

# Gauge-origin invariant calculations of excitation energies for molecules subject to strong magnetic fields

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Workshop on Quantum Chemistry in Strong Magnetic Fields,  
September 13–14, 2010

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# Outline

- 1 The LONDON program
  - Magnetic Periodic Boundary Conditions, hybrid basis sets
  - Reminder about gauge (in)variance, London orbitals
- 2 Finite magnetic fields in quantum chemistry: How strong?
- 3 Hartree–Fock ground state results
- 4 Random phase approximation for excitations
  - Formalism, technicalities
  - Some preliminary results
- 5 Differentiated integrals and related issues
  - Geometry optimization
- 6 Summary

# From MPBC to mixed basis sets & London orbitals

- (Collaboration with [A. Soncini](#))
- A Gaussian-type orbital approach to periodic systems in (finite) uniform magnetic fields...
- ...leads to integrals over mixed plane-wave/GTO functions:

$$\omega(\mathbf{r}) = (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-a(\mathbf{r}-\mathbf{A})^2} e^{-i\mathbf{q}\cdot\mathbf{r}} \quad (1)$$

- From a method-development P.O.V., no difference between matrix element evaluation for:
  - periodic systems, finite magnetic fields, GTOs
  - periodic systems, finite magnetic fields, London orbitals
  - molecular systems, finite magnetic fields, London orbitals
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# From MPBC to mixed basis sets & London orbitals

- 3rd alt.: molecular systems, finite magnetic fields, London orbitals
- Interesting in itself: Excepting a few studies on very small systems ( $H_2$ , Be atom, ...), it has not been done before
- Proof of concept for integrals arising in other cases
- All integrals now become complex-valued. In particular, Coulomb integrals involve the Boys function of a complex-valued argument<sup>1</sup>

$$F_n(z) = \int_0^1 t^n e^{-zt^2} dt \quad (2)$$

- Hard to reuse standard packages (e.g. DALTON), due their reliance on real-valued quantities

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# London orbitals: implementation issues

Brief (and incomplete) review of integral evaluation:

- Analytical expressions for Coulomb integrals (scattering):
  - N. Ostlund, *Chem Phys Lett* **34**:419 (1975)
  - T. Rescigno *et al.* *Phys Rev A* **11**:825 (1975)
- Integration schemes suitable for implementation (plane wave/Gaussian hybrid functions):
  - Rys quadrature: P. Čárský & M. Polášek, *J Comp Phys* **143**:266 (1998)
  - McMurchie–Davidson scheme (no implementation): M. Tachikawa & M. Shiga, *Phys Rev E* **64**:056706 (2001)
- Integration schemes suitable for implementation (London orbitals considered):
  - Obara–Saika scheme, application to  $H_2$ : S. Kiribayashi *et al.* *IJQC* **75**:637 (1999)
  - ACE scheme (no implementation): K. Ishida, *J Chem Phys* **118**:4819 (2003)
  - McMurchie–Davidson scheme: E. Tellgren, A. Soncini & T. Helgaker, *J Chem Phys* **129**:154114 (2008)

# London orbitals: **A** vs. **B**

- A *gauge transformation* using an arbitrary  $f(\mathbf{r}, t)$ ,

$$V' = V - \frac{\partial f(\mathbf{r}, t)}{\partial t} \quad (3)$$

$$\mathbf{A}' = \mathbf{A} + \nabla f(\mathbf{r}, t) \quad (4)$$

$$\psi' = e^{if(\mathbf{r}, t)}\psi \quad (5)$$

only affects the non-physical degrees of freedom.

- A finite basis set does not approximate all gauge transformed wave functions equally well.
- How well a wave function  $\psi' = e^{if(\mathbf{r})}\psi$  can be approximated depends on the gauge function  $f(\mathbf{r})$ .
- It is hopeless to achieve gauge invariance using Gaussian-type basis sets of reasonable size.

