Extended-Hückel Energy Band Structures of Transition Metal Compounds with One-Dimensional Crystal Geometries

Basic Equations and Computational Results
for Bis(2,5-dimethyl-N,N'-dicyanoquinonedimine) copper(I)

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Using symmetry adapted basis sets of linearly combined Bloch sums, we summarize the basic equations for one-dimensional energy band structure calculations of extended-Hückel type such as SCC (Self-Consistence of Charge) and SCCC (Self-Consistence of Charge and Configuration). In addition to the considerable computational savings achievable by this technique, its main advantage is that band indexing difficulties can be systematically excluded. Furthermore, it turns out that backtransformations into the original atomic orbital basis are unnecessary throughout. As an illustrative example, we document the energy band structure of a one-dimensional model geometry of highly conducting bis(2,5-dimethyl-N,N'-dicyanoquinonedimine)copper(I) (2,5-DM-DCNQI)₂Cu. In spite of its one-electron nature, the outlined energy band structure calculation method appears to be useful to rationalize the unusual electronic properties of this “organic metal”.

1. Introduction

In this paper we report the formalism to calculate the extended-Hückel energy band structure of transition metal compounds with purely one-dimensional model geometries of isolated stacks with translational symmetry in only one direction and additional spatial symmetries properly characterized by line groups. Such one-dimensional crystals are taken to be chemically homogeneous and to have no defects. They are assumed to consist of a finite but huge number of one-dimensional unit cells; different geometries and compositions of the terminating cells will be ignored.

Although the extended-Hückel procedure is methodically simple, a considerable amount of computer time and storage capacity is required for band-structure calculations of one-dimensional crystals with many basis orbitals per unit cell. Ab-initio methods based on the Hartree-Fock approximation cannot be applied in these cases. Some sophistication, however, has been brought into the semiempirical self-consistent field (SCF) treatment by Böhm who parametrized such approaches for transition metal compounds [1].

Recently, the synthesis of the highly conducting compound bis(2,5-dimethyl-N,N'-dicyanoquinonedimine)copper(I) (2,5-DM-DCNQI)₂Cu has been reported by Aumüller, Erk, Klebe, Hünig, Schütz, and Werner [2] together with the main features of its anisotropic crystalline structure. A one-dimensional model of this interesting “organic metal” will serve us as an example to illustrate the computational method which will be outlined in the following section.

2. Extended-Hückel Band Structure Calculations of One-Dimensional Crystals

The standard eigenvalue problem of one-dimensional one-electron band theory in a basis set of $M$ Bloch sums

$$\left| \phi_{\mu}(k) \right|, \mu = 1, 2, \ldots, M$$

for each wavenumber $k$ in the first Brillouin zone

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a}$$

reads:

$$H(k) C(k) = S(k) C(k) E(k).$$

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the expressions (19) and (20) are also valid for the modified Wolfsberg-Helmholz formula proposed by Ammeter et al. [7]. Like the overlap matrices \( S(k, \Gamma_m) \), extended-Hückel matrices \( H(k, \Gamma_m) \) are also Hermitian:

\[
H(k, \Gamma_m) = H^\dagger(k, \Gamma_m).
\]

2.4 Symmetrical Löwdin Orthogonalization

The symmetrical orthogonalization procedure which transforms the non-orthogonal symmetry orbitals (9) into an orthogonal basis set

\[
\{ \Phi^0_\mu(k, \Gamma_m) \} \quad \mu = 1, 2, \ldots, \dim V_{k, \Gamma_m}
\]

by means of the transformation matrix \( S^{-\frac{1}{2}}(k, \Gamma_m) \) consists of two steps [11]:

1. Since \( S(k, \Gamma_m) \) is Hermitian, it can be diagonalized [12] by a unitary matrix \( U(k, \Gamma_m) \):

\[
U^\dagger(k, \Gamma_m) S(k, \Gamma_m) U(k, \Gamma_m) = s(k, \Gamma_m).
\]

where \( s(k, \Gamma_m) \) is a diagonal matrix of the eigenvalues of \( S(k, \Gamma_m) \). The Hermitian transformation matrix \( S^{-\frac{1}{2}}(k, \Gamma_m) \) is constructed by taking the inverse square root of each of the eigenvalues [14] to form the diagonal matrix \( S^{-\frac{1}{2}}(k, \Gamma_m) \) and then “undiagonalizing” by the transformation

\[
U(k, \Gamma_m) S^{-\frac{1}{2}}(k, \Gamma_m) U^\dagger(k, \Gamma_m) = S^{-\frac{1}{2}}(k, \Gamma_m).
\]

2. Substitution of the relation

\[
C'(k, \Gamma_m) = S^{-\frac{1}{2}}(k, \Gamma_m) C(k, \Gamma_m)
\]

between the coefficient matrices \( C(k, \Gamma_m) \) and \( C'(k, \Gamma_m) \) of the non-orthogonal basis (9) and the orthogonal basis (24), respectively, into the eigenvalue equation (11) and multiplication on the left by

\[
(S^{-\frac{1}{2}}(k, \Gamma_m))^\dagger = S^{-\frac{1}{2}}(k, \Gamma_m)
\]

yields

\[
S^{-\frac{1}{2}}(k, \Gamma_m) H(k, \Gamma_m) S^{-\frac{1}{2}}(k, \Gamma_m) C'(k, \Gamma_m)
\]

\[
= S^{-\frac{1}{2}}(k, \Gamma_m) S(k, \Gamma_m) S^{-\frac{1}{2}}(k, \Gamma_m) C'(k, \Gamma_m) E(k, \Gamma_m).
\]

With the definition of new extended-Hückel matrices

\[
H'(k, \Gamma_m) = S^{-\frac{1}{2}}(k, \Gamma_m) H(k, \Gamma_m) S^{-\frac{1}{2}}(k, \Gamma_m)
\]

the expressions (19) and (20) are also valid for the modified Wolfsberg-Helmholz formula proposed by Ammeter et al. [7]. Like the overlap matrices \( S(k, \Gamma_m) \), extended-Hückel matrices \( H(k, \Gamma_m) \) are also Hermitian:

\[
H(k, \Gamma_m) = H^\dagger(k, \Gamma_m).
\]
in the orthogonalized symmetry orbital basis (24), the final eigenvalue problem reads

\[ \mathbf{H}'(k, \Gamma_m) \mathbf{C}'(k, \Gamma_m) = \mathbf{C}'(k, \Gamma_m) \mathbf{E}(k, \Gamma_m). \]  (31)

