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A CNDO/INDO Crystal Orbital Model for Transition Metal Polymers of the 3*d* Series—Basis Equations

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The crystal orbital formalism in the tight-binding approximation is combined with a recently developed CNDO/INDO model for transition metal species of the 3*d* series in order to allow band structure calculations on the Hartree–Fock (HF) SCF level for one-dimensional (1*D*) chains with organometallic unit cells. The band structure approach based on the CNDO and INDO approximation can be used for any atom combination up to bromine under the inclusion of the 3*d* series. The matrix elements for the tight-binding Hamiltonian are derived for an improved CNDO and INDO framework. The total energy of the 1*D* chain is partitioned into one-center contributions and into two-center increments of the intracell and intercell type. Semiempirical band structure calculations on simple model systems are compared with available *ab initio* data of high quality.

Key words: Tight-binding formalism for 3*d* polymers – Band structure approach in the CNDO/INDO approximation – Basis equations and parametrization.

1. Introduction

The chemical and physical properties of conducting and semiconducting organometallic chains have been studied extensively in the last decade [1, 2]. Important examples where metallic or near metallic conductivities have been detected are the partially oxidized tetracyanoplatinate, $Pt(CN)_4^{2-}$, (Krogmann's salt) [3], polyferrocenylene [4], nickel and palladium glyoximate derivatives [5], bisbenzoquinonedioximates of Ni and Pd [6], molecular metals produced by

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halogenation of phthalocyanines [7] as well as porphyrinato metallamacrocycles with transition metal atoms [8, 9] or SiO/GeO groups [10] as bridging units.

Unfortunately this experimental variety is accompanied by a deficit of theoretical models for the determination of the band structure of these one-dimensional ($1D$) polymers. Several band structure approaches with different degrees of sophistication (e.g. X_α method and one-electron calculations of the Wolfsberg–Helmholtz type) are only available for the tetracyanoplatinate chain [11–13]. In the case of the larger metallamacrocycles only sparse one-electron calculations of the Extended Hückel (EH) type have been published [14]. One-electron models are obviously no suitable tool for the investigation of electronic phase transitions in polymers (metallic vs. insulating state) due to the neglect of electron-electron interaction which determines the electrical and magnetic properties of the low-dimensional materials [15, 16].

It is clear that tight-binding approaches based on *ab initio* models are beyond the current computational capacities for nearly all of the aforementioned $1D$ chains with transition metal centers. Band structure calculations on these systems are therefore restricted to semiempirical frameworks which are based on the zero differential overlap (ZDO) approximation where two-electron integrals of the multicenter type are neglected. Recently we have developed an improved CNDO/INDO model for molecules that contain the atoms H to Br under the inclusion of the first transition metal series [17]. The semiempirical ZDO operators have been designed to reproduce the computational results of *ab initio* calculations of double-zeta quality. In the formulas for the various two-electron integrals, experimental quantities have been taken into account. Thus intraatomic and interatomic correlation effects are included partially even in the framework of the Hartree–Fock (HF) approximation. The molecular CNDO/INDO model has been successfully tested in investigations of ground state properties (e.g., geometries, conformational behaviour, and dipole moments) [18–20], excitation energies [18], ionization potentials [20–22] and many-body effects [23] in a large number of mononuclear and polynuclear transition metal compounds.

In the following we want to present the extension of this CNDO/INDO model [24] for atoms up to bromine to the self-consistent-field tight-binding approximation for polymers as developed by Del Re, Ladik and Biczó [25, 26]. Various CNDO and INDO studies based on the crystal orbital approach have been reported for atoms of the first two rows. Morokuma [27], Fujita and Imamura [28] as well as Perkins and coworkers [29, 30] have published the first band structure calculations based on the CNDO model, while the original INDO formalism has been adopted for the first time by O'Shea and Santry [31] and by Beveridge et al. [32]. Detailed reviews on the capability of semiempirical and ab initio band structure calculations are given in Refs. [26], [33] and [34].

Tight-binding models that are based on the CNDO or INDO approximation for polymers containing transition metal atoms of the $3d$ series have not been reported. One-electron band structure studies on organometallic $1D$ systems already have been mentioned [13, 14, 16], and EH type calculations for $3D$

solids with small unit cells (e.g. ScP, VP, CrP, MnP) have been published recently [35]. A review of APW and OPW approaches applied to smaller transition metal systems (e.g. dichalcogenides, trichalcogenides, and platinocarbonyls) can be found in Ref. [36].

We have adopted the CNDO/INDO parametrization of Ref. [17] for the implementation into the crystal orbital formalism in its original version. For the elements Ga to Br only the CNDO variant is available as the necessary Slater–Condon parameters for the INDO model are not known for these atoms. The elements of the third period (Na—Cl) can be treated with a *sp* basis in the INDO framework but alternatively with a *sp* and a *spd* basis in the CNDO approximation; the INDO restriction once again has its origin in the missing Slater–Condon factors for the virtual 3*d* set. The invariance criteria satisfied in the present semiempirical models differ from the original integral restrictions derived in the ZDO approximation [32, 37]. We have adopted an algorithm of Brown and Roby [38] where the matrix elements of the Fock operator are invariant under transformations of the local axes but not invariant under a transformation into such as a basis of hybrid orbitals. This degree of freedom allows the implementation of different one- and two-center two-electron integrals for different magnetic quantum numbers (*s*, *p*, *d* orbitals).

The basis equations of the CNDO/INDO tight-binding formalism for transition metal chains are presented in the next section. In the following semiempirical results are compared with available ab initio band structure calculations on smaller model systems. The band structure of nickel(II)glyoximate as derived in the INDO version of the present ZDO model is discussed in detail in an accompanying contribution.

2. Basis Equations

The one-electron crystal orbitals in the tight-binding approximation are given by the well-known Bloch sums [39]

$$\psi_{kl} = N^{-1/2} \sum_{j=0}^{(N-1)} \sum_{\mu=1}^{n} \exp(ijk) c_{\mu lk} \mu_j^{A_j}(r_A - ja). \tag{1}$$

where k is the wave vector which is defined in Eq. (2), l represents a band index, j symbolizes a cell in the chain ($j = 0$, origin) and μ labels the μth AO. Thus $\mu_j^{A_j}(r_A - ja)$ is the μth AO at center A in the jth unit cell, and a is the primitive vector characterizing the translational symmetry. The Bloch sums of course are subject to the periodic Born–von Karman boundary conditions [40].

$$k = 2\pi p/N \qquad p = 0, 1, 2, \ldots (N-1). \tag{2}$$

The complex eigenvalue problem for the coefficients $c_{\mu lk}$ is formulated in Eq. (3) [25]; the matrix elements of the Fock operator and the eigenvectors and eigenvalues depend parametrically on the wave vector k.

$$\boldsymbol{F}(\boldsymbol{k})\boldsymbol{C}(\boldsymbol{k}) = \boldsymbol{C}(\boldsymbol{k})\boldsymbol{\varepsilon}(\boldsymbol{k}). \tag{3}$$

Eq. (3) is already the ZDO adapted formulation of the self-consistent-field method in the tight-binding approximation.

