Closed-Shell Molecular Paramagnetism

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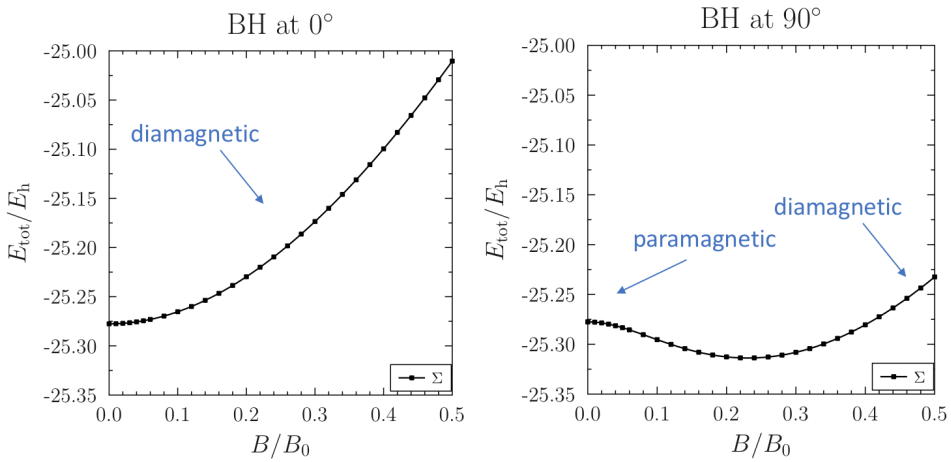
MAGIC 2018
The 3rd Workshop on Magnetically Induced Currents in Molecules
Hotel Kragujevac, Kragujevac, Serbia,
23–28 September 2018

Para- and diamagnetism

- When a magnetic field is applied to a molecule, one of two things can happen:
  - the energy decreases and the molecule moves into the field: paramagnetism
  - the energy increases and the molecule moves out of the field: diamagnetism
- We associate paramagnetism with open shells and diamagnetism with closed shells
  - nevertheless, some closed-shell paramagnetic molecules do exist



- Closed-shell paramagnetism has a long history of experiment and theory
  - experimental evidence since 1919
  - arguments were put forward that closed-shell systems cannot be paramagnetic
  - Rebane, Hegstrom and Lipscomb, and others resolved the paradox (1960s)
- All previous work is in terms of perturbation theory at zero field
  - we here study dia- and paramagnetism in a non-perturbative setting

Electronic Hamiltonian

- The one-electron Hamiltonian in the absence of a magnetic field (a.u.):

$$H_0 = \tfrac{1}{2}p^2 + V, \quad \mathbf{p} = -\mathrm{i}\boldsymbol{\nabla}$$

- In a magnetic field $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$, the kinetic-energy operator is modified and spin added:

$$H = \tfrac{1}{2}(\mathbf{p} + \mathbf{A}) \cdot (\mathbf{p} + \mathbf{A}) + \mathbf{B} \cdot \mathbf{S} + V$$

- For a uniform magnetic field in the z direction, expansion of the kinetic energy gives

$$H = H_0 + \tfrac{1}{2}BL_z + Bs_z + \tfrac{1}{8}B^2(x^2 + y^2)$$

- The linear paramagnetic Zeeman terms are easily understood:
  - the magnetic moments associated with L_z and s_z interact with B
- The quadratic diamagnetic term may be understood in the following manner:
  1. the field B induces a precession of the electrons with Larmor frequency $B/4\pi$
  2. this precession generates an induced magnetic moment proportional to the field

$$\text{charge} \times \text{frequency} \times \text{area} = -\frac{B}{4\pi}\pi(x^2 + y^2)$$

  3. this induced magnetic moment interacts with B, raising the energy quadratically

Para- and diamagnetic operators

- Consider the effects of the paramagnetic and diamagnetic operators:

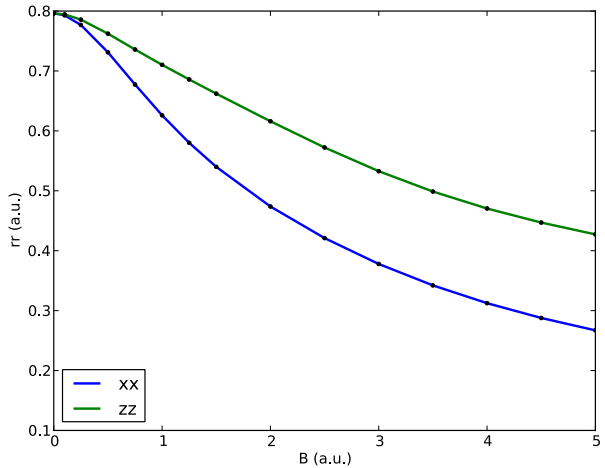
$$H = H_0 + Bs_z + \tfrac{1}{2}BL_z + \tfrac{1}{8}B^2\left(x^2 + y^2\right)$$

1. Effects of the paramagnetic Zeeman operators:
   1. they reduce symmetry and split energy levels
   2. energy is raised or lowered, depending on orientation

   - high-angular momentum states are favoured

2. Effects of diamagnetic operator:
   1. it raises the energy of all systems
   2. it squeezes all systems
   - transversal and longitudinal sizes of He
   - high-angular momentum states favoured

$$\langle\psi_{n\ell m}|r|\psi_{n\ell m}\rangle = \frac{3n^2 - \ell(\ell+1)}{2Z}$$

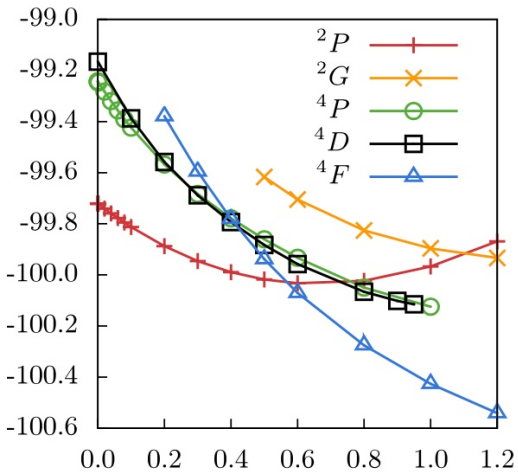


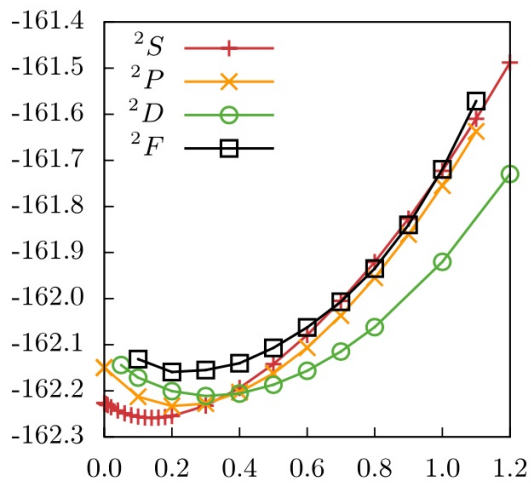
Quadratic Zeeman effect

- Initial energy lowering by the Zeeman terms is counteracted by the diamagnetic term

$$H = H_0 + Bs_z + \tfrac{1}{2}BL_z + \tfrac{1}{8}B^2\left(x^2 + y^2\right)$$

- Lowest states of the fluorine atom (left) and sodium atom (right) in a magnetic field
  - CCSD(T) calculations in uncontracted aug-cc-pCVQZ basis (atomic units)
  - Stopkowicz, Gauss, Lange, Tellgren, and Helgaker, JCP **143**, 074110 (2015)





  - what goes down, must come up
  - the last shall be the first, and the first will be last

- Note: one atomic unit of magnetic field strength B_0 corresponds to

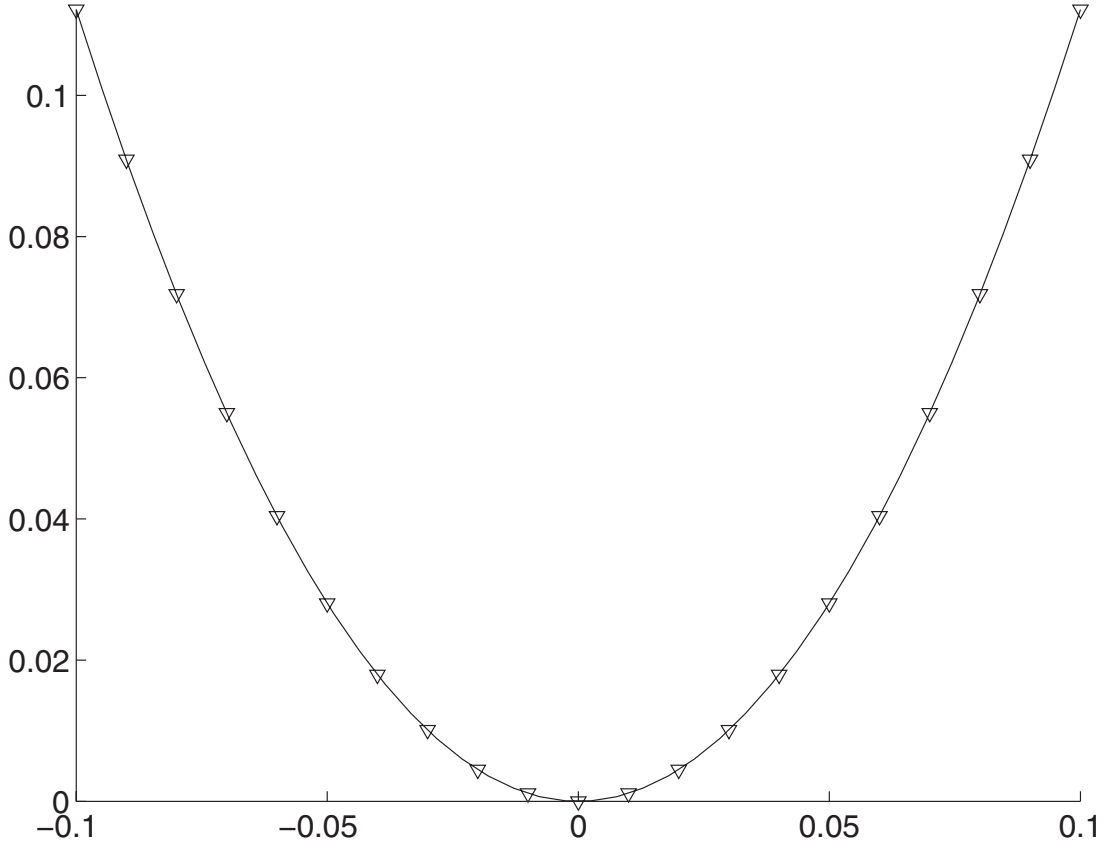
$$B_0 = 2.35 \times 10^5 \text{ T}$$

Closed-shell diamagnetism

- In a closed-shell system, the ground-state energy should (naively) increase diamagnetically:

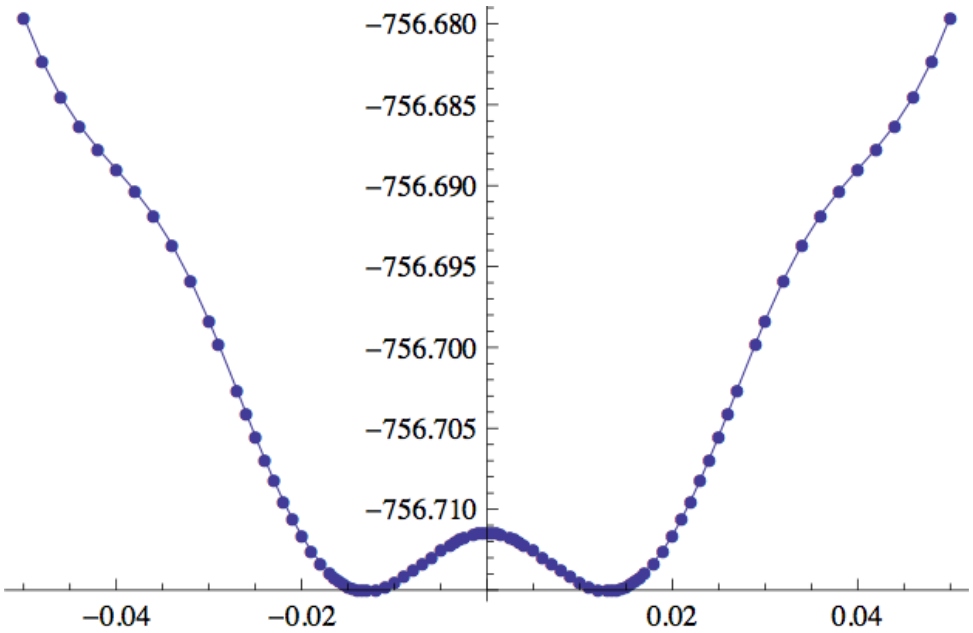
$$\langle 0|H|0\rangle = \langle 0|H_0|0\rangle + \tfrac{1}{8}B^2\langle 0|x^2+y^2|0\rangle, \quad \langle 0|L_z|0\rangle = \langle 0|S_z|0\rangle = 0$$

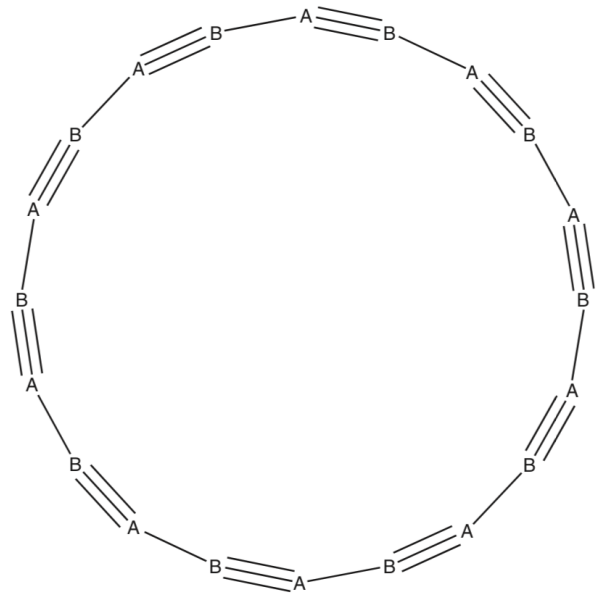
- Energy of benzene in a perpendicular magnetic field (atomic units):



Closed-shell paramagnetism

- Nevertheless, closed-shell paramagnetic molecules such as C_{20} do exist
  - the molecule is paramagnetic in 'weak fields', diamagnetic in 'strong fields'
  - notice undulating energy curve: what are the reasons for this?



