

Molecules in strong magnetic fields

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Outline

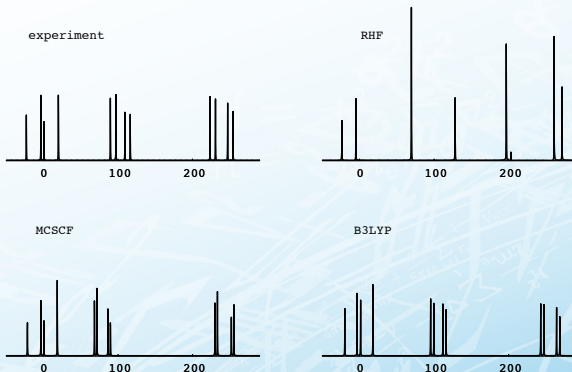
- 1 Molecular magnetism
- 2 London orbitals and the LONDON program
- 3 Molecular diamagnetism and paramagnetism
- 4 Atoms in strong fields
- 5 Excitations in strong fields
- 6 Molecular structure in strong fields
- 7 Conclusions

Molecules in weak magnetic fields

- ▶ Molecular magnetism is usually studied **perturbatively**

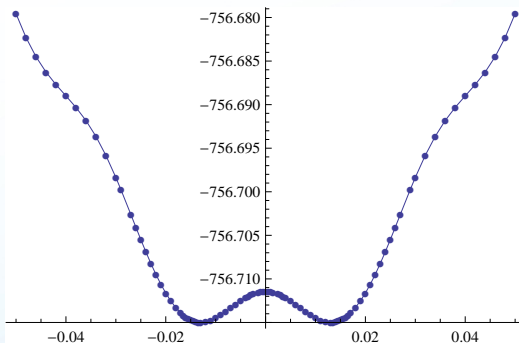
$$E(\mathbf{B}) = E(0) - \sum_{\alpha} \mu_{\alpha} B_{\alpha} - \frac{1}{2} \sum_{\alpha\beta} \chi_{\alpha\beta} B_{\alpha} B_{\beta} + \dots$$

- ▶ 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 vinyl lithium



Molecules in strong magnetic fields

- ▶ However, the field dependence of the energy can be complicated
 - ▶ the energy of C_{20} (ring conformation) plotted against B (atomic units)



- ▶ such behaviour cannot be described or understood perturbatively
- ▶ We have undertaken a **nonperturbative study** of molecular magnetism
 - ▶ gives new insight into molecular electronic structure
 - ▶ enables evaluation of many properties by finite-difference techniques
 - ▶ describes atomic and molecules observed in astrophysics (stellar atmospheres)
 - ▶ mimicks conditions in certain semiconductors
 - ▶ provides a framework for studying the current dependence of the universal density functional

The electronic Hamiltonian in an external magnetic field

- ▶ The **non-relativistic electronic Hamiltonian** (atomic units) in a magnetic field **B** is given by

$$H = T + V_{\text{Coulomb}} + \frac{1}{2} \mathbf{B} \cdot \mathbf{L} + \mathbf{B} \cdot \mathbf{s} + \frac{1}{8} \sum_i (\mathbf{B} \times \mathbf{r}_i) \cdot (\mathbf{B} \times \mathbf{r}_i)$$

- ▶ T is the kinetic-energy operator
- ▶ $V_{\text{Coulomb}} = V_{\text{ne}} + V_{\text{ee}} + V_{\text{nn}}$ are the Coulomb operators
- ▶ \mathbf{L} and \mathbf{s} are the orbital and spin angular momentum operators

- ▶ **Coulomb regime:** $B \approx 0$ a.u.

- ▶ earth-like conditions: Coulomb interactions dominate
- ▶ magnetic interactions are treated perturbatively

- ▶ **Landau regime:** $B \gg 1$ a.u.

