Hartree–Fock and Kohn–Sham theories for large molecular systems

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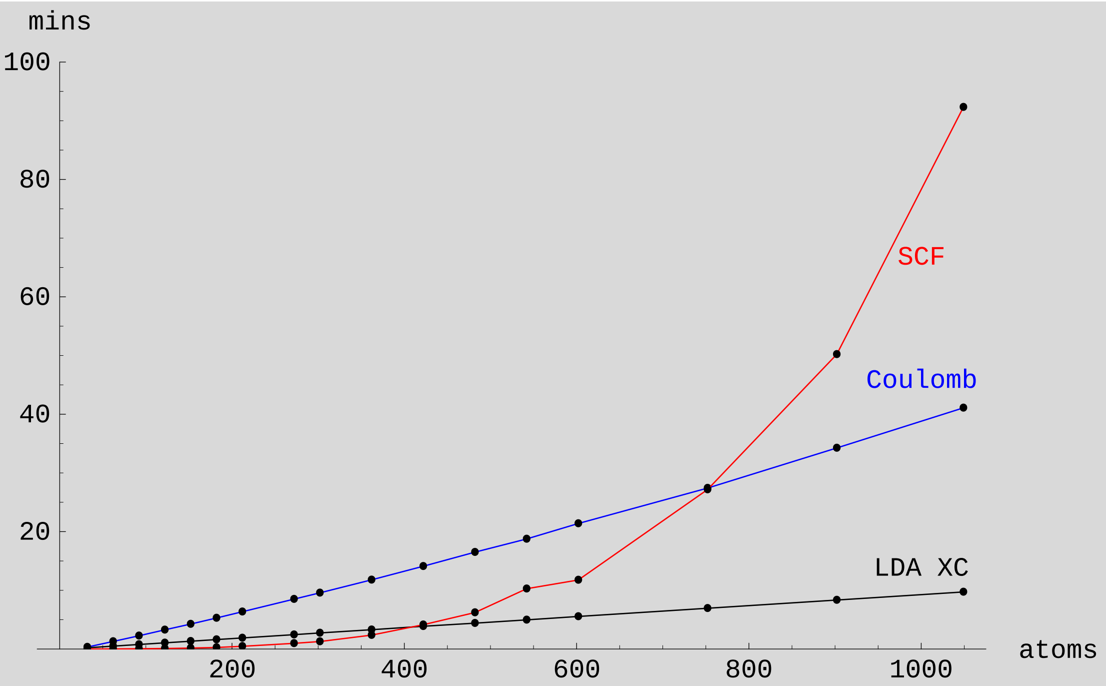
Self-consistent field (SCF) theory

- Consider the optimization of the SCF energy (here LDA) of molecular systems:
  - small systems dominated by KS-matrix evaluation, with linear scaling
  - large systems dominated by SCF diagonalization, with cubic scaling

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}$$

$$\mathbf{D}_{\mathrm{new}} = \mathbf{C}_{\mathrm{occ}}^{\mathrm{T}}\mathbf{C}$$



- To achieve linear scaling, we must avoid diagonalization and MOs!
- We shall here consider an alternative to diagonalization:
  - it optimizes the density matrix directly, avoiding MOs
  - involves only additions and multiplications of (sparse) one-electron matrices
  - for large (sparse systems), the calculations scale linearly with system size

Direct optimization of the density matrix

- Consider the direct optimization of the density matrix:

$$E(\mathbf{D}) = \mathrm{Tr}\,\mathbf{Dh} + \text{2-el. part}$$

  - there are constraints on the density matrix:

$$\underbrace{\mathbf{D} = \mathbf{D}^{\mathrm{T}}}_{\text{symmetry}}, \quad \underbrace{\mathrm{Tr}\,\mathbf{D} = N}_{\text{trace}}, \quad \underbrace{\mathbf{D}^2 = \mathbf{D}}_{\text{idempotency}} \quad \text{(orthonormal basis)}$$

  - any optimization must obey these constraints

- Many strategies are based on purification of the density matrix

$$\widetilde{\mathbf{D}} = 3\mathbf{D}^2 - 2\mathbf{D}^3 \quad \text{(McWeeny purification, 1960)}$$

  - Li, Nunes and Vanderbilt (1993)

$$\widetilde{E} = \mathrm{Tr}\,\widetilde{\mathbf{D}}\mathbf{h} + \mu(\mathrm{Tr}\,\mathbf{D} - N) + \text{2-el. part}$$

  - Millam and Scuseria (1997), Challacombe (1999)
  - Palser and Manolopoulos (1998), Niklasson (2002)

- We shall pursue a different approach, based on an explicitly parameterization of **D**

Exponential parameterization of the density matrix

- In a real, nonorthogonal AO basis, with $\mathbf{S} \neq \mathbf{I}$, let $\mathbf{D}$ be a valid HF/KS matrix:

$$\underbrace{\mathbf{D} = \mathbf{D}^{\mathrm{T}}}_{\text{symmetry}}, \quad \underbrace{\operatorname{Tr} \mathbf{DS} = N}_{\text{trace}}, \quad \underbrace{\mathbf{DSD} = \mathbf{D}}_{\text{idempotency}}$$

- Any other valid density matrix $\mathbf{D}(\mathbf{X})$ can then be generated from this matrix:

$$\underbrace{\mathbf{D}(\mathbf{X}) = \exp(-\mathbf{XS})\mathbf{D}\exp(\mathbf{SX})}_{\text{exponential parameterization}}, \quad \underbrace{\mathbf{X}^{\mathrm{T}} = -\mathbf{X}}_{\text{antisymmetric}}$$

  - Helgaker, Jørgensen and Olsen: *Molecular Electronic-Structure Theory* (Wiley, 2000)
  - Head-Gordon and coworkers, MolPhys **101**, 37 (2003), JCP **118**, 6144 (2003)

- We can obtain any valid density matrix, in the AO basis, without recourse to MOs!
  - in particular, we may optimize the energy by freely varying $X_{\mu\nu}$ with $\mu > \nu$:

$$E_{\min}(\mathbf{X}) = \min_{\mathbf{X}} \left[\operatorname{Tr} \mathbf{D}(\mathbf{X})\mathbf{h} + \text{2-el. part}\right]$$

- Is the use of $\mathbf{D}(\mathbf{X})$ a practical proposition?
  - we shall in this talk demonstrate that it is indeed so
  - we shall consider energy optimizations and property calculations

Two questions about $\mathbf{D}(\mathbf{X}) = \exp(-\mathbf{XS})\mathbf{D}\exp(\mathbf{SX})$

- Can it be evaluated efficiently?
  - we use a generalized Baker–Campbell–Hausdorff (BCH) expansion:

$$\mathbf{D}(\mathbf{X}) = \mathbf{D} + [\mathbf{D}, \mathbf{X}]_{\mathrm{S}} + \tfrac{1}{2}[[\mathbf{D}, \mathbf{X}]_{\mathrm{S}}, \mathbf{X}]_{\mathrm{S}} + \cdots$$

