Molecular Bonding, Structure, and Dynamics in a Strong Magnetic Field

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Introduction

- We have over the last decade studied atoms and molecules in (ultra)strong magnetic fields
  - one atomic unit of magnetic field strength B corresponds to

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

- Such field strengths have not been realized on Earth (yet) but exist on magnetic white dwarf stars
  - atoms have been observed under such conditions but not yet molecules
  - 'Matter in Strong Magnetic Fields', D. Lai, *Rev. Mod. Phys.* **73**, 629 (2001)
- Under such conditions chemistry becomes very different – it is an exotic, largely unexplored world
  - to unravel this chemistry is exciting in itself
  - it gives a fresh perspective on Earth chemistry and new insight into molecular electronic structure
  - it describes atoms (and molecules) observed in astrophysics
  - it is a stress test for quantum chemistry in a different environment
- Overview
  - background
  - atoms
  - chemical bonding
  - molecular structure
  - molecular dynamics
  - rovibrational spectra

Three field regimes

- The electronic Hamiltonian contains a field-free term H_0 and terms that are linear and quadratic in the field

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

- It is then useful to distinguish three field regimes:

1. Coulomb regime: $B \ll B_0$
   - Coulomb interactions dominate
   - familiar chemistry of spherical atoms
   - Earth: $10^{-10}B_0$, NMR $10^{-4}B_0$, pulsed fields $10^{-2}B_0$

2. Intermediate regime: $B \approx B_0$
   - Coulomb and magnetic interactions compete
   - exotic chemistry of small, ellipsoidal atoms
   - magnetic white dwarfs: 0.01–$1.0B_0$

3. Landau regime: $B \gg B_0$
   - magnetic interactions dominate
   - alien chemistry of tiny, needle-like atoms
   - neutron stars: 10^3–10^4B_0

White dwarf stars

- White dwarfs are the evolutionary end point of 97% of all stars
  - compact objects – comparable to Earth in size and to Sun in mass
  - core composed of C and O, with an atmosphere of mostly H and He

- About 10% of all white dwarfs are magnetized with surface field strengths up to about 10^4 T
  - field strengths are determined by matching observed H spectra with theoretical spectra
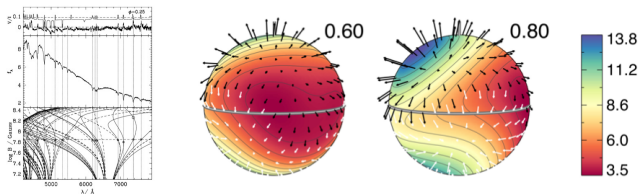
  - Euchner *et al.*, *Astron. Astrophys.* **451**, 671 (2006) (PG 1015+014); Landstreet *et al.*, *Astron. Astrophys.* **607**, A92 (2017) (WD2359-434)

- Do white dwarfs also contain molecules? – their atmospheres are very hot. . .
  - UV transitions in the Lyman band of H_2 detected on three white dwarfs in 2013
  - S. Xu *et al.*, *Astrophys. J. Lett.* **766**, L18 (2013)

- So far, molecules have not been detected on magnetized white dwarfs
 - they should be there – but what would their spectra look like?

Molecular Hamiltonian – para- and diamagnetism

- The Hamiltonian contains linear paramagnetic terms and quadratic diamagnetic term:

$$H = H_0 + \underbrace{\tfrac{1}{2}BL_z + Bs_z}_{\text{paramagnetic Zeeman terms}} + \underbrace{\tfrac{1}{8}B^2(x^2 + y^2)}_{\text{diamagnetic term}}$$
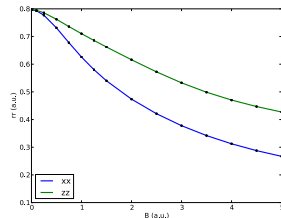
- Paramagnetic Zeeman operators:
    - couple the field to angular momentum of the electrons
    - reduce symmetry and split energy levels
   - raise or lower the energy, depending on orientation
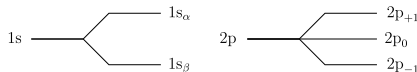
- Diamagnetic operator:
    - arises from induced angular momentum
    - raises the energy of all systems
    - squeezes all systems
        - helium transversal size $\propto 1/\sqrt{B}$
        - helium longitudinal size $\propto 1/\log B$

- All field operators favour high angular momentum

From Coulomb to Landau regime

- The splitting of levels observed in the laboratory is only the thin end of the wedge
- As the field increases, a complete state reordering occurs, driven by the magnetic quantum number m_ℓ
    - left: hydrogen energy levels in units of $\beta = B/B_0$ (Simola and Virtamo, 1978); right: wavelength spectrum against $\beta/2$ (Wunner and Ruder, 1987)
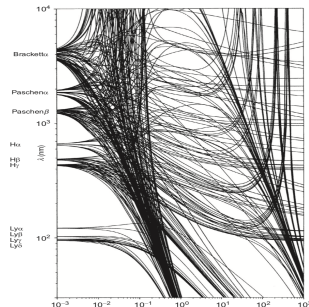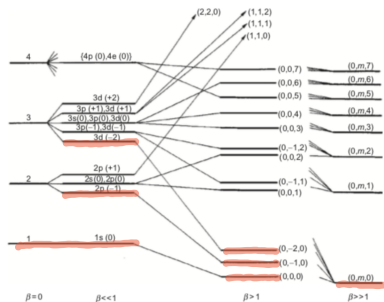

