Connections

- **Validity of Hellmann–Feynman theorem:** holds for a variational wavefunction within a fixed variational subspace; may fail when the subspace changes with the perturbation (e.g. perturbation-dependent basis → Pulay terms).
- **Then:** derivatives of wavefunction parameters may be required.
- **But:** these can still be avoided by using a Lagrangian approach and differentiating the stationarity/side conditions (connection to $2n + 1$ and $2n + 2$ rules, still need derivatives of overlap matrix though)
- **Also:** the theorem does not hold directly for non-variational approaches (e.g. CC theory); a Lagrangian approach can be used here as well.

Zeeman terms

Consider linear terms in the electronic Hamiltonian for molecule in a homogeneous magnetic field in *z*-direction (in a.u.)

$$\hat{H} = \hat{H}_0 + \frac{1}{2} B \hat{L}_z + B \hat{S}_z + \frac{1}{8} \sum_i^N B^2 \left(x_i^2 + y_i^2 \right)$$

Angular momenta L_z and s_z set up a magnetic moment

$$m_z = -\frac{1}{2} L_z - s_z$$

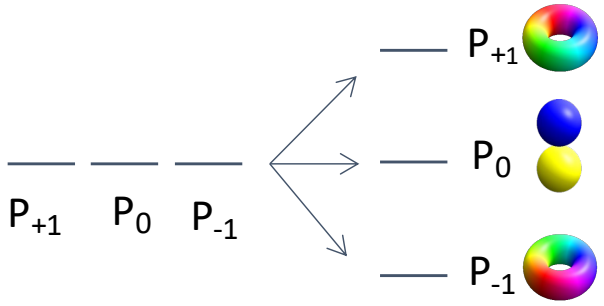
Magnetic moment interacts with magnetic field (dipolar interaction)

$$-B m_z = \frac{1}{2} B L_z + B s_z$$

Zeeman terms

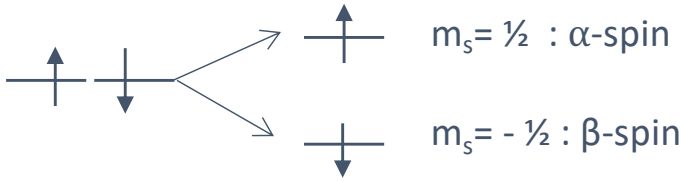
Consequences:

Reduction of symmetry and splitting of energy levels



$$p_{+1} = -\frac{1}{\sqrt{2}}(p_x + ip_y), \quad p_{-1} = \frac{1}{\sqrt{2}}(p_x - ip_y)$$

Orbital Zeeman



Spin Zeeman

Energy can be raised or lowered depending on the orientation

Zeeman terms

Orbital Zeeman:

- Trivial (WF is eigenfunction) for atoms and linear molecules when field is parallel
- Non-trivial, i.e., needs quantum-chemical calculation for general molecules $\frac{1}{2}\langle\Psi \mid \hat{L}_z \mid \Psi\rangle \underline{B}$

Spin Zeeman (assuming non-rel. wave function):

- Always trivial, WF is eigenfunction to $\hat{S}_z$

Perturbation theory

- Consider here closed-shell cases (no spin-Zeeman contribution)
- First-order perturbation theory: $\langle \Psi^{(0)} \mid \hat{H}^{(1)} \mid \Psi^{(0)} \rangle = E^{(1)}$

from general Hamiltonian

$$\underbrace{\langle \Psi^{(0)} \mid \frac{1}{2} \sum_{\alpha} \hat{\underline{l}}_{\alpha} \mid \Psi^{(0)} \rangle}_{\underline{m}} \underline{B} = E^{(1)}$$

vector which defines the negative „permanent magnetic moment“ $\underline{m}$ of molecule due to angular momentum

$$-\underline{m}\ \underline{B} = E^{(1)}$$

$$\underline{m} = -\langle \Psi^{(0)} \mid \frac{1}{2} \sum_{\alpha} \hat{\underline{l}}_{\alpha} \mid \Psi^{(0)} \rangle = -\gamma \langle \hat{L} \rangle$$

- $\underline{m}$ is zero for most molecules

gyromagnetic ratio $\gamma = -\frac{e}{2m_e} = -\frac{\mu_B}{\hbar}$

- atoms: this interaction is responsible for the normal Zeeman effect

Perturbation theory

- Most molecules can be described by a real wave function

→ $$\langle \Psi^{(0)} \mid \hat{O} \mid \Psi^{(0)} \rangle = \langle \Psi^{(0)} \mid \hat{O} \mid \Psi^{(0)} \rangle^*$$

for Hermitian operator $\hat{O}$

- But: $\langle \Psi^{(0)} \mid \frac{1}{2} \sum_\alpha \hat{\underline{l}}_\alpha \mid \Psi^{(0)} \rangle$

Imaginary! $\hat{\underline{l}}_\alpha = -i(\underline{r}_\alpha \times \nabla_\alpha)$

→ $$\langle \Psi^{(0)} \mid \sum_\alpha \hat{\underline{l}}_\alpha \mid \Psi^{(0)} \rangle = -\langle \Psi^{(0)} \mid \sum_\alpha \hat{\underline{l}}_\alpha \mid \Psi^{(0)} \rangle^*$$

Contradiction, except if = 0

→ No permanent magnetic moment due to Orbital-Zeeman
(But due to spin for open-shell cases)

→ No contribution from perturbation theory in first order

Perturbation theory

- Second-order PT

$$E^{(2)} = \underbrace{\langle \Psi^{(0)} \mid \hat{H}^{(2)} \mid \Psi^{(0)} \rangle}_{\text{diamagnetic contribution}} + \underbrace{\sum_{i \neq 0}^{\text{exc. states}} \frac{\langle \Psi^{(0)} \mid \hat{H}^{(1)} \mid \Psi^{(1)} \rangle \langle \Psi^{(1)} \mid \hat{H}^{(1)} \mid \Psi^{(0)} \rangle}{E_0^{(0)} - E_i^{(0)}}}_{\text{paramagnetic contribution}}$$

$E^{(2)}$ → Magnetizability, nonzero for all molecules!

Via derivative theory: expansion in B, compare to Taylor (see lecture 1)

$$E(\underline{B}) = E(B=0) + \left.\frac{\partial E}{\partial \underline{B}}\right|_{B=0}^{T} \underline{B} + \frac{1}{2}\underline{B}^T \left.\frac{\partial^2 E}{\partial \underline{B} \partial \underline{B}}\right|_{B=0} \underline{B} + \ldots$$

$$E(\underline{B}) = E(B=0) - \underline{m}^T \underline{B} - \frac{1}{2}\underline{B}^T \underline{\underline{\zeta}}\, \underline{B} + \ldots$$

Quantum-chemical calculation of magnetizabilities

- Component in the magnetizability tensor

$$\zeta_{ij} = \left. \frac{\partial^2 E}{\partial B_i \partial B_j} \right|_{B=0}$$

- Needed: $\dfrac{\partial \hat{H}}{\partial B_i} \xrightarrow{\hat{h} \to \hat{h} + \frac{1}{2}\hat{l}_i B_i + \ldots} \dfrac{\partial \hat{h}}{\partial B_i} = \dfrac{1}{2}\hat{l}_i = -i(\underline{r} \times \nabla)_i$

- Matrix elements: $h_{\mu\nu} + \underbrace{\langle \chi_\mu \mid \frac{1}{2}\hat{l}_i \mid \chi_\nu \rangle B_i}_{\text{complex}} + \ldots$

- Numerical differentiation for magnetic properties requires determination of complex wave function parameters → non-standard in most q.c. codes

Quantum-chemical calculation of magnetizabilities

$$2\zeta_{ij} = \frac{d^2 E^{\mathrm{HF}}}{dB_i dB_j} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial B_j} + \frac{1}{2} \sum_{\mu\nu\sigma\rho} D_{\mu\nu} D_{\sigma\rho} \left(\frac{\partial^2 \langle \mu\sigma \mid \nu\rho \rangle}{\partial B_i \partial B_j} - \frac{1}{2} \frac{\partial^2 \langle \mu\sigma \mid \rho\nu \rangle}{\partial B_i \partial B_j} \right)$$

$$- \sum_{\mu\nu} W_{\mu\nu} \frac{\partial^2 S_{\mu\nu}}{\partial B_i \partial B_j}$$

$$+ \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_i} \left(\frac{\partial h_{\mu\nu}}{\partial B_j} + \sum_{\sigma\rho} P_{\sigma\rho} \left(\frac{\partial \langle \mu\sigma \mid \nu\rho \rangle}{\partial B_j} - \frac{1}{2} \frac{\partial \langle \mu\sigma \mid \rho\nu \rangle}{\partial B_j} \right) \right)$$

$$- \sum_{\mu\nu} \frac{\partial W_{\mu\nu}}{\partial B_j} \frac{\partial S_{\mu\nu}}{\partial B_i}$$

Do the basis functions depend on the magnetic field?

No…

$$2\zeta_{ij} = \sum_{\mu\nu} D_{\mu\nu} \underbrace{\frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial B_j}}_{\langle \mu \mid r^2 \delta_{ij} - \underline{r}_i \underline{r}_j \mid \mu \rangle} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_i} \underbrace{\frac{\partial h_{\mu\nu}}{\partial B_j}}_{\langle \mu \mid \frac{1}{2} \hat{l}_j \mid \mu \rangle}$$

Derivatives of density wrt $\underline{B}$ via CPHF

Quantum-chemical calculation of magnetizabilities

- CPHF equations for B (again, no 2el terms):

$$U_{ai}^{B_\alpha}(\varepsilon_a - \varepsilon_i) + \sum_{bj} U_{bj}^{B_\alpha}(\langle aj \mid bi\rangle - \langle ab \mid ji\rangle) = h_{ai}^{B_\alpha}$$

- Overall, easy enough, no??

  Did we miss something??

Quantum-chemical calculation of magnetizabilities

- Magnetizabilities of Argon, HF, aug-pVDZ

R_O	ζ	ζ^{dia}	ζ^{para}
0.0	-4,353	-4,353	0
1.0	-6,020	-7.353	1,333
5.0	-46,039	-79,353	33,314
10.0	-171,100	-304,353	-133,253

- Changes in gauge origin → very large changes in magnetizability values
- Quantum-chemical calculations of magnetizabilities in finite basis are not gauge-origin independent!
- Gauge origin can be chosen randomly!

Quantum-chemical calculation of magnetizabilities

- Magnetizabilities of CO, HF, basis-set convergence, gauge origin in center of mass

basis	ζ	ζ^{dia}	ζ^{para}
cc-pVDZ	-4,224	-10,173	5,949
cc-pVTZ	-3,354	-10,157	6,804
cc-pVQZ	-2,882	-10,153	7,271

fast convergence

slow convergence

not particularly impressive…

Quantum-chemical calculation of magnetizabilities

- Reason for the bad convergence of the paramagnetic term? (see also exercise)
- Consider H atom with magnetic field along z
- Chose $\underline{R}_O = 0$:
  - diamagnetic contribution $\langle \phi_{1s} \mid \cdots \mid \phi_{1s} \rangle$
  - paramagnetic contrib. $\underbrace{\langle \phi_{1s} \mid \hat{l}_z \mid \phi_a \rangle}_{=0}$

    =0 (for whatever is in the ket, since eigenfunction to l_z)
- Chose $\underline{R}_O \neq 0$:
  - diamagnetic contribution $\langle \phi_{1s} \mid \cdots \mid \phi_{1s} \rangle$
  - paramagnetic contrib.

$$\hat{l}_z^O = [(\underline{r} - R_O) \times \hat{p}]_z$$

$$(\underline{r} - R_O) \times \hat{p} = \hat{l} - (\underline{R}_O \times \hat{p})$$

$$\langle \phi_{1s} \mid \hat{l}_z^O \mid \phi_a \rangle = \underbrace{\langle \phi_{1s} \mid \hat{l}_z \mid \phi_a \rangle}_{=0} - \underbrace{\langle \phi_{1s} \mid (\underline{R}_O \times \hat{p})_z \mid \phi_a \rangle}_{\neq 0}$$

Quantum-chemical calculation of magnetizabilities

Problem: momentum operator

$$\hat{p}\phi_{1\mathrm{s}} = \frac{\partial}{\partial x} e^{-\alpha r^2} \rightarrow \underbrace{x e^{-\alpha r^2}}_{\text{p function}}$$

Higher angular momentum functions

→ problem for incomplete basis

→ “bad” results for paramagnetic contribution

Our example:

$\langle \phi_{1s} \mid \hat{l}_z \mid \phi_a \rangle$ described without error

$\langle \phi_{1s} \mid \hat{l}_z^{\mathrm{O}} \mid \phi_a \rangle$ of worse quality, not exactly described

In the calculation, it matters where we put the gauge origin (unphysical!)

Quantum-chemical calculation of magnetizabilities

Conclusions:

Atoms: natural gauge origin in the center

Molecules: no natural gauge origin

Gauge transformation of the wave function

- Allowed gauge trafos (lead to same fields $\underline{E}$, $\underline{B}$)
- A general gauge trafo given by a unitary trafo

$$\Phi' = \Phi - \frac{\partial}{\partial t} f$$
$$\underline{A}' = \underline{A} + \nabla f$$

$$\left(H^{\mathrm{trans}} - i\frac{\partial}{\partial t} \right) = \exp\left(-if\right) \left(H^{\mathrm{orig}} - i\frac{\partial}{\partial t} \right) \exp\left(if\right)$$

- For the Schrödinger equation to still be satisfied, i.e.,

$$\left(\hat{H}^{\mathrm{trans}} - i\frac{\partial}{\partial t} \right) \Psi^{\mathrm{trans}} \quad \Longleftrightarrow \quad \left(\hat{H}^{\mathrm{orig}} - i\frac{\partial}{\partial t} \right) \Psi^{\mathrm{orig}}$$

the wave function compensates by phase oscillation

$$\Psi^{\mathrm{trans}} = \exp\left(-if\right) \Psi^{\mathrm{orig}}$$

Gauge transformation of the wave function

such that observables do not change

$$\langle \Psi^{\mathrm{trans}} \mid \hat{O}^{\mathrm{trans}} \mid \Psi^{\mathrm{trans}} \rangle = \langle \Psi^{\mathrm{orig}} \mid \hat{O}^{\mathrm{orig}} \mid \Psi^{\mathrm{orig}} \rangle$$

- Example: electron density

$$\rho^{\mathrm{trans}} \leftarrow (\Psi^{\mathrm{trans}})^* \Psi^{\mathrm{trans}} = [\exp(-if)\Psi^{\mathrm{orig}}]^* [\exp(-if)\Psi^{\mathrm{orig}}]$$
$$= \exp(0)(\Psi^{\mathrm{orig}})^* \Psi^{\mathrm{orig}} \rightarrow \rho^{\mathrm{orig}}$$

- Same properties for any choice of gauge related by allowed gauge trafos → gauge invariance

Gauge-origin transformation

- For static uniform magnetic field (using Coulomb gauge)

$B = \text{const.}$ $\qquad$ $\underline{B} = \nabla \times \underline{A}$

$$\underline{A}_{\mathrm{O}} = \frac{1}{2}(\underline{B} \times (\underline{r} - \underline{R}_{\mathrm{O}}))$$

contains arbitrary gauge-origin $\underline{R}_{\mathrm{O}}$

- Already discussed: any choice of R_O valid.
- Change of gauge-origin from the original one to the transformed one is related by gauge transformation

$$\underline{A}_{\mathrm{trans}}(\underline{r}) = \underline{A}_{\mathrm{orig}}(\underline{r}) - \underline{A}_{\mathrm{orig}}(\underline{R}_{\mathrm{trans}}) \qquad \text{see exercise}$$

$$= \underline{A}_{\mathrm{orig}}(\underline{r}) + \nabla f \qquad \text{with} \quad f(\underline{r}) = -\underline{A}_{\mathrm{orig}}(\underline{R}_{\mathrm{trans}}) \cdot \underline{r}$$

Hence indeed $\underline{A}' = \underline{A} + \nabla f$

Gauge-origin transformation

For a change from $\underline{R}_O=\underline{R}_{orig}$ to $\underline{R}_{trans}$ the exact wave function transforms as

$$\Psi_{trans}^{exact} = \exp\left[-if(\underline{r})\right]\Psi_{orig}^{exact}$$
$$= \exp\left[i\underline{A}_{orig}(R_{trans})\cdot\underline{r}\right]\Psi_{orig}^{exact}$$

$$\Psi_{trans}^{exact} = \exp\left(\frac{i}{2}\underline{B}\times(\underline{R}_{trans}-\underline{R}_{orig})\cdot\underline{r}\right)\Psi_{orig}^{exact}$$

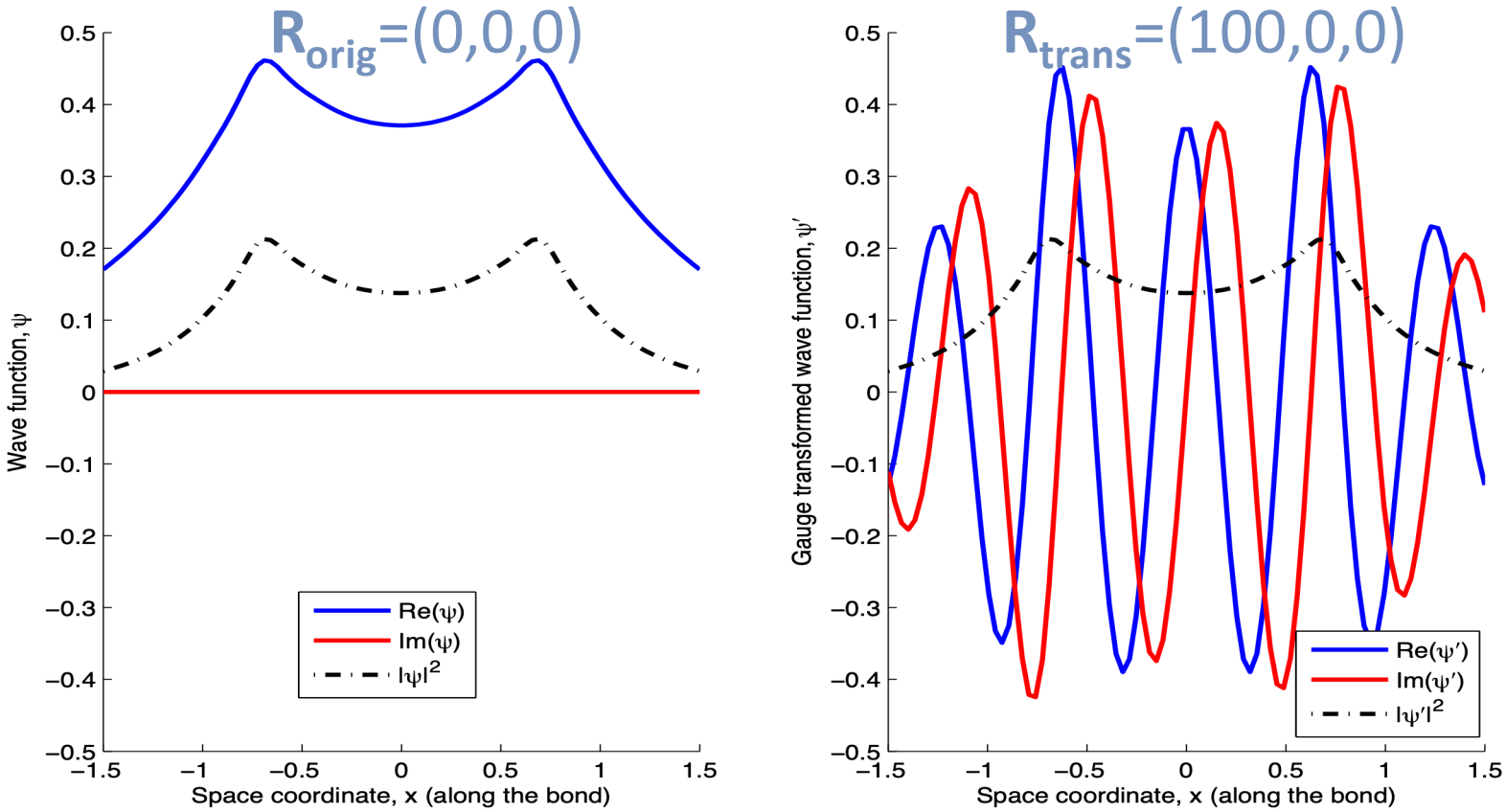
inducing phase oscillations and ensuring that observables do not change

→ ensures gauge-origin independence

→Not necessarily true for approximate wave functions!

Gauge-origin transformation

FCI Wave function of H_2 on z axis in a magnetic field of B=0.2 B_0 perpendicular to the bond



Observable quantity $|\Psi|^2$ same in both cases!

T. Helgaker lecture notes

Distinctions

- Gauge invariance
  General

$$\Phi' = \Phi - \frac{\partial}{\partial t} f$$
$$\underline{A}' = \underline{A} + \nabla f$$

- Gauge-origin independence
  within the specific case of static uniform field

- To be distinguished
  gauge-origin independence
  = gauge-origin invariance
  ≠ gauge invariance!

