Electron Correlation, Excitation and Magnetic Fields

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Objective

Study molecules placed in strong magnetic fields in order to understand the quantum mechanism of intramolecular interactions in highly magnetized stellar objects and gain insight into electronic structure changes on breaking of spin symmetry.

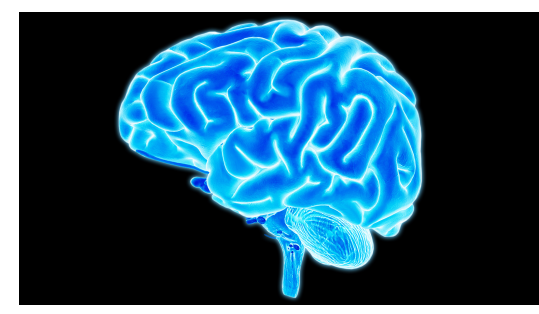## Magnetic Fields: How Strong is "Strong" ?
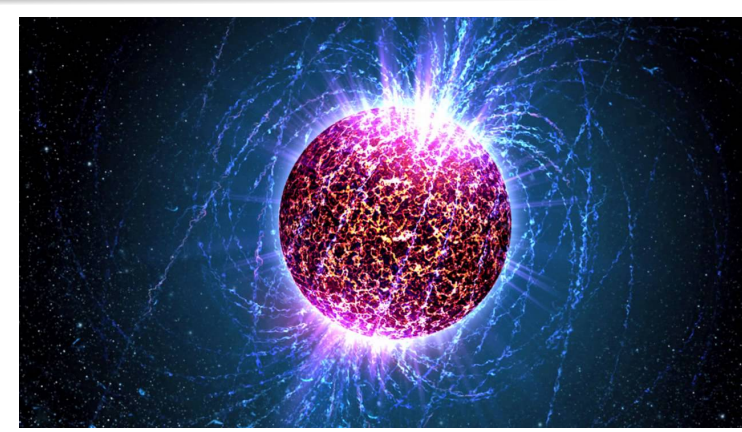

$$1\ au = 235kT$$

Figure 1: Brain: pT

Figure 2: Neutron Star: GT

Astrochemistry

- The spectra of molecules changes dramatically in strong magnetic fields
- Computations required to understand and interpret spectra for molecular detection in magnetic white dwarfs
- Currently, field strength is determined by comparing observed and predicted atomic lines in the visible spectrum, eg. $\Rightarrow$ He atom in figure
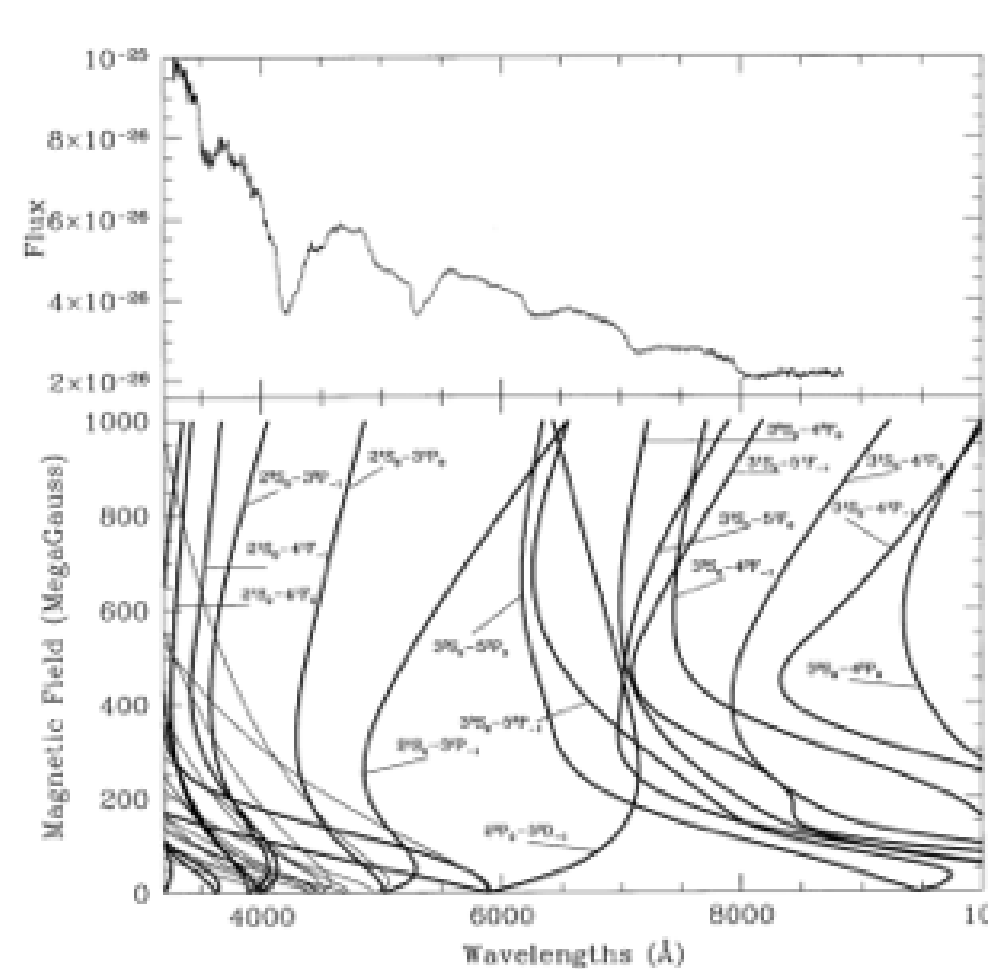- He_2 is predicted to exist in strong magnetic fields