- ▶ astrophysical conditions: magnetic interactions dominate

$$H = T + \frac{1}{2} B L_z + B s_z + \frac{1}{8} \sum_i (x_i^2 + y_i^2) B^2$$

- ▶ harmonic-oscillator Hamiltonian with force constant $B^2/4$: Landau levels
 - ▶ the electrons are confined in the transverse directions by the magnetic field
 - ▶ cyclotron energy proportional to B , cyclotron radius proportional to $B^{-1/2}$
 - ▶ Coulomb interactions are treated perturbatively
- ▶ **intermediate regime:** $B \approx 1$ a.u.
 - ▶ the Coulomb and magnetic interactions are equally important
 - ▶ complicated behaviour resulting from interplay of linear and quadratic terms
 - ▶ the linear term may lower or raise the energy
 - ▶ the quadratic term always raises the energy

The electronic Hamiltonian in an external magnetic field

- ▶ The **non-relativistic electronic Hamiltonian** (atomic units) in a magnetic field \mathbf{B} is given by

$$H = T + V_{\text{Coulomb}} + \frac{1}{2} \mathbf{B} \cdot \mathbf{L} + \mathbf{B} \cdot \mathbf{s} + \frac{1}{8} \sum_i (\mathbf{B} \times \mathbf{r}_i) \cdot (\mathbf{B} \times \mathbf{r}_i)$$

- ▶ We distinguish three **magnetic-field regimes**

- ▶ Coulomb regime: $B \approx 0$ a.u.
- ▶ intermediate regime: $B \approx 1$ a.u.
- ▶ Landau regime: $B \gg 1$ a.u.

- ▶ One **atomic unit** of B corresponds to 2.235×10^5 T = 2.235×10^9 G

- ▶ earth magnetism: 30–50 μ T
- ▶ fridge magnet: 1 mT
- ▶ loudspeaker magnet and medical MRI: 1 T
- ▶ strongest sustained laboratory fields: 45 T
- ▶ strongest pulsed laboratory fields: 100–1000 T
- ▶ white dwarfs: 10^1 – 10^5 T; neutron stars 10^8 – 10^9 T; magnetars 10^{10} T

- ▶ We shall here consider the **intermediate regime**

- ▶ Coulomb and magnetic interactions are both described nonperturbatively
- ▶ requires complex arithmetic
- ▶ gauge-origin invariance must be ensured (London orbitals)
- ▶ requires development of a non-standard code (LONDON)

London orbitals

- ▶ The external magnetic field is represented by a **vector potential**

$$\boldsymbol{\pi} = -i\hbar\nabla + e\mathbf{A}(\mathbf{r}), \quad \mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}), \quad \mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$$

- ▶ the position of the **gauge origin** \mathbf{O} is not unique
- ▶ approximate calculations may suffer from spurious **gauge-origin dependence**
- ▶ Gauge-origin invariance may be enforced by using **London atomic orbitals**:

$$\omega_{lm} = \exp[i\mathbf{A}_K(\mathbf{O}) \cdot \mathbf{r}] \chi_{lm}(\mathbf{r}_K)$$

- ▶ standard atomic orbitals equipped with a complex phase factor
- ▶ London orbitals are **correct to first-order** in the external magnetic field
 - ▶ for this reason, **basis-set convergence** is usually improved, as here illustrated for benzene:

	basis set	χ_{xx}	χ_{yy}	χ_{zz}	X_{xxxx}	X_{yyyy}	X_{zzzz}
London	STO-3G	-8.1	-8.1	-23.0	-211	-211	-52
	6-31G	-8.2	-8.2	-23.1	-219	-219	-64
	cc-pVDZ	-8.1	-8.1	-22.3	-236	-236	-120
	aug-cc-pVDZ	-8.0	-8.0	-22.4	-316	-316	-153
origin CM	STO-3G	-35.8	-35.8	-48.1	45	45	27
	6-31G	-31.6	-31.6	-39.4	29	29	-152
	cc-pVDZ	-15.4	-15.4	-26.9	9	9	-241
	aug-cc-pVDZ	-9.9	-9.9	-25.2	-413	-413	-159
origin H	STO-3G	-35.8	-176.3	-116.7	45	1477	-5340
	6-31G	-31.6	-144.8	-88.0	29	1588	-5866
	cc-pVDZ	-15.4	-48.0	-41.6	9	2935	-3355
	aug-cc-pVDZ	-9.9	-20.9	-33.9	-413	-3321	-1097

