Generalized Hartree Fock:
Symmetry breaking and magnetic ordering

Hartree-Fock seeks to minimize the energy of a
single Slater Determinant (independent particle model, IPM)

$$E \leq \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

The equality holds when the wave function is **variationally optimum**.

The Fock operator is the exact electronic Hamiltonian in the IPM.

In general, we expect that our solution has the same symmetries as the exact Hamiltonian (e.g. rotationally invariant).

All symmetry operations can be
represented by similarity transformations.

$$\hat{g}\hat{H}\hat{g}^{-1} = \hat{H}, \qquad (\forall \hat{g} \in \mathcal{G}).$$

It's usually the case that the similarity transformations
are also (anti-)unitary.

The electronic Hamiltonian is invariant to
unitary spin transformations about the z-axis.

$$\hat{U}(\theta, \mathbf{n}_z) = e^{i\theta \hat{S}_z}$$

So that: $$e^{i\theta \hat{S}_z} \hat{H} e^{-i\theta \hat{S}_z} = \hat{H}$$

For any real angle theta about the z-axis

We can write the most general Fock operator in the spin-half manifold as

$$\begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

We seek a unitary transformation such that

$$\hat{U} \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix} \hat{U}^{-1} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

In other words, find the constraints on the Fock matrix that satisfy the above for any arbitrary unitary transformation.

We often claim UHF is invariant to $\hat{S}_z$

Let's show this (overlooking a few details).

$$\hat{U} \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix} \hat{U}^{-1} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{F}_{\alpha\beta} \\ \mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & -\mathbf{F}_{\alpha\beta} \\ -\mathbf{F}_{\beta\alpha} & \mathbf{F}_{\beta\beta} \end{pmatrix}$$

Which is true if and only if $\mathbf{F} = \begin{pmatrix} \mathbf{F}_{\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{F}_{\beta\beta} \end{pmatrix}$

So this symmetry invariance leads to a decoupling
of the Fock operator into pure spin-up and spin-down manifolds

Any time we make the Fock operator invariant
to some symmetry, we add a constraint.

More constraints can only raise the energy
of a variationally optimized solution.

If we eliminate symmetry constraints related to spin and time reversal,
we get the **Generalized Hartree-Fock** solutions.

Solutions may be complex-valued and mixed spin.

We can get the lowest energy solution with GHF, but how can we ensure the solution we got is a true local minimum?

Electronic Hessian in Hartree-Fock (HF) theory

We want **stable** electronic solutions to the HF model.

Local minima guaranteed by
(a) First variation equal to zero.
(b) Second variation greater than or equal to zero.

In Hartree-Fock, we **minimize** the energy functional

$$E[\phi] = \langle \phi | \hat{H} | \phi \rangle$$

We can parameterize this using

$$|\tilde{\phi}\rangle = e^{\hat{T}_1} |\phi\rangle$$ (Thouless, 1960)

Where

$$\hat{T}_1 = \sum_{ia} t_i^a \{a_a^\dagger a_i\} \qquad \text{and} \qquad \hat{T}_1 = -\hat{T}_1^\dagger$$

Our new functional, parameterized with respect to T

$$E = \langle \tilde{\phi} | \hat{H}_N | \tilde{\phi} \rangle_c = \langle \phi | e^{\hat{T}_1^\dagger} \hat{H}_N e^{\hat{T}_1} | \phi \rangle_c$$

With our normal ordered* Hamiltonian

$$\hat{H}_N = \hat{H} - \langle \phi | \hat{H} | \phi \rangle = \hat{F}_N + \hat{V}_N = f_{pq} \{ a_p^\dagger a_q \} + \frac{1}{4} \langle pq || rs \rangle \{ a_p^\dagger a_q^\dagger a_s a_r \}$$

*Normal ordering makes the final evaluation of matrix elements easier because we can use diagrammatic tools to evaluate them. The results do not change if you use, e.g. Slater-Condon rules instead.

Expanding out the energy functional:

$$E = \langle 0|\hat{H}_N + \hat{T}_1^\dagger \hat{H}_N + \hat{H}_N \hat{T}_1 + \hat{T}_1^\dagger \hat{H}_N \hat{T}_1 + \frac{1}{2}\hat{T}_1^\dagger \hat{T}_1^\dagger \hat{H}_N + \frac{1}{2}\hat{H}_N \hat{T}_1 \hat{T}_1 + \cdots |0\rangle_c$$

Take **first variation** with respect to t_a^{i*} and t_i^a about zero.

$$\delta^{(1)} E = \langle \phi_i^a | \hat{H}_N | \phi \rangle_c = \langle \phi | \hat{H}_N | \phi_i^a \rangle_c = f_{ia} = f_{ai} = 0$$

This is **Brillouin's theorem**.

Taking the second variation

$$\delta^{(2)}E = \langle\phi_i^a|\hat{H}_N|\phi_j^b\rangle_c + \langle\phi_{ij}^{ab}|\hat{H}_N|\phi\rangle_c + \langle\phi|\hat{H}_N|\phi_{ij}^{ab}\rangle_c + \langle\phi_j^b|\hat{H}_N|\phi_i^a\rangle_c \geq 0$$

In matrix form, we have

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \geq 0$$

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle aj||ib\rangle$$

$$B_{ia,jb} = \langle ab||ij\rangle$$

This is the **Hessian**

Since all positive semi-definite matrices have positive (or zero) eigenvalues, we can determine if our solution is locally stable by diagonalizing the Hessian

If we run into negative eigenvalues, we pick the lowest one and its associated eigenvector (**J**).

We take a step (**s**) in the direction of the eigenvector and re-optimize.

$$\mathbf{C}' = e^{-s\mathbf{K}}\mathbf{C} \qquad \mathbf{K} = \begin{pmatrix} \mathbf{0} & -\mathbf{J}^\dagger \\ \mathbf{J} & \mathbf{0} \end{pmatrix}$$

J is steepest-descent eigenvector, **C** and **C'** are old and new orbitals

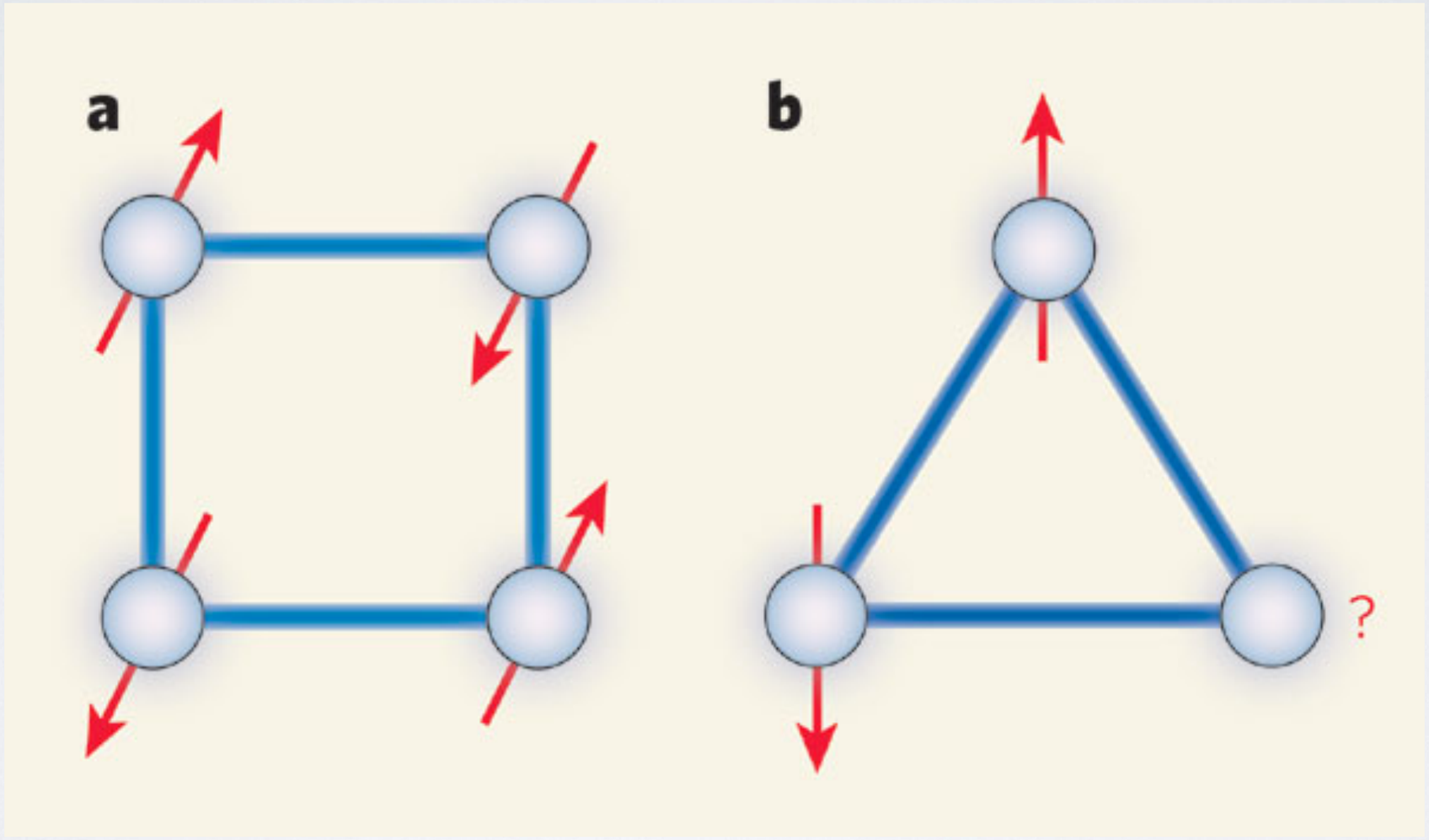
To recap, Generalized Hartree-Fock eliminates the constraints that our solutions must be invariant to spin rotations and time reversals.

