Quantum Chemistry of Periodic Systems

The Cyclic Cluster Model at *ab initio* Level

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2013/02/01

Outline

1. Introduction
2. Theoretical Framework
   - Periodic Boundary Conditions
   - From Wigner-Seitz cells to cyclic clusters
   - Treatment of Integrals
3. Implementation
   - Atomic Simulation Environment
   - AICCM Program
4. Results

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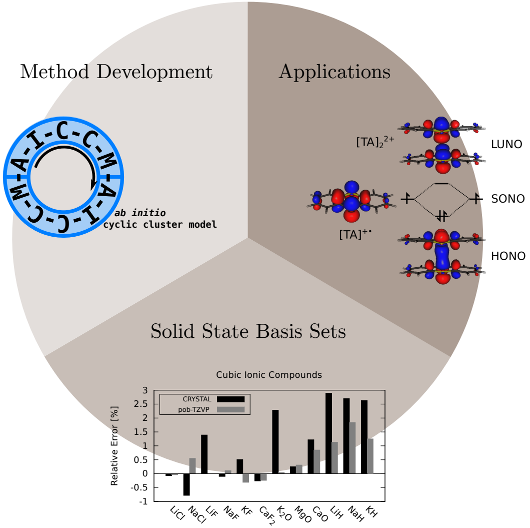

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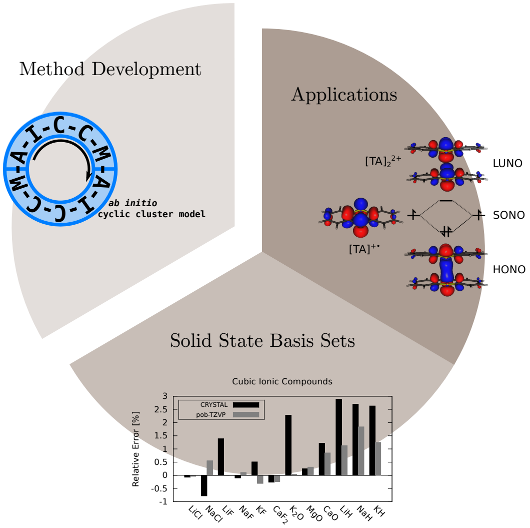

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Motivation

SFB813 Project C5: Spin centers in molecular solids - From paramagnetic salts to organic conductors

- Stacked arrangements of organic radical cations may lead to organic semiconductors exhibiting magnetic properties besides the conductivity
- Theoretical prediction of stacking behavior from first principles of donor molecules
- Investigation of intermolecular spin center interactions of molecular crystals that feature stacked arrangements of radical cations
- Development of new methods that combine advanced quantum chemical methods with periodic boundary conditions

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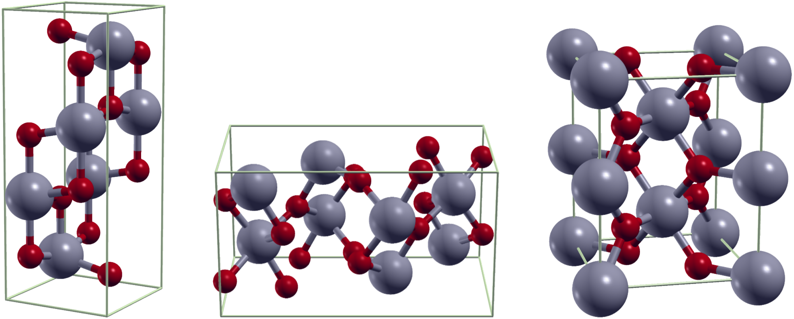
Correlated methods in solids?



(a) Anatase (b) Brookite (c) Rutile

The phase stability of TiO_2 modifications is still unsolved!