Hybrid plane-wave–Gaussians (PWG) orbitals

- ▶ London AOs are in fact hybrid **plane-wave–Gaussian (PWG)** orbitals

$$\omega_{\kappa,c}(\mathbf{r}) = \underbrace{\exp(i\kappa \cdot \mathbf{r})}_{\text{plane wave}} \underbrace{S_{lm}(\mathbf{r}) \exp(-a r_A^2)}_{\text{solid-harmonic Gaussian}}$$

- ▶ the wave vector κ 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
- ▶ PWGs necessitate 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)
 - ▶ previous work: M. Tachikawa and M. Shiga, Phys. Rev. E 64:056706 (2001)
- ▶ Integral evaluation in complex algebra
 - ▶ the Boys function with complex arguments

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

- ▶ more terms in the recurrence relations

PWG product rule and overlap integrals

- ▶ The Gaussian product rule still holds

$$\begin{aligned}
 \Omega_{ab}^{\kappa\lambda}(\mathbf{r}) &= \underbrace{\exp(i\kappa \cdot \mathbf{r})^* \exp(-a r_A^2)}_{\text{PWG at A}} \underbrace{\exp(i\lambda \cdot \mathbf{r}) \exp(-b r_B^2)}_{\text{PWG at B}} \\
 &= \underbrace{\exp\left(-\frac{ab}{a+b} R_{AB}^2\right)}_{\text{prefactor}} \underbrace{\exp[-i(\kappa - \lambda) \cdot \mathbf{r}] \exp[-(a+b)r_P^2]}_{\text{PWG at } \mathbf{P} = (a\mathbf{A} + b\mathbf{B})/(a+b)}
 \end{aligned}$$

- ▶ Integration over all space yields

$$\int \Omega_{ab}^{\kappa\lambda}(\mathbf{r}) d\mathbf{r} = \underbrace{\exp\left[-\frac{(\kappa - \lambda)^2}{4(a+b)} + i(\kappa - \lambda) \cdot \mathbf{P}\right]}_{\text{plane-wave contribution}} \underbrace{\frac{\pi^{3/2} \exp\left(-\frac{ab}{a+b} R_{AB}^2\right)}{(a+b)^{3/2}}}_{\text{standard Gaussian overlap}}$$

- ▶ As for standard Gaussians, Coulomb integrals reduce to the Boys function

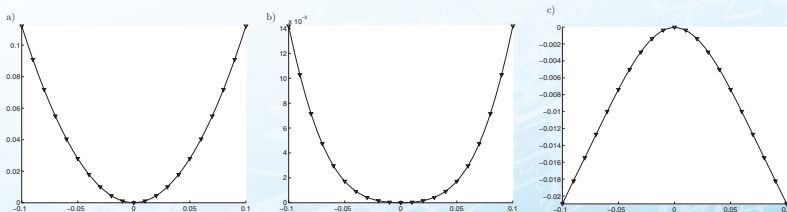
$$\begin{aligned}
 J &= \iint \frac{\exp(-i\kappa \cdot \mathbf{r}_1) \exp(-p r_{1P}^2) \exp(i\lambda \cdot \mathbf{r}_2) \exp(-q r_{2Q}^2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= \exp\left(-\frac{\kappa^2}{4p} - \frac{\lambda^2}{4q} - i\kappa \cdot \mathbf{P} - i\lambda \cdot \mathbf{Q}\right) \underbrace{\frac{2\pi^{5/2}}{pq\sqrt{p+q}} F_0\left[\frac{pq}{p+q} (\mathbf{P}' - \mathbf{Q}')^2\right]}_{\mathbf{P}' = \mathbf{P} - i\kappa/2p, \mathbf{Q}' = \mathbf{Q} - i\lambda/2q}
 \end{aligned}$$

The LONDON program

- ▶ an *ab initio* program for finite-field calculations with London orbitals
- ▶ some features of the present code
 - ▶ Hartree–Fock theory (RHF, UHF, GHF)
 - ▶ 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
 - ▶ C₂₀ is a “large” system

