Multiresolution Analysis in Extreme Magnetic Fields

Doctoral Defense

21.04.2026

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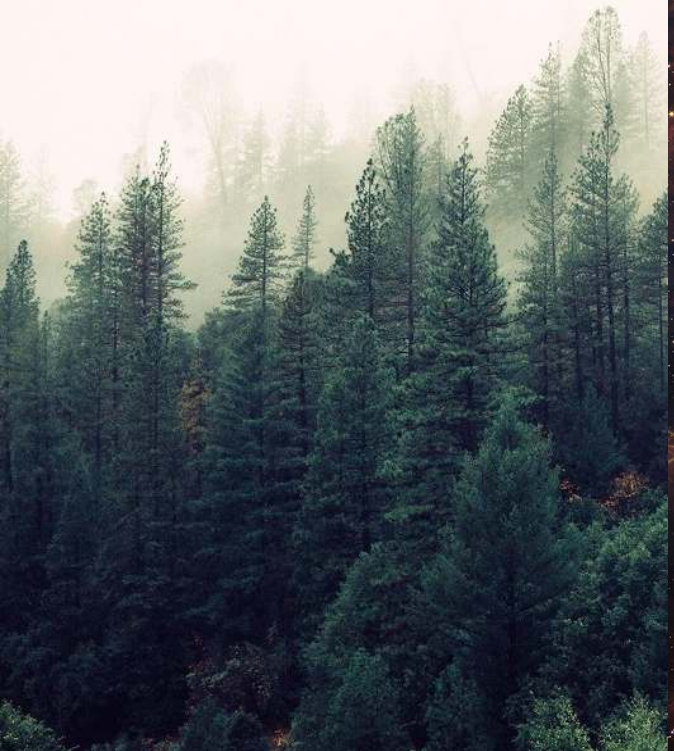
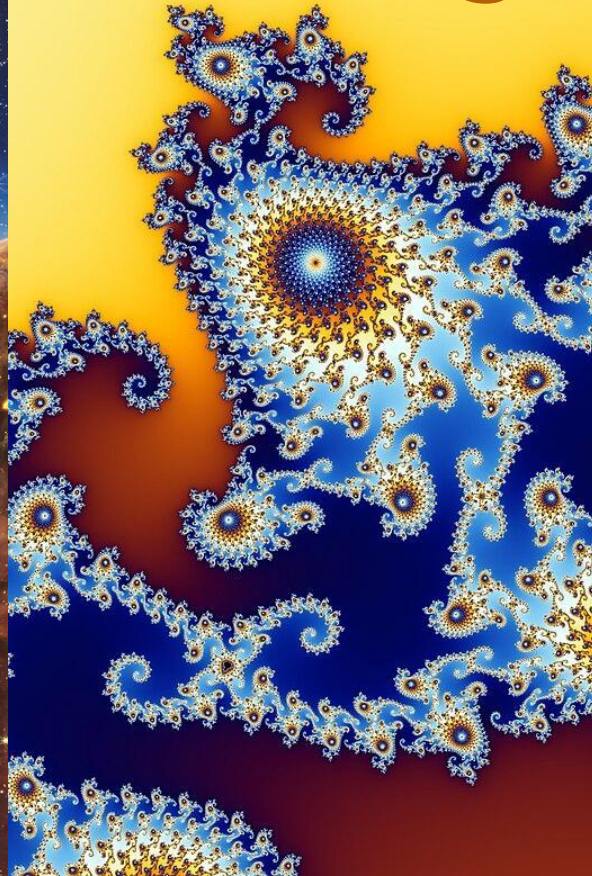
Life



Nature

Reality



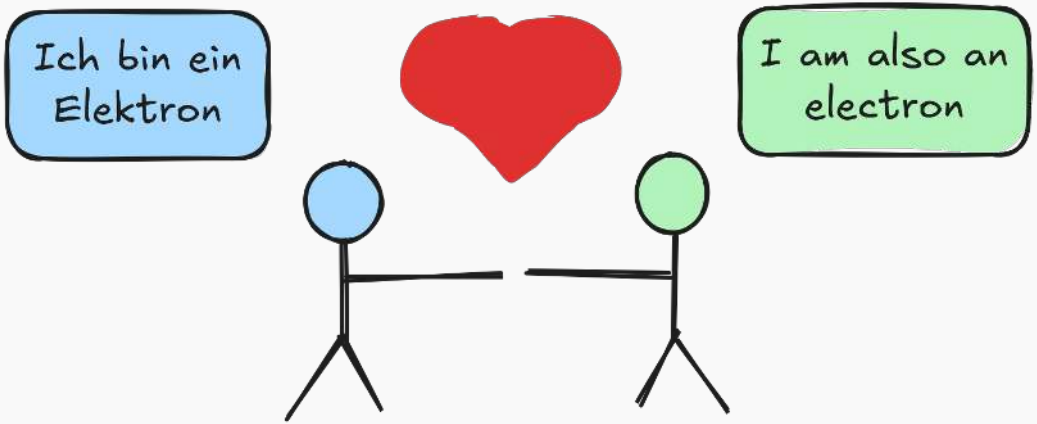

Chemical Bond

Chemical Bonding

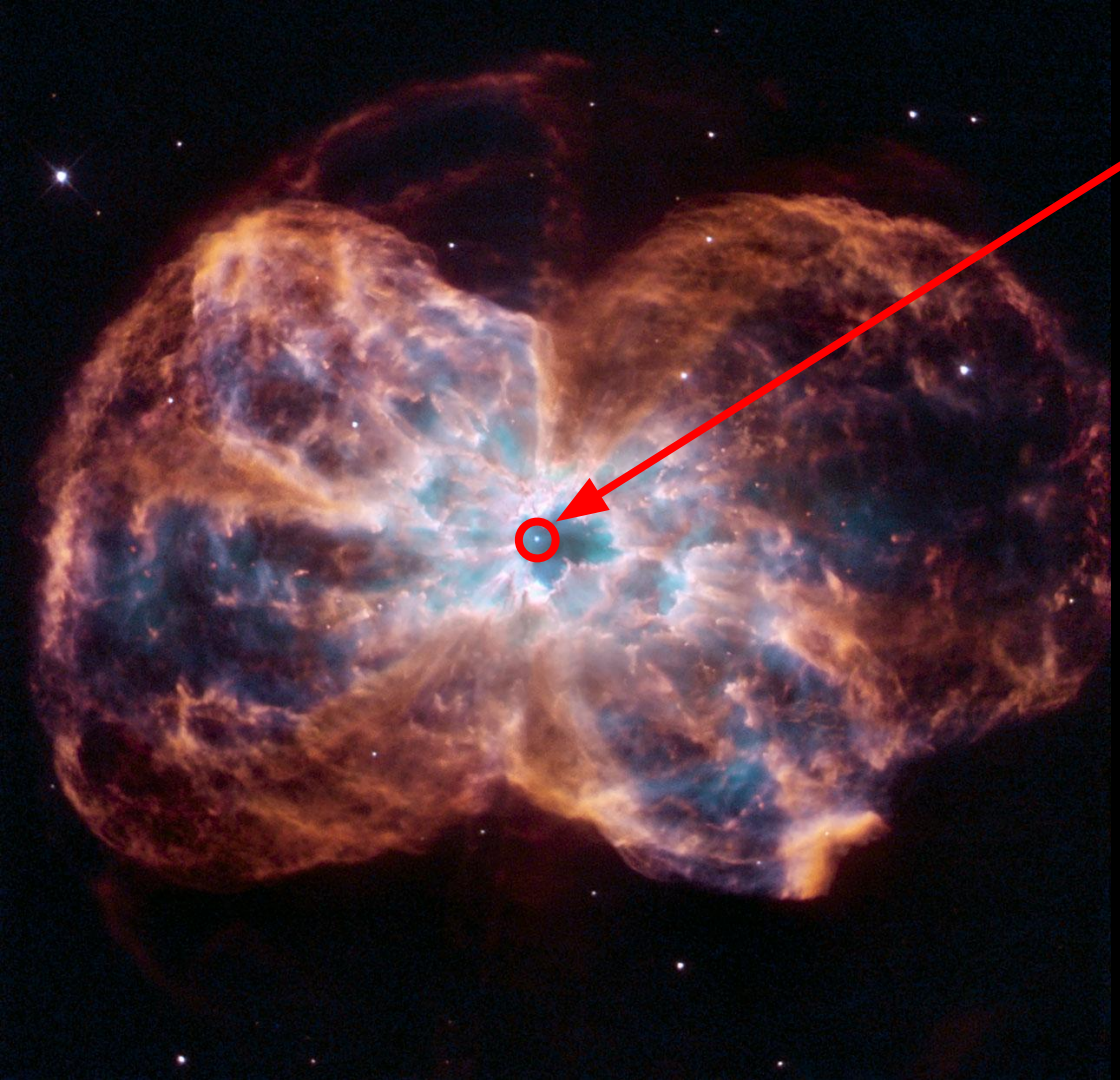
”

Das ganze Phänomen ist nahe verwandt mit dem von Heisenberg behandelten quantenmechanischen Resonanzphänomen.

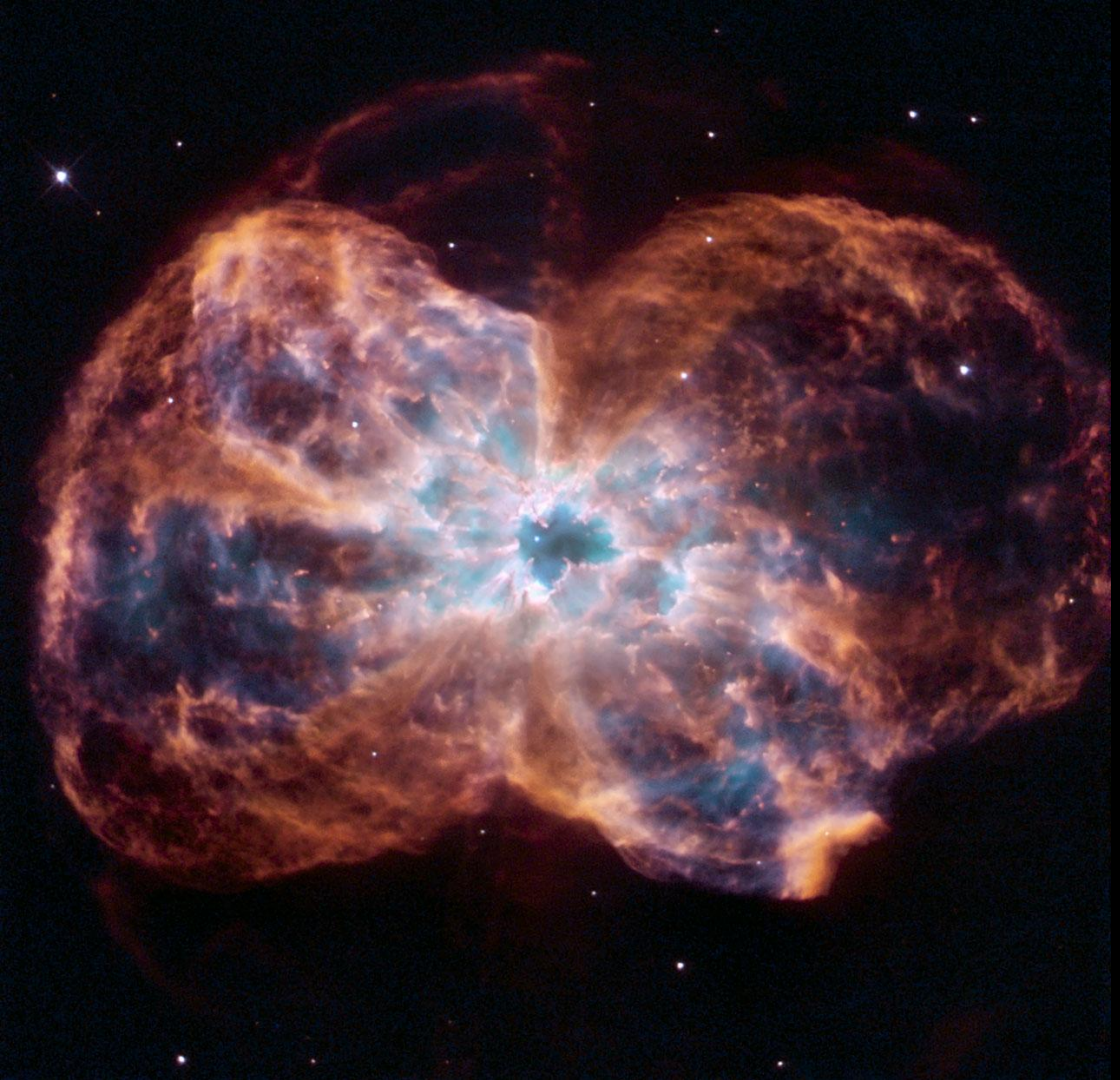
- Heitler and London (1927)



Molecules under ambient or earthly atmosphere have been studied to a greater extent.

