# The Cyclic Cluster Model at Hartree–Fock Level

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We present the implementation of the cyclic cluster model (CCM) formalism at the Hartree–Fock (HF) level. In contrast to other periodic models, the CCM is a Γ-point approach. Integration is carried out in real space within a finite interaction area determined by the size and the shape of the cluster that corresponds to a supercell of the solid, surface, or polymer. Particular care has to be taken for the proper treatment of three- and four-center integrals that involve basis functions located at the boundaries of the Wigner–Seitz supercell, which defines the interaction region. The similarity between the CCM formalism and molecular approaches allows in principle the application of sophisticated post HF methods to solid-state problems with only moderate modification of the molecular code. We show for selected model systems, that with our approach, the electronic structure and energetics obtained by the conventional supercell model is fully reproduced. © 2014 Wiley Periodicals, Inc.

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## Introduction

Molecular quantum-chemical methods are much more advanced than their periodic counterparts. Cluster models such as the free cluster model or the embedded cluster model allow in principle the application of sophisticated methods to model systems for crystals, surfaces and polymers. However, due to boundary effects and the neglect of long-range interactions, these models never reproduce the real electronic structure of such extended systems.[1]

Although the development of periodic methods based on the supercell model (SCM) has made substantial advances in the recent years,[2–4] it would be highly desirable to have a periodic approach that is closely related to the molecular case and does not require significant modifications in the molecular formalism and, therefore, in the program code.

The cyclic cluster model (CCM)[5] is such an approach. It is based on the Γ-point approximation and is closely related to the large unit cell (LUC) model proposed by Evarestov and coworkers.[6–9]

The CCM[5,10,11] applies periodic boundary conditions (PBC) to a cluster corresponding to a nonprimitive unit cell of a solid, surface, or infinite chain by directly employing the cyclic Born–von-Kármán boundary conditions to that cluster. Integration is carried out in real space and the number of crystalline orbitals is determined by the size of the cluster. However, it does not imply a geometric warping as it was proposed by Mattheiss[12] for the study of electronic and magnetic properties of hydrogen. The surrounding of each atom is replaced by a notional cyclic arrangement of the cluster atoms. The interaction range of every atom within the cyclic cluster is defined by a Wigner–Seitz supercell (WSSC), constructed by the translation vectors of the unit cell, and centered at the atom.

In periodic Hartree–Fock (HF) approaches, the exchange term converges comparably fast.[13] At variance, the long-range Coulomb interactions, namely the electron–nuclear attraction, the electron–electron, as well as the core–core repulsion terms only converge if they are treated together in a consistent scheme.[14,15]

In the CCM, the WSSC of each atom is stoichiometric, imposes proper site symmetry, and ensures electro-neutrality. Therefore, it is not necessary to group such Coulomb terms. Long-range Coulomb interactions with atoms outside the WSSCs can be taken into account with summation techniques.[16]

The basic ideas of the CCM date back more than 40 years. It was first implemented at semiempirical level.[10],[17–26] The name "cyclic cluster model" was first used in a study of the electronic structure of α-quartz.[5] With MSINDO-CIS,[27] there is a semiempirical CI-implementation. Later, there were attempts to implement the CCM at density functional theory, first within the local density approximation[28] and then within the generalized gradient approximation.[11] Through modifications of the integral tolerances of the CRYSTAL code[29,30] and the exploitation of the idempotency of the density matrix HF calculations were performed.[31,32] Noga and coworkers[33] have performed HF- and second-order Møller–Plesset perturbation theory (MP2)-calculations of one-dimensional (1D) periodic chains. But this implementation does not employ WSSCs. A chronology of all implementations is shown in Figure 1. But all the nonsemiempirical calculations were experiencing problems and, therefore, the only available quantum-chemical program

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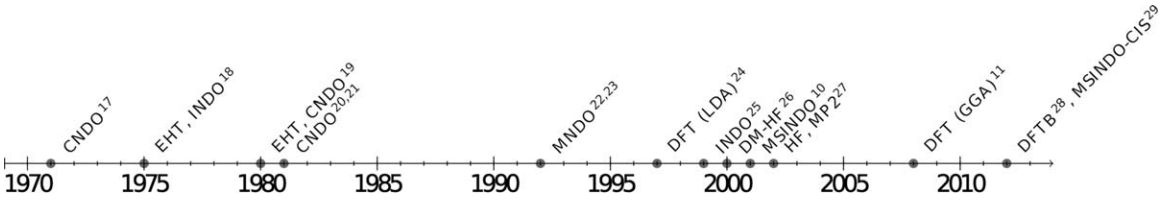


**Figure 1**. Implementations of the cyclic cluster model.

employing PBCs via the CCM is the semiempirical program MSINDO. A general *ab initio* CCM (AICCM) formalism was missing up to now.