Molecular diamagnetism and paramagnetism

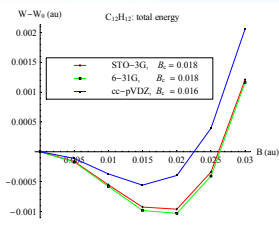
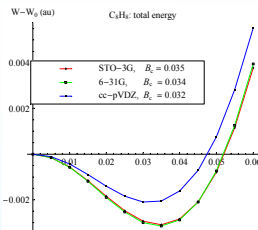
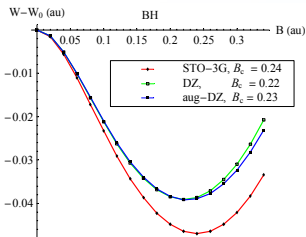
- ▶ When a magnetic field is applied to a molecule, one of two things can happen:
 - ▶ the energy is lowered: **molecular paramagnetism**
 - ▶ the energy is raised: **molecular diamagnetism**
- ▶ **Open-shell molecules are paramagnetic**
 - ▶ the molecule reorients the permanent magnetic moment and lowers the energy
- ▶ **Closed-shell molecules may be diamagnetic or paramagnetic**
 - ▶ the induced magnetic moment may oppose or enhance the external field
 - ▶ most molecules are diamagnetic (Lenz' law)
 - ▶ in some systems, orbital unquenching results in paramagnetism
- ▶ RHF calculations of the field-dependence for three closed-shell systems:



- a benzene (aug-cc-pVDZ): typical **diamagnetic quadratic dependence** on an out-of-plane field
- b cyclobutadiene (aug-cc-pVDZ): **diamagnetic non-quadratic dependence** on an out-of-plane field
- c BH (aug-cc-pVTZ): **paramagnetic dependence** on a perpendicular field

Stabilizing field strength for paramagnetic molecules

- ▶ However, plots over a larger range reveal that all closed-shell systems become diamagnetic in sufficiently strong fields:



- ▶ The transition occurs at a characteristic **stabilizing critical field strength B_c**
 - ▶ $B_c \approx 0.22$ perpendicular to principal axis for BH
 - ▶ $B_c \approx 0.032$ along the principal axis for antiaromatic octatetraene C_8H_8
 - ▶ $B_c \approx 0.016$ along the principal axis for antiaromatic [12]-annulene $C_{12}H_{12}$
- ▶ The stabilizing field strength **decreases with increasing molecular size**
 - ▶ strongest laboratory fields attainable: 10^{-3} a.u.
 - ▶ B_c is inversely proportional to the area of the molecule normal to the field
 - ▶ we estimate that B_c should be observable for $C_{72}H_{72}$
- ▶ We may in principle separate such molecules by applying a field gradient

Analytical model for the diamagnetic transition

- ▶ The diamagnetic transition arises from an interplay between linear and quadratic terms
 - ▶ it can be understood from a simple two-level model
- ▶ 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:

$$|0\rangle = |1s_B^2 2\sigma_{BH}^2 2p_z^2\rangle, \quad |x\rangle = |1s_B^2 2\sigma_{BH}^2 2p_z 2p_x\rangle, \quad |y\rangle = |1s_B^2 2\sigma_{BH}^2 2p_z 2p_y\rangle$$

- ▶ Let us apply a **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 **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 with $\chi_0 = -28$, $\chi_1 = -16$ and $\Delta = (E_1 - E_0)/2 = 0.01$:

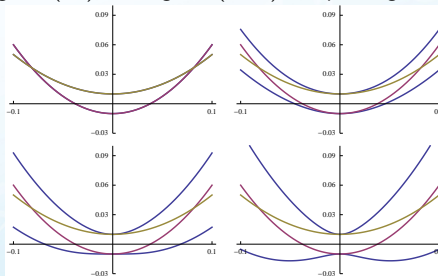
$$\mathbf{H}(B) = \begin{pmatrix} -\Delta - \frac{1}{2}\chi_0 B^2 & i\mu B \\ -i\mu B & \Delta - \frac{1}{2}\chi_1 B^2 \end{pmatrix} = \begin{pmatrix} -0.01 + 14B^2 & i\mu B \\ -i\mu B & 0.01 + 8B^2 \end{pmatrix}$$

- Eigenvalues:

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

- Plots for different values of μ :