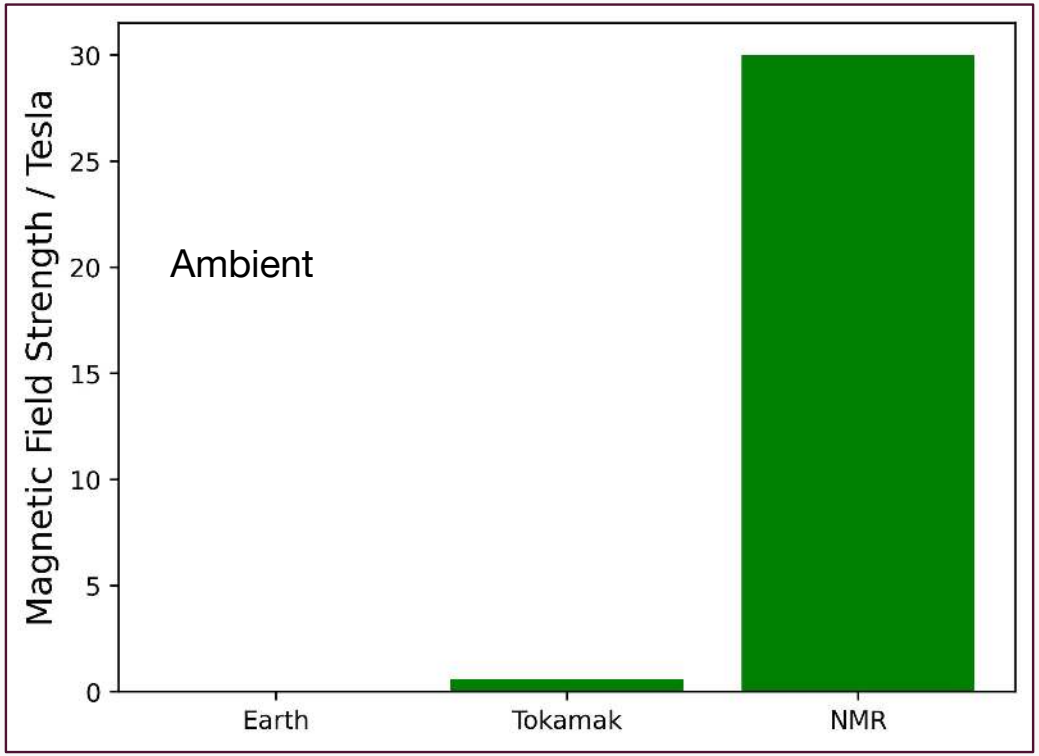


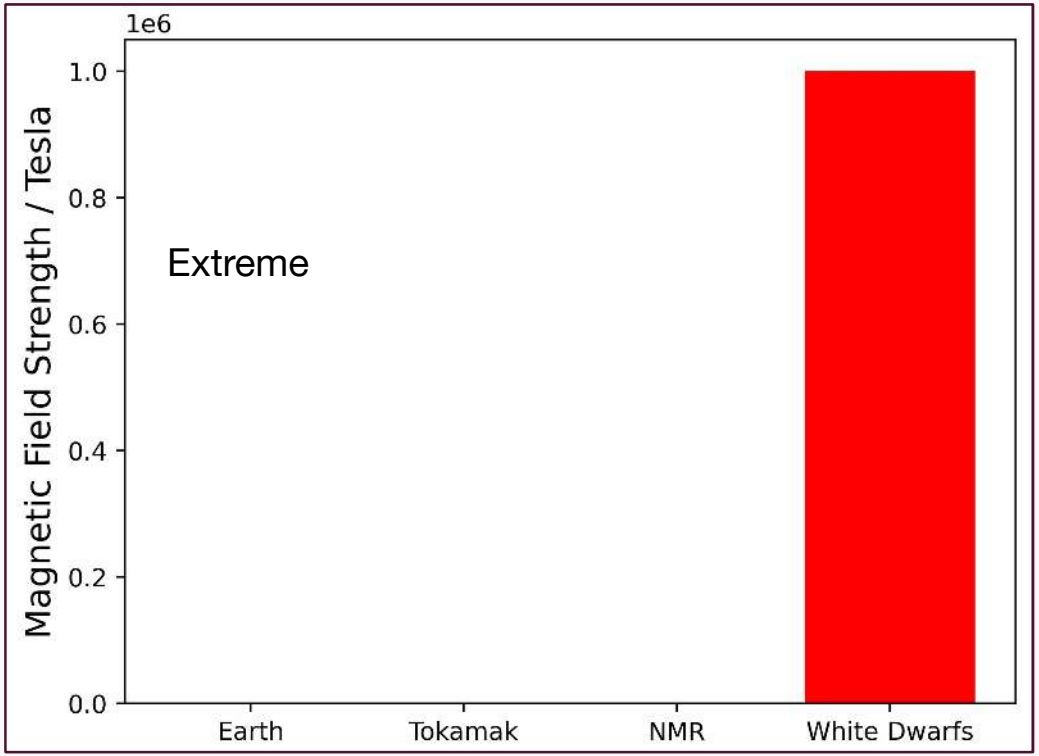
Source: https://images.nasa.gov



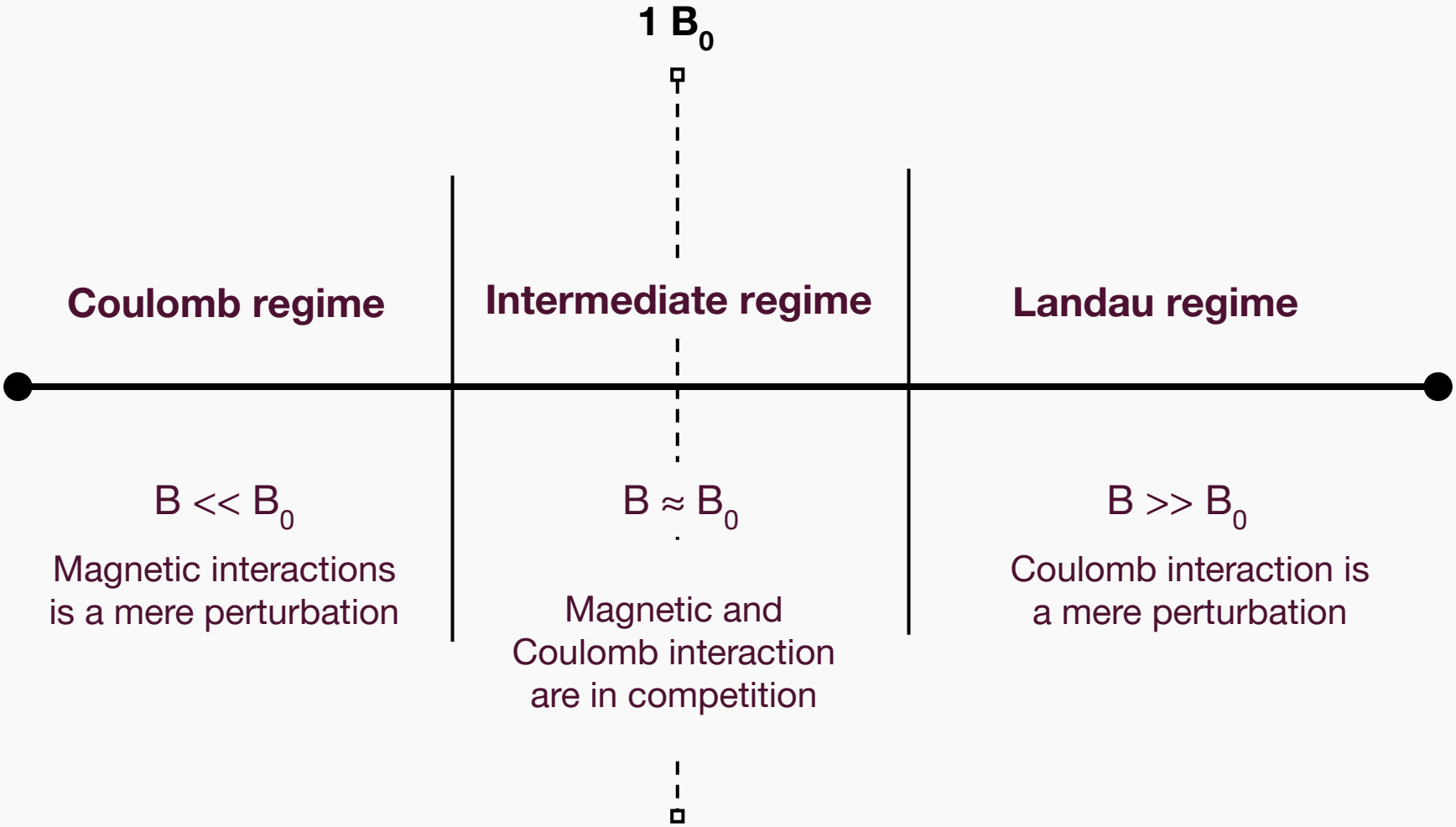
Magnetic fields upto 2 million times Earth's field

Source: https://images.nasa.gov


Magnetic Field Strength / Tesla
30
25
20
15
10
5
0
Ambient
Earth
Tokamak
NMR



$$1\ \mathrm{B}_0 = 2.35 \times 10^6\ \ \mathrm{T}$$


1 B0
Coulomb regime
Intermediate regime
Landau regime
B << B0
Magnetic interactions is a mere perturbation
B ≈ B0
Magnetic and Coulomb interaction are in competition
B >> B0
Coulomb interaction is a mere perturbation

Magnetic Fields and Quantum Chemistry

Hamiltonian in absence of **B**

$$\hat{H}_0 = \frac{\hat{p}^2}{2} + \hat{V}$$

B is introduced explicitly through kinetic momentum (π)

$$\frac{\hat{\pi}^2}{2} = \frac{\hat{p}^2}{2} + \frac{1}{2}B_z\hat{L}_z + \frac{1}{8}B_z^2(x^2 + y^2)$$

The resulting Hamiltonian in presence of field with the introduction of spin

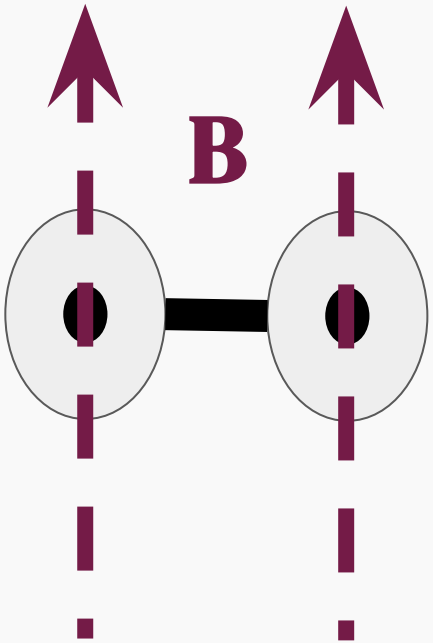
$$\hat{H} = \hat{H}_0 + \frac{1}{2}B_z\hat{L}_z + B_z\hat{S}_z + \frac{1}{8}B_z^2(x^2 + y^2)$$

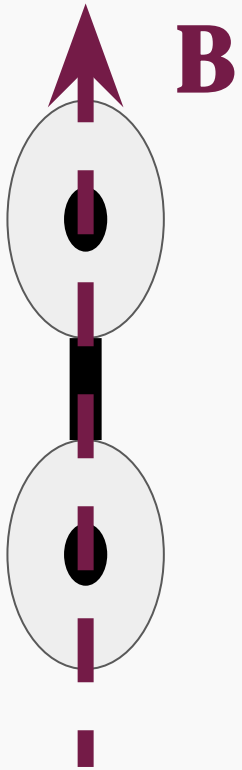
$$\hat{H} = \hat{H}_0 + \frac{1}{2} B_z \hat{L}_z + B_z \hat{S}_z + \frac{1}{8} B_z^2 (x^2 + y^2)$$

Field free Hamiltonian

Zeeman Terms
accounts for the interaction of orbital and spin magnetic moments of electron with external **B** field resulting in increase or decrease of energy

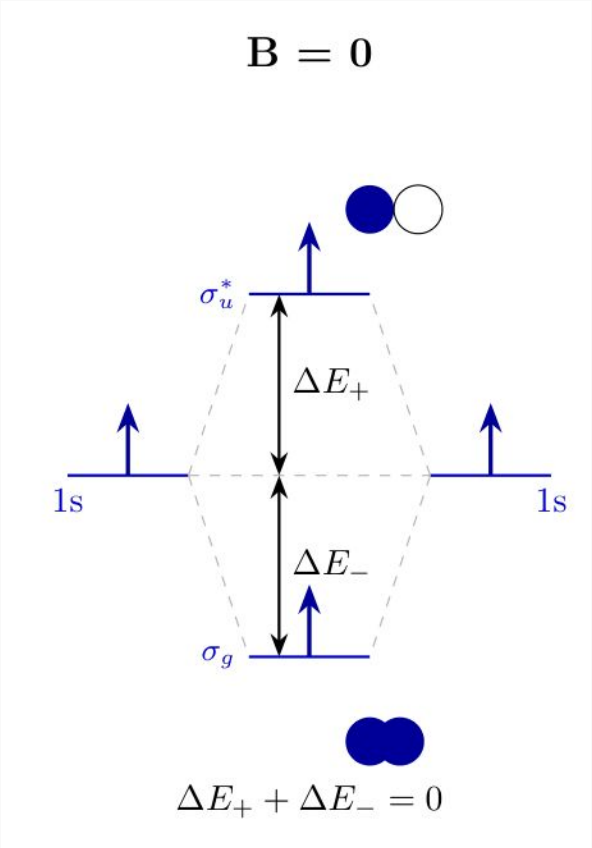
Diamagnetic Term
accounts for magnetic confinement resulting in increase of energy


