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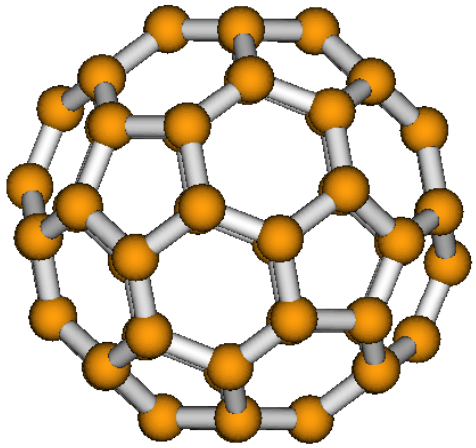
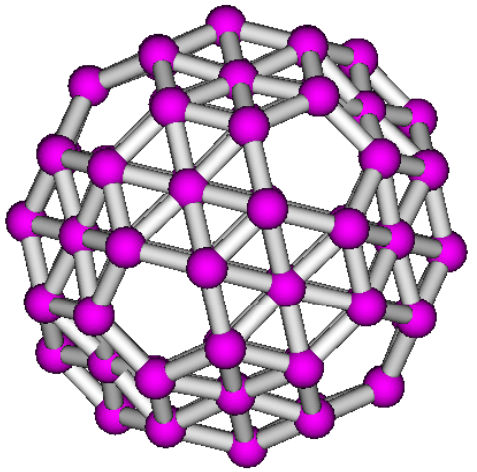
Chemical Bonding in C_{60} and B_{80}

Tshishimbi Muya, Jules
Quantum Chemistry
KULeuven





July 20th, 2012
VBW-UPMC, Paris

Introduction

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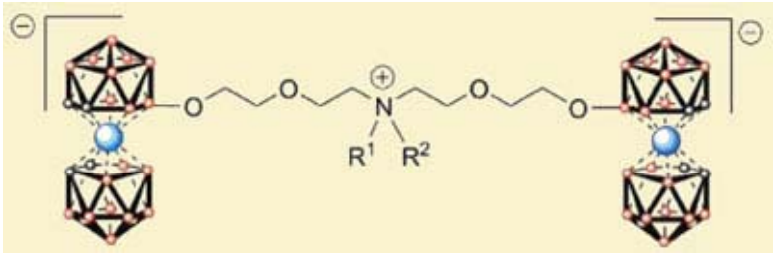
Polyhedral boranes

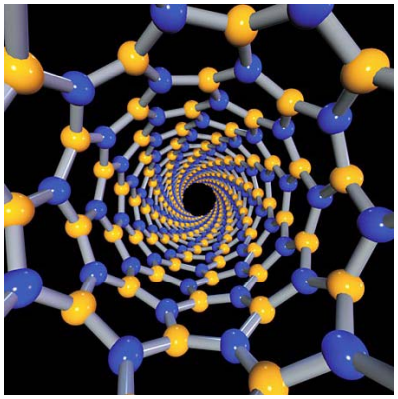
Carboranes

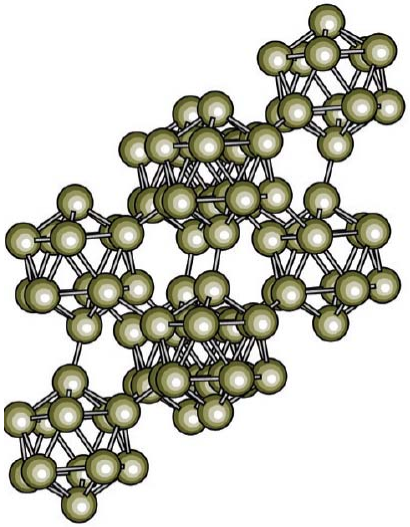
BNTs (BN)

