eV]



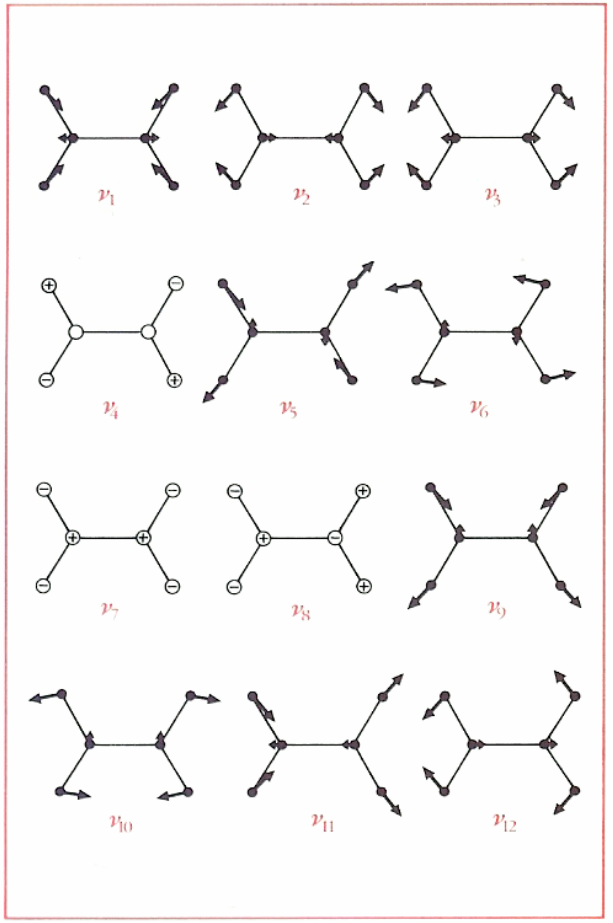
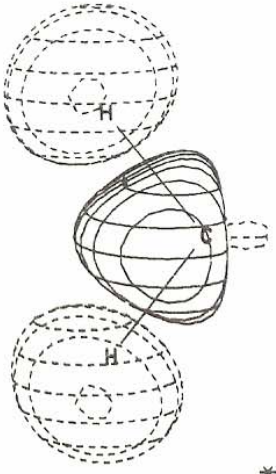


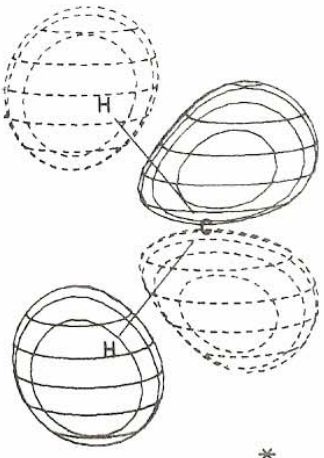
Abb. 17. Normalschwingungen des Ethylen-Moleküls. Die Schwingungen ν_4, ν_7 und ν_8 sind mit Bewegungen der Atome senkrecht zur Papierebene verbunden. „+“ bedeutet Bewegung nach oben (zum Betrachter hin), „−“ bedeutet Bewegung nach unten. Man erkennt, daß z.B. bei ν_4 die beiden CH_2-Gruppen gegeneinander verdreht werden, daß ν_4 also eine Torsionsschwingung darstellt

