Quantum Mechanical Optimization of Carbon Clusters

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The Paper

PHYSICAL REVIEW B VOLUME 51, NUMBER 19 15 MAY 1995-I

Construction of tight-binding-like potentials on the basis of density-functional theory: Application to carbon

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(Received 2 November 1994)

We present a density-functional-based scheme for determining the necessary parameters of common nonorthogonal tight-binding (TB) models within the framework of the linear-combination-of-atomic-orbitals formalism using the local-density approximation (LDA). By only considering two-center integrals the Hamiltonian and overlap matrix elements are calculated out of suitable input densities and potentials rather than fitted to experimental data. We can derive analytical functions for the C-C, C-H, and H-H Hamiltonian and overlap matrix elements. The usual short-range repulsive potential appearing in most TB models is fitted to self-consistent calculations performed within the LDA. The calculation of forces is easy and allows an application of the method to molecular-dynamics simulations. Despite its extreme simplicity, the method is transferable to complex carbon and hydrocarbon systems. The determination of equilibrium geometries, total energies, and vibrational modes of carbon clusters, hydrocarbon molecules, and solid-state modifications of carbon yield results showing an overall good agreement with more sophisticated methods.

Outline

- Introduction
  - Semi-empirical methods and Tight-Binding
  - The Paper
  - C_{60}
  - C_{20}
- Method
  - Simulated Annealing
  - Getting the Energy
- Results and Conclusions
  - From C_2 to C_{10}
  - C_{20}
  - C_{60}
- References

Semi-empirical methods

- **Energy calculation:** Empirical vs. Analytical (DFT, HF)
- Semi-empirical approximations:
  - Only valence electrons are considered
  - Uses just two-center integrals
  - Matrix elements are approximated by analytical functions of inter-atomic separation
  - Core-core Coulombic repulsion is replaced with a parameterized function

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Tight-Binding

- Features:
  - Simple and few parameters
  - Qualitative (and even quantitative) description of the system
  - Good transferability/complexity ratio and predictive power
  - Well suited for computational optimization
- Orthogonal TB:
- Non-orthogonal TB:

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- Orthogonal TB: $\mathbf{H}\Psi = E\Psi$
- Non-orthogonal TB: $\mathbf{H}\Psi = E\mathbf{S}\Psi$

Back to the Paper

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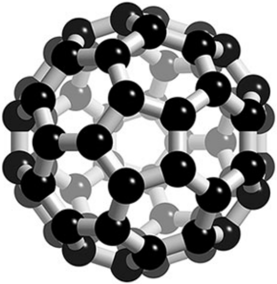
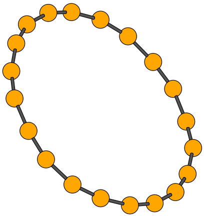
C_{60}