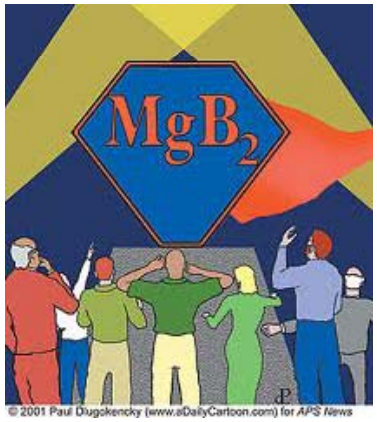
B_2Mg

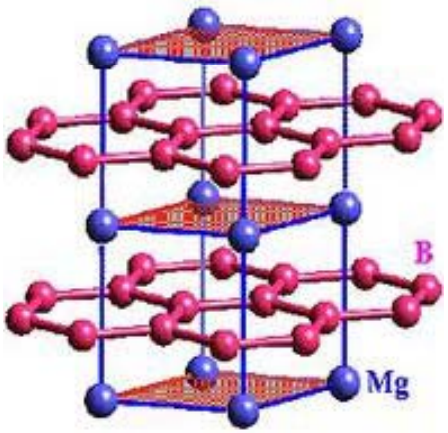
Alpha boron (rh. sol)

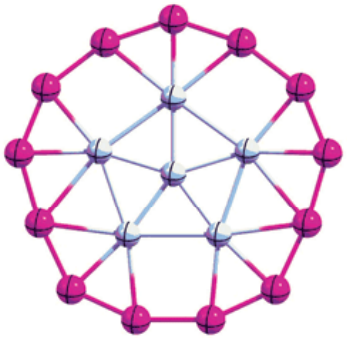












Introduction

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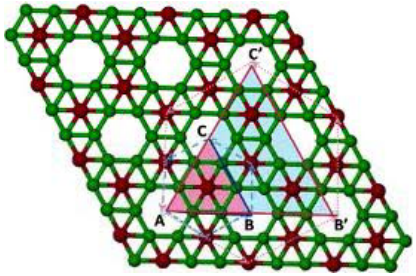
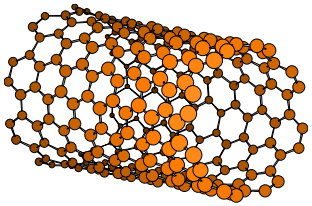
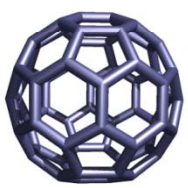
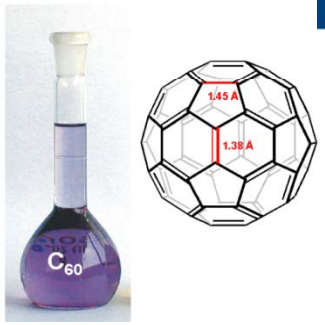
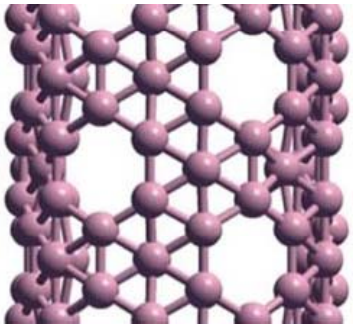
(A) Alpha Boron sheet