Arguably, one of the most important aspects of the CCM is the handling of charged defects. SCM calculations are in principle inadequate for charged systems, and one has to resort to a compensating jellium and to complicated correction schemes of limited generality.[34,35] This is especially interesting for the calculation of bulk defects in semiconductors and to photocatalysis and heterogeneous catalysis.[36] As the CCM is a finite-size model, there is no problem if the cluster carries a net charge. As we describe the basic theory in this article, the discussion of defects is out of scope of this article and will be discussed elsewhere.

One major advantage of this approach over the SCM,[2,29] PBC with density fitting,[37] or localized "resolution of identity"[38,39] is its similarity to molecular quantum-chemical methods. Therefore, the CCM can in principle be employed to post-HF methods with only moderate modifications that are described in the following.

## Theory

A cluster is chosen as a supercell of the primitive or conventional unit cell. By repeating the cell $N_1$, $N_2$, and $N_3$ times along the lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, a cluster of $N=N_1 \cdot N_2 \cdot N_3$ unit cells is created. The cyclic Born–von-Kármán boundary conditions

$$\psi\left(\mathbf{r}+\sum_{j=1}^{3} N_j \mathbf{a_j}\right)=\psi\left(\mathbf{r}+\mathbf{t}^N\right)=\psi(\mathbf{r}+\mathbf{T})=\psi(\mathbf{r}). \quad (1)$$

are directly applied to this cluster. The local environment of every single atom is conceptually replaced by a cyclic arrangement of the atoms of the cluster, which therefore corresponds to the "main region" of the periodic system. This way, the cluster is closed to form a ring (1D), torus (2D), or hypertorus (3D) and interactions of atoms in the reference cell, which corresponds to the cluster, with translationally equivalent atoms are reduced back to interactions of atoms within the cyclic cluster. The atoms in the reference cell are denoted as "real" atoms $u_j$. The translations vectors $\mathbf{T}$ create the so-called "virtual" atoms $u_j^{\pm}$.

As the translational symmetry is kept within the CCM, a transformation of periodic Bloch orbitals to the basis of atomic orbitals is possible. Neglecting contributions $t \neq 0$ in

$$\phi_\mu^{\mathbf{k}}=\frac{1}{\sqrt{N}}\sum_{\mathbf{t}}^{N} e^{i\mathbf{k}\cdot\mathbf{t}}\mu^{\mathbf{t}} \quad (2)$$

at the $\Gamma$-point gives $\phi_\mu^{\mathrm{CCM}} \approx \mu^0$. Therefore, the CCM basis is directly comparable to a molecular basis.

In contrast to the SCM, no summation over special **k**-points is carried out in the CCM formalism. Instead, a discrete number $N_{\mathbf{k}}$ of **k**-points, which are equally distributed in space, is contained implicitly. The number of **k**-points can be chosen by considering the coherence of reciprocal lattice vectors and the main region of the extended system

$$\{\mathbf{k}\}=\prod_{j}^{3}\frac{g_j}{N_j}\mathbf{b_j} \quad \text{with} \quad g_j=0,\ldots,N_j^{-1} \quad (3)$$

analogous to "shrinking"-factors in the Monkhorst–Pack lattice.

In the CCM, the integrals over Bloch functions are replaced by the corresponding integrals over atomic orbitals. With exception of the atoms at the borders of the WSSCs, every translationally equivalent atom exists only once in every WSSC (*vide infra*).

In the SCM, lattice sums over electron–nuclear attraction $V_{\mathrm{Ne}}$ and electron–electron repulsion $V_{\mathrm{ee}}$ are divergent, if treated separately. Only the balanced treatment of both interactions is convergent.

Contrary to the interaction regions of SCM and LUC, that determine the range of interaction terms by integral thresholds, which may lead to an unbalanced treatment of exchange and Coulomb interaction,[31] the CCM also guarantees stoichiometry within each individual WSSC. It is, therefore, not necessary to group Coulomb, electron–nuclear attraction, and nuclear repulsion terms. Electroneutrality is achieved by restricting the interaction range to the WSSC and introducing a weighting scheme for interactions with atoms at the border of the WSSC. Long-range interactions of Coulomb type can be taken into account, for example, by the Ewald summation technique.[16]

The challenge for the development of the CCM at *ab initio* level is the treatment of three- and four-center integrals. Here, these interactions are treated differently than in previous implementations.[11,28]

### Two-center interactions

Matrices of interactions involving up to two centers like the overlap matrix or the kinetic energy matrix are treated in the *ab initio* implementation in the same way as in previous semiempirical implementations.

