Derivatives and properties

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Acknowledgement

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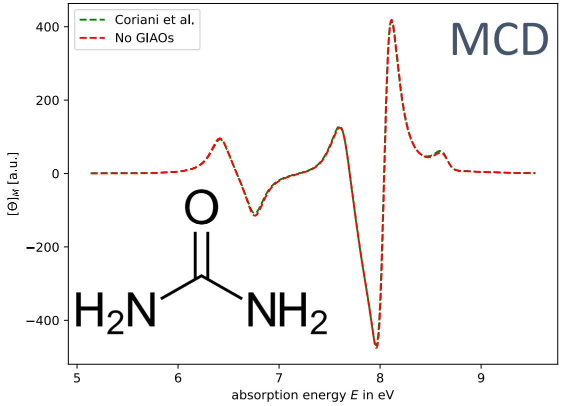
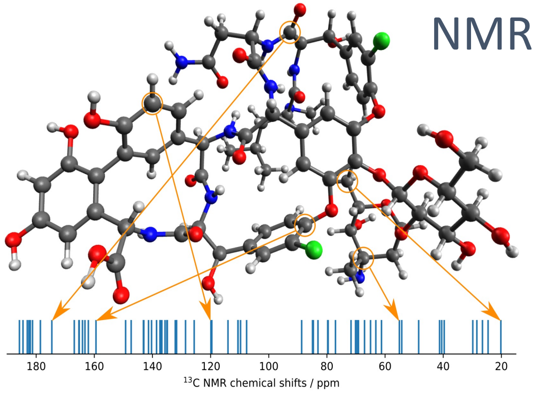
Content

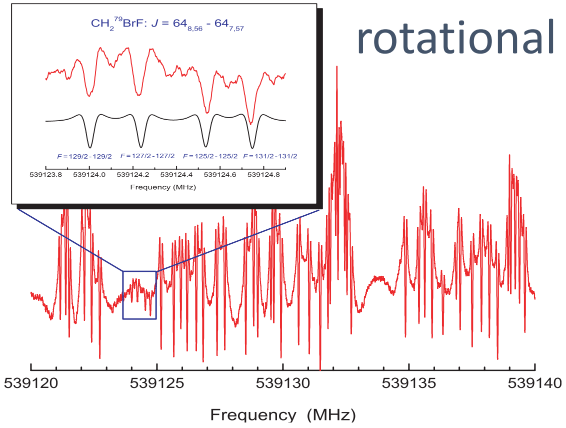
- Part 1: Derivative theory
- Part 2: Magnetic properties and molecules in magnetic fields

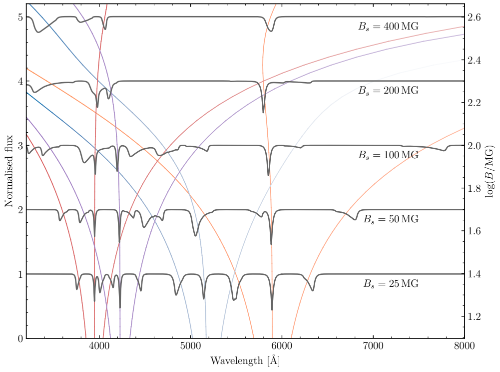
Molecular properties

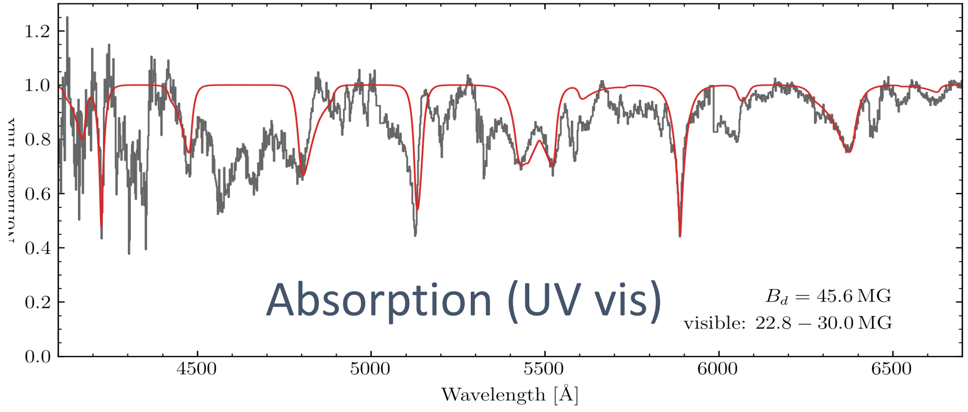
- Spectroscopy
  - NMR, EPR, IR, Raman, Rotational spectra, MCD, …


MCD


NMR


rotational




Absorption (UV vis)

- Time- (or frequency) dependent vs. **time independent**

Types of (time-independent) molecular properties

- State-specific properties
  - Equilibrium structure
  - Vibrational frequencies
  - Dipole moment and polarizability
  - NMR shielding
  - Magnetizability

  …

Focus of this lecture

- Transition properties
  - Electronic excitation energies
  - One- and two-photon transition strengths
  - Radiative lifetimes
  - Ionization potentials and electron affinities

  …
- Based on energy differences
  - Reaction energies
  - Stability of conformers/isomers
  - Atomization energies
  - Dissociation energies

  …

Part 1
Derivative theory

Contents

- Properties as expectation values
- Properties as energy derivatives
  - Numerical and analytical derivatives
- Hellman-Feynman theorem
- Derivative theory
  - Variational and non-variational wave functions
  - Lagrangian formalism
  - (2n+1) and (2n+2) rules
  - Examples for first- and second-order properties via Lagrangian approach

Calculation of molecular properties

Quantum mechanics suggest:

Calculate properties as

expectation value to a corresponding Hermitian operator $\hat{O}$!

$$\frac{\langle \Psi \mid \hat{O} \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle}$$

Molecular properties as expectation value

- Example: dipole moment
- Calculation via expectation value of respective operator

$$\hat{\boldsymbol{\mu}} = \sum_{\alpha}(-e\mathbf{r}_{\alpha}) + \sum_{A} Z_A \mathbf{R}_A$$

electronic part

nuclear part

$$\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}_{\mathrm{el}} + \hat{\boldsymbol{\mu}}_{\mathrm{nuc}}$$

- For quantum-chemical calculation: el. part relevant
- Expectation value: $\langle \Psi \mid \hat{\boldsymbol{\mu}}_{\mathrm{el}} \mid \Psi \rangle$

WF normalized

Molecular properties as energy derivatives

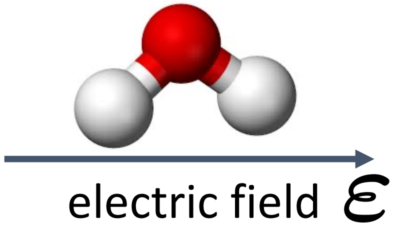
Alternative view: Property as a response of a system to a (small) perturbation

→ to be calculated as energy derivative with respect to a perturbation parameter to which to property is associated

→ sufficiently weak perturbation: Taylor expansion around x=0

Molecule in electric field

- Response of the system to a perturbation



→ $E(\varepsilon)$

Energy of the molecule changes and is a function of the electric field

Example: Perturbation by electric field

- Expansion with respect to electric field as perturbation

$$E(\boldsymbol{\varepsilon}) = \underbrace{E(\boldsymbol{\varepsilon} = 0)}_{\text{field-free energy}} \underbrace{\boxed{-\,\boldsymbol{\mu}^T}\,\boldsymbol{\varepsilon}\,\boxed{-}\,\frac{1}{2}\boldsymbol{\varepsilon}^T\boxed{\boldsymbol{\alpha}}\,\boldsymbol{\varepsilon}\ldots}_{\text{field – dependent terms}}$$

expansion coefficients characteristic of the molecule and its quantum states → molecular properties.

- Taylor expansion around the field-free case

$$E(\boldsymbol{\varepsilon}) = E(\boldsymbol{\varepsilon} = 0) + \boxed{\left.\frac{dE}{d\boldsymbol{\varepsilon}}\right|_{\boldsymbol{\varepsilon}=\mathbf{0}}^{T}}\,\boldsymbol{\varepsilon} + \frac{1}{2}\boldsymbol{\varepsilon}^T\boxed{\left.\frac{d^2E}{d\boldsymbol{\varepsilon}\,d\boldsymbol{\varepsilon}}\right|_{\boldsymbol{\varepsilon}=\mathbf{0}}}\,\boldsymbol{\varepsilon}\ldots$$

- Comparison:

$$\boxed{\boldsymbol{\mu} = -\left.\frac{dE}{d\boldsymbol{\varepsilon}}\right|_{\boldsymbol{\varepsilon}=\mathbf{0}}}$$ dipole moment

$$\boxed{\boldsymbol{\alpha} = -\left.\frac{d^2E}{d\boldsymbol{\varepsilon}\,d\boldsymbol{\varepsilon}}\right|_{\boldsymbol{\varepsilon}=\mathbf{0}}}$$ polarizability

Expectation value vs. derivative

- We have now seen two ways to calculate the dipole moment:

expectation value

$$\boxed{\boldsymbol{\mu} = \langle \Psi \mid \hat{\boldsymbol{\mu}} \mid \Psi \rangle}$$

vs.

energy derivative

$$\boxed{\boldsymbol{\mu} = - \left. \frac{dE}{d\boldsymbol{\varepsilon}} \right|_{\varepsilon = \mathbf{0}}}$$

Expectation value vs. derivative

- Equivalence? → Hellmann-Feynman theorem!

$$\boxed{\frac{dE}{dx} = \langle \Psi \mid \frac{d\hat{H}}{dx} \mid \Psi \rangle}$$

WF normalized:
$\langle \Psi \mid \Psi \rangle = 1$

with $\hat{H} = \hat{H}_0 - \underset{\searrow}{\hat{\boldsymbol{\mu}}\boldsymbol{\varepsilon}}$ such that

modifies V_{ne}

$$\boxed{-\frac{dE}{d\varepsilon} = \langle \Psi \mid \hat{\boldsymbol{\mu}} \mid \Psi \rangle = \boldsymbol{\mu}}$$

→ Dipole moment as energy derivative

→ Equivalence to perturbation theory expression

Proof of Hellmann-Feynman theorem for exact wave function

- Derivative of energy-expectation value:

only exact WF that solves Schrödinger equation

$$\frac{dE}{dx} = \frac{d}{dx}\langle \Psi \mid \hat{H} \mid \Psi \rangle = \langle \Psi \mid \frac{d\hat{H}}{dx} \mid \Psi \rangle + \underbrace{\left(\langle \frac{d\Psi}{dx} \mid \underset{E \mid \Psi \rangle}{\hat{H} \mid \Psi \rangle} + c.c. \right)}_{\underbrace{E \left(\langle \frac{d\Psi}{dx} \mid \Psi \rangle + c.c. \right)}_{E \underbrace{\left(\frac{d}{dx} \langle \Psi \mid \Psi \rangle \right)}_{0}}}$$

WF normalized

→ $$\boxed{\frac{dE}{dx} = \langle \Psi \mid \frac{d\hat{H}}{dx} \mid \Psi \rangle}$$

Implications of Hellmann-Feynman theorem

- Only derivatives of Hamiltonian with respect to the perturbation needed (integrals)
- No derivatives of wave function needed

Generally true?

What about approximate wave functions?

Example: Hartree-Fock wave function

Infinitesimal perturbation

$$\Psi_{\mathrm{HF}} \rightarrow \Psi_{\mathrm{HF}} + \delta\Psi_{\mathrm{HF}} \;= \Psi_{\mathrm{HF}} + \frac{\partial \Psi_{\mathrm{HF}}}{\partial \alpha}\partial\alpha$$

HF variation:

$$E_{\mathrm{HF}} \rightarrow E_{\mathrm{HF}} + \delta E_{\mathrm{HF}}$$

Normalized WF

$$= E_{\mathrm{HF}} + \langle \delta\Psi_{\mathrm{HF}} \mid \hat{H} \mid \Psi_{\mathrm{HF}} \rangle + \langle \Psi_{\mathrm{HF}} \mid \hat{H} \mid \delta\Psi_{\mathrm{HF}} \rangle$$

$$\underbrace{\left(\langle \frac{\partial \Psi_{\mathrm{HF}}}{\partial \alpha} \mid \hat{H} \mid \Psi_{\mathrm{HF}} \rangle + \langle \Psi_{\mathrm{HF}} \mid \hat{H} \mid \frac{\partial \Psi_{\mathrm{HF}}}{\partial \alpha} \rangle \right)}_{=0} \partial\alpha$$

HF variational condition:

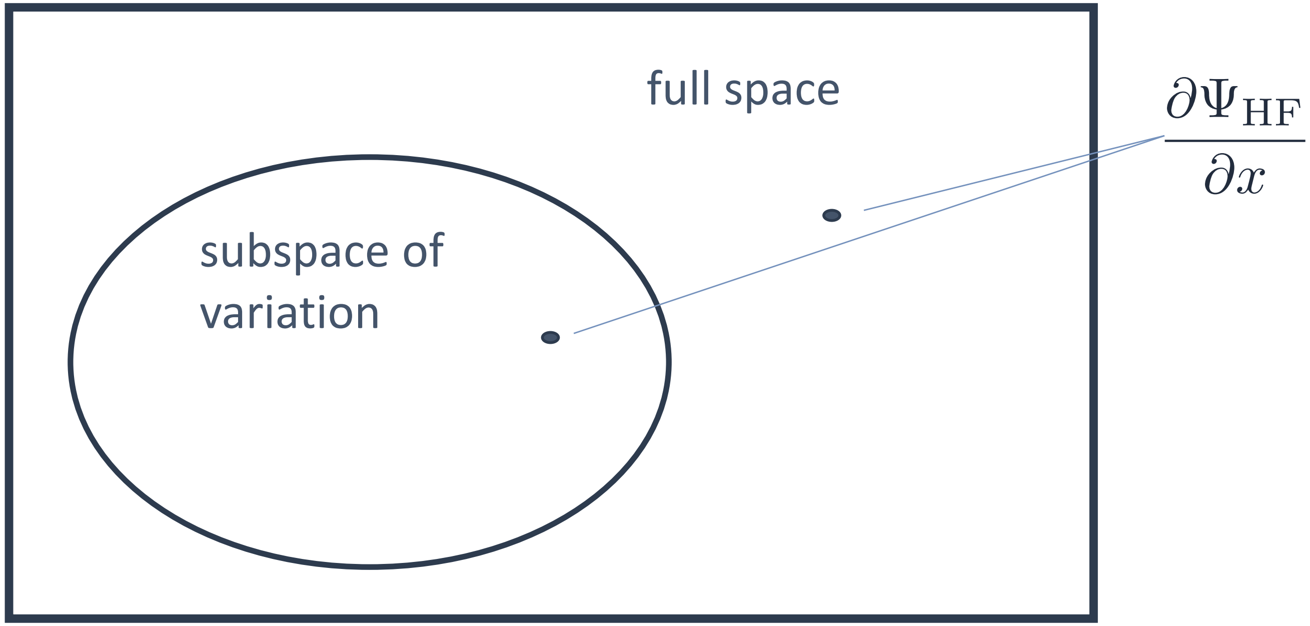
$$\delta E_{\mathrm{HF}} = 0$$

No derivative contributions in HF wave function

→ Hellman-Feynman theorem valid (in the basis-set limit)

Example: Hartree-Fock wave function

- Why Hellman-Feynman theorem not necessarily outside the basis-set limit for HF wave function?
- Incomplete basis → variation is being performed within a subspace
- Proof only valid if derivative and variation within the same space



Example: Hartree-Fock wave function

- Hellmann-Feynman theorem valid for Hartree-Fock wave function in the basis-set limit due to variational nature of theory
- Outside the basis-set limit: Does perturbation change metric?

$$\delta_{pq} = \langle \phi_p \mid \phi_q \rangle = \sum_{\mu\nu} c^*_{\mu p} c_{vq} S_{\mu\nu}$$

$$S_{\mu\nu} = \langle \chi_\mu \mid \chi_\nu \rangle$$

$$e^{(\underline{r}-\underline{R}_A)^2}$$

differentiate

$$0 = \sum_{\mu\nu} \left(\frac{\partial (c^*_{\mu p} c_{\nu q})}{\partial x} S_{\mu\nu} + c^*_{\mu p} c_{\nu q} \boxed{\frac{\partial S_{\mu\nu}}{\partial x}} \right)$$

Hellmann-Feynman theorem valid if $\frac{\partial S_{\mu\nu}}{\partial x} = 0$

→ If basis functions do not depend on perturbation → no change of the metric → Hellmann-Feynman theorem valid

✅ electric field (for dipole moment)

❌ nuclear coordinates (for geometric perturbations)

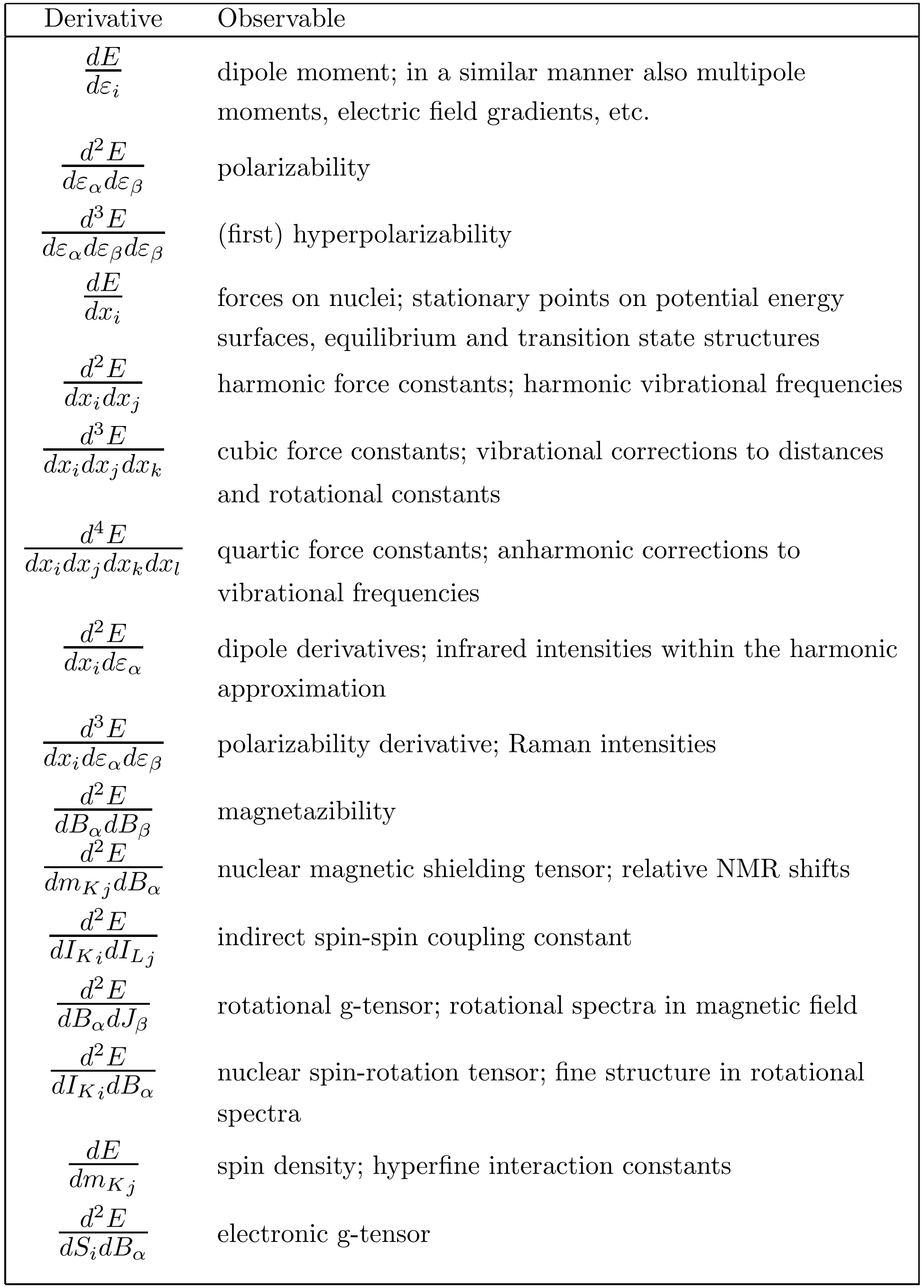
Derivative theory

→ Useful concept: we can calculate properties as energy derivatives

Examples of derivatives and their connection to properties

Response to

- Geometrical perturbations
  Forces and force constants
- External electric fields
  Permanent and induced moments, vibrational intensities
- Nuclear quadrupole moments
  Nuclear field gradients, quadrupole-coupling constants
- Magnetic fields
  magnetizabilities
- Magnetic fields and nuclear magnetic moments
  NMR and ESR parameters
- Magnetic and electric fields
  Magnetic circular dichroism, optical rotation
- Molecular rotation
  Spin-rotation constants and molecular g values



Derivative	Observable
$\frac{dE}{d\varepsilon_i}$	dipole moment; in a similar manner also multipole moments, electric field gradients, etc.
$\frac{d^2E}{d\varepsilon_\alpha d\varepsilon_\beta}$	polarizability
$\frac{d^3E}{d\varepsilon_\alpha d\varepsilon_\beta d\varepsilon_\beta}$	(first) hyperpolarizability
$\frac{dE}{dx_i}$	forces on nuclei; stationary points on potential energy surfaces, equilibrium and transition state structures
$\frac{d^2E}{dx_i dx_j}$	harmonic force constants; harmonic vibrational frequencies
$\frac{d^3E}{dx_i dx_j dx_k}$	cubic force constants; vibrational corrections to distances and rotational constants
$\frac{d^4E}{dx_i dx_j dx_k dx_l}$	quartic force constants; anharmonic corrections to vibrational frequencies
$\frac{d^2E}{dx_i d\varepsilon_\alpha}$	dipole derivatives; infrared intensities within the harmonic approximation
$\frac{d^3E}{dx_i d\varepsilon_\alpha d\varepsilon_\beta}$	polarizability derivative; Raman intensities
$\frac{d^2E}{dB_\alpha dB_\beta}$	magnetazibility
$\frac{d^2E}{dm_{Kj} dB_\alpha}$	nuclear magnetic shielding tensor; relative NMR shifts
$\frac{d^2E}{dI_{Ki} dI_{Lj}}$	indirect spin-spin coupling constant
$\frac{d^2E}{dB_\alpha dJ_\beta}$	rotational g-tensor; rotational spectra in magnetic field
$\frac{d^2E}{dI_{Ki} dB_\alpha}$	nuclear spin-rotation tensor; fine structure in rotational spectra
$\frac{dE}{dm_{Kj}}$	spin density; hyperfine interaction constants
$\frac{d^2E}{dS_i dB_\alpha}$	electronic g-tensor

and many more

J. Gauss, Modern Methods and Algorithms in Quantum Chemistry, 3, 541, (2000)

Potential-energy surfaces & geometrical derivatives

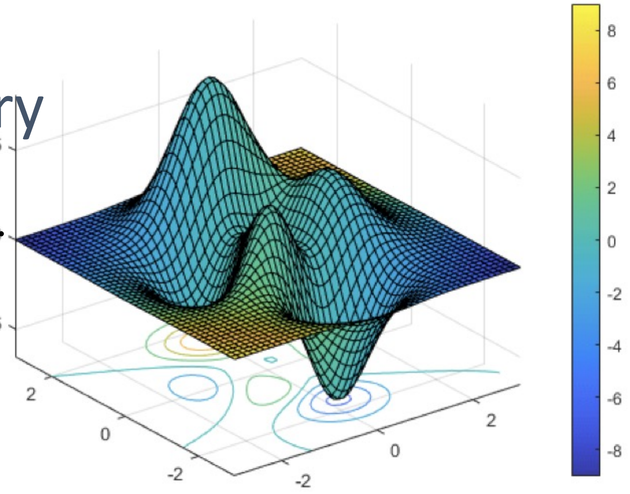
- In Born-Oppenheimer approximation, the potential-energy surface (PES) is a function of the molecular geometry

- Taylor expansion around a reference geometry

$$E(x) = E(x_0) + \underbrace{\left.\frac{dE}{dx}\right|_{x_0}}_{\downarrow} (x - x_0) + \frac{1}{2} \underbrace{\left.\frac{d^2E}{dx^2}\right|_{x_0}}_{\downarrow} (x - x_0)^2 + \ldots$$

molecular gradient
→ forces

molecular hessian
→ vib. frequencies



- Needed to locate and characterize critical points
  Minima → (meta-)stable geometries
  Saddle points → transition states

- Relation to IR → vibrational frequencies, spectroscopic constants, intensities

Fig: https://www.mathworks.com/help/matlab/ref/surfc.html

NMR parameters

Expansion of energy with respect to magnetic moments *m* and magnetic field *B*

(due to interaction with vector potential, see also part 2 on magnetic properties)

$$E(m,B) = E_0 + \frac{dE}{dm}m + \frac{dE}{dB}B + \underbrace{\frac{1}{2}\frac{d^2E}{dBdB}B^2}_{\text{related to magnetizabilites}} + \underbrace{\frac{1}{2}\frac{d^2E}{dmdm}m^2}_{\text{related to spin-spin coupling}} + \underbrace{\frac{d^2E}{dBdm}Bm}_{\text{related to NMR shielding (coupling between B and m)}} + \ldots$$

How to calculate the energy derivatives?

In principle two ways:
Numerical vs. analytical derivatives

Numerical differentiation

- Numerical differentiation (symmetric form)

$$\left.\frac{dE}{dx}\right|_{x_0} \approx \frac{E(x_0 + \Delta x) - E(x_0 - \Delta x)}{2\Delta x}$$

looks rather simple..., “no” new code needed

Why bother doing anything but this?

Important questions:

  - What does it cost?
  - How accurate is it?

Cost of numerical differentiation: Gradient

$$\left.\frac{dE}{dx}\right|_{x_0} \approx \frac{E(x_0+\Delta x) - E(x_0-\Delta x)}{2\Delta x}$$

Gradient, geometry optimization

- Example: differentiation wrt nuclear coordinates
  - Number of atoms N_{atom}
  - 3 per direction (x,y,z)
  - 2 per derivative

6 x N_{atom} calculations
(more for better approximations)

→ Scales with number of atoms
→ Will become prohibitive for larger molecules

Cost of analytical differentiation: Gradient

- For Hartree Fock, most time-consuming step is derivative of the two-electron integrals with respect to nuclear coordinates (see also later)
- Number of integrals $\langle \mu\sigma \mid \nu\rho \rangle \sim$ M^4
- Number nuclear coordinates $\sim$ 3 N$_{\text{atom}}$

~3N$_{\text{atom}}$ M^4?

$$\frac{\partial \langle \mu\sigma \mid \nu\rho \rangle}{\partial X_A} = \underbrace{\langle \frac{\partial \mu}{\partial X_A}\sigma \mid \nu\rho \rangle}_{\neq 0} + \langle \mu \frac{\partial \sigma}{\partial X_A} \mid \nu\rho \rangle + \ldots$$

Only if BF μ centered @ A

- Number of derivative integrals is 4 BF (centered @A) x 3 coordinates x M^4 = 12 M^4

Important: HF analytic gradient does NOT scale with number of atoms!

Cost comparison for HF gradient

Numerical differentiation

6 x N_{atom} x M^4

- Scales with number of atoms

Analytical differentiation

12 x M^4 (plus some extra)

Does not scale with number of atoms

Possible to go to larger molecules when analytical derivatives are available.