- The Landau levels are quantized as an harmonic oscillator except in the field direction
    - the lowest $m_\ell \leq 0$ component of each hydrogen level enters the infinitely degenerate Landau ground state

Evolution of atomic states in a magnetic field

▶ Lowest states of helium (left), fluorine (middle), and sodium (right) in a magnetic field

   ▶ Stopkowicz, Gauss, Lange, Tellgren, and Helgaker, JCP **143**, 074110 (2015)
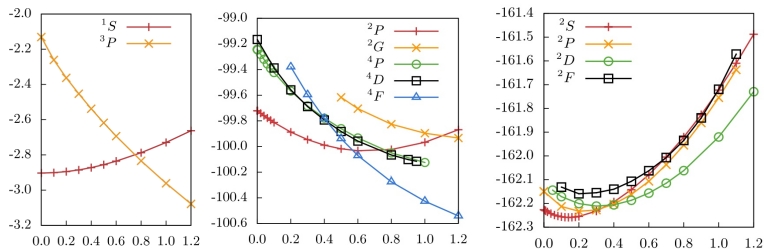
$$\langle H \rangle = \langle H_0 \rangle + B \langle S_z + \tfrac{1}{2} L_z \rangle + \tfrac{1}{8} B^2 \langle x^2 + y^2 \rangle$$

▶ Convex evolution of energy levels with increasing field strength:

   ▶ the initial slope is determined by the permanent magnetic moment through the Zeeman term
   ▶ the slope increases monotonically with increasing field strength by the quadratic diamagnetic term
   ▶ all curves therefore have a convex shape with a unique minimum, at a characteristic field strength (here lowest for sodium)
   ▶ beyond this minimum, the energy increases indefinitely – first quadratically, then linearly

Stability of atoms in a magnetic field

▶ A magnetic field stabilizes atoms and molecules towards ionization, unlike an electric field

▶ Ionization potentials (IPs) plotted against magnetic field strength B
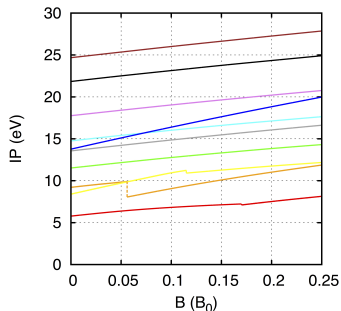
He = brown
Ne = black
F = violet
O = blue
N = cyan
H = gray
C = green
B = yellow
Be = orange
Li = red
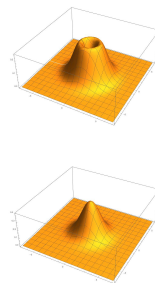
▶ C. Holzer, A. Teale, F. Hampe, S. Stopkowicz, T. Helgaker, W. Klopper, JCP **150** 214112 (2019)

▶ Reason for increased stability:

   ▶ the energy of the ionized electron increases linearly with the field strength
   ▶ the electron inside the atom is shielded from the field by the other electrons

Quantum chemistry in a (strong) magnetic field

- **Atoms in a strong magnetic field** have been studied for a long time
    - such calculations are comparatively simple
    - help identify atoms and determine field strength on white dwarfs
- **Molecules in a strong magnetic field** are much more difficult to study
    - complex arithmetic and gauge-origin invariance problem
    - *ab initio* studies became possible and routine only in 2008
    - *Nonperturbative ab initio calculations in strong magnetic fields using London orbitals*, E. I. Tellgren, A. Soncini, and T. Helgaker, *J. Chem. Phys.* **129**, 154114 (2008)
- **LONDON** is the first general code for molecules in magnetic fields
    - Erik Tellgren, Kai Lange, Stella Stopkowicz, Andy Teale, Tanner Culpitt, Laurens Peters
    - HF, FCI, MCSCF, MP2, CCSD(T), DFT, CDFT
- Other codes used by us:
    - QUEST – Andy Teale's group, Nottingham, UK
    - Turbomole – Wim Klopper's group, Karlsruhe, Germany
- Some functionality also available in these codes:
    - BAGEL – Toru Shiozaki's group, Northwestern
   - ChronusQ – Xiasong Li, David Williams-Young, Ed Valeev and others

Bonding in magnetic fields

- ▶ We have seen an interesting interplay of para- and diamagnetism in atoms
  - ▶ we shall now see how para- and diamagnetism may affect molecules and bonding
- ▶ How will the squeezed and distorted atoms bind in a magnetic field?
  - ▶ will bonds be strengthened or weakened?
  - ▶ what is the preferred orientation of the molecule in the field?
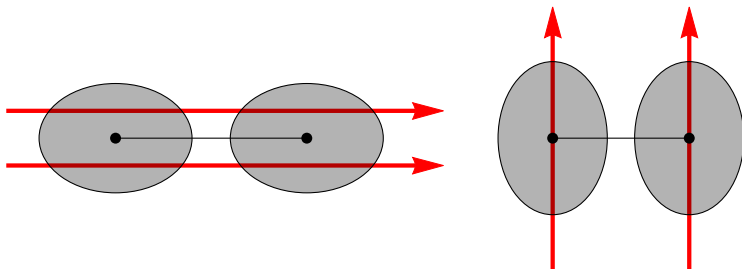
Zeeman interaction: bond breaker and bond maker

▶ Let us consider the ground-state H_2 molecule in an increasing magnetic field
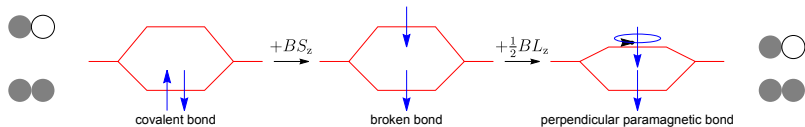
- ▶ The spin Zeeman interaction Bs_z breaks the covalent bond
  - ▶ the magnetic field favours beta spin over alpha spin
  - ▶ singlet–triplet transition: eventually, the alpha electron undergoes a spin flip, forcing it into the antibonding orbital
  - ▶ we expect the resulting molecule to be unstable and fall apart . . .