Figure 2 shows a 1D cluster of a fictive MNOP-system. The real atoms *M*, *N*, *O*, *P* with the atomic orbitals μ, *ν*, *ρ*, and *σ* are surrounded by the virtual atoms $M^-$, ... and $M^+$, ... with the virtual atomic orbitals $\mu^-$, ... and $\mu^+$, ....

Although interactions of real atoms with all atoms within their WSSC are taken into consideration, interactions with atoms outside their WSSC are neglected. That means that the interaction of basis function μ, which is centered on the real atom *M*, with basis function *σ*, which is centered at atom *P*, is replaced by the interaction with the closer translationally equivalent basis function $\sigma^-$ centered on the virtual atom $P^-$. In contrast to previous implementations,[40] which do not use WSSCs, it is not necessary, that the cluster contains an inversion center.

Special attention has to be paid to interactions with atoms that are exactly on the border of the WSSC and, therefore, occur more than once within the interaction range $\pm\frac{\mathbf{t}}{2}$. For example, the overlap integral $\langle\mu|\rho\rangle$ and $\langle\mu|\rho^-\rangle$ occurs twice. To avoid double-counting, the integrals are weighted according to the number of occurrences in the WSSC.[10,22] Therefore, the two-center weights are given by

$$\omega_{\mu\nu'}=\frac{1}{n_{\nu'}}. \tag{4}$$

and the entries of the cyclic overlap matrix $\mathbf{S}^{\mathrm{CCM}}$ are given by

$$\mathbf{S}^{\mathrm{CCM}}_{\mu\nu}=\sum_{\nu'}^{n_{\nu'}}\omega_{\mu\nu'}\langle\mu|\nu'\rangle. \tag{5}$$

The sum over $\nu'$ contains all translationally equivalent atoms within the WSSC and $n_{\nu'}$ is their number of occurrences in the WSSC.

The entries of the kinetic energy matrix consist also only of two-center interactions and are, therefore, written analogous to eq. (5).

$$T^{\mathrm{CCM}}_{\mu\nu}=\sum_{\nu'}\omega_{\mu\nu}\left\langle\mu\left|\frac{1}{2}\nabla^2\right|\nu'\right\rangle \tag{6}$$

The kinetic HF energy within the CCM formalism is then given as

$$\mathbf{T}^{\mathrm{CCM}}=\sum_{\mu,\nu}P^{\mathrm{CCM}}_{\mu\nu}T^{\mathrm{CCM}}_{\mu\nu}. \tag{7}$$

### Three-center interactions

The nuclear attraction energy is given in the molecular case as

$$\mathbf{V}=-\sum_{\mu,\nu}\sum_{C}P_{\mu\nu}\left\langle\mu\left|\frac{Z_C}{\mathbf{r}_C}\right|\nu\right\rangle\equiv\sum_{\mu\nu C}I_{\mu\nu C}. \tag{8}$$

As this equation contains interactions between up to three-centers, the two-center weighting scheme given above cannot be applied.

Janetzko and coworkers have proposed a three-center-weighting scheme[41,42] for their implementation of the CCM into the *deMon2k* program[43] at ADFT level (auxiliary density functional theory). In ADFT, the nuclear attraction integral $I_{\mu\nu C}$ is written as a product of the corresponding overlap integral and a scaling factor.

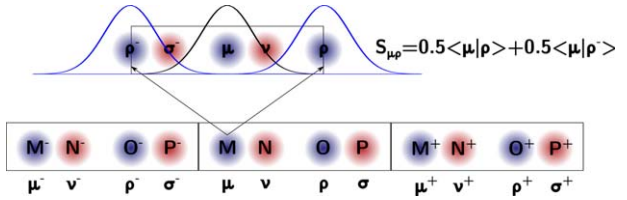


**Figure 2.** One-dimensional cluster of a linear MNOP-system is described. The real atoms *M*, *N*, *O*, *P* with the atomic orbitals μ, *ν*, *ρ*, and *σ* are surrounded by the virtual atoms $M^-$,...and $M^+$,...with the virtual atomic orbitals $\mu^-$, ... and $\mu^+$, ....

$$I^{\mathrm{ADFT\text{-}CCM}}_{\mu\nu C}=\frac{1}{n_{\mathrm{MNC}}}\left[\sum_{M'}^{\mathrm{WSSC}\,(C)}\sum_{\mu'}^{M'}\sum_{N'}^{\mathrm{WSSC}\,(M')}\sum_{\nu'}^{N'}S_{\mu'\nu'}f_{\mu'\nu'C}+\sum_{N'}^{\mathrm{WSSC}\,(C)}\sum_{\nu'}^{N'}\sum_{M'}^{\mathrm{WSSC}\,(N')}\sum_{\mu'}^{M'}S_{\mu'\nu'}f_{\mu'\nu'C}\right] \tag{9}$$

The three-center weighting scheme was derived from the two-center weighting scheme so that

$$n_{\mathrm{MNC}}=n_{MN}(n_{MC}+n_{NC})=\frac{1}{\omega_{MN}(\omega_{MC}+\omega_{NC})}=\frac{1}{\omega_{\mathrm{MNC}}}. \tag{10}$$

This scheme was also applied to the Coulomb repulsion over auxiliary functions, which also only contains up to three-center interactions.