Accuracy of numerical differentiation

$$\left.\frac{dE}{dx}\right|_{x_0} \approx \frac{E(x_0+\Delta x) - E(x_0-\Delta x)}{2\Delta x}$$

- Accuracy is dependent on step-size Δx
- In the limit of $\Delta x \longrightarrow 0$, we would get the exact results
- Hence one would in principle want to choose Δx *as small as possible*
- However, this in practice not a good idea…

Accuracy of numerical differentiation

Example: Energy converged to 10^{-10} E_h

This is already rather optimistic… Anyways: machine precision ~10^{-15}

→ Error in gradient: $$\frac{2 \cdot 10^{-10}}{2\Delta x}$$

According to 2-point formula

Δx	error
10^{-4}	10^{-6}
10^{-6}	10^{-4}
10^{-8}	10^{-2}

- Δx too small: Round-off errors!
- Even more problems with higher derivatives

Accuracy of numerical differentiation

- Δx too large: Contamination from higher derivatives!

$$E(x) = E(x_0) + \left.\frac{dE}{dx}\right|_{x_0} \underbrace{(x-x_0)}_{\Delta x} + \frac{1}{2}\left.\frac{d^2E}{dx^2}\right|_{x_0}(x-x_0)^2 + \frac{1}{3!}\left.\frac{d^3E}{dx^3}\right|_{x_0}(x-x_0)^3 + \dots$$

For $x=x_0+\Delta x$

$$E(x_0+\Delta x) = E(x_0) + \left.\frac{dE}{dx}\right|_{x_0}(\Delta x) + \frac{1}{2}\left.\frac{d^2E}{dx^2}\right|_{x_0}(\Delta x)^2 + \frac{1}{3!}\left.\frac{d^3E}{dx^3}\right|_{x_0}(\Delta x)^3 + \dots$$

For $x=x_0$-Δx

$$E(x_0-\Delta x) = E(x_0) + \left.\frac{dE}{dx}\right|_{x_0}(-\Delta x) + \frac{1}{2}\left.\frac{d^2E}{dx^2}\right|_{x_0}(-\Delta x)^2 + \frac{1}{3!}\left.\frac{d^3E}{dx^3}\right|_{x_0}(-\Delta x)^3 + \dots$$

$$\rightarrow \boxed{\frac{E(x_0+\Delta x) - E(x_0-\Delta x)}{2\Delta x} = \left.\frac{dE}{dx}\right|_{x_0} + \frac{1}{6}\left.\frac{d^3E}{dx^3}\right|_{x_0}\Delta x^2 + \dots}$$

contamination,
grows with Δx

Accuracy of numerical differentiation

$$\left.\frac{dE}{dx}\right|_{x_0} \approx \frac{E(x_0+\Delta x)-E(x_0-\Delta x)}{2\Delta x} + \mathcal{O}(\Delta x^3)$$

small step size

rounding errors, convergence, etc. δE

error: $\mathcal{O}\left(\frac{\delta E}{\Delta x}\right)$

tight convergence

larger step size

numerical differentiation *n* times $\mathcal{O}\left(\frac{\delta E}{\Delta x^n}\right)$

Accuracy of numerical differentiation

Possible to use higher-order polynomial for the to approximate the derivative but then even more calculations derivative needed:

(*n* points → (*n*-1)th order polynomial)

For example, rather than the 2-point formula the 4, 6, etc… formula can be used:

2pt: $$b = \frac{f(x) - f(-x)}{2x}$$

4pt: $$b = \frac{8[f(x) - f(-x)] - [f(2x) - f(-2x)]}{12x}$$

6pt: $$b = \frac{45[f(x) - f(-x)] - 9[f(2x) - f(-2x)] + [f(3x) - f(-3x)]}{60x}$$

Accuracy of numerical differentiation

- Or more generally:

$$f(k) = \underbrace{f(k_0)}_{a} + \underbrace{\left(\frac{\partial f(k)}{\partial k}\right)_{k=k_0}}_{b} \underbrace{(k-k_0)}_{x} + \underbrace{\frac{1}{2}\left(\frac{\partial^2 f(k)}{\partial k^2}\right)_{k=k_0}}_{c} \underbrace{(k-k_0)^2}_{x^2} + \dots$$

- Solve for coefficients

$$\begin{pmatrix} 1 & x & x^2 & x^3 & \dots \\ 1 & 2x & (2x)^2 & (2x)^3 & \dots \\ 1 & 3x & (3x)^2 & (3x)^3 & \dots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ \vdots \end{pmatrix} = \begin{pmatrix} f(x) \\ f(2x) \\ f(3x) \\ \vdots \end{pmatrix}$$

$$\mathbf{Ac} = \mathbf{f}$$

Accuracy of numerical differentiation

Remaining issues:

- More calculations needed for fits to higher-order polynomials
- Still unclear what a good step size is. This needs calibration (more calculations).

Analytical derivatives

- In principle exact

- Require explicit expressions and their implementation (traditionally new implementation per new method with some re-use)

- Often less computational cost (as compared to numerical differentiation)

- Differences whether or not methods are variational (constrained /unconstrained) or non-variational

Numerical vs analytical differentiation

	numerical	**analytical**
accuracy	limited	high
efficiency	low	high
freq. dependence	no	yes
imaginary pert.	only with complex wave function	yes
implementation	easy	demanding

→Analytic differentiation preferred if available

In the following we will deal with analytical derivatives and the „tricks“ to use in order to get the derivatives with as low computational cost as possible

Explicit and implicit dependence on perturbation

- Energy expression, dependence on the perturbation
- Wave function parameters *c* (MO coefficients, amplitudes)

$$E(x) = \langle \Psi(c(\underset{\substack{\downarrow\\ \text{implicit dependence}}}{x})) \mid \hat{H}(\underset{\substack{\downarrow\\ \text{explicit dependence}}}{x}) \mid \Psi(c(\underset{\substack{\downarrow\\ \text{implicit dependence}}}{x})) \rangle$$

- In general case need to consider both implicit as well as explicit dependence on perturbation when differentiating, i.e.

$$\frac{dE(x)}{dx} = \underset{\substack{\downarrow\\ \text{explicit dependence}}}{\frac{\partial E}{\partial x}} + \underbrace{\frac{\partial E}{\partial c}\frac{\partial c}{\partial x}}_{\text{implicit dependence}}$$

$\frac{\partial c}{\partial x}$ → change of WF wrt pertubation x = wave function response

Variational wave function

- When WF is determined in unconstrained variation then (as per definition!)

$$\boxed{\frac{\partial E}{\partial c} \overset{!}{=} 0}$$

- It follows: $$\frac{dE(x)}{dx} = \frac{\partial E}{\partial x} + \xcancel{\frac{\partial E}{\partial c}\frac{\partial c}{\partial x}}$$

=0

- This means the response of the wave-function parameters $\frac{\partial c}{\partial x}$ does not need to be calculated to obtain the gradient

Examples for variational wave functions

- Hartree-Fock (HF) energy in an unconstrained exponential parametrization

$$\mid \Psi^{\mathrm{HF}} \rangle = \exp(-\kappa) \mid 0 \rangle, \quad \kappa^{\dagger} = -\kappa$$

- Full CI (FCI) wave function as an expectation value

$$|\Psi^{\mathrm{FCI}}\rangle = \sum_{I} c_I |\Phi_I\rangle$$

$$E^{\mathrm{FCI}} = \frac{\langle \Psi^{\mathrm{FCI}} \mid \hat{H} \mid \Psi^{\mathrm{FCI}} \rangle}{\langle \Psi^{\mathrm{FCI}} | \Psi^{\mathrm{FCI}} \rangle} \qquad \frac{\partial E^{\mathrm{FCI}}}{\partial c} = 0$$

Constrained variation and non-variational wave functions

- If wave function is constructed via constrained variation or in a non-variational manner, in principle response of wave-function parameters needs to be calculated

$$\frac{dE(x)}{dx} = \frac{\partial E}{\partial x} + \boxed{\frac{\partial E}{\partial c}} \frac{\partial c}{\partial x}$$

🫠

doesn‘t vanish needs hence to be calculated!

- Possible…., will need a set of equations per perturbation

Example: HF gradient

- HF energy

$$E^{\mathrm{HF}} = \sum_{\mu\nu} D_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\sigma\rho} D_{\mu\nu} D_{\sigma\rho} \left(\langle \mu\sigma \mid \nu\rho \rangle - \frac{1}{2} \langle \mu\sigma \mid \rho\nu \rangle \right)$$

- Differentiate

$$\frac{dE(x)}{dx} = \frac{\partial E}{\partial x} + \frac{\partial E}{\partial c} \frac{\partial c}{\partial x}$$

$$\frac{dE^{\mathrm{HF}}}{dx} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial x} + \frac{1}{2} \sum_{\mu\nu\sigma\rho} D_{\mu\nu} D_{\sigma\rho} \left(\frac{\partial \langle \mu\sigma \mid \nu\rho \rangle}{\partial x} - \frac{1}{2} \frac{\partial \langle \mu\sigma \mid \rho\nu \rangle}{\partial x} \right)$$

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

- would need to solve for perturbed wave-function parameters → coupled-perturbed HF (CPHF) equations

Perturbed MO parameters

- CPHF equations from differentiating Brillouin condition

$$\frac{d}{dx} f_{ai} = 0$$

or Roothaan-Hall equations

- Parametrization

$$\frac{\partial c_{\mu r}}{\partial x} = \sum_p c_{\mu p} U^x_{pr}$$

CPHF coefficients

- Linear equations for U^x_{ai}

$$\underline{\underline{A}}\,\underline{U}^x = \underline{B}^x$$

$$(\varepsilon_a - \varepsilon_i) U^x_{ai} + \sum_b \sum_j (4\langle ab \mid ij\rangle - \langle ab \mid ji\rangle - \langle aj \mid bi\rangle)$$

$$= -f^{(x)}_{ai} + \varepsilon_i S^x_{ai} + \frac{1}{2} \sum_m \sum_j (4\langle am \mid ij\rangle - \langle am \mid ji\rangle - \langle aj \mid mi\rangle) S^x_{mj}$$

can be solved iteratively.

cost: N_{pert} x M^5 (integral transformation) → expensive!!!

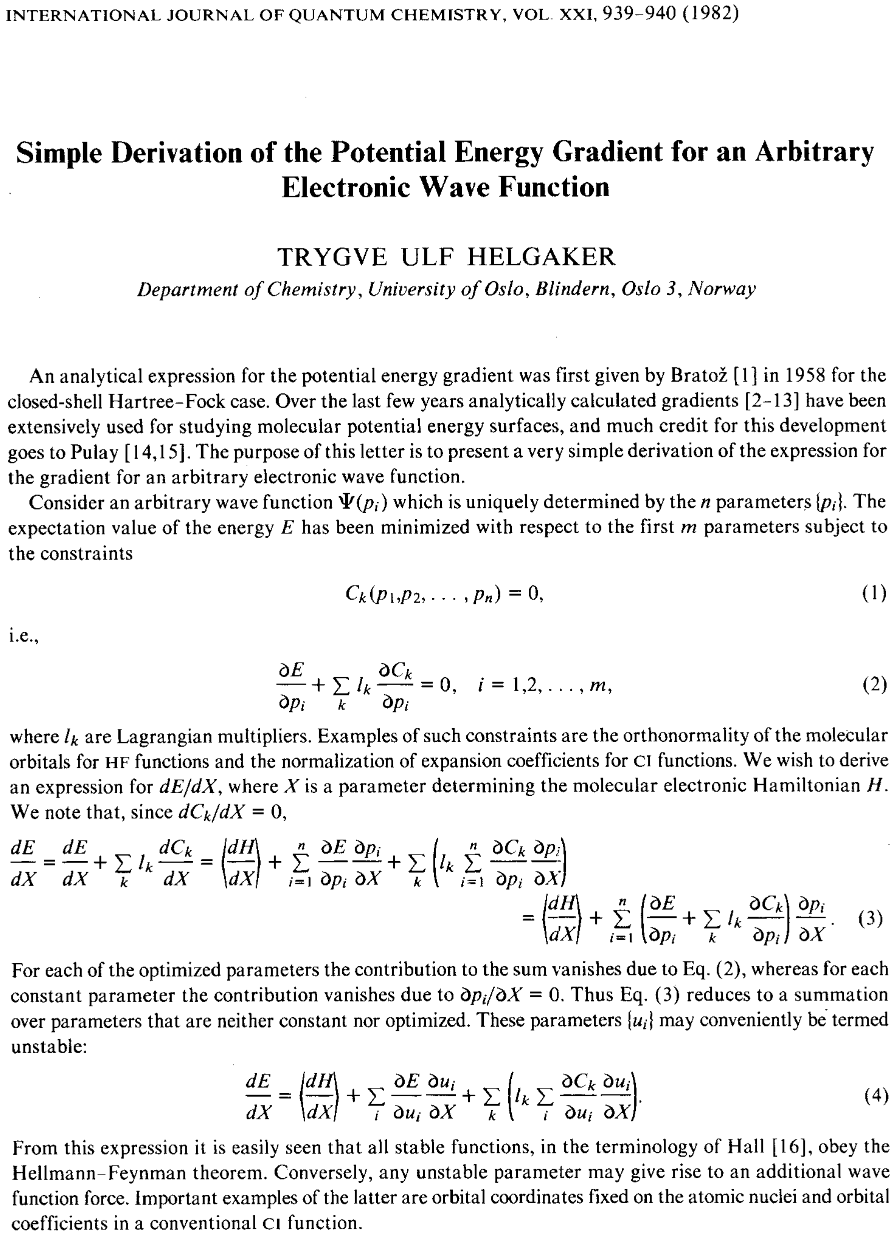
Perturbed MO parameters

- Do we *actually* need to calculate the perturbed wave-function parameters?

- Solution: enforce stationarity of energy expression with respect to perturbation-dependent parameters *c*

  → method of Lagrange multipliers!

Method of Lagrange multipliers



INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, VOL. XXI, 939–940 (1982)

Simple Derivation of the Potential Energy Gradient for an Arbitrary Electronic Wave Function

TRYGVE ULF HELGAKER

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An analytical expression for the potential energy gradient was first given by Bratož [1] in 1958 for the closed-shell Hartree–Fock case. Over the last few years analytically calculated gradients [2–13] have been extensively used for studying molecular potential energy surfaces, and much credit for this development goes to Pulay [14,15]. The purpose of this letter is to present a very simple derivation of the expression for the gradient for an arbitrary electronic wave function.

Consider an arbitrary wave function $\Psi(p_i)$ which is uniquely determined by the n parameters $\{p_i\}$. The expectation value of the energy E has been minimized with respect to the first m parameters subject to the constraints

$$C_k(p_1,p_2,\ldots,p_n)=0, \tag{1}$$

i.e.,

$$\frac{\partial E}{\partial p_i}+\sum_k l_k\frac{\partial C_k}{\partial p_i}=0,\quad i=1,2,\ldots,m, \tag{2}$$

where l_k are Lagrangian multipliers. Examples of such constraints are the orthonormality of the molecular orbitals for HF functions and the normalization of expansion coefficients for CI functions. We wish to derive an expression for dE/dX, where X is a parameter determining the molecular electronic Hamiltonian H. We note that, since $dC_k/dX=0$,

$$\begin{aligned}\frac{dE}{dX}=\frac{dE}{dX}+\sum_k l_k\frac{dC_k}{dX}&=\left\langle\frac{dH}{dX}\right\rangle+\sum_{i=1}^{n}\frac{\partial E}{\partial p_i}\frac{\partial p_i}{\partial X}+\sum_k\left(l_k\sum_{i=1}^{n}\frac{\partial C_k}{\partial p_i}\frac{\partial p_i}{\partial X}\right)\\&=\left\langle\frac{dH}{dX}\right\rangle+\sum_{i=1}^{n}\left(\frac{\partial E}{\partial p_i}+\sum_k l_k\frac{\partial C_k}{\partial p_i}\right)\frac{\partial p_i}{\partial X}.\end{aligned} \tag{3}$$

For each of the optimized parameters the contribution to the sum vanishes due to Eq. (2), whereas for each constant parameter the contribution vanishes due to $\partial p_i/\partial X=0$. Thus Eq. (3) reduces to a summation over parameters that are neither constant nor optimized. These parameters $\{u_i\}$ may conveniently be termed unstable:

$$\frac{dE}{dX}=\left\langle\frac{dH}{dX}\right\rangle+\sum_i\frac{\partial E}{\partial u_i}\frac{\partial u_i}{\partial X}+\sum_k\left(l_k\sum_i\frac{\partial C_k}{\partial u_i}\frac{\partial u_i}{\partial X}\right). \tag{4}$$

From this expression it is easily seen that all stable functions, in the terminology of Hall [16], obey the Hellmann–Feynman theorem. Conversely, any unstable parameter may give rise to an additional wave function force. Important examples of the latter are orbital coordinates fixed on the atomic nuclei and orbital coefficients in a conventional CI function.

← First paper on this (within quantum-chemical context)

- cited 12 times (according to google scholar)
- Trygve‘s first single-author paper (pre-PhD)

Better known:

- *A numerically stable procedure for calculating Møller–Plesset energy derivatives, derived using the theory of Lagrangians*, T. Helgaker, P. Jørgensen, and N. C. Handy, *Theor. Chim. Acta* **76**, 227–245 (1989) 124 citations
- *Coupled cluster energy derivatives. Analytic Hessian for the closed-shell coupled cluster singles and doubles wave function: Theory and applications*, H. Koch, H. J. Aa. Jensen, P. Jørgensen, T. Helgaker, G. E. Scuseria, and H. F. Schaefer III, *J. Chem. Phys.* **92**, 4924–4940 (1990) 281 citations

Method of Lagrange multipliers

- Set up energy functional (Lagrangian L) with side condition f
- Side condition written such that

$$\boxed{f(x, c(x)) = 0}$$

- If those side conditions are fulfilled, Lagrangian is equal to the energy itself: L=E
- Lagrangian:

$$\boxed{L = E + \lambda f}$$

side condition

Lagrange multiplier

- Enforce stationarity $\frac{\partial L}{\partial c} \overset{!}{=} 0$ and $\frac{\partial L}{\partial \lambda} \overset{!}{=} 0$

notice: L, not E!

Gives back side condition f

Method of Lagrange multipliers

$$\boxed{L = E + \lambda f}$$

- Stationarity

$$\boxed{\frac{\partial L}{\partial c} = \frac{\partial E}{\partial c} + \lambda \frac{\partial f}{\partial c} = 0}$$

← determines **λ**

Note: perturbation-independent (as compared to $\frac{\partial c}{\partial x}$)

$$\boxed{\frac{\partial L}{\partial \lambda} = f = 0}$$

← determines c

Gives back side condition

- Note: derivative wrt c → **λ**
  derivative wrt **λ** → c

Method of Lagrange multipliers

- Hence for the gradient:

$$\frac{dL(x)}{dx} = \frac{\partial L}{\partial x} + \underbrace{\cancel{\frac{\partial L}{\partial c}\frac{\partial c}{\partial x}}}_{=0} + \underbrace{\cancel{\frac{\partial L}{\partial \lambda}\frac{\partial \lambda}{\partial x}}}_{=0}$$

→We managed to avoid having to solve for response of wave function parameters to perturbation!

$$\boxed{\frac{dL(x)}{dx} = \frac{\partial L}{\partial x} = \frac{\partial E}{\partial x} + \underbrace{\lambda\frac{\partial f}{\partial x}}_{\text{In addition as compared to expression for variational methods.}}}$$

In addition as compared to expression for variational methods.

Method of Lagrange multipliers

- Constrained variation: side condition corresponds to constraints that need to be fulfilled. Example: orthogonality constraint of the orbitals for Hartree-Fock*

- Non-variational wave functions: side condition corresponds to the conditional equations that are needed to get the wave function parameters (solved anyways)

*note that HF can be formulated in unconstrained manner using orbital rotation

Lagrangian expressions: Hartree Fock

- Hartree-Fock Lagrangian:

$$L^{\mathrm{HF}} = \boxed{\sum_{\mu\nu} D_{\mu\nu} h_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\sigma\rho} D_{\mu\nu} D_{\sigma\rho}\left(\langle\mu\sigma \mid \nu\rho\rangle - \frac{1}{2}\langle\mu\sigma \mid \rho\nu\rangle\right)}$$

$$\boxed{-2\sum_{ij}\epsilon_{ij}\left(\sum_{\mu\nu} c^{*}_{\mu i} S_{\mu\nu} c_{\nu j} - \delta_{ij}\right)}$$

E^{HF}

$D_{\mu\nu} = 2\sum_{i} c^{*}_{\mu i} c_{\nu i}$

orthogonality constraint $\langle\phi_i \mid \phi_j\rangle = \delta_{ij}$

Lagrange multipliers (one per constraint)

$$\frac{\partial L^{\mathrm{HF}}}{\partial c} = 0$$

→ → Hartree-Fock equations

Hartree Fock gradient

- HF gradient:

$$\frac{dE^{\mathrm{HF}}}{dx} = \frac{\partial L^{\mathrm{HF}}}{\partial x} = \underbrace{\boxed{\sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial x} + \frac{1}{2} \sum_{\mu\nu\sigma\rho} D_{\mu\nu} D_{\sigma\rho} \left(\frac{\partial \langle \mu\sigma \mid \nu\rho \rangle}{\partial x} - \frac{1}{2} \frac{\partial \langle \mu\sigma \mid \rho\nu \rangle}{\partial x} \right)}}_{\frac{\partial E^{\mathrm{HF}}}{\partial x}}$$

$$\boxed{- \sum_{\mu\nu} \underbrace{W_{\mu\nu}}_{\text{Energy-weighted density matrix}} \frac{\partial S_{\mu\nu}}{\partial x}}$$

$$W_{\mu\nu} = 2 \sum_i c^*_{\mu i} \epsilon_i c_{\nu i}$$

- Essentially only integral derivatives required!
- No derivatives of the density matrices

Reminder Coupled Cluster

CC wave function

$$\boxed{|\,\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}\,|\,\Psi^{\mathrm{HF}}\rangle}$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N$$

$$\hat{T}_1 = \sum_{ai} t_i^a \hat{a}_a^\dagger \hat{a}_i \qquad \hat{T}_2 = \sum_{abij} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$$

amplitudes t_p

CC equations

Amplitude equations

$$\langle \Psi_p \,|\, e^{-\hat{T}} \hat{H} e^{\hat{T}} \,|\, \Psi^{\mathrm{HF}} \rangle = 0$$

CC energy

$$\langle \Psi^{\mathrm{HF}} \,|\, e^{-\hat{T}} \hat{H} e^{\hat{T}} \,|\, \Psi^{\mathrm{HF}} \rangle = E^{\mathrm{CC}}$$

Lagrangian expressions: Coupled Cluster

- Coupled-Cluster Lagrangian (non-variational!)

$$L^{\mathrm{CC}} = \boxed{\langle \Psi^{\mathrm{HF}} \mid \exp(-\hat{T})\hat{H}\exp(\hat{T}) \mid \Psi^{\mathrm{HF}} \rangle} \rightarrow E^{\mathrm{CC}}$$

$$\boxed{+ \sum_p \lambda_p \langle \Psi_p \mid \exp(-\hat{T})\hat{H}\exp(\hat{T}) \mid \Psi^{\mathrm{HF}} \rangle}$$

→ Amplitude equations (determine the CC amplitudes)

→ Lagrange multipliers (one per constraint)

- Often written as

$$\boxed{L^{\mathrm{CC}} = \langle \Psi^{\mathrm{HF}} \mid (1+\Lambda)\exp(-\hat{T})\hat{H}\exp(\hat{T}) \mid \Psi^{\mathrm{HF}} \rangle}$$

with deexcitation operator $\langle \Psi^{\mathrm{HF}} \mid \Lambda = \sum_p \lambda_p \langle \Psi_p \mid$

Lagrangian expressions: Coupled Cluster

- Full CC Lagrangian and required side conditions (from t-amplitudes and MO-coefficients → orbital relaxation)

$$L^{\mathrm{CC}} = \langle \Psi^{\mathrm{HF}} \mid (1+\Lambda) \exp(-\hat{T}) \hat{H} \exp(\hat{T}) \mid \Psi^{\mathrm{HF}} \rangle$$

E + amplitude equations

$$+ \sum_{ai} \underbrace{Z_{ai} f_{ai}}_{\downarrow} + \sum_{pq} \underbrace{I_{pq}(S_{pq} - \delta_{pq})}_{\downarrow}$$

← orbital relaxation part

Brillouin condition (HF minimal condition)

orthogonality condition of MOs

wf parameters 1: CC amplitudes t_p

wf parameters 2: MO coefficients c

→ Total of 3 types of Lagrange multipliers λ_p, Z_{ai}, I_{pq}

Lagrangian expressions: Coupled Cluster

or in terms of density matrices (general form)

$$L^{\mathrm{CC}} = \sum_{pq} \tilde{D}_{pq} f_{pq} + \sum_{pqrs} \Gamma_{pqrs} \langle pq \,||\, rs \rangle + \sum_{pq} I_{pq} S_{pq}$$

↓

Generalized 1-el density matrix
(contains Z_{ai} contribution)

density matrices (contain t_p and λ_p amplitudes)

$$D_{pq} = \langle \Psi^{\mathrm{HF}} \mid (1+\Lambda) e^{-\hat{T}} \{\hat{a}_p^\dagger \hat{a}_q\} e^{\hat{T}} \mid \Psi^{\mathrm{HF}} \rangle$$

$$\Gamma_{pqrs} = \langle \Psi^{\mathrm{HF}} \mid (1+\Lambda) e^{-\hat{T}} \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\} e^{\hat{T}} \mid \Psi^{\mathrm{HF}} \rangle$$

Lagrangian expressions: Coupled Cluster

- Derivatives with respect to the wave-function parameters

$$\frac{\partial L^{\mathrm{CC}}}{\partial t_p} = 0$$

$\mathit{\Lambda}$ equations (determine λ_p)
→ Needed to set up (unrelaxed) CC density

$$\frac{\partial L^{\mathrm{CC}}}{\partial c} = 0$$

Z-vector equations (determine Z_{ai}, I_{pq})

→ Perturbation-independent equations

$$\frac{\partial L^{\mathrm{CC}}}{\partial \lambda_p} = 0$$

gives back CC equations

Lagrangian expressions: Coupled Cluster

$$L^{\mathrm{CC}} = \sum_{pq} \tilde{D}_{pq} f_{pq} + \sum_{pqrs} \Gamma_{pqrs} \langle pq \,||\, rs \rangle + \sum_{pq} I_{pq} S_{pq}$$

- Gradient

$$\boxed{\frac{dE^{\mathrm{CC}}}{dx} = \frac{\partial L^{\mathrm{CC}}}{\partial x} = \sum_{pq} \tilde{D}_{pq} f_{pq}^{(x)} + \sum_{pqrs} \Gamma_{pqrs} \langle pq \,||\, rs \rangle^x + \sum_{pq} I_{pq} S_{pq}^x}$$

Notation: only the integrals (but not MO coefficients are differentiated!

$$f_{pq}^{(x)} = \sum_{\mu\nu} c_{\mu p}^* \left\{ \frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} D_{\sigma\rho}^{\mathrm{SCF}} \frac{\partial \langle \mu\sigma \,||\, \nu\rho \rangle}{\partial x} \right\} c_{\nu q}$$

$$\langle pq \,||\, rs \rangle^x = \sum_{\mu\nu\sigma\rho} c_{\mu p}^* c_{\sigma q}^* \frac{\partial \langle \mu\sigma \,||\, \nu\rho \rangle}{\partial x} c_{\nu r} c_{\rho s}$$

$$S_{pq}^x = \sum_{\mu\nu} c_{\mu p}^* \frac{\partial S_{\mu\nu}}{\partial x} c_{\nu q}$$

For implementation expressed in AO basis

Flowchart CC gradients

Solve CC and $\boldsymbol{\Lambda}$ equations (~N^6, N^8, …)

Build CC density matrices (~N^6, N^8, …)

Transformation of densities to AO basis (~N^5)

Contract with integrals derivatives (N^4, no storage)

Computation independent of N_{pert}
→ for geometrical gradients: independent of number of atoms

A note on orbital relaxation

- For the CC (or MP, CI, …) wave function:

$$\boxed{\Psi = \Psi(c, t)}$$

MO coefficients

amplitudes (or CI coefficients, …)

switch on perturbation x

$$\boxed{\Psi = \Psi(c(x), t(x))}$$

MOs may react to the perturbation

or

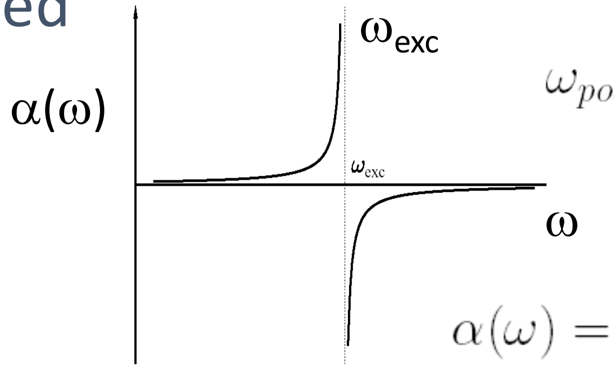
$$\boxed{\Psi = \Psi(c(0), t(x))}$$

Perturbation only switched on for correlation treatment
NO orbital relaxation

- Choice whether to include orbital relaxation, i.e., terms that stem from the HF wave-function parameters (Brillouin & orthogonality condition)

A note on orbital relaxation

- Relevance of inclusion depends on type of perturbation
  - Perturbation changes the metric $\frac{dS_{\mu\nu}}{dx} \neq 0$ → inclusion important
    - In particular for geometric perturbations a must (correct gradient)
  - Perturbation does not change the metric → free choice
    - Electric field
  - For frequency-dependent perturbations, consideration of orbital relaxation leads to additional unphysical poles (from HF) → not recommended



$$\omega_{pole} = \left(E_{exc} - E_0\right)/\hbar$$

$$\alpha(\omega) = \sum_i \frac{|\langle\Psi_0|\hat{\mu}|\Psi_i\rangle|^2}{\omega_{oi} - \omega} + \sum_i \frac{|\langle\Psi_0|\hat{\mu}|\Psi_i\rangle|^2}{\omega_{oi} + \omega}$$

$\Rightarrow$ pole position at excitation frequency

Take-home messages lecture 1

- Properties can be calculated as energy derivatives
- Analytic differentiation is preferred (accuracy + cost)
- Perturbations that change the metric can cause more work (validity of Hellman-Feynman theorem)
- Method of Lagrange multipliers is useful to get (efficient) expressions for the derivatives also for non-variational methods
- Usefulness of inclusion of orbital relaxation depends on property

Reminder: method of Lagrange multipliers

- Set up energy functional (Lagrangian L) with side condition f
- Side condition written such that $\boxed{f(x, c(x)) = 0}$

- If those side conditions are fulfilled, Lagrangian is equal to the energy itself: $L = E$

- Lagrangian: $$\boxed{L = E + \underbrace{\lambda}_{\text{Lagrange multiplier}} \underbrace{f}_{\text{side condition}}}$$

- Enforce stationarity $\frac{\partial L}{\partial c} \overset{!}{=} 0$ and $\frac{\partial L}{\partial \lambda} \overset{!}{=} 0$

notice: L, not E!