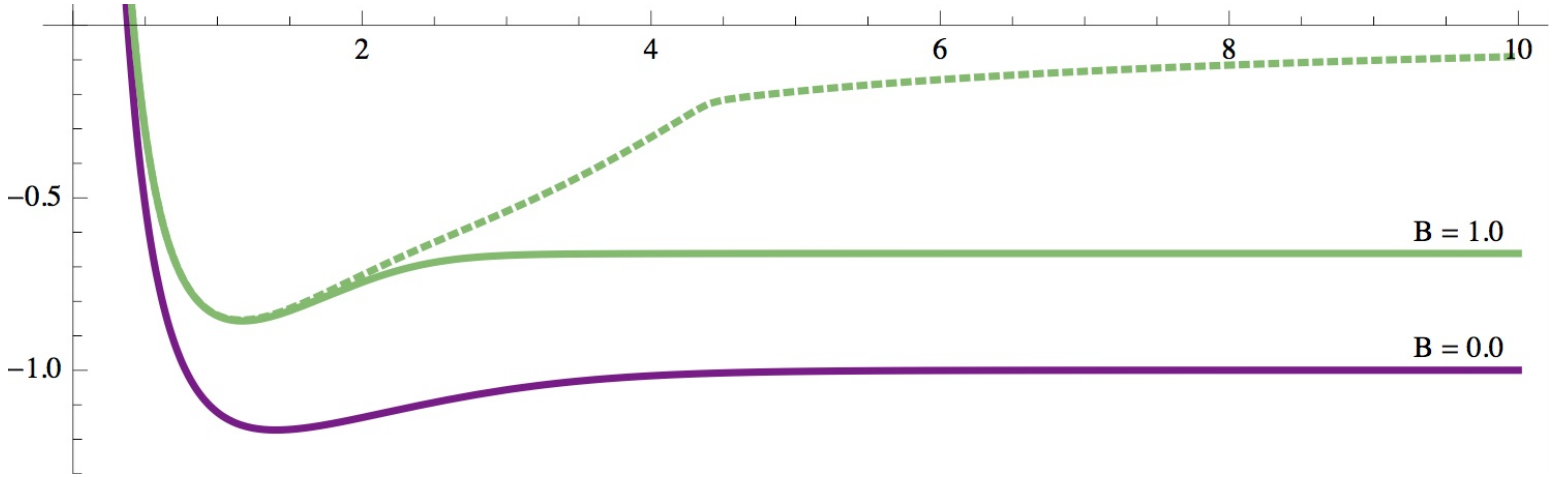


- Paramagnetism must in some way arise from field-induced changes in the ground state:

$$\langle 0\,|H|\,0\rangle = \langle 0\,|H_0 + \tfrac{1}{2}BL_z + \tfrac{1}{8}B^2(x^2+y^2)|\,0\rangle$$

Quantum chemistry in magnetic fields

- Standard quantum-chemistry programs cannot be used for molecules in magnetic fields
  - the wave function is complex – complex algebra cannot be avoided
  - London orbitals (GIAOs) must be used for gauge-origin invariance



- Quantum-chemistry codes for molecules in magnetic fields:
  - LONDON E. Tellgren, K. Lange, S. Stopkowicz, F. Hampe, A. Teale (Oslo)
  - QUEST A. Teale's group (Nottingham)
  - BAGEL T. Shiozaki's group (Northwestern)
- We have used the London (HF, DFT and CC) and Quest (DFT) codes

Closed-shell paramagnetism: BH molecule

- We will illustrate closed-shell paramagnetism with the BH molecule
  - R. A. Hegstrom & W. N. Lipscomb (1968), M. Jaszuński (1978), E. Tellgren *et al.* (2009)
- Molecular orbitals from the $1s_B^2\, 2s_B^2\, 2p_B^1$ AOs of B and $1s_H$ AO of H

$$\underbrace{1s_B}_{\text{core}} < \underbrace{1\sigma \approx 2s_B + 1s_H}_{\text{bonding orbital}} < \underbrace{2p_0}_{\text{lone pair HOMO}} < \underbrace{2\pi_{\pm 1}}_{\text{LUMOs}}$$

- Lowest electronic states of BH
  - MRCI, Miliordos and Mavridis, JCP **128**, 144308 (2008)
  - three lowest singlet states:

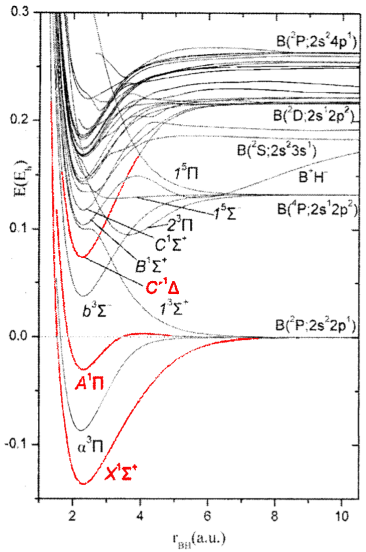
$$\left|{}^1\Sigma^+\right\rangle = \left|1s^2 1\sigma^2 2p_0^2\right\rangle \quad \leftarrow \text{ground state}$$

$$\left|{}^1\Pi\right\rangle = \left|1s^2 1\sigma^2 2p_0 2\pi_{\pm 1}\right\rangle \quad \leftarrow \text{singly excited}$$

$$\left|{}^1\Delta\right\rangle = \left|1s^2 1\sigma^2 2\pi_{\pm 1}^2\right\rangle \quad \leftarrow \text{doubly excited}$$

  - lowest triplet state:

$$\left|{}^3\Pi\right\rangle = \left|1s^2 1\sigma^2 2p_0 2\pi_{\pm 1}\right\rangle \quad \leftarrow \text{singly excited}$$



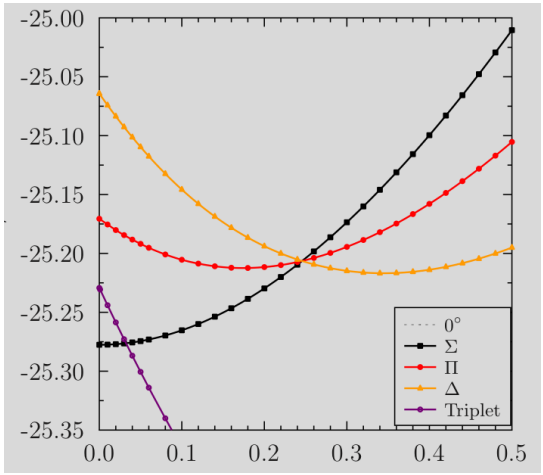
BH in a parallel magnetic field

- Consider the energy of the electronic states of BH in a parallel field:

$$\mathcal{E}_{\lambda,m_s}(B) = \langle \lambda, m_s \left| H_0 + \tfrac{1}{8}B^2(x^2+y^2) + \tfrac{1}{2}BL_z + BS_z \right| \lambda, m_s \rangle$$

  - CCSD and EOM-CCSD calculations in the aug-cc-pVQZ basis

$$\begin{aligned}
\left|{}^1\Delta\right\rangle &= \left|1s^2 1\sigma^2 2\pi_{-1}^2\right\rangle \\
\left|{}^1\Pi\right\rangle &= \left|1s^2 1\sigma^2 2p_0 2\pi_{-1}\right\rangle \\
\left|{}^3\Pi\right\rangle &= \left|1s^2 1\sigma^2 2p_0 2\pi_{-1}\right\rangle \\
\left|{}^1\Sigma\right\rangle &= \left|1s^2 1\sigma^2 2p_0^2\right\rangle
\end{aligned}$$



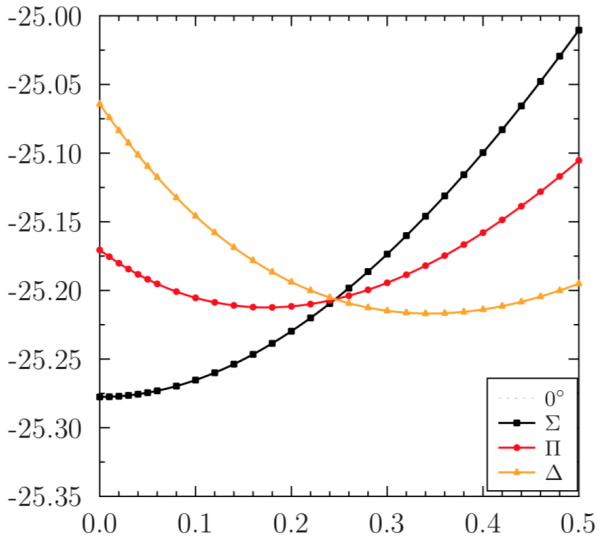
- The states do not mix, having different eigenvalues of the angular momentum operator
  - the initial slope is determined by the total angular momentum:

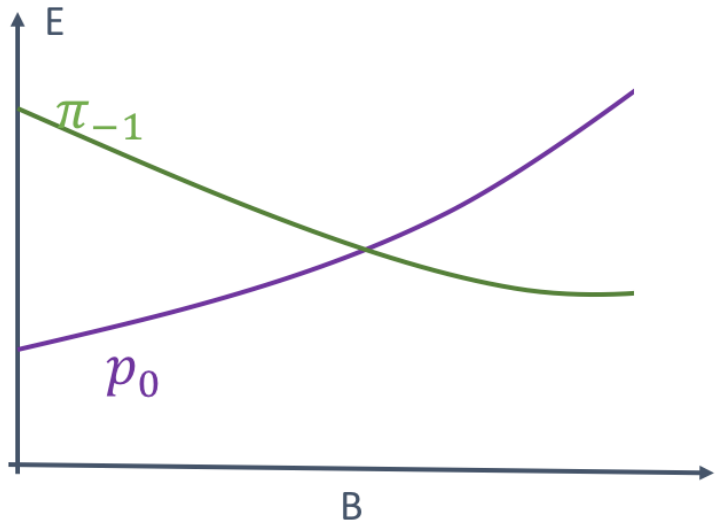
$$\langle \lambda, m_s \left| \tfrac{1}{2}L_z + S_z \right| \lambda, m_s \rangle = 0, -3/2, -1/2, -1$$

  - all states are paramagnetic except the singlet ground state
  - the triplet becomes the ground state at about $0.040B_0$
  - the three singlet states cross at about $0.25B_0$

Three-state crossing

- In a parallel field, the three singlet states of BH cross at about $B = 0.25B_0$:





- From the orbital occupations

$$|\Sigma\rangle = \left|1s^2 1\sigma^2 2p_0^2\right\rangle, \quad |\Pi\rangle = \left|1s^2 1\sigma^2 2p_0 2\pi_{-1}\right\rangle, \quad |\Delta\rangle = \left|1s^2 1\sigma^2 2\pi_{-1}^2\right\rangle,$$

  we see that triple crossing occurs when the $2p_0$ and $2\pi_{-1}$ orbitals become degenerate

- The Π curve is the average of the Σ and Δ curves:

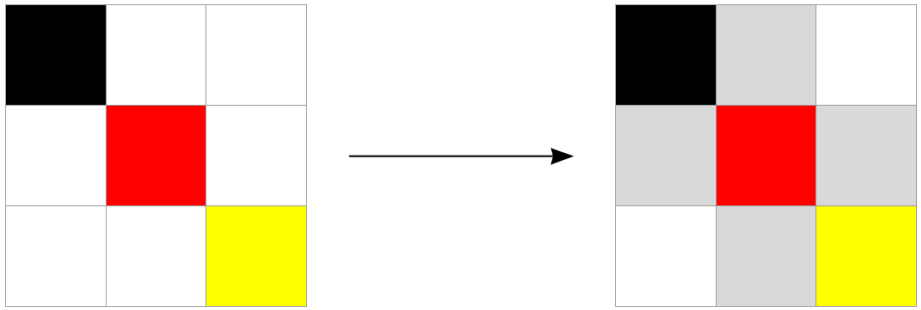
$$\mathcal{E}_\Pi(B) \approx \tfrac{1}{2}\mathcal{E}_\Sigma(B) + \tfrac{1}{2}\mathcal{E}_\Delta(B)$$

BH in a non-parallel magnetic field

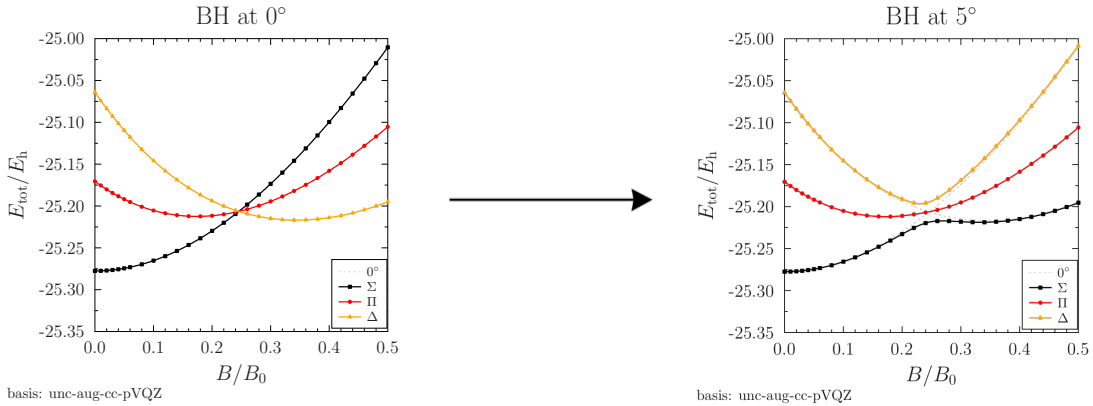
- In a parallel field, the three lowest singlet states of BH are of different symmetries

$$|\Sigma\rangle = \left|1s^2 1\sigma^2 2p_0^2\right\rangle, \quad |\Pi\rangle = \left|1s^2 1\sigma^2 2p_0 2\pi_{-1}\right\rangle, \quad |\Delta\rangle = \left|1s^2 1\sigma^2 2\pi_{-1}^2\right\rangle$$

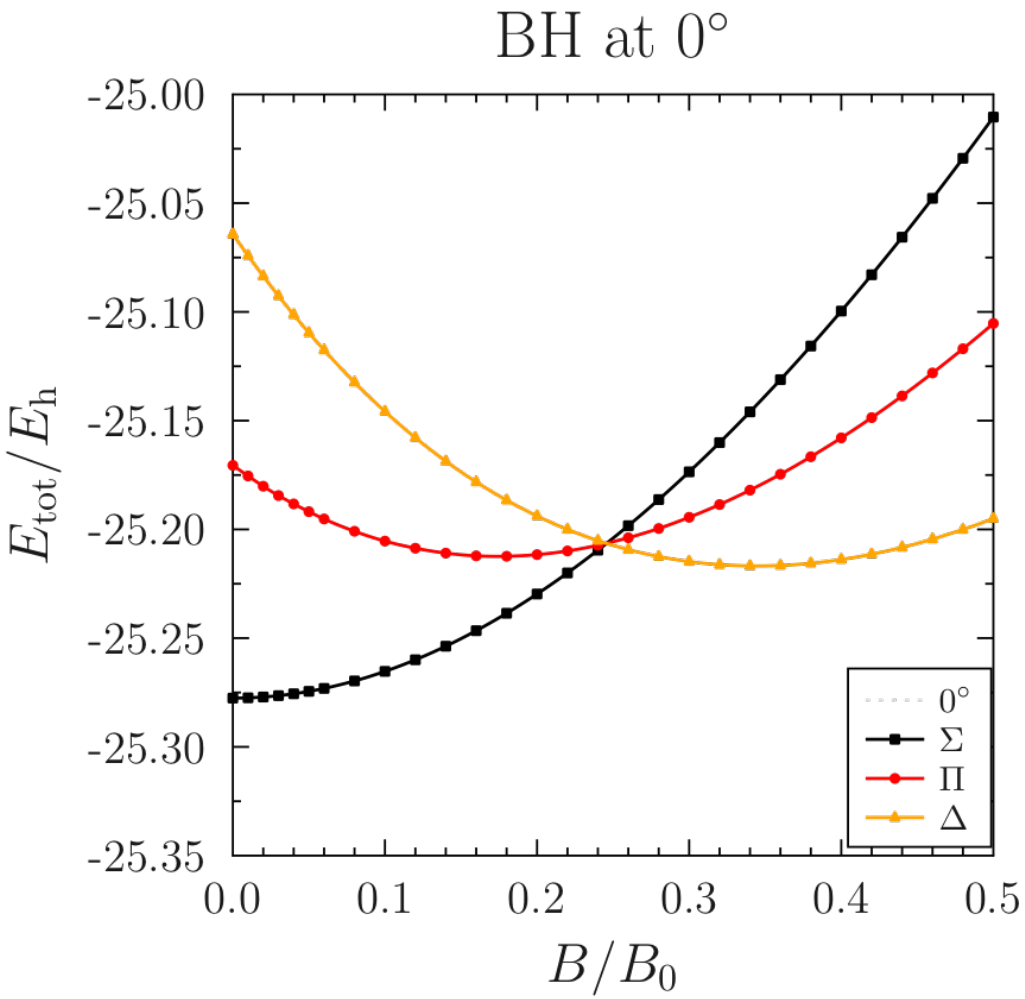
- In a non-parallel field, these states belong to the same symmetry
  - the orbital Zeeman operator $\frac{1}{2} L_z B$ couples states differing by a single excitation



  - this coupling generates a three-state avoided crossing



Emergence of paramagnetism in BH



basis: unc-aug-cc-pVQZ

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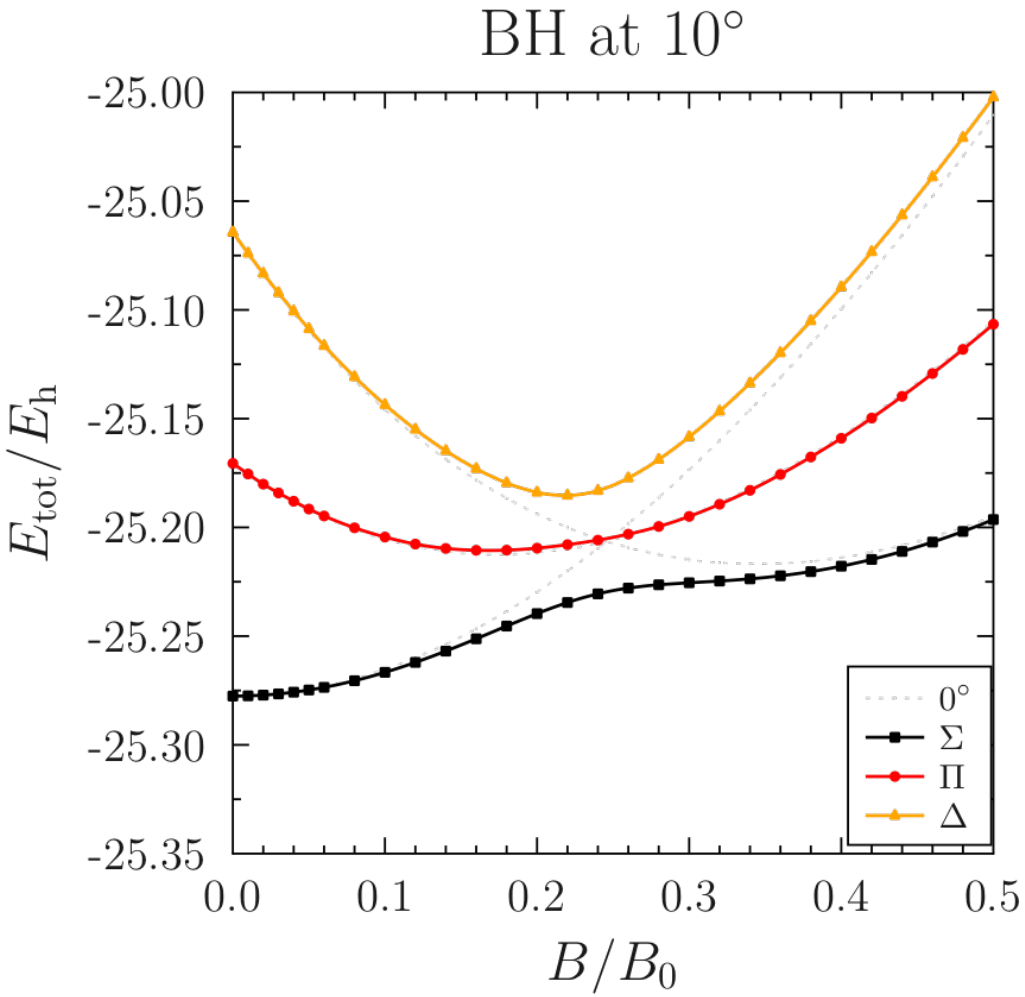

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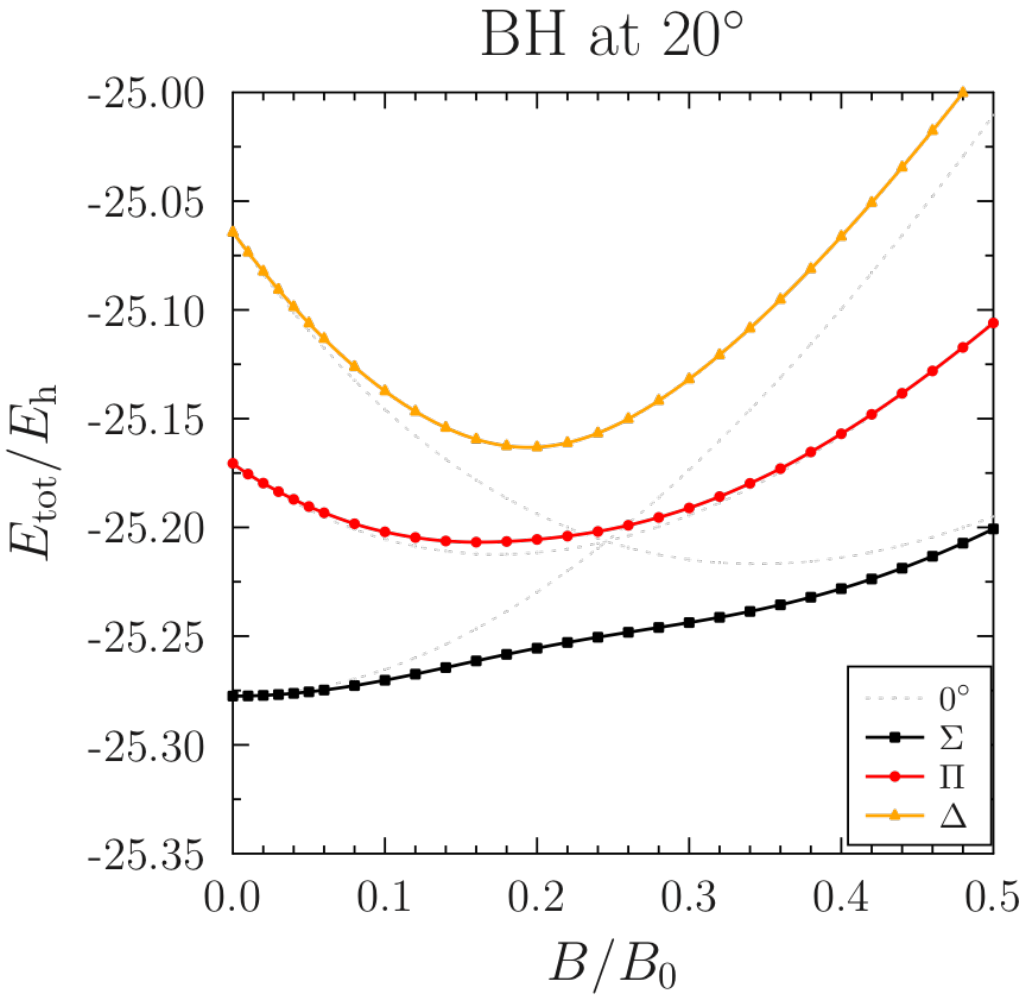