The k-dependent Fock matrix $F(k)$ and the k-dependent overlap matrix $S(k)$ are defined in Eqs. (4) and (5) by means of exp $(\pm ijk)$ modulated summations over the unit cells in the chain.

$$F(k)=F(0)+\sum_{j\neq 0}[\exp(ijk)F(j)+\exp(-ijk)F(-j)] \tag{4}$$

$$S(k)=S(0)+\sum_{j\neq 0}[\exp(ijk)S(j)+\exp(-ijk)S(-j)]. \tag{5}$$

The first elements on the right sides of Eqs. (4) and (5) are the Fockian and the overlap matrix at the origin while the summation over j spans the neighbouring elementary cells.

The complex Hermitian matrix $F(k)$ can be decomposed into a real (cos) and into an imaginary (sin) part by means of Euler's relation.

$$F(k)={}^{R}F(k)+(i\,{}^{I}F(k)) \tag{6}$$

$${}^{R}F(k)=F(0)+\sum_{j\neq 0}[F(j)+F(-j)]\cos(jk) \tag{7}$$

$${}^{I}F(k)=\sum_{j\neq 0}[F(j)-F(-j)]\sin(jk). \tag{8}$$

The Fock operator $F(k)$ is decomposed into the one-electron core operator $H(k)$ and into the two-electron operator $G(k)$ in order to come to a clear representation for the tight-binding matrix elements in the CNDO/INDO approximation.

$$F(k)=H(k)+G(k) \tag{9}$$

$$H(k)=H(0)+\sum_{j\neq 0}[\exp(ijk)H(j)+\exp(-ijk)H(-j)] \tag{10}$$

$$G(k)=G(0)+\sum_{j\neq 0}[\exp(ijk)G(j)+\exp(-ijk)G(-j)]. \tag{11}$$

The detailed formulas defined below differ from the definition given in Eqs. (10) and (11). We have rearranged the matrix elements in a way that only integrals with the coordinates from the reference cell (coordinates from the basis functions and from the Hamiltonian) are collected in $H(0)$ and $G(0)$; all contributions with coordinates from neighbouring cells are summarized in $H(j)$ and $G(j)$.

The diagonal and off-diagonal terms of $H(0)$ are respectively defined in Eqs. (12) and (13).

$$H(0)_{\mu\mu}=U^{A_0A_0}_{\mu_0\mu_0}+\sum_{B\neq A}V^{A_0B_0}_{\mu_0B_0} \tag{12}$$

$$H(0)_{\mu\nu}=H^{A_0B_0}_{\mu_0\nu_0}. \tag{13}$$

$U^{A_0A_0}_{\mu_0\mu_0}$ is the atomic core operator, Eq. (14), and $V^{A_0B_0}_{\mu_0B_0}$ the electron-core interaction between the μth AO at center A and the atomic core of atom B (A and B belong to the elementary cell at the origin).

$$U^{A_0A_0}_{\mu_0\mu_0} = (\mu^{A_0}_0|-\tfrac{1}{2}\nabla^2 - V_{A_0}|\mu^{A_0}_0) \tag{14}$$

$$V^{A_0B_0}_{\mu_0B_0} = (\mu^{A_0}_0|V_{B_0}|\mu^{A_0}_0). \tag{15}$$

The magnitude of the atomic core integrals of Eq. (14) differs in the CNDO and INDO approximation. The corresponding values which are based on spectroscopic data [41] are summarized in Ref. [17].

$H^{A_0B_0}_{\mu_0\nu_0}$ is the resonance integral between AO μ at center A and AO ν at B in the 0th cell. We have factorized the resonance integral into the following form:

$$H^{A_0B_0}_{\mu_0\nu_0} = (\mu^{A_0}_0|-\tfrac{1}{2}\nabla^2 - V_{A_0} - V_{B_0}|\nu^{B_0}_0) = A^{A_0B_0}_{\mu_0\nu_0} \cdot I^{A_0B_0}_{\mu_0\nu_0} \cdot M^{A_0B_0}_{\mu_0\nu_0}. \tag{16}$$

$A^{A_0B_0}_{\mu_0\nu_0}$ is a function of the AO's μ and ν, and contains valence state ionization potentials. $I^{A_0B_0}_{\mu_0\nu_0}$ is an interference term according to the suggestions of Ruedenberg and Kutzelnigg [42], and $M^{A_0B_0}_{\mu_0\nu_0}$ is a flexible function that has been designed for the simulation of *ab initio* results. These three quantities are discussed in detail in Ref. [17].

Different expressions for the CNDO and INDO variant are encountered in the two-electron elements $G(0)$. The CNDO formulas are displayed in Eqs. (17) and (18). Off-diagonal elements for AO's at one center and two-center terms have the same structure in the CNDO framework. In the INDO approximation different formulas are derived for off-diagonal elements where both AO's are localized at a common center, Eq. (20), and where μ and ν belong to two atoms, Eq. (21).

$$G(0)^{\text{CNDO}}_{\mu\mu} = \sum_{\lambda_0} P_{\lambda\lambda}(\mu_0\mu_0|\lambda_0\lambda_0) - (1/2)P_{\mu\mu}(\mu_0\mu_0|\mu_0\mu_0) \tag{17}$$

$$G(0)^{\text{CNDO}}_{\mu\nu} = -(1/2)P_{\mu\nu}(\mu_0\mu_0|\nu_0\nu_0) \tag{18}$$

$$\begin{aligned} G(0)^{\text{INDO}}_{\mu\mu} = {} & \sum_{\lambda_0 \in A_0} P_{\lambda\lambda}[(\mu_0\mu_0|\lambda_0\lambda_0) - (1/2)(\mu_0\lambda_0|\mu_0\lambda_0)] \\ & + \sum_{\substack{\sigma_0 \in B_0 \\ B_0 \neq A_0}} P_{\sigma\sigma}(\mu_0\mu_0|\sigma_0\sigma_0) \end{aligned} \tag{19}$$

$$G(0)^{\text{INDO}}_{\mu\nu} = 2P_{\mu\nu}(\mu_0\nu_0|\mu_0\nu_0) - (1/2)P_{\mu\nu}(\mu_0\mu_0|\nu_0\nu_0) - (1/2)P_{\mu\nu}(\mu_0\nu_0|\mu_0\nu_0) \tag{20}$$

$\mu|, \nu \in A_0$

$$G(0)^{\text{INDO}}_{\mu\nu} = -(1/2)P_{\mu\nu}(\mu_0\mu_0|\nu_0\nu_0). \tag{21}$$

$\mu \in A_0 \qquad \nu \in B_0.$

The general two-electron integral $(\mu_0\mu_0|\nu_j\nu_j)$ is defined in Eq. (22) in terms of AO basis functions localized at atom A of the 0th cell and atom B of the jth cell ($j = 0$ in Eqs. (17)–(21)).

$$(\mu_0\mu_0|\nu_j\nu_j) = \left\langle \mu_0^{A_0}(1)\mu_0^{A_0}(1) \left| \frac{1}{r_{12}} \right| \nu_j^{B_j}(2)\nu_j^{B_j}(2) \right\rangle = \gamma_{\mu_0\nu_j}^{A_0B_j} \tag{22}$$

The diagonal one-center Coulomb integrals in the CNDO approximation are given by means of a scaled monopole term $F_0^{\mu\mu}$ calculated for AO's of s symmetry with Burns' exponents [43] that correspond to the actual AO; the scaling factors f for the various atomic species are summarized in Table 2 of Ref. [17].

