Partial differential equations and graph theory from a perspective of a chemist

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1

Analytical form of helium wave function

2

Theory and applications of Zhang-Zhang polynomials

Goal

- Solve analytically Schrödinger equation for the helium atom

  - Ground state only (the lowest S state)
  - Fixed, point-like nuclues
  - Non-relativistic regime

Questions

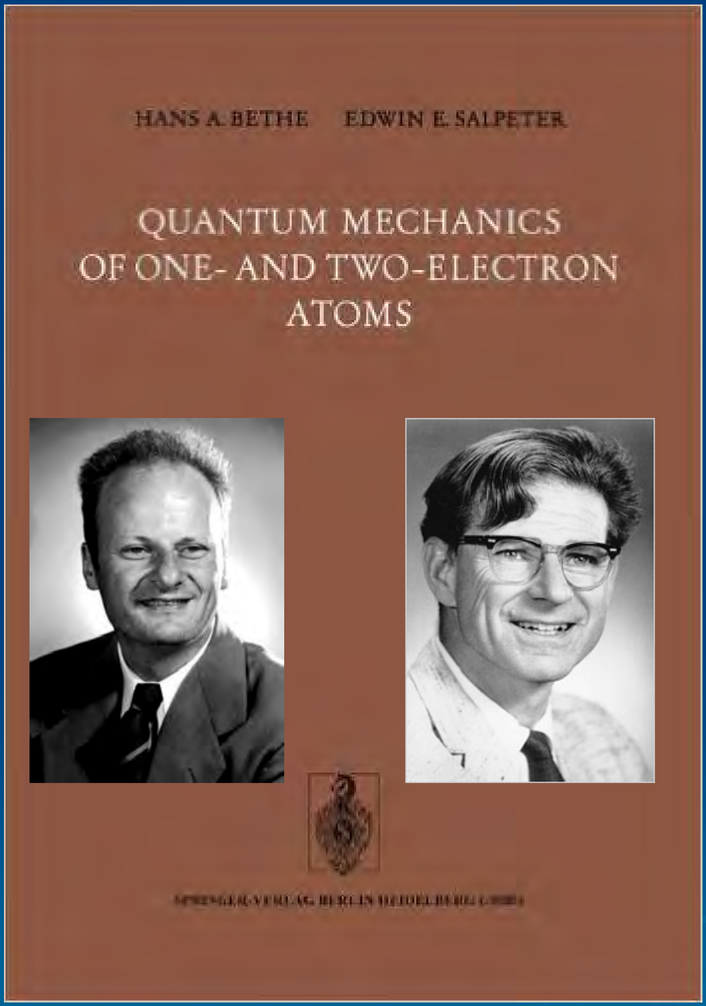
- Why to do it?
- Is it possible?
- How to do it?

Motivation

Why to do it?

- An important problem per se
- Possible gateway to analytical theory of atoms and molecules
- New quantum chemistry can be built upon a compact and correlated two-electron orbitals
- Personal reasons

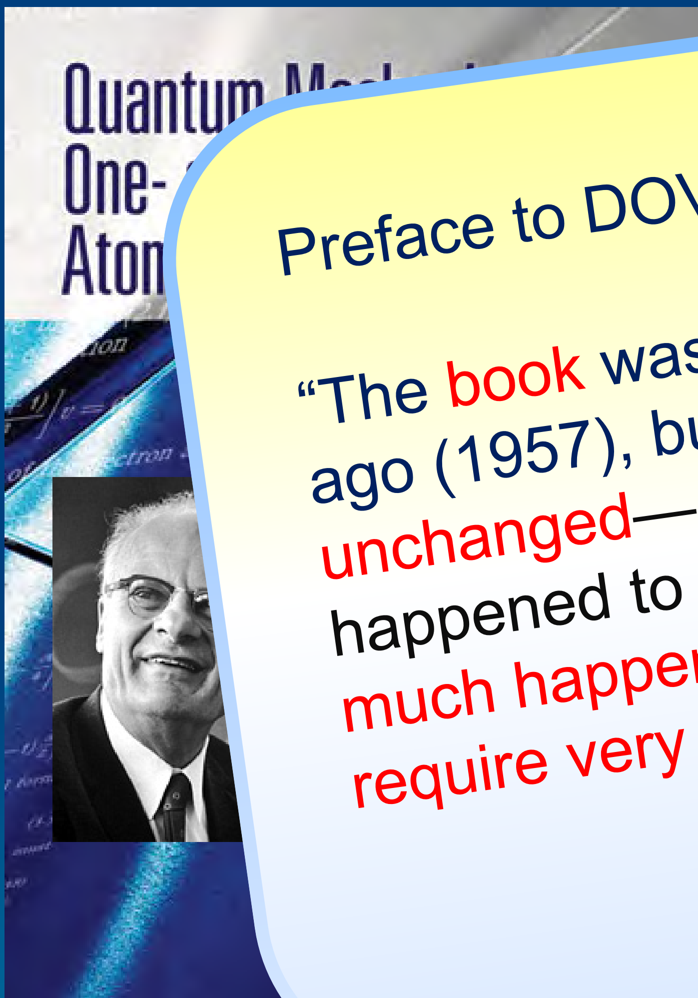
Perspectives of success



- “The differential equation for the two-electron system is not separable.”
- “Eigenfunctions and energy eigenvalues cannot be expressed in closed analytic form.”

Springer 1957

Perspectives of success



Preface to DOVER edition, Feb 2008

"The book was written just over fifty years ago (1957), but it is left almost unchanged—not because little has happened to the subject, but because so much happened that any change would require very major rewriting."

E. Salpeter

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print in 2008

Definition of the problem

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + \hat{V}$$

$$\hat{V} = -\frac{Z}{\|\boldsymbol{r}_1\|} - \frac{Z}{\|\boldsymbol{r}_2\|} + \frac{1}{\|\boldsymbol{r}_1 - \boldsymbol{r}_2\|} \qquad \boldsymbol{r}_i = \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix}$$

$$\Psi = \Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2)$$

Properties of the solution

$$\Psi = \Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2)$$

Boundary conditions

- Ψ antisymmetric (permutation symmetry $\hat{P}_{1\leftrightarrow 2}$)
- Ψ is an eigenfunction of operators $\hat{S}_z$, $\hat{S}^2$, $\hat{M}_z$, $\hat{L}^2$, and $\hat{\Pi}$
- Ψ finite and continuous everywhere
- Ψ' finite everywhere
- Ψ' continuous everywhere except for Coulomb singular points (so called Kato cusp conditions)
- Ψ square-integrable

Spin separation

$$\Psi = \Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2)$$

singlet states

$$\Psi = \underbrace{\Psi(x_1, y_1, z_1, x_2, y_2, z_2)}_{\text{symmetric wrt to the } 1 \leftrightarrow 2 \text{ interchange}} \cdot \underbrace{\Sigma^S(\sigma_1, \sigma_2)}_{\text{antisymmetric wrt } 1 \leftrightarrow 2}$$

triplet states

$$\Psi = \underbrace{\Psi(x_1, y_1, z_1, x_2, y_2, z_2)}_{\text{antisymmetric wrt to the } 1 \leftrightarrow 2 \text{ interchange}} \cdot \underbrace{\Sigma^T(\sigma_1, \sigma_2)}_{\text{symmetric wrt } 1 \leftrightarrow 2}$$

Angular momentum separation

$$\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$$

hyperspherical coordinates ↓

$$\Psi = \Psi(r, \alpha, \theta, \underbrace{\varepsilon_1, \varepsilon_2, \varepsilon_3}_{\text{Euler angles}})$$

Angular momentum eigenspace

(hyperspherical coordinates)

$$V_M^L = \mathrm{Span}\{\underbrace{D_{Mk}^L(\varepsilon_1, \varepsilon_2, \varepsilon_3)}_{\text{Wigner D matrices}} : k = -L, \dots, L\}$$

$$= V_M^{Ln} \oplus V_M^{Lu}$$

V_M^{Ln} ← Natural parity subspace

$\mathrm{Span}\{\Omega_{Mk}^{Ln} : k = 0, \dots, L\}$

$L + 1$ generators

V_M^{Lu} ← Unnatural parity subspace

$\mathrm{Span}\{\Omega_{Mk}^{Lu} : k = 1, \dots, L\}$

L generators

Angular momentum separation

natural parity subspace

$$\Psi_M^{Ln} = \sum_{k=0}^{L} \Phi_k^{Ln}(r,\alpha,\theta) \cdot \Omega_{Mk}^{Ln}(\varepsilon_1,\varepsilon_2,\varepsilon_3)$$

unnatural parity subspace

$$\Psi_M^{Lu} = \sum_{k=1}^{L} \Phi_k^{Lu}(r,\alpha,\theta) \cdot \Omega_{Mk}^{Lu}(\varepsilon_1,\varepsilon_2,\varepsilon_3)$$

Angular momentum separation

- Reduced Schrödinger equation for $\Phi^S(r, \alpha, \theta)$

E.A. Hylleraas, *Zeit. Phys.* **48**, 469 (1928)

- Reduced Schrödinger equations for $\Phi^P(r, \alpha, \theta)$, $\Phi_0^{P^\circ}(r, \alpha, \theta)$, and $\Phi_1^{P^\circ}(r, \alpha, \theta)$

G. Breit, *Phys. Rev.* **35**, 569 (1930)

- Reduced Schrödinger equations for general $\Phi_k^{Ln}(r, \alpha, \theta)$ and $\Phi_k^{Lu}(r, \alpha, \theta)$

A.K. Bhatia and A. Temkin, Rev. Mod. *Phys.* **36**, 1050 (1964)

Angular momentum separation

$$\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$$

hyperspherical coordinates

$$\Psi = \Psi(r, \alpha, \theta, \underbrace{\varepsilon_1, \varepsilon_2, \varepsilon_3}_{\text{Euler angles}})$$

bipolar spherical coordinates

$$\Psi = \Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

Angular momentum eigenspace

(bipolar spherical coordinates)

natural parity subspace $d = 0$

$$V_M^{Ln} = \mathrm{Span}\{\Omega_{Mk}^{Ln}(\theta_1, \phi_1, \theta_2, \phi_2) : k = d, \ldots, L\}$$

unnatural parity subspace $d = 1$

$$V_M^{Lu} = \mathrm{Span}\{\Omega_{Mk}^{Lu}(\theta_1, \phi_1, \theta_2, \phi_2) : k = d, \ldots, L\}$$

bipolar harmonics

$$\Omega_{Mk}^{L\pi}(\theta_1, \phi_1, \theta_2, \phi_2) = (-1)^{M+d}\sqrt{2L+1} \cdot \sum_{m=-k}^{k} \begin{pmatrix} k & L-k+d & L \\ m & M-m & -M \end{pmatrix} Y_m^k(\theta_1, \phi_1)\, Y_{M-m}^{L-k+d}(\theta_2, \phi_2)$$

$\pi = n \text{ or } u$

Angular momentum separation

natural parity subspace

$$\Psi_M^{Ln} = \sum_{k=0}^{L} \Phi_k^{Ln}(r_1, r_2, \theta) \cdot \Omega_{Mk}^{Ln}(\theta_1, \phi_1, \theta_2, \phi_2)$$

unnatural parity subspace

$$\Psi_M^{Lu} = \sum_{k=1}^{L} \Phi_k^{Lu}(r_1, r_2, \theta) \cdot \Omega_{Mk}^{Lu}(\theta_1, \phi_1, \theta_2, \phi_2)$$

$$\cos\theta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos\,(\phi_2 - \phi_1)$$

$$
\begin{aligned}
&\left[L_{\theta_{12}}+\frac{2m}{\hbar^2}(E-V)\right]F_l^{\kappa}-\left(\frac{1}{r_1{}^2}+\frac{1}{r_2{}^2}\right)\left[\left(\frac{l(l+1)-\kappa^2}{2\sin^2\theta_{12}}+\frac{\kappa^2}{4}\right)F_l^{\kappa}\right.\\
&\quad-\frac{\cot\theta_{12}}{4\sin\theta_{12}}l(l+1)\,\delta_{1\kappa}\tilde{F}_l^{\kappa}+\frac{\cot\theta_{12}}{4\sin\theta_{12}}B_l^{\kappa+2}\\
&\quad\times\left\{F_l^{\kappa+2}-\tfrac{1}{2}\delta_{0\kappa}\left(F_l^{\kappa+2}-\tilde{F}_l^{\kappa+2}\right)\right\}\\
&\quad\left.+\frac{\cot\theta_{12}}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa})B_{l\kappa}\left\{F_l^{\kappa-2}+\delta_{2\kappa}\tilde{F}_l^{\kappa-2}\right\}\right]\\
&+\left(\frac{1}{r_1{}^2}-\frac{1}{r_2{}^2}\right)\left[\kappa\left(\tfrac{1}{2}\cot\theta_{12}+\frac{\partial}{\partial\theta_{12}}\right)\tilde{F}_l^{\kappa}-\frac{l(l+1)}{4\sin\theta_{12}}\delta_{1\kappa}F_l^{\kappa}\right.\\
&\quad+\frac{B_l^{\kappa+2}}{4\sin\theta_{12}}\left\{-\tilde{F}_l^{\kappa+2}+\tfrac{1}{2}\delta_{0\kappa}\left(F_l^{\kappa+2}+\tilde{F}_l^{\kappa+2}\right)\right\}\\
&\quad\left.+\frac{B_{l\kappa}}{4\sin\theta_{12}}(1-\delta_{0\kappa}-\delta_{1\kappa})\left\{\tilde{F}_l^{\kappa-2}+\delta_{2\kappa}F_l^{\kappa-2}\right\}\right]=0.
\end{aligned}
$$

Resulting differential equation

the simplest case: even S state

$$-\frac{1}{2}\sum_{i=1,2}\frac{\partial^2\Psi}{\partial {r_i}^2}-\sum_{i=1,2}\frac{1}{r_i}\frac{\partial\Psi}{\partial r_i}-\frac{\partial^2\Psi}{\partial {r_{12}}^2}-\frac{2}{r_{12}}\frac{\partial\Psi}{\partial r_{12}}$$

$$-\frac{{r_1}^2-{r_2}^2+{r_{12}}^2}{2r_1r_{12}}\frac{\partial^2\Psi}{\partial r_1\partial r_{12}}-\frac{{r_2}^2-{r_1}^2+{r_{12}}^2}{2r_2r_{12}}\frac{\partial^2\Psi}{\partial r_2\partial r_{12}}$$

$$-\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r_{12}}\right)\Psi=0$$

kinetic energy $\hat{T}$

potential energy $\hat{V}$

Very accurate numerical solutions

Is it possible?

- We may consider this problem solved
  - Hylleraas (1929) → E correct to 3-4 digits
  - Pekeris (1958) → E correct to 7 digits
  - Schwartz (2006) → E correct to 36 digits
  - Nakatsuji (2007) → E correct to 40 digits

Classical three-body problem

- 3-body problem was solved by Karl Sundman in 1912
    - K. Sundman, *Acta Mathematica* **36**, 105-179 (1912)

- *n*-body problem was solved by Quidong Wang in 1991
    - Q. Wang, *Celestial Mechanics* **50**, 73-88 (1991)

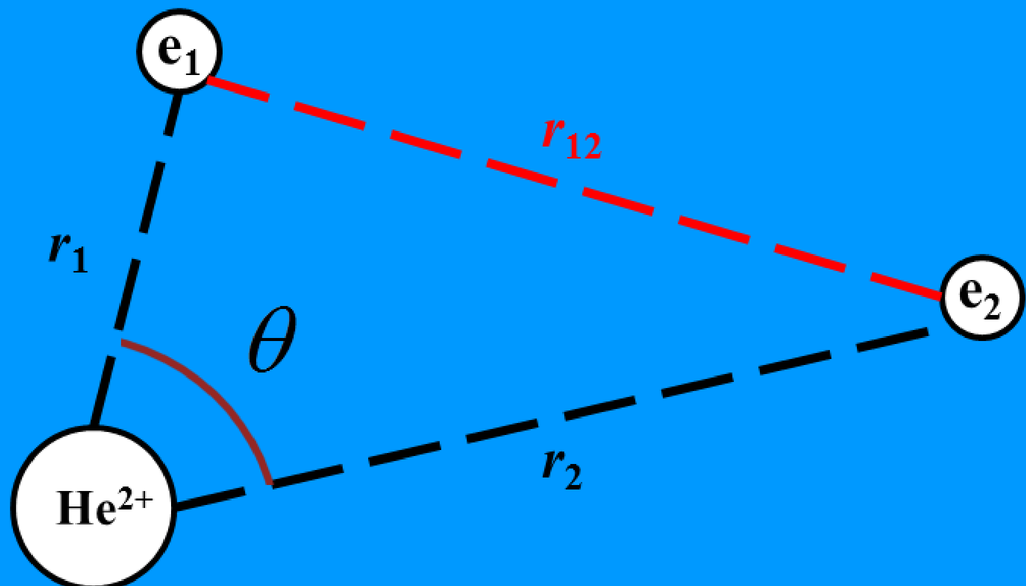
- Florin Diacu, "The solution of the *n*-body problem", *The Mathematical Intelligencer*, **18**, 66-70 (1996)

Quantum three-body problem

- 3-body problem
  - V.A. Fock, *Izv. Akad. Nauk SSSR Ser. Fiz.* **18**, 161 (1954)
  - V. Fock, *Nor. Vidensk. Selsk. Forh.* **31**, 138 (1958)

- Generalization to *n* bodies in a series of papers of Knirk
  - D.L. Knirk, JCP 60, 66, 1974
  - D.L. Knirk, JCP 60, 760, 1974
  - D.L. Knirk, PNAS 71, 1291 (1974)
  - D.L. Knirk, Phys. Rev. Lett. 32, 651 (1974)

Definition of the problem



Interparticle coordinates

Fock expansion

$$\Psi = \sum_{l=0}^{\infty} r^l \sum_{m=0}^{\lfloor l/2 \rfloor} (\ln r)^m \cdot f_{lm}(\alpha, \theta)$$

where

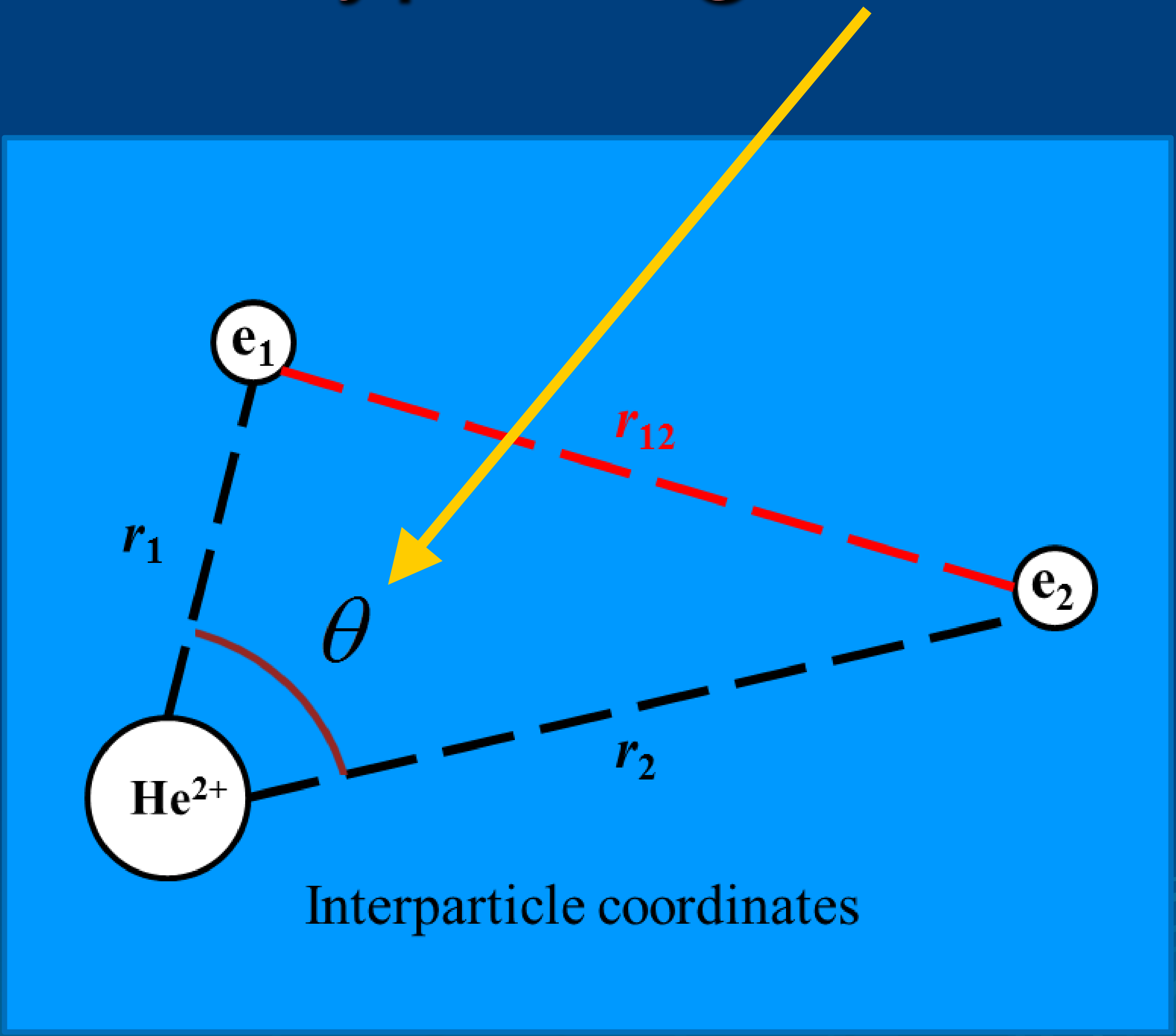
$$\alpha = \arccos \frac{{r_1}^2 - {r_2}^2}{{r_1}^2 + {r_2}^2}$$

$$r = \sqrt{{r_1}^2 + {r_2}^2}$$

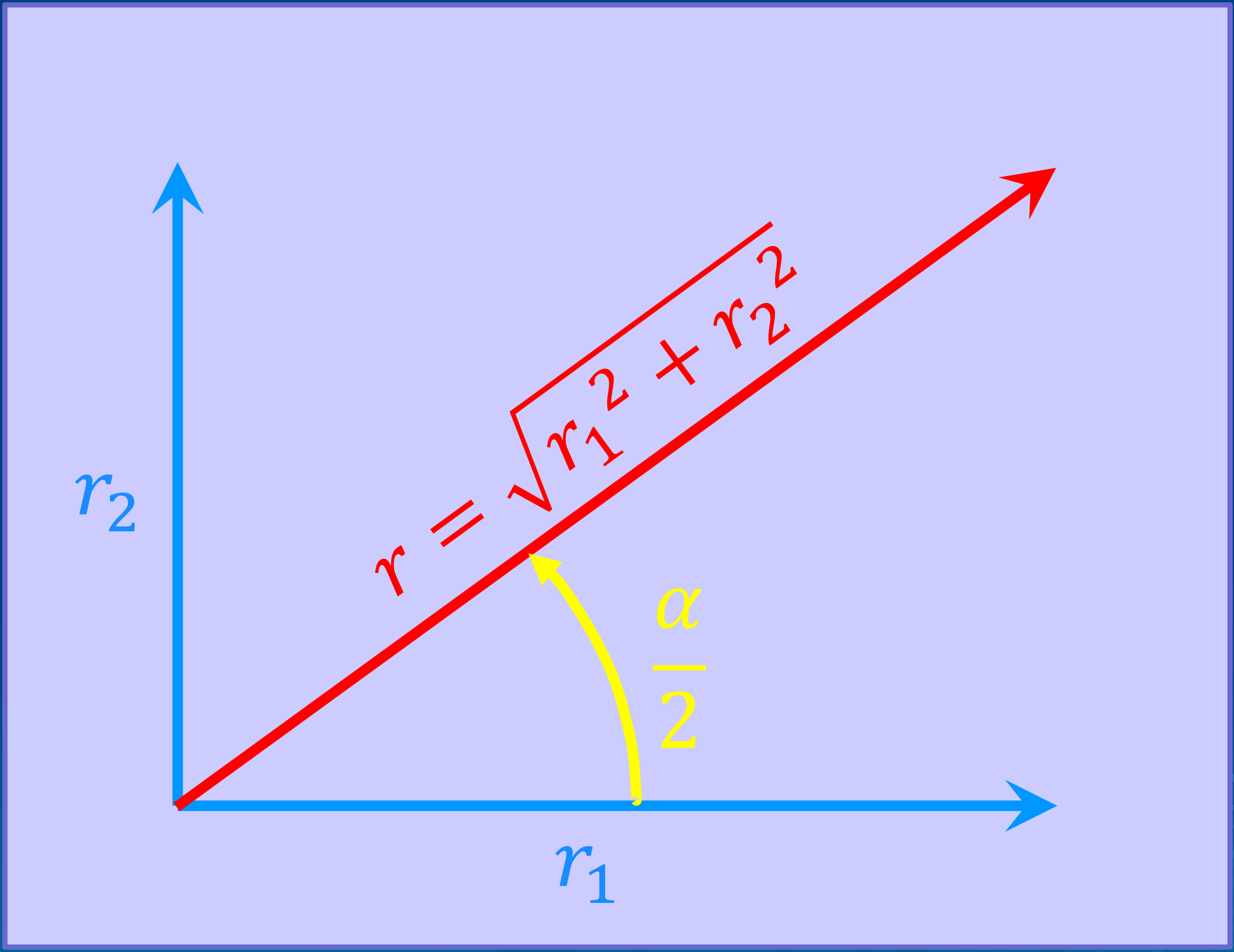
$$\theta = \arccos \frac{{r_1}^2 + {r_2}^2 - {r_{12}}^2}{2 r_1 r_2}$$

