

166. Molecular Geometries by the Extended-*Hückel* Molecular Orbital Method III: Band-Structure Calculations

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Geometries of extended structures can be evaluated with the extended-*Hückel* tight-binding method by inclusion of a distance-dependent weighted *Wolfsberg-Helmholz* formula and an approximate two-body electrostatic repulsive-energy term. We explain the theoretical procedure which is shown to be straightforward. Application to (all-*trans*)-polyacetylene yields alternating C,C bond lengths and a bandgap of 1.6 eV at the optimized geometry, in good agreement with the experimental finding.

Introduction. – Extended-*Hückel* band-structure calculations [1] have much contributed to the understanding of solid-state chemistry. The extended-*Hückel* molecular orbital (EHMO) method in its improved ASED (atom superposition and electron delocalization) form has been shown to be a useful tool for combining the information of the EHMO results with good geometry calculation for many organic and inorganic molecules [2]. We now show that the same procedure can be extended to infinite structures, and we apply it to the problem of bond alternation of (all-*trans*)-polyacetylene. Bond alternation of (all-*trans*)-polyacetylene has been subject to discussions since the early LCAO-MO studies of linear polyenes of *Lennard-Jones* [3] and *Coulson* [4]. It is now widely accepted that polyacetylene forms a *Peierls*-distorted ground state. Theoretical reasoning by *Longuet-Higgins* and *Salem* [5], X-ray scattering data [6], nutation NMR spectroscopy [7], and *ab initio* calculations [8] [9] do support bond alternation.

Theory. – Given a set of atomic basis functions χ_i for the unit cell, a set of *Bloch* basis functions $\phi_i(\vec{k})$ is formed by constructing *Bloch* sums over the N cells of the crystal [10]

$$\phi_i(\vec{k}) = N^{-1/2} \sum_l e^{i\vec{k} \cdot \vec{R}_l} \chi_i(\vec{r} - \vec{R}_l) \quad (1)$$

In this formula, \vec{R}_l is a direct space lattice vector, the wave vector \vec{k} ranges through the N values of the first *Brillouin* zone, and the summation runs over all direct lattice vectors. The LCAO crystal orbitals are given as

$$\psi_n(\vec{k}) = \sum_i C_i^n(\vec{k}) \phi_i(\vec{k}) \quad (2)$$

where n is the band index. The coefficients $C_i^n(\vec{k})$ and energies $\varepsilon^n(\vec{k})$ are determined by finding the solutions to the eigenvalue equation

$$[\mathbf{H}(\vec{k}) - E(\vec{k}) \mathbf{S}(\vec{k})] \cdot \mathbf{C}(\vec{k}) = 0 \quad (3)$$

where

$$H_{ii}(\vec{k}) = \langle \phi_i(\vec{k}) | \hat{H} | \phi_i(\vec{k}) \rangle \quad (4)$$

$$S_{ii}(\vec{k}) = \langle \phi_i(\vec{k}) | \phi_i(\vec{k}) \rangle$$

The off diagonal elements $H_{iu} = \langle \chi_i | \hat{H} | \chi_u \rangle$ are evaluated by the distance-dependent weighted *Wolfsberg-Helmholz* formula [2b].

$$H_{iu} = \frac{1}{2} K'_{iu} S_{iu} (H_{ii} + H_{uu}) \quad (5)$$

$$K'_{iu} = 1 + (K - 1) e^{-\delta(R_{iu} - d_0)} \quad \text{with} \quad K = 1 + \kappa + \Delta^2 - \Delta^4 \kappa \quad \text{and} \quad \Delta = \frac{H_{ii} - H_{uu}}{H_{ii} + H_{uu}} \quad (6)$$

κ and δ are positive parameters, d_0 is equal to the sum of the orbital radii, calculated from the *Slater* exponents, and R_{iu} denotes the distance between two atoms. The total electronic energy per unit cell is obtained by summation over all occupied energy levels $\epsilon_n(\vec{k})$ and integration over the first *Brillouin* zone BZ with volume V_{BZ} [1a].

$$E_{\text{EHMO}} = \frac{1}{V_{BZ}} \int_{BZ} 2 \sum_n^{\text{occ}} \epsilon_n(\vec{k}) d^3 \vec{k} \quad (7)$$

The total potential energy E_{tot} is calculated in the same way as for molecules by adding an approximate two-body repulsive electrostatic energy term E_{Rep} to the extended-*Hückel* binding energy ΔE_{EHMO} [2].

$$\Delta E_{\text{EHMO}} = E_{\text{EHMO}} - \sum_s b_s^0 E_s^0 \quad (8)$$

$$E_{\text{tot}}(\mathbf{R}) = \Delta E_{\text{EHMO}}(\mathbf{R}) + E_{\text{Rep}}(\mathbf{R}) \quad (9)$$

$\sum_s b_s^0 E_s^0$ is the sum of atomic valence orbital ionization potentials, each of them times the orbital occupation number b_s^0 of the free atoms and \mathbf{R} is the matrix of the coordinates.

