Molecules in strong magnetic fields

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Molecular para- and diamagnetism

- When a magnetic field is applied to a molecule, one of two things can happen:
  - the energy is lowered: molecular paramagnetism
  - the energy is raised: molecular diamagnetism

- Open-shell molecules are paramagnetic
  - permanent magnetic moments (unpaired spins)
  - the molecule reorients itself and moves into the field
  - temperature dependent

- Closed-shell molecules are nearly all diamagnetic
  - induced magnetic dipole only—no permanent magnetic moment
  - induced currents oppose the external field (Lenz’ law)
  - the molecule moves out of the field
  - temperature independent
  - much weaker than open-shell paramagnetism

- Some closed-shell molecules are paramagnetic
  - induced currents now support the external field
  - temperature independent
  - much weaker than the temperature-dependent open-shell paramagnetism
  - first discovered for MnO$_4^-$ (1914)
  - much studied: BH and CH$^+$

- General theory of Van Vleck (1932)
Electronic Hamiltonian in an external magnetic field $B$

- The external magnetic field is represented by a vector potential
  \[ B(r) = \nabla \times A(r), \quad A(r) = \frac{1}{2} B \times r \]

- The non-relativistic electronic Hamiltonian (atomic units)
  \[
  H = H_0 + A(r) \cdot p + B(r) \cdot s + \frac{1}{2} A(r)^2
  = H_0 + \frac{1}{2} B \cdot L + B \cdot s + \frac{1}{8} (B \times r) \cdot (B \times r)
  \]
  - $H_0$ is the field-free non-relativistic Hamiltonian
  - $p = -i\nabla$ is the generalized momentum operator
  - $L = r \times p$ is the orbital angular momentum operator
  - $s = \sigma/2$ is the spin angular momentum operator

- The Hamiltonian depends both linearly and quadratically on the field
  - the linear term may lower or raise the energy
  - the quadratic term will always raise the energy

- We can expect a rather complicated dependence of the energy on the field
  - for large $B$, the second-order term will dominate
  - but what happens for small and intermediate $B$?
  - we consider only closed-shell states
Magnetic interactions are usually studied by perturbation theory

\[ E(B) = E(0) - \sum_{\alpha} \mu_{\alpha} B - \frac{1}{2} \sum_{\alpha\beta} \chi_{\alpha\beta} B_{\alpha} B_{\beta} + \cdots \]

The first-order term represents interaction with the permanent magnetic moment

\[ \mu = - \langle 0 \mid \frac{1}{2} \mathbf{L} + \mathbf{s} \mid 0 \rangle \]

temperature-dependent paramagnetism (vanishes for closed-shell systems)

The second-order term represents interaction with the induced dipole moment

the induced dipole moment is governed by the magnetizability:

\[ \chi = - \frac{1}{4} \left\langle 0 \left| \mathbf{r} \mathbf{r}^T - (\mathbf{r}^T \mathbf{r}) \mathbf{l}_3 \right| 0 \right\rangle + \frac{1}{2} \sum_n \frac{\left\langle 0 \mid \mathbf{L} \mid n \right\rangle \left\langle n \mid \mathbf{L}^T \mid 0 \right\rangle}{E_n - E_0} \]

the Langevin term arises from precessional motion of the electrons

temperature-independent diamagnetism

the sum-over-states term arises from orbital unquenching

temperature-independent paramagnetism
The need for a nonperturbative treatment

- It is possible to go to higher orders by including hypermagnetizabilities

\[ E(B) = E(0) - \frac{1}{2} \sum_{\alpha\beta} \chi_{\alpha\beta} B_{\alpha} B_{\beta} - \frac{1}{24} \sum_{\alpha\beta\gamma\delta} \chi_{\alpha\beta\gamma\delta} B_{\alpha} B_{\beta} B_{\gamma} B_{\delta} + \ldots \]

- However, the field dependence of the energy can be very complicated

- the energy of C\textsubscript{20} (ring conformation) as a function of \( B \) (atomic units)