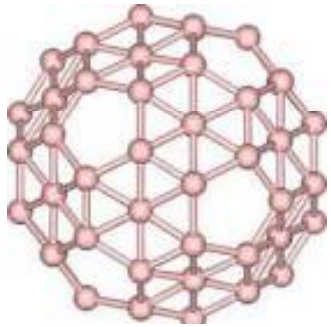




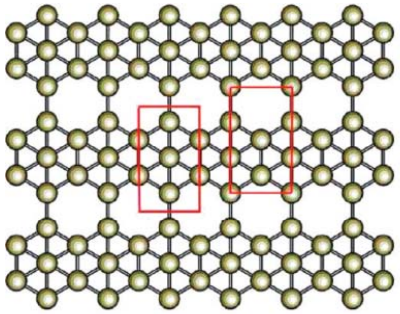




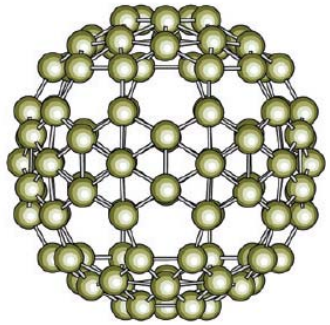




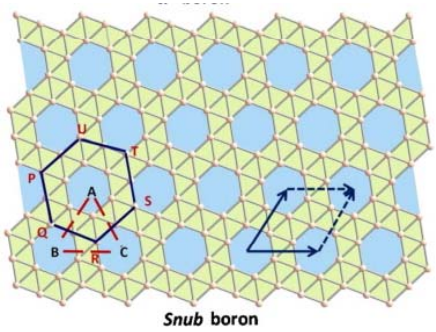
(B) Gamma boron sheet



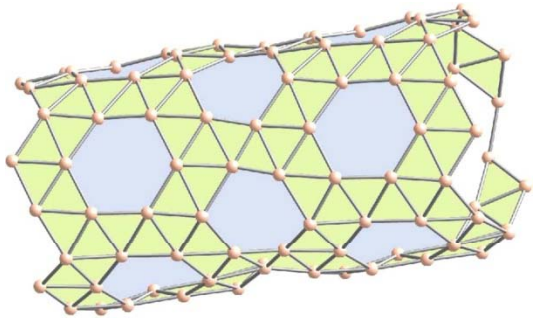
Insertion of pentagons

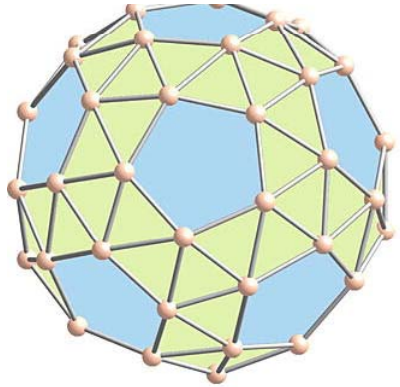


(C) Snub boron sheet



Snub boron





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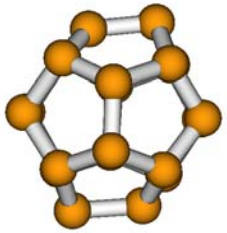
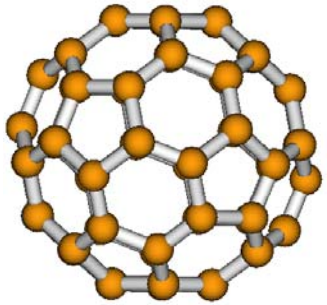
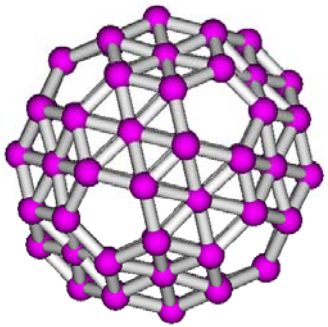
Boron Buckyball B_{80}:Leapfrog operation