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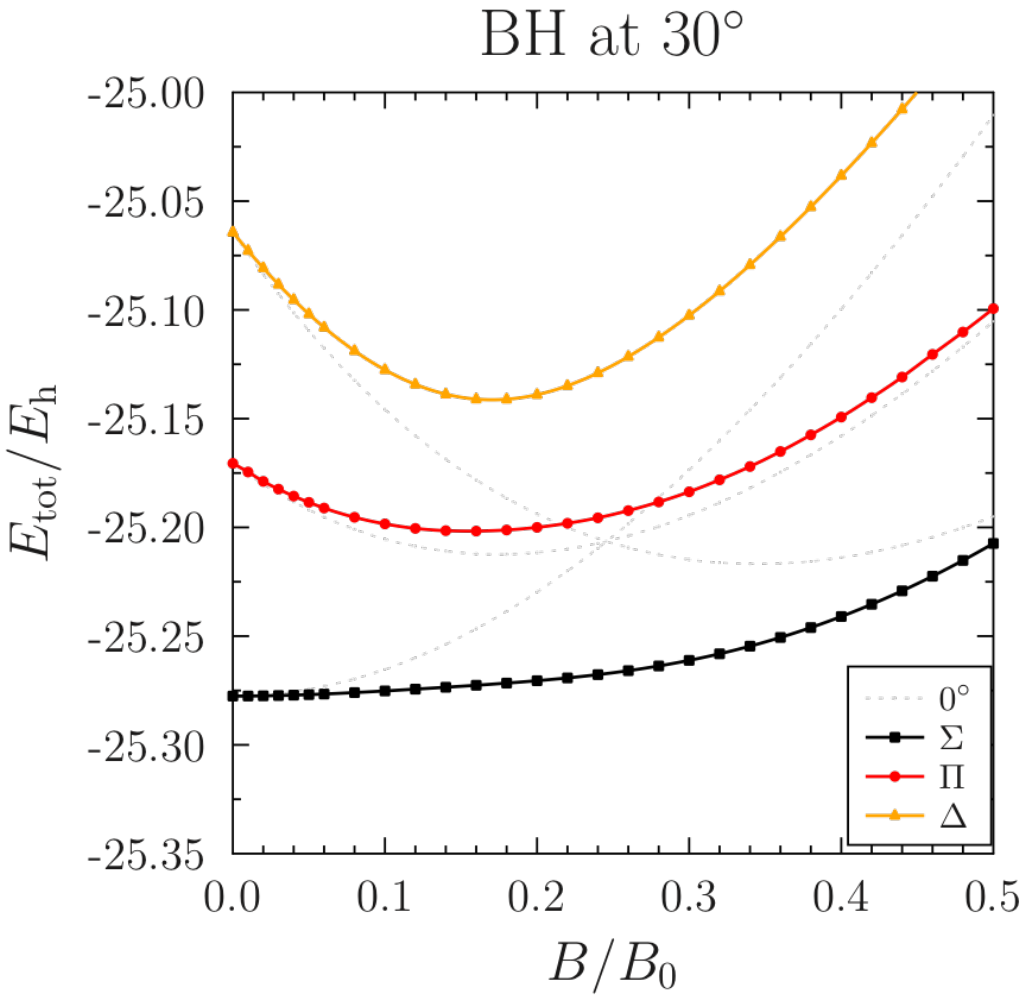

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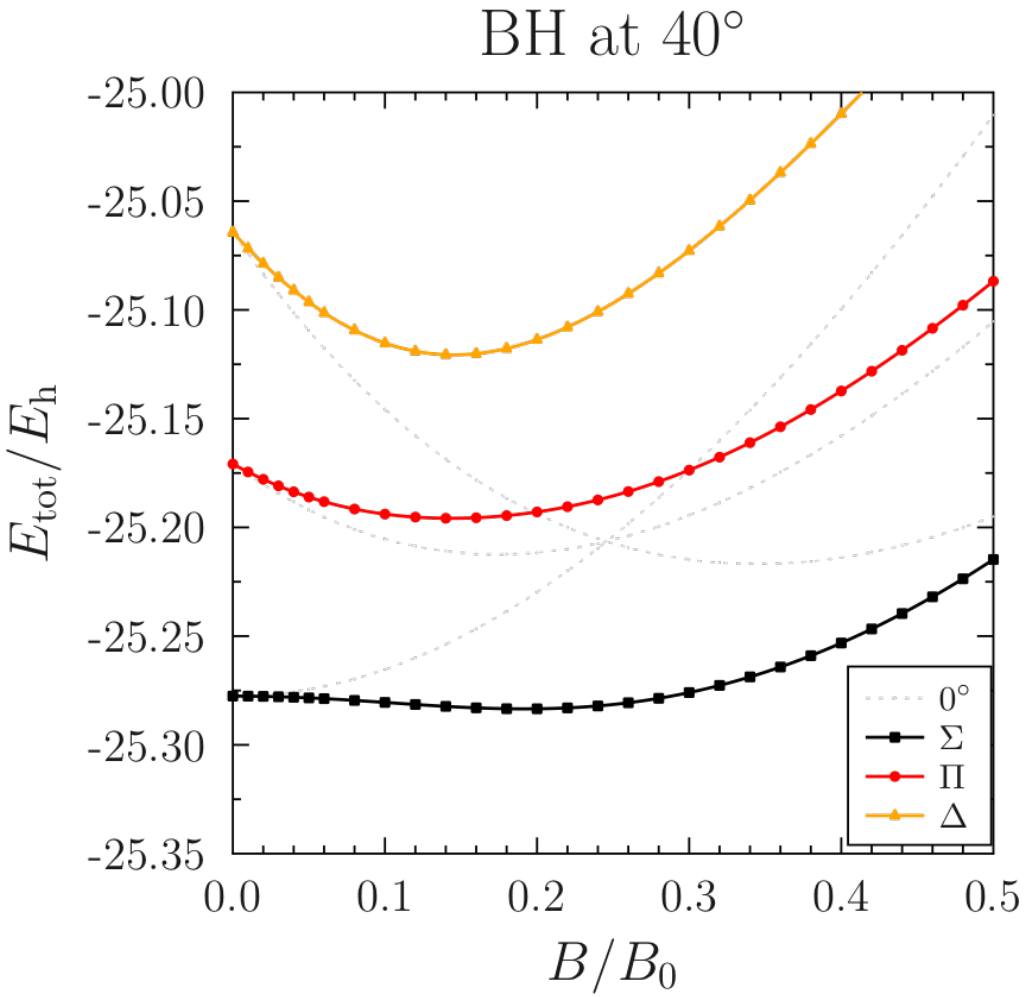

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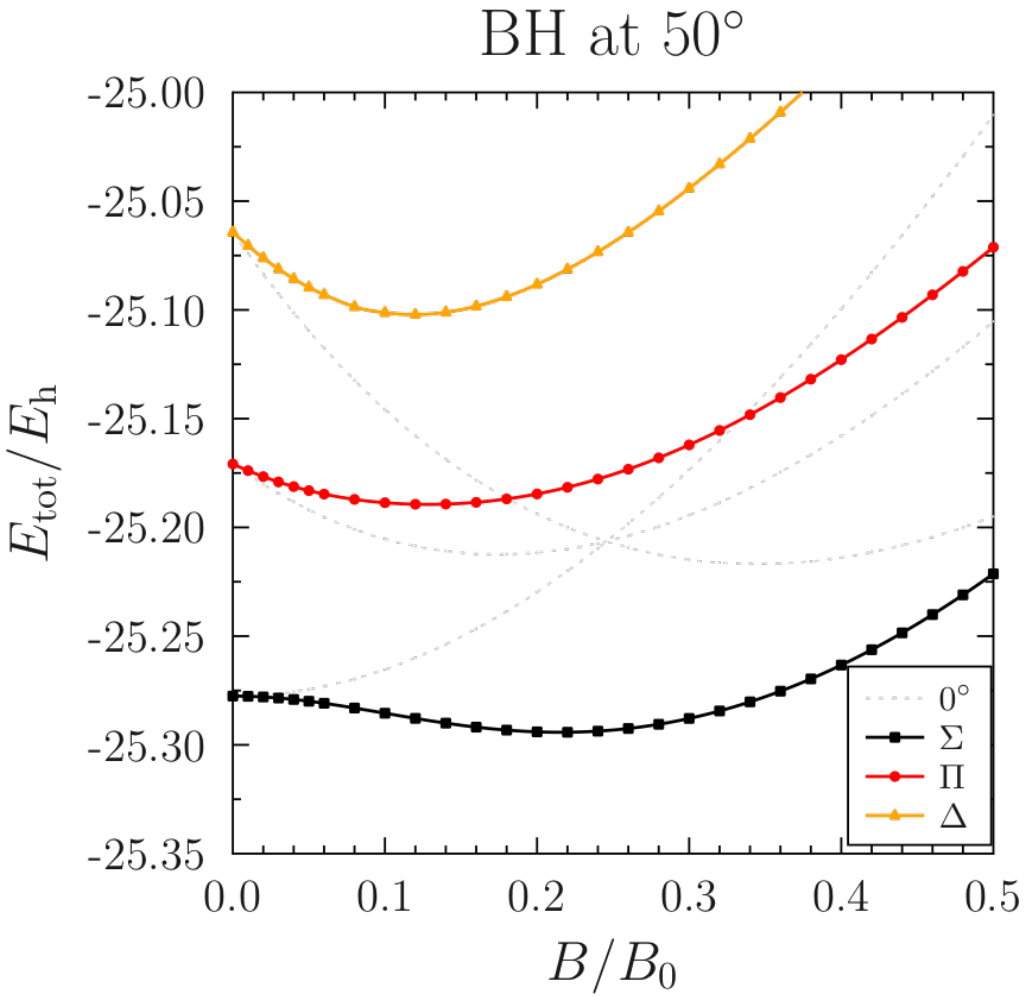

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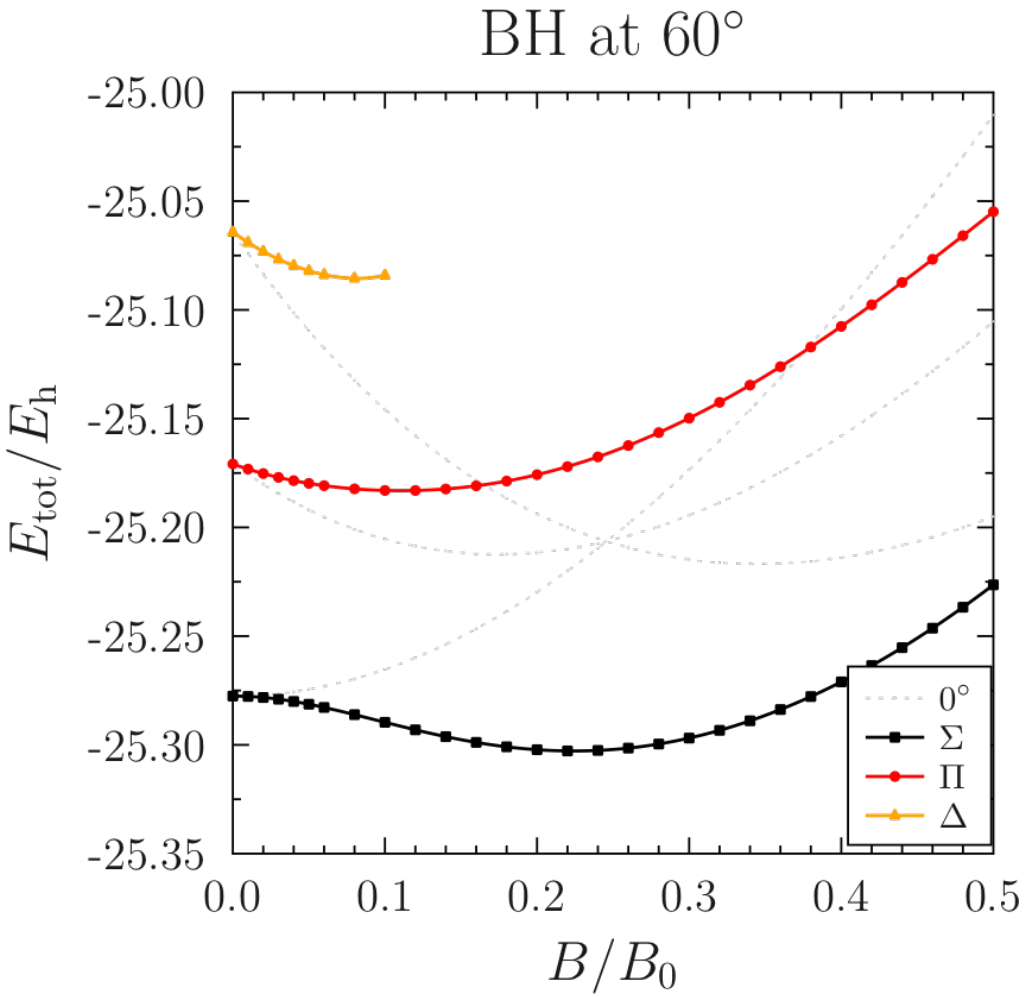