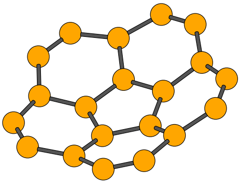


- Harold Kroto, Robert Curl and Richard Smalley, 1985

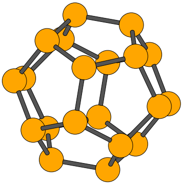
C_{20}



ring

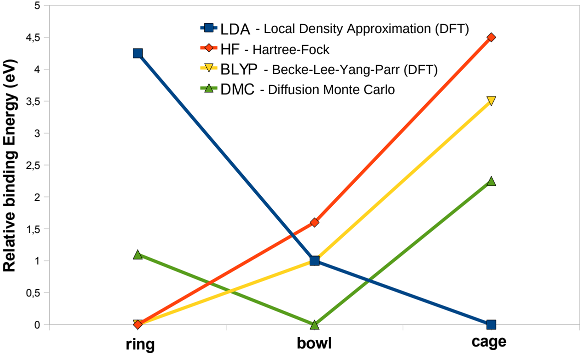


bowl



cage

C_{20}



http://altair.physics.ncsu.edu/projects/c20/c20.html

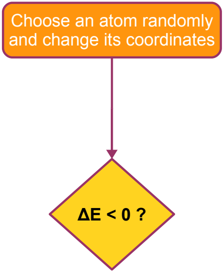
Method

Simulated Annealing

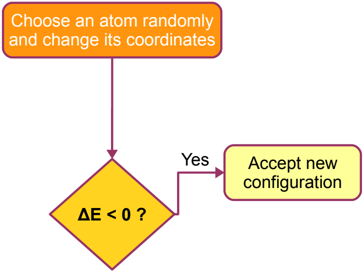
Simulated Annealing

Choose an atom randomly
and change its coordinates

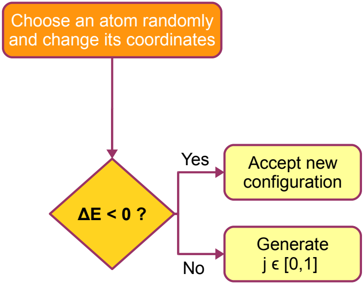
Simulated Annealing



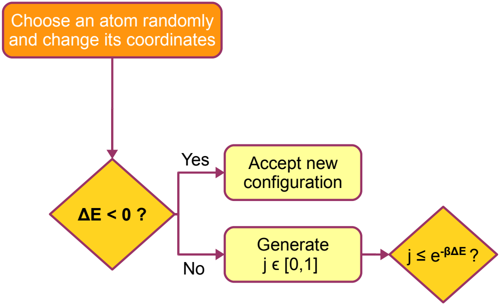
Simulated Annealing



Simulated Annealing



Simulated Annealing



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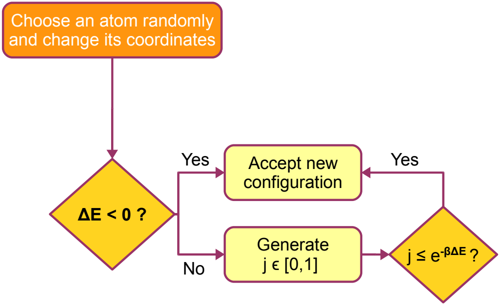
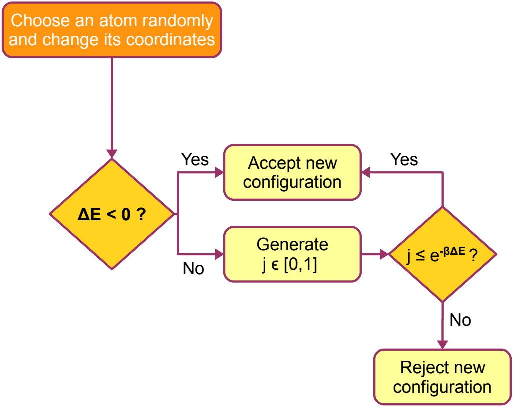


Simulated Annealing



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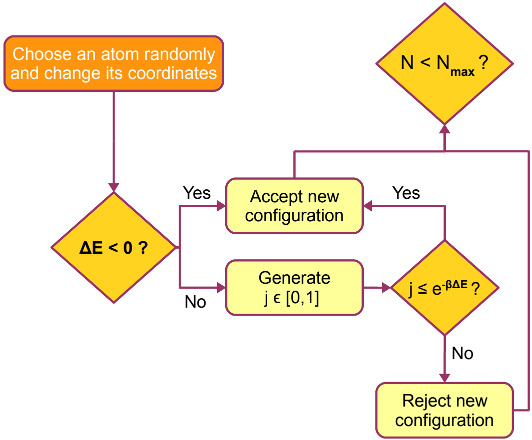

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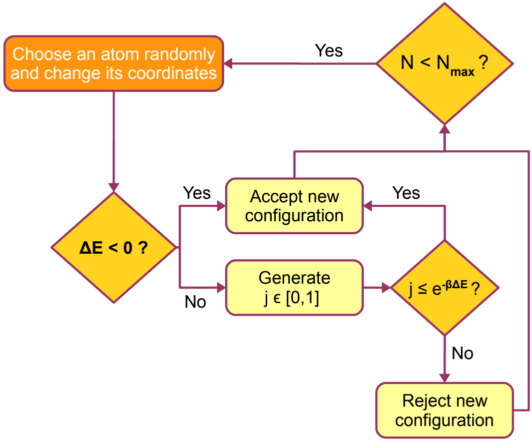