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

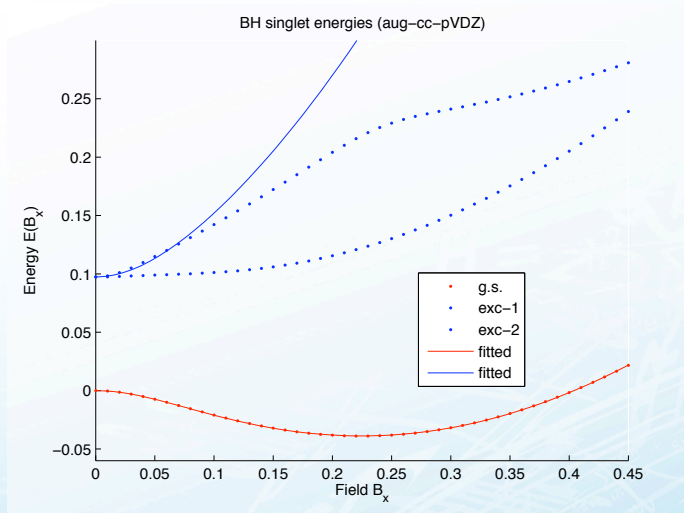


- magnetizability (negative second derivative at $B = 0$):

$$\chi(0) = -W_0''(0) = \chi_0 + \mu^2/2\Delta = -7, -5, 0, 11$$

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

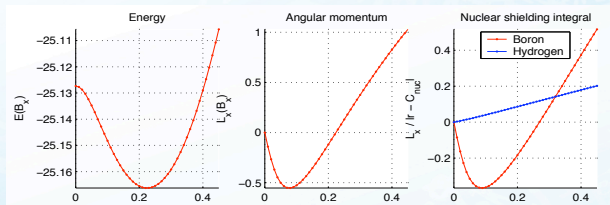


Induced magnetic moment and kinetic angular momentum

- ▶ The induced magnetic moment \mathbf{M} and the kinetic angular momentum $\mathbf{\Lambda}_{\text{kin}}$ are related as

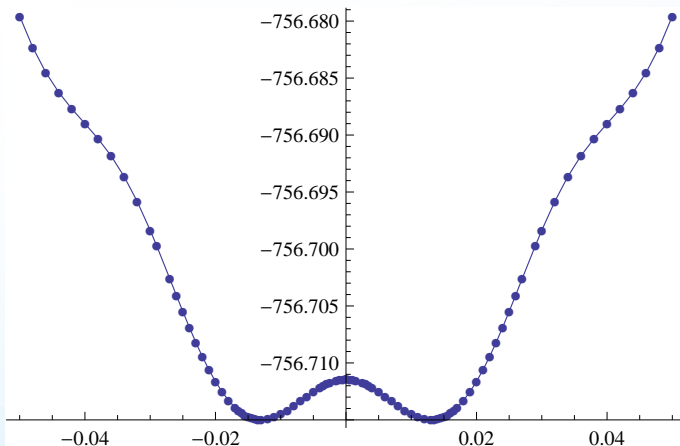
$$\mathbf{M} = -E'(\mathbf{B}) = -\frac{1}{2} \langle 0 | \mathbf{\Lambda} | 0 \rangle, \quad \mathbf{\Lambda} = \mathbf{r} \times \boldsymbol{\pi}, \quad \boldsymbol{\pi} = \mathbf{p} + \mathbf{A}$$

- ▶ the kinetic angular momentum represents the amount of rotation in the system
- ▶ it differs from the canonical momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ in an electromagnetic field
- ▶ Diamagnetic closed-shell molecules:
 - ▶ $\langle 0 | \mathbf{\Lambda} | 0 \rangle$ aligns with the field, increasing the energy $\frac{1}{2} \langle 0 | \mathbf{\Lambda} | 0 \rangle \cdot \mathbf{B}$
- ▶ Paramagnetic closed-shell molecules:
 - ▶ $\langle 0 | \mathbf{\Lambda} | 0 \rangle$ first aligns against the field, decreasing the energy
 - ▶ $\langle 0 | \mathbf{\Lambda} | 0 \rangle$ goes through a minimum at the inflection point $E''(\mathbf{B}) = 0$
 - ▶ $\langle 0 | \mathbf{\Lambda} | 0 \rangle$ then increases again until it vanishes at B_c
 - ▶ $\langle 0 | \mathbf{\Lambda} | 0 \rangle$ finally aligns with the field, making the system diamagnetic