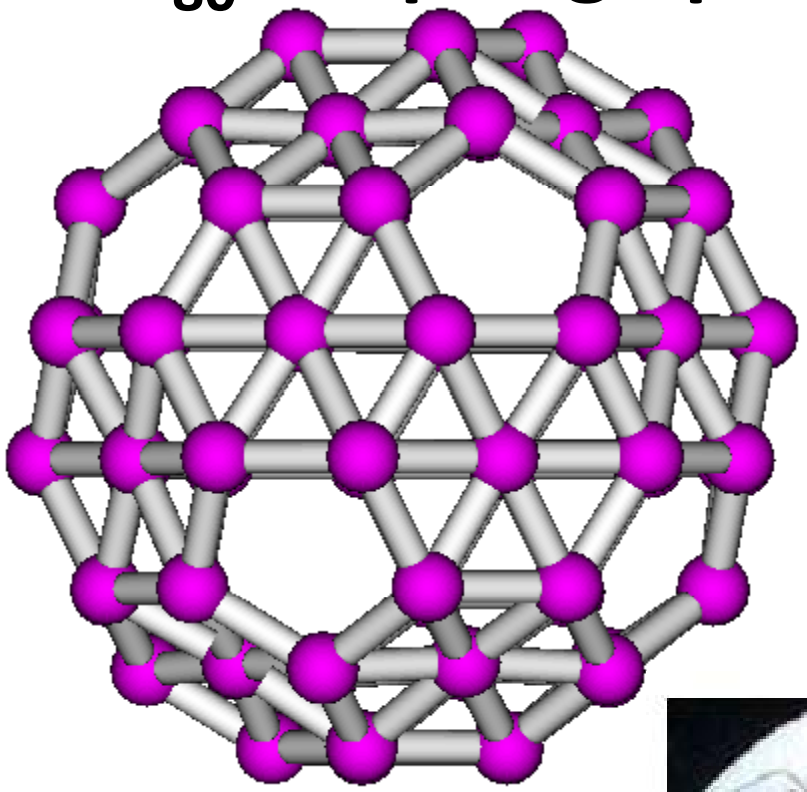
C_{20}



C_{60}



B_{80}



Group Theoretical Background

Ih	E	$12C_5$	$12C_5^2$	$20C_3$	$12C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ
A_g	1	1	1	1	1	1	1	1	1	1
T_{1g}	3	X	X'	0	-1	3	X'	X	0	-1
T_{2g}	3	X'	X	0	-1	3	X	X'	0	-1
G_g	4	-1	-1	1	0	4	-1	-1	1	0
H_g	5	0	0	-1	1	5	0	0	-1	1
A_u	1	1	1	1	1	-1	-1	-1	-1	-1
T_{1u}	3	X	X'	0	-1	-3	-X'	-X	0	1
T_{2u}	3	X'	X	0	-1	-3	-X	-X'	0	1
G_u	4	-1	-1	1	0	-4	1	1	-1	0
H_u	5	0	0	-1	1	-5	0	0	1	-1

$$x = \frac{1}{2}\left(1 + \sqrt{5}\right) \qquad x' = \frac{1}{2}\left(1 - \sqrt{5}\right)$$

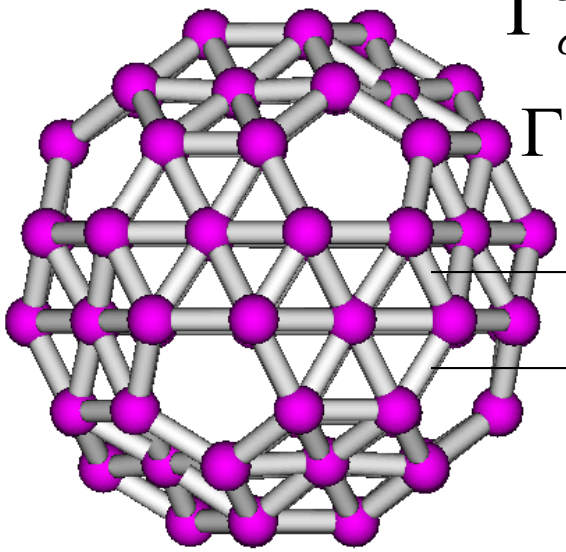
Reducible representation

$$\Gamma_{\sigma}^{60} = A_g + T_{1g} + 2T_{1u} + T_{2g} + 2T_{2u} + 2G_g + 2G_u + 3H_g + 2H_u$$

$$\Gamma_{\pi}^{60} = A_g + A_u + 3T_{1g} + 3T_{1u} + 3T_{2g} + 3T_{2u} + 4G_g + 4G_u + 5H_g + 5H_u$$

$$\Gamma_{\sigma}^{20} = A_g + T_{1u} + T_{2u} + G_g + G_u + H_g$$

$$\Gamma_{\pi}^{20} = T_{1g} + T_{1u} + T_{2g} + T_{2u} + G_g + G_u + 2H_g + 2H_u$$



$$\Gamma_{\sigma}^{30} = A_g + T_{1u} + T_{2u} + G_g + G_u + 2H_g + H_u$$

$$\Gamma_{\sigma^*}^{30} = T_{1g} + T_{1u} + T_{2g} + T_{2u} + G_g + G_u + H_g + H_u$$

