Semiempirical LCAO Methods for Molecules and Periodic Systems

6.1 Extended Hückel and Mulliken–Rüdenberg Approximations

6.1.1 Nonself-consistent Extended Hückel–Tight-binding Method

During the early days of molecular quantum chemistry, when computational power was minimal, the semiempirical LCAO methods were applied even for small molecules [204, 205]. Later, at the beginning of the 1970s, these approaches were extended to crystalline solids [206–208] and allowed calculations of their properties to be made in the period when the first-principles HF LCAO calculations for solids were practically unreliable. The limitations of the first-principles HF LCAO calculations are caused mainly by the necessity of evaluation of multicenter two-electron integrals whose number grows proportionally as $N^4$ ($N$ is the number of AOs used). Therefore, in the quantum chemistry of large molecules and solids the semiempirical calculations continue to appear in large numbers in chemical literature. We refer the reader to the recently published book [102], Chap.5, where the corresponding bibliography of semiempirical methods for molecules can be found.

In this chapter we discuss the extension of LCAO semiempirical methods of molecular quantum chemistry to periodic systems and provide a comparison between semiempirical Hamiltonians for molecules and crystals.

The approximate LCAO methods of quantum chemistry can be divided on empirical (semiquantitative) and semiempirical grounds.

The empirical (semiquantitative) methods are based on a one-electron effective Hamiltonian and may be considered as partly intuitive: extended Hückel theory (EHT) for molecules [204] and its counterpart for periodic systems – the tight-binding (TB) approximation. As, in these methods, the effective Hamiltonian is postulated there is no necessity to make iterative (self-consistent) calculations. Some modifications of the EHT method introduce the self-consistent charge-configuration calculations of the effective Hamiltonian and are known as the method of Mulliken–Rüdenberg [209].

The semiempirical methods are based on the simplification of the HF LCAO Hamiltonian and require the iterative (self-consistent) density matrix calculations: complete and intermediate neglect of differential overlap (CNDO and INDO – approximations), neglect of diatomic differential overlap (NDDO) and others, using the neglect of differential overlap (NDO) approximation.
Both groups of methods use the valence-electron approximation, i.e. all core electrons are ignored. It is assumed that core electrons are sufficiently invariant to differing chemical environments so that changes in their orbitals as a function of environment are of no chemical consequence, energetic or otherwise. The valence atomic orbitals are represented by a so-called Slater-type orbital (STO). The mathematical form of a normalized STO (in atom-centered polar coordinates) is

\[ \chi_{\mu}(r) = R_{\mu}(r)Y_{lm}(\theta, \varphi) = N_{\mu}r^{n-1}\exp(-\zeta_{\mu}r)Y_{lm}(\theta, \varphi) \]  

(6.1)

The radial part \( R_{\mu}(r) \) of STO \( \chi_{\mu}(r) \) depends on \( n \) (the principal quantum number for the valence orbital) and an orbital exponent \( \zeta_{\mu} \) that can be chosen according to a simple set of rules developed by Slater [210], (see Sect. 8.1.1), in EHT and TB methods or considered as semiempirical parameters. The angular parts are spherical harmonic functions \( Y_{lm}(\theta, \varphi) \) depending on the angular momentum quantum numbers \( l \) and \( m \) (in the majority of cases their real combinations \( Y_{lm}(\theta, \varphi) \pm Y_{l-m}(\theta, \varphi) \) are used, giving for \( l = 1, 2, 3 \) the angular part of \( p, d, f \) atomic functions, respectively). STOs have a number of features that make them attractive. The orbital has the correct exponential decay with increasing \( r \), the angular component is hydrogen-like, and the 1s orbital has, as it should, a cusp at the nucleus (i.e. is not smooth). More importantly, from a practical point of view, overlap integrals between two STOs as a function of interatomic distance are readily computed. In simple Hückel theory (SHT) all STOs in a molecule are supposed to be orthogonal, in EHT the AOs overlap matrix \( S \) is computed directly.

In EHT for molecules the MOs and the corresponding one-electron energies are found as the eigenfunctions and eigenvalues of the effective Hamiltonian \( H \):

\[ \det |H_{\mu\nu} - S_{\mu\nu}\epsilon_i| = 0 \]  

(6.2)

The dimension of the matrices \( H \) and \( S \) is equal to the whole number of the atomic STOs.

The values for diagonal elements \( H_{\mu\mu} \) are taken as the negative of the average ionization potential for an electron in the appropriate valence orbital. Of course in many-electron atoms, the valence-shell ionization potential (VSIP) for the ground-state atomic term may not necessarily be the best choice for the atom in a molecule, so this term is best regarded as an adjustable parameter, although one with a clear, physical basis. VSIPs have been tabulated for most of the atoms in the periodic table [211,212].

The nondiagonal elements (for the nearest neighbors known as resonance integrals) are more difficult to approximate. Wolfsberg and Helmholz [213] suggested the following convention:

\[ H_{\mu\nu} = \frac{K}{2} (H_{\mu\mu} + H_{\nu\nu}) S_{\mu\nu} \]  

(6.3)

where \( K \) is an empirical constant and \( S_{\mu\nu} \) is the overlap integral. Thus, the energy associated with the matrix element is proportional to the average of the VSIPs for the two orbitals \( \mu \) and \( \nu \) times the extent to which the two orbitals overlap in space (note that, by symmetry of angular parts the overlap between different valence STOs on the same atom is zero). Originally, the constant \( K \) was given a different value for matrix elements corresponding to \( \sigma \)- and \( \pi \)-type bonding interactions. In modern
EHT calculations, it is typically taken as 1.75 for all matrix elements, although it can still be viewed as an adjustable parameter when such adjustment is warranted.

Because the matrix elements do not depend on the final MOs in any way (unlike HF- theory), the process is not iterative, so it is very fast, even for very large molecules.

The very approximate nature of the resonance integrals in EHT makes it inaccurate for the calculation of the atomic positions in molecules so that use of EHT is best restricted to systems for which experimental geometries are available. For such cases EHT tends to be used today to generate qualitatively correct MOs in much the same fashion as it was used 50 years ago [102]. In the 21st century, such a molecular problem has become amenable to more accurate treatments (HF and post-HF methods, see Chapters 4 and 5), so the province of EHT is now primarily very large systems, like extended solids, where its speed makes it a practical option for understanding the band structure of bulk and surface states [214].

In the EHT method for solids, crystalline orbitals (4.55) are expanded over the Bloch sums (4.53) of valence AOs and the secular equation

$$\det |H_{\mu\nu}(k) - S_{\mu\nu}(k)\epsilon_i(k)| = 0 \quad (6.4)$$

is solved where $H_{\mu\nu}(k)$ and $S_{\mu\nu}(k)$ are, respectively, the matrix elements of the effective one-electron Hamiltonian and of the overlap integrals between two LCAO Bloch sums expressed as

$$H_{\mu\nu}(k) = \sum_{R_n} \exp(ikR_n)H_{\mu\nu}(r - R_n), \quad S_{\mu\nu}(k) = \sum_{R_n} \exp(ikR_n)S_{\mu\nu}(r - R_n) \quad (6.5)$$

The difference between the matrix elements $H_{\mu\nu}(k)$ (6.5) and $F_{\mu\nu}(k)$ (4.56) is due to the difference between HF and EHT Hamiltonians: the former includes one-electron and two-electron parts and depends on the crystalline density matrix (4.65), the latter are assumed to be proportional to the overlap matrix elements. The explicit form of $H_{\mu\nu}(r - R_n)$ is given as follows

$$H_{\mu\nu}(r - R_n) = \frac{1}{2}K_{1\mu
u}(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}(r - R_n) \quad (6.6)$$

where the proportionality constant $K_{1\mu\nu} = 1$ for $\mu = \nu$ and otherwise $K_{1\mu\nu}$ is an empirically adjustable parameter, $H_{\mu\nu}$ is the valence-state ionization potential (VSIP) of AO $\chi_\mu$. These matrix elements are fixed at the beginning of EHT calculations so that the secular equations (6.4) are solved independently for different wavevector $k$ values and the calculation does not require the self-consistency. Due to the translation symmetry the order of secular equation (6.4) is equal to the number of valence AOs per primitive cell. The field of lattice summations in matrix elements $H_{\mu\nu}(k)$, $S_{\mu\nu}(k)$ depends on the model chosen. In the infinite-crystal model the summations are made up to the distance when the overlap integrals $S_{\mu\nu}(r - R_n)$ become less than some threshold. In the cyclic-cluster model these summations are made in such a way that the lattice summation is restricted by the cyclic-cluster translation vector. As was already mentioned the shape and size of the cyclic cluster chosen defines the $k$-vectors set, for which the calculation is in fact made. As EHT is a nonself-consistent method (the matrix elements are calculated independently for different $k$-vectors) the choice of one or another restriction for summation in the direct lattice is mainly
a conceptual point. The EHT approach to solids (known also as the tight-binding (TB) approximation) is applied in many cases as an interpolation method, to be used in connection with more accurate calculation schemes or experimental data [58]. As an example, we consider the EHT band structure of Si crystal, fitted in [214] to reproduce the experimental bandgap and optical properties. The lattice summation was taken over all atoms within the sixth-nearest neighbors. In order to reproduce optical properties it turned out that four proportionality constants ($K_{ss}$, $K_{sp}$, $K_{pp}$ and $K_{pp\pi}$) are required for each shell of neighbors resulting in 24 fitting parameters. Adding the ionization potentials $I_s$, $I_p$ and orbital exponents $\zeta_s$, $\zeta_p$ for the Slater-type AOs (which are also treated as fitting parameters), this amounts to a total 28 adjustable fitting parameters. These parameters have been determined by fitting to the pseudopotential band-structure calculations for the experimental value of the cubic lattice constant [215] and experimental data. The best-fit parameters are listed in Table 6.1.

<table>
<thead>
<tr>
<th>Neighbors</th>
<th>(K_{ss})</th>
<th>(K_{sp})</th>
<th>(K_{pp})</th>
<th>(K_{pp\pi})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.403</td>
<td>1.409</td>
<td>1.890</td>
<td>2.290</td>
</tr>
<tr>
<td></td>
<td>1.523</td>
<td>1.931</td>
<td>3.050</td>
<td>2.570</td>
</tr>
<tr>
<td></td>
<td>0.955</td>
<td>2.095</td>
<td>3.780</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>1.355</td>
<td>0.375</td>
<td>1.750</td>
<td>2.150</td>
</tr>
<tr>
<td></td>
<td>5.450</td>
<td>2.485</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>4.550</td>
<td>1.750</td>
<td>1.600</td>
<td>4.500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.800</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In fitting the bands, special weight has been given to the valence and conduction bands at $\Gamma$, the conduction bands at $L$ and $K$, and the conduction-band minima at $+0.85(2\pi/a_0)$ along the (001) directions, which may influence the optical properties. These band states are somewhat sensitive to the change in the individual values of the fitting parameters and special attention has been paid to their determination. The energy eigenvalues at high-symmetry points of the BZ (see Fig. 3.2) are compared to the Hartree–Fock LCAO calculation and experimental values in Table 6.2.

The energies in eV are measured relative to the top of the valence band with the symmetry $\Gamma_5$. As is seen from Table 6.2 an excellent description of the valence and conduction bands has been achieved throughout the Brillouin zone. The main features of the bands are reproduced quite accurately. More specifically, the highest valence and lowest conduction bands run parallel along the $\Lambda$, $\Delta$, and $\Sigma$ lines and the indirect bandgap of Si, the $\Delta$ minima of which lie at 85% of the way along the $\Gamma - X$ directions, has been exactly reproduced. It is seen from Table 6.1 that the fitted values of EHT parameters are essentially different compared to those used for molecules. The orbital exponent value $\zeta_s = \zeta_p = 1.385$ found with Slater rules differs from the fitted values $\zeta_s = 1.656$, $\zeta_p = 1.728$. The neutral Si atom ionization potentials $I_s = 16.34$ eV, $I_p = 8.15$ eV also differ from the corresponding fitted values 15.55 eV and 7.62 eV, respectively. Analyzing the data given in Table 6.1 one sees that the proportionality constant is not the same for $2s$ and $2p$ orbitals (its value, 1.75, is taken in molecular calculations) and essentially depends on the interatomic distance.
Table 6.2. EHT fitted, HF and experimental eigenvalues (in eV) for Si crystal at \( \Gamma \), X, and L-points relative to the valence-band maxima

<table>
<thead>
<tr>
<th>Level</th>
<th>Fitted</th>
<th>HF</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma )</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00, ( \approx ) 0.00</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>(-12.32)</td>
<td>(-12.36)</td>
<td>(-12.4, -12.5)</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>3.43</td>
<td>3.43</td>
<td>3.45, 3.41</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>4.08</td>
<td>4.10</td>
<td>4.15</td>
</tr>
<tr>
<td>( L )</td>
<td>(-10.82)</td>
<td>(-9.55)</td>
<td>(-9.3)</td>
</tr>
<tr>
<td>( L )</td>
<td>(-6.20)</td>
<td>(-6.96)</td>
<td>(-6.4, -6.8)</td>
</tr>
<tr>
<td>( L )</td>
<td>(-1.12)</td>
<td>(-1.23)</td>
<td>(-1.2)</td>
</tr>
<tr>
<td>( L )</td>
<td>2.26</td>
<td>2.23</td>
<td>2.2, 2.3</td>
</tr>
<tr>
<td>( L )</td>
<td>4.43</td>
<td>4.34</td>
<td>3.9</td>
</tr>
<tr>
<td>( X )</td>
<td>(-7.92)</td>
<td>(-7.69)</td>
<td>(-2.5, -2.9)</td>
</tr>
<tr>
<td>( X )</td>
<td>(-2.95)</td>
<td>(-2.86)</td>
<td>(-2.5, -2.9)</td>
</tr>
<tr>
<td>( X )</td>
<td>1.33</td>
<td>1.17</td>
<td>1.13</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>1.13</td>
<td>1.10</td>
<td>1.13</td>
</tr>
<tr>
<td>( K )</td>
<td>1.62</td>
<td>1.66</td>
<td>1.66</td>
</tr>
</tbody>
</table>

