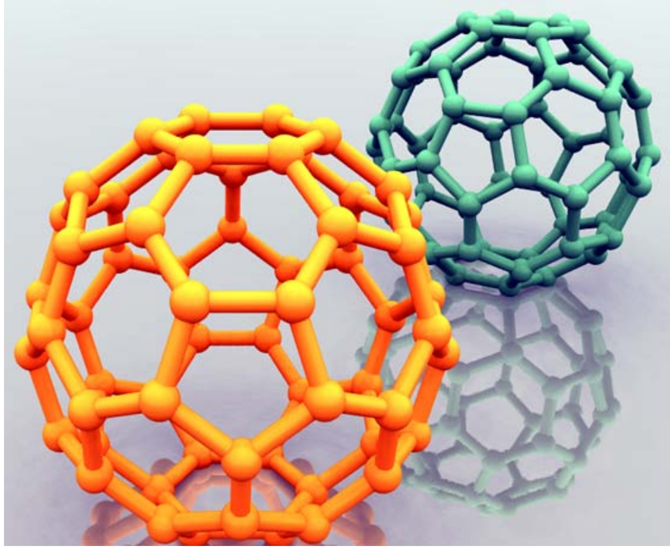
Graph Theoretic Approaches to Atomic Vibrations in Fullerenes



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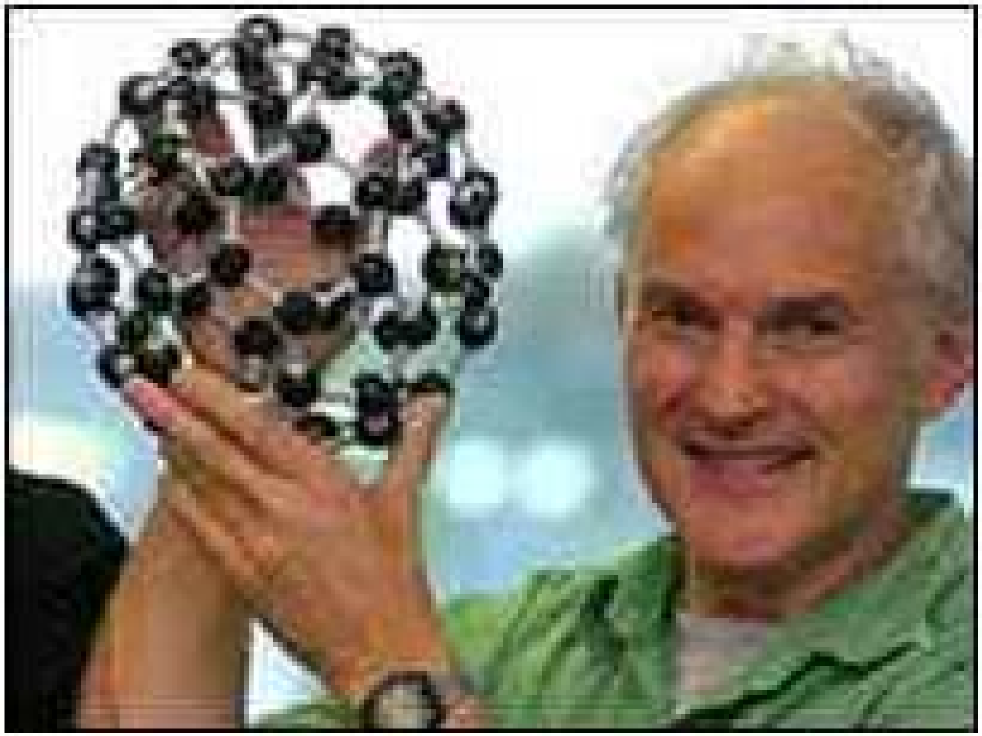
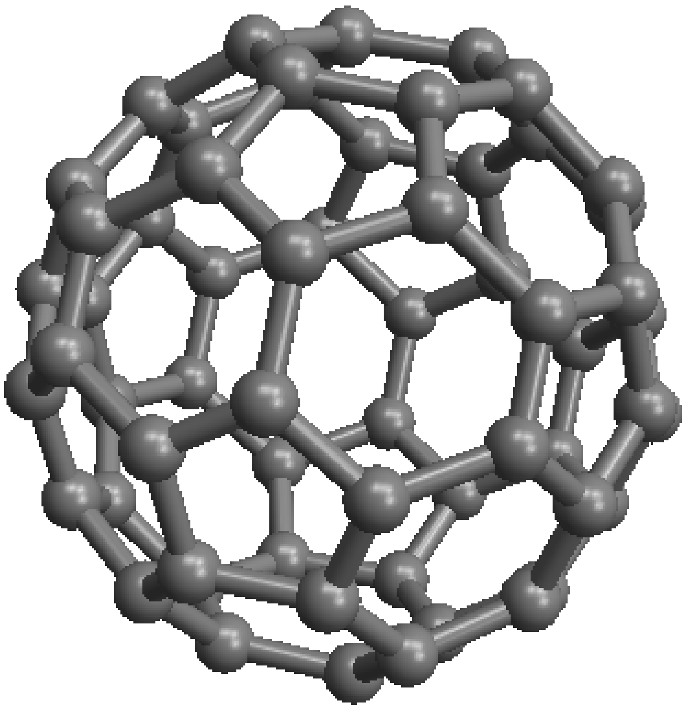
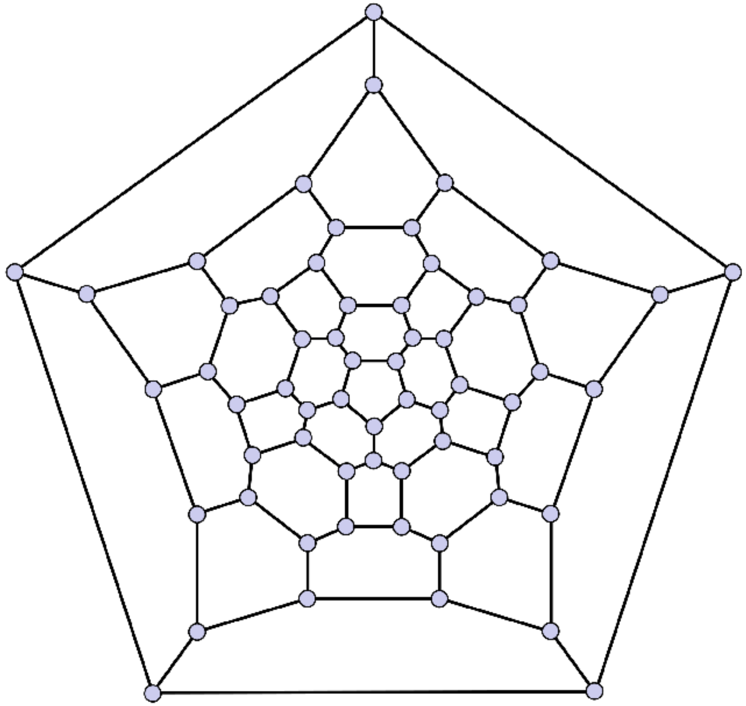


FULLERENES

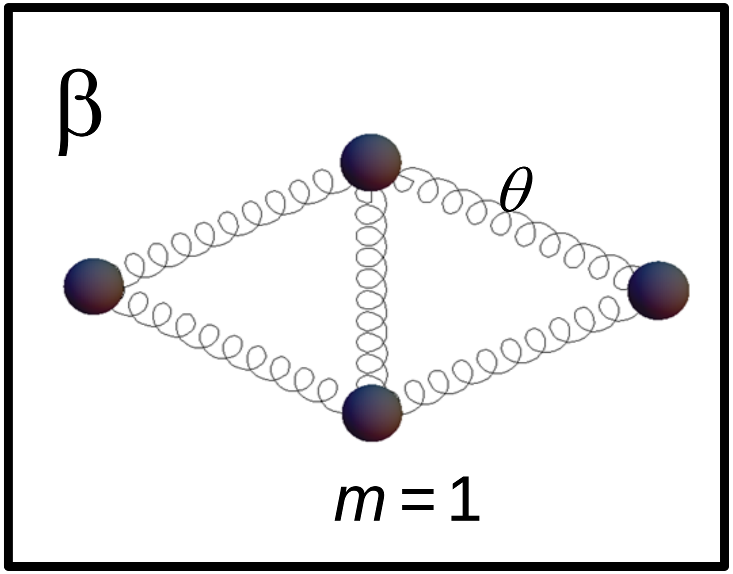




“A **fullerene**, by **definition**, is a closed convex cage molecule containing only hexagonal and pentagonal faces.”

R. E. Smalley

CLASSICAL MECHANICS PICTURE

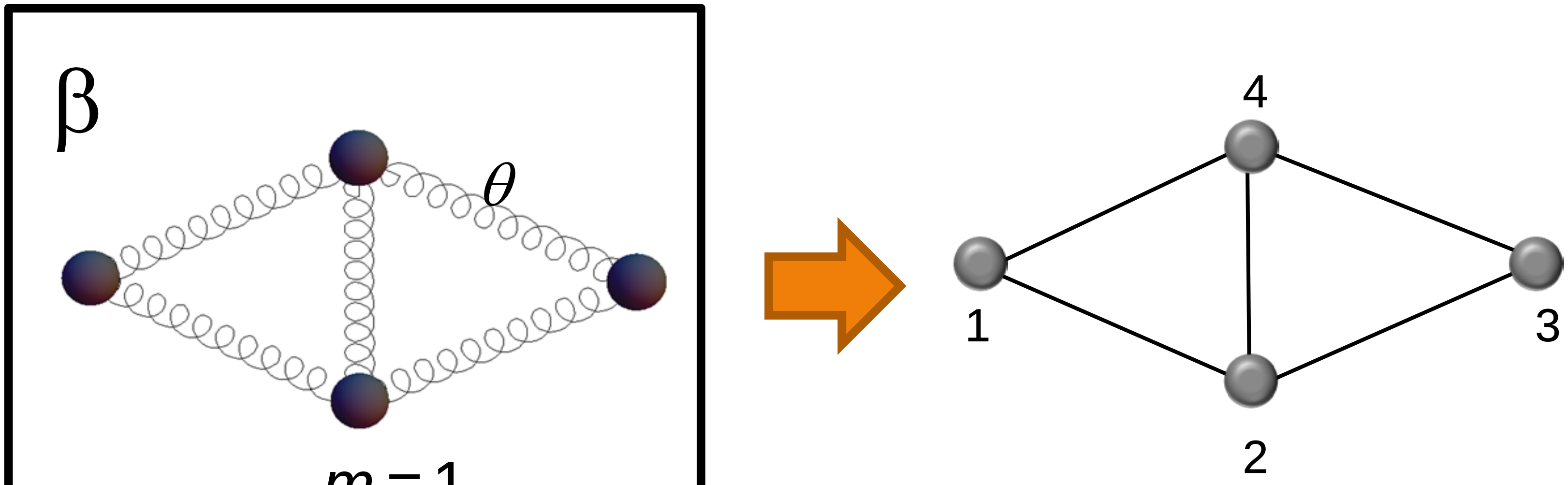


Equation of motion:

$$\mathbf{M}\ddot{\mathbf{x}} + \mathbf{L}\mathbf{x} = 0 \qquad (1)$$

Potential energy:

$$V(\vec{x}) = \frac{\theta}{2}\vec{x}^{T}\mathbf{L}\vec{x} \qquad (2)$$



Edge weight: βθ

$$\mathbf{L} = \mathbf{D} - \mathbf{A} = \begin{pmatrix} 2 & -1 & 0 & -1 \\ -1 & 3 & -1 & -1 \\ 0 & -1 & 2 & -1 \\ -1 & -1 & -1 & 3 \end{pmatrix}$$

Mean atomic displacement:

$$\Delta x_i \equiv \sqrt{\left\langle {x_i}^2 \right\rangle} = \sqrt{\int {x_i}^2 P(\vec{x}) d\vec{x}} \qquad (3)$$

Displacement correlation:

$$\left\langle x_i x_j \right\rangle = \int x_i x_j P(\vec{x}) d\vec{x} \qquad (4)$$