$$\text{CNDO} \quad (\mu_0\mu_0|\mu_0\mu_0) = f \cdot \left\langle s_\mu(1)s_\mu(1) \left| \frac{1}{r_{12}} \right| s_\mu(2)s_\mu(2) \right\rangle = F_0^{\mu\mu} \tag{23}$$

$$(s_0s_0|s_0s_0) = F_0^{ss} \tag{24}$$

$$(p_0p_0|p_0p_0) = F_0^{pp} \tag{25}$$

$$(d_0d_0|d_0d_0) = F_0^{dd}. \tag{26}$$

The CNDO off-diagonal elements in the one-center limit are defined in Eqs. (27)–(29) and are the result of the CNDO invariance criterion.

$$\text{CNDO} \quad (s_0s_0|p_0p_0) = (1/2)(F_0^{ss} + F_0^{pp}) \qquad s, p \in A_0 \tag{27}$$

$$(s_0s_0|d_0d_0) = (1/2)(F_0^{ss} + F_0^{dd}) \qquad s, d \in A_0 \tag{28}$$

$$(p_0p_0|d_0d_0) = (1/2)(F_0^{pp} + F_0^{dd}) \qquad p, d \in A_0. \tag{29}$$

The one-center integrals in the INDO approximation are given by multipole expansions constructed by means of theoretically calculated monopole terms which are multiplied by a scale factor and by rotationally invariant linear combinations [44] of Slater–Condon parameters [45] for the higher multipole contributions to the Laplace Neumann expansion. The one-center Coulomb elements are displayed in Eqs. (30)–(37), and the exchange parameters are given in Eqs. (38)–(42). Each primed basis function in the various formulas symbolizes the component of an AO pair with the same magnetic quantum number as the unprimed AO but with a different z component (m_z).

$$\text{INDO} \quad (s_0s_0|s_0s_0) = F_0^{ss} \tag{30}$$

$$(p_0p_0|p_0p_0) = F_0^{pp} + 4F_2^{pp} \tag{31}$$

$$(p_0p_0|p_0'p_0') = F_0^{pp} - 2F_2^{pp} \tag{32}$$

$$(d_0d_0|d_0d_0) = F_0^{dd} + 4F_2^{dd} + 36F_4^{dd} \tag{33}$$

$$(d_0d_0|d_0'd_0') = F_0^{dd} - F_2^{dd} - 9F_4^{dd} \tag{34}$$

$$(s_0s_0|p_0p_0) = F_0^{sp} \tag{35}$$

$$(s_0s_0|d_0d_0) = F_0^{sd} \tag{36}$$

$$(p_0p_0|d_0d_0) = F_0^{pd} \tag{37}$$

$$(s_0p_0|s_0p_0) = G_1^{sp} \tag{38}$$

$$(s_0d_0|s_0d_0) = G_2^{sd} \tag{39}$$

$$(p_0p_0'|p_0p_0') = 3F_2^{pp} \tag{40}$$

$$(p_0d_0|p_0d_0) = 2G_1^{pd} + 21G_3^{pd} \tag{41}$$

$$(d_0d_0'|d_0d_0') = 2.5F_2^{dd} + 22.5F_4^{dd}. \tag{42}$$

The necessary multipole components (F_2^{pp}, F_2^{dd}, F_4^{dd}, G_1^{sp}, G_2^{sd}, G_1^{pd}, G_3^{pd}) are summarized in Ref. [17].

All two-center Coulomb integrals are calculated by means of the empirical Dewar–Sabelli–Ohno–Klopman (DSOK) relation [46] (43) where two-center quantities are related to diagonal atomic Coulomb elements. The DSOK expression for the interaction between the μth AO at center A in the 0th cell and AOν at atom B in the jth cell reads:

$$\begin{aligned}\gamma_{\mu_0\nu_j}^{A_0B_j} &= \langle \mu_0^{A_0}(1)\mu_0^{A_0}(1)|\frac{1}{r_{12}}|\nu_j^{B_j}(2)\nu_j^{B_j}(2)\rangle \\ &= 1|\sqrt{R_{A_0B_j}^2 + 0.25(1|(\mu_0\mu_0|\mu_0\mu_0) + 1|(\nu_0\nu_0|\nu_0\nu_0))^2}.\end{aligned} \tag{43}$$

The elements $P_{\mu\mu}$ and $P_{\mu\nu}$ of the bond order matrices in Eqs. (17)–(21) will be defined below.

The intercell elements $H(j)$ and $G(j)$ are identical for both (CNDO/INDO) ZDO variants and are shown in Eqs. (44)–(49).

$${}^RH(j)_{\mu\mu} = V_{\mu_0B_j}^{A_0B_j} + V_{\mu_jB_0}^{A_jB_0} + 2\cos(kj)H_{\mu_0\mu_j}^{A_0A_j} \tag{44}$$

$${}^RH(j)_{\mu\nu} = \cos(kj)(H_{\mu_0\nu_j}^{A_0B_j} + H_{\mu_j\nu_0}^{A_jB_0}) \tag{45}$$

$${}^IH(j)_{\mu\nu} = \sin(kj)(H_{\mu_0\nu_j}^{A_0B_j} - H_{\mu_j\nu_0}^{A_jB_0}) \tag{46}$$

$${}^RG(j)_{\mu\mu} = P_{\mu\mu}\left[\sum_{\lambda_j}(\gamma_{\mu_0\lambda_j}^{A_0B_j} + \gamma_{\mu_j\lambda_0}^{A_jB_0})\right] - \cos(kj)q_{\mu\mu}^{+}\gamma_{\mu_0\mu_j}^{A_0A_j} \tag{47}$$

$${}^RG(j)_{\mu\nu} = -(1/2)\cos(kj)(q_{\nu\mu}^{+}\gamma_{\mu_0\nu_j}^{A_0B_j} + q_{\nu\mu}^{+}\gamma_{\mu_j\nu_0}^{A_jB_0}) \tag{48}$$

$${}^IG(j)_{\mu\nu} = -(1/2)\sin(kj)(q_{\nu\mu}^{-}\gamma_{\mu_0\nu_j}^{A_0B_j} - q_{\nu\mu}^{-}\gamma_{\mu_j\nu_0}^{A_jB_0}). \tag{49}$$

The physical meaning of the various integrals on the right sides of Eqs. (44–49) can be easily gathered from the intrasegment expressions. The intercell elements have been derived with the aid of the relations (50)–(52) which follow directly from the translational symmetry of the 1D chain.

$$H_{\mu_0B_{-j}}^{A_0B_{-j}} = H_{\mu_j\nu_0}^{A_jB_0} \tag{50}$$

$$V_{\mu_0B_{-j}}^{A_0B_{-j}} = V_{\mu_jB_0}^{A_jB_0} \tag{51}$$

$$\gamma_{\mu_0\nu_{-j}}^{A_0B_{-j}} = \gamma_{\mu_j\nu_0}^{A_jB_0} \tag{52}$$

The intrafragment charge density bond order matrix $P_{\mu\nu}$ is defined in Eq. (53); the bond orders $q_{\mu\nu}^{\pm}$ for AO's μ and ν that are j unit cells apart are given in Eq. (54).

