Molecular Dynamics and Rovibrational Spectra in a 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

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

- 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
  - 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
- We here consider molecules in ultrastrong magnetic fields with emphasis on molecular dynamics
  - background
  - molecular bonding and structure
  - molecular dynamics with the (screened) Lorentz force
  - rovibrational spectra
  - harmonic approximation

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

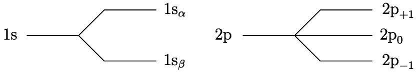
3. Landau regime: $B \gg B_0$
    - magnetic interactions dominate
    - alien chemistry of tiny, needle-like atoms
    - neutron stars: 10^3–$10^4 B_0$

Molecular Hamiltonian – para- and diamagnetism

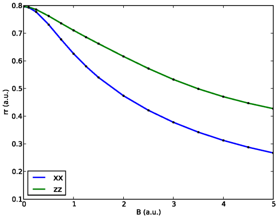
- The Hamiltonian contains linear paramagnetic terms and a quadratic diamagnetic term:

$$H = H_0 + \underbrace{\tfrac{1}{2}BL_z + Bs_z}_{\text{paramagnetic Zeeman terms}} + \underbrace{\tfrac{1}{8}B^2(x^2+y^2)}_{\text{diamagnetic term}}$$

- Paramagnetic Zeeman operators:
  - couple the field to the angular momentum of the electrons
  - reduce symmetry and split energy levels
  - raise or lower the energy, depending on orientation



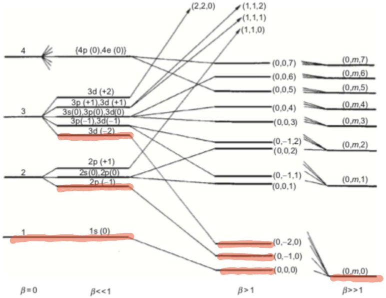
- Diamagnetic operator:
  - arises from induced angular momentum
  - raises the energy of all systems
  - squeezes all systems
    - helium transversal size $\propto 1/\sqrt{B}$
    - helium longitudinal size $\propto 1/\log B$

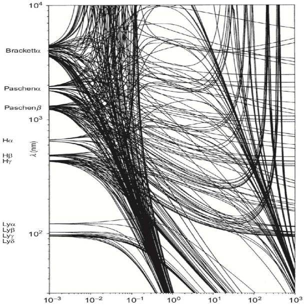


- All field operators favour high angular momentum

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)

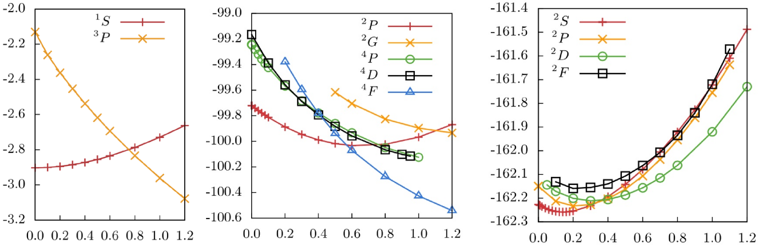




- The Landau levels are quantized as a harmonic oscillator except in the field direction
    - the lowest $m_\ell \leq 0$ component of each hydrogen level enters the infinitely degenerate Landau ground state

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)

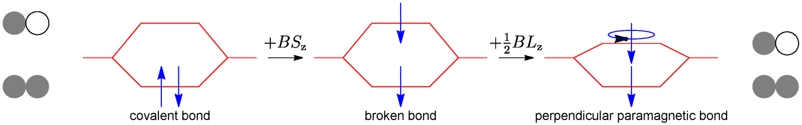


$$\langle H\rangle = \langle H_0\rangle + B\langle S_z + \tfrac{1}{2}L_z\rangle + \tfrac{1}{8}B^2\langle x^2 + y^2\rangle$$

- 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

Zeeman interaction: bond breaker and bond maker

- Let us consider the ground-state H_2 molecule in an increasing magnetic field

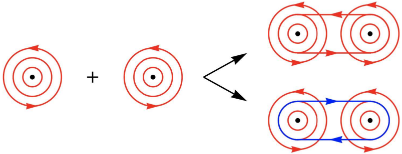


  - The spin Zeeman interaction Bs_z breaks the covalent bond
    - the magnetic field favours beta spin over alpha spin
    - eventually, the alpha electron undergoes a spin flip, forcing it into the antibonding orbital (singlet-triplet transition)
    - we expect the resulting molecule to be unstable 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