The fitted EHT parameters were used in [214] for the EHT calculations to study the molecular oxygen chemisorption and hydrogen-terminated Si(001) ultrathin films. Even when using modern computer codes and facilities the first-principles calculations would be, in this case, very complicated as is seen from the examples given in Chap. 11. In the example considered the remarkable fit for Si crystal has been achieved within the EHT formalism by defining a rather large parameter basis set that resembled a typical Slater–Koster (tight-binding) parametrization. However, it is surprising that, to our knowledge, a systematic quantitative study on the accuracy attainable with the EHT when applied to different bulk materials has been attempted only recently [216]. It was shown how the simple EHT method can be easily parametrized in order to yield accurate band structures for bulk materials, while the resulting optimized atomic orbital basis sets present good transferability properties. The number of parameters involved is exceedingly small, typically ten or eleven per structural phase. A new EHT parametrization scheme was applied to almost fifty elemental and compound bulk phases. An orthonormal AO basis set was chosen for each inequivalent atom \( M \). Generally, the basis involves rather extended radial wavefunctions, although any other type of basis set may be employed as well. In this work, the Hamiltonian matrix elements \( H_{\mu M,\nu N} \) were taken in the form

\[
H_{\mu M,\nu N} = K_{\text{EHT}} \left( I_{\mu M} + I_{\nu N} \right)/2
\]

where \( K_{\text{EHT}} \) is a constant traditionally set to a value of 1.75 and \( I_{\mu M}, I_{\nu N} \) are onsite energies of both elements \( M, N \). From the above formula it follows that the strength of the Hamiltonian matrix elements is weighted by the mean value of the onsite energies, so that a shift in energy of these onsite parameters does not translate into a rigid shift in energy of the EHT-derived band structure. Therefore, and in order to avoid any arbitrariness in the origin of the energy scales, the Fermi level for transition
metals to –10 eV was fixed and the top of the valence band for semiconductors at –13 eV. It was then found that increasing $K_{\text{EHT}}$ to 2.3 consistently provided better fits for all elements, although similar good fits may be obtained with $K_{\text{EHT}} = 1.75$ if the Fermi level is lowered to around –20 eV. A minimal spd basis set per element was employed, while each AO is described by a double Slater wavefunction. Apart from the onsite energies ($I_s$, $I_p$, and $I_d$), this leads to three parameters per $\ell$ quantum number: the exponents $\zeta_1$ and $\zeta_2$ (with $\zeta_1 < \zeta_2$), and the coefficient for the former, $C_1$. The second coefficient $C_2$ is determined by imposing normalization of the wavefunction. For transition metals the optimization of the three AO parameters was found to be redundant for the $s$ and $p$ orbitals, and equally good fits could be obtained by fixing $\zeta_2$ to a rather large value: $\zeta_2 > 20.0$. Since such a highly localized term gives a negligible contribution to the overlaps with neighboring orbitals, it was explicitly omitted, while allowing the coefficient $C_1$ to take values smaller than 1.0 (i.e. the $\zeta_2$ Slater orbital only contributes to the normalization of the wavefunction). For the $d$ orbitals, on the contrary, it was found necessary to include the $\zeta_2$ contribution. Hence, the transition-metal fits comprise 10 parameters per elemental phase. In order to improve the transferability of the EHT, the AO basis set of a given element simultaneously for different structural phases (e.g. Ti-fcc, -bcc, and -hex) has also been optimized, while the onsite energies have been treated as independent parameters for each phase. For the spin-polarized phases of Fe, Co, and Ni, the coefficient of the $d$ orbitals was additionally varied independently for each spin, since the $d$ bandwidths are larger for the spin minority bands than for the majority ones. The main difference from traditional TB schemes is clear – explicit definition of the AOs. This might look at first glance as a disadvantage, since it requires the calculation of the overlap matrix elements. However, the computational effort involved in constructing the actual overlap $S(k)$ and Hamiltonian $H(k)$ matrices is minimal (only two-center integrals plus the simple EHT formula are involved) and more importantly, for a fixed cutoff radius, it scales linearly with the number of orbitals in the unit cell. The explicit use of AOs can be regarded as advantageous, particularly in what concerns the transferability of the EHT parameters, since the dependence of the overlap terms $S_{\mu M, \nu N}$ on the interatomic distance $d_{MN}$ readily provides a natural scaling law that is not restricted to small variations of $d_{MN}$. A further advantage is the possibility to obtain the local density of states, while the traditional TB methods only provide real space-integrated quantities.

The empirically adjusted and consistent set of EHT valence orbital parameters for molecular calculations, based on the Hartree–Fock–Slater (see (4.23)) model of atoms, was recently suggested in [217] for all elements of the periodic table. The parametrization scheme uses individual values of the exchange parameter, $\alpha$, for each atom. Each value of $\alpha$ was adjusted to reproduce the empirical value of the first ionization energy of the atom considered. The expectation values, energies and radial functions for all elements of the periodic table have been evaluated on the basis of the Hartree–Fock–Slater model and individual exchange parameters. A consistent set of Slater-type orbital single $\zeta$ valence atomic orbital exponents and energies for all elements of the periodic table, suitable for orbital interaction analysis, was presented. These exponents were calculated by fitting the $\langle r \rangle_{\text{STO}}$ moments to numerical empirically adjusted $\langle r \rangle_{\text{HFS}}$ results. In future, these parameters may appear to be useful for TB method calculations of solids after some modifications.
6.1 Extended Hückel and Mulliken–Rüdenberg Approximations

The process in the EHT and TB methods does become iterative if VSIPs are not included in the set of fitted parameters but are adjusted as a function of partial atomic charge as described in the next subsection, since the partial atomic charge depends on the occupied orbitals. Such a scheme is applied for more ionic systems than those studied by the EHT method. The self-consistent one-electron Hamiltonian Mulliken–Rüdenberg calculation scheme is considered in the next subsection.

6.1.2 Iterative Mulliken–Rüdenberg Method for Crystals

The Rüdenberg’s integrals approximations for molecules has been described in [209] and in more detail in [218]. This approximation was introduced by Rüdenberg [219] to simplify the calculation of two-electron four-center integrals

\[
(\mu M, \nu N | \sigma P, \lambda L) = \int dr_1 \int dr_2 \chi_{\mu M}(r_1) \chi_{\nu N}(r_1) \frac{1}{r_{12}} \chi_{\sigma P}(r_2) \chi_{\lambda L}(r_2) \tag{6.8}
\]

where \(\chi_{\mu M}(r)\) is the \(\mu\)th AO on the \(M\)th atom in a molecule. Let \(\chi_{1M}, \chi_{2M}, \ldots\) be a complete set of orthogonal real orbitals on center \(M\) and analogously \(\chi_{1N}, \chi_{2N}, \ldots\) and \(\chi_{1L}, \chi_{2L}, \ldots\) on centers \(N, P\), and \(L\), respectively. If \(S_{\mu M, \nu N} = \int dr \chi_{\mu M}(r) \chi_{\nu N}(r)\) denotes the overlap integrals between the orbitals \(\chi_{\mu M}(r)\) and \(\chi_{\nu N}(r)\), then we have the expansions

\[
\chi_{\mu M}(r_1) = \sum_{\omega} S_{\mu M, \omega N} \chi_{\omega N}(r_1) \tag{6.9}
\]

\[
\chi_{\nu N}(r_2) = \sum_{\omega} S_{\omega M, \nu N} \chi_{\omega M}(r_2) \tag{6.10}
\]

whence

\[
\chi_{\mu M}(r_1) \chi_{\nu N}(r_2) = \frac{1}{2} \sum_{\omega} \left[ S_{\mu M, \omega N} \chi_{\nu N}(r_1) \chi_{\omega N}(r_2) + S_{\nu N, \omega M} \chi_{\mu M}(r_1) \chi_{\omega M}(r_2) \right] \tag{6.11}
\]

Insertion of (6.11) and the analogous formula for the centers \(L, K\) in (6.8) expresses the four-center integral in terms of two-center Coulomb integrals and overlap integrals:

\[
(\mu M, \nu N | \sigma P, \lambda L) = \frac{1}{4} \sum_{\omega} \sum_{\omega'} \left[ S_{\mu M, \omega N} S_{\sigma P, \omega' L} (\omega N, \omega' L) + S_{\nu N, \omega M} S_{\sigma P, \omega' L} (\mu M, \omega' L) + S_{\nu N, \omega M} S_{\lambda L, \omega' P} (\mu M, \sigma P) \right] \tag{6.12}
\]

In the Mulliken approximation [220] only the first term in expansion (6.12) is taken so that the one-electron distribution is approximated by

\[
\chi_{\mu M}(r_1) \chi_{\nu N}(r_1) \approx \frac{1}{2} S_{\mu M, \nu N} \left[ \chi_{\mu M}^2(r_1) + \chi_{\nu N}^2(r_1) \right] \tag{6.13}
\]

Using expansions (6.9) and (6.10) for the two-electron distribution and the Mulliken approximation we obtain
\[
\chi_{\mu M}(r_1)\chi_{\nu N}(r_2) \approx \frac{1}{2} S_{\mu M,\nu N} \left[ \chi_{\mu M}(r_1)\chi_{\mu M}(r_2) + \chi_{\nu N}(r_1)\chi_{\nu N}(r_2) \right]
\]  

(6.14)

In the Mulliken approximation the HF operator can be written in the form [221]

\[
\hat{F} = -\frac{\Delta}{2} + \sum_M \hat{V}_M
\]

(6.15)

where

\[
\hat{V}_M = \sum_{\mu} P_{\mu} \left[ 2(\cdots|\chi_{\mu M}\chi_{\mu M}) - (\cdots\chi_{\mu M}|\cdots\chi_{\mu M}) \right] - \frac{Z_M}{R_M}
\]

(6.16)

The summation in (6.16) is made over AOs of atom \( M \), \( P_{\mu} \) is the Mulliken population of the \( \mu \)th AO, defined as

\[
P_{\mu} = \sum_{i,\mu} C_{i,\mu M}^2 + \sum_{N \neq M}^{N_{\text{occ}}} \sum_{\nu} C_{i,\mu M} C_{i,\nu N} S_{\mu M,\nu N}
\]

(6.17)

The action of operator \( \hat{V}_M \) on the MO \( \varphi \) is defined by relations

\[
(\cdots|\chi_{\mu M}\chi_{\mu M})\varphi = (\varphi|\chi_{\mu M}\chi_{\mu M})
\]

(6.18)

\[
(\cdots\chi_{\mu M}|\cdots\chi_{\mu M})\varphi = (\varphi|\chi_{\mu M}|\varphi|\chi_{\mu M})
\]

(6.19)

As in (6.8) the functions depending on coordinates of the first electron are up to the vertical line, those depending on coordinates of the second electron – after the vertical line.

As the valence-electron approximation is supposed to be introduced, the term \( Z_M/R_M \) in (6.16) means the electron interaction with the core of atom \( M \) in the point-charge approximation. As AO \( \chi_{\mu M}(r) \) can be considered as an eigenfunction of operator \( -\Delta + \hat{V}_M \) and introducing the point-charge approximation for \( Z_M/R_N(N \neq M) \), we obtain the matrix elements of operator (6.15) in the form [222]

\[
F_{\mu M,\mu M} = \epsilon_{\mu M}(q_M) - \sum_{N \neq M} q_N(\chi_{\mu M}|\frac{1}{r_N}|\chi_{\mu M})
\]

(6.20)

\[
F_{\mu M,\nu N} = S_{\mu M,\nu N} (\epsilon_{\mu M}(q_M) + \epsilon_{\nu N}(q_N))
\]

\[
-\frac{1}{2} S_{\mu M,\nu N} \sum_{L \neq M,N} q_L \left( (\chi_{\mu M}|\frac{1}{r_L}|\chi_{\mu M}) + (\chi_{\nu N}|\frac{1}{r_L}|\chi_{\nu N}) \right) - T_{\mu M,\nu N}
\]

(6.21)

In these expressions, \( \chi_{\mu M} \) is the \( \mu \)th atomic orbital on the \( M \)th atom; \( \epsilon_{\mu M}(q_M) \) is the ionization potential of the \( \mu \)th valence orbital on the \( M \)th atom with charge \( q_M \); \( S_{\mu M,\nu N} \) and \( T_{\mu M,\nu N} \) are the overlap and kinetic energy integrals of the \( \mu \)th and \( \nu \)th orbitals on the \( M \)th and \( N \)th atom, respectively; \( (\chi_{\mu M}|\frac{1}{r_L}|\chi_{\mu M}) \) is the core-attraction integral. The effective charge \( q_M \) is calculated using the Mulliken population analysis, i.e. \( q_M = \sum_{\mu} P_{\mu} \) where the AO population \( P_{\mu} \) is defined by (6.17).

The application of the Mulliken–Rüdenberg (MR) approximation to calculate the electronic structure not of the free molecule, but of a fragment of an ionic crystal (also
called a molecular cluster), requires the summation over an infinite number of lattice sites in terms corresponding to the interaction of the fragment atoms with those of the remaining crystal. For the \( N \)th atom in a binary crystal the field of ions surrounding the considered fragment can be calculated in the point-charge approximation using the formula

\[
V_N = - \left( \frac{M_c}{a} + \sum_L \frac{\text{sgn}(q_L)}{R_{NL}} \right) |q_R| \tag{6.22}
\]

Here \( M_c \) is the Madelung constant, \( a \) the nearest-neighbor distance in crystal, \( q_R \) the charge ascribed to the lattice ions beyond the fragment under consideration, \( L \) numbers atoms in the fragment considered.

Taking into account (6.22) one can write expressions (6.20) and (6.21) in the form

\[
F_{\mu M, \mu M} = \varepsilon_{\mu M}(q_M) - \sum_{L \neq M} q_L (\chi_{\mu M})_L \frac{1}{r_L} |\chi_{\mu M}| + V^M \tag{6.23}
\]

\[
F_{\mu M, \nu N} = S_{\mu M, \nu N} (\varepsilon_{\mu M}(q_M) + \varepsilon_{\nu N}(q_N)) - \frac{1}{2} S_{\mu M, \nu N} \left\{ \sum_{L \neq M, N} q_L \left[ (\chi_{\mu M})_L \frac{1}{r_L} |\chi_{\mu M}| + (\chi_{\nu N})_L \frac{1}{r_L} |\chi_{\nu N}| \right] + V^M + V^N \right\} - T_{\mu M, \nu N} \tag{6.24}
\]

The MR approximation was extended to the periodic systems in [222,223].

To describe the band structure of an infinite perfect crystal in the framework of the LCAO method one should calculate the matrix elements of operator (6.15) using the Bloch sums of atomic orbitals (AO), defined in (4.53):

\[
\varphi_{\mu k}(r) = L^{-1/2} \sum_j \exp(i k R_j) \chi_{\mu}(r - R_j)
\equiv L^{-1/2} \sum_j \exp(i k R_j) \chi_{\mu j}(r) \tag{6.25}
\]

Here, \( k \) is the wavevector, \( \mu \) numbers the AOs in the unit cell, \( \varphi_{\mu k}(r) \) is the \( \mu \)th crystal orbital, \( \chi_{\mu j}(r) \) is the \( \mu \)th AO in the \( j \)th unit cell, and \( L \) the number of unit cells in the fundamental region of the crystal.

It is obvious that summation of core-attraction integrals over the whole lattice is very complicated. The values of these integrals decrease as \( 1/R_{MN} \) with increasing distance, i.e. special methods are required to estimate their sums. As the values of core-attraction integrals approximate rapidly the value \( 1/R \) when increasing the interatomic distance one can hope that the substitution of the Madelung energy for the sums of integrals would turn out to be a quite satisfactory approximation, at least for ionic crystals.