Gives back side condition f

Reminder: method of Lagrange multipliers

- Hence for the gradient:

$$\frac{dL(x)}{dx} = \frac{\partial L}{\partial x} + \xcancel{\underbrace{\frac{\partial L}{\partial c}}_{=0}\frac{\partial c}{\partial x}} + \xcancel{\underbrace{\frac{\partial L}{\partial \lambda}}_{=0}\frac{\partial \lambda}{\partial x}}$$

→We managed to avoid having to solve for response of wave function parameters to perturbation!

$$\boxed{\frac{dL(x)}{dx} = \frac{\partial L}{\partial x} = \frac{\partial E}{\partial x} + \lambda\underbrace{\frac{\partial f}{\partial x}}_{\text{In addition as compared to expression for variational methods.}}}$$

Only contributions from explicit dependence (perturbed integrals) needed

(2*n*+1) rule for wave-function parameters

- One can show that the *n*-th derivative of the wave-function parameters is sufficient for the calculation up to the (2*n*+1)-th derivative of the energy!

$$\boxed{c^{(n)} \rightarrow E^{(2n+1)}}$$

no response of the wave function parameters required

n=0 → 1st derivative of energy

n=1 → 2nd and 3rd derivative of the energy

n=2 → 4th and 5th derivative of the energy

- Holds for variational wave functions
- Holds for constrained variation and non-variational methods when Lagrangian is used

(2*n*+2) rule for Lagrange multipliers

- Similarly, one can show that the *n*-th derivative of the Lagrange multipliers is sufficient for the calculation up to the (2*n*+2)-th derivative of the energy!

$$\boxed{\lambda^{(n)} \rightarrow E^{(2n+2)}}$$

$n=0$ → 1st and 2nd derivative of energy

$n=1$ → 3rd and 4th derivative of the energy

$n=2$ → 5th and 6th derivative of the energy

First contribution appears for third derivative of the energy!

Second derivatives

- For the second derivative, according to the (2*n*+1) and (2*n*+2) rules, the first derivative of the wave-function parameters $c^{(1)}$ is required, no derivatives with respect to the Lagrange multipliers $\lambda^{(0)}$.

$$\boxed{\frac{d^2E}{dxdy} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial y \partial c}\frac{\partial c}{\partial x} + \frac{\partial^2 L}{\partial c^2}\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}}$$

- Equations for the perturbed wave-function parameters via differentiation of their conditional equations wrt to the perturbation.

Second derivatives

- Depending on the perturbation it can be advantageous to differentiate the first derivative leading to the so-called asymmetric expression

$$\boxed{\frac{d^2E}{dxdy} = \frac{d}{dy}\frac{\partial L}{\partial x} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial x \partial \lambda}\frac{\partial \lambda}{\partial y}}$$

- No derivative of c wrt to perturbation x needed.
- Instead, derivative of **λ** wrt to y needed.
- Order of differentiation: Example NMR shieldings:
  - Perturbation 1: Nuclear magnetic moment, N_{atom}*3 components
  - Perturbation 2: Magnetic field, 3 components, two sets

Harmonic frequencies

- Typical example: harmonic vibrational frequencies

- Taylor expansion of the BO potential around equilibrium geometry & cut after harmonic approximation

$$V^{\mathrm{BO}} \approx V_{\mathrm{eq}} + \frac{1}{2}\sum_{ij}^{3N_{\mathrm{atom}}} \left(\frac{\partial^2 V}{\partial X_i \partial X_j}\right)_{\mathrm{eq}} (X_i - X_i^{\mathrm{eq}})(X_j - X_j^{\mathrm{eq}})$$

elements H_{ij} of Hessian

$$\approx V_{\mathrm{eq}} + \frac{1}{2}\sum_{ij}^{3N_{\mathrm{atom}}} H_{ij}\Delta x_i \Delta x_j$$

- Insert into nuclear Hamiltonian $\hat{H}_{\mathrm{nuc}} = \hat{T}_{\mathrm{nuc}} + V^{\mathrm{BO}}$

$$\hat{H}_{\mathrm{nuc}} = -\frac{1}{2}\sum_{i}^{3N_{\mathrm{atom}}} \frac{1}{M_i}\frac{\partial^2}{\partial X_i^2} + \frac{1}{2}\sum_{i}^{3N_{\mathrm{atom}}} H_{ij}\Delta x_i \Delta x_j$$

couplings

Harmonic frequencies

- Introduce mass-weighted coordinates $\tilde{x}_i = \sqrt{M_i}\Delta x_i$

$$\hat{H}_{\text{nuc}} = -\frac{1}{2}\sum_i^{3N_{\text{atom}}} \frac{\partial^2}{\partial \tilde{x}_i^2} + \frac{1}{2}\sum_{ij}^{3N_{\text{atom}}} \underbrace{\frac{H_{ij}}{\sqrt{M_i M_j}}}_{K_{\text{ij}}} \tilde{x}_i \tilde{x}_j$$

- Diagonalize $\mathbf{K}$ matrix to construct new coordinates from the eigenvectors $\mathbf{L}$ $\quad \mathbf{KL} = \mathbf{L}\boldsymbol{\lambda}$
- Build normal coordinates $Q_i = \sum_j L_{ji}\tilde{x}_j$

$$\hat{H}_{\text{nuc}} = -\frac{1}{2}\sum_i^{3N_{\text{atom}}} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\sum_i^{3N_{\text{atom}}} \lambda_i Q_i^2 = \sum_i^{3N_{\text{atom}}} \hat{H}_i^{\text{HO}}$$

separable harmonic oscillator

no couplings

- vibrational frequencies $\omega_i = \sqrt{\lambda_i}$ normal-coordinate analysis

Expression for HF second derivatives

$$
\begin{aligned}
\frac{d^2E^{\mathrm{HF}}}{dxdy} = \frac{d}{dy}\frac{\partial L^{\mathrm{HF}}}{\partial x} = & \sum_{\mu\nu} D_{\mu\nu}\frac{\partial^2 h_{\mu\nu}}{\partial x\partial y} + \frac{1}{2}\sum_{\mu\nu\sigma\rho} D_{\mu\nu}D_{\sigma\rho}\left(\frac{\partial^2\langle\mu\sigma \mid \nu\rho\rangle}{\partial x\partial y} - \frac{1}{2}\frac{\partial^2\langle\mu\sigma \mid \rho\nu\rangle}{\partial x\partial y}\right) \\
& - \sum_{\mu\nu} W_{\mu\nu}\frac{\partial^2 S_{\mu\nu}}{\partial x\partial y} \\
& + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial y}\left(\frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} P_{\sigma\rho}\left(\frac{\partial\langle\mu\sigma \mid \nu\rho\rangle}{\partial x} - \frac{1}{2}\frac{\partial\langle\mu\sigma \mid \rho\nu\rangle}{\partial x}\right)\right) \\
& - \sum_{\mu\nu} \frac{\partial W_{\mu\nu}}{\partial y}\frac{\partial S_{\mu\nu}}{\partial x}
\end{aligned}
$$

with

$$
\frac{\partial D_{\mu\nu}}{\partial x} = 2\sum_i\left\{\frac{\partial c^*_{\mu i}}{\partial x}c_{\nu i} + c^*_{\mu i}\frac{\partial c_{\nu i}}{\partial x}\right\} \qquad \frac{\partial W_{\mu\nu}}{\partial x} = 2\sum_i\{\frac{\partial c^*_{\mu i}}{\partial x}\epsilon_i c_{\nu i} + c^*_{\mu i}\epsilon_i\frac{\partial c_{\nu i}}{\partial x}\} + \sum_{ij} c^*_{\mu i}\frac{\partial \epsilon_{ji}}{\partial x}c_{\nu j}.
$$

(2n+1) → Derivative of MO coefficients needed → CPHF equations

Shown here: asymmetric expression

Flowchart HF second derivatives

SCF calculation

Transform integrals

Solve CPHF equations, get U^{x}_{ai}

Obtain $\dfrac{\partial c_{\mu\nu}}{\partial x}$ and $\dfrac{\partial D_{\mu\nu}}{\partial x}$

Calculate second-order property

Expression for CC second derivatives

- symmetric expression: $\frac{d^2E}{dxdy} = \frac{\partial^2 L}{\partial x \partial y} + \frac{\partial^2 L}{\partial x \partial c}\frac{\partial c}{\partial y} + \frac{\partial^2 L}{\partial y \partial c}\frac{\partial c}{\partial x} + \frac{\partial^2 L}{\partial c^2}\frac{\partial c}{\partial x}\frac{\partial c}{\partial y}$

$$
\begin{aligned}
\frac{d^2E}{dxdy} = &\langle 0|(1+\Lambda)\exp(-T)\frac{\partial^2 H}{\partial x \partial y}\exp(T)|0\rangle \\
&+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial x}\exp(T), \frac{dT}{dy}]|0\rangle + \\
&+\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial y}\exp(T), \frac{dT}{dx}]|0\rangle + \\
&+\langle 0|(1+\Lambda)[[\exp(-T)H\exp(T), \frac{dT}{dx}], \frac{dT}{dy}]|0\rangle .
\end{aligned}
$$

Skipping here the contributions from orbital relaxation
(2n+1) rule → first derivatives of t amplitudes
(2n+2) rule → no derivative of λ amplitudes

Expression for CC second derivatives

- asymmetric expression: $\frac{d^2E}{dxdy} = \frac{d}{dy}\frac{\partial L}{\partial x} = \frac{\partial^2 L}{\partial x\partial y} + \frac{\partial^2 L}{\partial x\partial c}\boxed{\frac{\partial c}{\partial y}} + \frac{\partial^2 L}{\partial x\partial \lambda}\boxed{\frac{\partial \lambda}{\partial y}}$

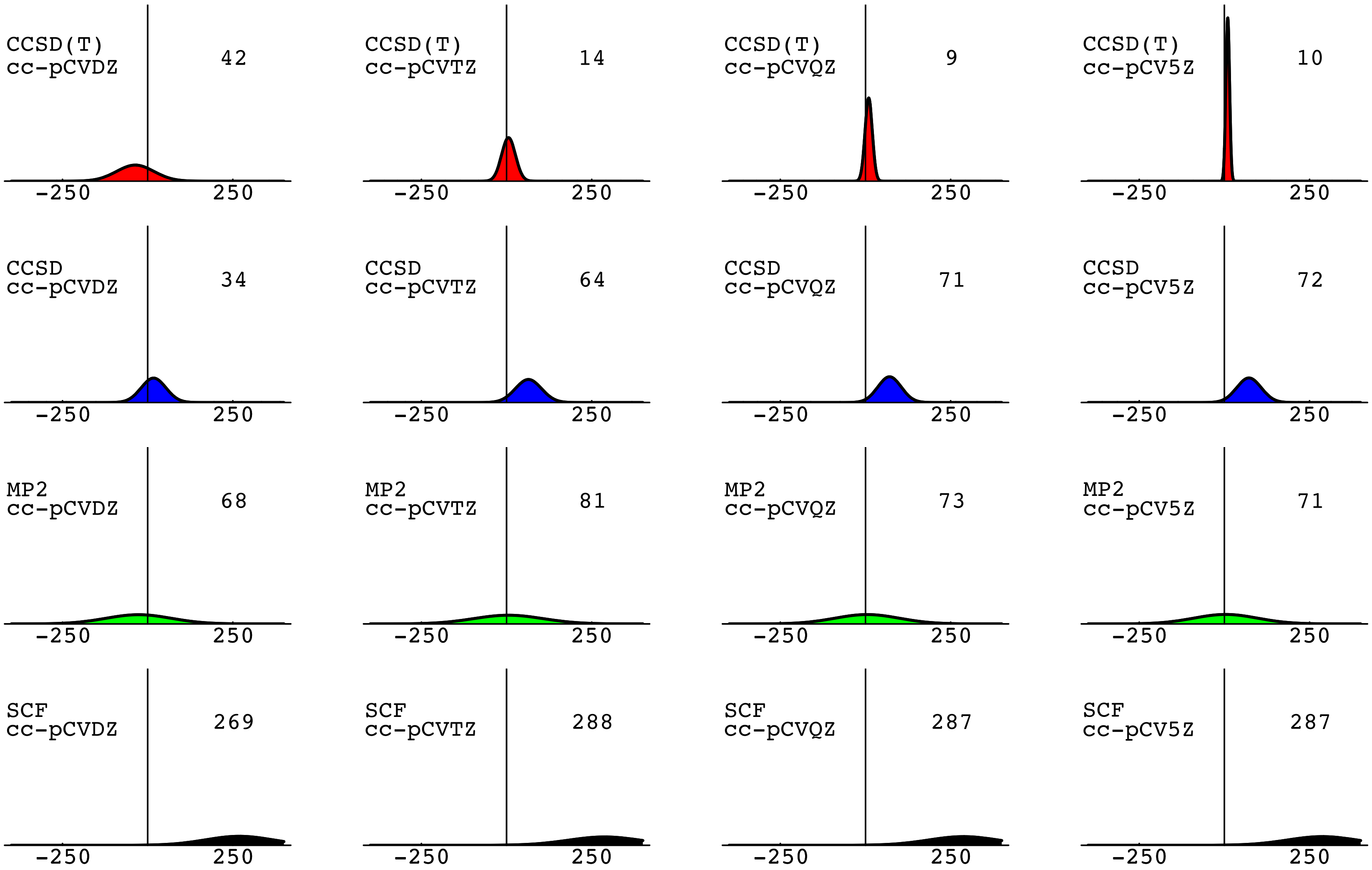
$$\begin{aligned}\frac{d^2E}{dxdy} = {} & \langle 0|(1+\Lambda)\exp(-T)\frac{\partial^2 H}{\partial x\partial y}\exp(T)|0\rangle \\ & +\langle 0|(1+\Lambda)[\exp(-T)\frac{\partial H}{\partial x}\exp(T),\boxed{\frac{dT}{dy}}]|0\rangle + \\ & +\langle 0|\boxed{\frac{d\Lambda}{dy}}\exp(-T)\frac{\partial H}{\partial x}\exp(T)|0\rangle .\end{aligned}$$

Skipping here the contributions from orbital relaxation
full differentiation of the gradient expression :

→ perturbed CC equations wrt *x*
→ perturbed *λ* equations wrt *y*

Harmonic constants ω_e of BH, CO, N_2, HF, F_2

in cm^{-1}



from T. Helgaker lecture notes on derivatives

Summary

- Properties as derivatives
- Numerical vs. analytical derivatives
- Lagrangian techniques for constrained variation and non-variational wave functions
  - Avoid calculation of response of wave function parameters if possible
- Expressions for gradients and second derivatives

Part 2
Magnetic properties and molecules in magnetic fields

Contents

- Introduction into electromagnetic fields
- Derivation of Hamiltonian with electromagnetic fields
- Magnetizabilities
- Gauge-origin dependence in quantum-chemical calculations
- Further magnetic properties
- Strong magnetic fields

Fields, Forces, and Potentials

- Particles can be charged
- Charged particles interact

charges z_1 and z_2

Coulomb force
(SI units)

$$\boxed{\underline{F}^{\text{Coul}} = \frac{1}{4\pi\varepsilon_0} \frac{z_1 z_2}{r^3} \underline{r}}$$

vacuum permittivity

- Charge generates electric field
- Second charge interacts with electric field (feels force in the electric field generated by z_1)

$$\boxed{\underline{E} = \frac{\underline{F}}{z_2} = \frac{1}{4\pi\varepsilon_0} \frac{z_1}{r^3} \underline{r}}$$

A quick reminder...

Nabla-operator (vector) $\nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}$

Gradient (on scalar) → vector $\nabla f = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{pmatrix}$

Divergence (on vector) → scalar $\nabla \underline{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$

Curl $\nabla \times \underline{A} = \begin{pmatrix} \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \\ \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \\ \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \end{pmatrix}$

Curl of gradient $\nabla \times \nabla f = \underline{0}$

Divergence of curl $\nabla \cdot (\nabla \times \underline{A}) = 0$

Fields, Forces, and Potentials

- Coulomb force is conservative! $\underline{F} = -\nabla V$
- Electrostatic potential generates the electric field

$$\underline{F} = \frac{1}{4\pi\varepsilon_0}\frac{z_1 z_2}{r^3}\underline{r}$$

Coulomb force

$$\underline{F}$$

$$-\nabla V$$

$$V$$

Coulomb potential

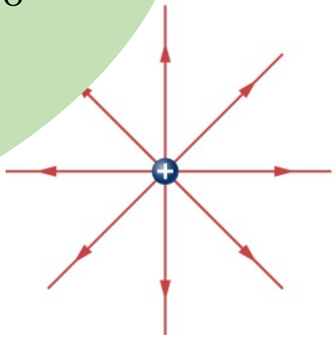
$$V = \frac{1}{4\pi\varepsilon_0}\frac{z_1 z_2}{r}$$

$$\underline{E} = \frac{\underline{F}}{z_2}$$

$$\underline{E} = \frac{1}{4\pi\varepsilon_0}\frac{z_1}{r^3}\underline{r}$$

electric field

$$\underline{E}$$



$$-\nabla\Phi$$

$$\Phi$$

Electrostatic potential

$$\Phi = \frac{1}{4\pi\varepsilon_0}\frac{z_1}{r}$$

For charge distribution $\rho(r)$

$$\Phi(r) = \frac{1}{4\pi\varepsilon_0}\int d^3r'\,\frac{\rho(r')}{|r - r'|}$$

Fields, Forces, and Potentials

- Fields are associated with forces
- In quantum-mechanics we work with potentials rather than forces (see Hamiltonian…)
- For conservative forces, the potential is related to the force simply via $F = -\nabla V$

→ Easy to work with potentials

Moving charges and magnetic fields

- A moving charge furthermore experiences a Lorentz-force

$$\boxed{\underline{F}^{\mathrm{Lorentz}} = z(\underline{v} \times \underline{B})}$$

force is dependent on velocity!

deflection perpendicular to $\underline{B}$

magnetic field

- Additional non-conservative force!
- Forces on matter through $\underline{E}$ and $\underline{B}$
  → Coulomb- and Lorentz forces

$$\boxed{\underline{F}^{\mathrm{tot}} = z(\underline{E} + \underline{v} \times \underline{B})}$$

often referred to as Lorentz force

electric part

magnetic part

Straightforward to be used within Newton‘s formulation of classical mechanics!

Moving charges and magnetic fields

- In the case of a non-conservative force, the relationship with the potential is not as simple…

$$F \neq -\nabla V$$

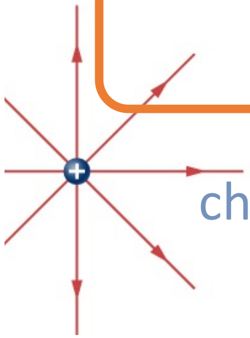
- How can we then get access to the potentials?

Maxwell Equations

- Maxwell equations provide basis for electrodynamics

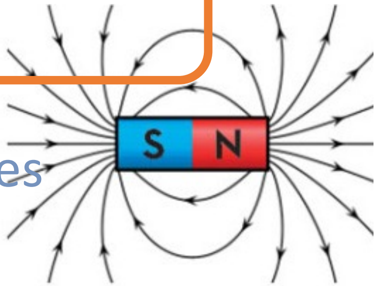
connect ***E*** and ***B*** as well as charge density ρ and current ***j***

$$\nabla \underline{E} = \frac{1}{\varepsilon_0}\rho$$



charges create electric field

$$\nabla \underline{B} = 0$$



no magnetic monopoles

$$\nabla \times \underline{E} = -\frac{\partial \underline{B}}{\partial t}$$

time-dependent magnetic field generates electric field

$$\nabla \times \underline{B} = -\mu_0 \underline{j} + \frac{1}{c^2}\frac{\partial \underline{E}}{\partial t}$$

currents generate magnetic field

Lorentz invariant

Potentials of electromagnetic fields

- Lorentz force not conservative → cannot be traced back to a simple scalar potential!
- Limiting cases:
  - E≠0, B=0 $\underline{E} = -\nabla\Phi$
  - B≠0, E=0 $\underline{B} = \nabla \times \underline{A}$ (fulfills 2.MEQ: $\nabla \underline{B} = 0$)

$\underline{A}$ is the so-called vector potential which is associated with the magnetic field. We define it such that it gives back $\underline{B}$

Potentials of electromagnetic fields

- Lorentz force not conservative → cannot be traced back to a simple scalar potential!
- Limiting cases:
  - E≠0, B=0 $\underline{E} = -\nabla\Phi$
  - B≠0, E=0 $\underline{B} = \nabla \times \underline{A}$ (fulfills 2.MEQ: $\nabla\underline{B} = 0$)
  - E≠0, B≠0 using 3. MEQ: $\nabla \times \underline{E} = -\frac{\partial}{\partial t}\underline{B}$

rearrange rhs

$$\nabla \times \underline{E} = -\frac{\partial}{\partial t}(\nabla \times \underline{A})$$

$$\nabla \times \underline{E} = \nabla \times \left(-\frac{\partial \underline{A}}{\partial t}\right)$$

$$\underline{E} = -\frac{\partial \underline{A}}{\partial t} + \nabla f$$

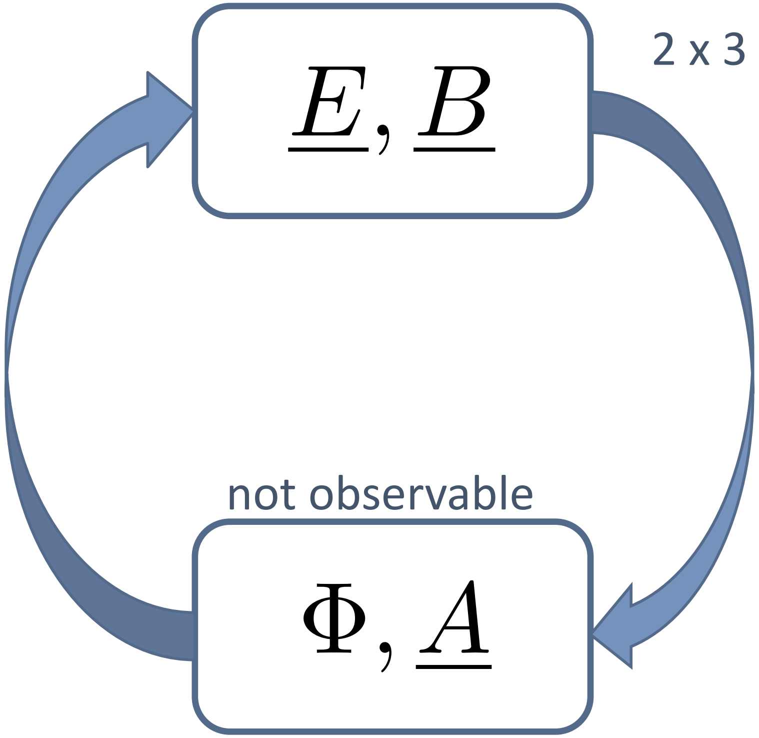
can be added since $\nabla \times \nabla f = 0$ hence no impact on 3. MEQ

$$\boxed{\underline{E} = -\nabla\Phi - \frac{\partial \underline{A}}{\partial t}}$$

Potentials of electromagnetic fields

unique!

$$\underline{E} = -\nabla\Phi - \frac{\partial \underline{A}}{\partial t}$$
$$\underline{B} = \nabla \times \underline{A}$$



observables

$\underline{E}, \underline{B}$

2 x 3 = 6 components

NOT unique!

not observable

$\Phi, \underline{A}$

1+3 = 4 components

This means: Many choices of vector and electrostatic potential lead to same observable electric and magnetic fields!

Choice of gauge

- Different choices of $\underline{A}$ and ϕ can generate same $\underline{E}$ and $\underline{B}$
  - Case 1: $\underline{E} = -\nabla\Phi, \quad \underline{B} = 0$

    can add a constant to ϕ (because gradient is taken)
  - Case 2: $\underline{E} = 0, \quad \underline{B} = \nabla \times \underline{A}$

    can add gradient of a scalar function to $\underline{A}$
  - General case: $\underline{E} = -\nabla\Phi - \frac{\partial \underline{A}}{\partial t}, \quad \underline{B} = \nabla \times \underline{A}$

Allowed trans-formations

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

$$\Phi' = \Phi - \frac{\partial}{\partial t} f$$

no change in $\underline{B}$: $\underline{B}(\underline{A}) = \underline{B}(\underline{A}')$
but change in $\underline{E}$, compensate by

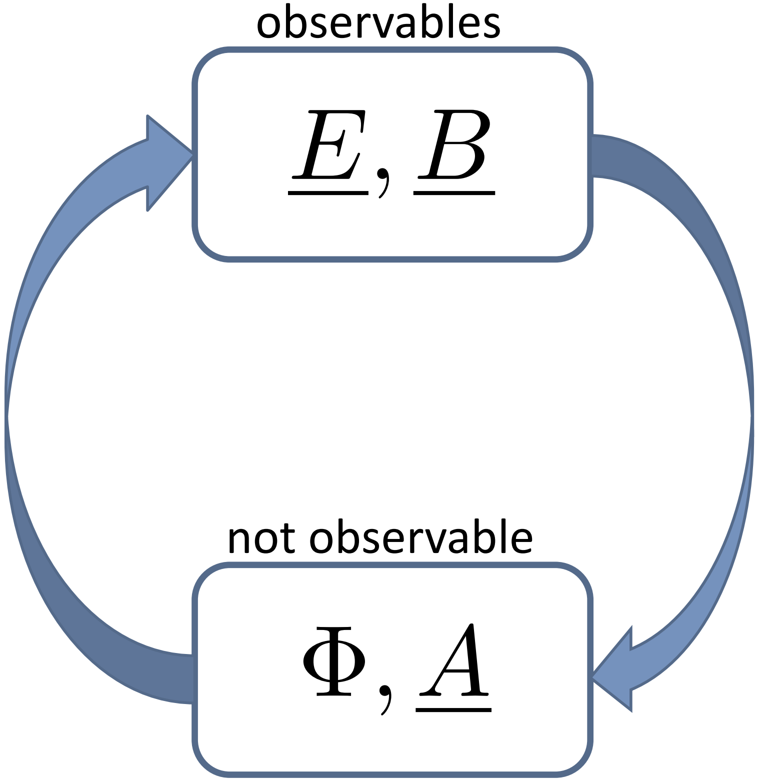
choice of arbitrary scalar function
f → choice of gauge!

$$\underline{E}(\Phi, \underline{A}) = \underline{E}(\Phi', \underline{A}')$$

$$\underline{B}(\underline{A}) = \underline{B}(\underline{A}')$$

electric and magnetic fields unchanged!

Choice of gauge



observables

$$\underline{E}, \underline{B}$$

not observable

$$\Phi, \underline{A}$$

unique!

$$\boxed{\begin{aligned} \underline{E} &= -\nabla\Phi - \frac{\partial \underline{A}}{\partial t} \\ \underline{B} &= \nabla \times \underline{A} \end{aligned}}$$

NOT unique!