→ Fixed gauge-origin does not fix gauge completely

Gauge-origin dependence

- Hamiltonian depends on gauge origin
- Physical properties should not depend on choice of gauge origin

  → ensured by according trafo of wave function
- Problem: approximate wave function does not reproduce phase oscillation seen before

$$\Psi_{\mathrm{trans}} = \exp\left(\frac{i}{2}\underline{B} \times (\underline{R}_{\mathrm{trans}} - \underline{R}_{\mathrm{orig}}) \cdot \underline{r}\right)\Psi_{\mathrm{orig}}$$

Gauge-Including Atomic Orbitals

- How to solve this problem? $\Psi_{\mathrm{trans}} = \exp\left(\frac{i}{2}\underline{B} \times (\underline{R}_{\mathrm{trans}} - \underline{R}_{\mathrm{orig}}) \cdot \underline{r}\right)\Psi_{\mathrm{orig}}$
  - build transformation behavior into the basis functions!

    gauge-including atomic orbitals
    (GIAOs, also known as London orbitals)

$$\chi_\mu(\underline{r}, \underline{B}) = \exp(-\frac{i}{2}\underline{B} \times ((\underline{R}_\mu - \underline{R}_{\mathrm{O}}) \cdot \underline{r})\chi_\mu(\underline{r})$$

(London, 1937)

  - equivalent to local gauge-origins $\underline{R}_\mu$ for AOs
  - unique results (but still no gauge invariance)
  - fast basis-set convergence

nowadays standard for magnetic properties

GIAO naming conventions

Gauge-including atomic orbitals

ok

London orbitals

ok

Gauge-invariant atomic orbitals

not ideal as AOs are explicitly dependent on gauge origin

Gauge-independent atomic orbitals

not ideal as AOs are explicitly dependent on gauge origin

Elimination of gauge origin

$\langle \chi_\nu(\underline{r}, \underline{B}) | \hat{\pi}^2 | \chi_\mu(\underline{r}, \underline{B}) \rangle$ independent of gauge origin $\underline{R}_O$

$$\int d\underline{r} \; \exp(\frac{i}{2}\underline{B} \times (\underline{R}_\nu - \underline{R}_O) \cdot \underline{r}) \chi_\nu(\underline{r}) \hat{\pi}^2 \exp(-\frac{i}{2}\underline{B} \times (\underline{R}_\mu - \underline{R}_O) \cdot \underline{r}) \chi_\mu(\underline{r})$$

$$= \int d\underline{r} \; \exp(\frac{i}{2}\underline{B} \times (\underline{R}_\nu - \underline{R}_\mu) \cdot \underline{r}) \chi_\nu(\underline{r}) (-i\nabla^2 + \frac{1}{2}\underline{B} \times (\underline{r} - \underline{R}_\mu))^2 \chi_\mu(\underline{r})$$

$\Rightarrow$ results of quantum-chemical calculations independent of $\underline{R}_O$
(see also exercise session)

Consequences of use of GIAOs for magnetizabilities?

$$\chi_\mu(\underline{r},\underline{B}) = \exp(-\frac{i}{2}\underline{B}\times((\underline{R}_\mu - \underline{R}_\mathrm{O})\cdot\underline{r})\chi_\mu(\underline{r})$$

- From before
- But now: the basis functions DO depend on the magnetic field

$$2\zeta_{ij} = \frac{d^2E^{\mathrm{HF}}}{dB_i dB_j} = \sum_{\mu\nu} D_{\mu\nu}\frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial B_j} + \cancel{\frac{1}{2}\sum_{\mu\nu\sigma\rho} D_{\mu\nu}D_{\sigma\rho}\left(\frac{\partial^2\langle\mu\sigma\mid\nu\rho\rangle}{\partial B_i\partial B_j} - \frac{1}{2}\frac{\partial^2\langle\mu\sigma\mid\rho\nu\rangle}{\partial B_i\partial B_j}\right)}$$

$$\cancel{-\sum_{\mu\nu} W_{\mu\nu}\frac{\partial^2 S_{\mu\nu}}{\partial B_i\partial B_j}}$$

$$+\sum_{\mu\nu}\frac{\partial D_{\mu\nu}}{\partial B_i}\left(\frac{\partial h_{\mu\nu}}{\partial B_j} + \cancel{\sum_{\sigma\rho} P_{\sigma\rho}\left(\frac{\partial\langle\mu\sigma\mid\nu\rho\rangle}{\partial B_j} - \frac{1}{2}\frac{\partial\langle\mu\sigma\mid\rho\nu\rangle}{\partial B_j}\right)}\right)$$

$$\cancel{-\sum_{\mu\nu}\frac{\partial W_{\mu\nu}}{\partial B_j}\frac{\partial S_{\mu\nu}}{\partial B_i}}$$

Consequences of use of GIAOs for magnetizabilities?

$$\chi_\mu(\underline{r},\underline{B}) = \exp(-\frac{i}{2}\underline{B}\times((\underline{R}_\mu - \underline{R}_O)\cdot\underline{r})\chi_\mu(\underline{r})$$

- From before
- The basis functions DO depend on the magnetic field

$$2\zeta_{ij} = \frac{d^2E^{HF}}{dB_i dB_j} = \sum_{\mu\nu} D_{\mu\nu}\frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial B_j} + \frac{1}{2}\sum_{\mu\nu\sigma\rho} D_{\mu\nu}D_{\sigma\rho}\left(\frac{\partial^2\langle\mu\sigma\mid\nu\rho\rangle}{\partial B_i\partial B_j} - \frac{1}{2}\frac{\partial^2\langle\mu\sigma\mid\rho\nu\rangle}{\partial B_i\partial B_j}\right)$$
$$- \sum_{\mu\nu} W_{\mu\nu}\frac{\partial^2 S_{\mu\nu}}{\partial B_i\partial B_j}$$
$$+ \sum_{\mu\nu}\frac{\partial D_{\mu\nu}}{\partial B_i}\left(\frac{\partial h_{\mu\nu}}{\partial B_j} + \sum_{\sigma\rho} P_{\sigma\rho}\left(\frac{\partial\langle\mu\sigma\mid\nu\rho\rangle}{\partial B_j} - \frac{1}{2}\frac{\partial\langle\mu\sigma\mid\rho\nu\rangle}{\partial B_j}\right)\right)$$
$$- \sum_{\mu\nu}\frac{\partial W_{\mu\nu}}{\partial B_j}\frac{\partial S_{\mu\nu}}{\partial B_i}$$

Consequences of use of GIAOs for magnetizabilities?

- Additional integrals that contain derviatives wrt GIAOs

$$\frac{\partial S_{\mu\nu}}{\partial B_\alpha} = \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} | \chi_\nu \right\rangle + \left\langle \chi_\mu | \frac{\partial \chi_\nu}{\partial B_\alpha} \right\rangle,$$

$$\frac{\partial^2 S_{\mu\nu}}{\partial B_\alpha \partial B_\beta} = \left\langle \frac{\partial^2 \chi_\mu}{\partial B_\alpha \partial B_\beta} | \chi_\nu \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} | \frac{\partial \chi_\nu}{\partial B_\beta} \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\beta} | \frac{\partial \chi_\nu}{\partial B_\alpha} \right\rangle + \left\langle \chi_\mu | \frac{\partial^2 \chi_\nu}{\partial B_\alpha \partial B_\beta} \right\rangle,$$

$$\frac{\partial h_{\mu\nu}}{\partial B_\alpha} = \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} | h | \chi_\nu \right\rangle + \frac{1}{2} \langle \chi_\mu | ((\mathbf{r} - \mathbf{R}_O) \times \mathbf{p})_\alpha | \chi_\nu \rangle + \left\langle \chi_\mu | h | \frac{\partial \chi_\nu}{\partial B_\alpha} \right\rangle,$$

$$\begin{aligned}\frac{\partial^2 h_{\mu\nu}}{\partial B_\alpha \partial B_\beta} = & \left\langle \frac{\partial^2 \chi_\mu}{\partial B_\alpha \partial B_\alpha} | h | \chi_\nu \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} | h | \frac{\partial \chi_\nu}{\partial B_\beta} \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\beta} | h | \frac{\partial \chi_\nu}{\partial B_\alpha} \right\rangle + \left\langle \chi_\mu | h | \frac{\partial^2 \chi_\nu}{\partial B_\alpha \partial B_\beta} \right\rangle + \frac{1}{2} \left\langle \frac{\partial \chi_\mu}{\partial B_\beta} | ((\mathbf{r} - \mathbf{R}_O) \times \mathbf{p})_\alpha | \chi_\nu \right\rangle \\ & + \frac{1}{2} \left\langle \chi_\mu | ((\mathbf{r} - \mathbf{R}_O) \times \mathbf{p})_\alpha | \frac{\partial \chi_\nu}{\partial B_\beta} \right\rangle + \frac{1}{2} \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} | ((\mathbf{r} - \mathbf{R}_O) \times \mathbf{p})_\beta | \chi_\nu \right\rangle + \frac{1}{2} \left\langle \chi_\mu | ((\mathbf{r} - \mathbf{R}_O) \times \mathbf{p})_\beta | \frac{\partial \chi_\nu}{\partial B_\alpha} \right\rangle \\ & + \frac{1}{4} \langle \chi_\mu | \delta_{\alpha\beta} (\mathbf{r} - \mathbf{R}_O)^2 - (\mathbf{r} - \mathbf{R}_O)_\beta (\mathbf{r} - \mathbf{R}_O)_\alpha | \chi_\nu \rangle,\end{aligned}$$

$$\frac{\partial \langle \mu\sigma | \nu\rho \rangle}{\partial B_\alpha} = \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} \chi_\sigma | \chi_\nu \chi_\rho \right\rangle + \left\langle \chi_\mu \frac{\partial \chi_\sigma}{\partial B_\alpha} | \chi_\nu \chi_\rho \right\rangle + \left\langle \chi_\mu \chi_\sigma | \frac{\partial \chi_\nu}{\partial B_\alpha} \chi_\rho \right\rangle + \left\langle \chi_\mu \chi_\sigma | \chi_\nu \frac{\partial \chi_\rho}{\partial B_\alpha} \right\rangle,$$

Consequences of use of GIAOs for magnetizabilities?

- Additional integrals (cont')

$$\frac{\partial^2\langle\mu\sigma|\nu\rho\rangle}{\partial B_\alpha \partial B_\beta} = \left\langle \frac{\partial^2\chi_\mu}{\partial B_\alpha \partial B_\beta}\chi_\sigma|\chi_\nu\chi_\rho\right\rangle + \left\langle \chi_\mu\frac{\partial^2\chi_\sigma}{\partial B_\alpha \partial B_\beta}|\chi_\nu\chi_\rho\right\rangle + \left\langle \chi_\mu\chi_\sigma|\frac{\partial^2\chi_\nu}{\partial B_\alpha \partial B_\beta}\chi_\rho\right\rangle + \left\langle \chi_\mu\chi_\sigma|\chi_\nu\frac{\partial^2\chi_\rho}{\partial B_\alpha \partial B_\beta}\right\rangle + \left\langle \frac{\partial\chi_\mu}{\partial B_\alpha}\frac{\partial\chi_\sigma}{\partial B_\beta}|\chi_\nu\chi_\rho\right\rangle$$
$$+ \left\langle \frac{\partial\chi_\mu}{\partial B_\beta}\frac{\partial\chi_\sigma}{\partial B_\alpha}|\chi_\nu\chi_\rho\right\rangle + \left\langle \frac{\partial\chi_\mu}{\partial B_\alpha}\chi_\sigma|\frac{\partial\chi_\nu}{\partial B_\beta}\chi_\rho\right\rangle + \left\langle \frac{\partial\chi_\mu}{\partial B_\beta}\chi_\sigma|\frac{\partial\chi_\nu}{\partial B_\alpha}\chi_\rho\right\rangle + \left\langle \frac{\partial\chi_\mu}{\partial B_\alpha}\chi_\sigma|\chi_\nu\frac{\partial\chi_\rho}{\partial B_\beta}\right\rangle + \left\langle \frac{\partial\chi_\mu}{\partial B_\beta}\chi_\sigma|\chi_\nu\frac{\partial\chi_\rho}{\partial B_\alpha}\right\rangle$$
$$+ \left\langle \chi_\mu\frac{\partial\chi_\sigma}{\partial B_\alpha}|\frac{\partial\chi_\nu}{\partial B_\beta}\chi_\rho\right\rangle + \left\langle \chi_\mu\frac{\partial\chi_\sigma}{\partial B_\beta}|\frac{\partial\chi_\nu}{\partial B_\alpha}\chi_\rho\right\rangle + \left\langle \chi_\mu\frac{\partial\chi_\sigma}{\partial B_\alpha}|\chi_\nu\frac{\partial\chi_\rho}{\partial B_\beta}\right\rangle + \left\langle \chi_\mu\frac{\partial\chi_\sigma}{\partial B_\beta}|\chi_\nu\frac{\partial\chi_\rho}{\partial B_\alpha}\right\rangle + \left\langle \chi_\mu\chi_\sigma|\frac{\partial\chi_\nu}{\partial B_\alpha}\frac{\partial\chi_\rho}{\partial B_\beta}\right\rangle$$
$$+ \left\langle \chi_\mu\chi_\sigma|\frac{\partial\chi_\nu}{\partial B_\beta}\frac{\partial\chi_\rho}{\partial B_\alpha}\right\rangle.$$

- These have to be implemented (but same for all methods)

Derivatives of the basis functions

$$\chi_\mu(\underline{r},\underline{B}) = \exp(\frac{i}{2}\underline{B} \times ((\underline{R}_O - \underline{R}_\mu)\cdot\underline{r})\chi_\mu(\underline{r})$$

- Derivative wrt to one component B_α

$$\frac{\partial\chi_\mu(\underline{r},\underline{B})}{\partial B_\alpha} = \chi_\mu(\underline{r})\frac{\partial}{\partial B_\alpha} e^{\frac{i}{2}(\underline{B}\times(\underline{R}_O-\underline{R}_\mu)\cdot\underline{r})}$$

$$= \frac{i}{2}\{(\underline{R}_O - \underline{R}_\mu)\times\underline{r}\}_\alpha \; e^{\frac{i}{2}(\underline{B}\times(\underline{R}_O-\underline{R}_\mu)\cdot\underline{r})}\chi_\mu(\underline{r})$$

$$= \frac{i}{2}\{(\underline{R}_O - \underline{R}_\mu)\times\underline{r}\}_\alpha \; \chi_\mu(\underline{r},\underline{B})$$

- In the limit *B*=0 (magnetic properties), the dependence on $\underline{B}$ is removed (e^0=1) and the corresponding integrals become purely imaginary

→ can deal with in real analytic code (bookkeeping of *i*)

→ not applicable in finite magnetic field (complex code)

Quantum-chemical calculation of magnetizabilities

- Was it worth it (to introduce the GIAOs)?
- Magnetizabilities of CO, HF, basis-set convergence

basis	$\zeta^{\text{without GIAOs}}$	$\zeta^{\text{with GIAOs}}$
cc-pVDZ	-4,224	-2,642
cc-pVTZ	-3,354	-2,612
cc-pVQZ	-2,882	-2,607

fast convergence

much improved basis-set convergence when GIAOs are used!

Terminology para- and diamagnetic

- Do not confuse:
  - paramagnetic/diamagnetic as linear/quadratic in B contributions to the energy
  - paramagnetic/diamagnetic as overall magnetizability response, i.e., molecule is attracted/repelled by magnetic field
    - → closed-shell molecules typically diamagnetic
      $E^{(1)}=0$, contributions only from $E^{(2)}$
    - → open-shell molecules typically paramagnetic

Magnetizabilities for paramagnetic molecules

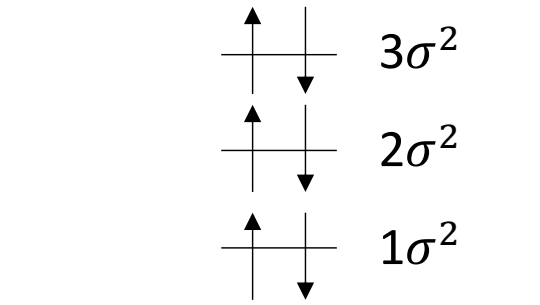
Paramagnetic molecules:		10^{-30} J T^{-2}
BH	$xx = yy$	418.7
	zz	−196.0
	total	213.8
CH^+	$xx = yy$	546.7
	zz	−113.6
	total	326.6
AlH	$xx = yy$	239.8
	zz	−358.9
	total	40.2
SiH^+	$xx = yy$	247.9
	zz	−247.3
	total	82.9
BeH^-	$xx = yy$	246.8
	zz	−588.4
	total	−31.6

Reimann et al., Mol. Phys., 117, 97, 2019

Calculated using CCSD(T), aug-cc-pCV5Z, using GIAOs

Unquenching of angular momentum due to **π** orbitals (from atomic p) and corresponding low-lying **Π** states

Field-free ground state: $^1\Sigma$



Magnetizabilities for paramagnetic molecules

- Similar results for ScH and YH

  ScH 18.7958

  YH 6.4492

CCSD(T), cc-pVQZ, using GIAOs, in a.u.

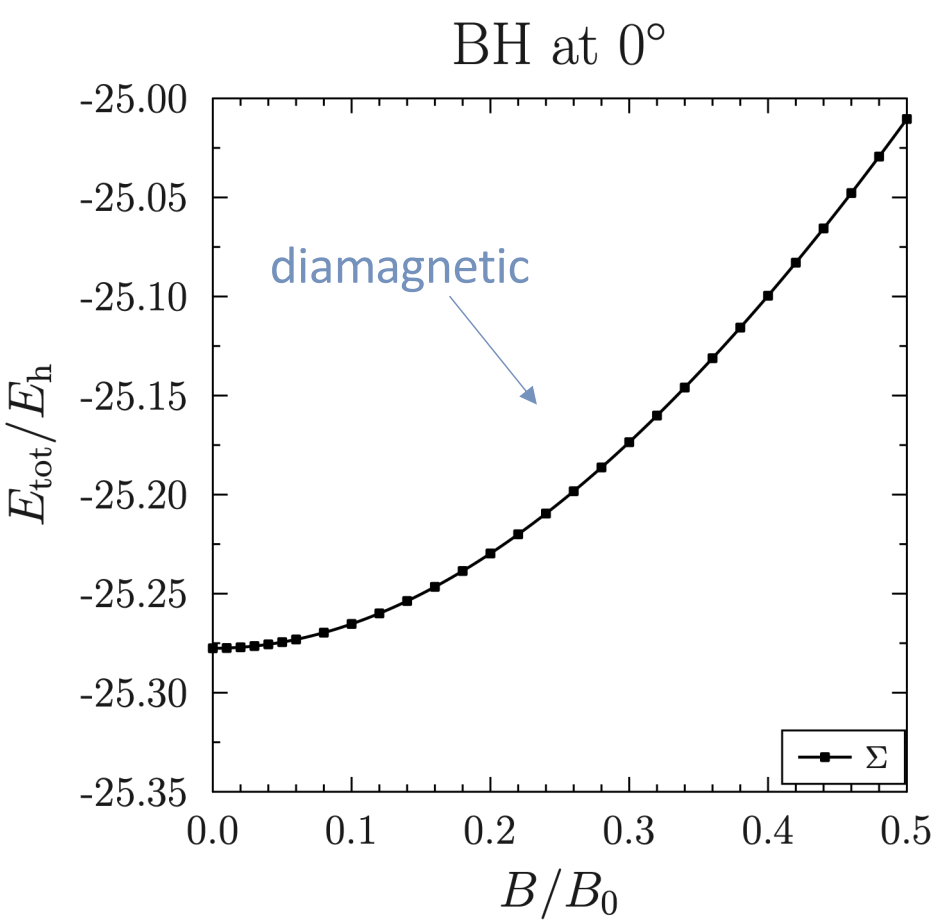
Similar effects also for π and δ orbitals (from atomic d)

Grazioli et al., J. Comp. Phys., 45, 1215, 2024

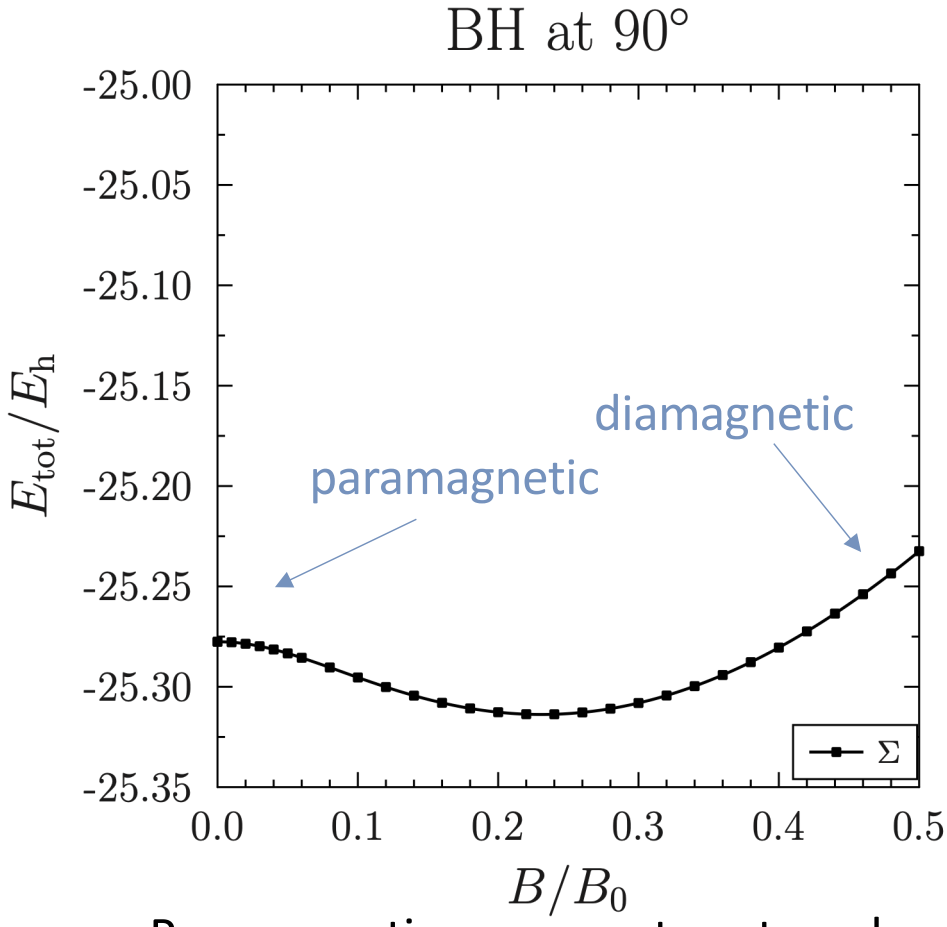
Energy of closed-shell paramagnetic molecules

