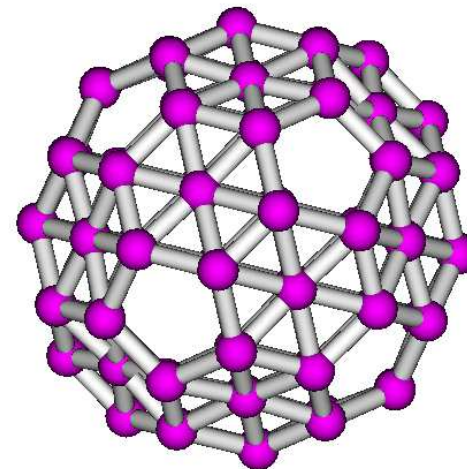
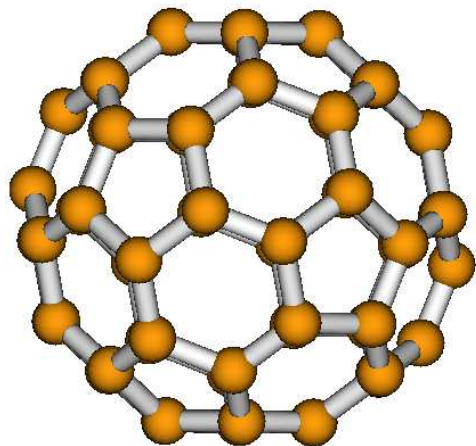


Chemical Bonding in C_{60} and B_{80}

Tshishimbi Muya, Jules
Quantum Chemistry
KULeuven



July 20th, 2012
VBW-UPMC, Paris

Introduction

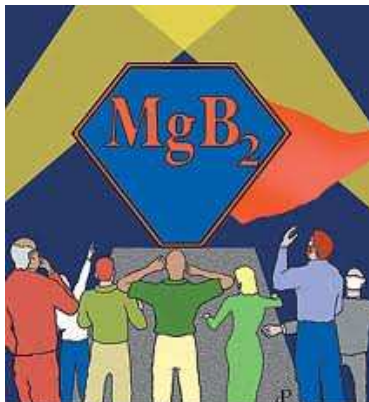
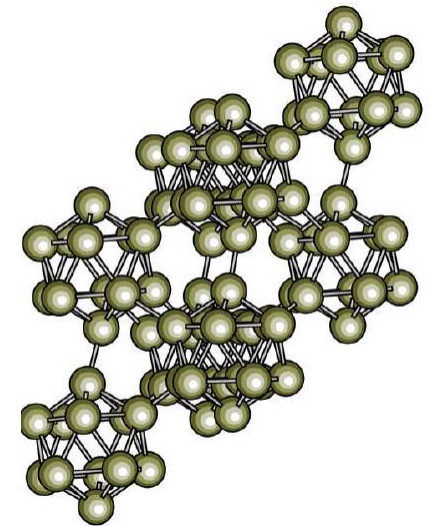
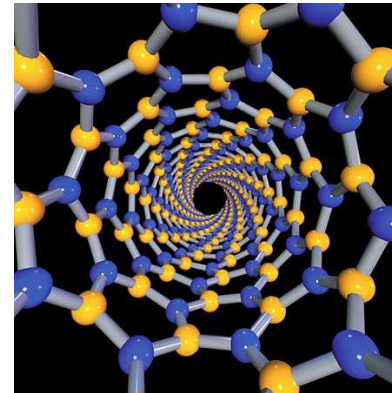
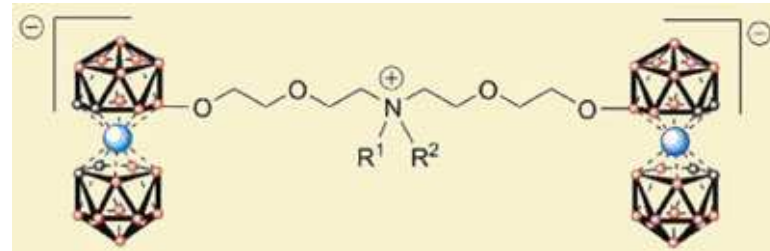
Polyhedral boranes