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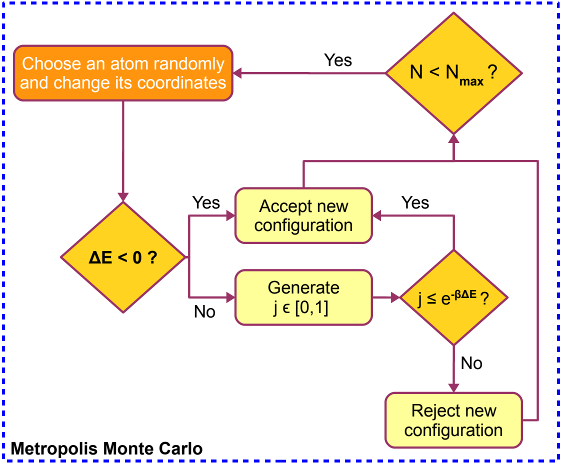
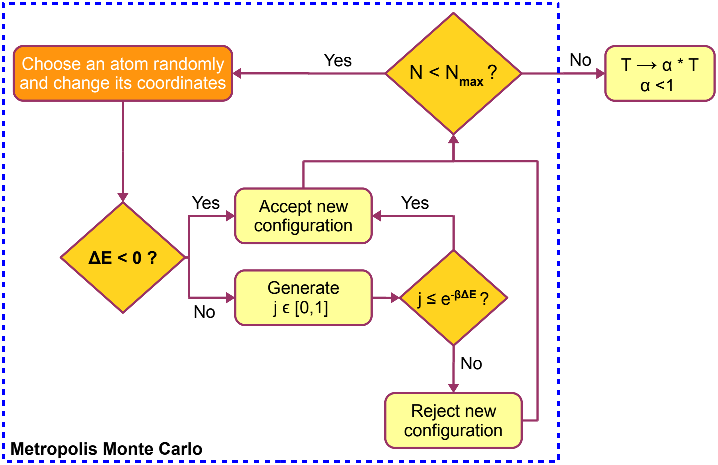


Simulated Annealing



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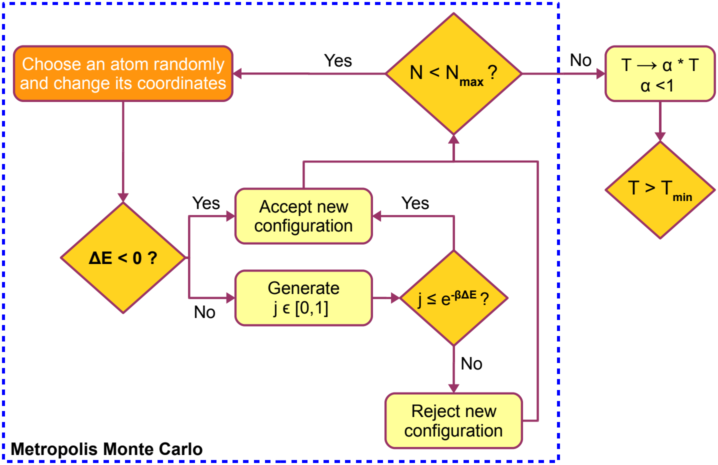

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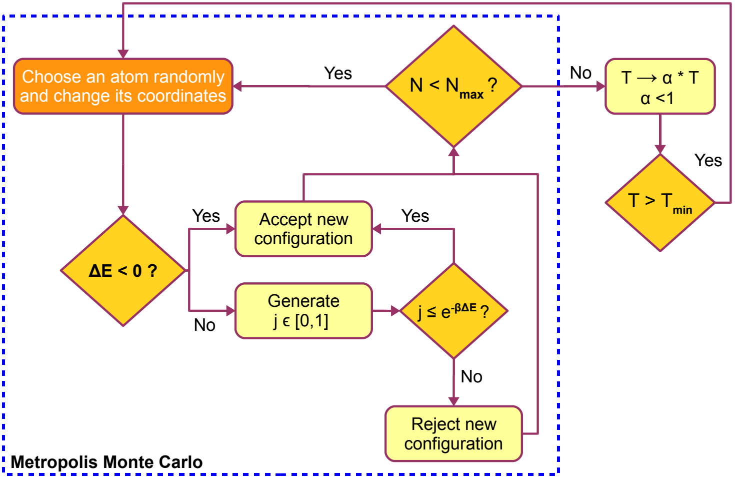

