Molecules in strong magnetic fields

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Molecular magnetism is usually studied perturbatively. Such an approach is highly successful and widely used in quantum chemistry. Molecular magnetic properties are accurately described by perturbation theory. Example: 200 MHz NMR spectra of vinyllithium.
We have undertaken a nonperturbative study of molecules up to the intermediate regime
- gives insight into molecular electronic structure
- describes atoms and molecules observed in astrophysics (stellar atmospheres)
- is of relevance to impurities in semi-conductions
- enables evaluation of many properties by finite-difference techniques
- provides a framework for studying the current dependence of the universal density functional

The nonrelativistic electronic Hamiltonian in a magnetic field $B$ along the z axis (a.u.):
\[ H = H_0 + \frac{1}{2} BL_z + Bs_z + \frac{1}{8} B^2 (x^2 + y^2) \]
- one atomic unit of magnetic field strength is very strong: 1 a.u. = $2.35 \times 10^5$ T

$B \ll 1$ a.u.: Coulomb regime — familiar chemistry
- earth-like conditions
- magnetic interactions treated perturbatively (NMR $\sim 10^{-4}$ a.u.)

$B \sim 1$ a.u.: Intermediate regime — exotic chemistry
- white dwarfs
- Coulomb and magnetic interactions compete

$B \gg 1$ a.u.: Landau regime — alien chemistry
- neutron stars
- magnetic interactions dominate (Landau levels)

For a review, see D. Lai, Rev. Mod. Phys. 73, 629 (2001)
London orbitals and gauge-origin invariance

- The non-relativistic electronic Hamiltonian in a magnetic field along the z axis:

\[ H = H_0 + \frac{1}{2} BL_z + Bs_z + \frac{1}{8} B^2 [(x - O_x)^2 + (y - O_y)^2] \]

- The orbital-angular momentum operator is imaginary and gauge-origin dependent:

\[ L = -i (r - O) \times \nabla, \quad A_O = \frac{1}{2} B \times (r - O) \]

- we must optimize a complex wave function and also ensure gauge-origin invariance

- Gauge-origin invariance is imposed by using London atomic orbitals (LAOs):

\[ \omega_{lm}(r_K, B) = \exp \left[ \frac{1}{2} i B \times (O - K) \cdot r \right] \chi_{lm}(r_K) \leftarrow \text{special integral code needed} \]

- London orbitals are absolutely necessary to ensure proper chemistry (e.g., dissociation)
  - FCI/un-aug-cc-pVTZ dissociation of H\(_2\) in a perpendicular field
  - with London orbitals (full lines) and without London orbitals (dashed lines)
The effect of gauge transformations

- Consider H$_2$ along the z axis in a uniform magnetic field in the y direction
  - the RHF wave function (real part blue, imaginary part red) and the corresponding density (black)
  - the gauge origin at $O = (0, 0, 0)$ (left) and $G = (100, 0, 0)$ (right)
  - the density remains the same but the wave function changes with changes in the gauge origin

London orbitals: do we need them?

Example: H$_2$ molecule, on the x-axis, in the field $B = \frac{1}{10} \hat{z}$.

$A = \frac{1}{20} \hat{z} \times r$

$\psi'' = \mathbf{RHF}/\text{aug-cc-pVQZ}$

Gauge-origin moved from 0 to $G = 100 \hat{y}$.

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Erik Tellgren 
Ab initio finite magnetic field calculations using London orbitals

Helgaker et al. (CTCC, University of Oslo)
Introduction
Calcutta, December 17, 2013
The London program

- We have developed the **London code** for calculations in finite magnetic fields
  - complex wave functions and London atomic orbitals
  - Hartree–Fock theory (RHF, UHF, GHF), MCSCF, MP2, CCSD, FCI theory, and KS-DFT
  - energy, molecular gradients, excitation energies
  - London atomic orbitals require a generalized integral code

\[ F_n(z) = \int_0^1 \exp(-zt^2)t^{2n} \, dt \quad \leftarrow \text{complex argument } z \]

- C++ code written by Erik Tellgren, Alessandro Soncini, and Kai Lange
- \( C_{20} \) is a “large” system
- Tellgren, Soncini and Helgaker, JCP **129**, 154114 (2008)

- **Overview:**
  - molecular dia- and paramagnetism
  - helium atom in strong fields: atomic distortion and electron correlation
  - \( \text{H}_2 \) and \( \text{He}_2 \) in strong magnetic fields: bonding, structure and orientation
  - molecular structure in strong magnetic fields