$$P_{\mu\nu} = \frac{2}{N}\int_0^{2\pi} P_{\mu\nu}(k)\,dk = \frac{2}{N}\int_0^{2\pi}\left[\sum_{l=1}^{\mathrm{occ}} (c^*_{\mu lk}c_{\nu lk})\right] dk$$

$$= \frac{2}{N}\int_0^{2\pi}\left[\sum_{l=1}^{\mathrm{occ}} ({}^Rc_{\mu lk}{}^Rc_{\nu lk} + {}^Ic_{\mu lk}{}^Ic_{\nu lk})\right] dk \tag{53}$$

$$q^{\pm}_{\mu\nu} = \frac{2}{N}\int_0^{2\pi}\left[\exp(\pm ijk)\left(\sum_{l=1}^{\mathrm{occ}} c^*_{\mu lk}c_{\nu lk}\right)\right] dk$$

$$= \frac{4}{N}\int_0^{\pi} \mathrm{Re}\left[\exp(\pm ijk)\left(\sum_{l=1}^{\mathrm{occ}} c^*_{\mu lk}c_{\nu lk}\right)\right] dk \tag{54}$$

$${}^*c_{\mu lk} = c_{\mu l(2\pi - k)}. \tag{55}$$

The coupled complex Hermitian eigenvalue problems, Eq. (3), can be either solved directly by standard routines [47], or alternatively the Fockian can be rearranged into the real form Eq. (56).

$$\begin{pmatrix} {}^R\boldsymbol{F}(\boldsymbol{k}) & -{}^I\boldsymbol{F}(\boldsymbol{k}) \\ {}^I\boldsymbol{F}(\boldsymbol{k}) & {}^R\boldsymbol{F}(\boldsymbol{k}) \end{pmatrix}\begin{pmatrix} {}^R\boldsymbol{C}(\boldsymbol{k}) \\ {}^I\boldsymbol{C}(\boldsymbol{k}) \end{pmatrix} = \begin{pmatrix} {}^R\boldsymbol{C}(\boldsymbol{k}) \\ {}^I\boldsymbol{C}(\boldsymbol{k}) \end{pmatrix}\boldsymbol{\varepsilon}(\boldsymbol{k}). \tag{56}$$

The eigenvalues of Eq. (56) of course are doubly degenerate. There are two important motives to avoid the diagonalization via the real problem (56). SCF iterations based on Eq. (56) need in any case an enhanced storage in the computer, a limiting factor that is of crucial importance in the case of large unit cell dimensions (e.g. large number of AO's). The second, even more restrictive condition lies in the degeneracy of the eigenvalues in Eq. (56). The formation of symmetry adapted Bloch sums is prevented in the case of $1D$ chains of spatial point groups $\{R|0\}$ and space groups $\{R|j\}$ with degenerate irreducible representations due to the artificial degeneracies in Eq. (56). For instance the symmetry of the Bloch sums is violated during the SCF iterations. Therefore we have solved Eq. (3) directly for the calculation of the crystal orbitals.

The convergence of the SCF iteration is in any case a serious problem in calculations on transition metal species [48]. Therefore it is necessary to allocate a set or various reliable sets of occupied bands after an one-electron calculation of the EH type. The trial Bloch sums are extremely illconditioned if the core operator of the present CNDO/INDO model is employed as zeroth order approximation. Matrix elements of a suitable one-electron Hamiltonian (EH) used in the first step are summarized below.

$$H(0)^{\mathrm{EH}}_{\mu\mu} = -I_{\mu\mu} \tag{57}$$

$$H(0)^{\mathrm{EH}}_{\mu\nu} = H^{A_0B_0}_{\mu_0\nu_0} \tag{58}$$

$${}^RH(j)^{\mathrm{EH}}_{\mu\mu} = 2\cos(kj)H^{A_0A_j}_{\mu_0\mu_j}. \tag{59}$$

$I_{\mu\mu}$ is the valence state ionization potential for an electron in the μth AO [17]. The remaining matrix elements (${}^RH(j)^{\mathrm{EH}}_{\mu\nu}$ and ${}^IH(j)^{\mathrm{EH}}_{\mu\nu}$) correspond to Eqs. (45) and (46). The bond order matrices of the $(n+1)$th iteration are calculated by means of an accelerated Hartree damping [49].

$$P_{\mu\nu,(n+1)}=(1-c(n)P_{\mu\nu,(n)}+c(n)P_{\mu\nu,(n-1)} \qquad 0\leq c(n)\leq 1. \tag{60}$$

A large number of calculations has shown that $c(1)=0.7$ is a suitable choice for the first diagonalization of the complete Fock operator; in the subsequent SCF steps $c(n)$ is always reduced by 0.1. The intercell bond order matrices are damped in the same way.

The total energy of the polymer is defined in Eqs. (61), (62) (electronic energy) and (63) (core-core repulsion).

$$E_{\text{tot}}=E_{\text{el}}+E_{\text{core}} \tag{61}$$

$$E_{\text{el}}=E_{\text{el}}(0)+\sum_{j\neq 0}[E_{\text{el}}(j)+E_{\text{el}}(-j)] \tag{62}$$

$$E_{\text{core}}=E_{\text{core}}(0)+\sum_{j\neq 0}E_{\text{core}}(j) \tag{63}$$

$$E_{\text{core}}(j)=\sum_{A_0}\sum_{B_j}E_{\text{core},A_0B_j} \tag{64}$$

$$E_{\text{core},A_0B_j}=z_Az_B(\mu^{A_0}\mu^{A_0}|\nu^{B_j}\nu^{B_j})+f_{\text{rep}}(R_{A_0B_j}). \tag{65}$$

Z_A and Z_B in the formula for the core-core repulsion represent the atomic core charges. The proper choices for the AO basis functions at centers A and B are formulated in Eqs. (55)–(58) of Ref. [17], and $f_{\text{rep}}(R_{A_0B_0})$ is defined in Eq. (59) of Ref. [17]. The electronic contributions of E_{tot} read:

$$E_{\text{el}}(0)=(1/2)\sum_{\mu_0}\sum_{\nu_0}P_{\mu\nu}[H(0)_{\mu\nu}+F(0)_{\mu\nu}] \tag{66}$$

$$E_{\text{el}}(j)=(1/2)\sum_{\mu}\sum_{\nu}q^{+}_{\mu\nu}[H(j)_{\mu\nu}+F(j)_{\mu\nu}]. \tag{67}$$

In order to understand the quantum chemical origin for the formation of 1D chains, the strength of intracell and intercell coupling, and the charge drifts in the system, we want to dissect the total energy into one-center contributions, two-center fragments of the intrasegment type, and two-center elements between neighbouring unit cells. The following formulas are an extension of the work of Pople and Santry [50] as well as of Fischer and Kollmar [51] on molecular CNDO Hamiltonians, of Imamura and Fujita on a CNDO/2 tight-binding approximation [52] and of Dewar and Lo [53] on the INDO descendant MINDO/2 (molecular fragmentation).