Carboranes

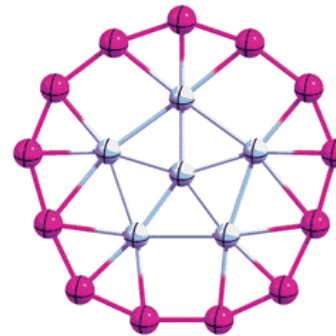
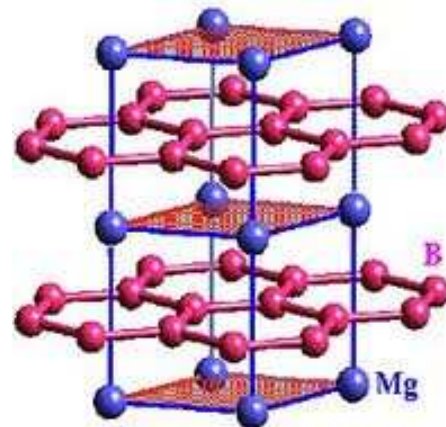
BNTs (BN)

B_2Mg

Alpha boron (rh. sol)

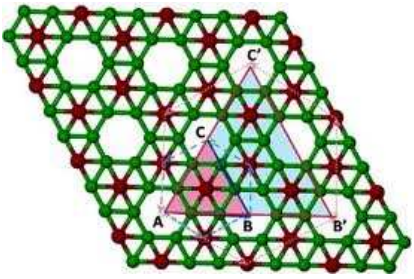


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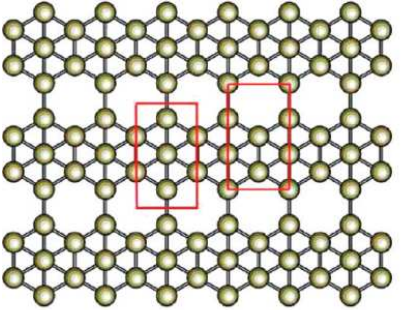


Introduction

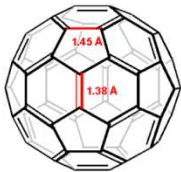
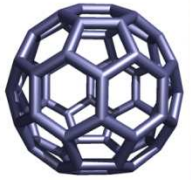
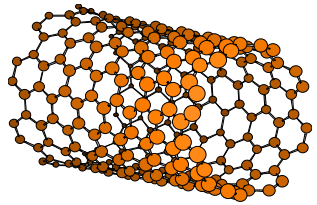
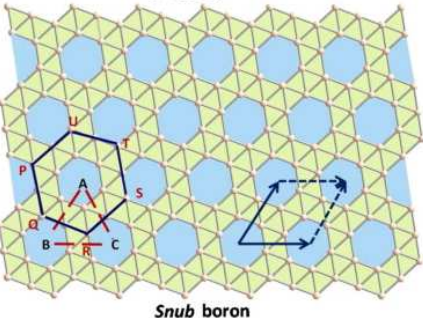
(A) Alpha Boron sheet