Gauge transformations:

$$\boxed{\begin{aligned} \Phi' &= \Phi - \frac{\partial}{\partial t} f \\ \underline{A}' &= \underline{A} + \nabla f \end{aligned}}$$

Using **Φ**‘ and $\underline{A}$‘ instead of **Φ** and $\underline{A}$ will describe the same fields $\underline{E}$ and $\underline{B}$

Usually we require the vector potential to obey: $\boxed{\nabla \underline{A} = 0}$ „Coulomb gauge“ $\longrightarrow$ implies also $\boxed{\nabla^2 f = 0}$

Choice of gauge-origin

- Example: Static homogenous magnetic field (independent of time and position)

$$\underline{B} = \underline{\mathrm{const.}}$$

$$\underline{B} = \nabla \times \underline{A}$$

$$\underline{A} = \frac{1}{2}(\underline{B} \times \underline{r})$$

Choice of gauge-origin

- Example: B in z-direction

$$\underline{B} = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix} \xrightarrow{\boxed{\underline{A} = \frac{1}{2}(\underline{B} \times \underline{r})}} \underline{A} = \frac{1}{2} \begin{pmatrix} -B_z y \\ B_z x \\ 0 \end{pmatrix}$$

$$B = \nabla \times \underline{A} = \frac{1}{2} \begin{pmatrix} 0 \\ 0 \\ \frac{\partial}{\partial x} A_y - \frac{\partial}{\partial y} A_x \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 0 \\ 0 \\ B_z + B_z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix}$$

Choice of gauge-origin

- Example: Static homogenous magnetic field (independent of time and position)

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

$$\boxed{\underline{A} = \frac{1}{2}(\underline{B} \times \underline{r})}$$

- Equivalent:

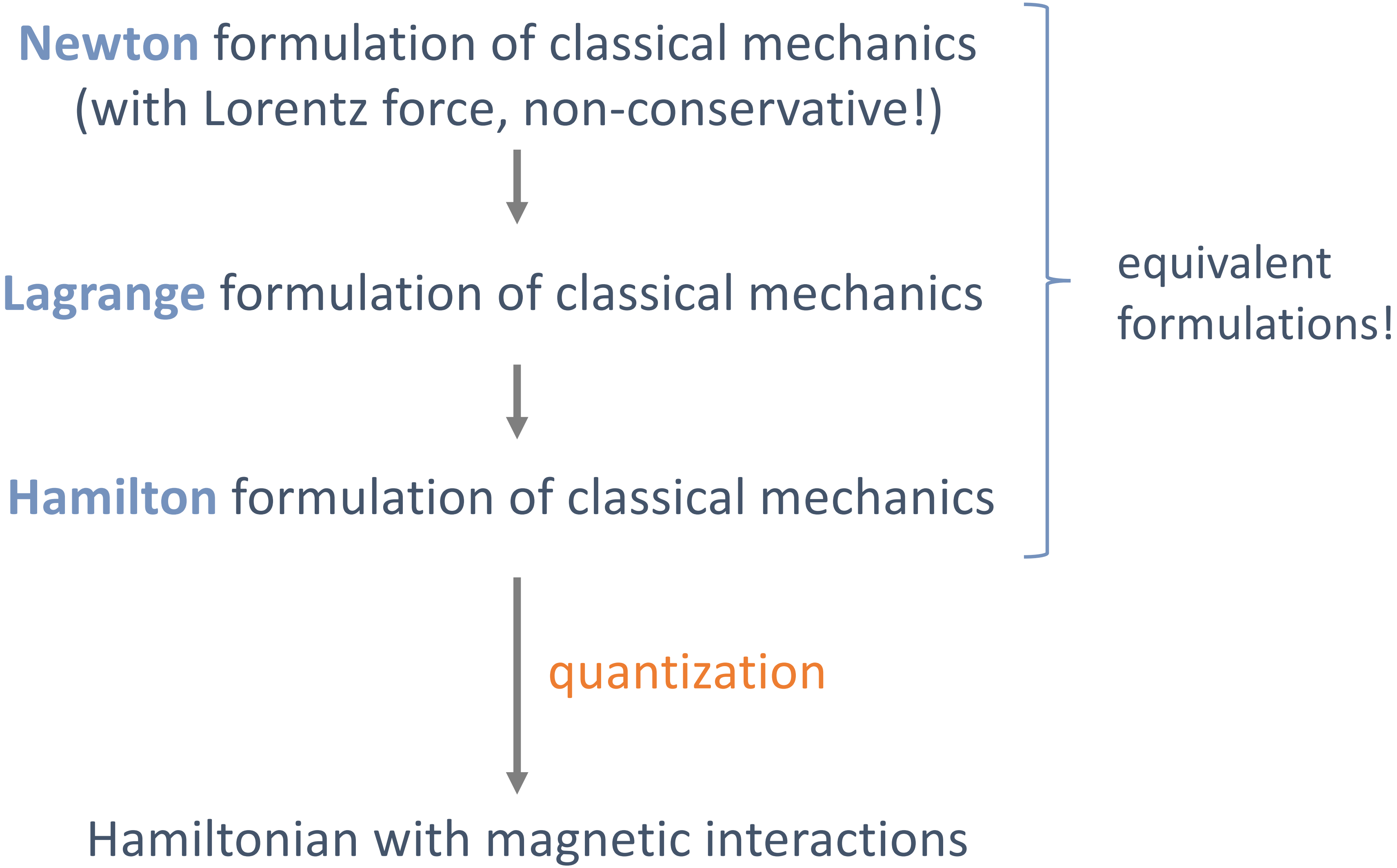
$$\underline{A}' = \frac{1}{2}(\underline{B} \times (\underline{r} - \underline{R}_{\mathrm{O}}))$$

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

$$\underline{A}' = \boxed{\underline{A}} \boxed{+ \nabla f} \qquad f = -\frac{1}{2}(\underline{B} \times \underline{R}_{\mathrm{O}})\underline{r}$$

- Any choice of $\underline{R}_{\mathrm{O}}$ is valid as it yields the same magnetic field!

Recipe to get the Hamiltonian for magnetic interactions



Newton formulation of classical mechanics (with Lorentz force, non-conservative!)

↓

Lagrange formulation of classical mechanics

↓

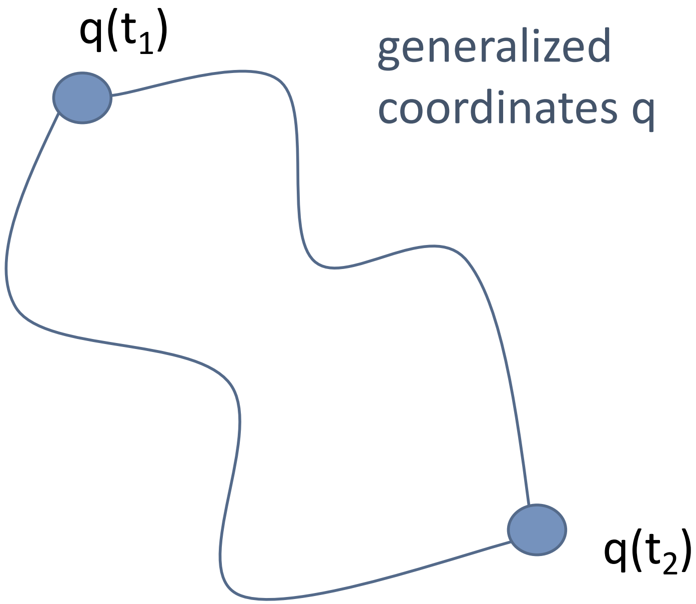
Hamilton formulation of classical mechanics

equivalent formulations!

↓ quantization

Hamiltonian with magnetic interactions

Lagrangian mechanics



Q: Which path is taken for a particle moving from q(t_1) → q(t_2)?

Hamilton principle: (least action) path minimizes action integral

$$S = \int_{t_1}^{t_2} L(q, \dot{q}, t) dt$$

Lagrange function L

meaning $\delta S = 0$

variation

Euler-Lagrange equations
(Lagrange equations of motion)

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \left(\frac{\partial L}{\partial q}\right) = 0$$

Note: Treat q and $\dot{q}$ as independent variables.
Note: For conservative force: $L(q, \dot{q}, t) = T(q, \dot{q}, t) - V(q)$
(does not hold for Lorentz force!)

Hamilton mechanics

Definition of conjugated canonical momentum $p = \frac{\partial L}{\partial \dot{q}}$

Hamilton function via Legendre transformation

$$H(q,p,t) = p\dot{q} - L(q,\dot{q},t)$$

basis for quantization

Hamilton eqs. of motion $\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}$

Equivalence of the 3 formulations of classical mechanics

Particle with coordinate x=q in 1-dim. potential V(x)

Newton

$$F = m\ddot{x}$$

$$-\frac{\partial V}{\partial x} = m\ddot{x}$$

$$0 = -\frac{\partial V}{\partial x} - m\ddot{x}$$

Lagrange

$$L = T - V$$

$$L = \frac{1}{2}m\dot{x}^2 - V(x)$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \left(\frac{\partial L}{\partial x}\right) = 0$$

$$0 = -\frac{\partial V(x)}{\partial x} - m\ddot{x}$$

Hamilton

$$p = \frac{\partial L}{\partial \dot{q}} = \boxed{m\dot{x}}$$

$$H(q,p) = p\dot{q} - L$$

$$= m\dot{x}^2 - \frac{m\dot{x}^2}{2} + V(x)$$

$$= \frac{p^2}{2m} + V(x)$$

$$\underset{\underset{m\ddot{x}}{\searrow}}{\boxed{\dot{p}}} = -\frac{\partial H}{\partial q} = -\frac{\partial V}{\partial x}$$

$$0 = -\frac{\partial V}{\partial x} - m\ddot{x}$$

Lagrangian in an electromagnetic field

Task: Set up Hamilton function! Needs Lagrange function L

→ Not known for non-conservative force!

→ But Newtonian eqs. of motion known!

Set up *L* in terms of $\boldsymbol{\Phi}$ and $\underline{A}$ *such that* resulting Lagrange eqs. of motion are equivalent

Lorentz force

$$\underline{F}^{\mathrm{tot}} = z(\underline{E} + \underline{v} \times \underline{B})$$

Newton‘s equation with Lorentz force and potentials

$$m\ddot{r} = z\left(-\nabla\Phi - \frac{\partial \underline{A}}{\partial t}\right) + z\underline{v} \times (\nabla \times \underline{A}))$$

Lagrange function that leads to Newton‘s equation

$$\boxed{L = \frac{mv^2}{2} - z\Phi + z\underline{v} \cdot \underline{A}}$$

Hamiltonian in an electromagnetic field

Define conj. canonical momentum: $$p = \frac{\partial L}{\partial \dot{q}} = m\underline{v} + z\underline{A}$$

$$L = \frac{mv^2}{2} - z\Phi + z\underline{v} \cdot \underline{A}$$

no longer just $m\underline{v}$!

Legendre trafo to get Hamilton function

$$\begin{aligned} H(q,p,t) &= p\dot{q} - L \\ &= (m\underline{v} + \cancel{z\underline{A}})\underline{v} - \frac{m\underline{v}^2}{2} + z\Phi - z\cancel{\underline{v}\,\underline{A}} \\ &= \frac{m\underline{v}^2}{2} + z\Phi \end{aligned}$$

No dependence on $\underline{A}$

Express using canonical momentum

$$= \frac{(p - z\underline{A})^2}{2m} + z\Phi$$

Basis for quantization!

Hamiltonian in an electromagnetic field

$$\boxed{H = \frac{(p - z\underline{A})^2}{2m} + z\Phi}$$

For electrons: z=-e, in atomic units: z=-1, m=m$_e$=1. Quantize!

$$\hat{p} = -i\nabla$$

$$\boxed{\begin{aligned}\hat{H} &= \frac{(\hat{p} + \underline{A})^2}{2} - \Phi \\ &= \frac{\hat{\pi}^2}{2} - \Phi\end{aligned}}$$

Comment: no quantization of fields here

$$\hat{\pi} = \hat{p} + \underline{A}$$

kinetic momentum

Non-relativistic Hamiltonian for electron in electromagnetic field!

Spin contribution in electromagnetic field

- Schrödinger equation does not contain spin
- Ad-hoc introduction of spin by Pauli (1927)

$$\boxed{\hat{H} = \frac{(\underline{\sigma}\hat{\pi})^2}{2} - \Phi}$$

vector of the Pauli spin matrices (2x2)

$$\underline{\sigma} = \begin{pmatrix}\boldsymbol{\sigma}_x \\ \boldsymbol{\sigma}_y \\ \boldsymbol{\sigma}_z\end{pmatrix} \qquad \boldsymbol{\sigma_x} = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \boldsymbol{\sigma_y} = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}, \boldsymbol{\sigma_z} = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$(\underline{\sigma}\hat{\pi})^2 = \hat{\pi}^2 + i\underline{\sigma}(\hat{\pi} \times \hat{\pi})$$

Dirac identity

$$= \hat{\pi}^2 + i\underline{\sigma}(\underset{0}{\cancel{\hat{p} \times \hat{p}}} + \underset{0}{\cancel{\underline{A} \times \underline{A}}} + \hat{p} \times \underline{A} + \cancel{\underline{A} \times \hat{p}})$$

$$\hat{p} \times \underline{A}f = (\hat{p} \times \underline{A})f - \cancel{\underline{A} \times \hat{p}f}$$

$\hat{p} = -i\nabla$

$$= \hat{\pi}^2 + \underline{\sigma}\underbrace{(\nabla \times \underline{A})}_{\underline{B}}$$

$\sigma = 2\hat{s}$

$$\Longrightarrow \quad \boxed{\hat{H} = \frac{\hat{\pi}^2}{2} + \underline{B}\hat{s} - \Phi}$$

Spin contribution in electromagnetic field

$$\boxed{H = \frac{(\underline{\sigma\pi})^2}{2} - \Phi} \xrightarrow{\boldsymbol{\sigma}_i = 2\hat{s}_i} \boxed{H = \frac{\pi^2}{2} + \underline{B\hat{s}} - \Phi}$$

- **same result** is obtained when taking non-relativistic limit (c→∞) of the (modified) Dirac equation
  - → arguments whether or not spin is a relativistic effect
  - → see Trond’s lectures (we agree that spin-orbit coupling is a relativistic effect 🙂)

- Note: magnetic field defines spin-quantization axis. Spin parallel or antiparallel wrt field (α & β).

Hamiltonian in electromagnetic field

$$\boxed{\frac{\hat{p}^2}{2}} \rightarrow \boxed{\frac{\hat{\pi}^2}{2} - \Phi} \rightarrow \boxed{\frac{\hat{\pi}^2}{2} + \underline{B}\,\underline{\hat{s}} - \Phi}$$

field-free

$\hat{p} = -i\nabla$

electromagn. field

$\hat{\pi} = \hat{p} + \underline{A}$

consideration of spin

- Expanding $\hat{\pi}^2$

$$\begin{aligned}\hat{\pi}^2 &= (\hat{p} + \underline{A})^2 \\ &= \hat{p}^2 + \underline{A}^2 + \boxed{\hat{p}\underline{A}} + \boxed{\underline{A}\hat{p}}\end{aligned}$$

be aware that the momentum operator does in general not commute with the vector potential!

Hamiltonian in electromagnetic field

$$\boxed{\frac{\hat{p}^2}{2}} \rightarrow \boxed{\frac{\hat{\pi}^2}{2} - \Phi} \rightarrow \boxed{\frac{\hat{\pi}^2}{2} + \underline{B}\,\underline{\hat{s}} - \Phi}$$

field-free

$\hat{p} = -i\nabla$

electromagn. field

$\hat{\pi} = \hat{p} + \underline{A}$

consideration of spin

- Expanding $\hat{\pi}^2$

$$\begin{aligned}\hat{\pi}^2 &= (\hat{p} + \underline{A})^2 \\ &= \hat{p}^2 + \underline{A}^2 + \hat{p}\underline{A} + \underline{A}\hat{p} \\ &= \hat{p}^2 + \underline{A}^2 + 2\underline{A}\hat{p}\end{aligned}$$

$$\hat{p}\underline{A}f = \cancel{(\hat{p}\underline{A})}f + \underline{A}\hat{p}f$$

Coulomb gauge! $\nabla\underline{A} = 0$

$$\boxed{\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2 - \Phi}$$

Hamiltonian

- Goal: Derive molecular Hamiltonian in electromagnetic field
- So far: Hamiltonian for 1 electron via use of the equivalence of Newtonian and Lagrange eqs. of motion:
  - Find L such that Lagrange eqs. of motion yield

$$\underline{F}^{\text{tot}} = z(\underline{E} + \underline{v} \times \underline{B})$$

$$m\ddot{r} = z\left(-\nabla\Phi - \frac{\partial \underline{A}}{\partial t}\right) + z\underline{v} \times (\nabla \times \underline{A}))$$

  - Determine p and set up Hamilton function H
  - Quantize $\hat{H} = \frac{(\hat{p} + \underline{A})^2}{2} - \Phi$
  - Consideration of spin and using Coulomb gauge

$$\boxed{\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2 - \Phi}$$

Molecular Hamiltonian in electromagnetic field

$$\boxed{\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2 - \Phi}$$

So far:

- 1 Electron in electromagnetic field

Now: Molecular Hamiltonian! (adding instantaneous Coulomb interaction, summing over all electrons)

$$\begin{aligned}\hat{H} =& \sum_{\alpha} \frac{1}{2}\hat{p}_{\alpha}^2 - \sum_{K\alpha} \frac{Z_K}{r_{\alpha K}} + \sum_{\alpha<\beta} \frac{1}{r_{\alpha\beta}} \\ &+ \sum_{\alpha} \underline{A}_{\alpha}\hat{p}_{\alpha} + \sum_{\alpha} \underline{B}_{\alpha}\hat{s}_{\alpha} - \sum_{\alpha} \Phi_{\alpha} \\ &+ \frac{1}{2}\sum_{\alpha} \underline{A}_{\alpha}^2\end{aligned}$$

Zeroth-order Hamiltonian (non-relativistic)

First-order Hamiltonian

Second-order Hamiltonian

Magnetic perturbations

$$\boxed{\hat{H} = \hat{H}_0 + \underbrace{\sum_{\alpha} \underline{A}_{\alpha} \hat{p}_{\alpha}}_{\textit{Orbital Zeeman paramagnetic}} + \underbrace{\sum_{\alpha} \underline{B}_{\alpha} \hat{s}_{\alpha}}_{\textit{Spin Zeeman paramagnetic}} - \sum_{\alpha} \Phi_{\alpha} + \frac{1}{2} \underbrace{\sum_{\alpha} \underline{A}_{\alpha}^2}_{\textit{diamagnetic}}}$$

- 1 atomic unit for B, B_0, corresponds to 235000 Tesla!
- 1 B_0 is very large in comparison to any field we would typically apply
- due to the “smallness” of typical magnet fields on Earth, perturbative treatment often sufficient

Magnetic perturbations

- For quantum chemistry with magnetic fields, we are typically interested in:
  - Uniform external magnetic field, with vector potential

$$\boxed{\underline{A}^{\text{ext}} = \frac{1}{2}\underline{B}^{\text{ext}} \times \underline{r}}$$

Or $\underline{r}\text{-}\underline{R}_{\mathbf{O}} \rightarrow \underline{A}_{\mathrm{O}}$

→ *Zeeman interactions*

  - Nuclear magnetic moments M_K with vector potential

$$\boxed{\underline{A}^{\text{nuc}} = \sum_K \underline{A}_K = \sum_K \alpha^2 \frac{\underline{M}_K \times \underline{r}_K}{r_K^3}}$$

α≈1/137 fine structure constant

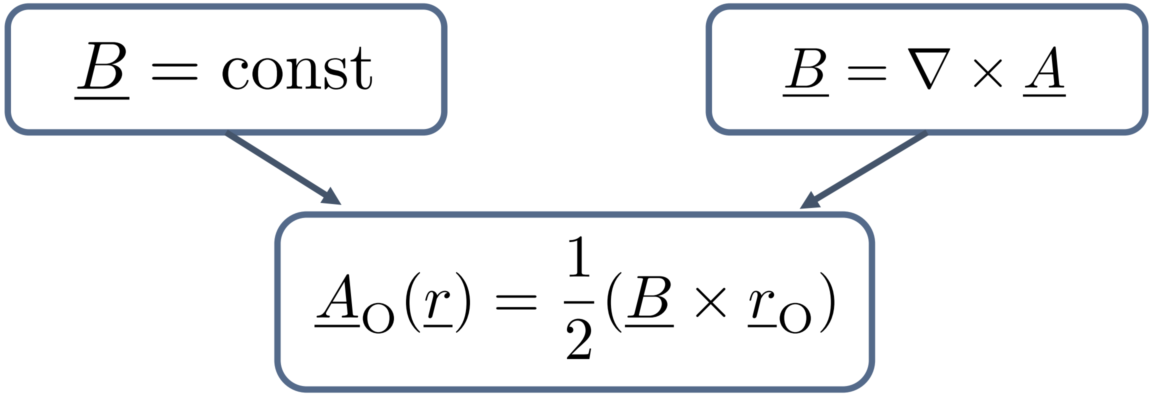
→ *Hyperfine interactions*

  - Combination: NMR

Hamiltonian for static uniform magnetic field

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

$$\boxed{\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2}$$



$$\underline{B} = \text{const}$$

$$\underline{B} = \nabla \times \underline{A}$$

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

$$\Phi = 0$$

$$\nabla \underline{A}_{\mathrm{O}} = 0$$

Rewrite terms with vector potential $\underline{A}$ in terms of $\underline{B}$

Hamiltonian in uniform magnetic field

$$\boxed{\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2}$$

Linear term (orbital Zeeman)

$$\underline{A}_{\mathrm{O}}\hat{p} = \frac{1}{2}(\underline{B} \times \underline{r}_{\mathrm{O}}) \cdot \hat{p} = \frac{1}{2}\underline{B} \cdot (\underline{r}_{\mathrm{O}} \times \hat{p}) = \frac{1}{2}\underline{B} \cdot \underline{\hat{l}}^{\mathrm{O}}$$

Angular momentum operator, dependent on gauge origin

Quadratic term (diamagnetic)

$$\frac{1}{2}\underline{A}_{\mathrm{O}}^2 = \frac{1}{8}(\underline{B} \times \underline{r}_{\mathrm{O}})^2 = \frac{1}{8}(\underline{B} \times \underline{r}_{\mathrm{O}})(\underline{B} \times \underline{r}_{\mathrm{O}}) = \frac{1}{8}[B^2 \cdot r_{\mathrm{O}}^2 - (\underline{B}\,\underline{r}_{\mathrm{O}})(\underline{B}\,\underline{r}_{\mathrm{O}})]$$

$$= \frac{1}{8}\underline{B}^T[\underline{r}_{\mathrm{O}} \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}\underline{r}_{\mathrm{O}}^T]\underline{B}$$

It follows for the Hamiltonian

$$\boxed{\hat{H} = \frac{1}{2}\hat{p}^2 + \frac{1}{2}\underline{Bl}^{\mathrm{O}} + \underline{Bs} = \frac{1}{8}\underline{B}^T[\underline{r}_{\mathrm{O}} \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}\underline{r}_{\mathrm{O}}^T]\underline{B}}$$

Hamiltonian in uniform magnetic field

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \underline{A}\hat{p} + \underline{B}\hat{s} + \frac{1}{2}\underline{A}^2$$

$$\hat{H} = \frac{1}{2}\hat{p}^2 + \frac{1}{2}\underline{B}\,\underline{l}^{\mathrm{O}} + \underline{B}\,\hat{s} + \frac{1}{8}\underline{B}^T[\underline{r}_{\mathrm{O}} \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}\underline{r}_{\mathrm{O}}^T]\underline{B}$$

Molecular Hamiltonian

$$\hat{H} = \hat{H}_0 + \underbrace{\sum_{\alpha}\frac{1}{2}\underline{B}\,\underline{l}_{\alpha}^{\mathrm{O}} + \sum_{\alpha}\underline{B}\hat{s}_{\alpha}}_{\hat{H}^{(1)}} + \underbrace{\frac{1}{8}\sum_{\alpha}\underline{B}^T[\underline{r}_{\mathrm{O}}(\alpha) \cdot \underline{\underline{1}} - \underline{r}_{\mathrm{O}}(\alpha)\underline{r}_{\mathrm{O}}^T(\alpha)]\underline{B}}_{\hat{H}^{(2)}}$$

Linear in B

Quadratic in B

Paramagnetism

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

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

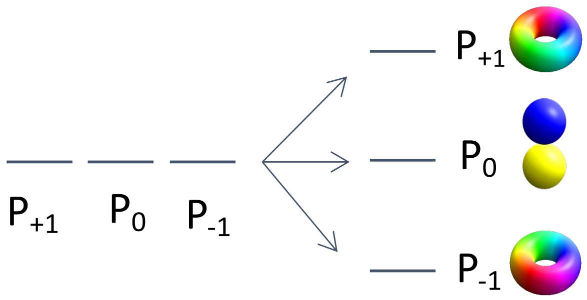
Magnetic moment interacts with magnetic field (dipolar interaction)

$$-Bm_z = \frac{1}{2}BL_z + Bs_z$$

Paramagnetism

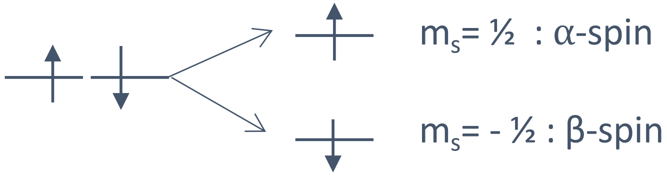
Consequences:

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

Paramagnetism

Note:

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:

- 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

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

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

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

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

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

gyromagnetic ratio $\gamma = -\frac{e}{2m_e} = -\frac{\mu_\mathrm{B}}{\hbar}$

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

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

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

  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

Take-Home messages from lecture 2

- For non-conservative forces, we cannot get the potential simply from $F = -\nabla V$
- Hamiltonian that involves electromagnetic-field interactions from Lorentz force → Newtonian mechanics → Lagrange → Hamilton → quantize
- Ad-hoc: spin → leads to spin-Zeeman contribution
- Observable: fields (E & B), not observable (A & Φ), gauge transformations allowed
- Static magnetic field: Free choice of gauge origin

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)

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

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

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

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

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

Quantum-chemical calculation of magnetizabilities

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

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 $\underline{R}_\mathrm{O} = 0$:
  - diamagnetic contribution $\langle \phi_{1s} \mid \cdots \mid \phi_{1s} \rangle$
  - paramagnetic contrib. $\underbrace{\langle \phi_{1s} \mid \hat{l}_z \mid}_{=0 \text{ (for whatever is in the ket)}} \phi_a \rangle$
- Chose $\underline{R}_\mathrm{O} \neq 0$:
  - diamagnetic contribution $\langle \phi_{1s} \mid \cdots \mid \phi_{1s} \rangle$
  - paramagnetic contrib.