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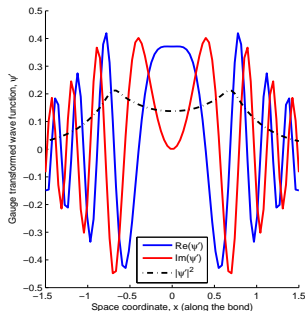
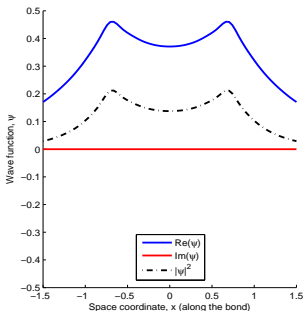
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# London orbitals: gauge invariance and finite basis sets

Example:  $H_2$  molecule, on the x-axis, in the field  $\mathbf{B} = \frac{1}{10}\hat{\mathbf{z}}$ .

$$\begin{aligned} \mathbf{A} &= \frac{1}{20}\hat{\mathbf{z}} \times \mathbf{r} & \longrightarrow & \mathbf{A}' = \mathbf{A} + \nabla(10x^2) \\ \psi &= \text{RHF/aug-cc-pVQZ} & \longrightarrow & \psi' = e^{i \cdot 10x^2} \psi \end{aligned} \quad (6)$$



# London orbitals: gauge invariance vs. gauge-origin invariance

- Gauge invariance is not practically feasible with Gaussian basis sets.
- Restrict attention to uniform fields, fix some of the gauge freedom by choosing  $\nabla \cdot \mathbf{A} = 0$ , and in addition take  $\mathbf{A}$  to be cylindrically symmetric.
- A magnetic field  $\mathbf{B}_0$  is then represented by 
$$\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B}_0 \times (\mathbf{r} - \mathbf{G}).$$
- The gauge origin  $\mathbf{G}$  contains the remaining gauge degrees of freedom.
- More modest goal: make finite basis set calculations independent of the gauge origin  $\mathbf{G}$ .



# London orbitals: definition of

- Consider an atomic orbital  $\chi_{\text{ao}}(\mathbf{r})$  centered at  $\mathbf{C}$ .
- Define the *London orbital*

$$\chi_{\text{lo}}(\mathbf{r}) = e^{-i\mathbf{A}(\mathbf{C})\cdot\mathbf{r}} \chi_{\text{ao}}(\mathbf{r}) \quad (7)$$

as the AO times a gauge factor.

- When the AOs are Gaussian-type orbitals, the London orbitals take the form

$$\chi(\mathbf{r}) = x^l y^m z^n e^{-\gamma(\mathbf{r}-\mathbf{C})^2 - i\mathbf{A}(\mathbf{C})\cdot\mathbf{r}}. \quad (8)$$

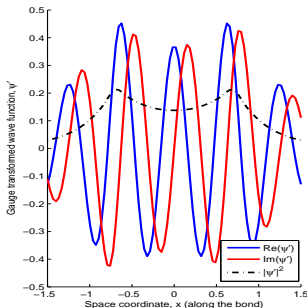
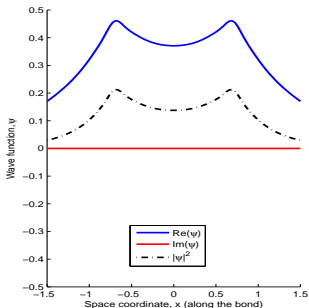
- London orbitals make all quantities gauge-origin independent.

# London orbitals: illustration

Example:  $H_2$  molecule, on the x-axis, in the field  $\mathbf{B} = \frac{1}{10}\hat{\mathbf{z}}$ .

$$\begin{aligned} \mathbf{A} &= \frac{1}{20}\hat{\mathbf{z}} \times \mathbf{r} & \longrightarrow & \mathbf{A}' = \mathbf{A} + \nabla(-\mathbf{A}(\mathbf{G}) \cdot \mathbf{r}) \\ \psi &= \text{RHF/aug-cc-pVQZ} & \longrightarrow & \psi' = e^{-i\mathbf{A}(\mathbf{G}) \cdot \mathbf{r}} \psi \end{aligned} \quad (9)$$

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



## The LONDON program

Reminder about gauge (in)variance, London orbitals

# The LONDON program

The LONDON program is an ab initio program for finite field calculations using London orbitals<sup>2</sup>:

- Hartree-Fock wave functions [RHF, UHF, GHF].
- DFT version?
- Quite general integral evaluation
- Excitation energies using RPA
- Geometrical gradients and geometry optimization functionality
- Automatic generation of current density grid files
- Not yet highly optimized for speed. C<sub>20</sub> is a “large” system.