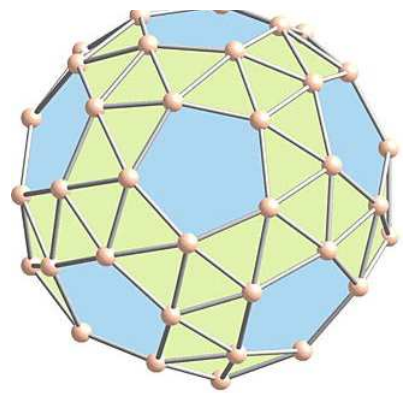
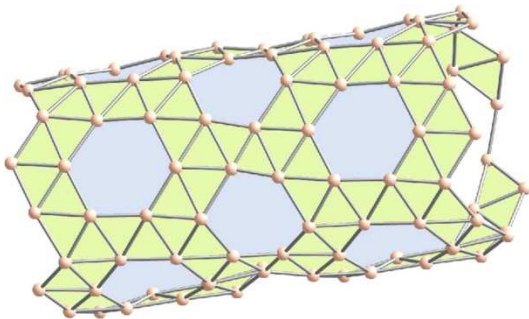
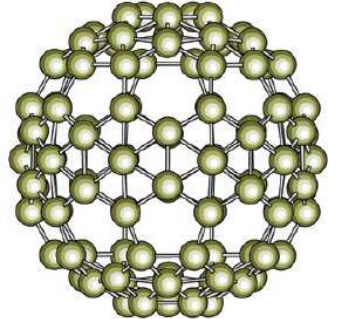
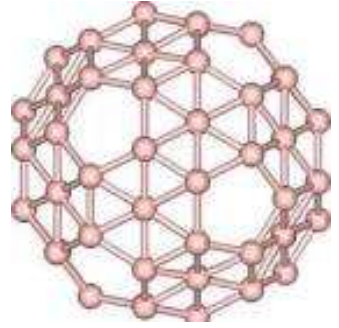
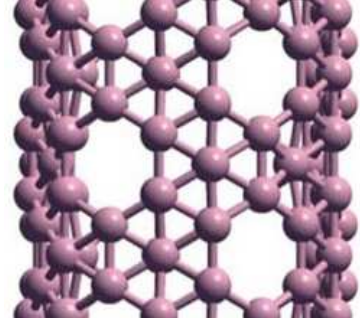
(B) Gamma boron sheet



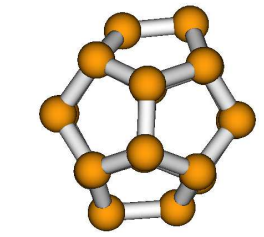
(C) Snub boron sheet



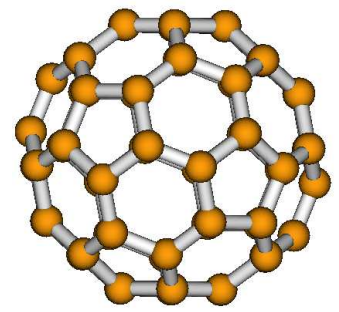
Insertion of pentagons



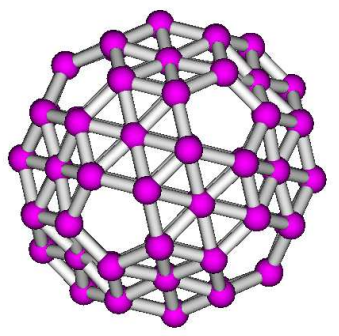
Boron Buckyball B_{80} : Leapfrog operation