3. Singulett-Methylen

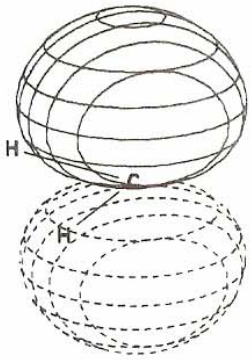
Symmetrie: C_{2v}



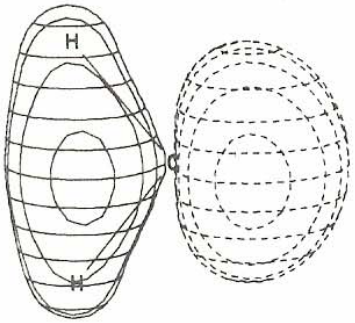
$4A_1$ E= 0.0753 $\sigma^*_{CH_2}$



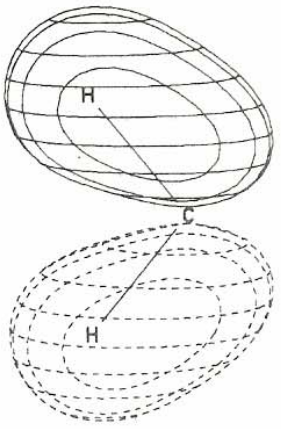
$2B_2$ E= 0.1214 $\pi^*_{CH_2}$



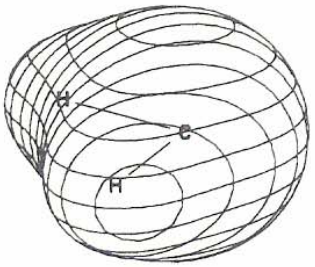
$1B_1$ E=-0.0369 P



$3A_1$ E=-0.3949 Π, (σ_{CH_2})

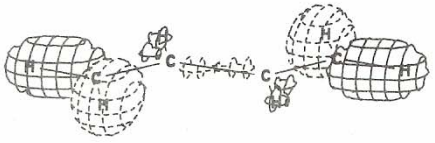


$1B_2$ E=-0.4860 π_{CH_2}

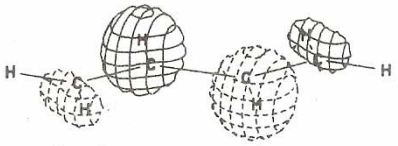


$2A_1$ E=-0.9553 σ_{CH_2}

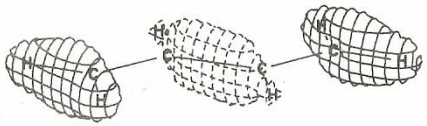
Symmetrie: C_{2h}



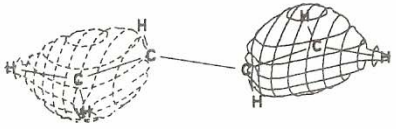
$5A_g$ E=-0.664 π'_{CH_2}



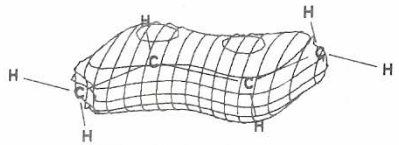
$4B_u$ E=-0.775 σ_{CH}, (σ_{CH_2})



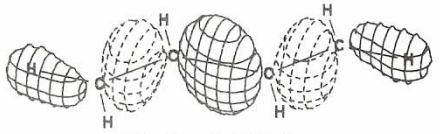
$4A_g$ E=-0.838 σ



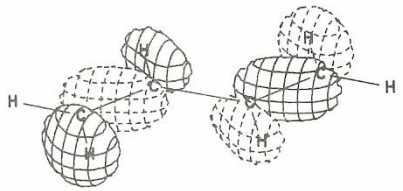
$3B_u$ E=-1.021 σ_{CC}, σ_{CH_2}



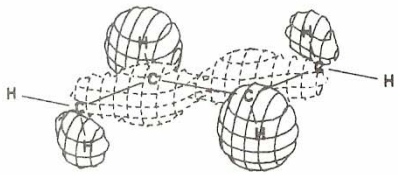
$3A_g$ E=-1.109 σ_{CC}



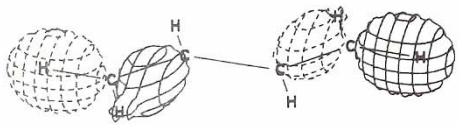
$7A_g$ E=-0.514 σ_{CC}



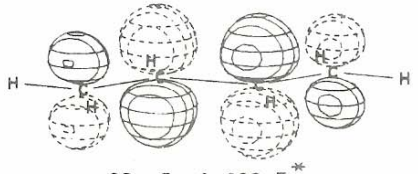
$6B_u$ E=-0.569 σ



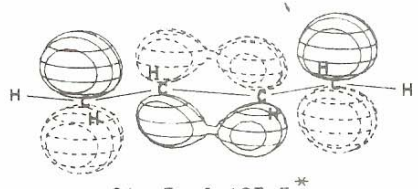
$6A_g$ E=-0.574 σ_{CH}, σ_{CC}



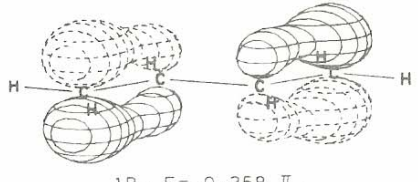
$5B_u$ E=-0.660 π'_{CH_2}, (σ_{CC})



