Studying basis set errors in strong magnetic fields with MRA

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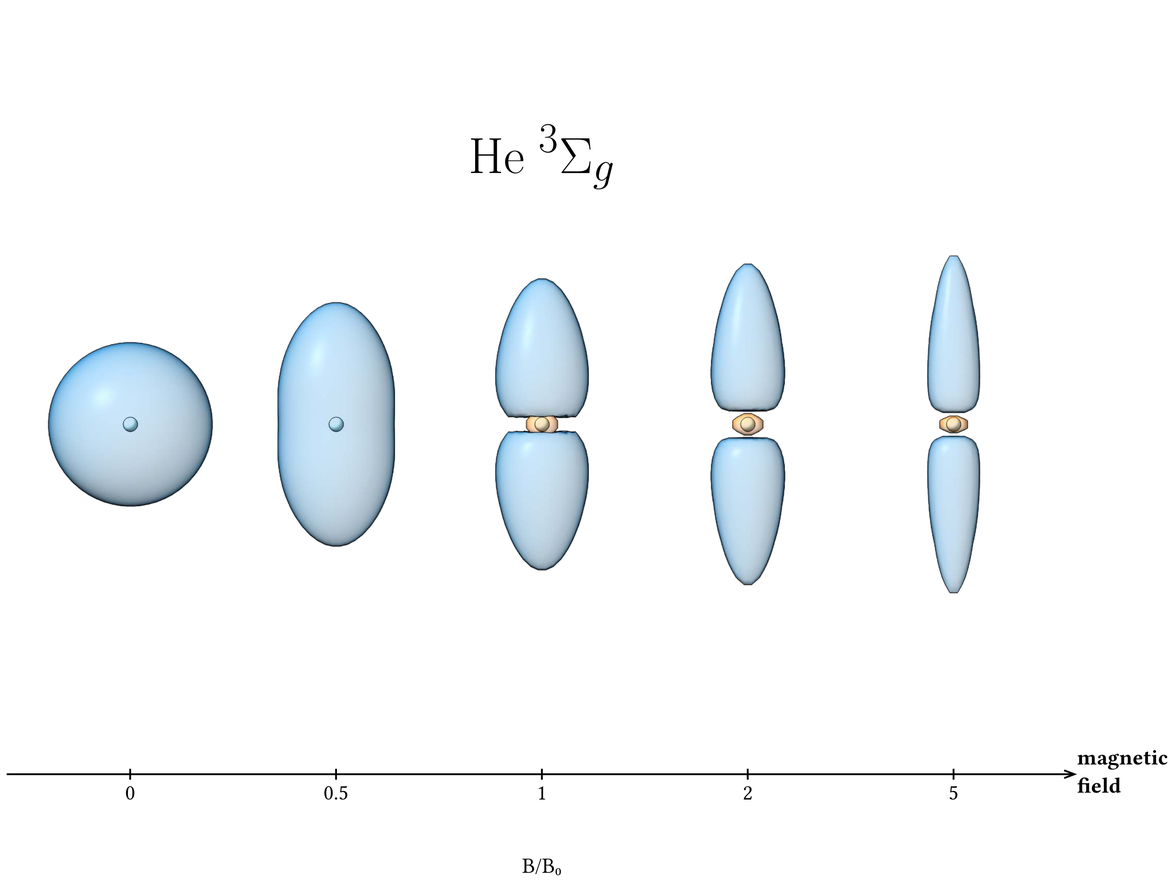

Figure 1: The orbital changes from s to d_{z^2} character once He atom is subjected to a strong magnetic field ranging from 0 to 5.0 B_0 which cannot be captured by both unc-(aug/d-aug)-cc-pVQZ basis sets.

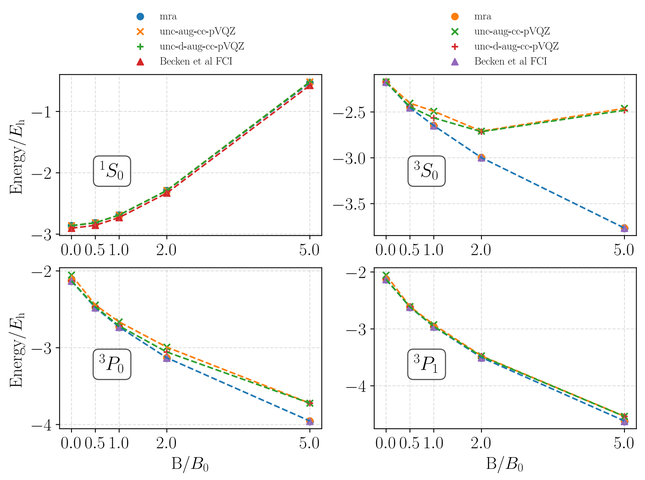

Figure 2: Total absolute energies of He atom using MRA, LCAO (unc-(aug and d-aug)-cc-pVQZ) basis set and literature FCI values from `Becken et. al. 1999 and 2000`