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<sup>2</sup>E. Tellgren, A. Soncini, T. Helgaker, *J Chem Phys*, 129:154114 (2008)

## Magnetic field strength in context

- 1 T is a large unit,  $1 \text{ au} = 2.35 \times 10^5 \text{ T}$
- National High Magnetic Field Lab (Florida): 45 T (sustained), 88.9 T (2 sec.), 1000 T ( $\sim 1 \text{ ms}$ )<sup>3</sup>
- For finite field calculations on diatomic molecules,  $\sim 0.1 \text{ au}$  is a natural field. . .
- . . . shows non-linear response clearly
- Larger molecules can be probed with smaller fields

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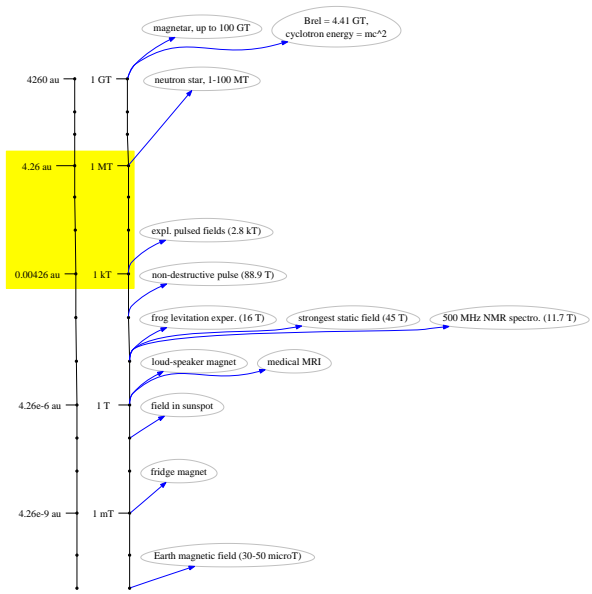
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# Hypermagnetizabilities (benzene)

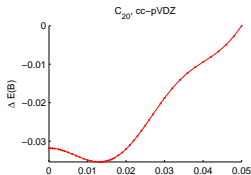
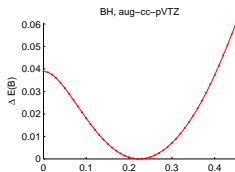
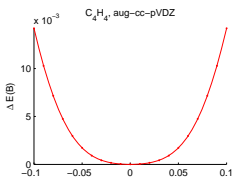
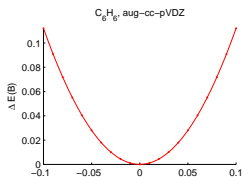
- compute points on  $E(\mathbf{B})$  curve, least-squares fit a polynomial  $\rightarrow$  estimate of Taylor coeff.
- Benzene ( $C_6H_6$ ) finite field results:

basis set	$\chi_{xx}$	$\chi_{yy}$	$\chi_{zz}$	$\chi_{xxxx}$	$\chi_{yyyy}$	$\chi_{zzzz}$
London orbitals						
STO-3G	-8.11	-8.11	-22.97	-211.17	-211.17	-52.08
6-31G	-8.24	-8.24	-23.14	-218.79	-218.79	-64.32
cc-pVDZ	-8.08	-8.08	-22.27	-235.96	-235.96	-120.11
aug-cc-pVDZ	-7.99	-7.99	-22.41	-316.46	-316.46	-152.67
common-origin: centre of mass						
STO-3G	-35.75	-35.75	-48.11	45.21	45.21	26.91
6-31G	-31.56	-31.56	-39.42	28.88	28.88	-151.57
cc-pVDZ	-15.38	-15.38	-26.93	8.90	8.90	-241.48
aug-cc-pVDZ	-9.91	-9.91	-25.22	-412.51	-412.51	-158.50
common-origin: hydrogen nucleus						
STO-3G	-35.75	-176.25	-116.69	45.19	1477	-5340
6-31G	-31.56	-144.81	-88.03	28.88	1588	-5866
cc-pVDZ	-15.38	-48.00	-41.56	9.11	2935	-3355
aug-cc-pVDZ	-9.91	-20.94	-33.86	-412.55	-3321	-1097

(N.B.: decontracted basis sets)

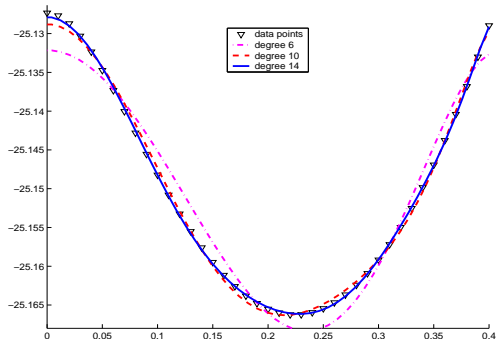
# Non-perturbative phenomena

- Benzene illustrates the typical case
- Some paratropic ( $C_4H_4$ ) and paramagnetic (BH,  $C_{20}$  ring) systems have slowly converging/diverging perturbation expansions