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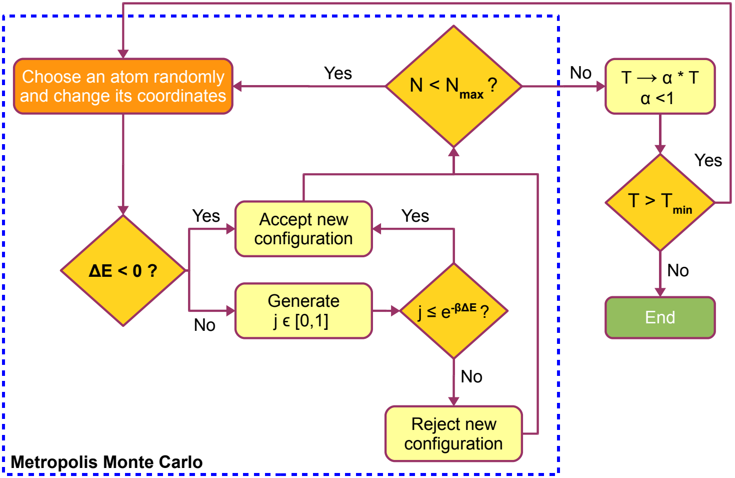
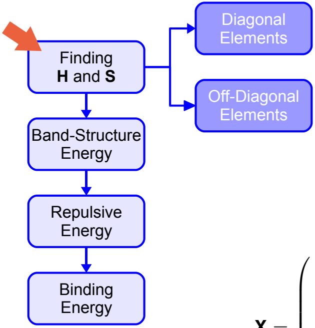


Getting the Energy



Overlap Matrix:

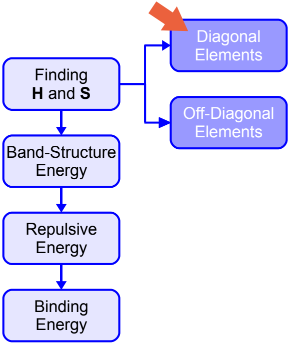
$$\mathbf{S}_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$$

Hamiltonian Matrix:

$$\mathbf{H}_{\mu\nu} = \langle \phi_\mu | \mathbf{H} | \phi_\nu \rangle$$

$$\mathbf{X} = \begin{array}{c} \overbrace{\begin{array}{cccc} s & p_x & p_y & p_z \end{array}}^{\text{Atom 1}} \\ \begin{pmatrix} \mathbf{X}_{1s1s} & \mathbf{X}_{1s1p_x} & \mathbf{X}_{1s1p_y} & \mathbf{X}_{1s1p_z} & \cdots \\ \mathbf{X}_{1p_x1s} & \mathbf{X}_{1p_x1p_x} & \mathbf{X}_{1p_x1p_y} & \mathbf{X}_{1p_x1p_z} & \cdots \\ \mathbf{X}_{1p_y1s} & \mathbf{X}_{1p_y1p_x} & \cdots & \cdots & \cdots \\ \mathbf{X}_{1p_z1s} & \mathbf{X}_{1p_z1p_x} & \cdots & \cdots & \cdots \\ \mathbf{X}_{2s1s} & \mathbf{X}_{2s1p_x} & \cdots & \cdots & \cdots \\ \vdots & \vdots & & & \end{pmatrix} \end{array} \begin{array}{l} \left.\begin{array}{l} s \\ p_x \\ p_y \\ p_z \end{array}\right\rangle \text{Atom 1} \\ \\ \\ \end{array}$$

Getting the Energy

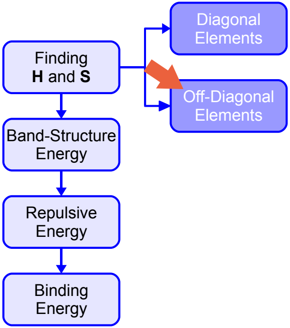


$$\mathbf{S}_{\mu\nu} = \int \phi_\mu \phi_\nu = 1, \qquad \mu = \nu$$

$$\mathbf{H}_{\mu\nu} = \int \phi_\mu \mathbf{H} \phi_\nu = \begin{cases} \varepsilon_s & \mu = \nu = s \\ \varepsilon_p & \mu = \nu = p \end{cases}$$

- $\varepsilon_s = -0.50097 E_h$
- $\varepsilon_{p_x} = \varepsilon_{p_y} = \varepsilon_{p_z} = -0.19930 E_h$