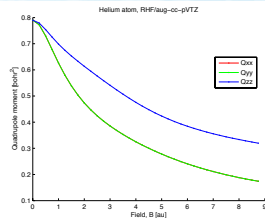
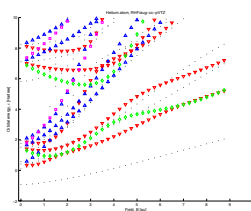
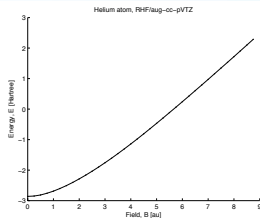
- ▶ there is no net induced rotation at the energy minimum

C_{20} : more structure



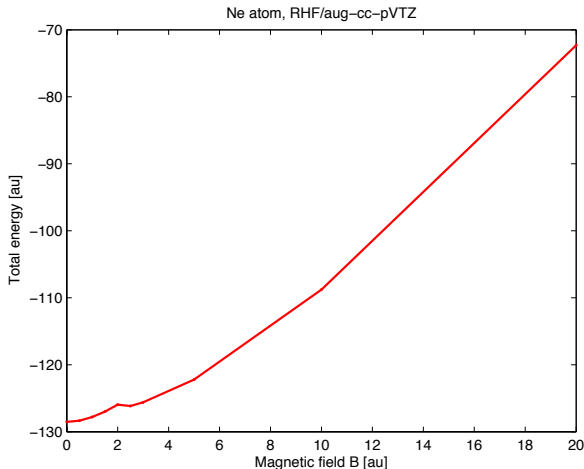
The helium atom in strong fields

- ▶ The **helium energy** behaves in simple manner in magnetic fields (left)
 - ▶ an initial quadratic diamagnetic behaviour is followed by linear increase in B
 - ▶ this is expected from the Landau levels (harmonic potential increases as B^2)
- ▶ The **orbital energies** behave in a more complicated manner (middle)
 - ▶ 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 **atom becomes squeezed** in the magnetic field (right)
 - ▶ this is particularly true for the **transverse directions**
 - ▶ the cyclotron radius is proportional to $B^{-1/2}$
 - ▶ special basis sets are needed for strong fields (Landau orbitals)



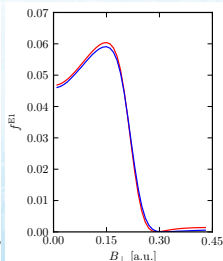
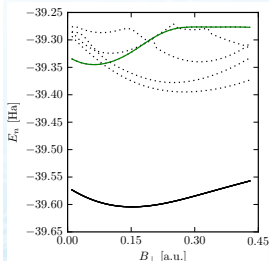
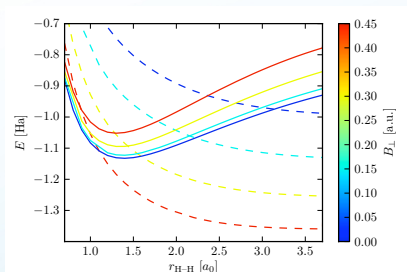
The neon atom in strong fields

- ▶ The field-dependence of the neon energy is more complicated
 - ▶ at $B \approx 2$, the ground state changes from $J_z = 0$ to $J_z = -1$



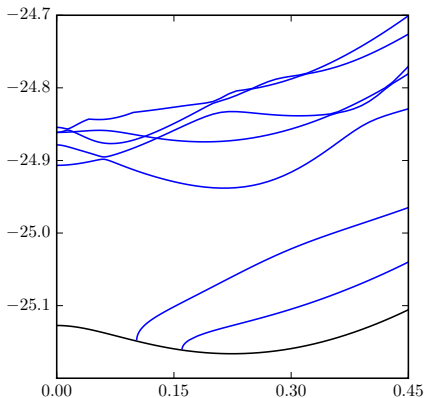
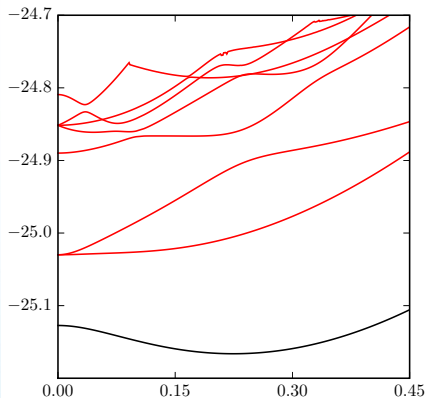
Linear response theory in finite magnetic fields