# Non-perturbative phenomena: perturbative divergence

Polynomials fitted to the BH energy curve (aug-cc-pVDZ):

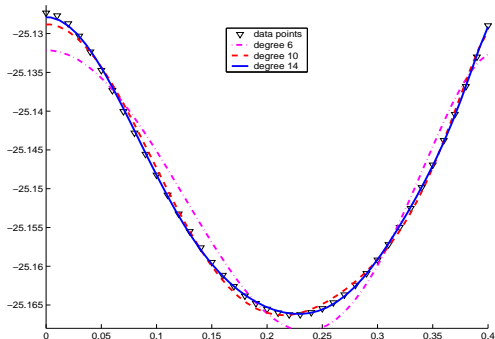


- Perturbative response calculations need to go to order  $> 14$ .
- A two-state model ( $2 \times 2$  Hamiltonian) accounts for this behavior (as well as the diamagnetic case)<sup>4</sup>

<sup>4</sup>E. Tellgren, T. Helgaker, A. Soncini *PCCP* 11:5489 (2009)

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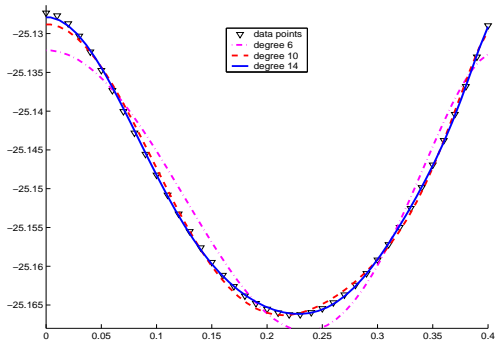


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# RPA formulation & implementation for LONDON

- Desiderata:

- linear basis transformations shouldn't change the form of the working equations<sup>5</sup> ("covariance")
- allow any basis (e.g. AOs), avoid MO basis in practice
- don't split complex quantities into real- and imaginary parts
- unified formulation & implementation for RHF, UHF and GHF

- Sample of recent non-MO formulations of RPA (TD-HF):

- H. Larsen et al. *JCP* 113:8908 (2000), S. Coriani et al. *JCP* 126:154108 (2007)
- M. Lucero et al. *JCP* 129:064114 (2008), T. Kjærgaard et al. *JCP* 129:054106 (2008)

- Rederiving RPA with the desiderata in mind, lead to a formulation essentially identical to that of Kjærgaard et al.

- Minor differences: complex quantities, notation reflects "covariance", indices may refer to either space orbitals, spin orbitals, 2-comp. orbitals.

- Davidson's method iteratively solves the eigenvalue problem, exploiting the paired structure of excitation operators

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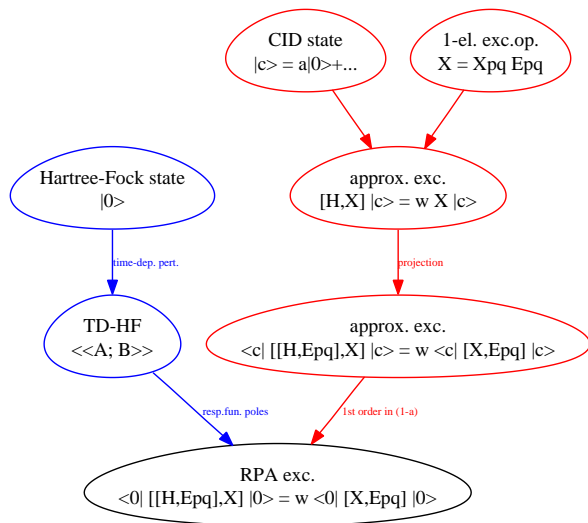
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# Different paths to RPA



# RPA formulation & implementation for LONDON

- Very tedious but straightforward to work out  
 $W_{\zeta\eta,\theta\kappa}^{[2]} = \langle 0 | [[\hat{H}, \hat{E}_{\zeta\eta}], \hat{E}_{\theta\kappa}] | 0 \rangle$  and  $S_{\zeta\eta,\theta\kappa}^{[2]} = \langle 0 | [\hat{E}_{\theta\kappa}, \hat{E}_{\zeta\eta}] | 0 \rangle$   
 explicitly in AO basis
- But only their effects on a trial vector are needed