B


B

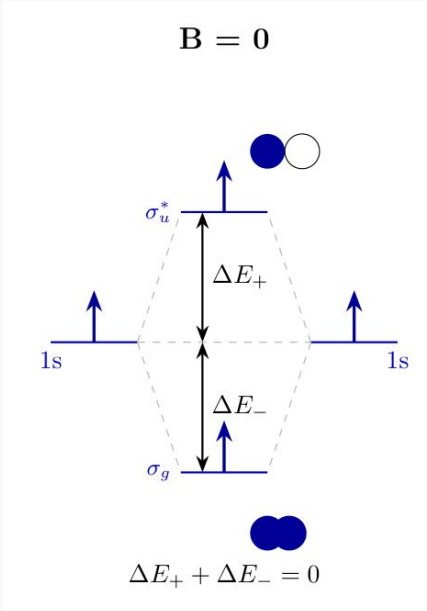
Triplet H_2

Formal bond order 0

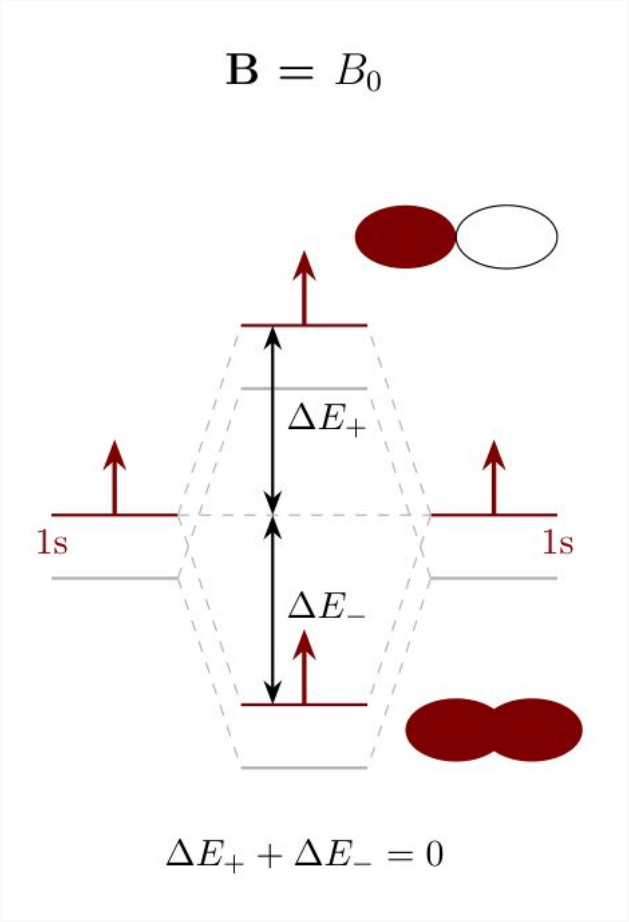


Perpendicular Paramagnetic Bonding

Triplet H_2 in strong **B**



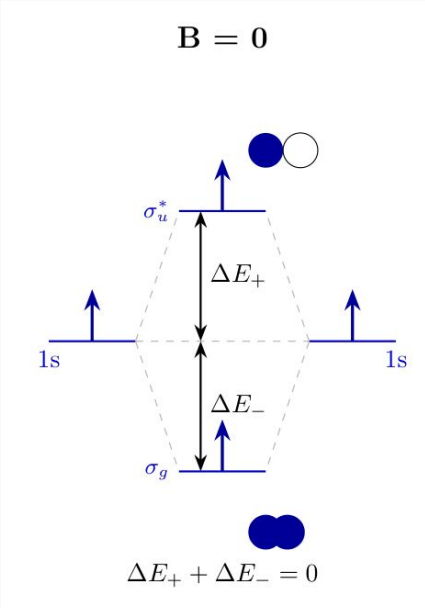
B parallel



Source: Lange et al. *Science* 2012

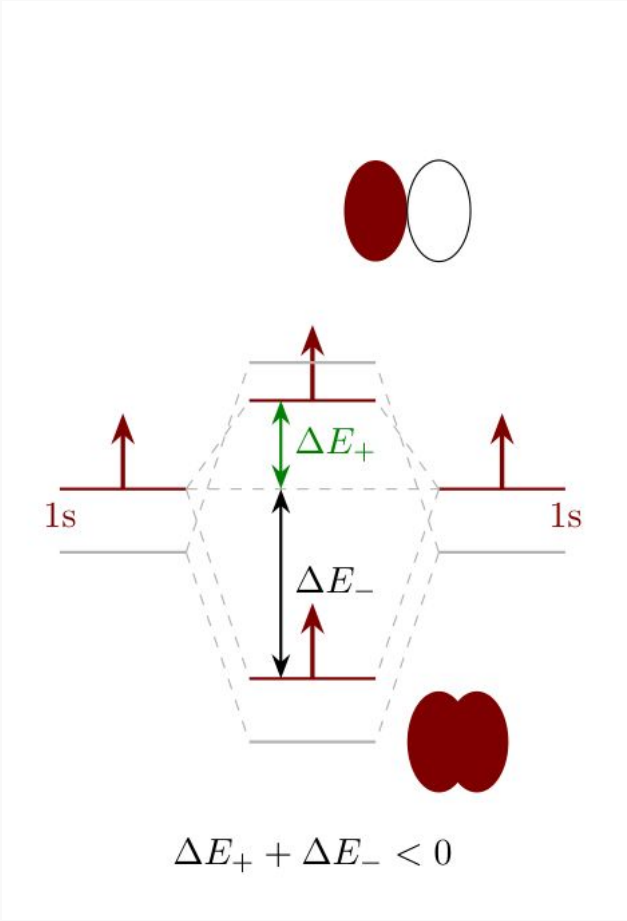
Perpendicular Paramagnetic Bonding

Triplet H_2 in strong **B**



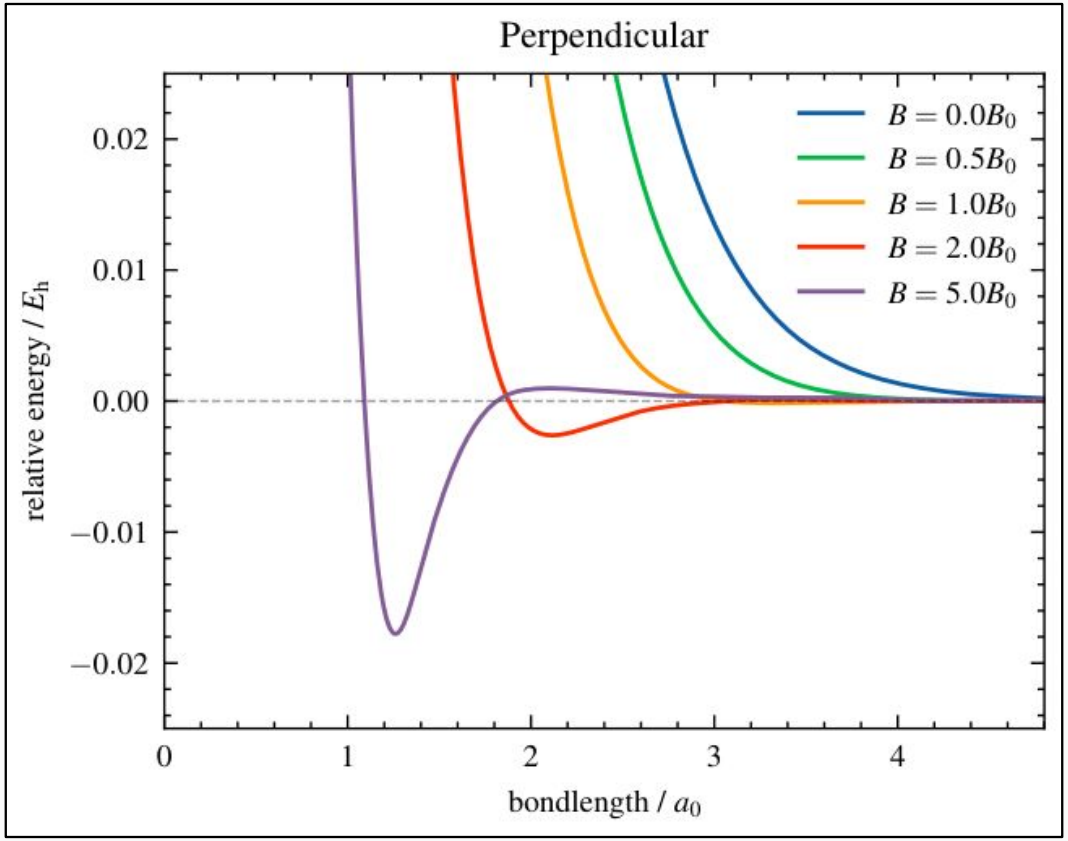
B perpendicular

Stabilization of the antibonding orbital due to orbital Zeeman term.



Source: Lange et al. *Science* 2012

Singlet He_2 in B



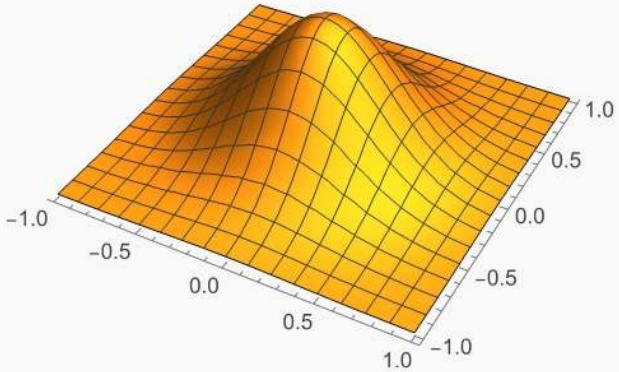
Non bonded singlet He_2 held by dispersion binds strongly in B

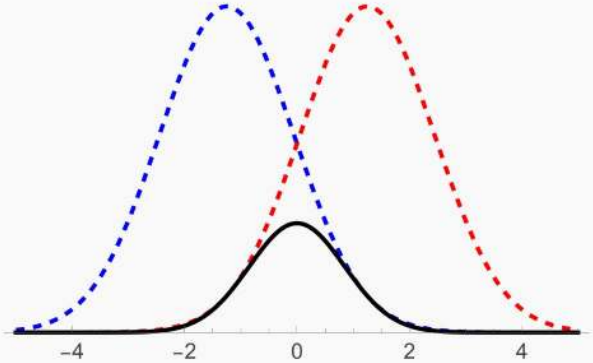
Linear Combination of Atomic Orbitals (LCAO)

Atom-centered basis sets

$$\Phi_i(\boldsymbol{r}) = \sum_{\mu} c_{\mu i}\ \chi_\mu(\boldsymbol{r}) \quad \left[c_{\mu i} \in \mathbb{R}\right]$$

$$\mathrm{GTO}_{nlm}(x, y, z) = N x^n y^l z^m e^{-\alpha r^2}$$





LONDON Orbitals

LONDON orbitals encorporate **gauge origin invariance**:

$$\omega_\mu(\boldsymbol{r}) = \mathrm{e}^{-i\boldsymbol{k}_\mu \cdot \boldsymbol{r}} \chi_\mu(\boldsymbol{r})$$

where

$$k_\mu = \frac{1}{2}\boldsymbol{B} \times (\boldsymbol{R}_\mu - \boldsymbol{O})$$

$\boldsymbol{R}_\mu \rightarrow$ center of the basis function

Source : Tellgren et. al *J. Chem. Phys.* 2008

Limitations of LCAO

Inaccurate physics in extreme fields

Isotropic GTOs cannot capture anisotropic effects in **B**

Basis Set Incompleteness Error (BSIE)

Finiteness of the basis set lacks flexibility to represent correct physics

Basis Set Superposition Error (BSSE)

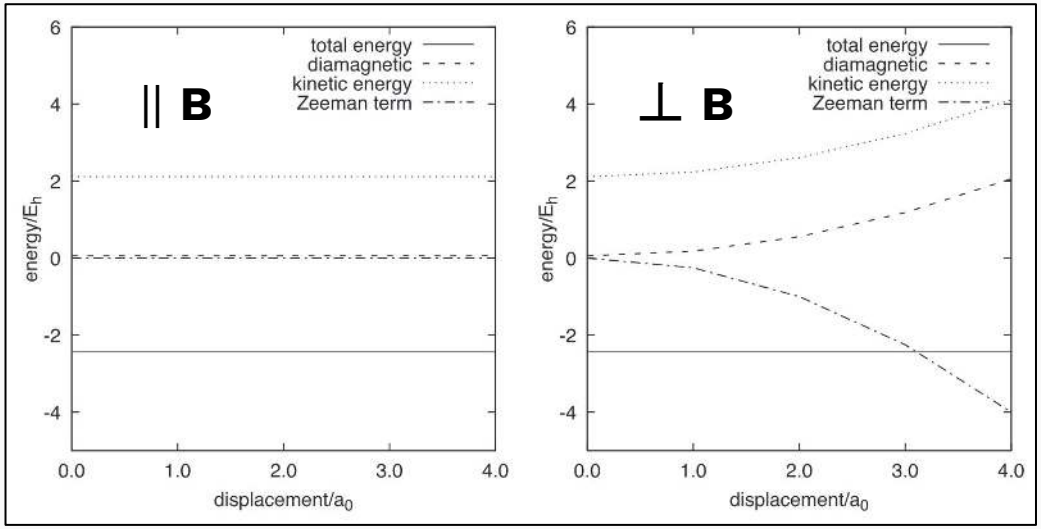
The artificial stabilization of a monomer's wavefunction through the utilization of basis functions centered on neighboring fragments.