  - we have here introduced the S commutator

$$[\mathbf{D}, \mathbf{X}]_{\mathrm{S}} = \mathbf{DSX} - \mathbf{XSD}$$

  - converges rapidly (purification may be necessary), in about 10 matrix multiplications
- Are redundancies a problem?
  - the AO space consists of two parts: the occupied space and the virtual space

$$\mathbf{P} = \mathbf{DS} \text{ (onto occupied space)}, \quad \mathbf{Q} = \mathbf{I} - \mathbf{DS} \text{ (onto virtual space)}$$

  - only rotations between the occupied and virtual spaces are nonredundant;

$$\mathbf{X} = \underbrace{\mathbf{PXP}^{\mathrm{T}} + \mathbf{QXQ}^{\mathrm{T}}}_{\text{redundant}} + \underbrace{\mathbf{PXQ}^{\mathrm{T}} + \mathbf{QXP}^{\mathrm{T}}}_{\mathbf{X}_{\mathrm{ov}}}$$

  - to avoid problems with redundancies, we use the projected parameterization

$$\mathbf{D}(\mathbf{X}) = \exp(-\mathbf{X}_{\mathrm{ov}}\mathbf{S})\mathbf{D}\exp(\mathbf{S}\mathbf{X}_{\mathrm{ov}}), \quad \mathbf{X}^{\mathrm{T}} = -\mathbf{X}$$

Diagonalization-free Roothaan–Hall SCF optimization

- The SCF (Fock or Kohn–Sham) energy may, in principle, be optimized directly:

$$E_{\min} = \min_{\mathbf{X}} E(\mathbf{X}) \quad \Leftrightarrow \quad \underbrace{\mathbf{F}(\mathbf{D})\mathbf{D}\mathbf{S} = \mathbf{S}\mathbf{D}\mathbf{F}(\mathbf{D})}_{\text{stationary condition}}$$

  - a difficult global minimization problem!

- In MO theory, the Roothaan–Hall SCF scheme works well, especially with DIIS:

$$\mathbf{F} = \mathbf{h} + \mathbf{g}(\mathbf{D}) \quad \underset{D}{\overset{F}{\rightleftarrows}} \quad \mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}; \; \mathbf{D}_{\text{new}} = \mathbf{C}_{\text{occ}}\mathbf{C}_{\text{occ}}^{\mathrm{T}}$$

  - each diagonalization is equivalent to minimizing the sum of the (occ.) orbital energies

$$\varepsilon(\mathbf{X}) = \sum_I \epsilon_I = \operatorname{Tr} \mathbf{D}(\mathbf{X})\mathbf{F}$$

- By analogy with MO theory, we set up the following Roothaan–Hall SCF scheme:

$$\mathbf{F} = \mathbf{h} + \mathbf{g}(\mathbf{D}) \quad \underset{D}{\overset{F}{\rightleftarrows}} \quad \varepsilon_{\min} = \min_{\mathbf{X}} \operatorname{Tr} \mathbf{D}(\mathbf{X})\mathbf{F}; \; \mathbf{D}_{\text{new}} = \mathbf{D}(\mathbf{X})$$

  - at each SCF iteration, we minimize $\operatorname{Tr} \mathbf{D}(\mathbf{X})\mathbf{F}$ with respect to $\mathbf{X}$
  - the new density is then obtained by expansion of $\mathbf{D}(\mathbf{X})$ with the minimizer $\mathbf{X}_*$

- We thus avoid MOs and diagonalization but retain the SCF iterations

Newton minimization of the Roothaan–Hall energy function

- At each SCF iteration, our task is to minimize the Roothaan–Hall energy function

$$\varepsilon(\mathbf{X}) = \mathrm{Tr}\,\mathbf{D}(\mathbf{X})\mathbf{F} = \mathrm{Tr}\,\mathbf{DF} + \mathrm{Tr}\big[\mathbf{D},\mathbf{X}\big]_{\mathrm{S}}\mathbf{F} + \tfrac{1}{2}\,\mathrm{Tr}\big[\big[\mathbf{D},\mathbf{X}\big]_{\mathrm{S}},\mathbf{X}\big]_{\mathrm{S}}\mathbf{F} + \cdots$$

- Truncating to second order and setting the gradient to zero, we obtain the Newton step:

$$\mathbf{HXS} + \mathbf{SXH} = \mathbf{G} \;\leftarrow \text{the Roothaan–Hall Newton equation}$$

  - where the (negative) gradient and Hessian matrices are given by

$$\mathbf{G} = \mathbf{F}^{\mathrm{vo}} - \mathbf{F}^{\mathrm{ov}} \qquad \mathbf{F} = \mathbf{F}^{\mathrm{oo}} + \mathbf{F}^{\mathrm{ov}} + \mathbf{F}^{\mathrm{vo}} + \mathbf{F}^{\mathrm{vv}}$$

$$\mathbf{H} = \mathbf{F}^{\mathrm{vv}} - \mathbf{F}^{\mathrm{oo}}$$

- A RH diagonalization corresponds to an exact minimization (many Newton steps)
  - however, a partial minimization will do
  - in fact, one RH Newton step is usually sufficient
- Because of their large dimensions, the Newton equations cannot be solved directly
  - we use an iterative scheme: the conjugate-gradient method
  - key step: repeated evaluation of the residual $\mathbf{R} = \mathbf{G} - \mathbf{HXS} - \mathbf{SXH}$
  - all operations are elementary (sparse) matrix manipulations

Solution of the Roothaan–Hall Newton equations

- At each SCF iteration, we solve the Roothaan–Hall Newton equations

$$\mathbf{HXS} + \mathbf{SXH} = \mathbf{G}$$

  - a naïve application of the CG method converges slowly
  - the equations are ill-conditioned since $\kappa(\mathbf{H})\kappa(\mathbf{S}) \gg 1$ (κ is the condition number)

- The equations may be made well-conditioned by a Löwdin orthonormalization

$$\widetilde{\mathbf{H}}\mathbf{Z} + \mathbf{Z}\widetilde{\mathbf{H}} = \widetilde{\mathbf{G}}, \quad \widetilde{\mathbf{A}} = \mathbf{S}^{-1/2}\mathbf{A}\mathbf{S}^{-1/2}$$

  - convergence is greatly improved since $\kappa(\widetilde{\mathbf{H}}) = \kappa(\mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2}) \ll \kappa(\mathbf{H})\kappa(\mathbf{S})$
  - we obtain $\mathbf{S}^{-1/2}$ by Taylor expansion
  - orthogonalization is also possible by Cholesky decomposition $\mathbf{S} = \mathbf{U}^{\mathrm{T}}\mathbf{U}$
  - Millam and Scuseria (1996), Challacombe (1998), Head-Gordon *et al.* (2003)