V.A. Fock, *Izv. Akad. Nauk SSSR Ser. Fiz.* **18**, 161 (1954)
V. Fock, *Nor. Vidensk. Selsk. Forh.* **31**, 138 (1958)

Hyperangle θ



Hyperradius r and hyperangle α



Fock expansion

$$\Psi = \sum_{l=0}^{\infty} r^l \sum_{m=0}^{\lfloor l/2 \rfloor} (\ln r)^m \cdot f_{lm}(\alpha, \theta)$$

$$\begin{aligned}
\Psi = \quad & f_{00}(\alpha,\theta) + \\
& + r\, f_{10}(\alpha,\theta) + \\
& + r^2 f_{20}(\alpha,\theta) + r^2 \ln r\, f_{21}(\alpha,\theta) + \\
& + r^3 f_{30}(\alpha,\theta) + r^3 \ln r\, f_{31}(\alpha,\theta) + \\
& + r^4 f_{40}(\alpha,\theta) + r^4 \ln r\, f_{41}(\alpha,\theta) + r^4 (\ln r)^2 f_{42}(\alpha,\theta) + \\
& + r^5 f_{50}(\alpha,\theta) + r^5 \ln r\, f_{51}(\alpha,\theta) + r^5 (\ln r)^2 f_{52}(\alpha,\theta) + \\
& + \cdots
\end{aligned}$$

Coefficients in Fock expansion

$$f_{00} = 1$$

Vladimir Fock
(1954)

$$r f_{10} = -Z(r_1 + r_2) + \frac{1}{2} r_{12}$$

Kato cusp parameters

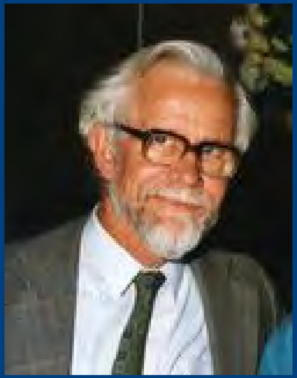
Tosio Kato
(1957)

$$r^2 \ln r \, f_{21} = Z \frac{\pi - 2}{12\pi} ({r_{12}}^2 - {r_1}^2 - {r_2}^2) \ln({r_1}^2 + {r_2}^2)$$

Alexei Ermolaev (1964)

$r^2 f_{20}$

$$
\begin{aligned}
12\pi r^2 f_{20}(\alpha,\theta) &= (1+4Z^2-2E)\,r_{12}^2\,\pi - 8Z\,r_{12}(r_1+r_2)\,\pi + 4(Z+3Z^2)\,r_1 r_2\,\pi \\
&- 4Z(r_1^2+r_2^2-r_{12}^2)\ln(r_1+r_2+r_{12})\,\pi + 2Z(r_1^2-r_2^2)\ln(r_1-r_2+r_{12})\,\pi \\
&+ 4Z(r_1^2+r_2^2-r_{12}^2)\ln(r_1^2+r_2^2) \\
&+ 2Z\left(\pi + 2\arcsin\left(\frac{r_1^2+r_2^2-r_{12}^2}{r_1^2+r_2^2}\right)\right) r_{12}\sqrt{2r_1^2+2r_2^2-r_{12}^2} \\
&- Z(r_1^2-r_2^2)\ln\left(r_{12}\sqrt{2r_1^2+2r_2^2-r_{12}^2}+r_1^2-r_2^2\right)\pi \\
&+ Z\arcsin\left(\frac{2r_1 r_2}{r_1^2+r_2^2}\right)\ln\left(\frac{(r_1+r_2+r_{12})(r_1+r_2-r_{12})}{(r_1-r_2+r_{12})(r_2-r_1+r_{12})}\right)(r_1^2-r_2^2) \\
&- Z(r_1^2-r_2^2)\arcsin\left(\frac{r_1^2+r_2^2-r_{12}^2}{r_1^2+r_2^2}\right)\ln\left(\frac{r_{12}\sqrt{2r_1^2+2r_2^2-r_{12}^2}+r_1^2-r_2^2}{r_{12}\sqrt{2r_1^2+2r_2^2-r_{12}^2}+r_2^2-r_1^2}\right) \\
&+ 2Z(r_1^2-r_2^2)\left(\mathrm{L}\left(\frac{\alpha}{2}-\frac{\beta}{2}\right)-\mathrm{L}\left(\frac{\alpha}{2}+\frac{\beta}{2}\right)+\mathrm{L}\left(\frac{\pi}{2}-\frac{\alpha}{2}+\frac{\beta}{2}\right)-\mathrm{L}\left(\frac{\pi}{2}-\frac{\alpha}{2}-\frac{\beta}{2}\right)\right)
\end{aligned}
$$



Edward (Ted) Maslen

Paul Abbott (1986)
Chris Davis (1981)
John Gottschalk (1987)
Kevin McIsaac (1993)

Philip Pluvinage (1955,1982,1985)

$f_{20}(\alpha, \theta)$ (cont.)

where $L\left(\frac{\alpha-\beta}{2}\right)$, $L\left(\frac{\alpha+\beta}{2}\right)$, $L\left(\frac{\pi-\alpha+\beta}{2}\right)$, and $L\left(\frac{\pi-\alpha-\beta}{2}\right)$ are Lobachevski functions

$$L(x) = -\int_0^x \ln(\cos t)\, dt$$

and

$$\alpha = \arcsin\frac{2r_1r_2}{{r_1}^2 + {r_2}^2}$$

$$\beta = \arcsin\frac{{r_1}^2 + {r_2}^2 - {r_{12}}^2}{{r_1}^2 + {r_2}^2}$$

Closed form?

- Lobachevski function

$$L(x) = -\int_0^x \ln(\cos t)dt$$

can be expressed as dilogarithm

$$\mathrm{Li}_2(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^2}$$

$$L(x) = \frac{i}{12}\pi^2 - \frac{1}{8}x^2 - x\frac{\ln 2}{2} + \frac{x}{2}\ln(1 - e^{ix}) - \frac{x}{2}\ln\left(\sin\frac{x}{2}\right) - \frac{i}{2}\mathrm{Li}_2(e^{ix})$$

Closed form?

- Lobachevski function

$$L(x) = -\int_0^x \ln(\cos t)dt$$

can be expressed as dilogarithm

$$\mathrm{Li}_2(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^2}$$

$$\exp(z) = \sum_{k=0}^{\infty} \frac{z^k}{k!} \qquad \ln(1-z) = -\sum_{k=1}^{\infty} \frac{z^k}{k}$$

How to do it?

OUR APPROACH

Homogeneity

- x is homogeneous of order 1
- x^k is homogeneous of order k
- ${r_1}^i {r_2}^j {r_{12}}^k$ is homogeneous of order $i + j + k$
- $\frac{\partial}{\partial x}$ is homogeneous of order -1
- $\ln(x)$ is homogeneous of order 0
  - since $\frac{\partial}{\partial x} \ln(x) = \frac{1}{x}$
- $\exp(x)$ has mixed homogeneity
  - since $\frac{\partial}{\partial x} \exp(x) = \exp(x)$ and $\exp(x) = \sum_{k=0}^{\infty} \frac{z^k}{k!}$

Resulting differential equation

$$-\frac{1}{2}\sum_{i=1,2}\frac{\partial^2\Psi}{\partial {r_i}^2}-\sum_{i=1,2}\frac{1}{r_i}\frac{\partial\Psi}{\partial r_i}-\frac{\partial^2\Psi}{\partial {r_{12}}^2}-\frac{2}{r_{12}}\frac{\partial\Psi}{\partial r_{12}}$$

$$-\frac{{r_1}^2-{r_2}^2+{r_{12}}^2}{2r_1r_{12}}\frac{\partial^2\Psi}{\partial r_1\partial r_{12}}-\frac{{r_2}^2-{r_1}^2+{r_{12}}^2}{2r_2r_{12}}\frac{\partial^2\Psi}{\partial r_2\partial r_{12}}$$

$$-\left(E+\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r_{12}}\right)\Psi=0$$

kinetic energy $\hat{T}$

potential energy $\hat{V}$

Solution based on the concept of homogeneity

$$\hat{T}\Psi + \hat{V}\Psi = E\Psi$$

$$\underbrace{\hat{T}}_{-2}\Psi + \underbrace{\hat{V}}_{-1}\Psi = \underbrace{E}_{0}\Psi$$

Ψ must have mixed homogeneity

$$\Psi = \underbrace{\Psi_0}_{0} + \underbrace{\Psi_1}_{1} + \underbrace{\Psi_2}_{2} + \underbrace{\Psi_3}_{3} + \cdots$$

E.A. Hylleraas, *Fest. til Prof. Bjorn Helland-Hansen (*Bergen*)* (1956)
E.A. Hylleraas, *Phys. Math. Univ. Osloensis Inst. Rep. No. 6* (1960)

Solution based on the concept of homogeneity

$$\underbrace{\hat{T}\Psi_0}_{-2} + \underbrace{\hat{T}\Psi_1 + \hat{V}\Psi_0}_{-1} + \underbrace{\hat{T}\Psi_2 + \hat{V}\Psi_1 - E\Psi_0}_{0}$$

$$+ \underbrace{\hat{T}\Psi_3 + \hat{V}\Psi_2 - E\Psi_1}_{1} + \cdots = \underbrace{0}_{-2} + \underbrace{0}_{-1} + \underbrace{0}_{0} + \cdots$$

$$\hat{T}\Psi_0 = 0$$

$$\hat{T}\Psi_1 = -\hat{V}\Psi_0$$

$$\hat{T}\Psi_2 = -\hat{V}\Psi_1 + E\Psi_0$$

$$\hat{T}\Psi_{k+2} = -\hat{V}\Psi_{k+1} + E\Psi_k$$

for $k = 1,2,3,\ldots$

Ψ_0 and Ψ_1

$$\hat{T}\Psi_0 = 0 \qquad \hat{T}\Psi_1 = Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - \frac{1}{r_{12}}$$

$$\Psi_0 = 1 \qquad \Psi_1 = -Z(r_1 + r_2) - \frac{1}{2} r_{12}$$

Space of polynomials of homogeneity 0

$$\mathcal{V}_0 = \mathrm{Span}\{1\}$$

Space of polynomials of homogeneity 1

$$\mathcal{V}_1 = \mathrm{Span}\{r_1, r_2, r_{12}\}$$

Ψ_2

$$\hat{T}\Psi_2 = -\hat{V}\Psi_1 + E\Psi_0$$

$$\hat{T}\Psi_2 = \left(E - \frac{1}{2} - 2Z^2\right) - Z^2\left(\frac{r_2}{r_1} + \frac{r_1}{r_2}\right) + Z\frac{r_1+r_2}{r_{12}} + \frac{Z}{2}\left(\frac{r_{12}}{r_1} + \frac{r_{12}}{r_2}\right)$$

Space of polynomials of homogeneity 2

$$\mathcal{V}_2 = \mathrm{Span}\{{r_1}^2, {r_2}^2, {r_{12}}^2, r_1 r_2, r_1 r_{12}, r_2 r_{12}\}$$

Symmetric sector

$$\mathcal{V}_2{}^S = \mathrm{Span}\{{r_1}^2 + {r_2}^2, {r_{12}}^2, r_1 r_2, r_1 r_{12} + r_2 r_{12}\}$$

Antisymmetric sector

$$\mathcal{V}_2{}^A = \mathrm{Span}\{{r_1}^2 - {r_2}^2, r_1 r_{12} - r_2 r_{12}\}$$

Ψ_2

$$\hat{T}\Psi_2 = -\hat{V}\Psi_1 + E\Psi_0$$

$$\hat{T}\Psi_2 = \left(E - \frac{1}{2} - 2Z^2\right) - Z^2\left(\frac{r_2}{r_1} + \frac{r_1}{r_2}\right) + Z\,\frac{r_1 + r_2}{r_{12}} + \frac{Z}{2}\left(\frac{r_{12}}{r_1} + \frac{r_{12}}{r_2}\right)$$

Ψ_{2c} Ψ_{2d}

Since $\hat{T}({r_{12}}^2) = -6$

$$\Psi_{2a} = \frac{1 + 4Z^2 - 2E}{12}{r_{12}}^2$$

Since

$$\hat{T}(r_1 \cdot r_2) = -\left(\frac{r_2}{r_1} + \frac{r_1}{r_2}\right)$$

$$\Psi_{2b} = Z^2 \cdot r_1 \cdot r_2$$

$$\Psi_{2c}$$

$$\hat{T}\Psi_{2c} = Z\frac{r_1+r_2}{r_{12}}$$

$$\hat{T}\left(r_1{}^i r_2{}^j r_{12}{}^k\right) =$$

$$= -\frac{r_1{}^i r_2{}^j}{2}\cdot\left\{\left[i(i+k+1)\frac{1}{r_1{}^2} + j(j+k+1)\frac{1}{r_2{}^2}\right] r_{12}{}^k + \left[-ik\frac{r_2{}^2}{r_1{}^2} - jk\frac{r_1{}^2}{r_2{}^2} + k(2k+i+j+2)\right] r_{12}{}^{k-2}\right\}$$

$$\hat{T}(f_0 r_{12}{}^1) \rightarrow -g_1 r_{12}{}^1 + g_0 r_{12}{}^{-1}$$
$$\hat{T}(f_1 r_{12}{}^3) \rightarrow -g_2 r_{12}{}^3 + g_1 r_{12}{}^1$$
$$\hat{T}(f_2 r_{12}{}^5) \rightarrow -g_3 r_{12}{}^5 + g_2 r_{12}{}^3$$
$$\hat{T}(f_3 r_{12}{}^7) \rightarrow -g_4 r_{12}{}^7 + g_3 r_{12}{}^5$$
$$\vdots$$

$$\hat{T}\left(\sum_{k=0}^{\infty} f_k r_{12}{}^{2k+1}\right) = g_0 r_{12}{}^{-1}$$

Ψ_{2c}

$$\hat{T}\Psi_{2c} = Z(r_1 + r_2) \cdot \frac{1}{r_{12}}$$

$$\Psi_{2c} = \sum_{k=0}^{\infty} f_k(r_1, r_2) \cdot r_{12}^{2k+1}$$

$$\hat{T}\Psi_{2c} = \left\{-\frac{1}{2}({r_1}^2 - {r_2}^2)\left[\frac{1}{r_1}\frac{\partial f_0}{\partial r_1} - \frac{1}{r_2}\frac{\partial f_0}{\partial r_2}\right] - 2f_0\right\} \cdot \frac{1}{r_{12}} +$$

$$+ \sum_{k=0}^{\infty}\left\{-\frac{1}{2}(2k+1)({r_1}^2 - {r_2}^2)\left[\frac{1}{r_1}\frac{\partial f_k}{\partial r_1} - \frac{1}{r_2}\frac{\partial f_k}{\partial r_2}\right] - (2k+1)(2k+2)f_k\right.$$

$$\left. - \frac{1}{2}\left[\frac{\partial^2 f_{k-1}}{\partial {r_1}^2} + \frac{\partial^2 f_{k-1}}{\partial {r_2}^2}\right] - \frac{1}{2}(2k+1)\left[\frac{1}{r_1}\frac{\partial f_{k-1}}{\partial r_1} + \frac{1}{r_2}\frac{\partial f_{k-1}}{\partial r_2}\right]\right\} \cdot {r_{12}}^{2k-1}$$

Ψ_{2c}

for $k = 0$:

$$(r_1{}^2 - r_2{}^2)\left[\frac{1}{r_1}\frac{\partial f_0}{\partial r_1} - \frac{1}{r_2}\frac{\partial f_0}{\partial r_2}\right] + 4f_0 = -2Z(r_1 + r_2)$$

for $k \neq 0$:

$$(r_1{}^2 - r_2{}^2)\left[\frac{1}{r_1}\frac{\partial f_k}{\partial r_1} - \frac{1}{r_2}\frac{\partial f_k}{\partial r_2}\right] + 4(k+1)f_k =$$

$$= -\frac{1}{(2k+1)}\left[\frac{\partial^2 f_{k-1}}{\partial r_1{}^2} + \frac{\partial^2 f_{k-1}}{\partial r_2{}^2}\right] - \left[\frac{1}{r_1}\frac{\partial f_{k-1}}{\partial r_1} + \frac{1}{r_2}\frac{\partial f_{k-1}}{\partial r_2}\right]$$

First-order differential equations!

Ψ_{2c}

for $k = 0$:

$$({r_1}^2 - {r_2}^2)\left[\frac{1}{r_1}\frac{\partial f_0}{\partial r_1} - \frac{1}{r_2}\frac{\partial f_0}{\partial r_2}\right] + 4f_0 = -2Z(r_1 + r_2)$$

$$f_0 = -\frac{2}{3}Z\frac{{r_1}^2 + r_1 r_2 + {r_2}^2}{r_1 + r_2} + \frac{F_0({r_1}^2 + {r_2}^2)}{{r_1}^2 - {r_2}^2}$$

where F_0 is an arbitrary function of the argument ${r_1}^2 + {r_2}^2$

$$\lim_{r_1 \to r_2}\left\{-\frac{2}{3}Z\frac{{r_1}^2 + r_1 r_2 + {r_2}^2}{r_1 + r_2} + \frac{F_0({r_1}^2 + {r_2}^2)}{{r_1}^2 - {r_2}^2}\right\} = \begin{cases} -Zr_2 & \text{when } F_0 = 0 \\ \infty & \text{when } F_0 \neq 0 \end{cases}$$

$$f_0 = -\frac{2}{3}Z\frac{{r_1}^2 + r_1 r_2 + {r_2}^2}{r_1 + r_2}$$

Ψ_{2c}

for $k \neq 0$: $$(r_1{}^2 - r_2{}^2)\left[\frac{1}{r_1}\frac{\partial f_k}{\partial r_1} - \frac{1}{r_2}\frac{\partial f_k}{\partial r_2}\right] + 4(k+1)f_k =$$

$$= -\frac{1}{(2k+1)}\left[\frac{\partial^2 f_{k-1}}{\partial r_1{}^2} + \frac{\partial^2 f_{k-1}}{\partial r_2{}^2}\right] - \left[\frac{1}{r_1}\frac{\partial f_{k-1}}{\partial r_1} + \frac{1}{r_2}\frac{\partial f_{k-1}}{\partial r_2}\right]$$

for $k = 1$: $$(r_1{}^2 - r_2{}^2)\left[\frac{1}{r_1}\frac{\partial f_1}{\partial r_1} - \frac{1}{r_2}\frac{\partial f_1}{\partial r_2}\right] + 8f_1 = -\frac{1}{3}\left[\frac{\partial^2 f_0}{\partial r_1{}^2} + \frac{\partial^2 f_0}{\partial r_2{}^2}\right] - \left[\frac{1}{r_1}\frac{\partial f_0}{\partial r_1} + \frac{1}{r_2}\frac{\partial f_0}{\partial r_2}\right]$$

$$f_0 = -\frac{2}{3}Z\frac{r_1{}^2 + r_1 r_2 + r_2{}^2}{r_1 + r_2}$$

$$f_1 = \frac{2}{9}Z\frac{r_1{}^2 + 3r_1 r_2 + r_2{}^2}{(r_1 + r_2)^3} + \frac{F_1(r_1{}^2 + r_2{}^2)}{(r_1{}^2 - r_2{}^2)^3}$$

where F_1 is an arbitrary function of the argument $r_1{}^2 + r_2{}^2$

$$f_1 = \frac{2}{9}Z\frac{r_1{}^2 + 3r_1 r_2 + r_2{}^2}{(r_1 + r_2)^3}$$

Ψ_{2c}

$$f_0 = -\frac{2}{3} Z \frac{{r_1}^2 + r_1 r_2 + {r_2}^2}{(r_1 + r_2)^1}$$

$$f_1 = \frac{2}{9} Z \frac{{r_1}^2 + 3 r_1 r_2 + {r_2}^2}{(r_1 + r_2)^3}$$

$$f_2 = \frac{2}{45} Z \frac{{r_1}^2 + 5 r_1 r_2 + {r_2}^2}{(r_1 + r_2)^5}$$

$$f_3 = \frac{2}{105} Z \frac{{r_1}^2 + 7 r_1 r_2 + {r_2}^2}{(r_1 + r_2)^7}$$

$$\vdots$$

$$f_k = \frac{2Z}{3(2k-1)(2k+1)} \frac{{r_1}^2 + (2k+1) r_1 r_2 + {r_2}^2}{(r_1 + r_2)^{2k+1}}$$

Ψ_{2c}

$$\hat{T}\Psi_{2c} = Z\frac{r_1+r_2}{r_{12}}$$

$$\hat{T}\left(r_1{}^i r_2{}^j r_{12}{}^k\right) = -g_k(r_1,r_2;i,j,k)r_{12}{}^k + g_{k+1}(r_1,r_2;i,j,k)r_{12}{}^{k-2}$$

$$\Psi_{2c} = \sum_{k=0}^{\infty} f_k(r_1,r_2)\cdot r_{12}{}^{2k+1}$$

$$f_k(r_1,r_2) = \frac{2Z(r_1{}^2 + (2k+1)r_1r_2 + r_2{}^2)}{3(2k+1)(2k-1)(r_1+r_2)^{2k+1}}$$

$$\Psi_{2c} = \frac{2Z}{3}(r_1{}^2 + r_2{}^2)\sum_{k=0}^{\infty}\frac{\left(\frac{r_{12}}{r_1+r_2}\right)^{2k+1}}{(2k-1)(2k+1)} + \frac{2Z}{3}r_1r_2\sum_{k=0}^{\infty}\frac{\left(\frac{r_{12}}{r_1+r_2}\right)^{2k+1}}{(2k-1)}$$

Ψ_{2c}

$$\Psi_{2c} = \frac{2Z}{3}({r_1}^2 + {r_2}^2)\sum_{k=0}^{\infty}\frac{\left(\frac{r_{12}}{r_1 + r_2}\right)^{2k+1}}{(2k-1)(2k+1)} + \frac{2Z}{3}r_1 r_2\sum_{k=0}^{\infty}\frac{\left(\frac{r_{12}}{r_1 + r_2}\right)^{2k+1}}{(2k-1)}$$

$$\sum_{k=0}^{\infty}\frac{\left(\frac{r_{12}}{r_1 + r_2}\right)^{2k+1}}{(2k-1)(2k+1)} = \frac{1}{2}\left(\frac{{r_{12}}^2}{(r_1 + r_2)^2} - 1\right)\operatorname{arctanh}\left(\frac{r_{12}}{r_1 + r_2}\right) - \frac{1}{2}\frac{r_{12}}{r_1 + r_2}$$

$$\sum_{k=0}^{\infty}\frac{\left(\frac{r_{12}}{r_1 + r_2}\right)^{2k+1}}{(2k-1)} = \frac{{r_{12}}^2}{(r_1 + r_2)^2}\operatorname{arctanh}\left(\frac{r_{12}}{r_1 + r_2}\right) - \frac{r_{12}}{r_1 + r_2}$$

$$\Psi_{2c} = \frac{Z}{3}({r_1}^2 + {r_2}^2 - {r_{12}}^2)\operatorname{arctanh}\left(\frac{r_{12}}{r_1 + r_2}\right) - \frac{Z}{3}r_{12}(r_1 + r_2)$$

Ψ_{2c}

$$\hat{T}\Psi_{2c} = Z\frac{r_1+r_2}{r_{12}}$$

$$\Psi_{2c} = \sum_{k=0}^{\infty} f_k(r_1, r_2) \cdot r_{12}{}^{2k+1}$$

$$f_k(r_1, r_2) = \frac{2Z(r_1{}^2 + (2k+1)r_1 r_2 + r_2{}^2)}{3(2k+1)(2k-1)(r_1+r_2)^{2k+1}}$$

$$\Psi_{2c} = \frac{Z}{3}(r_1{}^2 + r_2{}^2 - r_{12}{}^2)\,\mathrm{arctanh}\left(\frac{r_{12}}{r_1+r_2}\right) - \frac{Z}{3} r_{12}(r_1+r_2)$$

Ψ_{2d}

$$\hat{T}\Psi_{2d} = \frac{Z}{2}\left(\frac{r_{12}}{r_2} + \frac{r_{12}}{r_1}\right)$$

$$\hat{T}\left({r_1}^i {r_2}^j {r_{12}}^k\right) = F_1(r_1, r_2; i, j, k){r_{12}}^k + F_2(r_1, r_2; i, j, k){r_{12}}^{k-2}$$