Models for the quantum chemical treatment of solids

Free Cluster Model

- 🙂 Molecular model
  $\Rightarrow$ Full range of qc methods
- 🙁 Boundary effects
- 🙁 No translational symmetry

Embedded Cluster Model

- 🙂 Molecular model
  $\Rightarrow$ Full range of qc methods
- 🙁 Reduced boundary effects
- 🙁 No translational symmetry

Periodic Model

- 🙁 No molecular reference
  $\Rightarrow$ Limited range of qc methods
- 🙂 No boundary effects
- 🙂 Translational symmetry

Cyclic Cluster Model

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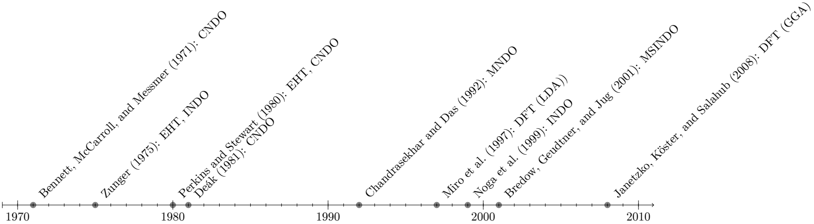
A brief history of the CCM



But the only code **available** employing PBC via the CCM is MSINDO!

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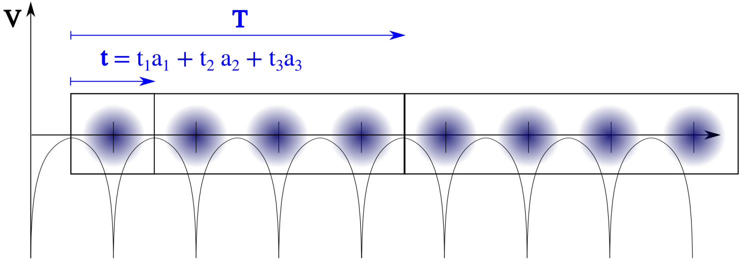
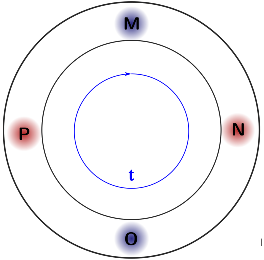
Periodic potentials and Bloch's theorem



Bloch's Theorem

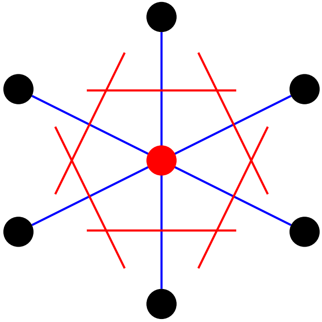
$$\hat{\mathbf{t}}\Psi^{\mathbf{k}}(\mathbf{r}) = \Psi^{\mathbf{k}}(\mathbf{r}+\mathbf{t}) = e^{\imath\mathbf{kr}}\Psi^{\mathbf{k}}(\mathbf{r})$$

$$\Psi^{\mathbf{k}}(\mathbf{r}) = e^{\imath\mathbf{kr}}u(\mathbf{r})$$



Wigner-Seitz cell (WSC)

- **Definition:** Part of space closer to the origin than any integer multiple of the real lattice vectors
- **Construction:**
  1. Draw lines from the reference lattice point to all closest lattice points
  2. At the midpoint of each line, draw another line normal to each of the first set of lines
- **Properties:**
  - unique
  - reflects the symmetry of the lattice
  - primitive



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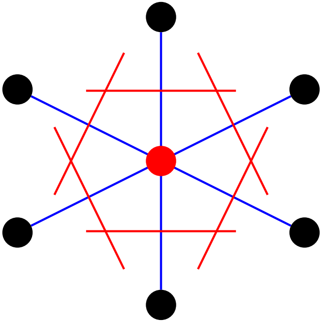

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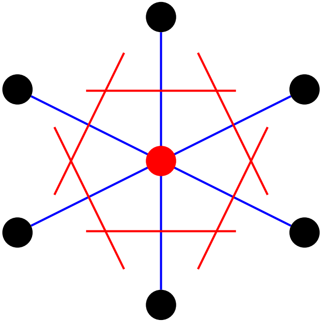

Reciprocal lattice and the Brillouin zone

Reciprocal lattice

$$\mathbf{b_1} = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot \mathbf{a_2} \times \mathbf{a_3}} \quad \mathbf{b_2} = 2\pi \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot \mathbf{a_2} \times \mathbf{a_3}} \quad \mathbf{b_3} = 2\pi \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot \mathbf{a_2} \times \mathbf{a_3}}$$