The total energy of the polymer is decomposed into the partial summations of Eq. (68).

$$E_{\text{tot}}=\sum_{A_0}E_{A_0}+\sum_{A_0<B_0}\sum E_{A_0B_0}+\sum_{j\neq 0}\sum_{A_0}\sum_{B_j}E_{A_0B_j}. \tag{68}$$

The one-center energies can be fragmented into core ($E^U_{A_0}$), Coulomb ($E^J_{A_0}$) and exchange ($E^K_{A_0}$) contributions.

$$E_{A_0}=E^U_{A_0}+E^J_{A_0}+E^K_{A_0} \tag{69}$$

$$E^U_{A_0}=\sum_{\mu}^{A_0} P_{\mu\mu}U^{A_0A_0}_{\mu_0\mu_0}. \tag{70}$$

The Coulomb and exchange elements in the CNDO approximation are displayed in Eqs. (71) and (72).

$$\text{CNDO}\quad E^J_{A_0}=(1/2)\sum_{\mu}^{A_0}\sum_{\nu}^{A_0} P_{\mu\mu}P_{\nu\nu}(\mu_0\mu_0|\nu_0\nu_0) \tag{71}$$

$$E^K_{A_0}=-(1/4)\sum_{\mu}^{A_0}\sum_{\nu}^{A_0} P^2_{\mu\nu}(\mu_0\mu_0|\nu_0\nu_0). \tag{72}$$

The corresponding expressions in the INDO framework are given in Eqs. (73) and (74), respectively. The various combinations of one-center charge density bond order elements (P_1-P_{12}) are derived in Eqs. (75)–(86).

$$\begin{aligned}\text{INDO}\quad E^J_{A_0}={}&(1/2)P^2_{ss}(s_0s_0|s_0s_0)+(1/2)P_1(p_0p_0|p_0p_0)\\&+(1/2)P_2(d_0d_0|d_0d_0)\\&+P_3(s_0s_0|p_0p_0)+2P_4(s_0p_0|s_0p_0)\\&+P_5(p_0p_0|p'_0p'_0)+2P_6(p_0p'_0|p_0p'_0)\\&+P_7(s_0s_0|d_0d_0)+2P_8(s_0d_0|s_0d_0)\\&+P_9(p_0p_0|d_0d_0)+2P_{10}(p_0d_0|p_0d_0)\\&+P_{11}(d_0d_0|d'_0d'_0)+2P_{12}(d_0d'_0|d_0d'_0)\end{aligned} \tag{73}$$

$$\begin{aligned}E^K_{A_0}={}&-(1/4)P^2_{ss}(s_0s_0|s_0s_0)-(1/4)P_1(p_0p_0|p_0p_0)\\&-(1/4)P_2(d_0d_0|d_0d_0)\\&-(1/2)P_4(s_0s_0|p_0p_0)-(1/2)(P_3+P_4)(s_0p_0|s_0p_0)\\&-(1/2)P_6(p_0p_0|p'_0p'_0)-(1/2)(P_5+P_6)(p_0p'_0|p_0p'_0)\\&-(1/2)P_8(s_0s_0|d_0d_0)-(1/2)(P_7+P_8)(s_0d_0|s_0d_0)\\&-(1/2)P_{10}(p_0p_0|d_0d_0)-(1/2)(P_9+P_{10})(p_0d_0|p_0d_0)\\&-(1/2)P_{12}(d_0d_0|d'_0d'_0)-(1/2)(P_{11}+P_{12})(d_0d'_0|d_0d'_0)\end{aligned} \tag{74}$$

$$P_1=\sum_{\mu\in p}^{A_0} P^2_{\mu\mu}=P^2_{xx}+P^2_{yy}+P^2_{zz} \tag{75}$$

$$P_2=\sum_{\mu\in d}^{A_0} P^2_{\mu\mu}=P^2_{z^2z^2}+P^2_{xzxz}+P^2_{yzyz}+P^2_{x^2-y^2x^2-y^2}+P^2_{xyxy} \tag{76}$$

$$P_3=P_{ss}\left(\sum_{\mu\in p}^{A_0} P_{\mu\mu}\right) \tag{77}$$

$$P_4=P^2_{sx}+P^2_{sy}+P^2_{sz} \tag{78}$$

$$P_5 = P_{xx}P_{yy} + P_{xx}P_{zz} + P_{yy}P_{zz} \tag{79}$$

$$P_6 = P^2_{xy} + P^2_{xz} + P^2_{yz} \tag{80}$$

$$P_7 = P_{ss}\left(\sum_{\mu \in d}^{A_0} P_{\mu\mu}\right) \tag{81}$$

$$P_8 = \sum_{\mu \in d}^{A_0} P^2_{s\mu} \tag{82}$$

$$P_9 = \sum_{\mu \in p}^{A_0} \sum_{\nu \in d}^{A_0} P_{\mu\mu}P_{\nu\nu} \tag{83}$$

$$P_{10} = \sum_{\mu \in p}^{A_0} \sum_{\nu \in d}^{A_0} P^2_{\mu\nu} \tag{84}$$

$$P_{11} = \sum_{\mu \in d}^{A_0} \sum_{\nu \in d}^{A_0} P_{\mu\mu}P_{\nu\nu} \tag{85}$$

$$P_{12} = \sum_{\mu \in d}^{A_0} \sum_{\nu \in d}^{A_0} P^2_{\mu\nu}. \tag{86}$$

All one-center formulas correspond to an atom with *s*, *p* and *d* orbitals. In the case of the *H* atom only the first element on the right sides of Eqs. (73) and (74) must be taken into account. The elements P_1, P_2, P_4–P_7 contribute to the one-center Coulomb and exchange contributions for an atom with *s* and *p* orbitals.

The two-center intrasegment energies are decomposed into the aforementioned two-electron components ($E^J_{A_0B_0}$: Coulomb, $E^K_{A_0B_0}$: exchange), into a resonance ($E^R_{A_0B_0}$), an electron-core ($E^{EC}_{A_0B_0}$) and a core-core ($E^C_{A_0B_0}$) parameter.

$$E_{A_0B_0} = E^R_{A_0B_0} + E^{EC}_{A_0B_0} + E^J_{A_0B_0} + E^K_{A_0B_0} + E^C_{A_0B_0} \tag{87}$$

$$E^R_{A_0B_0} = 2\sum_{\mu}^{A_0}\sum_{\nu}^{B_0} P_{\mu\nu}H^{A_0B_0}_{\mu_0\nu_0} \tag{88}$$

$$E^{EC}_{A_0B_0} = \sum_{\mu}^{A_0} P_{\mu\mu}V^{A_0B_0}_{\mu_0B_0} + \sum_{\nu}^{B_0} P_{\nu\nu}V^{B_0A_0}_{\nu_0A_0} \tag{89}$$

$$E^J_{A_0B_0} = \sum_{\mu}^{A_0}\sum_{\nu}^{B_0} P_{\mu\mu}P_{\nu\nu}\gamma^{A_0B_0}_{\mu_0\nu_0} \tag{90}$$

$$E^K_{A_0B_0} = -(1/2)\sum_{\mu}^{A_0}\sum_{\nu}^{B_0} P^2_{\mu\nu}\gamma^{A_0B_0}_{\mu_0\nu_0} \tag{91}$$

$$E^C_{A_0B_0} = E_{\text{core},A_0B_0}. \tag{92}$$

The intercell parameters are structurally related to the intracell components.