- **Previous work in this area:**
  - much work has been done on small atoms
  - Hartree–Fock with London orbitals on \( \text{H}_2 \)
  - FCI on two-electron molecules \( \text{H}_2 \) (parallel orientation only) and \( \text{H}^- \) (Cederbaum)
  - Nakatsuji’s free complement method
  - no general molecular code with London orbitals
Molecular diamagnetism and paramagnetism

- The Hamiltonian has **paramagnetic** and **diamagnetic** parts:

\[ H = H_0 + \frac{1}{2} B L_z + B s_z + \frac{1}{6} B^2 (x^2 + y^2) \leftarrow \text{linear and quadratic } B \text{ terms} \]

- Most closed-shell molecules are **diamagnetic**
  - their energy increases in an applied magnetic field: \( E(B) = E_0 + \frac{1}{6} B^2 \langle 0 | x^2 + y^2 | 0 \rangle \)
  - the induced currents oppose the field

- Some closed-shell systems are **paramagnetic**
  - their energy decreases in a magnetic field
  - relaxation of the wave function lowers the energy, dominating the diamagnetic term

- RHF calculations of the field dependence of the energy for two closed-shell systems:

  ![Graphs showing field dependence of energy](image)

  - left: benzene: **diamagnetic dependence** on an out-of-plane field, \( \chi < 0 \)
  - right: BH: **paramagnetic dependence** on a perpendicular field, \( \chi > 0 \)
C\textsubscript{20} in a perpendicular magnetic field

- All systems become diamagnetic in sufficiently strong fields:

\[ B_c \approx 0.01 \] for C\textsubscript{20} (ring conformation) above

\[ B_c \] is inversely proportional to the area of the molecule normal to the field

We may in principle separate such molecules by applying a field gradient
Closed-shell paramagnetism explained

The Hamiltonian has a linear and quadratic dependence on the magnetic field:

\[ H = H_0 + \frac{1}{2} B L_z + B s_z + \frac{1}{8} B^2 (x^2 + y^2) \]

Consider the effect of \( B \) on the ground state and on the first excited state:

- the quadratic term raises the energy of both states, creating 'diabatic energy curves'
- depending on the states, 'diabatic curve crossings' may occur at a given field strength
- the linear term couples the two states, creating 'adiabatic states' and 'avoiding crossings'

A sufficiently strong coupling gives a paramagnetic ground-state with a double minimum

Tellgren, Helgaker and Soncini, PCCP 11, 5489 (2009)
Induced electron rotation

- The magnetic field induces a rotation of the electrons about the field direction:
  - the derivative of the energy with the field is half the kinetic angular-momentum operator
    \[
    E'(B) = \frac{1}{2} \langle 0 | \mathbf{r} \times \pi | 0 \rangle, \quad \pi = p + A
    \]

- Paramagnetic closed-shell molecules (here BH):
  - there is no rotation at the field-free energy maximum: \( B = 0 \)
  - the onset of paramagnetic rotation (with the field) reduces the energy for \( B > 0 \)
  - the strongest paramagnetic rotation occurs at the energy inflexion point
  - the rotation comes to a halt at the stabilizing field strength: \( B = B_c \)
  - the onset of diamagnetic rotation in the opposite direction increases the energy for \( B > B_c \)

- Diamagnetic closed-shell molecules:
  - induced diamagnetic rotation always increases the energy
The hydrogen atom in a magnetic field

- The hydrogen Balmer spectrum for high-field magnetic white dwarfs

Illustration taken from B. N. Murdin et al., Nat. Commun. 4, 1469 (2013)
The helium atom: energy and orbital energies

- **The total energy** illustrates the complicated evolution of electronic states in the field (left)
  - the behaviour depends on orbital and spin angular momenta
  - eventually, all energies increase diamagnetically

- **The orbital energies** behave in an equally complicated manner (right)
  - the initial behaviour is determined by the angular momentum
  - beyond \( B \approx 1 \), all energies increase with increasing field
  - HOMO–LUMO gap increases, suggesting a decreasing importance of electron correlation
The helium atom: dynamical correlation

- The FCI occupation numbers approach 2 and 0 in strong fields
  - diminishing importance of dynamical (but not static) correlation in magnetic fields
  - the two electrons rotate in the same direction about the field direction
Atoms become squeezed and distorted in magnetic fields
- Helium $1s^2 \, 1S$ (left) is prolate in all fields
- Helium $1s2p \, ^3P$ (right) is oblate in weak fields and prolate in strong fields

- Transversal size proportional to $1/\sqrt{B}$, longitudinal size proportional to $1/\log B$