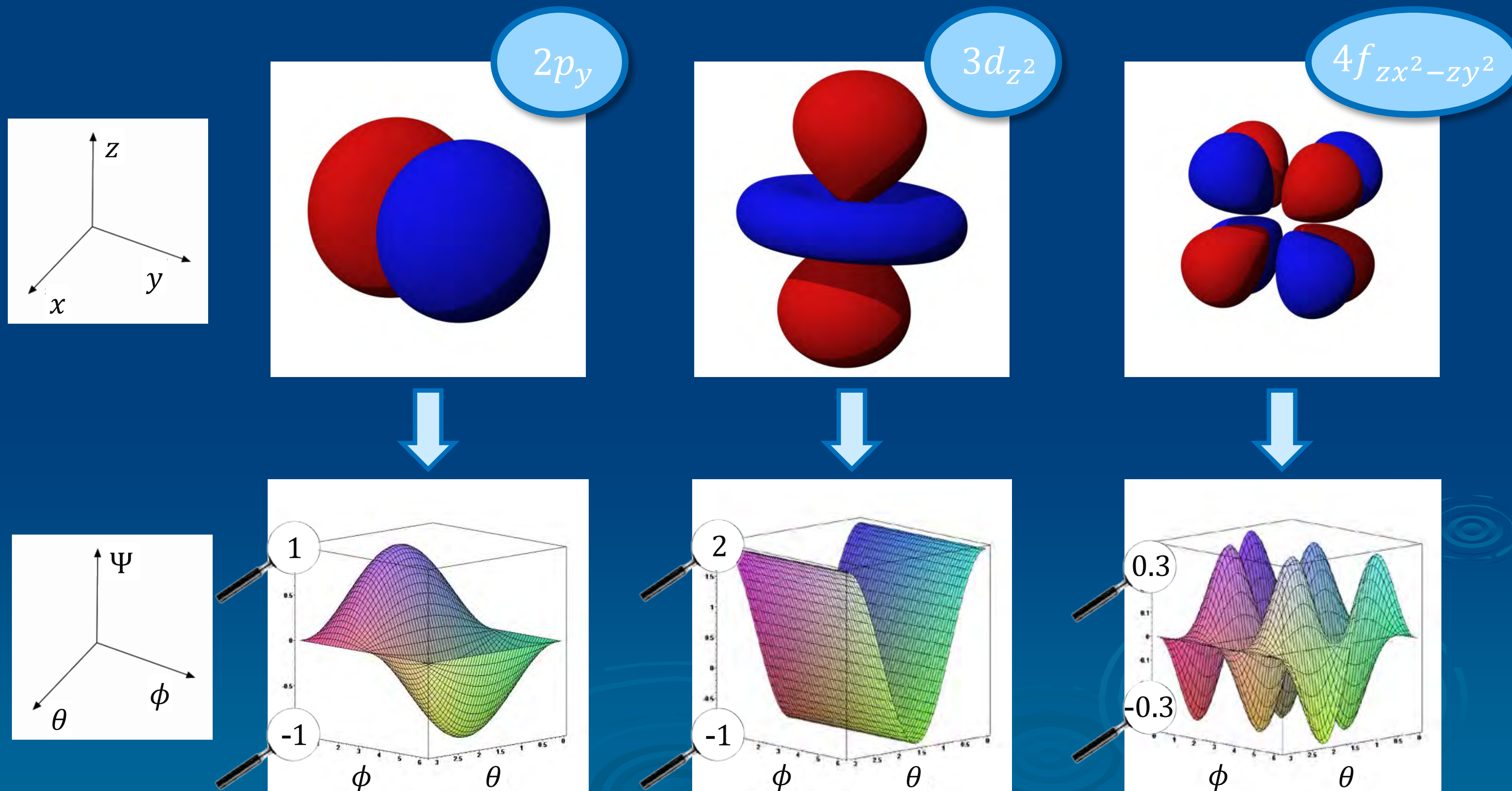
$$\Psi_{2d} = \sum_{k=0}^{\infty} f_k(r_1, r_2) \cdot {r_{12}}^{2k+3}$$

$$f_k(r_1, r_2) = \frac{2Z(-1)^{k+1}}{3(2k+3)({r_1}^2 + {r_2}^2)^{k+\frac{1}{2}}} \sum_{n=0}^{\infty} \left(\frac{{r_2}^2 - {r_1}^2}{{r_1}^2 + {r_2}^2}\right)^n \sum_{m=0}^{\infty} \binom{k+\frac{3}{2}}{m} \binom{\frac{m}{2}}{n+k+1}$$

$$\Psi_{2d} = \frac{2Z}{3}({r_1}^2 - {r_2}^2)\,\mathrm{arctanh}\left(\frac{r_{12}(r_1 + r_2)}{{r_1}^2 - {r_2}^2}\right) - \frac{2Z}{3} r_{12}(r_1 + r_2) - \frac{2Z}{3}({r_1}^2 - {r_2}^2)\,\mathrm{arctanh}\left(\frac{r_{12}\sqrt{2{r_1}^2 + 2{r_2}^2 - {r_{12}}^2}}{{r_1}^2 - {r_2}^2}\right) + \frac{2Z}{3} r_{12}\sqrt{2{r_1}^2 + 2{r_2}^2 - {r_{12}}^2}$$

Visualization of wave function

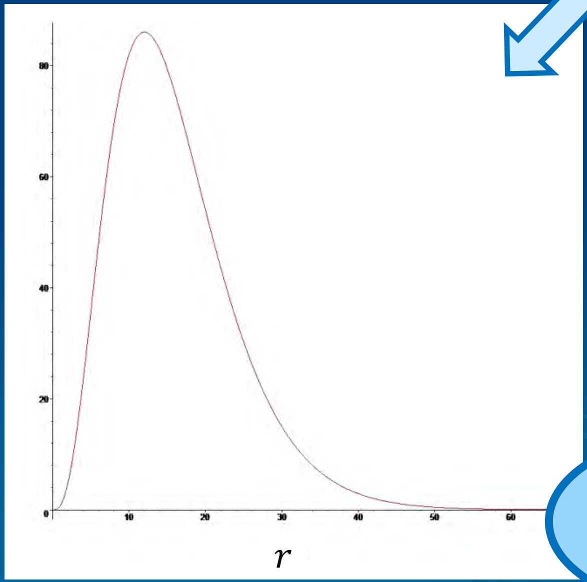
Hydrogenic orbitals (angular part)



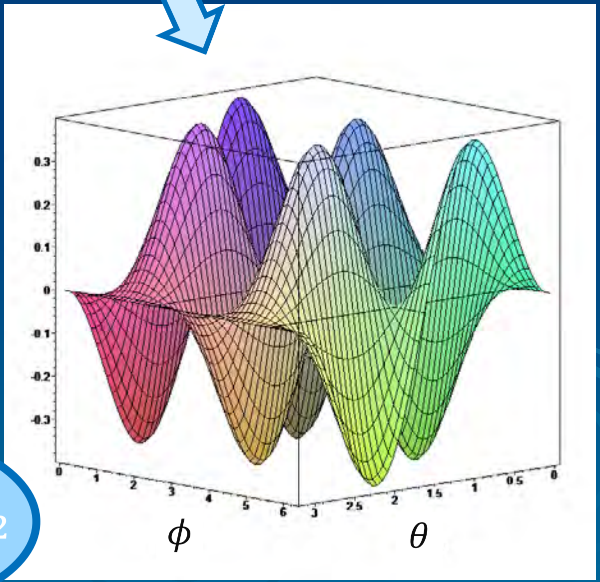
Visualization of wave function

Hydrogenic wave functions

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r) \cdot Y_{lm}(\theta,\phi)$$

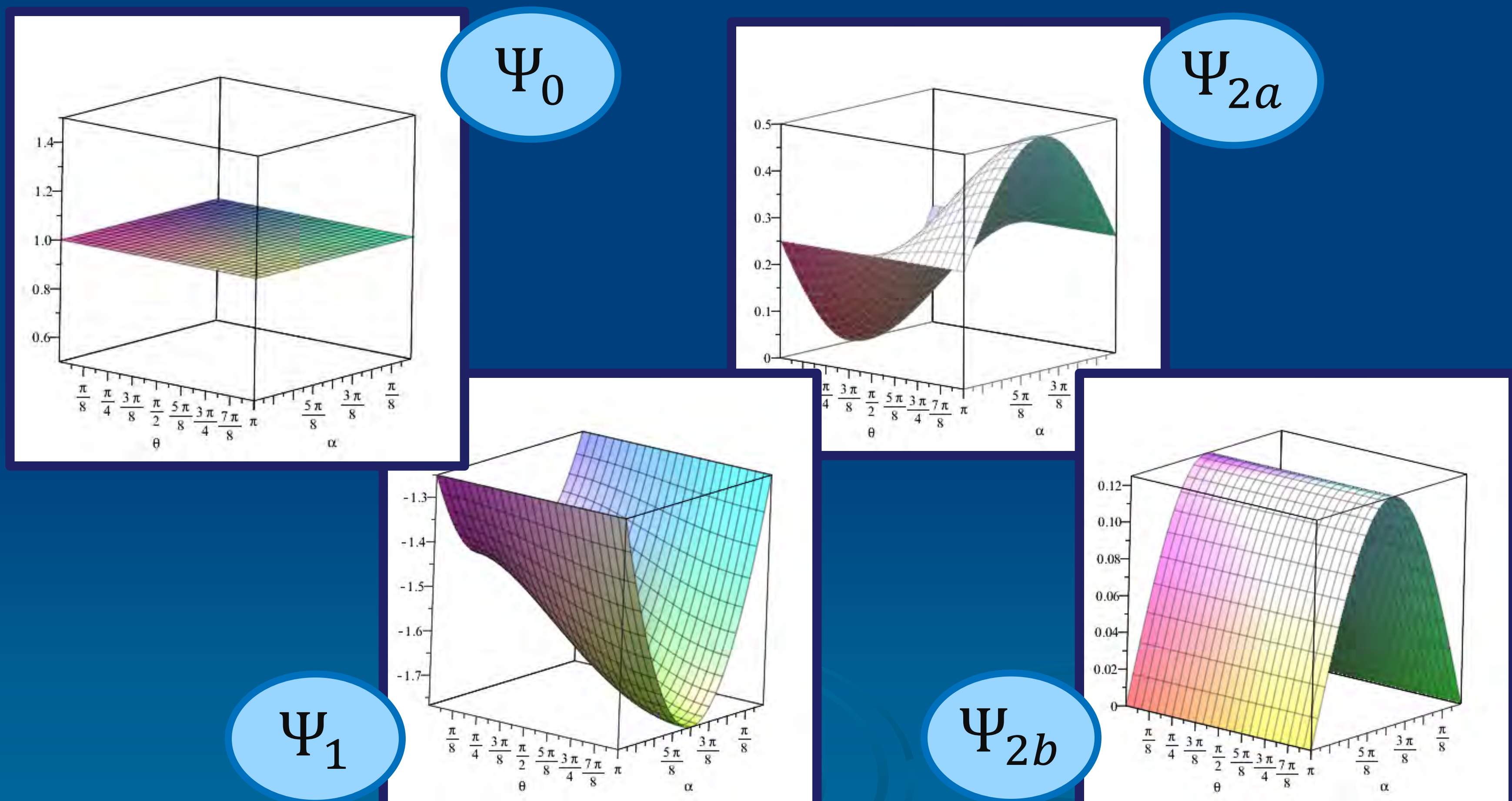


$4f_{zx^2-zy^2}$



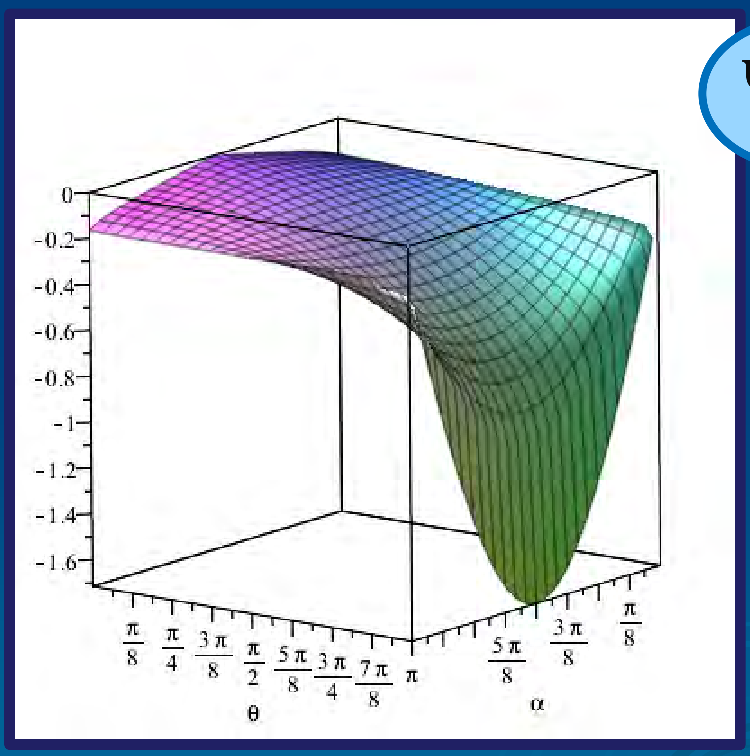
Visualization of wave function

Components of helium wave functions

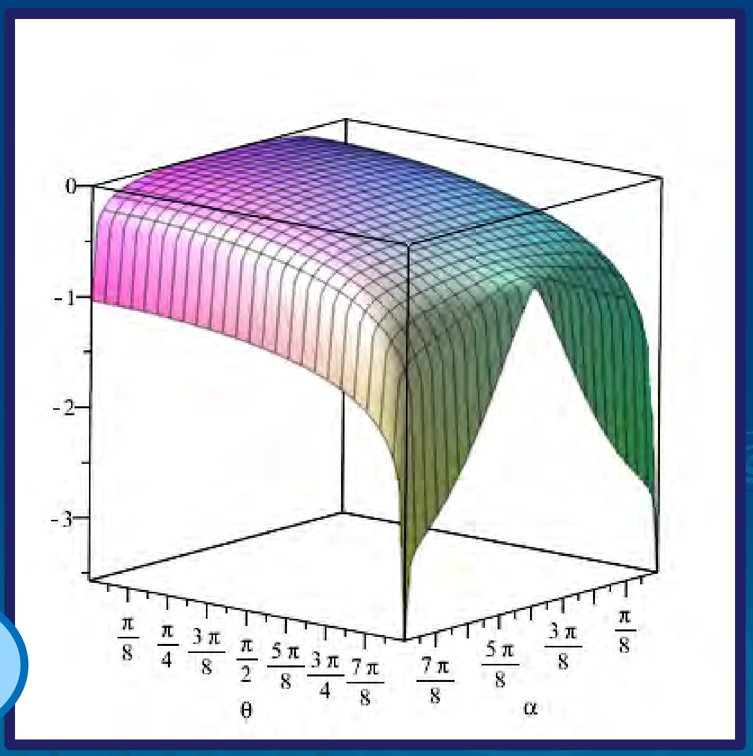


Visualization of wave function

Components of helium wave functions



Ψ_{2c}



Ψ_{2d}

Ψ_{2c}

$$\hat{T}\Psi_{2c} = Z\frac{r_1+r_2}{r_{12}}$$

Only odd powers of r_{12}

$$\Psi_{2c} = \sum_{k=0}^{\infty} f_k(r_1, r_2)\cdot {r_{12}}^{2k+1}$$

$$f_k(r_1, r_2) = \frac{2Z({r_1}^2 + (2k+1)r_1 r_2 + {r_2}^2)}{3(2k+1)(2k-1)(r_1+r_2)^{2k+1}}$$

$$\Psi_{2c} = \frac{Z}{3}({r_1}^2 + {r_2}^2 - {r_{12}}^2)\,\mathrm{arctanh}\left(\frac{r_{12}}{r_1+r_2}\right) - \frac{Z}{3}r_{12}(r_1+r_2)$$

Ψ_{2c}

$$\hat{T}\Psi_{2c} = Z\frac{r_1+r_2}{r_{12}}$$

$$\Psi_{2c} = \sum_{k=0}^{\infty} f_{2k+1}(r_1, r_2) \cdot {r_{12}}^{2k+1}$$

$$f_{2k+1}(r_1, r_2) = \frac{2Z({r_1}^2 + (2k+1)r_1 r_2 + {r_2}^2)}{3(2k+1)(2k+1-2)(r_1+r_2)^{2k+1}}$$

$$\Psi_{2c} = \frac{Z}{3}({r_1}^2 + {r_2}^2 - {r_{12}}^2)\,\mathrm{arctanh}\left(\frac{r_{12}}{r_1+r_2}\right) - \frac{Z}{3}r_{12}(r_1+r_2)$$

Ψ_{2c}

$$f_0(r_1, r_2) = \frac{r_1 r_2}{3} - \frac{1}{3}({r_1}^2 + {r_2}^2 \ldots$$

$$f_2(r_1, r_2) = \frac{1}{3}\ln(r_1 + r_2) + \frac{1}{6}\frac{({r_1}^2 + {r_2}^2)}{(r_1 + r_2)^2} - C_1$$

not working for
$k = 0$ and $k = 2$

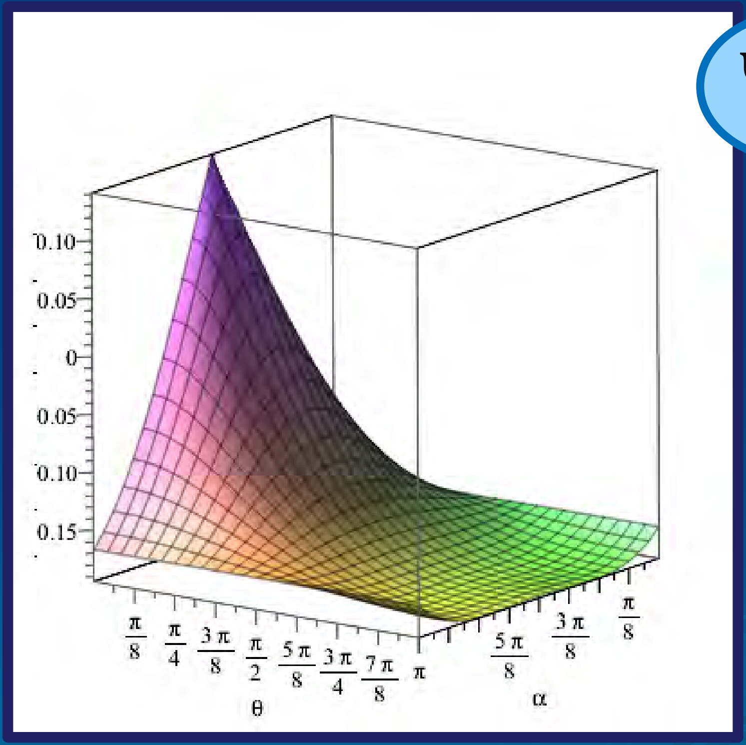
$$f_k(r_1, r_2) = \frac{2Z({r_1}^2 + k r_1 r_2 + {r_2}^2)}{3k(k-2)(r_1 + r_2)^k}$$

$$\Psi_{2c} = \frac{Z}{3} r_1 r_2 - \frac{Z}{3} r_{12}(r_1 + r_2) - \frac{Z}{3}({r_1}^2 + {r_2}^2 - {r_{12}}^2)\ln(r_1 + r_2 + r_{12})$$
$$+ C_1({r_1}^2 + {r_2}^2 - {r_{12}}^2)$$

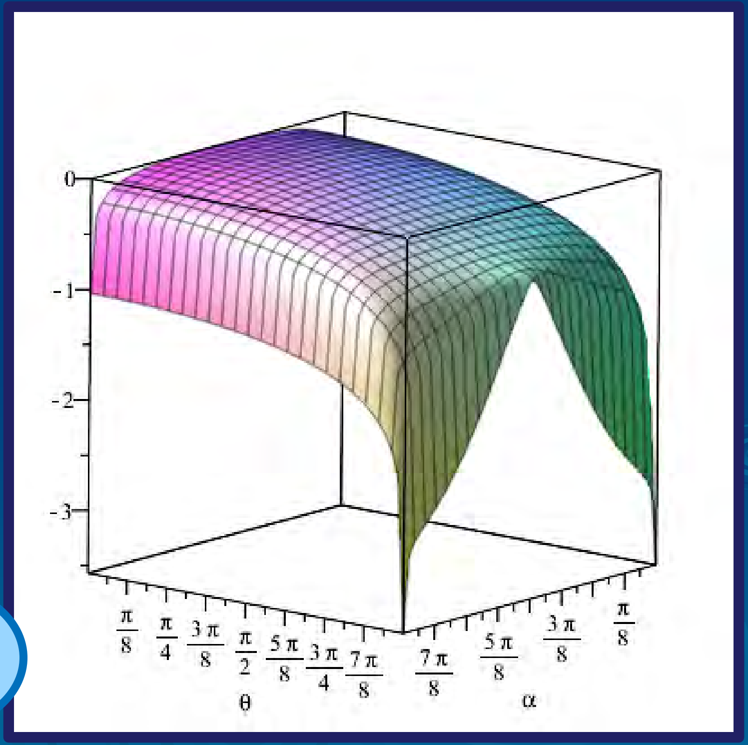
Visualization of wave function

Components of helium wave functions

Ψ_{2c}



Ψ_{2d}



Summary

$$\Psi = \Psi_0 + \Psi_1 + \Psi_2 + \Psi_3 + \cdots$$

$$\Psi_2 = \Psi_{2a} + \Psi_{2b} + \Psi_{2c} + \Psi_{2d}$$

$$\Psi_0 = 1$$

$$\Psi_1 = -Z(r_1 + r_2) - \frac{1}{2} r_{12}$$

$$\Psi_{2a} = \frac{1 + 4Z^2 - 2E}{12} {r_{12}}^2$$

$$\Psi_{2b} = Z^2 \cdot r_1 \cdot r_2$$

$$\Psi_{2c} = Z \sum_{k=0}^{\infty} c_k(r_1, r_2) {r_{12}}^k$$

$$\Psi_{2d} = \frac{Z}{2} \sum_{k=0}^{\infty} d_k(r_1, r_2) {r_{12}}^k$$

Summary

$$c_k = \begin{cases} \dfrac{r_1 r_2}{3} - \dfrac{1}{3}({r_1}^2 + {r_2}^2)\ln(r_1 + r_2) & \text{for} \quad k = 0 \\ \dfrac{1}{3}\ln(r_1 + r_2) + \dfrac{1}{6}\dfrac{({r_1}^2 + {r_2}^2)}{(r_1 + r_2)^2} & \text{for} \quad k = 2 \\ -\dfrac{(-1)^k({r_1}^2 + {r_2}^2)(k+2)}{3\,k\,(k-2)\sqrt{2{r_1}^2 + 2{r_2}^2}^{\,k}}\ {}_2F_1\left[\begin{matrix}\frac{k}{4}, \frac{k}{4} - \frac{1}{2} \\ \frac{k}{2} + 1\end{matrix}; \dfrac{({r_1}^2 - {r_2}^2)^2}{({r_1}^2 + {r_2}^2)^2}\right] & \end{cases}$$

$$\Psi_{2c} = Z \sum_{k=0}^{\infty} c_k(r_1, r_2) {r_{12}}^k \qquad \Psi_{2d} = \frac{Z}{2} \sum_{k=0}^{\infty} d_k(r_1, r_2) {r_{12}}^k$$

Summary

$$d_k = \begin{cases} \frac{2}{3\pi}({r_1}^2 - {r_2}^2)\left[\int_{\frac{\pi}{2}}^{2\arctan\left(\frac{r_2}{r_1}\right)} \operatorname{arctanh}(\sin t)\,dt + \arcsin\left(\frac{{r_1}^2 - {r_2}^2}{{r_1}^2 + {r_2}^2}\right)\operatorname{arctanh}\left(\frac{2r_1 r_2}{{r_1}^2 + {r_2}^2}\right)\right] \\ -\frac{2}{3\pi}({r_1}^2 + {r_2}^2)(\ln({r_1}^2 + {r_2}^2) - 1) & \text{for} \quad k = 0 \\ 0 & \text{for} \quad k = 1 \\ \frac{2}{3\pi}\ln({r_1}^2 + {r_2}^2) + \frac{4r_1 r_2}{3\pi({r_1}^2 - {r_2}^2)}\arcsin\left(\frac{{r_1}^2 - {r_2}^2}{{r_1}^2 + {r_2}^2}\right) & \text{for} \quad k = 2 \\ -\frac{2\,({r_1}^2 + {r_2}^2)\Gamma\left(\frac{k}{2} - 1\right)}{3\,\Gamma\left(\frac{k}{2} + \frac{1}{2}\right)\sqrt{\pi}\sqrt{2{r_1}^2 + 2{r_2}^2}^{\,k}}\, {}_3F_2\left[\begin{matrix} 1, \frac{k}{4}, \frac{k}{4} - \frac{1}{2} \\ \frac{1}{2}, \frac{k}{2} + \frac{1}{2} \end{matrix}; \frac{({r_1}^2 - {r_2}^2)^2}{({r_1}^2 + {r_2}^2)^2}\right] & \text{for} \quad k > 2 \end{cases}$$

$$\Psi_{2c} = Z\sum_{k=0}^{\infty} c_k(r_1, r_2){r_{12}}^k \qquad \Psi_{2d} = \frac{Z}{2}\sum_{k=0}^{\infty} d_k(r_1, r_2){r_{12}}^k$$

Acknowledgments

- E. A. Hylleraas (1928-1964)
- V. A. Fock (1954-1958)
  - A. M. Ermolaev, G. B. Sochilin, Y. N. Demkov
- Ph. Pluvinage (1950-1985)
- E. D. Maslen (1978-1987)
  - P. C. Abbott, J. Gottschalk, C. Davis, K. McIsaac
- J. D. Morgan (1977-)
- Bing-hou, Johanna and Wen-yang
- Jacek Karwowski and Andreas Savin ☺
- and many, many others….