$$E_{A_0B_j} = E^R_{A_0B_j} + E^{EC}_{A_0B_j} + E^J_{A_0B_j} + E^K_{A_0B_j} + E^C_{A_0B_j} \tag{93}$$

$$E^R_{A_0B_j} = \sum_{\mu}^{A_0}\sum_{\nu}^{B_j} q^+_{\mu\nu}H^{A_0B_j}_{\mu_0\nu_j} \tag{94}$$

$$E^{EC}_{A_0B_j} = \sum_{\mu}^{A_0} P_{\mu\mu} V^{A_0B_j}_{\mu_0B_j} + \sum_{\nu}^{B_0} P_{\nu\nu} V^{B_0A_j}_{\nu_0A_j} \tag{95}$$

$$E^{J}_{A_0B_j} = (1/2) \sum_{\mu}^{A_0} \sum_{\nu}^{B_j} P_{\mu\mu} P_{\nu\nu} (\gamma^{A_0B_j}_{\mu_0\nu_j} + \gamma^{A_jB_0}_{\mu_j\gamma_0}) \tag{96}$$

$$E^{K}_{A_0B_j} = -(1/4) \sum_{\mu}^{A_0} \sum_{\nu}^{B_j} q^{+}_{\mu\nu} q^{+}_{\mu\nu} \gamma^{A_0B_j}_{\mu_0\nu_j} \tag{97}$$

$$E^{C}_{A_0B_j} = E_{\mathrm{core},A_0B_j}. \tag{98}$$

In recent years several theoretical investigations on the electronic structure of long (infinite) polymers have been published where long-range exchange interactions or antiferromagnetic coupling have been suggested [54, 55]. Tight-binding calculations in connection with the aforementioned fragmentation scheme into physically feasible elements should be a suitable tool to quantify the nature of these solid state effects.

The ensemble of two-electron integrals and electron-core elements of the CNDO/INDO Fockian in the tight-binding approximation consists of spherical averages. The integrals are a function of the magnetic quantum number m (s, p, d), but they are independent from the z-component (m_z) of m. This restriction follows from the employed invariance critera of the present ZDO model. The intracell ($H^{A_0B_0}_{\mu_0\nu_0}$) and intercell ($H^{A_0B_0}_{\mu_0\nu_0}$) resonance integrals on the other hand depend on m_z (σ, π and δ overlap). The intracell elements are at first calculated in the diatomic coordinate system where the z-axis corresponds to $m_z = 0$. In a subsequent step these diatomic integrals are rotated into the coordinate system of the unit cell in the origin.

$$H^{A_0B_0}_{\mu_0\nu_0} = \sum_{\alpha_0} \sum_{\beta_0} O_{\alpha_0\mu_0} O_{\beta_0\nu_0} H^{A_0B_0}_{\alpha_0\beta_0}. \tag{99}$$

The same procedure for $H^{A_0B_j}_{\mu_0\nu_j}$ is only valid if the polymer has no combined symmetry operation (e.g. translation along a primitive or a helical axis combined with a rotation around the axis). In this case it is impossible to represent the atoms in the 0'th cell and the atoms in the neighbouring cells ($j \neq 0$) by a common coordinate system because the cyclic boundary conditions would be violated. The frame in the jth cell(s) has to be rotated with the molecules in order to preserve the symmetry of the Bloch sums. The intersegment resonance integrals are therefore determined in three steps. The transformation from the diatomic system into the global (common) coordinate system is displayed in Eq. (100). The deconvolution of the resonance integrals to the j'th cell is symbolized in Eq. (101). Two important examples of the transformation matrices U for an atomic *spd* basis are summarized in the Appendix (primitive translation coupled to a rotation, screw axis combined with a rotation).

$$H^{A_0B_j}_{\mu_0\gamma_j} = \sum_{\alpha_0} \sum_{\gamma_j} O_{\alpha_0\mu_0} O_{\beta_j\gamma_j} H^{A_0B_j}_{\alpha_0\beta_j} \tag{100}$$

$$H^{A_0B_j}_{\mu_0\nu_j} = \sum_{\gamma_j} U_{\gamma_j\nu_j} H^{A_0B_j}_{\mu_0\gamma_j}. \tag{101}$$

3. Comparison with *ab initio* Band Structure Calculations

In the subsequent semiempirical calculations always the INDO version of the ZDO operator has been employed, the density matrices have been calculated at ten points within the first Brillouin zone, and the lattice summations are extended to five neighbours. The geometries have been adopted from the cited *ab initio* studies. We have compared the INDO results with available *ab initio* band structure calculations of high quality in a series of simple model systems.

In Table 1 we have symmarized INDO crystal orbital data on an idealized linear HF chain together with *ab initio* calculations with different basis sets [56]. The *ab initio* bases in Table 1 symbolize uncontracted gaussians (first elements: *F*, latter ones: *H*, see Ref. [56]). It is seen that both the absolute positions of the bands as well as the bandwidths are satisfactorially reproduced by the approximate crystal orbital formalism. The width of the π band is slightly overestimated while the width of the highest σ band is close to the $\Delta\varepsilon_3$ value of the extended basis set (10, 6, 2/6, 1) calculation. The difference in the $\Delta\varepsilon$ values of the INDO and the *ab initio* approaches is large in the case of the inner valence band ε_2. This behaviour is typical for band structure calculations based on ZDO models and has been analyzed in various contributions [27, 30, 57]. The INDO net charges are between the 8, 4/4 populations on one side and the extended basis set results on the other side.

In Table 2 INDO results on all-trans-polyacetylene are compared with two *ab initio* crystal orbital data [58] as well as with an approach based on an one-electron nonempirical effective Hamiltonian (VEH) [57]. Once again a sufficient conformity between the INDO model and the sophisticated band structure approaches is encountered; the width of the σ bands is slightly overestimated.

Table 1. Comparison of the band structure data ($\varepsilon(k)$ at the marginal k-points and net charges) for the linear hydrogen fluoride chain calculated by means of the INDO operator (INDO) and by means of *ab initio* calculations with different degrees of sophistication. All values in a.u. $\Delta\varepsilon$ = bandwidth; q = net charge; a = unit cell dimension. π band = ε_4

	INDO		*ab initio* [56]	
		8, 4/4	9, 5, 1/5, 1	10, 6, 2/6, 1
$\varepsilon_4(0)$	−0.6542	−0.6739	−0.6779	−0.6823
$\varepsilon_4(\pi/a)$	−0.6073	−0.6525	−0.6609	−0.6655
$\Delta\varepsilon_4$	0.0469	0.0214	0.0170	0.0168
$\varepsilon_3(0)$	−0.6586	−0.6816	−0.7332	−0.7432
$\varepsilon_3(\pi/a)$	−0.7670	−0.8840	−0.8655	−0.8663
$\Delta\varepsilon_3$	0.1084	0.2025	0.1323	0.1231
$\varepsilon_2(0)$	−1.7881	−1.6374	−1.6333	−1.6381
$\varepsilon_2(\pi/a)$	−1.5606	−1.5983	−1.6100	−1.6170
$\Delta\varepsilon_2$	0.2275	0.0391	0.0234	0.0211
q_H	0.488	0.435	0.576	0.571

Table 2. Comparison of the band structure data for all-trans-polyacetylene at $k = 0$ and $k = \pi/a$ for calculations with the semiempirical INDO operator (INDO), *ab initio* calculations with the STO-3G basis with fourth neighbour's interactions (STO-3G) and the $8s/4p$ basis with second neighbour's interactions ($8s/4p$) as well as an *ab initio* effective Hamiltonian (VEH). All values in a.u. $\Delta\varepsilon' = \varepsilon(0) - \varepsilon(k/a)$; a unit cell dimension