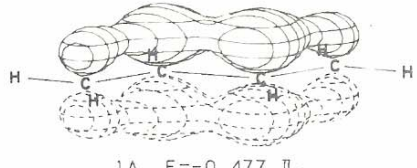
$2B_g$ E= 0.283 π^*_4



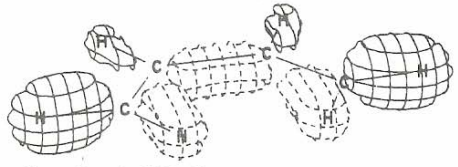
$2A_u$ E= 0.127 π^*_3



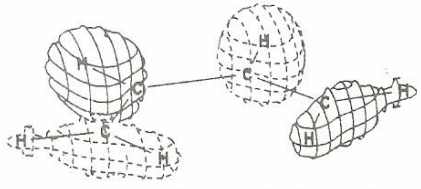
$1B_g$ E=-0.358 π_2



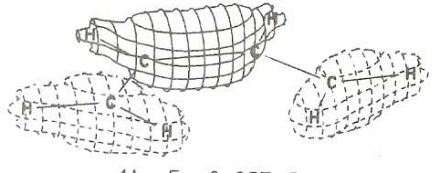
$1A_u$ E=-0.477 π_1



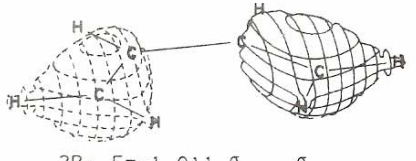
$5A_1$ E=-0.707 σ



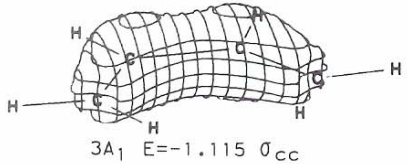
$4B_2$ E=-0.744 σ_{CH}, σ_{CH_2}



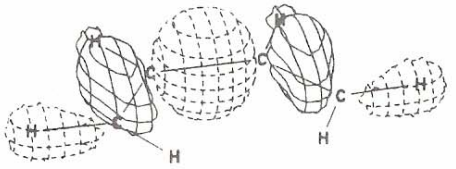
$4A_1$ E=-0.857 σ



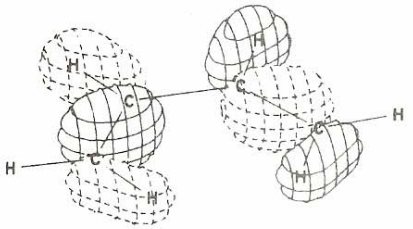
$3B_2$ E=-1.011 σ_{CC}, σ_{CH_2}



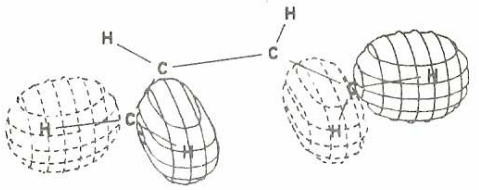
$3A_1$ E=-1.115 σ_{CC}



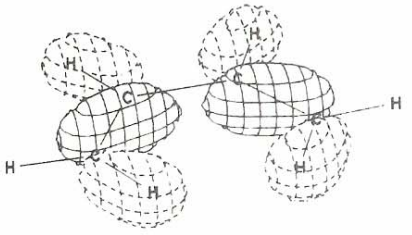
$7A_1$ E=-0.526 σ



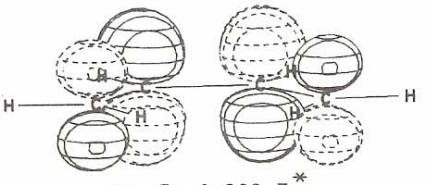
$6B_2$ E=-0.537 σ



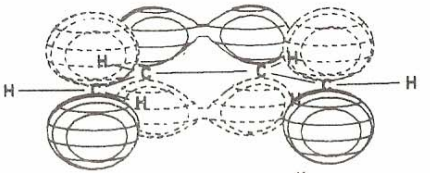
$5B_2$ E=-0.602 π_{CH_2}



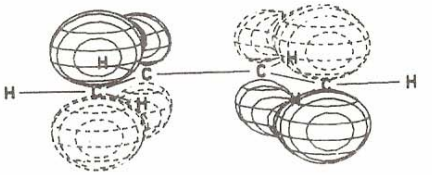
$6A_1$ E=-0.629 σ