Using the spectral decomposition of the Laplacian and some algebra:

$$\begin{aligned} Z &= \int d\vec{y} \exp\left(-\frac{\beta\theta}{2} \vec{y}^T \mathbf{M} \vec{y} \right) \\ &= \prod_{\alpha=1}^{n} \int_{-\infty}^{+\infty} dy_\alpha \exp\left(-\frac{\beta\theta}{2} \mu_\alpha {y_\alpha}^2 \right). \end{aligned} \qquad (5)$$

where:

$$0 = \mu_1 < \mu_2 \leq \cdots \leq \mu_n$$

Because $\mu_1 = 0$ we modify the partition function:

$$\tilde{Z} = \prod_{\alpha=2}^{n} \int_{-\infty}^{+\infty} dy_\alpha \exp\left(-\frac{\beta\theta}{2} \mu_\alpha y_\alpha{}^2 \right) = \prod_{\alpha=2}^{n} \sqrt{\frac{2\pi}{\beta\theta\mu_\alpha}}. \qquad (6)$$

and transform the RHS of (3):

$$\tilde{I}_i \equiv \sum_{\nu=2}^{n} \int_{-\infty}^{+\infty} dy_\nu (U_{i\nu} y_\nu)^2 \exp\left(-\frac{\beta\theta}{2} \mu_\nu y_\nu{}^2 \right) \times \prod_{\substack{\alpha=2 \\ \alpha\neq\nu}}^{n} \int_{-\infty}^{+\infty} dy_\alpha \exp\left(-\frac{\beta\theta}{2} \mu_\alpha y_\alpha{}^2 \right)$$

$$= \sum_{\nu=2}^{n} \frac{U_{i\nu}{}^2}{2} \sqrt{\frac{8\pi}{(\beta\theta\mu_\nu)^3}} \times \prod_{\substack{\alpha=2 \\ \alpha\neq\nu}}^{n} \sqrt{\frac{2\pi}{\beta\theta\mu_\nu}}$$

$$= \tilde{Z} \times \sum_{\nu=2}^{n} \frac{U_{i\nu}{}^2}{\beta\theta\mu_\nu}. \qquad (7)$$

The atomic displacement is given by:

$$\Delta x_i \equiv \sqrt{\left\langle {x_i}^2 \right\rangle} = \sqrt{\frac{\tilde{I}_i}{\tilde{Z}}} = \sqrt{\sum_{\nu=2}^{n} \frac{{U_{i\nu}}^2}{\beta\theta\mu_\nu}}, \qquad (8)$$

or, equivalently as:

$$\left(\Delta x_i\right)^2 = \frac{1}{\beta\theta}\left(\mathbf{L}^+\right)_{ii} \qquad (9)$$

where $\mathbf{L}^+$ is the *Moore-Penrose* generalised inverse of the *Laplacian*.

Estrada, E., Hatano, N. *Chem. Phys. Lett*. 486 **2010**, 166.

The displacement correlation is:

$$\langle x_i x_j \rangle = \sum_{\nu=2}^{n} \frac{U_{i\nu} U_{j\nu}}{\beta\theta\lambda_\nu} = \frac{1}{\beta\theta} \left(\mathbf{L}^{+} \right)_{ij} \qquad (10)$$

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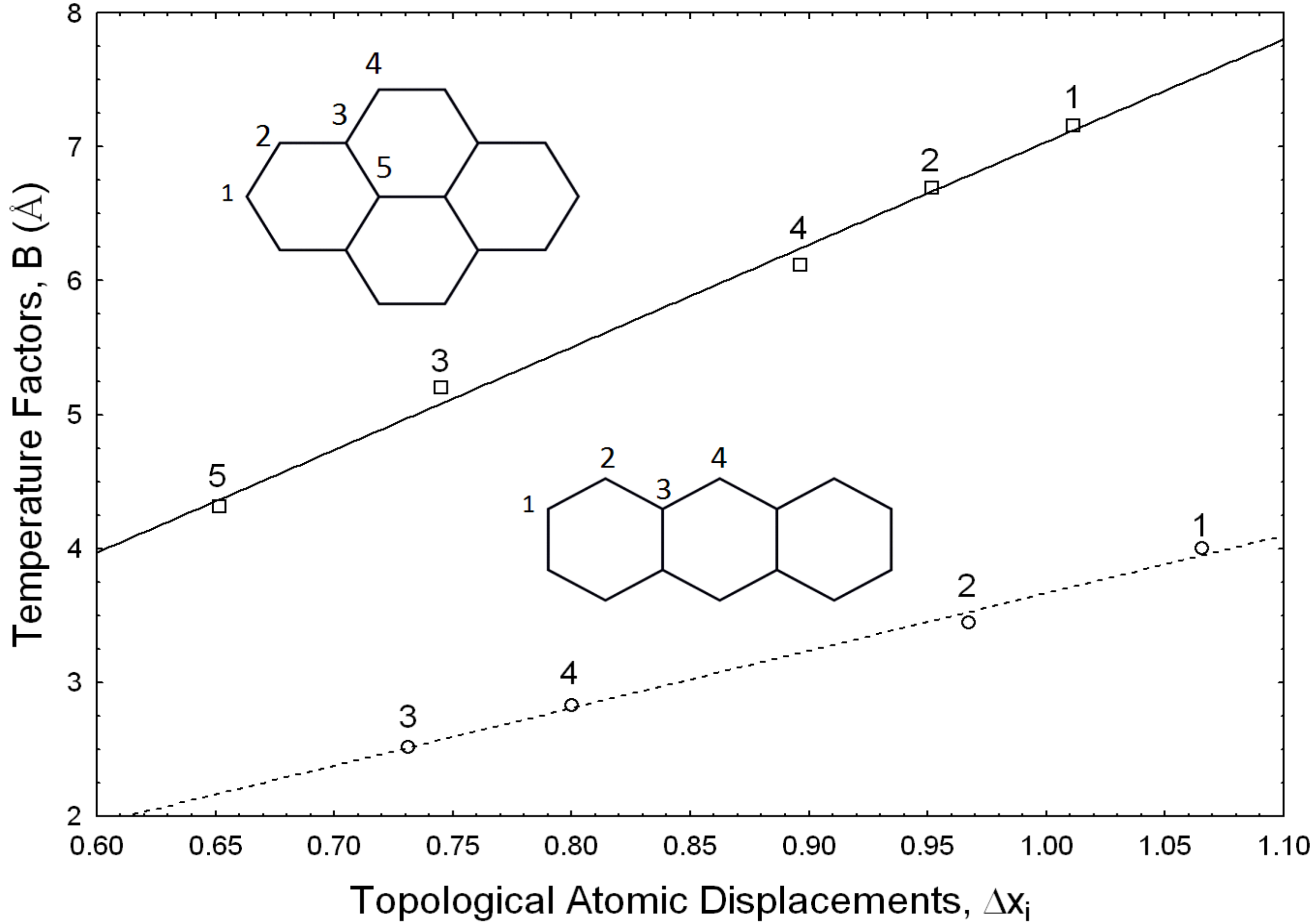
Atomic Displacements: Theory vs. Experiment



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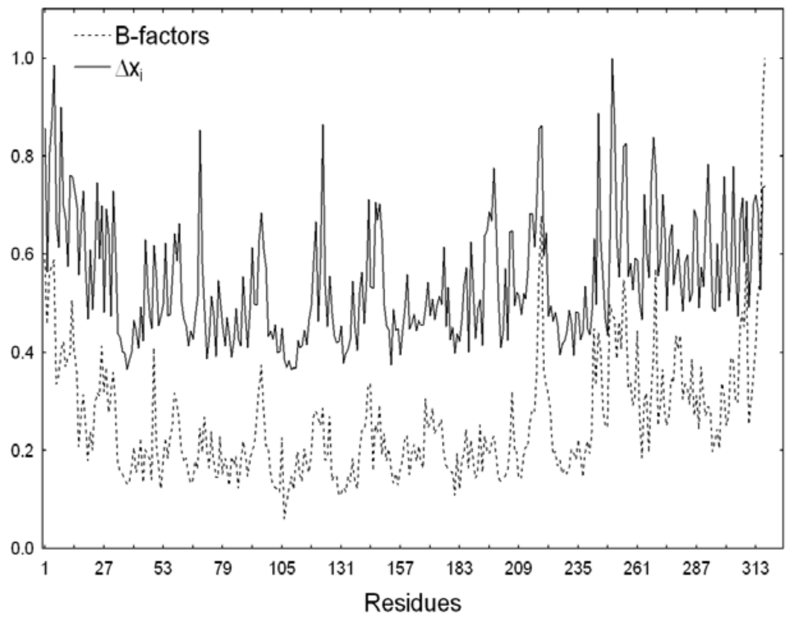
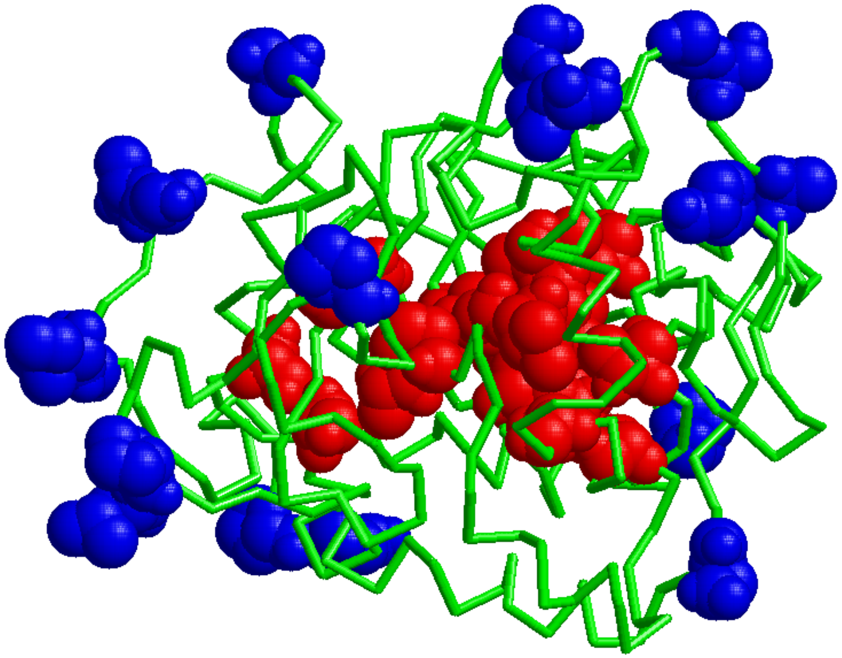
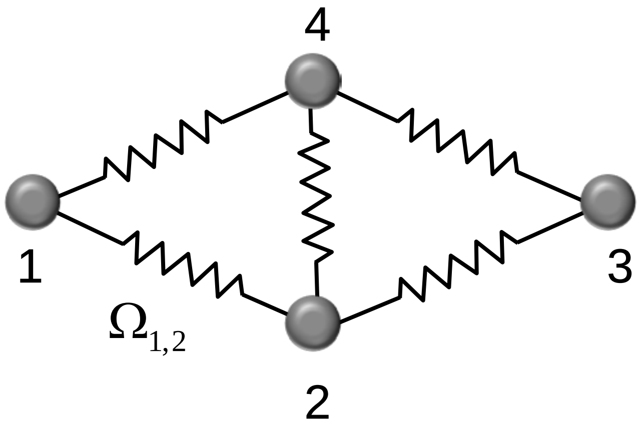
Atomic Displacements: Theory vs. Experiment





Estrada, E., Hatano, N. *Chem. Phys. Lett*. 486 **2010**, 166.

ELECTRICAL NETWORK PICTURE



Effective resistance:

$$\Omega_{1,2} = \left(\mathbf{L}^{+}\right)_{1,1} + \left(\mathbf{L}^{+}\right)_{2,2} - 2\left(\mathbf{L}^{+}\right)_{1,2}$$

Kirchhoff index:

$$Kf\left(G\right) = \frac{1}{2}\sum_{i}\sum_{j}\Omega_{i,j} = \sum_{i} R_i$$

$$R_i = \sum_{j \in V(G)} \Omega_{i,j}$$

Klein, D.J. , Randić, M. *J. Math. Chem*. **12** (1993) 81.

Atomic displacements and Effective resistance:

$$\left(\Delta x_i\right)^2 = \left(\mathbf{L}^+\right)_{ii} = \frac{1}{n}\left(R_i - \frac{Kf}{n}\right) \quad (11)$$

$$\left\langle x_i x_j \right\rangle = \left(\mathbf{L}^+\right)_{ij} = -\frac{1}{2}\left(\Omega_{ij} - \frac{1}{n}\left(R_i + R_j\right) + \frac{2Kf}{n^2}\right) \quad (12)$$

$$\left\langle V\left(\vec{x}\right)\right\rangle = \frac{1}{2n}\sum_{i=1}^{n} k_i R_i - \frac{1}{2n}\sum_{i,j\in E}\left(R_i + R_j - n\Omega_{ij}\right) \quad (13)$$

Estrada, E., Hatano, N. *Physica A*. 389 **2010**, 3648.