- ▶ The orbital Zeeman interaction $\frac{1}{2}BL_z$ makes a paramagnetic bond
  - ▶ however, $1\sigma_u^*$ has the shape of a $2p_{-1}$ orbital, if properly oriented
  - ▶ the $1\sigma_u^*$ energy is increasingly lowered as the atoms come together
  - ▶ by this mechanism, the triplet $1\sigma_g 1\sigma_u^*$ configuration becomes bonding

- ▶ Perpendicular paramagnetic bonding
 - ▶ Lange, Tellgren, Hoffmann and Helgaker, *Science* **337** 327 (2012)

The H_2 molecule in a strong magnetic field

- Singlet H_2 $\left|1\sigma_g^2\right\rangle$ aligns itself with the field and becomes more strongly bound
- Triplet H_2 $\left|1\sigma_g 1\sigma_u^*\right\rangle$ becomes bound in a perpendicular field orientation

	singlet			triplet		
B	R_e	D_e	ΔE_{rot}	R_e	D_e	ΔE_{rot}
0.0	74 pm	459 kJ/mol	0	∞	0	0
1.0	66 pm	594 kJ/mol	83 kJ/mol	136 pm	12 kJ/mol	12 kJ/mol

- Polar plots of $E(R, \Theta)$ in the singlet (left) and triplet (right) states
 - red for high energy; blue for low energy
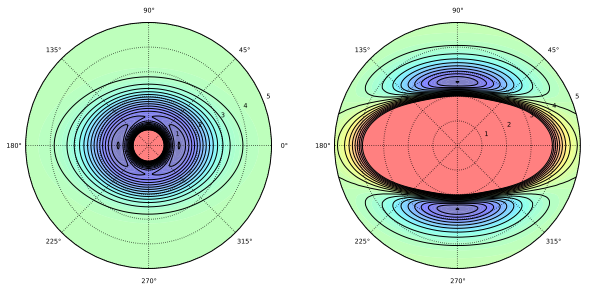
Diamagnetic and paramagnetic currents

- The field sets up counter-clockwise currents in each atom
    - these diamagnetic currents increase the energy of each atom
- As the atoms come closer together, molecular currents appear
    - in singlet H_2, these are counter clockwise, raising the energy
    - in triplet H_2, these are clockwise, lowering the energy
- Induced currents in singlet (left) and triplet (right) H_2 (relative to free atoms)
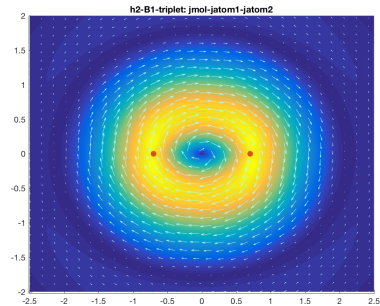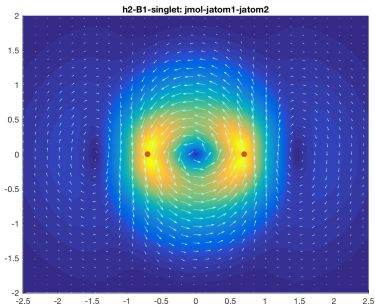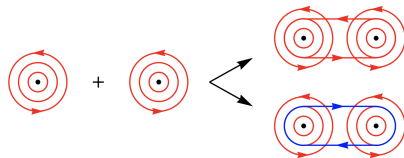
Bonding in helium trimer

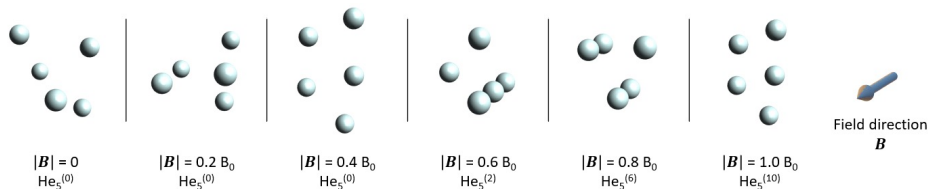▶ Electron correlation significantly enhances paramagnetic bonding
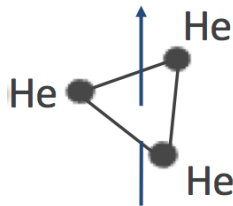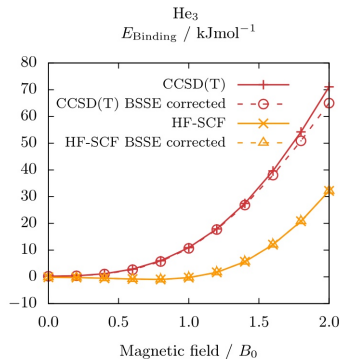
Stopkowicz, Gauss, Lange, Tellgren, and Helgaker, JCP **143**, 074110 (2015)

▶ Bond creation: the clustering atoms are shielding themselves from the field in the same way that huddling penguins are protecting themselves against the cold in the Antarctic winter.