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

$$(\underline{r} - R_\mathrm{O}) \times \hat{p} = \hat{l} - (\underline{R}_\mathrm{O} \times \hat{p})$$

$$\langle \phi_{1s} \mid \hat{l}_z^\mathrm{O} \mid \phi_a \rangle$$

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

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

$$\boxed{\begin{aligned}\Phi' &= \Phi - \frac{\partial}{\partial t} f \\ \underline{A}' &= \underline{A} + \nabla f\end{aligned}}$$

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

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

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

the wave function compensates by phase oscillation

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

Gauge transformation of the wave function

such that observables do not change

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

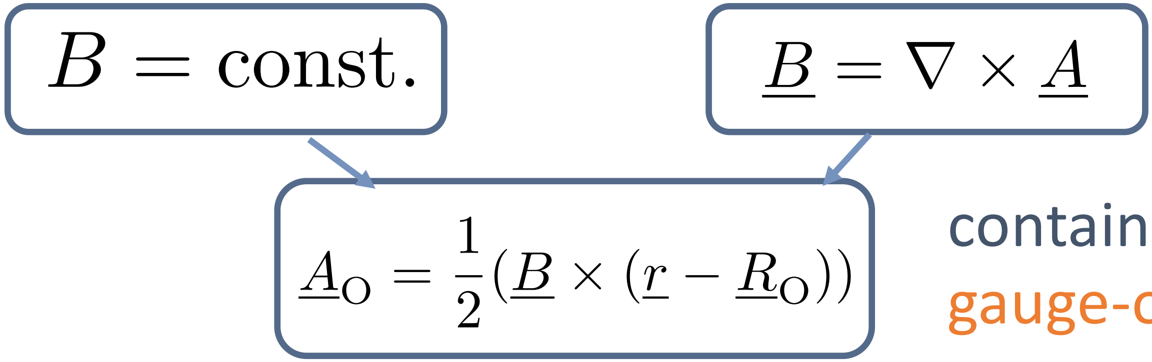
- Example: electron density

$$\begin{aligned}\rho^{\text{trans}} \leftarrow (\Psi^{\text{trans}})^* \Psi^{\text{trans}} &= [\exp(-if)\Psi^{\text{orig}}]^* [\exp(-if)\Psi^{\text{orig}}] \\ &= \exp(0)(\Psi^{\text{orig}})^* \Psi^{\text{orig}} \rightarrow \rho^{\text{orig}}\end{aligned}$$

- 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)



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

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

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

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

see exercise

$$= \underline{A}_\mathrm{orig}(\underline{r}) + \nabla f$$

with $f(\underline{r}) = -\underline{A}_\mathrm{orig}(\underline{R}_\mathrm{trans}) \cdot \underline{r}$

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

Gauge-origin transformation

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

$$\begin{aligned}\Psi_{\mathrm{trans}}^{\mathrm{exact}} &= \exp\left[-if(\underline{r})\right]\Psi_{\mathrm{orig}}^{\mathrm{exact}} \\ &= \exp\left[i\underline{A}_{\mathrm{orig}}(\underline{R}_{\mathrm{trans}})\cdot\underline{r}\right]\Psi_{\mathrm{orig}}^{\mathrm{exact}}\end{aligned}$$

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

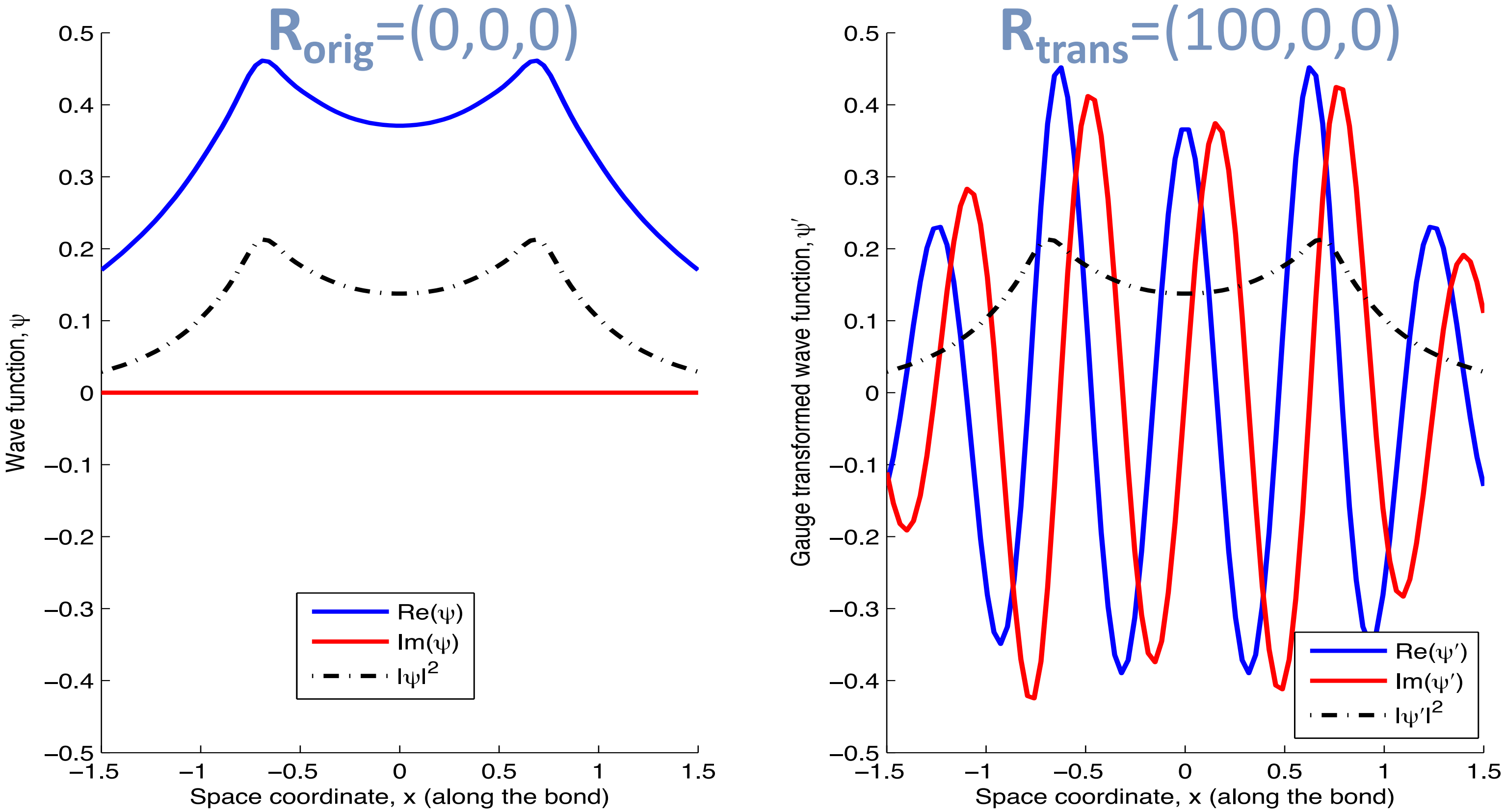
inducing phase oscillations and ensuring that observables do not change

→ 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



$\mathbf{R}_{\mathbf{orig}}=(0,0,0)$ $\mathbf{R}_{\mathbf{trans}}=(100,0,0)$

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

T. Helgaker lecture notes

Distinctions

- Gauge invariance

  General

$$\boxed{\begin{aligned}\Phi' &= \Phi - \frac{\partial}{\partial t} f \\ \underline{A}' &= \underline{A} + \nabla f\end{aligned}}$$

- 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

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

Gauge-Including Atomic Orbitals

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

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

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

(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?

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

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

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

Consequences of use of GIAOs for magnetizabilities?

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

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

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

Consequences of use of GIAOs for magnetizabilities?

- Additional integrals

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

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

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

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

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

Consequences of use of GIAOs for magnetizabilities?

- Additional integrals (cont')

$$
\begin{aligned}
\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 \middle| \chi_\nu \chi_\rho \right\rangle + \left\langle \chi_\mu \frac{\partial^2 \chi_\sigma}{\partial B_\alpha \partial B_\beta} \middle| \chi_\nu \chi_\rho \right\rangle + \left\langle \chi_\mu \chi_\sigma \middle| \frac{\partial^2 \chi_\nu}{\partial B_\alpha \partial B_\beta} \chi_\rho \right\rangle + \left\langle \chi_\mu \chi_\sigma \middle| \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} \middle| \chi_\nu \chi_\rho \right\rangle \\
& + \left\langle \frac{\partial \chi_\mu}{\partial B_\beta} \frac{\partial \chi_\sigma}{\partial B_\alpha} \middle| \chi_\nu \chi_\rho \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} \chi_\sigma \middle| \frac{\partial \chi_\nu}{\partial B_\beta} \chi_\rho \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\beta} \chi_\sigma \middle| \frac{\partial \chi_\nu}{\partial B_\alpha} \chi_\rho \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\alpha} \chi_\sigma \middle| \chi_\nu \frac{\partial \chi_\rho}{\partial B_\beta} \right\rangle + \left\langle \frac{\partial \chi_\mu}{\partial B_\beta} \chi_\sigma \middle| \chi_\nu \frac{\partial \chi_\rho}{\partial B_\alpha} \right\rangle \\
& + \left\langle \chi_\mu \frac{\partial \chi_\sigma}{\partial B_\alpha} \middle| \frac{\partial \chi_\nu}{\partial B_\beta} \chi_\rho \right\rangle + \left\langle \chi_\mu \frac{\partial \chi_\sigma}{\partial B_\beta} \middle| \frac{\partial \chi_\nu}{\partial B_\alpha} \chi_\rho \right\rangle + \left\langle \chi_\mu \frac{\partial \chi_\sigma}{\partial B_\alpha} \middle| \chi_\nu \frac{\partial \chi_\rho}{\partial B_\beta} \right\rangle + \left\langle \chi_\mu \frac{\partial \chi_\sigma}{\partial B_\beta} \middle| \chi_\nu \frac{\partial \chi_\rho}{\partial B_\alpha} \right\rangle + \left\langle \chi_\mu \chi_\sigma \middle| \frac{\partial \chi_\nu}{\partial B_\alpha} \frac{\partial \chi_\rho}{\partial B_\beta} \right\rangle \\
& + \left\langle \chi_\mu \chi_\sigma \middle| \frac{\partial \chi_\nu}{\partial B_\beta} \frac{\partial \chi_\rho}{\partial B_\alpha} \right\rangle .
\end{aligned}
$$

- These have to be implemented (all methods)

Derivatives of the basis functions

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

- Derivative wrt to one component B_α

$$\begin{aligned}
\frac{\partial \chi_\mu(\underline{r},\underline{B})}{\partial B_\alpha} &= \chi_\mu(\underline{r})\frac{\partial}{\partial B_\alpha} e^{\frac{i}{2}(\underline{B}\times(\underline{R}_O - \underline{R}_\mu)\cdot\underline{r})} \\
&= \frac{i}{2}\{(\underline{R}_{\mathrm{O}} - \underline{R}_\mu) \times \underline{r}\}_\alpha \; e^{\frac{i}{2}(\underline{B}\times(\underline{R}_O - \underline{R}_\mu)\cdot\underline{r})}\chi_\mu(\underline{r}) \\
&= \frac{i}{2}\{(\underline{R}_{\mathrm{O}} - \underline{R}_\mu) \times \underline{r}\}_\alpha \; \chi_\mu(\underline{r},\underline{B})
\end{aligned}$$

- 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 analyticcode (bookkeeping of *i*)

→ not true in finite field

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

- Reminder: 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

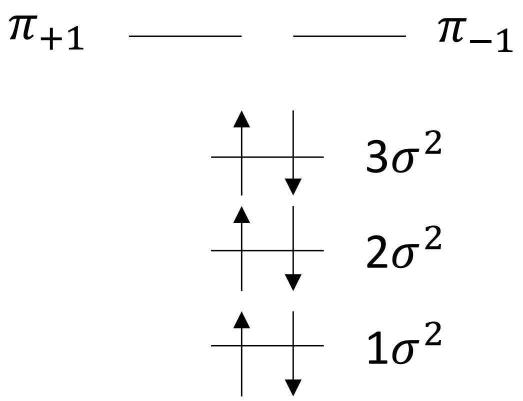
Paramagnetic molecules:		10^{-30} J T^{-2}
BH	$xx = yy$	418.7
	zz	−196.0
	total	213.8
CH^+	$xx = yy$	546.7
	zz	−113.6
	total	326.6
AlH	$xx = yy$	239.8
	zz	−358.9
	total	40.2
SiH^+	$xx = yy$	247.9
	zz	−247.3
	total	82.9
BeH^-	$xx = yy$	246.8
	zz	−588.4
	total	−31.6

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.

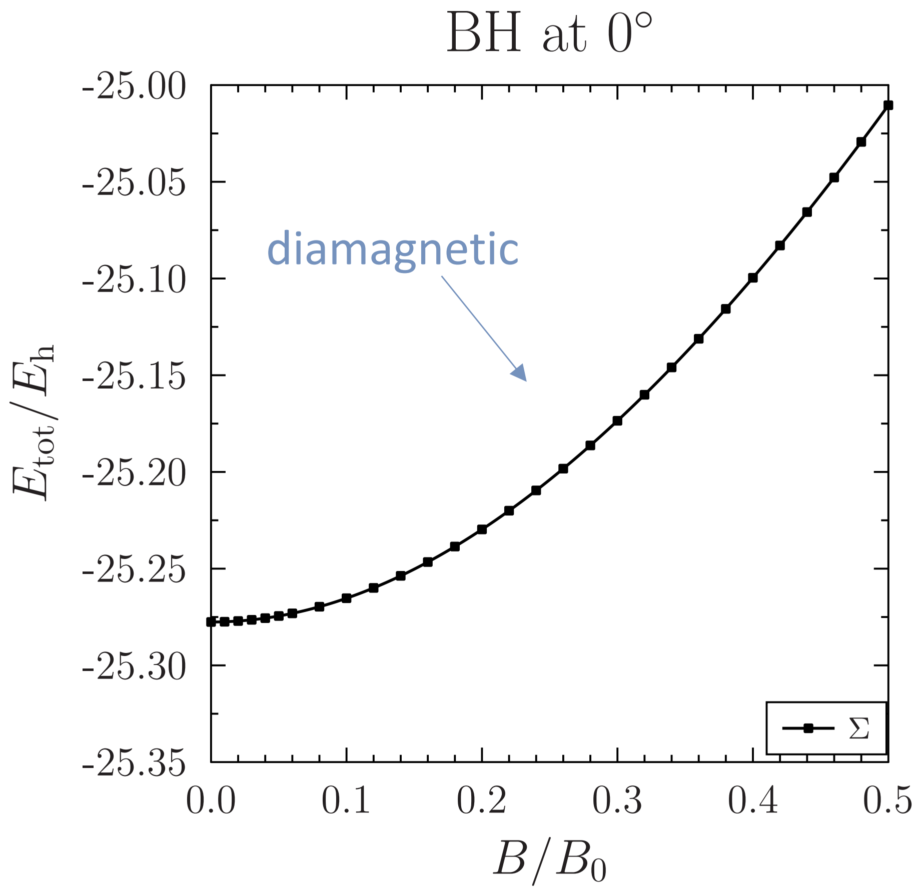
Similar effects also for **π** and **δ** orbitals (from atomic d)

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

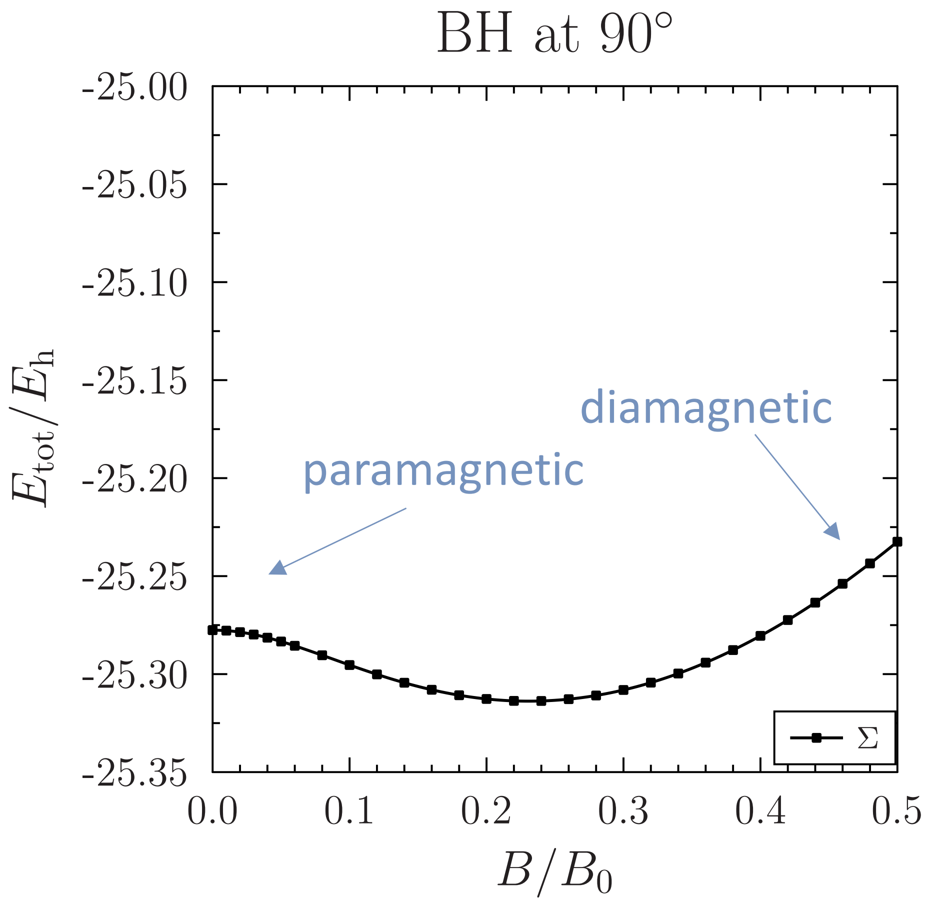
Energy of closed-shell paramagnetic molecules

Development of the energy as a function of a magnetic field

PARALLEL



PERPENDICULAR



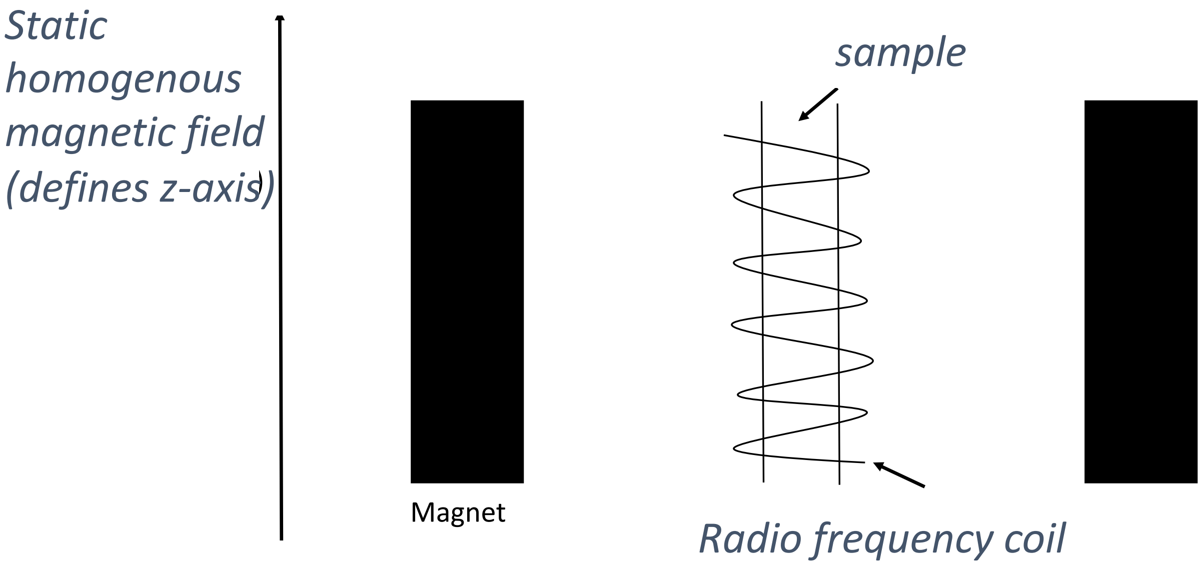
Paramagnetic response to external perpendicular magnetic field (up to ~0.2 B_0~50000T)

1 B_0 = 235 000 T

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

Nuclear Magnetic Resonance (NMR) experiment

- Setup



characterize molecules!

- Nuclear spin → nuclear magnetic moment → interacts with external magnetic field → Magnetic field splits energy levels of nuclear spins (Zeeman)
- Larmor-frequency: Transitions between energy levels of the nuclear spins.

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

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

Zeeman and hyperfine interactions

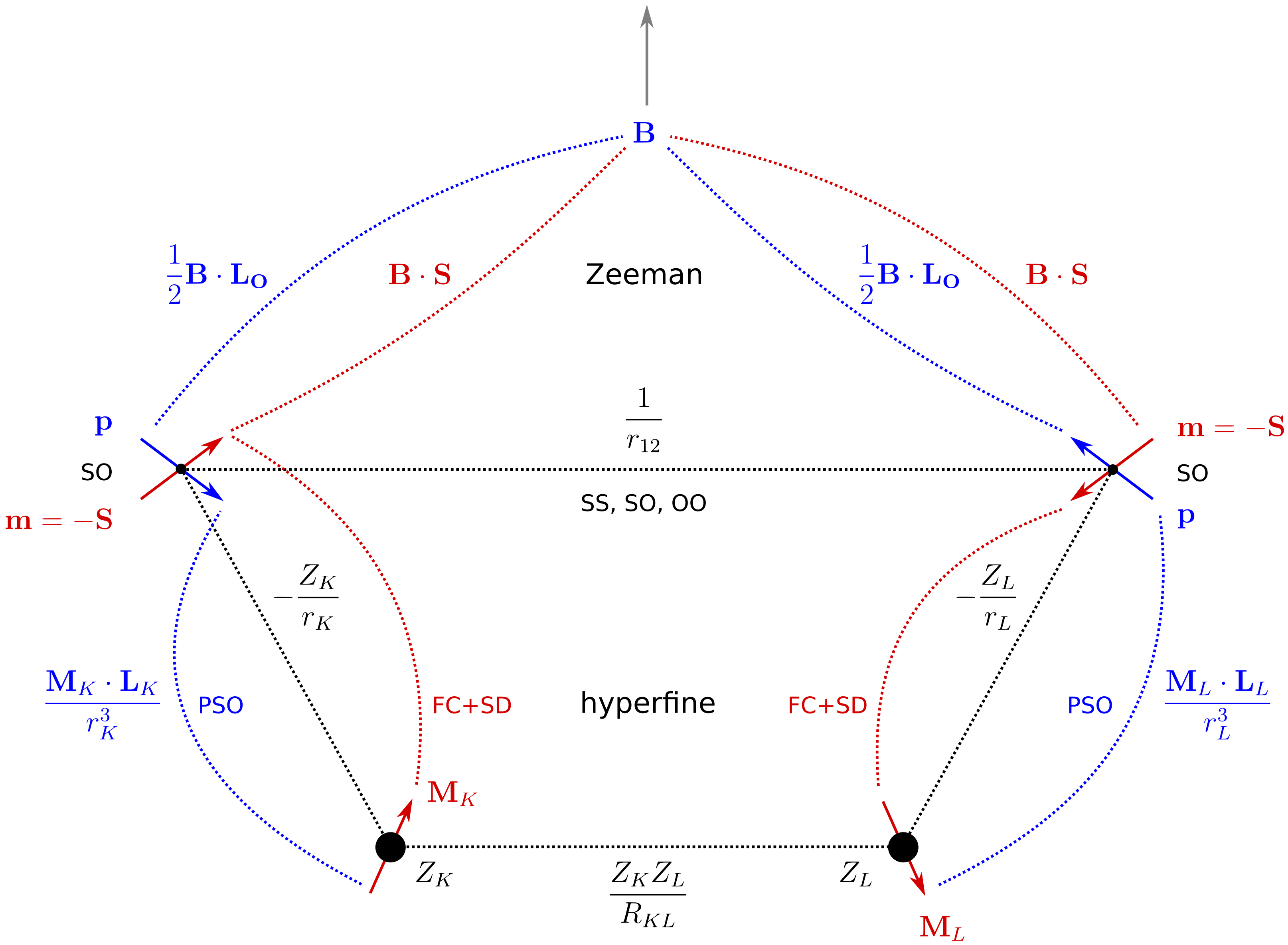


Fig. from ESQC books, chapter by T. Helgaker

Calculation of nuclear shielding constants

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

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

→ 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 $H_{\mathrm{nuc}}^{(1,1)} = -\sum_K \underline{M}_K^\top \underline{B}$
  - in molecule: coupling is modified by nuclear shielding tensor

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

electronic contribution!

Calculation of nuclear shielding constants

Perturbations

$$\lambda_1 = \sum_K \underline{M}_K \qquad \lambda_2 = \sum_K \underline{B}^{\mathrm{ext}}$$

Perturbed Hamiltonian more complicated:

$$\hat{H} = \hat{H}^{(0)} + \lambda_1 \hat{H}^{(1,0)} + \lambda_2 \hat{H}^{(0,1)} + \lambda_1^2 \hat{H}^{(2,0)} + \lambda_2^2 \hat{H}^{(0,2)} + \lambda_1 \lambda_2 \hat{H}^{(1,1)}$$

Expansion of energy and wave function:

$$E(\lambda_1, \lambda_2) = E_0 + \lambda_1^2 E^{(2,0)} + \lambda_2^2 E^{(0,2)} + \lambda_1 \lambda_2 \boxed{E^{(1,1)}}$$

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

Insert into Schrödinger-eq, collect terms of order $\lambda_1 \lambda_2$, project onto $\Psi_0^{(0)}$:

$$E^{(1,1)} = \langle \Psi_0^{(0)} \mid \hat{H}^{(1,1)} \mid \Psi_0^{(0)} \rangle + \langle \Psi_0^{(0)} \mid \hat{H}^{(0,1)} \mid \Psi_0^{(1,0)} \rangle + \langle \Psi_0^{(0)} \mid \hat{H}^{(1,0)} \mid \Psi_0^{(0,1)} \rangle$$

$$\mid \Psi_0^{(0,1)} \rangle = \sum_n \frac{\langle \Psi_n^{(0)} \mid \hat{H}^{(0,1)} \mid \Psi_n^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \mid \Psi_n^{(0)} \rangle$$

Calculation of nuclear shielding constants

- From second-order perturbation theory:

$$E^{(1,1)\mathrm{el}} = \langle \Psi_0 \mid \hat{H}^{(1,1)}_{\mathrm{el.}} \mid \Psi_0 \rangle + 2\sum_n \frac{\langle \Psi_0 \mid \hat{H}^{(1,0)}_{\mathrm{el.}} \mid \Psi_n \rangle \langle \Psi_n \mid \hat{H}^{(0,1)}_{\mathrm{el.}} \mid \Psi_0 \rangle}{E_0^{\mathrm{el.}} - E_n^{\mathrm{el.}}}$$

- Identify the operators!

since

$$\hat{H} = \hat{H}_0 + \sum_i \underline{A}(r_i)\hat{p}_i + \frac{1}{2}\sum_i \underline{A}(r_i)^2$$

and

$$\underline{A}^{\mathrm{tot}} = \underline{A}^{\mathrm{ext}} + \sum_K \underline{A}_K$$

$$\hat{H}^{(1,0)} \leftarrow \sum_{iK} \underline{A}_{Ki}\hat{p}_i$$

$$\hat{H}^{(0,1)} \leftarrow \sum_i \underline{A}_i^{\mathrm{ext}}\hat{p}_i$$

$$\hat{H}^{(2,0)} \leftarrow \frac{1}{2}\sum_{Ki} A_{Ki}^2,$$

$$\hat{H}^{(0,2)} \leftarrow \frac{1}{2}\sum_i A_i^{\mathrm{ext}\,2},$$

$$\hat{H}^{(1,1)} \leftarrow \frac{1}{2}\sum_{Ki} 2\underline{A}_{Ki}\underline{A}_i^{\mathrm{ext}}$$

Calculation of nuclear shielding constants

- Term 1, diamagnetic (comes from $\underline{A}^2$)

$$
\begin{aligned}
H^{(1,1)} \leftarrow \sum_i \sum_K \mathbf{A}_{G_i}(\mathbf{r}_i)\mathbf{A}_{K_i}(\mathbf{r}_i) &= \frac{\alpha^2}{2}\sum_{iK}\frac{(\mathbf{B}\times\mathbf{r}_{iG})(\mathbf{M}_K\times\mathbf{r}_{iK})}{r_{iK}^3} \\
&= \sum_K \mathbf{M}_K^\top \underbrace{\left(\frac{\alpha^2}{2}\sum_i \frac{\mathbf{r}_{iG}^\mathrm{T}\mathbf{r}_{iK}\mathbf{1}_3 - \mathbf{r}_{iG}\mathbf{r}_{iK}^\mathrm{T}}{r_{iK}^3}\right)}_{\mathbf{H}_{K0}^{\mathrm{dia}}}\mathbf{B}
\end{aligned}
$$

- Term 2, paramagnetic (comes from $\underline{A}$)

$$
\begin{aligned}
\hat{H}^{(0,1)} \leftarrow \mathbf{A}_{G_i}(\mathbf{r}_i)\mathbf{p}_i &= \frac{1}{2}\sum_i \mathbf{B}\times\mathbf{r}_{iG}\cdot\mathbf{p}_i \\
&= \frac{1}{2}\sum_i \mathbf{B}\times l_{iG} \\
&= \mathbf{B}\frac{1}{2}\mathbf{L}_G \\
&= \mathbf{B}\mathbf{H}_0^{\mathrm{zmL}}
\end{aligned}
$$

Calculation of nuclear shielding constants

- Term 2 continued:

$$\hat{H}^{(1,0)} \leftarrow \sum_K \mathbf{A}_{K_i}(\mathbf{r}_i)\mathbf{p}_i = \alpha^2 \sum_{iK} \frac{(\mathbf{M}_K \times \mathbf{r}_{iK}) \cdot \mathbf{p}_i}{r_{iK}^3}$$

$$= \sum_K \mathbf{M}_K \underbrace{\alpha^2 \sum_i \frac{\mathbf{l}_{iK}}{r_{iK}^3}}_{\mathbf{H}_K^{\text{pso}}}$$

- Collect:

$$E_K^{(1,1)\text{el.}} = \langle \Psi_0 \mid \mathbf{H}_{K0}^{\text{dia}} \mid \Psi_0 \rangle + 2 \sum_n \frac{\langle \Psi_0 \mid \mathbf{H}_0^{\text{zmL}} \mid \Psi_n \rangle \langle \Psi_n \mid \mathbf{H}_K^{\text{pso}} \mid \Psi_0 \rangle}{E_0 - E_n}$$

Calculation of nuclear shielding constants

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

Connect to Taylor expansion

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

Calculation in quantum chemistry via derivative theory!