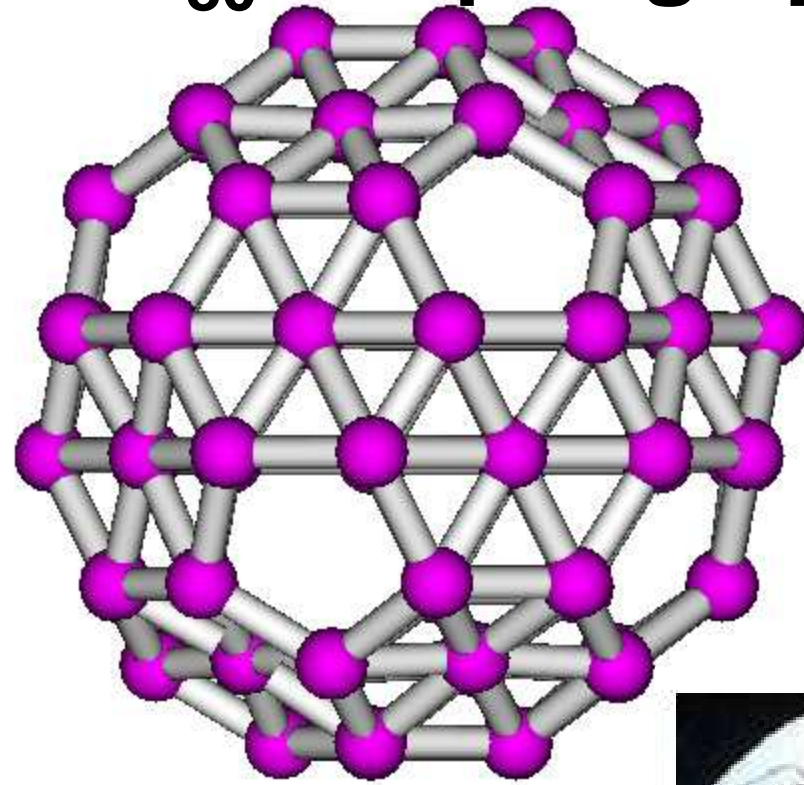
C_{20}



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

$$X = \frac{1}{2} (1 + \sqrt{5})$$

$$X^- = \frac{1}{2} (1 - \sqrt{5})$$

Reducible representation

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

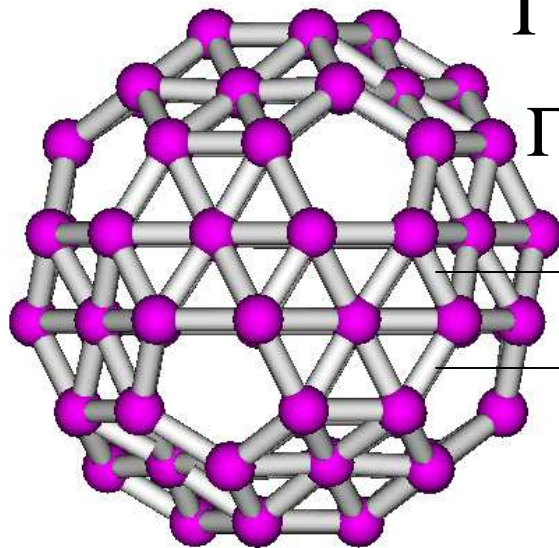
$$\Gamma_{\pi}^{60} = A_g + A_u + 3T_{1g} + 3T_{1u} + 3T_{2g} + 3T_{2u} + 4G_g + 4G_u + 5H_g + 5H_u$$

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

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

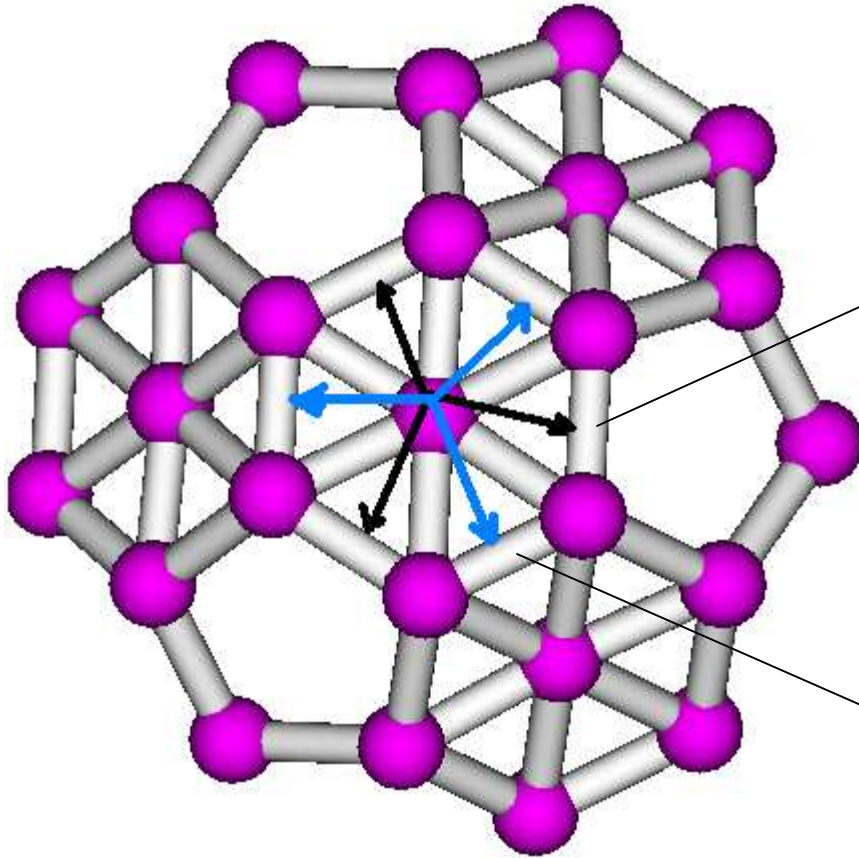
$$\Gamma_{\sigma}^{30} = A_g + T_{1u} + T_{2u} + G_g + G_u + 2H_g + H_u$$