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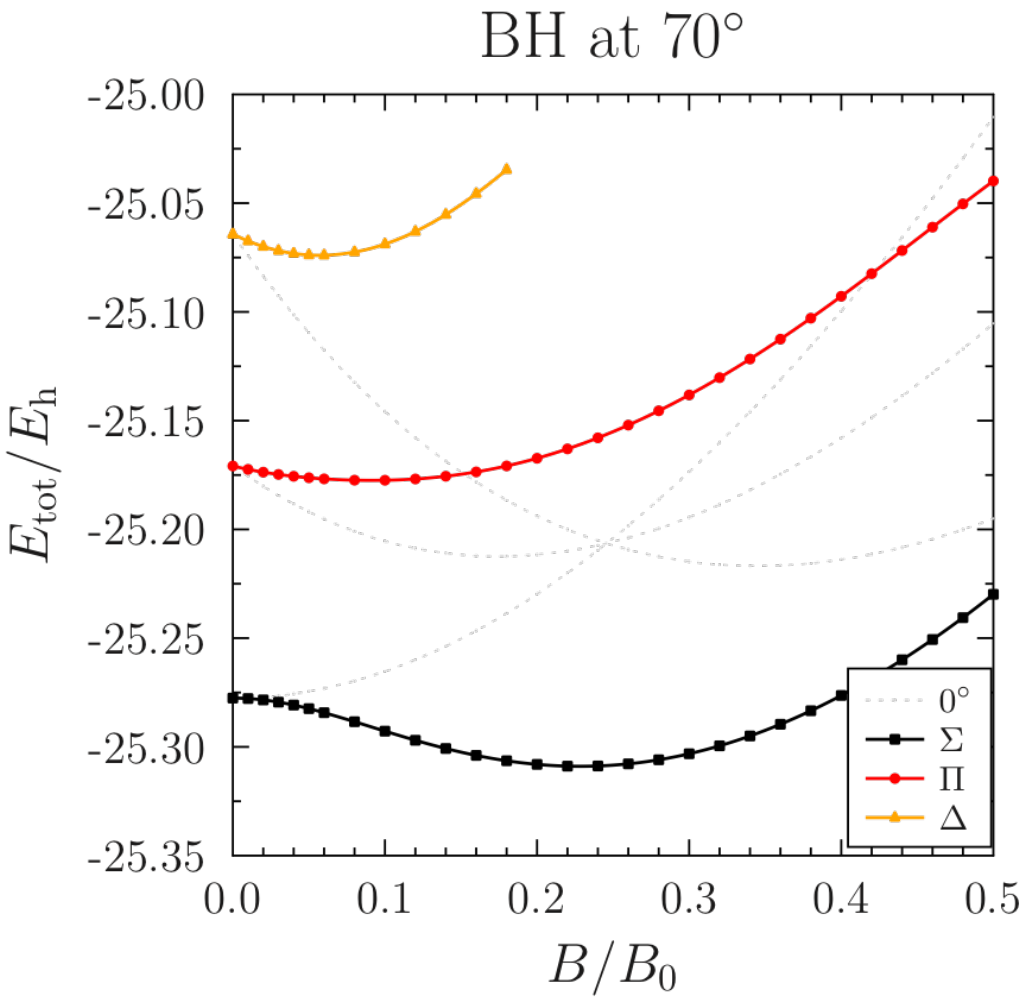

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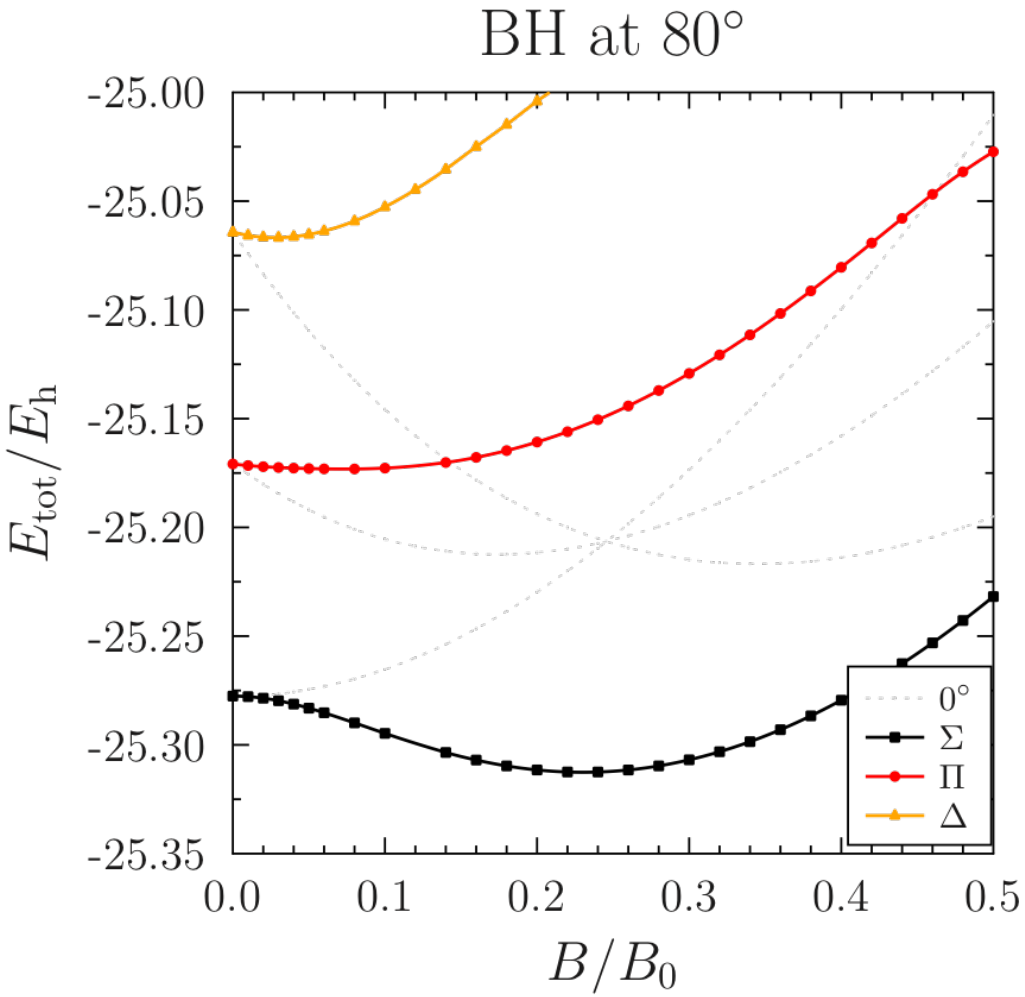

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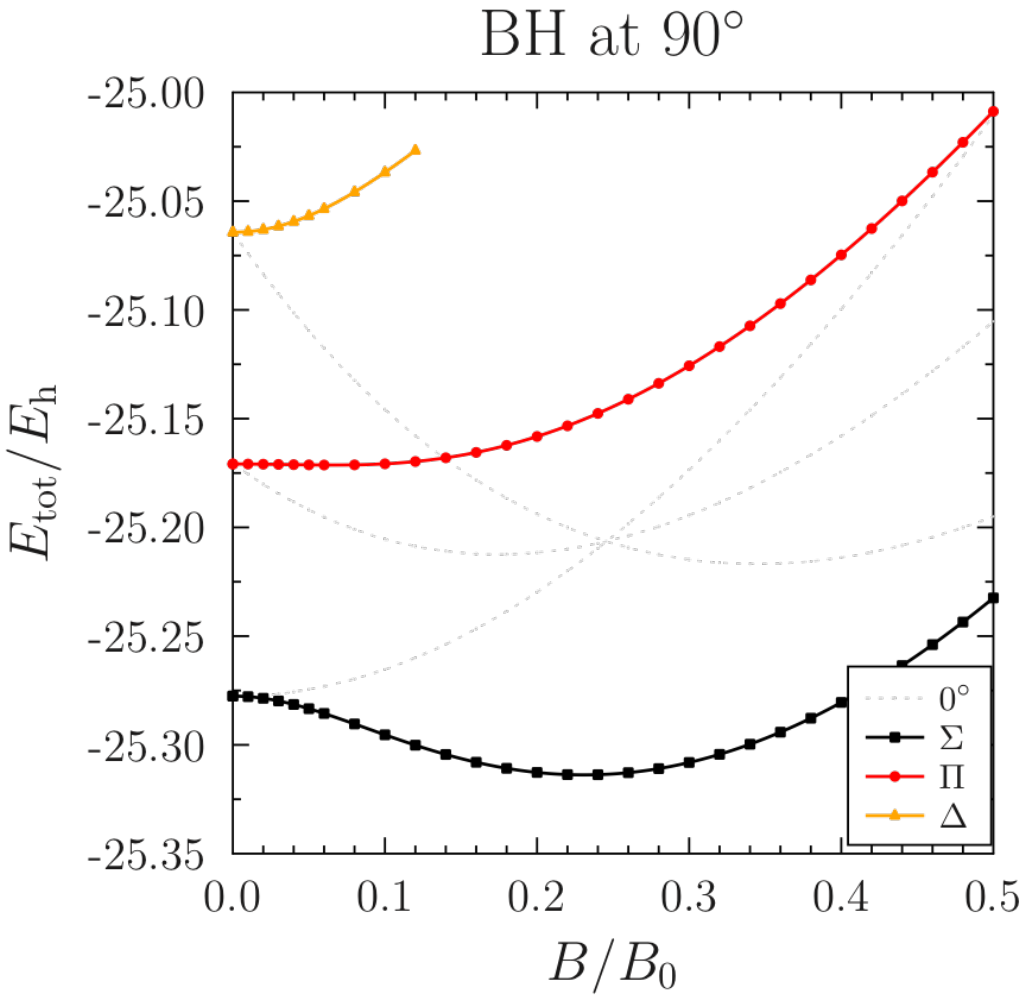
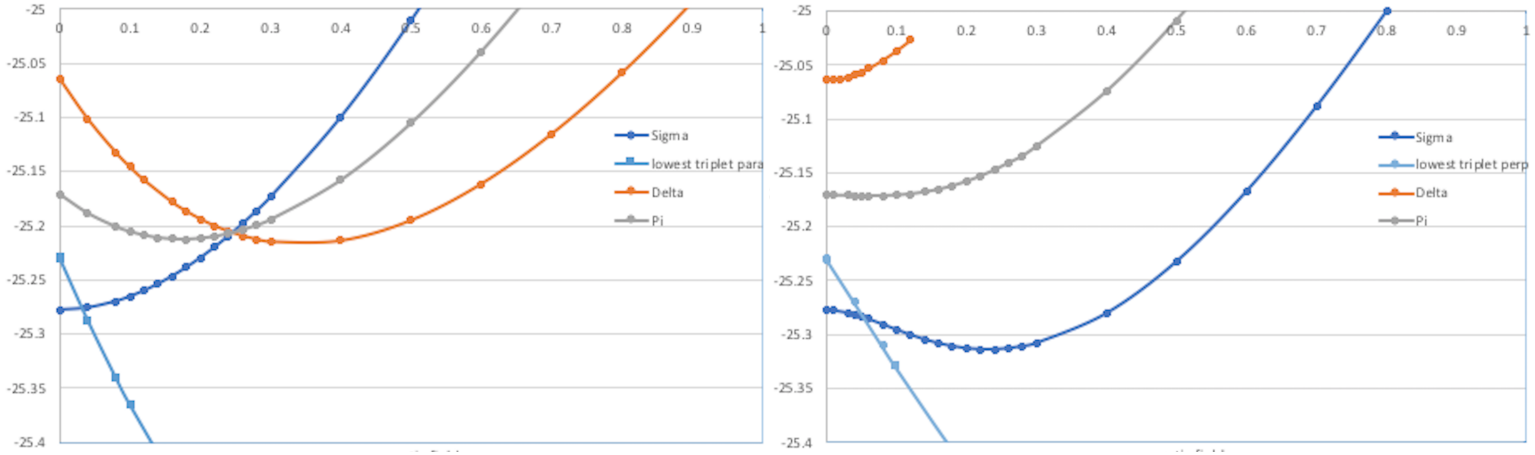
Emergence of paramagnetism in BH