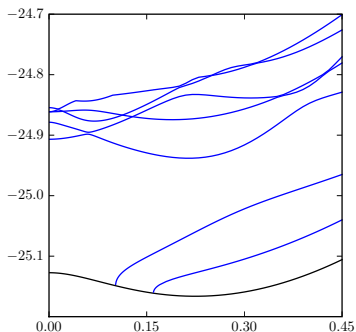
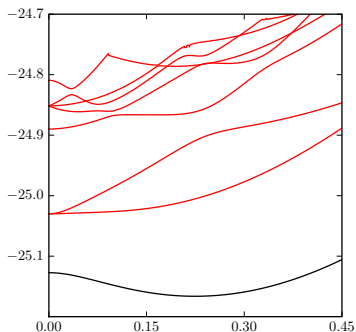
## Hessian and metric transformations

$$W_{\zeta\eta,\theta\kappa}^{[2]} X^{\theta\kappa} = -[[\hat{P}, \hat{X}], \hat{F}(P)]_{\eta\zeta} - [\hat{P}, \hat{G}([P, X])]_{\eta\zeta} \quad (10)$$

$$S_{\zeta\eta,\theta\kappa}^{[2]} X^{\theta\kappa} = [\hat{P}, \hat{X}]_{\eta\zeta} \quad (11)$$

# RPA spectrum of boronmonohydride (BH)

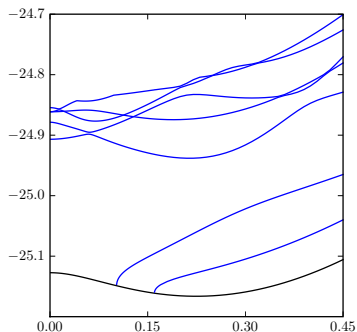
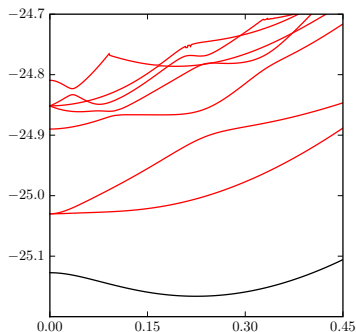
Singlet and triplet energies vs. field for BH [RHF/aug-cc-pVDZ]



The field is perpendicular to the bond axis. Instabilities at  $B_{\perp} \approx 0.1, 0.16$  au.

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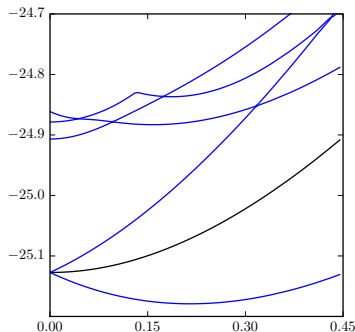
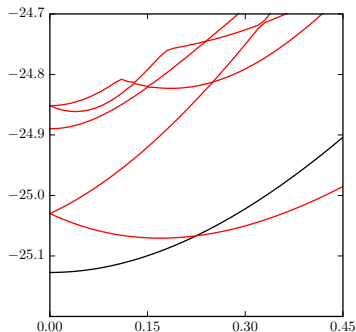
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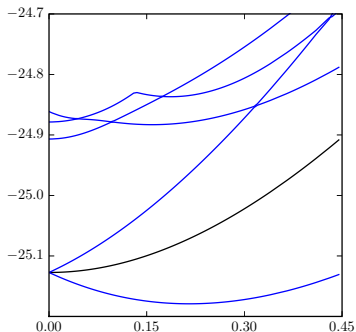
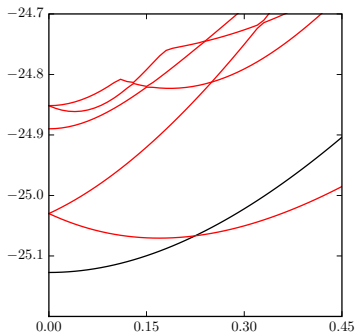
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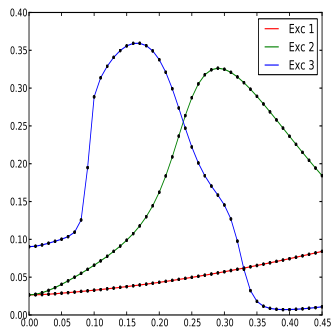
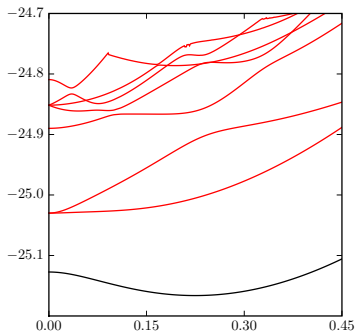