Brillouin zone

The irreducible Brillouin zone (IBZ) is the Wigner-Seitz cell in reciprocal space. It is the part of space closer to the origin than any integer multiple of the reciprocal lattice vectors

$$\mathbf{k} = k_1\mathbf{b_1} + k_2\mathbf{b_2} + k_3\mathbf{b_3} \quad \text{with} \quad k_j \in \mathbb{Z}.$$

Born-von Kármán boundary conditions

Cyclic Born-von Kármán boundary conditions

$$\Psi\left(\mathbf{r} + N_j \mathbf{a_j}\right) = \Psi\left(\mathbf{r} + \mathbf{t}^N\right) = \Psi\left(\mathbf{r}\right) \quad \text{mit} \quad j = \{1, 2, 3\} \tag{1}$$

Fundamental region

Selected large supercell where tho supercell tranformation matrix $\mathbf{N}$ contains only integers ($N_{ij} \in \mathbb{Z}$).

Integration over reciprocal space

- The summation over infinite number of translations ($N \rightarrow \infty$) becomes an integral over the first Brillouin zone:

$$\sum_{\mathbf{k}} \phi^{\mathbf{k}}(\mathbf{r}) \quad \Rightarrow \quad \int_{1BZ} \phi(\mathbf{r}, \boldsymbol{\kappa})\, d\kappa$$

- The integral is in practice replaced by a weighted, finite sum of discrete points

$$\int_{1BZ} \phi(\mathbf{r}, \boldsymbol{\kappa})\, d\boldsymbol{\kappa} \approx \sum_{\boldsymbol{\kappa}} \omega_{\boldsymbol{\kappa}} \phi(\mathbf{r}, \boldsymbol{\kappa})$$

$\rightarrow$ Monkhorst-Pack algorithm

Periodic Hartree-Fock equations

Periodic Hartree-Fock equations

$$\mathbf{F}^{\kappa}\mathbf{C}^{\kappa} = \mathbf{S}^{\kappa}\mathbf{C}^{\kappa}\mathbf{E}^{\kappa}$$

Atom-centered Gaussian basis functions

$$\phi_{\mu}^{\kappa}(\mathbf{r}) = \sum_{\mathbf{t}} e^{i\kappa\mathbf{t}}\mu(\mathbf{r}+\mathbf{t})$$

Overlap matrix in reciprocal space

$$\mathbf{S}_{\mu\nu}^{\kappa} = \sum_{\mathbf{t}} e^{i\kappa\mathbf{t}}\mathbf{S}_{\mu\nu}(\mathbf{t})$$

Reciprocal Fock matrix

$$\mathbf{F}^{\kappa} = \sum_{\mathbf{t}} \mathbf{F}^{\mathbf{t}} e^{i\kappa\mathbf{t}}$$

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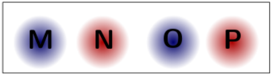
Construction of cyclic clusters



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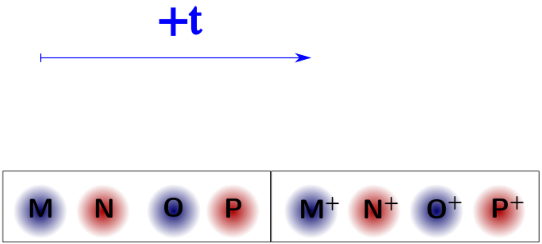

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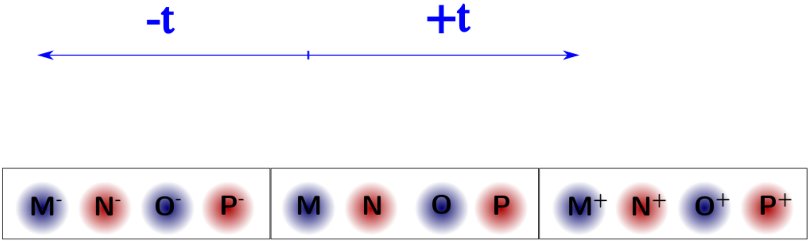

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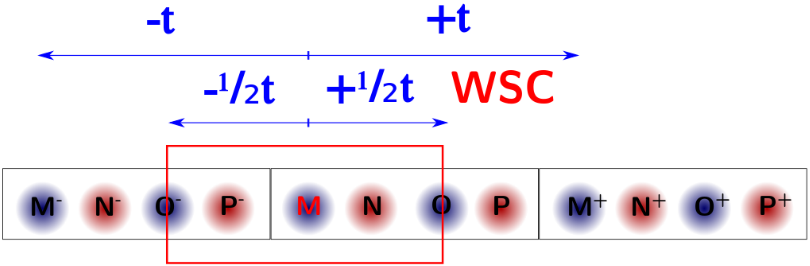