Gauge Origin Invariance of Observables

- Gauge origin invariance ensures that observables remain meaningful

- Total energy is gauge origin invariant, components not

Triplet He atom

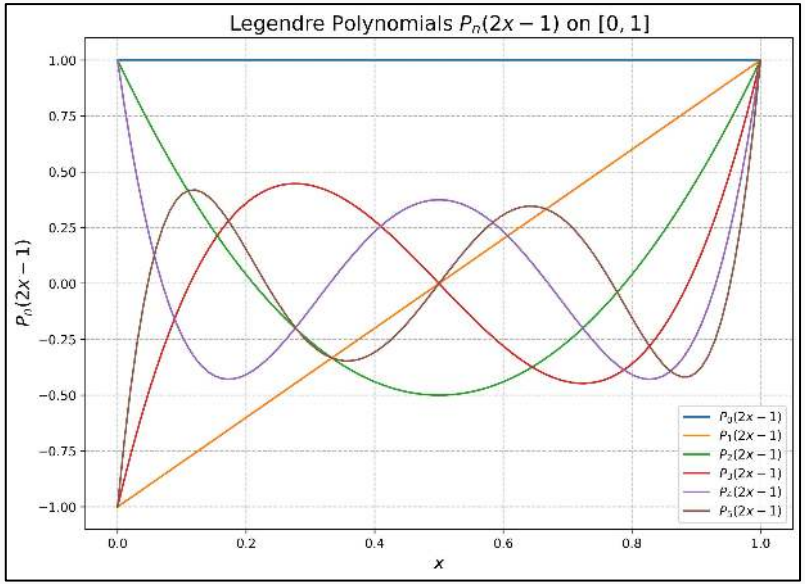


Source : Bischoff *Phys. Rev. A.* 2020

How decisive is the advantage of MRA over LCAO in finite field calculations?

Multiresolution Analysis (MRA)

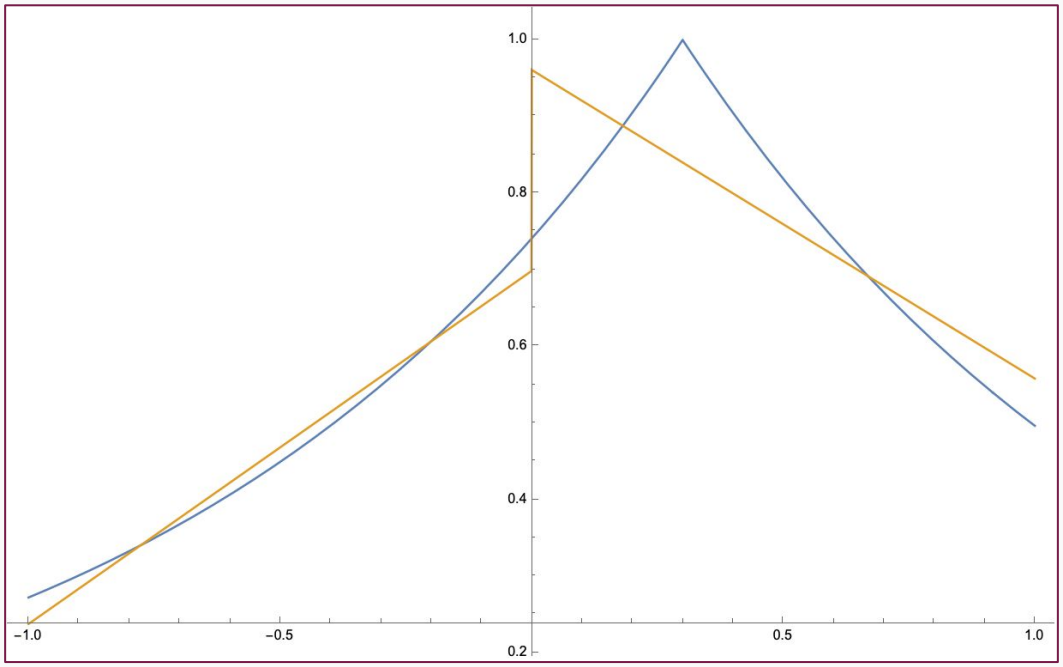
MRA is a method of **projecting functions and operators** of arbitrary dimensions **using orthonormal polynomials adaptively.**



1. Harrison et. al *J. Chem. Phys.* 2004
2. Bischoff *Adv. in Quant. Chem.* Ch-1 2019 (book chapter)

Function representation

Order = 1



2 boxes

$$f^n(x) = \sum_{i=0}^{k} \sum_{l=0}^{2^n-1} s_{il}^n \phi_{il}^n(x)$$

n = level of resolution

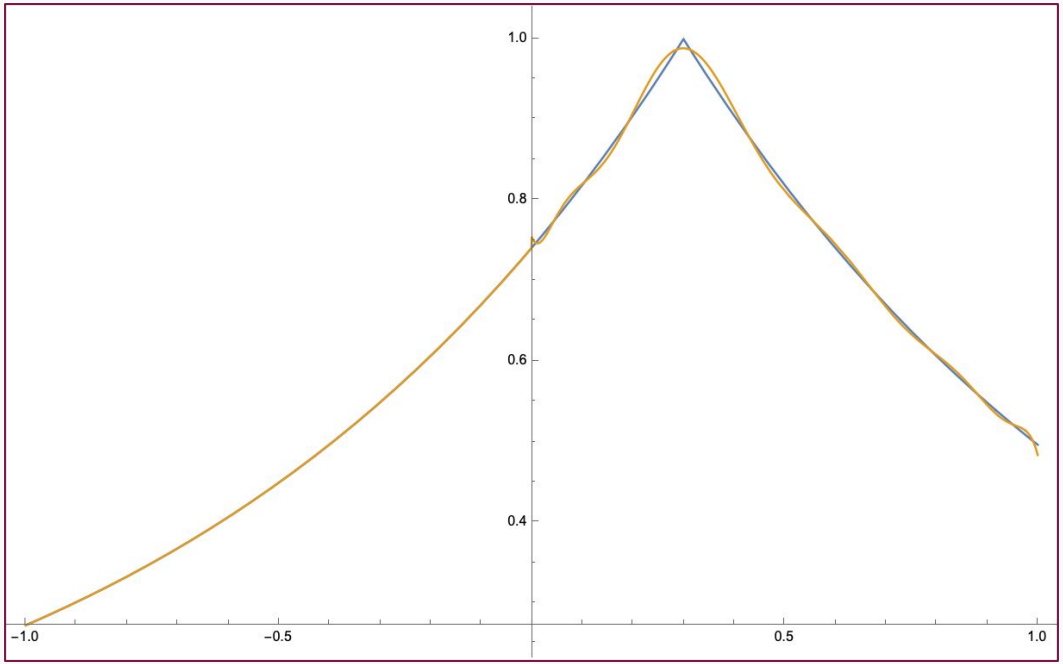
i = order of the polynomial

l = translation index

Resolving with higher order polynomials wherever necessary gives MRA adaptiveness

Function representation

Order = 5



2 boxes

$$f^n(x) = \sum_{i=0}^{k} \sum_{l=0}^{2^n-1} s_{il}^n \phi_{il}^n(x)$$

n = level of resolution

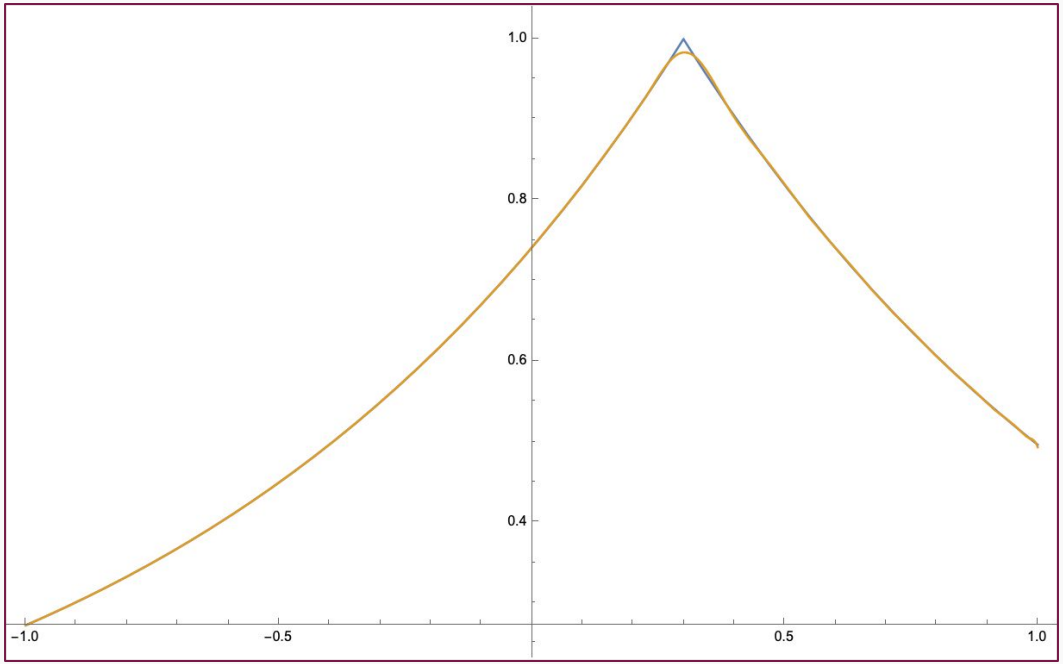
i = order of the polynomial

l = translation index

Resolving with higher order polynomials wherever necessary gives MRA adaptiveness

Function representation

Order = 15



2 boxes

$$f^n(x) = \sum_{i=0}^{k} \sum_{l=0}^{2^n-1} s_{il}^n \phi_{il}^n(x)$$

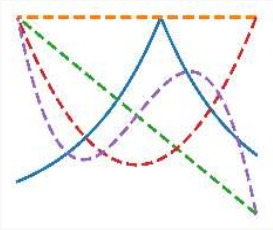
n = level of resolution

i = order of the polynomial

l = translation index

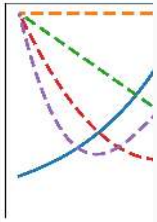
Resolving with higher order polynomials wherever necessary gives MRA adaptiveness