Using the Mulliken approximation in the three-center integrals, and the point-charge approximation for \( V_M \) it is shown in [222,224] that the MR operator matrix elements for a periodic system are given by
\[ F_{\mu M,\nu N}(k) = \frac{1}{2} \left[ 2\varepsilon_\mu(q_M, n_M) - ME_M(q_M) + 2\varepsilon_\nu(q_N, n_N) - ME_N(q_N) \right] \]

\[ \cdot \sum_j \exp(i\mathbf{kR}_j)S_{\mu Mj,\nu N0} + \frac{1}{2}(q_M + q_N) \sum_j \exp(i\mathbf{kR}_j)S_{\mu Mj,\nu N0} \frac{1}{R_{Mj,N0}} \]

\[ - \sum_j \exp(i\mathbf{kR}_j)T_{\mu Mj,\nu N0} - \delta_{MN}\delta_{\mu\nu}\varepsilon_\mu(q_M, n_M) \quad (6.26) \]

Here, the indices \( \mu Mj \) denote the element of the \( \mu \)th AO on atom \( M \) from primitive unit cell \( j \), defined by translation vector \( \mathbf{R}_j \); \( \varepsilon_\mu(q_M, n_M) \) is the ionization potential of the orbital on atom \( M \) with the atomic charge \( q_M \) and orbital population \( n_M \), \( S_{\mu Mj,\nu N0} \) and \( T_{\mu Mj,\nu N0} \) are overlap and kinetic energy integrals, respectively. The iteration procedure continues until self-consistent effective atomic charges \( q_M \) and electronic configuration \( n_M \) are obtained. The Madelung energy \( ME_M \) at the site of atom \( M \) is recalculated at each step of the iterative calculation. It is worth noting that the population-analysis scheme developed for molecules should be applied with caution to calculate the effective charges of atoms in crystals. Thus, according to the Mulliken population analysis that is widespread in molecular calculations, the contribution to the total atomic population is computed proportional to the atomic orbital overlap integrals. In the case of crystals the overlap integrals should be computed with the Bloch sums and, generally speaking, have some meaning other than the molecular ones. To avoid this difficulty Löwdin’s population analysis [225] can be used [224] that is based on a symmetrically orthogonalized basis set and that has therefore no problems connected with the distribution of the overlap population.

In the cyclic-cluster model the matrix elements (6.26) should be modified, [222]. The AOs \( \chi_\mu(\mathbf{r}) \) have to belong now not only to the atoms in the reference cell but to all the atoms included in the cyclic-cluster. Matrix elements (6.26) are calculated only for \( k = 0 \), the summation over the crystal is changed by the summation over the cyclic-cluster atoms. For ionic systems the Madelung field of the surrounding crystal can be taken into account by subtracting from the Madelung energy at the site of an atom the part due to the interaction with atoms directly included in the cyclic cluster. To satisfy the PBC introduction for the cyclic cluster the overlap integrals have to satisfy the condition \( (\chi_\mu M(\mathbf{r} - \mathbf{R}_j + \mathbf{A})\chi_\nu N(\mathbf{r})) = S_{\mu Mj,\nu N} \) where \( \mathbf{A} \) is the translation vector of the cyclic cluster as a whole (see Chap. 3).

The MR approximation was applied for electronic structure calculations of both perfect crystals (alkali halides [222], MgO and CaO [226], PbO [227], corundum [228]), point defects in solids ([229–234]) and surfaces [224].

The general analysis of Rödenberg’s approximation in the HF LCAO method for molecules [218] and solids [223] has shown that EHT and zero differential overlap (ZDO) approximations can be considered as particular cases of Rödenberg’s integral approximation. ZDO methods, considered in the next section, were applied to a wide class of molecules and solids, from purely covalent to purely ionic systems. Therefore, they are more flexible compared to the MR approximation, which is more appropriate for ionic systems.
6.2 Zero-differential Overlap Approximations for Molecules and Crystals

6.2.1 Zero-differential Overlap Approximations for Molecules

As was seen in Sec. 6.1 in EHT the AO basis functions are only used for the calculation of overlap integrals (molecules) or lattice sums of overlap integrals (crystals). In the MR method kinetic energy integrals or their lattice sums are also included. These integrals in fact can be expressed through overlap integrals. All other contributions to the one-electron Hamiltonian matrix elements are based on empirical parameters.

As we have seen, EHT is a nonself-consistent method but the self-consistency over charge and configuration is included in the MR approximation. The \textit{Ab-initio} HF SCF method requires the self-consistent calculation of the density matrix (see Chap. 4). This feature of the HF approach is maintained in the semiempirical methods, based on the zero differential overlap (ZDO) approximation. This approximation is used to reduce the number of multicenter integrals appearing in HF LCAO calculations.

In the ZDO approximation the differential overlap \( \chi_\mu(r_1)\chi_\nu(r_2)dr_1dr_2 \) of valence AO basis functions is supposed to be zero for any \( \mu \neq \nu \) both for \( r_1 = r_2 \) and \( r_1 \neq r_2 \). The ZDO approximation means that the AO basis is assumed to be orthogonal \((S_{\mu\nu} = \int \chi_\mu(r)\chi_\nu(r)dr = \delta_{\mu\nu})\). A recent review by Bredow and Jug \cite{235} gives a brief summary of the basis features of ZDO semiempirical methods together with examples of their use. These authors are convinced that “the development of semiempirical methods and their extension to a growing number of research areas has been a continuous process over the last 4 decades and there is apparently no end to be seen”. This is demonstrated by the large number of semiempirical studies in organic, inorganic and physical chemistry, biochemistry, drug design, crystallography and surface science.

Depending on the level of the approximations used for other integrals ZDO methods differ. In the CNDO (complete neglect of differential overlap) method \cite{205,236} all two-electron integrals are approximated by Coulomb integrals according to

\[
(\mu\nu|\lambda\sigma) = \int \chi_\mu(r_1)\chi_\nu(r_1)\frac{1}{r_{12}}\chi_\lambda(r_2)\chi_\sigma(r_2)dr_1dr_2 = \delta_{\mu\nu}\delta_{\lambda\sigma}(\mu\mu|\lambda\lambda) \tag{6.27}
\]

and only two-center electron-repulsion integrals \((\mu\mu|\lambda\lambda) = \gamma_{MN}\) are retained \((M\) and \(N\) are the atoms on which basis functions \(\chi_\mu(r)\) and \(\chi_\nu(r)\) reside, respectively). The independence of this integral on the angular part of AOs restores the AOs hybridization invariance of the original HF operator matrix elements, \textit{i.e.} it is supposed that \((S_M S_M|S_N S_N) = (P_M P_M|P_N P_N) = (P_M S_M|P_N S_N) = \gamma_{MN}\). The two-center Coulomb integral \(\gamma_{MN}\) can either be computed explicitly from \(s\)-type STOs (6.1) or it can be treated as a parameter. The one-center Coulomb integral \(\gamma_M\) is parametrized using a so-called Pariser–Parr \cite{237} approximation \(\gamma_M = I_M - A_M\), where \(I_M\) and \(A_M\) are the atomic ionization potential and electron affinity, respectively. The parameter \(\gamma_M\) can be expressed with a commonly tabulated semiempirical parameter \(U_{\mu\nu}\) (the energy of interaction of electron-occupying AO \(\chi_\mu(r)\) with the core of atom \(M\)):

\[
U_{\mu\nu} = -I_\mu - (Z_\mu - 1)\gamma_M \tag{6.28}
\]
Equations (6.28) and (6.29) are used in CNDO/1 and CNDO/2 methods, respectively. For the two-center integral $\gamma_{MN}$, the Mataga–Nishimoto [238]

$$
\gamma_{MN}(eV) = \frac{14.3986}{R_{AB} + \delta}, \quad \delta(eV) = \frac{14.3986}{(\gamma_{AA} + \gamma_{BB})^{1/2}}
$$

(6.30)
or Ohno [239]

$$
\gamma_{AB}(eV) = \frac{14.3986}{\sqrt{R_{AB} + \delta}}
$$

(6.31)
formulas are adopted, where $R_{AB}(\text{Å})$ is the interatomic distance. At large distance, $\gamma_{AB}$ in both cases goes to $1/R_{AB}$, as expected for widely separated charge clouds, while at short distances, it approaches the average of the two one-center parameters.

The one-electron terms for offdiagonal matrix elements are defined as

$$
h_{\mu\nu} = \beta_{\mu\nu} = 0.5(\beta_M + \beta_N)S_{\mu\nu}
$$

(6.32)

where $S_{\mu\nu}$ is the overlap matrix element computed using Slater-type basis functions $\chi_\mu(r)$ and $\chi_\nu(r)$, centered on atoms $M$ and $N$, respectively; the $\beta_M, \beta_N$ values are semiempirical parameters. Note that computation of the overlap is carried out for every combination of basis functions, even though in the secular equation $FC = CE$ itself $S$ is defined in ZDO approximation as $S_{\mu\nu} = \delta_{\mu\nu}$. There are, in effect, two different $S$ matrices, one for each purpose. The $\beta$ parameters are entirely analogous to the parameters $\beta$ in EHT – they provide a measure of the strength of through-space interactions between atoms [240]. As $\beta$ parameters are intended for completely general use it is not necessarily obvious how to assign them a numerical value, unlike the situation that obtains in EHT. Instead, $\beta$ values for CNDO were originally adjusted to reproduce certain experimental quantities.

The diagonal $F_{\mu\mu}$ and nondiagonal $F_{\mu\nu}$ matrix elements in the CNDO approximation for molecules are defined by

$$
F_{\mu\mu} = U_{\mu\mu} + (P_M - 1/2P_{\mu\mu})\gamma_M + \sum_{N \neq M}(P_N - Z_N)\gamma_{MN}
$$

(6.33)

$$
F_{\mu\nu} = -0.5P_{\mu\nu}\gamma_M
$$

(6.34)

$$
F_{\mu\nu} = \beta_{MN}S_{\mu\nu} - 0.5P_{\mu\nu}\gamma_{MN}
$$

(6.35)

AOs $\chi_\mu$ and $\chi_\mu'$ in (6.34) are supposed to belong to the same atom $M$. In (6.34) $Z_M$ is the atomic-core charge, $P_{\mu\nu}$ are the density matrix elements in the LCAO approximation (see (4.37)), $P_M = \sum_{\mu}P_{\mu\mu}$ is the electron population of atom $M$, the resonance integral $\beta_{\mu\nu}$ is taken as $\beta_{MN}$, i.e. depends only on the atom type, but not on a particular orbital of this atom. The CNDO method represents a vast simplification of HF theory, reducing the number of two-electron integrals having nonzero values from formally $N^4$ to $N^2$. Furthermore, these integrals are computed by trivial algebraic formulae, not by explicit integration, and between any pair of atoms all of the integrals have the same value irrespective of the atomic orbitals involved. Similarly, evaluation of one-electron integrals is also entirely avoided (excluding overlap integrals), with numerical values for those portions of the relevant matrix elements coming from easily
evaluated formulae. Historically, a number of minor modifications to the conventions outlined above were explored, and the different methods had names like CNDO/1, CNDO/2, CNDO/BW, etc. [205].

The computational simplifications inherent in the CNDO method are not without chemical cost, as might be expected. Like EHT, CNDO is quite incapable of accurately predicting good molecular structures. Furthermore, the electronic interactions on a single atom are not correctly reproduced due to the ZDO approximation for the different AOs of the same atom. In an attempt to overcome this deficiency of the CNDO scheme the intermediate neglect of differential overlap (INDO) approximation was introduced [241] to permit a more flexible handling of electron–electron interactions on the same center. In this case, the different values of one-center two-electron integrals are used for different AOs: \((ss|ss) = G_{ss}, (ss|pp) = G_{sp}, (pp|pp) = G_{pp}, (sp|sp) = L_{sp}\). These integrals are in practice estimated from spectroscopic data. In the INDO scheme the valence bond angles are predicted with much greater accuracy than is the case for CNDO. Nevertheless, overall molecular geometries predicted from INDO tend to be rather poor. Preliminary efforts to address this problem have been reported only recently [242]. A careful parametrization of INDO for spectroscopic problems [243] was described in an INDO/S calculation scheme whose parametrization was later extended to most of the elements in the periodic table [244]. In a purely terminological sense one can make a distinction between the INDO semiempirical method and the INDO/S model [102]. The latter is a particular parametrization of the INDO method designed for spectroscopic applications. The MINDO/3 model [245], the third version of the modified INDO method, included some modifications: different orbital exponents were used for \(s\)- and \(p\)-orbitals on the same atom, resonance integrals \(\beta_{MN}\) between two atoms were split into pairs corresponding to \(s-s\), \(s-p\), \(p-p\) orbital interactions, some empirical modifications to the nuclear repulsion energy were introduced. The MINDO/3 model allowed prediction of heats of formation with the mean absolute error of 11 kcal/mole, 0.7 eV for ionization potentials, 0.022˚A for bond lengths.

In both CNDO and INDO methods the two-center two-electron integral takes the value \((\mu\mu|\nu\nu) = \beta_{MN}\), irrespective of which orbitals on atoms \(M\) and \(N\) are considered.

The neglect of diatomic differential overlap (NDDO) method [236] is an improvement over the INDO approximation, since the ZDO approximation is applied only for orbital pairs centered at different atoms. Thus, all integrals \((\mu\nu|\lambda\sigma)\) are retained provided \(\mu\) and \(\nu\) are on the same atomic center and \(\lambda\) and \(\sigma\) are on the same atomic center, but not necessarily the center hosting \(\mu\) and \(\nu\). In principle, the NDDO approximation should describe long-range electrostatic interactions more accurately than INDO. Most modern semiempirical models (MNDO, AM1, PM3) are NDDO models.

The modified neglect of the diatomic overlap (MINDO) method [246] led to improved agreement with experiment. In the two-electron integrals calculation the continuous charge clouds were replaced with classical multipoles. Thus, an \(ss\) product was replaced with a point charge, an \(sp\) product was replaced with a classical dipole (represented by two point charges slightly displaced from the nucleus along the \(p\) orbital axis), and a \(pp\) product was replaced with a classical quadrupole (again represented by point charges). The magnitudes of the moments, being one-center in nature, are related to the parameterized integrals appearing in the INDO method. By adopting such a form for the integrals, their evaluation is made quite simple, and so too is
evaluation of their analytic derivatives with respect to nuclear motion. To complete
the energy evaluation by the MNDO method, the nuclear repulsion energy is added
to the SCF energy. The parameters of the MNDO model were optimized against a
large test set of molecular properties (within the assumption of a valence orbital set
comprised only of $s$ and $p$ orbitals).

In addition, a modified MNDO model explicitly adding electron-correlation effects
(MNDOC) by second-order perturbation theory was described by Thiel [247]. By
explicitly accounting for electron correlation in the theory, the parameters do not
have to absorb the effects of its absence from HF theory in some sort of average way.

Later, two modifications of MNDO were introduced [102,235]. The most prominent
of these are the Austin model 1 (AM1) by Dewar et al. [246] and the parametric
method 3 (PM3) by Stewart [248]. In principle MNDO, AM1 and PM3 methods
differ only in the parametrization and in the empirical function $f_{MN}$ in the core–core
repulsion

$$V_{nn} = \sum_{M>N} Z_M^* Z_N^* \gamma_{MN} + f_{MN}$$

(6.36)

where

$$f_{MN} = Z_M^* Z_N^* \gamma_{MN} \left( \exp(-\alpha_M R_{MN}) + \exp(-\alpha_N R_{MN}) \right)$$

and $Z^*$ is the effective core charge.

A variety of modifications of the original methods is now available. AM1 and
PM3 have been extended for the treatment of transition-metal compounds by in-
clusion of $d$ orbitals in the valence basis; the Green’s function technique has been
implemented in MNDO-type methods for the calculation of ionization potentials and
electron affinities; a parameterized variational technique is used for the calculation of
molecular polarizabilities and hyperpolarizabilities within the MNDO, AM1 and PM3
methods [235].

The most important modifications of the MNDO method are the use of effective
core potentials for the inner orbitals and the inclusion of orthogonalization corrections
in a way as was suggested and implemented a long time ago in the SINDO1 method
[249] at first developed for organic compounds of first-row elements and later extended
to the elements of the second and third row [250,251].