He$_5$ from dispersion to paramagnetic bonding

▶ CDFT calculations with the QUEST program

| $\lvert\boldsymbol{B}\rvert = 0$ He$_5^{(0)}$ | $\lvert\boldsymbol{B}\rvert = 0.2$ B$_0$ He$_5^{(0)}$ | $\lvert\boldsymbol{B}\rvert = 0.4$ B$_0$ He$_5^{(0)}$ | $\lvert\boldsymbol{B}\rvert = 0.6$ B$_0$ He$_5^{(2)}$ | $\lvert\boldsymbol{B}\rvert = 0.8$ B$_0$ He$_5^{(6)}$ | $\lvert\boldsymbol{B}\rvert = 1.0$ B$_0$ He$_5^{(10)}$ | Field direction $\boldsymbol{B}$ |

▶ The dissociation energy of the lowest dissociation pathway

B/B_0	0.0	0.2	0.4	0.6	0.8	1.0
$\Delta E/\text{kJ mol}^{-1}$	0.3	0.4	1.2	8.8	73.4	136.0

  ▶ convex evolution of the energy is similar to that of neon
  ▶ but only if geometry is carefully optimized at each field strength
  ▶ ab initio random structure search (AIRSS) (Pickard and Needs)

▶ Pemberton, Irons, Helgaker, and Teale, JCP **156**, 204113 (2022)
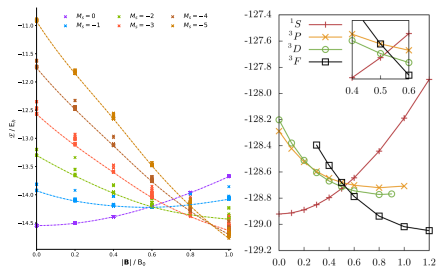
Methane from tetrahedron to fan shape

▶ CH_4 becomes paramagnetically bonded and fan-shaped in a strong field

$0.0B_0 - CH_4^{(0)}$ $\quad$ $0.2B_0 - CH_4^{(-2)}$ $\quad$ $0.4B_0 - CH_4^{(-4)}$ $\quad$ $0.6B_0 - CH_4^{(-4)}$ $\quad$ $0.8B_0 - CH_4^{(-4)}$ $\quad$ $1.0B_0 - CH_4^{(-4)}$
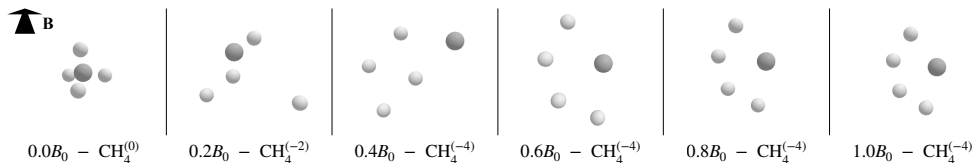
▶ The CDFT dissociation energy of lowest dissociation pathway

B/B_0	0.0	0.2	0.4	0.6	0.8	1.0
$\Delta E/\text{kJ mol}^{-1}$	546.7	0.3	5.2	32.0	41.9	49.3
mean C–H distance (Å)				2.46	2.14	1.95
mean H–H distance (Å)				1.87	1.59	1.41

▶ Pemberton, Irons, Helgaker, and Teale, JCP **156**, 204113 (2022)
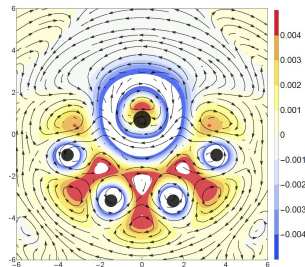
Molecular dynamics in a magnetic field

▶ To calculate spectra in a field, we must be able to do molecular dynamics (eventually with surface hopping)

   ▶ it is then necessary to integrate equations motion with the Lorentz force acting on each atom

$$\mathbf{F}(\mathbf{r}, \mathbf{v}) = z\mathbf{E}(\mathbf{r}) + z\mathbf{v} \times \mathbf{B}(\mathbf{r}) \qquad \leftarrow \text{velocity-dependent Lorentz force}$$

▶ Each nucleus experiences a local field, which is the total field screened by the electrons:

$$\mathbf{B}_{\text{loc}}(\mathbf{r}) = \mathbf{B} + \mathbf{B}_{\text{el}}(\mathbf{r}) \qquad \leftarrow \text{screened magnetic field}$$

▶ Illustration: calculations on the He atom with and without screening

    ▶ with screening ($\Omega \neq 0$): $\mathbf{B}_{\text{loc}}(\mathbf{r}) = \mathbf{0}$, giving perfect translation

    ▶ without screening ($\Omega = 0$): $\mathbf{B}_{\text{loc}}(\mathbf{r}) = \mathbf{B}$, giving circular motion with frequency $\tilde{\nu}_1 \approx 60 \, \text{cm}^{-1}$ at $B = B_0$
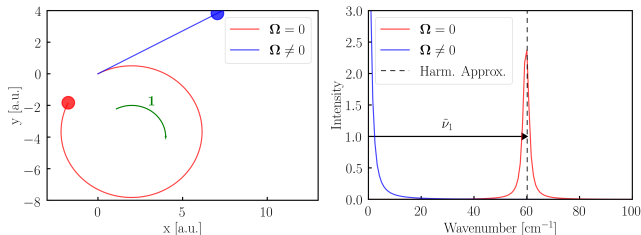
Born–Oppenheimer approximation in a magnetic field

