Modern finite-element methods applied to non-relativistic atomic calculations

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Basis sets in chemistry

Most quantum chemical calculations are performed with atomic basis sets

- linear combination of atomic orbitals (LCAO) approach

The LCAO approach has many benefits

- compact basis, only tens–few hundred functions per atom
- all-electron calculations feasible!
- straightforward chemical interpretation
- (usually) systematic error cancellation $\implies$ relative energies order(s) of magnitude more accurate than total energies

Basis sets: cardinal number

The quality of the basis is typically reported in terms of the cardinal number n. For instance, for oxygen ($1s^2 2s^2 2p^4$)

- single-ζ, minimal basis (MB); 2s1p
- polarized double-ζ (pVDZ) $\rightarrow$: 3s2p1d
- polarized triple-ζ (pVTZ) $\rightarrow$: 4s3p2d1f
- polarized quadruple-ζ (pVQZ) $\rightarrow$ 4s3p2d1f
- polarized quintuple-ζ (pV5Z) $\rightarrow$ 5s4p3d2f1g
- polarized hextuple-ζ (pV6Z) $\rightarrow$ 6s5p4d3f2g1h
- ...

Basis sets: quality

Linear combination of atomic orbitals (LCAO) often yields reliable results at low cost

- single-ζ: qualitative results; symmetry of ground state wave function?
  - atoms can't breathe or polarize $\implies$ **useless for chemistry**
- double-ζ: semi-quantitative accuracy for DFT
- triple-ζ: semi-quantitative accuracy for DFT, "minimal basis" for post-Hartree–Fock calculations
- quadruple-ζ and higher
  - **excellent accuracy for DFT, "basis set limit"**; useful for benchmark studies
  - **good for post-HF**; should also extrapolate to CBS

Types of radial basis sets

The atomic basis sets are of the form

$$\psi_{nlm} = R_{nl}(r) Y_{lm}(\hat{\mathbf{r}})$$

- almost all quantum chemistry is done with Gaussian basis sets

$$R_{nl}(r) = \sum_k d_{kn} r^l \exp(-\alpha_k r^2)$$

- Slater orbitals found usually in textbooks, not in practice

$$R_{nl}(r) = r^l \exp(-\zeta_n r)$$

- numerical atomic orbitals (NAOs) typically not even mentioned
  - but approach common in solid-state physics in density functional calculations (with pseudopotentials / PAWs)
  - all-electron approaches: proprietary Dmol^3, FHI-aims programs

Promise of numerical orbitals

NAOs are promising for quantum chemistry

- limited applications so far with high-level methods, e.g. coupled-cluster theory
- NAOs have local support: $\psi(\mathbf{r}) = 0$ for $r > r_\infty \implies$ better sparsity for molecular integrals
- modern parallel computers excellent for quadrature

$$O_{\mu\nu} = \int \chi_\mu(\mathbf{r}) \hat{O} \chi_\nu(\mathbf{r}) \mathrm{d}^3 r = \sum_p w_p \chi_\mu(\mathbf{r}_p) \hat{O} \chi_\nu(\mathbf{r}_p)$$

Few systematic basis sets published so far

- limited to density functional calculations
- established methods for building Gaussian basis sets can be used to build NAO basis sets
- could e.g. pseudopotentials / PAW setups be generated with higher-accuracy calculations?

History of atomic and diatomic calculations

Fully numerical approaches have a long history in quantum chemistry both for atoms and diatomic molecules, as discussed in a recent review paper (696 references).

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REVIEW

International Journal of QUANTUM CHEMISTRY WILEY

A review on non-relativistic, fully numerical electronic structure calculations on atoms and diatomic molecules

Susi Lehtola

Limitations of existing approaches

Most programs are limited

- low-order numerical methods require $\mathcal{O}(10^4\text{–}10^5)$ radial points to converge energy tightly i.e. to sub-μE_h level
- self-consistent field convergence slow (large # of dofs!), no modern convergence accelerators used
- programs have only had few density functionals, no support for hybrid functionals and/or meta-GGA functionals
- usually not parallellized and written in Fortran 77

Computers and algorithms have developed a lot in the past 40 years $\implies$ new implementations beneficial

New code: HelFEM

I have written a finite element program for electronic structure calculations on atoms and diatomic molecules: $\hat{H}_{\mathrm{el}}$FEM or HelFEM. A version of the code is available on GitHub (`https://github.com/susilehtola/HelFEM`).