30 bonds

60 bonds

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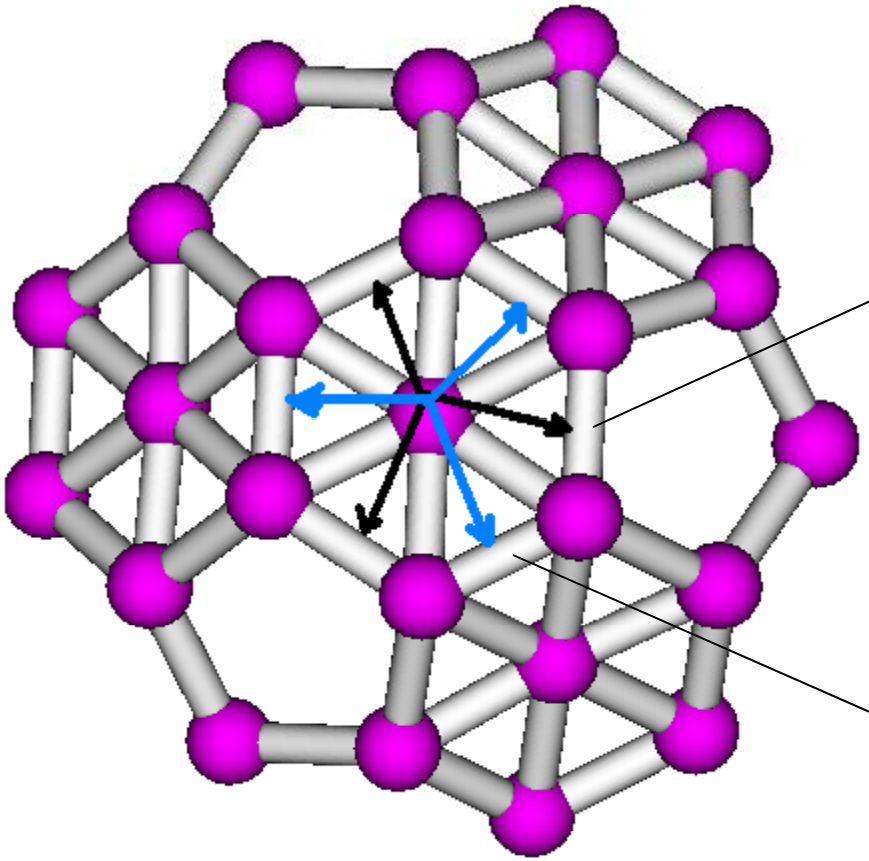

$$\Gamma_{\sigma}^{20} + \Gamma_{\pi}^{20} = \Gamma_{\sigma}^{60}$$

$$\Gamma_{\sigma}^{20} + \Gamma_{\pi}^{20} = \Gamma_{\sigma}^{30} + \Gamma_{\sigma^*}^{30}$$

Chemical Bonding in C_{60}

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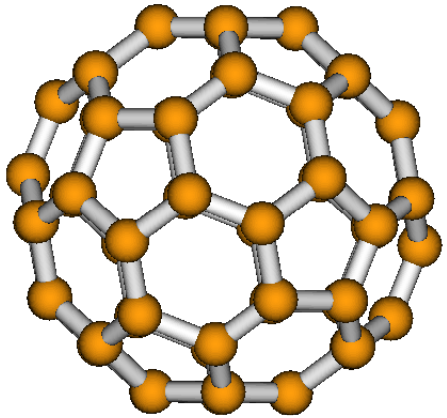

sp^2 + p orbitals

$$\Gamma_{bond}(C_{60}) = \Gamma_{\sigma}^{60} + 2\Gamma_{\sigma}^{30}$$

$$\Gamma_{bond}(C_{60}) = 3A_g + T_{1g} + 4T_{1u} + T_{2g} + 4T_{2u} + 4G_g + 4G_u + 7H_g + 4H_u$$