▶ Molecular Hamiltonian in a magnetic vector potential $\mathbf{A}$:

$$H_{\text{mol}} = \tfrac{1}{2} \sum_I M_I^{-1} \Pi_I^2 + H_{\text{el}}(\mathbf{r}, \mathbf{R}, \mathbf{A}), \quad \boldsymbol{\Pi}_I = \mathbf{P}_I - Z_I e \mathbf{A}(\mathbf{R}_I), \quad \mathbf{P}_I = -\mathrm{i}\hbar \boldsymbol{\nabla}_I$$

   ▶ electronic coordinates $\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \dots\}$ and nuclear coordinates $\mathbf{R} = \{\mathbf{R}_1, \mathbf{R}_2, \dots\}$

▶ Born–Oppenheimer wave-function ansatz:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \Theta(\mathbf{R}, t)\Phi(\mathbf{r}; \mathbf{R}) \quad \leftarrow \text{ nuclear wave function} \times \text{electronic wave function}$$

▶ Project the molecular Schrödinger equation by the electronic wave function to obtain nuclear Schrödinger equation

$$\mathrm{i}\hbar\partial_t \Psi(\mathbf{r}, \mathbf{R}, t) = H_{\text{mol}}\Psi(\mathbf{r}, \mathbf{R}, t) \implies \mathrm{i}\hbar\partial_t \Theta(\mathbf{R}, t) = (T + U)\Theta(\mathbf{R}, t)$$

▶ The nuclear Hamiltonian has contributions from nonadiabatic coupling matrix elements (NACMEs):

$$T = \tfrac{1}{2} \sum_I M_I^{-1} \left(\boldsymbol{\Pi}_I + \langle\Phi|\mathbf{P}_I|\Phi\rangle\right)^2 \qquad \leftarrow \text{Berry connection (geometric vector potential)}$$

$$U = \langle\Phi|H_{\text{el}}|\Phi\rangle + \tfrac{1}{2} \sum_I M_I^{-1} \left(\langle\Phi|P_I^2|\Phi\rangle - |\langle\Phi|\mathbf{P}_I|\Phi\rangle|^2\right) \qquad \leftarrow \text{diagonal Born–Oppenheimer correction (DBOC)}$$

Born–Oppenheimer dynamics with the Lorentz force

▶ The nuclear Schrödinger equation for a molecule in a magnetic field is given by:

$$\tfrac{1}{2} \sum_I M_I^{-1} \left(\mathbf{P}_I - Z_I e \mathbf{A}_I + \langle \Phi | \mathbf{P}_I | \Phi \rangle \right)^2 \Theta(\mathbf{R}, t) + U(\mathbf{R})\Theta(\mathbf{R}, t) = i\hbar \partial_t \Theta(\mathbf{R}, t)$$

▶ The corresponding classical equations of motion for nucleus I at $\mathbf{R}_I$ become:

$$M_I \ddot{\mathbf{R}}_I = - \underbrace{\boldsymbol{\nabla}_I U(\mathbf{R})}_{\text{gradient force}} - \underbrace{Z_I e\, \mathbf{B} \times \dot{\mathbf{R}}_I}_{\text{Lorentz force}} + \underbrace{\sum_J \boldsymbol{\Omega}_{IJ}(\mathbf{R})\, \dot{\mathbf{R}}_J}_{\text{Berry force}} \quad \leftarrow \text{screened Lorentz force}$$

▶ The Berry force provides the screening and is obtained from the Berry-curvature tensor:

$$\boldsymbol{\Omega}_{IJ}(\mathbf{R}) = 2\hbar \operatorname{Im}\langle \boldsymbol{\nabla}_I \Phi | \boldsymbol{\nabla}_J^{\mathsf{T}} \Phi \rangle \quad \leftarrow \text{Berry curvature}$$

   ▶ evaluation by response theory, making trajectory calculations in a field more expensive

▶ LONDON is the first general code for molecular dynamics in a magnetic field

   ▶ Tanner Culpitt, Laurens Peters, Erik Tellgren, and Trygve Helgaker, *J. Chem. Phys.* **155**, 024104 (2021)
   ▶ Laurens Peters, Tanner Culpitt, Laurenz Monzel, and Trygve Helgaker, *J. Chem. Phys.* **155**, 024105 (2021)
   ▶ Ceresoli, Marchetti, and Tosatti, *Phys. Rev. B* **75**, 161101 (2007) – perpendicular orientation, minimal Slater basis

# Berry curvature and magnetic field

- ▶ The Berry curvature contains complete information about the magnetic field
  - ▶ if not, neutral atoms would not move in a straight line in a magnetic field
- ▶ The important relation is the magnetic-translational sum rule:

$$2\hbar \,\mathrm{Im} \sum_{IJ} \langle \boldsymbol{\nabla}_I \Phi | \boldsymbol{\nabla}_J^{\mathsf{T}} \Phi \rangle = e N_{\mathrm{el}} \begin{pmatrix} 0 & -B_z & B_y \\ B_z & 0 & -B_x \\ -B_y & B_x & 0 \end{pmatrix} \qquad \leftarrow \text{ wave function determines the field}$$

  - ▶ Peters, Culpitt, Tellgren, and Helgaker, JCP **157**, 134108 (2022)
- ▶ The sum rule is a consequence of the translational symmetry of the electronic wave function

$$\Phi(\mathbf{r}; \mathbf{R} + \mathbf{T}) = \exp\left[-\tfrac{\mathrm{i}e}{2\hbar} \mathbf{B} \times \mathbf{T} \cdot (\mathbf{r} - \mathbf{R})\right] \Phi(\mathbf{r} - \mathbf{T}; \mathbf{R}) \quad \leftarrow \text{ translation of nuclear coordinates by } \mathbf{T}$$