basis: unc-aug-cc-pVQZ

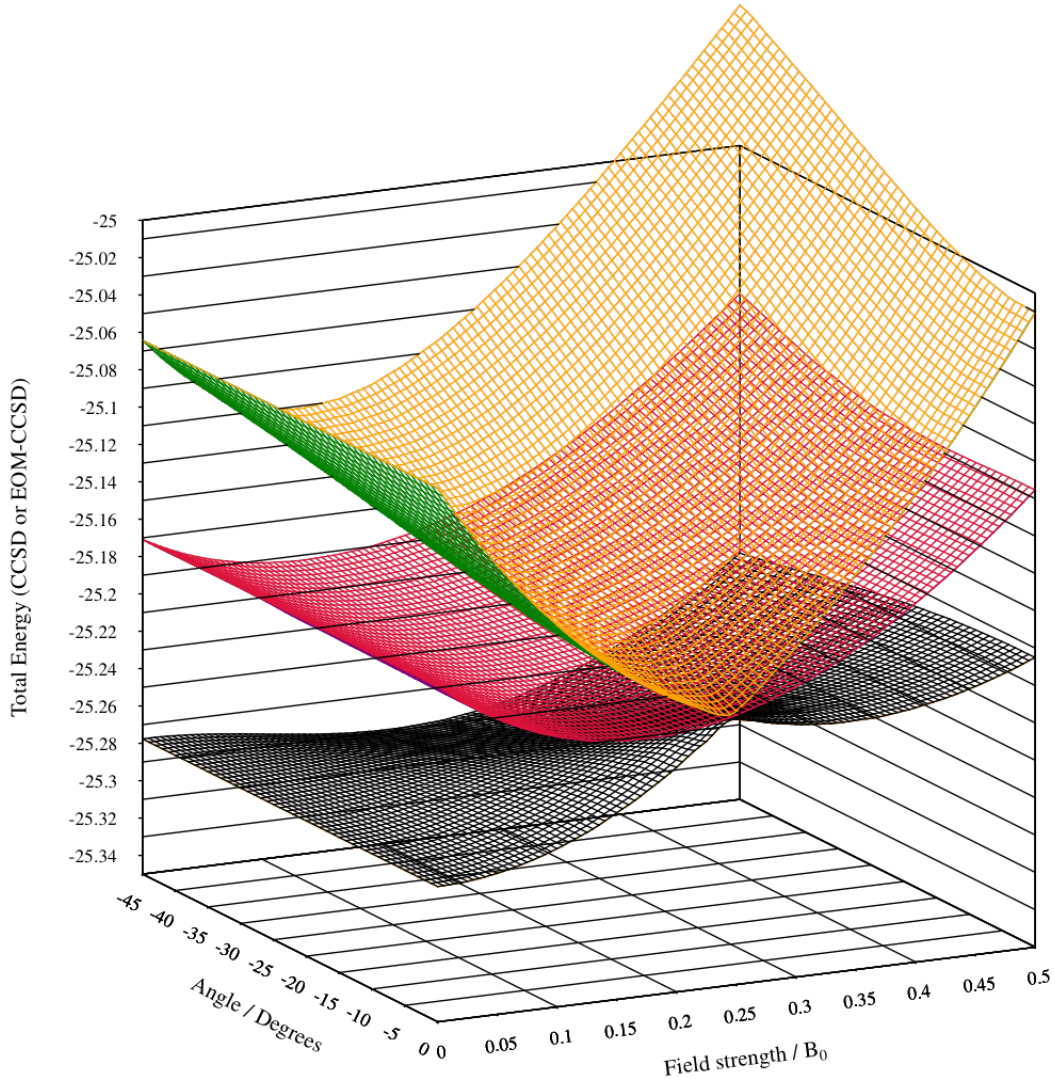
BH in parallel and perpendicular fields

- BH behaves very differently in parallel (left) and perpendicular (right) fields



- At zero field, the closed-shell singlet ground state is paramagnetic
  - an avoided crossing unquenches the angular momentum
- Paramagnetism is a magnetic Jahn–Teller effect
  - open-shell paramagnetism: Jahn–Teller effect
  - closed-shell paramagnetism: pseudo Jahn–Teller effect
- The lowest triplet becomes the ground state in relatively weak fields
  - crossing before $0.04B_0$ ($0.08B_0$) in the parallel (perpendicular) field orientation
- The magnetic field orients the molecule
  - preferred perpendicular (parallel) orientation in the singlet (triplet) state

Three lowest singlet states of BH



Modelling of three-state (avoided) crossing

- The three-state avoided crossing can easily be modelled for the diabatic states $|\lambda\rangle$:

$$|0\rangle = \left|1s^2 1\sigma^2 2p_0^2\right\rangle, \quad |1\rangle = \left|1s^2 1\sigma^2 2p_0 2\pi_{-1}\right\rangle, \quad |2\rangle = \left|1s^2 1\sigma^2 2\pi_{-1}^2\right\rangle$$

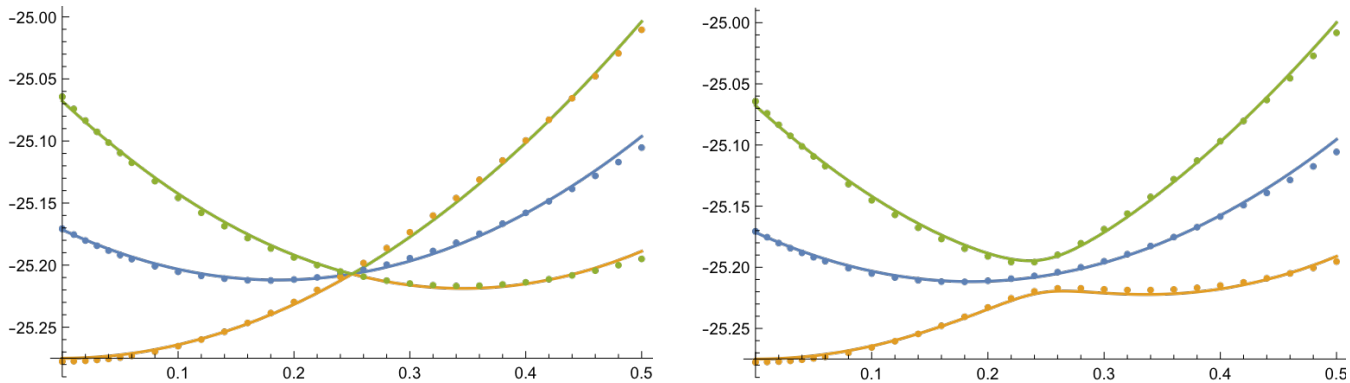
- The diabatic energies are modelled in the manner

$$\mathcal{E}_\lambda(B) = E_\lambda - \tfrac{1}{2}\lambda\cos(\theta)B + \tfrac{1}{2}a_\lambda B^2$$

- Introducing the coupling parameter μ, we obtain the Hamiltonian

$$H(B,\theta) = \begin{pmatrix} \mathcal{E}_0(B) & \mathrm{i}\mu B\sin(\theta) & 0 \\ -\mathrm{i}\mu B\sin(\theta) & \frac{1}{2}\mathcal{E}_0(B) + \frac{1}{2}\mathcal{E}_2(B) & \mathrm{i}\mu B\sin(\theta) \\ 0 & -\mathrm{i}\mu B\sin(\theta) & \mathcal{E}_2(B) \end{pmatrix}$$

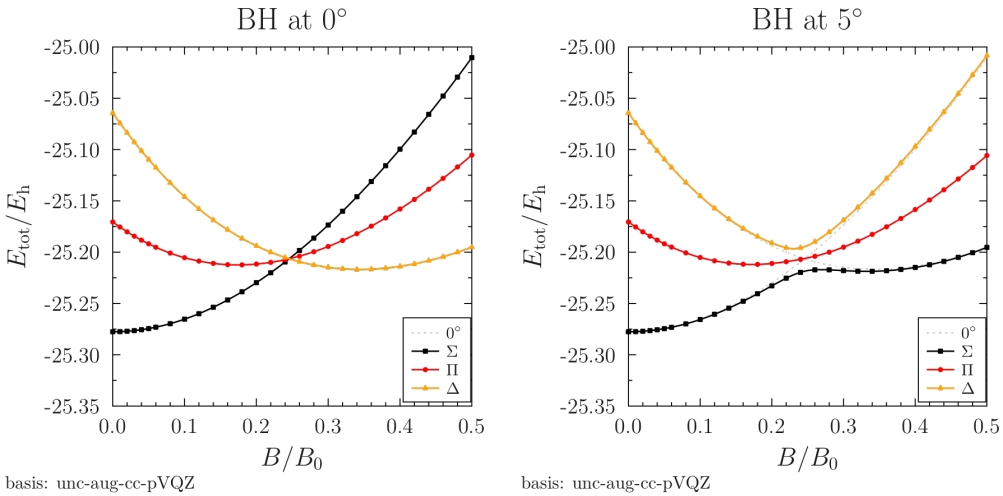
- This 5-parameter Hamiltonian accurately reproduces the CCSD energies at all angles:



- Note: the middle state is an active spectator, mediating the coupling

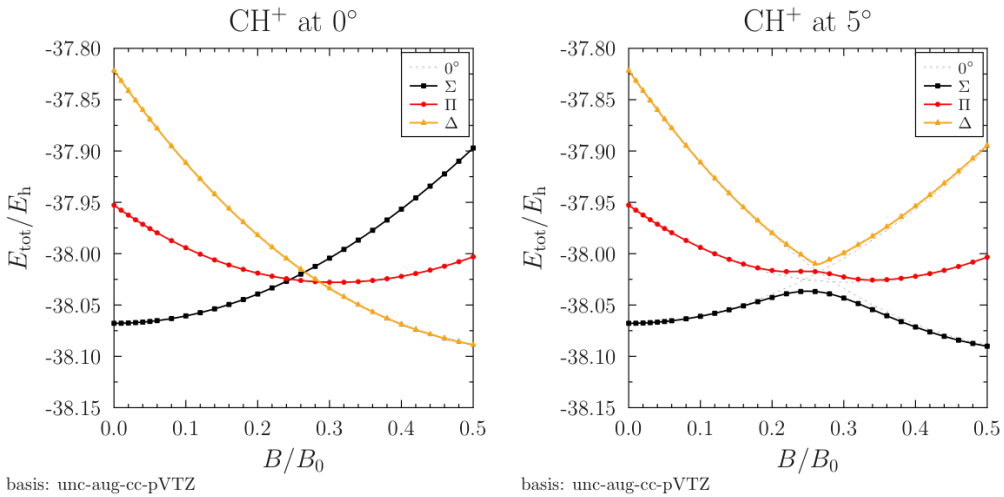
Near three-state crossing

- The three-state crossing in BH is not exact...



basis: unc-aug-cc-pVQZ basis: unc-aug-cc-pVQZ

- ...as is clearly demonstrated by the isoelectronic CH^+ molecule

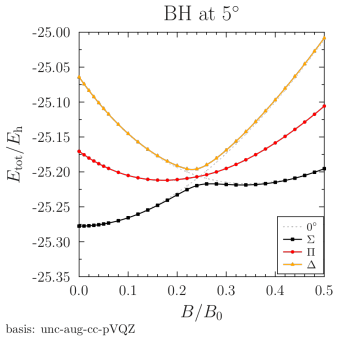


basis: unc-aug-cc-pVTZ basis: unc-aug-cc-pVTZ

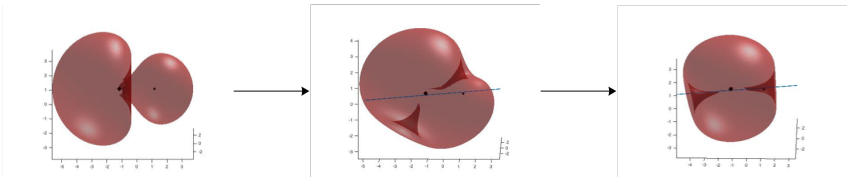
Evolution of BH orbitals and states in a non-parallel field

- As we increase the (non-parallel) field, the Σ state takes on the character of the Δ state

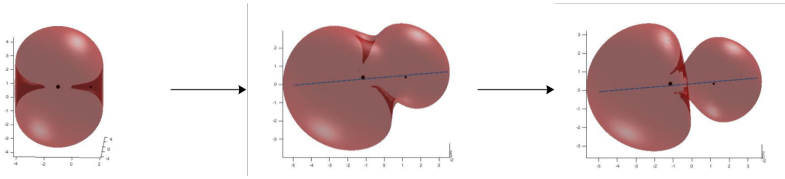
$$|2\rangle = |1s^2 1\sigma^2 2\pi_{-1}^2\rangle \longrightarrow |1s^2 1\sigma^2 2p_0^2\rangle$$
$$|1\rangle = |1s^2 1\sigma^2 2p_0 2\pi_{-1}\rangle \longrightarrow |1s^2 1\sigma^2 2\pi_{-1} 2p_0\rangle$$
$$|0\rangle = |1s^2 1\sigma^2 2p_0^2\rangle \longrightarrow |1s^2 1\sigma^2 2\pi_{-1}^2\rangle$$