Atomic distortion affects chemical bonding

- Which orientation is favored?
H$_2$ singlet ($1\sigma_g^2$) and triplet ($1\sigma_g 1\sigma_u^*$) molecule ($M_S = 0$)

- FCI/un-aug-cc-pVTZ curves in parallel (full) and perpendicular (dashed) orientations
- Singlet (blue) and triplet (red) energies increase diamagnetically in all orientations

- Earlier onset of singlet–triplet separation with increasing field strength (smaller systems)
  - the singlet–triplet separation is greatest in the parallel orientation (larger overlap)
  - the singlet state favors a parallel orientation (full line)
  - the triplet state favors a perpendicular orientation (dashed line) and becomes bound
  - parallel orientation studied by Schmelcher et al., PRA 61, 043411 (2000); 64, 023410 (2001)
  - Hartree–Fock studies by Žaucer and and Ažman (1977) and by Kubo (2007)
Zeeman splitting of H$_2$ spin components ($M_S = -1, 0, 1$)

- The spin Zeeman interaction splits the triplet, lifting $\alpha \alpha$ and lowering $\beta \beta$:

- The $\beta \beta$ triplet component becomes the ground state at $B \approx 0.4$ a.u.
  - eventually, all triplet components will be pushed up in energy diamagnetically...
The H$_2$ molecule in a strong magnetic field

- Singlet H$_2$ $|1\sigma_g^2\rangle$ aligns itself with the field and becomes more strongly bound
- Triplet H$_2$ $|1\sigma_g 1\sigma_u^*\rangle$ becomes bound in a perpendicular field orientation

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<thead>
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<th>triplet</th>
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<td>66 pm</td>
<td>594 kJ/mol</td>
<td>83 kJ/mol</td>
<td>136 pm</td>
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- Polar plots of $E(R, \Theta)$ in the singlet (left) and triplet (right) states
  - red for high energy; blue for low energy
Perpendicular paramagnetic bonding

- The magnetic field modifies the MO energy level diagram
  - **parallel orientation**: both MOs are unaffected relative to the AOs
  - **perpendicular orientation**: antibonding MO is stabilized, while bonding MO is (less) destabilized
  - A qualitatively correct description does not require electron correlation

In the He limit, the bonding and antibonding London MOs transform into 1s and 2p AOs:

\[
\lim_{R \to 0} 1\sigma^*_u = \begin{cases} 
2p_0, & \text{parallel orientation} \\
2p_{-1}, & \text{perpendicular orientation (stabilized)} 
\end{cases}
\]

Rewriting the rules of the universe: Mysterious new atomic bond found in white dwarf stars could change computing forever

- Third kind of bond after ionic and covalent
- Found only in white dwarf stars - with magnetic fields 10,000 times stronger than any on Earth
- Find rewrites rules of universe
- Could lead to new discoveries in quantum physics
- Techniques used to analyse bonds could lead to new computers

By ROB WAUGH

A new kind of bond between atoms found only in the crushingly intense magnetic fields of white dwarf stars could unlock new secrets of quantum physics.

The find - a ‘third kind’ of bond between atoms, unknown on Earth - could also unlock the secrets of ultra-powerful new computers.
Molecular formation in ultrahigh magnetic fields

P. Schmelcher, Science 337, 302 (2013)

Molecule formation in ultrahigh magnetic fields

It might seem that this world is hidden from us by the requirement of enormous laboratory field strengths. However, available field strengths are progressively increasing, in particular for pulsed magnetic fields in the milli- or microsecond regime that are already achieving fields of hundreds of teslas. Besides this, standard laboratory magnetic fields of a few teslas are sufficient to introduce novel magnetic properties into highly excited Rydberg states, for which the weakened Coulomb force is comparable to the paramagnetic or diamagnetic forces, or both. In this respect, the very weakly bound Rydberg molecules with a huge bond length and a large electric dipole moment [...] are of particular interest and might be an ideal system to probe strong magnetic field effects in the laboratory.

Stronger against the field. A schematic illustration of (A) a rotating diatomic molecule in field-free space and (B) the parallel and orthogonal configuration of the molecule in the presence of a high magnetic field. Lange et al. show that the bond strength increases for the perpendicular case through paramagnetic interactions.
Here we demonstrate Lyman series spectra for phosphorus impurities in silicon up to the equivalent field, which is scaled to 32.8 T by the effective mass and dielectric constant. The spectra reproduce the high-field theory for free hydrogen, with quadratic Zeeman splitting and strong mixing of spherical harmonics. They show the way for experiments on He and $H_2$ analogues, and for investigation of $He_2$, a bound molecule predicted under extreme conditions.
Molecules in stars

Are stars too hot for molecules to exist?
- most white dwarf atmospheres are hotter (8000–40000 K) than the sun’s photosphere (6000 K)
- but there is also an enormous pressure...