Conclusions

- Three-body problem in QM is difficult but solvable
- The solution may not be easy but serious simplifications can be possible by re-summations
- Various approaches remain to be tested
  - Expansion and recurrence techniques
  - Lie group symmetries
  - Generating functions
  - and many, many others…
- A lot of work is left in the field and everybody is invited to join the collaboration or start its own activity
- I would be happy to share all the information

Warning from classical physics

- F. Diacu, “The solution of the *n*-body problem”, *The Mathematical Intelligencer*, **18**, 66-70 (1996)

- “Did this mean the end of the n-body problem? Paradoxically […] not; […] in fact we know nothing more than before having this solution. […] These series solutions […] have very slow convergence. One would have to sup up millions of terms to determine the motion of particles for insignificantly short intervals of time. […] Hundred years later […] solution presents only historical interest.”

1

Analytical form of helium wave function

2

Theory and applications of Zhang-Zhang polynomials

Plan of the talk

- Basic definitions
- Properties of ZZ polynomials
- Various techniques for computing ZZ polynomials
- Free software for ZZ polynomials manipulations
- Applications of ZZ polynomials
- List of open problems

General references

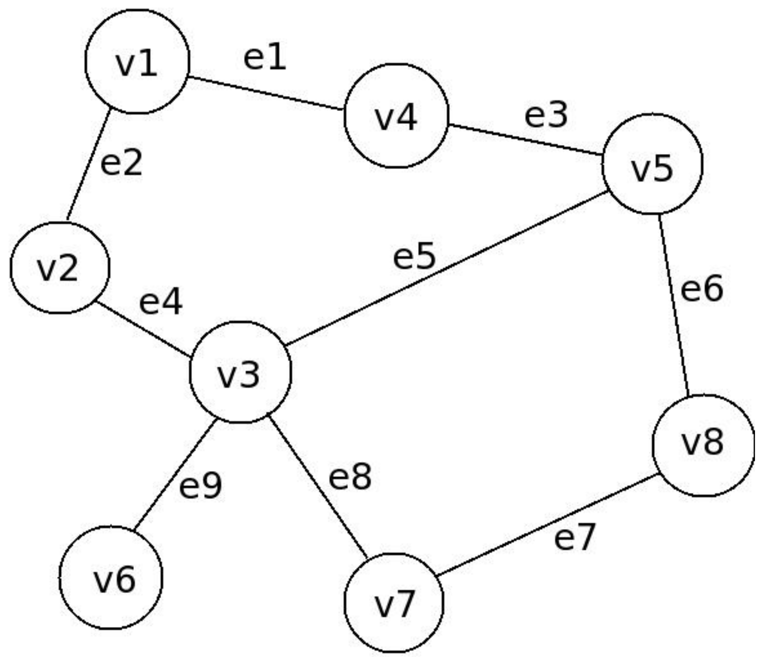
- Benzenoid structures: S. J. Cyvin and I. Gutman, “Kekule structures in benzenoid hydrocarbons”, Lecture Notes in Chemistry, vol. 46, Springer, 1988
- ZZ polynomials: H. Zhang and F. Zhang, Discr. Appl. Math. 69 (1996) 147-167 (~30 citations)
- Computing ZZ polynomials: C.-P. Chou and H.A. Witek, MATCH Commun. Math. Comput. Chem. 68 (2012) 3-30 and 31-64

Complete literature

- Zhang & Zhang (6 papers)
- Gutman & colaborators (6 papers)
- Our group (8 papers)
- Other groups (~10 papers)

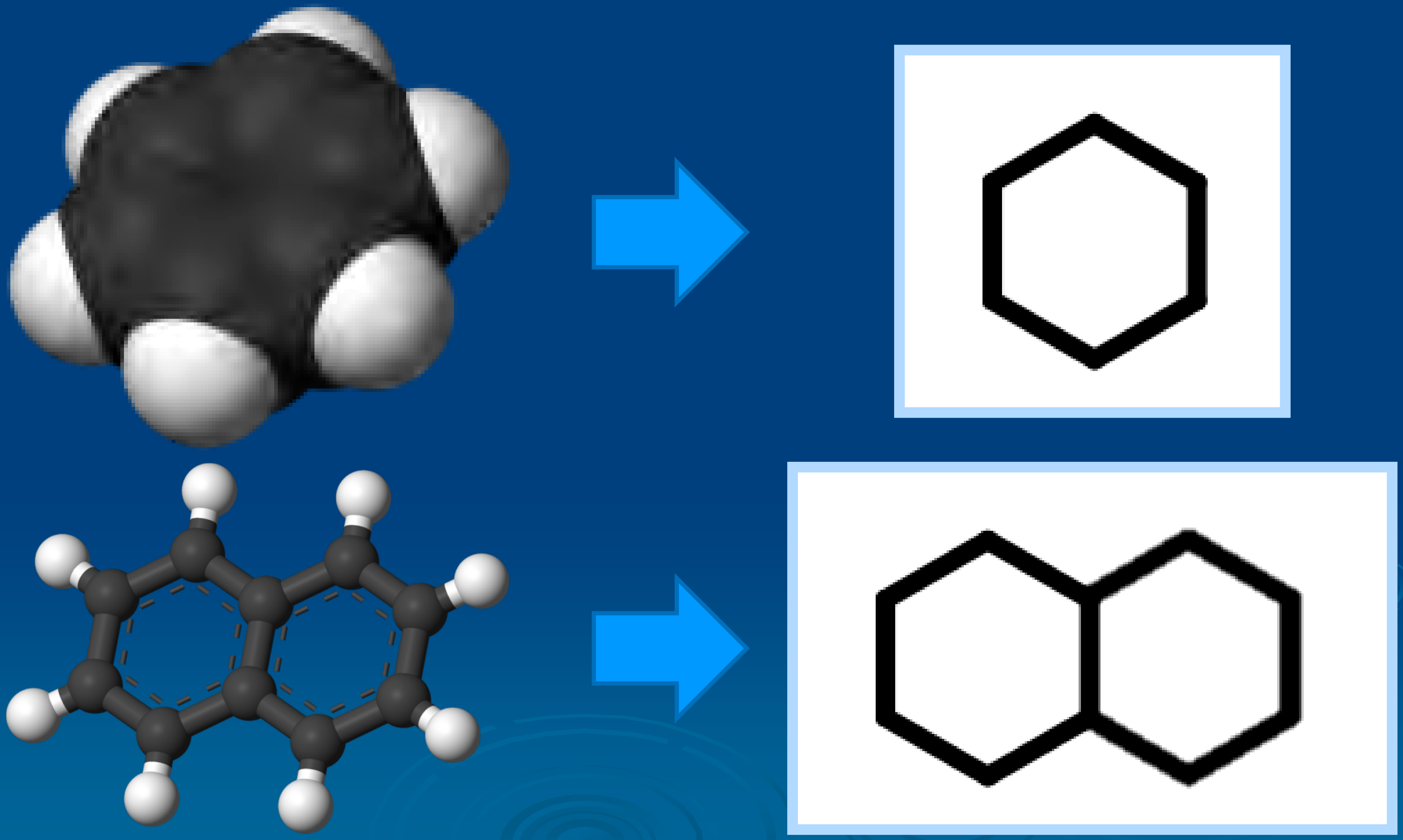
Concept of a graph

$$G = (V, E)$$



An undirected graph with 8 vertices and 9 edges

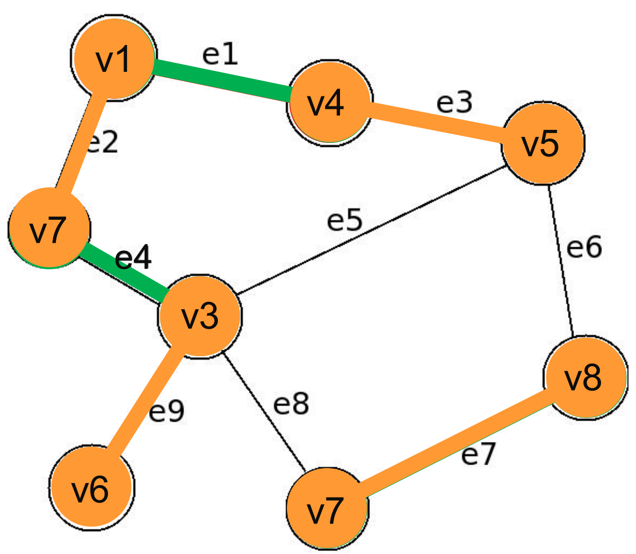
Graphs in chemistry



Definitions $G = (V, E)$

Does a graph G permits a perfect matching?

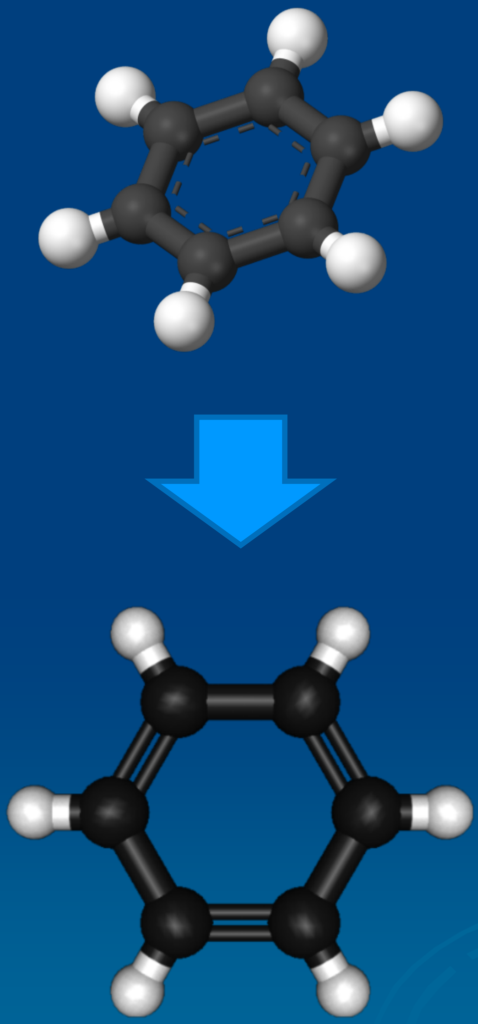
How many perfect matchings does a graph G permit?

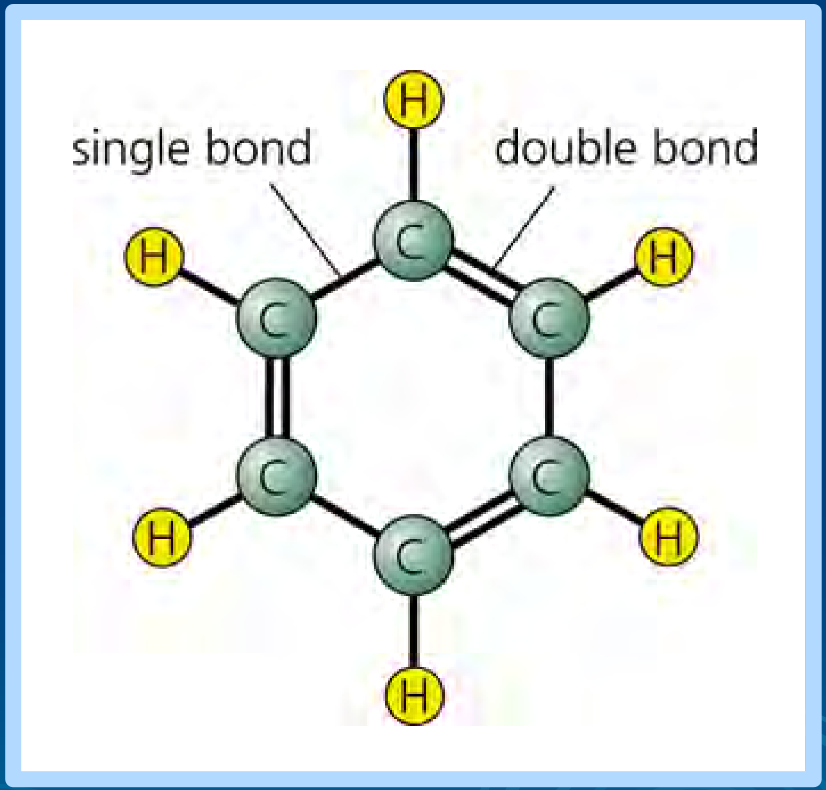


An undirected graph with 8 vertices and 9 edges

- We say that $\{e2, e3, e7, e9\} \subset E$ is a perfect matching of G if every vertex is covered once and only once

Perfect matching in chemistry





Kekule structures
of benzenoid structures
(chemistry)

=

Perfect matchings
in polyhexes
(graph theory)

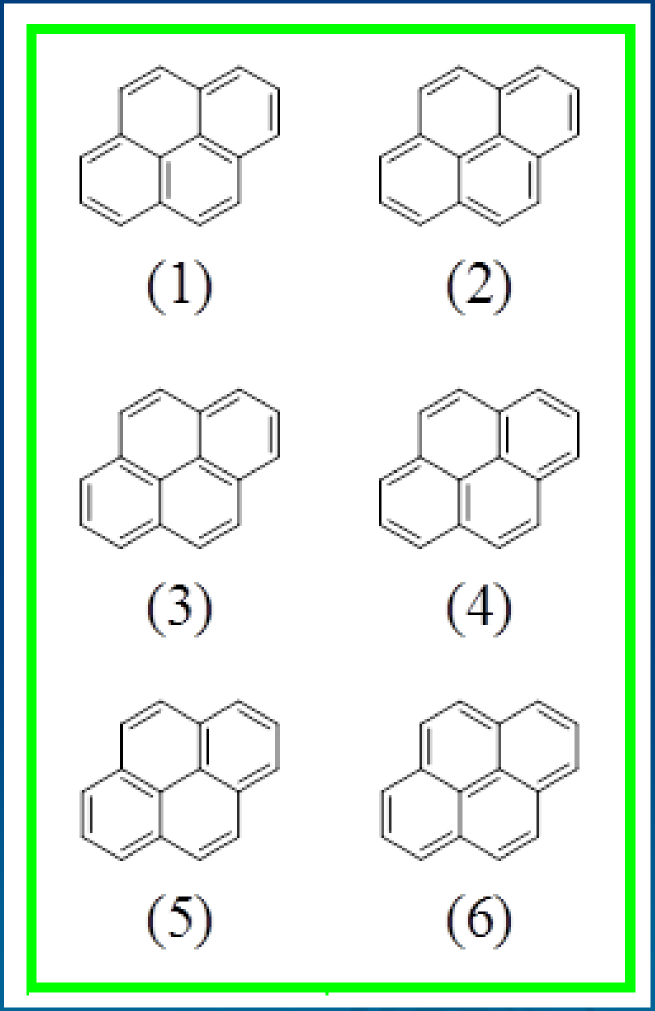
Kekule structures of benzene

K=2

Kekule structures of naphthalene

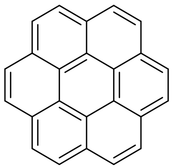
K=3

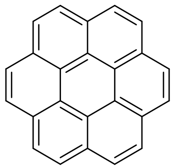
Kekule structures of pyrene



K=6

Kekule structures of coronene


(1)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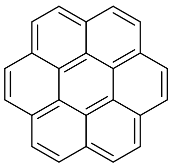
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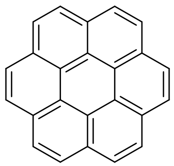
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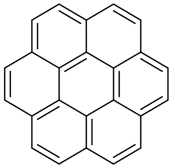
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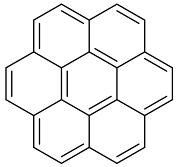
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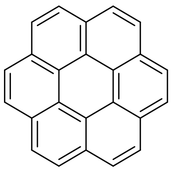
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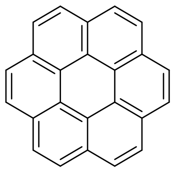
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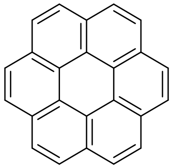
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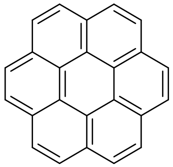
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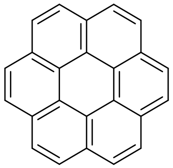
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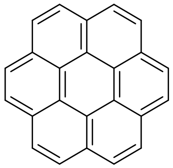
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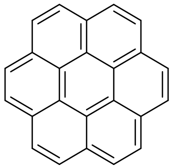
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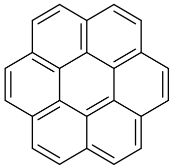
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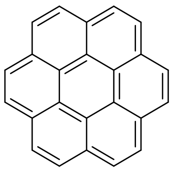
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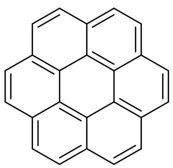
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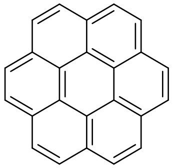
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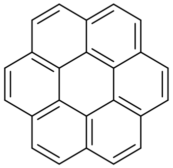
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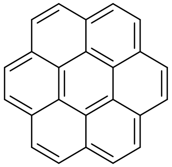
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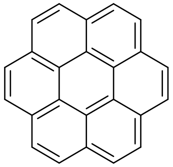
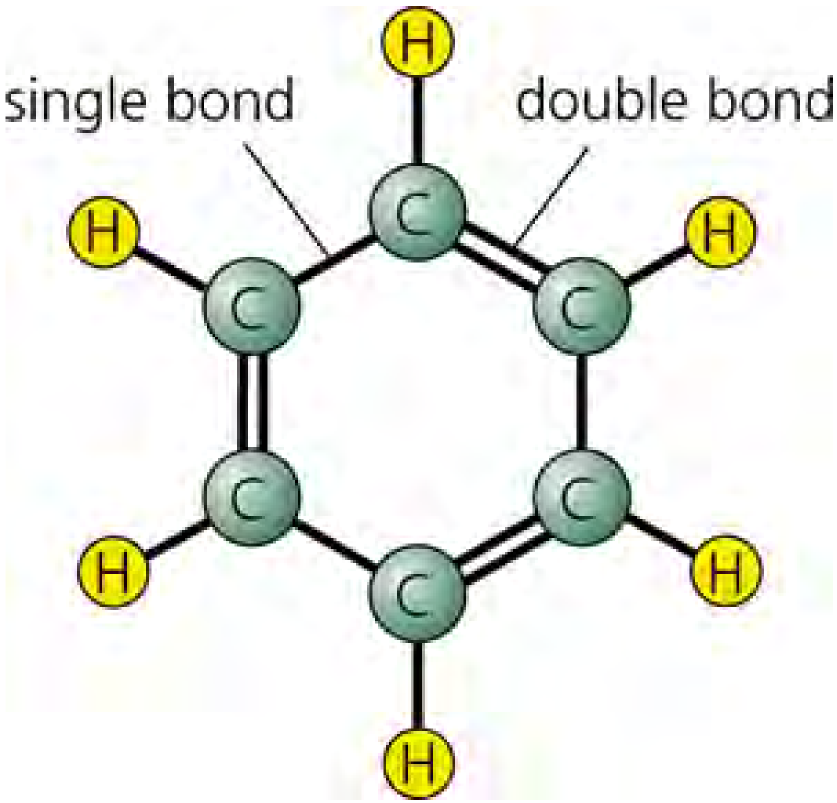
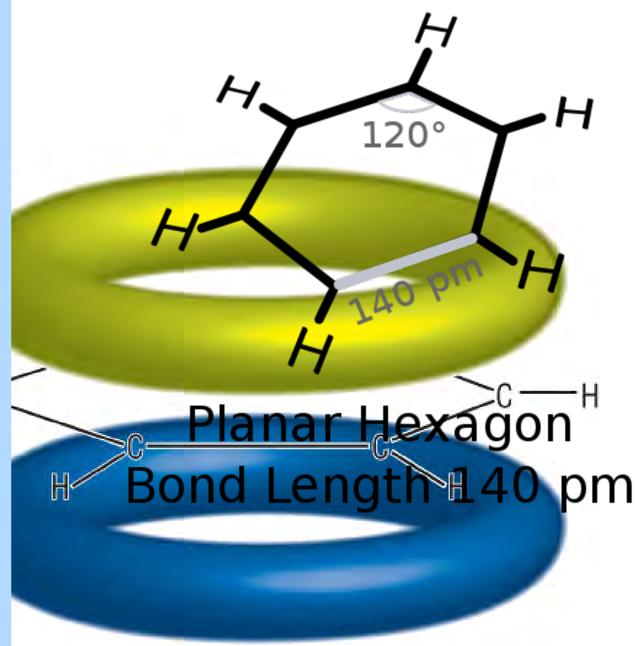

(20)