- Taylor expansions useless for strong fields

- How does this complicated field dependence arise?
Most studies of molecular magnetism are based on low-order expansions
- magnetizabilities and hypermagnetizabilities
- such studies provide much useful information

However, expansions around zero field have many limitations
- the behaviour in strong fields cannot be studied
- many phenomena may remain unnoticed

We have undertaken a nonperturbative study of molecules in strong fields
- this necessitated the development of a new code
- complex orbitals and complex wave functions
- London atomic orbitals to remove gauge-origin dependence

In the remainder of the talk, we will discuss the following points
- the need for London orbitals
- London-orbital integral evaluation in strong fields
- the energy in strong magnetic fields
- two-level analytic model for strong fields
- molecular properties in strong fields
A uniform external field may be represented by any potential of the form

\[ A_0(r) = \frac{1}{2} B \times (r - O) \]

- the vector potential vanishes at the gauge origin \( O \)
- the position of the origin is not unique

In exact theory, this non-uniqueness does not matter
- a change in the origin from \( O \) to \( K \) represents a gauge transformation
- the exact wave function undergoes a corresponding gauge transformation

\[ \psi_O = \exp[iA_K(O) \cdot r] \psi_K \]

- all choices of gauge origin \( O \) then lead to the same (observable) results

In approximate calculations, our results in general do depend on the origin
- approx. wave functions are not sufficiently flexible to be properly gauge transformed

This problem is solved by using gauge transforming the individual atomic orbitals (AOs)
- each AO has a unique “best” or “favoured” gauge origin: its atomic center

\[ \omega_{lm} = \exp[iA_K(O) \cdot r] \chi_{lm}(r_K) \leftarrow \text{gauge transformation from AO to global origin} \]

- each AO behaves as if the gauge origin were at its center
- the use of such London orbitals removes the gauge-origin dependence
The efficacy of London orbitals

- London orbitals are AOs with an attached complex phase factor
  \[ \omega_{lm} = \exp[i\mathbf{A}_K(O) \cdot \mathbf{r}] \chi_{lm}(r_K) \]
  - gauge factor removes gauge-origin dependence of magnetic properties
- London orbitals are correct to first-order in the external magnetic field
  - for this reason, basis-set convergence is usually improved
- Calculations on the water molecule

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<td>CM</td>
<td>H</td>
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<td>-2.7</td>
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<tr>
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<tr>
<td>aug-cc-pVDZ</td>
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- London orbitals greatly improve convergence of magnetizabilities
- they are less efficacious for hypermagnetizabilities
Hybrid plane-wave–Gaussians (PWG) orbitals

- London AOs are in fact hybrid **plane-wave–Gaussian (PWG) orbitals**
  \[
  \omega_{\kappa,c}(r) = \exp(i\kappa \cdot r) S_{lm}(r) \exp(-ar^2)
  \]
  - the wave vector $\kappa$ is the AO-centered vector potential at the gauge origin

- More generally, PWGs have several uses:
  - mixed basis for periodic boundary conditions and scattering studies
  - gauge-origin independent magnetic properties at zero field

- Necessitates a **generalization of GTO integral-evaluation techniques**
  - at zero field, complex algebra may be avoided
  - at finite field, complex algebra cannot be avoided

- We have developed and implemented a **McMurchie–Davidson PWG scheme**
  - Tellgren *et al.*, JCP 129, 154114 (2008)
PVG product rule and overlap integrals

- In many respects, a straightforward generalization of GTO integral evaluation
- The Gaussian product rule still holds

\[
\Omega_{ab}^{\kappa\lambda}(r) = \exp(i\kappa \cdot r)^* \exp(-ar_A^2) \exp(i\lambda \cdot r) \exp(-br_B^2)
\]

PWG at A \quad PWG at B

= \exp\left( -\frac{ab}{a+b} R_{AB}^2 \right) \exp[-i(\kappa - \lambda) \cdot r] \exp[-(a + b)r_P^2] \quad \text{prefactor}