Or, if you prefer:

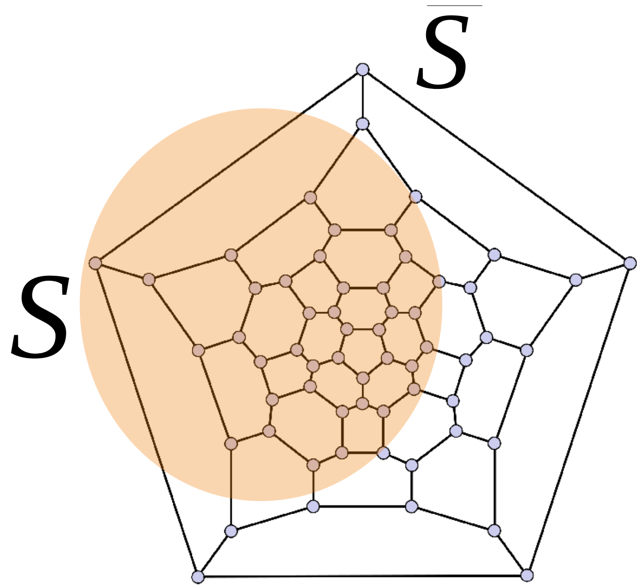
$$\Omega_{ij} = \left[\left(\Delta x_i \right)^2 + \left(\Delta x_j \right)^2 - 2 \left\langle x_i x_j \right\rangle \right] = \left\langle \left(x_i - x_j \right)^2 \right\rangle \qquad (14)$$

$$R_i = n \left(\Delta x_i \right)^2 + \sum_{i=1}^{n} \left(\Delta x_i \right)^2 = n \left[\left(\Delta x_i \right)^2 + \overline{\left(\Delta x \right)^2} \right] \qquad (15)$$

$$Kf = n \sum_{i=i}^{n} \left(\Delta x_i \right)^2 = n^2 \overline{\left(\Delta x \right)^2} \qquad (16)$$

Estrada, E., Hatano, N. *Physica A*. 389 **2010**, 3648.

ISOPERIMETRIC CONSTANT



Edge boundary of *S*:

$$\partial S = \{U \subset E \mid (u,v) \in U \Rightarrow u \in S, v \in \bar{S}\}$$

Set of edges connecting S to its complement

A graph *G* is said to have edge expansion (*K*, ϕ) if

$$|\partial(S)| \geq \phi |S|, \qquad \forall S \subseteq V \text{ with } |S| \leq K$$

$$\phi \equiv \min_{S:|S| \leq n/2} \frac{|\partial S|}{|S|}$$

For regular graphs, like fullerenes:

$$\mu_j = \lambda_1 - \lambda_j$$

where:

$$\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n$$

are the eigenvalues of the adjacency matrix.

Let $\beta\theta \equiv 1$ **and** $\Delta = \lambda_1 - \lambda_2$. **Then,**

$$(\Delta x_i)^2 = \frac{[\phi_2(i)]^2}{\Delta} + \sum_{j=3}^{n} \frac{\phi_j(i)^2}{\lambda_1 - \lambda_j}. \quad (17)$$

Estrada, E.; Hatano, N.; Matamala, A. R. **In the book**: Mathematics and Topology of Fullerenes, A. Graovac; O. Ori; F. Cataldo, Eds.; Springer, 2010 to appear.

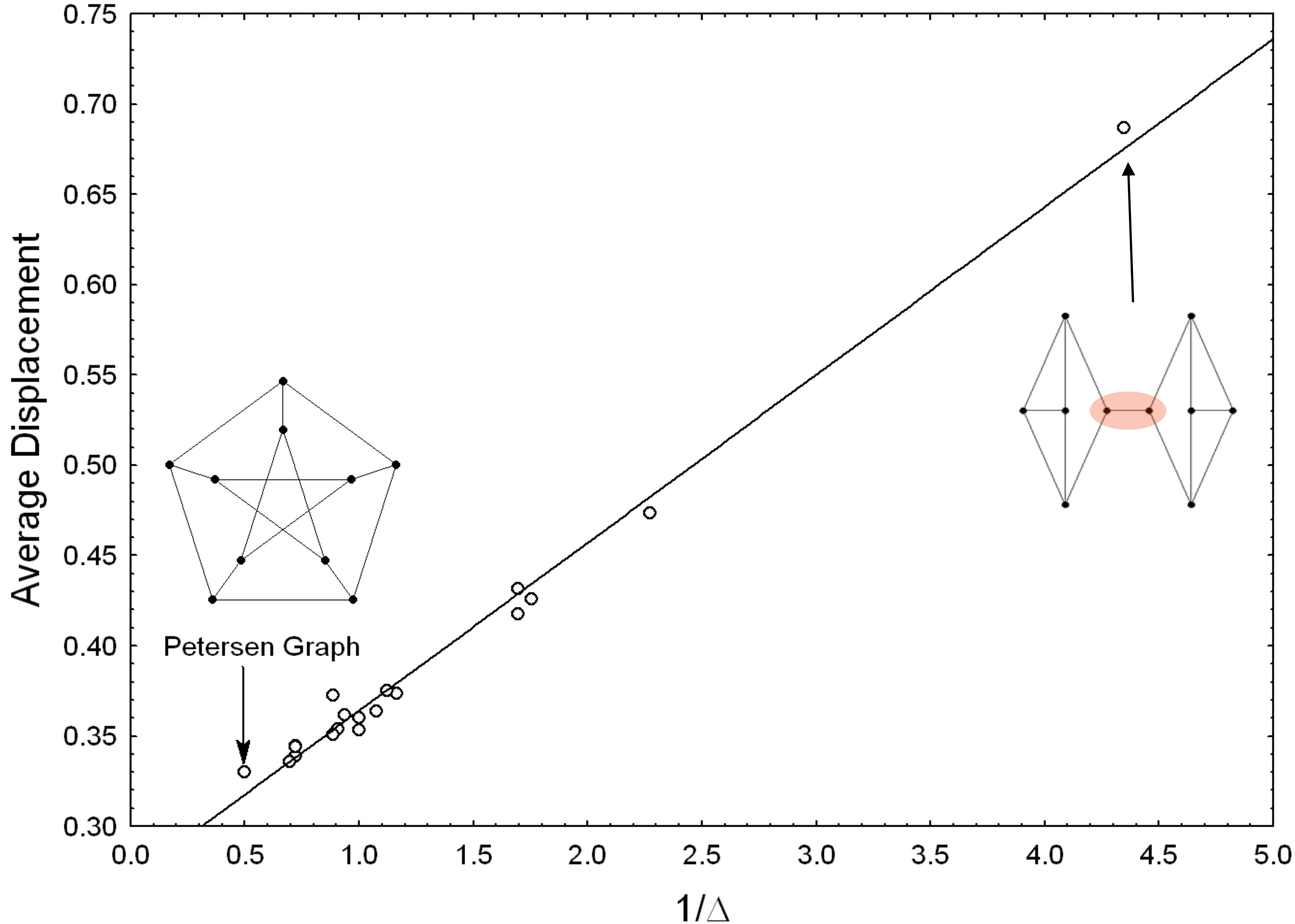
Thus:

$$\overline{(\Delta x_i)^2} = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{[\phi_2(i)]^2}{\Delta} + \sum_{j=3}^{n}\frac{\phi_j(i)^2}{\lambda_1 - \lambda_j}\right) = \frac{1}{n}\left(\frac{1}{\Delta} + \sum_{j=3}^{n}\frac{1}{\lambda_1 - \lambda_j}\right).$$

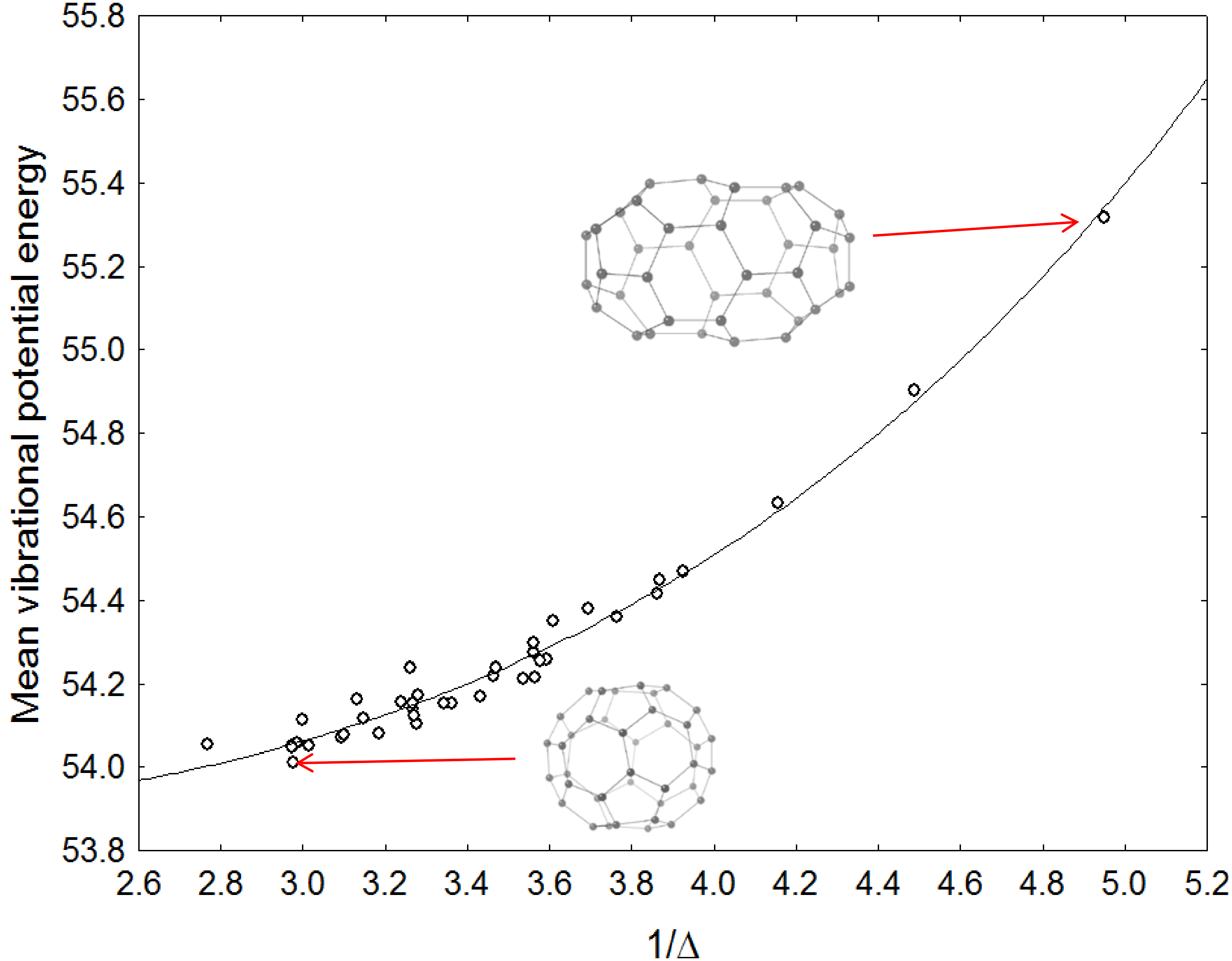
Among all graphs with *n* nodes, those having good expansion display the smallest topological displacements for their nodes.

Estrada, E.; Hatano, N.; Matamala, A. R. **In the book**: Mathematics and Topology of Fullerenes, A. Graovac; O. Ori; F. Cataldo, Eds.; Springer, 2010 to appear.