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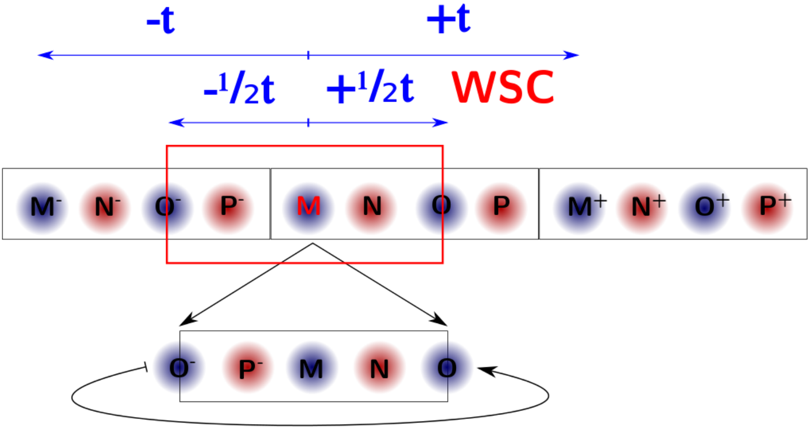

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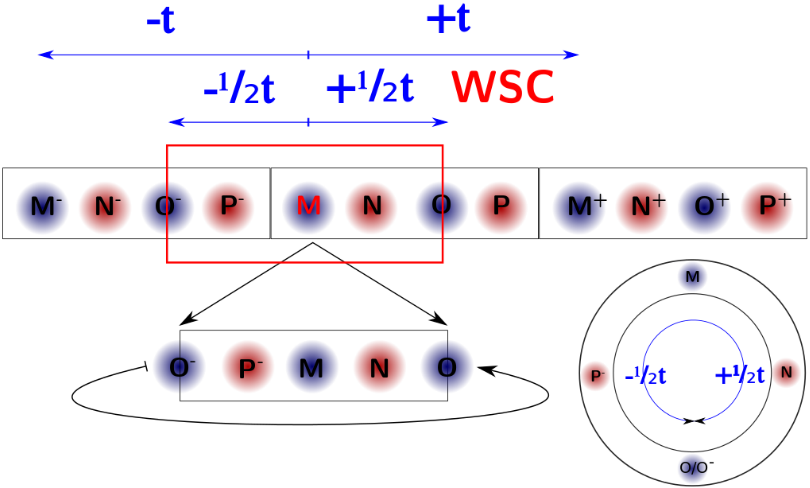

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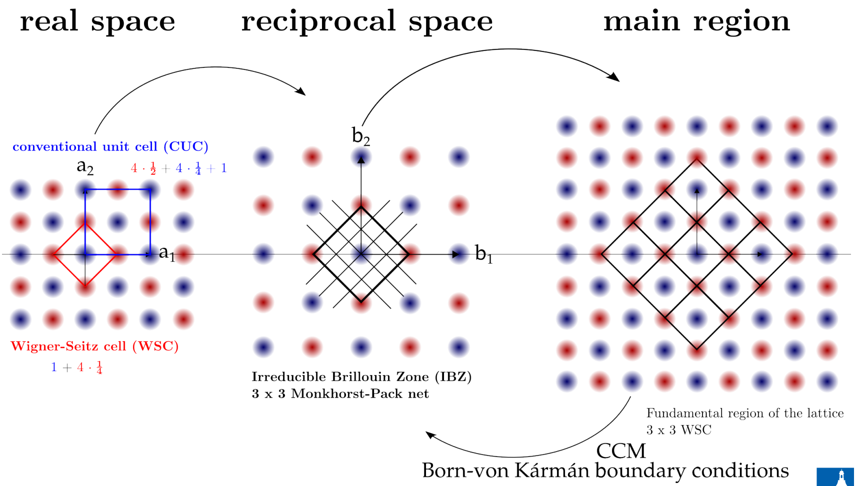
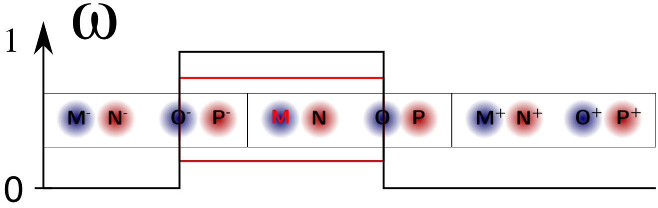
Selection of **k**-points versus choice of cyclic cluster