But the three-center weights can be much easier derived from the two-center weights if the unions over WSSCs are used as reference. Therefore, we propose a new weighting scheme based on this approach.

$$\mathrm{WSSC}\,(\overline{MN})=\mathrm{WSSC}\,(M)\cup\mathrm{WSSC}\,(N), \tag{11}$$

The union of WSSCs of atoms *M* and *N*, where basis functions μ and *ν* are centered is formed. In contrast to all other approaches, for the nuclear attraction term, the basis functions and not the atoms are used as reference, like in the molecular case (Fig. 3).

$$\mathbf{V}^{\mathrm{CCM}}=-\sum_{\mu}\sum_{\nu'}^{\mathrm{WSSC}\,(M)}\sum_{C}^{\mathrm{WSSC}\,(\overline{MN})}\omega_{\mu\nu C}\;I_{\mu\nu C} \tag{12}$$

The weighting factors are the product of $\omega_{\mu\nu}$ and the averaged two-center weights, which are given by the union of the WSSC of atom *M* and *N* WSSC $(\overline{MN})$. In Figure 3, this is shown for an explicit example.

$$\omega_{\overline{\mu\nu}C}=\omega_{\mu\nu}\cdot\frac{\omega_{\mu C}+\omega_{\nu C}}{2} \tag{13}$$

The difference to previous implementations lies in the considered interaction range. Using the union of WSSCs, the maximum

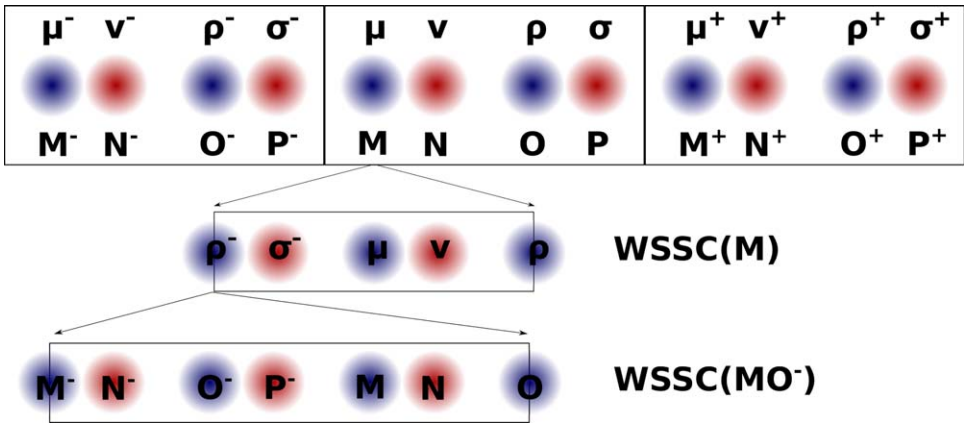


**Figure 3**. The interaction of the orbital product $\mu\rho^{-}$ with cores C that have to be taken into consideration for the nuclear attraction integral $I_{\mu\rho-c}$ is described.

interaction range is increased from $\pm\frac{1}{2}\mathbf{t}$ to $\pm\mathbf{t}$. As the interaction range of an atom at the edge of the cluster *M* spans from atom $O^{-}(-\frac{\mathbf{t}}{2})$ to $O(+\frac{\mathbf{t}}{2})$. If one then again looks at the interaction range of the border atoms $O^{-}$ ranges from $M^{-}(-\frac{\mathbf{t}}{2})$ to $M(+\frac{\mathbf{t}}{2})$. Therefore, a consistent treatment of three-center interactions needs one full translation of the cluster by $(\pm\mathbf{t})$.

The total nuclear attraction energy within the CCM formalism can be written similar to the molecular case as

$$\mathbf{V}^{\mathrm{CCM}} = -\sum_{\mu}\sum_{v}^{\mathrm{WSSC}\,(M)}\sum_{C}^{\mathrm{WSSC}\,(\overline{MN})} P_{\mu v}\omega_{\mu vC}I_{\mu vC} \tag{14}$$

We will use the short-hand notation

$$\mathbf{V}^{\mathrm{CCM}} = \sum_{\mu v'\overline{C}} P_{\mu v'}\omega_{\mu vC}I_{\mu vC} \tag{15}$$

in the following.