2.5 Eigenvectors and Eigenvalues

Solving the eigenvalue equation (31) for each wavenumber \( k \) and each irreducible representation \( \Gamma_m \) means finding a unitary coefficient matrix \( \mathbf{C}'(k, \Gamma_m) \) which transforms the Hermitian matrix \( \mathbf{H}'(k, \Gamma_m) \) into the diagonal matrix \( \mathbf{E}(k, \Gamma_m) \) of its eigenvalues:

\[ (\mathbf{C}'(k, \Gamma_m))^\dagger \mathbf{H}'(k, \Gamma_m) \mathbf{C}'(k, \Gamma_m) = \mathbf{E}(k, \Gamma_m). \]  (32)

This standard problem of numerical quantum chemistry can be solved efficiently by means of the already mentioned diagonalization algorithms [12].

Backtransformation of the eigenvector matrix \( \mathbf{C}'(k, \Gamma_m) \) according to (27) leads to the corresponding matrix \( \mathbf{C}(k, \Gamma_m) \) in the original non-orthogonal symmetry orbital basis (9).

The energy band structure of occupied valence bands and unoccupied conduction bands is recognizable whenever a band index can be assigned to the eigenvalues of each wavenumber \( k \) and each irreducible representation \( \Gamma_m \).

To decide whether a one-dimensional crystal will be electronically conducting, semiconducting or insulating, the electronic crystal orbital occupancy is crucial. Band indexing and band occupation determine the prediction of qualitative electronic and magnetic properties of the one-dimensional system under consideration.

2.5.1 Indexing of Energy Bands

The \( \mu \)th energy band of an irreducible representation \( \Gamma_m \) is formed from the ensemble of all crystal orbitals \( \Phi_{\mu}(k, \Gamma_m) \) of the first Brillouin zone

\[ -\frac{\pi}{a} < k \leq \frac{\pi}{a}. \]

In practice, however, only crystal orbitals of those \( N_k \) wavenumbers \( k \) will be known, for which the corresponding eigenvalue equation (11) has been solved. The assignment \( \Gamma_m \) to each orbital \( \Phi_{\mu}(k, \Gamma_m) \) prevents that crystal orbitals of different irreducible representations are collected within the same energy band.

Assuming cyclic translational symmetry for a considered one-dimensional crystal, it is sufficient to solve (11) only for wavenumbers \( k \) within the range \( 0 \leq k \leq \frac{\pi}{a} \), because crystal orbital energies are symmetric with respect to the center of the first Brillouin zone [15]:

\[ E_{\mu}(k, \Gamma_m) = E_{\mu}(-k, \Gamma_m). \]  (33)

The assignment of a band index \( \mu \) to a crystal orbital, characterized by a wavenumber \( k \) and an irreducible representation \( \Gamma_m \), has to be performed in energetically ascending order. The energy range between the lowest and the highest eigenvalue with band index \( \mu \) and symmetry label \( \Gamma_m \) is the \( \mu \)th allowed zone of the irreducible representation \( \Gamma_m \).

The essential advantages of this band indexing procedure using the symmetry label \( \Gamma_m \) are:

- Band indexing difficulties [16] do not occur [17].
- Linearly interpolated, continuous curves \( E_{\Gamma_m,\mu}(k) \) with equal \( \Gamma_m \) and different \( \mu \) do not intersect each other.
- Misinterpretations of the qualitative characteristic of electronic conductivity caused by a wrong band-index assignment can be excluded.

2.5.2 Occupation of Energy Bands

Electronic and magnetic properties of one-dimensional crystals are essentially determined by the kind and degree of occupation of the highest occupied energy band. If \( N_k \) is the number of \( k \)'s, for which the eigenvalue equation (11) had been solved, then \( N_k \cdot K \) electrons have to be distributed in the total number of \( N_k \cdot M \) crystal orbitals.

A non-magnetic insulating state is characterized by completely filled valence bands and a broad energy gap between the highest occupied (HOCO) and the lowest unoccupied crystal orbital (LUCO). A small energy gap leads to a semiconducting state. Metallic conductivity occurs only if the energy gap vanishes.

One-dimensional crystals with an odd number of electrons per unit cell have at least one partially occupied valence band. If the unit cell contains an even number of electrons, partially filled valence bands occur only in the case of an overlap of
different energy bands near the Fermi level. In one-electron band theory, a metallic state which arises whenever only the lowest orbitals of an incomplete filled energy band are occupied, is always predicted to be most stable because the total electronic energy $\mathcal{E}$ of the ground state is equal to the sum of its orbital energies multiplied by their corresponding occupation numbers $n_\mu(k, \Gamma_m) \in \{0, 1, 2\}$:

$$\mathcal{E} = \sum_k \sum_{\Gamma_m} \sum_\mu n_\mu(k, \Gamma_m) E_\mu(k, \Gamma_m).$$

(34)

Additional reductions of the total electronic ground state energy $\mathcal{E}$ may be caused by geometric Peierls distortions of the one-dimensional lattice, by means of which a metallic characteristic may change into a non-magnetic insulating one. But even if Peierls distortions can be excluded, several insulating states [19] are imaginable, whose total electronic ground state energies are lower than that of a metallic state, because they may reduce electron repulsion which has not been treated explicitly in the one-electron description. Therefore one-electron total electronic energies $\mathcal{E}$ often are basically inappropriate to predict the relative stability of the metallic and the insulating states of a partially filled energy band. Only the prediction of non-magnetic insulating states characterized by completely filled valence bands and broad HOCO-LUCO energy gaps seems to be unambiguous.