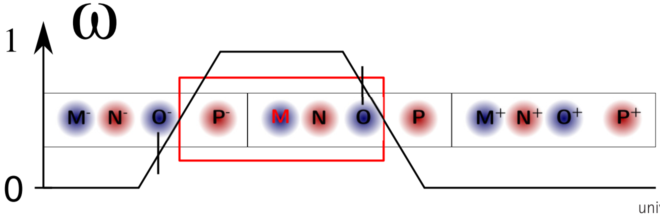


Weighting schemes

- Step function



- Linear function



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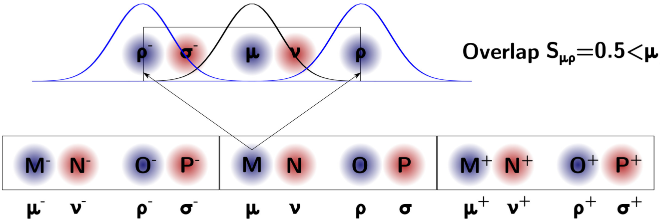
Two center integrals: Overlap matrix



Overlap $S_{\mu\rho} = 0.5\langle\mu|\rho\rangle + 0.5\langle\mu|\rho^-\rangle$

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

$$\mathbf{s} = \begin{vmatrix} 0.14 & 0.40 & 1.12 & 2.34 \end{vmatrix}$$

$$\mathbf{S}^{CCM}_{H4} = \begin{vmatrix} 1.00 & 0.66 & 0.26 & \mathbf{0.66} \\ 0.66 & 1.00 & 0.66 & 0.26 \\ 0.26 & 0.66 & 1.00 & 0.66 \\ \mathbf{0.66} & 0.26 & 0.66 & 1.00 \end{vmatrix}$$

$$\mathbf{s} = \begin{vmatrix} \mathbf{-0.06} & 0.74 & 0.74 & 2.58 \end{vmatrix}$$

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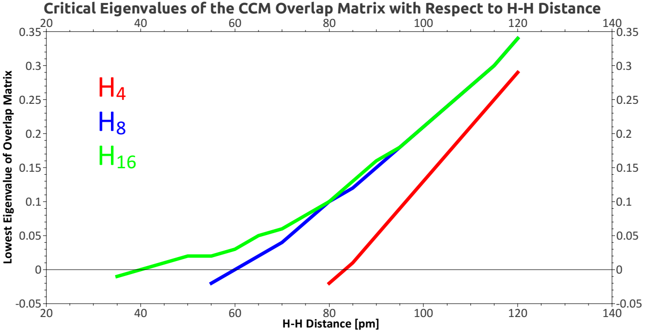
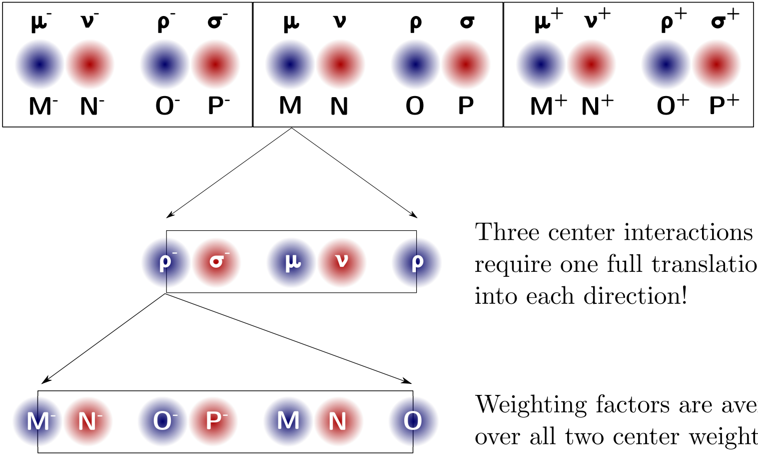
Critical eigenvalues of the overlap matrix



- Increasing the cluster size
- Screening via single value decomposition (SVD)
- Increase the interaction range

Three center integrals: Nuclear attraction $(\mu\nu|M)$



Three center interactions require one full translation into each direction!