Figure 3: Spectra of He atom from a magnetized white dwarf

High-field Analogues in Semi-conductors

At field strength B_0, the magnetic cyclotron energy of the electron is one hartree:

$$B_0 = \frac{e^3 m_e^2}{(4\pi\epsilon_0)^2\hbar^3} = 2.35 \times 10^5 T$$

- In semiconductors, **effective mass and dielectric constant may reduce B_0 dramatically**. The donated P electron in Si:P behaves as a hydrogen electron with $B_0 = 32.8$ T
- **Si:P as a laboratory analogue for hydrogen on high magnetic field white dwarf stars**
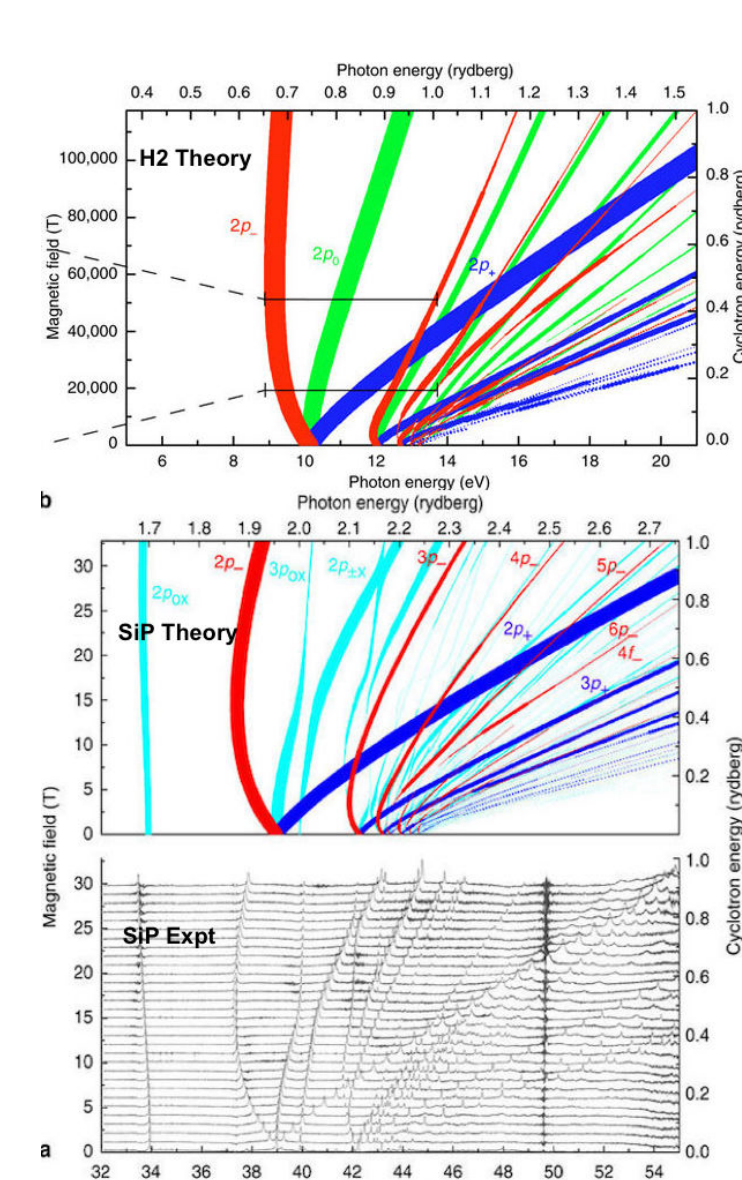
B. N. Murdin et al., Nat. Commun. 4, 1469 (2013): "The spectra reproduce the high-field theory for free hydrogen, with quadratic Zeeman splitting[...] They show the way for experiments on He and H_2 analogues, and for investigation of He_2, a bound molecule predicted under extreme conditions."

Figure 4: Lyman series of Si:P vs H_2 Theoretical Spectrum

Insight into DFT and CDFT

- An external B can be used to distort the electronic density in various ways as a probe to test the DFT exchange-correlation functionals.
- DFT in magnetic fields requires the introduction of the **paramagnetic current density** into the universal functional $\Rightarrow$ **CDFT**. CDFT is still in its infancy.
- Exchange-correlation functionals need to be tested and improved.
- mGGAs show promise
- CDFT will make it possible to study **larger molecules** and **semiconductor analogues** which ought to show exotic magnetic behaviour even at laboratory field strengths.