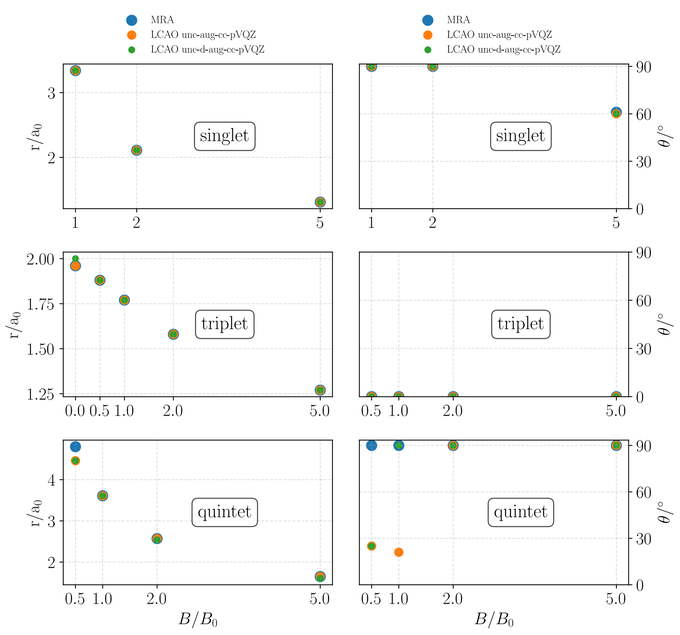

Figure 3: r in a.u. is bond length of He_2 and θ is the angle between the C_∞ axis of He_2 and the magnetic field axis in degrees. Figure shows variations of predicting the energy minima structure as well as its angular dependence with B for different spin symmetry of He_2.