2.6 Mulliken Population Analysis

In a basis of $\dim V_k, r_m$ symmetry orbitals (14), the density matrix $P(k, \Gamma_m)$ is defined by

$$P(k, \Gamma_m) \equiv C(k, \Gamma_m) n(k, \Gamma_m) C^\dagger(k, \Gamma_m).$$

(35)

where $n(k, \Gamma_m)$ is the diagonal matrix of the occupation numbers. There is no unique definition of the number of electrons to be associated with a given atom or atomic core in a one-dimensional crystal, but it is still sometimes useful to perform such population analyses [11]. Since $K$ is the total number of all valence electrons per unit cell of a one-dimensional crystal, we get for a given set of $N_k$ wavenumbers $k$ (using (14) and (35))

$$N_k \cdot K = \sum_k \sum_{\Gamma_m} \sum_\mu n_\mu(k, \Gamma_m) \langle \Psi_i(k, \Gamma_m) | \Psi_j(k, \Gamma_m) \rangle$$

$$= \sum_k \sum_{\Gamma_m} \sum_\mu (P(k, \Gamma_m) S(k, \Gamma_m))_{\mu \mu}$$

$$= \sum_k \sum_{\Gamma_m} \text{tr}(Q(k, \Gamma_m)),$$

(36)

where we have introduced the abbreviating notation

$$Q(k, \Gamma_m) \equiv P(k, \Gamma_m) S(k, \Gamma_m).$$

(37)

The Mulliken population analysis interprets $Q_{\mu \mu}(k, \Gamma_m)$ as the number of electrons to be associated with the symmetry orbital $\Phi_\mu(k, \Gamma_m)$.

Because these symmetry-adapted Bloch sums are centered on equivalent atomic nuclei, the number of electrons to be associated with a given atom are obtained by taking the arithmetic mean over all symmetry orbitals centered on the corresponding atomic family. The net charge $q_A$ associated with an atom $A$ representing $N_A$ equivalent atoms within one unit cell is then given by

$$q_A = Z_A - \frac{1}{N_k N_A} \sum_k \sum_{\Gamma_m} \sum_{\mu \in A} Q_{\mu \mu}(k, \Gamma_m),$$

(38)

where $Z_A$ is the charge of the atomic core of $A$; the indices of summation indicate that we only sum over the basis functions centered on equivalent nuclei of type $A$ as well as over all irreducible representations $\Gamma_m$ and all wavenumbers $k$ of the line group symmetry under consideration.

It is a well-known feature of Mulliken population analysis that a slightly negative gross population occurs in cases where a sum of negative overlap populations predominates the positive Mulliken net population of the corresponding real basis orbital [21]. A similar artifact of complex Mulliken population analysis is, that imaginary parts of such gross populations sometimes do not vanish completely which is physically unreasonable.

2.7 Valence Orbital Ionization Potentials

As already mentioned, the VOIP of electrons in diverse atomic orbitals are taken to parametrize the diagonal elements of an extended-Hückel matrix $H(k, \Gamma_m)$.

Unlike atoms in a homogeneous chemical environment of the same kind, heteropolarly bound atoms
are partially charged. Moreover, the sums $\Delta$, $\Sigma$ and $\Pi$ of their d, s, and p valence orbital populations considerably differ from the configurations $d^J s^p p^\Omega$ of the neutral atoms in uniform surroundings. Atomic charges $q$ and valence orbital configurations $d^J s^p p^\Omega$, however, exercise an un neglectable influence on the VOIP of a valence electron. According to the Mulliken population scheme, valence orbital populations $A_A$, $I_A$, and $\Pi_A$ of an atom $A$ representing $N_A$ equivalent atoms within one unit cell can be calculated as follows:

$$A_A = \frac{1}{N_k N_{d,A}} \sum_k \sum_{\Gamma_{\mu} \in d,A} Q_{\mu\mu}(k, \Gamma_m),$$

$$\Sigma_A = \frac{1}{N_k N_{s,A}} \sum_k \sum_{\Gamma_{\mu} \in s,A} Q_{\mu\mu}(k, \Gamma_m),$$

$$\Pi_A = \frac{1}{N_k N_{p,A}} \sum_k \sum_{\Gamma_{\mu} \in p,A} Q_{\mu\mu}(k, \Gamma_m).$$

The sum of $A_A$, $\Sigma_A$, and $\Pi_A$ is equal to the atomic population of a representative center within a whole family $A$ of symmetrically equivalent atoms:

$$A_A + \Sigma_A + \Pi_A = \frac{1}{N_k N_A} \sum_k \sum_{\Gamma_{\mu} \in A} Q_{\mu\mu}(k, \Gamma_m).$$

For some first row transition metals ($A \in \{Ti, V, Cr, Mn, Fe, Co, Ni\}$), Basch, Viste, and Gray [10] fitted quadratic polynomials in $q_A$:

$$V_{i,A}^{[j]}(q_A) = A_{i,A}^{[j]} q_A^2 + B_{i,A}^{[j]} q_A + C_{i,A}^{[j]}$$

with the adjustable coefficients $A_{i,A}^{[j]}$, $B_{i,A}^{[j]}$ and $C_{i,A}^{[j]}$ on the empirically observed dependence of a VOIP $V_{i,A}^{[j]}$ from the corresponding integer atomic and ionic charges $q_A$ with respect to some selected electronic configurations $[j]$ ($j \in \{1, 2, 3\}$).

With such standard configurations listed in Table 1, the VOIP for fractional valence orbital configurations of these first row transition metals can be evaluated by means of the following formulas (Ballhausen and Gray [10]):

$$V_{d,A}(A_A, \Sigma_A, \Pi_A) = (1 - \Sigma_A - \Pi_A) V_{d,A}^{[1]}_A + \Sigma_A V_{d,A}^{[2]}_A + \Pi_A V_{d,A}^{[3]}_A,$$

$$V_{s,A}(A_A, \Sigma_A, \Pi_A) = (2 - \Sigma_A - \Pi_A) V_{s,A}^{[1]}_A + (\Sigma_A - 1) V_{s,A}^{[2]}_A + \Pi_A V_{s,A}^{[3]}_A,$$

$$V_{p,A}(A_A, \Sigma_A, \Pi_A) = (2 - \Sigma_A - \Pi_A) V_{p,A}^{[1]}_A + (\Pi_A - 1) V_{p,A}^{[2]}_A + A_A V_{p,A}^{[3]}_A.$$

Table 1. Standard configurations for valence orbitals of Ti, V, Cr, Mn, Fe, Co, and Ni.