- Further diagonal preconditioning cuts the number of iterations by one half

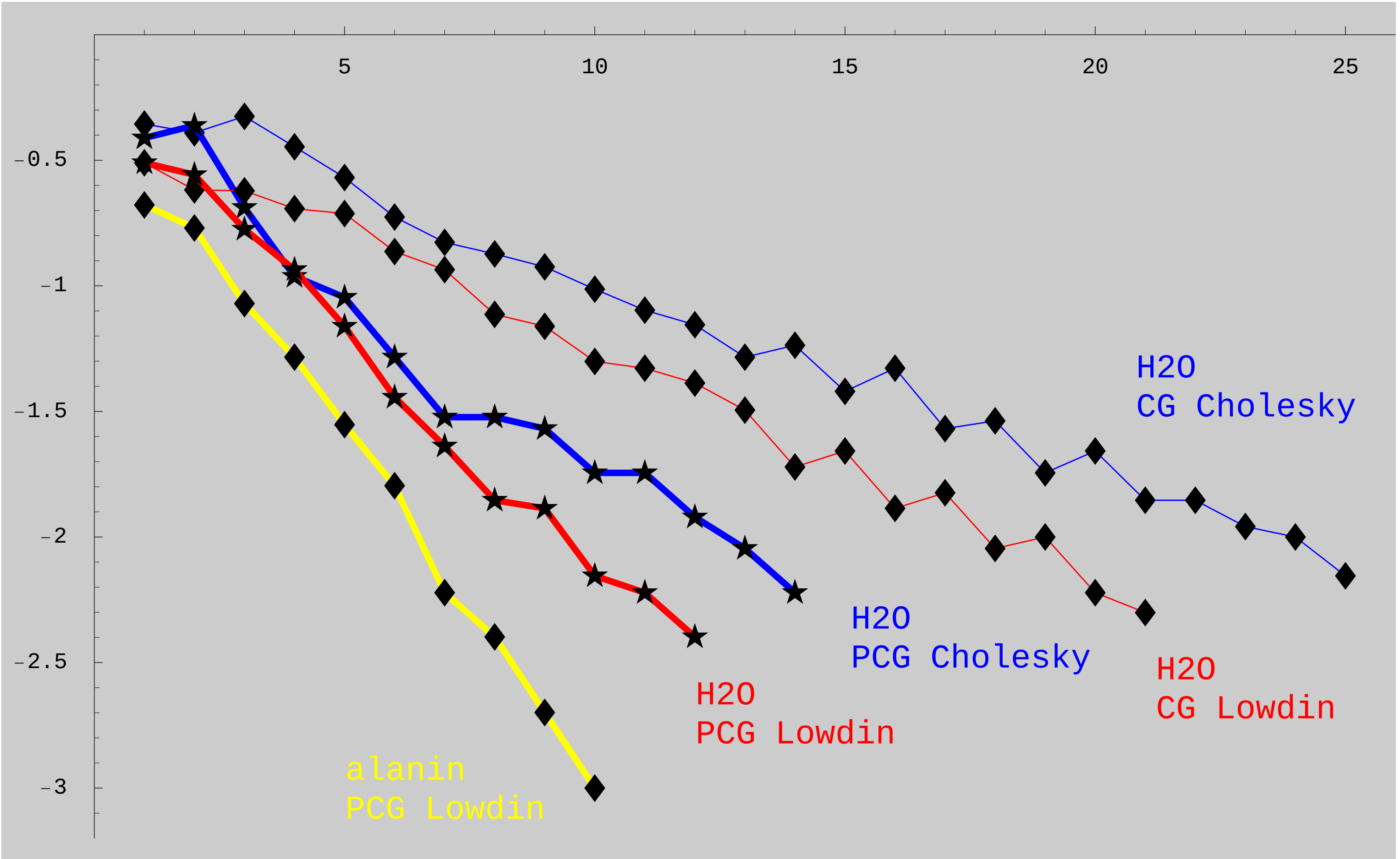
$$\widetilde{\widetilde{\mathbf{H}}} = \widetilde{\mathbf{H}}_{\mathrm{diag}}^{-1}\widetilde{\mathbf{H}}$$

  - 10 iterations typically reduce the residual by two orders of magnitude

- About 70 multiplications needed for one Newton iteration with density-matrix generation

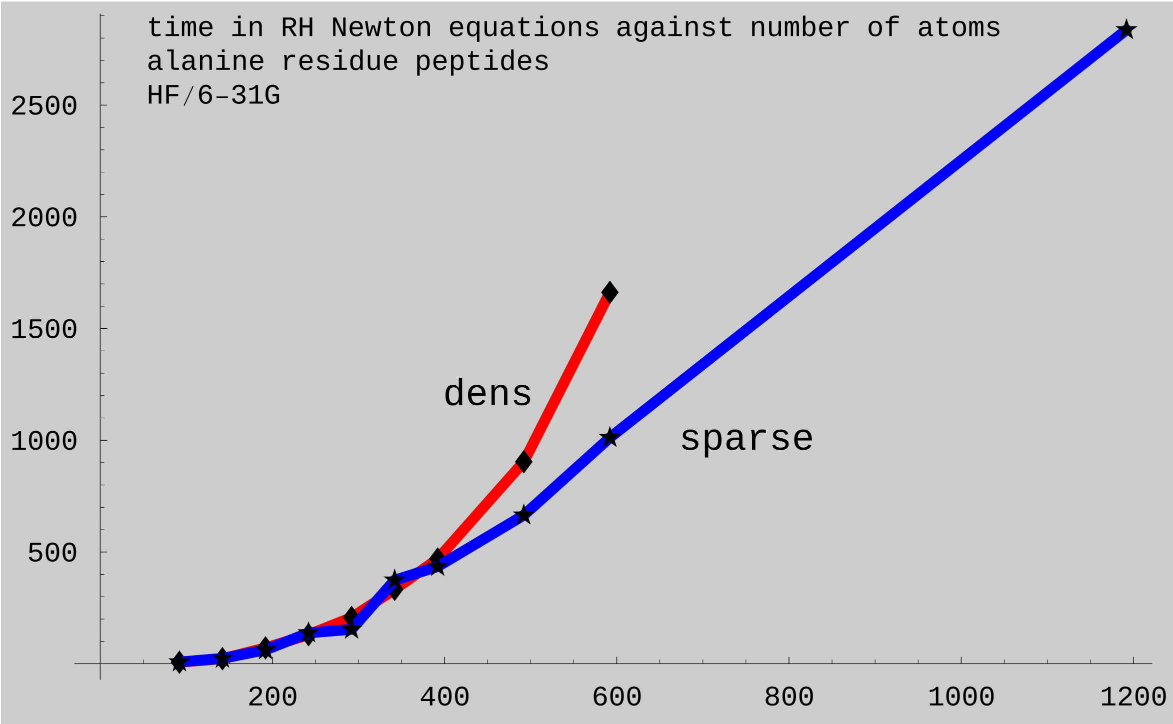
Iterative solution of Roothaan–Hall Newton equations