Development of the energy as a function of a magnetic field

PARALLEL



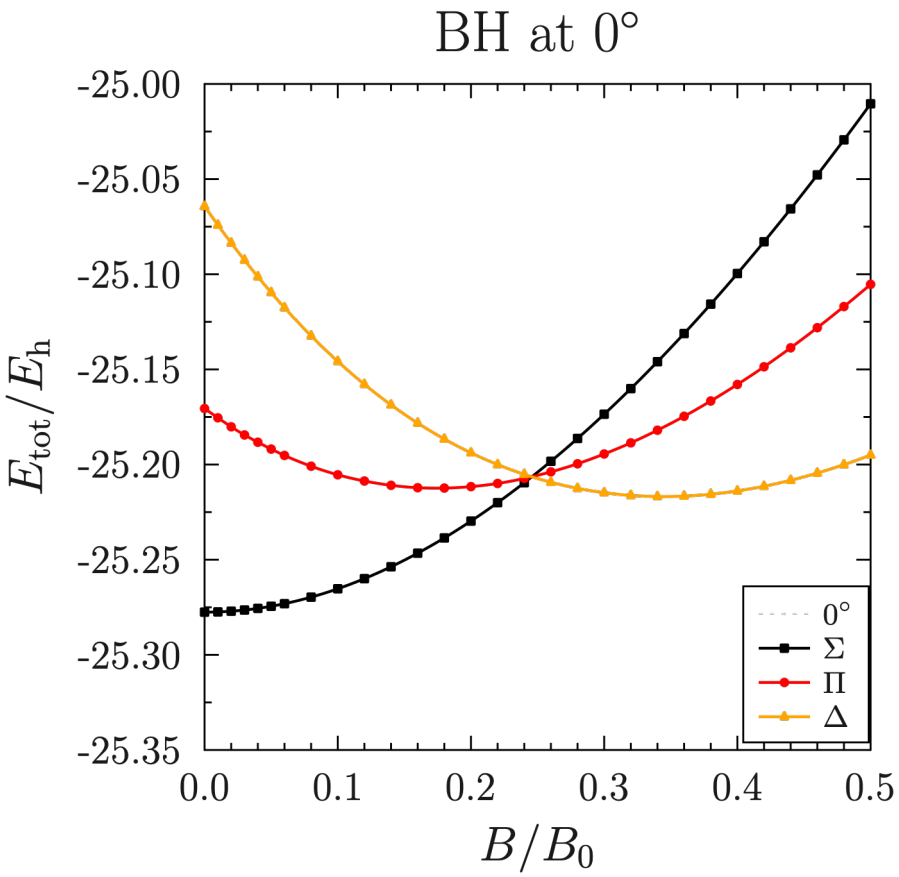
PERPENDICULAR



Paramagnetic response to external perpendicular magnetic field (up to ~0.2 B_0~50000T)

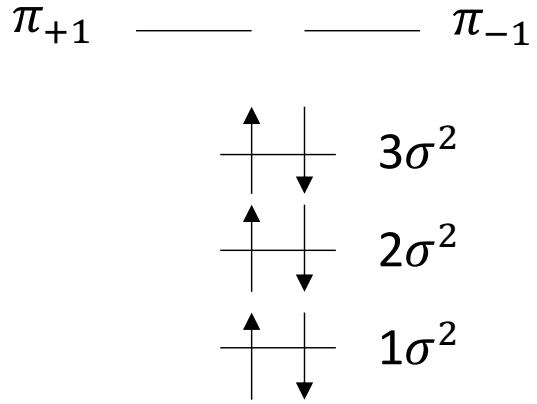
1 B_0 = 235 000 T

BH: Emergence of paramagnetism

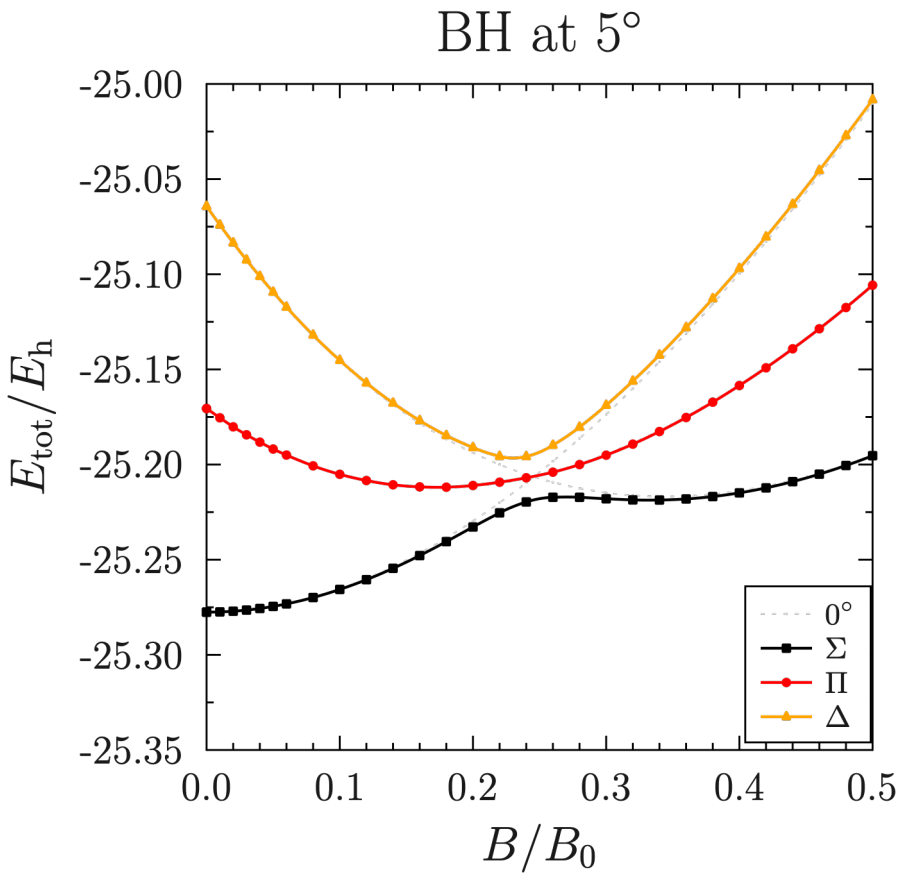


basis: unc-aug-cc-pVQZ

Field-free ground state: $^1\Sigma$

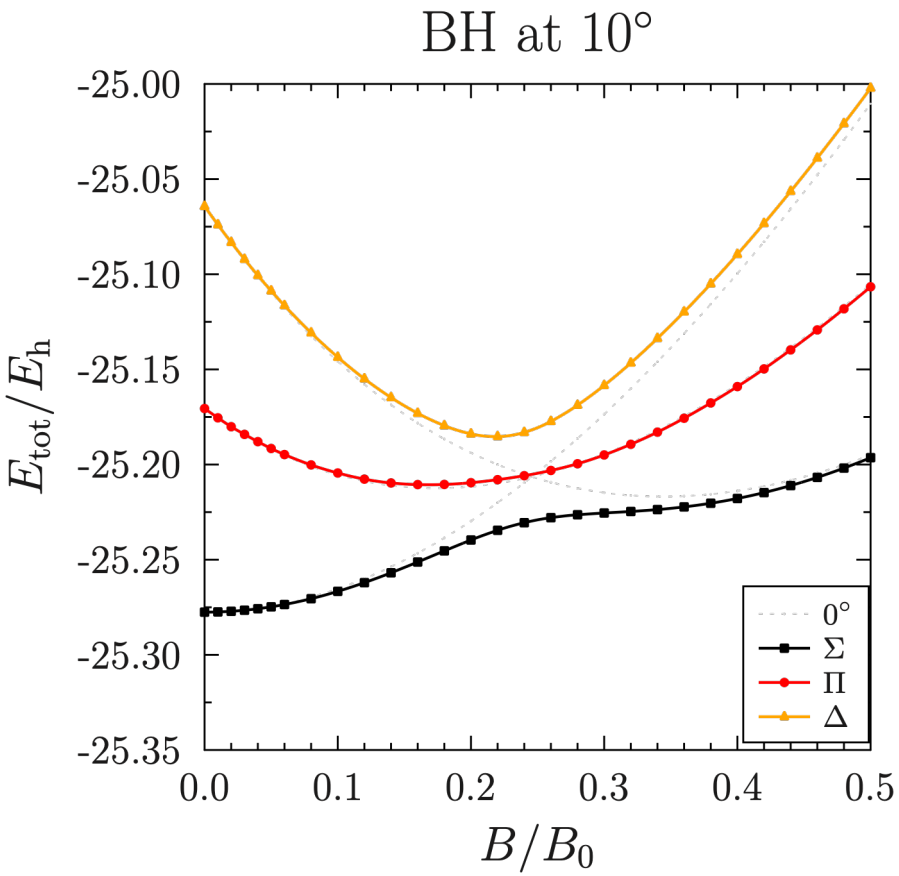


BH: Emergence of paramagnetism



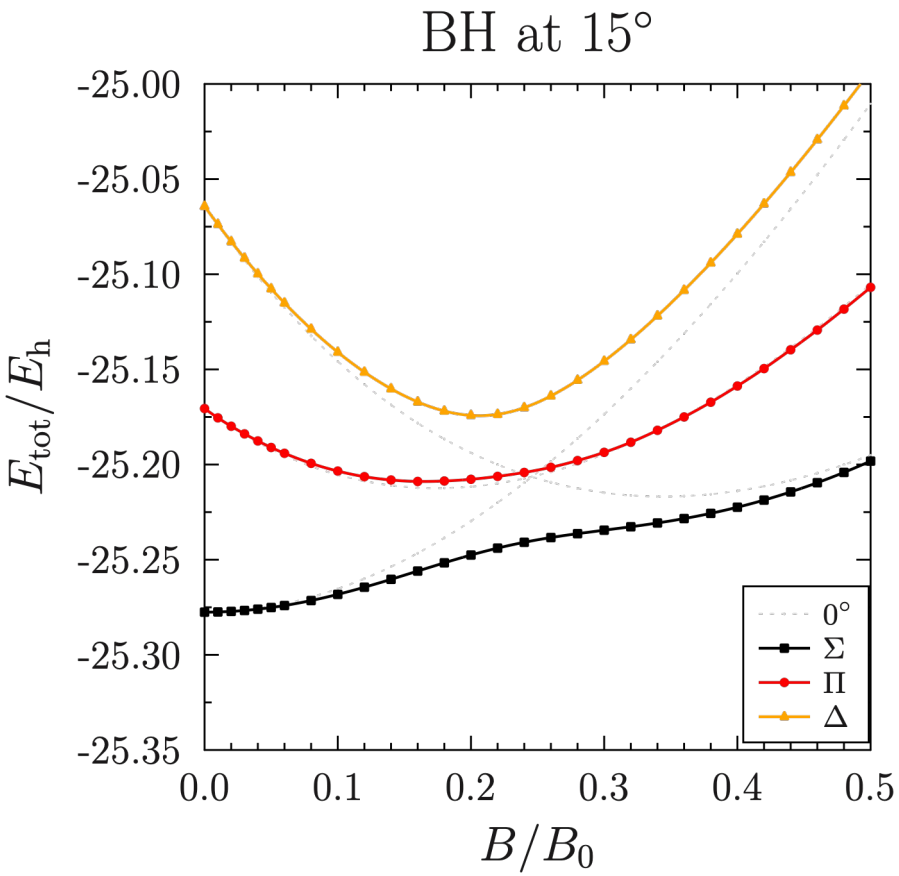
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



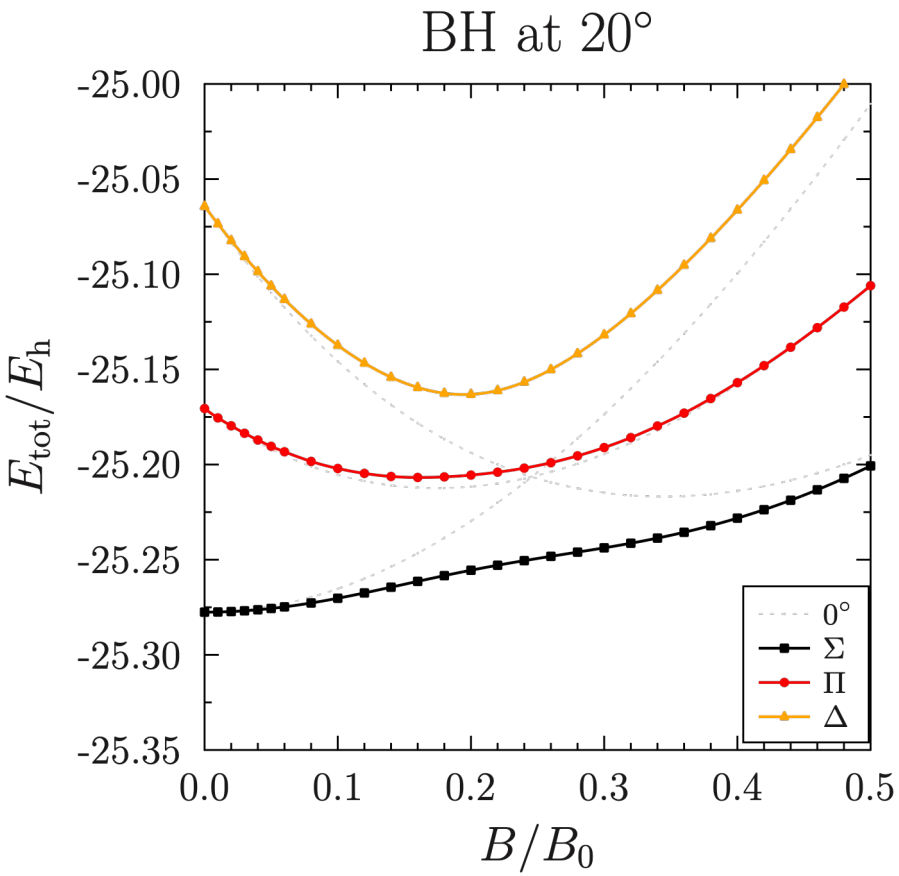
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



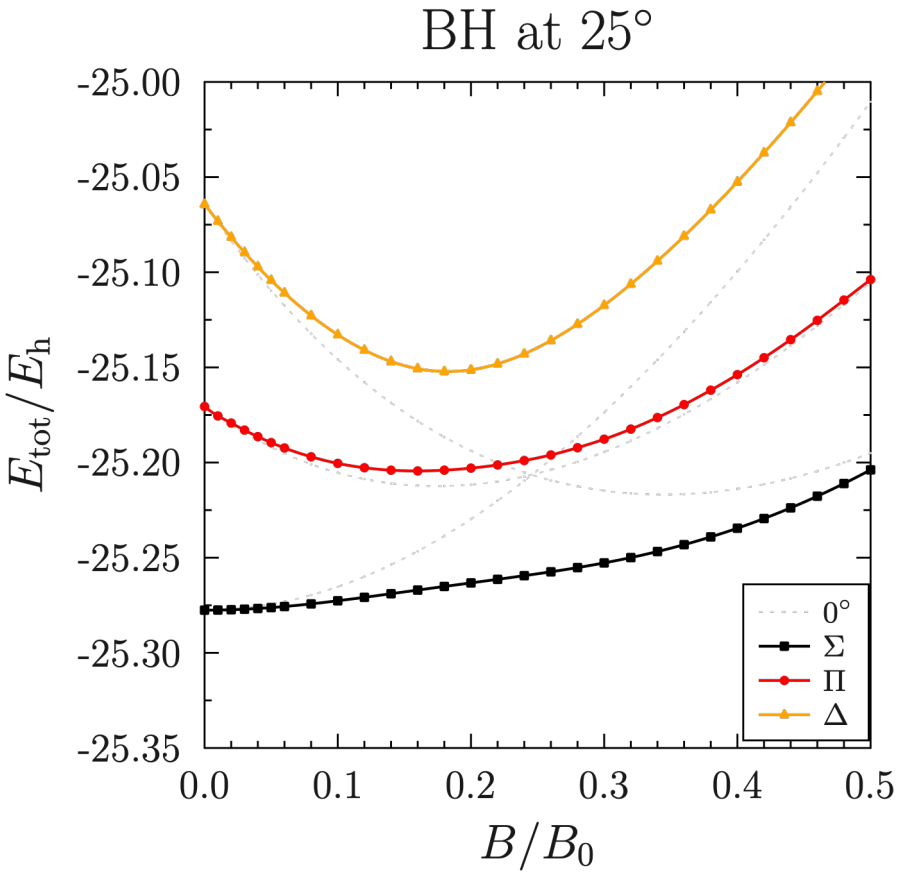
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



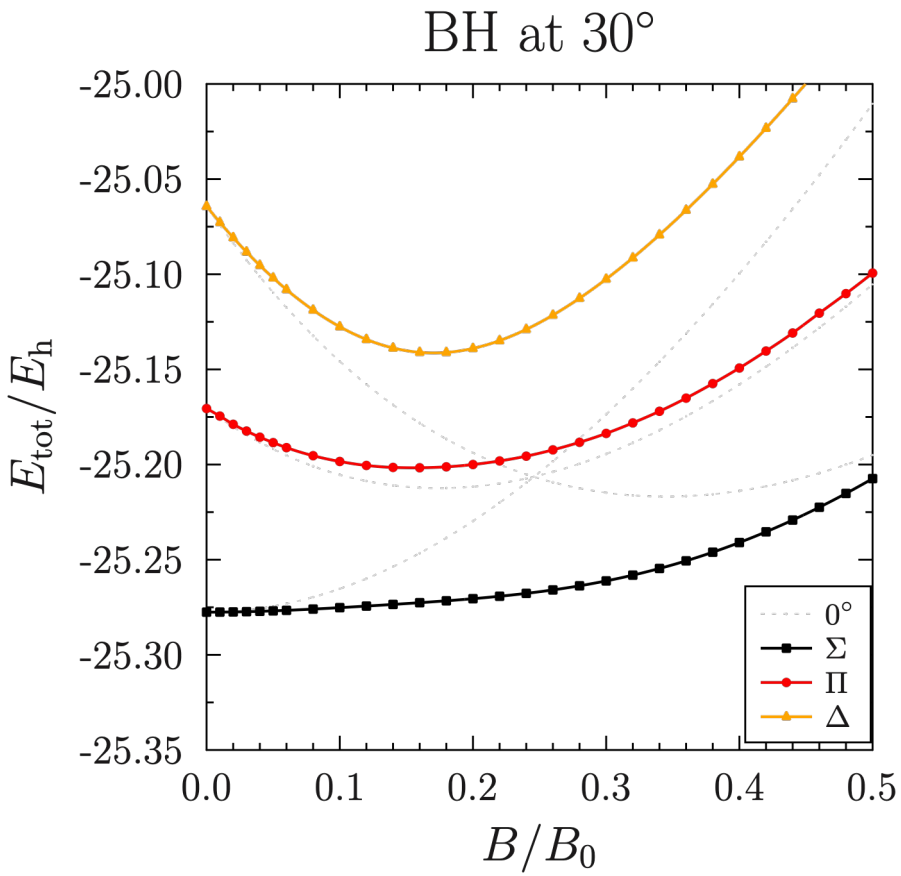
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