The most important feature of the SINDO1 method is that an orthogonalization
transformation of the basis functions is taken into account explicitly in solving the
HF LCAO equations. The one-electron integral matrix $H$ is transformed to Löwdin
symmetrically orthogonalized [225] AOs $\chi^\lambda = S^{-1/2}\chi$

$$H^\lambda = S^{-1/2}H S^{-1/2}$$

(6.37)

Matrix $S^{-1/2}$ can be expanded in a series

$$S = I + \sigma$$

$$S^{-1/2} = I - 1/2\sigma + 3/8\sigma^2 - \cdots$$

(6.38)

where $I$ is the unit matrix and $\sigma$ the remaining two-center overlap matrix. The ex-
pansion is truncated in such a way that only terms up to second order in the overlap
are retained.
Another special feature of SINDO1 is the treatment of inner orbitals by a local pseudopotential introduced in [252]. Two-center one-electron integrals $H_{\mu\nu}^{\lambda}$ are calculated by the following empirical formula:

$$H_{\mu\nu}^{\lambda} = L_{\mu\nu} + \Delta H_{\mu\nu}, \quad \mu \in M, \quad \nu \in N$$  (6.39)

Here, $L$ is a correction to the Mulliken approximation for the kinetic energy, and $\Delta H$ is entirely empirical and contains adjustable bond parameters. These are optimized in order to minimize the deviation from experiment for a set of reference compounds.

Two sets of Slater-orbital exponents are used. One ($\zeta^U$) for intra-atomic integrals, and the other ($\zeta^L$) for interatomic integrals. Experimental heats of formation are calculated from binding energies $E_B$, which are corrected by the zero-point energies obtained from vibration analyses. This is theoretically more sound than in MNDO, AM1 and PM3, where binding energies are parameterized directly to reproduce experimental heats of formation without reference to zero-point energies.

Recently, a new version MSINDO was developed by substantial modifications in the SINDO1 formalism. The parameters are now available for the elements H, C–F, Na–Cl, Sc–Zn, and Ga–Br [253–256] for Li–B and K–Ca, [257].

In MSINDO the standard basis set for elements Al–Cl has been changed from \{3s, 3p\} to \{3s, 3p, 3d\} in order to account for hypervalent compounds [253]. For compounds containing Na and Mg an inclusion of 3d functions was considered inconsistent, because these atoms already contain 3p functions for polarization. Moreover, test calculations showed that the 3d functions on these atoms had only insignificant effects on the molecular properties. As for SINDO1 the H basis set can be augmented with a 2p shell for the treatment of hydrogen bonds. All Slater–Condon atomic parameters are calculated analytically for the one-center two-electron integrals and one-electron integrals $U_{\mu\mu}$. For the higher multipole terms, this differs from SINDO1, where these terms were taken from experimental spectra. The MSINDO procedure is more consistent since all parameters are derived at the same level of theory. To maintain rotational invariance a number of one-center hybrid integrals have to be included in the case of $d$ functions [258]. This was already implemented in SINDO1 and was kept in MSINDO.

The core integrals $U_{3d}$ of second- and third-row elements were scaled by a screening potential $K_{sc}$ in order to avoid unrealistically high populations for the 3d shell:

$$U_{3d}^\prime = (1 - K_{sc})U_{3d}$$  (6.40)

For second-row elements a fixed value of $K_{sc} = 0.15$ is used. For third-row elements $U_{3d}, U_{4s}$ and $U_{4p}$ were scaled with different screening potentials [256].

The most important change in MSINDO with respect to SINDO1 is a modification of the approximate Löwdin orthogonalization of the basis [253]. Only the first-order terms in overlap are retained in (6.38). In SINDO1 the expansion was to second order. If only first-order terms are taken into account, no transformation of the two-electron integrals is necessary. The one-electron integrals are transformed

$$\tilde{H}_{\mu\mu'}^{\lambda} = H_{\mu\mu'}^{\lambda} - f^M \frac{1}{2} \sum_{N \neq M} \sum_{\nu} (L_{\mu\nu} S_{\nu\mu'} + S_{\mu\nu} L_{\nu\mu'})$$  (6.41)

The correction factor, $f^M$, accounts for the neglect of higher-order terms in the truncated expansion (6.38). Its value depends on the number of basis functions on atom $M$. $f^M$ is 1 for an \{s\} basis, 0.75 for an \{s, p\} basis and 0.5 for an \{s, p, d\} basis.
We considered SINDO1-MSINDO methods in more detail as these methods were successfully applied in calculations of bulk solids and surfaces in the embedded and cyclic-cluster models (see Sect. 6.3). The role of long-range interactions in solids increases, compared to the case of molecules. In order to better describe long-range interactions, in particular at surfaces, dipole–monopole and dipole–dipole terms were added to the MSINDO formalism following an early suggestion by Voigt [259]. After modification of the formalism a complete reparameterization of all elements had to be performed. The new version, called MSINDO+, was tested for some cases where SINDO1 and MSINDO gave results in disagreement with experiment.

It should be noted that an analysis of some systematic errors of the ZDO approximation [260] allowed an improved semiempirical approach to be developed [261]. In this approach the Rüdenberg approximation is used for diatomic overlap densities appearing in Coulomb integrals, the Fock matrix is simplified such that its construction scales with $N^2$ instead of $N^4$ in ab-initio methods, if $N$ is the dimension of the basis set. Thus, the one-electron and two-electron Coulomb parts of the Fock matrix are formulated explicitly in an atomic orbital (AO) basis, whereas the ZDO approximation is restricted to the two-electron exchange part. The complete two-electron Coulomb part of the Fock matrix is explicitly subjected to the Löwdin transformation. The proposed formalism is not necessarily an empirical one because, in principle, all matrix elements can be calculated exactly. Since only two-center integrals appear one can use a Slater instead of the Gaussian basis of ab-initio methods. However, if the formalism is restricted to the valence electrons as in normal semiempirical methods some parametrization is unavoidable. In this case, an additional pseudopotential accounting for the effects of core-valence orthogonality should be implemented. It may also be useful to absorb possible errors arising from the Rüdenberg approximation into the parametrization of the two-electron integrals.

Hybrid approaches combining ab-initio or DFT and semiempirical approaches have become popular. As an example, we can refer to LEDO (limited expansion of differential overlap) densities application to the density-functional theory of molecules [262]. This LEDO-DFT method should be well suited to the electronic-structure calculations of large molecules and in the authors’ opinion its extension to Bloch states for periodic structures is straightforward. In the next sections we discuss the extension of CNDO and INDO methods to periodic structures – models of an infinite crystal and a cyclic cluster.

### 6.2.2 Complete and Intermediate Neglect of Differential Overlap for Crystals

The first applications of ZDO methods for extended systems refer to the electronic-structure calculations of regular polymer chains when the one-dimensional (1D) periodicity is taken into account. The corresponding modifications of molecular ZDO equations can be found in the literature: for the CNDO method in [263–266], for the INDO and MINDO methods in [267, 268], for the MNDO, PM3 and AM1 methods in [269–272].

The CNDO method extended to the two-dimensional (2D) periodicity case was applied in regular chemisorption studies of hydrogen and oxygen on a graphite surface [207, 273–275]. The equations of the CNDO method for three-dimensional (3D) solids...
were given in [207, 273, 275–281]; the periodic MINDO method is considered in [282–284].

The main features of the CNDO and INDO approaches to periodic systems are similar to those used for molecules. A valence-electron approximation is adopted, which implies that only the valence electrons are in the bonding region and are polarized by the presence of neighboring atoms [277]. For periodic systems the LCAO approximation is based on use of the Bloch sums (4.53) of AOs \( \chi_n(r) = \chi_n(r - R_n) \) numbered by index \( \mu \) (labels all AOs in the reference primitive unit cell) and by the direct lattice translation vector \( R_n \) (\( n = 0 \) for the reference cell).

In the ZDO approximation AOs are supposed to be orthogonal both in the intracell and intercell overlap integrals

\[
S_{\mu 0, \nu n} = \int \chi_{\mu 0}(r)\chi_{\nu n}(r)\,dr = \delta_{0n}\delta_{\mu\nu} \tag{6.42}
\]

The two-electron integrals are approximated by Coulomb integrals \( \gamma_{00, MN} \), calculated with \( s \) functions of the \( M \)th atom from reference cell and the \( N \)th atom from the cell \( n \):

\[
\langle \mu 0, \nu n | \lambda i, \sigma i' \rangle = \delta_{0n}\delta_{\mu\nu}\delta_{i i'}\delta_{\lambda\sigma}\gamma_{00, MN} \tag{6.43}
\]

The one-electron matrix elements \( H_{\mu 0, \nu n} \) are approximated by \( \beta_{0N, MN}S_{0, 0, MN} \), where the resonance integrals \( \beta_{MN} \) depend only on the type of atoms \( M \) and \( N \) to which the AOs \( \mu \) and \( \nu \) refer. In particular, in the CNDO/2 version of the CNDO method for the crystal the diagonal one-electron matrix elements are taken in the form

\[
H_{\mu 0, \mu 0} = U_{\mu\mu} + Z_M\gamma_{00, MM} - \sum_{n, N} Z_N\gamma_{0n, MN} \tag{6.44}
\]

The difference of (6.44) from its molecular analog is defined by the lattice summation over all atoms \( N \) (including \( M = N \)) in the reference cell and in different unit cells of a crystal. In the model of an infinite crystal these lattice sums are infinite. All the simplifications mentioned are introduced in the Fock and overlap matrices (4.56) and HF LCAO equations (4.57) for periodic systems so that one obtains instead of (4.56) and (4.57):

\[
S^{ZDO}_{\mu\nu}(k) = \sum_n \delta_{0n}\delta_{\mu\nu}\exp(ikR_n) = \exp(ikR_0) \tag{6.45}
\]

\[
\sum_{\nu} \{ F^{ZDO}_{\mu\nu}(k) \exp(ik(R_n - R_0)) - E_i(k)C_{i\mu}(k) \} = 0 \tag{6.46}
\]

Let \( R_0 \), the lattice vector of the reference cell, correspond to the origin of the coordinate system. Then the core (H) and Fock (F) matrix elements have the following form within the CNDO formalism

\[
H_{\mu\mu}(k) = U_{\mu\mu} + Z_M\gamma_{00, MM} - \sum_{N} Z_N\gamma_{0n, MN} + \sum_{n=1}^{L-1} \beta_{0N}S_{0n, MN} \exp(ikR_n) \tag{6.47}
\]

\[
H_{\mu\nu} = \sum_{n=0}^{L-1} \beta_{MN}S_{0n, MN} \exp(ikR_n)
\]
\[ F_{\mu\nu}(k) = H_{\mu\nu}(k) + \frac{1}{L} \sum_{N,\nu} \sum_{n=0}^{L-1} P_{\nu\nu}(k') \gamma_{\alpha M N}^{0n} \]

\[ - \frac{1}{2L} \sum_{n=0}^{L-1} \sum_{k'} P_{\mu\mu}(k') \gamma_{\alpha M N}^{0n} \exp(i(k - k')R_n) \]

\[ F_{\mu\nu}(k) = H_{\mu\nu}(k) - \frac{1}{2L} \sum_{n=0}^{L-1} \sum_{k'} P_{\mu\nu}(k') \gamma_{\alpha M N}^{0n} \exp(i(k - k')R_n) \quad (6.48) \]

As in the HF LCAO method the calculation of the wavevector of the \( k \)-dependent density matrix

\[ P_{\mu\nu}(k) = 2 \sum_{i}^{\text{occ}} C_{i\mu}^*(k) C_{i\nu}(k) \quad (6.49) \]

requires the summation over occupied crystalline orbitals \((i)\) that are themselves defined as a linear combination of the basis atomic orbitals. The HF method allows both an all-electron calculation and a valence-electron approximation when the atomic cores pseudopotentials are introduced. In both cases the AO are represented by GTO. In the CNDO method for crystals only the valence atomic orbitals are included and represented by a minimal Slater basis set. We return to the basis-sets consideration in Chap. 8.

Equations (6.47) and (6.48) contain an explicit \( k \) dependence via the phase factors \( \exp(i k R_n) \) and an implicit \( k \)-dependence via summations over \( k' \). Invoking the special \( k \)-points theory (see Sect. 4.2.2) one need only use a small set of \( k' \)-points to approximate the integral over BZ.

In (6.48) and (6.49), \( S_{\mu\nu}^{0n} \) and \( \gamma_{\alpha M N}^{0n} \) are the overlap and Coulomb integrals for atomic orbital \( \mu \) on atom \( M \) in the primitive unit cell 0 and atomic orbital \( \nu \) on atom \( N \) in the cell \( R_n \). \( U_{\mu\mu} \) describes the interaction of an electron with the atomic core of atom \( M \) with the core charge \( Z_M \) (this is equal to the number of valence electrons of atom \( M \)). The Coulomb integrals \( \gamma_{MN} \) and the bonding parameters \( \beta_{MN} \) are assumed to be orbitally independent.

It follows from (6.49) that in the CNDO approximation the nonlocal exchange is taken into account as nondiagonal elements of the Fock matrix contain nondiagonal elements \( P_{\mu\nu}(k') \) of the density matrix. This means that lattice sums in this case are divergent, see Sect. 4.3.3. Indeed for sufficiently large \( R_n \) the two-electron integrals \( \gamma_{\alpha M N}^{0n} \) in the exchange part of (6.48) may be approximated by \( 1/|r_M + r_N - R_n| \) where \( r_M, r_N \) are the vectors defining the positions of atoms \( M \) and \( N \) in the reference cell. Therefore, the convergence of the lattice sum over \( n \) is defined by the convergence of the lattice sum

\[ S_j(k) = \sum_n \exp(i(k - k_j)R_n) \]

\[ |R_n + r_m - r_N| \quad (6.50) \]

The sum (6.50) can be calculated for \( k \neq k_j \), for example, by the Ewald method. However, for \( k = k_j \) the series (6.50) appears to be divergent [95]. This divergence is the result of the general asymptotic properties of the approximate density matrix calculated by the summation over the special points of BZ (see Sect. 4.3.3). The difficulties connected with the divergence of lattice sums in the exchange part have been resolved in CNDO calculations of solids by introduction of an interaction radius.
for exchange [276, 277] or of distance-dependent modulating functions that weight certain Coulomb interaction terms [280]. Detailed studies of the HF LCAO density matrix properties (see Sect. 4.3.3) allow an interpolation procedure to be suggested for constructing an approximate density matrix for periodic systems, which ensures a balance between the direct lattice and BZ summations. Furthermore, this analysis is important for the cyclic-cluster ZDO calculations as it allows an additional parameter (exchange radius) introduction to be omitted (see Sect. 6.3).

The extension of INDO and MINDO semiempirical methods to periodic systems has no principal differences compared with the CNDO method. The advantage of these methods is the possibility to make spin-dependent calculations as is done in the UHF method.

The considered CNDO method for periodic systems formally corresponds to the model of an infinite crystal or its main region consisting of \( L \) primitive cells. This semiempirical scheme was also applied for the cyclic-cluster model of a crystal allowing the BZ summation to be removed from the two-electron part of matrix elements. In the next section we consider ZDO methods for the model of a cyclic cluster.

6.3 Zero-differential overlap Approximation in Cyclic-cluster Model

6.3.1 Symmetry of Cyclic-cluster Model of Perfect Crystal

In Sect. 4.2.1 we introduced supercell transformation (4.77) in the direct lattice allowing generation of special points of the BZ in the calculation of the one-electron density matrix of the perfect crystal. In this consideration, the perfect crystal was supposed to be infinite or represented by its main region. The latter was defined as a block on which opposite-sides periodic boundary conditions are imposed. The main region of a crystal can be called a cyclic cluster of huge size (in the shape of a parallelepiped with large edges) modeling the infinite crystal and maintaining its translation symmetry.