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



→ 30 bonds

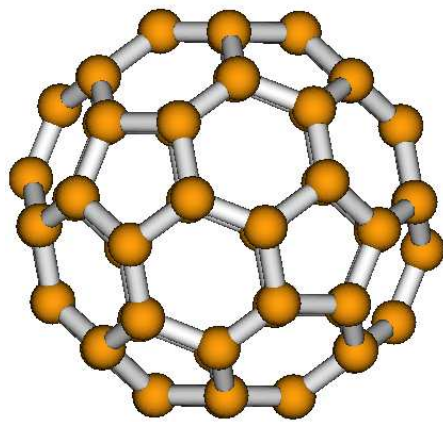
→ 60 bonds



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

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

Chemical Bonding in C₆₀



sp² + p orbitals

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

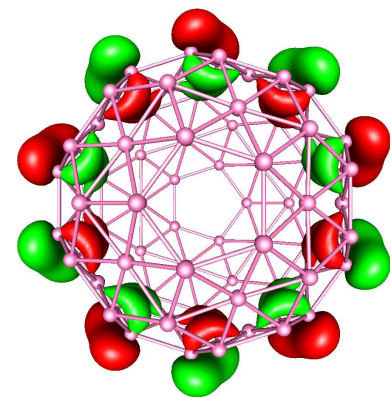
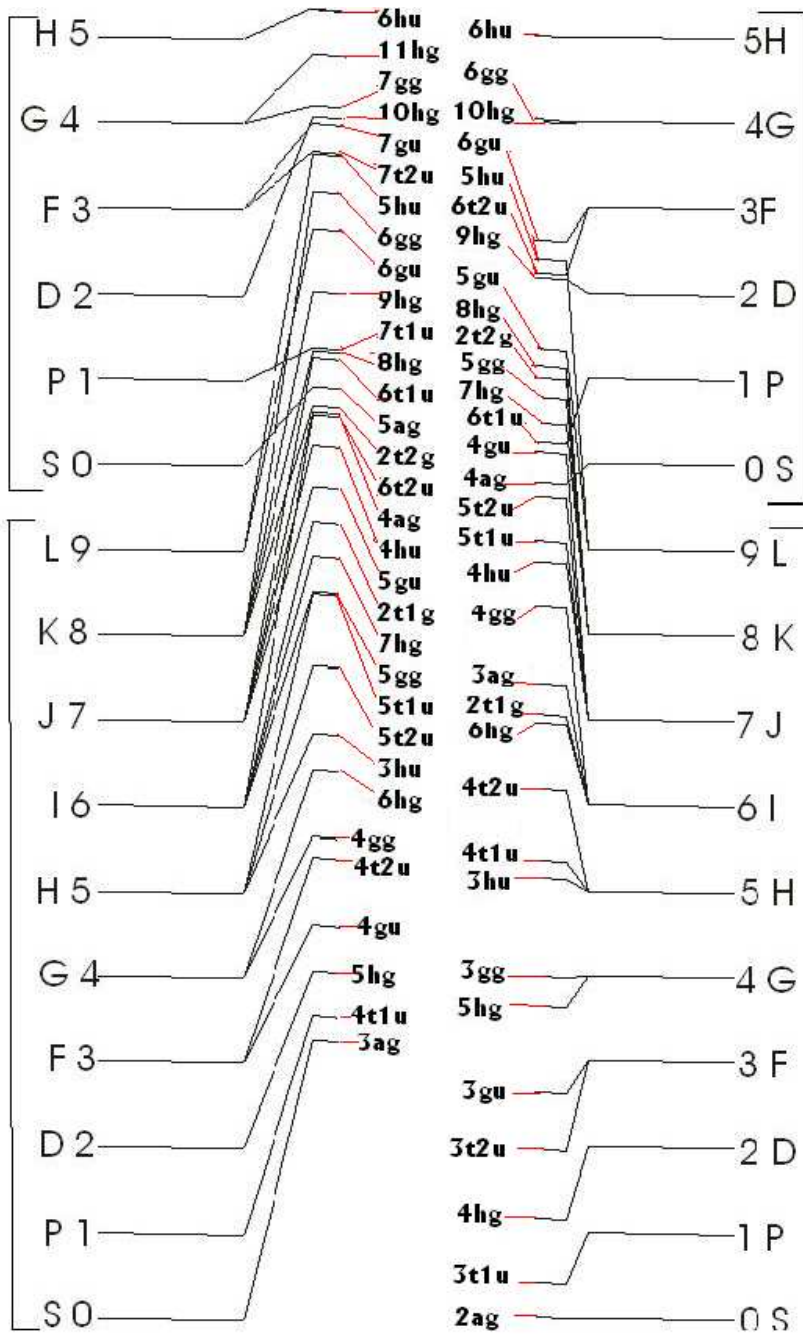
$$\Gamma_{bond}(C_{60}) = 3A_g + T_{1g} + 4T_{1u} + T_{2g} + 4T_{2u} + 4G_g + 4G_u + 7H_g + 4H_u$$