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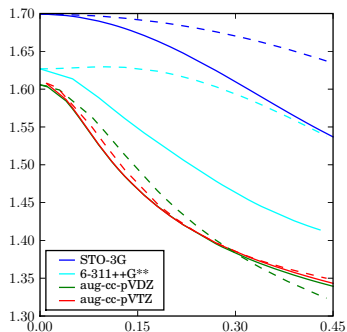
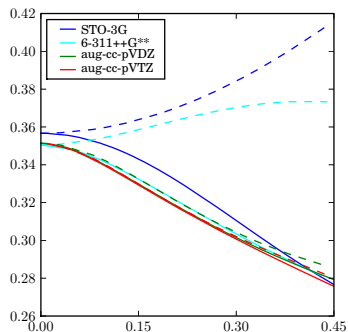
Singlet dip. oscillator strengths vs. field for BH



Field is perpendicular to the bond axis. Osc.str. for lowest 3 exc. shown.

# Lowest triplet in $H_2$ : Basis set convergence

Energy (left) and dipole trans.mom. (right) vs. perpendicular field.



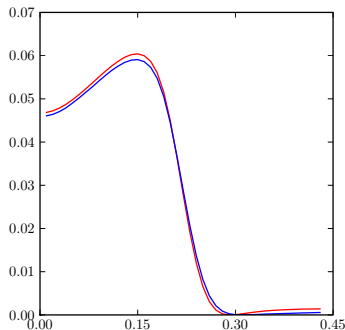
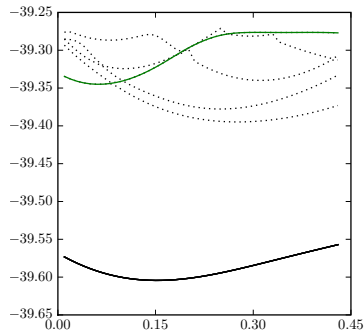
Solid lines: London orbitals

Dashed lines: Gaussian orbitals (g.o. on H)

# Methyl radical $\text{CH}_3$ (UHF/aug-cc-pVDZ)

*Left:* Energy spectrum vs. field [dashed lines dip. forbidden]

*Right:* Dip. osc. strength vs. field

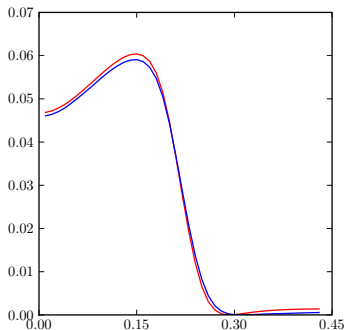
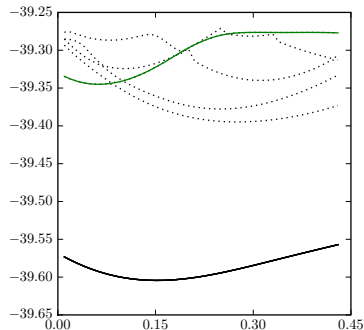


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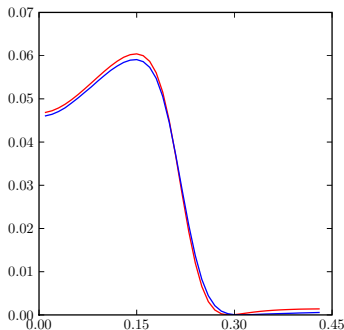
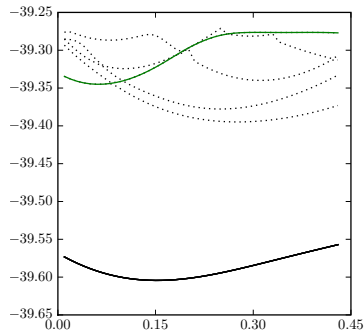