- Logarithmic plots of the residual against the number of iterations
  - H_2O, LDA/t-aug-cc-pVTZ
  - 99 alanine residue peptides, LDA/6-31G (5449 AOs)



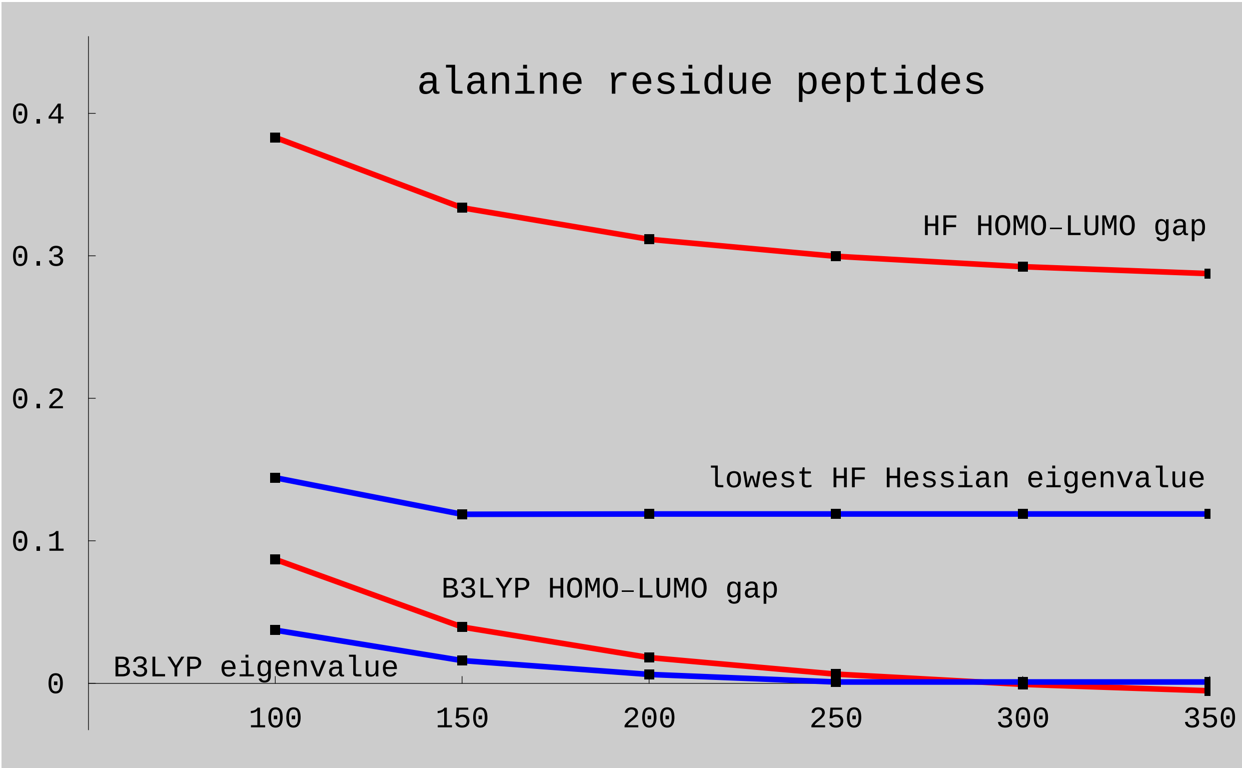
CPU time spent in Roothaan–Hall Newton equations

- We have successfully avoided Fock/Kohn–Sham diagonalization
  - minimization rather than the solution of a generalized eigenvalue problem
  - rapidly convergent: 50–100 sparse matrix multiplications needed
- Linear scaling is obtained by employing sparse-matrix algebra
  - compressed sparse-row (CSR) representation of few-atom blocks



SCF optimizations in small and large molecules

- Diagonalization can be avoided by solving Newton equations
- However, SCF convergence is typically more difficult in larger systems
  - small (or negative) HOMO-LUMO gaps and small Hessian eigenvalues in DFT
  - lowest Hessian eigenvalue and HOMO-LUMO gap in alanine residue peptides (6-31G)



- We have modified the standard SCF scheme, to make it more robust

The trust-region self-consistent field (TRSCF) method

- SCF optimizations have two ingredients
  1. Roothaan–Hall minimization (diagonalization): $\min_{\mathbf{X}} \operatorname{Tr} \mathbf{D}(\mathbf{X})\mathbf{F}$
  2. DIIS-type averaging of density matrices: $\overline{\mathbf{D}} = \sum_{i=0}^{n} c_i \mathbf{D}_i, \; \sum_i c_i = 1$
- In the Roothaan–Hall step, we minimize subject to a constraint on the step size:
  - this amounts to a simple level shifting of the Fock/Kohn–Sham matrix

$$\mathbf{F} \;\rightarrow\; \mathbf{F}(\mu) = \mathbf{F} - \mu \mathbf{S}^{\mathrm{oo}} \quad \text{(only occupied–occupied part shifted)}$$

  - for $\mu > 0$, the HOMO–LUMO gap increases, making large steps unfavourable
  - μ is adjusted until step is of desired length, during the iterative solution
- In the averaging step, we construct a second-order model of the SCF energy

$$E_{\mathrm{DSM}}(c_i) \approx E_{\mathrm{SCF}}(3\overline{\mathbf{D}}\mathbf{S}\overline{\mathbf{D}} - 2\overline{\mathbf{D}}\mathbf{S}\overline{\mathbf{D}}\mathbf{S}\overline{\mathbf{D}})$$

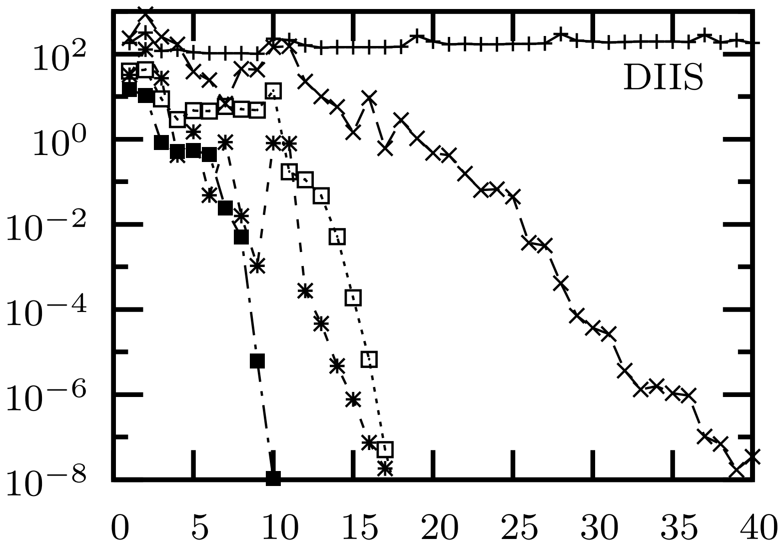
  - it has the correct gradient but an approximate Hessian
  - the best density matrix is obtained by minimization, subject to step-size constraint