Level 0

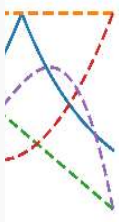


Translation 0

Level 1



Translation 0



Translation 1

Level 2

No refinement

Translation 0

Translation 1

Electronic Structure Theory with MRA

$$(T+V)\Psi = E\Psi \Leftrightarrow \Psi = -(T-E)^{-1}V\Psi$$

$$\therefore \Psi_{\text{final}} = -(T-E)^{-1}V\Psi_{\text{initial}}$$

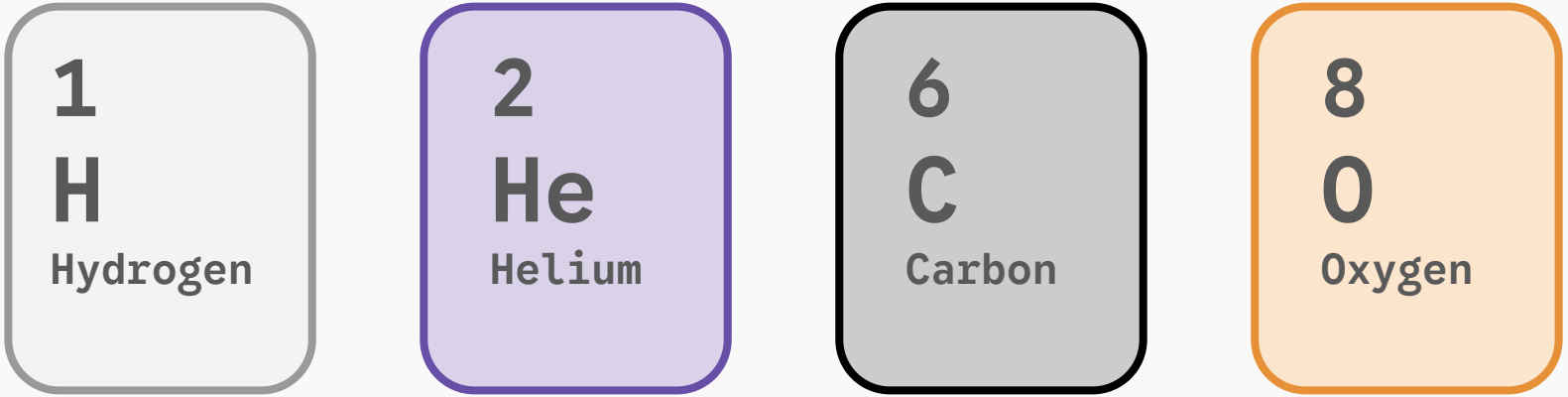
Advantages of MRA

No basis set errors

No gauge origin invariance problem

Accurate representation of physics even Landau regime

Results

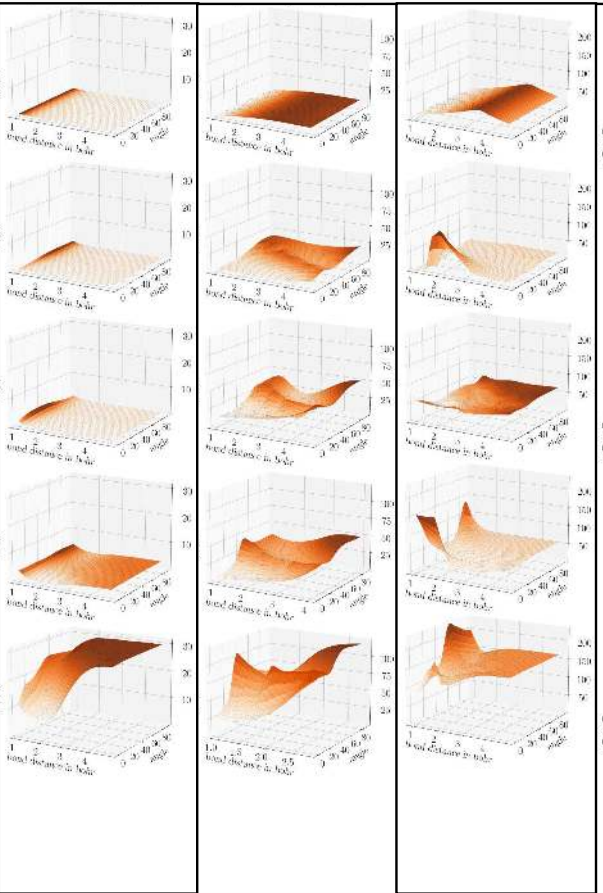

1
H
Hydrogen
2
He
Helium
6
C
Carbon
8
O
Oxygen

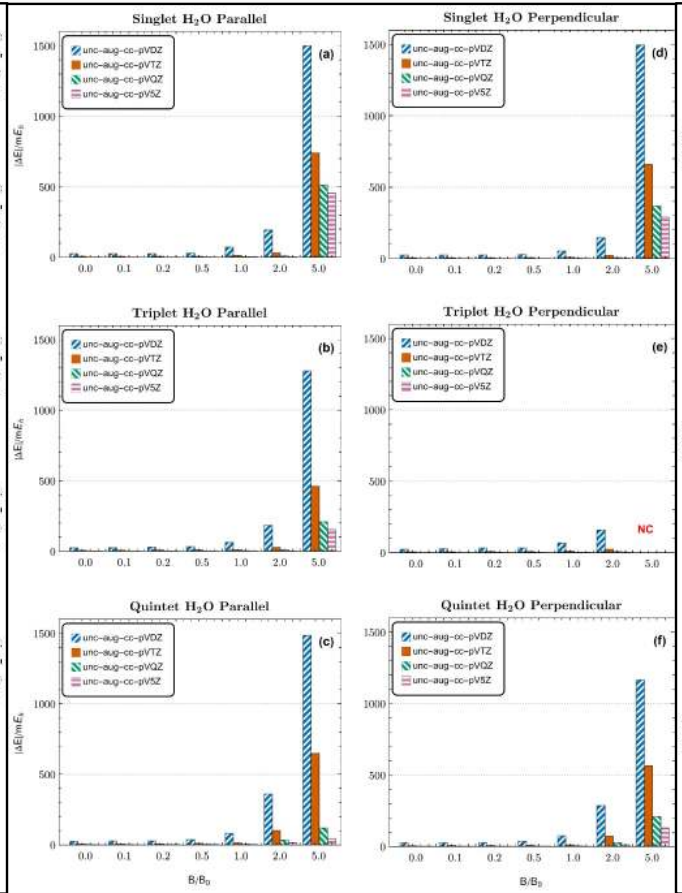
Systems under study

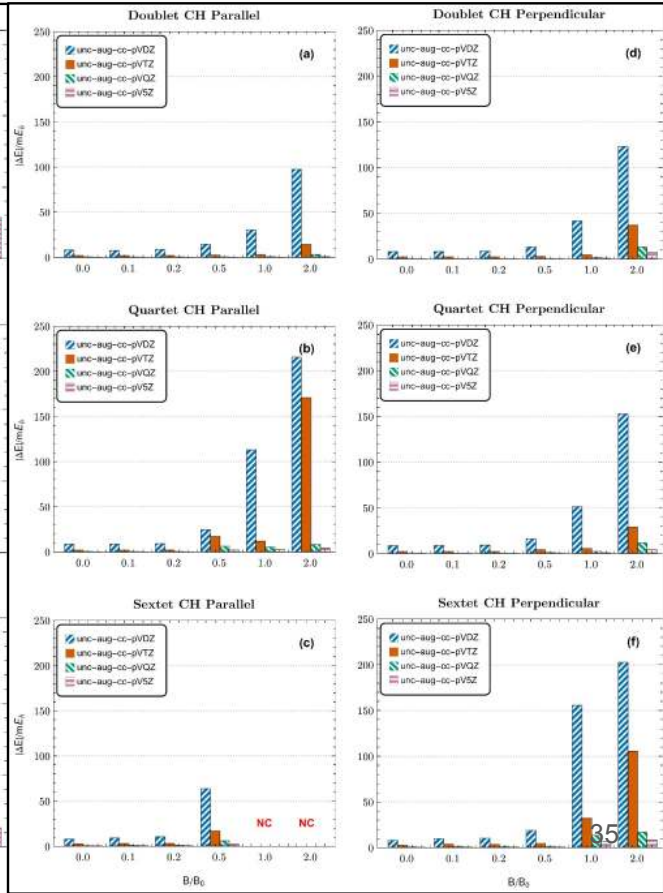
- Helium atom [singlet, triplet]
- Helium dimer (He_2) [singlet, triplet, quintet]
- Methylidyne (CH) radical [doublet, quartet, sextet]
- Water (H_2O) [singlet, triplet, quintet]

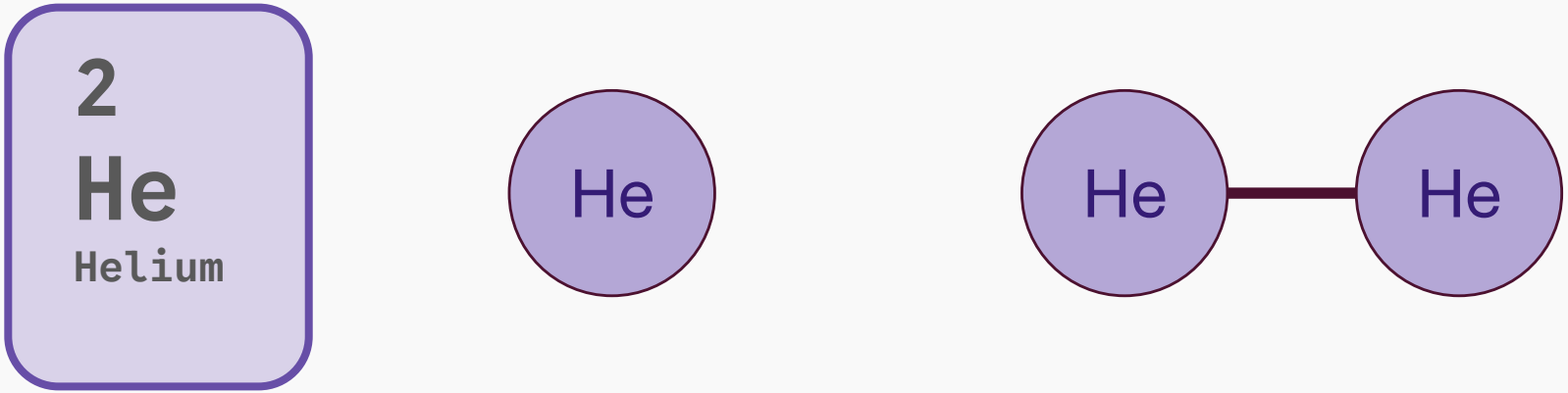
Source : Farhaz et. al *J. Chem. Phys.* 2025

Basis Set error study





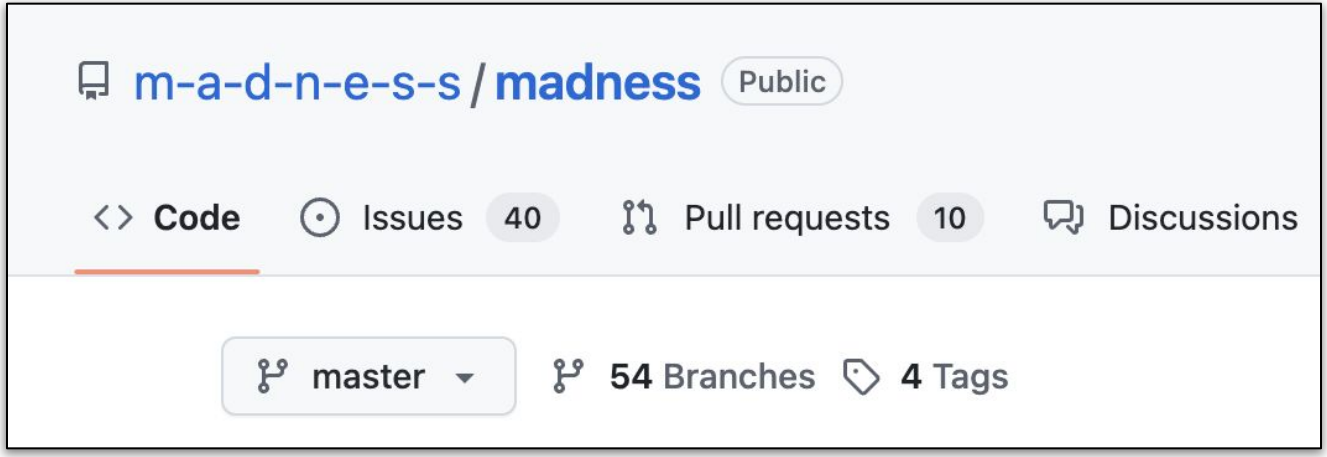




Source : Farhaz et. al *J. Chem. Phys.* 2025

Methodology

	LCAO	MRA
Basis set	unc-(aug/d-aug)-cc-pVQZ	CBS
Method	UHF	UHF
Polynomial Order	NA	9
Gauge Origin Invariance Treatment	LONDON Orbitals	NA