- HOMO in the $|0\rangle$ ground state at $0.00B_0$, $0.26B_0$ and $0.40B_0$



- HOMO in the $|2\rangle$ doubly excited state at $0.00B_0$, $0.26B_0$ and $0.40B_0$



- Note: nodal plane rotated by the field as the angular momentum is unquenched

Closed-shell diamagnetism by gauge transformations

- The vector potential $\mathbf{A}$ that satisfies $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$ is nonunique but takes the general form

$$\mathbf{A} = \mathbf{A}_0 + \boldsymbol{\nabla} f, \quad \boldsymbol{\nabla} \times \mathbf{A}_0 = \mathbf{B}, \quad \boldsymbol{\nabla} \cdot \mathbf{A}_0 = 0 \quad \text{(arbitrary gauge function } f\text{)}$$

- The lowest-order energy of a closed-shell system in the field represented by $\mathbf{A}$ is given by:

$$\Delta E^{(2)} = \underbrace{\frac{1}{2}\langle 0|A^2|0\rangle}_{\text{diamagnetic term}} \underbrace{- \sum_{n>0} \frac{\langle 0|\mathbf{A}\cdot\boldsymbol{\nabla} + \boldsymbol{\nabla}\cdot\mathbf{A}|n\rangle\langle n|\mathbf{A}\cdot\boldsymbol{\nabla} + \boldsymbol{\nabla}\cdot\mathbf{A}|0\rangle}{E_n - E_0}}_{\text{paramagnetic term}}$$

- If the paramagnetic term vanishes, then the lowest-order energy is positive:

$$(\mathbf{A}\cdot\boldsymbol{\nabla} + \boldsymbol{\nabla}\cdot\mathbf{A})\,\Psi_0 = 0 \implies \Delta E^{(2)} = \tfrac{1}{2}\langle 0|A^2|0\rangle > 0$$

- Closed-shell diamagnetism therefore follows if a solution f can be found for the equation

$$(\mathbf{A}_0 + \boldsymbol{\nabla} f)\cdot\boldsymbol{\nabla}\Psi_0 + \tfrac{1}{2}(\nabla^2 f)\Psi_0 = 0$$

- Rebane (1960) gave an explicit solution by expansion in excited states:

$$f(\mathbf{r}) = \sum_{n>0} \frac{\langle n|\mathbf{A}_0\cdot\boldsymbol{\nabla}|0\rangle}{E_n - E_0} \times \frac{\Psi_n(\mathbf{r})}{\Psi_0(\mathbf{r})}$$

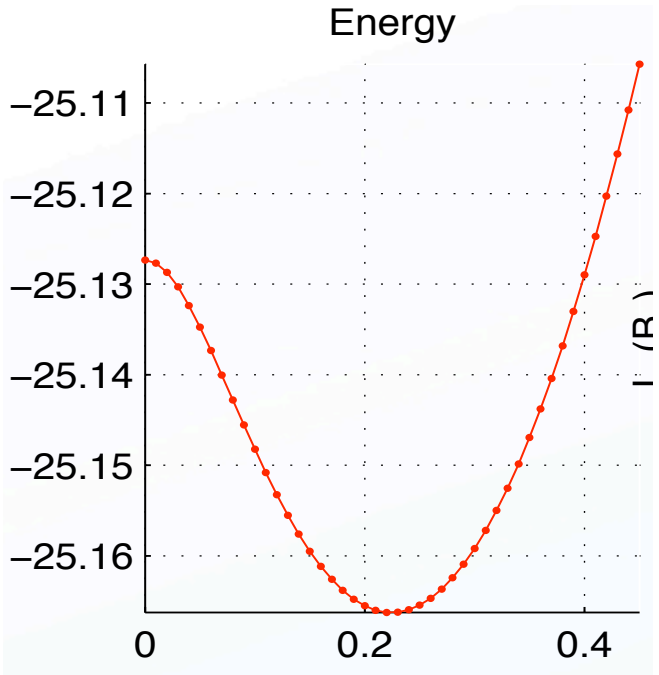
  - but a solution is guaranteed only if Ψ_0 is nodeless or has the same nodes as Ψ_n
  - ground states with more than two electrons can have nodal surfaces

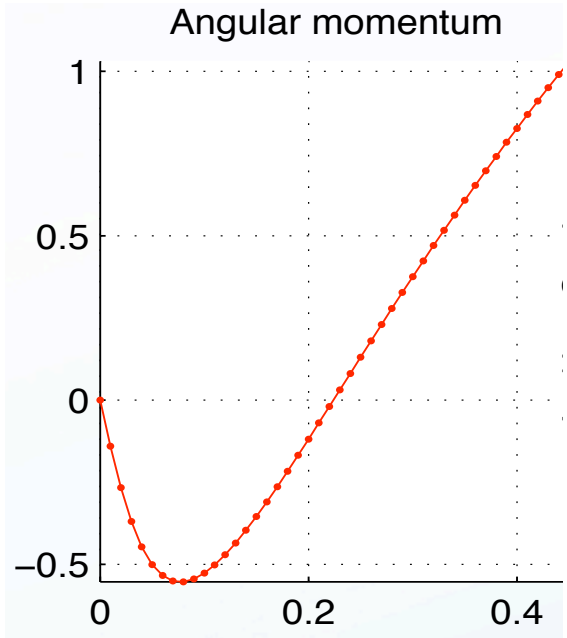
Induced electron rotation in BH

- The magnetic field induces a rotation of the electrons about the field direction:
  - the amount of rotation is the expectation value of the kinetic angular-momentum operator

$$\langle 0|\mathbf{\Lambda}|0\rangle = 2E'(\mathbf{B}), \quad \mathbf{\Lambda} = \mathbf{r} \times \boldsymbol{\pi}, \quad \boldsymbol{\pi} = \mathbf{p} + \mathbf{A}$$

- The induced rotation is twice the derivative of the energy with respect to the field
  - negative rotation reduces the energy: paramagnetism
  - positive rotation increases the energy: diamagnetism
- The energy and electron rotation of BH in a perpendicular field



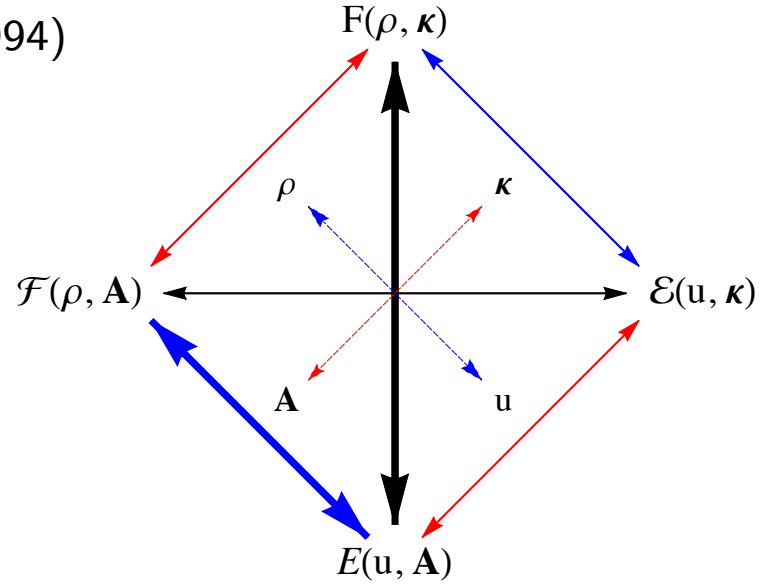


DFT in magnetic fields

- Magnetic perturbations are driven by changes in the kinetic energy
- In Kohn–Sham DFT, we model the noninteracting kinetic energy exactly
  - we therefore expect DFT to do well for magnetic properties
  - however, we are dependent on a good representation of the zero-field density
- Magnetic-field DFT (BDFT) (Grayce & Harrison 1994)

$$E(u,\mathbf{A}) = \inf_{\rho} \big(\mathcal{F}(\rho,\mathbf{A}) + (u|\rho)\big)$$

$$\mathcal{F}(\rho,\mathbf{A}) = \sup_{u} \big(E(u,\mathbf{A}) - (u|\rho)\big)$$



- Current DFT (CDFT) (Vignale & Rasolt 1987)

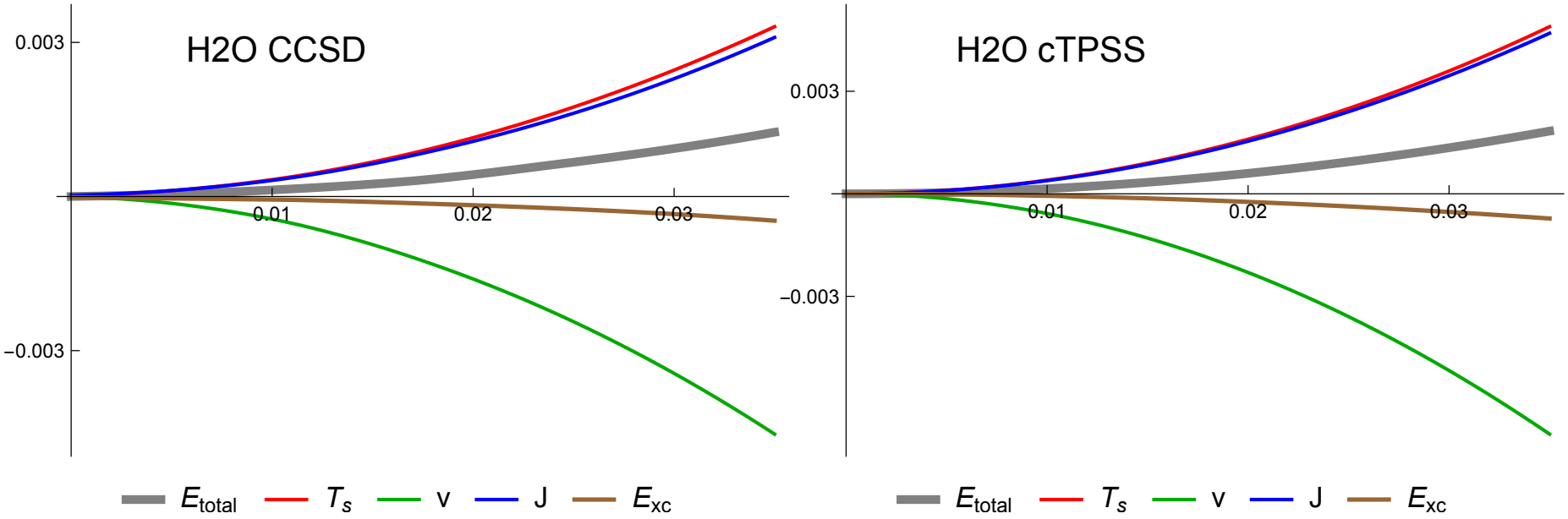
$$E(u,\mathbf{A}) = \inf_{\rho,\boldsymbol{\kappa}} \big(F(\rho,\boldsymbol{\kappa}) + (u|\rho) + (\mathbf{A}|\boldsymbol{\kappa})\big)$$

$$F(\rho,\boldsymbol{\kappa}) = \sup_{u,\mathbf{A}} \big(E(u,\mathbf{A}) - (u|\rho) - (\mathbf{A}|\boldsymbol{\kappa})\big)$$

- Observations regarding exchange–correlation functional:
  - the Vignale–Rasolt–Geldart (VRG) correction is not useful
  - the meta-GGA is the first satisfactory rung of DFT
  - the local kinetic energy demands a field or current dependence
- 'Kohn–Sham decomposition for molecules in a magnetic field', S. Reimann *et al.* (2018)