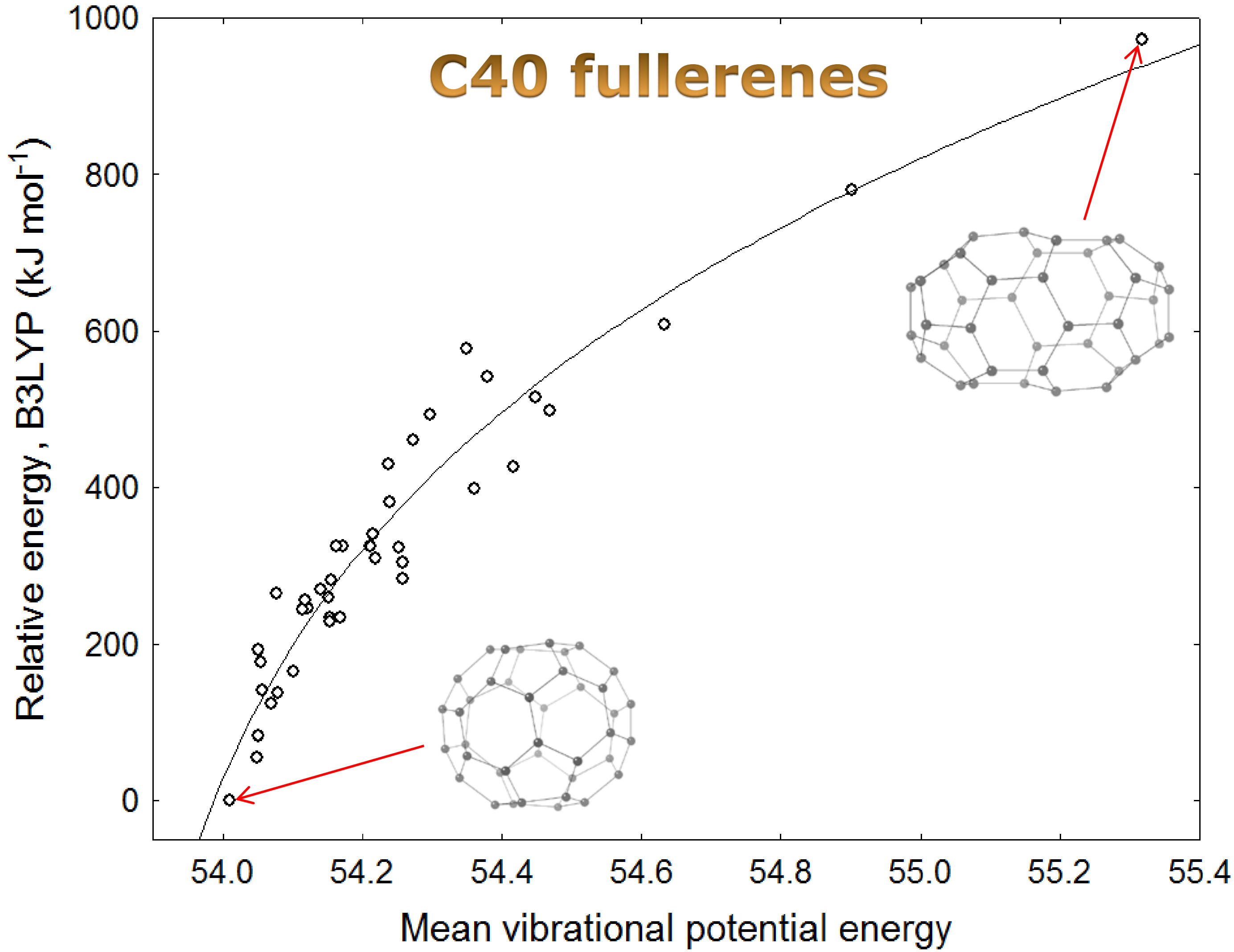
CUBIC GRAPHS WITH 8 NODES



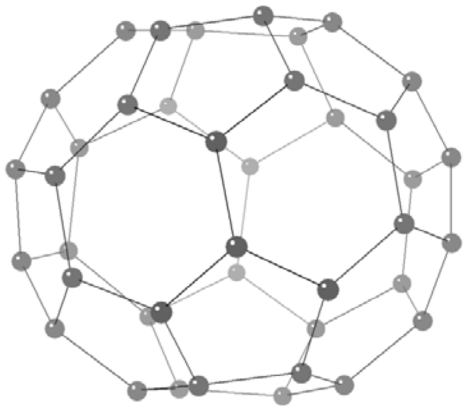
C40 FULLERENES



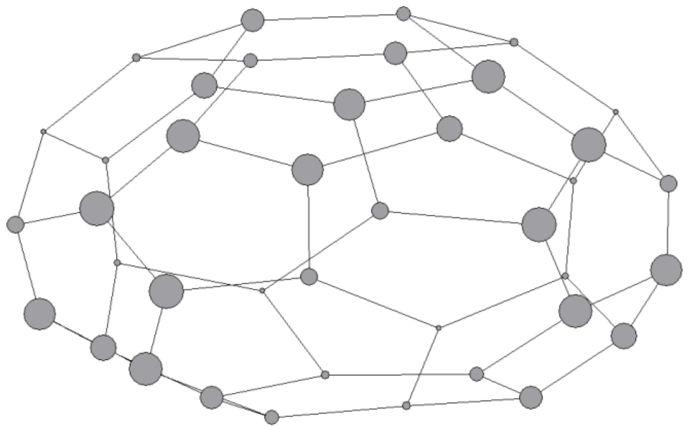
THE ENERGY CONNECTION

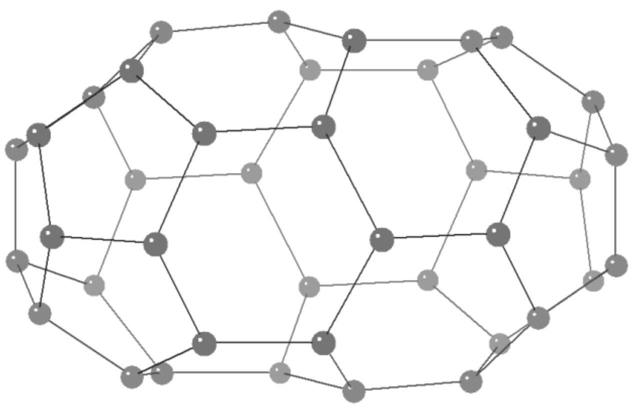


STABILITY & ATOMIC DISPLACEMENTS

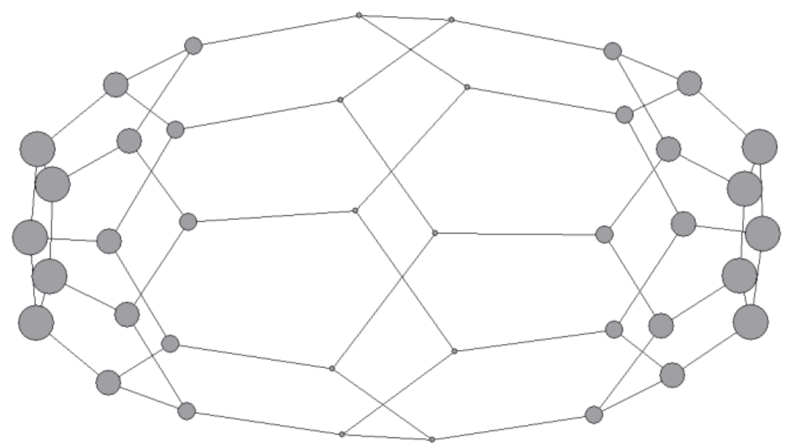


Most stable

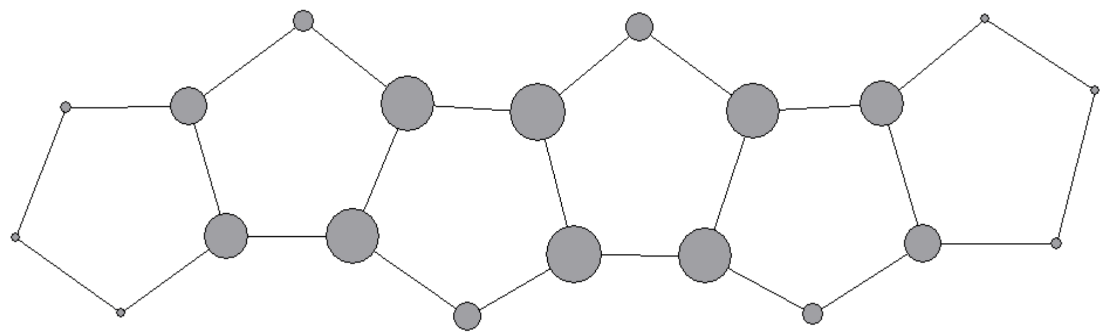




Least stable



DISPLACEMENT & PENTAGON ADJACENCY



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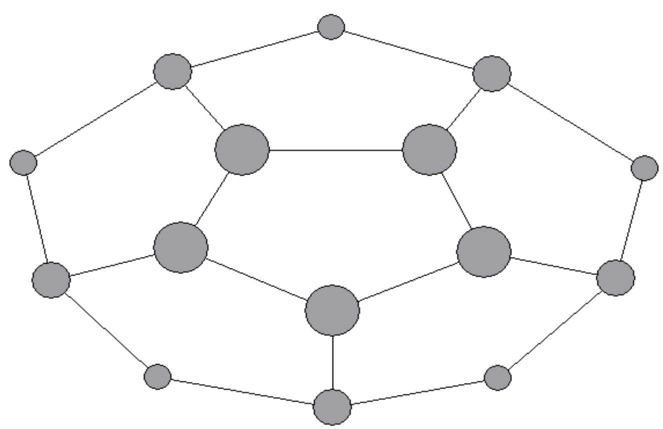