	INDO			STO-3G [58]			$8s/4p$ [58]			VEH [57]		
Band	$k = 0$	$k = \pi/a$	$\Delta\varepsilon'$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon'$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon'$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon'$
ε_8 (first virtual π band)	0.041	−0.092	0.135	0.463	0.101	0.362	0.232	−0.051	0.283			
$\varepsilon_7(\pi)$	−0.550	−0.276	0.274	−0.480	−0.195	0.285	−0.554	−0.262	0.292	−0.482	−0.243	0.239
ε_6	−0.464	−0.532	0.068	−0.450	−0.577	0.127	−0.542	−0.658	0.116	−0.401	−0.588	0.147
ε_5	−0.516	−0.547	0.031	−0.497	−0.587	0.090	−0.592	−0.664	0.072	−0.479	−0.616	0.137
ε_4	−0.749	−0.940	0.191	−0.759	−0.863	0.104	−0.836	−0.962	0.126	−0.781	−0.876	0.095

Table 3. Comparison of the π band characteristics in all-trans, cis-transoid and trans-cisoid polyacetylene calculated by means of the INDO operator and by means of an *ab initio* effective Hamiltonian (VEH). Unit cell is C_2H_2, i.e. unfolding of the π bands in the latter two polymers is applied. All values in a.u. $\Delta\varepsilon$ = bandwidth; a = unit cell dimension

	INDO			VEH		
Polymer	$k=0$	$k=\pi/a$	$\Delta\varepsilon$	$k=0$	$k=\pi/a$	$\Delta\varepsilon$
all-trans polyacetylene	−0.550	−0.276	0.274	−0.482	−0.243	0.239
cis-transoid polyacetylene	−0.540	−0.333	0.207	−0.482	−0.246	0.236
trans-cisoid polyacetylene	−0.539	−0.329	0.210	−0.482	−0.242	0.240

In Table 3 π band characteristics for all-trans, cis-transoid and trans-cisoid polyacetylene as derived in the INDO framework and in the VEH formalism [57] are summarized. The differences (position and width of the bands) between both models are less than 10%.

Band structure calculations on the acetylenic and butatrienic backbone of polydiacetylene are collected in the Tables 4 and 5. The *ab initio* calculations correspond to the minimal STO-3G basis and to an extended $7s/3p$ approach [59]; in the last columns of the two tables once again VEH data are shown. The absolute positions of the INDO bands are close to the $7s/3p$ results. The width of the valence band $\varepsilon_9(\pi)$ is slightly underestimated in comparison to the *ab initio* data, while $\Delta\varepsilon_7(\pi)$ in the INDO model comes close to the results of the timeconsuming calculations.

In Table 6, the STO-3G, $7s/3p$ and $7s/3p/1d$ calculations on polyyne [60] are compared with the present semiempirical data. The INDO results for the valence band are in almost perfect agreement with the two extended basis set ($7s/3p$, $7s/3p/1d$) calculations. In analogy to the foregoing examples the width of the σ bands is overestimated.

The STO-3G [61] and INDO results on some boron containing polymers are displayed in Table 7. We have compared the calculated band gaps as well as the ionization potentials. It is seen that the theoretically determined ionization energies in both types of band structure calculations are close to each other. The band gaps however differ significantly in both procedures. The INDO differences are smaller than the *ab initio* gaps. It is wellknown that HF *ab initio* band gaps are too large in comparison to experimental values as a result of the neglected correlation contributions [62]. Effective Hamiltonians with dressed two-electron interactions lead to a renormalization of the one-particle spectrum (orbital energies in molecules, band energies in polymers) [63]. The INDO gaps therefore should be a more realistic description of the energetic separation between the top of the valence band and the bottom of the conduction band.

Table 4. Comparison between the band structure data for polydiacetylene (acetylenic backbone) at $k = 0$ and $k = \pi/a$ for calculations based on the semiempirical INDO operator (INDO), *ab initio* calculations with the STO-3G basis with third neighbour's interactions (STO-3G) and the $7s/3p$ basis with first neighbour's interactions ($7s/3p$) as well as an *ab initio* effective Hamiltonian approach (VEH). All values in a.u. $\Delta\varepsilon$ = bandwidth; a unit cell dimension

	INDO			STO-3G [59]			$7s/3p$ [59]			VEH [57]		
Band	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$
$\varepsilon_9\ (\pi)$	−0.374	−0.458	0.084	−0.250	−0.418	0.169	−0.358	−0.532	0.174	−0.266	−0.412	0.146
ε_8	−0.444	−0.417	0.027	−0.382	−0.364	0.018	−0.491	−0.481	0.010	−0.398	−0.369	0.029
$\varepsilon_7\ (\pi)$	−0.578	−0.478	0.100	−0.502	−0.421	0.081	−0.616	−0.549	0.067	−0.510	−0.444	0.066
ε_6	−0.506	−0.508	0.013	−0.519	−0.558	0.038	−0.633	−0.661	0.028	−0.491	−0.558	0.067
ε_5	−0.606	−0.637	0.036	−0.606	−0.657	0.050	−0.746	−0.789	0.043	−0.597	−0.677	0.080
ε_4	−0.825	−0.639	0.186	−0.700	−0.657	0.043	−0.819	−0.797	0.022	−0.721	−0.680	0.041
ε_3	−0.960	−0.817	0.143	−0.864	−0.788	0.076	−1.005	−0.923	0.082	−0.891	−0.810	0.081

Table 5. Comparison of the band structure data for polyacetylene (butatrienic backbone) at $k = 0$ and $k = \pi/a$; see legend Table 4

	INDO			STO-3G [59]			$7s/3p$ [59]			VEH [57]		
Band	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$	$k = 0$	$k = \pi/a$	$\Delta\varepsilon$
$\varepsilon_9(\pi)$	−0.291	−0.440	0.149	−0.167	−0.393	0.226	−0.260	−0.490	0.230	−0.277	−0.404	0.177
ε_8	−0.421	−0.375	0.046	−0.370	−0.322	0.048	−0.452	−0.417	0.035	−0.383	−0.328	−0.055
$\varepsilon_7(\pi)$	−0.586	−0.485	0.101	−0.501	−0.425	0.076	−0.584	−0.506	0.078	−0.514	−0.449	0.065
ε_6	−0.542	−0.532	0.012	−0.536	−0.567	0.031	−0.617	−0.643	0.027	−0.530	−0.585	0.055
ε_5	−0.607	−0.647	0.040	−0.585	−0.648	0.063	−0.705	−0.748	0.043	−0.585	−0.670	0.085
ε_4	−0.805	−0.646	0.159	−0.686	−0.649	0.037	−0.775	−0.759	0.016	−0.717	−0.679	0.038
ε_3	−0.945	−0.818	0.127	−0.900	−0.793	0.107	−1.015	−0.903	0.112	−0.946	−0.827	0.119

Table 6. Comparison of the band structure data for linear polyyne at $k=0$ and $k=\pi/a$ for calculations with the semiempirical INDO operator (INDO) and *ab initio* calculations with different degrees of sophistication (STO-3G with fourth neighour's interaction, $7s/3p$ with fourth neighbour's interaction, $7s/3p/1d$ with second neighbour's interaction) [60]. All values in a.u. $\Delta\varepsilon$ = bandwidth; a unit cell dimension