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FULL PAPER

International Journal of Quantum Chemistry WILEY

Fully numerical Hartree-Fock and density functional calculations. I. Atoms

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FULL PAPER

International Journal of Quantum Chemistry WILEY

Fully numerical Hartree-Fock and density functional calculations. II. Diatomic molecules

Susi Lehtola

Note language barrier!

Quantum chemistry and atomic physics are closely related disciplines separated by the same language

- quantum chemists' Hartree–Fock $\neq$ atomic physicists' Hartree–Fock
  - single-configuration = single-determinant *vs* single-configuration = multi-determinant
- physicists' Hartree–Fock = chemists' multiconfigurational self-consistent field (MCSCF) or complete active space (CAS)
- physicists' multiconfiguration Hartree–Fock = chemists' state interation configuration interaction
- chemists' single-determinant calculations typically break symmetry for open-shell atoms
  - single-determinant HF yields lower energies than multideterminant HF (Löwdin's symmetry dilemma!); radial orbitals not spin-restricted
  - need flexible approaches to describe symmetry breaking

New code: HelFEM, cont'd

HelFEM follows the standard LCAO-type quantum chemistry formulation – full diagonalization is possible even with tens of thousands of numerical basis functions. Variational results guaranteed; symmetry breaking can be studied.

Further benefit: maximal reuse of code from Gaussian programs, include powerful convergence acceleration methods, e.g. Pulay DIIS and GDM.

Hundreds of LDA, GGA, and meta-GGA functionals supported via Libxc.

Original software publication

Recent developments in libxc — A comprehensive library of functionals for density functional theory

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Fock matrix

Standard LCAO quantum chemistry formulation: Fock matrix is given by

$$\mathbf{F}(\mathbf{C}) = \mathbf{T} + \mathbf{V} + \mathbf{J}(\mathbf{C}) - \mathbf{K}(\mathbf{C})$$

where $\mathbf{T}$ is kinetic energy, $\mathbf{V}$ is nuclear attraction, $\mathbf{J}(\mathbf{C})$ is Coulomb matrix, and $\mathbf{K}(\mathbf{C})$ is exchange matrix. In addition, $\mathbf{S}$ is overlap.

Fock matrix $\hat{F}$ depends on the electron density: $\mathbf{F} = \mathbf{F}(\mathbf{C}) \implies$ minimization of the total energy is a difficult problem. But, problem is independent of basis set

- We can adopt a variety of algorithms for accelerating self-consistent field convergence in LCAO calculations
- Employ modern convergence accelerators: ADIIS followed by DIIS. Also other choices possible.

New code: HelFEM, cont'd

Code is still actively worked upon. Current capabilities

- spin-restricted, spin-restricted open shell and spin-unrestricted calculations
- quick SCF convergence with ADIIS+DIIS
- Hartree–Fock or DFT with LDA, GGA and meta-GGA functionals including global hybrids
- range separated hybrids also supported in the case of atoms

Basis set limit

In LCAO, the electronic orbitals (1-particle states) are written in terms of basis functions as

$$|\psi\rangle = \sum_i \langle i|\psi\rangle \, |i\rangle = \sum_i c_i \, |i\rangle$$

The expansion implicitly assumes that the basis set is complete

$$\sum_i |i\rangle \langle i| = \mathbf{1}$$

which is never really the case, since the basis is finite.

Basis set limit: Addition of more basis functions changes result only negligibly. Easy to do in a fully numerical approach.

Finite elements

Fully numerical calculations employ basis sets that are not motivated by chemistry.

Finite elements: divide space into regions, represent functions (electronic structure) within each region. Glue the element functions together so continuity is ensured.

Elements can be of various sizes and accuracies. How do we describe the electronic structure within a single element?

Lagrange interpolating functions (LIPs)

Math formulation: we have a region $\xi \in [\xi_0, \xi_1]$ where we want to represent function $f(\xi)$. How to formulate a suitable basis to do this with arbitrary accuracy?