### Four-center interactions

The classical Coulomb term and the nonclassical exchange term involve interactions of atomic orbitals of up to four centers. The entries of the Coulomb-matrix **J** in the molecular case are given by

$$J_{\mu v} = \sum_{\sigma\rho} P_{\sigma\rho}(\mu v|\rho\sigma). \tag{16}$$

The entries of the exchange matrix **K** are given as

$$K_{\mu v} = \sum_{\sigma\rho} P_{\sigma\rho}(\mu\sigma|\rho v). \tag{17}$$

The treatment of these interactions in the CCM formalism makes use of the definition, that for the integral $(\mu v|\rho\sigma)$ the basis functions $\mu, v$ represent electron one and $\rho, \sigma$ represent electron two.

Therefore, interactions on the four centers *M, N, O,* and *P* can be consistently treated employing an analogous procedure as in the three-center case, forming the union of the WSSCs of atom *M* and Atom *N*. In Figure 4, an example is shown where electron one is described with $\mu v^{-}$. Interactions with atom $O^{-}$ within the WSSC ($\overline{MN}$) are taken into consideration. The fourth center *P* is then again selected from WSSC(*O*).

Interactions up to $\pm\frac{3}{2}\mathbf{t}$ are included. Consider, for example, the union of WSSCs of basis function μ centered at atom *M*

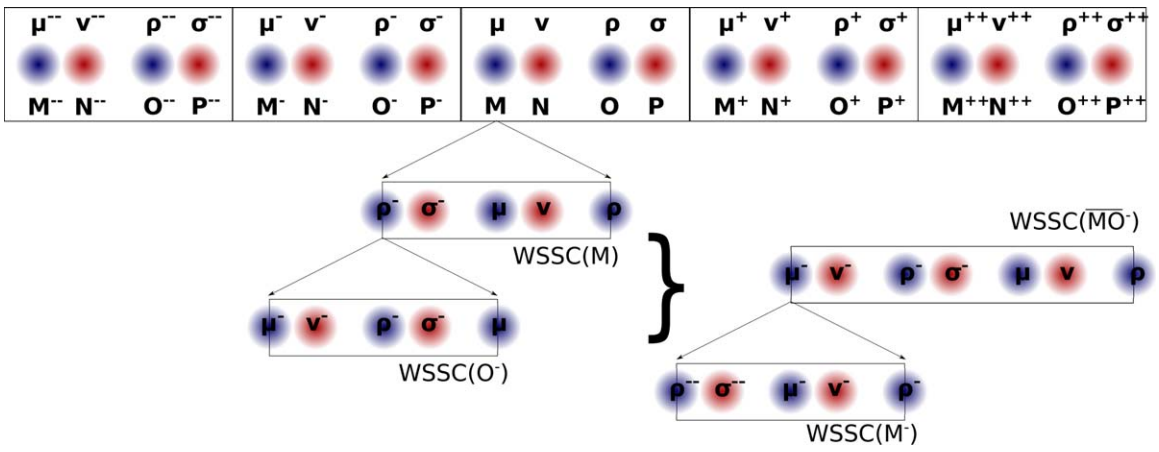


**Figure 4**. WSSCs for orbital products that have to be taken into consideration for four-center interactions of the reference orbital μ is described. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table 1.** The weighting scheme for electronic integrals involving up to four centers $(\mu\nu|\rho\sigma)$ is illustrated.

| $x$ | $\mu^{--}$ | $\nu^{--}$ | $\rho^{--}$ | $\sigma^{--}$ | $\mu^{-}$ | $\nu^{-}$ | $\rho^{-}$ | $\sigma^{-}$ | $\mu$ | $\nu$ | $\rho$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\omega_{\mu x}$ | 0 | 0 | 0 | 0 | 0 | 0 | $\frac{1}{2}$ | 1 | 1 | 1 | $\frac{1}{2}$ | 0 |
| $\omega_{\rho^- x}$ | 0 | 0 | 0 | 0 | $\frac{1}{2}$ | 1 | 1 | 1 | $\frac{1}{2}$ | 0 | 0 | 0 |
| $\bar{\omega}$ | 0 | 0 | 0 | 0 | $\frac{1}{4}$ | $\frac{1}{2}$ | $\frac{3}{4}$ | 1 | $\frac{3}{4}$ | $\frac{1}{2}$ | $\frac{1}{4}$ | 0 |
| $\omega_{\mu^- x}$ | 0 | 0 | $\frac{1}{2}$ | 1 | 1 | 1 | $\frac{1}{2}$ | 0 | 0 | 0 | 0 | 0 |

As an example, the derived weighting factor for the integral $\omega_{\mu\rho^-\mu^-\rho^{--}}=\frac{1}{2}\cdot\frac{1}{4}\cdot\frac{1}{2}$ equals to $\frac{1}{16}$. Here, $\bar{\omega}$ is the averaged weighting factor of center one and two with center three.

with virtual basis function $\rho^-$ centered at atom $O^-$ at the border of the WSSC of μ. Selecting the pair of basis functions representing electron two again from the borders of the WSSCs results in the electron repulsion integral (ERI) $(\mu\rho^-|\mu^-\rho^{--})$.