Roald Hoffmann in Letters to Editors, American Scientist 101, 403 (2013)

I was mistaken in implying that the surfaces of stars are too hot for molecules to exist. For instance, evidence for H$_2$O on the Sun was adduced by L. Wallace and others in a study published in Science in 1995. Evidence for H$_2$ in white dwarf atmospheres was demonstrated by S. Xu, M. Jura, D. Koster, B. Klein, and B. Zuckerman in a 2013 publication in Astrophysical Journal Letters. And molecules are found in abundance in stellar ejecta.

Discovery of molecular hydrogen in white dwarf atmospheres

With the Cosmic Origins Spectrograph on board the Hubble Space Telescope, we have detected molecular hydrogen in the atmospheres of three white dwarfs with effective temperatures below 14,000 K, G29-38, GD 133, and GD 31. This discovery provides new independent constraints on the stellar temperature and surface gravity of white dwarfs.
The helium dimer $^1\Sigma_g^+(1\sigma_g^21\sigma_u^*)$ singlet state

- The field-free He$_2$ is bound by dispersion in the ground state
  - our FCI/un-aug-cc-pVTZ calculations give $D_e = 0.08$ kJ/mol at $R_e = 303$ pm

- In a magnetic field, He$_2$ shrinks and becomes more strongly bound
  - perpendicular paramagnetic bonding (dashed lines) as for H$_2$
  - for $B = 2.5$, $D_e = 31$ kJ/mol at $R_e = 94$ pm and $\Theta_e = 90^\circ$
The helium dimer $^3\Sigma^+_u (1\sigma^2_g 1\sigma^*_u 2\sigma_g)$ triplet state

- The covalently bound triplet state becomes further stabilized in a magnetic field
  - $D_e = 178 \text{ kJ/mol}$ at $R_e = 104 \text{ pm}$ at $B = 0$
  - $D_e = 655 \text{ kJ/mol}$ at $R_e = 80 \text{ pm}$ at $B = 2.25$ (parallel orientation)
  - $D_e = 379 \text{ kJ/mol}$ at $R_e = 72 \text{ pm}$ at $B = 2.25$ (perpendicular orientation)

- The molecule begins a transition to diamagnetism at $B \approx 2$
  - Eventually, all molecules become diamagnetic

\[ T = \frac{1}{2} \left( \sigma \cdot \pi \right)^2 = \frac{1}{2} \left( \sigma \cdot (p + A) \right)^2 = \frac{1}{2} \left( \sigma \cdot (p + \frac{1}{2} B \times r) \right)^2 \]
Helium clusters

- We have studied helium clusters in strong magnetic fields (here $B = 2$)
  - RHF/u-aug-cc-pVTZ level of theory
  - all structures are planar of zero bond order and consist of equilateral triangles
  - suggestive of hexagonal 2D crystal lattice ($^3\text{He}$ crystallizes into an hcp structure at about 10 MPa)
  - $\text{He}_3$ and $\text{He}_6$ bound by 3.7 and 6.8 m$E_h$ per atom
  - 'vibrational frequencies' in the range 200–2000 cm$^{-1}$ (for the $^4\text{He}$ isotope)

- Tellgren, Reine and Helgaker, PCCP 14, 9492 (2012)
Molecular structure

- **Ammonia** for $0 \leq B \leq 0.06$ a.u. at the RHF/cc-pVTZ level of theory

- Bond length (left), bond angle (middle) and inversion barrier (right)
- Ammonia shrinks and becomes more planar (from shrinking lone pair?)
- In the parallel orientation, the inversion barrier is reduced by $-0.001 \text{ cm}^{-1}$ at 100 T

- **Benzene** in a field of 0.16 along two CC bonds (RHF/6-31G**)
  - It becomes 6.1 pm narrower and 3.5 pm longer in the field direction
  - Agrees with perturbational estimates by Caputo and Lazzeretti, IJQC 111, 772 (2011)
Conclusions

- We have developed the LONDON program for molecules in magnetic field
- We have studied closed-shell paramagnetic molecules in strong fields
  - all paramagnetic molecules attain a global minimum at a characteristic field $B_c$
- We have studied $H_2$ and $He_2$ in magnetic fields
  - atoms and molecules shrink; molecules are stabilized and oriented by magnetic fields
- We have studied molecular structure in magnetic fields
  - bond distances are typically shortened in magnetic fields
- Support: The Norwegian Research Council; ERC Advanced Grant