→ Beginning lecture 1: order of differentiation?

Calculation of nuclear shielding constants

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

Connect to Taylor expansion

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

Calculation in quantum chemistry via derivative theory!

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

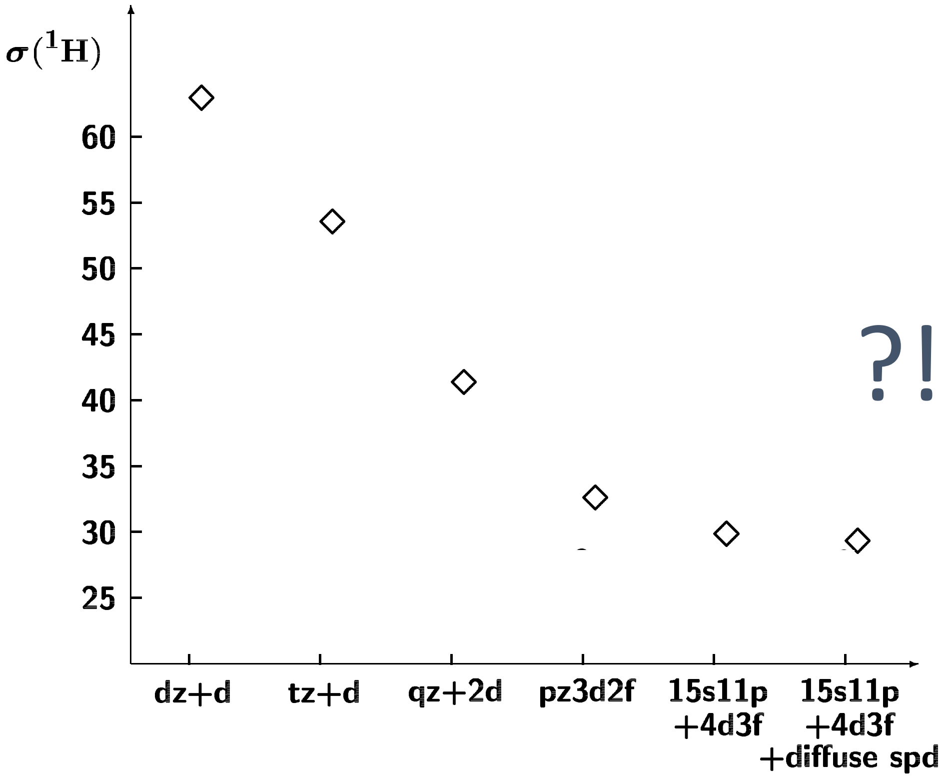
$$E = \sum_{\mu,\nu} D_{\mu\nu} h_{\mu\nu} + \sum_{\mu,\sigma,\nu,\rho} \Gamma_{\mu\nu\sigma\rho} \langle \mu\sigma \mid \nu\rho \rangle$$

Differentiate wrt. M_K and B

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

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

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.

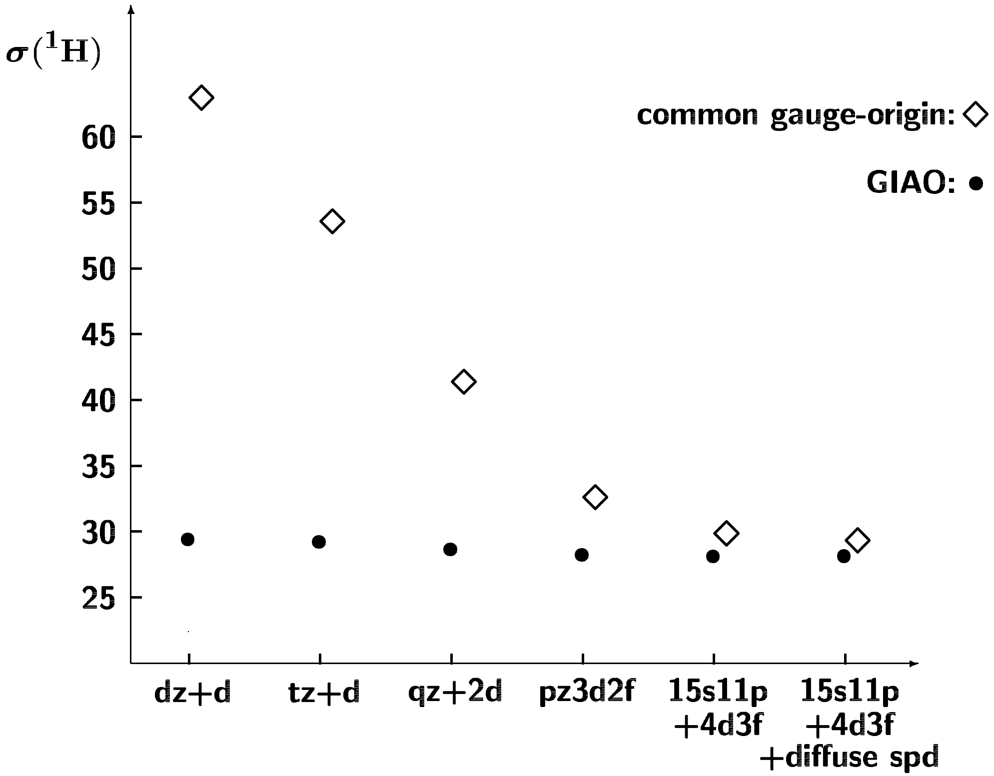
Gauge-origin dependence

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!

Basis-set convergence

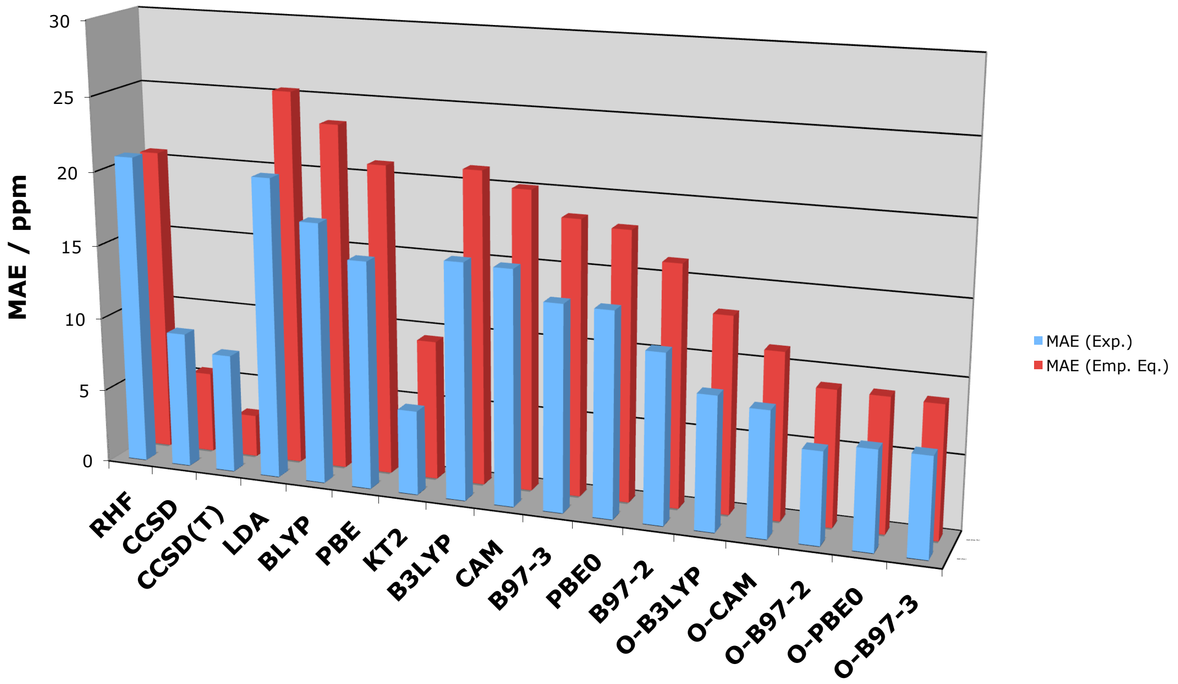


^{1}H shielding of hydrogen fluoride

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 uneven quality
- 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

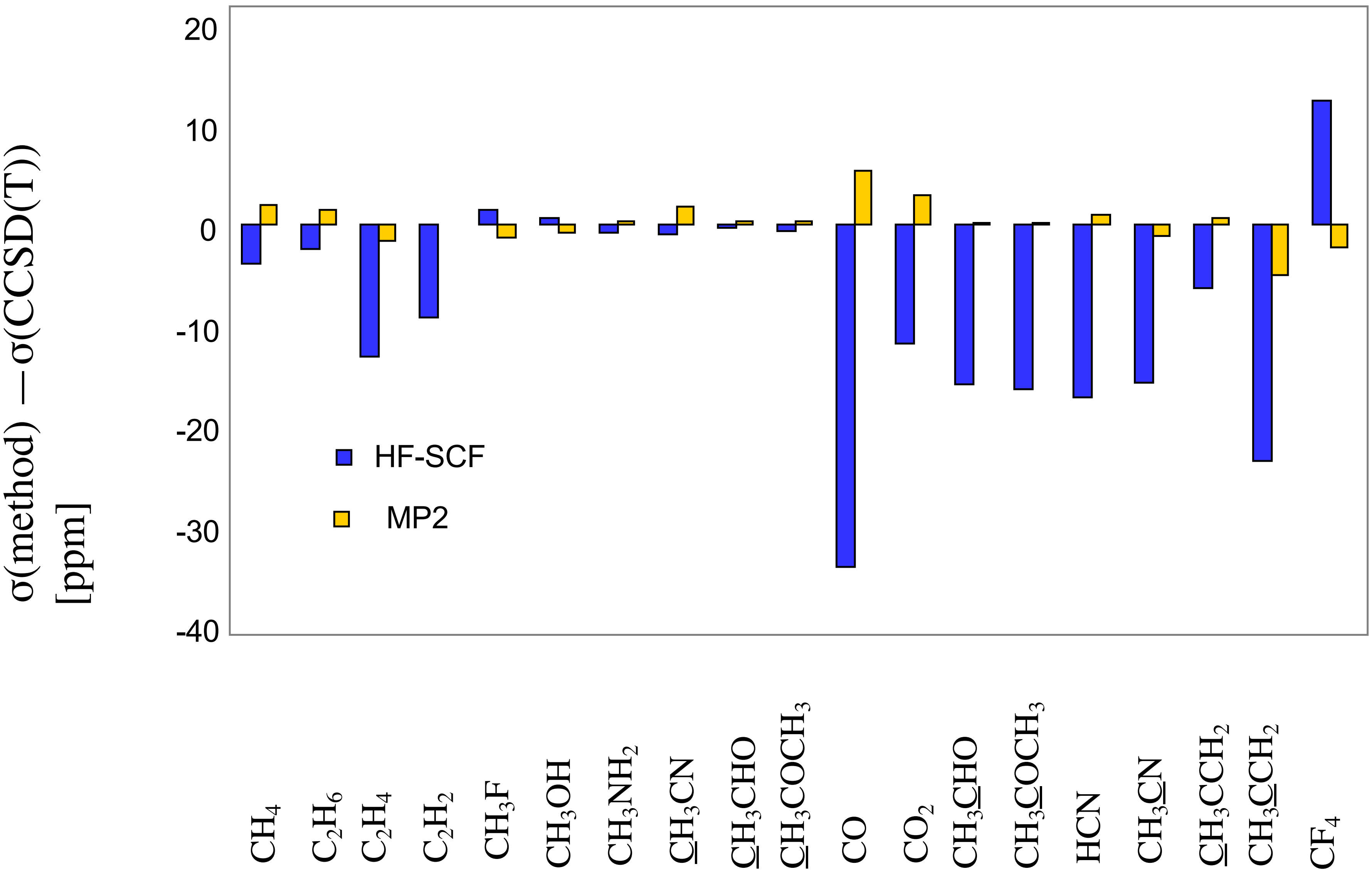


Figure from J. Gauss

Summary

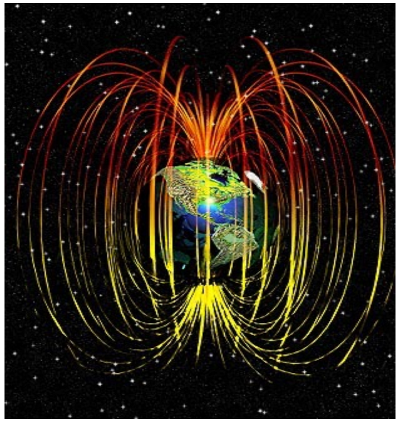
- Hamiltonian for molecule in electromagnetic field
- Calculation of NMR shieldings
- Important to ensure gauge-origin independence via use of GIAOs

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: **$1B_0 = 235000\ \mathrm{T}$**

Distinguish 3 regimes:

Increase magnetic field B

$B \ll B_0$ Coulomb regime

$B \approx B_0$ Mixing regime

$B \gg B_0$ Landau regime

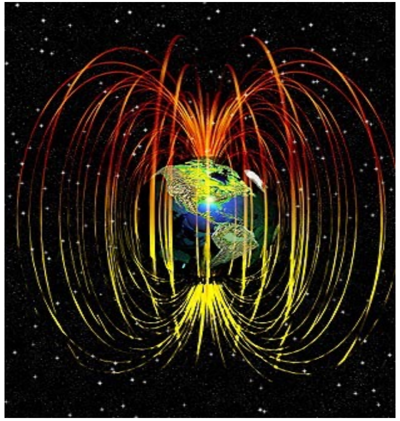
Magnetic fields on Earth

Human brain

$4.35\ \mathrm{aB}_0$

Earth magnetic field

$260\ \mathrm{pB}_0$



Refrigerator magnet

$17\ \mathrm{nB}_0$

NMR

$51\ \mu\mathrm{B}_0$

Levitate a frog

$68\ \mu\mathrm{B}_0$

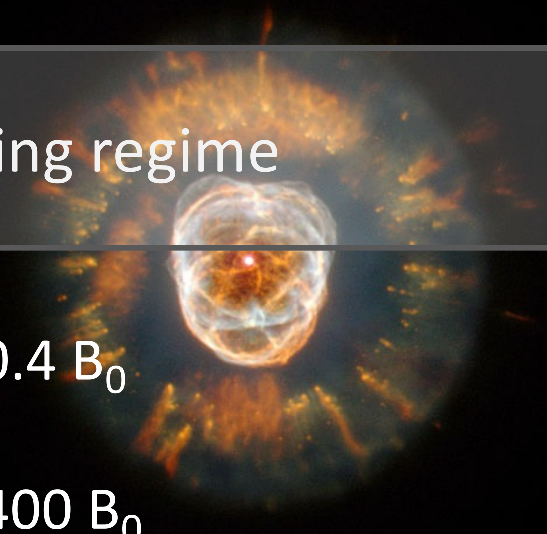
Strongest non-destructive magnet

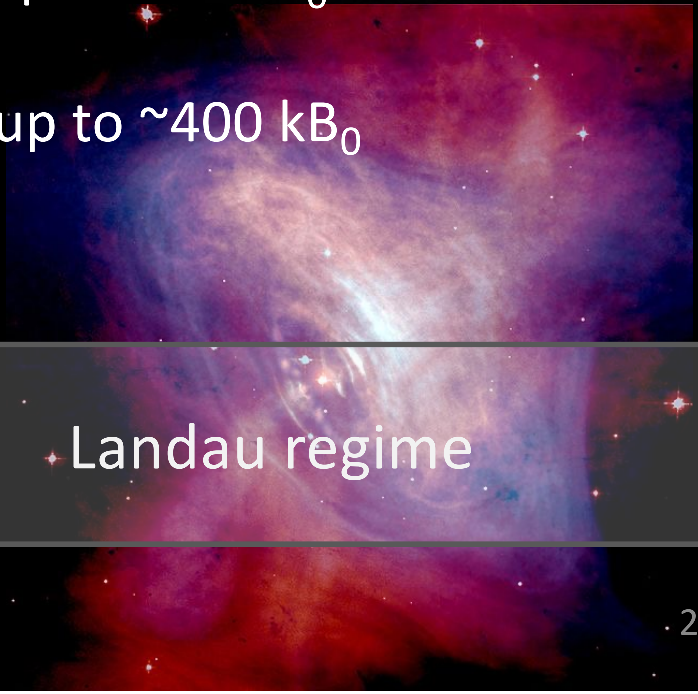
$0.4\ \mathrm{mB}_0$

Z-machine

$0.04\ \mathrm{B}_0$

Magnetic fields in space





Compact stars

Mixing regime

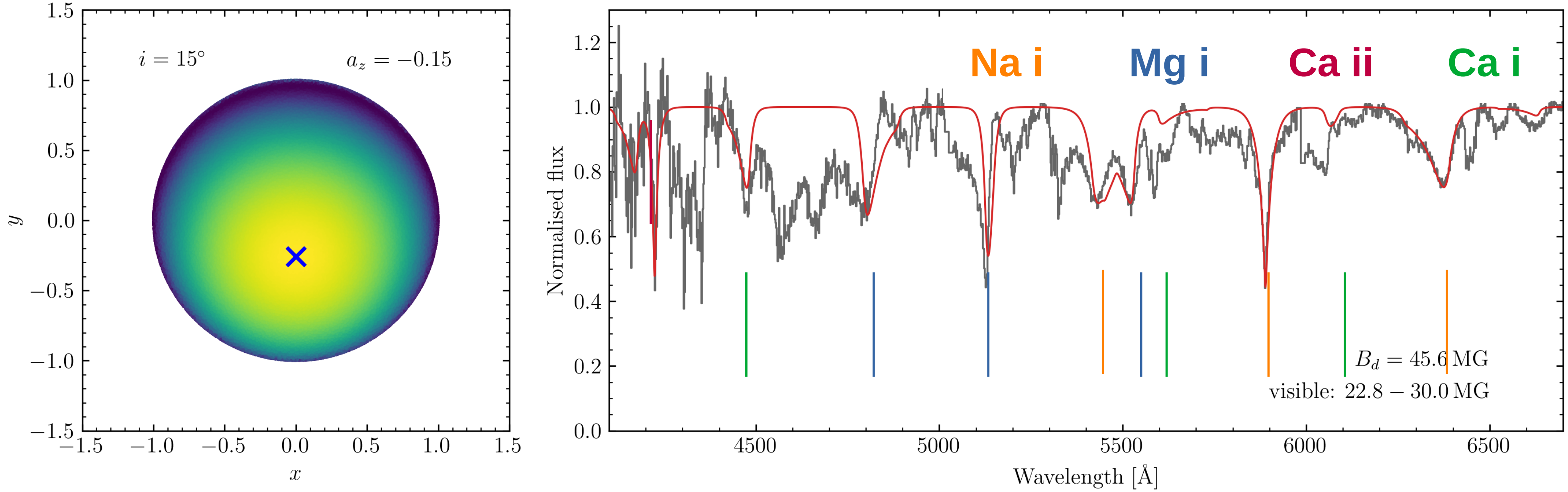
Magnetic White Dwarf stars ~3T – 100kT → up to ~0.4 B_0

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**

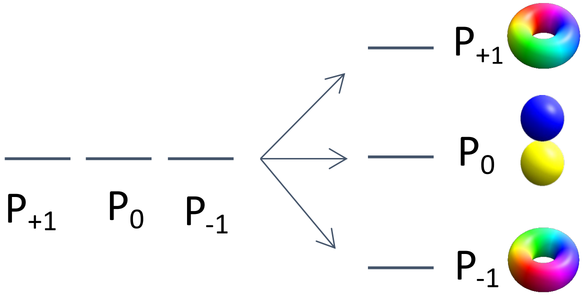
- leads to complex wave function
- gauge-origin dependent

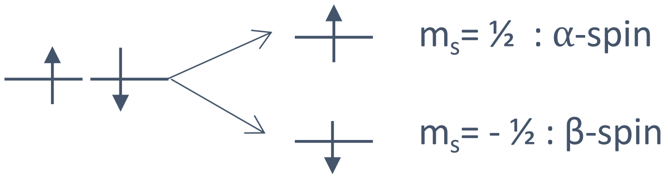
***Spin-Zeeman* term**

- 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

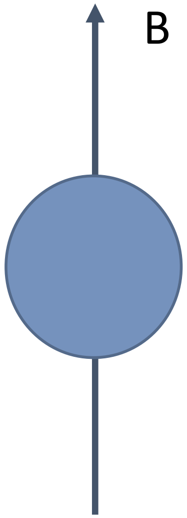




$$p_{+1} = -\frac{1}{\sqrt{2}}(p_x + ip_y), \quad p_{-1} = \frac{1}{\sqrt{2}}(p_x - ip_y)$$

Atom in magnetic field

- Symmetry

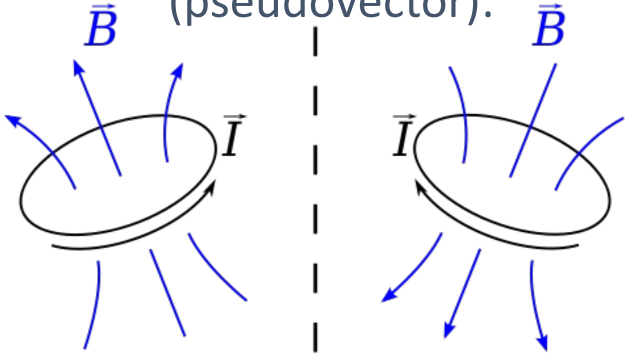


- Only **rotation** along B, but **any angle** C_∞
- **Mirror** planes?

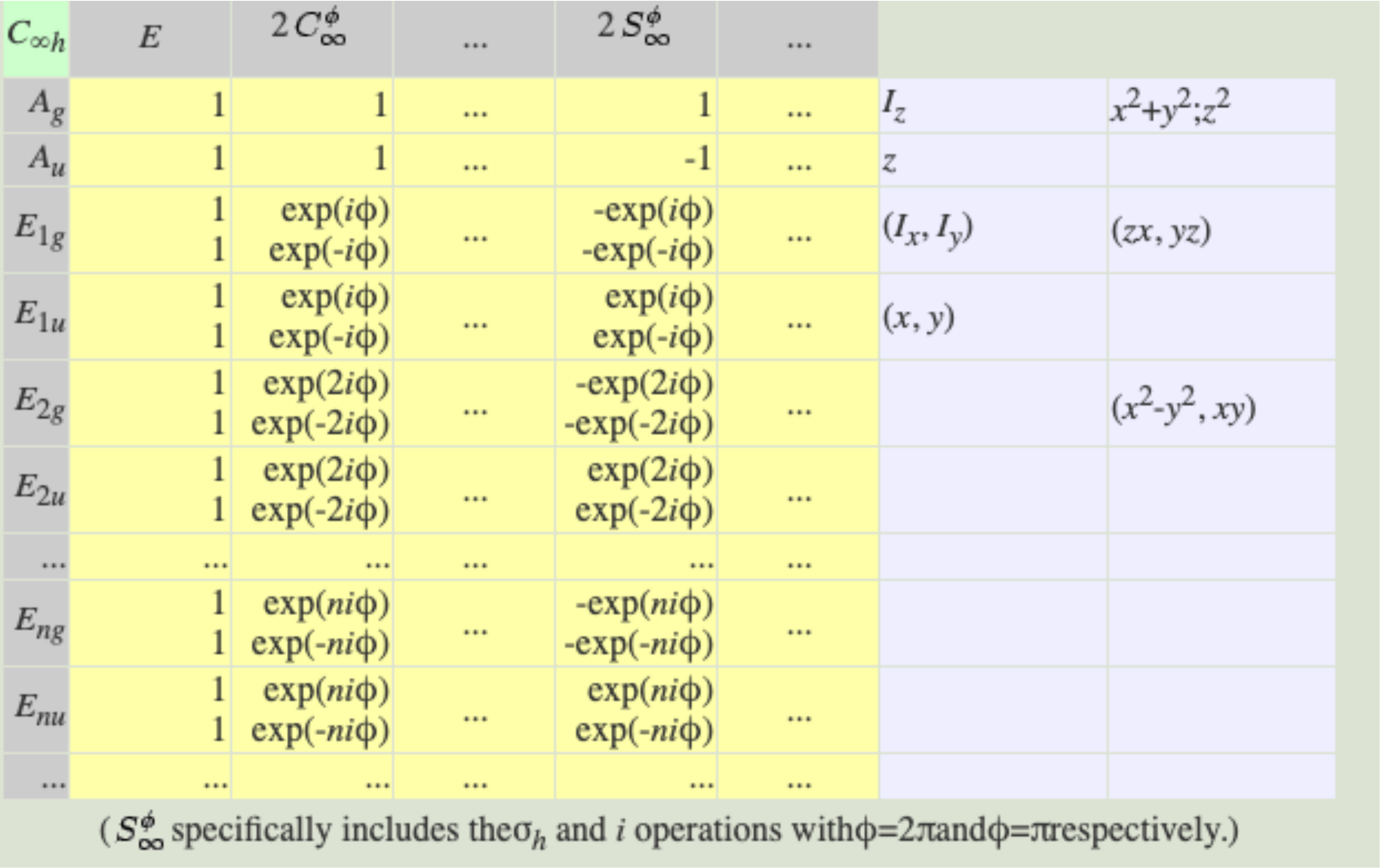
→ **Perpendicular** to B (non-intuitive)

$$\boxed{C_{\infty h}}$$

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	$\pi_{+1,g}$	$\delta_{+2,g}$

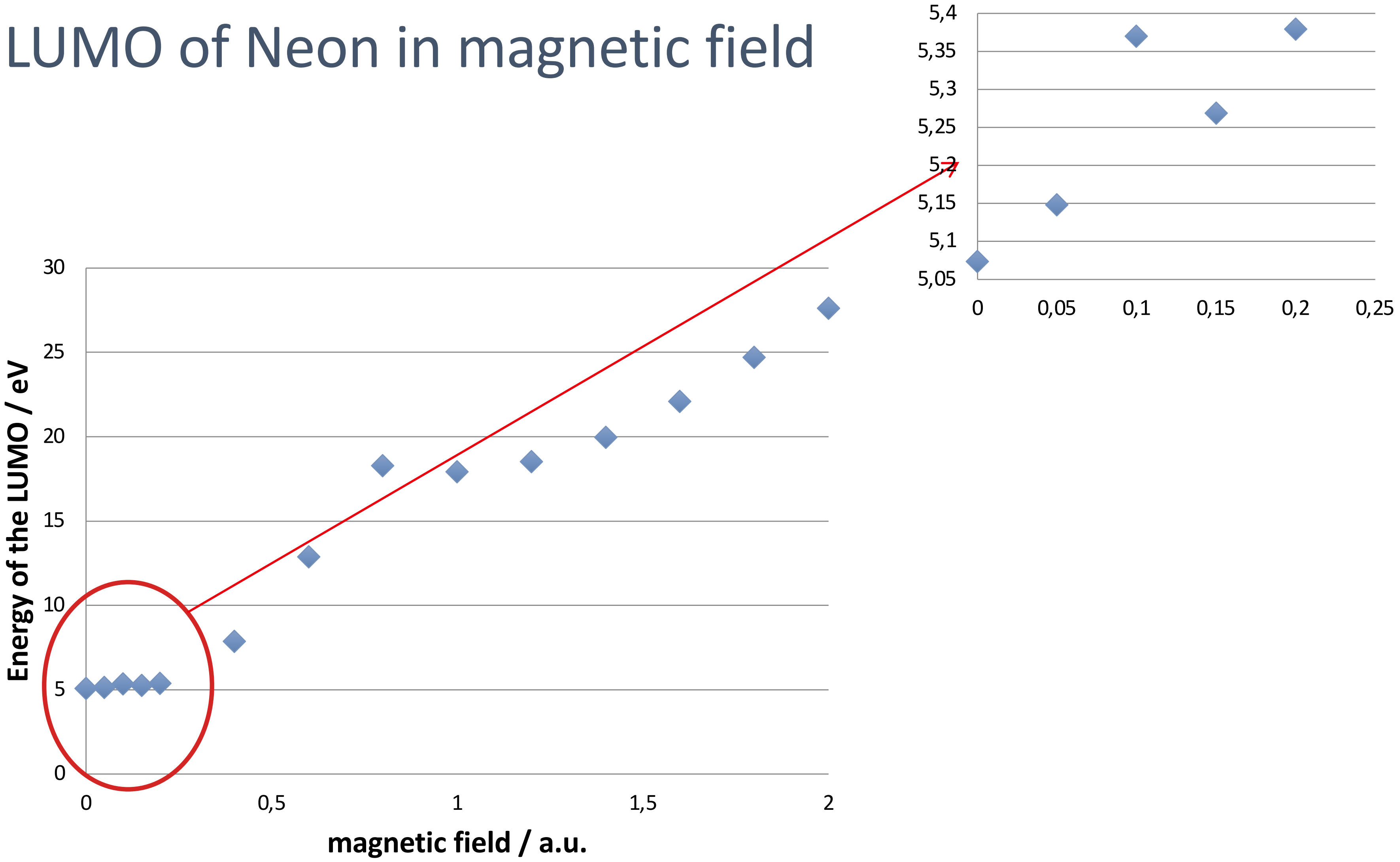
$$\hat{H} = \hat{H}_0 + \frac{1}{2}B\hat{L}_z + B\hat{S}_z + \frac{1}{8}\sum_i^N B^2\left(x_i^2 + y_i^2\right)$$