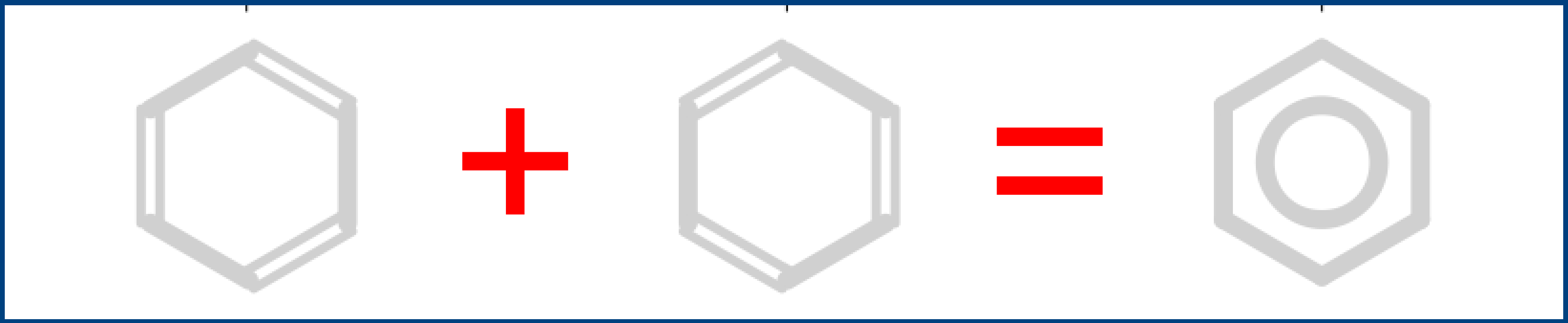
K=20

Aromatic ring

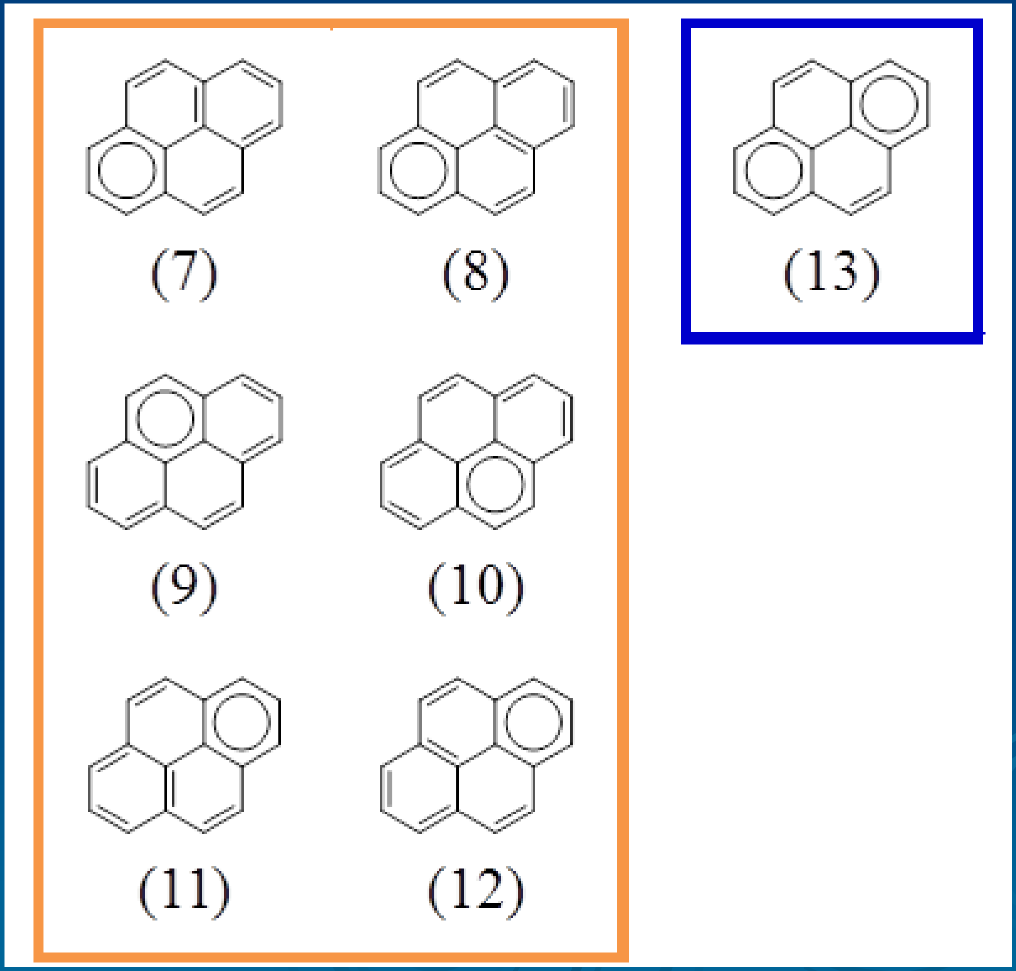




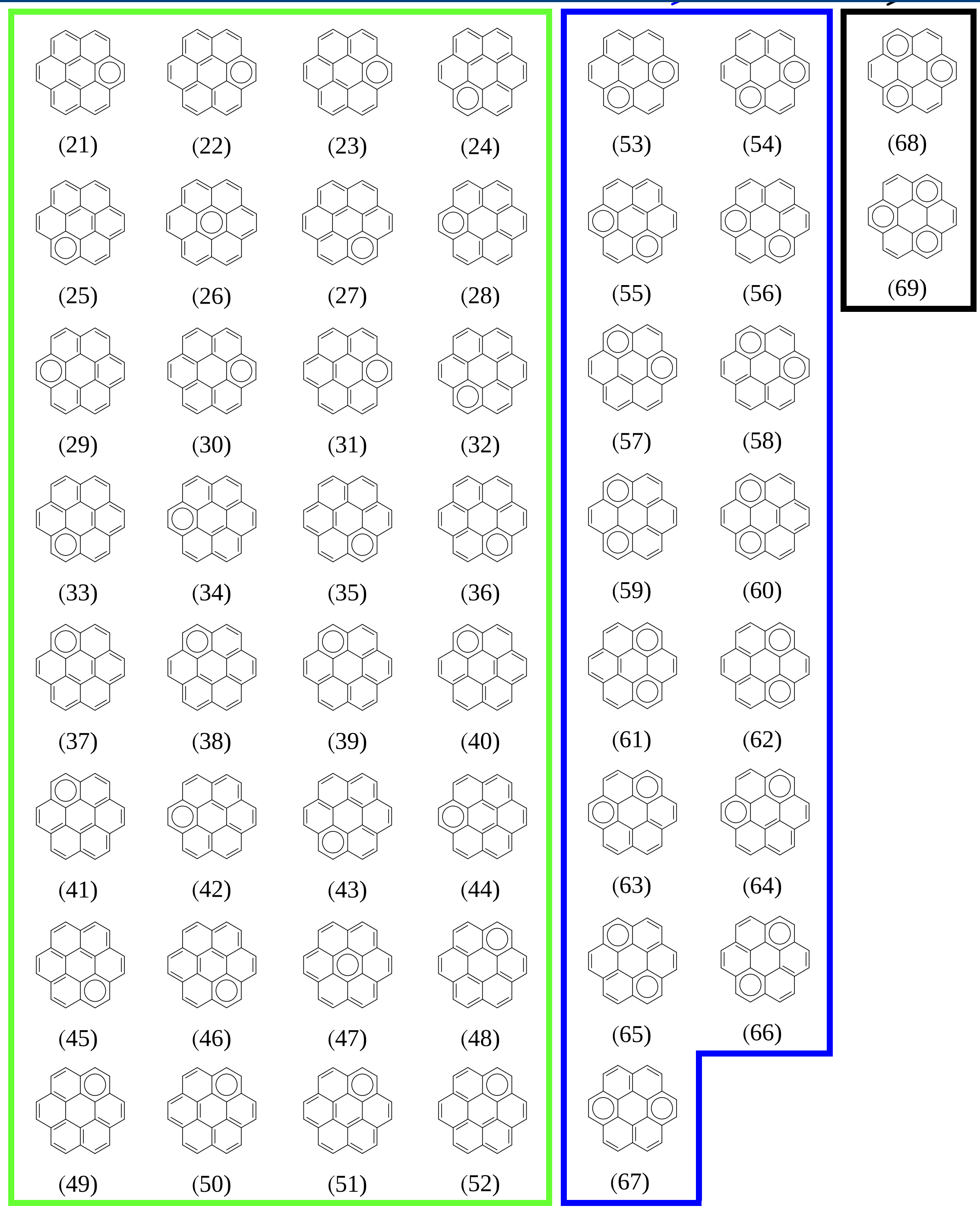
Clar sextet



Generalized Kekule structures of pyrene



Generalized Kekule structures of coronene



Generalized Kekule structures
of benzenoid structures
(chemistry)

=

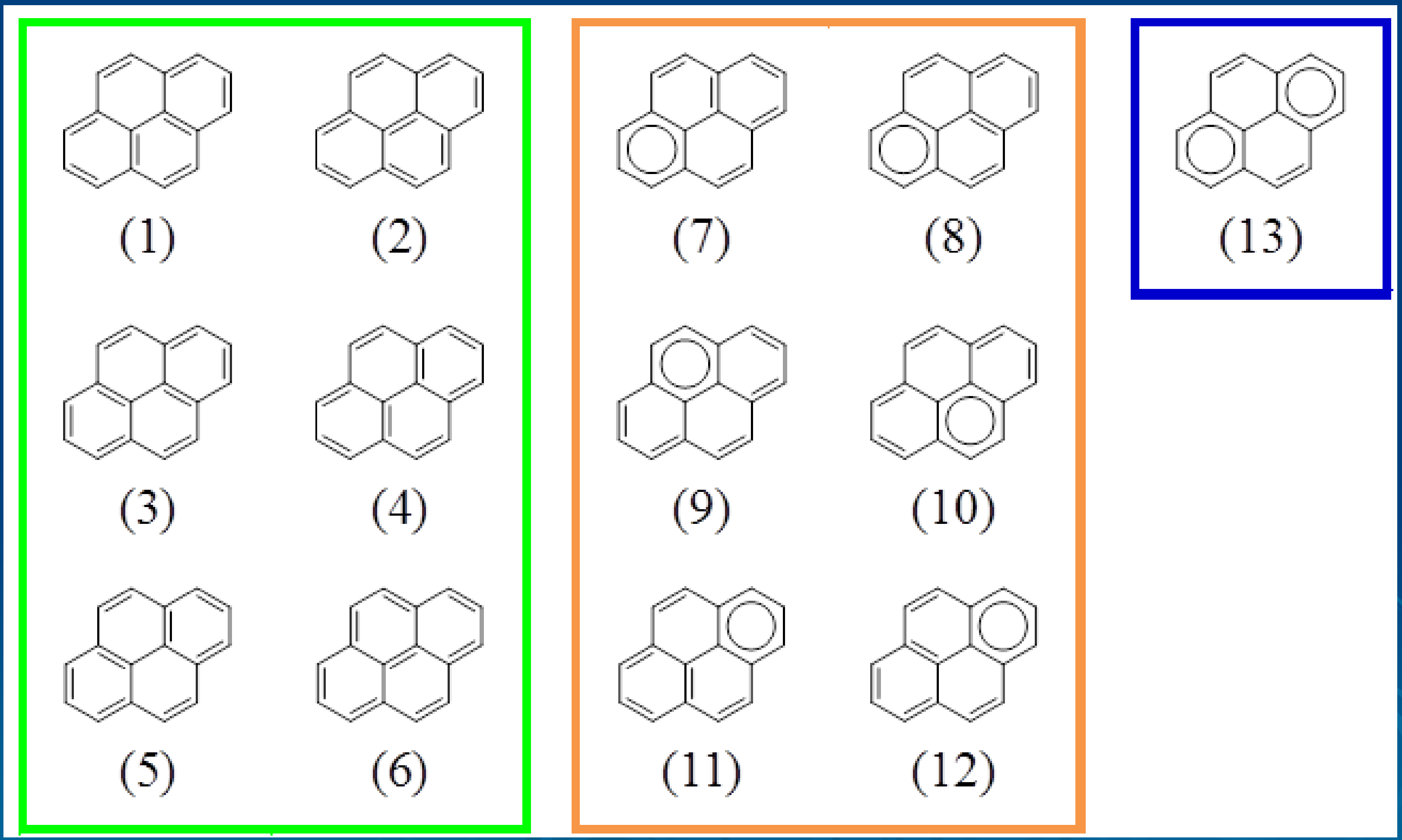
Clar covers
of benzenoid structures
(chemistry)

Clar covers of benzenoid structures (chemistry)

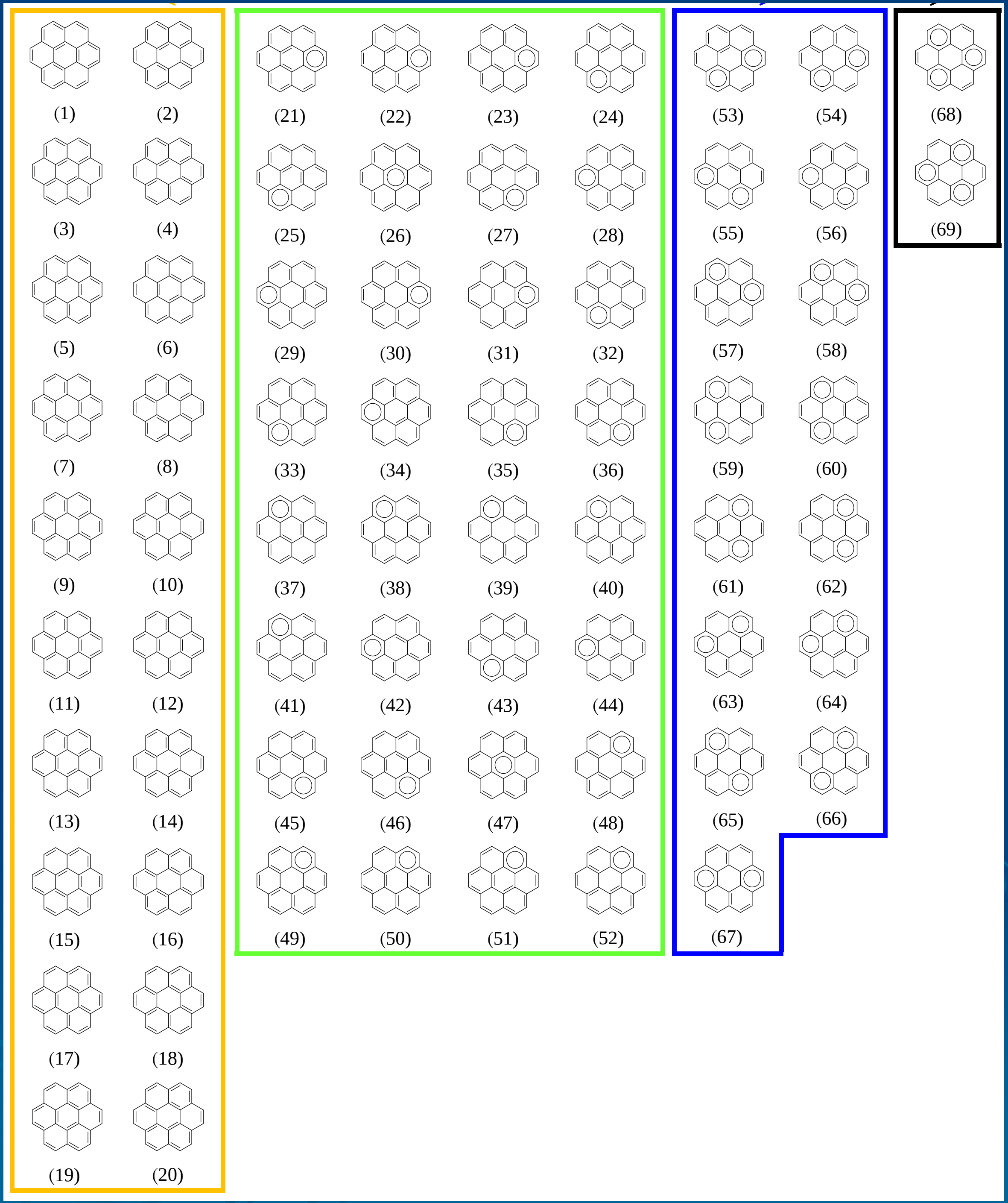
=

Generalized perfect matchings in polyhexes (graph theory)

Clar covers of pyrene



Clar covers of coronene



Important questions

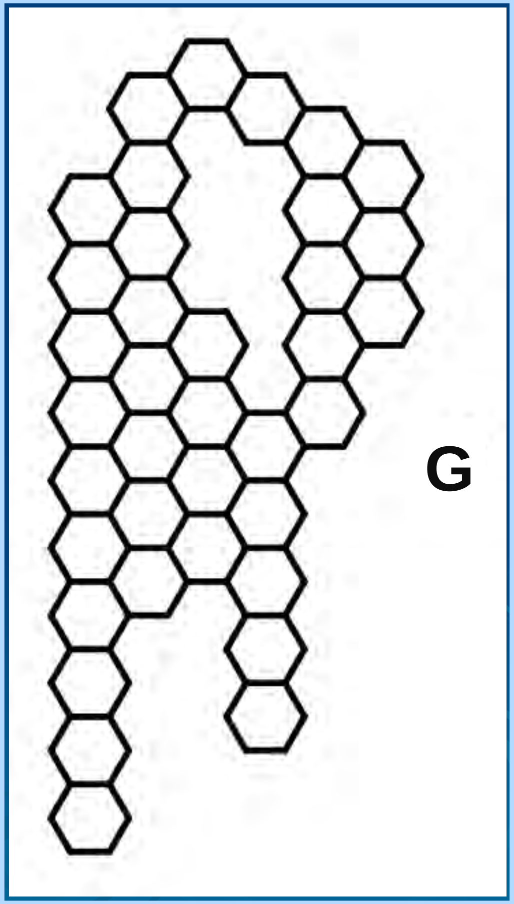
Does a graph G permits a generalized perfect matching?

How many generalized perfect matchings does a graph G permit?

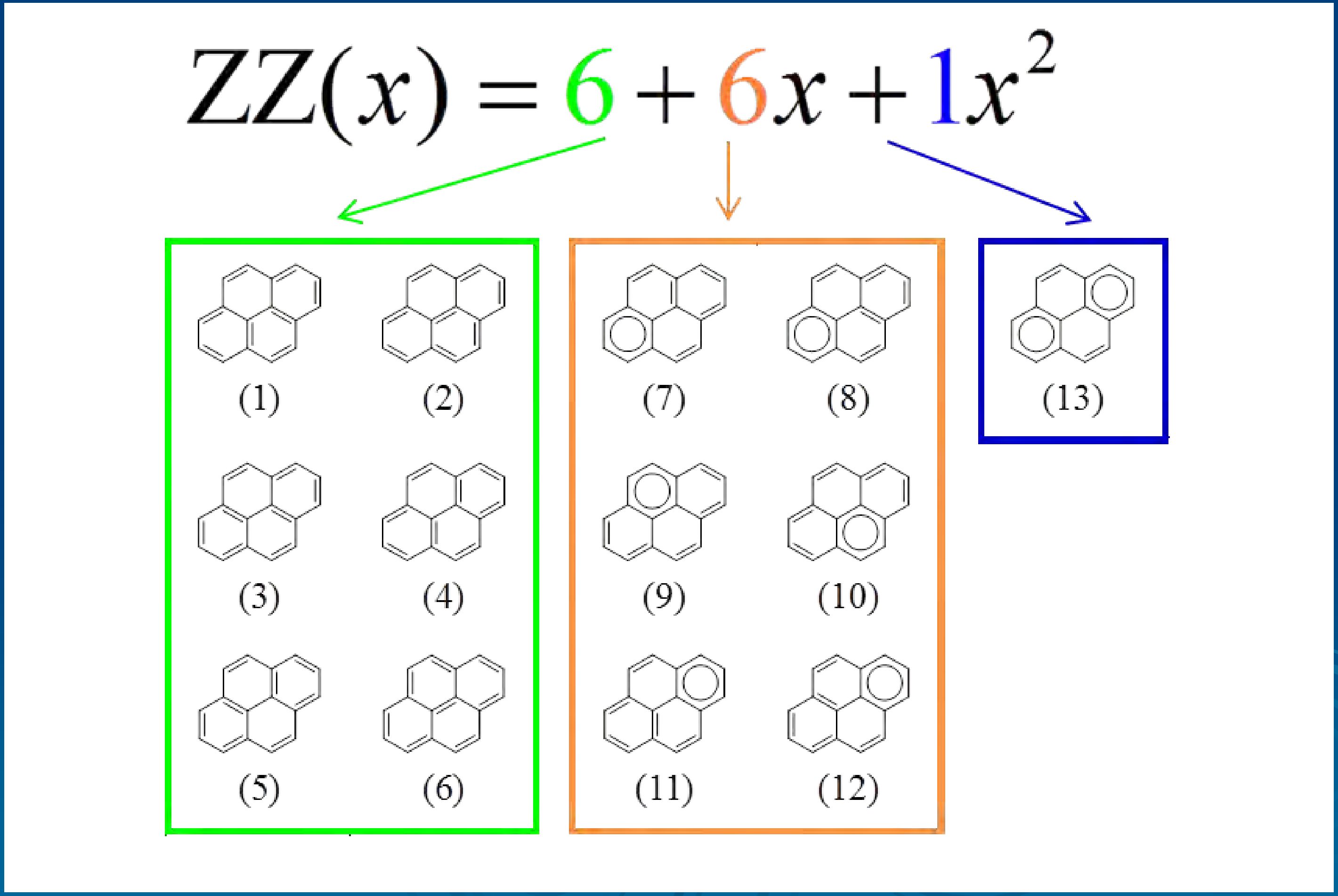
What is the maximal permissible number of Clar sextets?

How many Clar covers with maximal number of Clar sextets does a graph G permit?

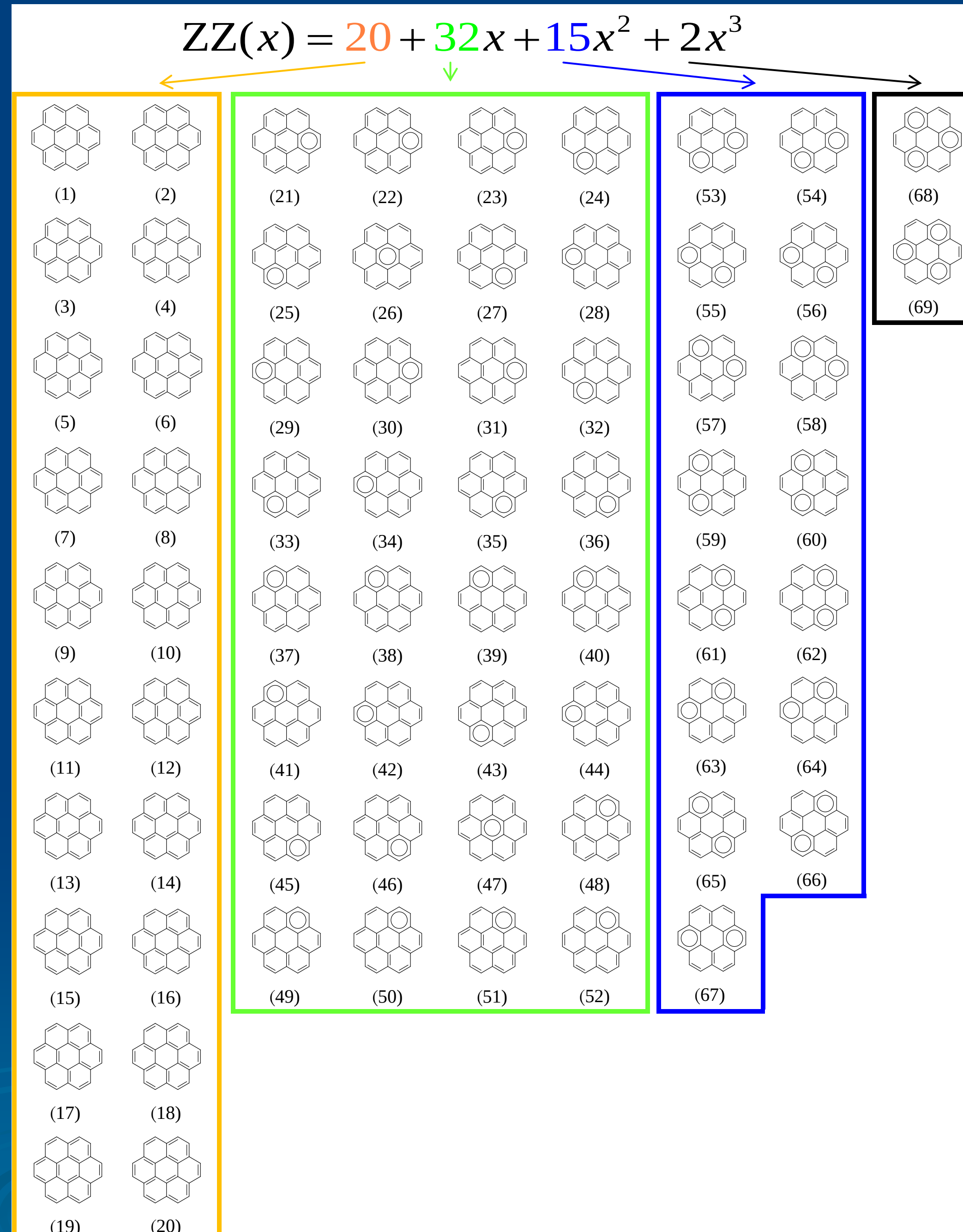
How to count Clar covers?