The idea to use relatively small cyclic clusters for comparative perfect-crystal and point-defect calculations appeared as an alternative to the molecular-cluster model in an attempt to handle explicitly the immediate environment of the chemisorbed atom on a crystalline surface [285] and the point defects in layered solids [286, 287] or in a bulk crystal [288, 289, 292, 293]. The cluster is formed by a manageable group of atoms around the defect and the difference between the molecular-cluster model (MCM) and the cyclic cluster model (CCM) is due to the choice of boundary conditions for the one-electron wavefunctions (MOs). Different notations of CCM appeared in the literature: molecular unit cell approach [288], small periodic cluster [286], large unit cell [289, 290]. We use here the cyclic cluster notation.

In MCM (as in molecules) MOs are supposed to be orthonormalized in the whole space; this condition is also fulfilled for the molecular clusters embedded by some or another means into the crystalline environment. Recent applications of the molecular-cluster model and MO calculations for materials design in the Hartree–Fock–Slater method are discussed in [291].

In the CCM model the periodic boundary conditions are introduced for MOs of a cluster having the shape of a supercell of a perfect crystal so that MOs are
orthonormal in the field of the cyclic cluster chosen. Postponing to Chap. 10 the more
detailed discussion of molecular models of defective crystals we would like to note
here the difference between the supercell model (SCM) and CCM for point defects.
In the former, PBC are introduced for the main region of a crystal so that the point
defect is periodically repeated over the crystalline lattice, in the latter the single point
defect is considered. This means that CCM is conceptually a supercell-type approach
but is technically more closely related to the simple MCM [294].

We discuss here the symmetry of CCM for perfect crystal [13, 295–299]. The sym-
mometry of defective crystal in CCM is considered in Chap. 10.

To define a finite cyclic system, let us make a linear transformation of the primitive-
lattice translation vectors

$$A_j = \sum_i l_{ji}a_j, \quad L = |\det l| \geq 1$$  \hspace{1cm} (6.51)

where the integer coefficients $l_{ji}$ form the matrix $l$. The transformation (6.51) for $L > 1$
determines a supercell (large unit cell) of the direct lattice. It may be chosen in the
form of a parallelepiped with vectors $A_j$ as edges or in the form of the corresponding
Wigner–Seitz unit cell.

The particular form of the matrix $l$ in (6.51) defines the supercell shape and its
volume (which is $L$ times larger than that of a primitive unit cell) and the symmetry
of the direct lattice based on the group $T_A$ of the translations

$$A_n = \sum_{j=1}^{3} n_jA_j, \quad n_j \text{ are arbitrary integers}$$  \hspace{1cm} (6.52)

The group $T_A$ is an invariant subgroup of $T_a$ (translation group of the infinite lattice
with primitive translation vectors $a_i$) so that the cosets $(E|\alpha^{(i)})T_A(i = 1, 2, \ldots, L)$
in the decomposition

$$T_a = \sum_{i=1}^{L} (E|\alpha^{(i)})T_A$$  \hspace{1cm} (6.53)

form the factor group $T_a/T_A = T^{(A)}$ of order $L$. The so-called inner translations of
the supercell are assumed to be chosen as $\alpha^{(i)}$ in (6.53).

Figure 6.1a shows the supercell of the plane hexagonal lattice of boron nitride,
BN, formed by the diagonal $l = \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$ matrix, with $L = 9$.

A cyclic cluster $C^{(A)}$ is defined as a supercell with identical opposite faces, i.e.
the periodic boundary conditions are introduced for the chosen supercell itself (not
for the main region of a crystal!). In particular, in the supercell, shown on Fig. 6.1a,
the atoms with the primed numbers are supposed to be identical with the atoms of
the supercell, having the same unprimed numbers. This means that the translation
of a supercell as a whole is equivalent to the zero translation.

The translation symmetry of $C^{(A)}$ is characterized by a three-dimensional cyclic
group $\hat{T}^{(A)}$ of order $L$ with the elements $(E|\alpha^{(i)})$ from (6.53) and multiplication law
modulo $T_A$. In our example, this group consists of 9 inner translations of the $B_9N_9$
supercell, i.e. translations of the BN primitive unit cell, consisting of one formula
unit. The group $\hat{T}^{(A)}$ is isomorphic to the factor group $T^{(A)}$. 
Fig. 6.1. Supercell (a) and small Brillouin zone (b) for hexagonal plane lattice of boron nitride BN. Atoms 1–18 belong to the supercell, the atoms with the primed numbers are supposed to be identical with the corresponding atoms, belonging to the supercell.

Let \( l^{(a)}(R) \) be the transformation matrix of the translation vectors \( a_i \) under the point-symmetry operation \( R \in F \)

\[
Ra_i = \sum_{i'} l^{(a)}_{i'i}(R)a_{i'}
\]  

(6.54)

The corresponding transformation matrix for the translation vectors \( A_j \) in (6.51) is

\[
RA_j = \sum_{j'} l^{(A)}_{j'j}(R)A_{j'}, \quad l^{(A)}(R) = l^{-1}l^{(a)}(R)l
\]  

(6.55)

The operation \( (R'|v' + a_n) \in G \) is compatible with the translation symmetry of the lattice composed of supercells, if the vectors \( R'A_j \) are integer linear combinations of
the vectors $\mathbf{A}_j$, i.e. the matrix $l^{(A)}(R')$ is integer. All these operations $(R'|\mathbf{v'} + \mathbf{a}_n)$ form a group $G' \subset G$. The rotations $R'$ form a point group $F' \subset F$ of order $n_{F'} \leq n_F$. As

\[(R'|\mathbf{v'} + \mathbf{a}_n)(E|\mathbf{A}_j)(R'|\mathbf{v'} + \mathbf{a}_n)^{-1} = (E|R'\mathbf{A}_j) \quad (6.56)\]

the translation group $T_A$ is an invariant subgroup of the group $G'$. The cosets in the decomposition

\[G' = \sum_{i=1}^{L} \sum_{s=1}^{n_{F'}} (R'_s|\mathbf{v}'_s + \mathbf{a}^{(i)}_s)T_A \quad (6.57)\]

form the factor group $G^{(A)} = G'/T_A$ of the order $n_{F'}L$.

The coset representatives $(R'_s|\mathbf{v}'_s + \mathbf{a}^{(i)}_s)$ in (6.57) contain the inner translations $\mathbf{a}^{(i)}$ of the supercell ($i = 1, 2, \ldots, L$) and rotational parts $R' \in F'$ forming the point group of the space group $G'$.

Let us introduce a modified multiplication law modulo $T_A$, which does not distinguish between the translations of the group $T_A$. The set of $n_{F'}L$ elements $(R'_s|\mathbf{v}'_s + \mathbf{a}^{(i)}_s)$ forms a group $\tilde{G}^{(A)}$ (modulo $T_A$), which is the symmetry group of the cyclic cluster $C^{(A)}$. The group $\tilde{G}^{(A)}$ is isomorphic to the factor group $G^{(A)}$. Both groups $(\tilde{G}^{(A)}$ and $G^{(A)}$) are homomorphic images of the space group $G'$. The translation group $T_A$ is the kernel of this homomorphism. If the space group $G'$ coincides with the space group $G$ the transformation (6.51) is called symmetric. In this case, the point symmetry of a cyclic cluster coincides with that of an infinite crystal. In our example, the cyclic cluster consisting of 9 primitive unit cells of hexagonal BN (see Fig. 6.1a) has the same point symmetry as the hexagonal BN in the one-layer model. The symmetric transformation (6.51) retains the point symmetry of the Bravais lattice, but it is compatible with a change of its type in the framework of the same crystalline system. As an example, one can consider the cyclic cluster defined by a crystallographic unit cell for face-centered cubic lattice (see Chap. 2) or the supercell of a hexagonal lattice, generated by the transformation with nondiagonal matrix $l = \begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$, with $L = 3$. In the first case, the translation vectors of the cubic cluster of 4 primitive unit cells ($l = \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}$, $L = 4$) form a simple cubic lattice. In the second case the lattice of supercells remains hexagonal. The nonsymmetric transformation (6.51) leads to a cyclic cluster with the point-symmetry group $F'$ that is lower than that of an infinite crystal. The smallest possible cyclic cluster $C^{(A)}$ is a primitive unit cell with the symmetry group $\hat{G}^{(a)}$ of the order $n_{F'} (\hat{F}^{(a)} \leftrightarrow F)$. The so-called main region of a crystal is also a cyclic cluster corresponding to the transformation (6.51) with very large $L = N_1N_2N_3$; it is assumed that there are $N_i$ primitive unit cells in direction $\mathbf{a}_i$ ($i = 1, 2, 3$) (where $N_i$ is a very large number). When the cyclic boundary conditions are introduced for the main region of a crystal, the translation group $T_A$ consists of translations $\mathbf{A}_i = N_ia_i(i = 1, 2, 3)$, i.e. the transformation matrix $l$ in (6.51) is assumed to be diagonal. Usually no attention is paid to the fact that the main region possesses the point symmetry of an infinite crystal only if the corresponding transformation (6.51) is symmetric. For example, the main region for a cubic crystal has to be defined with $N_1 = N_2 = N_3$. The space group $G$ of the infinite
crystal may be obtained as a limit of the symmetry groups of a sequence of increasing cyclic systems.

As is seen, the symmetry operations in the cyclic-cluster symmetry group are defined with the modified multiplication law modulo $T_A$. These groups were named by Stewart [299] “the symmetry groups of unit cells in solids” and interpreted as a new type of group being intermediate between point-symmetry groups of molecules and space groups of infinite crystals. The irreducible representations of these groups are defined by those of space groups for the points of the BZ satisfying the condition $\exp(i\mathbf{k}A_j) = 1$ where $A_j$ are the translation vectors of the cyclic-cluster as a whole. These points are given by (4.84) for $k = 0$ and can be easily found. All the possible transformation matrices, given in Appendix A, can be used to generate the symmetric cyclic clusters of any of the 14 Bravais lattices. In the cyclic-cluster calculations both the point and inner translation symmetry can be taken into account [300].

The CCM model allows real-space calculations (formally corresponding to the BZ center for the infinite crystal composed of the supercells). From this point of view the cyclic cluster was termed a quasimolecular large unit cell [289] or a molecular unit cell [288].

The practical cyclic-cluster calculations for crystals were made by EHT, MR and different ZDO methods. In these calculations one has to take into account the multiplication law of the cyclic-cluster symmetry group. This requires the modifications (compared with molecules) of Fock matrix elements in the LCAO approximation. These modifications are considered in the next sections.

6.3.2 Semiempirical LCAO Methods in Cyclic-cluster Model

In cyclic-cluster calculations we return to the molecular level without the loss of the symmetry, replacing a whole crystal by one supercell (multiple of the primitive unit cell), applying to it PBC and embedding a cyclic cluster in the Madelung field of the surrounding crystal. Instead of the system of coupled LCAO equations (4.57) for different wavevectors in the BZ we have one equation to be solved in each iteration as in the case of molecules.

In EHT for crystals the one-electron Hamiltonian and overlap integrals matrix elements (6.4) and (6.5) depend on wavevector $k$ and are the sums over a direct lattice. The order $M$ of the corresponding matrices $H$ and $S$ is equal to the number of AOs in the primitive unit cell.

In the CCM the supercell is introduced so that the order of the matrices in the secular equation (6.4) is equal to $L \times M$, where $L$ is defined in (6.51) and means the number of primitive cells in a supercell. The calculation is made only for $k = 0$ so that instead of (6.4) we obtain the molecular-type secular equation

$$\det |H_{\mu \nu} - \varepsilon_i S_{\mu \nu}| = 0$$

(6.58)

where $\mu, \nu, i$ change from 1 to $L \times M$. The difference between the Hamiltonian and overlap matrices in (6.58) from the molecular analog (when the supercell atoms are taken as a free molecular cluster) is due to the introduction of PBC for the supercell chosen. Instead of lattice sums (6.5) we have now the matrix elements calculated for all $L \times M$ AOs of a supercell. PBC are taken into account by modification of these matrix
elements. To show this modification let us consider a cyclic cluster \(B_9N_9\) of the one-layer model of hexagonal boron nitride \(BN_{\text{hex}}\), see Fig. 6.1. The primitive unit cell in this case contains one formula unit BN, the cyclic cluster chosen is formed by threefold increase in both translation vectors of the primitive unit cell. The central cyclic cluster and the nearest translated atoms are shown in Fig. 6.1. The primed B and N atoms are not included in the cyclic cluster explicitly but are translation equivalent (with the supercell translation vectors) to the corresponding nonprimed atoms inside the cyclic cluster. As was shown in Sect. 6.3.1, due to PBC introduction the cyclic-cluster translations are multiplied \textit{modulo} the translation group \(T_A\) of supercell as a whole (in our example this group consists of two supercell basic translations \(A_1 = 3a_1, A_2 = 3a_2\) and all their combinations \(A_n = \sum_{i=1}^{2} n_i A_i\) with integer coefficients \(n_i\)). As a result the matrix elements of \(H\) and \(S\) matrices are modified. The interactions between atoms in the supercell and those outside are then used to replace their weaker analog within the supercell [285]. For example, boron atom 1 interacts with nitrogen atoms 14 and 6 in the supercell as with the nearest neighbors because in atomic pairs 14–14’, 6–6’ two atoms are connected by the translation vectors of a cyclic cluster as a whole (see Fig. 6.1). Thus, we have no more “central” and “boundary” atoms in the cyclic cluster – for all of them the interactions with the nearest, next-nearest and next-next-nearest neighbors are taken into account.

The cyclic cluster can be chosen in the form of the Wigner–Seitz unit cell (shown by the dotted line in Fig. 6.1 with the center at boron atom 1). A connection of the interaction range to this cells atoms was discussed in [301].

PBC introduction for the cyclic cluster chosen allows connection by of symmetry the MOs of the cyclic cluster with some COs of a whole crystal [297]. Let a perfect crystal be described in terms of supercells composed of \(L\) primitive unit cells. Correspondingly, the reduced (small) BZ of the supercell is a factor of \(L\) smaller than the original BZ of the primitive unit cell. If wavevectors in the original BZ are denoted by \(K\) and wavevectors in the reduced (small) BZ by \(k\), a calculation at a single \(k\)-point is equivalent to a calculation at a particular set of \(K\)-points satisfying relation (4.84) determined by the translation vectors \(A_n\) of the supercell chosen. This “folding back” of information was used to generate special points of BZ in the model of an infinite crystal, see Sect. 4.2.2 and also forms the basis of the cyclic-cluster model. When the whole crystal is replaced by a cyclic cluster, the \(k' = 0\) approximation in the reduced BZ is made and (4.84) can be written in the form

\[
\vec{K}_i^{(0)} = \sum_j q_{ij} b_j
\]

(6.59)

where \(q_{ij}\) are integers, \(b_j\) are translation vectors of a reduced BZ and \(\vec{K}_i^{(0)}\) form the set of \(K\)-points of the original BZ folding down onto the \(k = 0\) point of a reduced BZ. Due to the relation \(\langle A_i, b_j \rangle = 2\pi\delta_{ij}\) between supercell translation vectors \(A_i, i = 1, 2, 3\) and small BZ translation vectors \(b_j, j = 1, 2, 3\), (6.59) becomes equivalent to the condition

\[
\exp(i\vec{K}_i^{(0)} A_j) = 1, \quad j = 1, 2, 3
\]

(6.60)

that has to be satisfied for those \(K\)-points of the original BZ that fold down on \(k = 0\) point of the reduced BZ.