<table>
<thead>
<tr>
<th>Valence orbital</th>
<th>Standard configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>{1}</td>
<td>{2}</td>
</tr>
<tr>
<td>3d</td>
<td>d&quot;</td>
</tr>
<tr>
<td>4s</td>
<td>d&quot;-1 s</td>
</tr>
<tr>
<td>4p</td>
<td>d&quot;-1 p</td>
</tr>
</tbody>
</table>

$n$: number of valence electrons of the transitional metal ($n = q + \Delta + \Sigma + \Pi$).

Table 2. Standard configurations for valence orbitals of second period elements.

<table>
<thead>
<tr>
<th>Valence orbital</th>
<th>Standard configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>{1}</td>
<td>{2}</td>
</tr>
<tr>
<td>2s</td>
<td>s^2 p^3-2</td>
</tr>
<tr>
<td>2p</td>
<td>s^2 p^3-2</td>
</tr>
</tbody>
</table>

$n$: number of valence electrons of the second period element ($n = q + \Sigma + \Pi$).

A similar set of standard configurations (cf. Table 2) and interpolation formulas can be set up for elements with only s and p valence electrons:

$$V_{s,A}(\Sigma_A, \Pi_A) = (\Sigma_A - 1) V_{s,A}^{[1]}_A + (2 - \Sigma_A) V_{s,A}^{[2]}_A,$$

$$V_{p,A}(\Sigma_A, \Pi_A) = (\Sigma_A - 1) V_{p,A}^{[1]}_A + (2 - \Sigma_A) V_{p,A}^{[2]}_A.$$

Methodical refinements for the parametrization of the diagonal elements of an extended-Hückel matrix $H(k, \Gamma_m)$ can be introduced using iterative one-electron SCC (Self-Consistence of Charge) and SCCCE (Self-Consistence of Charge and Configuration) procedures.

2.7.1 Self-Consistence of Charge

The flow chart in Fig.1 explains the iterative algorithm of the SCC model.

One starts with guessed charges $q_A^{(0)}$ for the representatives of all $N_F$ symmetrically inequivalent atomic families $A$, and evaluates the corresponding $V_{i,A}^{[j]}(q_A^{(0)})$ for all valence orbitals of one chosen configuration $[j]$.

Self-consistence of charge has been achieved whenever the atomic charges $q_A$ of all $N_F$ inequivi-
alient atoms do not change essentially within two subsequent iterative cycles $I$. The quality of the self-consistence procedure can be influenced by a suitable choice of the parameter $\varepsilon_{SCC}$ which determines the break-off of the iteration. If convergence cannot be reached, the SCC procedure stops after having exceeded a previously set up maximum number $I_{\text{max}}$ of steps.

If the energetical order of differently occupied crystal orbitals changes in the course of the iterative process, charge oscillations with a period of only a few cycles may occur. Particularly, if nearly degenerate crystal orbitals belong to energy bands of different symmetry labels $\Gamma_m$, a damping factor

$$0 \leq D_{\text{SCC}} < 1$$

has to be introduced in order to throttle charge oscillations and to promote the convergence.

2.7.2 Self-Consistence of Charge and Configuration

The SCCC procedure differs from the SCC iteration in guessing not only the charges $q^{(0)}_A$, but also the start configurations $d^{A(b)}_s, s^{A(c)} p^{A(d)}$ of all $N_F$
symmetrically inequivalent atoms. The iteration is continued until the atomic charges $q_A$ as well as their corresponding populations $J_A$, $\Sigma_A$, and $\Pi_A$ do not differ essentially between two subsequent cycles. Like in the SCC model we introduce $\varepsilon_{SCCC}$ and $D_{SCCC}$ as convergence and damping parameters of the SCCC approach.

For the second row elements with a valence orbital configuration $s^2 p^n$, the evaluation of populations $\Pi_A^{(I)}$ and VOIP $V_{d,A}(q_A^{(I)})$ is actually not
needed (cf. Fig. 2, where these quantities have been put in brackets).

2.8 Orbital Composition, Bond Order, Valence, and Free Valence

In addition to atomic charges $q$ and valence orbital populations $\Delta, \Sigma$ and $\Pi$, there are still some other quantities suitable to connect quantum chemical results and traditional chemical concepts.

100 $O_{i_A}^{(o)} (k, \Gamma_m)$, for instance, is a number which represents the percentage of the i-type symmetry orbitals ($i \in \{ s, p, d \}$) of an atomic family $A$ in a crystal orbital $\Psi_i (k, \Gamma_m)$ [22]:

$$O_{i_A}^{(o)} (k, \Gamma_m) = \sum_{\mu \in \Lambda_A} C_{\mu i} (k, \Gamma_m) (S(k, \Gamma_m) C(k, \Gamma_m)_{\mu \nu}$$

As in Mulliken population analysis it may happen that some $O_{i_A}^{(o)} (k, \Gamma_m)$ show a small non-vanishing imaginary part.

For the calculation of on-site bond orders between the nearest neighbors of two atomic families such as valences and free valences of single centers, we used the recommended definitions of Mayer [23] to specify analogous expressions for one-dimensional crystals:

Bond order $B_{AA'}$ between next neighbors of two atomic families $A$ and $A'$:

$$B_{AA'} = \frac{1}{N_k N_A N_A'} \sum_k \sum_{\mu \in A} \sum_{\nu \in A'} \sum_{i \in A} Q_{\mu \nu} (k, \Gamma_m) Q_{i \mu} (k, \Gamma_m).$$

Valence $V_A$ of an atom belonging to the family $A$:

$$V_A = \frac{1}{N_k N_A} \sum_k \sum_{\mu \in A} 2 \sum_{\nu \in A} Q_{\mu \nu} (k, \Gamma_m) - \sum_{\mu \in A} \sum_{\nu \in A} Q_{\mu \nu} (k, \Gamma_m) Q_{\nu \mu} (k, \Gamma_m).$$

Free valence $F_A$ of an atom belonging to the family $A$:

$$F_A = V_A - \sum_{A \neq A'} N_{AA'} B_{AA'}. \quad (53)$$

For (closed-shell) systems without partially filled crystal orbitals, $F_A$ is always equal to zero.