This means orbitals can be **complex** and contain both **spin-up** and **spin-down** components.

If a lower-energy, lower-symmetry solution to the IPM exists, GHF can (in theory) find it.

We guarantee we are at a local minima by examining the eigenvalues of our Hessian. If we aren't, we have a defined method to move towards a local minima.

One area where GHF routinely obtains lower energies is geometrically frustrated systems

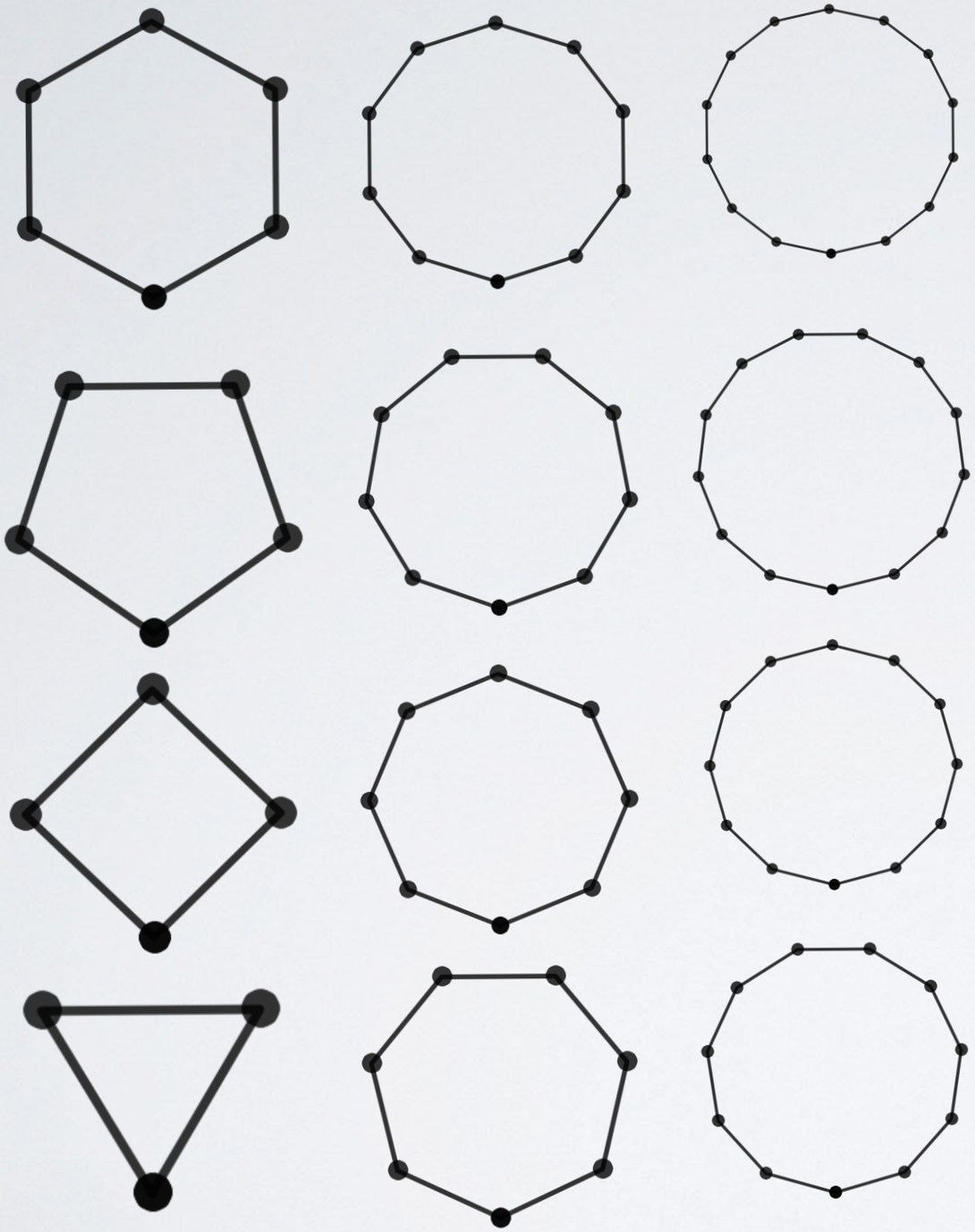


Condensed-matter physics: The eternal triangle

Mark Harris

Nature 456, 886-887(18 December 2008)

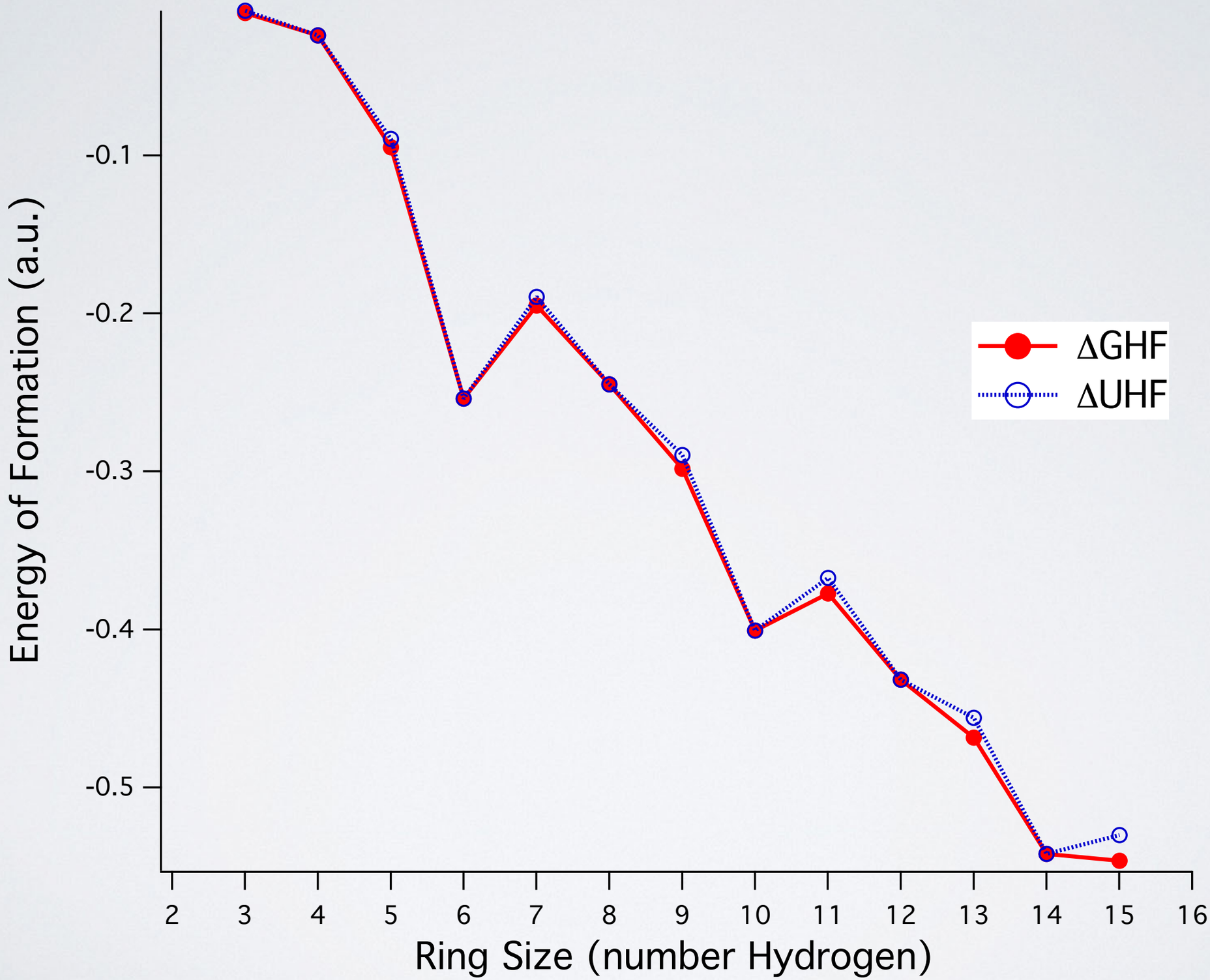
Symmetry Breaking in Hydrogen Rings.