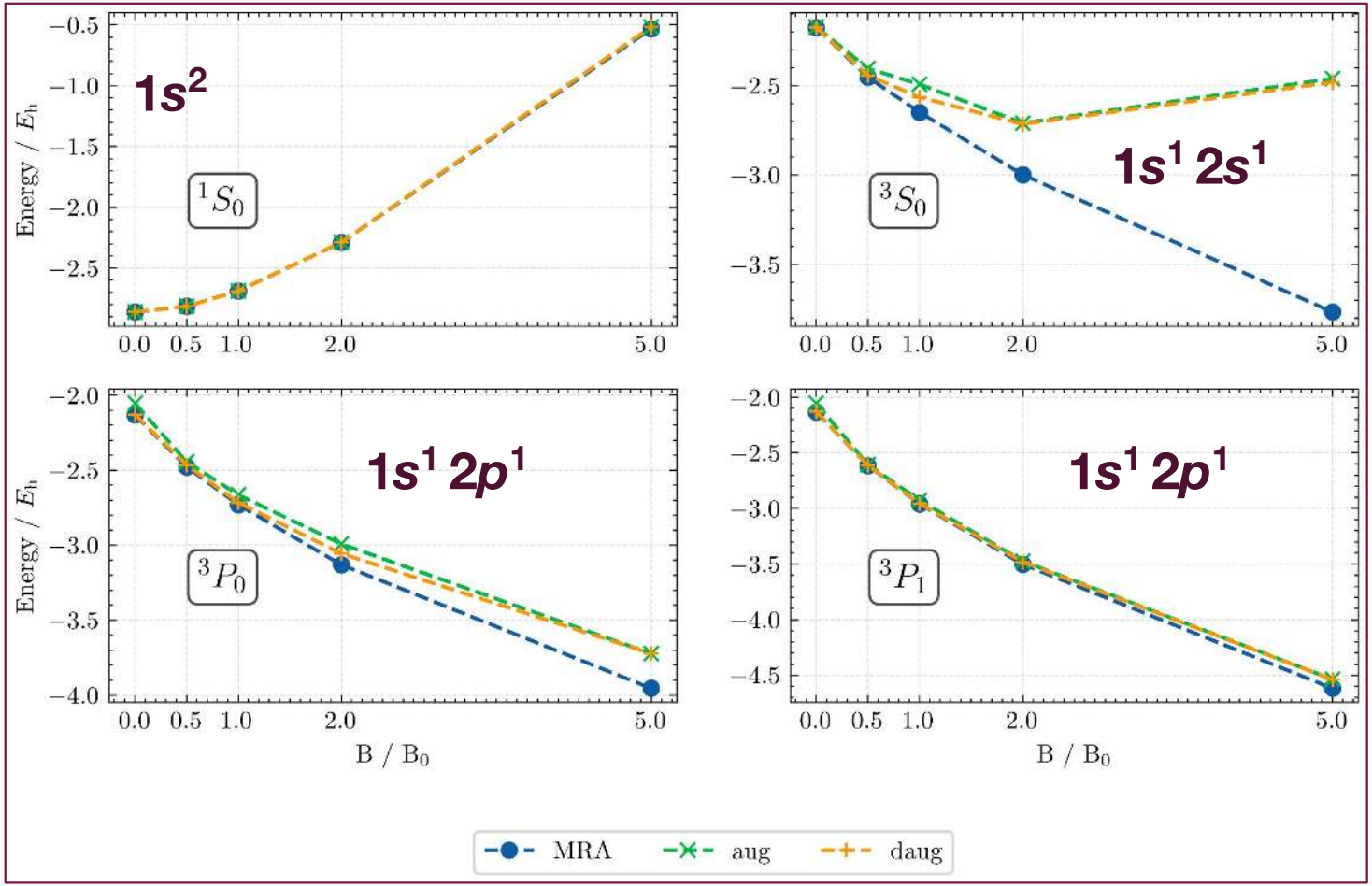


Source : Harrison et. al *SIAM J. Sci. Comput.* 2016

Helium Atom

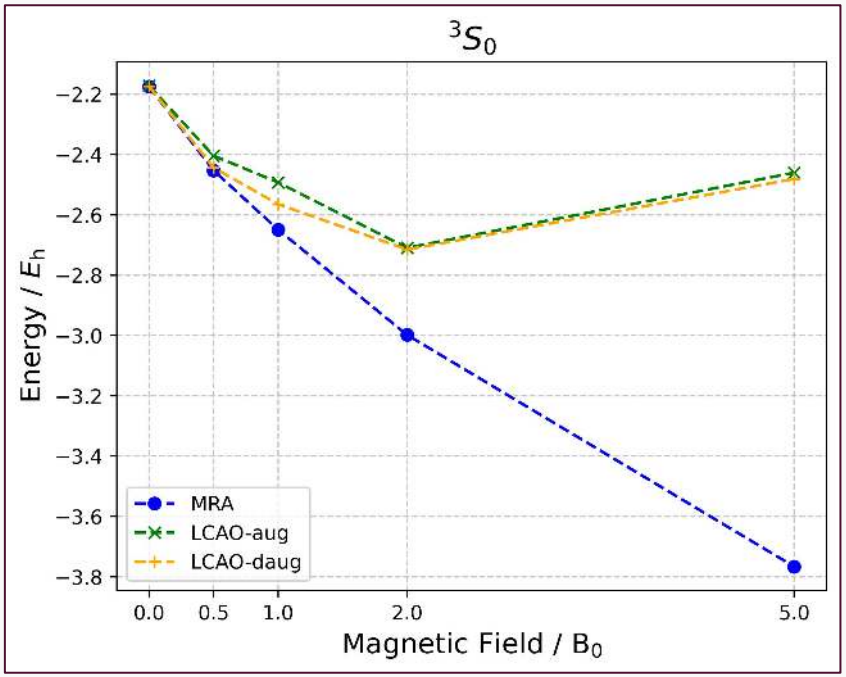
Total HF energies of He atom

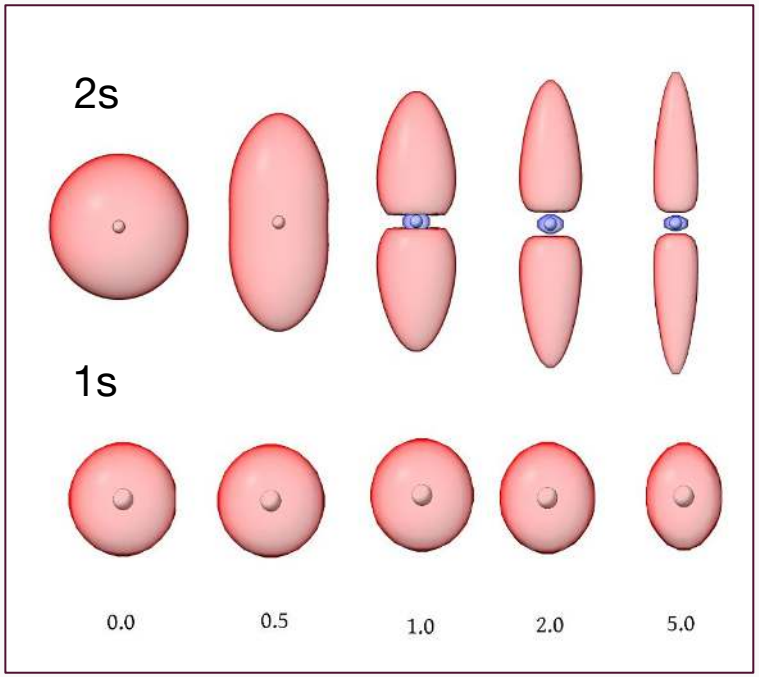
Source : Farhaz et. al *J. Chem. Phys.* 2025



Total HF energies of $^3S_0$ He atom

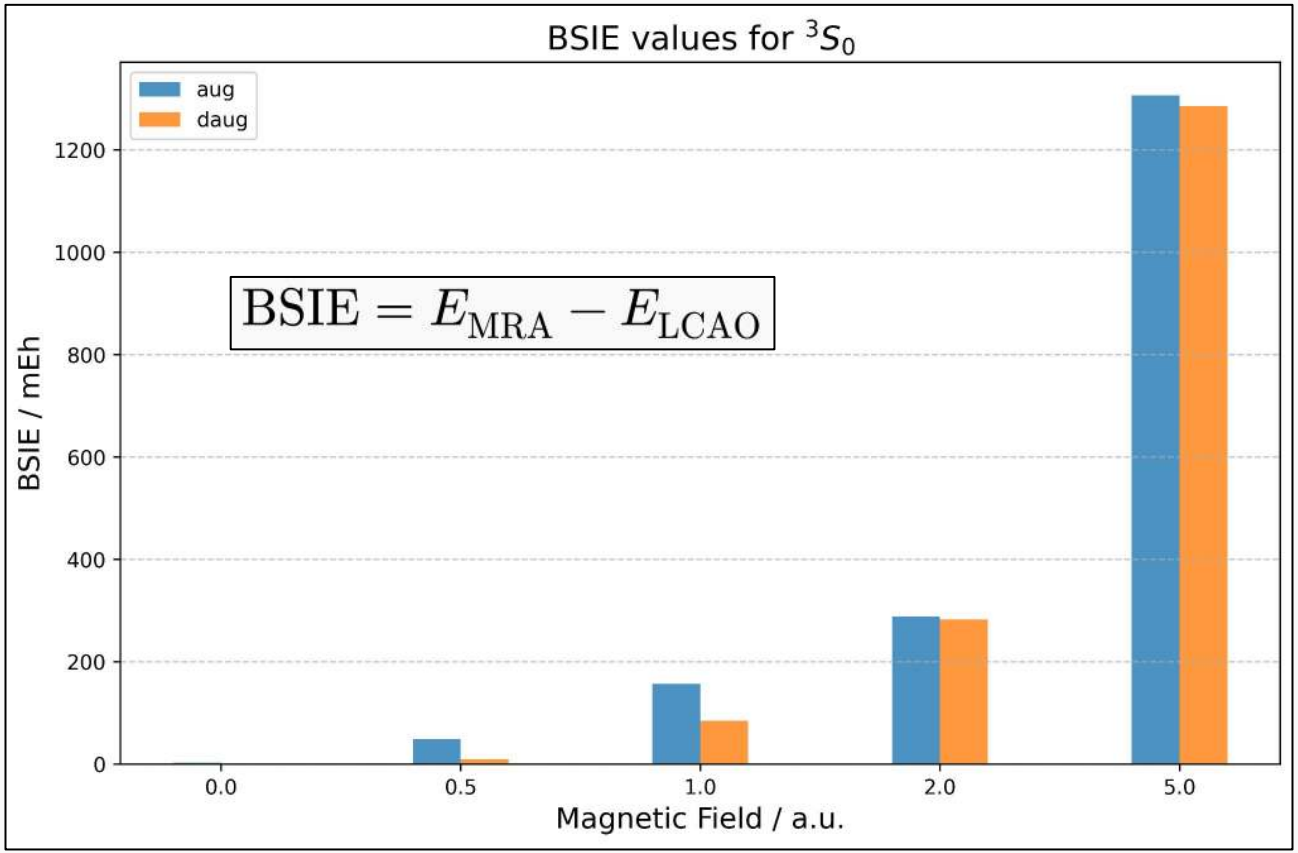
Source : Farhaz et. al *J. Chem. Phys.* 2025