- ▶ It holds in a finite basis only if London atomic orbitals (GIAOs) are used:
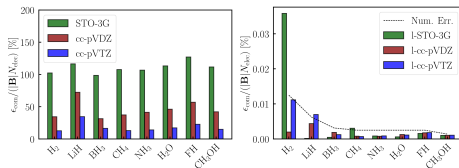
London orbitals

- London atomic orbitals are Gaussians with built-in field oscillations

$$\omega(\mathbf{r};\mathbf{R}) = \exp\left[-\tfrac{\mathrm{i}e}{2\hbar}\mathbf{B}\times(\mathbf{R}-\mathbf{O})\cdot\mathbf{r}\right]G(\mathbf{r}-\mathbf{R}) \ \leftarrow \text{London atomic orbital at } \mathbf{R} \text{ with gauge origin } \mathbf{O}$$

  - they ensure gauge-origin invariance of all calculations

- Use of London orbitals is essential to ensure proper chemistry in a magnetic field – for example,

  - translation of neutral atom in a uniform magnetic field
  - correct dissociation of molecules in a magnetic field


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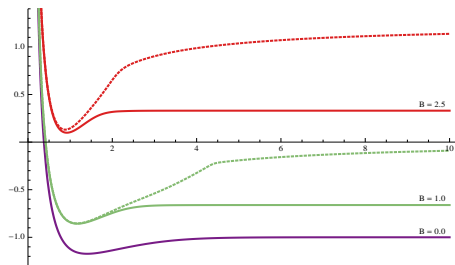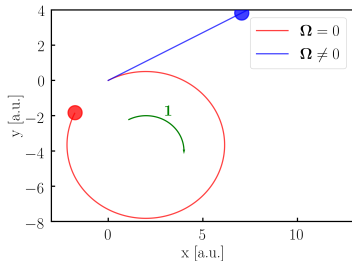
Rovibrational coordinates for singlet H_2

- Singlet H_2 has a preferred parallel field orientation, with a field-dependent barrier at perpendicular field orientation
- There are three degrees of freedom, in addition to translation:
    - ϕ: azimuthal motion: rotation about field axis
    - θ: polar motion: hindered rotation or libration (wagging)
    - r: radial motion: bond stretching
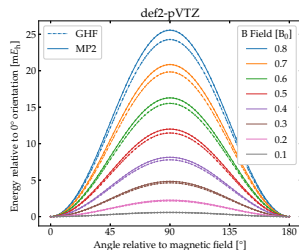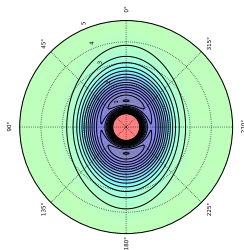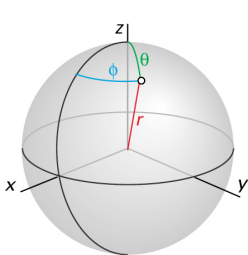
- For singlet H_2, the barrier is equatorial, occuring in the xy plane

Hindered rotation vs. libration of H_2

▶ A molecule may or may not have sufficient energy to cross the equatorial barrier, with very different dynamics

  ▶ trajectories initiated at equilibrium with energies 2.8 mH give libration (left)
  ▶ trajectories initiated at equilibrium with energies 3.5 mH give (hindered) rotation (right)
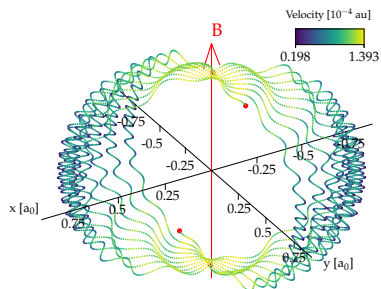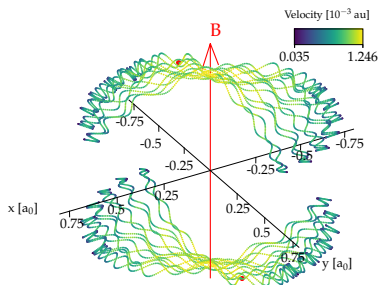
▶ Lorentz force acting on the partially screened nuclei induces precession of the atoms about the field axis

▶ Monzel, Pausch, Peters, Tellgren, Helgaker, and Klopper, *J. Chem. Phys.* **157**, 054106 (2022)
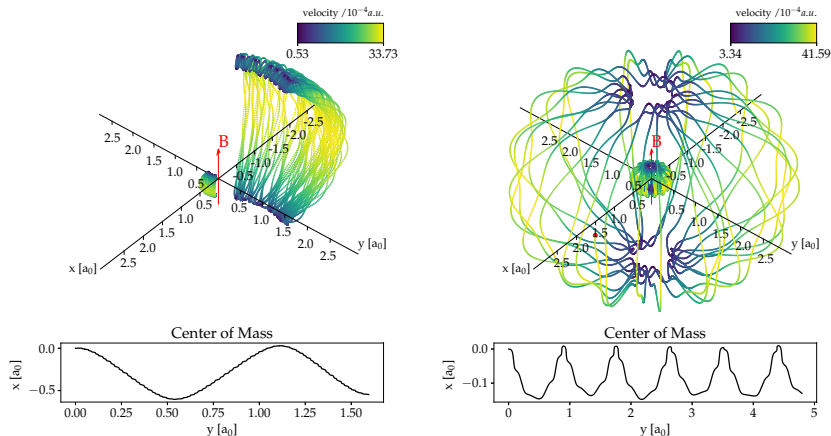
Rovibrational spectrum of H_2 at 1500 K