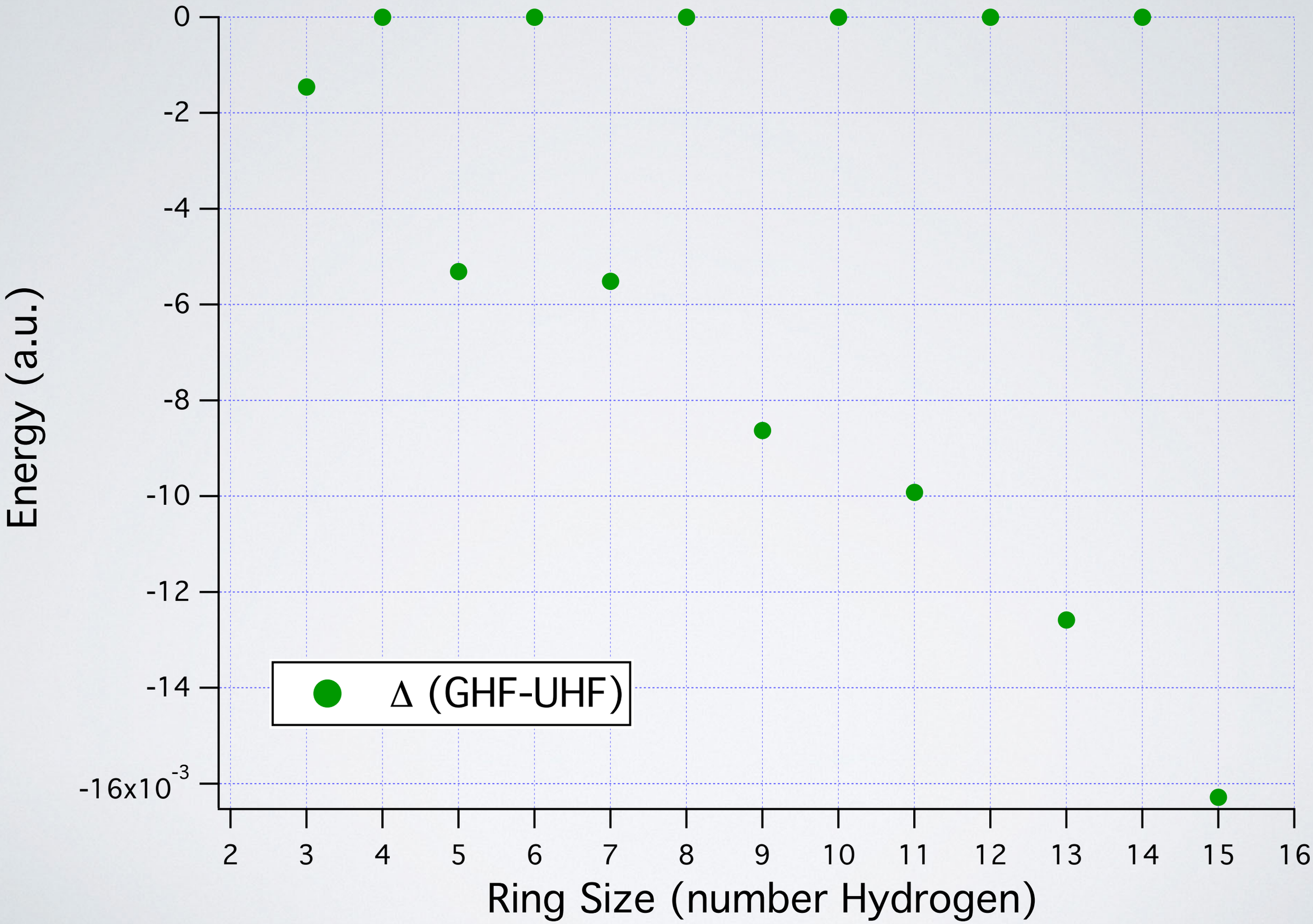
13 rings, ranging
from 3 to 15 hydrogens