Simplest solution: Lagrange interpolating polynomials (LIPs). Choose a set of control points ξ_i on the interval. Identify the value $f(\xi_i)$ at any point to arise from a single LIP:

$$\phi_i(\xi_j) = \delta_{ij}$$

which is solved by

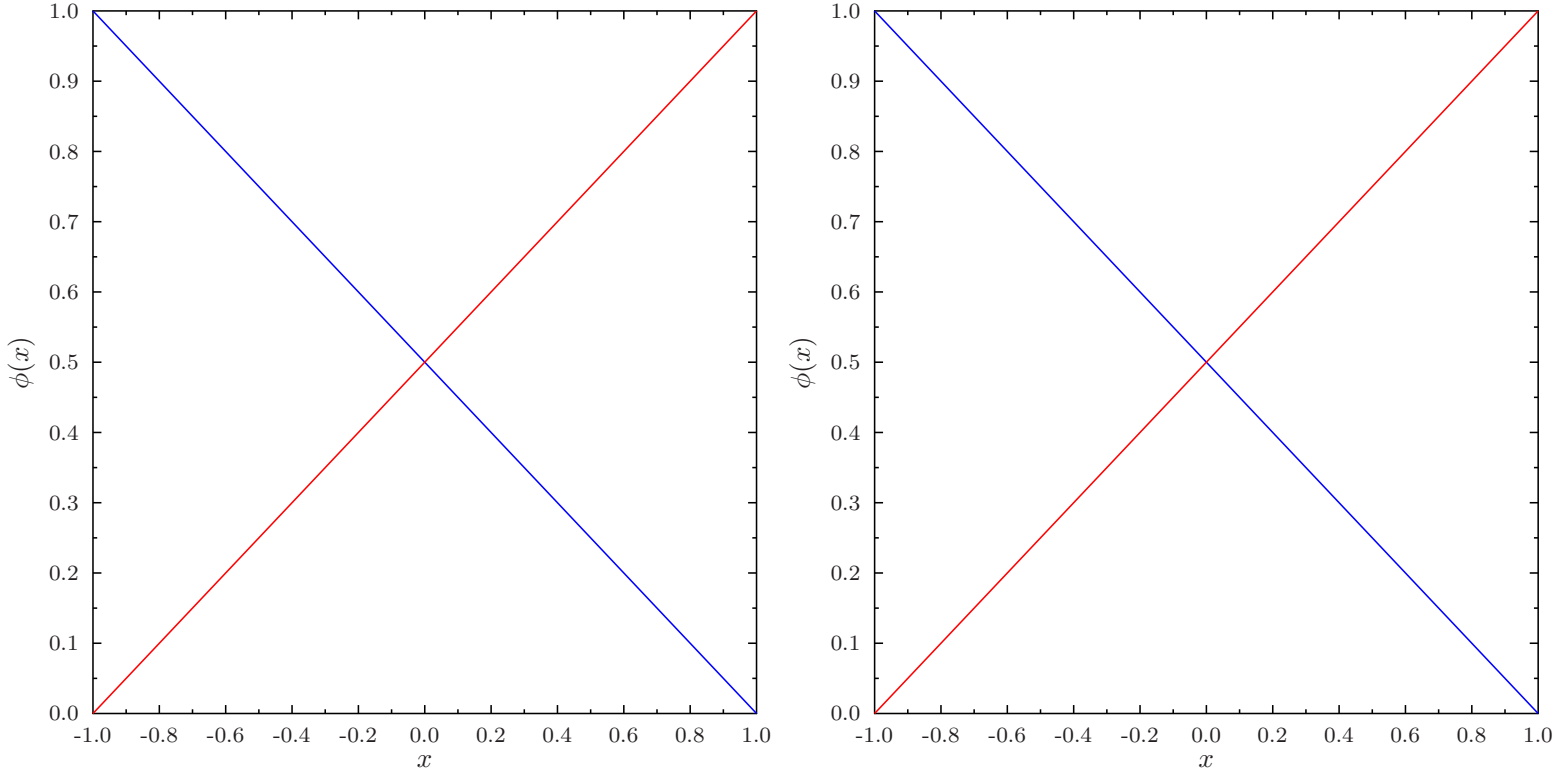
$$\phi_i(\xi) = \prod_{k \neq i} \frac{\xi - \xi_k}{\xi_i - \xi_k}$$