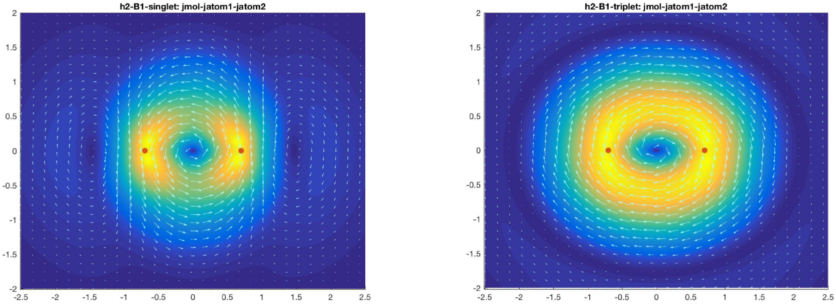
- Perpendicular paramagnetic bonding
  - Lange, Tellgren, Hoffmann and Helgaker, *Science* **337** 327 (2012)

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

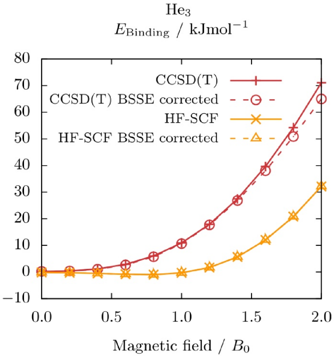


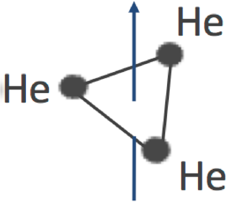
- Induced currents in singlet (left) and triplet (right) H_2 (relative to free atoms)



Bonding in helium trimer

- Electron correlation significantly enhances paramagnetic bonding



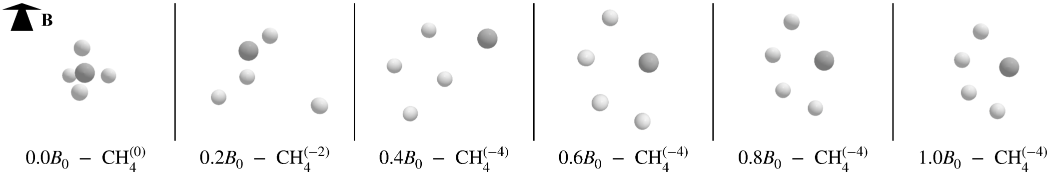


- Stopkowicz, Gauss, Lange, Tellgren, and Helgaker, JCP **143**, 074110 (2015)

- Bond creation: clustering atoms shield themselves from the field in the same way that huddling penguins protect themselves against the cold in the Antarctic winter.

Methane from tetrahedron to fan shape

- Parmagnetically bound molecules have structures vastly different from those on Earth
- CH_4, for example, is no longer tetrahedral but fan-shaped (half moon) in a sufficiently strong field



- The CDFT dissociation energy of lowest dissociation pathway

B/B_0	0.0	0.2	0.4	0.6	0.8	1.0
ΔE/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, *J. Chem. Phys.* **156**, 204113 (2022)

Molecular dynamics in a magnetic field

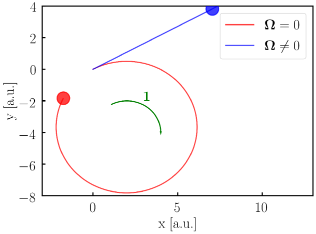
- To calculate spectra in a field, we have carried out semi-classical molecular dynamics calculations
  - it is then necessary to integrate the classical equations motion with the Lorentz force acting on each atom

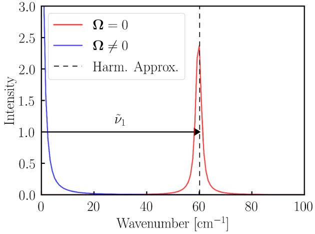
$$\mathbf{F}(\mathbf{r},\mathbf{v}) = z\mathbf{E}(\mathbf{r}) + z\mathbf{v}\times\mathbf{B}(\mathbf{r}) \qquad \leftarrow \text{velocity-dependent Lorentz force}$$