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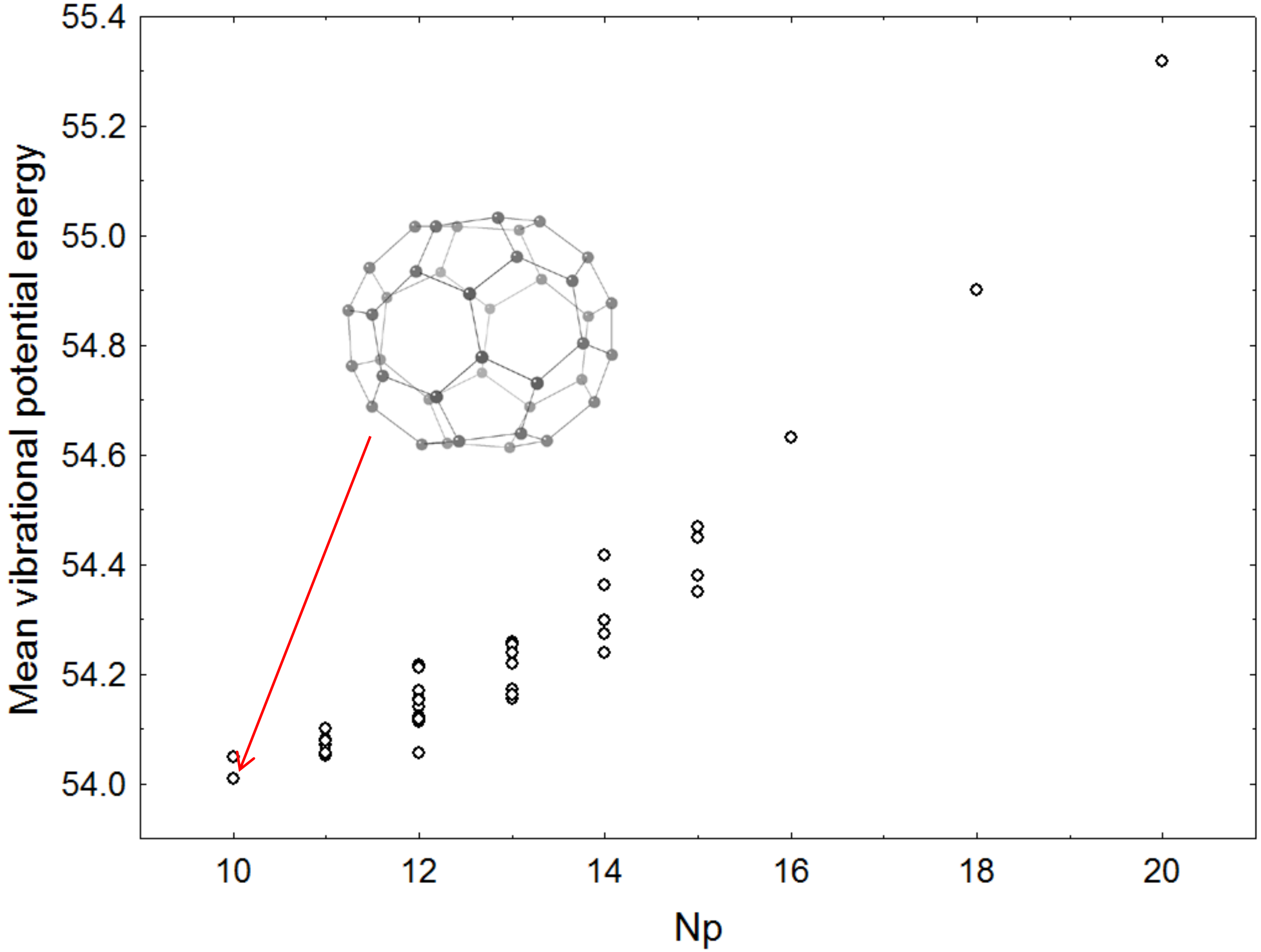
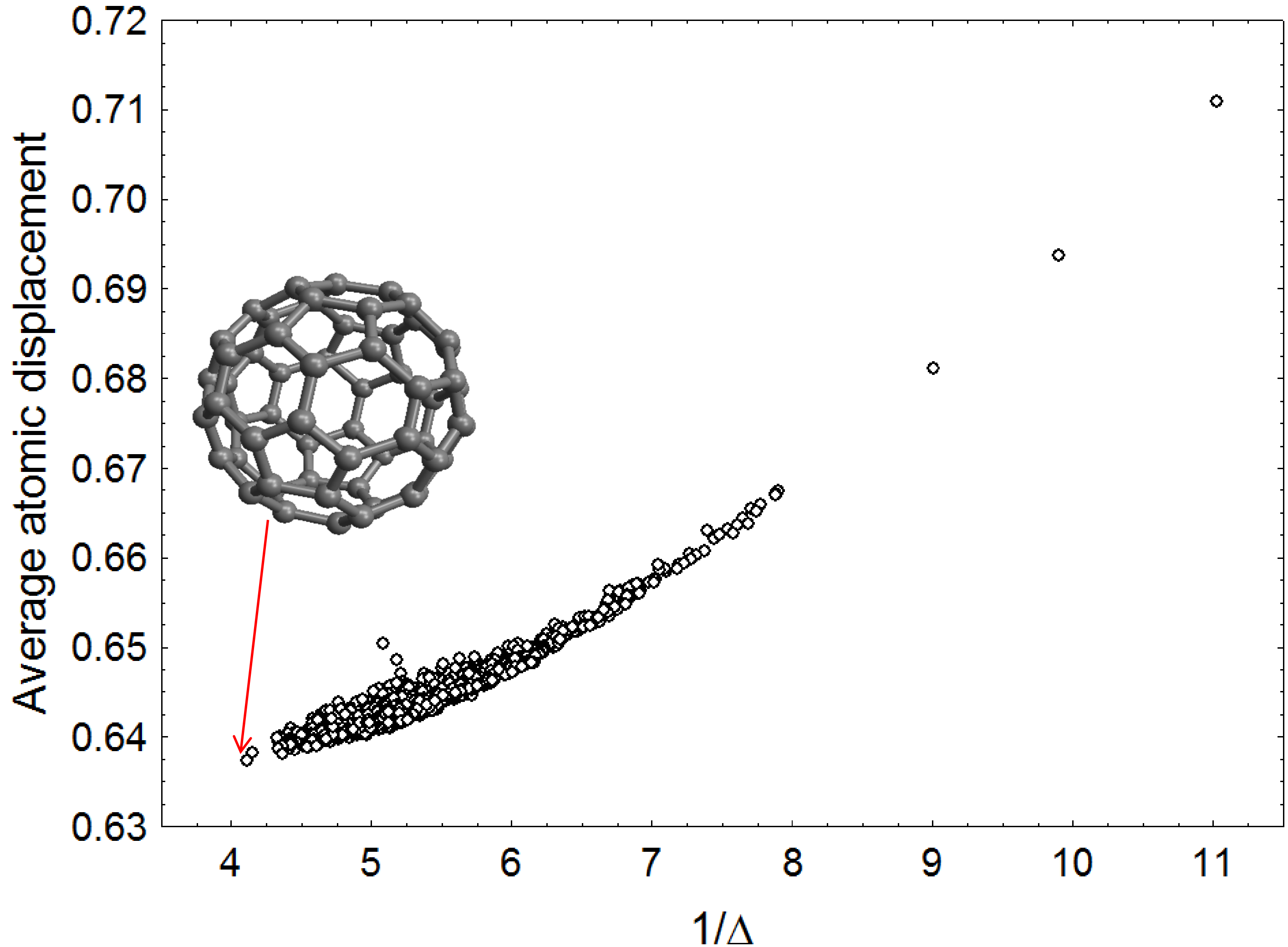
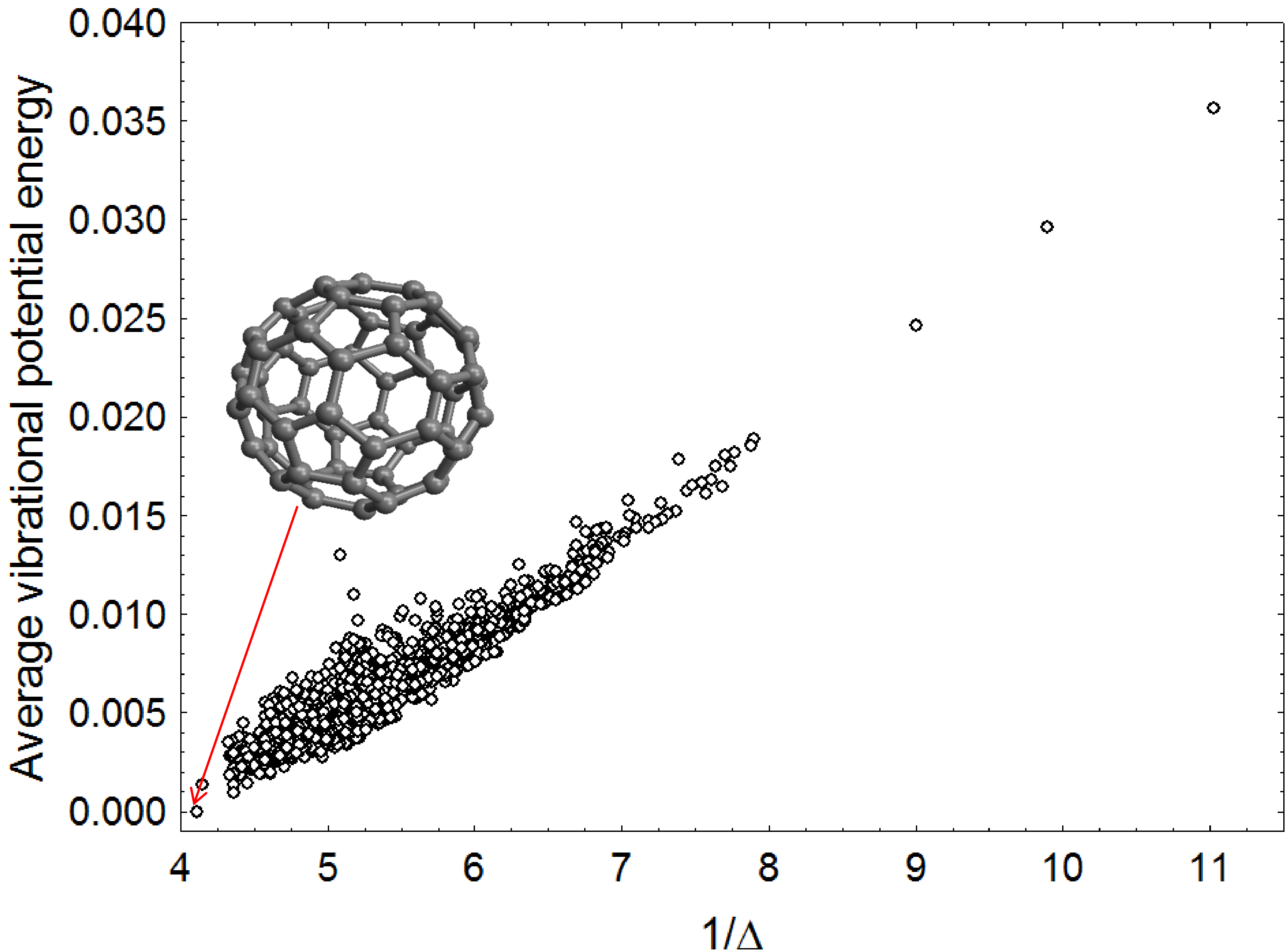
DISPLACEMENTS & PENTAGON ADJACENCY



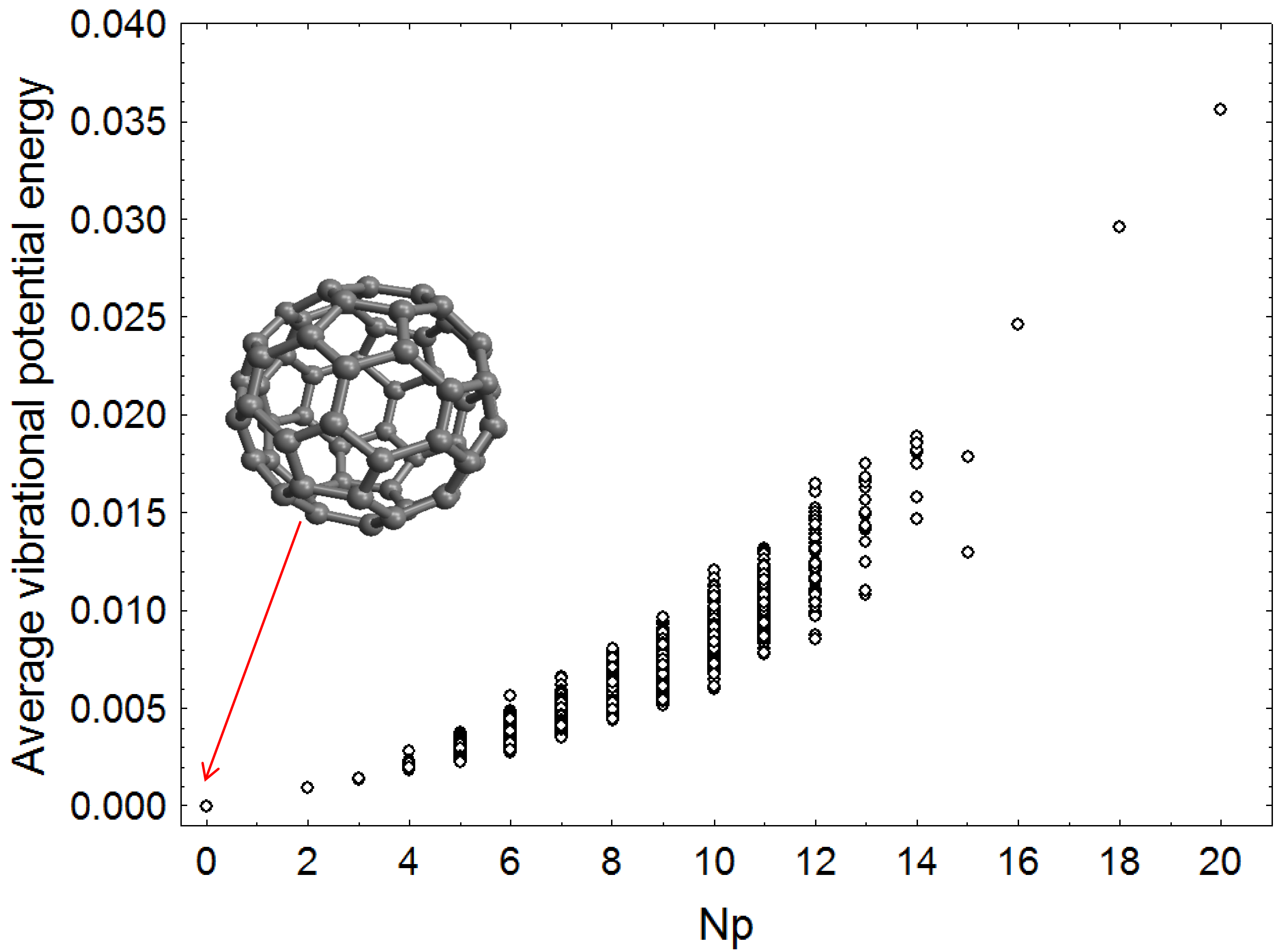
EXTENSIONS: C60 FULLERENES



C60 POTENTIAL ENERGIES



POTENTIAL ENERGY & PENTAGON ADJACENCY



QUANTUM MECHANICS PICTURE

Hamiltonian:

$$\hat{H} = \sum_s \frac{\hat{p}_s}{2m} + \sum_{r,s} \frac{\omega}{2}(x_r - x_s)^2 A_{rs} - \sum_s \frac{\omega}{2}(k_s - 1)x_s^2 \qquad (18)$$

where:

$\hat{p}_s \equiv \frac{\hbar}{i}\frac{d}{dx}$ **, and** k_s **is the degree of node *s***

Let:

$$\hat{a}_s^+ = \frac{1}{\sqrt{2\hbar}}\left(x_s\sqrt{m\varpi} - \frac{i}{\sqrt{m\varpi}}\hat{p}_s\right) \qquad \hat{a}_s^- = \frac{1}{\sqrt{2\hbar}}\left(x_s\sqrt{m\varpi} + \frac{i}{\sqrt{m\varpi}}\hat{p}_s\right)$$

where: $\varpi \equiv \sqrt{\frac{\omega}{m}}$

Hamiltonian in terms of *ladder operators*:

$$\hat{H} = \sum_s \left(\frac{\hat{p}_s}{2m} + \frac{\omega}{2} x_s^2 \right) - \omega \sum_{r,s} x_r A_{rs} x_s$$
$$= \sum_s \hbar \varpi \left(\hat{a}_s^+ \hat{a}_s^- + \frac{1}{2} \right) - \frac{\hbar \varpi}{2} \sum_{r,s} \left(\hat{a}_r^+ + \hat{a}_r^- \right) A_{rs} \left(\hat{a}_s^+ + \hat{a}_s^- \right) \quad (19)$$