Zhang-Zhang (ZZ) polynomial of pyrene



ZZ polynomial of coronene

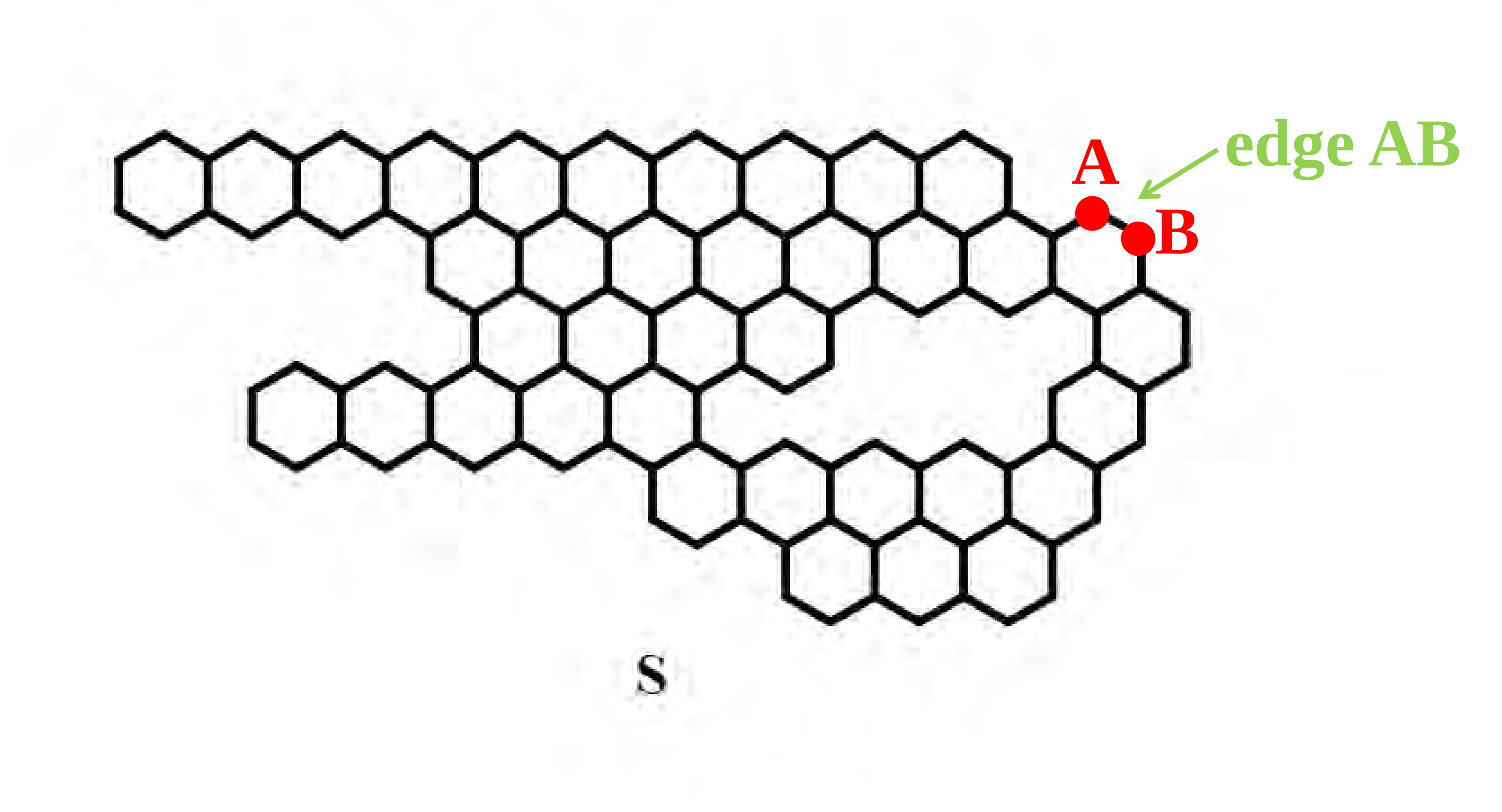


Generating Clar covers of S

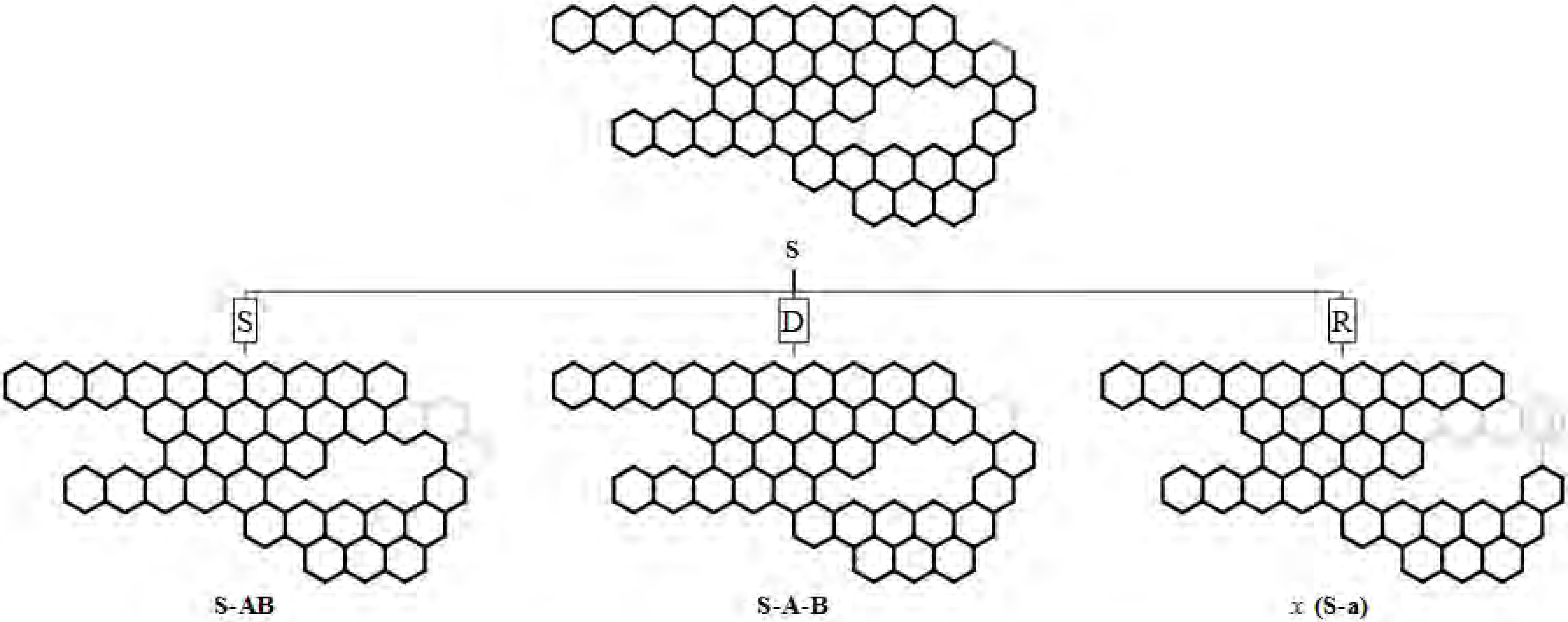
Recursive algorithm

- Choose a peripheral edge AB
- Make 3 copies of S and assign AB to
  - single bond or
  - double bond or
  - aromatic sextet
- Simplify the copies of S by removing single bonds and tetravalent atoms
- Enter next level of recursion

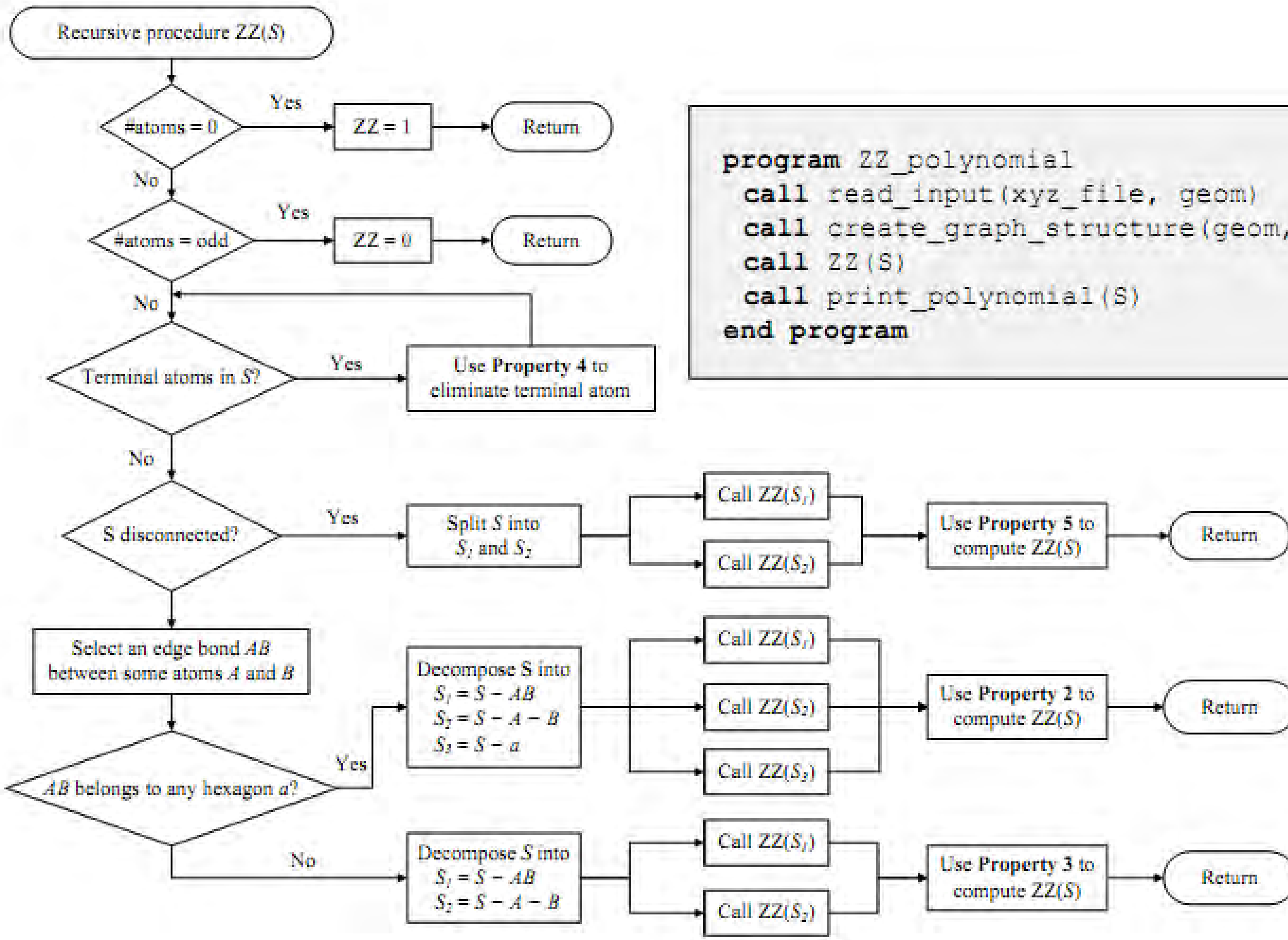
Example



Example

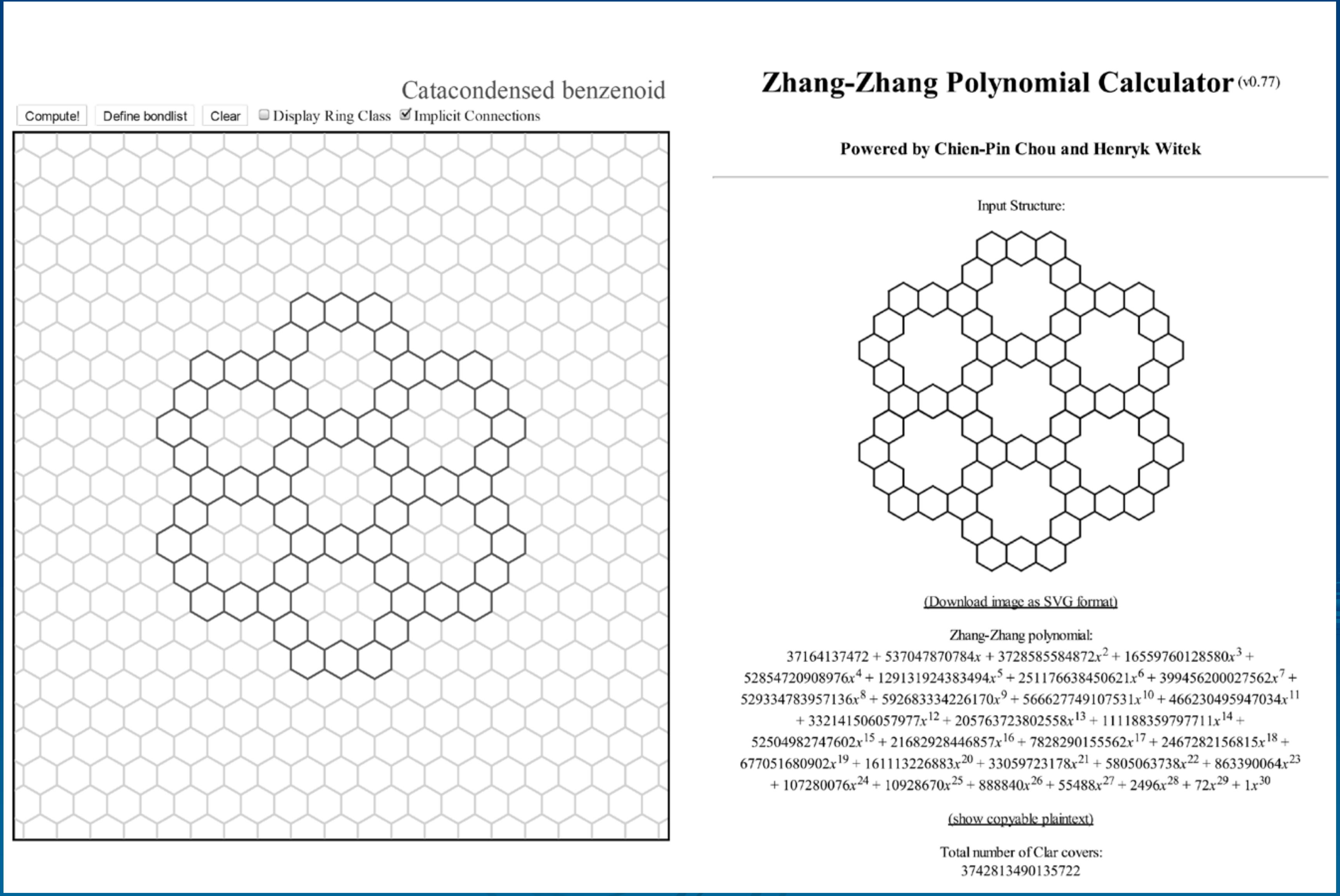


Computing ZZ polynomial




```
program ZZ_polynomial
  call read_input(xyz_file, geom)
  call create_graph_structure(geom, S)
  call ZZ(S)
  call print_polynomial(S)
end program
```

ZZ polynomial calculator



ZZ polynomial calculator

Zhang-Zhang polynomial:

$$37164137472 + 537047870784x + 3728585584872x^{2} + 16559760128580x^{3} + 52854720908976x^{4} + 129131924383494x^{5} + 251176638450621x^{6} + 399456200027562x^{7} + 529334783957136x^{8} + 592683334226170x^{9} + 566627749107531x^{10} + 466230495947034x^{11} + 332141506057977x^{12} + 205763723802558x^{13} + 111188359797711x^{14} + 52504982747602x^{15} + 21682928446857x^{16} + 7828290155562x^{17} + 2467282156815x^{18} + 677051680902x^{19} + 161113226883x^{20} + 33059723178x^{21} + 5805063738x^{22} + 863390064x^{23} + 107280076x^{24} + 10928670x^{25} + 888840x^{26} + 55488x^{27} + 2496x^{28} + 72x^{29} + 1x^{30}$$

(show copyable plaintext)

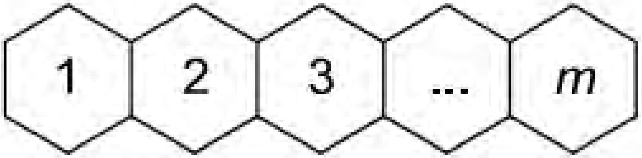
Total number of Clar covers:
3742813490135722

ZZ polynomial calculator

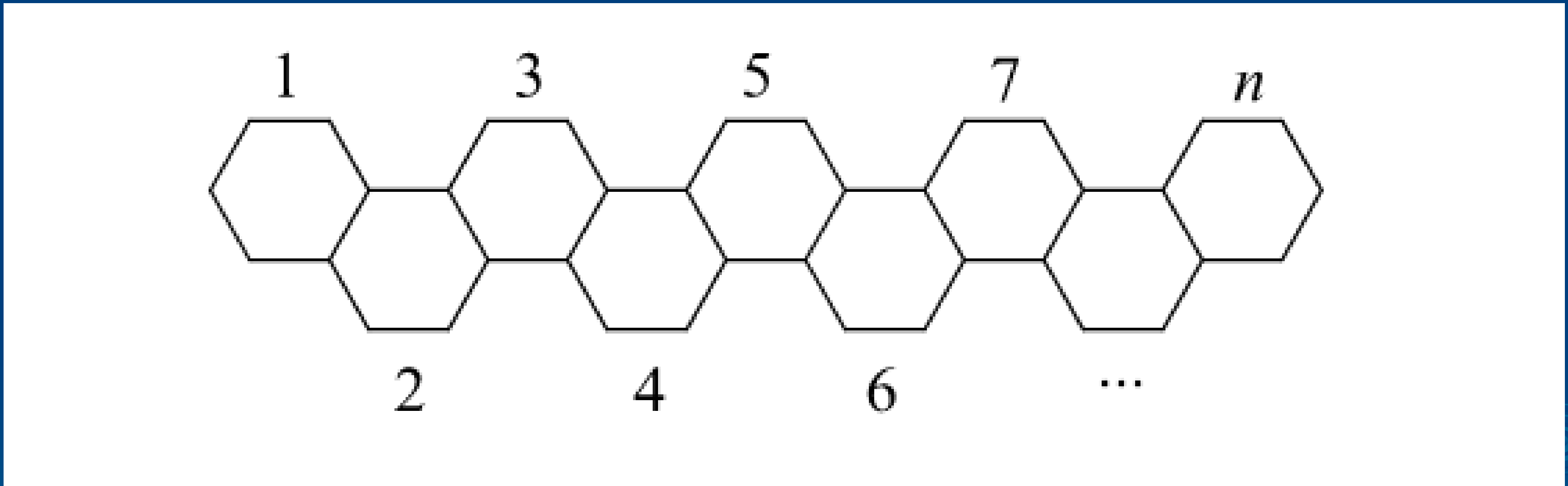
- Written in Fortran 95
- Applicable to
  - catacondensed graphs up to 10000 vertices
  - pericondensed graphs up to 500 vertices
- Uses large integers up to 10^{1000}
- Free to download
- Available also via online pluglet at
  http://qcl.ac.nctu.edu.tw/zzpolynomial

ZZ polynomial of polyacenes (zigzag chains)

$$\left.\begin{aligned}
ZZ\left(L(1),x\right) &= 2+x \\
ZZ\left(L(2),x\right) &= 3+2x \\
ZZ\left(L(3),x\right) &= 4+3x \\
ZZ\left(L(4),x\right) &= 5+4x \\
ZZ\left(L(5),x\right) &= 6+5x
\end{aligned}\right] \Rightarrow ZZ\left(L(m),x\right) = 1+m(1+x)$$



ZZ polynomial of armchair chains



ZZ polynomial of armchair chains

recursion relation

$$ZZ(N(n),x) = ZZ(N(n-1),x) + (x+1)\cdot ZZ(N(n-2),x).$$

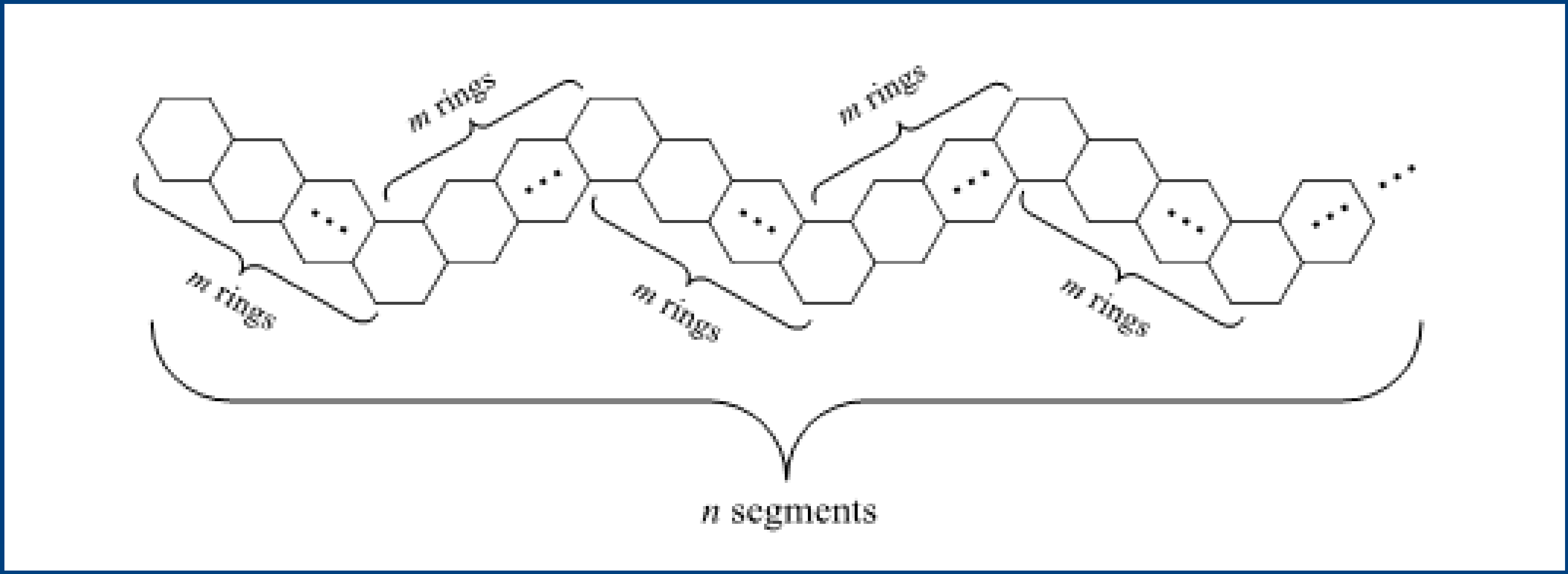
closed form solution

$$ZZ(N(n),x) = \frac{1}{2}\left(1+\frac{2x+3}{\sqrt{4x+5}}\right)\left(\frac{1+\sqrt{4x+5}}{2}\right)^n + \frac{1}{2}\left(1-\frac{2x+3}{\sqrt{4x+5}}\right)\left(\frac{1-\sqrt{4x+5}}{2}\right)^n.$$

additive form

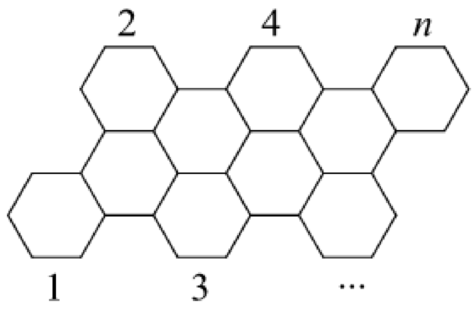
$$ZZ(N(n),x) = \sum_{k=0}^{n}\binom{n+1-k}{k}(1+x)^k,$$

Segmented polyacenes



$$ZZ(L(m,n),x) = \frac{1}{2}\left((x+2) + \frac{(2-m)x^2+(5-m)x+4}{\sqrt{k}}\right)\left(\frac{(m-1)+(m-2)x+\sqrt{k}}{2}\right)^n$$
$$+\frac{1}{2}\left((x+2) - \frac{(2-m)x^2+(5-m)x+4}{\sqrt{k}}\right)\left(\frac{(m-1)+(m-2)x-\sqrt{k}}{2}\right)^n,$$

ZZ polynomials of S_n structures



$$ZZ\big(S(n),x\big) = (2+x)\,ZZ\big(S(n-1),x\big) + (1+x)\,ZZ\big(S(n-2),x\big) - (1+x)^2\,ZZ\big(S(n-3),x\big).$$

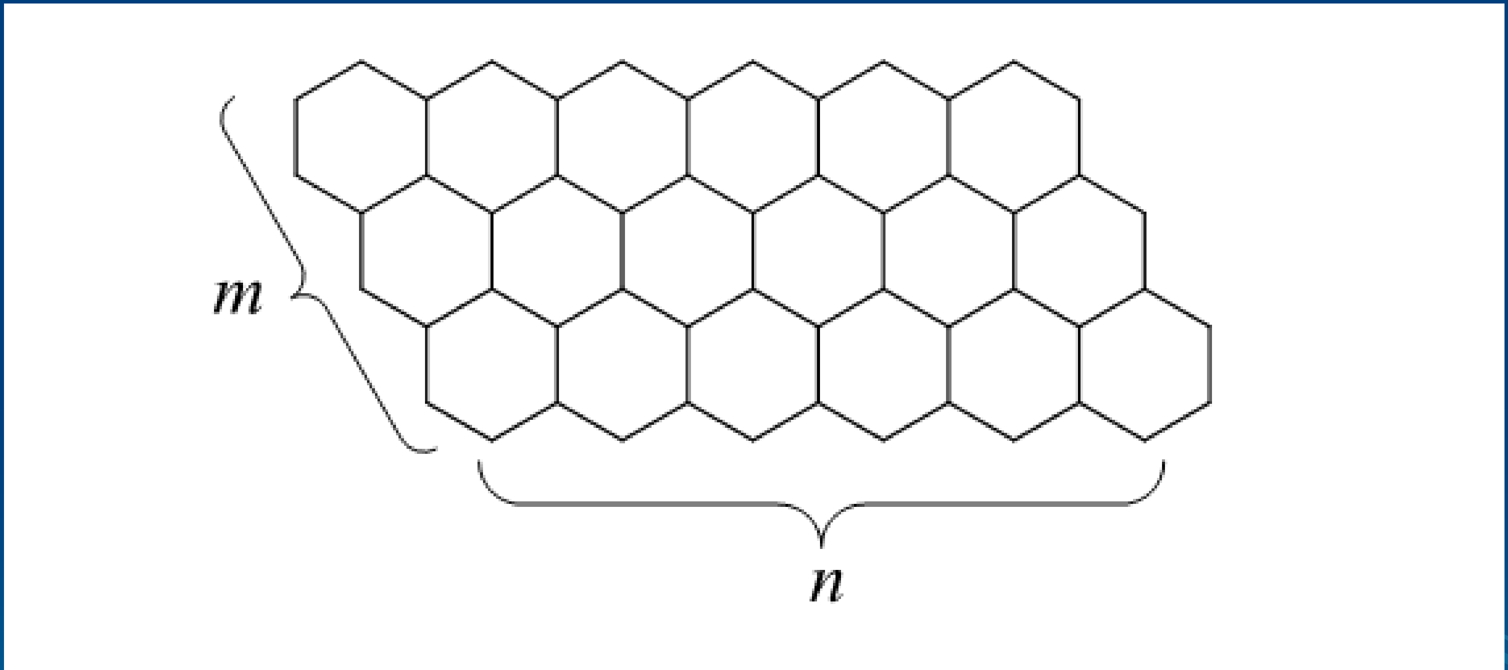
$$F(z) = \frac{1-(x+1)z^2}{(x+1)^2 z^3 - (x+1)z^2 - (x+2)z + 1}.$$

$$\begin{cases} ZZ\big(S(1),x\big) = 2+x \\ ZZ\big(S(2),x\big) = 4+4x+x^2 \\ ZZ\big(S(3),x\big) = 9+13x+6x^2+x^3 \\ ZZ\big(S(4),x\big) = 20+38x+26x^2+8x^3+x^4 \end{cases}$$

$$ZZ\big(S(n),x\big) = \frac{1}{n!}\frac{d}{dz^n}F(z)\Big|_{z=0}.$$

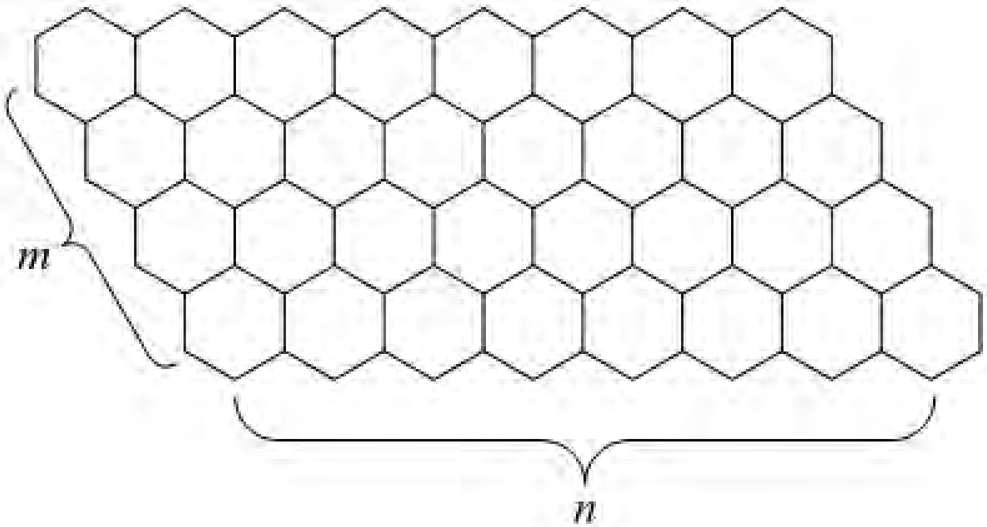
$$ZZ\big(S(n),x\big) = \sum_{k=0}^{\left\lfloor \frac{n}{2} \right\rfloor} \sum_{l=0}^{\left\lfloor \frac{n-2k}{3} \right\rfloor} (-1)^l (1+x)^{2l+k} (2+x)^{n-3l-2k} \frac{n-2l-2k}{n-2l-k} \binom{n-2l-k}{l} \binom{n-3l-k}{k}$$