The four-center weighting scheme can also be derived from the two-center weights. An example is shown in Table 1.

The total four-center weight is the product of an averaged weighting factor and two two-center weighting factors.

$$\omega_{\mu\nu\rho\sigma}=\omega_{\mu\nu}\cdot\frac{\omega_{\mu\rho}+\omega_{\nu\rho}}{2}\cdot\omega_{\rho\sigma} \tag{18}$$

So the two-center weights of *M*, *N* ($\omega_{\mu\nu}$) as well as *P*, *O* ($\omega_{\rho\sigma}$) are multiplied with the averaged weighting factor over the weighting factors of *M*, *P* ($\omega_{\mu\rho}$) and *N*, *P* ($\omega_{\nu\rho}$). The cluster has to be translated twice in every direction $(\pm 2\mathbf{t})$, as the maximum interaction range of four-centers is $\pm\frac{3}{2}\mathbf{t}$.

The cyclic Coulomb energy is then given as

$$J^{\mathrm{CCM}}=\sum_{\mu}^{\mathrm{WSSC}(M)}\sum_{\nu'}\omega_{\mu\nu'}P_{\mu\nu'}\sum_{\rho'}^{\mathrm{WSSC}(\overline{MN})}\omega_{\overline{\mu\rho,\nu\rho}}\sum_{\sigma'}^{\mathrm{WSSC}(O)}P_{\rho'\sigma'}\ \omega_{\rho\sigma}(\mu\nu'|\rho'\sigma') \tag{19}$$

and the cyclic exchange term is given as

$$K^{\mathrm{CCM}}=\sum_{\mu}^{\mathrm{WSSC}(M)}\sum_{\nu'}\omega_{\mu\nu'}P_{\mu\nu'}\sum_{\sigma'}^{\mathrm{WSSC}(\overline{MN})}\omega_{\overline{\mu\sigma,\nu\sigma}}\sum_{\rho'}^{\mathrm{WSSC}(O)}P_{\rho'\sigma'}\omega_{\rho\nu}(\mu\sigma'|\rho'\nu'). \tag{20}$$

The cyclic Coulomb matrix $J^{\mathrm{CCM}}$, therefore, has the entries

$$J^{\mathrm{CCM}}_{\mu\nu}=\sum_{\sigma'}^{\mathrm{WSSC}(\overline{MN})}\omega_{\overline{\mu\rho,\nu\rho}}\sum_{\rho'}^{\mathrm{WSSC}(O)}P_{\rho'\sigma'}\omega_{\rho\sigma}(\mu\nu'|\rho'\sigma') \tag{21}$$

and the cyclic exchange matrix has the entries

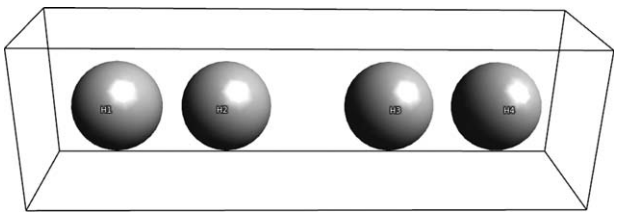


**Figure 5**. One-dimensional $H_4$-cluster containing two hydrogen pairs with alternating H—H distances of 0.8 and 1.2 Å.

$$K^{\mathrm{CCM}}_{\mu\nu}=\sum_{\sigma'}^{\mathrm{WSSC}(\overline{MN})}\omega_{\overline{\mu\sigma,\nu\sigma}}\sum_{\rho'}^{\mathrm{WSSC}(O)}P_{\rho'\sigma'}\omega_{\rho\nu}(\mu\sigma'|\rho'\nu'). \tag{22}$$

We again propose the shorthand notation

$$J^{\mathrm{CCM}}_{\mu\nu}=\sum_{\sigma\rho}^{\mathrm{WSSC}(\overline{MN})}P_{\rho\sigma}\omega_{\mu\nu\rho\sigma}(\mu\nu|\rho\sigma) \tag{23}$$

for the entries of the Coulomb matrix and

$$K^{\mathrm{CCM}}_{\mu\nu}=\sum_{\sigma\rho}^{\mathrm{WSSC}(\overline{MN})}P_{\rho\sigma}\omega_{\mu\sigma\rho\nu}(\mu\sigma|\rho\nu) \tag{24}$$

for the entries of the exchange matrix.

This is in agreement with the observation in the SCM, that the Coulomb term is very long range and the exchange term is a comparably short-range interaction.