PWG at P = (aA + bB)/(a + b)

- Integration over all space yields

\[
\int \Omega_{ab}^{\kappa\lambda}(r) \, dr = \exp\left[ -\frac{(\kappa - \lambda)^2}{4(a+b)} + i(\kappa - \lambda) \cdot P \right] \frac{\pi^{3/2} \exp\left( -\frac{ab}{a+b} R_{AB}^2 \right)}{(a + b)^{3/2}}
\]

plane-wave contribution \quad standard Gaussian overlap
As for standard Gaussians, Coulomb integrals reduce to the Boys function

\[
J = \frac{\int \int \exp(i\kappa \cdot r_1) \exp(-pr_1^2) \exp(i\lambda \cdot r_2) \exp(-qr_2^2)}{r_{12}} dr_1 dr_2
\]

\[
= \exp \left[ -\frac{\kappa^2}{4p} - \frac{\lambda^2}{4q} - i\kappa \cdot P - i\lambda \cdot Q \right] \frac{2\pi^{5/2}}{pq\sqrt{p+q}} F_0 \left[ \frac{pq}{p+q} \left( P' - Q' \right)^2 \right]
\]

\[
P' = P - i\kappa/2p, \quad Q' = Q - i\lambda/2q
\]

The Boys function is given by

\[
F_0(x) = \int_0^1 \exp(-xt^2) \, dt \quad \leftarrow \text{complex argument } x
\]

- evaluated in the usual manner by expansion and recursion
- For functions of higher angular momentum, recurrence relations are used
  - some translational symmetry lost
  - more complicated recurrence relations
The LONDON program

- an *ab initio* program for finite-field calculations with London orbitals

- some features of the present code
  - restricted, unrestricted and generalized unrestricted Hartree–Fock theory
  - Kohn–Sham theory
  - many first-order properties $(x - C_x)^m(\partial/\partial x)^n$
  - molecular gradients
  - excitation energies using response theory (RPA)

- some restrictions of the present code
  - lacks functionality for correlated wave functions

- code written by Erik Tellgren and Alessandro Soncini
  - mostly C++, some Fortran 77
  - modular but not highly optimized yet
  - $C_{20}$ is a “large” system
The dependence of total energy on the magnetic field

- RHF calculations of $B$ dependence for different systems

a) benzene (aug-cc-pVDZ): typical case of diamagnetic quadratic dependence
b) cyclobutadiene (aug-cc-pVDZ): non-quadratic dependence on an out-of-plane field
c) BH (aug-cc-pVTZ): paramagnetic dependence for a perpendicular field
d) BH (aug-cc-pVTZ): larger range of the perpendicular field reveals nonperturbative behaviour
The field dependence of paramagnetic molecules

- We have studied the field-dependence of a number of molecules

For all these systems, the field dependence takes on a sombrero shape

- we will give some examples
- we will explain this behaviour by means of a simple analytical model
Three closed-shell paramagnetic molecules: BH, CH⁺, and MnO₄⁻

- field applied perpendicularly for BH and CH⁺
- aug-cc-pVDZ on all atoms except Wachters-f for Mn

Energy minimum occurs at a characteristic critical field $B_c$

- we may in principle separate molecules by applying a field gradient
- $B_c = 0.2–0.5$ a.u. for these small systems
- strongest fields attainable: 100 T ($4.3 \cdot 10^{-4}$ a.u.)
Their linear response is characterized by strong ring currents
- cyclobutadiene $C_4H_4$, cyclo-octatetraene $C_8H_8$ and [12]-annulene $C_{12}H_{12}$
- magnetic field along principal axis

The critical field is now one order of magnitude smaller
- $B_c \approx 0.032$ for $C_8H_8$; $B_c \approx 0.016$ for $C_{12}H_{12}$
- the critical field decreases with increasing size of the system
- $B_c$ is inversely proportional to the area of the molecule
- we estimate that $B_c$ should be observable for $C_{72}H_{72}$
The field-dependence of closed-shell energies