Each ring has atoms
separated by one Angstrom

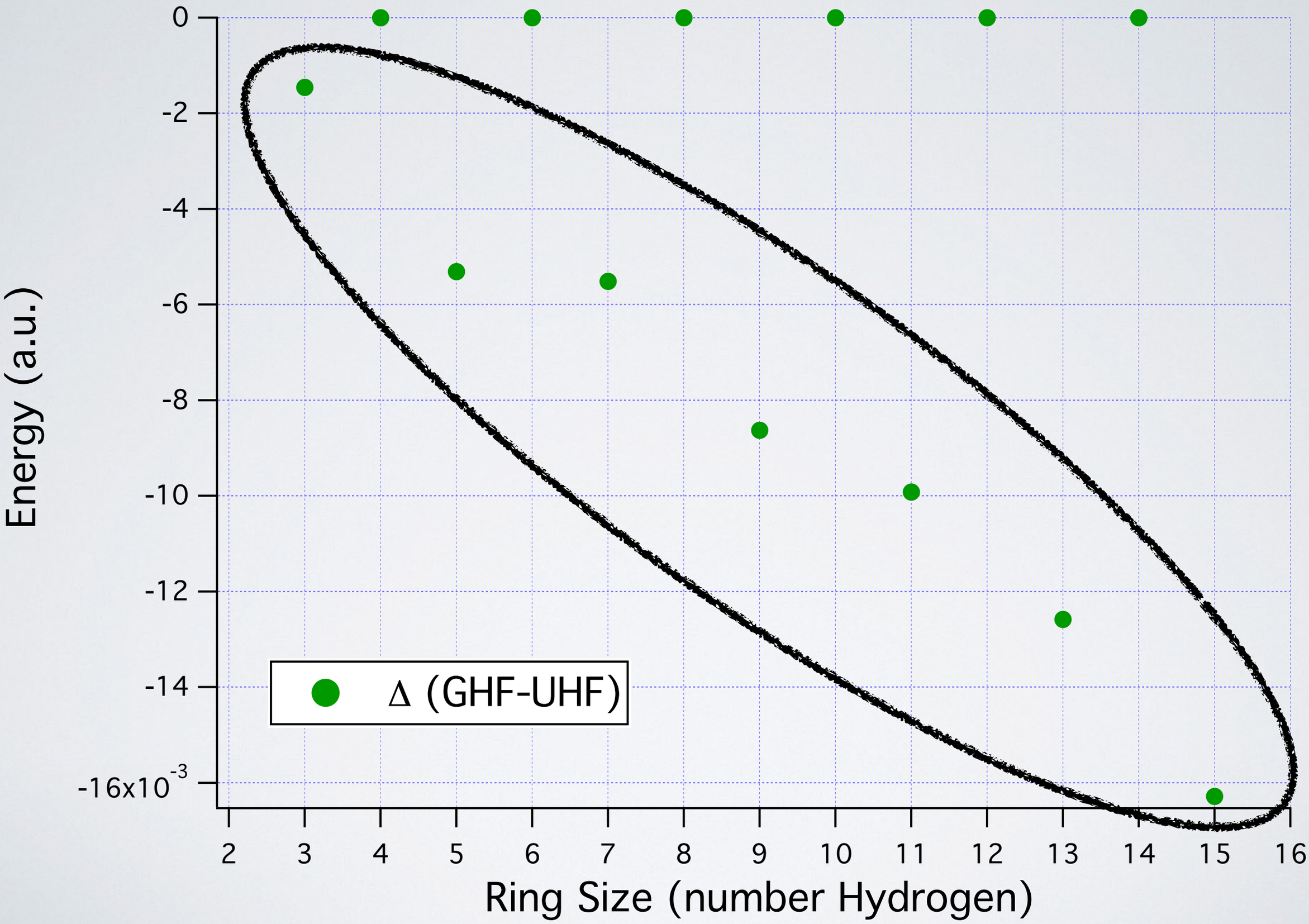
Energy of Formation vs Ring Size

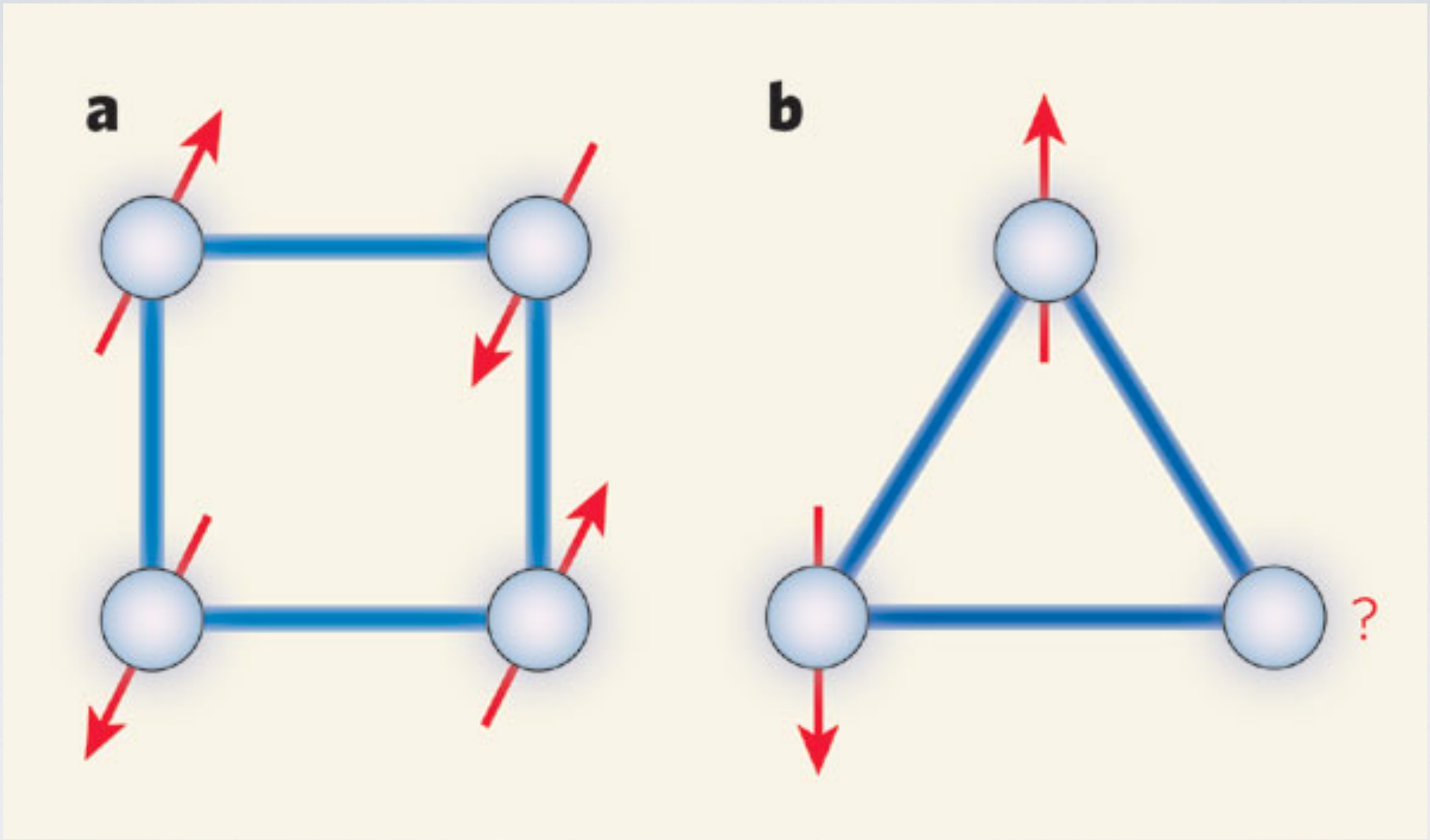


Difference between GHF and UHF energies by ring size



Difference between GHF and UHF energies by ring size





Condensed-matter physics: The eternal triangle

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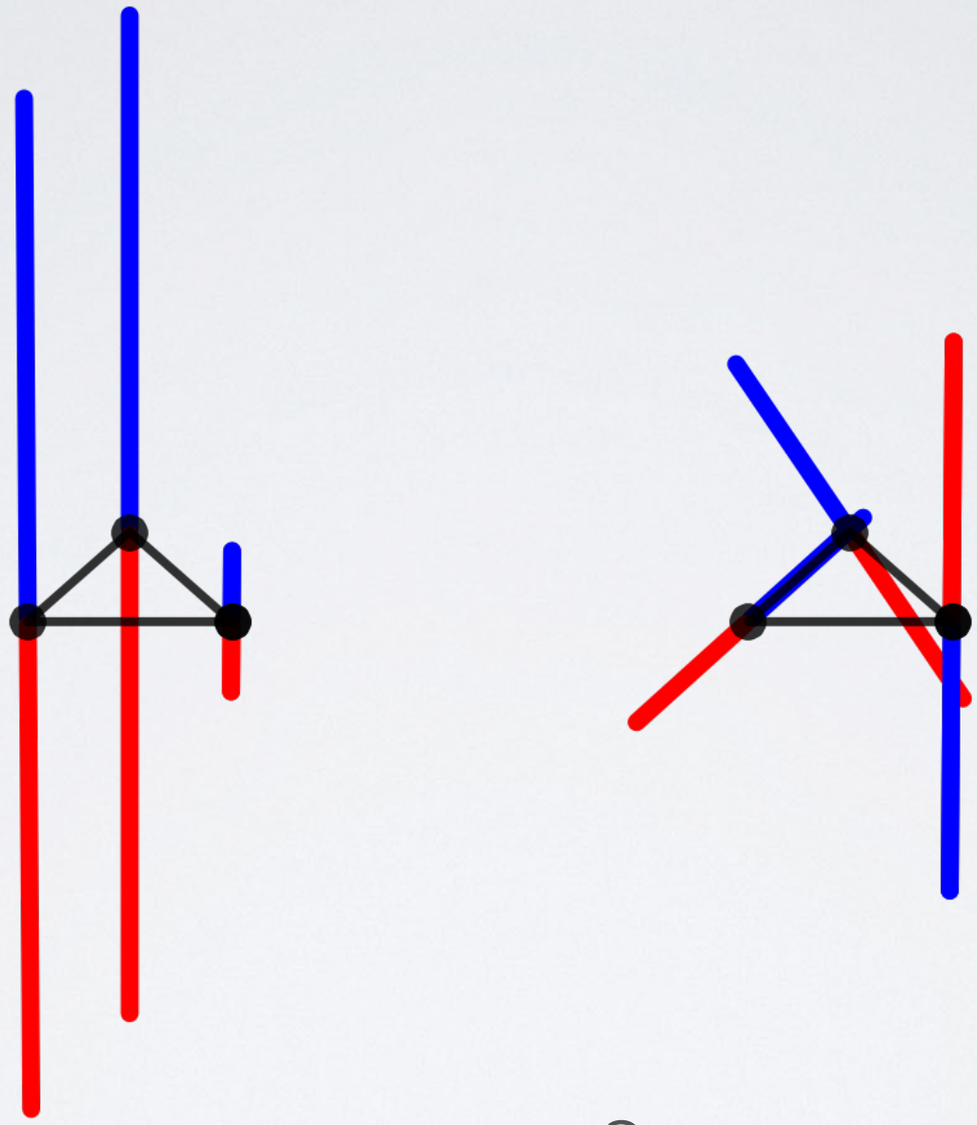
Nature 456, 886-887(18 December 2008)