Function is approximated on interval as

$$f(\xi) \approx \sum_j f(\xi_j)\phi_j(\xi)$$

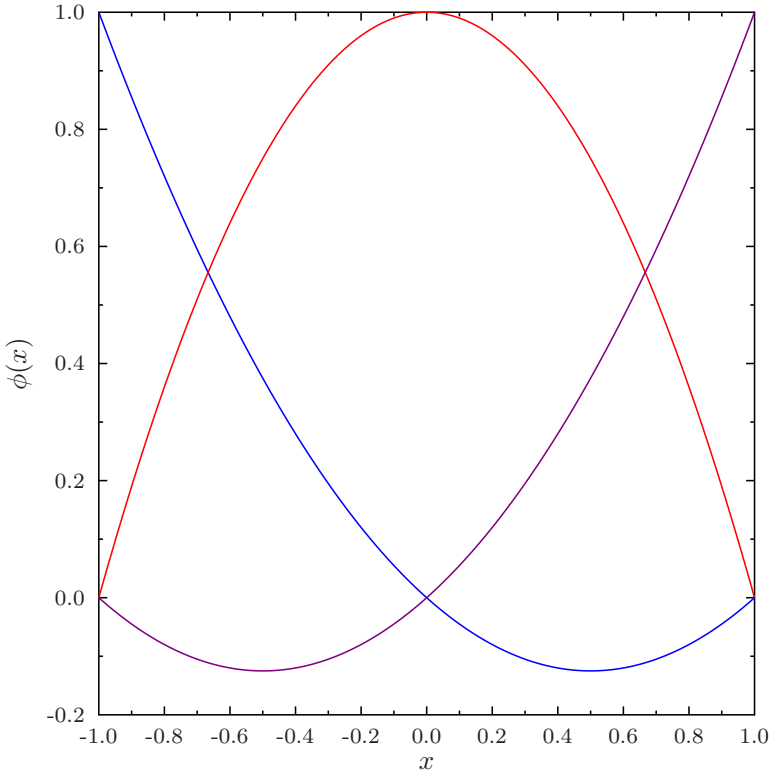
2-node LIPs

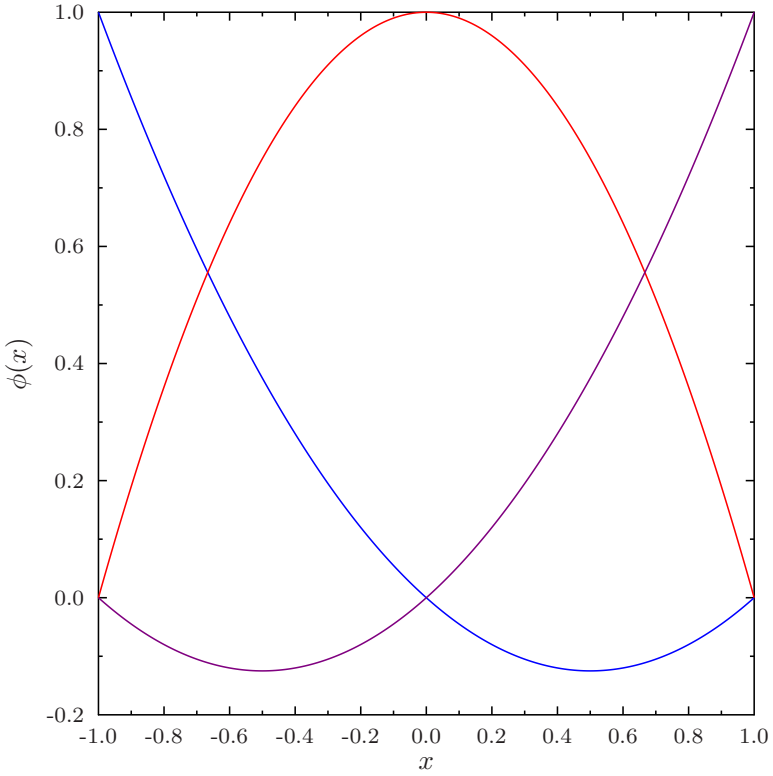
For two nodes in an element, we get the triangle functions, since the function value has to be continuous over the edges of the elements. (Function 2 continued to the right becomes function 1, since both are defined by the same control node.)



