Ab initio treatment of systems with translational symmetry using confined Gaussians

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Treatment of periodic systems

Approaches for finite systems:

- Very versatile Gaussian-based quantum chemistry codes
  $\longrightarrow$ do not use translational symmetry.

Treatment of periodic systems

Approaches for finite systems:

- Very versatile Gaussian-based quantum chemistry codes
  ⟶ do not use translational symmetry.

Approaches for infinite periodic systems:

- Periodic boundary conditions ⟶ Bloch waves.
  - ⋆ Plane-wave basis sets (and its variants).
  - ⋆ CRYSTAL: Bloch *ansatz* using Gaussians.
- Cluster calculations (extrapolation to infinite size)
  ⟶ method of increments.
- Cellular method (based on concept of Wigner and Seitz)
  ⟶ single cell, periodicity encoded in boundary conditions.

Finite systems with translational symmetry

Motivation:

- Real systems are not infinite (important example: nanophysics).
- Effects of terminal end groups may be important for properties.
- Defects (may be responsible for the “interesting” physics).
- Assumed infinity may cause trouble
  (calculation of polarizability etc. see, e. g. project Springborg).

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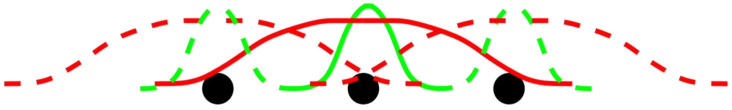
Natural starting point: standard quantum chemistry approaches.

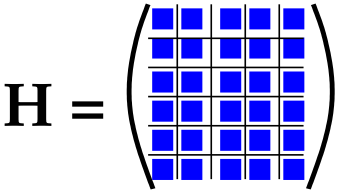
Question:

How can the translational symmetry efficiently be used???

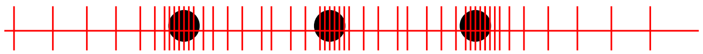
Basis functions

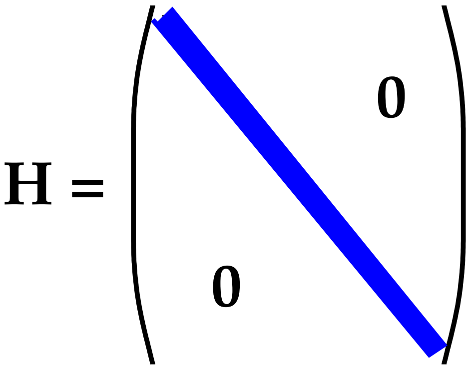
Global basis functions (Gaussians):



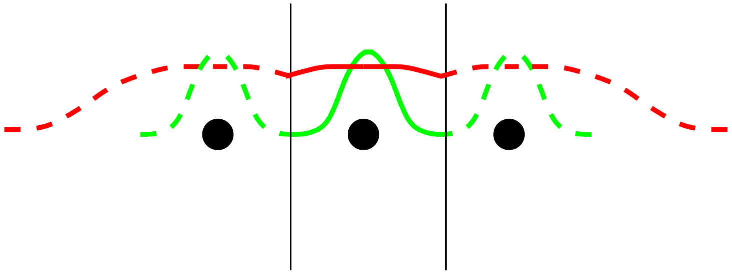


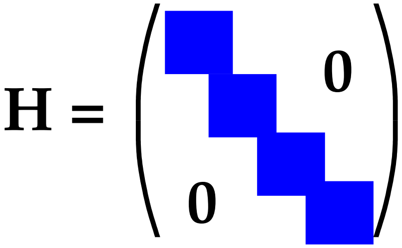
Local basis functions (FEM):





Confined Gaussians:





Finite systems

- The wavefunction is expressed in terms of confined Gaussians, non-zero only within a single unit cell.
- **Non-zero integrals only for Gaussians in the same cell.**
- Interaction with next-neighbour cell Gaussians (but only with them!) through **connectivity requirement**.
- No new integrals appear when adding a further monomer unit!
- **Finiteness, terminal groups, and defects can be considered.**
- **The locality can be used for an iterative procedure:**
  Update wavefunction in one cell while keeping it fixed in the others, continue with next cell, . . . , start again with first cell, . . . , proceed until full convergence is reached.