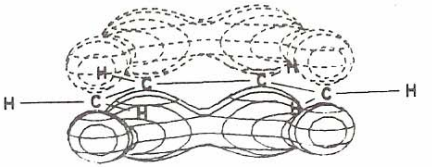
$2A_2$ E= 0.289 π^*_4



$2B_1$ E= 0.120 π^*_3

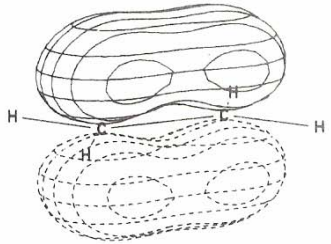


$1A_2$ E=-0.354 π_2

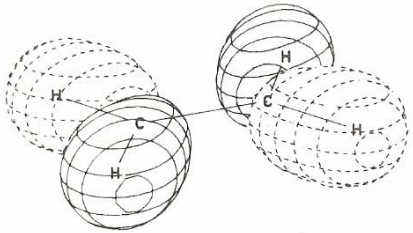


$1B_1$ E=-0.477 π_1

Symmetrie: D_{2h}

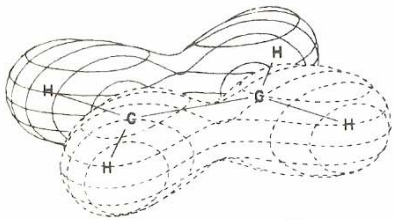


$1B_{2u}$ E=-0.3709 π_{CC}

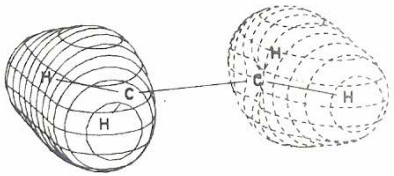


$1B_{2g}$ E=-0.5061 π'_{CH_2}

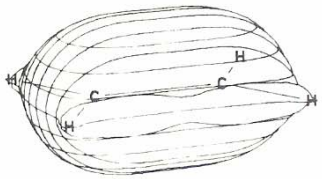
$3A_g$ E=-0.5616 σ_{CH_2}, σ_{CC}



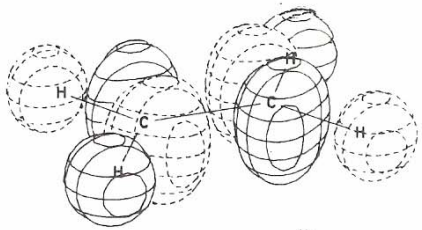
$1B_{3u}$ E=-0.6438 π'_{CH_2}



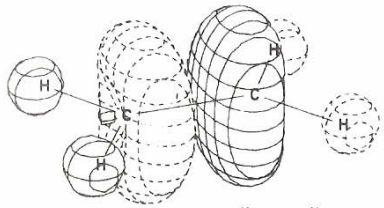
$2A_u$ E=-0.7823 σ_{CH_2}



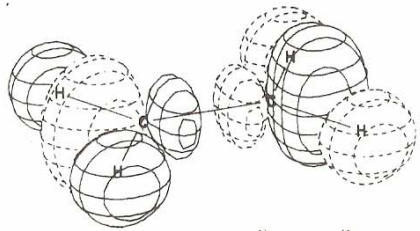
$2A_g$ E=-1.0144 σ_{CC}, σ_{CH_2}



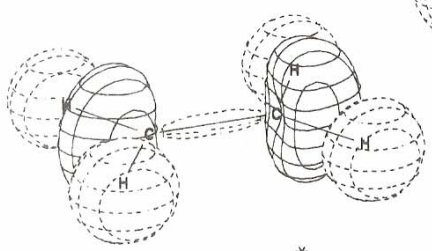
$2B_{2g}$ E= 0.8917 $\pi^*_{CH_2}$



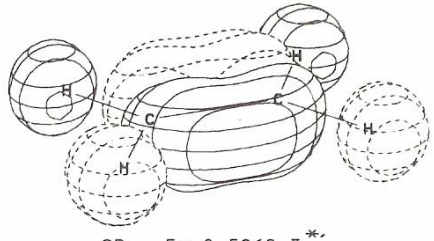
$4A_u$ E= 0.8453 σ^*_{CC}, $\sigma^*_{CH_2}$