Vignale and Rasolt, PRL, **59**, 2360 (1987); Tellgren, Teale, Furness, Lange, Ekström, and Helgaker, JCP, **140**, 034101 (2014)

The LONDON package

- First code for **molecules in finite magnetic fields**
- **Complex wave-function**: All MO coefficients, integrals are complex valued in our general implementation
- Equations were re-derived using complex algebra
- London orbitals used
- HF, FCI, MCSCF, MP2, CCSD(T), DFT capabilities
- Handle non-uniform magnetic fields
- **Latest**: Linear Response to compute excited states
- EOMCC is interfaced to it (Dr. S. Stopkowicz)
- Other software: BAGEL, QUEST

http://folk.uio.no/eriktel/london/index.html

Linear Response of RHF/UHF/GHF

- The orbitals are optimized in the presence of uniform and non-uniform magnetic fields.
- For GHF: **Spin and Spatial parts of the orbital are coupled** during optimization
- Final **orbitals are 2-component** with both a spatial density and a spin density.
- Excitation energies and oscillator strengths are computed using the Random Phase Approximation (**RPA**)/Tamm-Dancoff approximation (**TDA or Singles-CI**).
- The set of single excitation and de-excitation operators contain both spin-conserving and spin-flip operators.
- The implementation allows the use of LAOs.
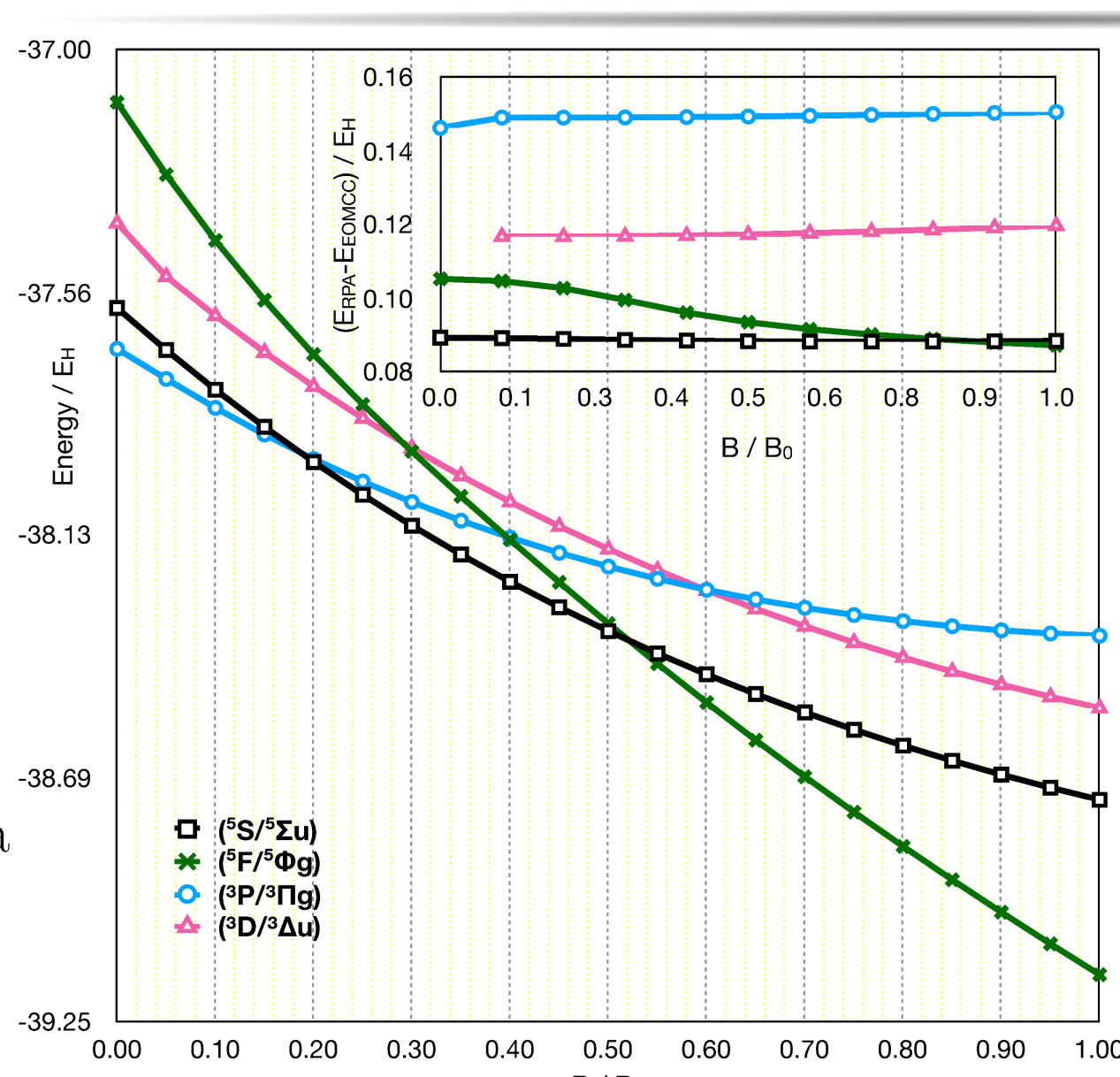- A general implementation for RHF/UHF/GHF allows access to states of various spin multiplicities.

C atom

The inset shows the difference of the energies of the excited states between Hartree-Fock linear response and EOM-CCSD