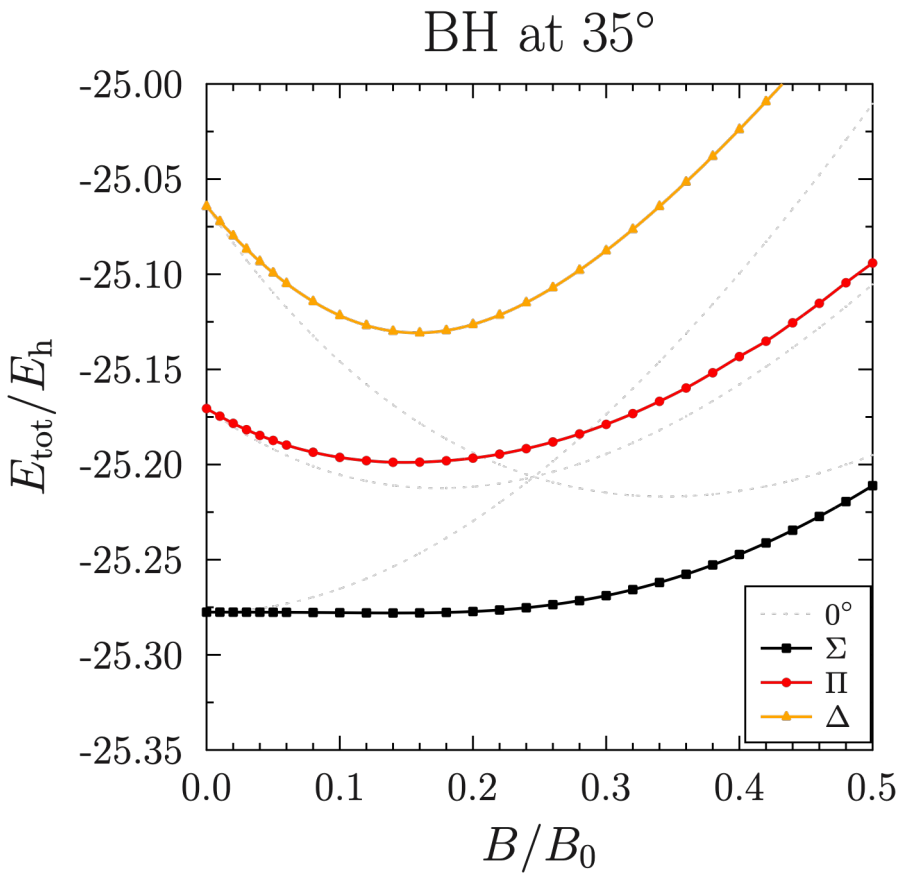
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



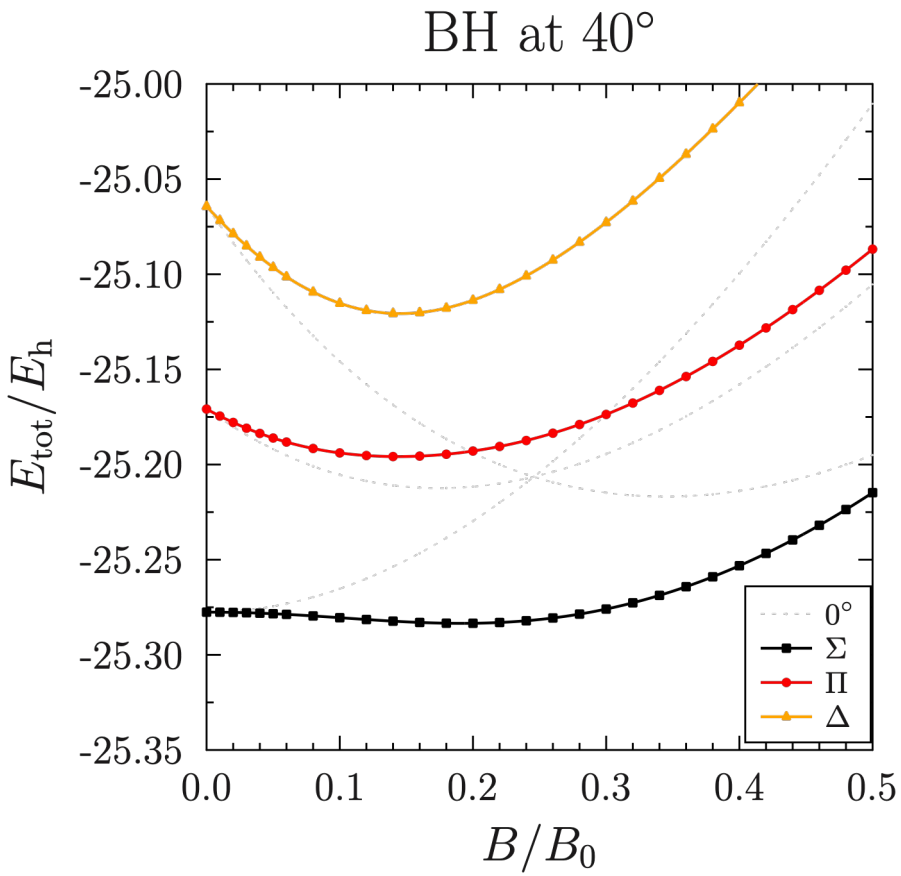
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



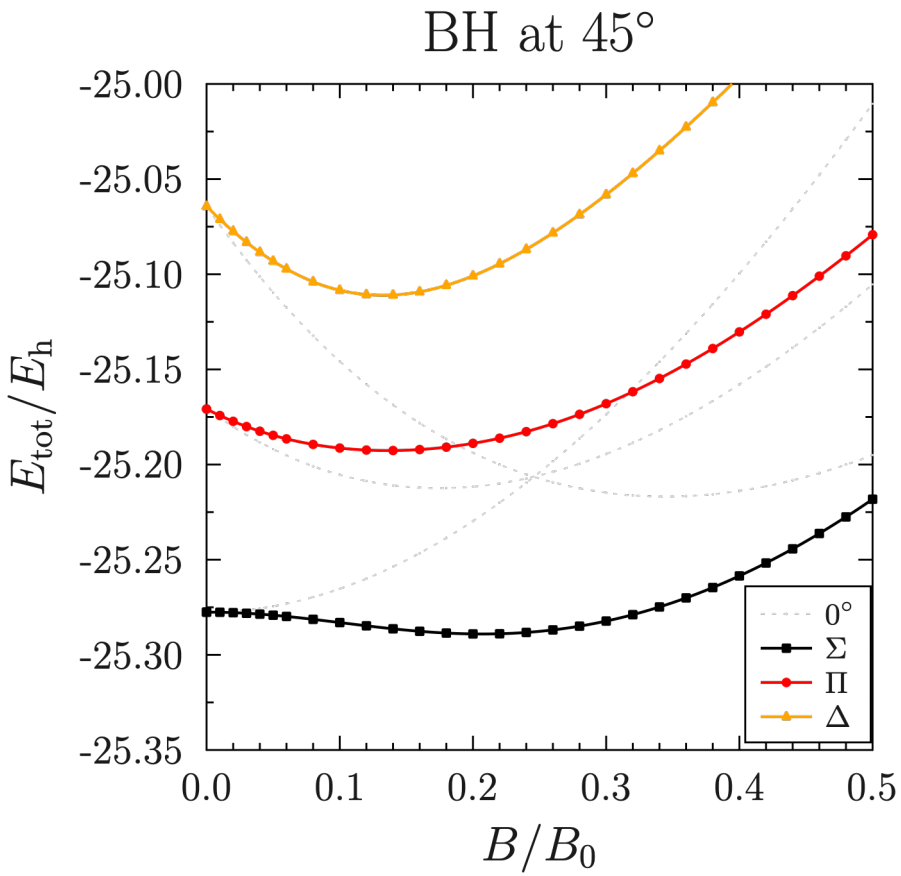
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



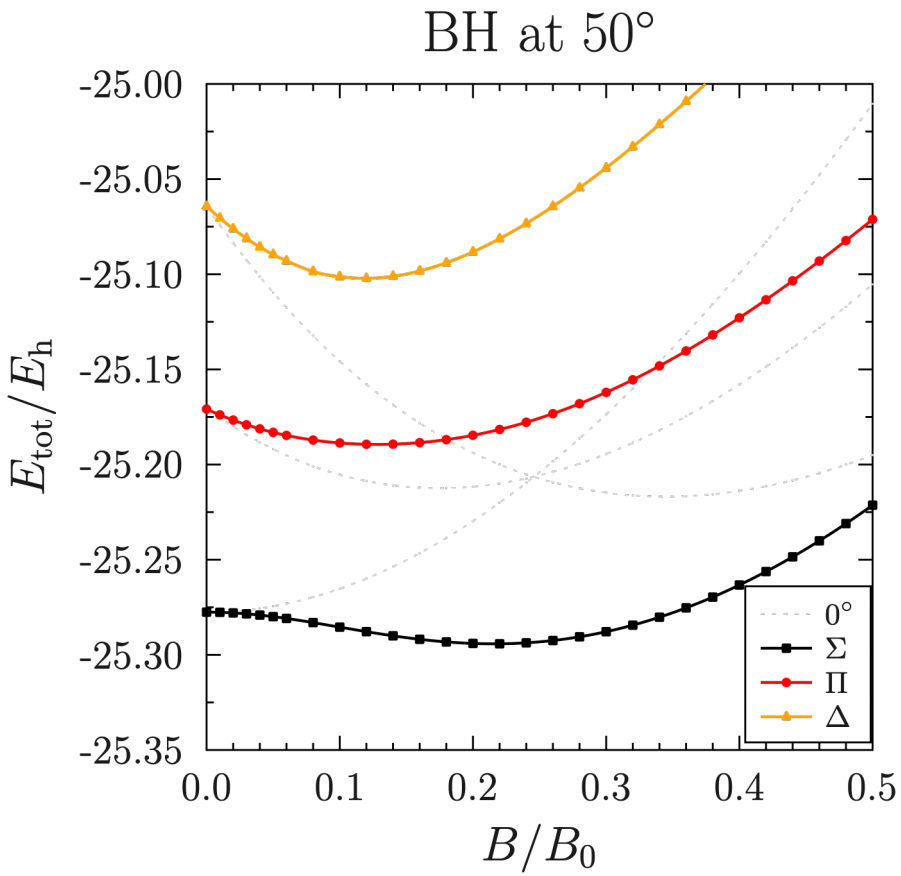
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



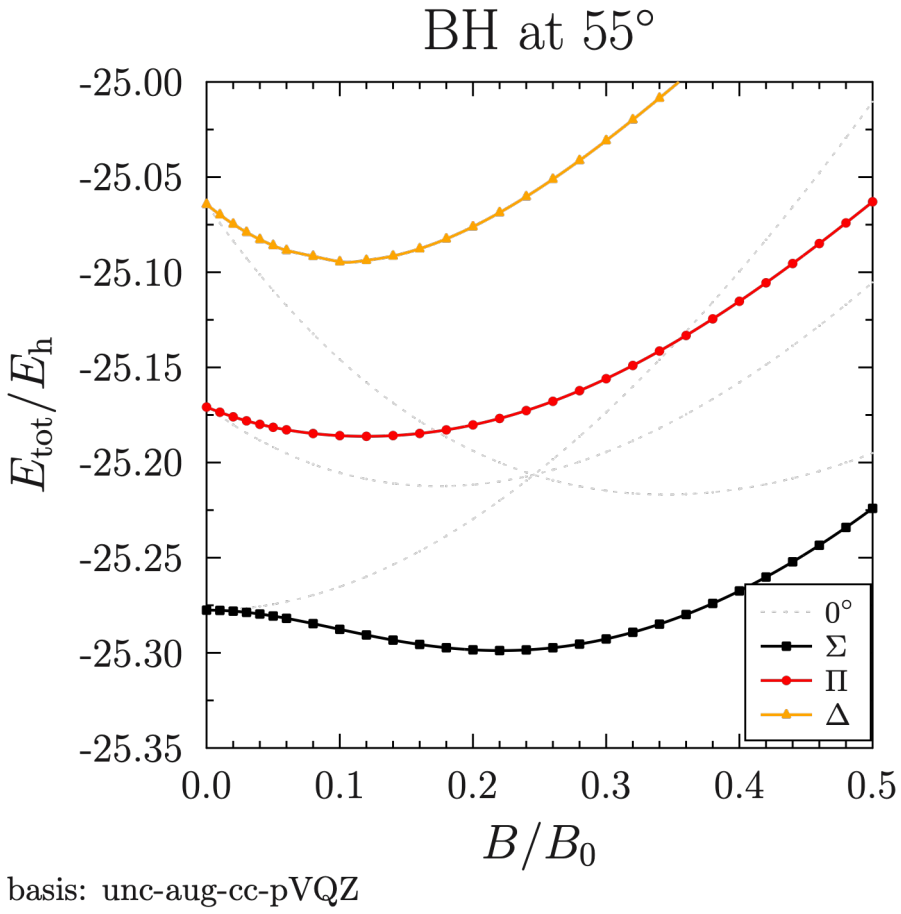
basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



basis: unc-aug-cc-pVQZ

BH: Emergence of paramagnetism



basis: unc-aug-cc-pVQZ

Becomes paramagnetic!

Paramagnetism in closed-shell molecules can also be understood as a result from Zeeman coupling between electronic states in the magnetic field

Zeeman and hyperfine interactions

FC = Fermi Contact
SD = Spin Dipolar
PSO = Paramagnetic Spin–Orbit

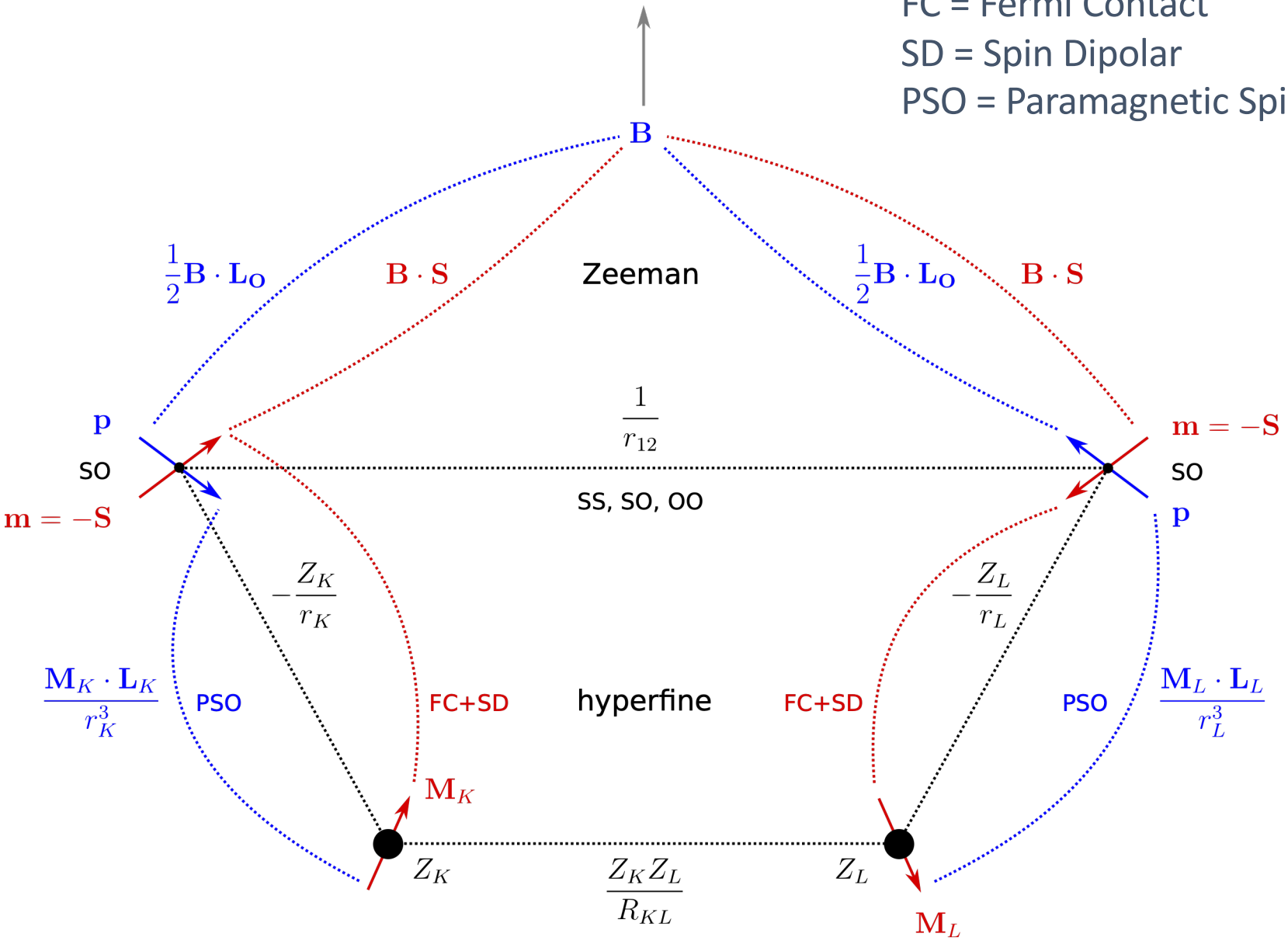


Fig. from ESQC books, chapter by T. Helgaker

Nuclear Magnetic Resonance (NMR) experiment

- Important: Shielding through electrons! Movement of electrons induces magnetic field → nuclei experience different strengths of magnetic fields

$$\underline{B}^{\text{local}} = \underline{B}^{\text{ext}} + \underline{B}^{\text{ind}}$$

$$\underline{B}^{\text{ind}} = -\underline{\sigma}_K \, \underline{B}^{\text{ext}}$$

shielding tensor: different for different molecules and nuclei, hyperfine-interaction between electrons and nuclear spins

- Interaction energy

$$E^{\text{interaction}} = -\underline{M}^{\top} \underline{B}^{\text{local}} = -\underline{M}^{\top} (\underline{I}_3 - \underline{\sigma}) \underline{B}^{\text{ext}}$$

Calculation of nuclear shielding constants

- Taylor expansion of the energy as function of magnetic moments $\underline{M}_K$ and external magnetic field $\underline{B}$ (closed-shell → no first-order terms)

$$E(\underline{M},\underline{B}) = E_0 + \sum_{KL} \underline{M}_K^\top E_{KL}^{(2,0)} \underline{M}_L + \sum_K \underline{M}_K^\top E_K^{(1,1)} \underline{B} + \underline{B}^\top E^{(0,2)} \underline{B} + \dots$$

→ NMR spin-spin couplings → NMR shieldings → magnetizability

- Perturbation theory adequate since
  - weak magnetic induction (~ 10^{-4} B_0, 1 B_0 ~ 235 000 Tesla)
  - magnetic moments couple weakly as well
- $E_K^{(1,1)}$: interaction of magnetic field and nuclear moment
  - without electrons: coupling= $-I_3$ $\quad H_{\text{nuc}}^{(1,1)} = -\sum_K \underline{M}_K^\top \underline{B}$
  - in molecule: coupling is modified by nuclear shielding tensor

$$E_K^{(1,1)} = -\underline{I}_3 + \underline{\sigma}_K$$

→ electronic contribution!

Calculation of nuclear shielding constants

$$E(\underline{M},\underline{B}) = E_0 + \sum_{KL} \underline{M}_K^\top E_{KL}^{(2,0)} \underline{M}_L + \sum_K \underline{M}_K^\top E_K^{(1,1)} \underline{B} + \underline{B}^\top E^{(0,2)} \underline{B} + \ldots$$

Connect to Taylor expansion

$$E_K^{(1,1)} = \left(\frac{\partial^2 E}{\partial \mathbf{M}_K \partial \mathbf{B}} \right)_{m_K, B=0}$$

Calculation in quantum chemistry via derivative theory!

→ Beginning lecture 1: order of differentiation?

Calculation of nuclear shielding constants

$$E(\underline{M},\underline{B}) = E_0 + \sum_{KL} \underline{M}_K^{\top} E_{KL}^{(2,0)} \underline{M}_L + \sum_{K} \underline{M}_K^{\top} E_K^{(1,1)} \underline{B} + \underline{B}^{\top} E^{(0,2)} \underline{B} + \ldots$$

Connect to Taylor expansion

$$E_K^{(1,1)} = \left(\frac{\partial^2 E}{\partial \mathbf{M}_K \partial \mathbf{B}} \right)_{m_K, B=0}$$

Calculation in quantum chemistry via derivative theory!