After some algebra we arrive at:

$$\hat{H} = \sum_j \hat{H}_j \quad (20)$$

Hamiltonian for *j*th C atom:

$$\hat{H}_j \equiv \hbar\varpi\left(\hat{b}_j^{+}\hat{b}_j^{-} + \frac{1}{2}\right) - \frac{\hbar\varpi}{2}\lambda_j\left(\hat{b}_j^{+} + \hat{b}_j^{-}\right)^2 \qquad (21)$$

$$= \hbar\varpi\left(\hat{b}_j^{+}\hat{b}_j^{-} + \frac{1}{2}\right) - \frac{\hbar\varpi}{2}\lambda_j\left(\hat{b}_j^{+2} + \hat{b}_j^{-2} + 2\hat{b}_j^{+}\hat{b}_j^{-} + 1\right)$$

where:

$$\hat{b}_j^{+} = \sum_s \varphi_j(s)\hat{a}_j^{+} \qquad \hat{b}_j^{-} = \sum_s \varphi_j(s)\hat{a}_j^{-}$$

which obey the following commutation:

$$\left[\hat{b}_j^{-}, \hat{b}_j^{+}\right] = \sum_{r,s}\left[\varphi_j(r)\hat{a}_r^{-}, \varphi_l(s)\hat{a}_s^{+}\right]$$

$$= \sum_{r,s}\varphi_j(r)\varphi_l(s)\delta_{rs}$$

$$= \sum_s \varphi_j(s)\varphi_l(s) = \delta_{jl},$$

Eigenvectors of **H**

THERMAL GREEN'S FUNCTION

$$G_{rs}\left\langle x_r x_s \right\rangle \equiv \frac{1}{Z}\left\langle 0 \middle| x_r e^{-\beta \hat{H}} x_s \middle| 0 \right\rangle \tag{22}$$

where:

$$Z \equiv \left\langle 0 \middle| e^{-\beta \hat{H}} \middle| 0 \right\rangle . \tag{23}$$

After some algebra we arrive at:

$$\begin{aligned} G_{rs} &= \frac{1}{Z}\sum_{j,l} \varphi_j(r)\varphi_l(s)\left\langle 0 \middle| \left(\hat{b}_j^+ + \hat{b}_j^-\right)\left(\prod_i e^{-\beta \hat{H}_i}\right)\left(\hat{b}_l^+ - \hat{b}_l^-\right) \middle| 0 \right\rangle \\ &= \frac{1}{Z}\sum_{j,l} \varphi_j(r)\varphi_l(s)\delta_{jl}\left\langle 0 \middle| \hat{b}_j^- e^{-\beta \hat{H}_j} \hat{b}_j^+ \middle| 0 \right\rangle \times \prod_{i(\neq j)} \left\langle 0 \middle| e^{-\beta \hat{H}_i} \middle| 0 \right\rangle \\ &= \frac{1}{Z}\sum_{j} \varphi_j(r)\varphi_j(s) \exp\left[-\frac{3\beta\hbar\varpi}{2}\left(1+\lambda_j\right)\right] \times \prod_{i(\neq j)} \exp\left[-\frac{\beta\hbar\varpi}{2}\left(1+\lambda_i\right)\right] \end{aligned} \tag{24}$$

THERMAL GREEN'S FUNCTION

For $\hbar\varpi \equiv 1$ **and** $H = -A$**:**

$$G_{rs} = C\left(e^{\beta \mathbf{A}}\right)_{rs} = C\sum_j \varphi_j(r)\varphi_j(s)e^{\beta\lambda_j}. \qquad (25)$$

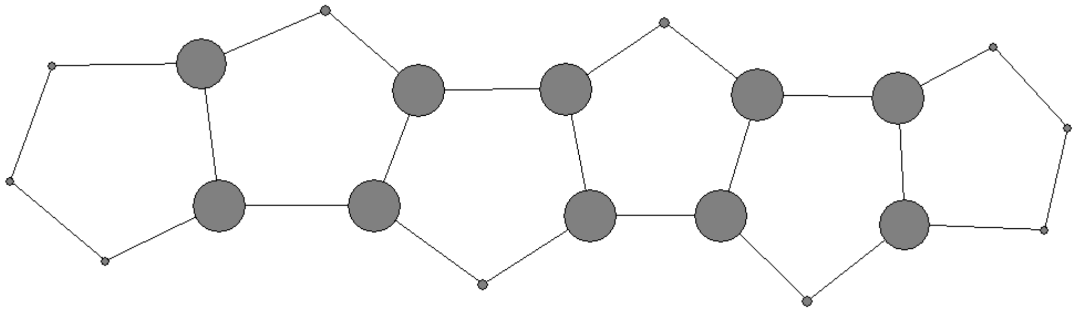
And:

$$Z \equiv EE(G) = tr\left(e^{\beta \mathbf{A}}\right) = \sum_j e^{\beta\lambda_j} \qquad (26)$$

$$\Delta x_r = \sum_j \left[\varphi_j(r)\right]^2 e^{\beta\lambda_j} \qquad (27)$$

Estrada, E., Rodriguez-Velazquez, A. *Phys. Rev*. *E* 71 **2005**, 056103.
Estrada, E., Hatano, N. *Phys. Rev*. *E* 77 **2008**, 036111.
Estrada, E., Hatano, N. *Chem. Phys. Lett* 439 **2007**, 247.

Quantum Atomic Displacements



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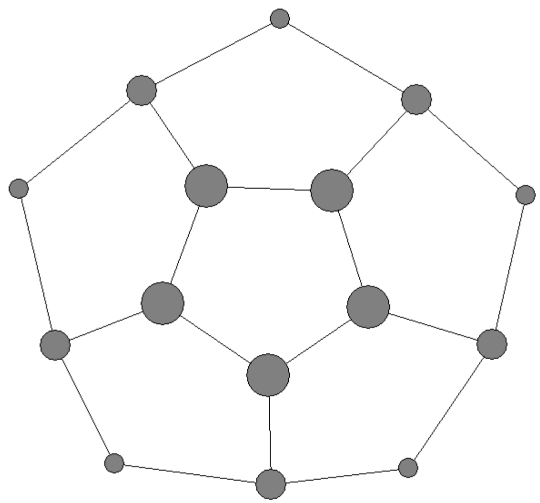

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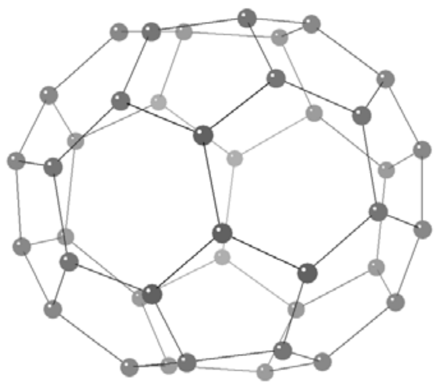
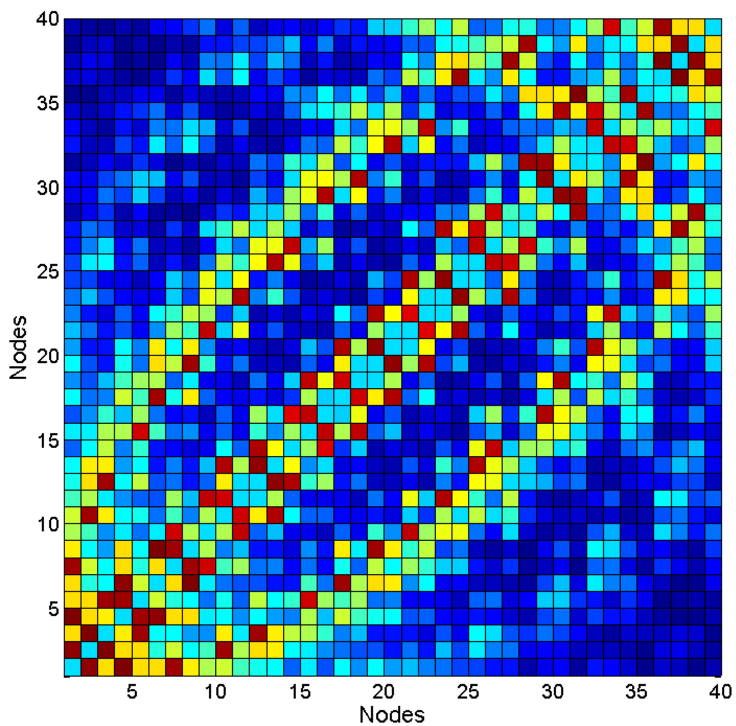
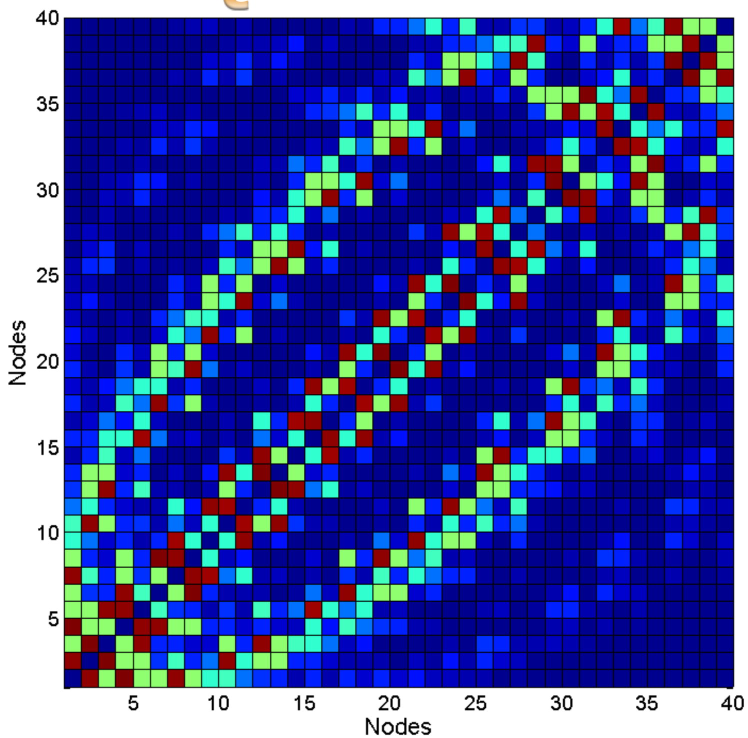
Classical vs. Quantum Displacements