The Valence shell of B_{80}

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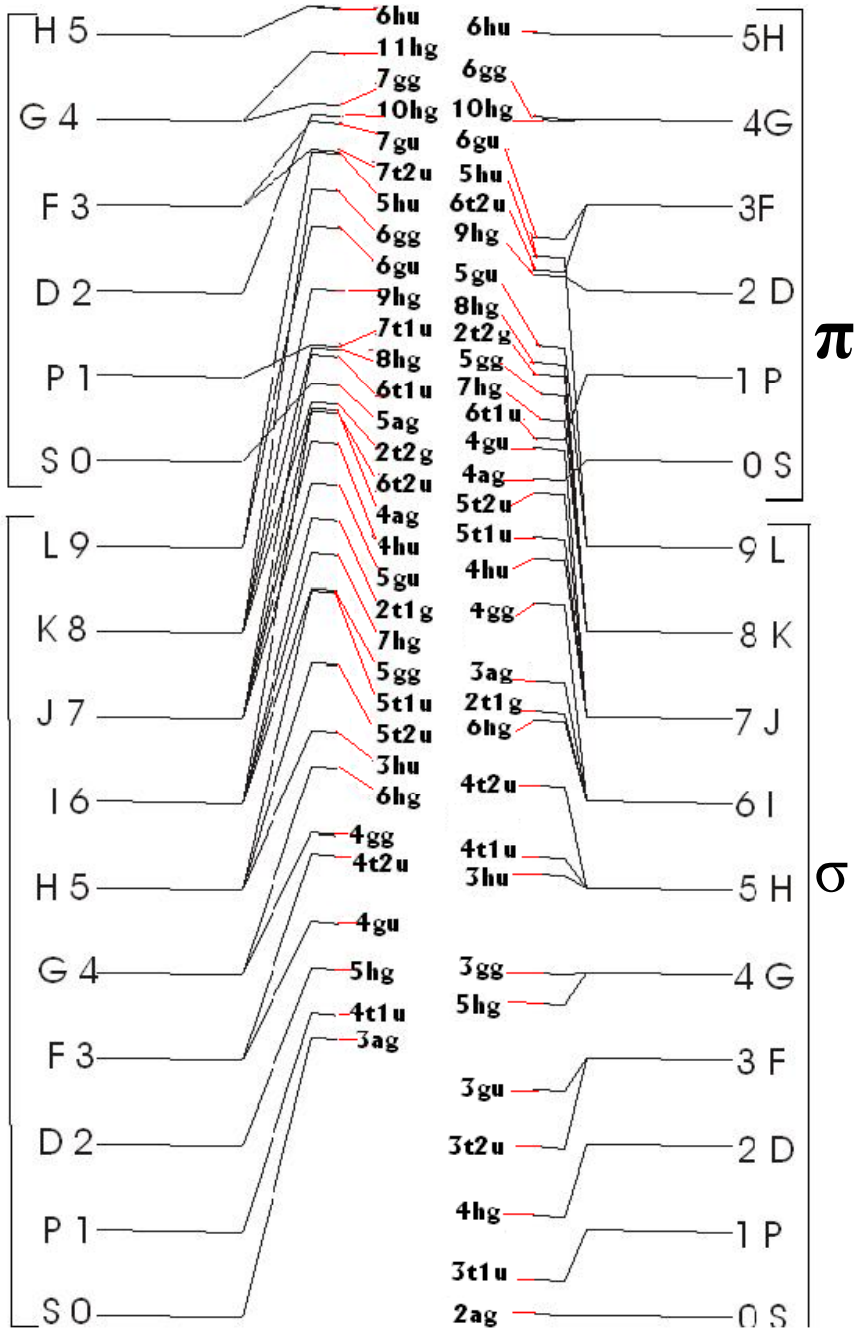
mos	Energy (e.V)	mos	Energy (e.V)	mos	Energy (e.V)
$3a_g$	-21.968	$2t_{1g}$	-13.837	$6g_g$	-8.664
$4t_{1u}$	-21.593	$5g_u$	-13.06	$5h_u$	-8.085
$5h_g$	-20.889	$4h_u$	-12.649	$7t_{2u}$	-8.049
$4g_u$	-20.161	$4a_g$	-12.157	$7g_u$	-7.607
$4t_{2u}$	-19.096	$6t_{2u}$	-12.115	$10h_g$	-7.5
$4g_g$	-18.776	$2t_{2g}$	-12.005	$7g_g$	-7.312
$6h_g$	-17.728	$5a_g$	-11.726	$11h_g$	-6.497
$3h_u$	-17.166	$6t_{1u}$	-11.263	$6h_u$	-5.633
$5t_{2u}$	-16.091	$8h_g$	-11.147	$8t_{1u}$	-3.711
$5t_{1u}$	-14.972	$7t_{1u}$	-11.102	$3t_{1g}$	-3.197
$5g_g$	-14.940	$9h_g$	-10.217	$8t_{2u}$	-3.031
$7h_g$	-14.376	$6g_u$	-9.226		