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

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

- Illustration: calculations on the He atom with and without screening
  - without screening: $\mathbf{B}_{\mathsf{loc}}(\mathbf{r}) = \mathbf{B}$, giving circular motion with frequency $\tilde{\nu}_1 \approx 60\,\mathrm{cm}^{-1}$ at $B = B_0$
  - with screening: $\mathbf{B}_{\mathsf{loc}}(\mathbf{r}) = \mathbf{0}$, giving perfect translation





Born–Oppenheimer approximation in a magnetic field

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

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

  - 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:

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

- Project molecular Schrödinger equation against 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 $T+U$ has contributions from nonadiabatic coupling matrix elements (NACMEs):

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

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

Born–Oppenheimer dynamics with the Lorentz force

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

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

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

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

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

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

  - 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

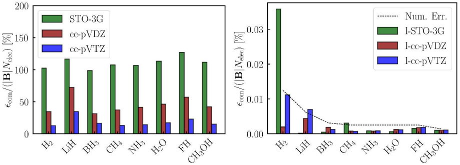
- The Berry curvature contains complete information about the magnetic field
  - if not, neutral atoms would undergo cyclotron motion in a magnetic field
- The important relation is the magnetic-translational sum rule:

$$2\hbar\,\mathrm{Im}\sum_{IJ}\langle \boldsymbol{\nabla}_I\Phi|\boldsymbol{\nabla}_J^{\mathsf{T}}\Phi\rangle = eN_{\mathsf{el}}\begin{pmatrix} 0 & -B_z & B_y \\ B_z & 0 & -B_x \\ -B_y & B_x & 0 \end{pmatrix}$$ ← 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

$$\Phi(\mathbf{r};\mathbf{R}+\mathbf{T}) = \exp\left[-\tfrac{ie}{2\hbar}\mathbf{B}\times\mathbf{T}\cdot(\mathbf{r}-\mathbf{R})\right]\Phi(\mathbf{r}-\mathbf{T};\mathbf{R})$$ ← translation of nuclear coordinates by $\mathbf{T}$

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

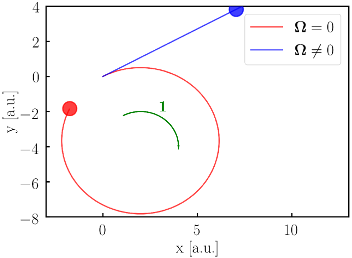


London orbitals

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

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

  - 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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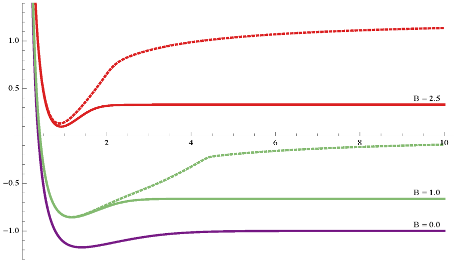
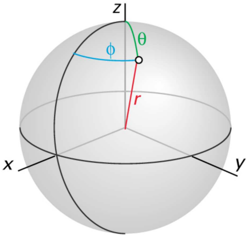
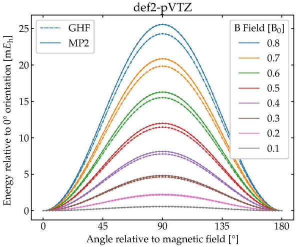
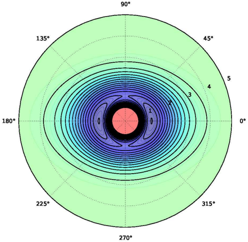


Rovibrational coordinates for singlet H_2

- 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



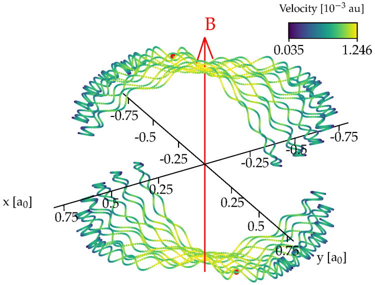


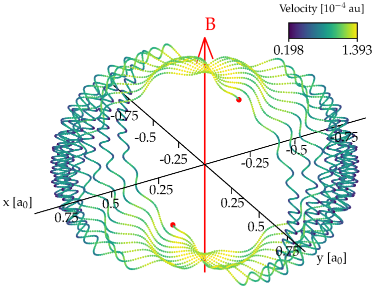


- For singlet H_2, the barrier is equatorial, occuring in the xy plane

Hindered rotation vs. libration of H_2

- A molecule may or may not have sufficient energy to cross the equatorial barrier, giving 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)