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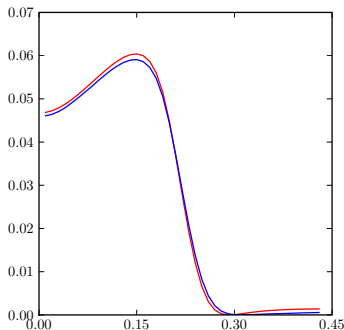
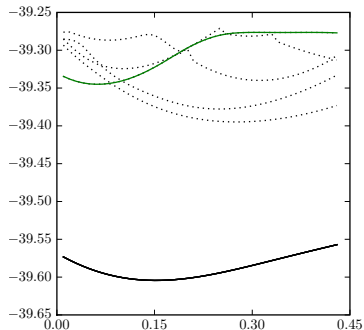


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# Differentiated GTO integrals

## Hermite scheme for differentiated GTO integrals<sup>6</sup>

- Expands spherical GTOs in Hermite GTOs rather than Cartesian GTOs
- Exploits special properties of Hermite GTOs
- Simple unified implementation of arbitrary order derivatives
- (Some other benefits as well, some speed-up ...)
- Not obvious how to generalize to London orbitals

Is there a (analogous or disanalogous) way to achieve the same unification & simplicity for finite-field London orbitals?

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# One approach to differentiated London orbitals

- Think of a basis set as a pair  $\mathcal{B} = (M, \mathcal{P})$
- $\mathcal{P}$  is a set of primitive GIAOs
- $M$  is a linear basis mapping that...
  - ...defines linear combinations of prim. GIAOs
  - ...is typically highly block diagonal in a matrix repr.

Some examples of such mappings:

- **Cartesian-to-spherical transformation**: maps prim. GIAOs to lin.comb. within the same (sub)shell
- **Contraction**: maps prim. GIAOs to lin.comb. with same ang.mom., different exponents
- If block-diagonality isn't required, also:
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# One approach to differentiated London orbitals

When higher-order derivatives/several basis sets are involved, another operation is useful:

- Given  $\mathcal{B}_1 = (M_1, \mathcal{P}_1)$  and  $\mathcal{B}_2 = (M_2, \mathcal{P}_2)$ , reexpress as  $\mathcal{B}'_1 = (M'_1, \mathcal{P}_1 \cup \mathcal{P}_2)$  and  $\mathcal{B}'_2 = (M'_2, \mathcal{P}_1 \cup \mathcal{P}_2)$
- $M_i[\mathcal{P}_i] = M'_i[\mathcal{P}_1 \cup \mathcal{P}_2] \implies \mathcal{B}_i, \mathcal{B}'_i$  define the same basis functions
- Enables reuse of intermediate integrals (e.g. gradients for free when computing Hessians)

# Current status

- Geometrical gradients have been implemented in LONDON using the above scheme
- (When the density matrix response is available, it should also be easy to implement Hessians.)
- BFGS geometry optimization implemented
  - works OK, but struggles to rotate molecules into optimal alignment with the external field
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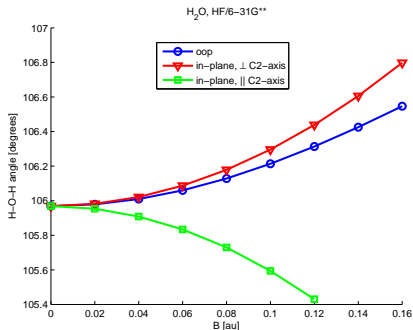
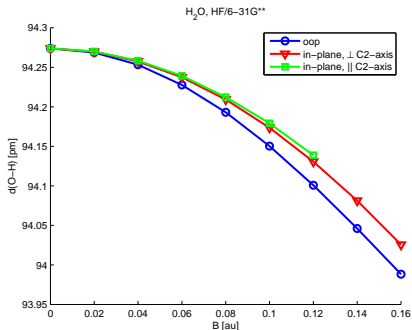
- Geometrical gradients have been implemented in LONDON using the above scheme
- (When the density matrix response is available, it should also be easy to implement Hessians.)
- BFGS geometry optimization implemented
  - works OK, but struggles to rotate molecules into optimal alignment with the external field
  - need to incorporate some extra coordinate that responds directly to the total torque
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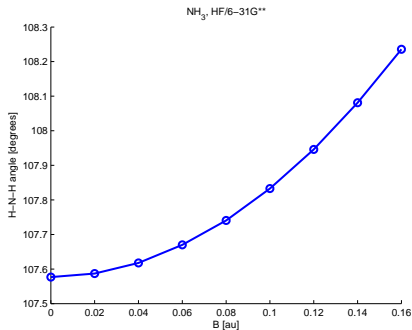
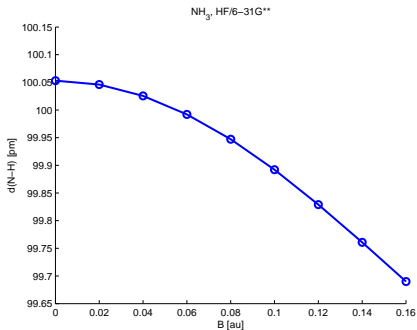
# Example: $\text{H}_2\text{O}$ geometry in strong fields