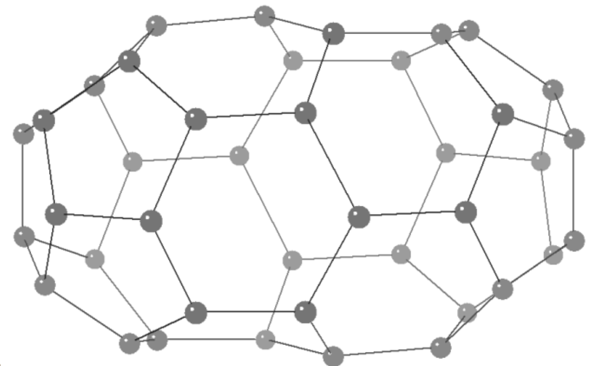
Classical



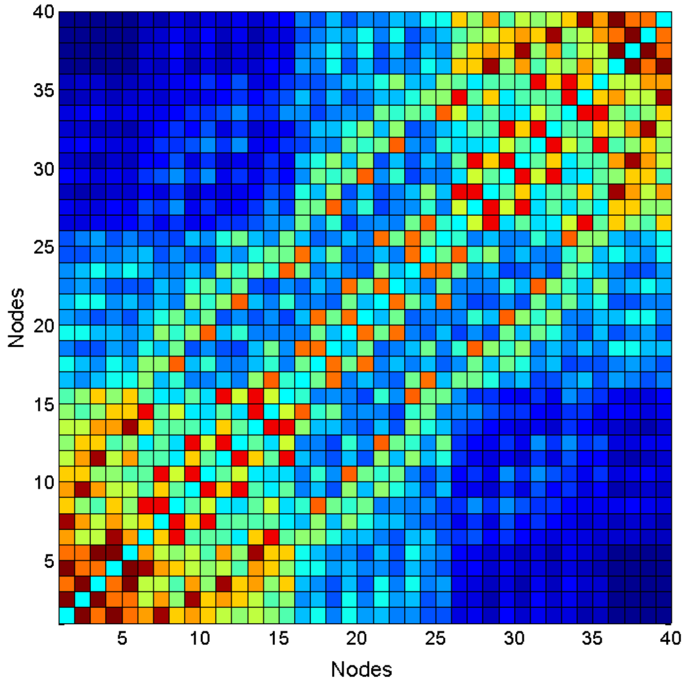
Quantum



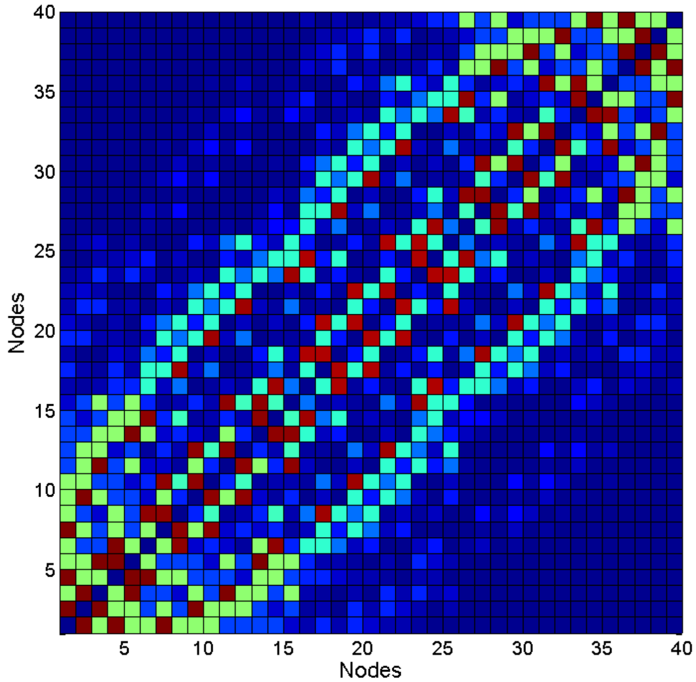
Classical vs. Quantum Displacements



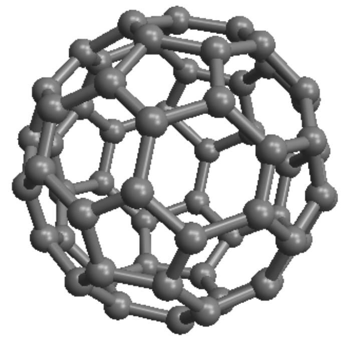
Classical



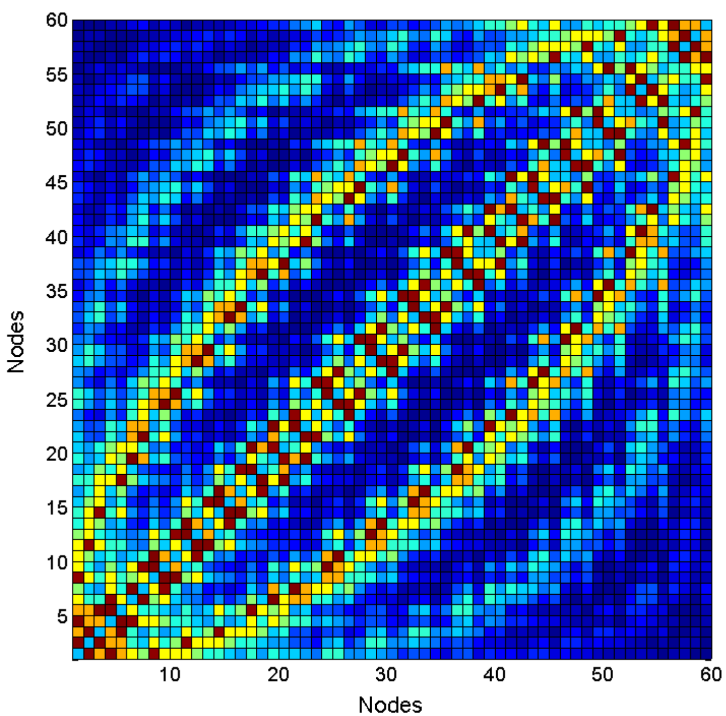
Quantum



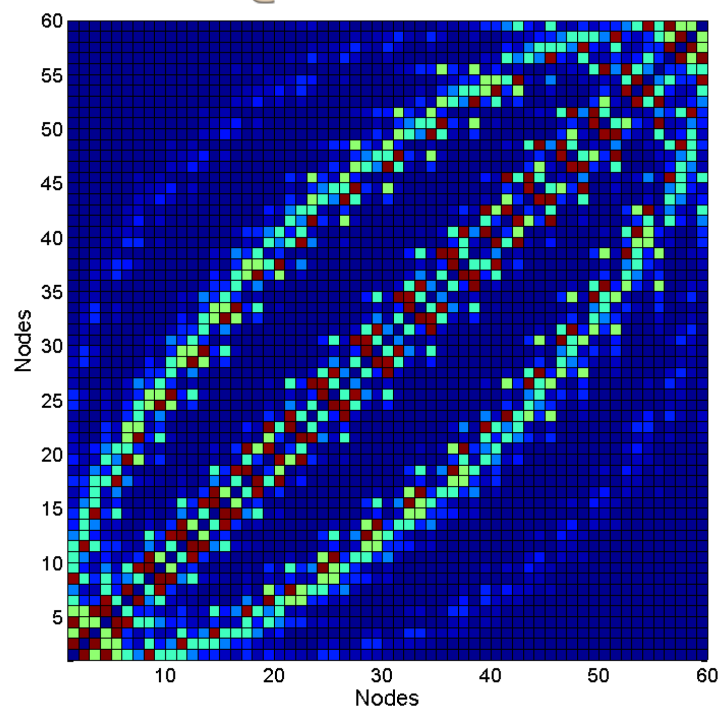
Displacements in Buckminsterfullerene



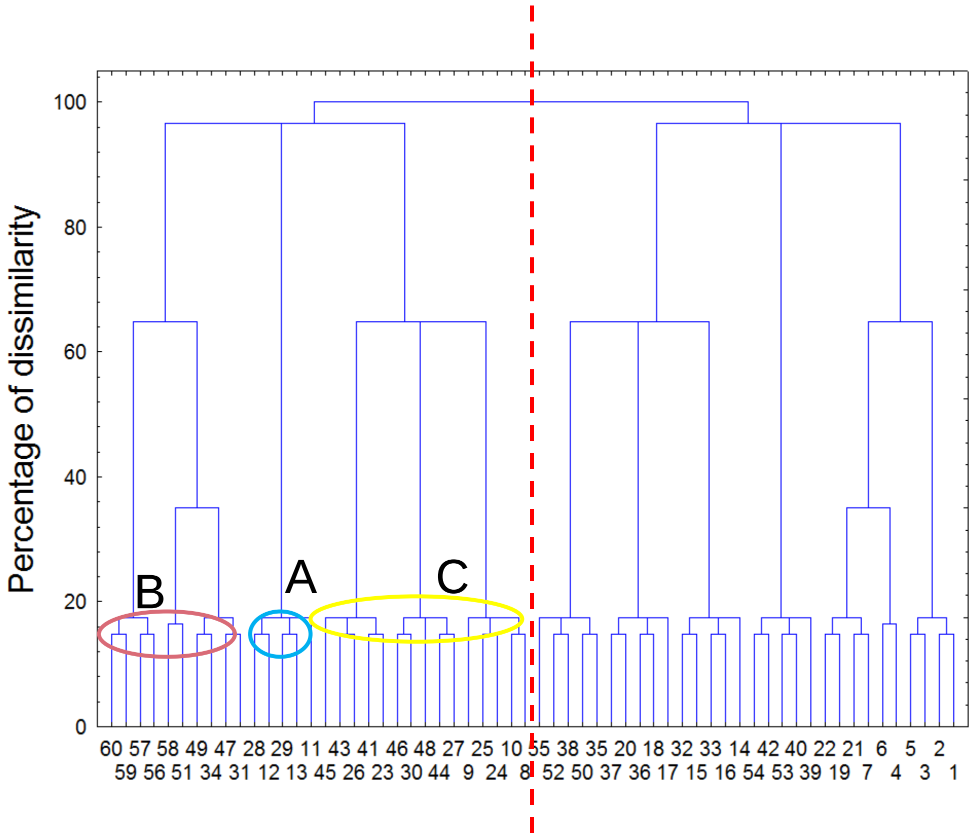
Classical



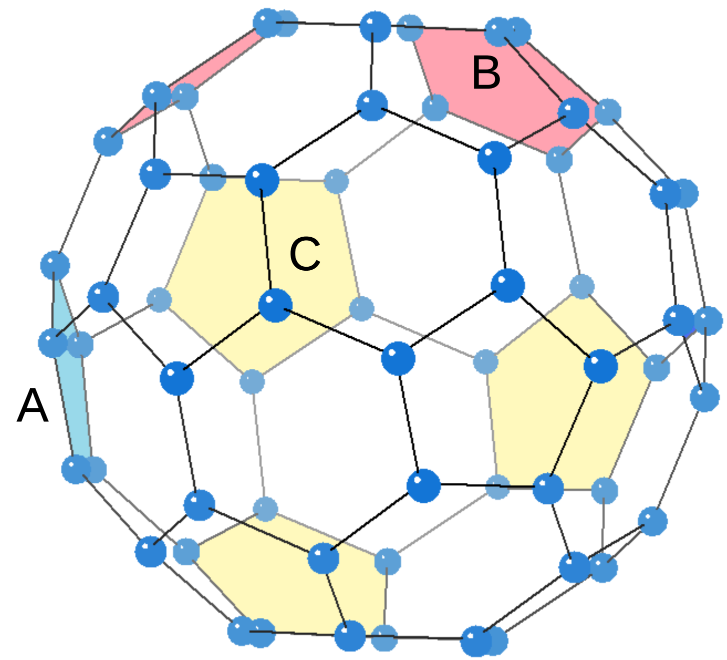
Quantum



Classical

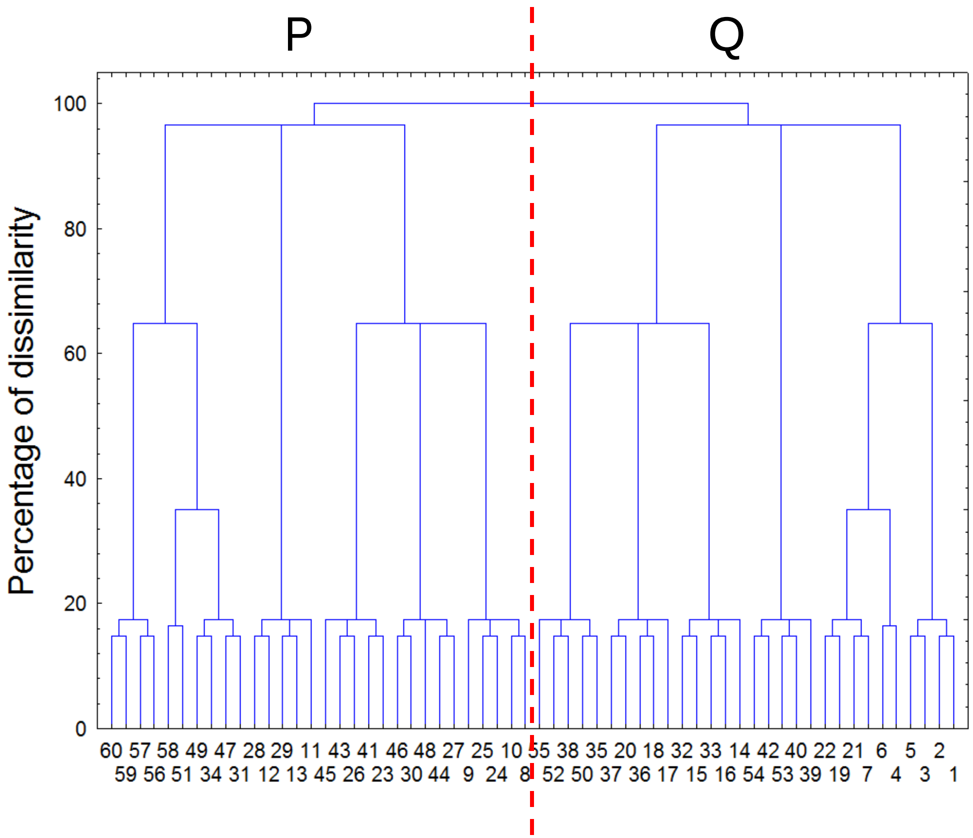


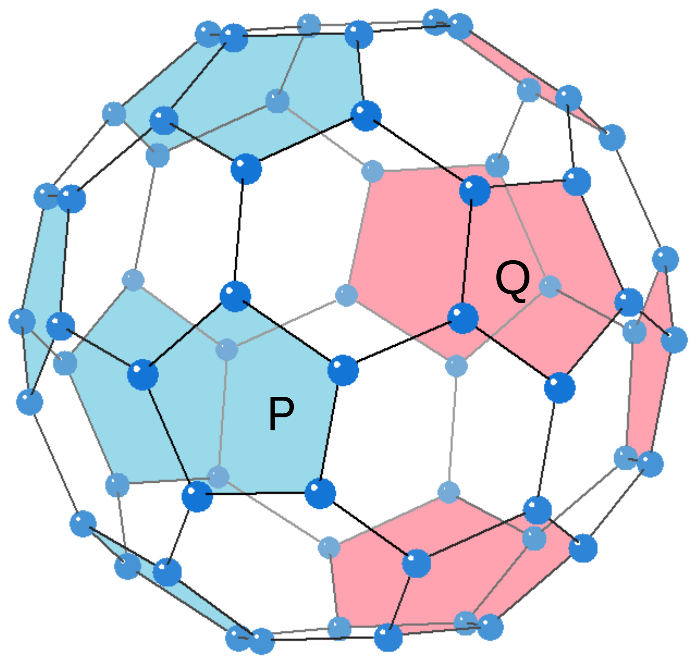
Percentage of dissimilarity
100
80
60
40
20
0
B
A
C
60 57 58 49 47 28 29 11 43 41 46 48 27 25 10 55 38 35 20 18 32 33 14 42 40 22 21 6 5 2
59 56 51 34 31 12 13 45 26 23 30 44 9 24 8 52 50 37 36 17 15 16 54 53 39 19 7 4 3 1