Bond orders, valences and free valences which have been computed according to the above definitions usually are not integers, but they do not deviate very much from the integer numbers of classical valence theory. Slightly negative values and small imaginary parts cannot be excluded, however.

2.9 Density of States Histogram

The $i$th segment $D(E_i)$ of a density of states histogram

$$|D(E_i)| i = 1, \ldots, n_E$$

may be regarded as a measure for the number of allowed crystal orbital energies within a small energy interval $\Delta E$ of average energy $E_i$.

In this section we describe the construction of a density of states histogram for a non-degenerate energy band $\Gamma_m$ whose energy values $E_{\Gamma_m, \mu} (k)$ are only known for the $N_k$ considered wavenumbers $k_1 < k_2 < k_3 < \ldots < k_{N_k}$.

If we divide the range $0 \leq k \leq \frac{\pi}{a}$ into $n_k$ intervals of length $\Delta k$, and the energy scale spanned by all eigenvalues $E_{\Gamma_m, \mu} (k)$ into $n_E$ intervals of length $\Delta E$ with average energies $E_i (i = 1, \ldots, n_E)$, we get a grid of $n_k \cdot n_E$ rectangles with side lengths $\Delta k$ and $\Delta E$.

For each irreducible representation $\Gamma_m$ and each energy band $\mu$ we define a function $I_{\Gamma_m, \mu} (E_i)$ as

$$I_{\Gamma_m, \mu} (E_i) = \frac{n_k}{n_E} \sum_{j=1}^{n_k} \left\{ \begin{array}{ll} 1 & \text{if } \left( E_i - \frac{\Delta E}{2} \right) < E_{\Gamma_m, \mu} (k) \equiv \left( E_i + \frac{\Delta E}{2} \right) \\ 0 & \text{otherwise} \end{array} \right.$$  

$$= \frac{1}{n_k (j - 1)} \pi < k \leq \frac{1}{n_k} j \pi$$

The sum $I(E_i)$ over all $\Gamma_m$ and all $\mu$ of these functions

$$I(E_i) = \sum_{\Gamma_m} \sum_{\mu} I_{\Gamma_m, \mu} (E_i)$$

is equal to the number of grid rectangles which are intersected by the continuously interpolated curve $E_{\Gamma_m, \mu} (k)$. 
Finally, the density of states $D(E_i)$ in an interval of average energy $E_i$ is defined as

$$D(E_i) = I(E_i)/I_{\text{max}},$$

where $I_{\text{max}}$ is the maximum of all integers $|I(E_i)|, i = 1, \ldots, n_E$.

The basic requirement for such a construction of a density of states histogram is, that the energy band structure, i.e. the continuous curves $E_{\mu,m}(k)$ are known for all band indices $\mu$ and all irreducible representations $\Gamma_m$. This complete energy band structure can be gained only approximately by means of an appropriate interpolation procedure.

We use a cubic spline function $E_{\mu,m}(k)$ composed of $N_k - 1$ cubic polynomials

$$f_i(k) = A_i(k - k_i)^3 + B_i(k - k_i)^2 + C_i(k - k_i) + D_i,$$

defined in the ranges $[k_i, k_{i+1})$, respectively. With the spline conditions:

$$f_i(k_i) = f_{i-1}(k_i) = E_{\mu,m}(k_i, \Gamma_m),$$

$$f_i'(k_i) = f_{i-1}'(k_i), \quad i = 2, \ldots, N_k - 1$$

and two additional boundary conditions:

$$f_1'(k_1) = 0 \quad \text{and} \quad f_{N_k-1}'(k_{N_k}) = 0$$

we can get a system of $N_k$ equations for the $N_k$ unknown second derivatives $f''_i(k_i), i = 1, \ldots, N_k$, from which the $4(N_k - 1)$ spline coefficients $A_i, B_i, C_i,$ and $D_i$ can be determined.

3. One-Dimensional Energy Band Structure of Bis(2,5-dimethyl-N,N'-dicyanoquinonediimine)-copper(I)

The first task of any one-dimensional energy band structure calculation is to choose an appropriate one-dimensional model geometry which can be assumed to represent the spatial and chemical structure of the real three-dimensional crystal. Figure 3 shows the one-dimensional unit cell (length $a = 3.881 \text{ Å}$) of line group symmetry $L_2$, because of its 2-fold rotation axis $C_2$ identical with the invariant line. Atomic coordinates (cf. Table 6) have been taken from crystallographic data, documented in reference [2]. Equivalent atomic families have been labelled as shown in Figure 3.

3.1 Parametrization

The band structure calculation has been performed according to the following list of standard choices:

1. The range $0 \leq k \leq \frac{\pi}{a}$ of the first Brillouin zone has been subdivided into five equidistant intervals; the $N_k = 6$ values of the wavenumber $k$ therefore are 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 in units of $\left(\frac{\pi}{a}\right)$.

2. Starting with the VOIP recommended by Ballhausen and Gray [10] (cf. Table 3), valence orbital ionization potentials generally have been...
evaluated by means of the iterative SCC and SCCC procedures, namely:
- VOIP of the elements H and Cu according to SCC.
- VOIP of the elements C and N according to SCCC.

We used the standard interpolation parameter sets of Basch, Viste, and Gray [10] for H, C, and N. SCC-parameters for Cu have been taken from reference [25] (cf. Table 5).

3. Convergence and damping parameters have been chosen in such a way that no charge oscillations could be observed:
\[ \xi_{\text{SCC}} = \xi_{\text{SCCC}} = 0.05, \]
\[ D_{\text{SCC}} = D_{\text{SCCC}} = 0.95. \]

In this way, convergence could be achieved within only a few iterative cycles. Unlike non-iterative extended-Hückel charge distributions, SCC and SCCC charges are in good agreement with chemical intuition.