In our example of a hexagonal lattice supercell with \(L = 9\) (Fig. 6.1b) the relation (6.60) is satisfied for three points of the plane hexagonal BZ, \(\Gamma(0,0), 2P(1/3,1/3),\)
6G(1/3, 0) (the integer numbers mean the number of rays in the stars, the coordinates of stars representatives from the irreducible part of the BZ are given in brackets). These points formally become equivalent to the $\Gamma(k = 0)$ point of the primitive-cell BZ [289].

Therefore, the cyclic-cluster energy level degeneration differs from that which would be for the corresponding free cluster of the same atoms. In the latter case, the point symmetry of the cluster is $C_{3v}$, so that only the degeneracy of levels can be one or two (dimensions of irreps of point group $C_{3v}$). In the former case, the degeneracy of MOs remains at 1, 2 only at the $\Gamma$ point of the BZ. The one-electron states at $P$ and $G$ points are 2-, 4- and 6-times degenerate, respectively. It becomes clear when one takes into account that the space-group irrep dimension is the product of the dimension of the irrep of the wavevector point group ($C_3$ for $P$ point, $C_1$ for $G$ point) times the number of rays in wavevector star (2, 6 for $P$ and $G$ points, respectively, see Chap. 3). It is also necessary to take into account the time-inversion symmetry making additional degeneracy for $k$ and $-k$ values of the wavevector.

What happens when the cyclic cluster is increased? Depending on its shape and size different sets of $k$-points are reproduced, but in the EHT matrix elements the number of interactions included (interaction radius) increases as the periodically reproduced atomic sites distance is defined by the translation vector of a cyclic cluster as a whole. It is important to reproduce in the cyclic-cluster calculations the states defining the bandgap. As the overlap matrix elements decay exponentially with the interatomic distance one obtains the convergence of results with increasing cyclic cluster. Of course, this convergence is slower the more diffuse are the AOs in the basis. From band-structure calculations it is known that for BN$_\text{hex}$ in the one-layer model the top of the valence band and the bottom of the conduction band are at the point $P$ of the BZ reproduced in the cyclic cluster considered.

We note that the symmetry connection of crystal and cyclic-cluster one-electron states is defined only by the supercell choice and therefore does not depend on the method used in the Hamiltonian matrix-elements calculations.

The EHT method is noniterative so that the results of CCM application depend only on the overlap interaction radius. The more complicated situation takes place in iterative Mulliken–Rüdenberg and self-consistent ZDO methods. In these methods for crystals, the atomic charges or the whole of the density matrix are calculated by summation over $k$ points in the BZ and recalculated at each iteration step. The direct lattice summations have to be made in the surviving integrals calculation before the iteration procedure. However, when the nonlocal exchange is taken into account (as is done in the ZDO methods) the balance between direct lattice and BZ summations has to be ensured. This balance is automatically ensured in cyclic-cluster calculations as was shown in Chap. 4. Therefore, in iterative MR and self-consistent ZDO methods the increase of the cyclic cluster ensures increasing accuracy in the direct lattice and BZ summation simultaneously. This advantage of CCM is in many cases underestimated.

In the MR method the matrix elements of a cyclic cluster are obtained from those for the crystal, taking $k = 0$ in (6.26). The modification of matrix elements due to PBC introduction has to be introduced in overlap and kinetic-energy integral calculation. The latter are expressed through overlap integrals so that there are no principal differences in the EHT and MR methods in the matrix-element modification, ensuring periodicity of the cluster chosen. The only difference is connected with the iterative
procedure of atomic charge and configuration self-consistency in the MR method, requiring the calculation of diagonal elements of the density matrix. In this calculation the summation over occupied MOs of the cyclic cluster is made that is equivalent to summation over those $K$-points of the original BZ that satisfy relation (6.60). The diagonal elements of the MR method Hamiltonian are corrected by the point-charge (Madelung) field of the surrounding crystal acting on cyclic-cluster atoms, see (6.26).

In fact, the embedded cyclic cluster is considered. For ionic systems such a correction (Madelung) field of the surrounding crystal acting on cyclic-cluster atoms, see (6.26). In CCM the iterative calculations the atomic charges are used at any step of the iterative procedure to recalculate the Madelung energy for all atoms of a cyclic cluster and at the next step the atomic charges are recalculated with the matrix elements corrected by a recalculated Madelung energy.

Within the $k = 0$ approximation the CNDO Hamiltonian for the supercell becomes

$$F_{\mu\nu}(0) = U_{\mu\mu} + Z_M\gamma_{MM}^{00} + \sum_{N} \left( \frac{1}{L} \sum_{k'} P_N(k') - Z_N \right) \sum_{n=0}^{L'-1} \gamma_{MM}^{0n}$$

$$+ \sum_{n=0}^{L'-1} \beta_M^{0n} \left( S_{\mu\mu}^{0n} - \delta_{0n} \right) - \frac{1}{2L'} \sum_{n=0}^{L'-1} \sum_{k'} P_{\mu\nu}(k') \exp(-ik'R_n) \gamma_{MM}^{0n}$$

(6.61)

$$F_{\mu\nu}(0) = \sum_{n=0}^{L'-1} \beta_{MN}^{0n} S_{\mu\mu}^{0n} - \frac{1}{2L'} \sum_{n=0}^{L'-1} \sum_{k'} P_{\mu\nu}(k') \exp(-ik'R_n) \gamma_{MM}^{0n}$$

(6.62)

where $L'$ is the number of supercells in the main region of a crystal and $k'$-summation is made over the reduced BZ.

A calculation performed solely at the $\Gamma(k' = 0)$ point of the supercell BZ would become entirely equivalent to special $K$-points (6.59) calculation if all the direct lattice summations were be made over the whole crystal. However, in CCM the interaction range depends on the cyclic-cluster size. To determine the $k' = 0$ Fock matrix elements we need the full $k'$ dependence of the supercell density matrices $P_{\mu\nu}(k')$, see (6.61) and (6.62). Meanwhile, each iteration in a cyclic-cluster calculation only provides the eigenvector coefficients $C_{i\mu}(0)$ at $k' = 0$, and hence only $P_{\mu\nu}(0)$. Therefore, it is necessary to relate the reduced BZ integrals over the fully $k'$-dependent density matrices, namely $\sum_{k'} P_{\mu\nu}(k')$ and $\sum_{k'} P_{\mu\nu}(k') \exp(-ik'R_n)$ to $P_N(0)$ and $P_{\mu\nu}(0)$, respectively [280]. For sufficiently large supercells all the values of $k'$ in the reduced BZ will lie near $k' = 0$, so that it should be valid to ignore the effect of the phase factor and use the fact that the reduced BZ is spanned by $L$ $k$-points to obtain

$$\frac{1}{L} \sum_{k'} P_{\mu\nu}(k') \exp(-ik'R_n) \rightarrow P_{\mu\nu}(0)$$

(6.63)

Simple substitution of (6.63) into (6.61) and (6.62) would introduce divergent lattice sums of $\gamma_{MM}^{0n}$ integrals. Therefore, a distance-dependent modulating function $\omega(R_{MN}^{0n})$ was introduced [280] such that

$$\frac{1}{L} \sum_{k'} P_{\mu\nu}(k') \exp(-ik'R_n) = \omega(R_{MN}^{0n}) P_{\mu\nu}(0)$$

(6.64)
6.3 Zero-differential overlap Approximation in Cyclic-cluster Model

To find an approximate form of this modulating function a tight-binding description of a one-dimensional chain of atoms possessing one atom per primitive unit cell and two orbitals per atom was studied [280]. The \( \text{sinc}^2\left(\frac{\pi}{a} R_{MN}^{0n}\right) \) function found was simply extended to the three-dimensional cubic lattice case. Unfortunately, the form of this modulating function depends on the direct lattice of supercells and its extension to noncubic lattices is nontrivial.

In some cases the modulating function \( \omega(R_{MN}^{0n}) \) is taken as the simple step function

\[
\omega(R_{MN}^{0n}) = \begin{cases} 
1 & \text{if } R_{MN}^{0n} \leq R_c \\
0 & \text{if } R_{MN}^{0n} > R_c 
\end{cases} 
\] (6.65)

where the exchange cutoff radius \( R_c \) in (6.65) was a variable parameter or taken intuitively to be about a half of the cyclic cluster smallest translation vector length. As was shown in Sect. 4.3.3, the modulating (weighting) function explicit form (4.157) can be found in the interpolation procedure for constructing an approximate density matrix. The modulating step function suggested in (4.157) is easily applied to any type of lattice and was incorporated into both HF and CNDO cyclic-cluster calculations [70]. It was shown that the exchange interaction range should be chosen such that the corresponding sphere of radius \( R_c \) differs only slightly from the Wigner–Seitz supercell, corresponding to the cyclic cluster. This gave a theoretical background to the former intuitive choice (6.65) of the exchange interaction radius \( R_c \).

Cyclic-cluster CNDO Hamiltonian matrix elements may be written in the following form

\[
F_{\mu\mu}(0) = U_{\mu\mu} + Z_M \gamma_{MM}^{00} + \sum_{N} \sum_{n=0}^{L'-1} \sum_{\nu \in N} (P_{\mu\mu}(0) - Z_N) \gamma_{MN}^{0n} \nonumber \\
+ \sum_{n=0}^{L'-1} \beta_M^0 S_{\mu\mu}^0 - \frac{1}{2} \sum_{n=0}^{L'-1} P_{\mu\mu}(0) \omega(R_{MN}^{0n}) \gamma_{MM}^{0n} 
\] (6.66)

\[
F_{\mu\nu}(0) = \sum_{n=0}^{L'-1} \rho_{MN}^0 S_{\mu\nu}^0 - \frac{1}{2} \sum_{n=0}^{L'-1} P_{\mu\nu}(0) \omega(R_{MN}^{0n}) \gamma_{MN}^{0n} 
\] (6.67)

Comparing CCM Hamiltonian matrix elements (6.66) and (6.67) with those for a free molecule, Equations (6.33)–(6.35), one can see the differences. Equations (6.66) and (6.67) formally include summation over the main region of a crystal composed of the equivalent supercells. The lattice sums containing overlap integrals are truncated for a cyclic cluster in the CNDO method in the same way as is done in the EHT and MR methods. For the Coulomb interaction sums (third item in (6.66)) the Ewald method can be used to calculate the Madelung energy of a crystal surrounding the cyclic cluster. The modulating function \( \omega(R_{MN}^{0n}) \) ensures the truncation of the diverging lattice sums appearing in the nonlocal exchange interactions (last items in (6.66) and (6.67)).

CCM has been implemented in various ZDO methods: CNDO-INDO [276,277,280, 303–310], MINDO/3 [311], MNDO [271], NDDO(AM1, PM3), [312]. All the semiempirical methods stand or fall by their parameter set. The ZDO methods parameter
sets suitable for molecular calculations will not necessarily be suitable for the solid state. The parametrization scheme may be dependent on the chemical bonding in the crystal (different sets of parameters are suitable for ionic and covalent crystals), introducing additional difficulties.

The main ZDO parameters for each orbital type are: the orbital exponent $\zeta$ entering the radial part of Slater-type AOs, the diagonal matrix elements $U_{\mu\mu}$ of the interaction of an electron occupying AO $\chi_\mu$ with its own core expressed through electronegativity $E_{neg}^M = -1/2(I_\mu + A_\mu)$ of this AO, the resonance integrals $\beta$ depending only on the atom type. Additional parameters appear in the matrix elements of an interaction of an electron on the $\mu$th AO belonging to atom $M$ with the core of another atom $N$, [313]:

$$V_{\mu N} = Z_N \left\{ \frac{1}{R_{MN}} + \left[ \langle \mu\mu|\nu\nu \rangle - \frac{1}{R_{MN}} \right] \exp(-\alpha_N R_{MN}) \right\} \quad (6.68)$$

where $R_{MN}$ is the distance between $M$ and $N$, $Z_N$ is the core charge of atom $N$, $\alpha_N$ is an adjustable parameter characterizing the nonpoint nature of the atom $N$ core. AOs $\chi_\mu$ and $\chi_\nu$ belong to atoms $M$ and $N$, respectively, the two-center Coulomb integral $\langle \mu\mu|\nu\nu \rangle$ may be calculated with STOs or considered as $\gamma_{MN}$ depending only on atoms types. The detailed discussion of parameter choice in CCM ZDO methods can be found for different types of crystalline solids: ionic crystals of alkali halides [300, 304, 314, 315] and simple oxides MgO, CaO [313], covalent and partly covalent semiconductors [276, 293, 310, 312, 316, 317], crystalline oxides with different structure [318], including high-$T_c$ superconductors [318].

In the next section we discuss MSINDO semiempirical and HF nonempirical methods implementation of CCM for the calculation of bulk properties of rutile crystal. The efficiency of the MSINDO method will be demonstrated that gives reasonable agreement with the results of HF calculations and at the same time is essentially simpler in practical realization.

6.3.3 Implementation of the Cyclic-cluster Model in MSINDO and Hartree–Fock LCAO Methods

The cyclic-cluster approach was implemented in the semiempirical SCF-MO method SINDO1 [319] and its recent modification MSINDO [301] and has been successfully applied for bulk and surface properties of oxides [302, 320].

The underlying strategy of the CCM implementation in MSINDO was to start from a molecular system and to introduce PBC in such a way that both local point symmetry and stoichiometry of the system are conserved. Within this approach the local environment of each cyclic-cluster atom is replaced by that of a fictitious cyclic arrangement. A cluster of $n$ atoms in one dimension is treated in the same way as a cyclic arrangement of the same number of atoms on a ring. Two- and three-dimensional systems are treated as arrangements on a torus and a hypertorus, respectively. All interactions for each atom $M$ are then calculated within an interaction region around that atom, corresponding to its Wigner–Seitz cell (WSC). For two-center integrals (overlap, nuclear attraction, electron repulsion) between the $M$ atom of the interaction region and atoms at the boundaries of its WSC [301] weighting factors are used to retain the proper symmetry. In this approach, the cyclicity and summation
6.3 Zero-differential overlap Approximation in Cyclic-cluster Model

regions are the same and not dependent on integral thresholds as for periodic LCAO methods [23]. Long-range Coulomb interactions have been taken into account by additional finite point charge fields outside the cyclic cluster [302]. A scheme for the calculation of analytical gradients has been developed for structure optimization of cyclic clusters [301].

In MSINDO only two-center two-electron integrals of the form $(\mu\mu\nu\nu)$ are taken into account. Atomic orbitals $\chi_\mu$ and $\chi_\nu$ are taken as $s$-type functions. Therefore, these integrals have no angular dependence and an averaging over integrals between different atoms on the same radius around the considered atom causes no problems.