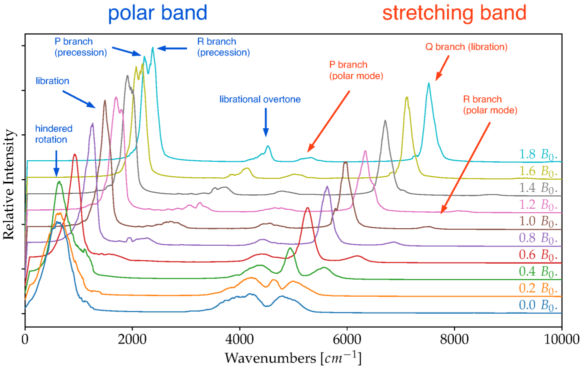




  - Lorentz force acting on the partially screened nuclei induces precession of the atoms about the field axis
- Monzel, Pausch, Peters, Tellgren, Helgaker, and Klopper, *J. Chem. Phys.* **157**, 054106 (2022)

Rovibrational spectrum of H_2 at 1500 K

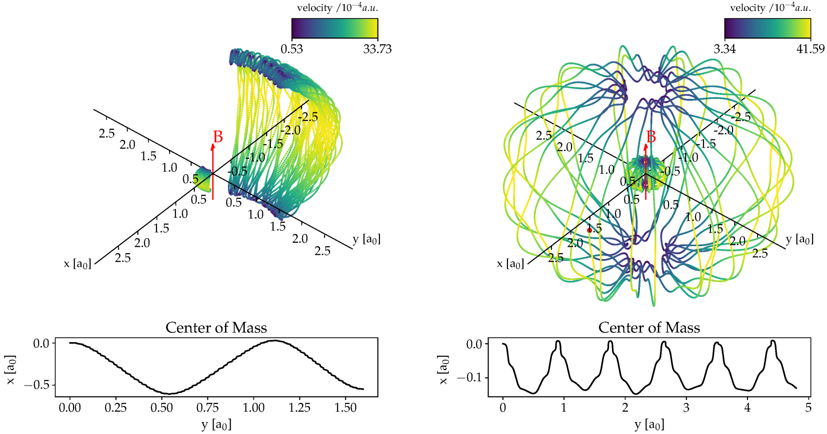
- NVT ensemble averaged over 2000 trajectories of 1 ps duration with initial velocities from Maxwell–Boltzmann distribution
  - power spectrum by Fourier transformation of velocities recorded during the simulation – intensities reflect how often a mode is visited during the simulation



- polar band:
  - initial (red-shifted) hindered rotation followed by (blue-shifted) libration at about $0.4B_0$ – 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 $0.4B_0$
  - 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

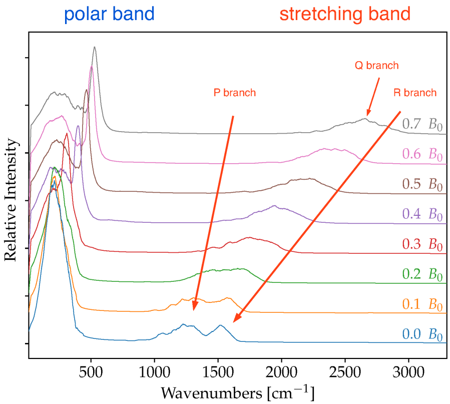
- Trajectories with libration (left) and hindered rotation (right) of LiH at $0.2B_0$



- 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

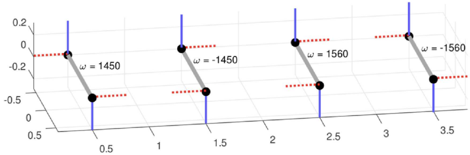
- In the quadratic eigenvalue problem, distinct eigenvalues $\omega_1 \neq \omega_2$ may have the same eigenvector $\boldsymbol{\eta}$:

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

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

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

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



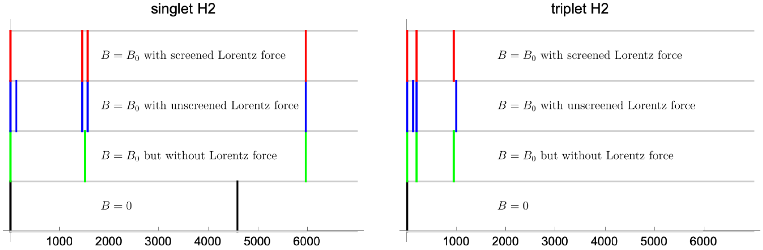
  - the frequencies 1450 and $-1560\,\mathrm{cm}^{-1}$ belong to $\boldsymbol{\eta}$, while -1450 and $1560\,\mathrm{cm}^{-1}$ belong to $\boldsymbol{\eta}^*$
  - at the same time $\boldsymbol{\eta}$ satisfies two linear eigenvalue problems

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

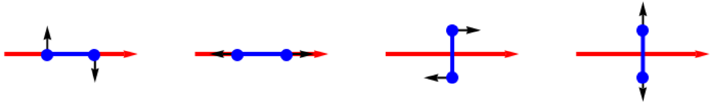
$$\mathrm{i}\boldsymbol{\Lambda}\boldsymbol{\eta} = 110\,\mathrm{cm}^{-1} \mathbf{M}\boldsymbol{\eta} \quad \leftarrow \quad \text{splitting of degenerate frequencey by the screened Lorentz force}$$

Harmonic spectra of singlet and triplet H_2

- Spectra at $B = 0$ and at $B = B_0$ with and without (un)screened Lorentz contributions
  - restricted Hartree–Fock calculations in the uncontracted aug-cc-pVTZ London basis

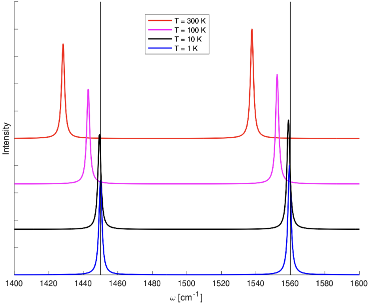


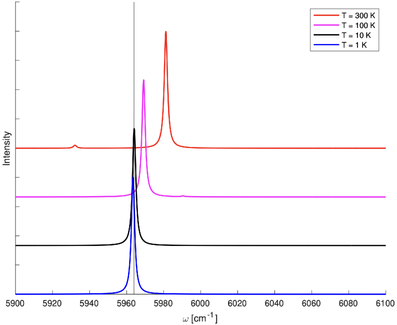
- Lorentz force only affects modes that have a component perpendicular to the field vector:



Harmonic and anharmonic frequencies of singlet H_2

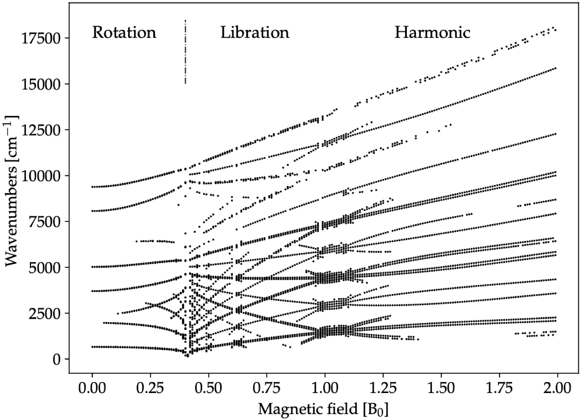
- As the temperature of molecular dynamics calculations is lowered, the harmonic frequencies are recovered
  - this comparison represents an excellent test on our calculations





- 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)

Conclusions and acknowledgements

- Concluding remarks
    - molecular dynamics in a magnetic field requires evaluation of Lorentz force
    - screening of the Lorentz force calculated from the Berry curvature
    - London atomic orbitals essential for accurate calculation of Berry curvature
    - diatomic spectra reveal hindered rotation and libration in the field
    - Lorentz force responsible for splitting of otherwise degenerate levels
    - harmonic frequencies and normal coordinates obtained from quadratic eigenvalue problem

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