The electrostatic two-body repulsion term $E_{\text{Rep},\alpha,\beta}$ is derived as described in the appendix of [2b]. It takes the following form:

$$E_{\text{Rep}}(\mathbf{R}) = \sum_{\alpha < \beta} \left[\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \frac{1}{2} \left(Z_\alpha \int_0^\infty \frac{\rho_\beta(r)}{|R_{\alpha\beta} - r|} dr + Z_\beta \int_0^\infty \frac{\rho_\alpha(r)}{|R_{\alpha\beta} - r|} dr \right) \right] \quad (10)$$

$$\int_0^\infty \frac{\rho_\alpha(r)}{|R_{\alpha\beta} - r|} dr = \frac{1}{R_{\alpha\beta}} \sum_{nl} b_{\alpha,nl}^0 \left[1 - \frac{e^{-2\zeta_{\alpha,nl} R_{\alpha\beta}}}{2n} \sum_{p=1}^{2n} (2R_{\alpha\beta} \zeta_{\alpha,nl})^{2n-p} \frac{p}{(2n-p)!} \right]$$

with (Z_α, Z_β) being the nuclear charges, $(\zeta_{\alpha,nl}, \zeta_{\beta,nl})$ the *Slater* exponents, $(\rho_\alpha, \rho_\beta)$ the electron densities, $R_{\alpha\beta}$ the distances between atoms α and β , nl the principal and azimuthal quantum numbers, and $b_{\alpha,nl}^0$ the occupation numbers of the free atoms. The indices α and β run over all atoms in the unit cell and the M nearest next neighbour cells.

We now calculate the matrix elements $H_{iu}(\vec{k})$. Given the *Bloch* sum $S_{iu}(\vec{k})$ of the overlap integrals [10b]

$$S_{iu}(\vec{k}) = S_{iu}^{(0,0)} + \sum_{m=1}^M \cos(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} + S_{iu}^{(m,0)}) + i \sum_{m=1}^M \sin(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} - S_{iu}^{(m,0)}) \quad (11)$$

the implementation of the distance-dependent weighted *Wolfsberg-Helmholz* approximation into the *Bloch* hamiltonian $H(\vec{k})$ yields for its diagonal elements $H_{ii}(\vec{k})$ and its off-diagonal elements $H_{iu}(\vec{k})$

$$H_{ii}(\vec{k}) = H_{ii}^{(0,0)} S_{ii}(\vec{k}) + 2H_{ii}^{(0,0)}(K-1) \sum_{m=1}^M \cos(m\vec{k} \cdot \vec{R}) S_{ii}^{(0,m)} e^{-\delta(R_{ii}^{(0,m)} - d_0)} \quad (12)$$

$$H_{iu}(\vec{k}) = 1/2 (H_{ii}^{(0,0)} + H_{uu}^{(0,0)}) [S_{iu}(\vec{k}) + (K-1) S'_{iu}(\vec{k})] \quad (13)$$

with

$$S'_{iu}(\vec{k}) = S_{iu}^{(0,0)} e^{-\delta(R_{iu}^{(0,0)} - d_0)} + \sum_{m=1}^M \cos(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} e^{-\delta(R_{iu}^{(0,m)} - d_0)} + S_{ui}^{(0,m)} e^{-\delta(R_{ui}^{(0,m)} - d_0)}) \quad (14)$$

$$+ i \sum_{m=1}^M \sin(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} e^{-\delta(R_{iu}^{(0,m)} - d_0)} - S_{ui}^{(0,m)} e^{-\delta(R_{ui}^{(0,m)} - d_0)})$$