UHF

GHF

$\langle S_z \rangle = 0.5$
$\langle S^2 \rangle = 0.77$
$S = 0.51$



$\langle S_z \rangle = 0.0$
$\langle S^2 \rangle = 0.78$
$S = 0.51$

n = 3

GHF more stable by 0.9 kcal/mol

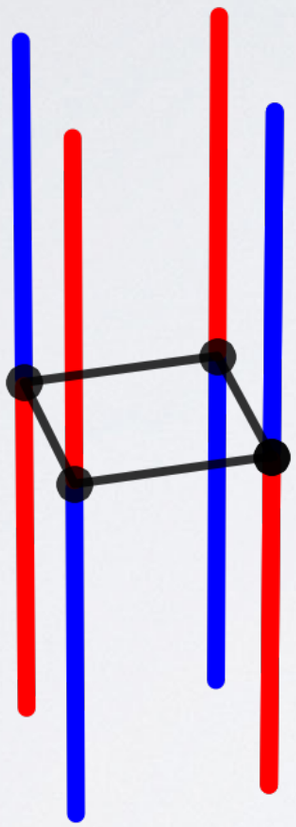
UHF

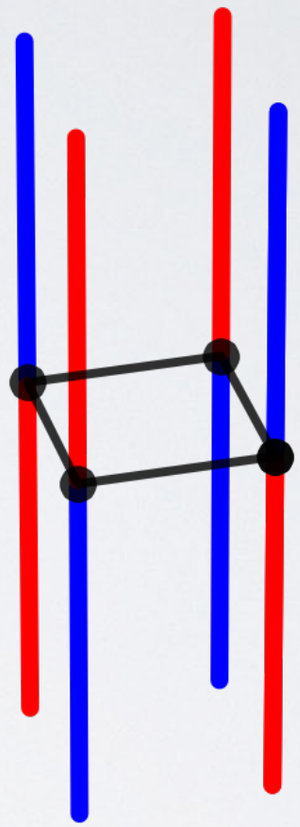
GHF

$\langle S_z \rangle = 0.00$

$\langle S^2 \rangle = 1.06$

$S = 0.64$





$\langle S_z \rangle = 0.00$

$\langle S^2 \rangle = 1.06$

$S = 0.64$

n = 4

Solutions have identical energy

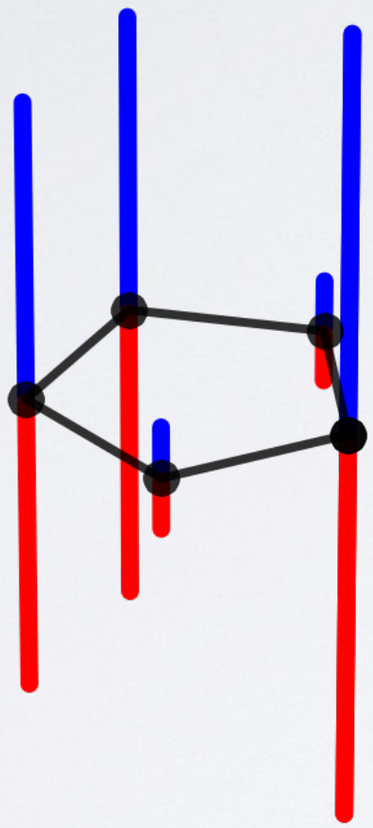
UHF

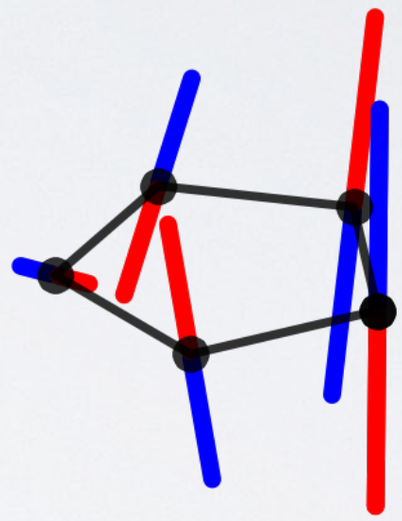
GHF

$\langle S_z \rangle = 0.5$

$\langle S^2 \rangle = 0.78$

$S = 0.51$





$\langle S_z \rangle = 0.00$

$\langle S^2 \rangle = 0.80$