ZZ polynomials of parallelograms



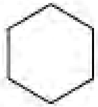
ZZ polynomials of parallelograms

$$ZZ(M(m,n),x) = \sum_{i=0}^{m} \binom{m}{i} \binom{n+m-i}{m} x^i$$



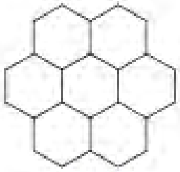
$$ZZ(M(m,n),x) = {}_2F_1\left[\begin{matrix} -m, -n \\ 1 \end{matrix}; 1+x\right]$$

ZZ polynomials of hexagons



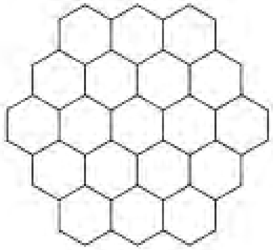
(0,0)

$2 + x$



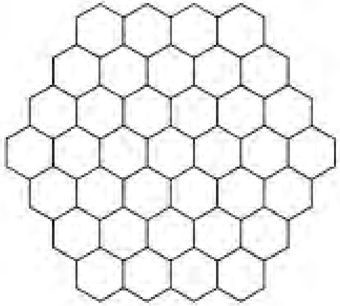
(1,0)

$20 + 32x + 15x^2 + 2x^3$



(2,0)

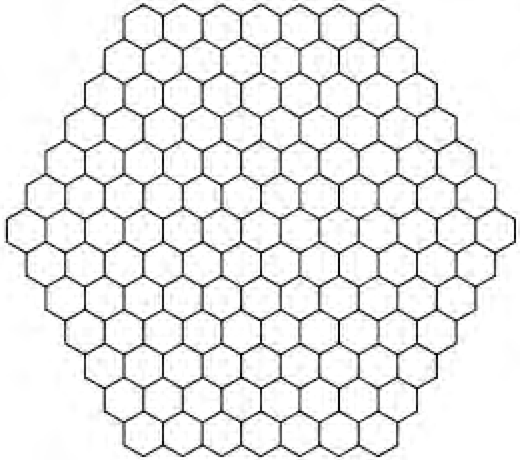
$980 + 3308x + 4458x^2 + 3065x^3 + 1140x^4 + 225x^5 + 22x^6 + x^7$



(3,0)

$232848 + 1355752x + 3482400x^2 + 5198238x^3 + 5001260x^4$
$+ 3252588x^5 + 1459605x^6 + 453642x^7 + 96753x^8 + 13860x^9$
$+ 1285x^{10} + 72x^{11} + 2x^{12}$

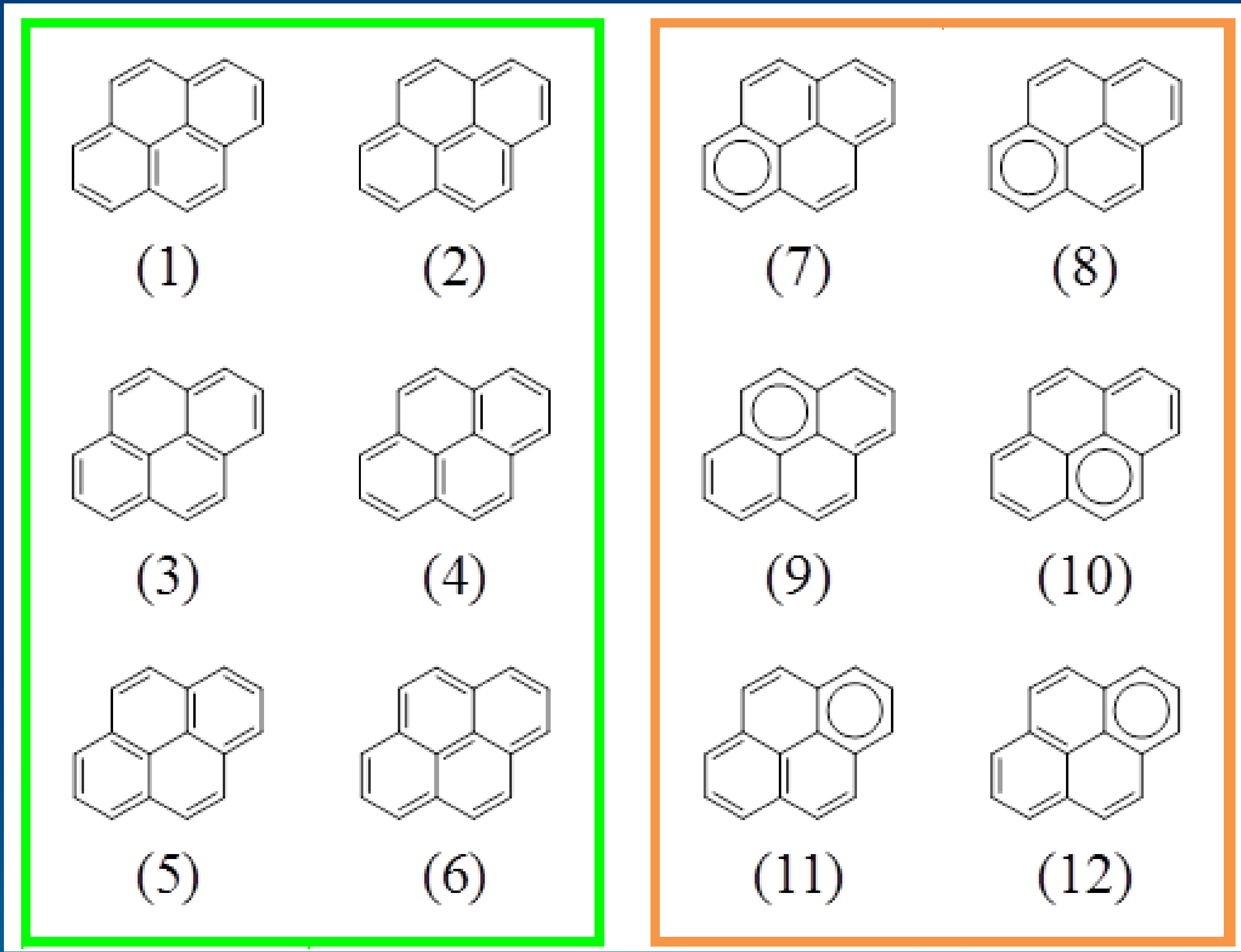
ZZ polynomials of hexagons

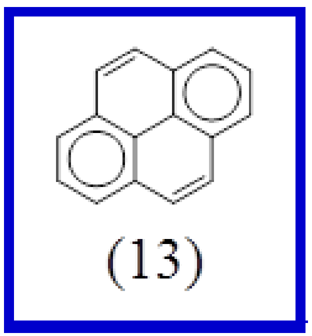


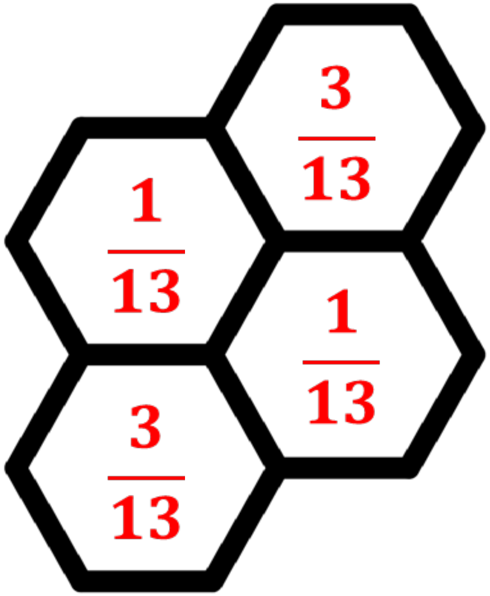
(6,0)

$$
\begin{aligned}
&3940599631842016 0 + 6782440227039852 96\, x + 5603836250880131466\, x^{2} \\
&+ 2959951711887778 3236\, x^{3} + 11230412721437819 5316\, x^{4} + 32604677144766042 1002\, x^{5} \\
&+ 75347614220565721 3552\, x^{6} + 14235468318821004 97662\, x^{7} + 22412049036390396 95772\, x^{8} \\
&+ 29822470584891322 26339\, x^{9} + 33901686226666332 28088\, x^{10} + 33197746672490565 97278\, x^{11} \\
&+ 28183663345154715 66982\, x^{12} + 20847710437342588 96273\, x^{13} \\
&+ 13488604991553456 19560\, x^{14} + 7655882492924396 46709\, x^{15} + 3820131183227457 67186\, x^{16} \\
&+ 1678285419445889 76642\, x^{17} + 649773500643014 87814\, x^{18} + 221797987568592 85180\, x^{19} \\
&+ 66750975057410494 92\, x^{20} + 17705406001157220 70\, x^{21} + 4136267487438368 94\, x^{22} \\
&+ 85027057142421642\, x^{23} + 15362049506580008\, x^{24} + 2436147310614634\, x^{25} \\
&+ 338577307537590\, x^{26} + 41164773295262 x^{27} + 4367930475858\, x^{28} + 403064458752\, x^{29} \\
&+ 32160857490\, x^{30} + 2197642843\, x^{31} + 126580890\, x^{32} + 5991030\, x^{33} + 223802\, x^{34} + 6180\, x^{35} \\
&+112\, x^{36} + x^{37}
\end{aligned}
$$

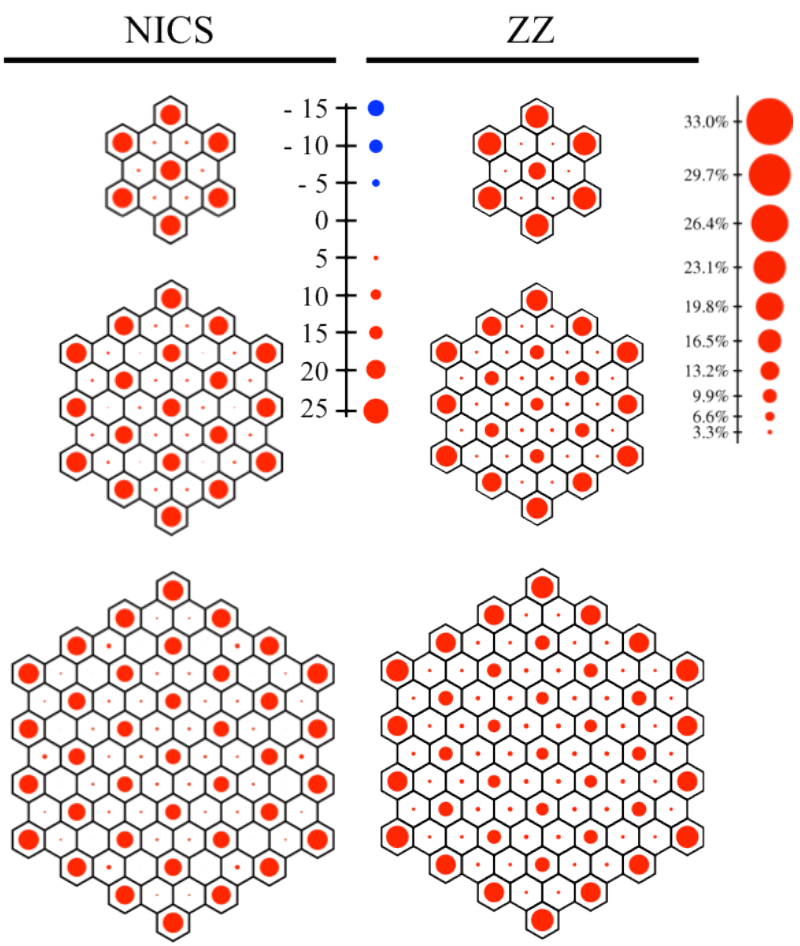
Aromaticity of graphene flakes



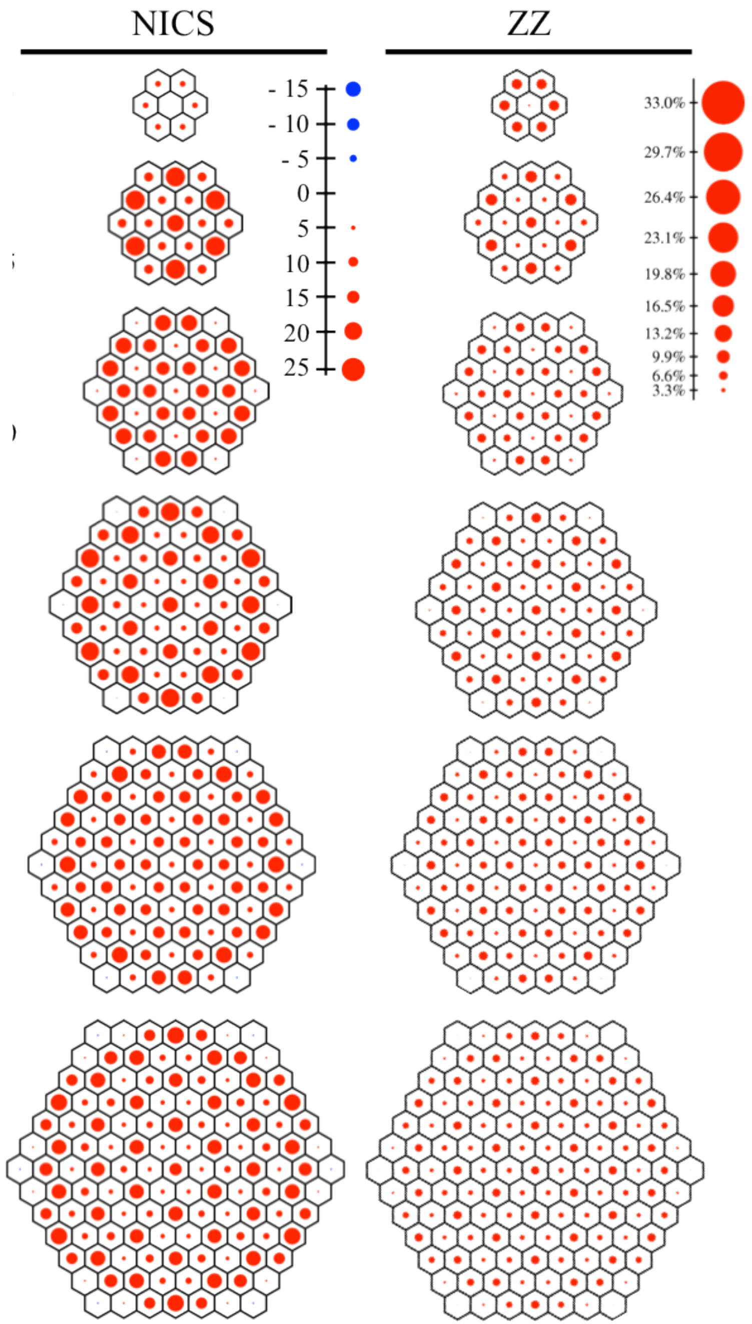




Aromaticity of graphene flakes

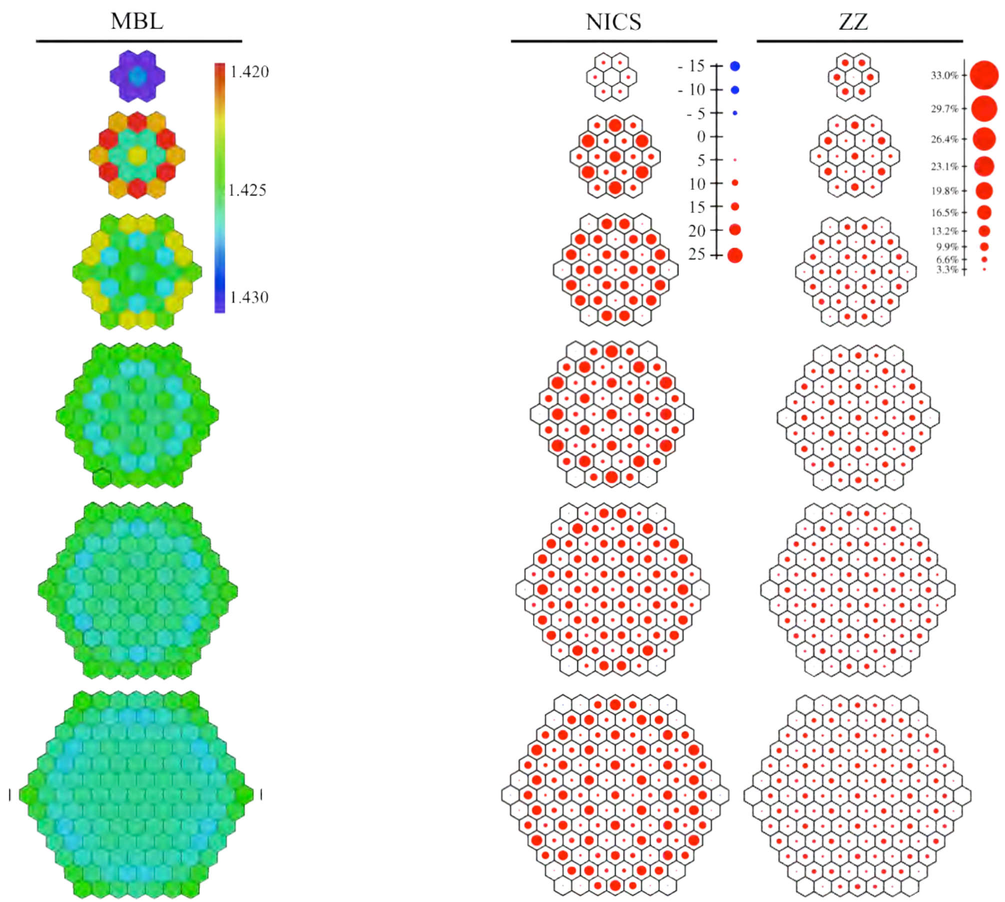


Aromaticity of graphene flakes

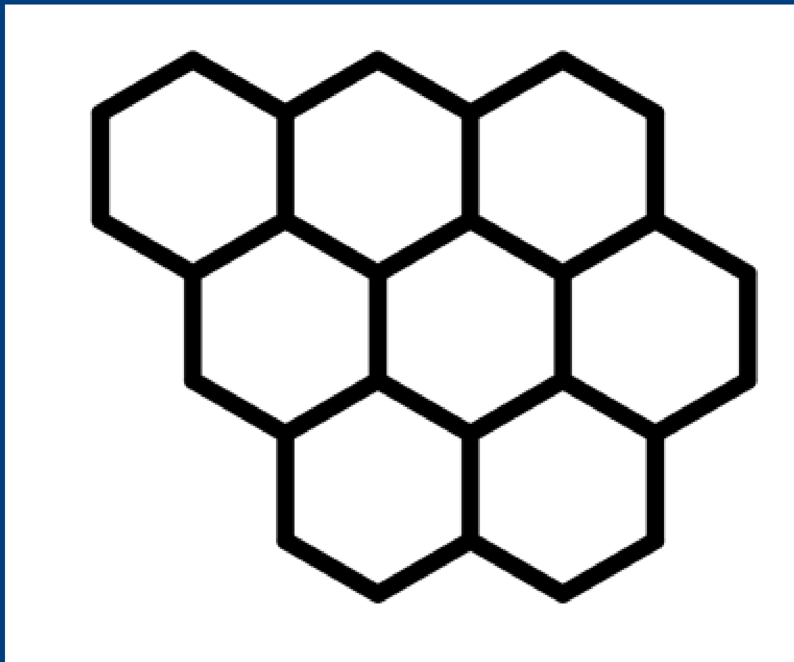


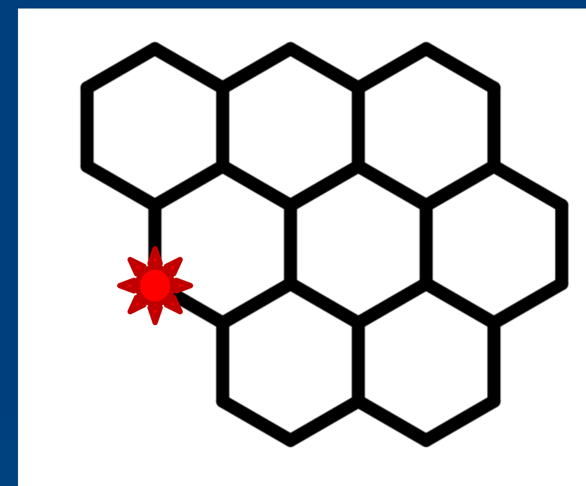
Page, Chou, Pham, Witek, Irle, and Morokuma, *Phys Chem Chem Phys*, 15, 3725-3735 (2013)