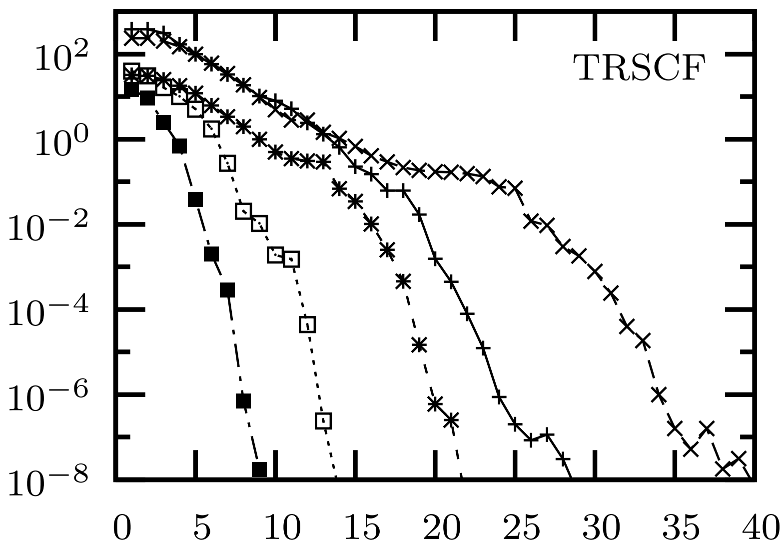
$$\min_{c_i} E_{\mathrm{DSM}}(c_i) \;\leftarrow \text{density-subspace minimization (DSM)}$$

- JCP **121**, 15 (2004); **123**, 074103 (2005)

The TRSCF method (continued)

- The TRSCF method gives a stable and uniform convergence towards the SCF minimum
- Convergence of LDA calculations for a variety of molecules
  - zinc complex(+), rhodium complex(×), cadmium complex(∗), CH_3CHO(□) and H_2O(■)



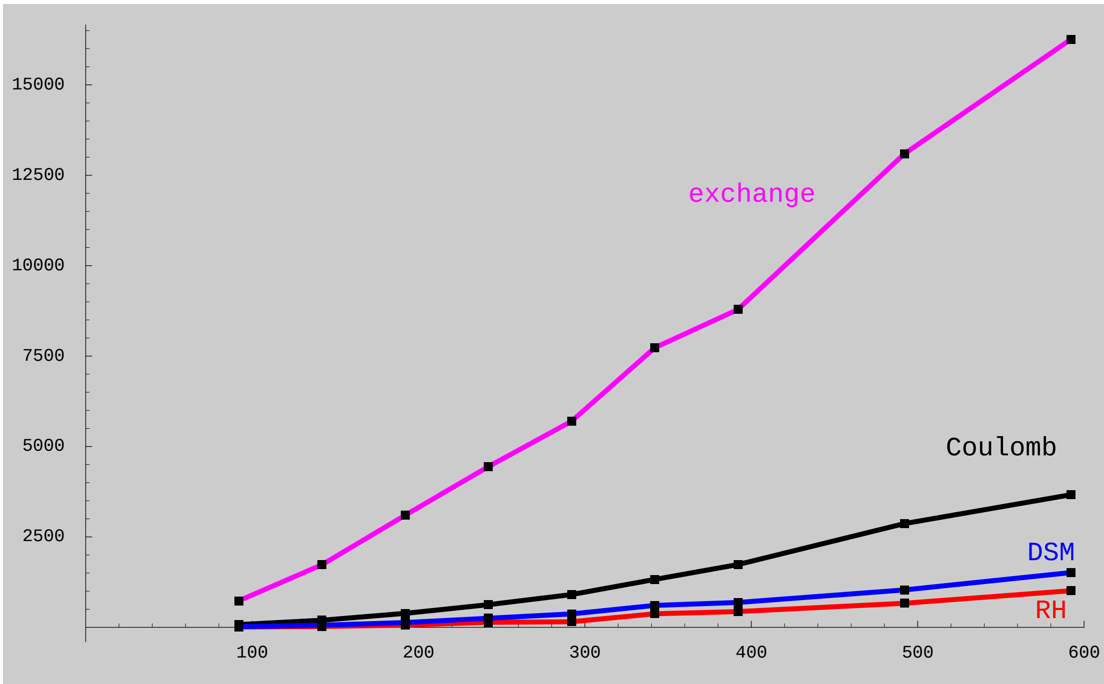


- Problems arise with small Hessian eigenvalues and small (negative) HOMO–LUMO gaps
  - Note: a Newton step of $\mathrm{Tr}\,\mathbf{FD}$ is a quasi-Newton step of $E_{\mathrm{SCF}}(\mathbf{D})$
  - we are doing a quasi-Newton optimization of the energy
  - the quasi-Newton step is poor for small or negative HOMO–LUMO gaps
  - revert to full Newton if necessary: $\min \mathrm{Tr}\,\mathbf{FD} \rightarrow \min E_{\mathrm{SCF}}(\mathbf{D})$

Illustration: alanine residue peptides

- Features of the code
  - diagonalization-free trust-region Roothaan–Hall (TRRH) energy minimization
  - trust-region density-subspace minimization (TRDSM) for density averaging
  - boxed density-fitting with FMM for Coulomb evaluation (Simen Reine)
  - LinK for exact exchange, linear-scaling exchange-correlation evaluation
  - compressed sparse-row (CSR) representation of few-atom blocks

- alanine residue peptides
  - CPU time against atoms
  - HF/6-31G
  - 5th SCF iteration
  - dominated by exchange
  - RH step least expensive
  - full lines: sparse algebra
  - dashed lines: dens algebra



Response theory

- The expectation value of $\hat{A}$ in the presence of a perturbation $\hat{V}_\omega$ of frequency ω:

$$\langle t|\hat{A}|t\rangle = \langle 0|\hat{A}|0\rangle + \int \langle\langle \hat{A}; \hat{V}_\omega \rangle\rangle_\omega \exp(-\mathrm{i}\omega t)\, \mathrm{d}\omega + \cdots$$

  – the linear-response function $\langle\langle \hat{A}; \hat{V}_\omega \rangle\rangle_\omega$ carries information about the first-order change in the expectation value

- The linear-response function may be represented compactly as:

$$\langle\langle \hat{A}; \hat{V}^\omega \rangle\rangle_\omega = -\mathbf{A}^{[1]\,\mathrm{T}} \underbrace{\left(\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]}\right)^{-1} \mathbf{V}_\omega^{[1]}}_{\text{linear equations}} \quad \longleftarrow \begin{cases} \mathbf{E}^{[2]} & \text{electronic Hessian} \\ \mathbf{S}^{[2]} & \text{metric matrix} \\ \mathbf{A}^{[1]} = \mathrm{vec}\left(\mathbf{ADS} - \mathbf{SDA}\right) \end{cases}$$

- In practice, the response functions are evaluated by solving linear equations

$$\left(\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]}\right)\mathbf{N}^{[1]} = -\mathbf{V}_\omega^{[1]}$$

$$\langle\langle \hat{A}; \hat{V}^\omega \rangle\rangle_\omega = \mathbf{A}^{[1]\,\mathrm{T}} \mathbf{N}^{[1]}$$

  – can this be accomplished efficiently in the AO basis?