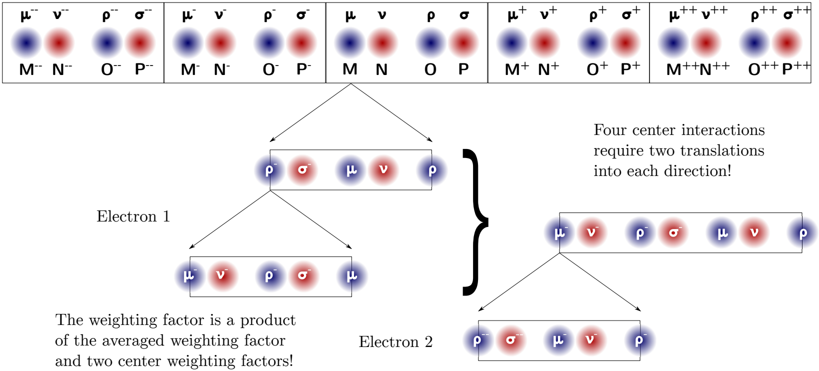
Weighting factors are averaged over all two center weights!

Three center integrals: Nuclear attraction (μν|C)

Weighting scheme for integral $(\mu\nu|C)$

	ρ^-	σ^-	μ	ν	ρ	σ
μ	$\frac{1}{2}$	1	1	1	$\frac{1}{2}$	0
ν	0	$\frac{1}{2}$	1	1	1	$\frac{1}{2}$
C	$\frac{1}{4}$	$\frac{3}{4}$	1	1	$\frac{3}{4}$	$\frac{1}{4}$

Four center integrals: Electron repulsion (μν|ρσ)



Four center interactions require two translations into each direction!

The weighting factor is a product of the averaged weighting factor and two center weighting factors!

Four center integrals: Electron repulsion $(\mu\nu|\rho\sigma)$

Weighting scheme for electronic integrals $(\mu\nu|\rho\sigma)$

	μ^{--}	ν^{--}	ρ^{--}	σ^{--}	μ^{-}	ν^{-}	ρ^{-}	σ^{-}	μ	ν	ρ	σ
μ	0	0	0	0	0	0	$\frac{1}{2}$	1	1	1	$\frac{1}{2}$	0
ρ^{-}	0	0	0	0	$\frac{1}{2}$	1	1	1	$\frac{1}{2}$	0	0	0
$\overline{\omega}$	0	0	0	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	0
μ^{-}	0	0	$\frac{1}{2}$	1	1	1	$\frac{1}{2}$	0	0	0	0	0

$$\Rightarrow \omega_{\mu\rho^{-}\mu^{-}\rho^{--}} = \frac{1}{2}\cdot\frac{1}{4}\cdot\frac{1}{2} = \frac{1}{16}$$

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Cyclic cluster Hartree-Fock equations

$$\mathbf{FC} = \mathbf{SCE}$$

$$\mathbf{F} = \mathbf{H}^{\text{core}} + \sum_a (2\mathbf{J}_a + \mathbf{K}_a)$$

$$J_{\mu\nu} = \sum^{WSSC(e1)} \sum^{WSSC(e2)} P_{\sigma\rho}\omega_{MNRS}(\mu\nu|\rho\sigma)$$

$$K_{\mu\nu} = \sum^{WSSC(e1)} \sum^{WSSC(e2)} P_{\sigma\rho}\omega_{MSRN}(\mu\sigma|\rho\nu).$$

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Differences and similiarities between SCM and CCM

- CCM applies periodic boundary conditions directly to a finite free cluster
- Hartree-Fock-Roothaan equations can be solved as in the molecular case
- WSSCs define the interaction range of atoms
- Number of **k**-points implicitly included via cluster size
- Weighting scheme ensures electroneutrality and imposes proper symmetry
- Γ-point approach and integration is carried out in real space
- Post-Hartree-Fock methods can be applied without further modifications

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Atomic Simulation Environment (ASE)

The **A**tomic **S**imulation **E**nvironment (Bahn and Jacobsen (2002)) provides Python modules for manipulating atoms, analyzing simulations and visualization.