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

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

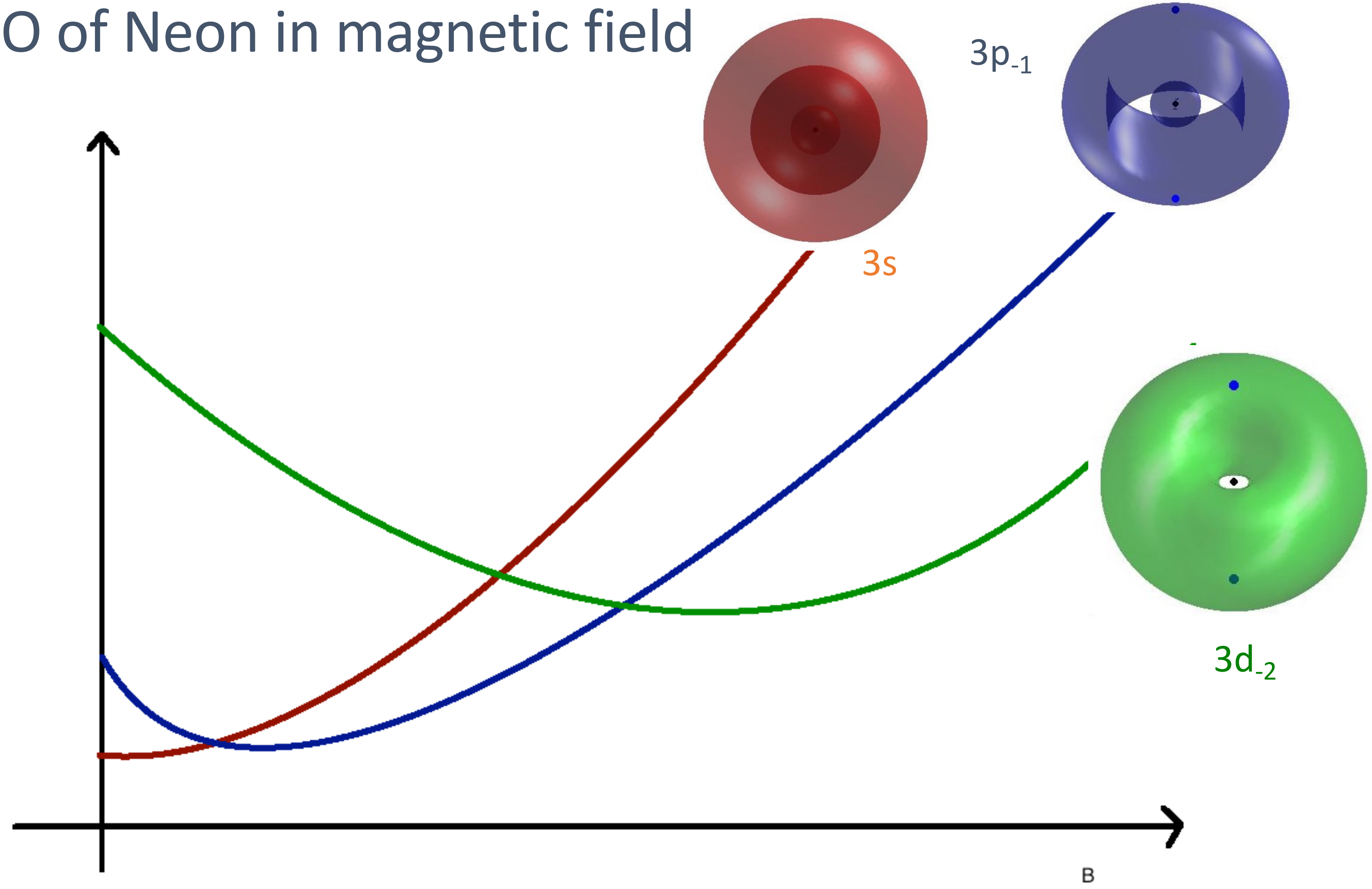
Paramagnetic effects

- LUMO of Neon in magnetic field



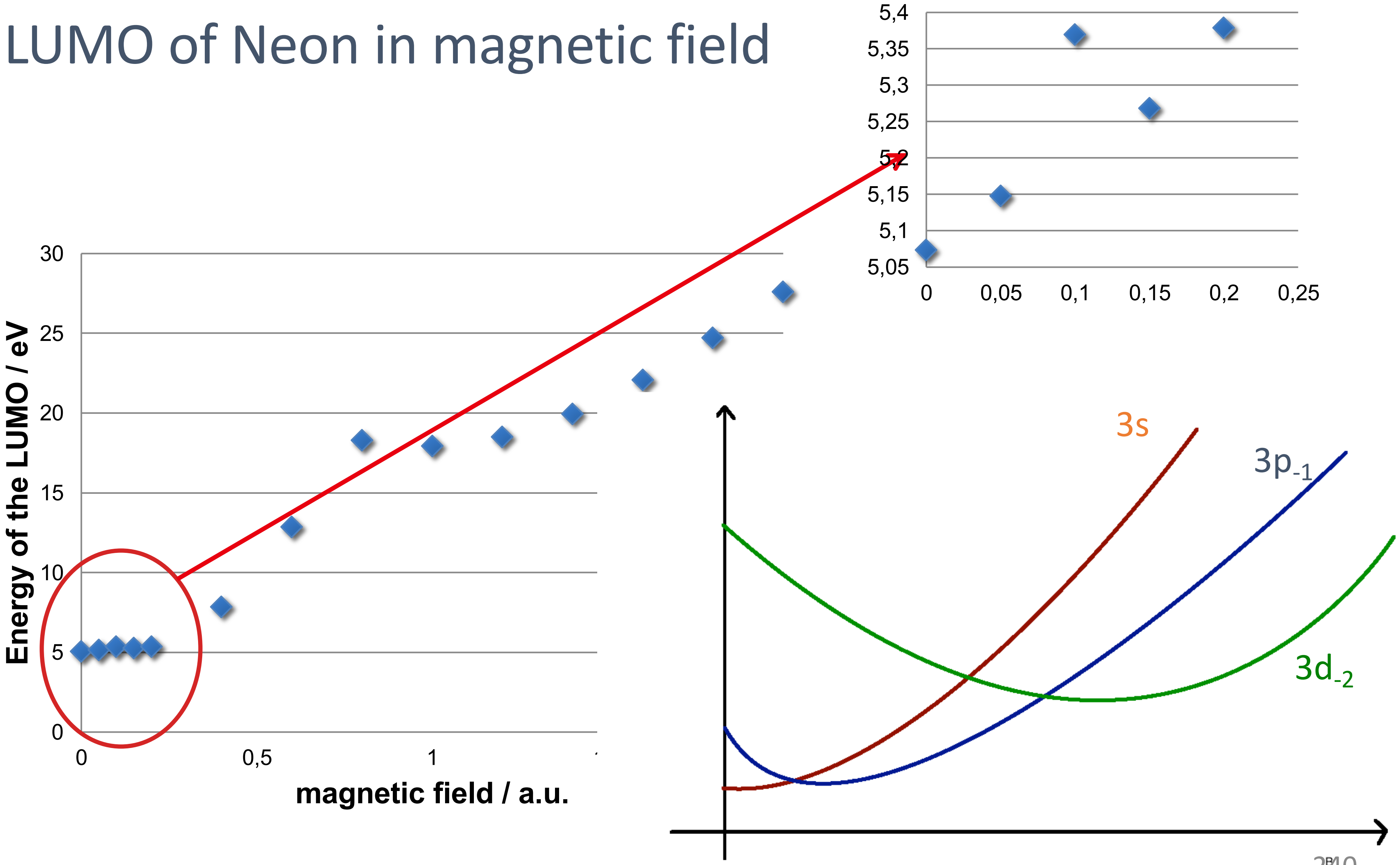
Paramagnetic effects

- LUMO of Neon in magnetic field



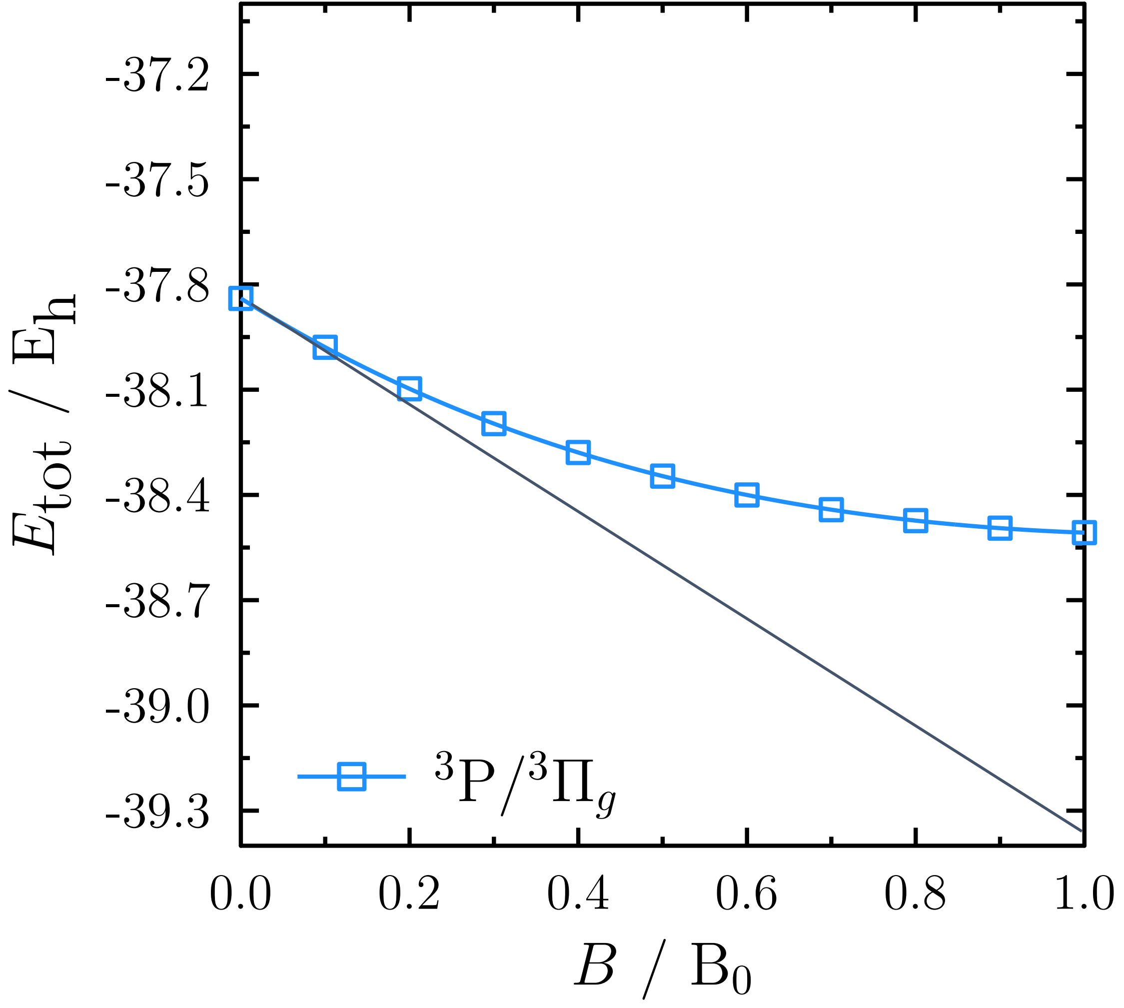
Paramagnetic effects

- LUMO of Neon in magnetic field



Ground state of the C atom in a magnetic field

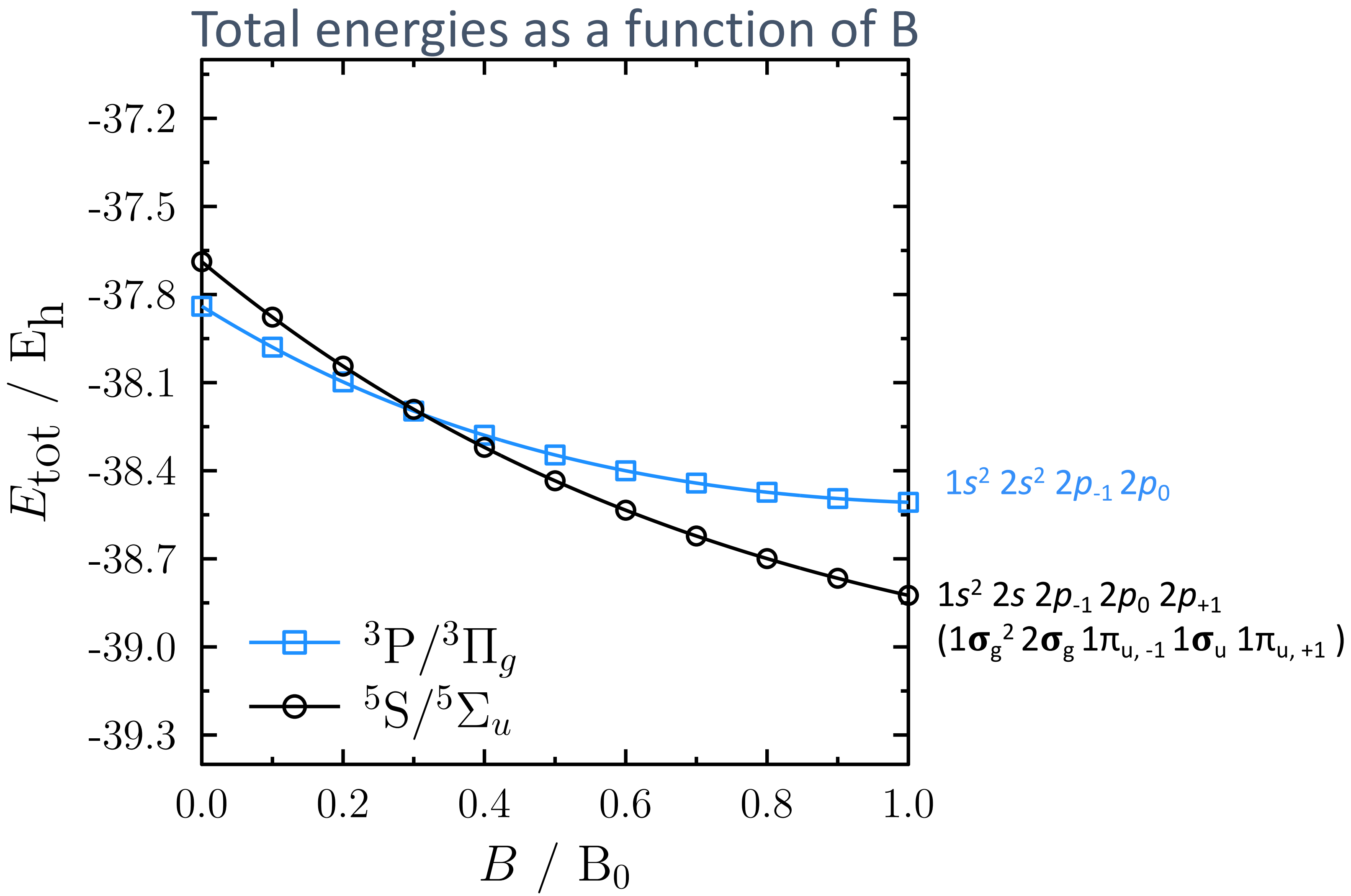
Total energies as a function of B



$1s^2\ 2s^2\ 2p_{-1}\ 2p_0$
$(1\boldsymbol{\sigma}_g{}^2\ 2\boldsymbol{\sigma}_g{}^2\ 1\pi_{u,\,-1}\ 1\boldsymbol{\sigma}_u)$

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

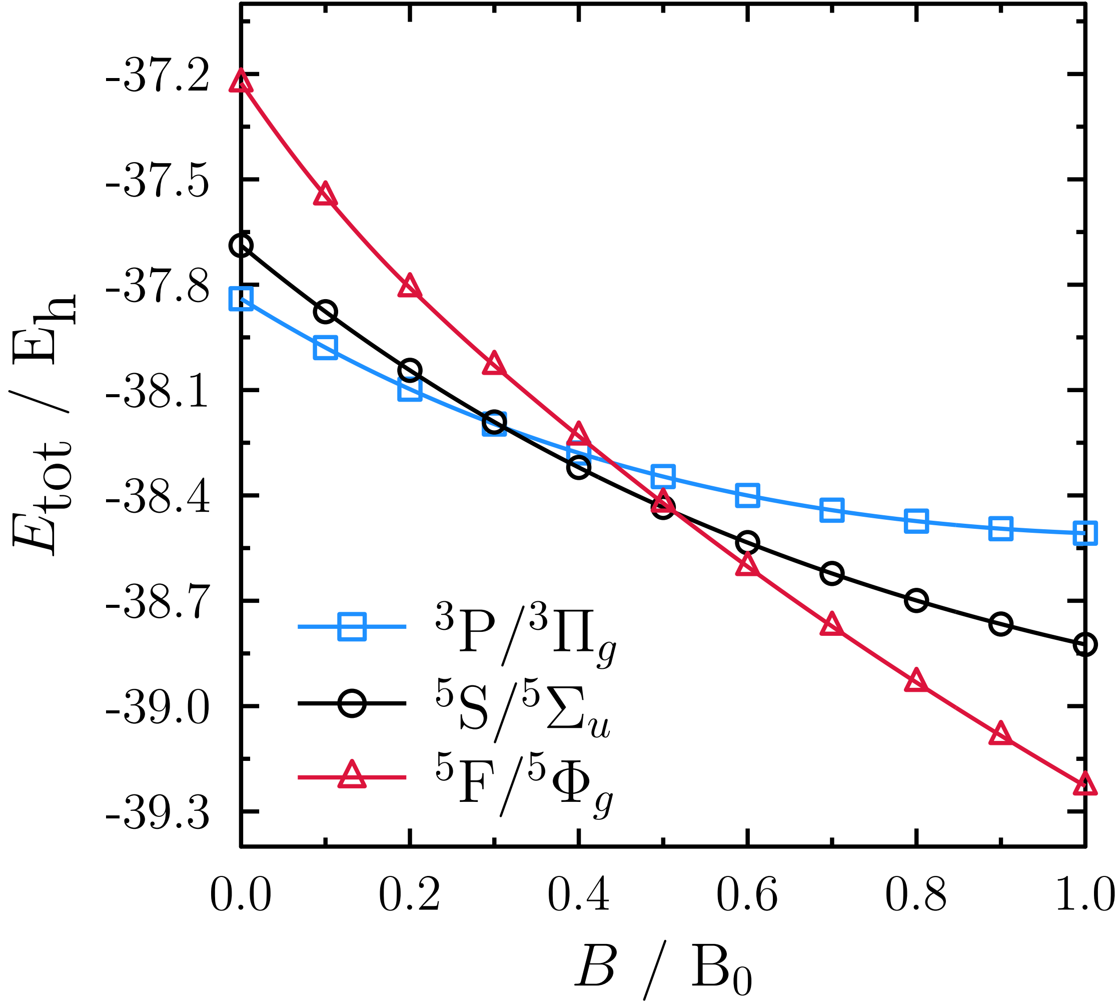
Ground state of the C atom in a magnetic field



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



$1s^2\ 2s^2\ 2p_{-1}\ 2p_0$

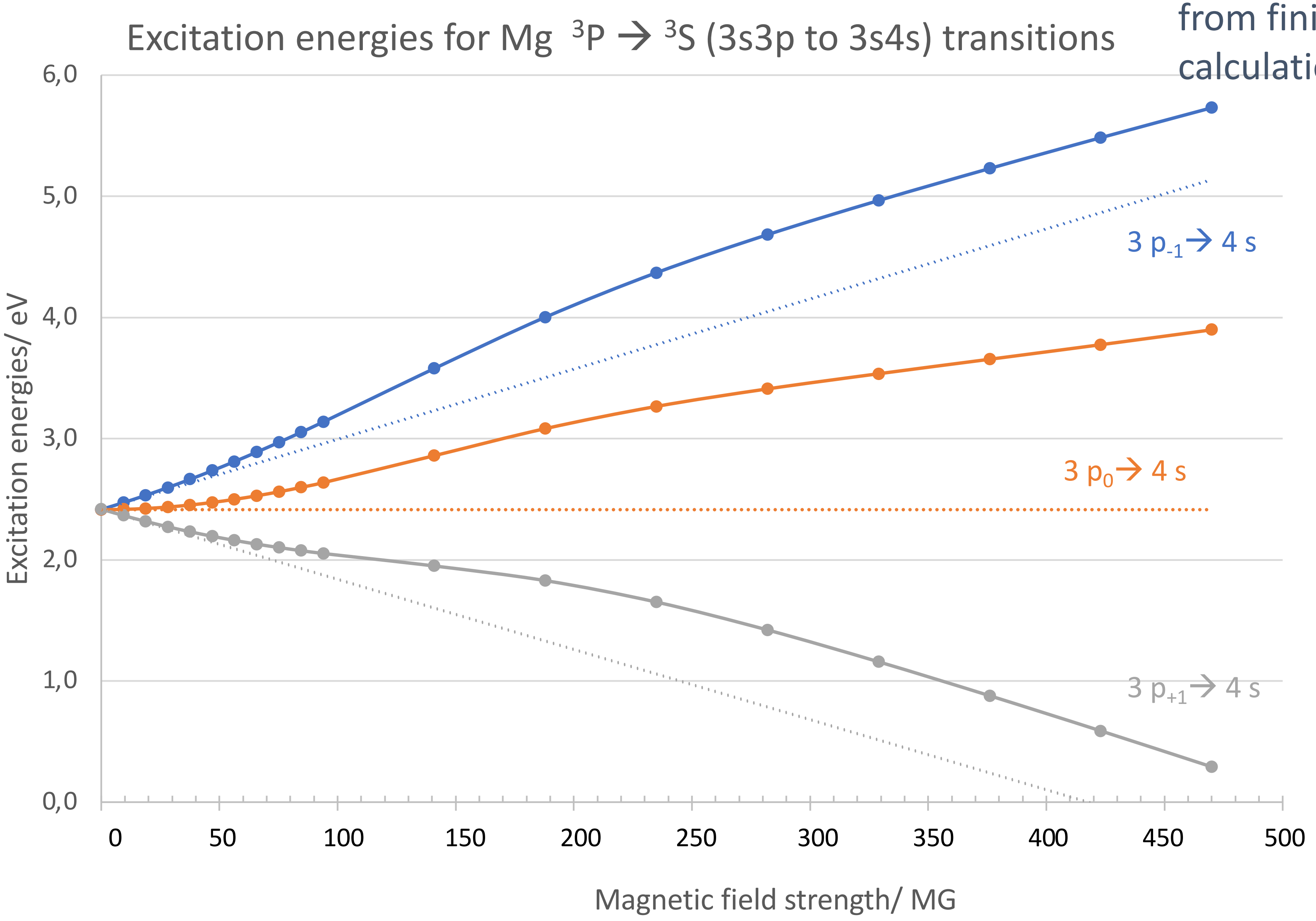
$1s^2\ 2s\ 2p_{-1}\ 2p_0\ 2p_{+1}$

$1s^2\ 2s\ 2p_{-1}\ 2p_0\ 3d_{-2}$
$(1\sigma_g^2\ 2\sigma_g\ 1\pi_{u,-1}\ 1\sigma_u\ 1\delta_{g,-2})$

Exotic states become ground states in strong field!

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

Excitation energies for Mg in magnetic field



from finite-field calculations!

Atom in magnetic field

- Consequences

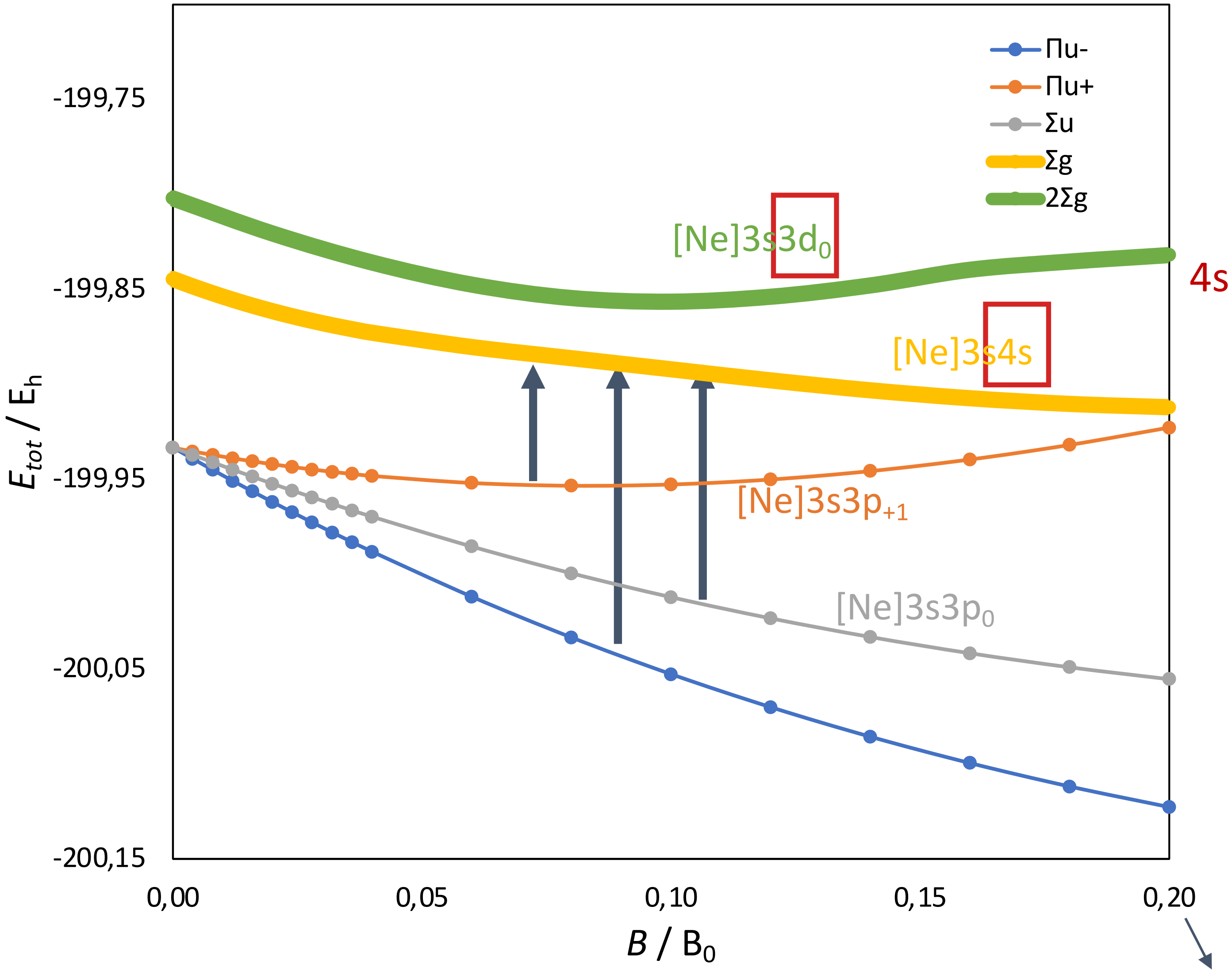
s	p_{-1}	p_0	p_{+1}	d_{-2}	d_{-1}	d_0	d_{+1}	d_{+2}
σ_g	$\pi_{-1,u}$	σ_u	$\pi_{+1,u}$	$\delta_{-2,g}$	$\pi_{-1,g}$	σ_g	$\pi_{+1,g}$	$\delta_{+2,g}$

not distinguishable, may not cross

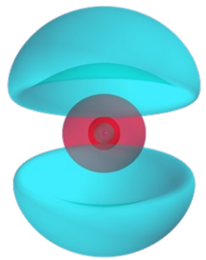
Still eigenfunctions to L_z $L_z = m\hbar$

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

Excitation energies for Mg in magnetic field



4s & 3d$_0$: σ_g

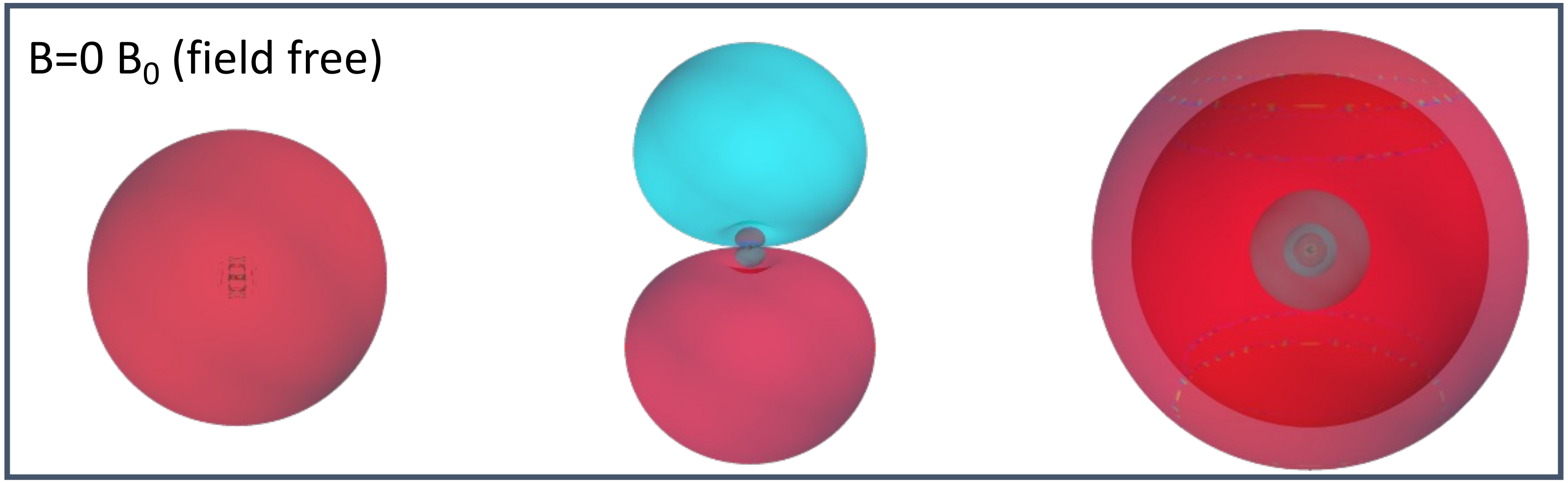


470 MG

Avoided crossings occuring!