3-node LIPs

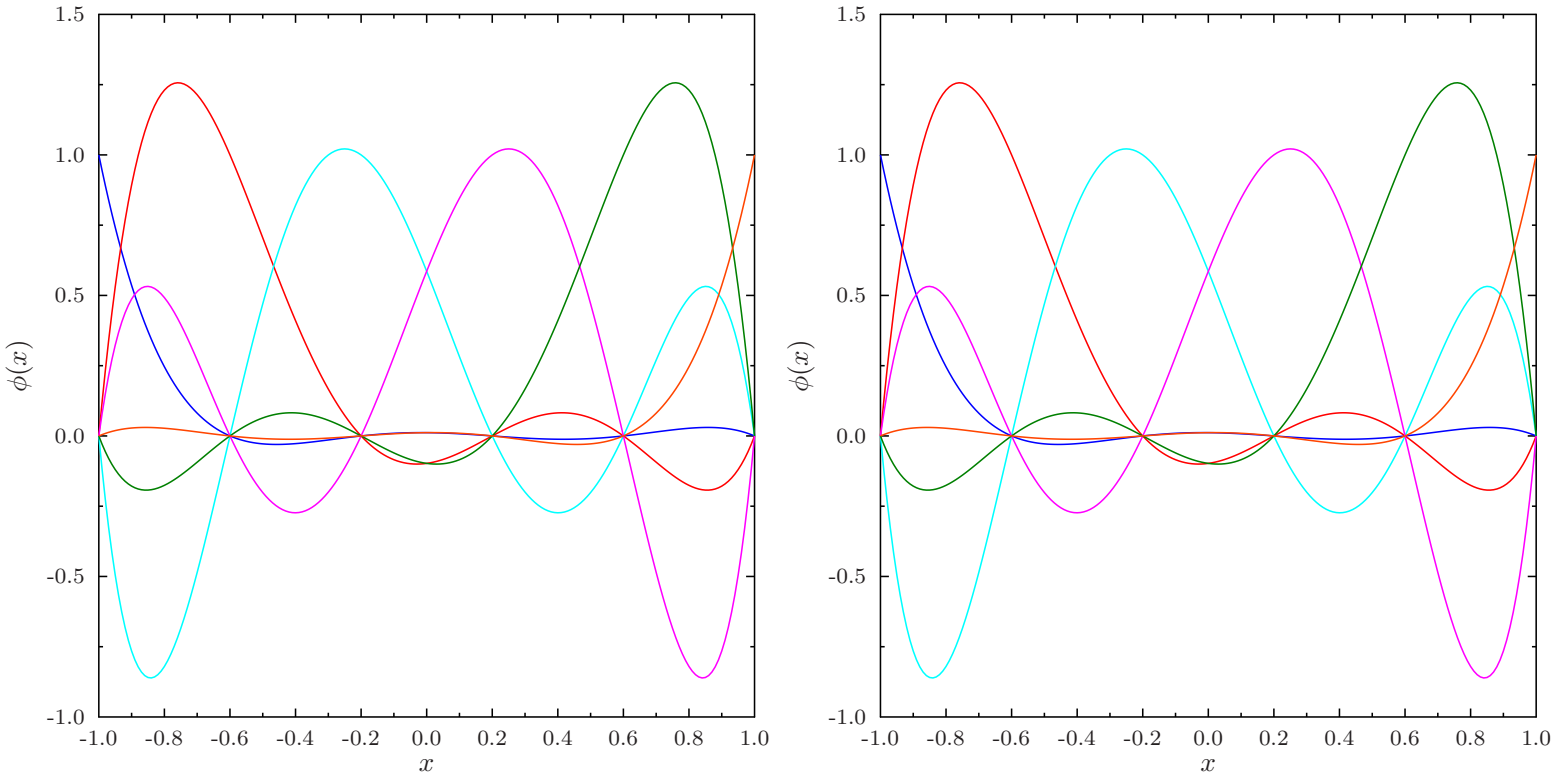
For three nodes, we get the following. The function corresponding to the middle node is purely in-element.