▶ NVT ensemble averaged over 2000 trajectories of 1 ps duration with initial velocities from Maxwell–Boltzmann distribution

    ▶ power spectrum by Fourier transformation of velocities recorded during the simulation – intensities reflect how often a mode is visited during the simulation
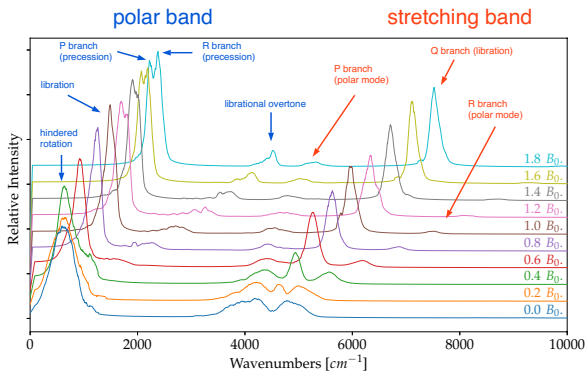
▶ polar band:

    ▶ initial (red-shifted) hindered rotation followed by (increasingly blue-shifted) libration at about $0.4\,B_0$ – overtone is visible

    ▶ coupling to precession gives P and Q branches in a strong field

▶ stretching band:

    ▶ coupling to rotation gives P and R branches at zero field – Q branch arises by coupling to libration from about $0.4\,B_0$

    ▶ blue shift occurs as the bond becomes stronger with increasing field strength – increased P–R splitting reflects the blue shift of libration

Trajectories of polar LiH in a magnetic field

▶ Trajectories with libration (left) and hindered rotation (right) of LiH at $0.2B_0$

▶ LiH has a preferred perpendicular orientation and avoids the parallel orientation altogther
▶ LiH has a permanent dipole moment, which induces centre-of-mass motion

Rovibrational spectrum of LiH at 1500 K

▶ NVT ensemble averaged over 2000 spectra of 1 ps duration with initial velocities from Maxwell–Boltzmann distribution
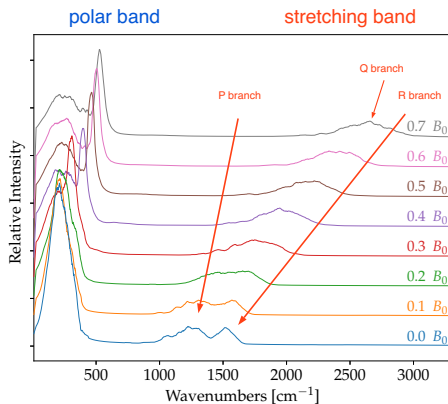
▶ Laurens Peters, Tanner Culpitt, Laurenz Monzel, Erik Tellgren, and Trygve Helgaker, *J. Chem. Phys.* **155**, 024105 (2021)
Laurenz Monzel, Ansgar Pausch, Laurens Peters, Erik Tellgren, Trygve Helgaker, and Wim Klopper, *J. Chem. Phys.* **157**, 054106 (2022)

Harmonic approximation and normal modes

▶ Field-free harmonic rovibrational frequencies and normal modes are obtained from an $3N \times 3N$ eigenvalue problem

$$\left(\mathbf{H} - \omega^2 \mathbf{M}\right) \boldsymbol{\eta}_\omega = \mathbf{0}$$

   ▶ $\mathbf{H}$ and $\mathbf{M}$ are the real symmetric Hessian (force-constant) and nuclear–mass matrices, respectively
   ▶ a quadratic eigenvalue problem where $(\pm\omega, \boldsymbol{\eta}_\omega)$ describe excitations and deexcitations

▶ In a magnetic field, the quadratic eigenvalue problem contains both linear and quadratic terms:

$$\left(\mathbf{H} - \mathrm{i}\omega\boldsymbol{\Lambda} - \omega^2 \mathbf{M}\right) \boldsymbol{\eta}_\omega = \mathbf{0}, \quad \Lambda_{I\alpha, J\beta}(\mathbf{R}) = Z_I e\, \delta_{IJ}\epsilon_{\alpha\beta\gamma}B_\gamma(\mathbf{R}) + \Omega_{I\alpha, J\beta}(\mathbf{R})$$

   ▶ the real antisymmetric screened Lorentz matrix $\boldsymbol{\Lambda}$ accounts for the screened Lorentz force
   ▶ the $6N$ solutions occur in complex conjugate pairs describing excitations and deexcitations

$$(\omega, \boldsymbol{\eta}_\omega) \leftrightarrow (-\omega^*, \boldsymbol{\eta}_\omega^*)$$

▶ The quadratic eigenvalue problem can be linearized in different ways by doubling the dimensions, for example:

$$\begin{pmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{H} & \boldsymbol{\Lambda} \end{pmatrix} \begin{pmatrix} \boldsymbol{\eta}_\omega \\ \boldsymbol{\gamma}_\omega \end{pmatrix} = \mathrm{i}\omega \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ 0 & \mathbf{M} \end{pmatrix} \begin{pmatrix} \boldsymbol{\eta}_\omega \\ \boldsymbol{\gamma}_\omega \end{pmatrix} \quad \leftarrow \quad 6N \times 6N \text{ linear eigenvalue problem}$$

▶ Tellgren, Culpitt, Peters, and Helgaker, *J. Chem. Phys.* **158**, 124124 (2023)