- bonds contract
- for  $\mathbf{B}$  parallel to the  $C_2$ -axis, the bond angle decreases (reducing the diamagnetic term)
- otherwise the bond angle increases

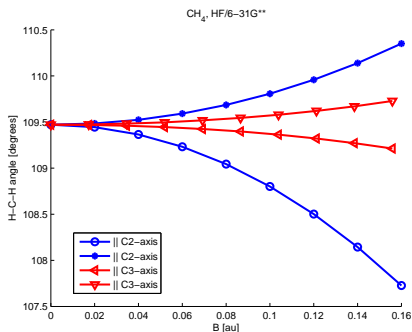
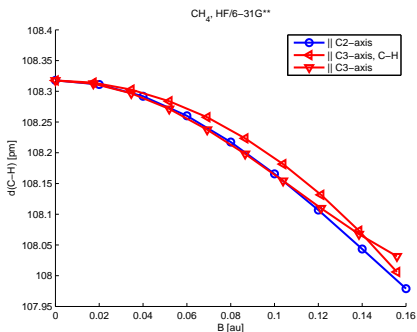
# Example: $\text{NH}_3$ geometry in strong fields

Field along symmetry axis:



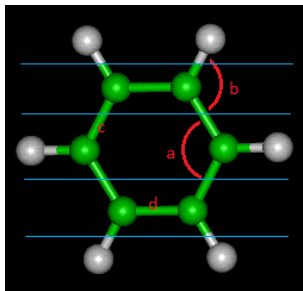
- bonds contract
- bond angle increases  $\longrightarrow$  more planar geometry

# Example: CH<sub>4</sub> geometry in strong fields

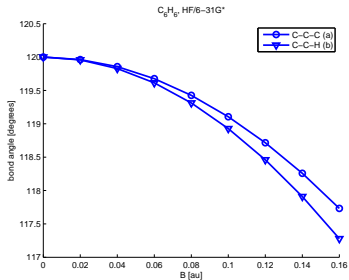
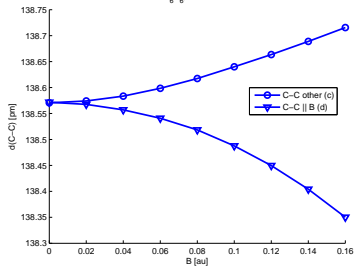
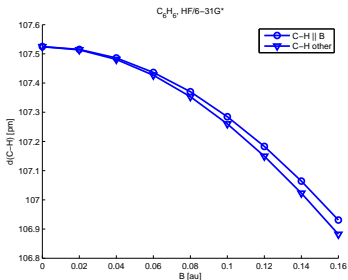


- C<sub>2</sub> case: reduces extent  $\perp$   $\mathbf{B}$  & the diamagnetic term
- C<sub>3</sub> case: angle between bond parallel to the field & other bonds decreases  $\rightarrow$  C & the 3 other H become more planar
- C<sub>3</sub> case: hint of non-linearity in crossing bond length curves

# Example: $C_6H_6$ geometry in strong fields



$C_6H_6$ , HF/6-31G\*



Fits with Caputo & Lazzeretti *IJQC* (online 31 aug 2010)

# Summary

- LONDON opens up for several applications, from an alternative method to compute static response properties to investigation of intrinsically non-perturbative phenomena
- Functionality for RPA excitations recently added
  - AO-/arbitrary basis formulation
  - unified handling of RHF/UHF/GHF
- Functionality related to gradients recently added
  - part of quite simple & general scheme for derivatives
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- Future goals include
  - Correlation: CI, etc.
  - Study of CDFT functionals using Adiabatic Connection methods (with A. Teale)

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# Thanks to...

- Trygve Helgaker
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- Paweł Sałek, Simen Reine
- The audience