Solution of the response equations

- The response equations are solved in the same manner as the RH Newton equations:

$$\left(\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]}\right)\mathbf{x} = \mathbf{V}^{[1]}$$

  - transformation to orthogonal basis (Cholesky or Löwdin)
  - generation of an iterative subspace until the residual is sufficiently small

$$\mathbf{R} = \left(\mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]}\right)\mathbf{x} - \mathbf{V}^{[1]}$$

- Key step: multiplication of Hessian and metric matrices with trial vectors

$$\mathbf{E}^{[2]}(\mathbf{X}) = \mathbf{HXS} + \mathbf{SXH} + \mathbf{g}^{\mathrm{vo}}([\mathbf{D}, \mathbf{X}]_{\mathrm{S}}) - \mathbf{g}^{\mathrm{ov}}([\mathbf{D}, \mathbf{X}]_{\mathrm{S}})$$

$$\mathbf{S}^{[2]}(\mathbf{X}) = \mathbf{S}^{\mathrm{oo}}\mathbf{X}\mathbf{S}^{\mathrm{vv}} - \mathbf{S}^{\mathrm{vv}}\mathbf{X}\mathbf{S}^{\mathrm{oo}}$$

  - requires recalculation of Fock/Kohn–Sham matrix with modified AO density matrix

- For rapid convergence, the residual vector is preconditioned

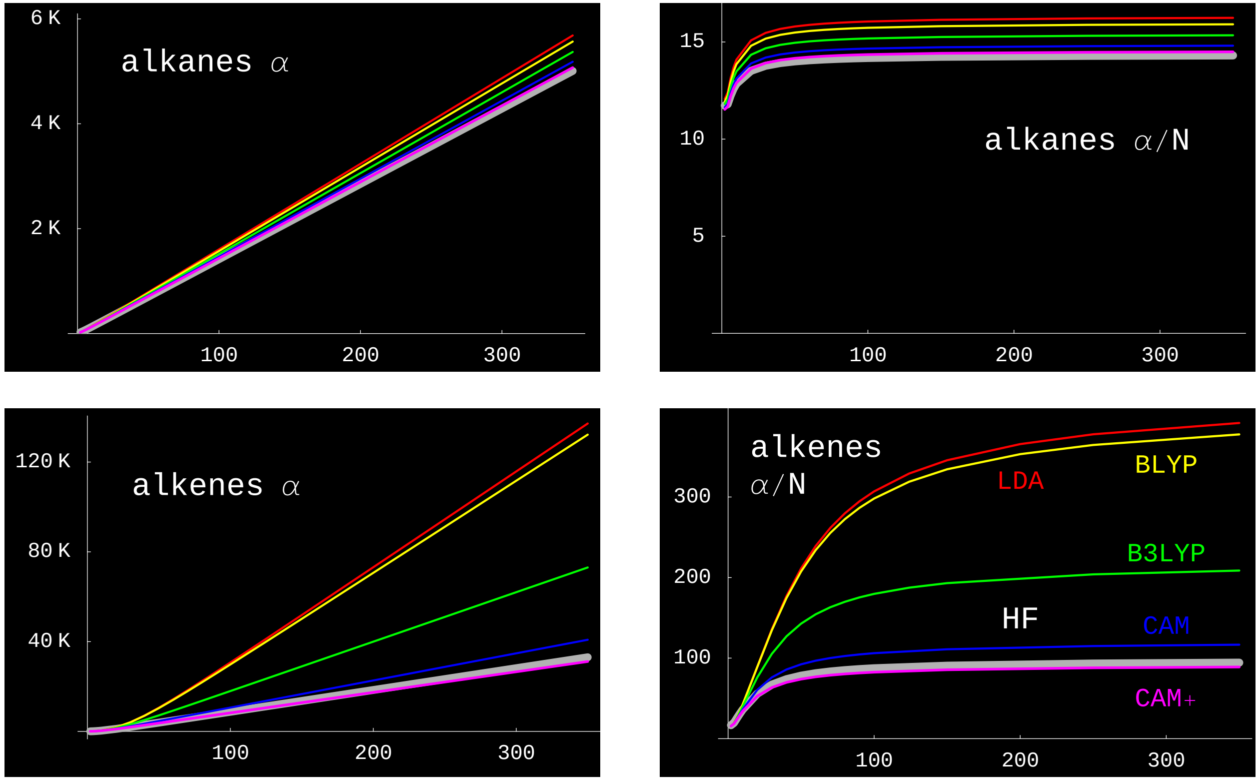
$$\widetilde{\mathbf{R}} = \mathbf{M}^{-1}\mathbf{R}, \quad \mathbf{M} = \mathbf{E}^{[2]} - \omega \mathbf{S}^{[2]} \text{ – expensive parts}$$

  - nondiagonal preconditioning requires about 5 conjugate-gradient steps

- With this preconditioner, the response equations converge in about 4 iterations
  - indeed, this is the same convergence as in the canonical MO basis
  - total cost: 4 Fock/Kohn–Sham evaluations, 100 matrix multiplications