Figure 5: C atom in a uniform field, Luaug-cc-pCVQZ.
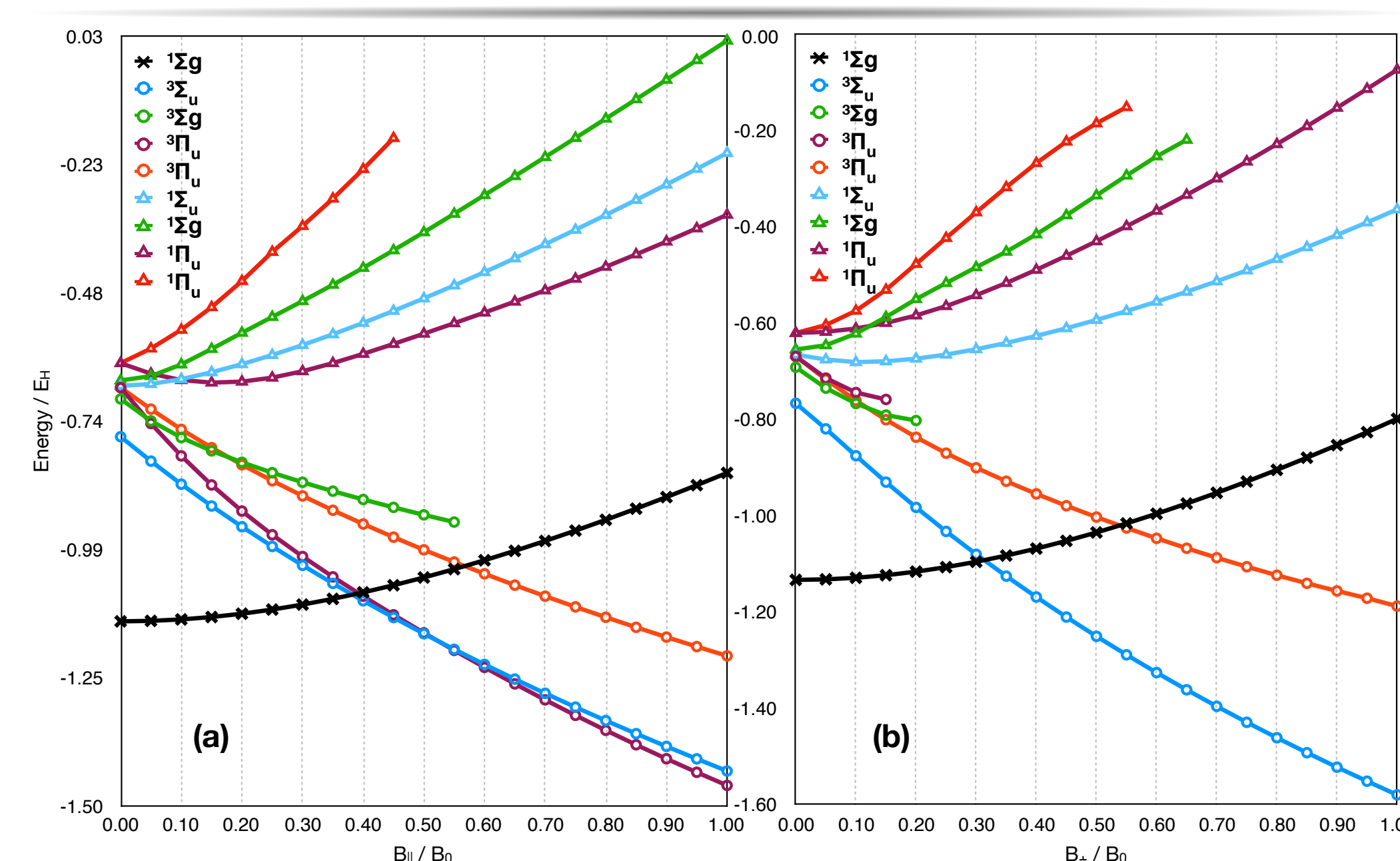
H_2

Figure 6: H_2 in a uniform field (a) parallel and (b) perpendicular to the bond axis, Luaug-cc-pCVQZ
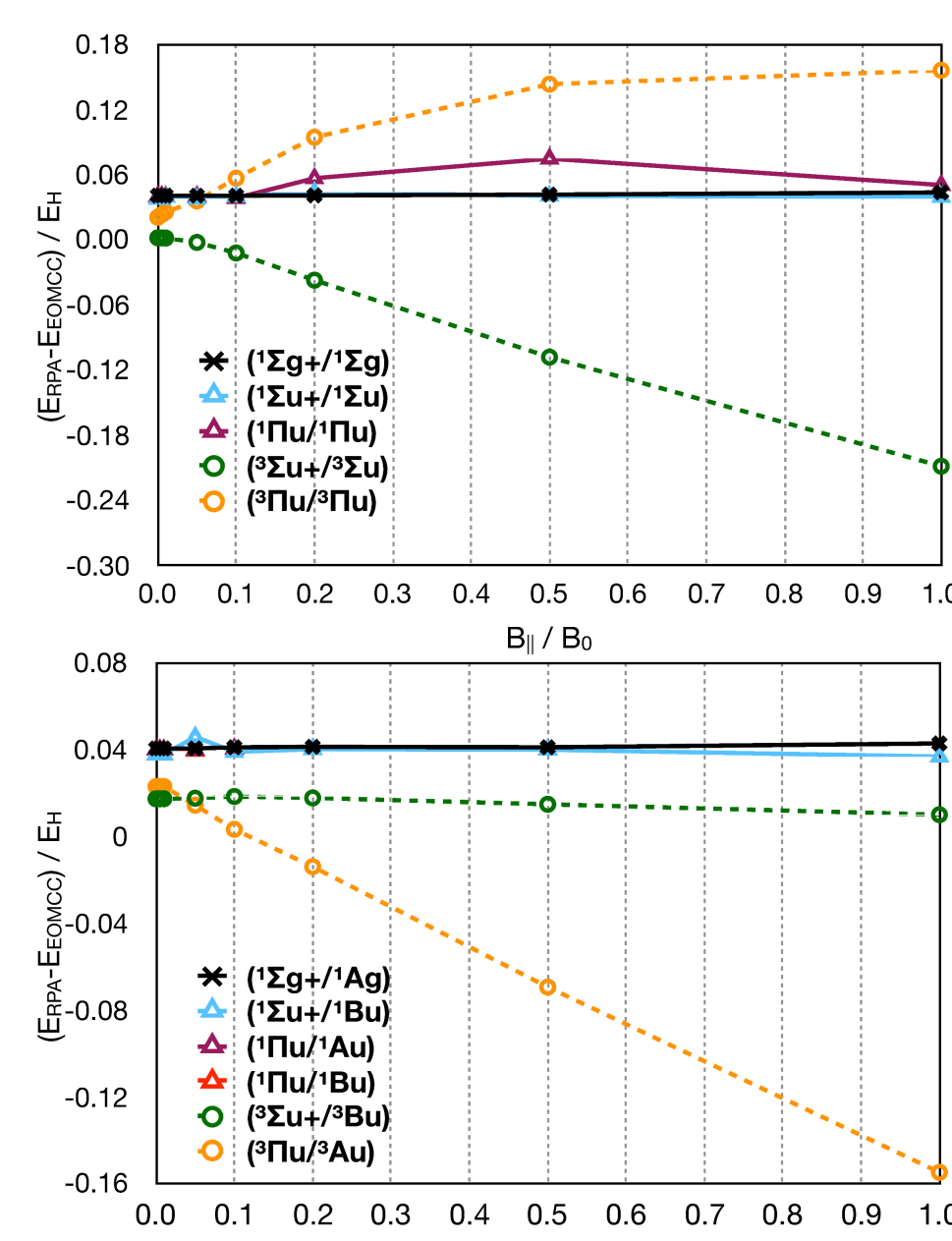