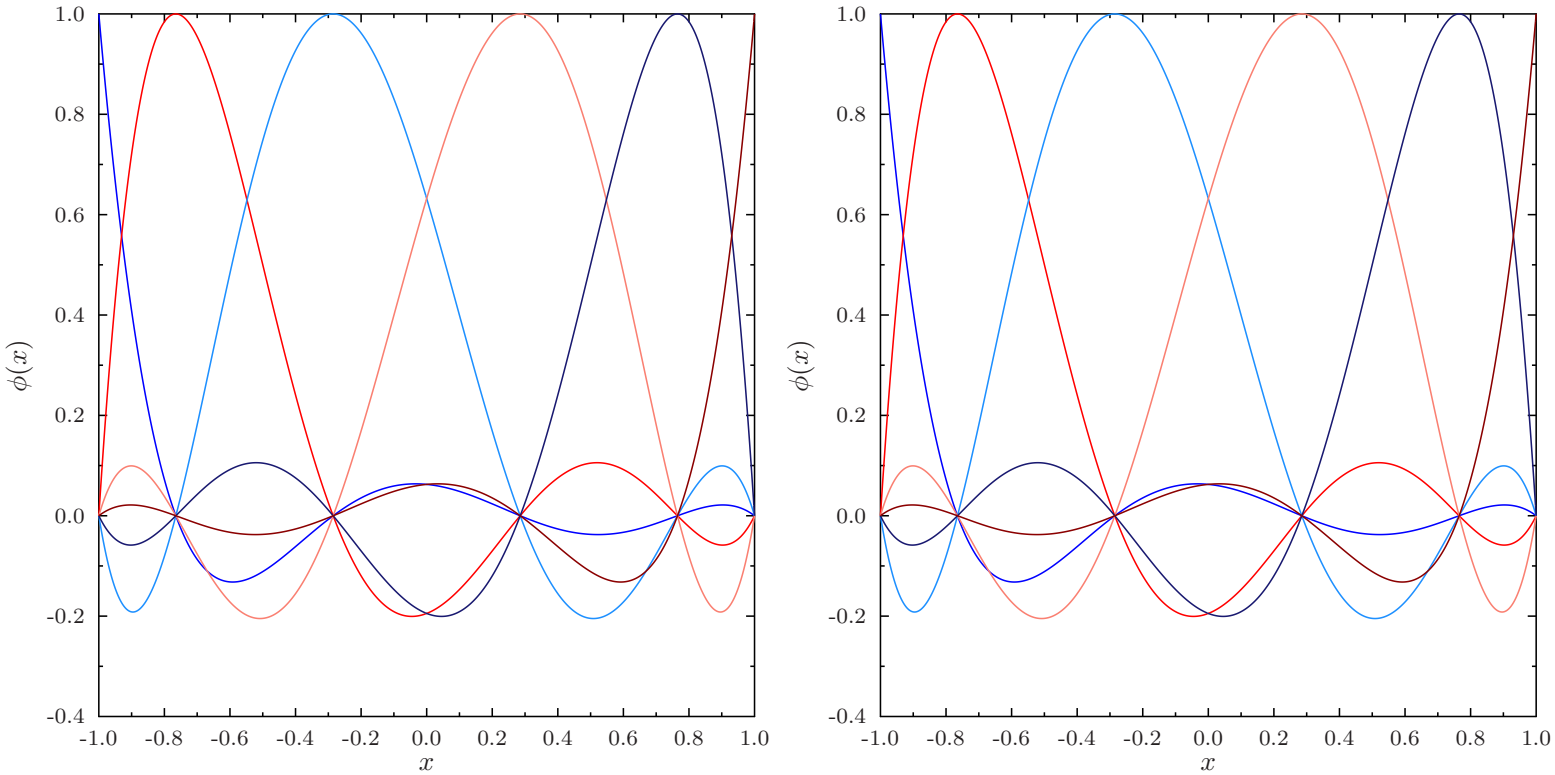
6-node LIPs

Six-node LIPs are quintic polynomials.