Getting the Energy

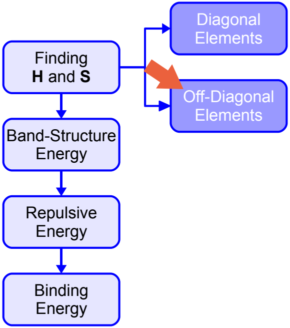


Matrix	c_1	c_2	c_3	c_4	c_5
(a,b)	c_6	c_7	c_8	c_9	c_{10}
$H_{ss\sigma}$	-0,4663805	0,3528951	-0,1402985	0,0050519	0,0269723
(1,0;7,0)	-0,0158810	0,0036716	0,0010301	-0,0015546	0,0008601
$H_{sp\sigma}$	0,3395418	-0,2250358	0,0298224	0,0653476	-0,0605786
(1,0;7,0)	0,0298962	-0,0099609	0,0020609	0,0001264	-0,0003381
$H_{pp\sigma}$	0,2422701	-0,1315258	-0,0372696	0,0942352	-0,0673216
(1,0;7,0)	0,0316900	-0,0117293	0,0033519	-0,0004838	-0,0000906
$H_{pp\pi}$	-0,3793837	0,3204470	-0,1956799	0,0883986	-0,0300733
(1,0;7,0)	0,0074465	-0,0008563	-0,0004453	0,0003842	-0,0001855
$S_{ss\sigma}$	0,4728644	-0,3661623	0,1594782	-0,0204934	-0,0170732
(1,0;7,0)	0,0096695	-0,0007135	-0,0013826	0,0007849	-0,0002005
$S_{sp\sigma}$	-0,3662838	0,2490285	-0,0431248	-0,0584391	0,0492775
(1,0;7,0)	-0,0150447	-0,0010758	0,0027734	-0,0011214	0,0002303
$S_{pp\sigma}$	0,3715732	-0,3070867	0,1707304	-0,0581555	0,0061645
(1,0;7,0)	0,0051460	-0,0032776	0,0009119	-0,0001265	-0,0000227
$S_{pp\pi}$	-0,1359608	0,0226235	0,1406440	-0,1573794	0,0753818
(1,0;7,0)	-0,0108677	-0,0075444	0,0051533	-0,0013747	0,0000751

$$V(\mathbf{r}) = \sum_{m=1}^{10} c_m T_{m-1}(y) - \frac{c_1}{2}, \; y = \frac{r - \frac{b+a}{2}}{\frac{b-a}{2}}$$

$$T_0(x) = 1, \quad T_1(x) = x, \quad T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$$

Getting the Energy



$\mathbf{H}_{ss\sigma}(r)$ $\mathbf{H}_{sp\sigma}(r)$ $\mathbf{H}_{pp\sigma}(r)$
$\mathbf{H}_{pp\pi}(r)$ $\mathbf{S}_{ss\sigma}(r)$ $\mathbf{S}_{sp\sigma}(r)$
$\mathbf{S}_{pp\sigma}(r)$ $\mathbf{S}_{pp\pi}(r)$

$\{s, p_x, p_y, p_z\}$

Slater-Koster table:

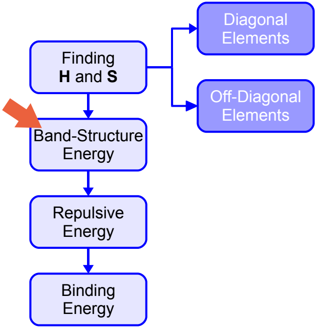
$$\mathbf{X}_{ss} = \mathbf{X}_{ss\sigma}$$
$$\mathbf{X}_{sp_i} = c_i \mathbf{X}_{sp\sigma}$$
$$\mathbf{X}_{p_i,p_i} = c_i^2 \mathbf{X}_{pp\sigma} + (1 - c_i^2)\mathbf{X}_{pp\pi}$$
$$\mathbf{X}_{p_i,p_j} = c_i c_j (\mathbf{X}_{pp\sigma} - \mathbf{X}_{pp\pi}) \qquad (i \neq j)$$

$x_1 = x,\ x_2 = y,\ x_3 = z$

$c_i = \frac{x_{ib} - x_{ia}}{r_{ab}}$

$\mathbf{X}_{sp\sigma} = -\mathbf{X}_{ps\sigma}$

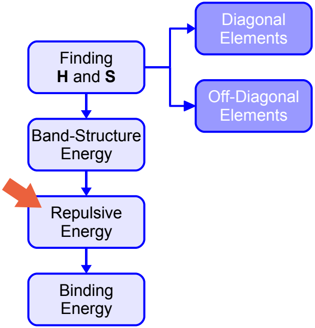
Getting the Energy



$$\mathbf{H}\Psi_i - \varepsilon_i \mathbf{S}\Psi_i = 0$$

$$E_{BS} = \sum_{i=1}^{2N} 2\varepsilon_i .$$

Getting the Energy



V_{rep}	c_1	c_2	c_3	c_4	c_5
(a,b)	c_6	c_7	c_8	c_9	c_{10}
V_{rep}	2,2681036	-1,9157174	1,1677745	-0,5171036	0,1529242
(1,0;4,10)	-0,0219294	-0,0000002	-0,0000001	-0,0000005	0,0000009