Table 3. Valence orbitals, exponents, and initial VOIP.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Valence orbital</th>
<th>( \zeta )</th>
<th>VOIP (10(^3) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1 s</td>
<td>1.0000</td>
<td>110</td>
</tr>
<tr>
<td>C</td>
<td>2 s</td>
<td>1.6250</td>
<td>157</td>
</tr>
<tr>
<td>C</td>
<td>2 p</td>
<td>1.6250</td>
<td>86</td>
</tr>
<tr>
<td>N</td>
<td>2 s</td>
<td>1.9500</td>
<td>206</td>
</tr>
<tr>
<td>N</td>
<td>2 p</td>
<td>1.9500</td>
<td>106</td>
</tr>
<tr>
<td>Cu</td>
<td>3 d</td>
<td>32.91</td>
<td>86</td>
</tr>
<tr>
<td>Cu</td>
<td>4 s</td>
<td>1.0000</td>
<td>62</td>
</tr>
<tr>
<td>Cu</td>
<td>4 p</td>
<td>1.0000</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 4. Double-\( \zeta \) exponents and coefficients.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Valence orbital</th>
<th>( \zeta_1 )</th>
<th>( c_1 )</th>
<th>( \zeta_2 )</th>
<th>( c_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3 d</td>
<td>5.95</td>
<td>0.5933</td>
<td>2.30</td>
<td>0.5744</td>
</tr>
</tbody>
</table>

Table 5. SCC and SCCC interpolation parameters (in 10\(^3\) cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Valence orbital</th>
<th>( A_1 )</th>
<th>( B_1 )</th>
<th>( C_1 )</th>
<th>( A_2 )</th>
<th>( B_2 )</th>
<th>( C_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1 s</td>
<td>109.84</td>
<td>219.20</td>
<td>109.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2 s</td>
<td>27.95</td>
<td>141.60</td>
<td>156.60</td>
<td>28.00</td>
<td>141.20</td>
<td>171.00</td>
</tr>
<tr>
<td>C</td>
<td>2 p</td>
<td>27.95</td>
<td>118.20</td>
<td>85.80</td>
<td>28.03</td>
<td>111.95</td>
<td>86.90</td>
</tr>
<tr>
<td>N</td>
<td>2 s</td>
<td>28.16</td>
<td>162.20</td>
<td>206.20</td>
<td>28.05</td>
<td>163.30</td>
<td>226.00</td>
</tr>
<tr>
<td>N</td>
<td>2 p</td>
<td>28.16</td>
<td>133.20</td>
<td>106.40</td>
<td>30.01</td>
<td>114.00</td>
<td>129.40</td>
</tr>
<tr>
<td>Cu</td>
<td>3 d</td>
<td>32.91</td>
<td>45.41</td>
<td>85.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>4 s</td>
<td>7.60</td>
<td>71.30</td>
<td>62.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>4 p</td>
<td>8.47</td>
<td>53.55</td>
<td>32.10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Extended-Hückel matrices \( H(k, \Gamma_m) \) have been calculated according to (19) and (20) with the scaling factor \( F' \) defined in (21) and (22). Using this modified Wolfsberg-Helmholz formula, negative orbital populations can be avoided [7]. As usual, \( F \) has been set equal to 1.75 [26].

5. For the orbital exponents \( \zeta \) we took the approved parameter sets of Whangbo, Hoffmann, and coworkers [27] (cf. Table 3):
- \( s \) and \( p \) exponents have been taken from Slater [4],
- linear combinations of two transition metal 3d Slater type orbitals have been used according to Richardson, Nieuwpoort, Powell, and Edgell [5] (cf. Table 4).

6. We set \( \delta \) which controls the break-off of Bloch summation (6) equal to 10^{-12}.

7. Nearly degenerate crystal orbitals with an energy difference less than 10^{-6} eV have been occupied according to Hund's rule in the course of the iterative procedure.

8. We took \( n_F = 1000 \) and \( n_k = 30000 \) to construct an appropriately resolved density of states grid (cf. (54) and (55)).

3.2 Computational Results

With the chosen set of valence orbitals (cf. Table 3), (2,5-DM-DCNQI)\(_2\)Cu contains 147 valence electrons. The SCC/SCCC procedure converged after 7 iteration cycles. Overlap integrals of 15 unit cells have been added according to (4) until condition (6) could be fulfilled (\( N_{\text{max}} = 7 \)).

Using symmetry adapted linear combinations of Bloch sums, the eigenvalue problem (2) splitted into two equations (11) with the matrix dimensions \( V_{k,A_0} = 69 \) and \( V_{k,A_1} = 68 \), respectively.
Fig. 4. One-dimensional energy band structure and density of states histogram.

Table 6. Cartesian coordinates $X$, $Y$ and $Z$, valence orbital ionization potentials $V$, configurations $d^4 s^2 p^7$ and charges $q$ for all representative atoms of (2,5-DM-DNCQI)$_2$Cu.