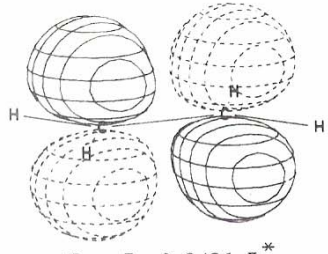
$3A_u$ E= 0.6395 $\sigma^*_{CH_2}$, σ^*_{CC}



$4A_g$ E= 0.6206 $\sigma^*_{CH_2}$

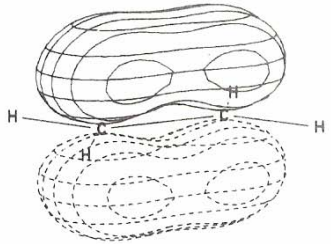


$2B_{3u}$ E= 0.5868 $\pi^*_{CH_2}$

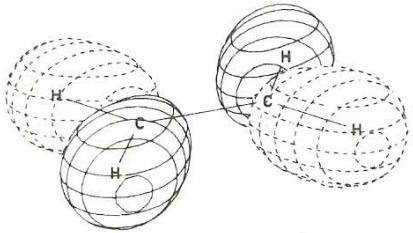


$1B_{3g}$ E= 0.2426 π^*_{CC}

Symmetrie: D_{2h}

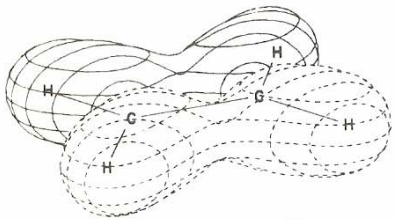


$1B_{2u}$ E=-0.3709 π_{CC}

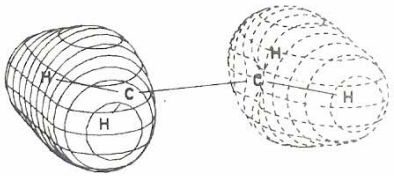


$1B_{2g}$ E=-0.5061 π'_{CH_2}

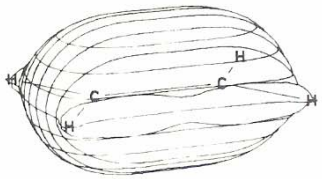
$3A_g$ E=-0.5616 σ_{CH_2}, σ_{CC}



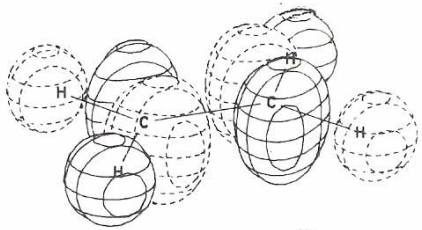
$1B_{3u}$ E=-0.6438 π'_{CH_2}



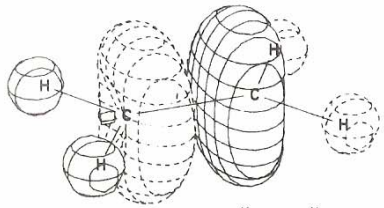
$2A_u$ E=-0.7823 σ_{CH_2}



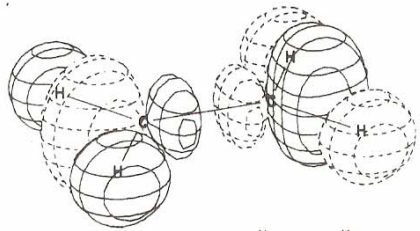
$2A_g$ E=-1.0144 σ_{CC}, σ_{CH_2}



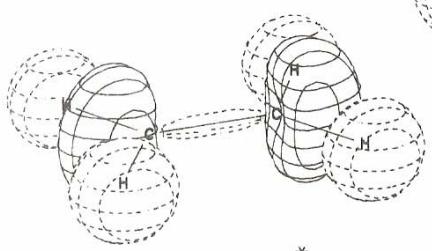
$2B_{2g}$ E= 0.8917 $\pi^*_{CH_2}$



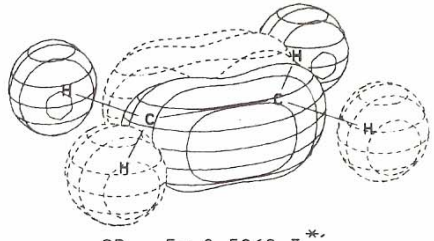
$4A_u$ E= 0.8453 σ^*_{CC}, $\sigma^*_{CH_2}$