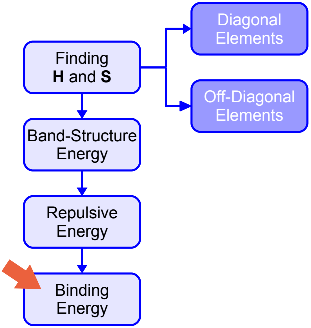
$$V(\mathbf{r}) = \sum_{m=1}^{10} c_m T_{m-1}(y) - \frac{c_1}{2}$$

$$y = \frac{r - \frac{b+a}{2}}{\frac{b-a}{2}}$$

$$T_0(x) = 1 \qquad T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$$
$$T_1(x) = x$$

$$E_{rep} = \sum_{k=0}^{N-2} \sum_{l=k+1}^{N-1} V_{rep}(r_{kl}).$$

Getting the Energy

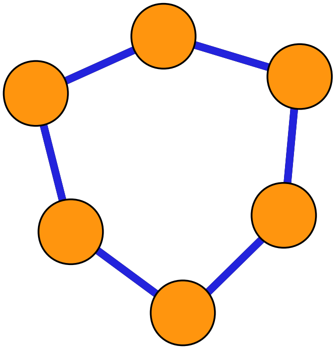


Binding Energy:

$$\sum_{i=1}^{2N} 2\varepsilon_i + \sum_{k=0}^{N-2} \sum_{l=k+1}^{N-1} V_{rep}(r_{kl}) - 2N(\varepsilon_s + \varepsilon_p)$$

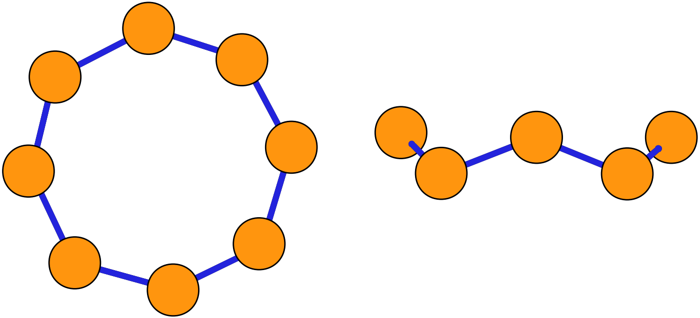
Results and Conclusions

From C_2 to C_{10}



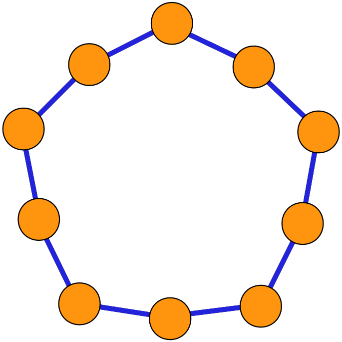
Isomer C_6 in D_{3h} configuration

From C_2 to C_{10}

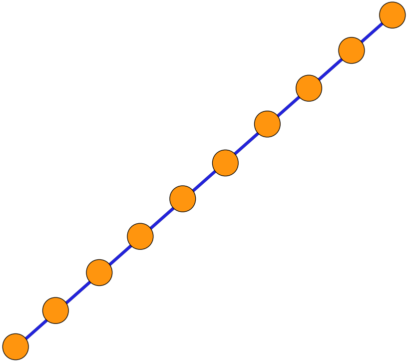


Isomer C_8 in C_{8v} configuration (top and side view)

From C_2 to C_{10}



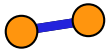
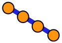
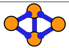
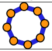
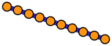
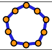
Isomer C_{10} in D_{5h} configuration