In MSINDO also two-center one-electron integrals are replaced by empirical formulas that do not contain any angular dependence, so that the two-center elements of the Fock matrix have the following form [249]:

$$F_{\mu\nu} = H_{\mu\nu} + P_{\mu\nu}(\mu\mu|\nu\nu) = \Delta H_{\mu\nu} + L_{\mu\nu} + P_{\mu\nu}(\mu\mu|\nu\nu) \quad (\mu \in M, \nu \in N) \quad (6.69)$$

with the two parametrized empirical functions

$$\Delta H_{\mu\nu} = \frac{1}{4} (K_M + K_N) S_{\mu\nu} (f_M h_{\mu\mu} + f_N h_{\nu\nu}) ; \quad f_M = 1 - \exp(-\alpha_M R_{MN})$$

$$L_{\mu\nu} = -\frac{1}{2} (\zeta_\mu^2 + \zeta_\nu^2) \frac{S_{\mu\nu}(1 - S_{\mu\nu})}{1 + 1/2(\zeta_\mu + \zeta_\nu)R_{MN}} \quad (6.70)$$

where $\zeta_\mu$, $\zeta_\nu$ are orbital exponents, $K_M$, $K_N$, and $\alpha_M$ are empirical parameters optimized for a given set of reference molecules. In CCM calculations these matrix elements remain unchanged when atom $N$ is in the inner part of the interaction region of atom $M$. In the case that $N$ is on the border of the interaction region around $M$, the contributions from all $n_{MN}$ atoms $N'$ that are translationally equivalent to $N$ and appear at the same radius are summed up into one matrix element with weighting coefficient [301]:

$$H_{\mu\nu} = \sum_{N'}^{\text{equiv}} \omega_{MN'} H_{\mu\nu'}, \quad \nu' \in N$$

$$G_{\mu\nu} = \sum_{N'}^{\text{equiv}} \omega_{MN'} (\mu\mu|\nu'\nu') \quad (6.71)$$

The construction of the Fock matrix and the SCF procedure to obtain a converged density matrix of the cyclic system are essentially identical to the molecular case. The only extension is the inclusion of an external point charge field that is added to the diagonal terms of $F$. As the calculations for the cyclic clusters are performed in real space, no Bloch functions are used as the basis set. This strategy makes a direct comparison between calculations for free and cyclic clusters possible. Because of the quadratic increase of the number of two-center integrals with the number of cluster atoms a special technique can be used to reduce the computational effort [321]. This technique is based on the sorting of the interatomic distances because equal atom pairs with the same distance have identical integrals in a local coordinate system. With this technique the number of calculated integrals can be decreased by a factor of
1000 or more. All features available in the molecular version of MSINDO, for example, configuration interaction, geometry optimization, or vibration analysis, can also be used for the cyclic clusters. This also includes the treatment of charged systems that are generally difficult to treat with periodic methods.

Interactions of an ion $M$ with ions $N''$ at a distance beyond the borders of the WSC will decrease rapidly with increasing interatomic distance in covalent systems. This does not hold for ionic systems, since Coulomb-type interactions fall off slowly. If the ions $N''$ are approximated as point charges with a net charge $q$, the Madelung potential due to these charges, which can be calculated by the Ewald summation technique as shown in [302], will modify the Fock matrix and the total energy in the following way

$$F_{\text{MAD}}(P) = F(P) + V_{\text{MAD}}(P)$$  \hspace{1cm} (6.72)

$$E_{\text{tot}} = \frac{1}{2} \text{Tr} [P(H + F_{\text{MAD}})] + V_{NN} + E_{\text{MAD}}$$  \hspace{1cm} (6.73)

Here $F$ denotes the Fock matrix, $F_{\text{MAD}}$ the Madelung-corrected Fock matrix, $P$ the density matrix, $H$ is the core Hamiltonian matrix, $E_{\text{tot}}$ the total energy of the system and $V_{NN}$ the nuclear repulsion term. The terms $V_{\text{MAD}}(P)$ and $E_{\text{MAD}}$ denote the Madelung correction of the Fock matrix and of the nuclear repulsion, respectively. Due to the application of the ZDO approximation in MSINDO, $V_{\text{MAD}}(P)$ is a diagonal matrix,

$$V_{\mu M \mu M}^{\text{MAD}} = \Phi_{mD}(\vec{d}_M) - \sum_{N''} \omega_{MN''} \frac{q_{N''}}{|\vec{d}_M - \vec{d}_{N''}|}$$  \hspace{1cm} (6.74)

$$E_{\text{MAD}} = \frac{1}{2} \sum_M Z_M^* \left[ \Phi_{mD}(\vec{d}_M) - \sum_{N''} \omega_{MN''} \frac{q_{N''}}{|\vec{d}_M - \vec{d}_{N''}|} \right]$$  \hspace{1cm} (6.75)

$Z_M^*$ is the effective nuclear charge of atom $M$. The corrections are implemented in a self-consistent manner, since the net charges $q_{N''}$ are calculated from the cluster density matrix $P$ using a Löwdin population analysis. The electrostatic interactions of the ion $M$ with the ions in its WSC must be subtracted from the Madelung potential $\Phi_{mD}$, because these interactions are already considered in the unmodified Fock matrix $F(P)$. To avoid double counting of interactions the factor 1/2 is introduced in (6.75).

It has to be mentioned that the simple procedure used in CCM MSINDO of an averaging of two-center integrals between the central atom of the interaction region and atoms at the boundaries of its WSC is not possible for $ab$-initio Hartree–Fock methods due to the presence of three- and four-center integrals.

The implementation of the CCM in the HF LCAO method is based on the use of the idempotency property of a one-electron density matrix (DM) of crystalline systems [100]. The underlying strategy in this case was to start from a periodic system and to make small modifications in the corresponding LCAO computer codes. It has to be mentioned that the CCM realization in PW basis seems to be impossible as the interaction region in this case can not be defined.

The idempotency of the DM is a consequence of the orthonormality of the one-electron Bloch functions that are the basis of the crystalline orbitals. In the CCM the DM has to be idempotent when a one-determinant wavefunction is used and convergence with cluster size is achieved. The infinite DM of a solid formally does not have this property, but the infinite solid itself is modeled by a very large cyclic cluster.
describing the main region of the crystal when Born–von Karman PBC are introduced to ensure macroscopic periodicity of a crystal model. In Sect. 4.3.3 the CCM of the infinite crystal was deduced from the study of the approximate DM (4.164). The supercell corresponding to the cyclic cluster under consideration was taken as the Wigner–Seitz supercell; to have the proper point symmetry the weighting function (4.165) was introduced. Defining an atomic covalence as the sum of Wiberg indices for an atom in the cyclic cluster or all the other atoms of a crystal the relation (4.140) was obtained. This relation means that the atomic covalence in a cyclic cluster may be calculated as a lattice sum

\[ \sum_{M} C_{M}^{(2)} = \sum_{M} \sum_{M \neq N} \omega_{N}(\bar{R}_{N})W_{MN}(\bar{R}_{n}) + \sum_{M} W_{MM}(0) = N_{e}^{C} \]

\[ \sum_{M} C_{M}^{(1)} = \sum_{M} \left( 2 \sum_{\mu \in M} P_{\mu\mu}(0) - W_{MM}(0) \right) = N_{e} \]  

(6.76)

where \( N_{e}^{C}, N_{e} \) is the number of electrons in the primitive unit cell. For each cyclic cluster there are certain weighting coefficients \( \omega_{N}(\bar{R}_{N}) \) of neighbor atoms in spheres around atom \( M \). For the inner atoms of a cyclic cluster \( \omega_{N} = 1 \), while for border atoms \( \omega_{N} < 1 \).

Relation (6.76) provides a simple way to check the idempotency property of the DM. Therefore, it can be used to implement the CCM in HF LCAO calculations.

This implementation requires simple modifications in the property part of the CRYSTAL program [23]. A Löwdin population analysis is introduced for self-consistent DM and the bond-order sums are calculated for atoms of the crystal. The lattice summation in (6.76) is made over the same part of the lattice that has been used in the integrals calculation for the self-consistent procedure (the lattice summation field is defined by the most severe tolerance used in the two-electron exchange integrals calculation).

In order to receive results for a cyclic cluster, relation (6.76) is checked for different choices of tolerances in the integrals calculations and \( Q \) sets of wavevectors in the BZ, corresponding to those \( K \)- sets that satisfy (6.60). The implementation of a cyclic cluster for perfect crystals is realized in most cases by using the primitive unit cell and taking into account that the cyclicity field of the DM is defined by the choice of \( Q \). The implementation of the CCM in HF LCAO calculations is demonstrated for the rutile structure.

The tetragonal rutile structure belongs to space group \( P4_2/mnm(D_{14h}^{14}) \) and contains two TiO\(_2\) units per cell. The two Ti atoms are located at the Wyckoff \( 2a \) sites \((0, 0, 0)\) and \((1/2, 1/2, 1/2)\) with \( D_{2h} \) site symmetry, while the four O atoms are located at the \( 4f \) sites \( \pm (u, u, 0) \) and \( \pm (u + 1/2, 1/2 - u, 1/2) \) with site symmetry \( C_{2v} \) (see Sect. 2.3.3). The primitive unit cell of rutile is illustrated in Fig. 6.2. Each Ti atom is surrounded by a slightly distorted octahedron of O atoms with two different Ti–O distances. In connection with the cyclic-cluster choice it is useful to label the atoms surrounding Ti\((1)\) and O\((3)\) in the primitive cell \((000)\) by the translation vectors of the corresponding unit cells (see Fig. 6.2). From Fig. 6.2 it is seen that the inclusion of all nearest neighbors for a Ti atom requires at least a cyclic cluster with translation vectors \( \mathbf{a}_4(0, 0, a), \mathbf{a}_2(0, a, 0), 2\mathbf{a}_3(0, 0, 2c) \). The smallest cyclic cluster
that contains the nearest neighbors to an O atom is formed by translation vectors $2a_1(2a,0,0), 2a_2(0,2a,0), 2a_3(0,0,2c)$. For simple tetragonal lattices the symmetric supercells can be made in four different ways while maintaining tetragonal symmetry:

1. By simple extension of translation vectors $(n_1a_1, n_2a_2, n_3a_3)$. The corresponding transformation matrix is given in Table 6.1 at the bottom of the first column.

2. By rotation of vectors $a_1$ and $a_2$ by 45° in their plane and extension of the vector. The transformation matrix is given in the second column of Table 6.1.

3. By changing from a simple to a body-centered tetragonal lattice. This can be achieved in two different ways. The corresponding transformation matrices are given in columns 3 and 4 of Table 6.3.

In Table 6.3 cyclic clusters representing the rutile bulk structure are given that are generated from the primitive bulk unit cell by applying the above-mentioned four types of LUC transformations. The cluster size was restricted to $L = 24$ (144 atoms).

As it was noted in Sect. 6.3.2 CCM allows us to connect by symmetry the MOs of cyclic cluster with those COs of a whole crystal for which (6.60) is satisfied.

The BZ for the simple tetragonal lattice was shown in Fig. 3.7. The $K$ symmetry points and $K$-points in symmetry lines (in units of the basic translation vectors of the reciprocal simple tetragonal lattice) are the following (for lines of symmetry the parameter $p < 1$ has to be introduced). Symmetry points $\Gamma(0,0,0), M(\frac{1}{4}, \frac{1}{4}, 0), Z(0,0,\frac{1}{2}), A(\frac{1}{4},\frac{1}{4},\frac{1}{4}), 2X(0,\frac{1}{4},0), 2R(0,\frac{1}{2},\frac{1}{2})$; symmetry lines $\Gamma - X = \Delta(0,p,0), \Gamma - M = \Sigma(p,p,0), \Gamma - Z = \Lambda(0,0,p), M - X = Y(p,\frac{1}{2},0), A - R = T(p,\frac{1}{2},\frac{1}{2}), Z - A = S(p,p,\frac{1}{2}), M - A = V(\frac{1}{2},\frac{1}{2},p), Z - R = U(0,p,\frac{1}{2}), X - R = W(0,\frac{1}{2},p), \Gamma - A = \varepsilon(p,p,p)$.

In Table 6.3 are given $K$-point sets of the primitive cell BZ satisfying (6.60) and folding down on the $k = 0$ point of the reduced BZ. The interaction region in CCM may be defined by WSC around each atom of a cyclic cluster or by the number $J$ of spheres of direct lattice translation vectors $A_n$ with smallest nonzero length, also given in Table 6.3.

To implement CCM into the HF LCAO calculations [100] the periodic crystalline-orbital program CRYSTAL95 [322] was used with the modifications [97] allow the DM idempotency (6.76) to be checked. In rutile TiO$_2$ calculations the AO bases, lattice parameters and effective core potentials were taken to be the same as those used in [323] to calculate the optimized lattice parameters. In the CRYSTAL code
Table 6.3. Cyclic clusters used for the representation of the rutile bulk; special point (SP)-set and its accuracy $J$

<table>
<thead>
<tr>
<th>$n_1$</th>
<th>$n_2$</th>
<th>CL*1 cluster</th>
<th>SP-set</th>
<th>$J$</th>
<th>CL*2 cluster</th>
<th>SP-set</th>
<th>$J$</th>
<th>CL*3 cluster</th>
<th>SP-set</th>
<th>$J$</th>
<th>CL*4 cluster</th>
<th>SP-set</th>
<th>$J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>C2.2</td>
<td>$\Gamma, Z$</td>
<td>1</td>
<td>C2.3</td>
<td>$\Gamma, A$</td>
<td>3</td>
<td>C4.4</td>
<td>$\Gamma, M, 2R$</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>C2.1</td>
<td>$\Gamma, M$</td>
<td>2</td>
<td>C4.2</td>
<td>$\Gamma, M, A, Z$</td>
<td>4</td>
<td>C4.3</td>
<td>$\Gamma, Z, 2V$</td>
<td>5</td>
<td>C8.4</td>
<td>$\Gamma, M, Z, A,$</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>C4.1</td>
<td>$\Gamma, M, 2X,$</td>
<td>1</td>
<td>C8.2</td>
<td>$\Gamma, M, 2X, \quad 4\Sigma(p = \frac{1}{4})$</td>
<td>1</td>
<td>C8.3</td>
<td>$\Gamma, M, 2X, \quad 4S(p = \frac{1}{4})$</td>
<td>4</td>
<td>C16.4</td>
<td>$\Gamma, M, 2X, \quad 4\Sigma, 4U, 4T(p = \frac{1}{4})$</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>C8.1</td>
<td>$\Gamma, M, Z, \quad A, 2X, 2R$</td>
<td>4</td>
<td>C16.2</td>
<td>$A, 2X, 2R, \quad 4\Sigma, 4S(p = \frac{1}{4})$</td>
<td>4</td>
<td>C16.3</td>
<td>$A, 2R, \quad 8\epsilon(p = \frac{1}{4})$</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>C12.1</td>
<td>$\Gamma, M, 2X, \quad 2A, 2V, \quad 2W(p = \frac{1}{3})$</td>
<td>9</td>
<td>C24.2</td>
<td>$\Gamma, M, 2X, \quad 2V, 2A, 4W, \quad 4\Sigma(p = \frac{1}{4}), 8(\frac{1}{4}, \frac{1}{3})$</td>
<td>9</td>
<td>C24.3</td>
<td>$2V, 2A, 4W, \quad 4S(p = \frac{1}{4}), 8(\frac{1}{3}, \frac{1}{2})$</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>C16.1</td>
<td>$\Gamma, M, 2X, \quad Z, A, 2R, 2A, \quad 2V, 4W(p = \frac{1}{4})$</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$L = n_1^2 n_2 = \begin{bmatrix} n_1 & 0 & 0 \\ 0 & n_1 & 0 \\ 0 & 0 & n_2 \end{bmatrix}$  
$L = 2n_1^2 n_2 = \begin{bmatrix} n_1 & -n_1 & 0 \\ n_1 & n_1 & 0 \\ 0 & 0 & n_2 \end{bmatrix}$  
$L = 2n_1^2 n_2 = \begin{bmatrix} 0 & n_1 & n_2 \\ n_1 & 0 & n_2 \\ n_1 & n_1 & 0 \end{bmatrix}$  
$L = 4n_1^2 n_2 = \begin{bmatrix} -n_1 & n_1 & n_2 \\ n_1 & -n_1 & n_2 \\ n_1 & n_1 & -n_2 \end{bmatrix}$

$L$ is the number of primitive unit cells in the large unit cell defining the cyclic cluster. The number $m$ in CL.$m$ defines the choice of the corresponding transformation matrix given at the bottom of each column.
the lattice sums of the integrals are truncated when the integrals values are smaller than $10^{-t_i}$. The tolerances $t_i (i = 1 - 5)$ define the accuracy of the lattice-sums calculation. The band-structure calculations using the primitive unit cell of the rutile, the tolerances $t_1 = t_2 = t_3 = t_4 = 6, t_5 = 12$ (the latter is used for exchange interactions) and shrinking factor IS=6 (216 $k$-points of $6 \times 6 \times 6$ Monkhorst–Pack special points in the BZ) ensure the converged results for the total energy per primitive cell, top of the valence band and Löwdin charge on the Ti-atom ($-69.7758$ a.u., $-0.3028$ a.u and $q=1.73$, respectively).