$S = 0.53$

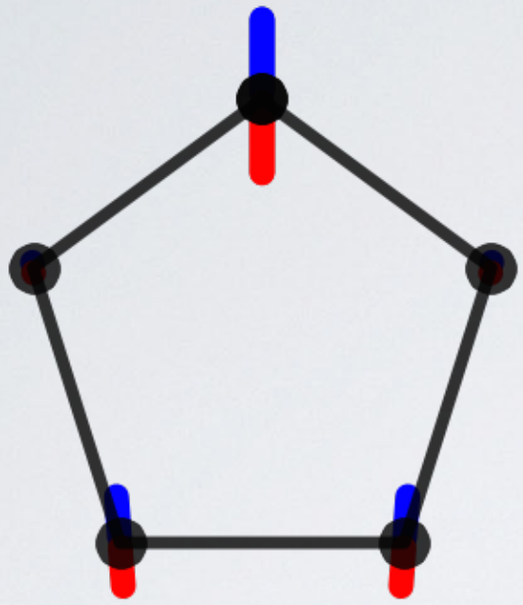
n = 5

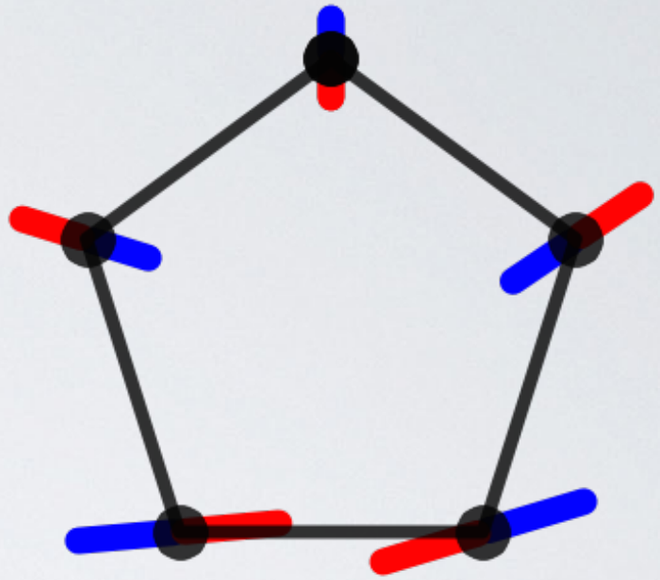
GHF more stable by 3.3 kcal/mol

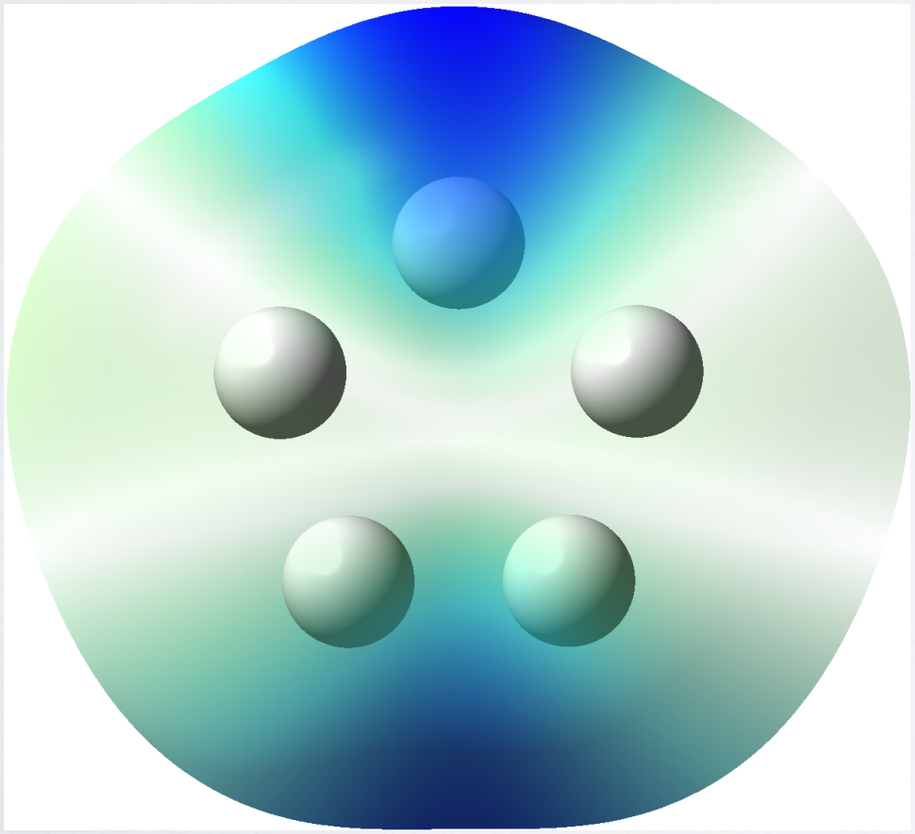
UHF

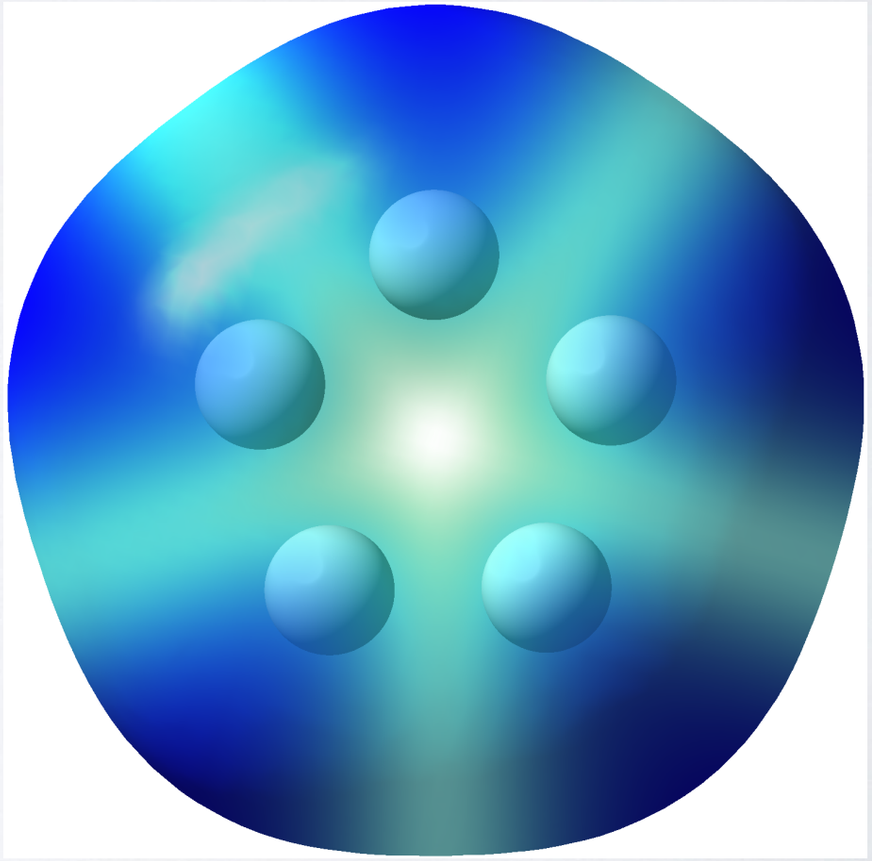
Spin density

GHF









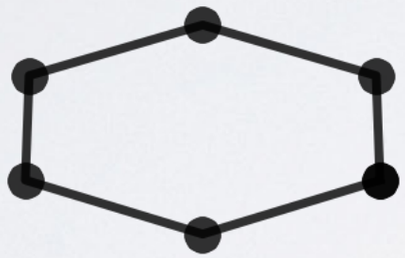
-1.823e-3 1.823e-3

UHF

$\langle S_z \rangle = 0.00$

$\langle S^2 \rangle = 0.00$

$S = 0.00$

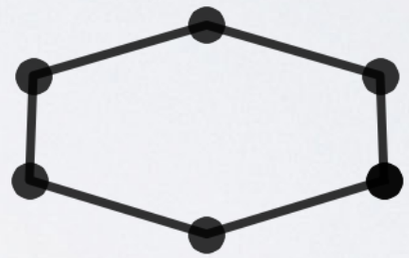


GHF

$\langle S_z \rangle = 0.00$

$\langle S^2 \rangle = 0.00$

$S = 0.00$



n = 6

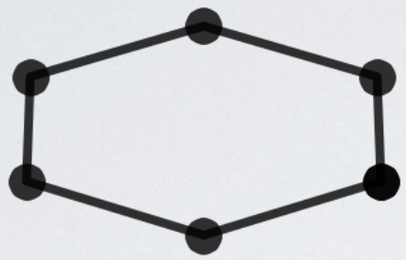
Solutions have identical energy

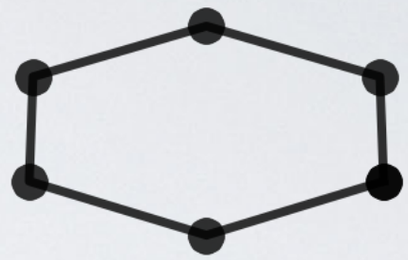
Huckel: 4n+2

UHF

GHF

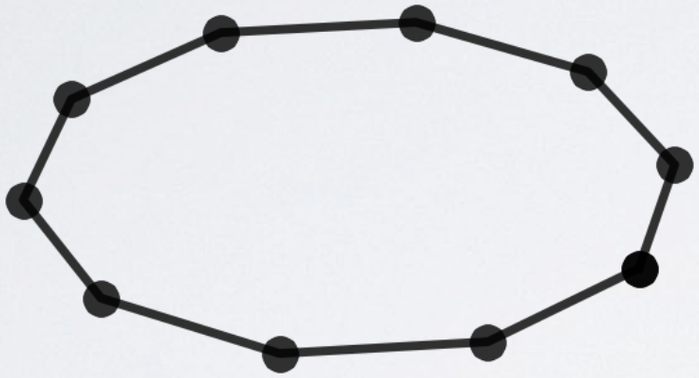
n = 6