Isomer C_{10} in $D_{\infty h}$ configuration

From C_2 to C_{10}

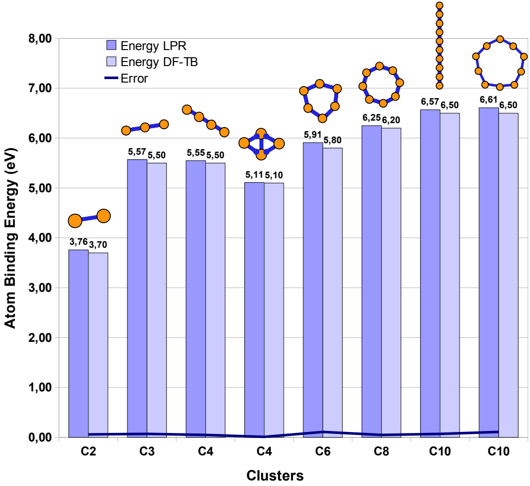
Comparing our results with theirs

Cluster	Method	Simmetry	Configuration	Bond length (Å)	Angle (°)	E^{at}_{bind} (eV)
C_2	LPR	$D_{\infty h}$		1,245	180,0	3,76
	DF-TB			1,244	180,0	3,70
C_3	LPR	$D_{\infty h}$		1,288	180,0	5,57
	DF-TB			1,288	180,0	5,50
C_4	LPR	$D_{\infty h}$		1,287 1,319	180,0	5,55
	DF-TB			1,288 1,321	180,0	5,50
	LPR	D_{2h}		1,442	70,7 109,3	5,11
	DF-TB			1,443	70,7	5,10
C_6	LPR	D_{3h}		1,346	100,1 139,9	5,91
	DF-TB			1,346	100,1	5,80
C_8	LPR	C_{8v}		1,347	120,2	6,25
	DF-TB			1,348	120,3	6,20
C_{10}	LPR	$D_{\infty h}$		1,247 1,342 1,270 1,309 1,284	180,0	6,57
	DF-TB			1,246 1,345 1,269 1,311 1,284	180,0	6,50
	LPR	D_{5h}		1,312	124,5 163,5	6,61
	DF-TB			1,311	125,3	6,50

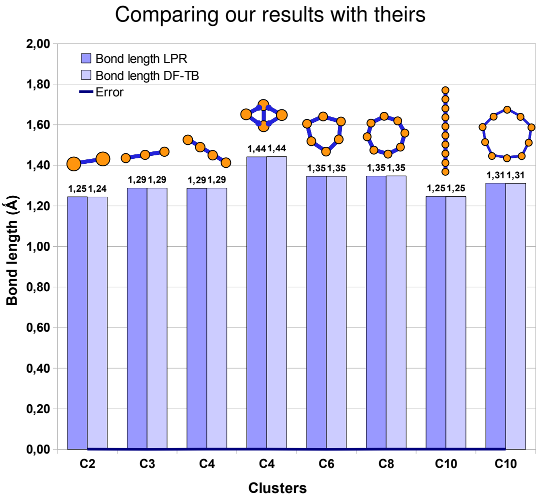
DF-TB - Nonorthogonal DF-based TB
LPR - Lara Pedro Rui

From C_2 to C_{10}

Comparing our results with theirs

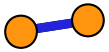
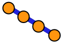
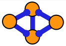
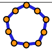