Polarizabilities of linear alkanes and alkenes

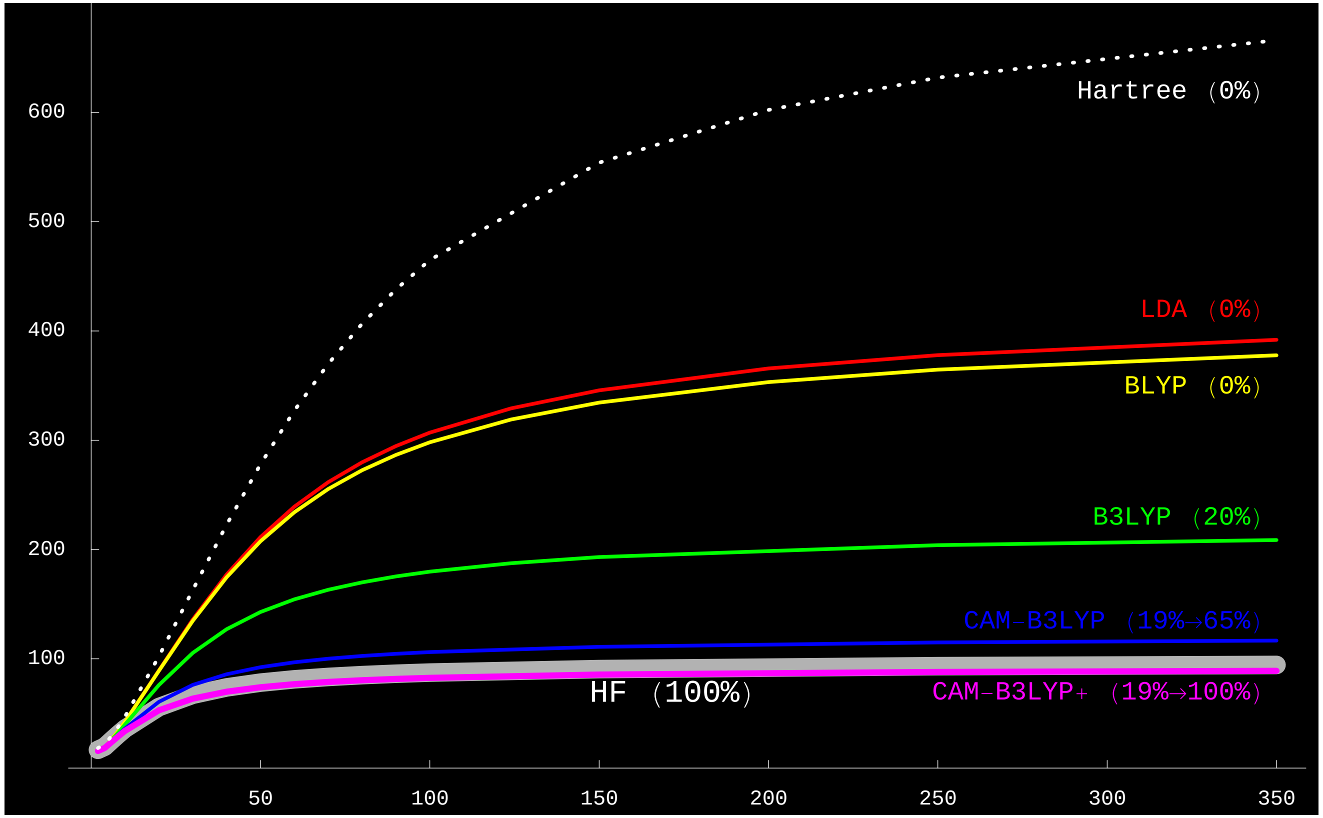
- To illustrate, we have calculated longitudinal polarizabilities in linear polymeric chains
  - HF and DFT α and α/N in 6-31G basis, plotted against the number of carbons N



- The alkenes are about an order of magnitude more polarizable than the alkanes
  - all models agree on alkanes (α/N-limit: HF 14.4; LDA 16.3)
  - widely different results for alkenes (α/N-limit: HF 97; LDA 427)

The importance of exact exchange for longitudinal polarizabilities

- Without a good description of long-range exchange, the systems become too polarizable



  - the Hartree model neglects all exchange and overestimates by a factor of eight
  - pure DFT has a poor long-range exchange and overestimates by a factor of four
  - hybrid functionals improve the situation, introducing some exact exchange
  - compromise solution: standard DFT at short range, full exchange at long range

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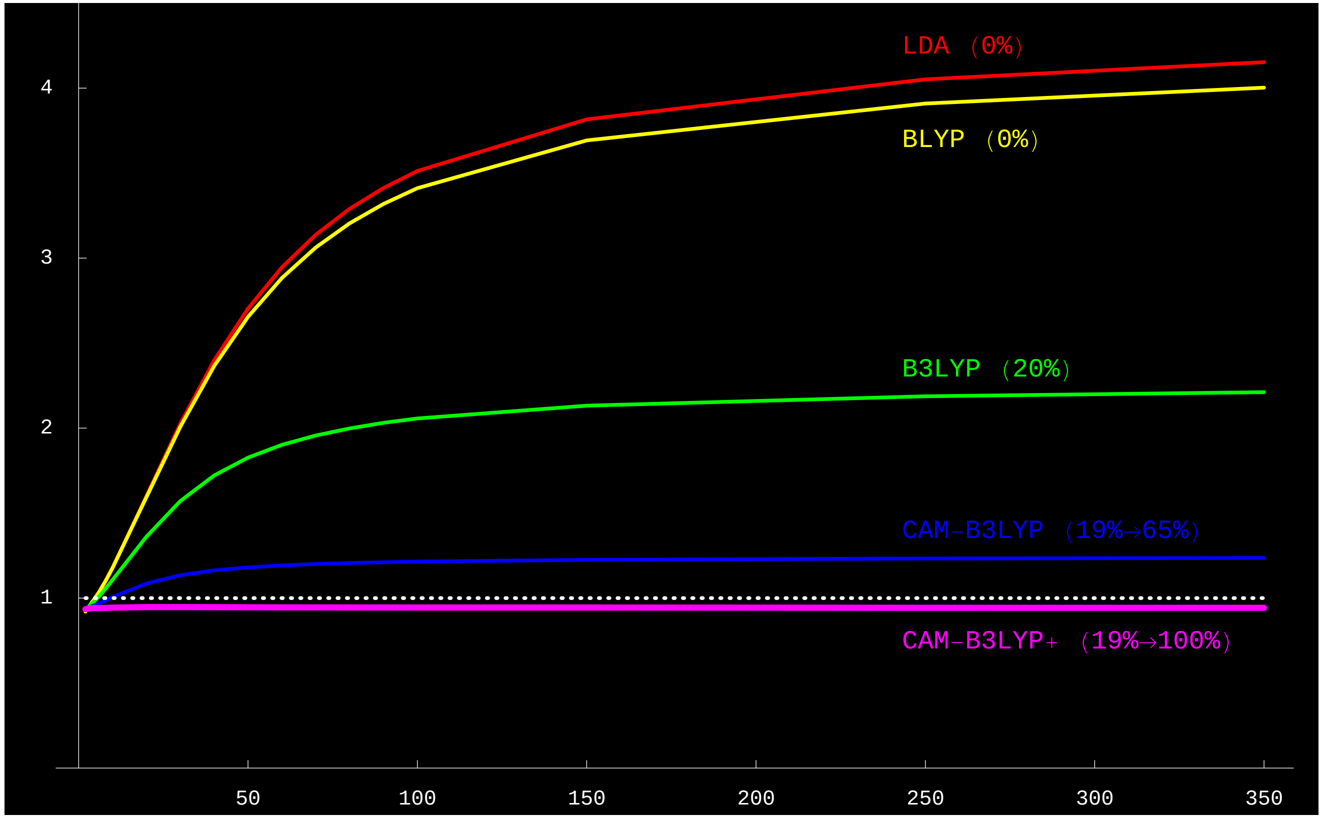