Infinite periodic systems

Cellular method for infinite periodic systems:

- Based on Wigner-Seitz approach, uses translational symmetry in real (not k) space.
- *Ansatz:* Infinite periodicity $\longrightarrow$ full solution contained in a single cell (volume Ω), periodicity enters via boundary conditions.

Weak formulation (Pask *et al.*, Comp. Phys. Comm. **135**, 1 (2001):

$$\mathbf{H}\,\mathbf{c} \;=\; \epsilon_{\vec{k}}\,\mathbf{S}\,\mathbf{c}$$

$$H_{i,j} \;=\; \int_{\Omega} [\,\nabla\phi_i\cdot\nabla\phi_j \;-\; 2i\,\vec{k}\cdot\phi_i\nabla\phi_j \;+\; (V+k^2)\,\phi_i\phi_j\,]\,\mathrm{d}\Omega$$

Note: The ϕ need only be **value periodic**, $\phi(\vec{r}\,) \;=\; \phi(\vec{r}+\vec{R})$.

Connectivity problem

Final wavefunction must be continuous across boundaries!

- Note, value continuity (C^0) at the boundaries is sufficient!
- As Pask *et al.* have shown: for the cellular method value periodicity is sufficient.

Possible solutions:

- For cell-centred Gaussians value continuity and periodicity are relatively easy to fulfill (but this results in strong limitation).
- Use of compact atom-centred and diffuse cell-centred Gaussians.
- Add polynomial basis functions (at mirror positions).
  [Identical geometrical shape, no difficult new integrals.]

The key integrals

Required: Calculation of the integrals within the cell volume Ω

$$H_{i,j} = \int_\Omega \phi_i \, \hat{\mathrm{H}} \, \phi_j \, \mathrm{d}\Omega \qquad \text{and} \qquad S_{i,j} = \int_\Omega \phi_i \, \phi_j \, \mathrm{d}\Omega$$

where the volume boundaries may be finite or infinite.

Preliminary work:

- All integral types (overlap, kinetic energy, nuclear attraction, and electron repulsion) have been formulated and tested.
- Approach is limited to orthogonal cells (at most orthorhombic).
- Worst case (all boundaries finite) was tested, partly infinite boundaries (easier!) and other efficiency issues have still to be addressed.

Goals:

Implement and test performance of three methods (starting with 1D periodicity [polymers] and pseudopotentials, DFT, or RHF):

Method 1:

- Use global Gaussians, but implement translational symmetry on the level of integral calculation.
- Analyse the unit-cell contributions to properties.