The cyclic-cluster calculations were performed using the SUPERCCELL option of CRYSTAL95 and setting the shrinking factors IS to unity (corresponding to the $k = 0$ point in the BZ), defining the DM cyclicity region as the cyclic-cluster region itself. For the calculation of the total number of electrons per primitive cell ($6.76$) can be used. For each cyclic cluster there are certain weighting coefficients of neighbor atoms in spheres $i$ around Ti($\omega_{Ti}(i)$) and O($\omega_{O}(i)$). At the same time the above-mentioned tolerance $t_5$ defines the interaction radius for the exchange-integral truncation. For the given structural parameters and basis sets this radius is $8.16$ Å around a Ti atom and $7.84$ Å around an O atom, respectively (for rutile TiO$_2$ with the optimized structures parameters $a=4.555$ Å, $c=2.998$ Å, $u=0.306$). The total number of electrons per unit cell $N_e$ within the interaction radius calculated by summing bond orders over spheres $i$, containing a total number $N(i)$ of atoms as given in the second line of Table 6.4. An analysis of Table 6.4 allows a cyclic cluster of relatively small size to be chosen in such a way that it still reproduces bulk properties with reasonable accuracy.

For the small-size clusters ($L = 4, 8$) the imbalance of the cyclicity region and the interaction radius causes a huge difference between $N_e^C$ and $N_e^s$ as the sum of bond orders inside the interaction radius includes the neighboring cyclic clusters around the central cyclic cluster. The PBCs force atoms outside the central cyclic cluster to be equivalent to the corresponding atoms inside the cluster. At the same time the summation of bond orders inside a cyclicity region gives $N_e^C$ values that are largely model-size independent, as the DM is calculated for the cyclic cluster under consideration.

From Table 6.4 one concludes also that even for the same size $L$ of a cyclic cluster the difference of the calculated properties $E_{tot}, \varepsilon_{top}$, and atomic charges $q$ strongly depends on the “compactness” of a cluster. The compactness is defined by the number of spheres $i$ of neighboring atoms with $\omega(i) = 1$ inside the cyclic cluster. This property of cyclic clusters is important as, for example, the more compact cluster C4.3 gives results closer to the band calculation limit than the larger but less compact cluster C8.2. In order to construct more compact clusters, the anisotropy of the rutile structure ($a \approx 1.5c$) has to be taken into account.

Table 6.5 shows the effect of integral thresholds on the calculated properties of cyclic clusters. For the cyclic cluster C12.1 the calculated properties are close to those for C16.3, but the difference $N_e^s - N_e^C$ is much larger, 3.2, i.e. the DM is nonidempotent. It is well known that small changes of only the most severe integral threshold do not essentially affect the results [324]. Therefore, its decrease may restore the DM idempotency while the calculated properties are only slightly changed. It is demonstrated in Table 6.5 that by using $t_5 = 9$ instead of 12, the difference $N_e^s - N_e^C$ decreases drastically to 0.10 for the same cluster, C12.1. For C16.1 the influence of $t_5$ is also small. For a
Table 6.4. Results of HF LCAO calculations of cyclic clusters for bulk rutile. Quality $J$, the difference of the total energy $\Delta E$ and the energy of the valence band top $\Delta \epsilon$ (a.u.) with respect to the largest cluster C216.1, total number of electrons per unit cell calculated with (6.76) within the corresponding cyclic cluster ($N_v^C$) and within the interaction radius defined by the integral thresholds ($N_S^e$), weighting coefficients of neighboring atoms in spheres $i$ around Ti ($\omega_{Ti}(i)$) and O ($\omega_{O}(i)$), total number of atoms $N(i)$ in sphere $i$, Löwdin charge $q_{Ti}$ on Ti.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$J$</th>
<th>$\Delta E$</th>
<th>$\Delta \epsilon$</th>
<th>$N_v^C$</th>
<th>$N_S^e$</th>
<th>$\omega_{Ti}(i)$</th>
<th>$\omega_{O}(i)$</th>
<th>$q_{Ti}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL4.1</td>
<td>1</td>
<td>$-4.4041$</td>
<td>$-0.2856$ 63.91</td>
<td>245.80</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.97</td>
</tr>
<tr>
<td>CL4.2</td>
<td>4</td>
<td>$-0.0302$</td>
<td>$-0.0136$ 63.85</td>
<td>199.57</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.60</td>
</tr>
<tr>
<td>CL4.3</td>
<td>5</td>
<td>$-0.0138$</td>
<td>$-0.0134$ 63.89</td>
<td>185.90</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.60</td>
</tr>
<tr>
<td>CL4.4</td>
<td>4</td>
<td>$-0.0248$</td>
<td>$-0.0170$ 63.73</td>
<td>248.79</td>
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<td>CL8.1*</td>
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<td>$-0.0167$</td>
<td>$-0.0127$ 63.77</td>
<td>111.32</td>
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<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
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</tr>
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<td>CL8.2</td>
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<td>$-0.2854$ 63.92</td>
<td>241.76</td>
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<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
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<td>CL8.3</td>
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<td>$-0.0183$</td>
<td>$-0.0124$ 63.74</td>
<td>108.95</td>
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<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
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<td>CL8.4</td>
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<td>$-0.0040$ 63.81</td>
<td>74.66</td>
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<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
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</tr>
<tr>
<td>CL12.1</td>
<td>9</td>
<td>0.0014</td>
<td>$-0.0001$ 63.77</td>
<td>70.17</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.73</td>
</tr>
<tr>
<td>CL16.1</td>
<td>10</td>
<td>0.0010</td>
<td>$-0.0003$ 63.79</td>
<td>67.04</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
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<tr>
<td>CL16.2</td>
<td>4</td>
<td>$-0.0178$</td>
<td>$-0.0125$ 63.76</td>
<td>108.14</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
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</tr>
<tr>
<td>CL16.3</td>
<td>15</td>
<td>0.0018</td>
<td>$-0.0002$ 63.83</td>
<td>63.86</td>
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<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.73</td>
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<td>$-0.0125$ 63.75</td>
<td>108.15</td>
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<tr>
<td>CL24.2</td>
<td>9</td>
<td>0.0014</td>
<td>$-0.0001$ 63.78</td>
<td>66.94</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.73</td>
</tr>
<tr>
<td>CL24.3</td>
<td>19</td>
<td>0.0005</td>
<td>$-0.0006$ 63.80</td>
<td>63.80</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.73</td>
</tr>
<tr>
<td>CL27.1*</td>
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<td>0.0008</td>
<td>0.0005 63.79</td>
<td>66.93</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.73</td>
</tr>
<tr>
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<td>0.0002</td>
<td>$-0.0002$ 63.80</td>
<td>63.80</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.73</td>
</tr>
<tr>
<td>CL216.1*</td>
<td>33</td>
<td>0.0000</td>
<td>0.0000 63.79</td>
<td>63.79</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1.73</td>
</tr>
</tbody>
</table>

*Band calculations (the shrinking factors are 2, 3, 4, 6 for CL8.1, CL27.1, CL64.1, and CL216.1, respectively)
Table 6.5. Effect of integral thresholds on calculated properties of cyclic clusters CL12.1 and CL16.3; total energy $E$ and top of valence band $\epsilon$ (a.u.), L"owdin charge $q_{Ti}$ of Ti, total number of electrons per unit cell calculated using (6.76) within the corresponding cyclic cluster ($N_{Ce}^C$) and within the interaction radius defined by the integral thresholds ($N_{Se}^S$)

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Integral thresholds</th>
<th>$E$</th>
<th>$\epsilon$</th>
<th>$q_{Ti}$</th>
<th>$N_{Ce}^C$</th>
<th>$N_{Se}^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL12.1</td>
<td>6 12</td>
<td>-69.7744</td>
<td>-0.3029</td>
<td>1.73</td>
<td>63.77</td>
<td>70.17</td>
</tr>
<tr>
<td></td>
<td>6 9</td>
<td>-69.7747</td>
<td>-0.3032</td>
<td>1.73</td>
<td>63.81</td>
<td>64.01</td>
</tr>
<tr>
<td></td>
<td>6 9$a$</td>
<td>-69.7760</td>
<td>-0.3032</td>
<td>1.73</td>
<td>63.74</td>
<td>63.75</td>
</tr>
<tr>
<td></td>
<td>6 8</td>
<td>-69.7746</td>
<td>-0.3034</td>
<td>1.73</td>
<td>63.75</td>
<td>63.94</td>
</tr>
<tr>
<td></td>
<td>6 8$a$</td>
<td>-69.7758</td>
<td>-0.3028</td>
<td>1.73</td>
<td>63.72</td>
<td>63.73</td>
</tr>
<tr>
<td>CL16.3</td>
<td>6 12</td>
<td>-69.7740</td>
<td>-0.3030</td>
<td>1.73</td>
<td>63.83</td>
<td>63.86</td>
</tr>
<tr>
<td></td>
<td>6 12$a$</td>
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<td>-0.3029</td>
<td>1.73</td>
<td>63.83</td>
<td>63.83</td>
</tr>
<tr>
<td></td>
<td>6 13</td>
<td>-69.7740</td>
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<td>63.83</td>
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<td>6 13$a$</td>
<td>-69.7758</td>
<td>-0.3029</td>
<td>1.73</td>
<td>63.79</td>
<td>63.79</td>
</tr>
</tbody>
</table>

band calculation$^b$ 6 12

-69.7758 $-0.3028$ 1.73 63.79 63.79

$^a$increased by a factor of 8 with shrinking factors $s_1 = s_2 = s_3 = 2$

$^b$primitive unit cell with shrinking factors $s_1 = s_2 = s_3 = 6$

Cyclic cluster that has been chosen properly, an increase of the cyclicity region has to give only small changes in the calculated results.

Table 6.6. MSINDO CCM results for bulk rutile; total energy per unit cell $E_{tot}$ (a.u.), binding energy per unit $E_B$ (kJ/mol), HOMO energy $\epsilon_{top}$ (a.u.), atomic L"owdin charge on Ti $q_{Ti}$.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$E_{tot}$</th>
<th>$E_B$</th>
<th>$\epsilon_{top}$</th>
<th>$q_{Ti}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL8.1</td>
<td>-70.2164</td>
<td>1880</td>
<td>-0.2947</td>
<td>1.74</td>
</tr>
<tr>
<td>CL12.1</td>
<td>-70.0959</td>
<td>1722</td>
<td>-0.2910</td>
<td>1.77</td>
</tr>
<tr>
<td>CL24.2</td>
<td>-70.3774</td>
<td>2092</td>
<td>-0.2898</td>
<td>1.77</td>
</tr>
<tr>
<td>CL32.2</td>
<td>-70.3428</td>
<td>2046</td>
<td>-0.2885</td>
<td>1.77</td>
</tr>
</tbody>
</table>

In CCM calculations of defective crystals such an increase of the cyclicity region allows investigation of the convergence of the results with cluster size. As is seen from Table 6.4, the $k$-sets accuracy $J$ is important to reproduce the total energy. The cyclic-cluster increase without change of $J$ (clusters C4.1 and C8.2 with $J = 1$, clusters C8.1, C16.1 and C16.4 with $J = 4$) gives only small changes in total energy. The cyclic clusters C12.1 and C16.3 generate highly accurate SP-sets ($J = 9$ and $J = 15$, respectively) and therefore the corresponding total energies are close to that of the infinite crystal. The same applies to the one-electron energy at the top of the valence band.
The idempotency of the DM in MSINDO cyclic-cluster calculations is guaranteed for all cases as the periodic boundary conditions were introduced into the molecular code. This was tested in [100] for the cyclic cluster C12.1 in two ways:

1. by calculating the difference $C_M^{(1)} - C_M^{(2)}$ obtained with relation (6.76);
2. by directly calculating $P^2 - 2P$ and summing the absolute values of the differences over all matrix elements, $\Delta = \sum_{\mu \nu} |P_{\mu \nu}^2 - 2P_{\mu \nu}|$.

By both ways of calculation it was clearly demonstrated that the MSINDO CCM density matrix is exactly idempotent. The differences of covalencies $C_M^{(1)}$ and $C_M^{(2)}$ as well as $\Delta$ are in the same order of magnitude as the SCF threshold, $10^{-8}$. At the same time the symmetry of the crystalline system was correctly reproduced as checked by counting the degenerate one-electron levels in the oxygen 2s valence-band region and comparison with the results of a symmetry analysis. The symmetry of the cyclic cluster is different from the molecular cluster due to the presence of additional translation symmetry elements. Therefore, highly degenerate (8,4 degenerated) one-electron levels appear that are not present in any molecular model of rutile.

The calculated binding energies per unit cell $E_B$, HOMO orbital energies $\varepsilon_{\text{top}}$, and atomic Löwdin charges $q$ for a number of cyclic clusters embedded in an infinite Madelung field, C8.1, C12.1, C24.2, and C32.2, are given in Table 6.6 [321].

The geometry of the four clusters has been optimized in terms of the three structural parameters $c$, $R_{\text{TiO}(5)}$, and $R_{\text{TiO}(3)}$. At low temperatures, the experimental references are $c = 2.954$ Å, $R_{\text{TiO}(5)} = 1.946$ Å, and $R_{\text{TiO}(3)} = 1.976$ Å. For the largest cyclic cluster, C32.3, the corresponding MSINDO values are 2.96 Å, 1.90 Å, and 1.91 Å, which are in reasonable agreement with experiment. From Table 6.6 it can be seen that the convergence of $E_{\text{tot}}$ is much slower than for the periodic HF calculations, see Table 6.3. On the other hand, $\varepsilon_{\text{top}}$ and $q_{\text{Ti}}$ show a similar convergence behavior. The MSINDO binding energies per TiO$_2$ unit $E_B$ vary between 1722 and 2096 kJ/mol and are close to the experimental value of 1900 kJ/mol. The calculated HOMO orbital energies for MSINDO (Table 6.6) and HF (Table 6.5) are similar. The MSINDO $\varepsilon_{\text{top}}$ is only 0.6 eV less negative than the HF result.

The density matrix idempotency relations described here may be easily extended to the unrestricted Hartree–Fock (UHF) method when the orbitals for $\alpha$ and $\beta$ spins are treated independently.

As it is seen from the HF calculations of bulk rutile structure the CCM technique produces a good representation of the perfect crystal, which is essential for point-defect studies.