Figure 7: H_2, Luaug-cc-pCVQZ, Difference of the energies of the excited states between Hartree-Fock linear response and EOM-CCSD
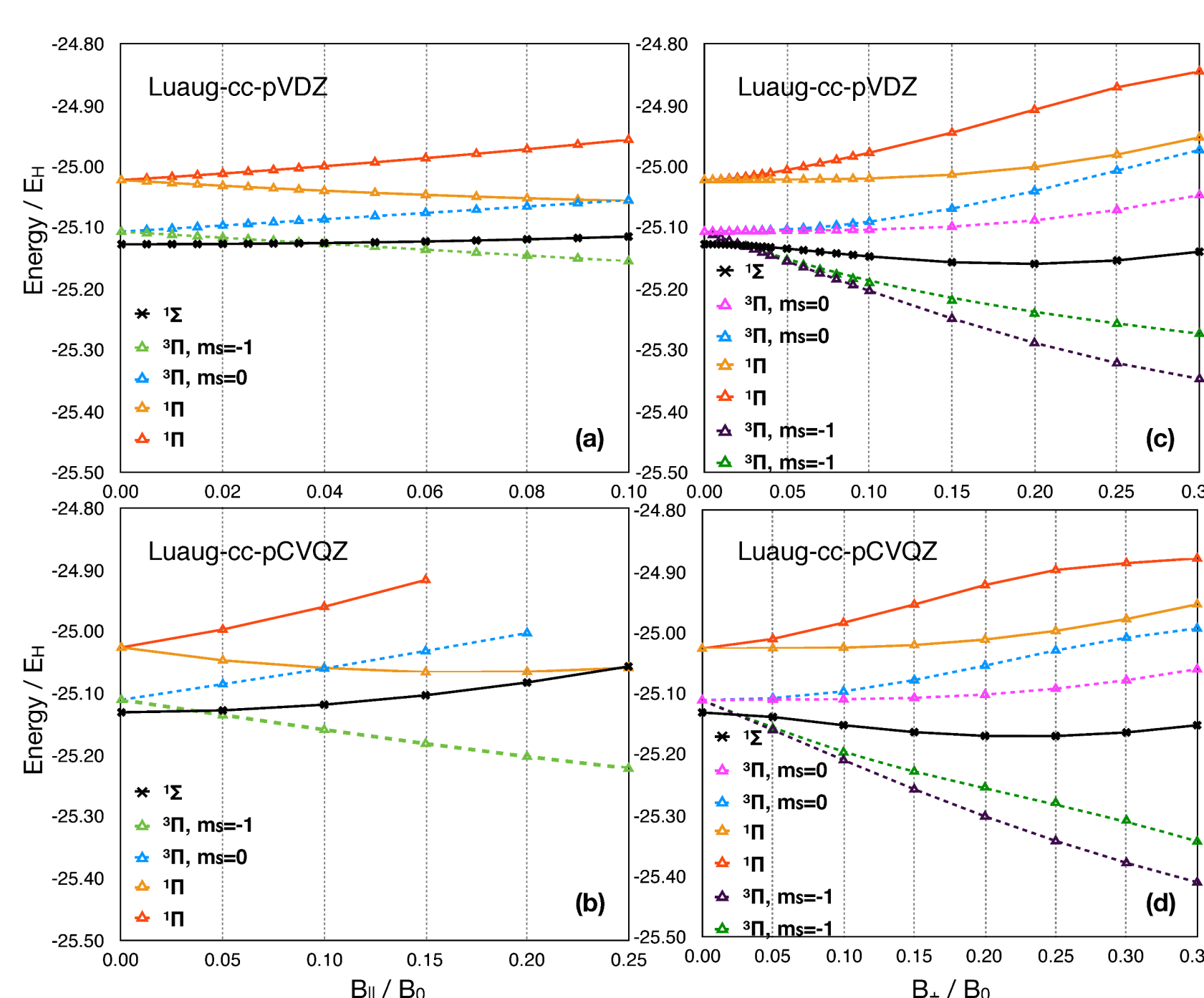
BH