The indices $(0, m)$ describe elements between the 0th and the m th unit cell. The gradients $\partial \varepsilon^n(\vec{k}) / \partial \vec{k}$ which are needed for the *Fourier* fitting of the energy bands [11] can be derived as follows:

$$\frac{\partial \varepsilon^n(\vec{k})}{\partial \vec{k}} = C^{rn}(\vec{k}) \left(\frac{\partial \mathbf{H}(\vec{k})}{\partial \vec{k}} - \varepsilon^n(\vec{k}) \frac{\partial \mathbf{S}(\vec{k})}{\partial \vec{k}} \right) C^n(\vec{k}) \quad (15)$$

$$\frac{\partial}{\partial \vec{k}} H_{iu}(\vec{k}) = \frac{1}{2} (H_{ii}^{(0,0)} + H_{uu}^{(0,0)}) \left[\frac{\partial}{\partial \vec{k}} S_{iu}(\vec{k}) + (K-1) \frac{\partial}{\partial \vec{k}} S'_{iu}(\vec{k}) \right] \quad (16)$$

$$\frac{\partial}{\partial \vec{k}} S_{iu}(\vec{k}) = \sum_{m=1}^M -m \sin(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} + S_{ui}^{(0,m)}) + i \sum_{m=1}^M m \cos(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} - S_{ui}^{(0,m)}) \quad (17)$$

$$\frac{\partial}{\partial \vec{k}} S'_{iu}(\vec{k}) = \sum_{m=1}^M -m \sin(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} e^{-\delta(R_{iu}^{(0,m)} - d_0)} + S_{ui}^{(0,m)} e^{-\delta(R_{ui}^{(0,m)} - d_0)}) \quad (18)$$

$$+ i \sum_{m=1}^M m \cos(m\vec{k} \cdot \vec{R}) (S_{iu}^{(0,m)} e^{-\delta(R_{iu}^{(0,m)} - d_0)} - S_{ui}^{(0,m)} e^{-\delta(R_{ui}^{(0,m)} - d_0)})$$

These equations have been implemented into the QCPE571 extended-*Hückel* band-structure program [12].

Bond Alternation in (all-*trans*)-Polyacetylene. – We now explain the calculated energy surfaces as function of the two C–C bond lengths in the unit cell of (all-*trans*)-polyacetylene in *Fig. 1*. The results have been obtained by applying the standard parameters [2d] listed in the *Table*. 101 equidistant k points have been used for the integration in the first *Brillouin* zone. The *Bloch* sum and the two-body repulsion term have been summed up over four nearest next neighbor cells which has been found to be sufficient. The C–C bond lengths have been varied by 0.02 Å steps at fixed C–H bond length and fixed α (C–C–C) angle of 1.08 Å and 120°, respectively. The energy surfaces have been interpolated to a resolution of 0.01 Å by a cubic spline function.

The reason for the *Peierls* distortion which leads to bond alternation, well reflected in both hypersurfaces $\Delta E_{\text{EHMO}}(r_1(\text{C–C}), r_2(\text{C–C}))$ and $E_{\text{tot}}(r_1(\text{C–C}), r_2(\text{C–C}))$, has been discussed in detail recently [1d]. The tendency to bond alternation is reflected by the lower

energies of $\Delta E_{\text{EHMO}}(r_1(\text{C}-\text{C}), r_2(\text{C}-\text{C}))$ along the diagonal from the upper left corner to the lower right corner for the distorted structures. It is, however, largely overestimated resulting in a collapse of always two atoms. Addition of the two-body electrostatic repulsion E_{Rep} remedies this deficiency as illustrated on the right of *Fig. 1*. The minima in the total-energy hypersurface are located at $r(\text{C}-\text{C}) = 1.50 \text{ \AA}$ and $r(\text{C}=\text{C}) = 1.36 \text{ \AA}$. This result has to be compared with the reported experimental values of $r(\text{C}-\text{C}) = 1.44 \text{ \AA}$ and $r(\text{C}=\text{C}) = 1.36 \text{ \AA}$ [7]. If desired, optimized κ, δ parameters can be applied to reproduce the reported experimental value in the same manner as described for molecules [2d].