- Input is written in Python scripting language
- Can be used interactively and in scripts
- External calculators provide total energies, forces, etc.
- Open Source (GNU LGPL Version 3)
- Supported calculators: ABINIT, **AICCM**, **Asap**, **DACAPO**, DFTB+, elk, exciting, **EMT**, FHI-aims, FLEUR, **GPAW!**, **Hotbit**, siesta, Turbomole, VASP

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ab initio Cyclic Cluster Model (AICCM)

The ***ab initio*** **C**yclic **C**luster **M**odel (AICCM) is a quantum chemical code which aims at the implementation of the CCM at various levels of theory.

- Written in Python/Cython and C++
- Depends on the ASE (calculator)
- Depends on Python modules, LAPACK routines, etc.
- Uses modern tools for software development like **git** (version control), spinx (manual), epydoc (code documentation), etc.
- Open Source (GNU GPL Version 3)

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AICCM Features

- (Un)restricted Hartree-Fock, MP2, DFTB/DFTB-SCC
- Uses **libint**, a library of C/C++ functions for efficient evaluation of several kinds of two-body integrals over Gaussian functions
- Gaussian basis sets in CRYSTAL, TURBOMOLE and deMon format
- Convergence Accelerators (Level shifting, DIIS, Fock matrix mixing)
- Plotting of molecular and crystalline orbitals (Gabedit, Molden)
- Parallelization (OpenMP)

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Periodic H_2: Convergence of total energy

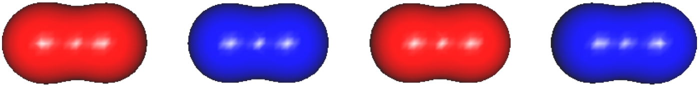
AICCM : Convergence with respect to cluster size

Cells	Atoms	E/Atom [a.u.]	ΔE [a.u.]
2	8	-0.540663	
4	16	-0.542819	0.002156
6	24	-0.542873	0.000054
8	32	**-0.542875**	0.000002
10	40	-0.542875	0.000000

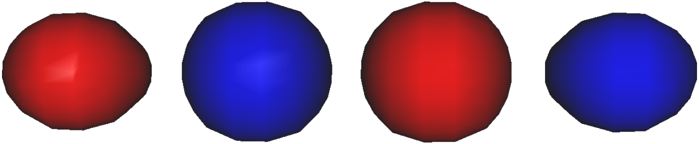
CRYSTAL09 : Convergence with respect to ITOL and SHRINK

k	ITOL	E/Atom [a.u.]	ΔE [a.u.]
1	2 4	-0.545025	
2	4 8	-0.541987	-0.00303752
4	8 16	-0.542822	0.00083454
8	12 24	-0.542874	0.00005204
16	16 32	**-0.542875**	0.00000055

Periodic H_2: Crystalline vs. molecular orbitals



Highest occupied crystalline orbital of H_8 cyclic cluster



Highest occupied molecular orbital of H_8 free cluster

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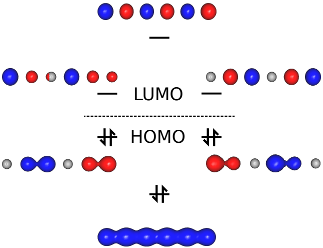
Equidistant Hydrogen Chain: Crystalline Orbitals



Orbital	Occupancy	E [a.u.]
1	2.00	-0.74295
2	2.00	-0.45266
3	2.00	-0.45266
4	0.00	+0.44076
5	0.00	+0.44076
6	0.00	+1.30010

Crystalline orbital coefficients for H_6

+0.272185	-0.078775	-0.488949	+0.906090	-0.083848	+0.856484
+0.272185	+0.384055	-0.312696	-0.525660	-0.742773	-0.856484
+0.272185	+0.462830	+0.176253	-0.380430	+0.826621	+0.856484
+0.272185	+0.078775	+0.488949	+0.906090	-0.083848	-0.856484
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Summary

- The cyclic cluster model allows the quantum chemical treatment of periodic systems in real space.
- It is a promising model for the application of advanced quantum chemical methods to periodic systems.

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- Outlook:

  Implementation into the program system?

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FIN

Thank you!