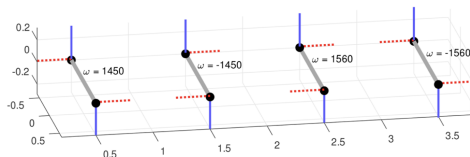# Distinct eigenvalues belonging to the same eigenvector

▶ In the quadratic eigenvalue problem, distinct eigenvalues $\omega_1 \neq \omega_2$ may have the same eigenvector $\boldsymbol{\eta}$:

$$\left(\mathbf{H} - i\omega_1\boldsymbol{\Lambda} - \omega_1^2\mathbf{M}\right)\boldsymbol{\eta} = \mathbf{0}, \quad \left(\mathbf{H} - i\omega_2\boldsymbol{\Lambda} - \omega_2^2\mathbf{M}\right)\boldsymbol{\eta} = \mathbf{0},$$

▶ This happens if and only if $\boldsymbol{\eta}$ is a simultaneous eigenvector of $\mathbf{H}$ and $i\boldsymbol{\Lambda}$:

$$\left(\mathbf{H} + \omega_1\omega_2\mathbf{M}\right)\boldsymbol{\eta} = \mathbf{0}, \quad \left(i\boldsymbol{\Lambda} + (\omega_1 + \omega_2)\mathbf{M}\right)\boldsymbol{\eta} = \mathbf{0}$$

▶ Illustration: hindered rotation of singlet H_2 at $B = B_0$

▶ the frequencies 1450 and $-1560\,\mathrm{cm}^{-1}$ belong to $\boldsymbol{\eta}$, while -1450 and $1560\,\mathrm{cm}^{-1}$ belong to $\boldsymbol{\eta}^*$
▶ at the same time $\boldsymbol{\eta}$ satisfies two linear eigenvalue problems

$$\mathbf{H}\boldsymbol{\eta} = (1504\,\mathrm{cm}^{-1})^2\mathbf{M}\boldsymbol{\eta} \quad \leftarrow \quad \text{degenerate frequency in the limit of complete screening}$$

$$i\boldsymbol{\Lambda}\boldsymbol{\eta} = 110\,\mathrm{cm}^{-1}\mathbf{M}\boldsymbol{\eta} \quad \leftarrow \quad \text{splitting of degenerate frequencey by the screened Lorentz force}$$

Harmonic and anharmonic frequencies of singlet H_2

▶ As the temperature of molecular dynamics calculations is lowered, the harmonic frequencies are recovered

   ▶ this comparison represents an excellent test on our calculations
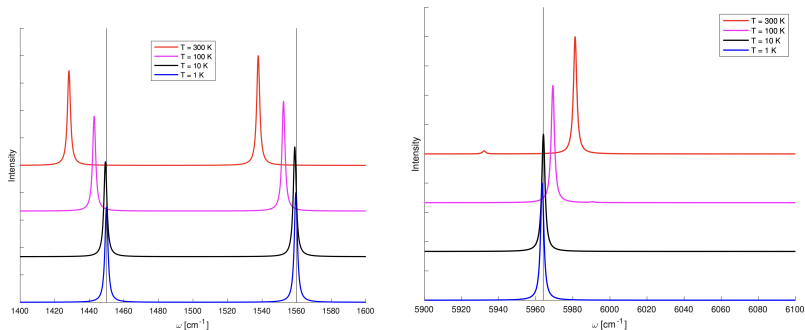
▶ Note: anharmonic corrections may be positive as well as negative

   ▶ rotational mode becomes redshifted as rotation becomes less hindered at higher temperatures
   ▶ stretching mode becomes blueshifted as more non-parallel orientations with a stiffer bond are explored at higher temperatures

Rovibrational spectrum of H_2 from Coulomb to Landau regime
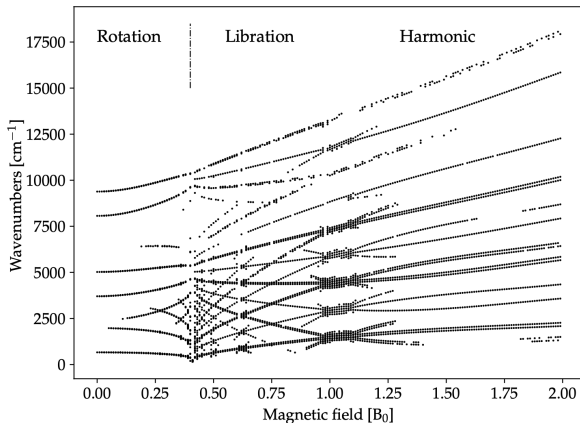
▶ Three regimes: rotation (Coulomb), libration (intermediate), harmonic (Landau)

▶ Monzel, Pausch, Peters, Tellgren, Helgaker, and Klopper, JCP (submitted)

Conclusions and acknowledgements

► Concluding remarks
  ► Chemistry in an ultrastrong magnetic field differs dramatically from chemistry on Earth
    ► puts our familiar chemistry in a fresh perspective
    ► so far only explored theoretically and computationally – stress test for our methods
    ► may be observable on magnetic white dwarfs, if reliably predicted
    ► connections with quantum dots and artificial molecules (coupled quantum dots)

► Co-workers:
  ► Erik Tellgren, Tanner Culpitt, Laurens Peters (University of Oslo)
  ► Andy Teale, Tom Irons, Miles Pemberton (University of Nottingham)
  ► Jürgen Gauss, Florian Hampe, Stella Stopkowicz (University of Mainz)
  ► Wim Klopper, Ansgar Pausch, Christof Holzer, Laurenz Monzel (KIT)

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