### Cyclic HF–Roothaan equations

With the equations given above, we can formulate the cyclic Fock matrix as

$$\mathbf{F}^{\mathrm{CCM}}=\mathbf{h}^{\mathrm{CCM}}+\sum_{n}\left(2\mathbf{J}^{\mathrm{CCM}}_{n}+\mathbf{K}^{\mathrm{CCM}}_{n}\right). \tag{25}$$

The HF–Roothaan equations in the CCM formalism

**Table 2.** Convergence of the AICCM total energy with respect to cluster size, STO-3G basis set.

| Cells | Atoms | Energy/atom (a.u.) | $\Delta E$ |
|---|---|---|---|
| 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 |

Energies are given in Hartree.

**Table 3.** Convergence of reference Hartree–Fock energy with respect to integral tolerances and **k**-points.

| SHRINK | ITOL | Energy/atom | $\Delta E$ |
|---|---|---|---|
| 1 1 | 2 2 2 2 4 | −0.545025 | |
| 2 2 | 4 4 4 4 8 | −0.541987 | −0.003037 |
| 4 4 | 8 8 8 8 16 | −0.542822 | 0.000834 |
| 8 8 | 12 12 12 12 24 | −0.542874 | 0.000052 |
| 16 16 | 16 16 16 16 32 | −0.542875 | 0.000001 |

Energies are given in Hartree.

**Table 4.** Convergence of the AICCM energy with increasing cluster size for hydrogen chains (DZVP basis set).

| Cells | Atoms | Energy | $\Delta E$ |
|---|---|---|---|
| 4 | 16 | −0.552529 | |
| 6 | 24 | −0.552588 | 0.000059 |
| 8 | 32 | −0.552591 | 0.000003 |
| 10 | 40 | −0.552592 | 0.000000 |

$$\mathbf{F}^{CCM}\mathbf{C}^{CCM} = \mathbf{S}^{CCM}\mathbf{C}^{CCM}\mathbf{E}^{CCM} \quad (26)$$

are solved in the same way as in the molecular case. The cyclic HF energy is given as

$$E^{CCM} = \sum_{i}^{N_e} \epsilon_i - \frac{1}{2}\sum_{ij}^{N_e}(J_{ij}^{CCM} - K_{ij}^{CCM}) + V_{nn}^{CCM}. \quad (27)$$

### Implementation and computational details

All CCM calculations have been carried out employing our quantum-chemical code AICCM.[26] It is written in object-oriented Python/Cython with C/C++ extensions as a native calculator for the atomic simulation environment.[44] It features DFTB/DFTB-SCC-, RHF-, and UHF- as well as MP2 calculations. The atomic orbitals are expanded in Gaussian basis functions. Convergence accelerators (Levelshift, Fock-Matrix-Mixing, and DIIS) and Mulliken as well as Löwdin population analysis are implemented. Molecular and crystalline orbitals can be visualized with Gabedit.[45] ERIs over Gaussians are calculated by interfacing the ERI library libint.[46]

The SCM reference calculations have been carried out employing the crystalline orbital program CRYSTAL09.[29,30]

**Table 5.** Orbital energies (Hartree) of the equidistant cyclic $H_6$ cluster.

| Orbital | Occupancy | Energy | k |
|---|---|---|---|
| 1 | 2.00 | −0.74295030 | $\Gamma$ |
| 2 | 2.00 | −0.45266305 | $+\frac{1}{6}$ |
| 3 | 2.00 | −0.45266305 | $-\frac{1}{6}$ |
| 4 | 0.00 | +0.44076948 | $+\frac{1}{3}$ |
| 5 | 0.00 | +0.44076948 | $-\frac{1}{3}$ |
| 6 | 0.00 | +1.30010143 | $+\frac{1}{2}$ |

## Results

To verify the results obtained with our method, we compare AICCM total energies with those obtained with the crystalline orbital program CRYSTAL. The integral tolerances and **k**-points are increased simultaneously, which corresponds to enlarging the unit cell in the $\Gamma$-point approach.

As first model system, we chose a unit cell containing two hydrogen pairs with alternating H—H distances of 0.8 and 1.2 Å (Fig. 5). In this way, artifacts due to orbital degeneracy are avoided. The total energy per atom converges rapidly with increasing cluster size (Table 2). The total energy per atom converges within $10^{-6}$ with respect to integral tolerances and