For any quantum-chemical method, the energy can be written as

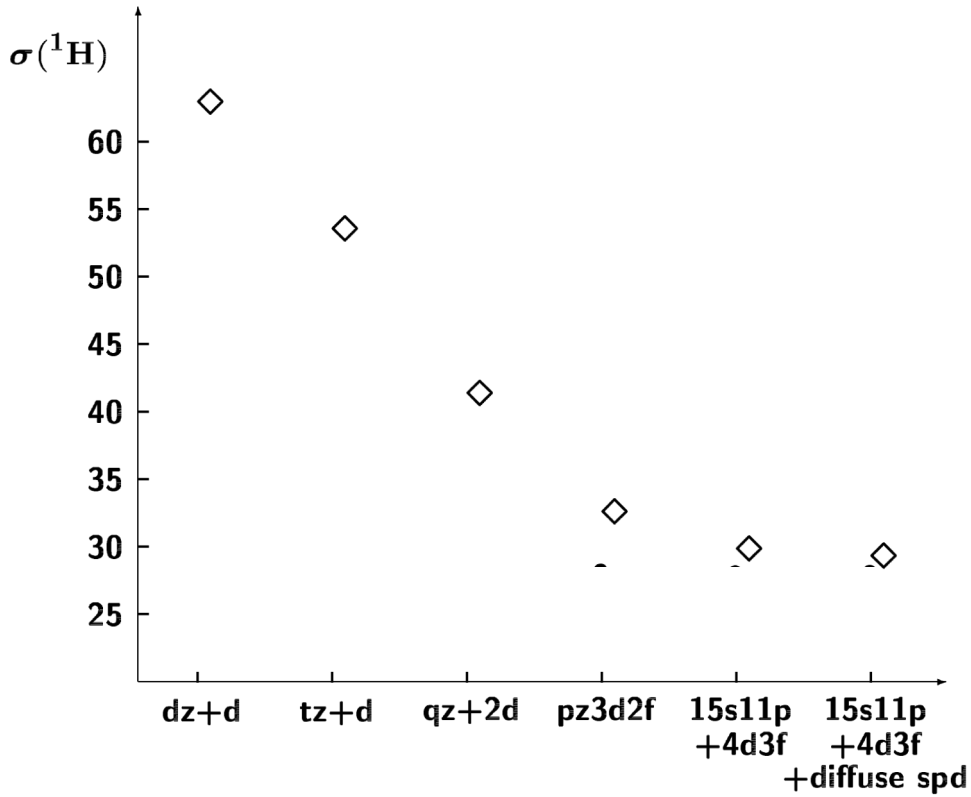
$$E = \sum_{\mu,\nu} D_{\mu\nu} h_{\mu\nu} + \sum_{\mu,\sigma,\nu,\rho} \Gamma_{\mu\nu\sigma\rho} \langle \mu\sigma \mid \nu\rho \rangle$$

Differentiate wrt. M_K and B

$$E_K^{(1,1)\mathrm{el.}} = \sum_{\mu,\nu} D_{\mu\nu} \underbrace{\left(\frac{\partial h_{\mu\nu}}{\partial B \partial M_K} \right)_{M_K, B=0}}_{\mathbf{H}_{K0}^{\mathrm{dia}}} + \sum_{\mu,\nu} \left(\frac{\partial D_{\mu\nu}}{\partial B} \right)_{B=0} \left(\frac{h_{\mu\nu}}{\partial M_K} \right)_{M_K=0}$$

$$\sigma_K = \frac{1}{3} \mathrm{Tr} \left(E_K^{(1,1)\mathrm{el.}} \right) = \frac{1}{3} \mathrm{Tr} \left(\frac{\partial^2 E^{\mathrm{el.}}}{\partial \mathbf{M}_K \partial \mathbf{B}} \right)$$

Basis-set convergence



^{1}H shielding of hydrogen fluoride

Very poor convergence wrt to basis-set limit…

J. Gauss, „Molecular properties“, published in „*Modern Methods and Algorithms of Quantum Chemistry*“ , 2000.

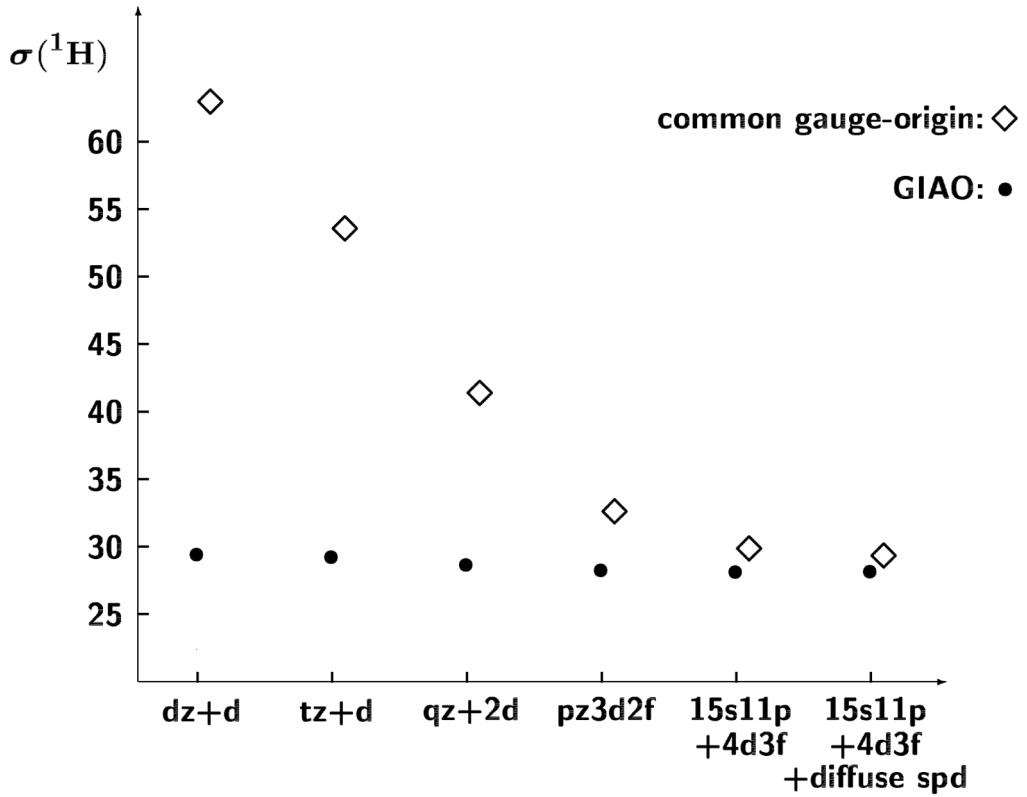
Gauge-origin dependence

basis set	gauge-origin		
	center of mass	fluorine	hydrogen
dz+d	29.3	27.6	60.1
tz+d	28.4	27.2	50.8
qz+2d	27.7	27.0	40.4

HF-SCF calculations for the proton shielding of HF

- results are not unique and depend on arbitrary choice of gauge-origin
- Again, fix by using GIAOs

Basis-set convergence

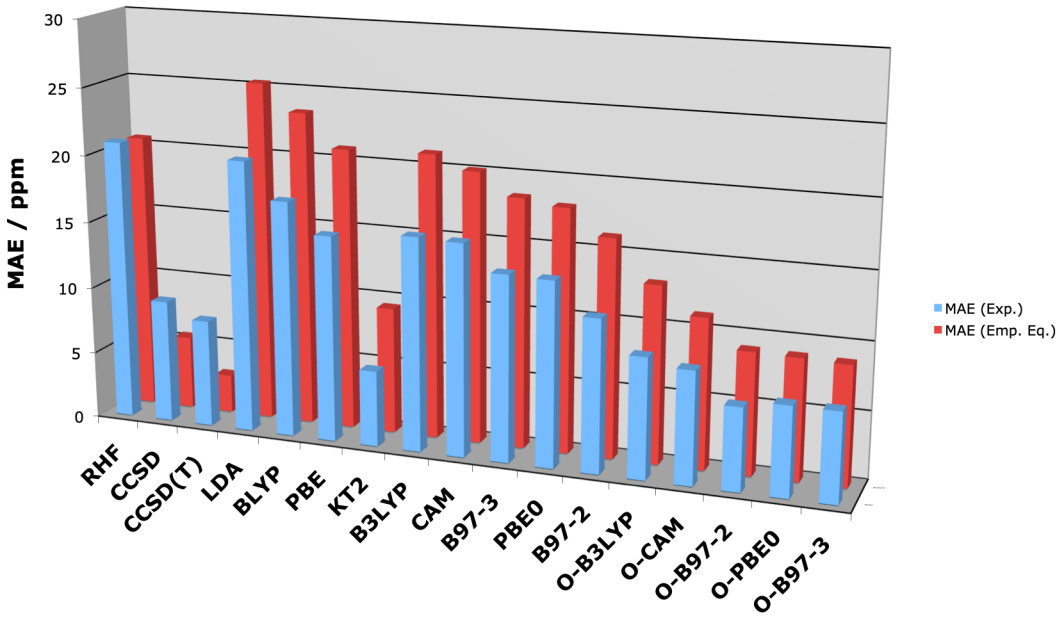


^{1}H shielding of hydrogen fluoride

J. Gauss, „Molecular properties“, published in „*Modern Methods and Algorithms of Quantum Chemistry“ ,* 2000.

NMR shieldings for various methods

- Mean absolute errors relative to experimental (blue) and empirical (red) equilibrium values



- DFT results can be of uneven quality, often ok for organic molecules and H shieldings, varies for other nuclei and more complicated electronic structures (e.g., charge-transfer etc.)
- Errors increase when vibrational corrections included

Figure from T. Helgaker. See also Teale et al. JCP 138, 024111 (2013)

^{13}C NMR chemical shieldings: accuracy of MP2

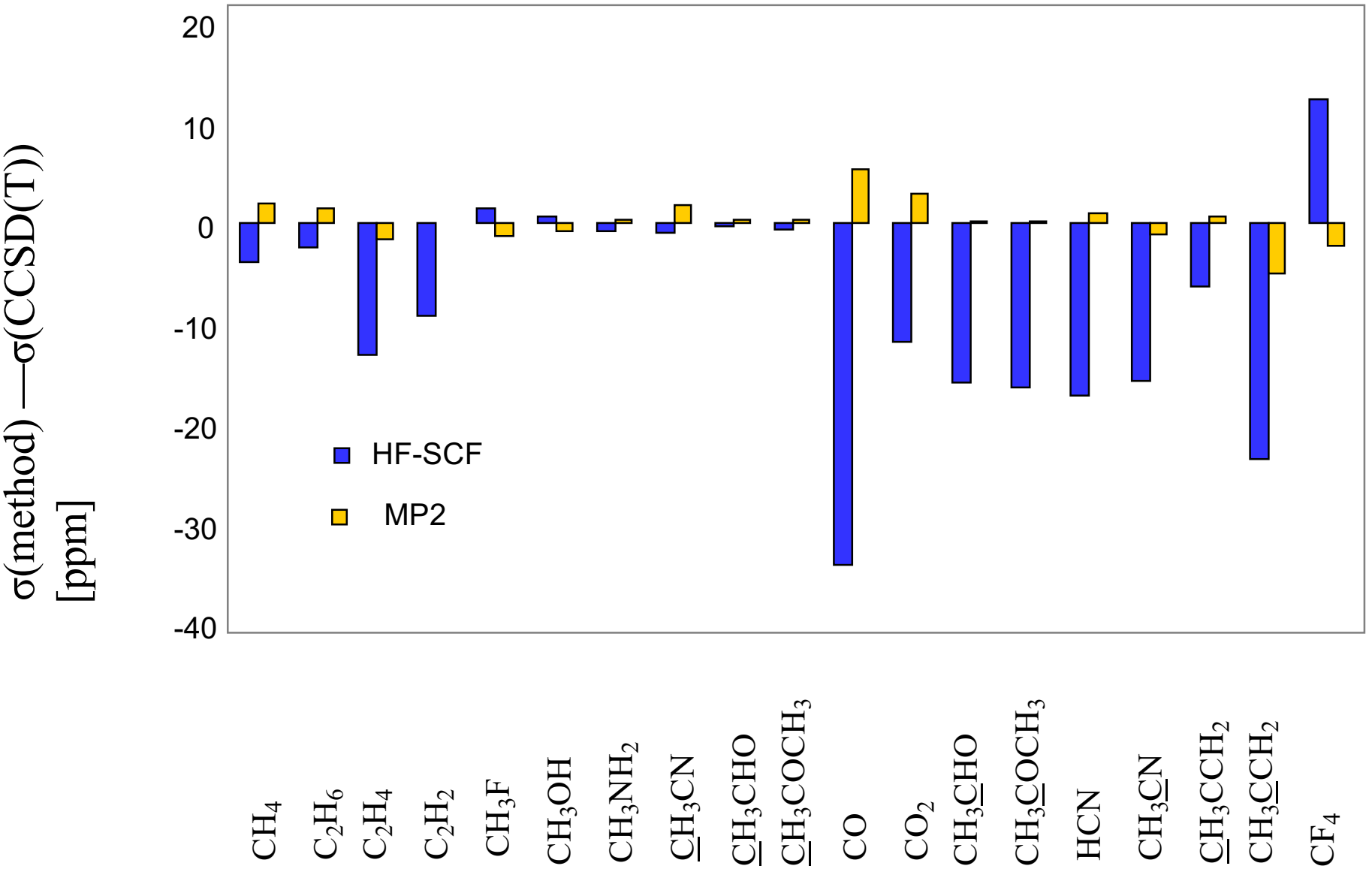


Figure from J. Gauss

Summary

- Hamiltonian for molecule in electromagnetic field
- Calculation of Magnetizabilities and NMR shieldings
- Important to ensure gauge-origin independence via use of GIAOs

Strong magnetic fields

Magnetic fields on Earth

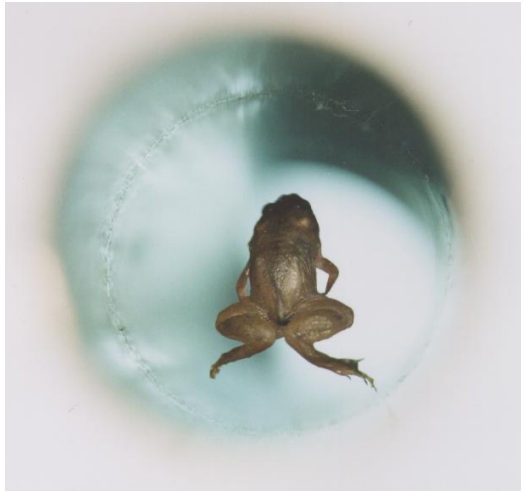
Human brain
1pT

Earth magnetic field
60μT

Refrigerator magnet
4mT

NMR
12 T

Levitate a frog
16T



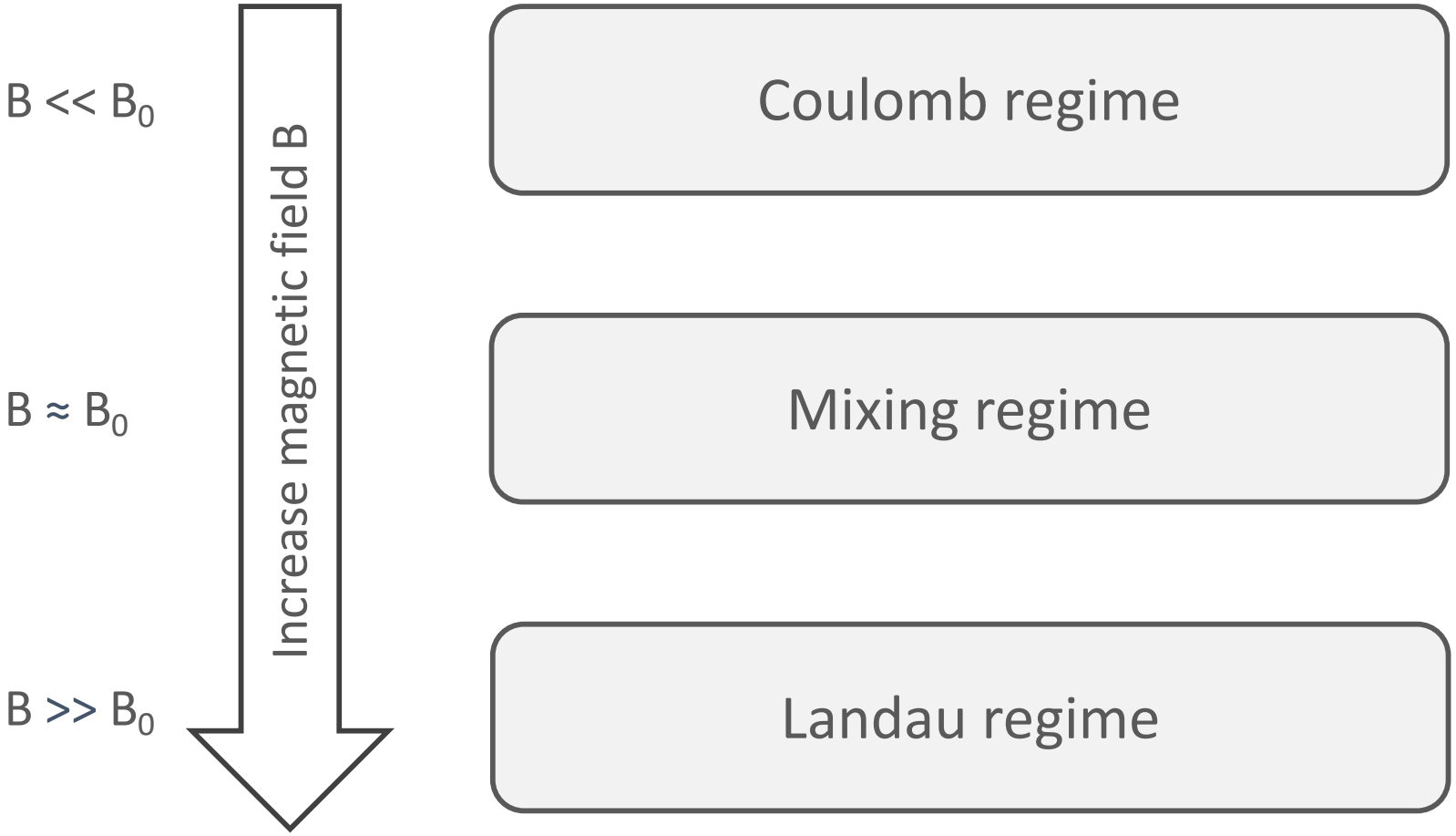
Strongest non-destructive magnet
100 T

Z-machine
~10.000 T

Cranking up the magnetic field

Atomic unit of the magnetic field B: $1B_0 = 235000\ T$

Distinguish 3 regimes:



Magnetic fields on Earth

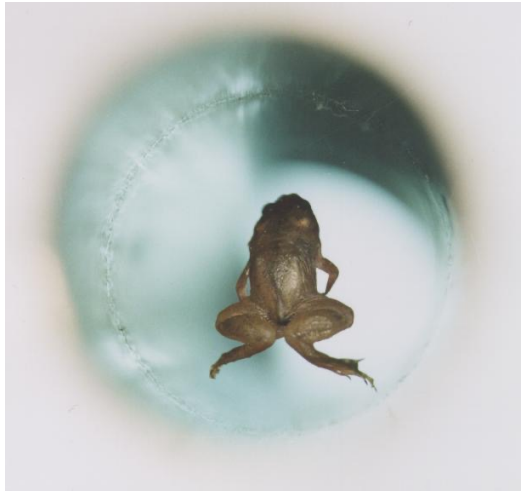
Human brain
4.35 aB_0

Earth magnetic field
260 pB_0

Refrigerator magnet
17 nB_0

NMR
51 μB_0

Levitate a frog
68 μB_0



Nelemans / HFML · CC BY-SA 3.0

Strongest non-destructive magnet
0.4 mB_0

Z-machine
0.04 B_0

Magnetic fields in space

Compact stars

Mixing regime

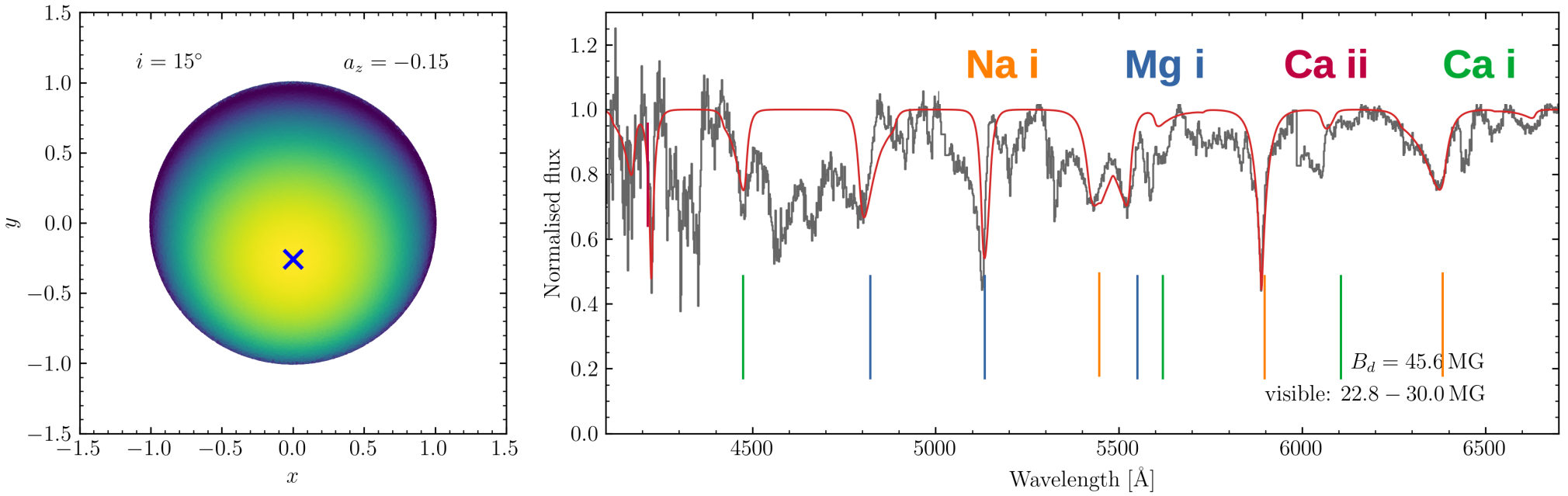
Magnetic White Dwarf stars ~3T – 100kT → up to ~0.4 B_0

Neutron stars ~1-100MT → up to ~400 B_0

Magnetars ~100MT-100GT → up to ~400 kB_0

Landau regime

Magnetic White Dwarf spectra with metals



- First assignment of metals in the spectrum of a strongly magnetic WD (~3000 T) using finite-field CC theory
- Further elements/transitions present – possibly iron …

Hollands, Stopkowicz, Hermes, Kitsaras, Hampe, Blaschke, MNRAS 520, 3560 (2023)

Molecular Hamiltonian

- Electronic Hamiltonian in homogeneous magnetic field (in a.u., with gauge origin O)

$$\hat{H} = \hat{H}_0 + \frac{1}{2}\mathbf{B}\mathbf{L}_\mathrm{O} + \mathbf{B}\mathbf{S} + \frac{1}{8}\sum_i^N \left(B^2 r_{i\mathrm{O}}^2 - (\mathbf{B}\mathbf{r}_{i\mathrm{O}})^2\right)$$

angular momentum operator

$$\mathbf{L}_\mathrm{O} = -\sum_k^N i\mathbf{r}_k^\mathrm{O} \times \boldsymbol{\nabla}_k$$

→ complex wave function!