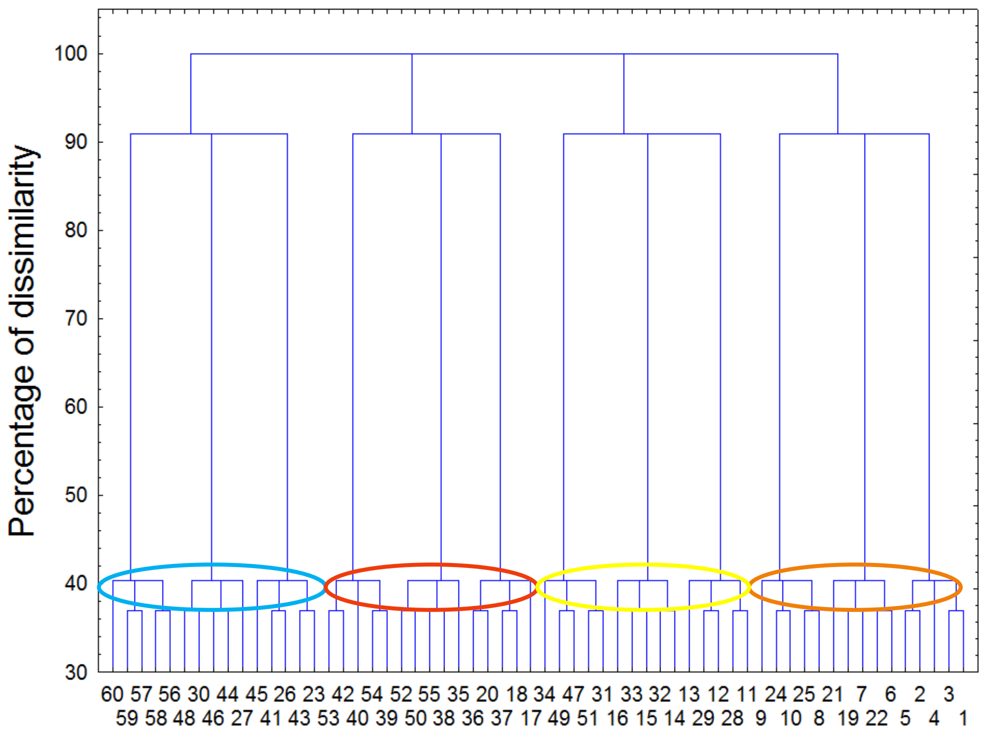
B
C
A

Classical

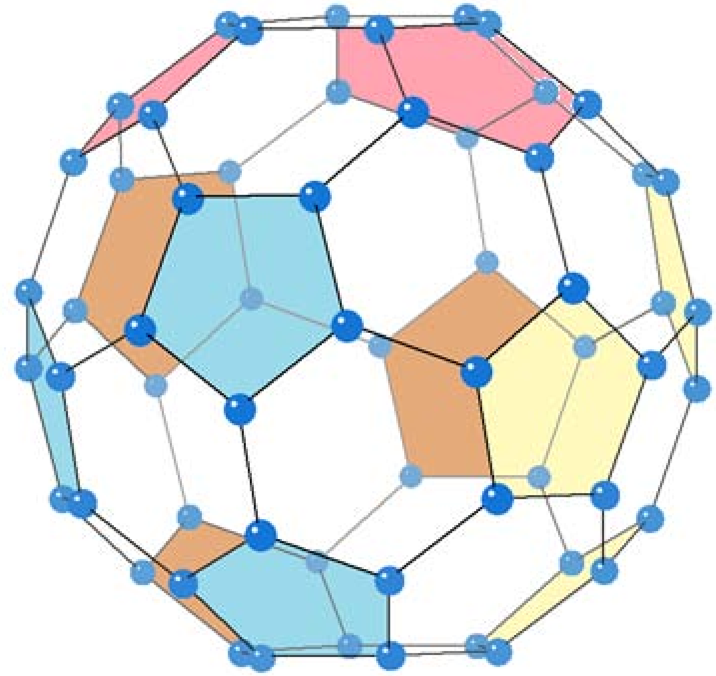

P
Q
Percentage of dissimilarity
0
20
40
60
80
100
60 57 58 49 47 28 29 11 43 41 46 48 27 25 10 55 38 35 20 18 32 33 14 42 40 22 21 6 5 2
59 56 51 34 31 12 13 45 26 23 30 44 9 24 8 52 50 37 36 17 15 16 54 53 39 19 7 4 3 1


Q
P

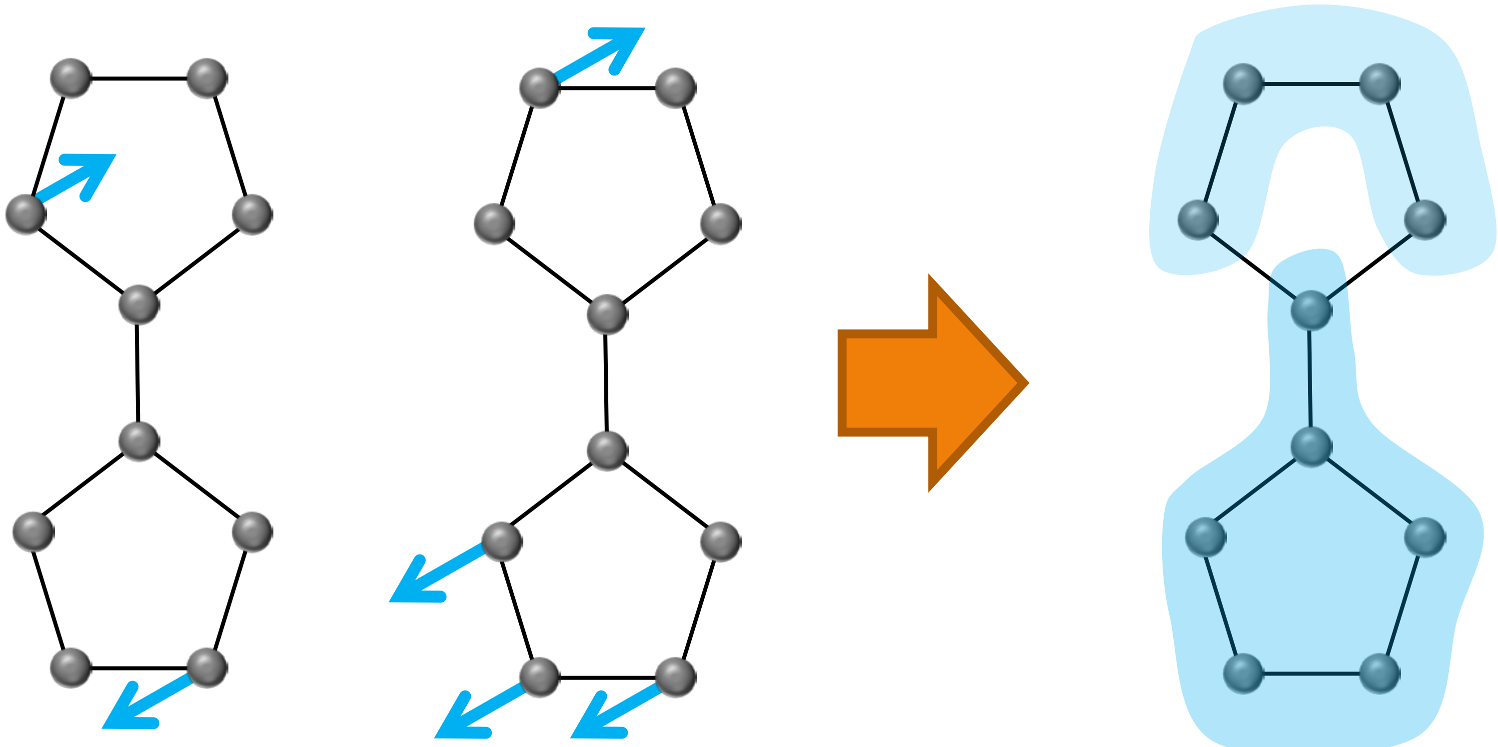
Quantum



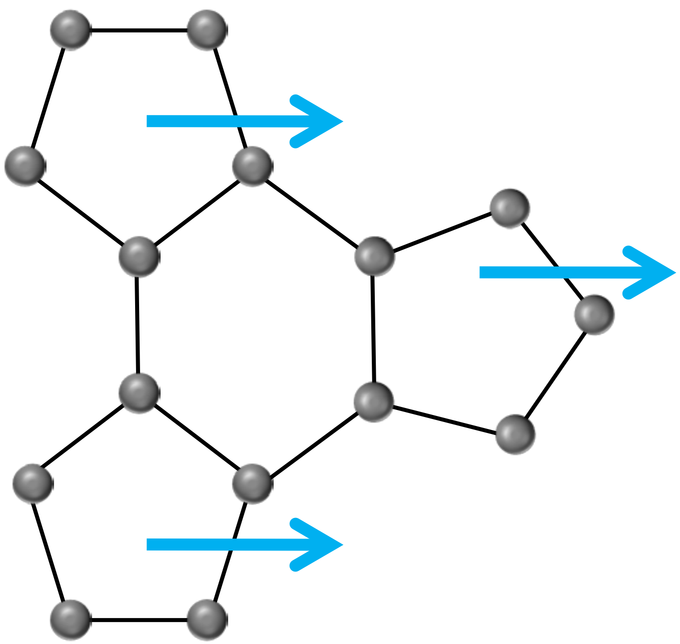
Percentage of dissimilarity
100
90
80
70
60
50
40
30
60 57 56 30 44 45 26 23 42 54 52 55 35 20 18 34 47 31 33 32 13 12 11 24 25 21 7 6 2 3
59 58 48 46 27 41 43 53 40 39 50 38 36 37 17 49 51 16 15 14 29 28 9 10 8 19 22 5 4 1

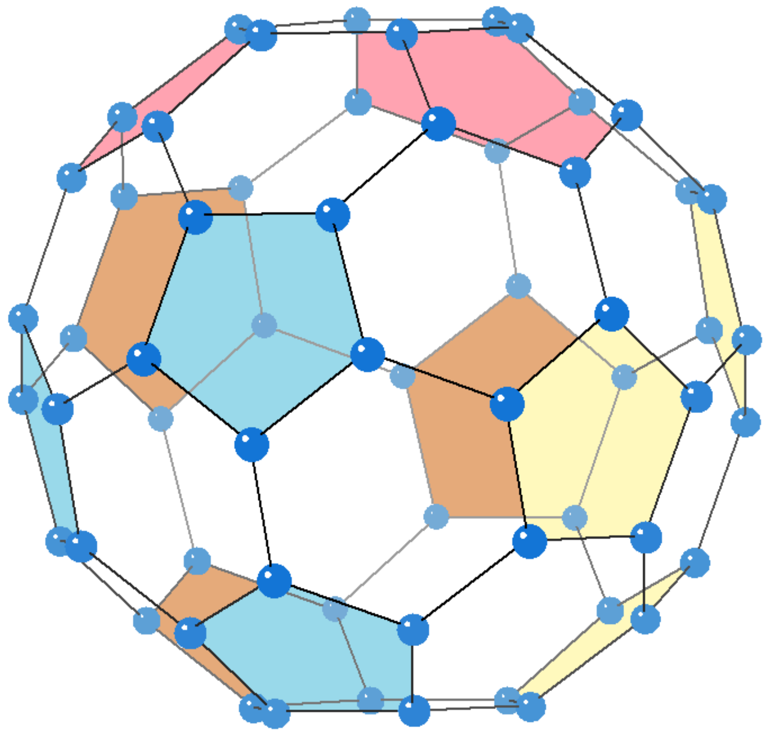


'Classical' Anti-correlated Vibrations



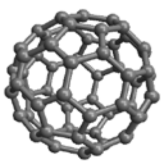
'Quantum' Correlated Vibrations





CONCLUSIONS

A classical mechanics approach to vibrations in molecules can be formulated on the basis of the generalised Moore-Penrose inverse of the graph Laplacian.



A quantum mechanics approach to vibrations in molecules based on coupled harmonic oscillators can be formulated on the basis of the exponential adjacency matrix of the graph representing the molecular system.

Both approaches give important information about the energetic and stability of fullerene isomers, as well as provide a theoretical framework for empirical observations such as the '*isolated pentagon rule*'.

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