**Table 6.** Crystalline orbital coefficients of the equidistant cyclic $H_6$ cluster.

| H | CO 1 | CO 2 | CO 3 | CO 4 | CO 5 | CO 6 |
|---|---|---|---|---|---|---|
| $H_1$ | +0.272185 | −0.078775 | −0.488949 | +0.906090 | −0.083848 | +0.856484 |
| $H_2$ | +0.272185 | +0.384055 | −0.312696 | −0.525660 | −0.742773 | −0.856484 |
| $H_3$ | +0.272185 | +0.462830 | +0.176253 | −0.380430 | +0.826621 | +0.856484 |
| $H_4$ | +0.272185 | +0.078775 | +0.488949 | +0.906090 | −0.083848 | −0.856484 |
| $H_5$ | +0.272185 | −0.384055 | +0.312696 | −0.525660 | −0.742773 | +0.856484 |
| $H_6$ | +0.272185 | −0.462830 | −0.176253 | −0.380430 | +0.826621 | −0.856484 |

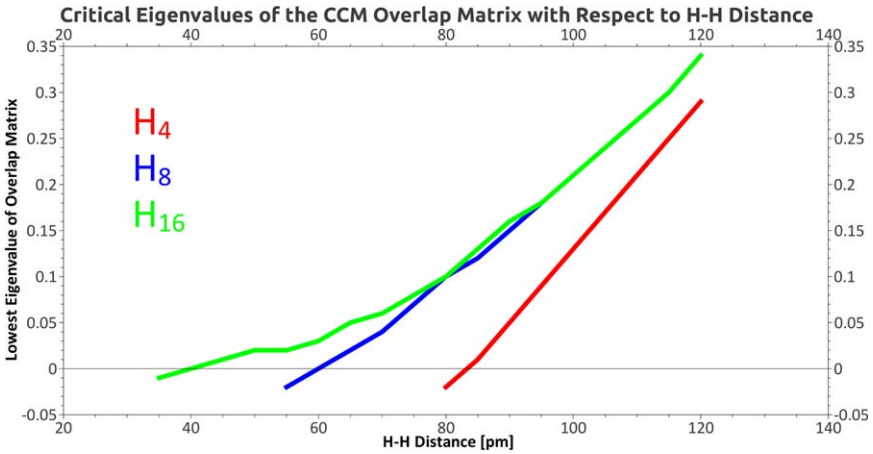


**Figure 6.** Critical eigenvalues of the CCM overlap matrix with respect to cluster size and bonding distance for equidistant hydrogen chains. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**k**-points (Table 3) at the corresponding cluster size in the CCM. This provides strong evidence that the AICCM scheme is correct.

### Basis sets

To check that our implementation is also correct for anisotropic integrals, for example, interactions of p-orbitals, we calculated total energies with larger basis sets and polarization functions. As expected, a calculation with a larger solid-state basis sets is lower in energy ($5-11G^* : \left(-0.552024 \ \frac{\text{Hartree}}{\text{cell}}\right)$.[14] For an unmodified molecular double-$\zeta$ basis set,[43] the convergence of the total energy with respect to cluster size was tested (Table 4).

As a second test system, we chose the equidistant hydrogen chain with a H—H distance of 1.0 Å. The cyclic cluster contains six atoms. Orbital energies are given in Table 5. The coefficients of the crystalline orbitals are given in Table 6. They show perfect symmetry degeneracy.

### Critical eigenvalues of the overlap matrix

One known problem of the CCM is, that with small clusters or the use of basis sets with very diffuse functions, the overlap matrix becomes indefinite.[11] This is similar to the SCM, where diffuse basis sets might lead to problems.[47,48] Figure 6 shows the eigenvalues of the overlap matrix of the equidistant cyclic hydrogen clusters depending on the interatomic distances and cluster sizes. For small clusters or interatomic distances, the overlap matrix becomes indefinite and the $\Gamma$-point approximation becomes unphysical. Therefore, this has to be checked before running CCM calculations. The small eigenvalues must be screened and removed, for example, by a canonical orthogonalization, or the cluster size must be increased.

## Conclusions and Outlook

Our preliminary results suggest that the AICCM implementation is a real alternative to other periodic approaches. Due to the modification of the interaction ranges, prior problems with negative eigenvalues of the Coulomb matrix do not occur in our approach with reasonable cluster sizes. For the simulation of ionic crystals, the inclusion of long-range interactions is mandatory. This can be achieved by various summation techniques.

The examples given above are restricted to the 1D case. This covers the applicability to, for example, nanotubes and nanowires. However, the formalism is general and can in principle be applied to 2D and 3D cases, depending on the efficiency of the implementation. We are currently working on a reimplementation in one major quantum-chemical program that provides the necessary infrastructure.

Inclusion of analytic gradients and implementation of electron correlation methods, for example, MP, seems to be relatively straightforward, due to the similarity of the CCM to molecular approaches. The problem that arises is that the hard cutoffs at the border of the WSSCs leads to discontinuities during structure optimizations. This can be overcome by using weighting functions depending on the distance from the border instead of fixed values. This is currently under development in our group.

**Keywords:** cyclic cluster model • solid-state • Hartree · Fock

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