Ab Initio Cyclic Cluster Model

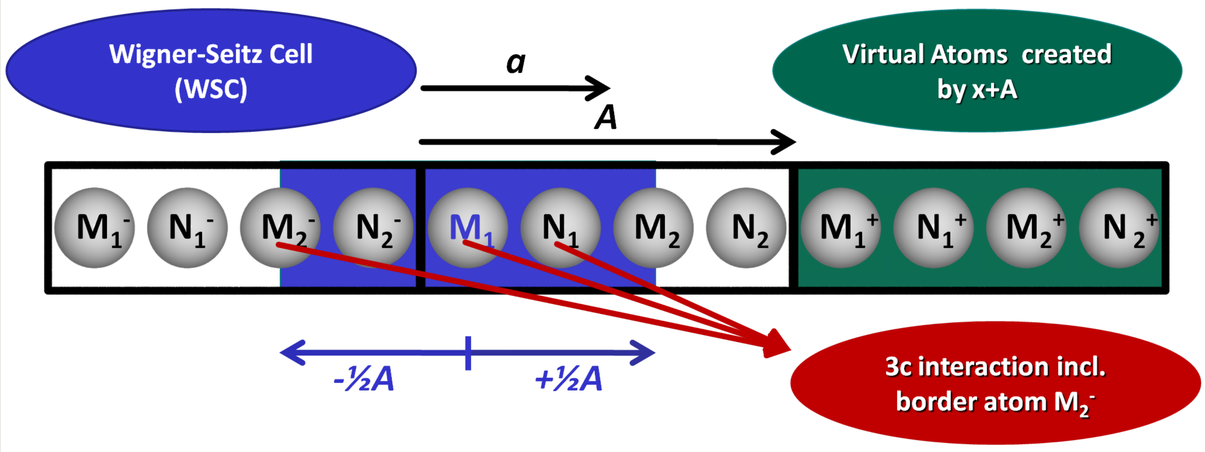
Michael F. Peintinger and Thomas Bredow

Institute of Physical and Theoretical Chemistry, University of Bonn

Introduction

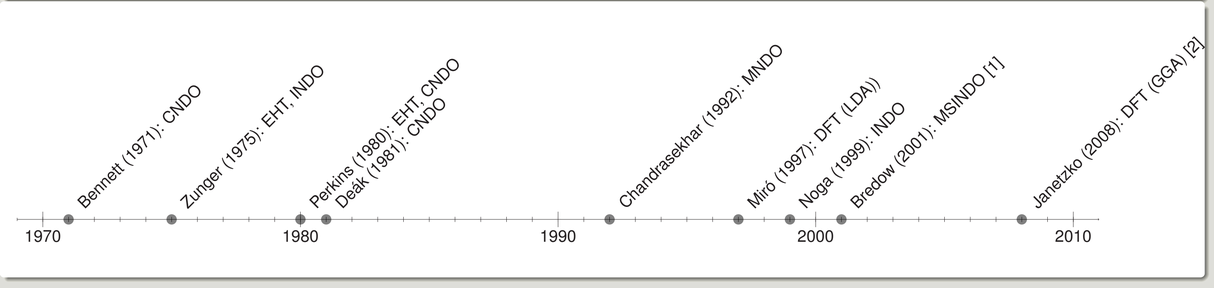
- The Cyclic Cluster Model (CCM) directly applies periodic boundary conditions (PBC) to a finite free cluster corresponding to a non-primitive unit cell
- The interaction range of every atom within the cluster is defined by its Wigner-Seitz Cell (WSC) defined by the translation vectors
- In contrast to conventional periodic models, the CCM is a Γ point approach and integration is carried out in real space
- The challenge for the development of the CCM at *ab initio* level is the treatment of three- and four-center integrals
- Special attention has to be paid to atoms at the border of WSCs, interactions have to be weighted correctly
- Post-Hartree-Fock methods can in principle be applied to the CCM without further modifications

The Cyclic Cluster Model in a Nutshell



The figure shows a one-dimensional Cyclic Cluster of a fictive MN system. The primitive cell vector is given by **a**, the non-primitive CCM translation vector is by **A**. The WSC of atom M_1 is highlighted in blue. M_1, N_1, M_2, N_2 are the so called *real* atoms. *Virtual* atoms are created by linear combination of atomic positions and the CCM translation vectors and are denoted by superscripted "+" for +**A** and "-" for -**A**. *Virtual* atoms created by +**A** are highlighted in green. A three-center (3c) interaction including an atom at the cell border, that has to be weighted accordingly is indicated in red.

Implementations of the Cyclic Cluster Model



Cyclic Cluster Hartree-Fock Theory

The *overlap matrix* $\mathbf{S}^{CCM}$, the *Coulomb matrix* $\mathbf{J}^{CCM}$ and the *exchange matrix* $\mathbf{K}^{CCM}$ have the elements

$$S_{\mu\nu} = \sum^{WSC(\mu)} \omega_{MN} \langle \mu | \nu \rangle \quad (1)$$

$$J_{\mu\nu} = D_{\sigma\rho} \sum^{WSC(\mu)} \omega_{MNRS} (\mu\nu|\rho\sigma) \quad (2)$$

$$K_{\mu\nu} = D_{\sigma\rho} \sum^{WSC(\mu)} \omega_{MNRS} (\mu\sigma|\rho\nu) \quad (3)$$

The Hartree-Fock-Roothaan equations can be solved as in the molecular case. The weighting scheme ensures electroneutrality and imposes proper symmetry.