Figure 8: BH in a uniform field: parallel to the bond, (a) Luaug-cc-pVDZ (b) Luaug-cc-pCVQZ and perpendicular to the bond, (c) Luaug-cc-pVDZ (d) Luaug-cc-pCVQZ
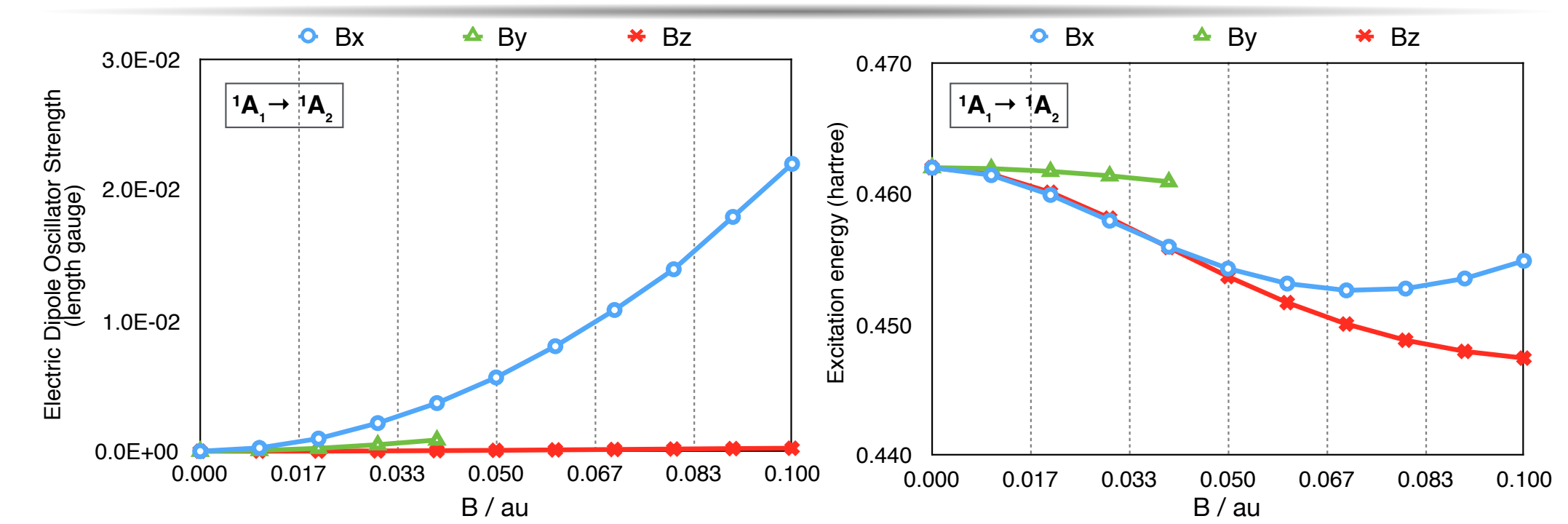
Allowing Spatially Forbidden Transitions