 BH energy in a perpendicular magnetic field

Polynomial fits to the BH energy in perpendicular magnetic field

- HF/aug-cc-pVDZ level of theory
- only even-order terms are included by symmetry
- expansions of order 14 or greater are needed

The BH curve clearly diverges from a parabolic behavior as we leave the region close to $B=0$. Using the energies obtained with the largest basis set, we can afford for this system the very small out-of-plane diamagnetizability of $-0.15$ a.u., resulting from cancellations between $-4$-electron paramagnetism and the $-3$-electron diamagnetizability, and the very large hypermagnetizability of $25.135$ a.u., resulting from cancellations between the $4$-electron paramagnetism and the $10$-electron diamagnetizability. These estimates are based on 41 uniformly spaced field values in the range $0–0.1$ a.u. and a fitting polynomial of degree 14, and are converged to the precision quoted.

An even more dramatic behavior is observed if we extend the magnetic field range up to 0.45 a.u. The plot of the BH energy curve in this range is shown in Fig. 2. Interestingly, at a field strength of about 0.20–0.25 a.u. we can observe a transition from paramagnetic to diamagnetic behavior, which calculations with high-quality GTO basis sets are infeasible and the choice of an optimal gauge origin is less efficient. In this intermediate region of space corresponding to about 0.2 a.u., the center of mass is not an efficient gauge origin.

Finally, paratropic and paramagnetic systems such as BH provide interesting examples of cases where finite-field calculations are not just an alternative to response calculations, but a necessity due to either slow convergence or divergence of the perturbative approach.

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Analytical model for the diamagnetic transition

- Molecular orbitals relevant for BH:
  \[ 1s_B, 2\sigma_{BH}, 2p_x, 2p_y, 2p_z \quad \text{(molecule along } z \text{ axis)} \]

- Ground and excited states:
  \[ |0\rangle = |1s_B^22\sigma_{BH}^22p_z^2\rangle, \quad |x\rangle = |1s_B^22\sigma_{BH}^22p_z2p_x\rangle, \quad |y\rangle = |1s_B^22\sigma_{BH}^22p_z2p_y\rangle \]

- Let us apply a \textit{perpendicular magnetic field} in the \( y \) direction:
  \[ H_B = \frac{1}{2} BL_y + \frac{1}{8} B^2(x^2 + z^2) \]

- This leads to the following \textbf{Hamiltonian matrix}:
  \[
  \mathbf{H}(B) = \begin{pmatrix}
  \langle 0|H|0\rangle & \langle 0|H|x\rangle \\
  \langle x|H|0\rangle & \langle x|H|x\rangle 
  \end{pmatrix} = \begin{pmatrix}
  E_0 - \frac{1}{2} \chi_0 B^2 & i\mu B \\
  -i\mu B & E_1 - \frac{1}{2} \chi_1 B^2 
  \end{pmatrix}
  \]

  where we have introduced
  \[ \chi_0 = \frac{1}{4} \langle 0|x^2 + z^2|0\rangle, \quad \chi_1 = \frac{1}{4} \langle x|x^2 + z^2|x\rangle, \quad \mu = -\frac{1}{2} i \langle 0|L_y|x\rangle \]
Energy levels of the two-level model

▶ Two-level Hamiltonian:

\[
H(B) = \begin{pmatrix}
-\Delta - \frac{1}{2} \chi_0 B^2 & i\mu B \\
-i\mu B & \Delta - \frac{1}{2} \chi_1 B^2
\end{pmatrix} = \begin{pmatrix}
-0.01 + 7B^2 & i\mu B \\
-i\mu B & 0.01 + 4B^2
\end{pmatrix}
\]