	INDO			STO-3G			$7s/3p$			$7s/3p/1d$		
Band	$k=0$	$k=\pi/a$	$\Delta\varepsilon$	$k=0$	$k=\pi/a$	$\Delta\varepsilon$	$k=0$	$k=\pi/a$	$\Delta\varepsilon$	$k=0$	$k=\pi/a$	$\Delta\varepsilon$
$\varepsilon_5(\pi)$	−0.622	−0.358	0.264	−0.559	−0.299	0.260	−0.621	−0.348	0.273	−0.661	−0.385	0.276
ε_4	−0.652	−0.947	0.295	−0.705	−0.899	0.194	−0.826	−1.005	0.179	−0.862	−1.055	0.193
ε_3	−1.305	−0.960	0.345	−1.104	−0.989	0.115	−1.212	−1.091	0.121	−1.254	−1.121	0.133

Table 7. Comparison of the band gap and the ionization potential in some boron containing polymers as predicted by the INDO model (INDO) and *ab initio* calculations with the STO-3G basis (STO) [61]

	$(HBBe)_n$		$(HBBH)_n$		$(HBCH_2)_n$		$(HBNH)_n$		$(HBO)_n$	
	INDO	STO	INDO	STO	INDO	STO	INDO	STO	INDO	STO
Band gap (eV)	2.06	5.79	2.23	7.48	9.64	13.57	10.08	11.86	10.91	12.81
Ionization potential (eV)	6.62	7.36	7.25	10.40	9.57	11.88	9.27	10.61	10.24	12.05

4. Conclusion

The band structure formalism in the tight-binding approximation has been implemented into a recently developed CNDO/INDO approach for atoms up to bromine under the inclusion of the 3*d* elements. The semiempirical MO model had been designed to reproduce the computational results of time-consuming *ab initio* calculations. The various parameters of the ZDO Hamiltonian have been optimized on the basis of more than 100 *ab initio* studies on a large variety of molecules (organic compounds, 3*d* complexes). The comparison of the semiempirical band structure data with high quality *ab initio* calculations presented in section 3 has shown that the CNDO/INDO crystal orbital formalism should be a suitable tool for the determination of band structure characteristics of reliable quality.

The SCF crystal orbital model has been developed in order to calculate the band structure of those extended organometallic polymers on the level of the HF approximation that are beyond current computational capacities for *ab initio* studies. The necessary CPU times for the present CNDO/INDO tight-binding approach span a range between 1 h for nickel(II)glyoximate and 3–4 h for metallamacrocycles with the porphyrine ribbon on an IBM 370/168 computer (lattice sums extended to 5–7 neighbours, 10 calculations in the first Brillouin zone of the *k*-space). The band structures of these systems are reported in subsequent publications.

The ZDO approximation allows a straightforward partitioning of the total energy of the polymer into one-center and two-center (intracell and intercell) contributions. This energy partitioning scheme will be used in further studies for the investigation of solid state effects in organometallic chains such as the nature of the *dd* interactions, exchange coupling, antiferromagnetic long-range contributions etc. The implementation of an effective Hamiltonian with dressed two-electron interactions should allow a reliable assessment of band gaps even in the HF framework because correlation effects are partially included in the model operator.

Appendix

The 0 matrices in Eqs. (99) and (100) have been defined in Ref. [24]. For the construction of the U matrix in Eq. (101), it is assumed that the rotated functions (s, p, d) for the atoms in the jth cell $(j \neq 0)$ are described with respect to the space-fixed AO's at the origin. The general strategy for this basis transformation is described in the literature [64]. The matrix elements for a rotation α between two unit cells related by a primitive translation are defined below. The rotational axis is the z-axis. The standard sequence of the AO basis functions is assumed $(s, p_x, p_y, p_z, d_{z^2}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{xy})$.

$U(R_z(\alpha))$:

$(1, 1) = 1$
$(2, 2) = \cos\alpha$
$(2, 3) = \sin\alpha$
$(3, 2) = -\sin\alpha$
$(3, 3) = \cos\alpha$
$(4, 4) = 1$
$(5, 5) = 1$
$(6, 6) = \cos\alpha$
$(6, 7) = \sin\alpha$
$(7, 6) = -\sin\alpha$
$(7, 7) = \cos\alpha$
$(8, 8) = \cos 2\alpha$
$(8, 9) = \sin 2\alpha$
$(9, 8) = -\sin 2\alpha$
$(9, 9) = \cos 2\alpha.$

All other matrix elements of $U(R_z(\alpha))$ are zero.

Two angles are necessary to describe the basis transformation in the case of a helical axis combined with a rotation between the molecules of the various unit cells. Without loss of generality we can select $R_z(\alpha)$ and $R_y(\beta)$. The summarized matrix elements of $U(R_z(\alpha)R_y(\beta))$ are none other than the well-known $F^{(1)}(\phi, \Theta)$ elements of the angular overlap model [65] in a slightly rearranged form.

$U(R_z(\alpha)R_y(\beta))$:

$(1, 1) = 1$
$(2, 2) = \cos\alpha \cos\beta$
$(2, 3) = \sin\alpha$
$(2, 4) = -\cos\alpha \sin\beta$
$(3, 2) = -\sin\alpha \cos\beta$
$(3, 3) = \cos\alpha$
$(3, 4) = \sin\alpha \sin\beta$
$(4, 2) = \sin\beta$
$(4, 4) = \cos\beta$
$(5, 5) = (1/4) + (3/4)\cos 2\beta$

$$(5,6) = (\sqrt{3}/2)\sin 2\beta$$

$$(5,8) = (\sqrt{3}/4) - (\sqrt{3}/4)\cos 2\beta$$

$$(6,5) = -(\sqrt{3}/2)\cos\alpha\sin 2\beta$$

$$(6,6) = \cos\alpha\cos 2\beta$$

$$(6,7) = \sin\alpha\cos\beta$$

$$(6,8) = (1/2)\cos\alpha\sin 2\beta$$

$$(6,9) = \sin\alpha\sin\beta$$

$$(7,5) = (\sqrt{3}/2)\sin\alpha\sin 2\beta$$

$$(7,6) = -\sin\alpha\cos 2\beta$$

$$(7,7) = \cos\alpha\cos\beta$$

$$(7,8) = -(1/2)\sin\alpha\sin 2\beta$$

$$(7,9) = -\cos\alpha\sin\beta$$

$$(8,5) = \cos 2\alpha[(\sqrt{3}/4) - (\sqrt{3}/4)\cos 2\beta]$$

$$(8,6) = -(1/2)\cos 2\alpha\sin 2\beta$$

$$(8,7) = -\sin 2\alpha\sin\beta$$

$$(8,8) = \cos 2\alpha[(3/4) + (1/4)\cos 2\beta]$$

$$(8,9) = \sin 2\alpha\cos\beta$$

$$(9,5) = -\sin 2\alpha[(\sqrt{3}/4) - (\sqrt{3}/4)\cos 2\beta]$$

$$(9,6) = (1/2)\sin 2\alpha\sin 2\beta$$

$$(9,7) = -\cos 2\alpha\sin\beta$$

$$(9,8) = -\sin 2\alpha[(3/4) + (1/4)\cos 2\beta]$$

$$(9,9) = \cos 2\alpha\cos\beta.$$

All other matrix elements are zero.

Both U matrices correspond to an atom with s, p and d orbitals; in the case of a reduced number of AO's only the $1X1$ or $4X4$ subunits have to be considered.

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