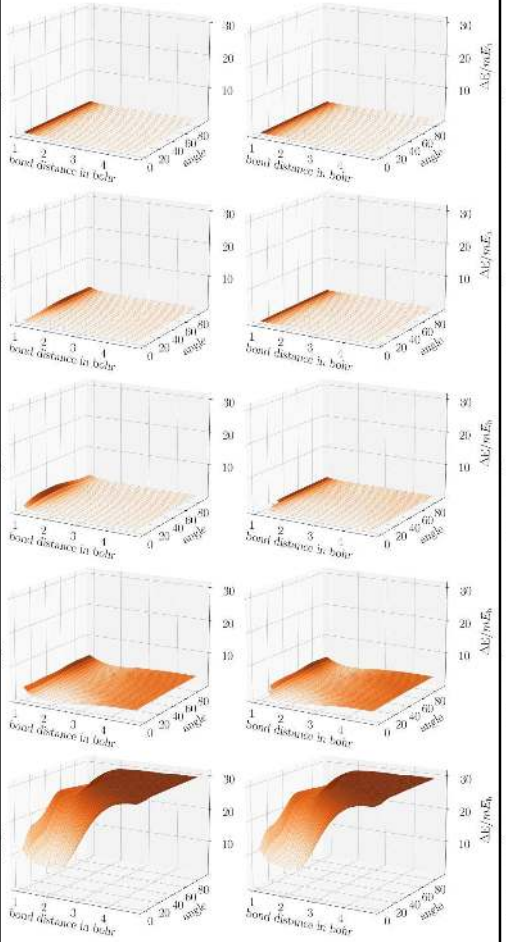


Well description demands addition of higher angular momentum functions

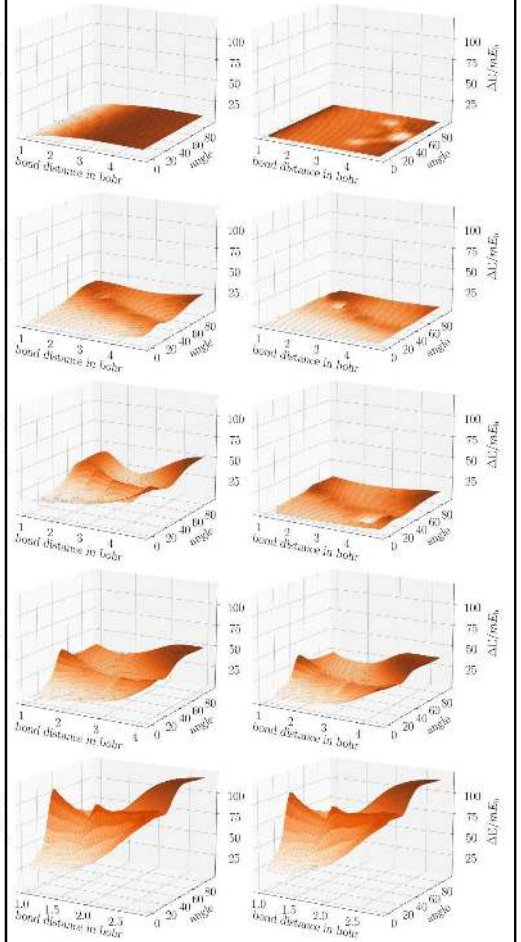
BSIE of $^3S_0$ He



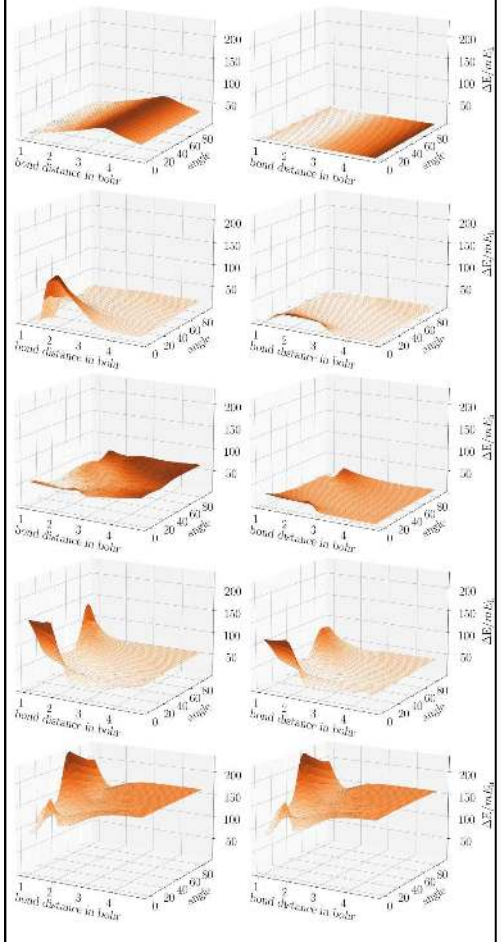
Helium Dimer



Singlet



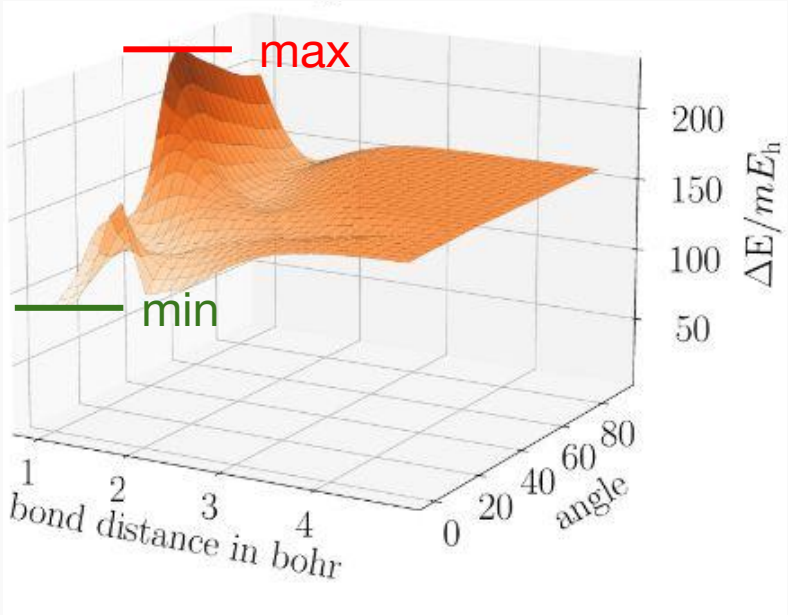
Triplet



Quintet

Basis set incompleteness errors in He dimer

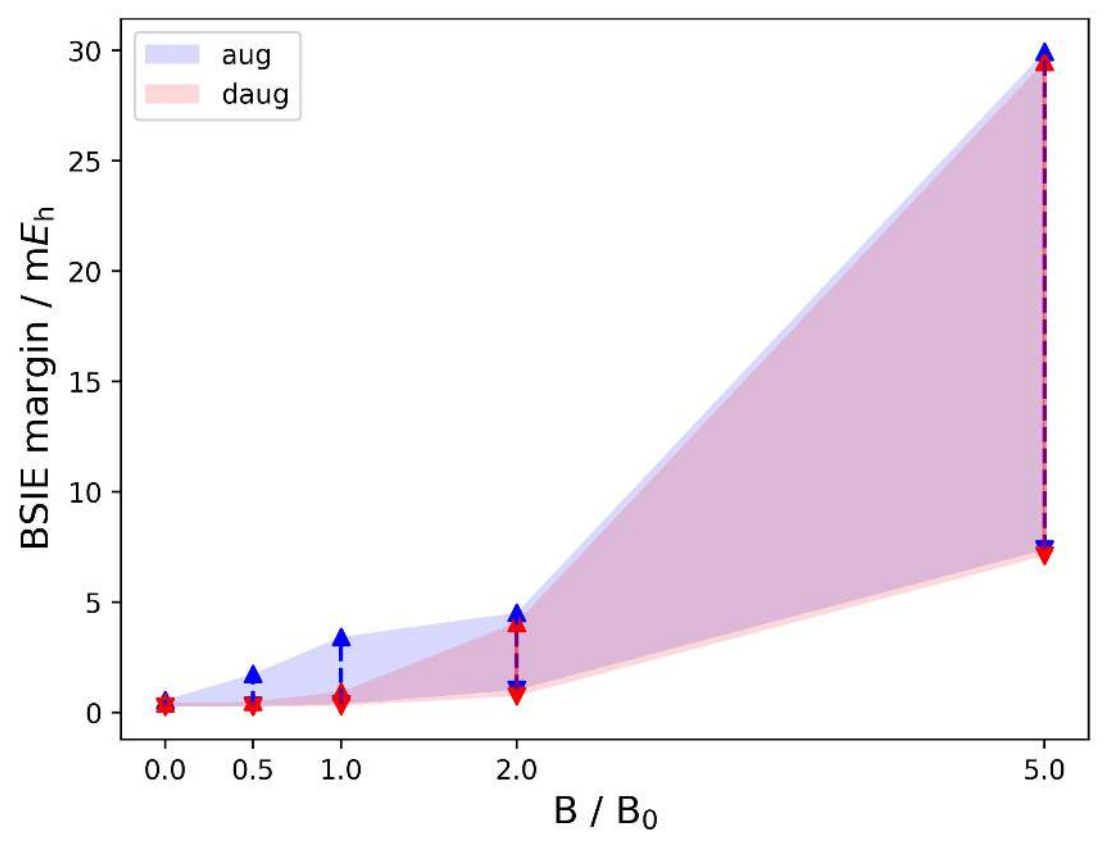
$$\mathrm{BSIE} = E_{\mathrm{MRA}} - E_{\mathrm{LCAO}}$$



The variation of the BSIE across the complete PES over all orientations and bondlengths