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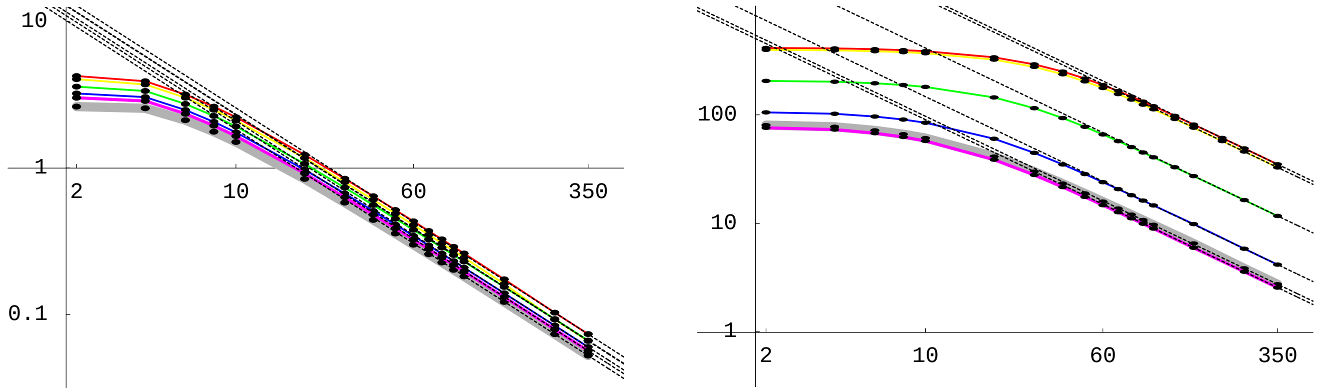
Asymptotic behaviour of group polarizabilities

- How does the group polarizability converge towards the infinite limit?

$$\overline{\alpha}_\infty - \overline{\alpha}_N = eN^{-1} + \mathcal{O}(N^{-2})$$ Kudin *et al.*, JCP **122**, 134907 (2005)

  – this behaviour is universal, holding at all levels of theory

- Log–log plots of $\overline{\alpha}_\infty - \overline{\alpha}_N$ for alkanes and alkenes:



  – limit obtained by extrapolation $\overline{\alpha}_\infty = (\alpha_N - \alpha_M)/(N - M)$

  – straight lines of slope -1 superimposed through the points at $N = 350$

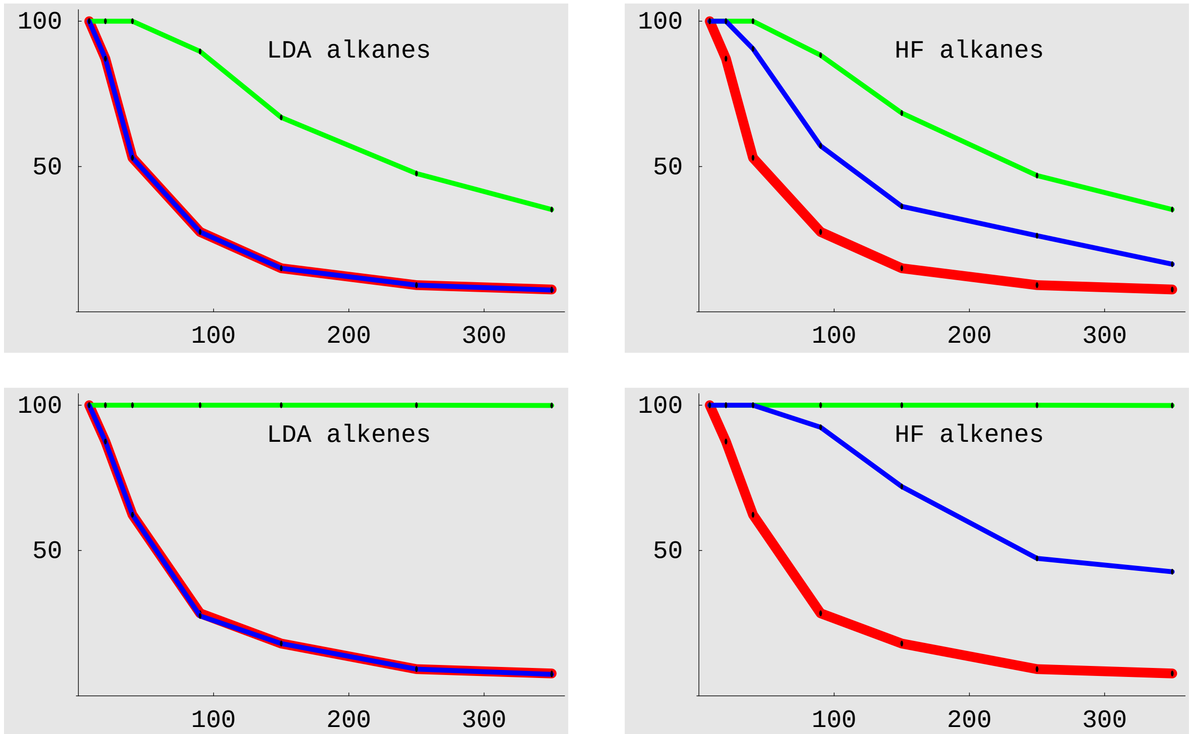
- The asymptotic region is reached with $C_{30}H_{62}$ (alkanes) and $C_{60}H_{62}$ (alkenes)

  – alkane $\overline{\alpha}_\infty$ predicted to within 1% from $C_{30}H_{62}$

  – alkene $\overline{\alpha}_\infty$ predicted to within 1% from $C_{60}H_{62}$ for HF and from $C_{150}H_{152}$ for LDA

Sparsity of linear alkanes and alkenes

- Each energy optimizations were converged in 6–14 SCF iterations
  - about 70 matrix multiplications for each TRRH step (diagonalization)
  - about 50 matrix multiplications for each TRDMS step (DIIS)
- Each polarizability component required 3–4 response iterations
  - about 20 matrix multiplications in each iteration
- Percentage of matrix elements greater than 10^{-6} in alkane and alkene chains
  - overlap matrix:
    - sparse
  - density matrix:
    - nonsparse for alkenes
    - sparse for alkanes
  - Fock/KS matrices:
    - KS matrix like overlap
    - Fock matrix intermediate between overlap and density matrices



Conclusions

- We have discussed the optimization of SCF energies without MOs
  - in each SCF iteration, we replace diagonalization by minimization
  - minimization by Newton's method, one step is usually enough
  - minimization stable and fast, highly competitive with diagonalization
  - 50–100 sparse matrix multiplications required
- Large molecules represent a more difficult minimization problem
  - small Hessian eigenvalues for pure DFT
  - trust-region SCF: careful step-size control
  - revert to second-order if necessary
- Linear-response is straightforward in the AO basis
  - one Fock/Kohn–Sham matrix build and 20 matrix multiplications pr. iteration
  - stable convergence in 3–5 iterations