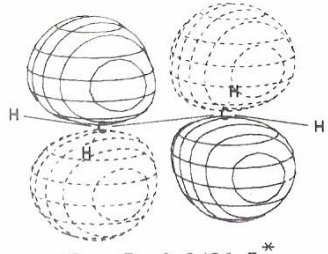
$3A_u$ E= 0.6395 $\sigma^*_{CH_2}$, σ^*_{CC}



$4A_g$ E= 0.6206 $\sigma^*_{CH_2}$

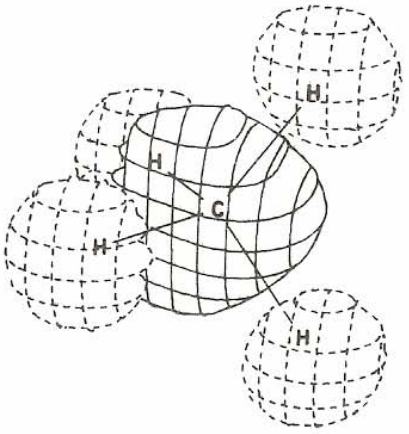


$2B_{3u}$ E= 0.5868 $\pi^*_{CH_2}$

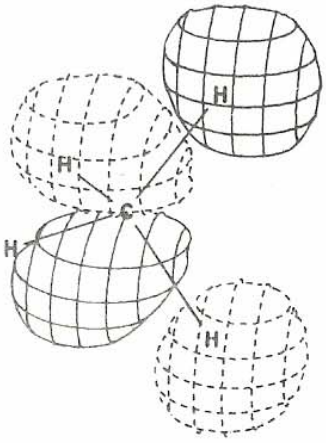


$1B_{3g}$ E= 0.2426 π^*_{CC}

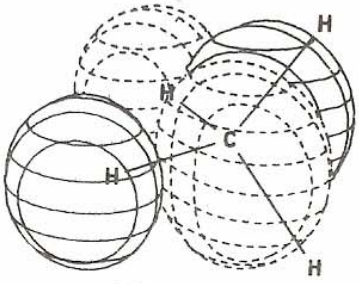
Symmetrie: T_d



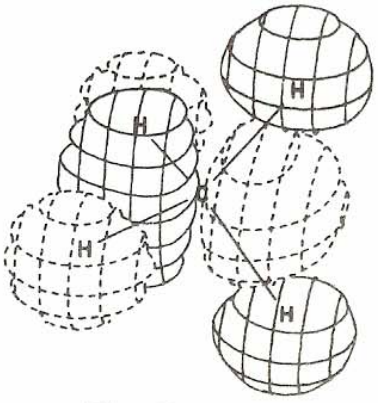
$3A_1$ E= 0.6887



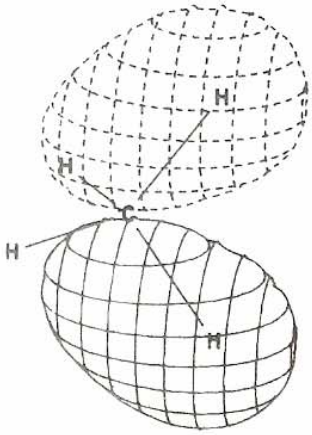
$2T_2$ E= 0.6441



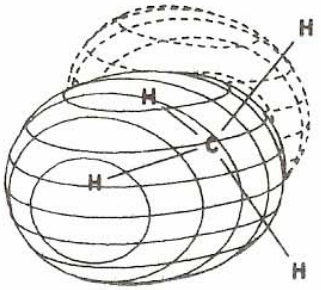
$2T_2$ E= 0.6441



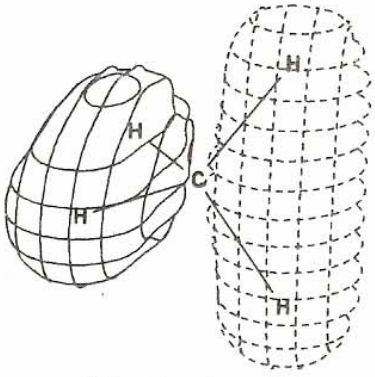
$2T_2$ E= 0.6441



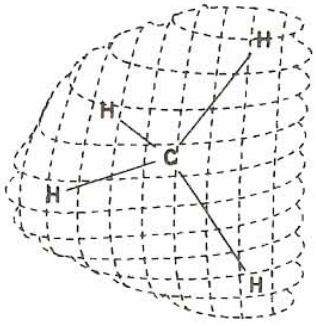
$1T_2$ E=-0.5418

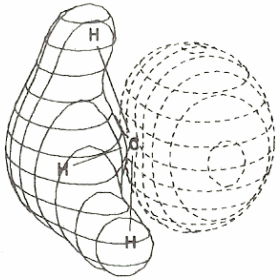


$1T_2$ E=-0.5418

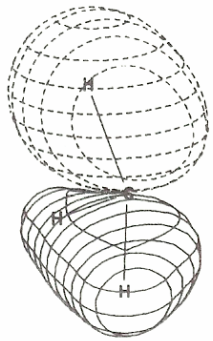


$1T_2$ E=-0.5418

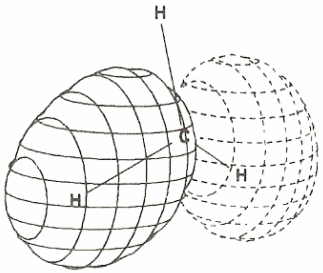




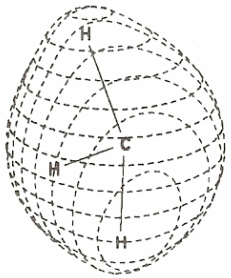
$3A_1$ E=-0.4315 Π, (σ_{CH_3})



1E E=-0.5117 π_{CH_3}

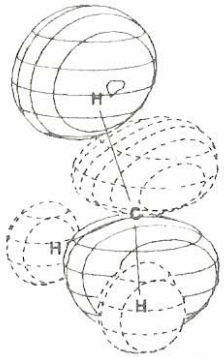


1E E=-0.5117 π_{CH_3}

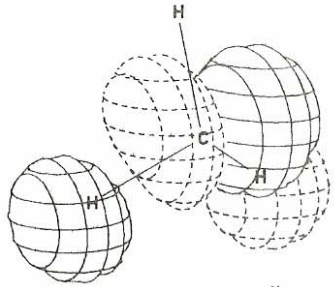


$2A_1$ E=-1.0653 σ_{CH_3}