- ▶ We have implemented **linear response theory** (RPA) in finite magnetic fields
- ▶ lowest singlet and triplet states of H_2 (left)
 - ▶ singlet state (full line) triplet state (dashed line)
 - ▶ at $B \approx 0.25$, the (weakly bound) triplet state becomes the ground state
- ▶ lowest CH_3 radical states in magnetic fields (middle)
 - ▶ transitions to the green state are electric-dipole allowed
- ▶ oscillator strength for transition to green CH_3 state
 - ▶ length (red) and velocity (blue) gauges



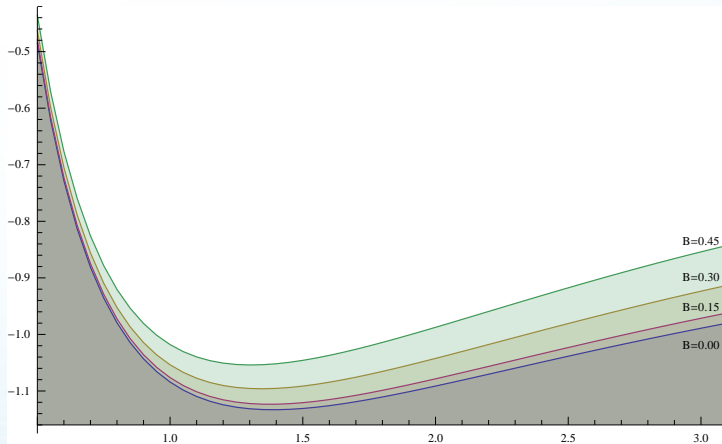
RPA spectrum of BH

- ▶ **Singlet** and **triplet** energies vs. field for BH [RHF/aug-cc-pVDZ]
 - ▶ the field is perpendicular to the bond axis
 - ▶ instabilities at $B_{\perp} \approx 0.1, 0.16$ au.



H₂ potential-energy curve in a perpendicular magnetic field

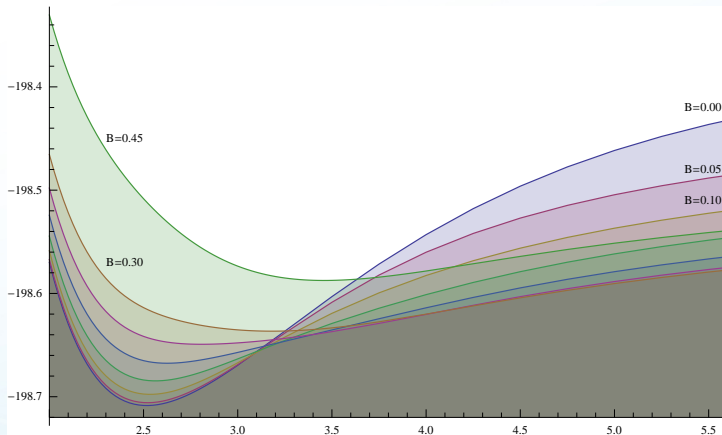
- ▶ The magnetic field changes the shape of the potential-energy curve



- ▶ diamagnetic behaviour at all separations
- ▶ most pronounced for atoms (no paramagnetic term)
- ▶ The bond length **decreases** with increasing magnetic field