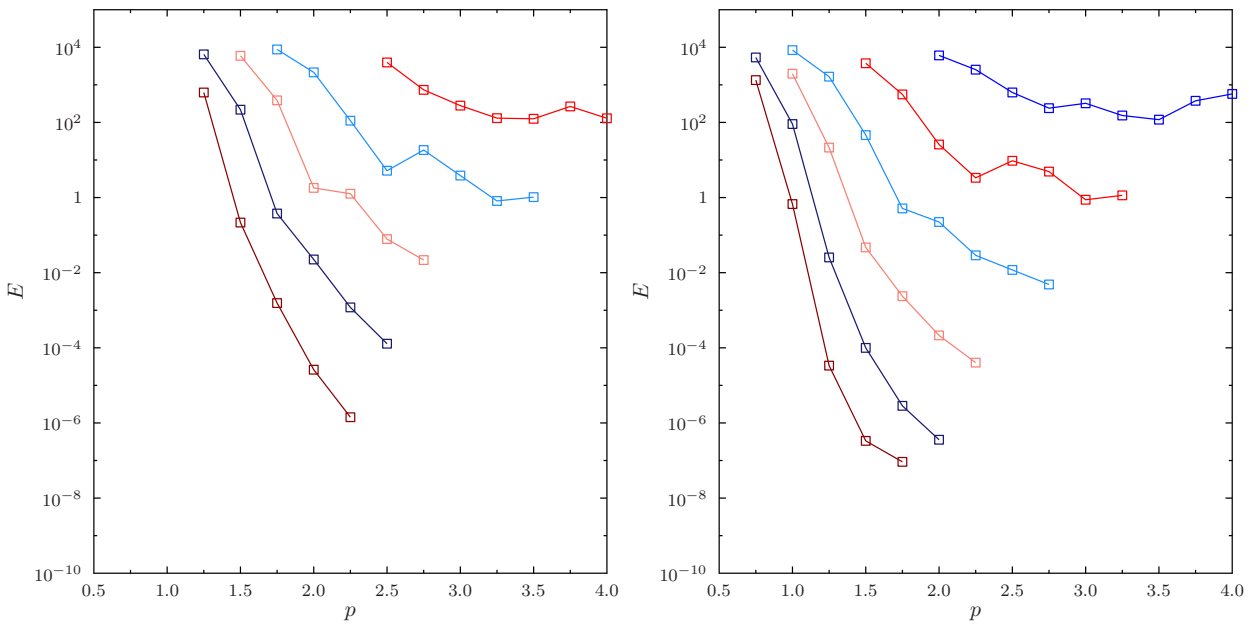
LIPs with Lobatto nodes

Going to higher order elements it becomes beneficial to employ non-uniform nodes, as this yields better numerical stability. An especially accurate basis is obtained by choosing the nodes from Gauss–Lobatto quadrature, e.g. six-node ones look like