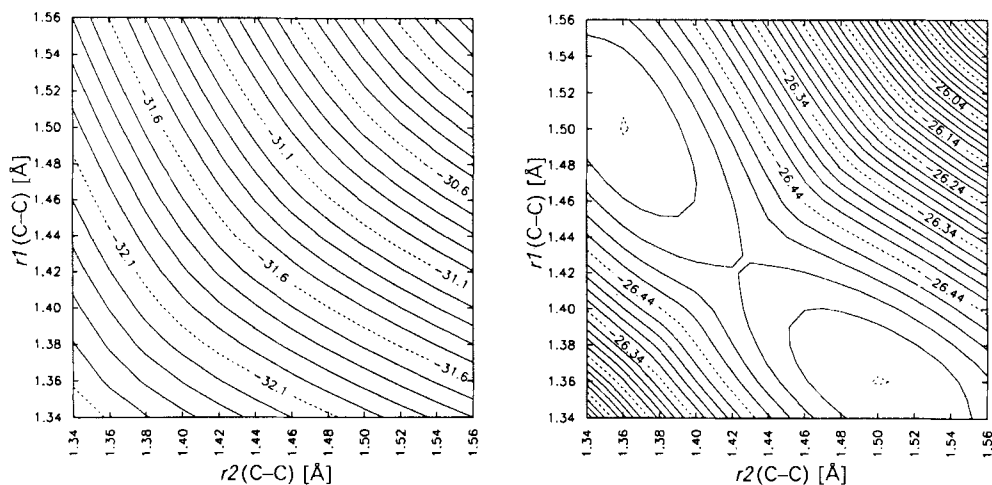


Fig. 1. Energy surfaces [eV] for the C–C bond stretching motion in (all-trans)-polyacetylene. Electronic stabilization energy ΔE_{EHMO} (Eqn. 8; left) and total energy E_{tot} (Eqn. 9; right).

The activation barrier for the single-double bond interconversion is calculated as 0.04 eV. The saddle point of the total-energy surface is located at the mean of the C–C and C=C bond length. *Ab initio* calculations report barriers in the order of 0.06 to 0.09 eV. This small barrier allows fast valence isomerization. In *Fig. 2*, we show that the band structure calculated by us is very similar to the one obtained by other extended-Hückel calculations [1c] [1d]. The two-body electrostatic repulsion does, of course, not affect the band structure at all. The band gap of 1.6 eV calculated at the theoretical geometry is in good agreement with the reported experimental value of 1.4 eV [13] [14]. There is much more information in this type of calculations as has been discussed recently by *Hoffmann*,

Table. Slater Parameters and Coulomb Integrals. $\kappa = 1.0$ and $\delta = 0.35 \text{ \AA}^{-1}$ [2d].

Element	n	ζ_{ns}	H_{ss}/eV	ζ_{np}	H_{pp}/eV
H	1	1.300	-13.6		
C	2	1.71	-21.4	1.625	-11.4

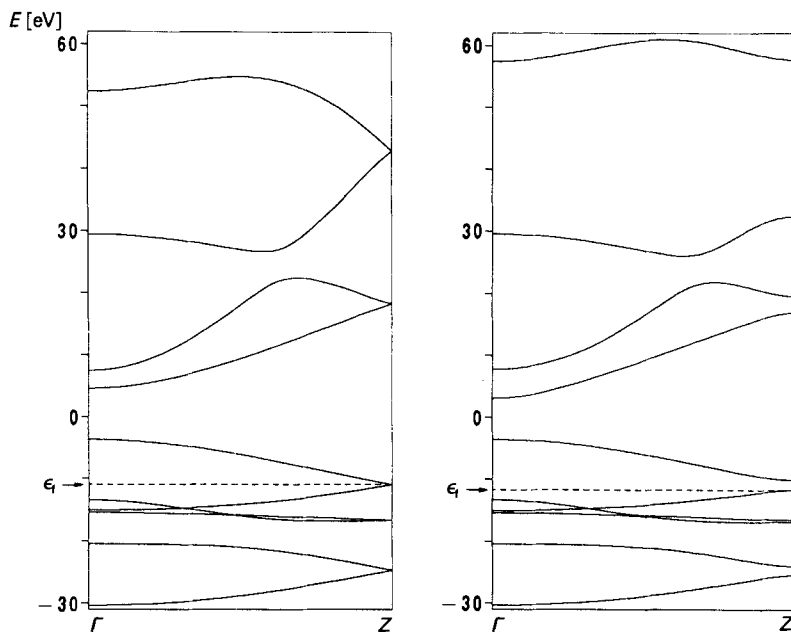


Fig. 2. Band structure of (all-trans)-polyacetylene with bond alternation (right; C=C 1.36 Å, C-C 1.50 Å) as compared to the one for equal C-C bond lengths (left; C-C 1.43 Å)

for a comprehensive report, we refer to [1d]. Inclusion of the distance-dependent *Wolfsberg-Helmholz* formula and the electrostatic two-body repulsive term into the extended-*Hückel* tight-binding band structure method allows to calculate geometries of extended structures without affecting the transparency of the extended-*Hückel* treatment. This offers the possibility of molecular modeling of solid matter, studies of site occupation in zeolites and adsorbate-surface interactions.

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