→ origin dependence in $\hat{H}$: use of GIAOs important

Finite-field methods

- Magnetic field treated non-perturbatively
  Example: Static magnetic field input: (B_x, B_y, B_z)
- Wave-function is complex → complex orbitals and other wave-function parameters → complex integrals
  In particular: New software implementations needed!
- Efficiency:
  - Larger computational cost (Factor 4 in matrix multiplication (Factor 3 with specialized BLAS routines)
  - Larger memory requirements (Factor 2 and more)
  - Less permutational symmetry: Factor 4 instead of 8 in 2-electron integrals

$$h_{pq} \neq h_{qp}, \quad h_{pq} = h^*_{qp}$$

$$< pq|rs > = < rs|pq >^* = < qp|sr > = < sr|qp >^*$$

$$(\neq < ps|rq > \neq < rq|ps > \neq < qr|sp > \neq < sp|qr >)$$

Molecular Hamiltonian

- Electronic Hamiltonian in homogeneous magnetic field (in a.u.)

$$\hat{H} = \hat{H}_0 + \frac{1}{2}\mathbf{B}\mathbf{L}_\mathrm{O} + \mathbf{B}\mathbf{S} + \frac{1}{8}\sum_i^N \left(B^2 r_{i\mathrm{O}}^2 - (\mathbf{B}\mathbf{r}_{i\mathrm{O}})^2\right)$$

for a field in z-direction

$$\underline{B} = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix}$$

$$\hat{H} = \hat{H}_0 + \frac{1}{2}B\hat{L}_z + B\hat{S}_z + \frac{1}{8}\sum_i^N B^2 \left(x_i^2 + y_i^2\right)$$

Molecular Hamiltonian

Electronic Hamiltonian for molecule in a homogeneous magnetic field in *z*-direction (in a.u.)

$$\hat{H} = \hat{H}_0 + \frac{1}{2}B\hat{L}_z + B\hat{S}_z + \frac{1}{8}\sum_i^N B^2\left(x_i^2 + y_i^2\right)$$

***Orbital-Zeeman* term**

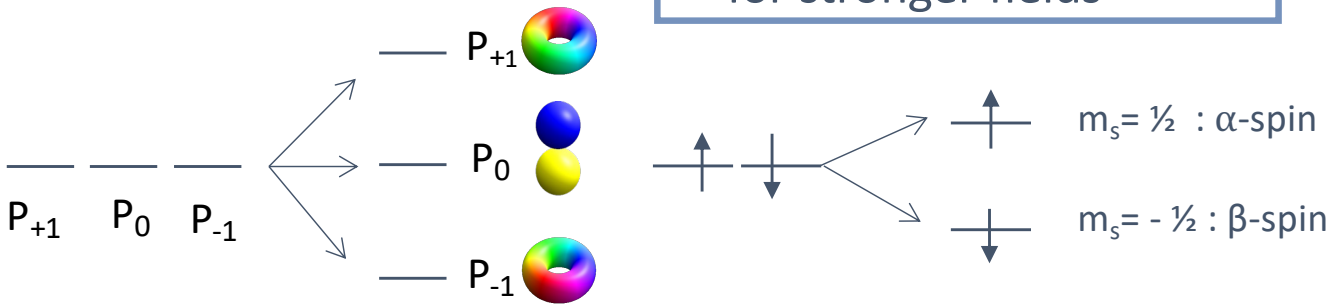
- leads to complex wave function
- gauge-origin dependent

***Spin-Zeeman* term**

- lifts degeneracy of alpha and beta spin
- favorization of high-spin states open-shell states for stronger fields

***diamagnetic* term**

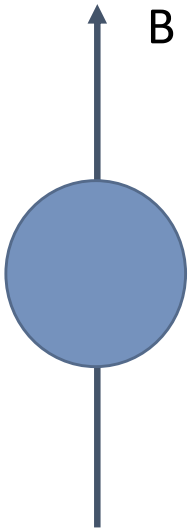
- always positive
- confinement
- gauge-origin dependent



$$p_{+1} = -\frac{1}{\sqrt{2}}(p_x + ip_y), \quad p_{-1} = \frac{1}{\sqrt{2}}(p_x - ip_y)$$

Atom in magnetic field

- Symmetry

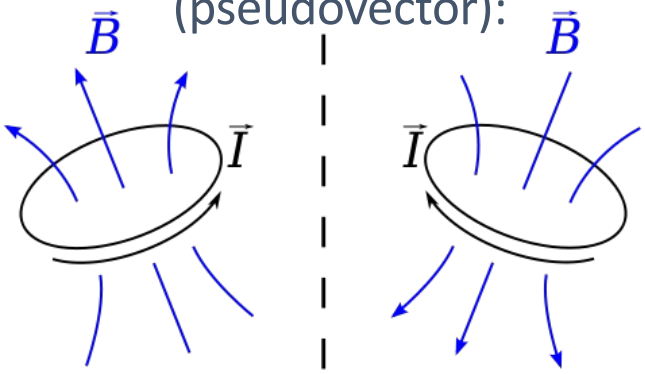


- Only rotation along B, but any angle C_∞
- Mirror planes?

→ Perpendicular to B (non-intuitive)

$C_{\infty h}$

B is an axial vector (pseudovector):



$C_{\infty h}$ character table

	$C_{\infty h}$	E	$2C_\infty^\phi$	...	$2S_\infty^\phi$	...		
σ_g	A_g	1	1	...	1	...	I_z	$x^2+y^2;z^2$
σ_u	A_u	1	1	...	-1	...	z	
$\pi_{+1,g}$ $\pi_{-1,g}$	E_{1g}	1 1	$\exp(i\phi)$ $\exp(-i\phi)$	...	$-\exp(i\phi)$ $-\exp(-i\phi)$	...	(I_x, I_y)	(zx, yz)
$\pi_{+1,u}$ $\pi_{-1,u}$	E_{1u}	1 1	$\exp(i\phi)$ $\exp(-i\phi)$	...	$\exp(i\phi)$ $\exp(-i\phi)$	...	(x, y)	
$\delta_{+2,g}$ $\delta_{-2,g}$	E_{2g}	1 1	$\exp(2i\phi)$ $\exp(-2i\phi)$	...	$-\exp(2i\phi)$ $-\exp(-2i\phi)$	...		(x^2-y^2, xy)
$\delta_{+2,u}$ $\delta_{-2,u}$	E_{2u}	1 1	$\exp(2i\phi)$ $\exp(-2i\phi)$	...	$\exp(2i\phi)$ $\exp(-2i\phi)$	...		
	...	...	...	...	...	...		
	E_{ng}	1 1	$\exp(ni\phi)$ $\exp(-ni\phi)$	...	$-\exp(ni\phi)$ $-\exp(-ni\phi)$	...		
	E_{nu}	1 1	$\exp(ni\phi)$ $\exp(-ni\phi)$	...	$\exp(ni\phi)$ $\exp(-ni\phi)$	...		
	...	...	...	...	...	...		

(S_∞^ϕ specifically includes the σ_h and i operations with $\phi=2\pi$ and $\phi=\pi$ respectively.)

https://www.staff.ncl.ac.uk/j.p.goss/symmetry/Categorisation.html

Symmetry of the orbitals of atoms in a magnetic field

- Consequences

s	p_{-1}	p_0	p_{+1}	d_{-2}	d_{-1}	d_0	d_{+1}	d_{+2}
σ_g	$\pi_{-1,u}$	σ_u	$\pi_{+1,u}$	$\delta_{-2,g}$	$\pi_{-1,g}$	σ_g	$\pi_{+1,g}$	$\delta_{+2,g}$

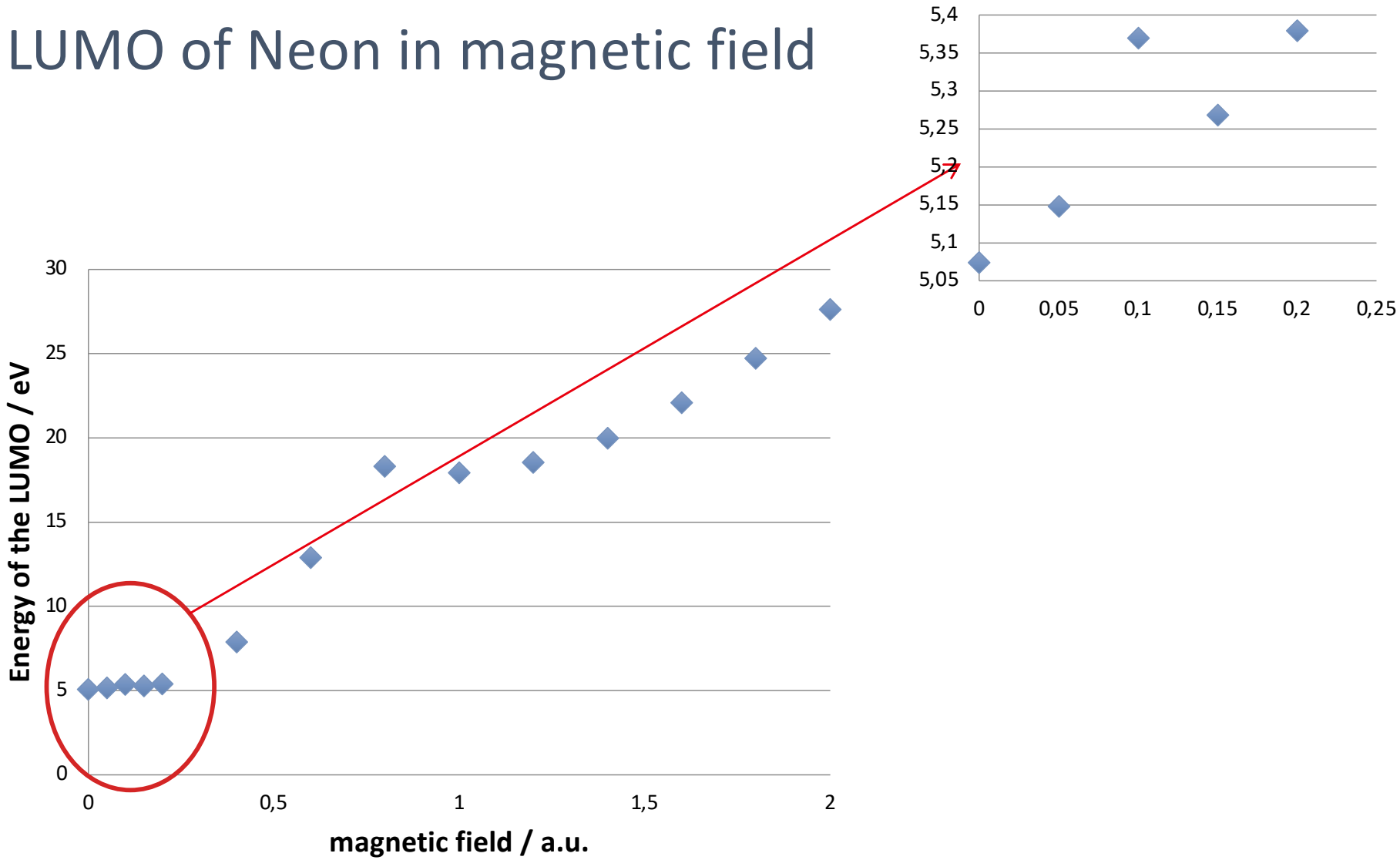
$$\hat{H} = \hat{H}_0 + \frac{1}{2}B\hat{L}_z + B\hat{S}_z + \frac{1}{8}\sum_i^N B^2\left(x_i^2 + y_i^2\right)$$

Still eigenfunctions to L_z $\quad L_z = m\hbar$

Same is true for linear molecules ($C_{\infty h}$ or C_∞)