AICCM: Implementation of the CCM at *Ab Initio* Level

The Atomic Simulation Environment (ASE) [3] provides Python modules for manipulating atoms, analyzing simulations and visualization and is interfaced by various quantum chemical codes.
AICCM is an object oriented, educational quantum chemical code written in the Python scripting language with C extensions.

- Depends on the ASE ("calculator")
- Makes heavy use of Python modules (NumPy, SciPy, matplotlib) and LAPACK routines
- Routines that require fast implementations are written in C (integral handlers)
- An interface to Libint [4], a library of C/C++ functions for efficient evaluation of several kinds of two-body molecular integrals over Gaussian functions, is currently under development
- Open Source (GNU General Public License Version 3)

AICCM Features

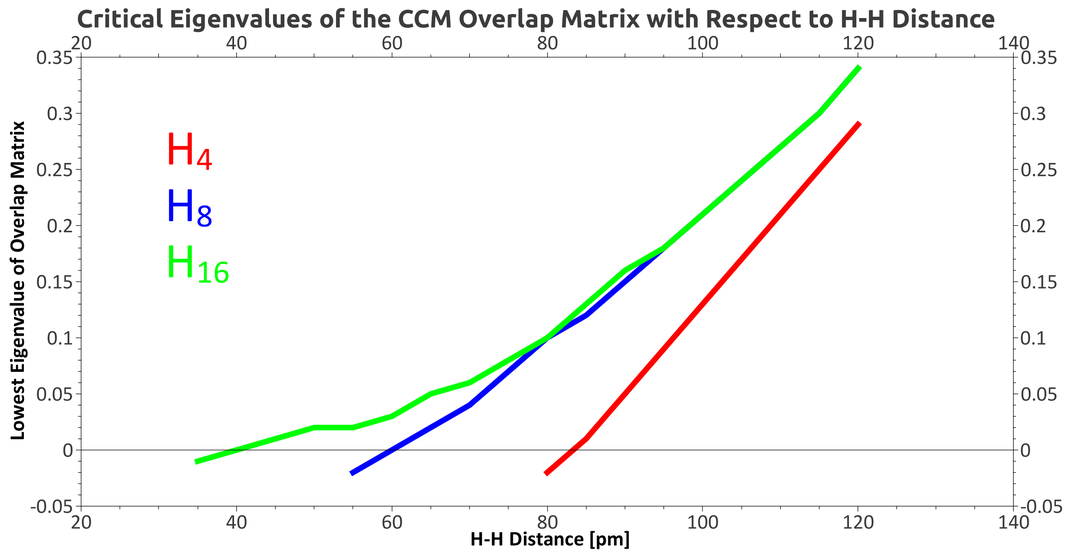
- Supports restricted and unrestricted molecular Hartree-Fock calculations (RHF, UHF), periodic RHF/UHF via the CCM under development
- Linear Combination of atomic orbitals (LCAO)
- Gaussian basis sets in CRYSTAL or TURBOMOLE format
- Convergence acceleration: Direct Inversion in Iterative Subspace (DIIS), Fock matrix mixing (FMixing), Level shift and Second-Order SCF (SOSCF)
- Simple weighting scheme for CCM calculations
- Parallelization via the multiprocessing module (OpenMP)
- Plotting of SCF convergence, Density of States (DOS) via matplotlib
- Interfaces to external graphical tools for plotting molecular and crystalline orbitals (Gabedit, Molden)

Critical Eigenvalues of the Overlap Matrix

By applying PBC to the overlap matrix, a small atomic overlap of one atom with a distant atom is replaced by a larger overlap with an equivalent *(virtual)* atom created by the translation vector **A**, if this is closer. The CCM *overlap matrix* $\mathbf{S}^{CCM}$ might become **indefinite**.

FCM and CCM overlap matrices of H_4 (H-H=0.74 Å, STO-3G basis):

$$\mathbf{S}^{FCM}_{H4} = \begin{pmatrix} 1.00 & 0.66 & 0.26 & 0.08 \\ 0.66 & 1.00 & 0.66 & 0.26 \\ 0.26 & 0.66 & 1.00 & 0.66 \\ 0.08 & 0.26 & 0.66 & 1.00 \end{pmatrix} \quad \mathbf{S}^{CCM}_{H4} = \begin{pmatrix} 1.00 & 0.66 & 0.26 & \mathbf{0.66} \\ 0.66 & 1.00 & 0.66 & 0.26 \\ 0.26 & 0.66 & 1.00 & 0.66 \\ \mathbf{0.66} & 0.26 & 0.66 & 1.00 \end{pmatrix}$$



- Cluster size has to be increased which leads to more demanding calculations
- Screening out negative eigenvalues via single value decomposition (SVD)
- Algorithms that can be applied to indefinite matrices?
- Extension of Wigner-Seitz Cell size leading to longer interaction ranges?

Future Developments

- Analytical Hartree-Fock gradients for molecular and periodic CCM calculations
- Development of a new weighting scheme based on spheres
- Implementation of the Split-RI-chain-of-spheres algorithm (RIJCOSX) [5]
- Approximate inclusion of long-range Coulomb interactions via Ewald summation
- Solve linear dependency via canonical orthogonalization (Cutoff for small entries in the overlap matrix that lead to indefinite matrices) or new algorithms

Literature

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[5] F. Neese, F. Wennmohs, A. Hansen, U. Becker, Efficient, approximate and parallel Hartree-Fock and hybrid DFT calculations. A Chain-of-spheres algorithm for the Hartree-Fock exchange, Chemical Physics 356 (1-3) (2009) 98 – 109, moving Frontiers in Quantum Chemistry: - Electron Correlation, Molecular Properties and Relativity.

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mpei@thch.uni-bonn.de