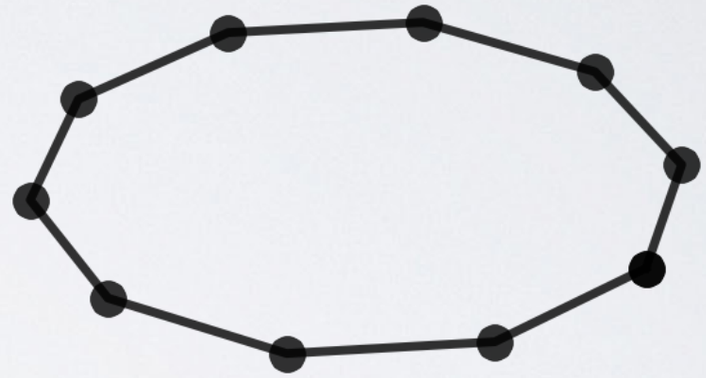




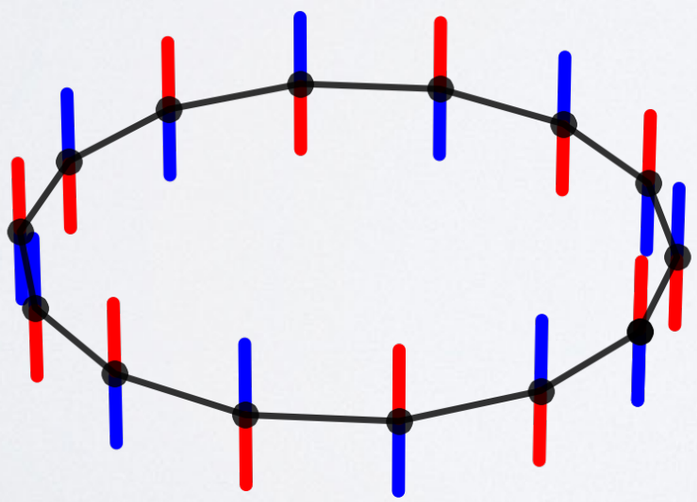
Increasing linearity

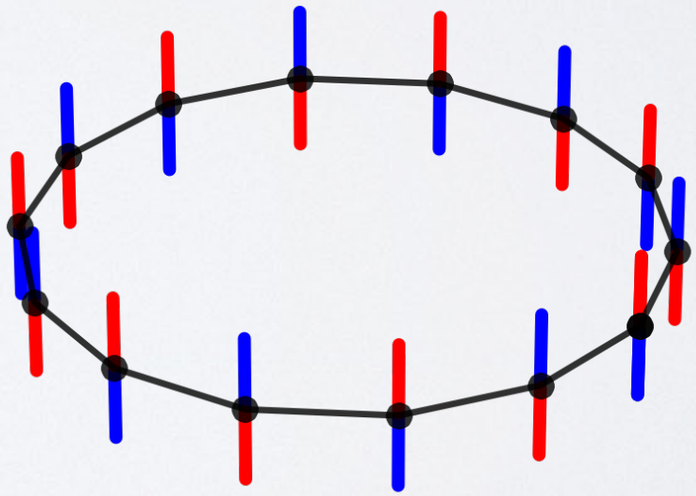
n = 10



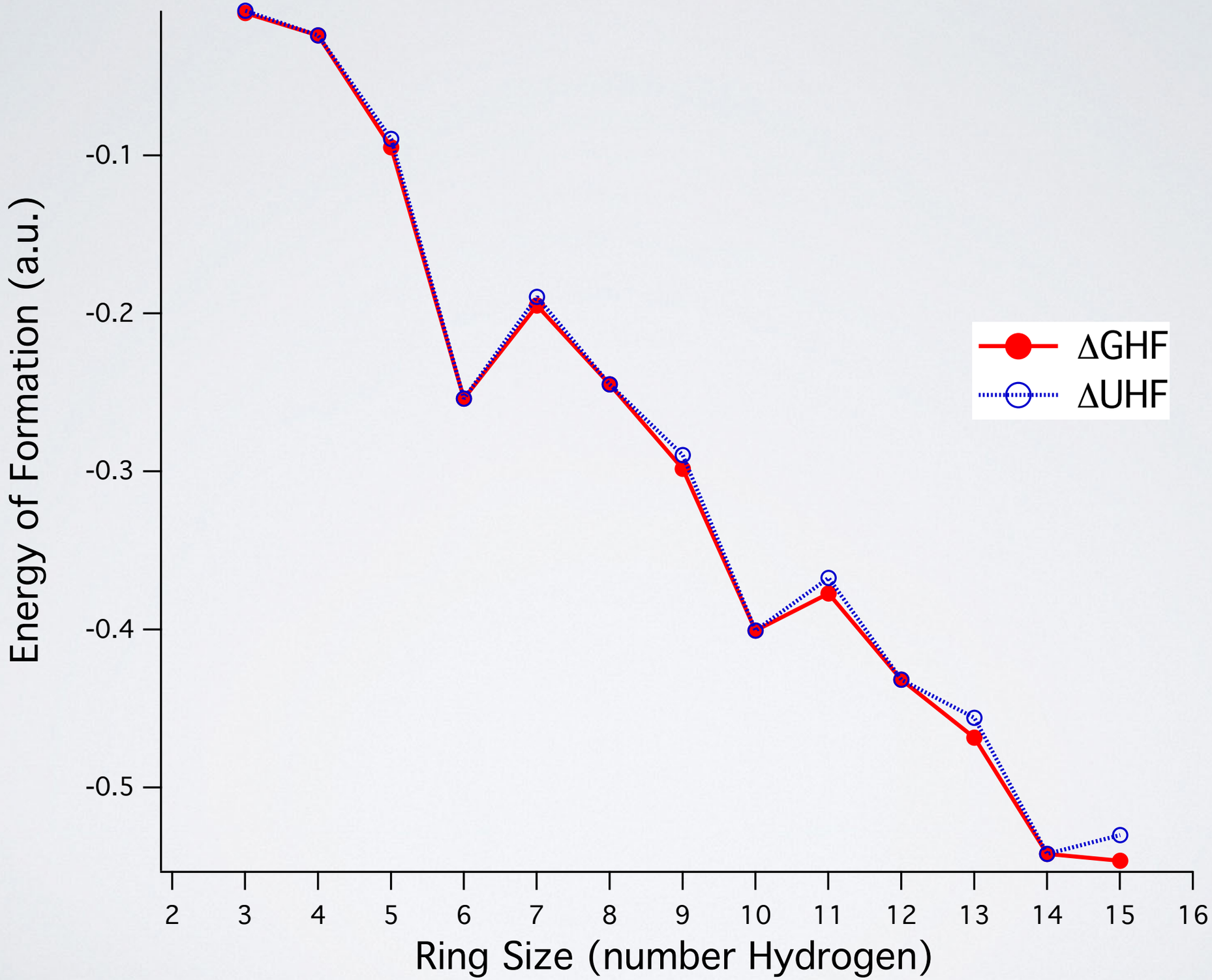


n = 14

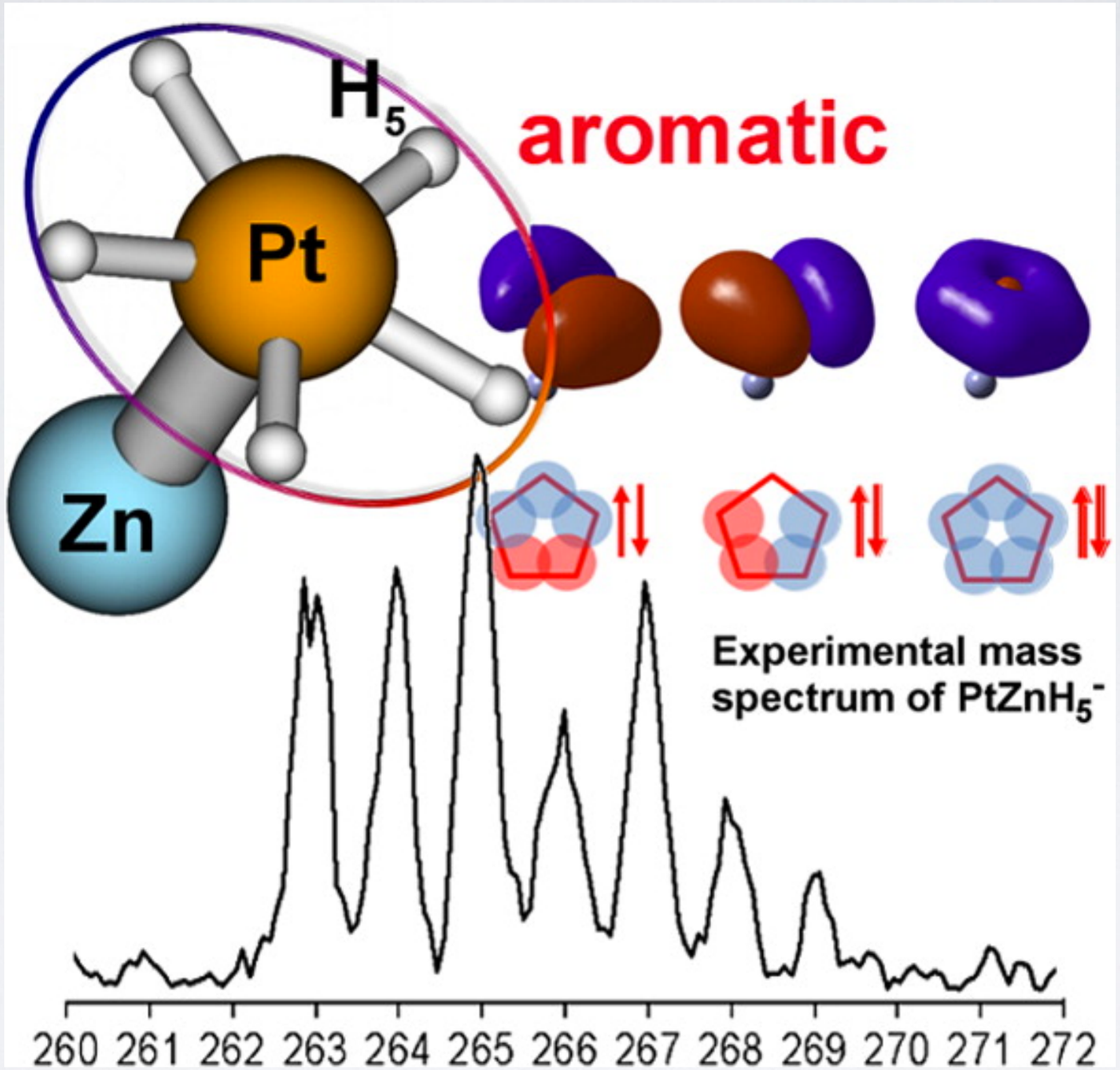




weak magnetic ordering starts to show


Energy of Formation (a.u.)
-0.1
-0.2
-0.3
-0.4
-0.5
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Ring Size (number Hydrogen)
ΔGHF
ΔUHF

σ-aromaticity in Hydrogen Rings?

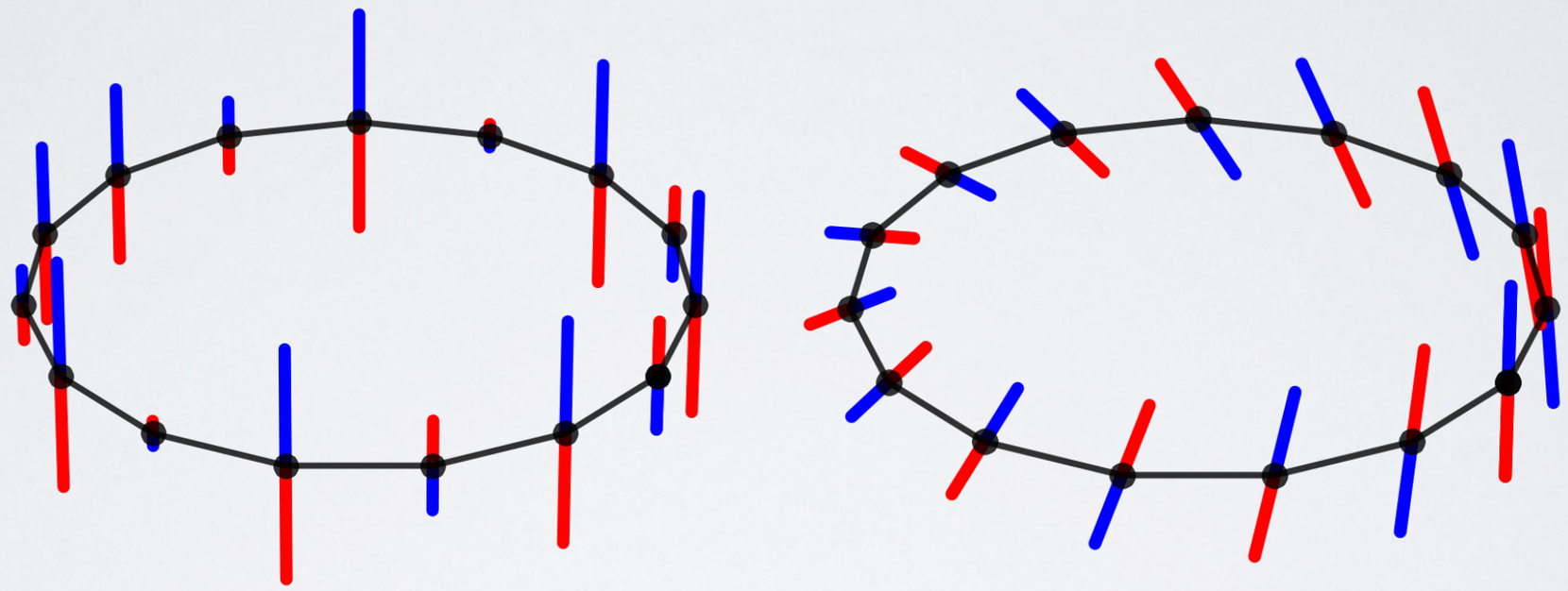


PtZnH5⁻, A σ-Aromatic Cluster. Xinxing Zhang, Gaoxiang Liu, Gerd Ganteför, Kit H. Bowen, and Anastassia N. Alexandrova
The Journal of Physical Chemistry Letters **2014** 5 (9), 1596-1601