The Valence shell of B₈₀

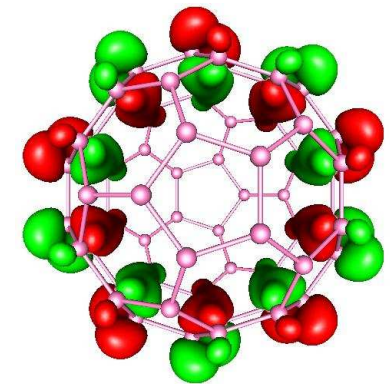
mos	Energy (e.V)	mos	Energy (e.V)	mos	Energy (e.V)
3a _g	-21.968	2t _{1g}	-13.837	6g _g	-8.664
4t _{1u}	-21.593	5g _u	-13.06	5h _u	-8.085
5h _g	-20.889	4h _u	-12.649	7t _{2u}	-8.049
4g _u	-20.161	4a _g	-12.157	7g _u	-7.607
4t _{2u}	-19.096	6t _{2u}	-12.115	10h _g	-7.5
4g _g	-18.776	2t _{2g}	-12.005	7g _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

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



HOMO(B_{80})



HOMO(C_{60})

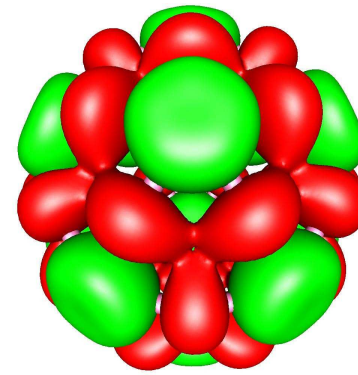


Fig3.3ag

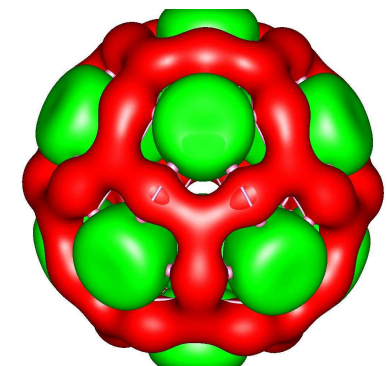


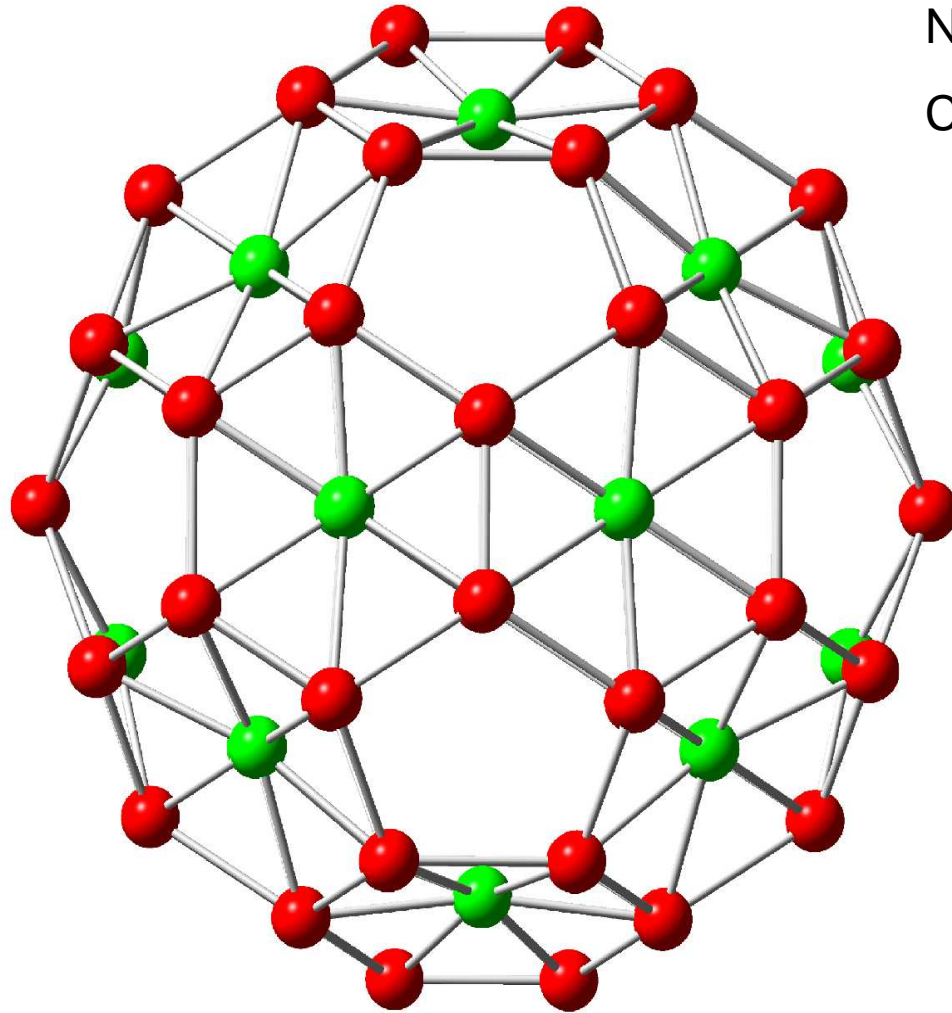
Fig4. 4ag

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

L	I_h	σ -band	π -band
0	A_g	$3a_g$	$5a_g$
1	T_{1u}	$4t_{1u}$	$7t_{1u}$
2	H_g	$5h_g$	$10h_g$
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

		Mos	2s	2p	2s + 2p	Γ^{30}
$\Gamma_{\sigma}^{20} + \Gamma_{\pi}^{20}$ Γ_{σ}^{60} (upward arrow) $\Gamma_{\sigma}^{30} + \Gamma_{\sigma^*}^{30}$ (downward arrow)	a_u	0	0	0	0	0
	a_g	0.51	0.31	0.82	1	1
	t_{1g}	0	0.94	0.94	0	0
	t_{1u}	1.21	2.40	3.62	3	3
	t_{2g}	0	0.40	0.40	0	0
	t_{2u}	1.84	1.05	2.89	3	3
	g_g	2.06	2.12	4.18	4	4
	g_u	1.53	1.03	2.56	4	4
	h_g	2.87	6.35	9.21	10	10
	h_u	0	4.68	4.68	5	5
Total		10.01	19.28	29.29	30	30



NBO charges

Computed at B3LYP/6-31G(d)

Caps transfer $\sim 3e$

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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GOA