Kohn–Sham decomposition of H_2O in a magnetic field

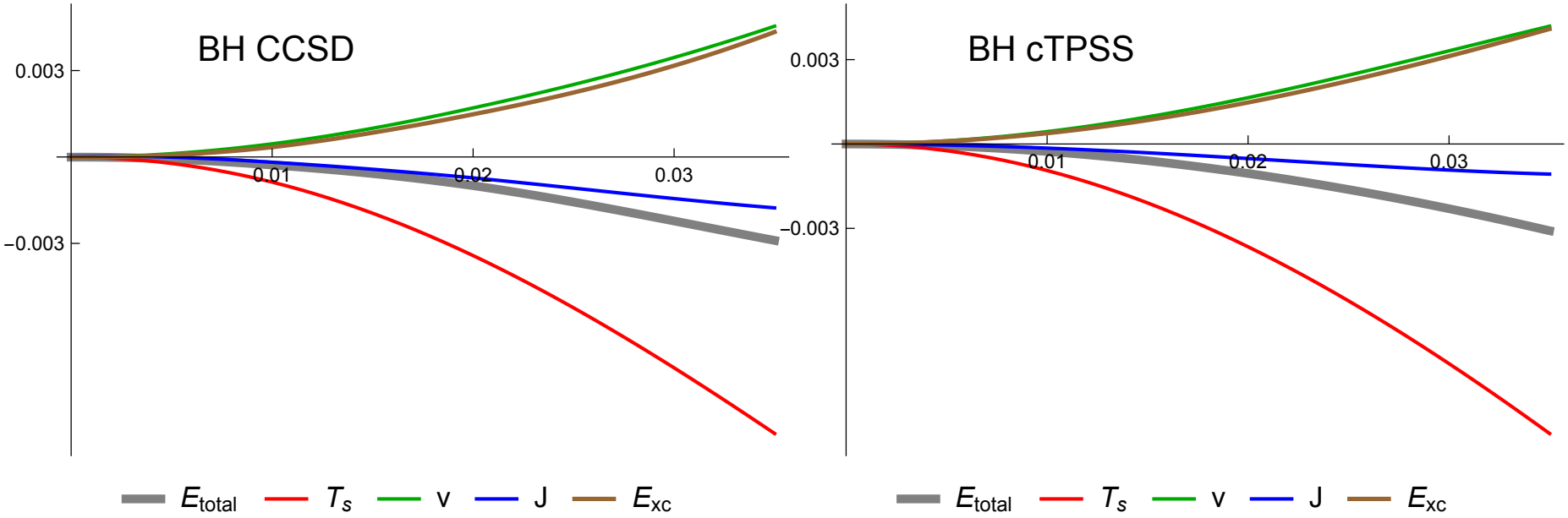
- Changes in the CCSD and cTPSS Kohn–Sham energy components with field strength



- Water is diamagnetic, with an overall quadratic energy increase in the field
  - the changes are driven by the increasing kinetic energy $T_s(\rho, \mathbf{B})$
  - a resulting compression of the density increases $J(\rho)$ and decreases $(v|\rho)$
  - the exchange–correlation energy decreases slightly
- cTPSS performs well but overestimates the overall energy variation
  - the quality of the density is important for a correct diamagnetic behaviour

Kohn–Sham decomposition of BH in a magnetic field

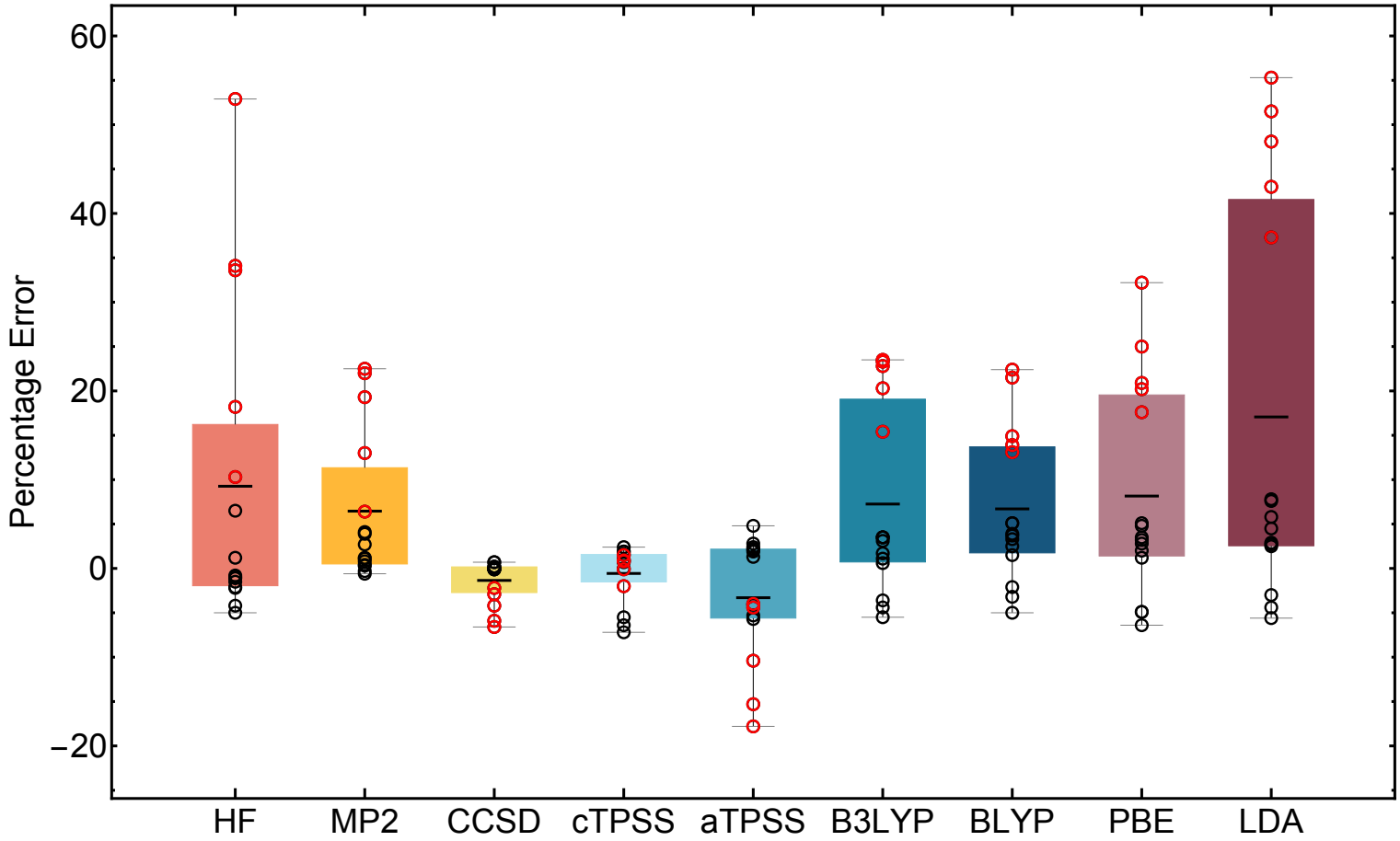
- Changes in the CCSD and cTPSS Kohn–Sham energy components with field strength



- BH is paramagnetic, with an overall quadratic energy decrease in the field
  - the changes are driven by the decreasing kinetic energy $T_s(\rho, \mathbf{B})$
  - a resulting decompression of the density decreases $J(\rho)$ and increases $(v|\rho)$
  - the exchange–correlation energy increases strongly in the field (mostly exchange)
- cTPSS performs well but error cancellation between exchange and correlation

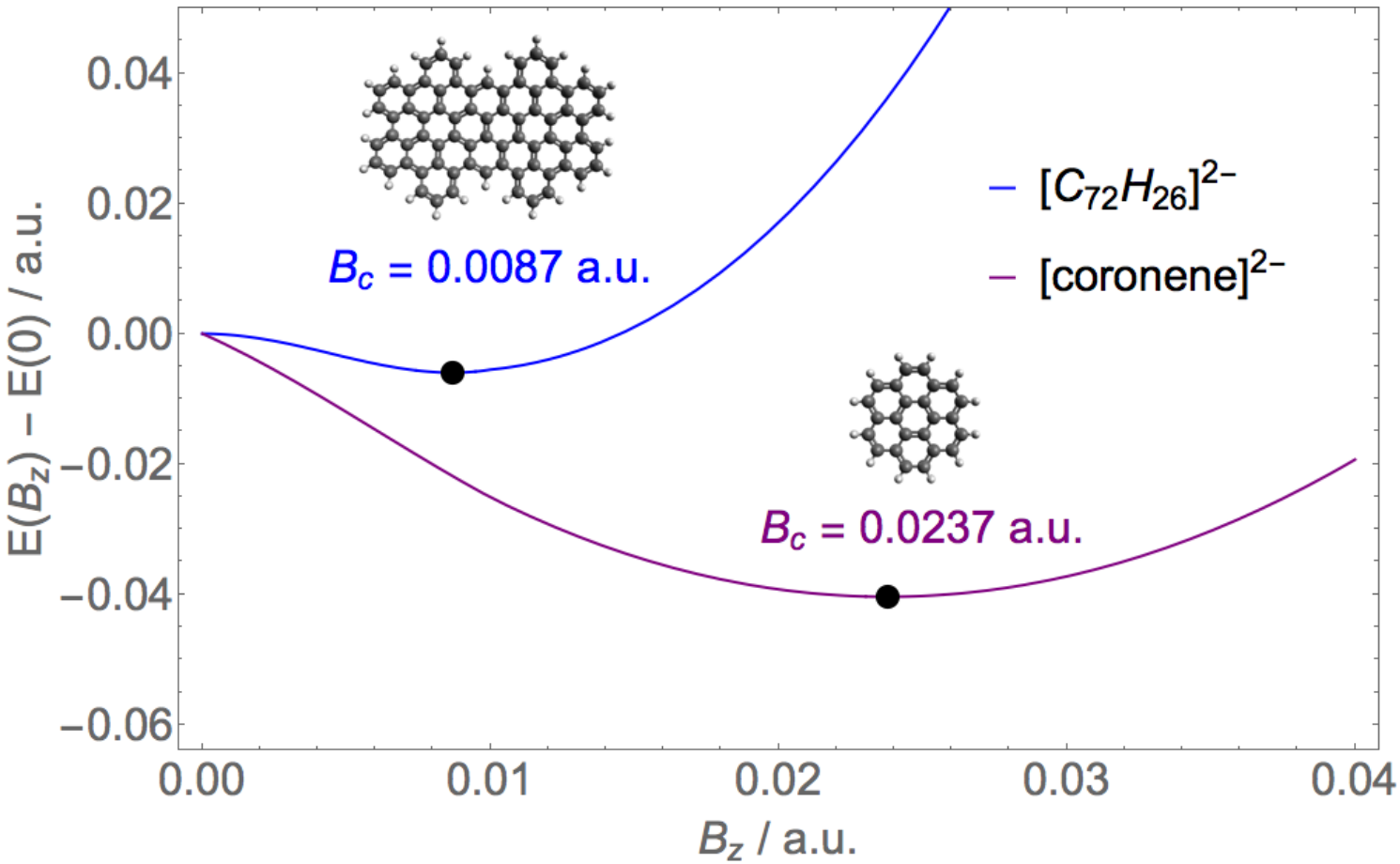
Magnetizabilities

- magnetizability $-\mathrm{d}^2E(B)/\mathrm{d}B^2|_{B=0}$ for perpendicular field (parallel for NH_3);
- diamagnetic He, H_2, He_2, Be, H_2O, HF, Ne, N_2, CO, NH_3, C_6H_6, C_4H_5N (black circles)
- paramagnetic BH, CH^+, AlH, SiH^+, BeH^- (red circles)
- mean percentage error of method/unc-aug-cc-pVTZ relative to CCSD(T)/aug-cc-pCVQZ



Closed-shell paramagnetic molecules

- We now have confidence in meta-GGA functionals in magnetic fields
- We are now in a position to study large molecules in magnetic fields



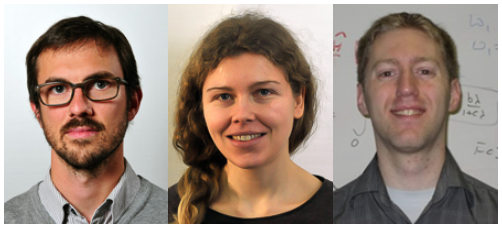
- calculations by Andy Teale's group using QUEST

Conclusions

- Closed-shell paramagnetism
  - the field couples the ground state to a low-lying paramagnetic doubly excited state
  - this coupling is mediated by a singly excited spectator state
  - the ground states takes on the paramagnetic character of the excited state
  - as a result, angular momentum of the ground state is unquenched
- Quantum chemistry in magnetic fields
  - complex algebra and GIAOs for gauge-origin invariance
  - special codes developed: LONDON, QUEST, BAGEL
  - Hartree–Fock, coupled-cluster, and density-functional theory
- Density-functional theory
  - meta-GGA functionals describe molecular magnetism well

Acknowledgements

- Co-workers:
  - Alex Borgoo, Sarah Reimann, Erik Tellgren (University of Oslo, CAS)
  - Jürgen Gauss, Florian Hampe, Stella Stopkowicz (University of Mainz, CAS)
  - Andy Teale (University of Nottingham, CAS)
  - Wim Klopper (Karlsruhe Institute of Technology, CAS)



- Special thanks:
  - to Michal Jaszuński for pointing out earlier work; Trond Saue and Peter Schwerdtfeger
- Funding:
  - Centre for Advanced Study (CAS) at the Norwegian Academy of Science and Letters
  - Norwegian Research Council for Centres of Excellence CTCC & Hylleraas
  - ERC Advanced Grant ABACUS