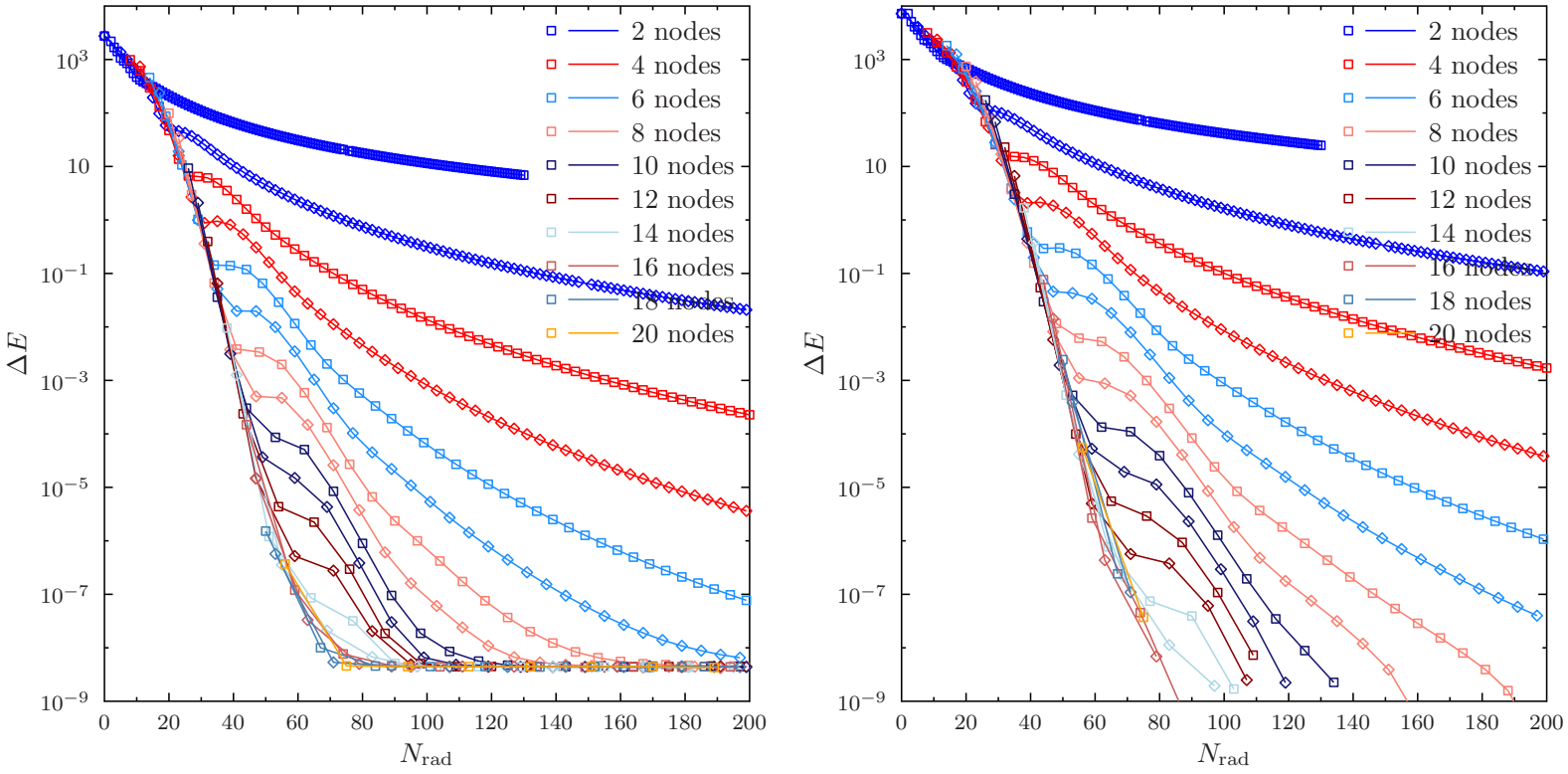
Convergence

Very accurate solutions can be obtained with suitable tuning of the radial element grid. Example: Hartree–Fock energy for Og atom ($Z = 118$) with a polynomial (left) or exponential (right) grid, with 5, 10, 20, 40, 80, and 160 six-node elements.



Convergence, cont'd

The accuracy can be further increased by using higher-order elements. Example: Hartree–Fock energy for Kr ($Z = 36$) and Xe ($Z = 54$) atoms with various elements.



- **nE_h level accuracy achievable with just $\mathcal{O}(100)$ radial functions**

New initial guesses

JCTC Journal of Chemical Theory and Computation Article
Cite This: J. Chem. Theory Comput. 2019, 15, 1593–1604 pubs.acs.org/JCTC

Assessment of Initial Guesses for Self-Consistent Field Calculations. Superposition of Atomic Potentials: Simple yet Efficient

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HelFEM has been used to generate atomic potentials for an alternative initial guess for electronic structure calculations: use sum of converged atomic $V(r)$ to initialize calculations on polyatomic systems.

Efficient implementation of the superposition of atomic potentials initial guess for electronic structure calculations in Gaussian basis sets

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Fractional occupations

The atomic approach has recently been extended to range-separated exchange functionals (error function or Yukawa kernel) as well as fractional occupations that make density spherically symmetric $n_\sigma = n_\sigma(r)$

PHYSICAL REVIEW A **101**, 012516 (2020)

Fully numerical calculations on atoms with fractional occupations and range-separated exchange functionals

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Resulting finite element calculations afford accurate atomic potentials for use in SAP guess.

Atomic configurations

Physicists' density functional calculations on atoms usually employ fractional occupations

- same technique used in atomic Hartree–Fock for forming initial guesses for polyatomic systems (both SAP and SAD)

Problem: using fractional occupations changes the functional; what are the corresponding occupations for the ground state?

- new ground states identified for non-relativistic Hartree–Fock
  - spin-restricted calculations, $n_\alpha(r) = n_\beta(r)$: Phys. Rev. A 101, 012516 (2020); doi:10.1103/PhysRevA.101.012516
  - spin-unrestricted calculations, $n_\alpha(r) \neq n_\beta(r)$: J. Chem. Phys. 152, 144105 (2020); doi:10.1063/5.0004046
- differences found for transition metals and lanthanides/actinides; new configurations yield much better guesses than experimental ground state

Atoms and density functionals

Atomic calculations can also be used to assess density functionals

- a good density functional should
  1. allow accurate energy of the total energy $E_{\mathrm{xc}} = \int n(\mathbf{r})\epsilon_{\mathrm{xc}}(n, \dots)\mathrm{d}^3 r$ at fixed density
  2. allow converging the density tightly in a fixed basis set in a SCF calculation
  3. converge quickly to the complete basis set limit when running larger and larger basis sets

The work in HelFEM on density functionals revealed issues in many functionals; several recent ones fail already for criterion 1!

Many recent density functionals are numerically ill-behaved

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Wrapup

Current status

- modern numerical methods allow for extremely compact radial expansions
- orbitals converge within a dozen iterations with established self-consistent field accelerators
- convergence can be speeded up by using guess orbitals from pretabulated potentials

On-going work

- new modular libraries for electronic structure theory
  - implement state-of-the-art orbital optimizers and convergence accelerator algorithms in a method-agnostic manner
  - implement atomic guesses in a portable manner

Future work

- include electron correlation with CASSCF/RASSCF
- extend to relativistic (X2C or four-component) calculations and finite nuclei

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