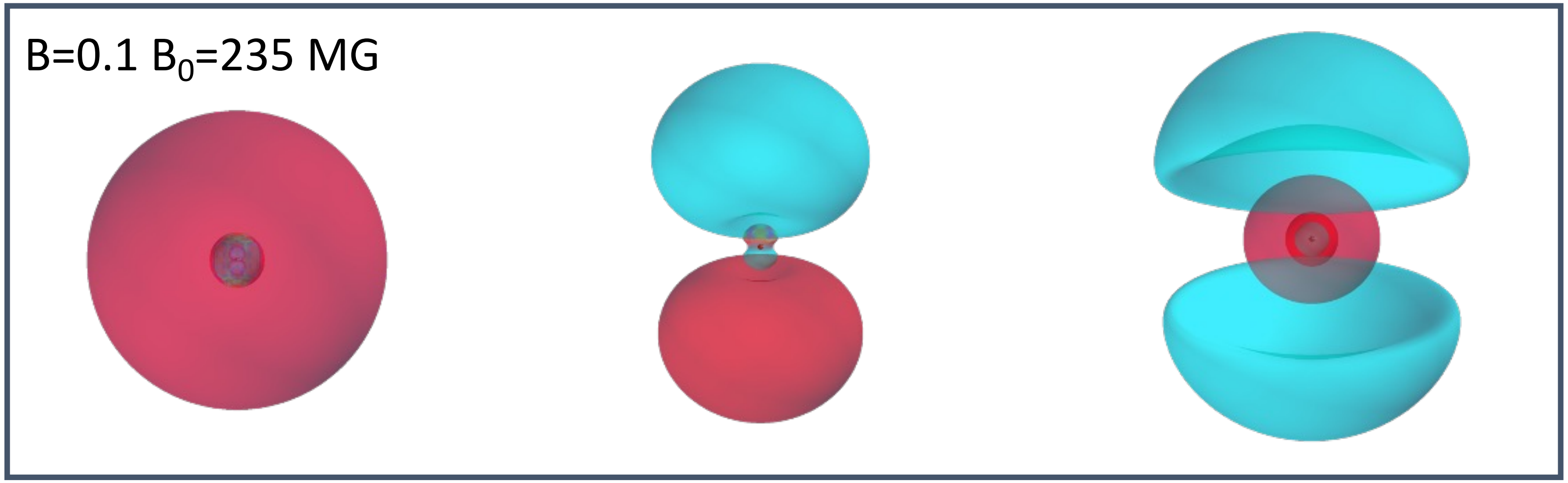
Kitsaras, Grazioli, Stopkowicz, JCP **160**, 094112 (2024)

Mg Orbitals



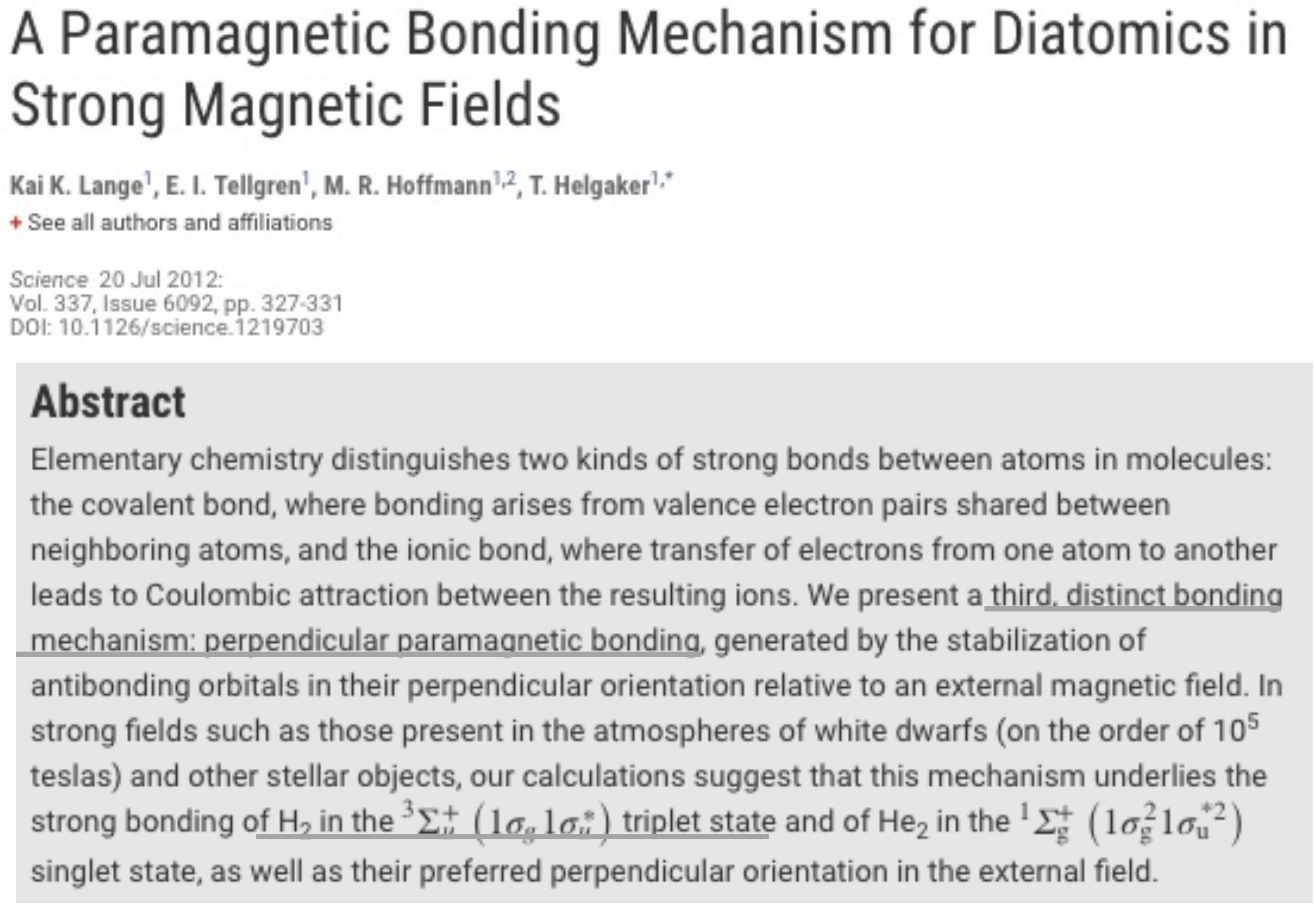
B=0 B_0 (field free)

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

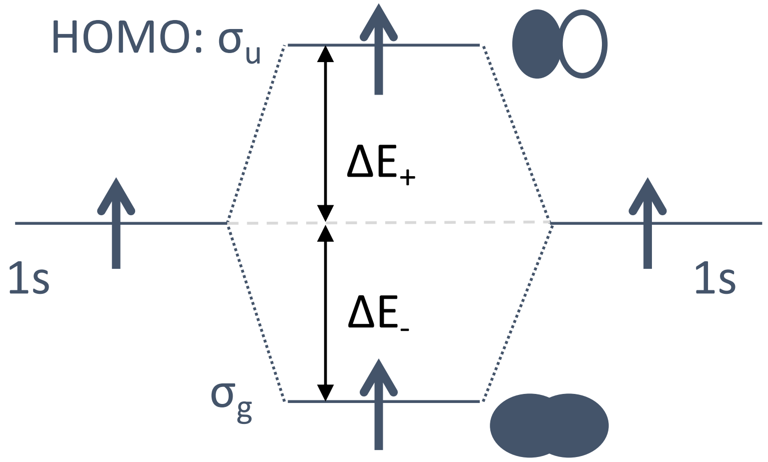
Abstract

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)

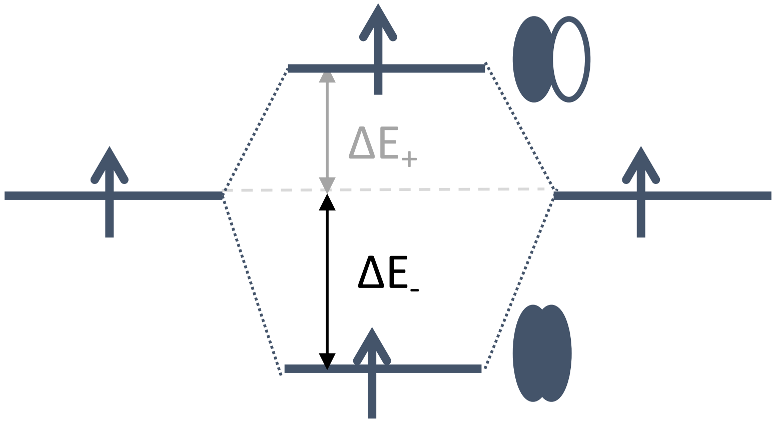
Paramagnetic bonding in H_2^+

field-free



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

perpendicular magnetic field



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

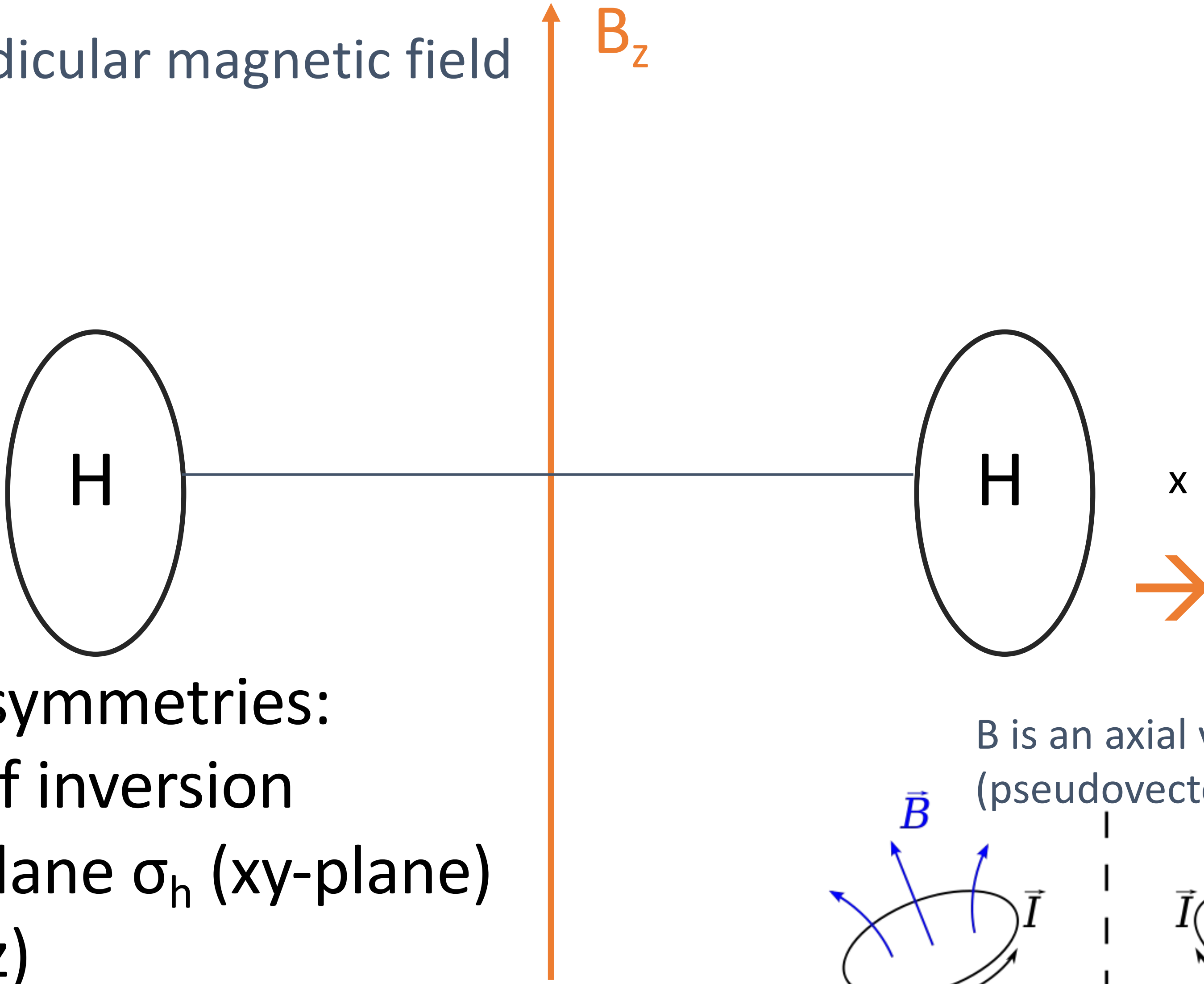
Bonding with formal bond order 0!

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

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

Symmetry considerations

H_2 in perpendicular magnetic field

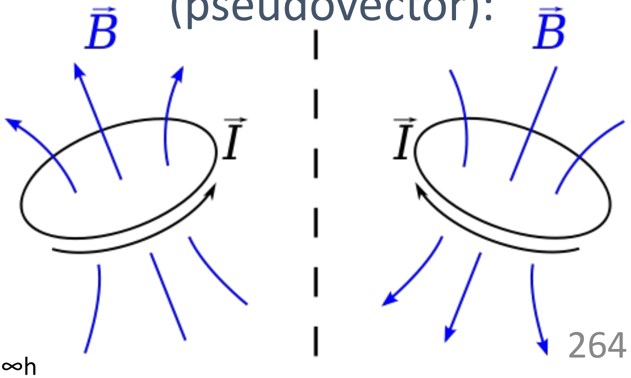


→ C_{2h}

Remaining symmetries:

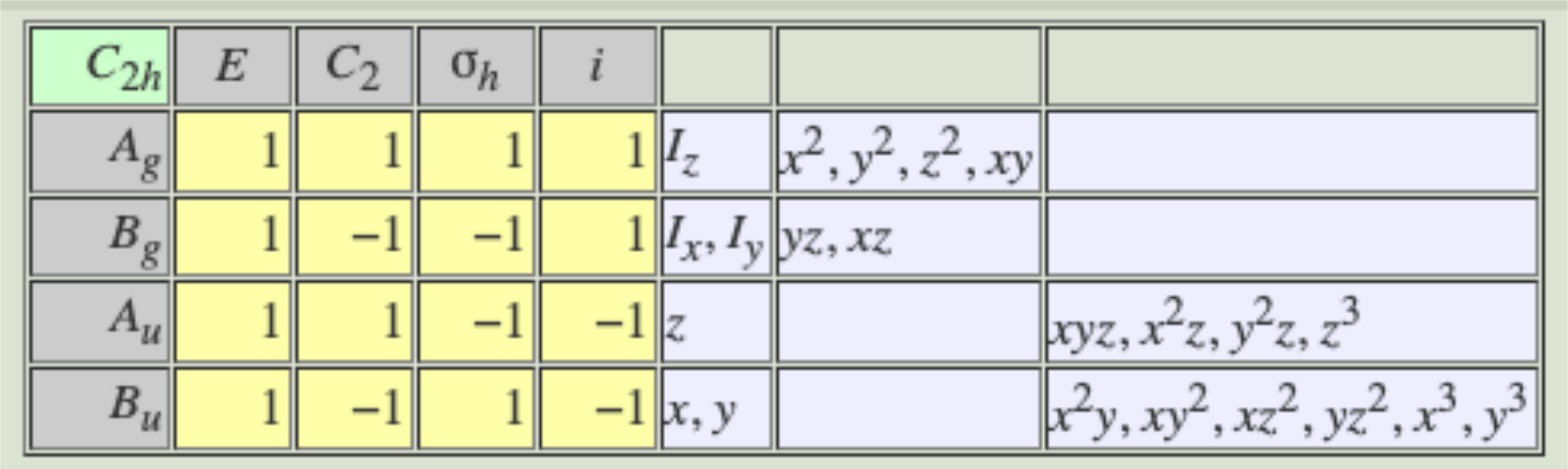
- Center of inversion
- Mirror plane σ_h (xy-plane)
- C_2-axis (z)

B is an axial vector (pseudovector):



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

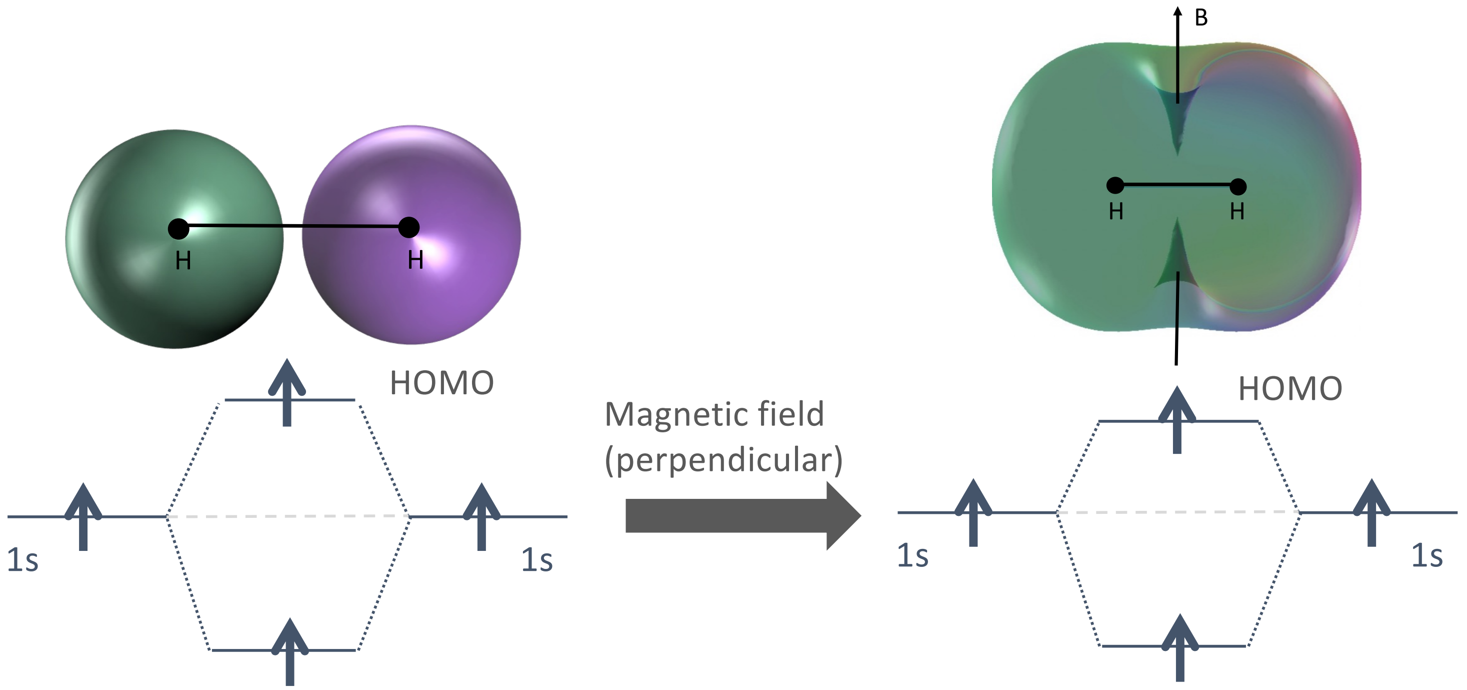
C_{2h} character table



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



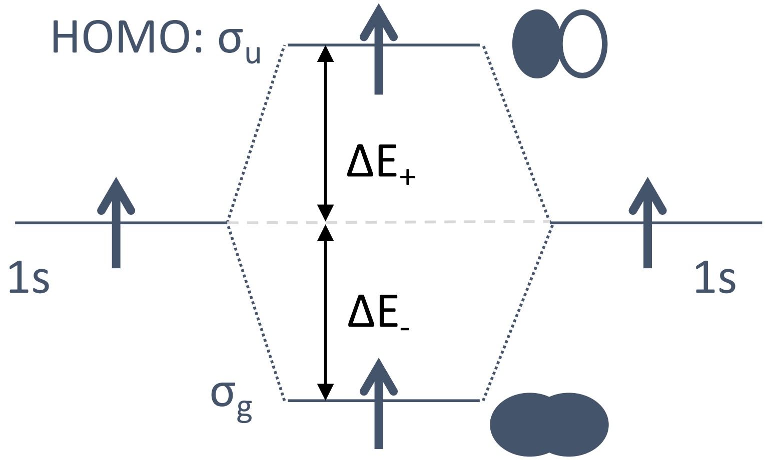
Field-free: highest occupied MO (HOMO) is antibonding

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

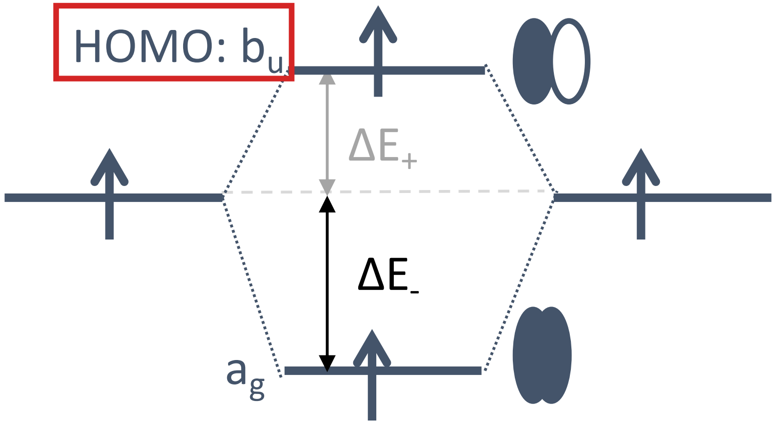
field-free



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

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

perpendicular magnetic field



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

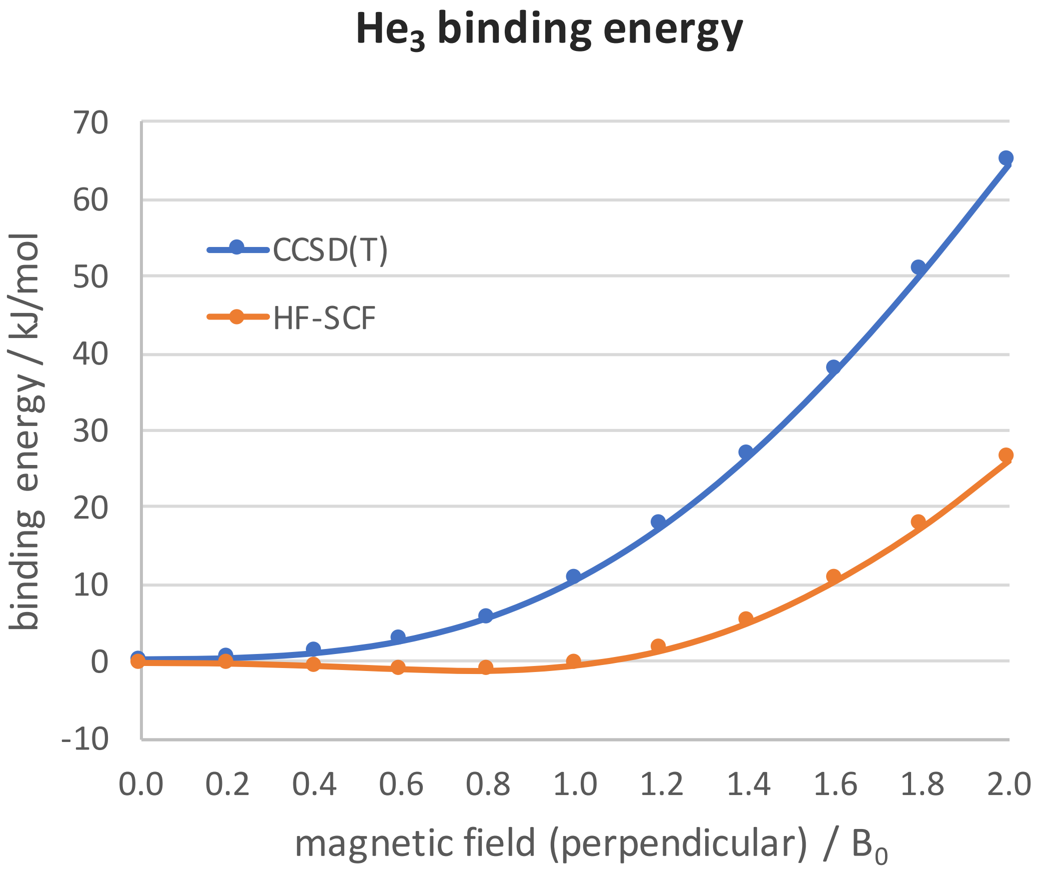
Bonding with formal bond order 0!

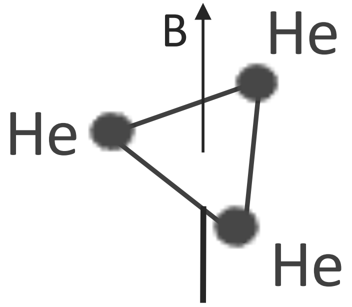
$$\hat{H} = \hat{H}_0 + \boxed{\frac{1}{2} B \hat{L}_z} + B \hat{S}_z + \frac{1}{8} \sum_i^N B^2 \left(x_i^2 + y_i^2 \right)$$

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