<table>
<thead>
<tr>
<th>Atomic family</th>
<th>$X$ (Å)</th>
<th>$Y$ (Å)</th>
<th>$Z$ (Å)</th>
<th>$V(d)$ ($10^3$ cm$^{-1}$)</th>
<th>$V(s)$ ($10^3$ cm$^{-1}$)</th>
<th>$V(p)$ ($10^3$ cm$^{-1}$)</th>
<th>$\Delta$</th>
<th>$\Sigma$</th>
<th>$\Pi$</th>
<th>$q$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$</td>
<td>0.000</td>
<td>0.000</td>
<td>-3.881</td>
<td>112.51752</td>
<td>83.05280</td>
<td>49.07945</td>
<td>9.92</td>
<td>0.32</td>
<td>0.29</td>
<td>0.47</td>
</tr>
<tr>
<td>C$_2$</td>
<td>4.526</td>
<td>0.757</td>
<td>-1.256</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.15</td>
<td>2.75</td>
<td>0.10</td>
</tr>
<tr>
<td>C$_3$</td>
<td>4.189</td>
<td>-0.558</td>
<td>-0.925</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.09</td>
<td>2.88</td>
<td>0.04</td>
</tr>
<tr>
<td>C$_4$</td>
<td>4.000</td>
<td>1.349</td>
<td>-0.154</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.06</td>
<td>2.77</td>
<td>0.07</td>
</tr>
<tr>
<td>C$_5$</td>
<td>6.285</td>
<td>-0.800</td>
<td>0.302</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.03</td>
<td>2.66</td>
<td>0.03</td>
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<tr>
<td>C$_6$</td>
<td>6.558</td>
<td>0.607</td>
<td>-0.056</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.07</td>
<td>2.60</td>
<td>0.03</td>
</tr>
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<td>C$_7$</td>
<td>5.801</td>
<td>1.351</td>
<td>-0.782</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.11</td>
<td>2.81</td>
<td>0.05</td>
</tr>
<tr>
<td>C$_8$</td>
<td>6.041</td>
<td>2.795</td>
<td>-1.176</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.98</td>
<td>3.12</td>
<td>-0.10</td>
</tr>
<tr>
<td>C$_9$</td>
<td>4.636</td>
<td>-2.777</td>
<td>0.121</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.98</td>
<td>3.10</td>
<td>-0.09</td>
</tr>
<tr>
<td>N$_{10}$</td>
<td>3.718</td>
<td>1.539</td>
<td>-2.005</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.34</td>
<td>3.90</td>
<td>-0.24</td>
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<td>N$_{11}$</td>
<td>2.607</td>
<td>1.074</td>
<td>-2.468</td>
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<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.14</td>
<td>2.80</td>
<td>0.06</td>
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<tr>
<td>N$_{12}$</td>
<td>1.558</td>
<td>0.789</td>
<td>-2.934</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.42</td>
<td>3.83</td>
<td>-0.25</td>
</tr>
<tr>
<td>N$_{13}$</td>
<td>7.064</td>
<td>-1.552</td>
<td>1.064</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.35</td>
<td>3.89</td>
<td>-0.25</td>
</tr>
<tr>
<td>N$_{14}$</td>
<td>8.226</td>
<td>-1.048</td>
<td>1.542</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.14</td>
<td>2.83</td>
<td>0.03</td>
</tr>
<tr>
<td>N$_{15}$</td>
<td>9.210</td>
<td>-0.739</td>
<td>2.012</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>1.46</td>
<td>3.83</td>
<td>-0.30</td>
</tr>
<tr>
<td>H$_{16}$</td>
<td>3.346</td>
<td>-0.925</td>
<td>-1.203</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.94</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>H$_{17}$</td>
<td>7.360</td>
<td>0.999</td>
<td>0.297</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.93</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>H$_{18}$</td>
<td>6.778</td>
<td>2.929</td>
<td>-0.576</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.93</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>H$_{19}$</td>
<td>5.350</td>
<td>3.445</td>
<td>-0.995</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.95</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>H$_{20}$</td>
<td>6.346</td>
<td>2.890</td>
<td>-2.081</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.94</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>H$_{21}$</td>
<td>3.763</td>
<td>-3.158</td>
<td>-0.012</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.95</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>H$_{22}$</td>
<td>4.945</td>
<td>-2.993</td>
<td>1.004</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.94</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>H$_{23}$</td>
<td>5.244</td>
<td>-3.138</td>
<td>-0.528</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00</td>
<td>0.92</td>
<td>0.00</td>
<td>0.08</td>
</tr>
</tbody>
</table>
In Table 6, valence orbital ionization potentials $V$, populations $A$, $\Sigma$ and $\Pi$ such as atomic charges $q$ of the 7th iteration step have been listed. It shows that copper 4s and 4p orbitals are only slightly populated. As expected, atomic charges of the electronegative nitrogen atoms are always negative; copper atoms are positively charged (0.47 a.u.).

Calculated valences and bond orders have been inserted into Figure 3. The discrepancy between these valences and the integer values of chemical valence theory is very small. Bond orders in the range between 1 and 2 emphasize the aromatic character of the quinoid ring systems. Cu atoms are strongest bound to next neighbor nitrogens, of course, with a bond order of 0.47.

Figure 4 shows the energy band structure and the density of states histogram in the energy range between $-17 \text{ eV}$ and $-5 \text{ eV}$. Each point of the central diagram represents the energy $E_\mu(k, \Gamma_m)$ of the crystal orbital $\Phi_\mu(k, \Gamma_m)$. Allowed and forbidden zones, band widths and band gaps can be recognized best by inspecting the left block chart. Near the Fermi level ($-10.84 \text{ eV}$) there are only two energy bands belonging to the irreducible representations $A_0$ and $A_1$, respectively, which nearly overlap each other completely.

If we focus on the two antipodal possibilities of band occupancy, namely the metallic versus the magnetic insulating (MOTT) state, a complete occupation of both energy bands with electrons of identical spin is not achievable because only $1/3$ of the $37A_1$ band is occupied (wavenumbers $k = 0$ and $k = 0.2 \pi$) and only $1/6$ of the $38A_0$ band (wavenumber $k = 0$). Although the combined width (0.42 eV) of both energy bands is rather small, we therefore predict a metallic state to be most stable, resulting from the incomplete occupancy of both $38A_0$ and $37A_1$ energy bands. This is the most important result; it is in good agreement with the experiment [2]. For the non-magnetic metallic characteristic the total electronic ground state energy $\varepsilon$ (cf. (34)) yields $-2496.35 \text{ eV}$.

Table 7 shows the percental composition (50) of the crystal orbitals $\Psi_{37}(k, A_1)$ and $\Psi_{38}(k, A_0)$; in both energy bands there is no significant participation of Cu electrons at all. We conclude that the copper atoms do not play any role in the mechanism of electronic conductivity, as already presumed in [2].

4. Conclusion

Though we cannot expect that relative stabilities of metallic and insulating states are unambiguously determinable within one-electron theories, one-dimensional band structure calculations of extended-Hückel type may be useful to rationalize the observed electronic properties of quasi one-dimensional crystals, as could be demonstrated for the highly conducting compound $(2,5\text{-DM-DNCQI})_2\text{Cu}$.