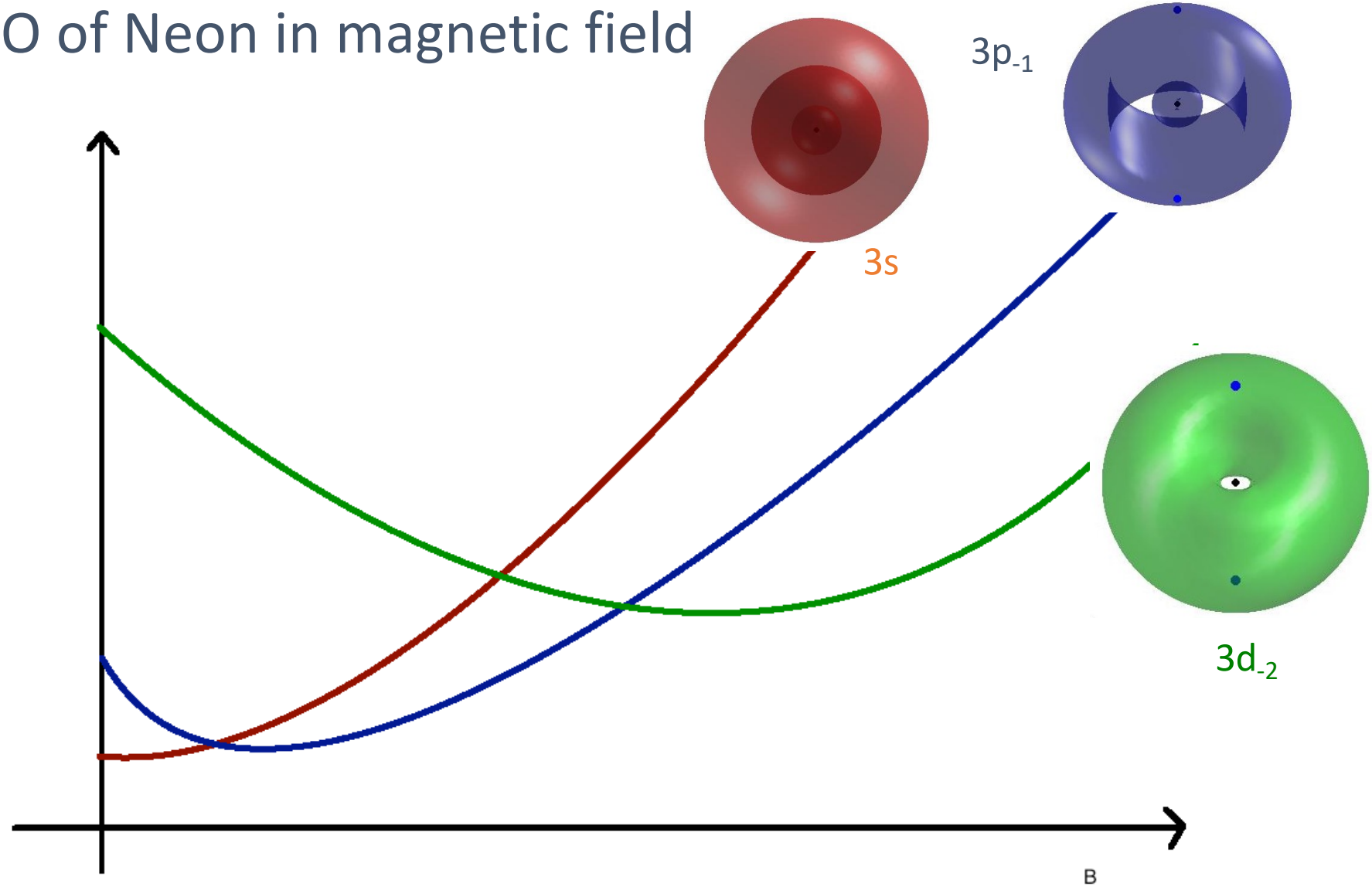
Paramagnetic effects

- LUMO of Neon in magnetic field



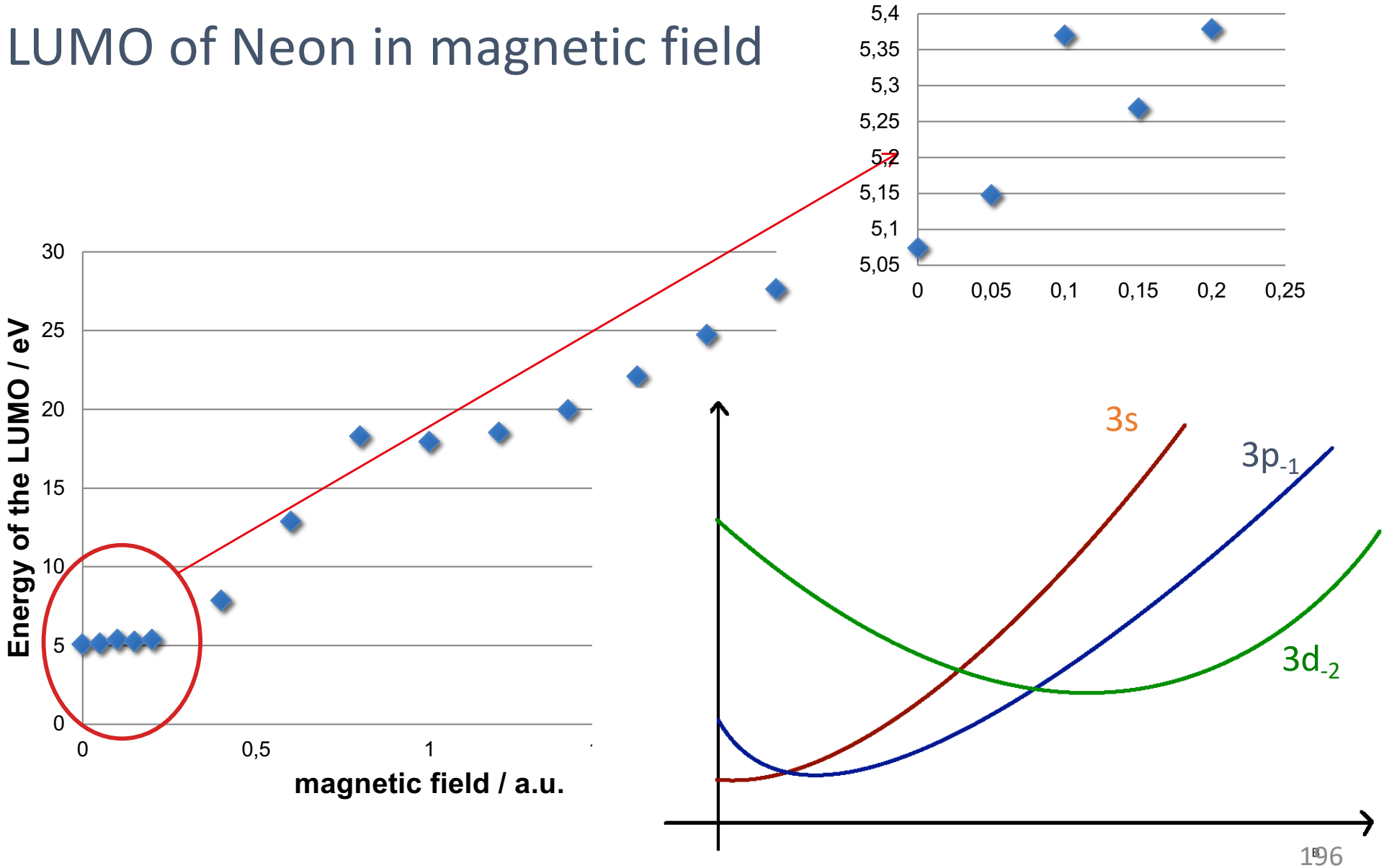
Paramagnetic effects

- LUMO of Neon in magnetic field

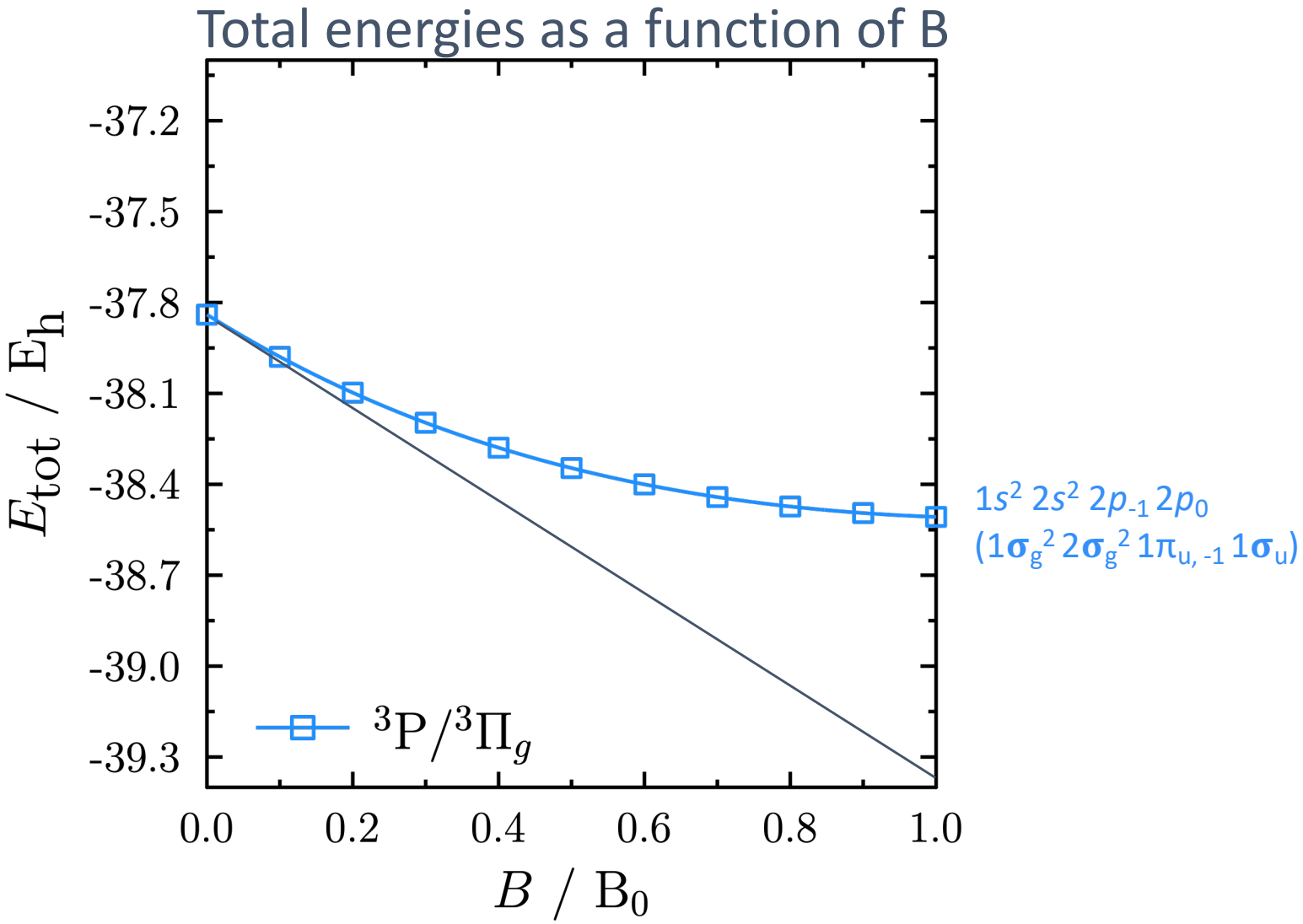


Paramagnetic effects

- LUMO of Neon in magnetic field



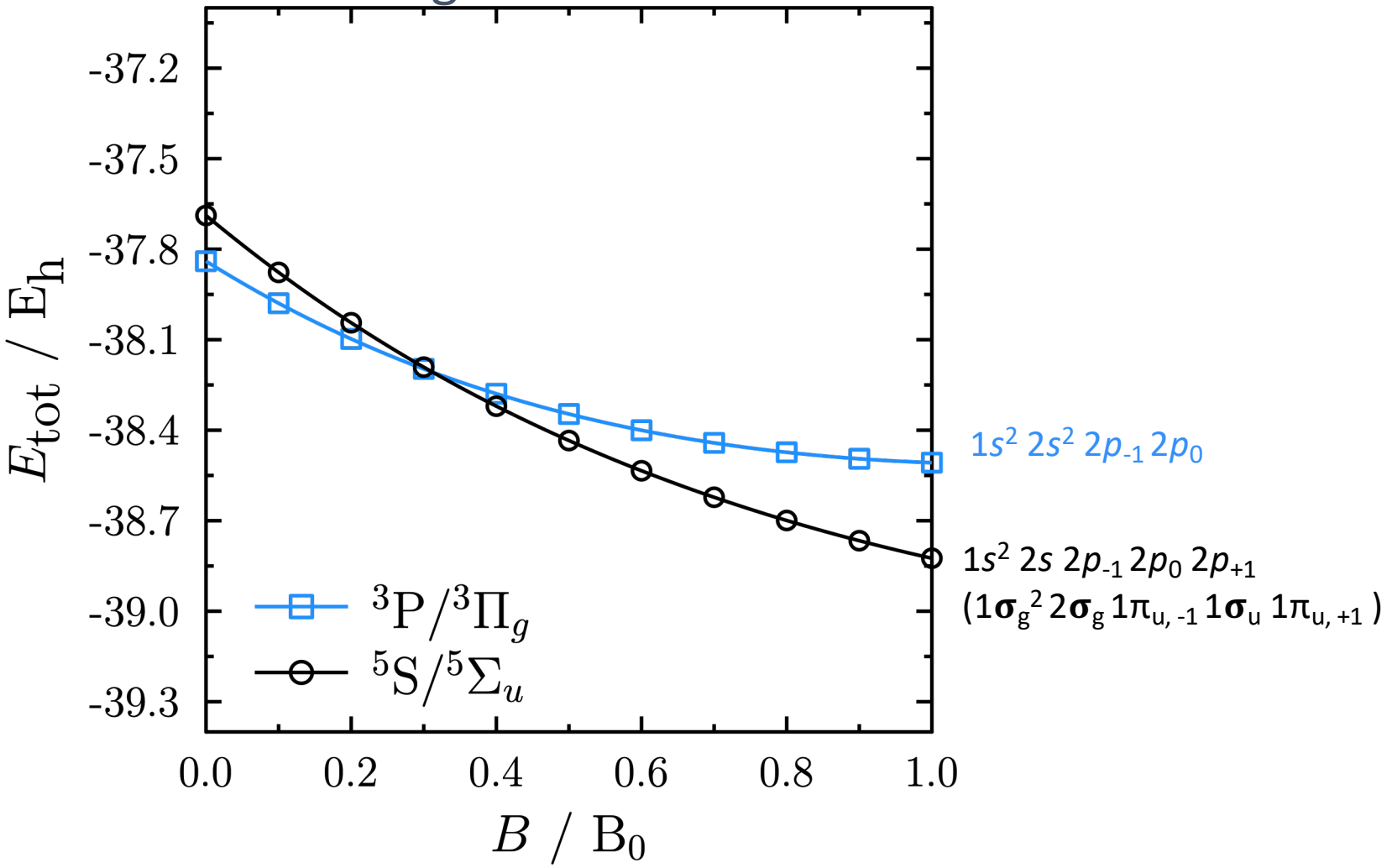
Ground state of the C atom in a magnetic field



Hampe and Stopkowicz, J. Chem. Phys., 146, 154105 (2017)

Ground state of the C atom in a magnetic field

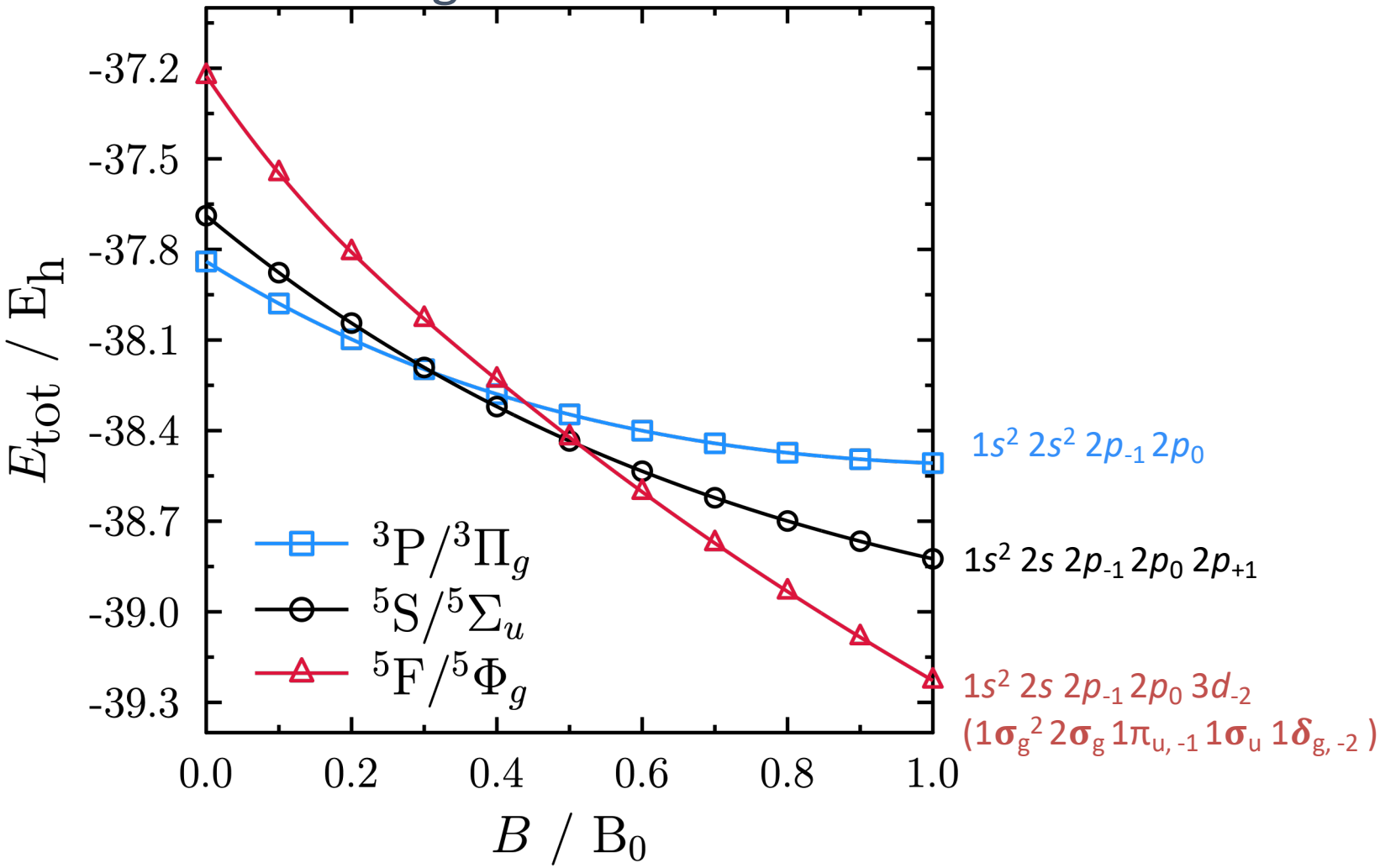
Total energies as a function of B



Hampe and Stopkowicz, J. Chem. Phys., 146, 154105 (2017)

Ground state of the C atom in a magnetic field

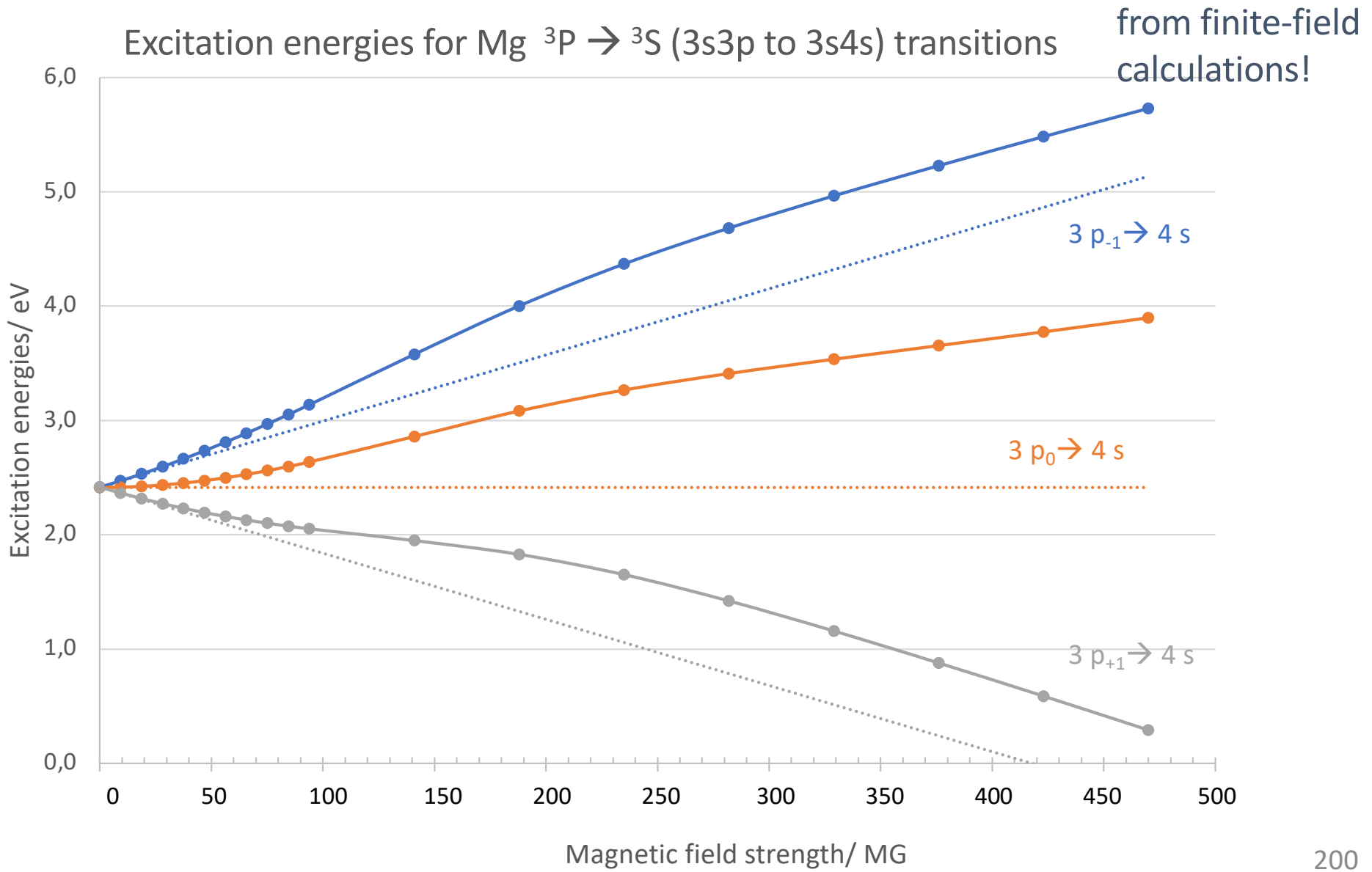
Total energies as a function of B



Exotic states become ground states in strong field!

Hampe and Stopkowicz, J. Chem. Phys., 146, 154105 (2017)

Excitation energies for Mg in magnetic field



Atom in magnetic field

- Consequences

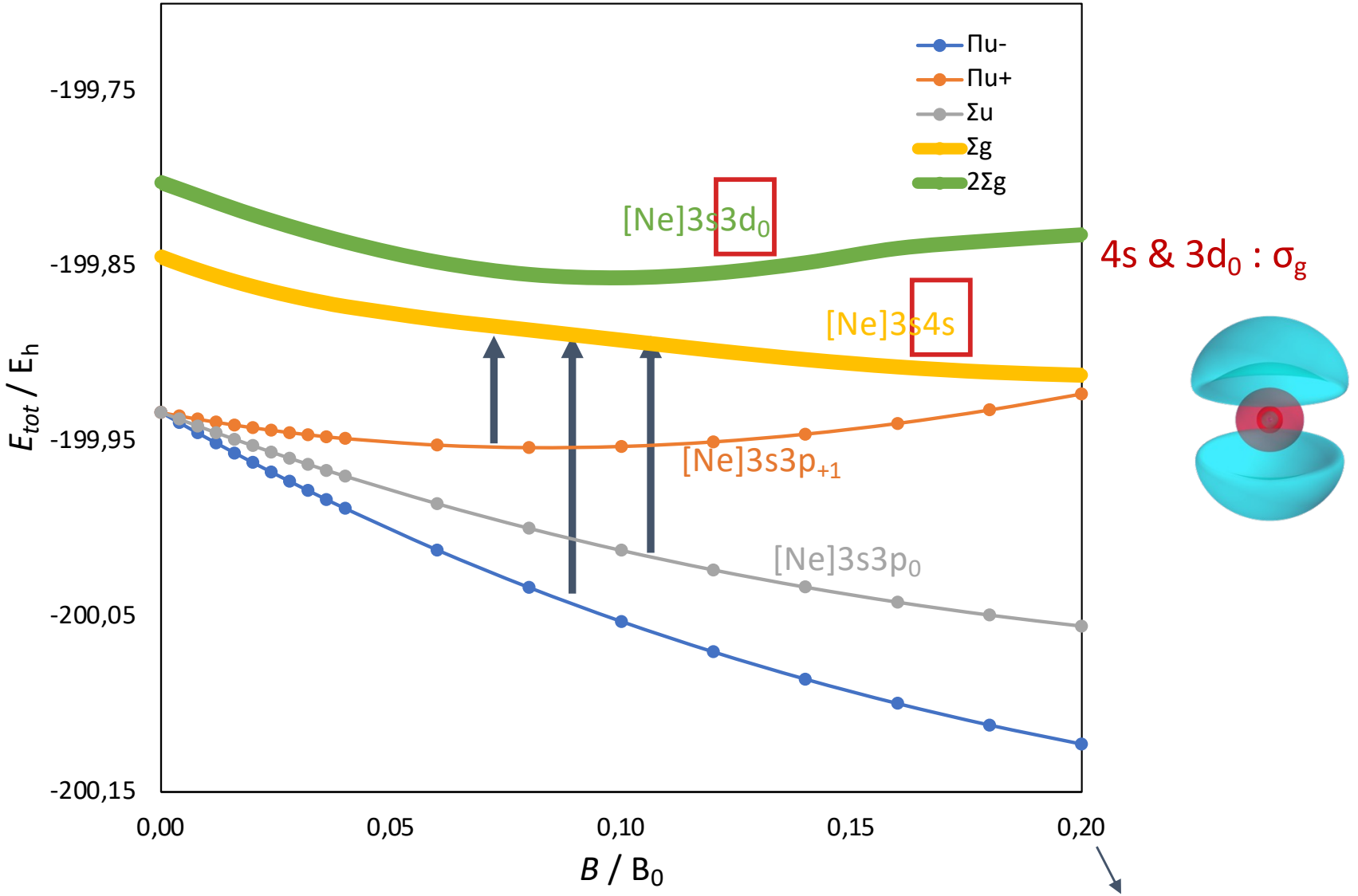
s	p_{-1}	p_0	p_{+1}	d_{-2}	d_{-1}	d_0	d_{+1}	d_{+2}
σ_g	$\pi_{-1,u}$	σ_u	$\pi_{+1,u}$	$\delta_{-2,g}$	$\pi_{-1,g}$	σ_g	$\pi_{+1,g}$	$\delta_{+2,g}$

not distinguishable, may not cross

Still eigenfunctions to L_z $\quad L_z = m\hbar$

Same is true for linear molecules ($C_{\infty h}$ or C_∞)

Excitation energies for Mg in magnetic field

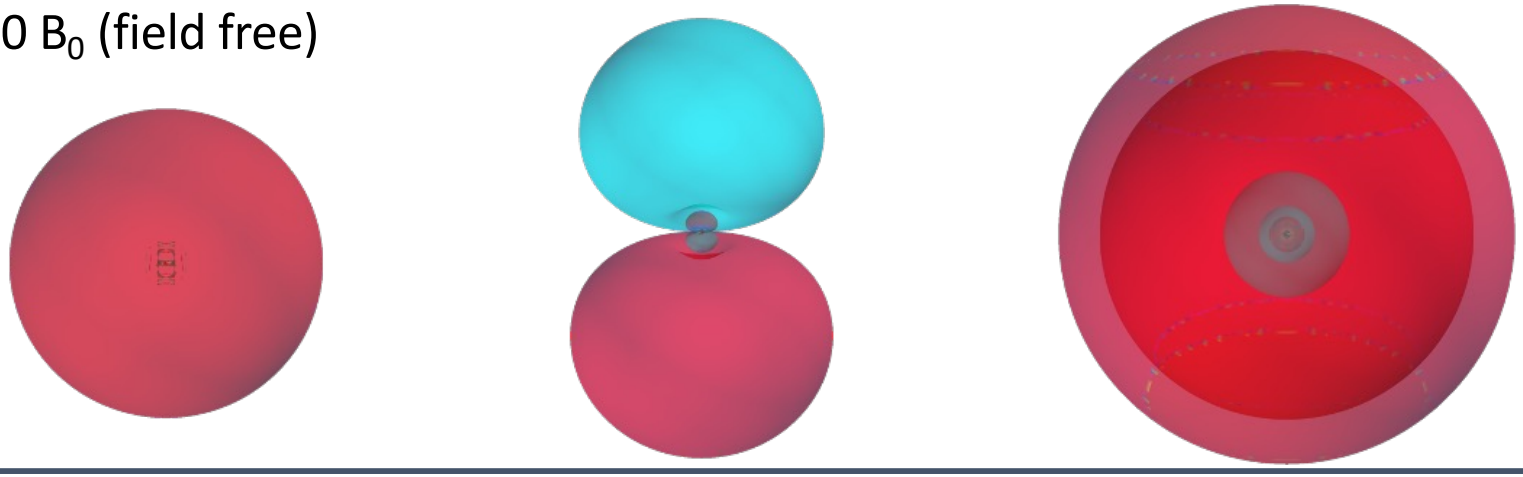


Avoided crossings occuring!