F_2 potential-energy curve in a perpendicular magnetic field

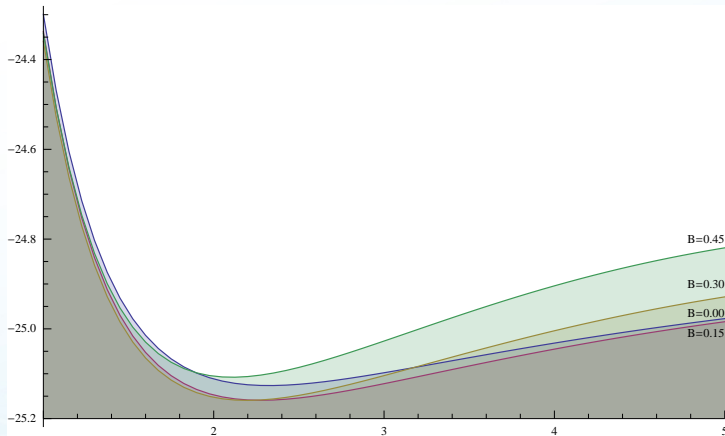
- ▶ The magnetic field changes the shape of the potential-energy curve



- ▶ diamagnetic behaviour in the molecular limit
- ▶ paramagnetic then diamagnetic behaviour in the atomic limit
- ▶ The bond length **increases** with increasing magnetic field

BH potential-energy curve in a perpendicular magnetic field

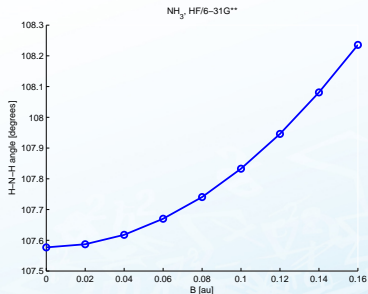
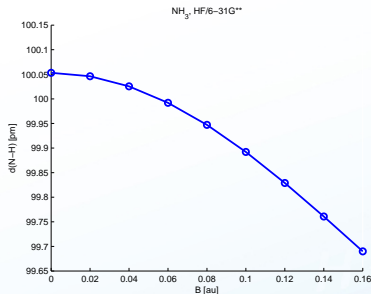
- ▶ The magnetic field changes the shape of the potential-energy curve



- ▶ mixed para- and diamagnetic behaviour at all separations
- ▶ mostly diamagnetic in the atomic limit
- ▶ The bond length of **decreases** with increasing magnetic field

The structure of NH_3 in strong fields

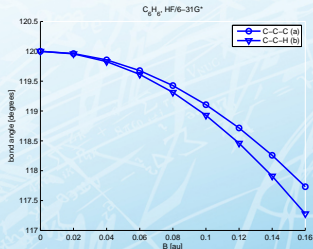
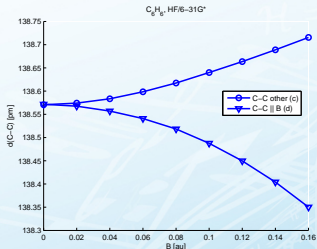
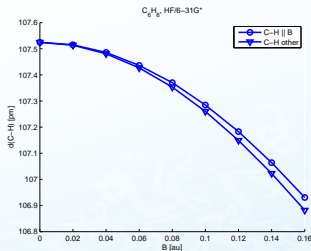
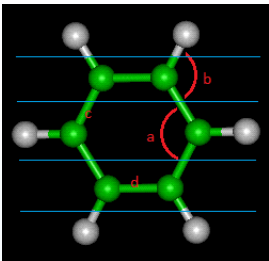
- ▶ Magnetic field applied along the symmetry axis



- ▶ As expected the molecule shrinks
 - ▶ bonds contract by 0.7 pm in a field of 0.15 a.u.
- ▶ Less intuitively, the molecule becomes more planar
 - ▶ could this be caused by the shrinking lone pair?

The structure of C_6H_6 in strong fields

- ▶ At $B = 0.16$, the molecule is 6.1 pm narrower and 3.5 pm longer in the field direction
 - ▶ in agreement with perturbational estimates by Caputo and Lazzeretti *IJQC* (online 31 aug 2010)



Conclusions

- ▶ 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
- ▶ We have studied excitation energies in magnetic fields
 - ▶ excitation energies typically increase in magnetic fields
- ▶ We have studied molecular structure in magnetic fields
 - ▶ atoms are squeezed in magnetic fields—in particular, perpendicular to the field
 - ▶ bond distances are typically reduced in magnetic fields
- ▶ We are in the process of introducing electron correlation
 - ▶ complete-active-space self-consistent field (CASSCF) theory