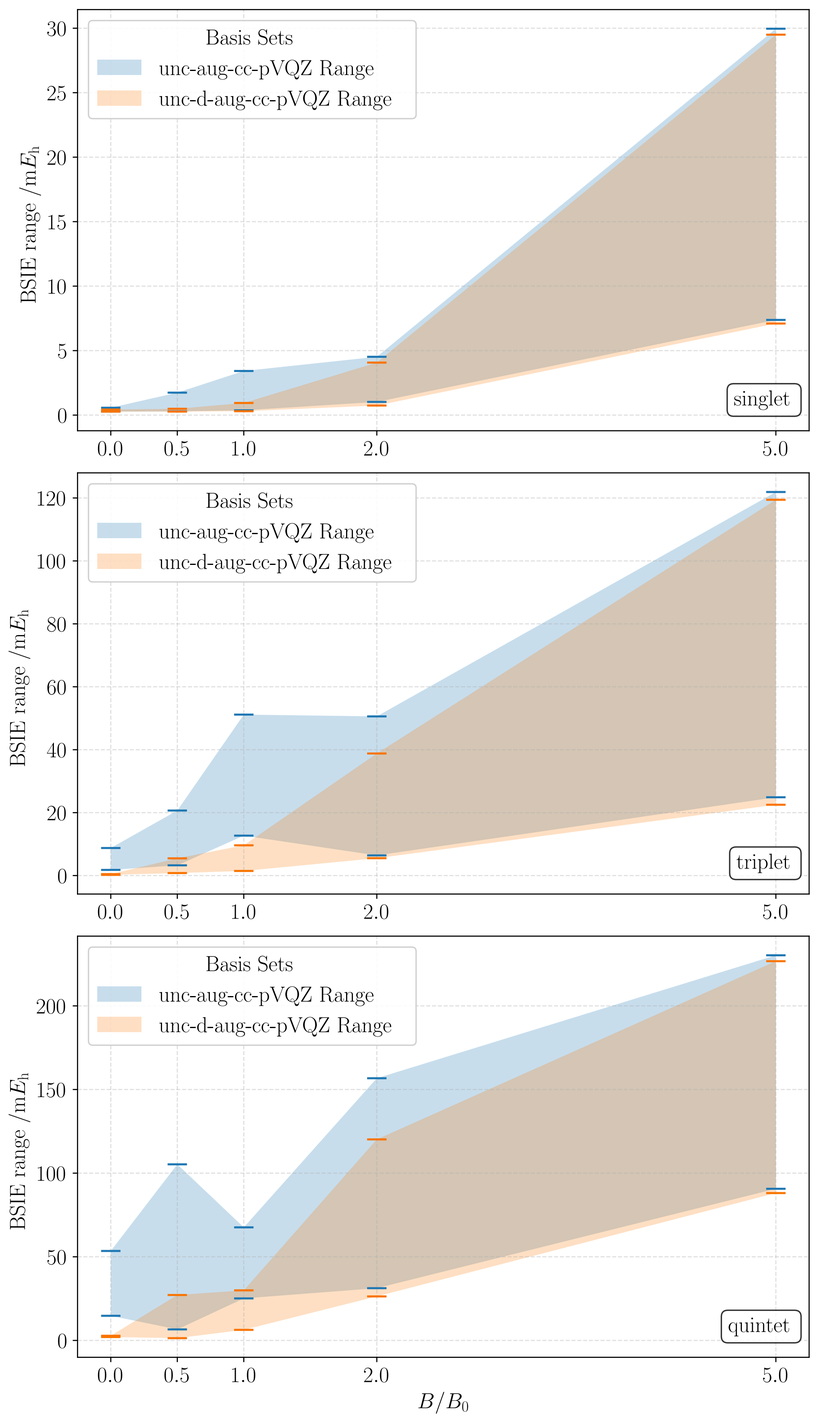

Figure 4: The BSIE range as a function of θ and r for different spin multiplicities and magnetic fields for He_2 molecule.

Background: Bonding Beyond Earthly Limits

- *Earth vs. Stellar Magnetic Fields*:

  Chemical bonding (covalent/ionic) is well-understood under weak terrestrial magnetic fields (**B**) ($\ll 10^5$ T). White dwarfs ($\sim 10^5$ T) and neutron stars ($\sim 10^{10}$ T) exhibit fields where magnetism rivals coulomb electrostatic forces

- *The Puzzle*:

  Early Hartree-Fock studies hinted that unbound species (e.g., triplet H_2) form bonds in perpendicular orientations to strong **B** (`See Kubo 2007`)

- *Key Insight*:

  Antibonding orbitals (e.g., triplet H_2 $1\sigma_u^*$) undergo paramagnetic stabilization when it is oriented $\perp$ **B**, reducing kinetic energy and enabling bonding for otherwise dissociative states

Mechanism: Perpendicular Paramagnetic Bonding

- *Orbital Transformation*:

  In strong fields, antibonding MOs (e.g., $1\sigma_u^*$) evolve into lower-energy 2p-like orbitals when perpendicular to B (`see Lange et. al. Science 2012`)

- *Energy Reduction*:

  Field-induced kinetic energy lowering in antibonding orbitals drives bonding

- *Generality*:

  Confirmed for H_2 ($^3\Sigma_g^+$) and He_2 ($^1\Sigma_g^+$), enabling bonding in species with formal bond order zero making it a distinct bonding mechanism besides covalent bonding, ionic bonding

What is Multiresolution Analysis (MRA)?

- grid-based numerical method to represent arbitrary multidimensional function and operators

$$f(x) = \sum_{n,l} \sum_{k} \varphi_{kl}^{n}(x) s_{kl}^{n}$$

- time independent Schrödinger equation can be solved by

$$\psi_{\text{new}} = -\hat{V}(T - E)^{-1}\psi_{\text{old}}$$

How is it applied to B?

$$\hat{H} = \hat{T} + \frac{1}{2}B\hat{L}_z + B\hat{s}_z + \frac{1}{8}B(x^2 + y^2)$$
$$+\hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn}$$

Core Findings

Standard basis sets reliably model molecules in magnetic fields up to 0.2 B_0 (47,000 T), with errors comparable to field-free calculations

Proceed With Caution

Between 0.5 B_0 – 1.0 B_0, BSIE grow significantly (up to 50%), but qualitative physics remains intact

A Threshold for Reliability

For fields above 1.0 B_0, BSIEs become large and unsystematic, limiting quantitative accuracy in Hartree-Fock calculations

Pathways for Progress

MRA provides benchmark-quality references to guide future basis-set development for high-field chemistry

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