Kitsaras, Grazioli, Stopkowicz, JCP **160**, 094112 (2024)

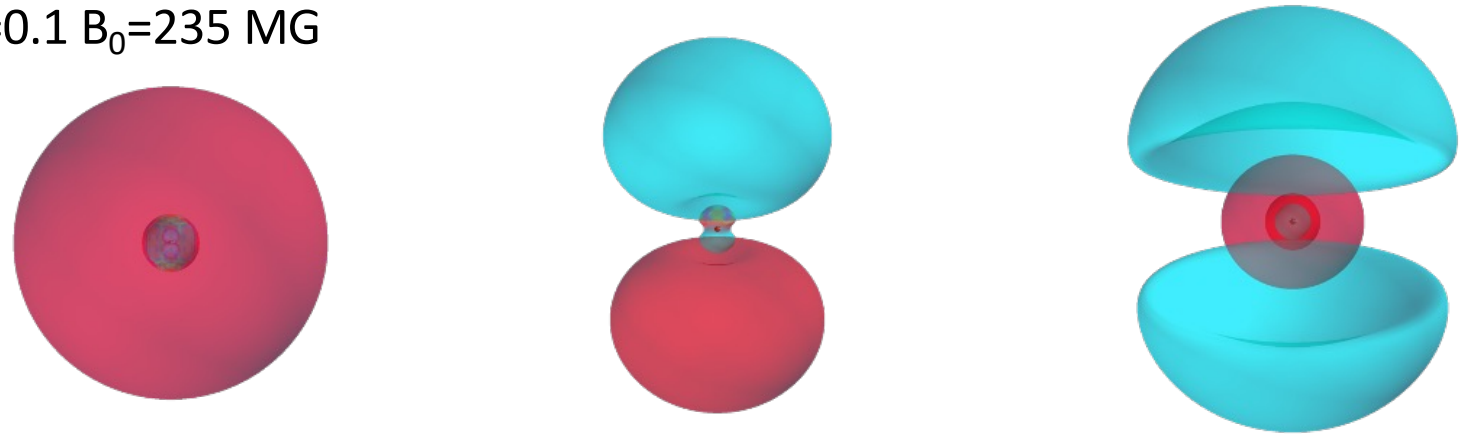
Mg Orbitals

B=0 B_0 (field free)



3s $3p_0$ 4s

B=0.1 B_0=235 MG



Paramagnetic bonding

A Paramagnetic Bonding Mechanism for Diatomics in Strong Magnetic Fields

Kai K. Lange[1], E. I. Tellgren[1], M. R. Hoffmann[1,2], T. Helgaker[1,*]

+ See all authors and affiliations

Science 20 Jul 2012:
Vol. 337, Issue 6092, pp. 327-331
DOI: 10.1126/science.1219703

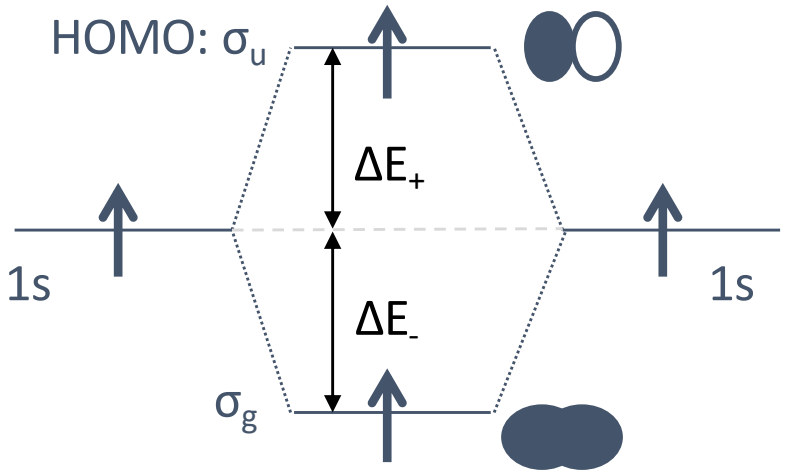
Abstract

Elementary chemistry distinguishes two kinds of strong bonds between atoms in molecules: the covalent bond, where bonding arises from valence electron pairs shared between neighboring atoms, and the ionic bond, where transfer of electrons from one atom to another leads to Coulombic attraction between the resulting ions. We present a third, distinct bonding mechanism: perpendicular paramagnetic bonding, generated by the stabilization of antibonding orbitals in their perpendicular orientation relative to an external magnetic field. In strong fields such as those present in the atmospheres of white dwarfs (on the order of 10^5 teslas) and other stellar objects, our calculations suggest that this mechanism underlies the strong bonding of H_2 in the $^3\Sigma_u^+\left(1\sigma_g 1\sigma_u^*\right)$ triplet state and of He_2 in the $^1\Sigma_g^+\left(1\sigma_g^2 1\sigma_u^{*2}\right)$ singlet state, as well as their preferred perpendicular orientation in the external field.

Lange, Tellgren, Hoffmann, Helgaker, Science *337*, 327 (2012)

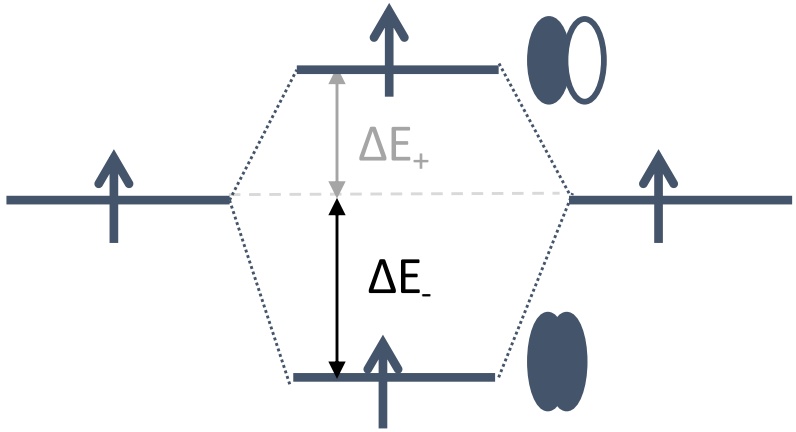
Paramagnetic bonding in H_2 triplet

field-free



$\Delta E_+ + \Delta E_- = 0$

perpendicular magnetic field



$\Delta E_+ + \Delta E_- < 0$

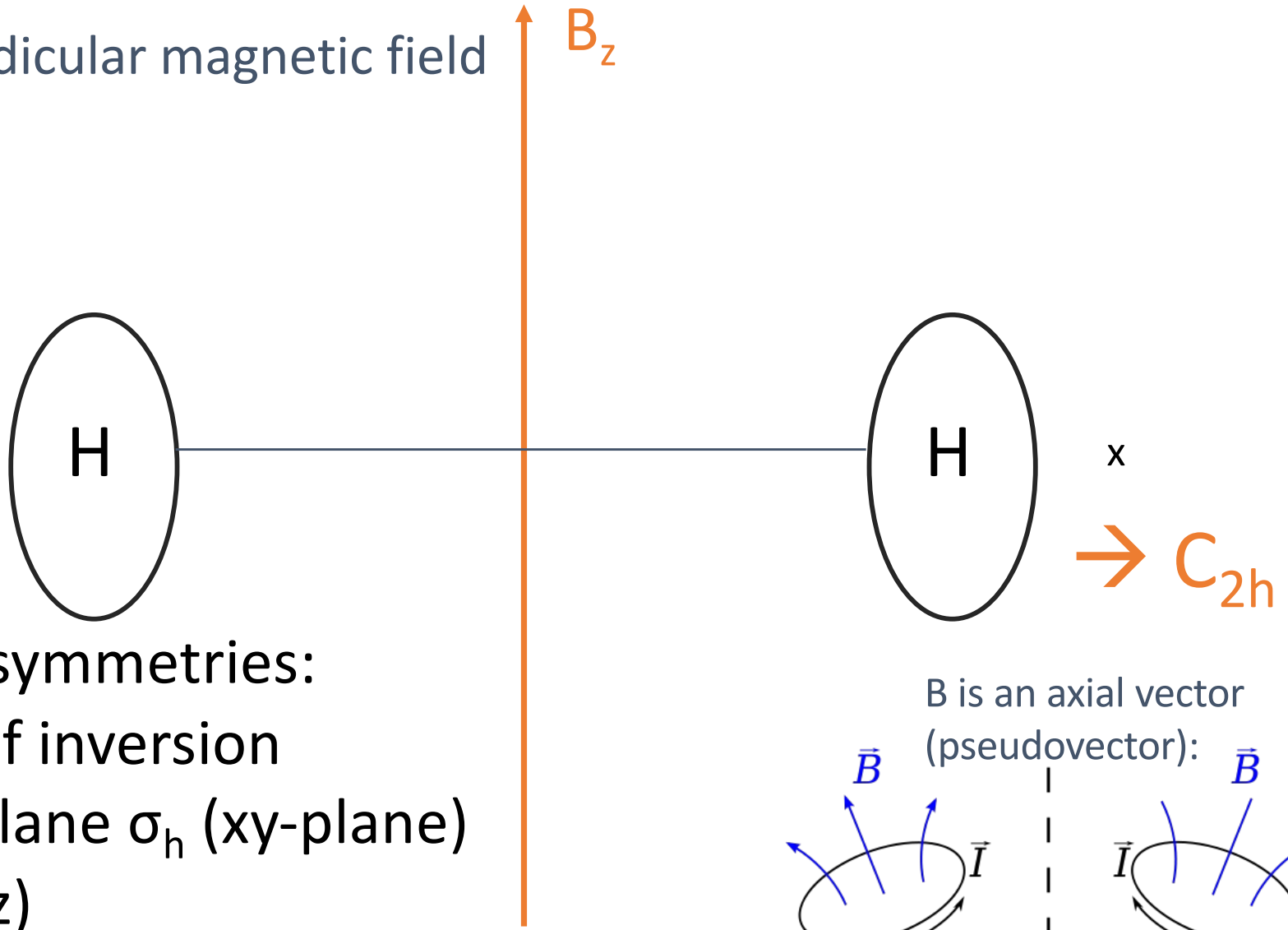
$$\hat{H} = \hat{H}_0 + \frac{1}{2}B\hat{L}_z + B\hat{S}_z + \frac{1}{8}\sum_i^N B^2\left(x_i^2 + y_i^2\right)$$

Bonding with formal bond order 0!

- Perpendicular magnetic field lowers symmetry to C_{2h}

Symmetry considerations

H_2 in perpendicular magnetic field



→ C_{2h}

Remaining symmetries:

- Center of inversion
- Mirror plane σ_h (xy-plane)
- C_2-axis (z)

B is an axial vector (pseudovector):

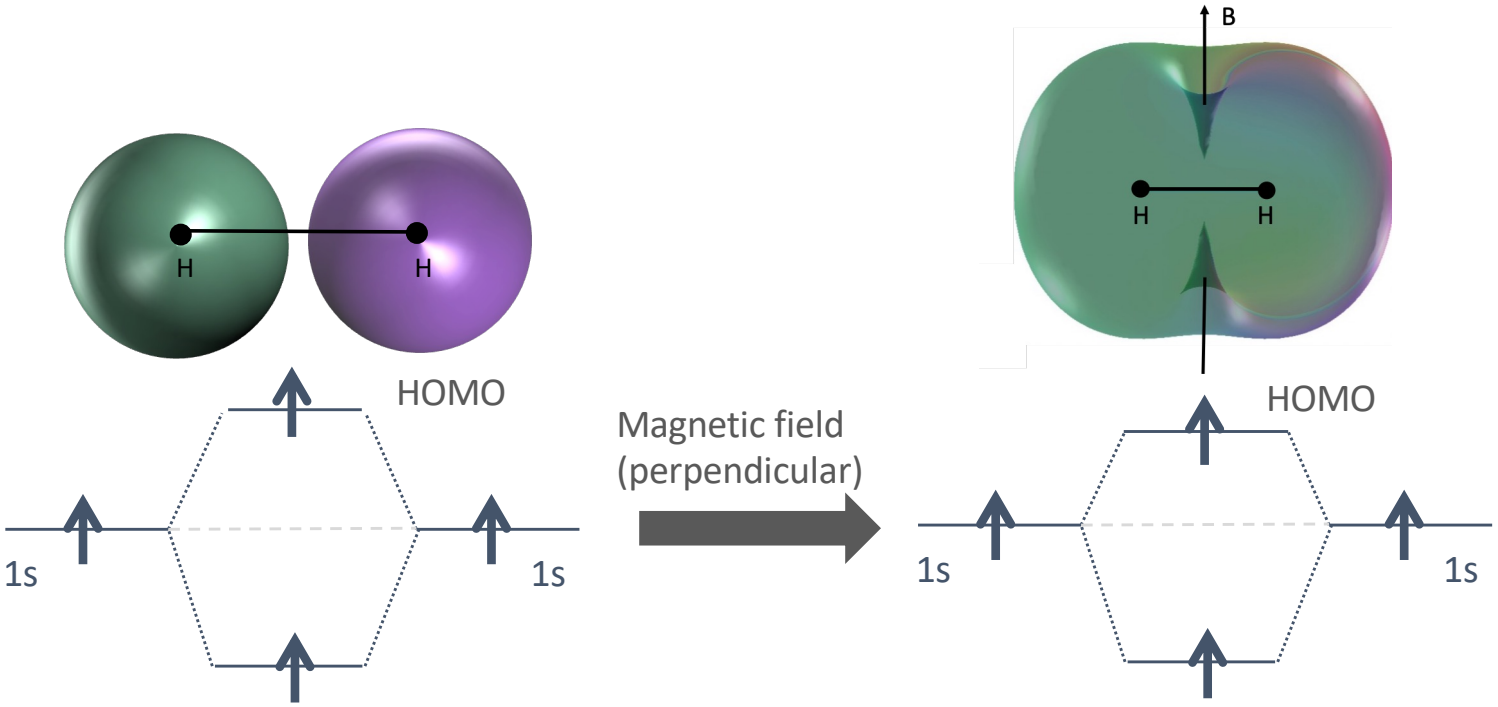
Parallel case: B coincides with molecular axis, no mirror planes that include z → $C_{\infty h}$

C_{2h} character table

C_{2h}	E	C_2	σ_h	i			
A_g	1	1	1	1	I_z	x^2, y^2, z^2, xy	
B_g	1	−1	−1	1	I_x, I_y	yz, xz	
A_u	1	1	−1	−1	z		xyz, x^2z, y^2z, z^3
B_u	1	−1	1	−1	x, y		$x^2y, xy^2, xz^2, yz^2, x^3, y^3$

https://www.staff.ncl.ac.uk/j.p.goss/symmetry/Categorisation.html

Paramagnetic bonding in H_2 triplet

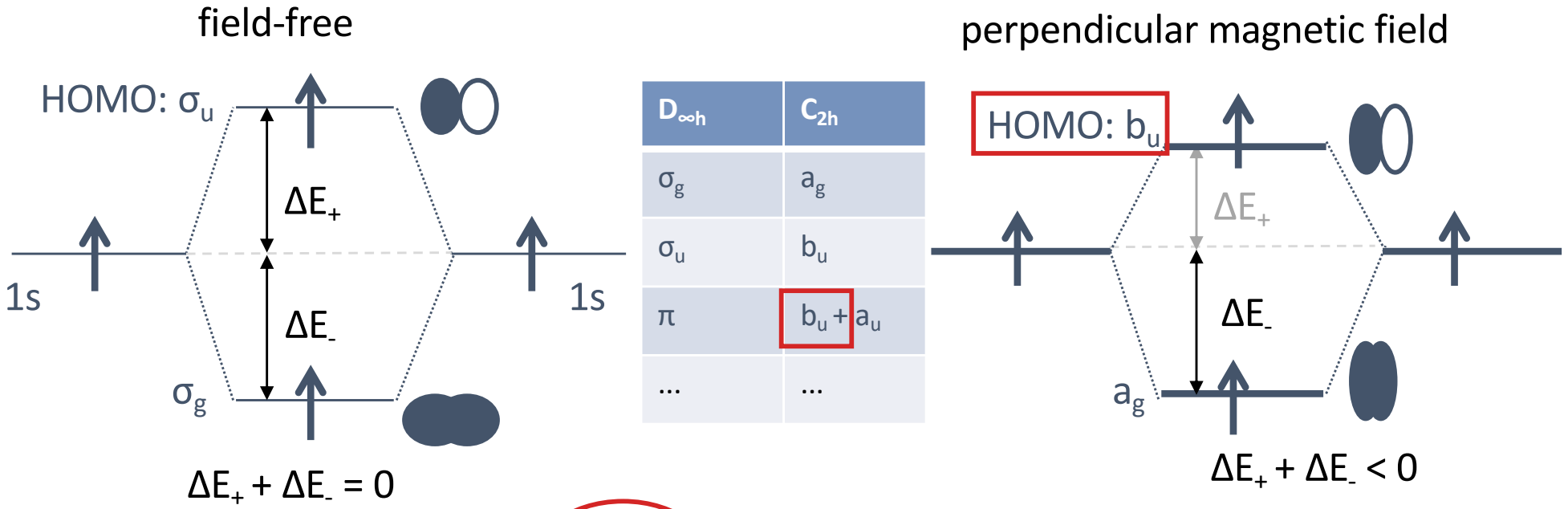


Field-free: highest occupied MO (HOMO) is antibonding

In magnetic field (ca. 200000 T): HOMO is bound via perpendicular bonding

Lange, Tellgren, Hoffmann, Helgaker, *Science* 337, 327 (2012)
Stopkowicz, *Nachr. Chem.* **70**, 11, 62-66 (2022)

Paramagnetic bonding in H_2



$D_{\infty h}$	C_{2h}
σ_g	a_g
σ_u	b_u
π	$b_u + a_u$
...	...

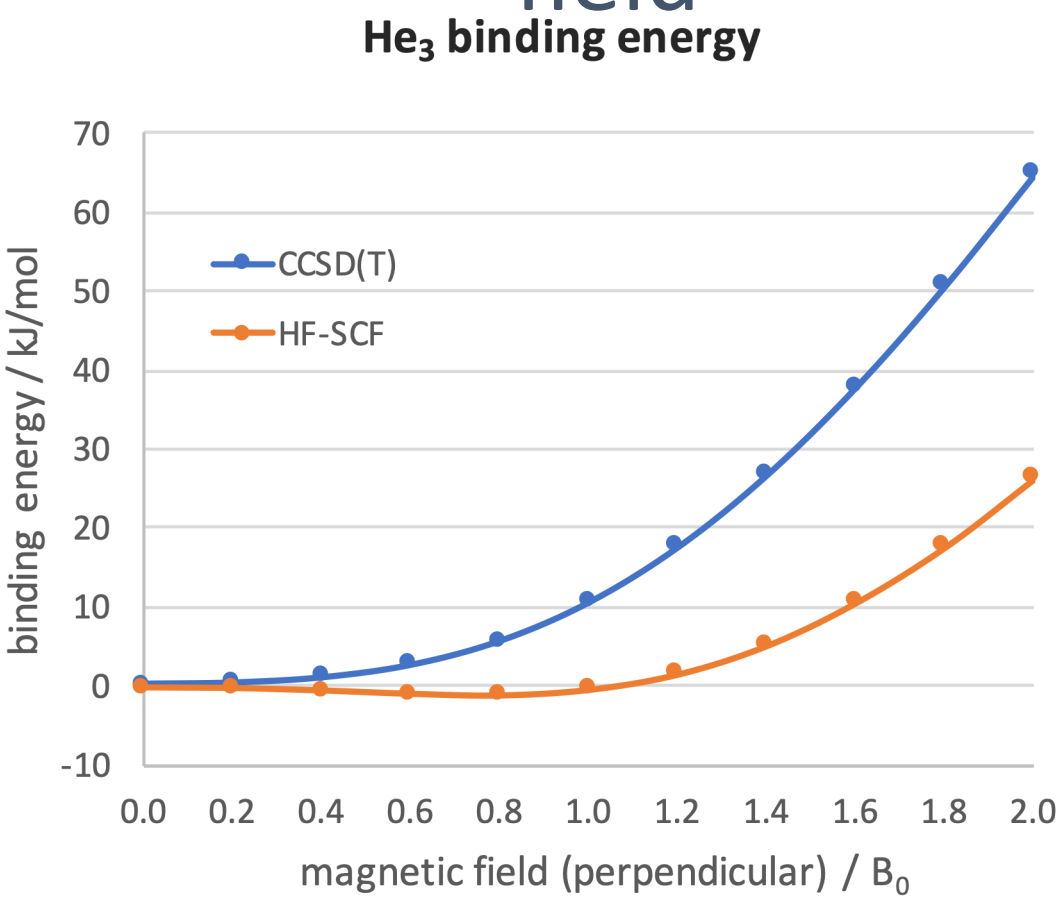
$$\hat{H} = \hat{H}_0 + \frac{1}{2}B\hat{L}_z + B\hat{S}_z + \frac{1}{8}\sum_i^N B^2\left(x_i^2 + y_i^2\right)$$

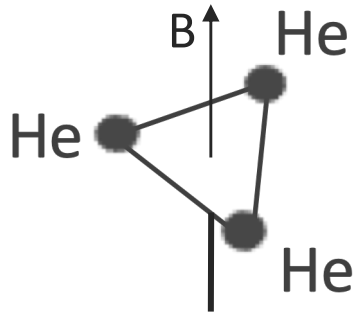
Bonding with formal bond order 0!

- Perpendicular magnetic field lowers symmetry to C_{2h}
- m_l no longer good quantum number, π/σ symmetry broken
  - Higher-lying π splits into b_u and a_u
  - Mixing with HOMO allowed
  - Induces angular momentum and lowers $\langle L_z \rangle$
  - Paramagnetic stabilization (GENERAL!): Here: Induces a bond

Binding energies of He_3 in perpendicular field

perpendicular
paramagnetic
bonding





- Becomes paramagnetically bound (not to be confused with van der Waals interaction)
- Correlation contribution more important with increasing field

Summary strong magnetic fields

- Strong fields exists on magnetic White Dwarf stars
- Assignment of spectra
- Lowering of symmetry
- Exotic states become ground states
- Paramagnetic bonding