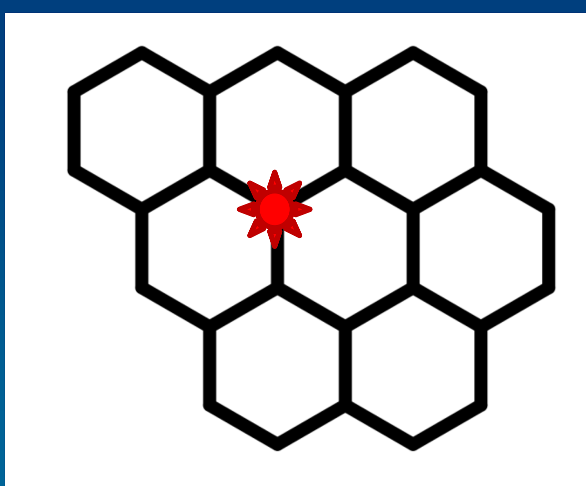
Aromaticity of graphene flakes

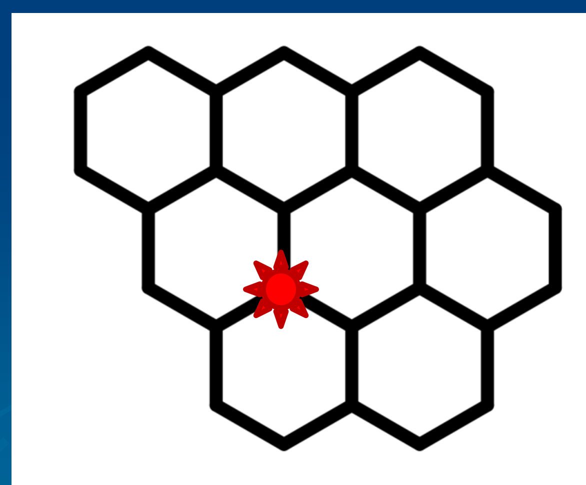


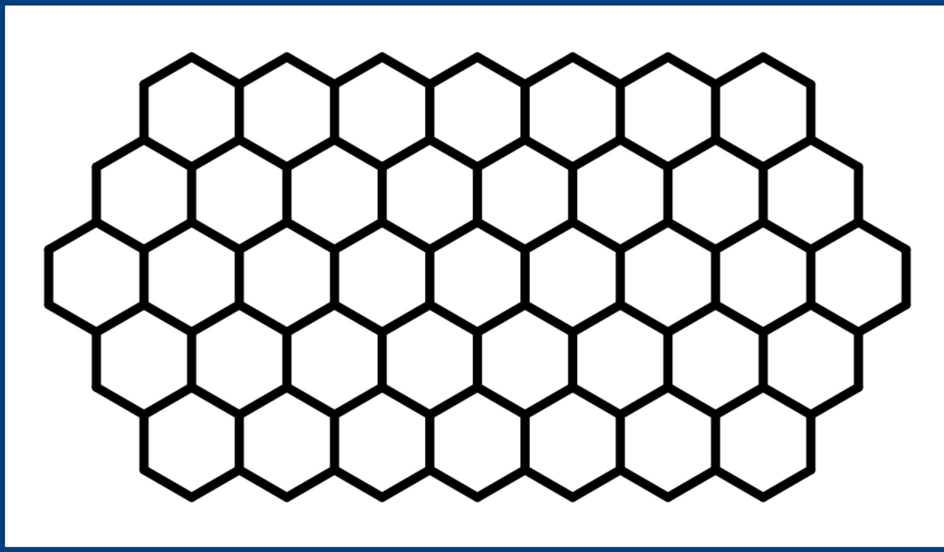
Stability of graphene-like radicals



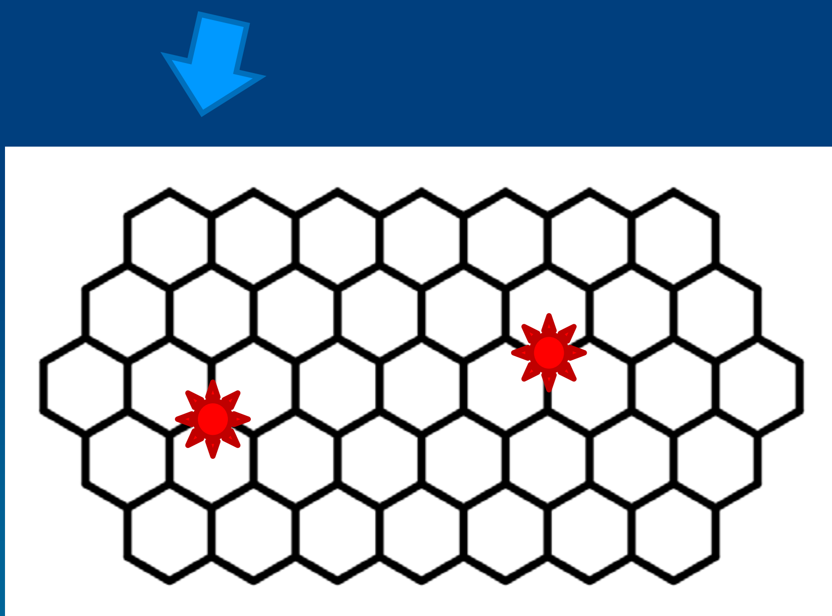






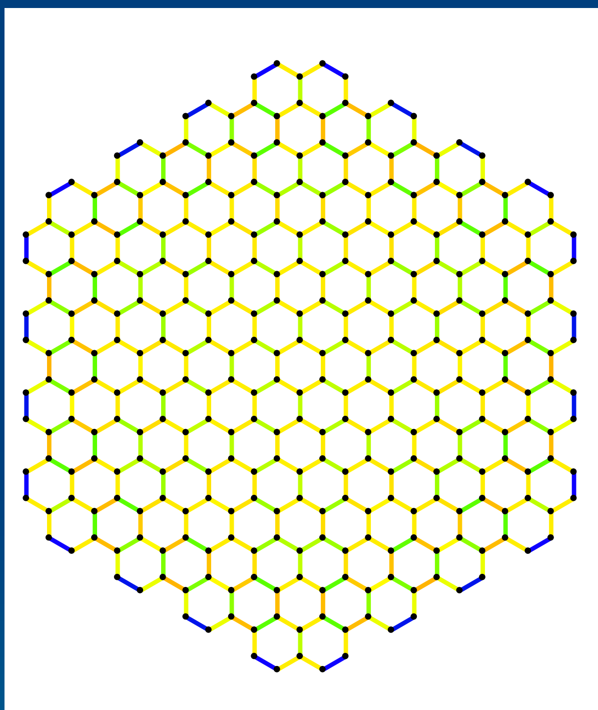


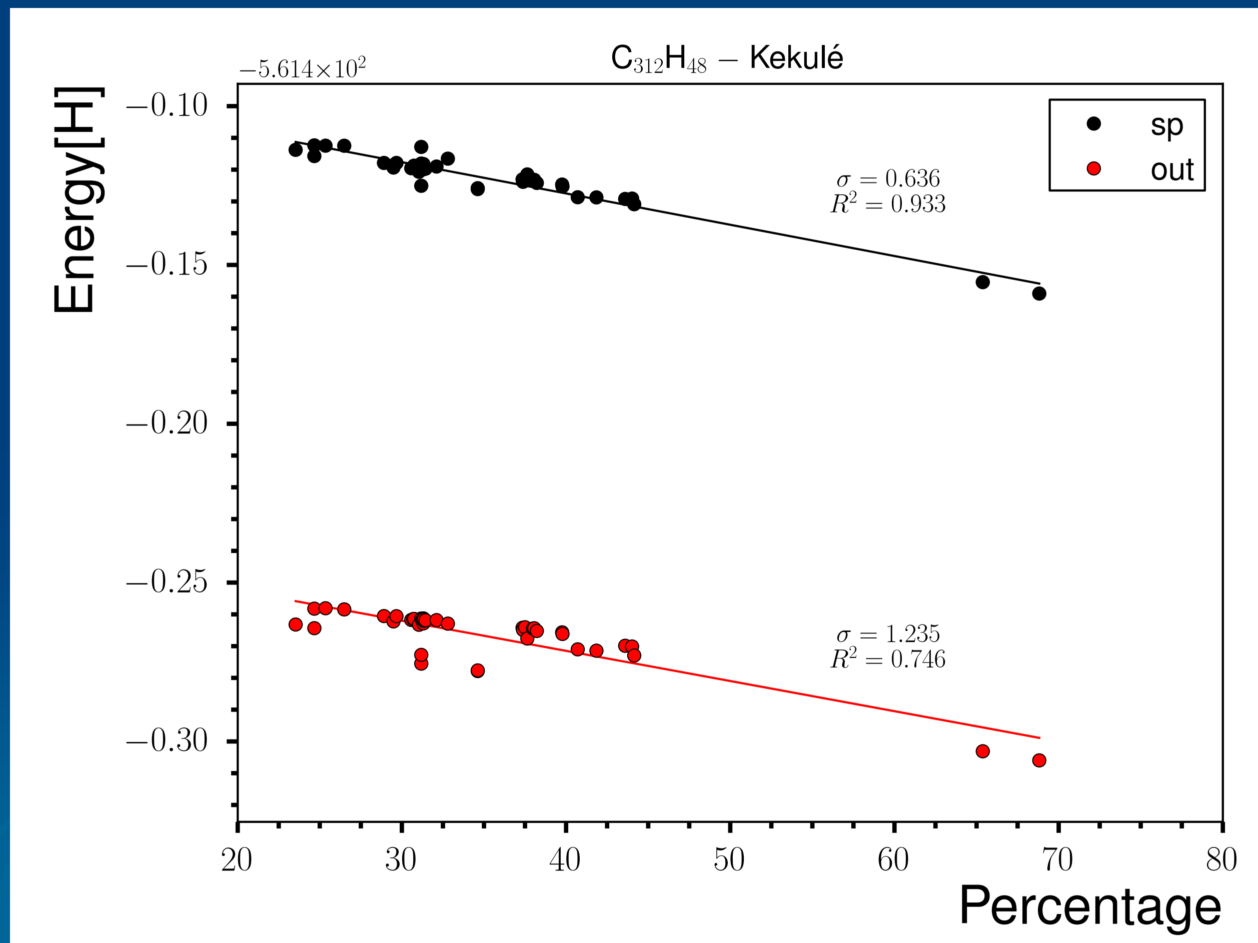
Stability of oxidized graphene like flakes



Stability of oxidized graphene flake isomers

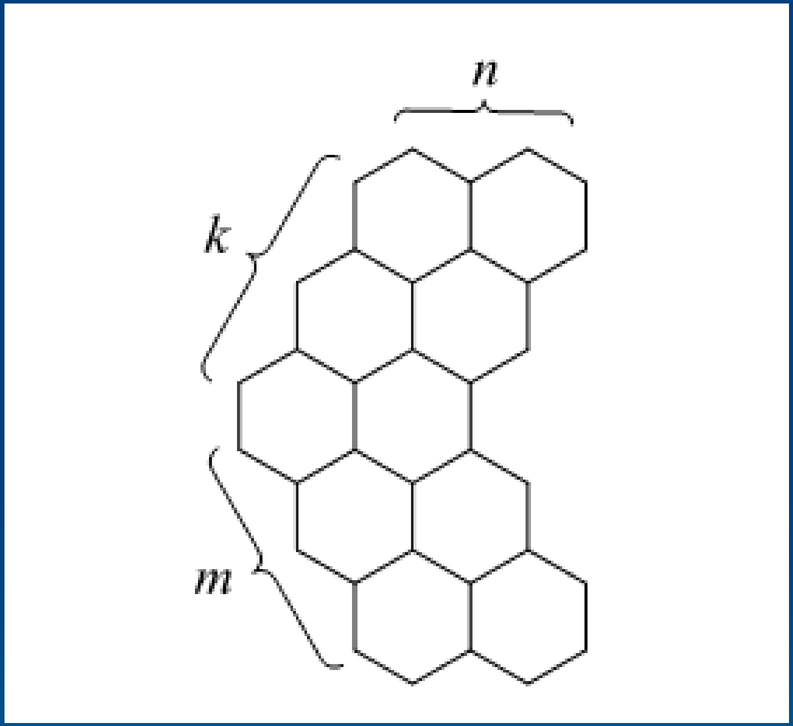
correlation between energy and percentage of surviving Kekule structures

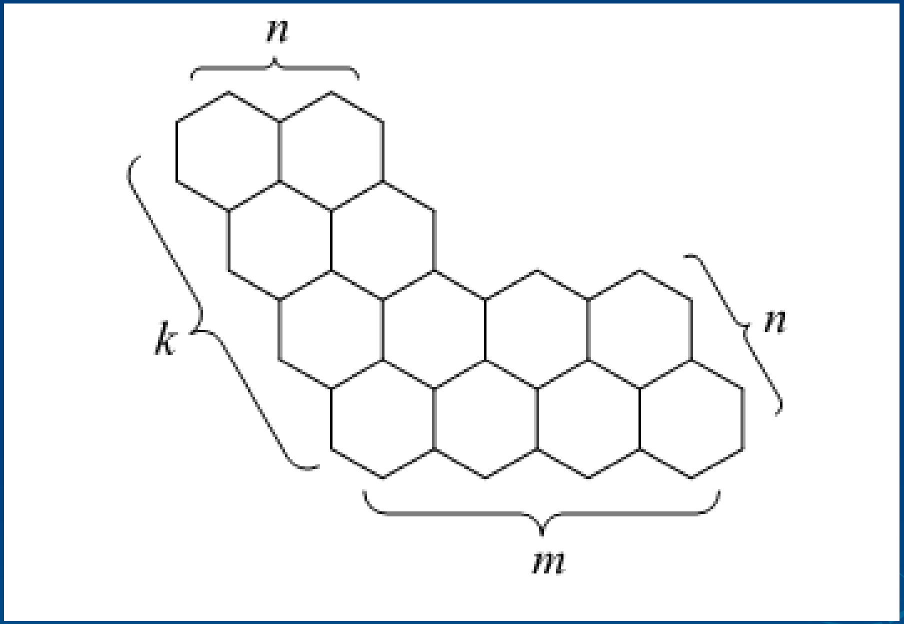




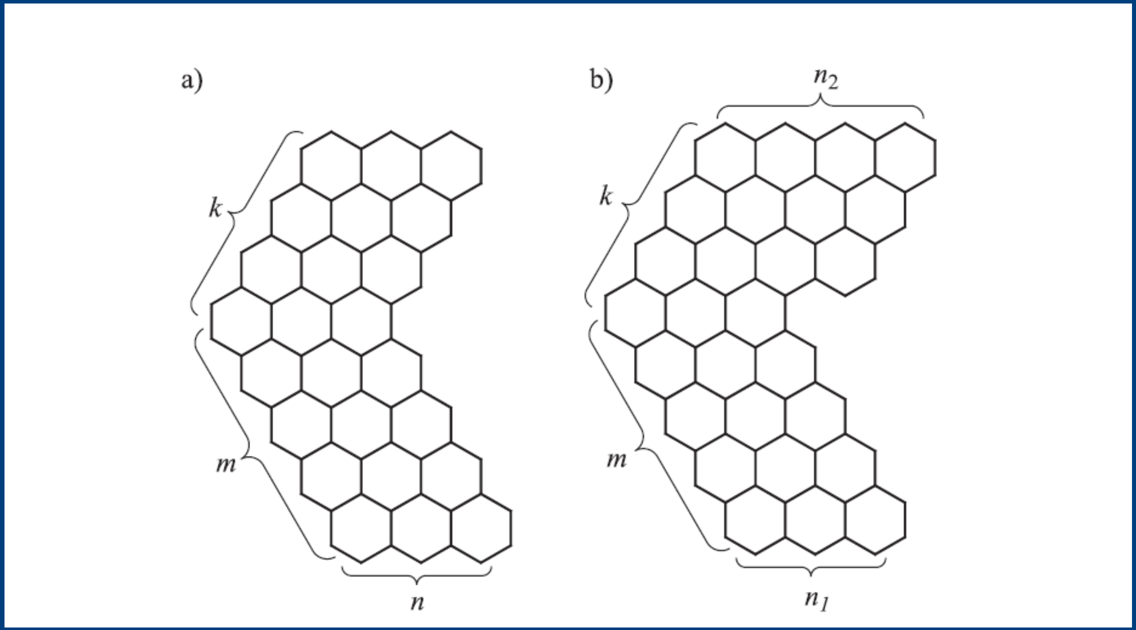
Page, Chou, Pham, Witek, Irle, and Morokuma, *Phys Chem Chem Phys*, 15, 3725-3735 (2013)

Chevrons & ribbons





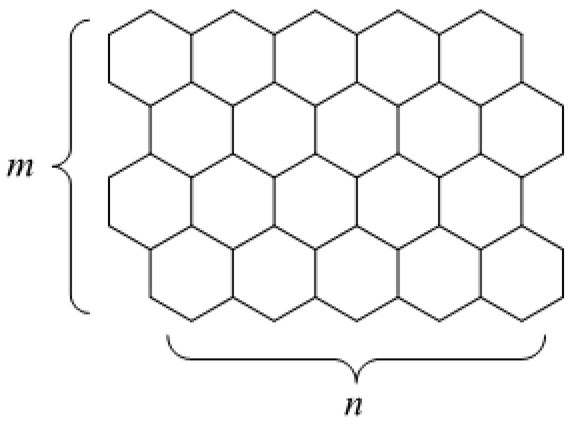
Chevrons



$$ZZ\left(Ch\left(k,m,n\right),x\right)=\sum_{i=0}^{n-1}\left(1+x\right)\cdot {}_2F_1\left[\begin{matrix}1-k,-i\\ 1\end{matrix};x+1\right]\cdot {}_2F_1\left[\begin{matrix}1-m,-i\\ 1\end{matrix};x+1\right]$$
$$+{}_2F_1\left[\begin{matrix}1-k,-n\\ 1\end{matrix};x+1\right]\cdot {}_2F_1\left[\begin{matrix}1-m,-n\\ 1\end{matrix};x+1\right]$$

$$ZZ\left(Ch\left(k,m,n_1,n_2\right),x\right)=\sum_{i=1}^{\min(n_1,n_2)}\left(1+x\right)\cdot {}_2F_1\left[\begin{matrix}1-k,i-n_2\\ 1\end{matrix};x+1\right]\cdot {}_2F_1\left[\begin{matrix}1-m,i-n_1\\ 1\end{matrix};x+1\right]$$
$$+{}_2F_1\left[\begin{matrix}1-k,-n_2\\ 1\end{matrix};x+1\right]\cdot {}_2F_1\left[\begin{matrix}1-m,-n_1\\ 1\end{matrix};x+1\right]$$

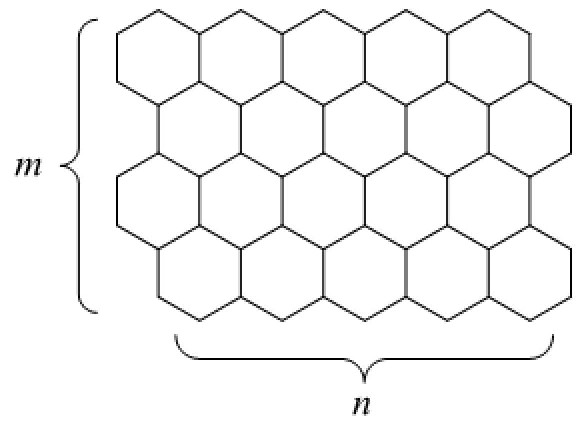
Multiple zigzag chains



$$ZZ\left(Z(4,n),x\right) = 1 + 4n(1+x) + \frac{3}{2}n(3n-1)(1+x)^2 + \frac{1}{3}(n-1)n(5n-1)(1+x)^3 + \frac{1}{24}(n-1)n(5n^2-5n+2)(1+x)^4.$$

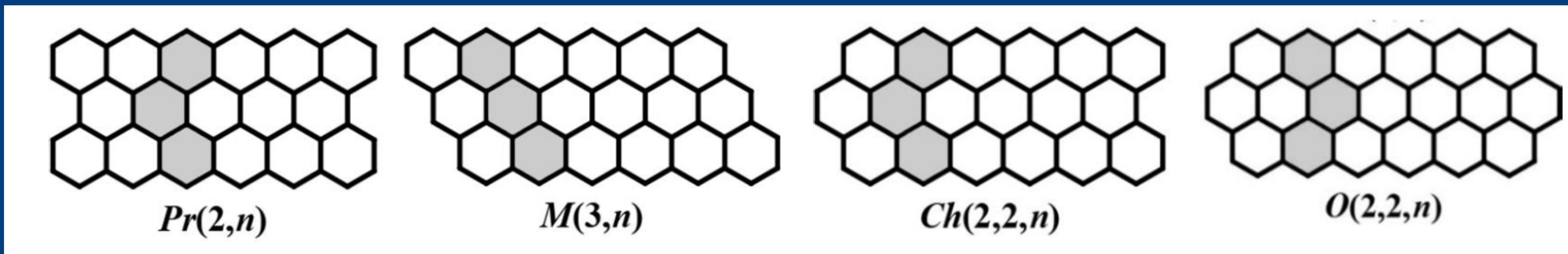
$$ZZ\left(Z(5,n),x\right) = 1 + 5n(1+x) + 2n(4n-1)(1+x)^2 + \frac{1}{2}n(1-9n+10n^2)(1+x)^3 + \frac{1}{6}(n-1)n(2n-1)(4n-1)(1+x)^4 + \frac{1}{30}(n-1)n(2n-1)(1-2n+2n^2)(1+x)^5.$$

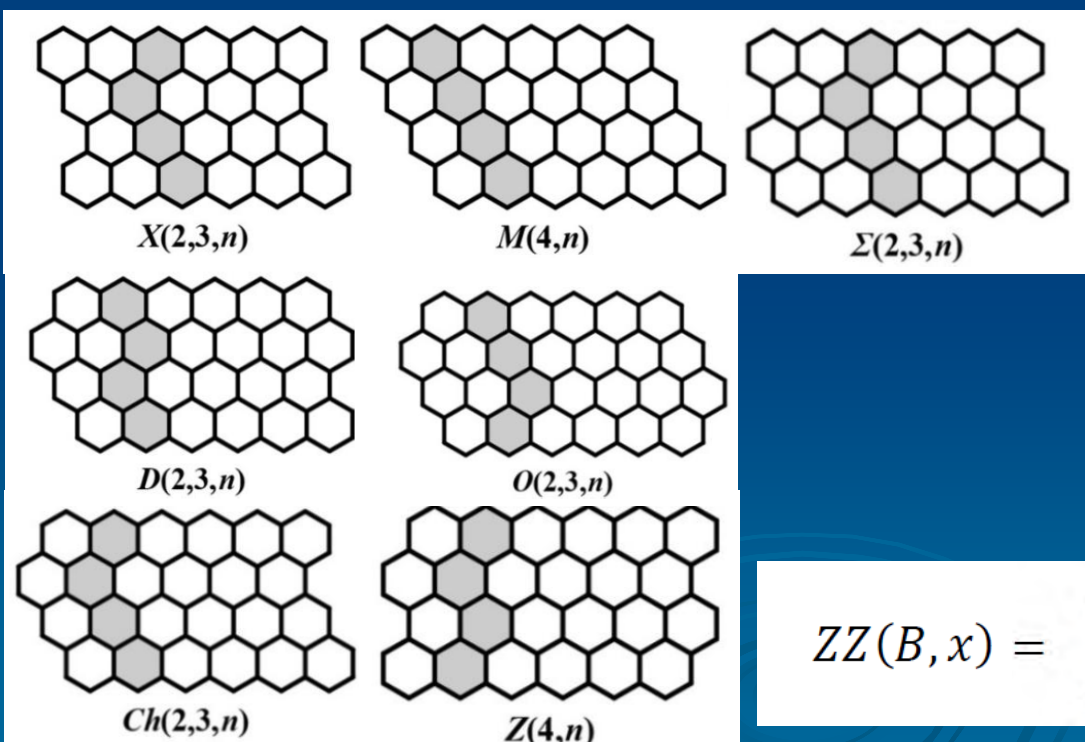
Multiple zigzag chains



$$ZZ\left(Z(m,n),x\right)=\sum_{k=0}^{m}(-1)^{\left\lfloor \frac{k}{2}\right\rfloor}(x+1)^{k}\left((x+1)\binom{\left\lfloor \frac{k+m}{2}\right\rfloor}{k+1}+\binom{\left\lfloor \frac{k+m}{2}\right\rfloor}{k}\right)\cdot ZZ\left(Z(m,n-k-1),x\right),$$

Regular 3 and 4-tier strips



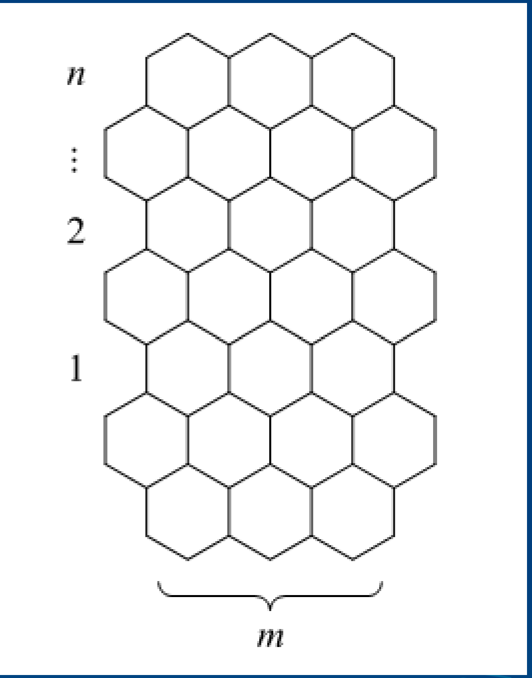


superfamily	B	Cl	a_1	a_2
1	$M(3,n)$	3	0	0
	$M(4,n)$	4	0	0
$M(1,n)\cdot M(1,n)$	$Pr(2,n)$ $X(2,3,n)$	2	1	0
	$Ch(2,2,n)$	3	1	0
	$O(2,2,n)$	4	1	0
$M(1,n)\cdot M(2,n)$	$\Sigma(2,3,n)$	3	2	0
	$Ch(2,3,n)$	4	2	0
$Z(4,n)$	$Z(4,n)$	4	3	1
	$D(2,3,n)$	5	3	1
	$O(2,3,n)$	6	3	1

$$ZZ(B,x) = \sum_{k=0}^{Cl}\sum_{l=0}^{2} a_l \binom{Cl-2l}{k-2l}\binom{n+l}{k}(1+x)^k$$

Most important open problems

- Solve hexagons
- Solve oblate rectangle
- Solve catacondensed structures with a single hexagon removed
- Find complete set of recurrence equations
- Study asymptotics



Stephan Irle

Conclusions

- Clar covers: new dimension in chemical graph theory
- Easy and pretty field for new results
- Programs are ready and available
- Wonderful MS projects for your students