▶ Eigenvalues:

\[
W_{0/1}(B) = -\frac{1}{2}(\chi_0 + \chi_1)B^2 \pm \frac{1}{2} \sqrt{[2\Delta + (\chi_0 - \chi_1)B^2]^2 + 4\mu^2 B^2}
\]

▶ Plots for different values of \(\mu\):

▶ uncoupled (0), diamagnetic (0.2), nonmagnetic (0.374), and paramagnetic (0.6)

▶ magnetizability (negative second derivative at \(B = 0\)):

\[
\chi(0) = -W_0''(0) = \chi_0 + \mu^2 / 2\Delta = -7, -5, 0, 11
\]
Two-level model fitted to experimental data

- The two-level model contains four parameters
  - may be fitted to experimental data
  - provides excellent fits, superior to polynomial fits

![Graph of BH singlet energies (aug-cc-pVDZ)]

Example 2: A two-state model
Setting $\Delta E = 0.097$ (zero field excitation energy) and fitting the other parameters to the ground energies yields:
Two-level model fitted to experimental data

- The two-level model contains four parameters
  - may be fitted to experimental data
  - provides excellent fits, superior to polynomial fits
  - comparisons with 6- and 8-order polynomial fits

![Graph showing BH and CH+ Polynomial and two-level model fits](image-url)
$C_{20}$: more structure
The induced magnetic moment \( M \) and angular momentum \( L \) are related as
\[
M = -\frac{1}{2}L = -E'(B), \quad \Delta E = -MB
\]

Diamagnetic molecules:
- \( M \) is always aligned against the field, increasing the energy

Paramagnetic molecules:
- \( M \) first aligns with the field, decreasing the energy
- \( M \) reaches its maximum value at the inflection point \( E''(B) = 0 \)
- \( M \) then decreases again until it vanishes at \( B_c \)
- \( M \) then aligns against the field, making the system diamagnetic

There is no net induced angular momentum at the energy minimum
We have implemented linear response theory in finite magnetic fields
BH orbital energies, HOMO–LUMO gap and singlet excitations

- the HOMO and LUMO orbital energies decrease and increase, respectively, with $B$
- the HOMO–LUMO gap opens up with increasing $B$
- most excitation energies increase with increasing $B$
**H₂ and CH₃ in magnetic fields**

- lowest singlet and triplet states of H₂ (left)
  - singlet state (full line) triplet state (dashed line)
- lowest CH₃ radical states in magnetic fields (middle)
  - transitions to green state electric-dipole allowed
- oscillator strength for transition to green state
  - length (red) and velocity (blue) gauges
The magnetic field changes the shape of the potential-energy curve.

- Diamagnetic behaviour at all separations
- Most pronounced for atoms (no paramagnetic term)

The bond length of $\text{H}_2$ decreases with increasing magnetic field.
The magnetic field changes the shape of the potential-energy curve

- diamagnetic behaviour in the molecular limit
- paramagnetic behaviour in the atomic limit

The bond length of F₂ increases with increasing magnetic field
The magnetic field changes the shape of the potential-energy curve

- mixed para- and diamagnetic behaviour at all separations
- mostly diamagnetic in the atomic limit

The bond length of BH decreases with increasing magnetic field
We have developed the LONDON program

- complex orbitals and wave functions
- restricted, unrestricted and generalized Hartree–Fock and Kohn–Sham theories
- London atomic orbitals for gauge-origin independence
- expectation values of one-electron operators
- molecular gradients
- linear response theory (RPA)

The LONDON program may be used for

- finite-difference alternative to analytical derivatives
- studies of molecules in strong magnetic fields
- studies of exchange–correlation functional in magnetic fields

We have studied the behaviour of paramagnetic molecules in strong fields

- all paramagnetic molecules attain a global minimum at a characteristic field $B_c$
- $B_c$ decreases with system size and should be observable for $C_{72}H_{72}$

This behaviour can be understood from a simple two-level model

- explains the existence of a global minimum at $B_c$
- at $B_c$, the induced angular momentum vanishes