From C_2 to C_{10}



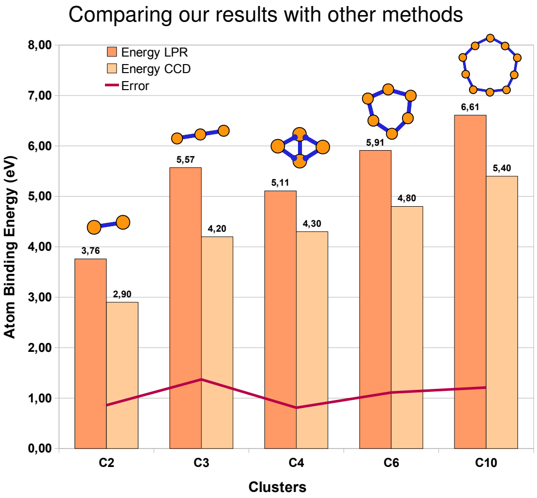
From C_2 to C_{10}

Comparing our results with other methods

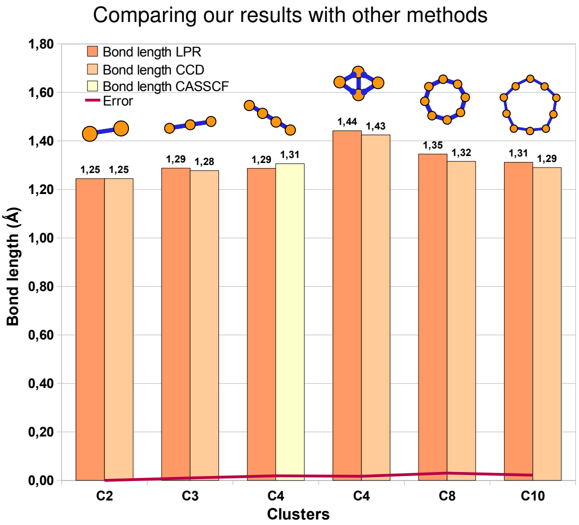
Cluster	Method	Simmetry	Configuration	Bond length (Å)	Angle (°)	E^{at}_{bind} (eV)
C_2	LPR	$D_{\infty h}$		1,245	180,0	3,76
	CCD			1,245	180,0	2,90
C_3	LPR	$D_{\infty h}$		1,288	180,0	5,57
	CCD			1,278	180,0	4,20
C_4	LPR	$D_{\infty h}$		1,287 1,319	180,0	5,55
	CASSCF			1,306 1,287	180,0	-
	LPR	D_{2h}		1,442	70,7 109,3	5,11
	CCD			1,425	61,5	4,30
C_6	LPR	D_{3h}		1,346	100,1 139,9	5,91
	CCD			1,316	90,4	4,80
C_{10}	LPR	D_{5h}		1,312	124,5 163,5	6,61
	CCD			1,290	119,4	5,40

CCD - Coupled-Cluster Doubles
CASSCF - Complete Active Space Self-Consistent Field
LPR - Lara Pedro Rui

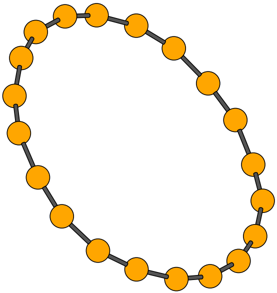
From C_2 to C_{10}



From C_2 to C_{10}



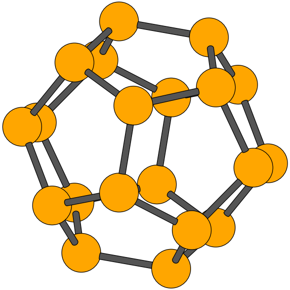
C_{20}



Isomer C_{20} in ring configuration

Energy -7.96 eV

Bond lenght 1.24Å and 1.37Å



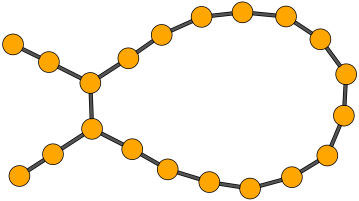
Isomer C_{20} in cage configuration

Energy -7.91 eV

Bond lenght 1.44Å

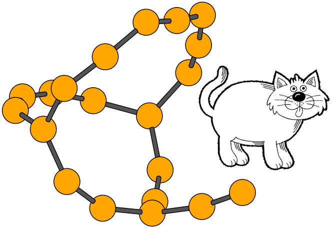
Angle 109°

C_{20} aberrations



Isomer C_{20} in 'fish' configuration

Energy -7.95 eV



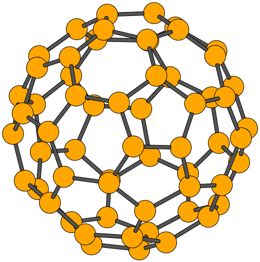
Isomer C_{20} in 'opened-by-cat cage' configuration

Energy -7.86 eV

C_{60}

Comparing bond lengths of C_{60}

Method	Bond length (Å)
LPR	1,38 1,46
DF-TB	1,397 1,449
LDA	1,398 1,450
Experimental	1,402 1,462



Counterfeit C_{60}
in cage configuration

Energy -8.60 eV (-8.85 eV)

Bond lenght 1.38 Å (1.397 Å)
and 1.46 Å (1.449 Å)

References

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- R. O. Jones, *Density functional study of carbon clusters C2n - Structure and bonding in the neutral clusters*, J. Chem. Phys. **110**, 5189 (1999).
- R. M. Martin, *Electronic Structure - Basic Theory and Practical Methods*, Cambridge University Press, 2004 (1a Edição).
- Arkady Krasheninnikov, *Introduction to electronic structure simulations - Lecture 5 - Semi-empirical and tight-binding methods*, University of Helsinki and Helsinki University of Technology, `http://tfy.tkk.fi/~asf/physics/lectures/PDF/lect5.pdf` (2008).

"Never discourage anyone who continually makes progress, no matter how slow."

Plato (427BC - 347BC)