In addition to considerable computational savings which can be achieved by using symmetry adapted linear combinations of Bloch sums as basis func-

### Table 7. Composition of the two incompletely occupied energy bands $38A_0$ and $37A_1$.  

#### $38A_0$

<table>
<thead>
<tr>
<th>$k$</th>
<th>21% N$<em>{12}$p, 15% N$</em>{10}$p, 12% N$<em>{12}$p, 12% N$</em>{15}$p, 9% C$_2$p, 9% C$_5$p, 8% C$_4$p, 4% C$_7$p, 2% C$_1$p, 2% C$_4$p</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k=0.0$</td>
<td>21% N$<em>{13}$p, 15% N$</em>{10}$p, 12% N$<em>{12}$p, 12% N$</em>{15}$p, 9% C$_2$p, 9% C$_5$p, 8% C$_4$p, 4% C$_7$p, 2% C$_1$p, 2% C$_4$p</td>
</tr>
<tr>
<td>$k=0.2$</td>
<td>21% N$<em>{13}$p, 15% N$</em>{10}$p, 12% N$<em>{12}$p, 12% N$</em>{15}$p, 9% C$_2$p, 9% C$_5$p, 8% C$_4$p, 4% C$_7$p, 2% C$_1$p, 2% C$_4$p</td>
</tr>
<tr>
<td>$k=0.4$</td>
<td>21% N$<em>{13}$p, 13% N$</em>{10}$p, 11% N$_{12}$p, 10% C$_2$p, 10% C$<em>5$p, 10% N$</em>{15}$p, 9% C$_4$p, 4% C$_7$p, 3% C$_3$p, 3% C$_6$p</td>
</tr>
<tr>
<td>$k=0.6$</td>
<td>21% N$<em>{13}$p, 13% N$</em>{10}$p, 12% C$_2$p, 11% C$<em>5$p, 9% C$<em>4$p, 9% N$</em>{15}$p, 9% N$</em>{15}$p, 5% C$_3$p, 4% C$_7$p, 3% C$_6$p</td>
</tr>
<tr>
<td>$k=0.8$</td>
<td>21% N$_{13}$p, 13% C$<em>2$p, 13% N$</em>{10}$p, 12% C$<em>5$p, 10% C$<em>4$p, 9% N$</em>{15}$p, 8% N$</em>{15}$p, 5% C$_3$p, 4% C$_6$p, 4% C$_7$p</td>
</tr>
<tr>
<td>$k=1.0$</td>
<td>21% N$_{13}$p, 13% C$<em>2$p, 13% N$</em>{10}$p, 12% C$<em>5$p, 10% C$<em>4$p, 8% N$</em>{15}$p, 8% N$</em>{15}$p, 5% C$_3$p, 4% C$_6$p, 4% C$_7$p</td>
</tr>
</tbody>
</table>

#### $37A_1$

<table>
<thead>
<tr>
<th>$k$</th>
<th>23% N$<em>{13}$p, 13% N$</em>{10}$p, 12% N$<em>{12}$p, 12% N$</em>{15}$p, 10% C$_2$p, 10% C$_4$p, 9% C$_5$p, 4% C$_7$p, 2% C$_1$p, 2% C$_4$p</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k=0.0$</td>
<td>22% N$<em>{13}$p, 13% N$</em>{10}$p, 12% N$<em>{12}$p, 11% N$</em>{15}$p, 10% C$_2$p, 10% C$_4$p, 9% C$_5$p, 4% C$_7$p, 2% C$_1$p, 2% C$_4$p</td>
</tr>
<tr>
<td>$k=0.2$</td>
<td>22% N$<em>{13}$p, 13% N$</em>{10}$p, 12% N$<em>{12}$p, 11% N$</em>{15}$p, 10% C$_2$p, 10% C$_4$p, 9% C$_5$p, 4% C$_7$p, 2% C$_1$p, 2% C$_4$p</td>
</tr>
<tr>
<td>$k=0.4$</td>
<td>22% N$<em>{13}$p, 13% N$</em>{10}$p, 11% C$<em>2$p, 11% N$</em>{15}$p, 10% C$_4$p, 10% C$<em>5$p, 10% N$</em>{15}$p, 4% C$_7$p, 3% C$_3$p, 3% C$_6$p</td>
</tr>
<tr>
<td>$k=0.6$</td>
<td>21% N$<em>{13}$p, 13% N$</em>{10}$p, 12% C$<em>2$p, 11% N$</em>{15}$p, 9% C$<em>4$p, 9% N$</em>{15}$p, 9% N$_{15}$p, 5% C$_3$p, 4% C$_7$p, 3% C$_6$p</td>
</tr>
<tr>
<td>$k=0.8$</td>
<td>21% N$<em>{13}$p, 14% N$</em>{10}$p, 13% C$_2$p, 12% C$<em>5$p, 9% C$<em>4$p, 9% N$</em>{15}$p, 8% N$</em>{15}$p, 5% C$_3$p, 4% C$_6$p, 4% C$_7$p</td>
</tr>
<tr>
<td>$k=1.0$</td>
<td>21% N$<em>{13}$p, 14% N$</em>{10}$p, 13% C$_2$p, 12% C$<em>5$p, 10% C$<em>4$p, 8% N$</em>{15}$p, 7% N$</em>{15}$p, 5% C$_3$p, 4% C$_6$p, 4% C$_7$p</td>
</tr>
</tbody>
</table>
tions, the main advantage of our treatment is that band indexing difficulties and any consequent misinterpretations of the electronic band structure are systematically excluded. Moreover, it has the nice feature that the evaluation of extended-Hückel matrix elements as well as the computation of atomic charges, populations, valences, and bond orders can be performed within this symmetry basis throughout, so that no backtransformations into the original atomic orbital basis are ever needed.

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[8] In a symmetry-adapted linear combination \( \Phi_{s}(k, \Gamma_m) \) only equivalent Bloch sums \( \Phi_{s}(k) \) with identical valence orbital ionization potentials \( \nu \) are combined.
[12] There exist numerous efficient algorithms for the diagonalization of Hermitian matrices. FORTRAN eigenvalue routines which base upon such algorithms can be taken from the program package EISPACK [13], for instance.
[14] Since \( S(k, \Gamma_m) \) is positive definite, i.e. its eigenvalues are all positive, there is in principle no difficulty of taking square roots.
[17] As a consequence, there is no need for an indexing procedure of an energy band \( E(k) \) without symmetry label \( \Gamma_m \) by means of the first derivative with respect to \( k \) [18].
[19] In addition to the non-magnetic insulating states arising from completely occupied valence bands, other insulating states caused by partially filled energy bands may be distinguishable [20], namely: magnetic insulating (MOTT) states, spin density wave states, charge density wave states, bond density wave states.
[27] There are numerous contributions which are closely related to our treatment, for instance [28].