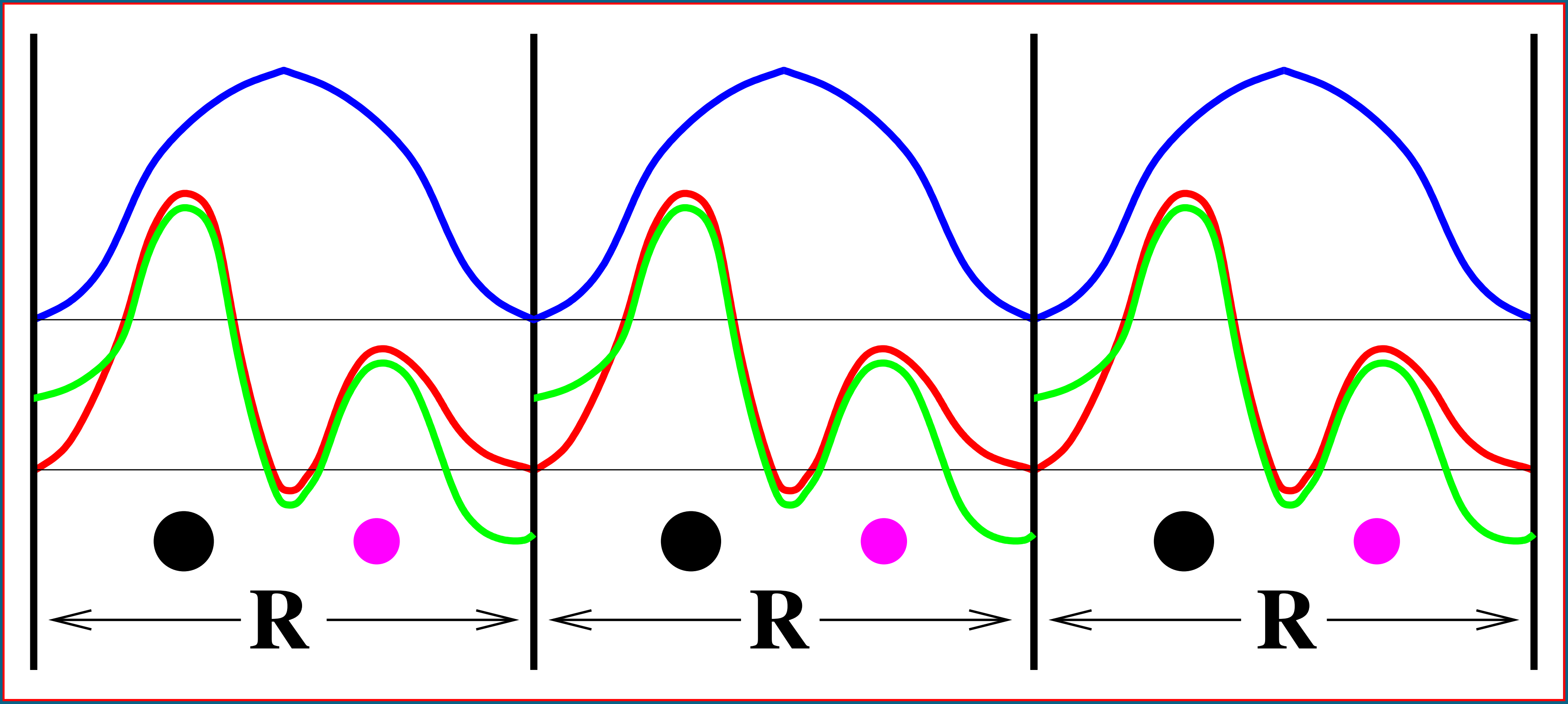
Method 2:

Combine the advantages of Gaussians (describing molecular orbitals) with the advantages of finite-element approaches.

2A: Use spatially confined Gaussians for finite periodic systems.

2B: Use spatially confined Gaussians for infinite periodic systems.

Connectivity (II)



Method 1: Basics

- Consider a polymer consisting of 5 monomers, A to C, where (in general) A, C $\neq$ B (see Fig. 1).
- The space may be divided into 5 (semi-infinite) subspaces.
- The Hamiltonian can be partitioned into contributions from those spatial volumes.
- This is a consequence of the additivity property of integrals.
- Every integral (example: one-electron operator $\hat{\mathrm{O}}$) may be written:

$$O_{i,j} = \sum_{m=1}^{5} I_{i,j}^{(m)} = \sum_{m=1}^{5} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{z_{m-1}}^{z_m} \phi_j^* \, \hat{\mathrm{O}} \, \phi_i \, \mathrm{d}V \quad \text{where} \quad \begin{array}{l} z_0 = -\infty \\ z_5 = +\infty \end{array}$$

Method 1: Discussion

- Many integral pieces $I_{i,j}^{(m)}$ will identically occur for different integrals $\longrightarrow$ no recalculation is needed.
- The gain should be most pronounced when considering sequences of polymers with N, $N+1$, $N+2$, . . . monomers.
- Applicability to finite systems (including the explicit consideration of terminal groups and possible defects).
- Could also be used for infinite systems (cluster calculations).
- Of interest for orbital localization or analysis of properties (dipole moments etc.; also using, e. g., cluster-calculation wavefunctions)?
- Efficiency of $I_{i,j}^{(m)}$ calculation in comparison to standard integrals and index-based consideration of translational symmetry?