Singlet BSIE

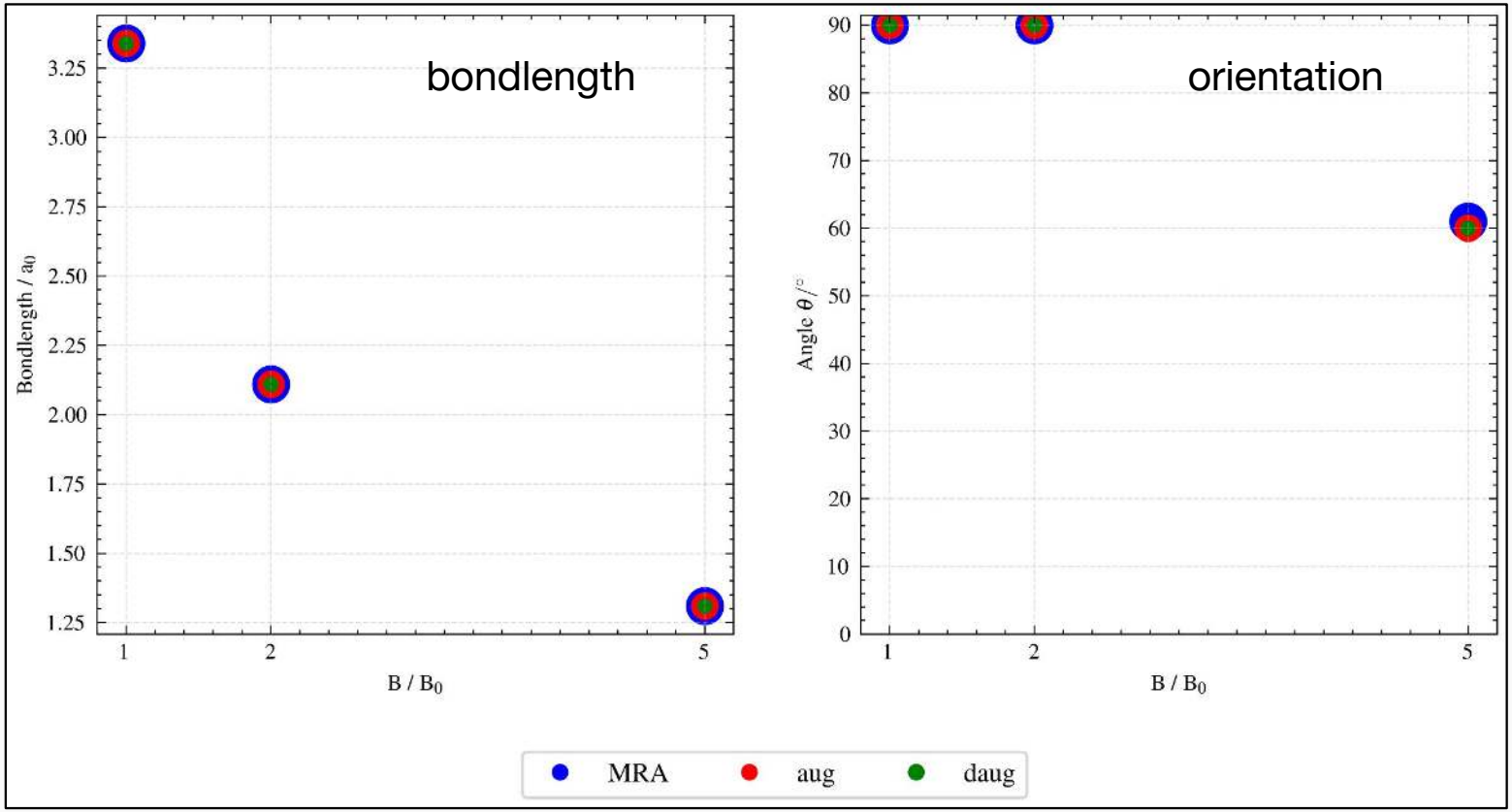
Helium Dimer



Dissociates into two $^1S_0$ He atoms

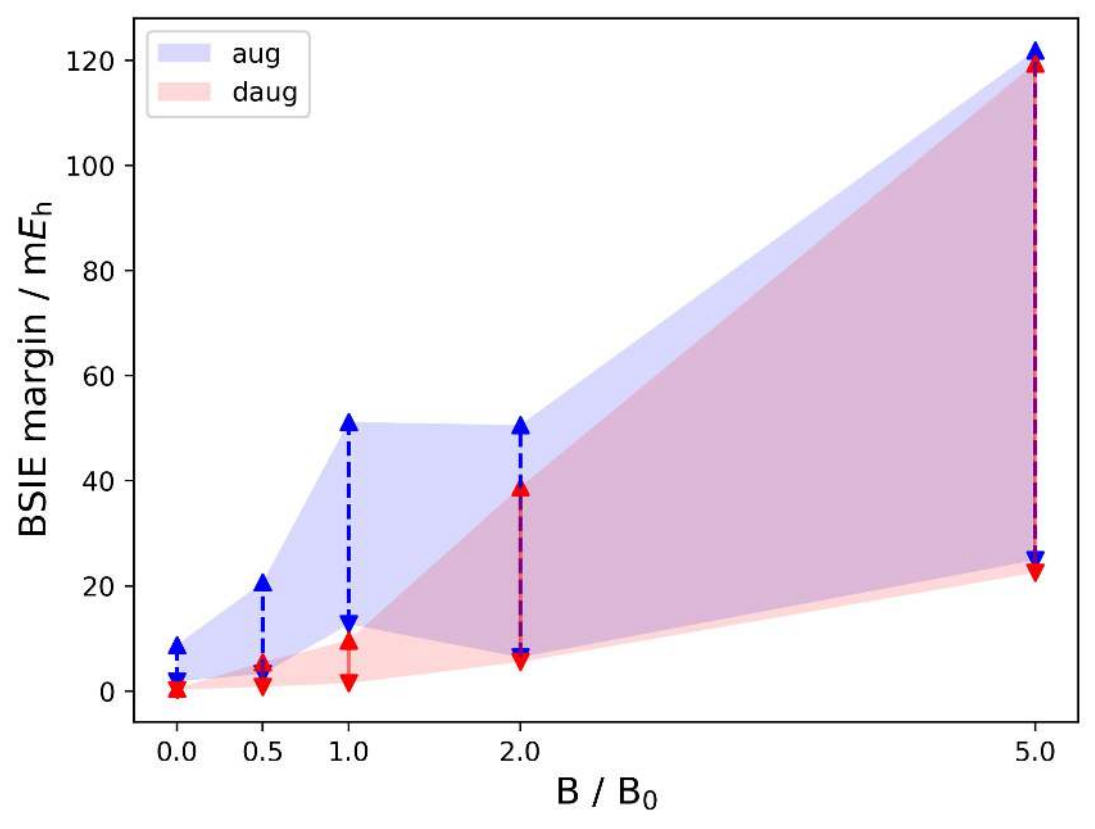
Singlet PES

Helium Dimer



Triplet BSIE

Helium Dimer



Dissociation

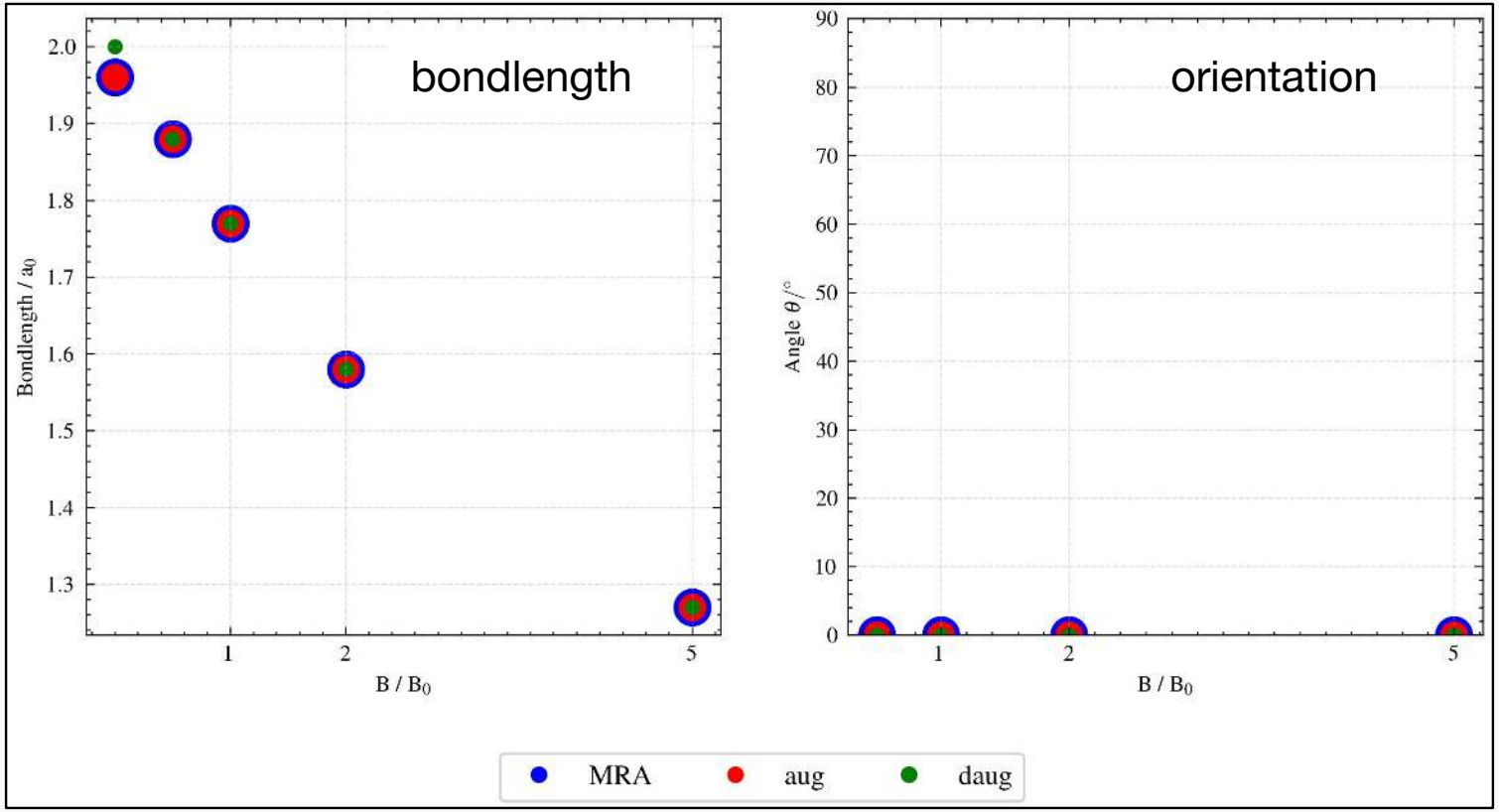
$^1S_0 + {}^3S_0$ in field free

$^1S_0 + {}^3P_1$ in **B**

The interest lies in the minima region so symmetric triplet of interest

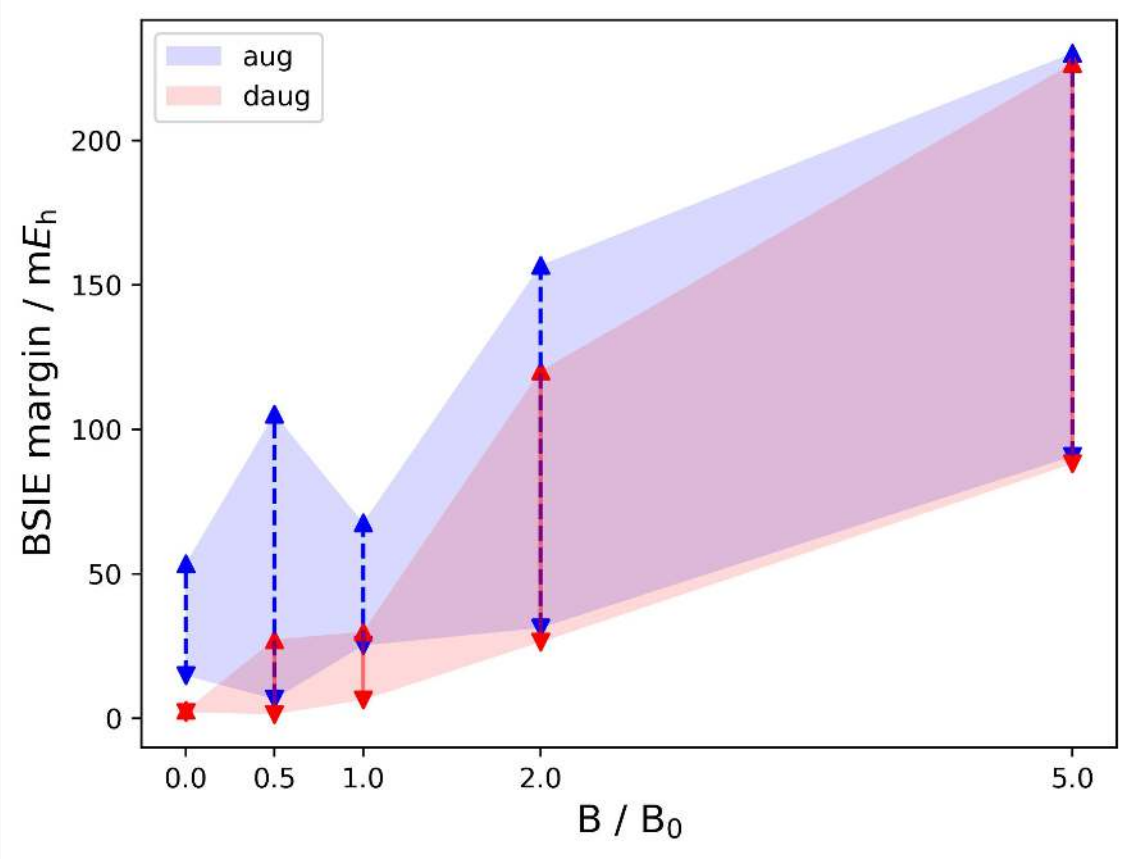
Triplet PES

Helium Dimer



Quintet BSIE

Helium Dimer



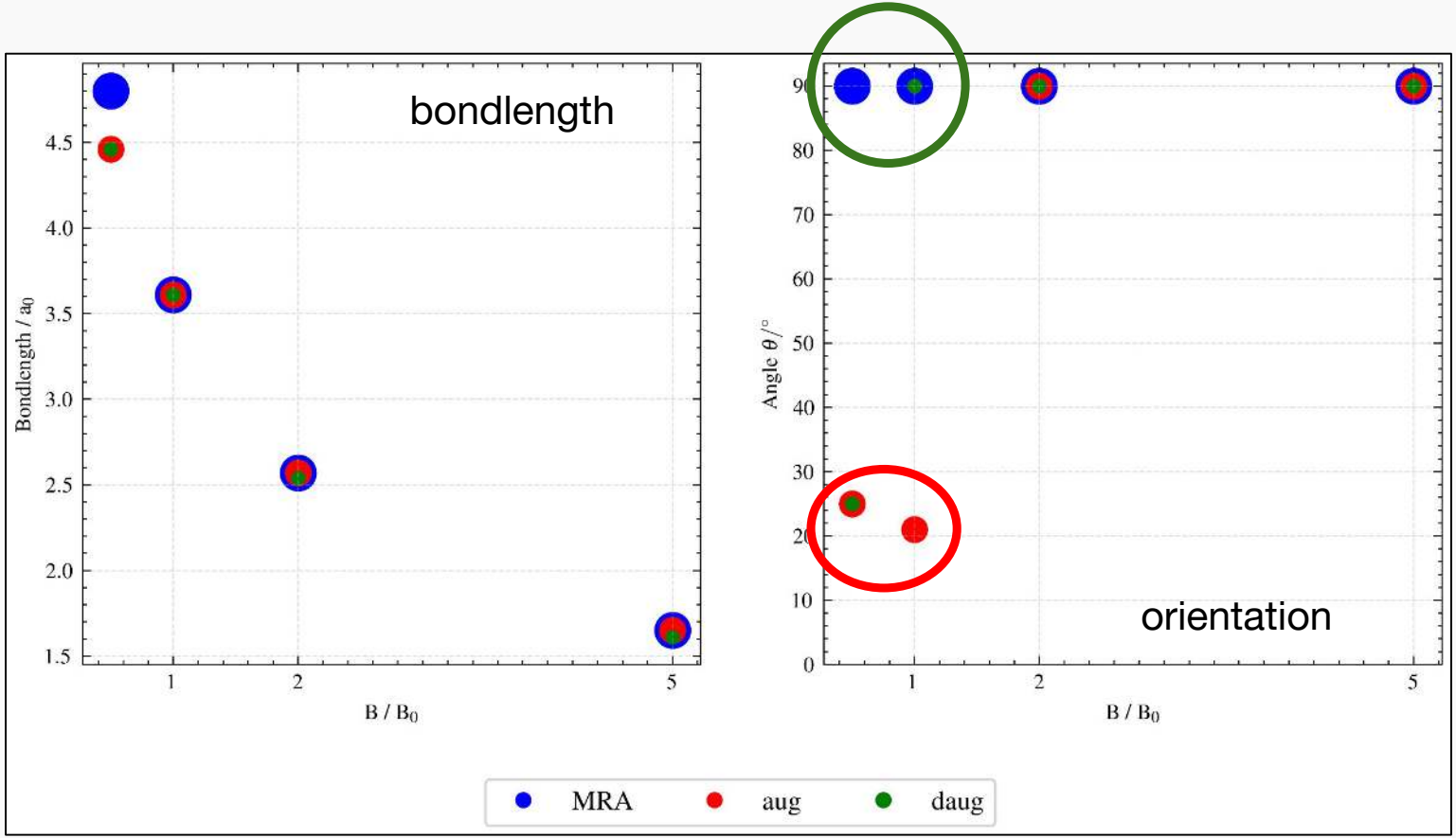
Dissociation

Two $^3S_0$ in field free

Two $^3P_1$ in **B**

Quintet PES

Helium Dimer



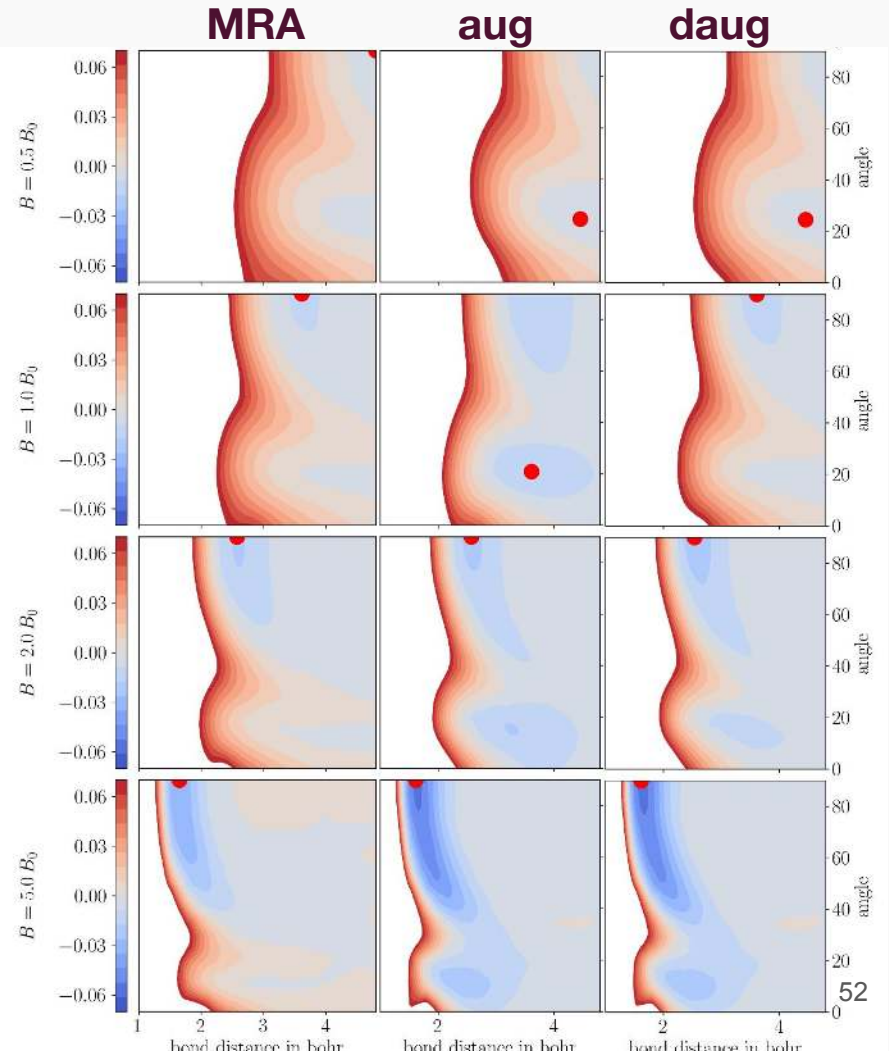
Quintet PES

Helium Dimer

Quintet state becomes the ground state in **B** with perpendicular orientation

Competition of two minima : double well like potential

LCAO fails to predict the correct minima



Source : Farhaz et. al *J. Chem. Phys.* 2025

Conclusions

- LCAO is unreliable beyond ~ 0.5 B_0
- MRA reliable candidate for post HF methods in B
- MRA as reference for future basis set optimization

Vielen Dank!