UHF

GHF

$S = 0.63$
$\langle S_z \rangle = 0.50$
$\langle S^2 \rangle = 1.01$

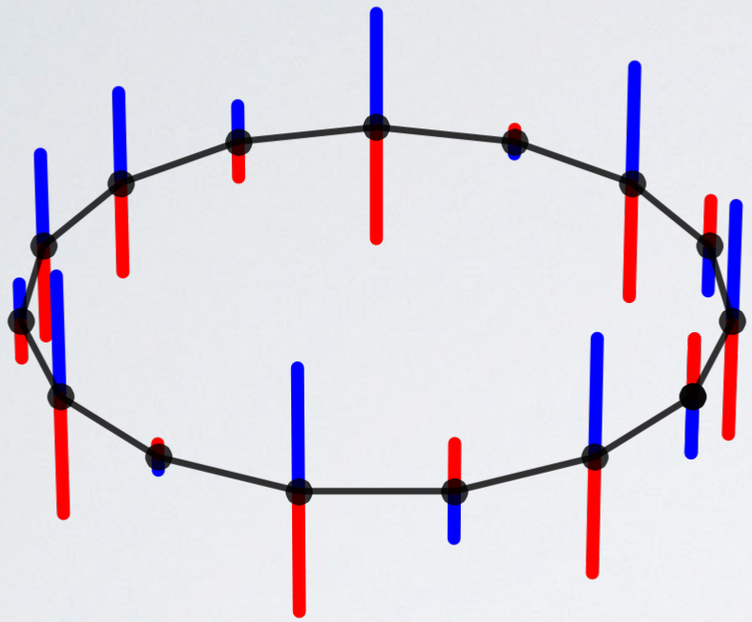


$S = 0.74$
$\langle S_z \rangle = 0.00$
$\langle S^2 \rangle = 1.29$

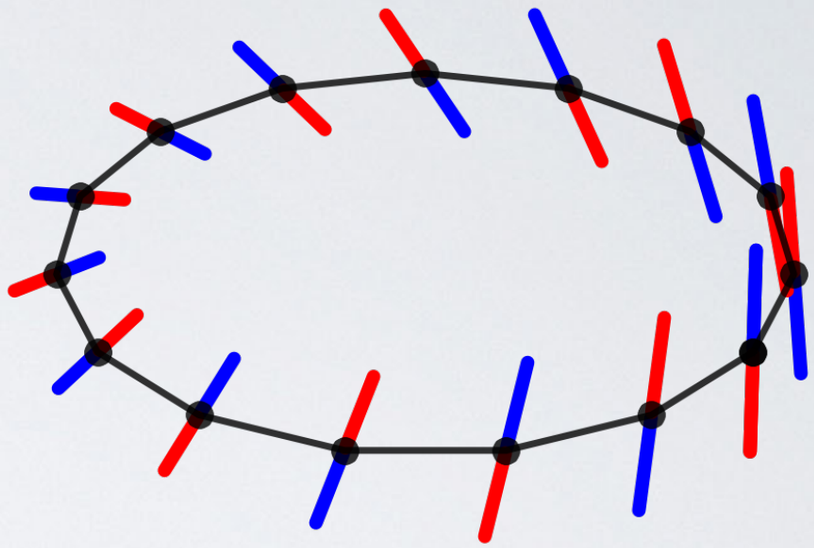
n = 15

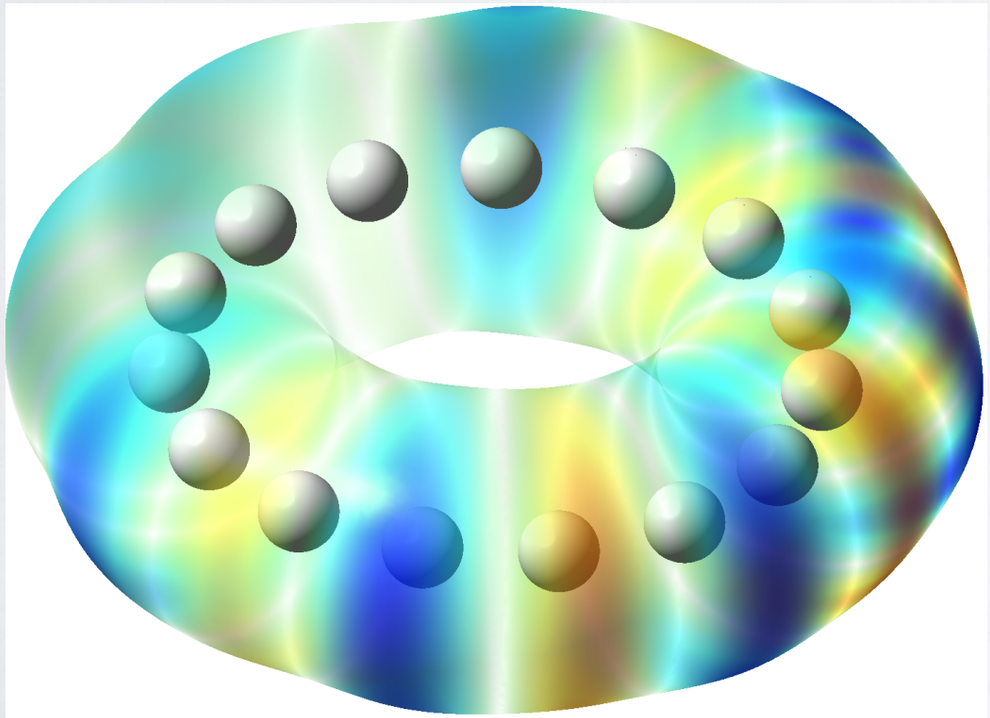
GHF more stable by 10.2 kcal/mol

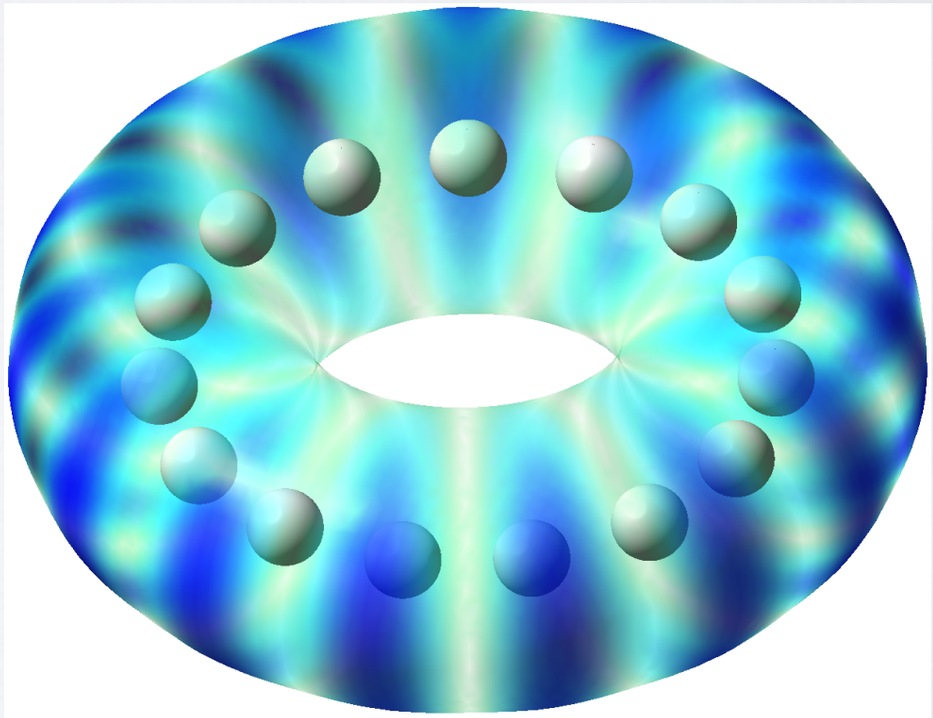
UHF



GHF







n = 15

GHF is (local) energetic minimum, but by no means unique

$$|\phi\theta\rangle = e^{\theta\hat{S}}|\phi\rangle \qquad e^{-\theta\hat{S}}\hat{H}e^{\theta\hat{S}} = \hat{H}$$

$$\hat{S} = -\hat{S}^\dagger \qquad |\phi\theta\rangle \neq |\phi\rangle$$

Infinitely-many degenerate solutions related by theta

$$E = \langle\phi\theta|\hat{H}|\phi\theta\rangle = \langle\phi|e^{-\theta\hat{S}}\hat{H}e^{\theta\hat{S}}|\phi\rangle = \langle\phi|\hat{H}|\phi\rangle$$

Broken-symmetry requires us to have zeros in our Hessian

$$E = \langle \phi\theta | \hat{H} | \phi\theta \rangle = \langle \phi | e^{-\theta \hat{S}} \hat{H} e^{\theta \hat{S}} | \phi \rangle = \langle \phi | \hat{H} | \phi \rangle$$

$$\langle \phi | \hat{H} | \phi \rangle = \langle \phi | e^{\theta \hat{S}^\dagger} \hat{H} e^{\theta \hat{S}} | \phi \rangle$$

$$= \langle \phi | \hat{H} | \phi \rangle + \left. \frac{\partial E}{\partial \mathbf{s}} \right|_{\mathbf{s}=0} \mathbf{s} + \frac{1}{2} \left. \frac{\partial^2 E}{\partial \mathbf{s} \partial \mathbf{s}} \right|_{\mathbf{s}=0} \mathbf{s}^2 + \cdots$$

All variations must be zero. First is satisfied by Brillouin's theorem, second (our Hessian) will have at least one zero.

This is a finite version of Goldstone's theorem: if the system spontaneously breaks a continuous symmetry, we get zero-energy excitations along the mode of the symmetry.

Thank you to the Li group.