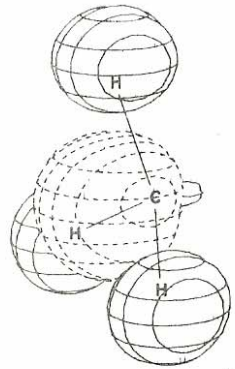
Pyramidales Methyl-Radikal (Fortsetzung)



2E E= 0.1216 $\pi^*_{CH_3}$



2E E= 0.1216 $\pi^*_{CH_3}$



$4A_1$ E= 0.0593 $\sigma^*_{CH_3}$

lineare, unverzweigte Polyene:

$E_i = \alpha + 2\beta \cos \frac{i\pi}{n+1}$ $\quad c_{iv} = \sqrt{\frac{2}{n+1}} \sin \frac{iv\pi}{n+1}$

Beispiel Butadien $=\backslash/=$

Säkulardeterminante

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} \xrightarrow[\frac{\alpha-E}{\beta}=x]{:\beta} 0 = \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = x \cdot \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \cdot \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix}$$

$= x(x^3 - 2x) - (x^2 - 1) = x^4 - 3x^2 + 1$ $\quad$ via $y = x^2$

$\Rightarrow y(y-3) = -1$

Nullstellen: $x = \pm\sqrt{2{,}62}\ ;\ \pm\sqrt{0.382}$

$= \pm 1{,}618 \quad \pm 0.6181$

$\Rightarrow E_{1,4} = \alpha \pm 1.618\beta \qquad E_{2,3} = \alpha \pm 0.6181\beta$

mit $E_i = \alpha + 2\beta \cos \frac{i\pi}{4+1} = \alpha \pm 1{,}618\beta\ ;\ \alpha \pm 0{,}618\beta$