Calculated at B3LYP/SV(P) level using TURBOMOLE program package



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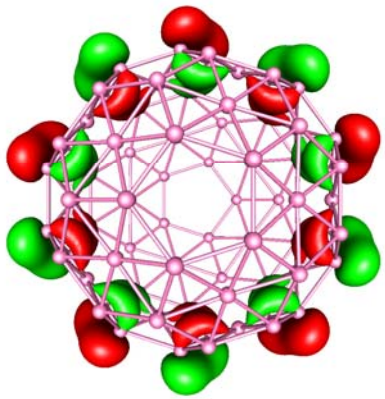
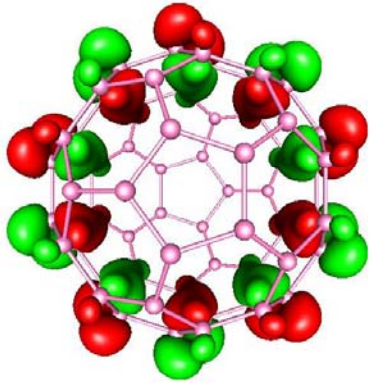
Comparison between valence orbitals occupied MOs of B_{80} and C_{60} B3LYP/SV(P)



HOMO(B_{80})



HOMO(C_{60})

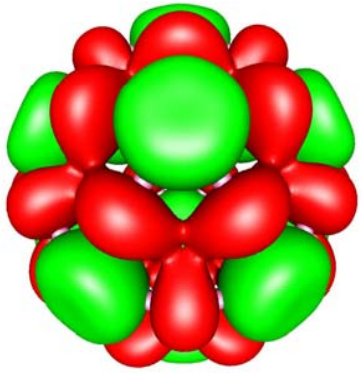


Fig3.3ag

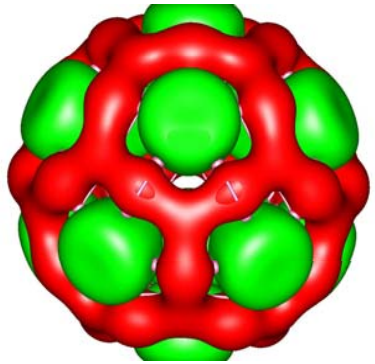


Fig4. 4ag

Spherical shells and σ- and π-band of B_{80}

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L	I_h	σ-band	π -band
0	A_g	$3a_g$	$5a_g$
1	T_{1u}	$4t_{1u}$	$7t_{1u}$
2	H_g	$5\,h_g$	$10h_g$
3	$T_{2u}+G_u$	$4t_{2u}+4g_u$	$7t_{2u}+7g_u$
4	G_g+H_g	$4g_g+6h_g$	$7g_g+11h_g$
5	$T_{1u}+T_{2u}+H_u$	$5t_{1u}+5t_{2u}+3h_u$	$6h_u$
6	$A_g+T_{1g}+G_g+H_g$	$4a_g+2t_{1g}+5g_g+7h_g$	
7	$T_{1u}+T_{2u}+G_u+H_u$	$6t_{1u}+6t_{2u}+5g_u+4h_u$	
8	$T_{2g}+G_g+2H_g$	$2t_{2g}+6g_g+8h_g+9h_g$	
9	$T_{1u}+T_{2u}+2G_u+H_u$	$6g_u+5h_u$	

The bonding role of the caps

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Γ_{σ}^{60}

$\square$

$\Gamma_{\sigma}^{20} + \Gamma_{\pi}^{20}$

$\square$

$\Gamma_{\sigma}^{30} + \Gamma_{\sigma^*}^{30}$

Mos	2s	2p	2s + 2p	Γ^{30}
a_u	0	0	0	0
a_g	0.51	0.31	0.82	1
t_{1g}	0	0.94	0.94	0
t_{1u}	1.21	2.40	3.62	3
t_{2g}	0	0.40	0.40	0
t_{2u}	1.84	1.05	2.89	3
g_g	2.06	2.12	4.18	4
g_u	1.53	1.03	2.56	4
h_g	2.87	6.35	9.21	10
h_u	0	4.68	4.68	5
Total	10.01	19.28	29.29	30