Figure 9: H_2O: Electric Dipole forbidden transition in uniform B

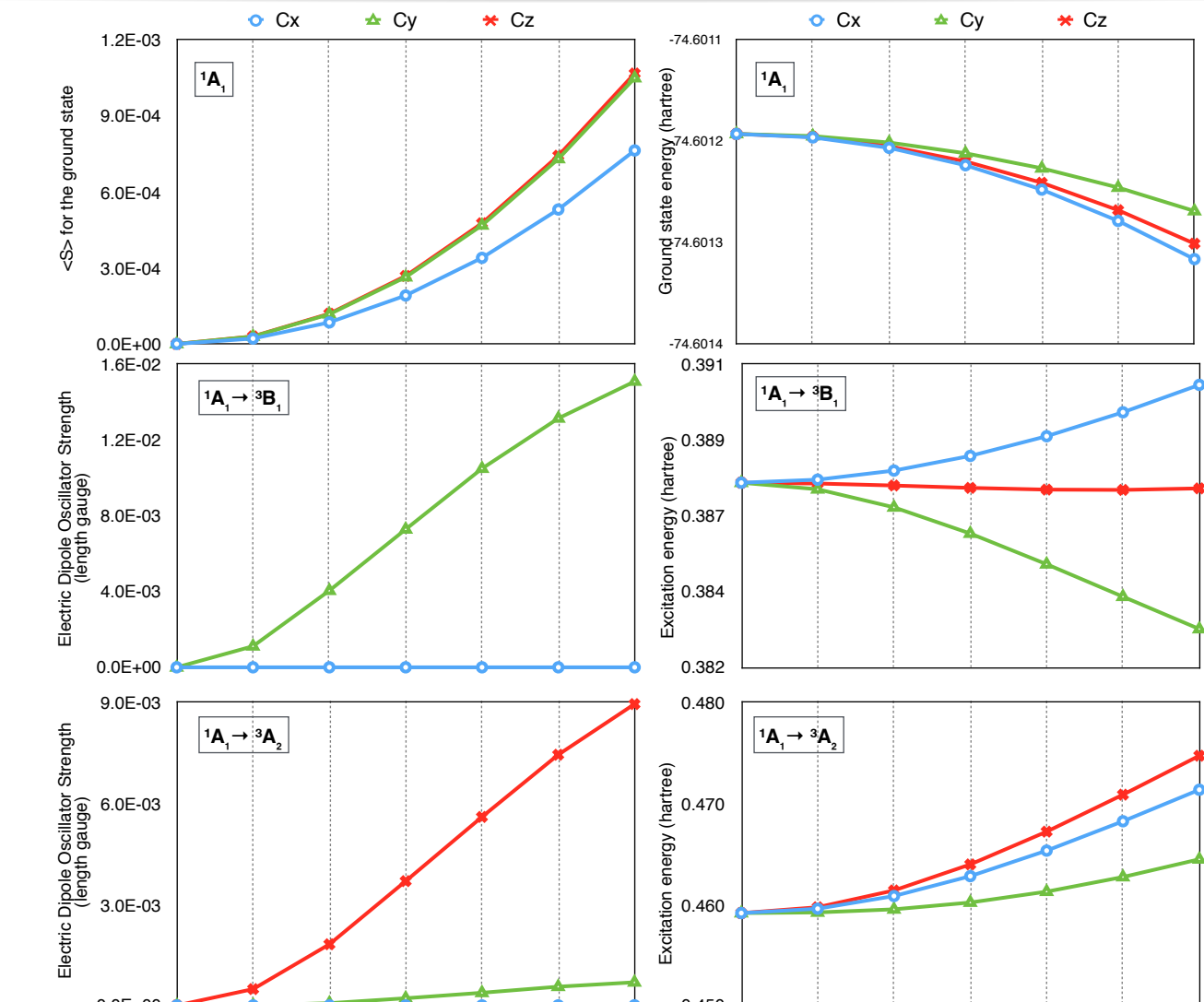## Allowing Spin Forbidden Transitions

Figure 10: H_2O: Spin forbidden transition allowed in non-uniform B

Equivalence of Length and Velocity Gauge for RPA with complex orbitals
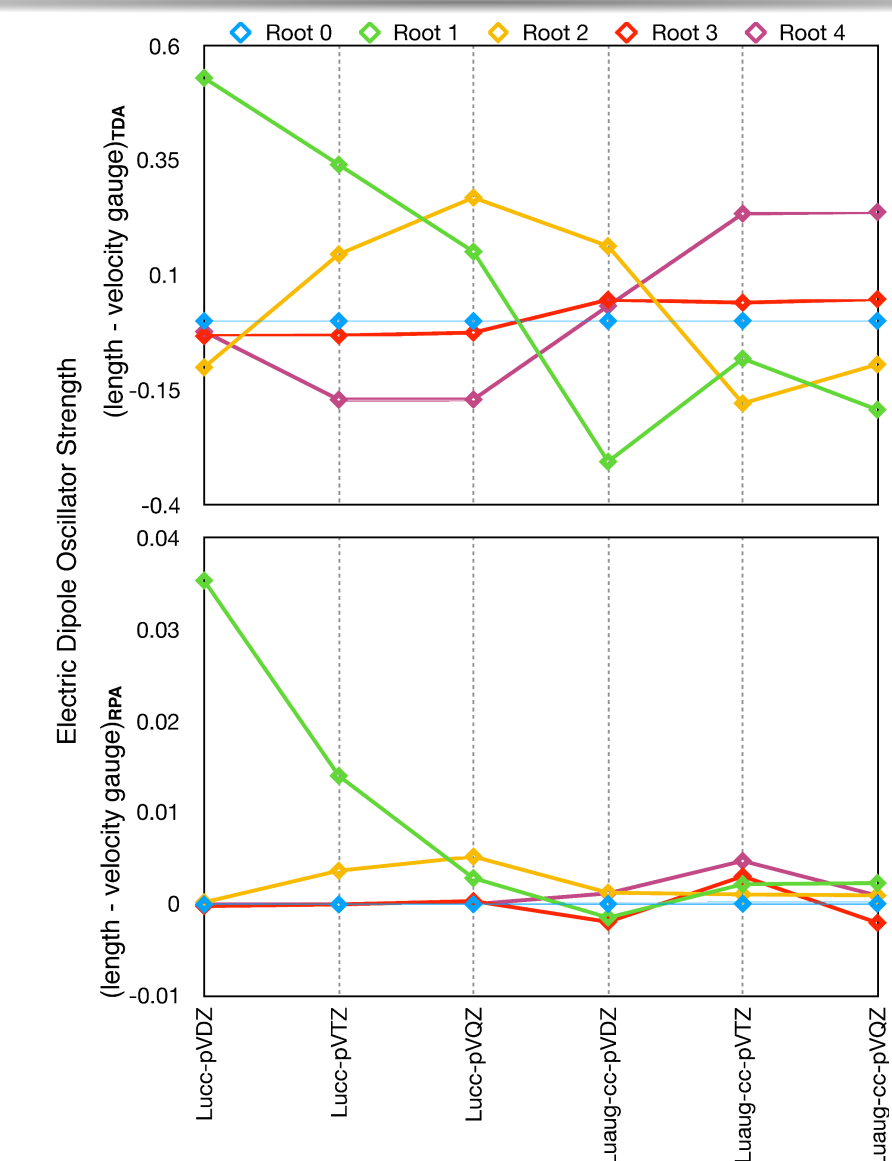

Figure 11: H_2: Numerical demonstration of the equivalence of the electric dipole oscillator strengths in length and velocity gauge for RPA but not the Tamm-Dancoff approximation with complex orbitals

Tensor-DFT

We present a **kinetic energy tensor** (**Q**) that unifies a scalar kinetic energy density commonly used in mGGA functionals (τ_D) and the vorticity density (ν) that appears in CDFT. Functionals depending on **Q** may be naturally placed on the third rung of Jacob's ladder.
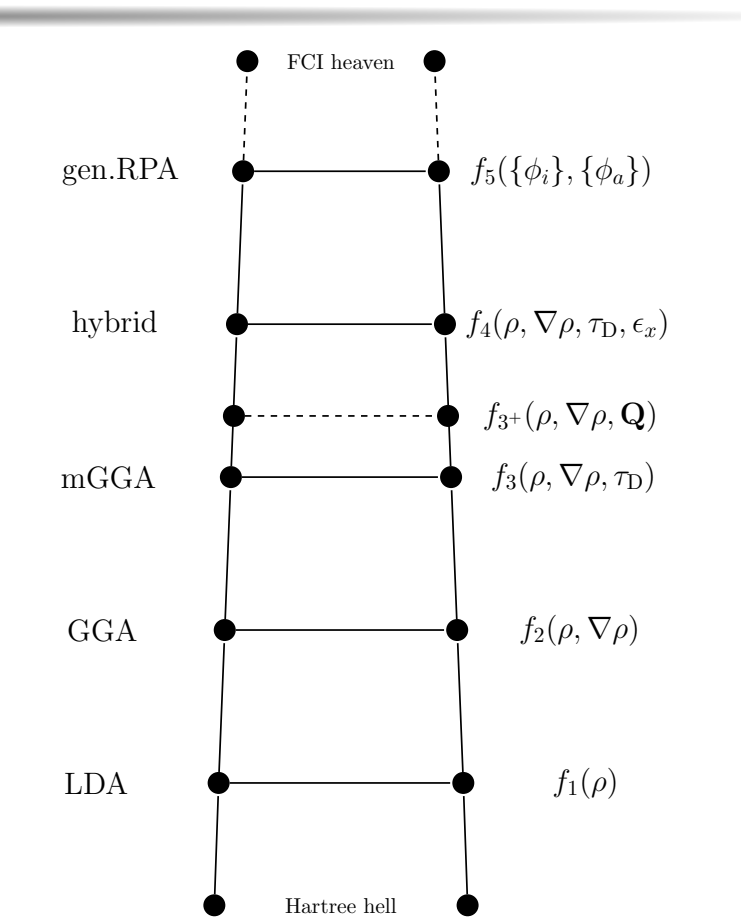

Figure 12: Jacob's Ladder

The Electron Localization Function (ELF) can discriminate effective one-orbital regions from other regions, **Q can discriminate between one-, two-, three-, and four-or-more orbital regions**.
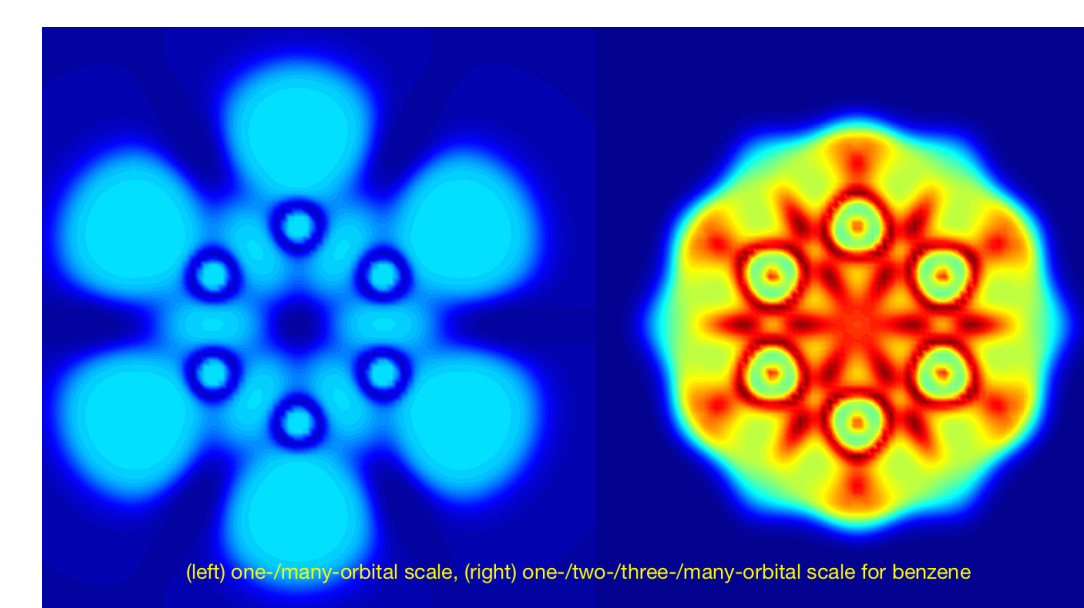

Figure 13: Benzene in **B**=[0,0,0] au. Left: ELF. Right: QELF.

Acknowledgements