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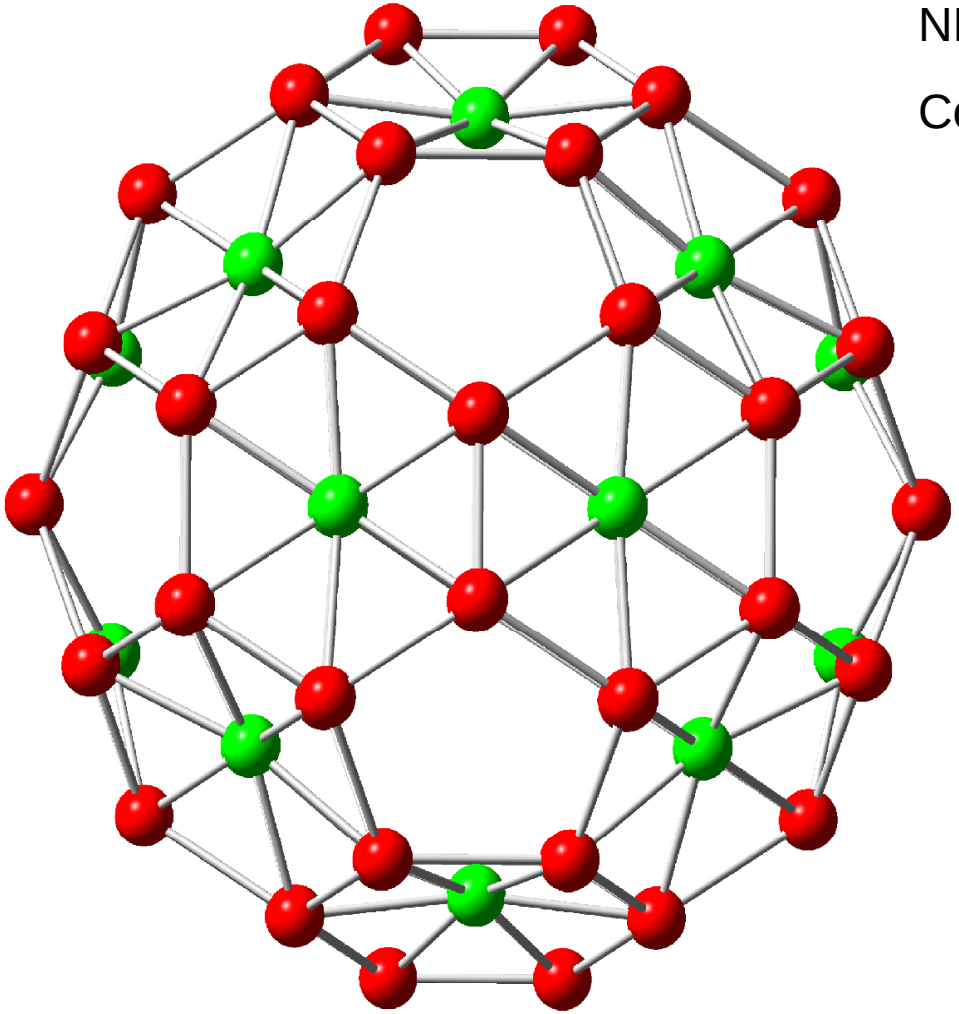

NBO charges

Computed at B3LYP/6-31G(d)

Caps transfer ~3e

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Concluding Remarks

-B_{80} is isoelectronic to C_{60}

-The chemical bonding in B_{80} is similar to that of C_{60}

-The caps contribute to reinforce essentially 30 sigma bonds along the 6-6 edges

-The HOMO in B_{80} is $6h_u$ and is located on the truncated icosahedral frame and its shape is similar to that of C_{60}

References

[1] A Ceulemans, JT Muya, G Gopakumar, MT Nguyen, Chem. Phys. Lett. 461 (2008), p. 226.

[2] D Bean, JT Muya, P Fowler,MT Nguyen, A Ceulemans, Phys. Chem. Chem. Phys. 13 (2011), p.20855.

[3]JT Muya, F De Proft, P Geerlings, MT Nguyen, A Ceulemans, J. Phys. Chem. A 115 (2011), p.9069.

[4] JT Muya, E Lijnen,M Nguyen,A Ceulemans,J.Phys.Chem. A 115 (2011), p.2268.

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FWO VLAANDEREN

GOA