有限系電子状態からの ab initio エネルギーバンド
の構築と有機導体設計への応用

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Introduction.　In this report an ab initio method to build the band structure of polymers from oligomer elongation calculations is presented. The elongation method mimics the mechanism of polymerization in experiment and yields the electronic structure of very large systems. It gives possibility to treat the molecular systems big enough to be representative of infinite system and reflect the periodic character of the corresponding infinite polymer.

Periodic properties imply energy dependence on wave vector. However band structure of periodic system naturally obtained from calculations with periodic boundary conditions (PBC), is problematic to be obtained from finite cluster calculations.

To derive the band structure of infinite polymer from the quantum chemical computations of a finite oligomer the method based on Hueckel Molecular Orbital relationships between chain and ring system has been developed.

Method. Crystal orbitals (COs) of polymer can be treated as states of ring where degenerated states' energies coincide with energies of the linear chain. Because ring is a periodic system, the eigenstates and eiganvalues of it associated with wave vector. It becomes possible for every state of a linear chain to put into corresponding an appropriate wave vector as well. Thus, k-values for the states of the chain are defined by

$$k = \frac{q}{M+1}\frac{\pi}{a}, q = 1,2,...M, \quad 0 < k < \frac{\pi}{a} \tag{1}$$

Where M is number of repeated units of the oligomer (in the approximation of one atomic orbital (AO) per unit) and a is the translation vector.　To find the correspondence between the states of the oligomer and the ring we can look for the maximum of overlap of the MO with real linear combinations of the COs of degenerated energies.

$$X_q^{m,r} = \sum_j C_{jr}^m \sum_{j'} \sin\left(\frac{\pi j' q}{M+1}\right)\langle \chi_j^r | \chi_{j'}^r \rangle,$$

$$Y_q^{m,r} = \sum_j C_{jr}^m \sum_{j'} \cos\left(\frac{\pi j' q}{M+1}\right)\langle \chi_j^r | \chi_{j'}^r \rangle. \tag{2}$$

Where χ refers to AO with number r, j and j' refer to numbers of repeat units. Expansion coefficients C refer to m^{th} eigenvector of oligomer and q is running from 1 to M. Since the COs are determined only up to a phase factor it is reasonable for every m^{th} MO to look for the maximum with respect to q of the following function.

$$R_q^m = \sum_r \sqrt{\left(X_q^{m,r}\right)^2 + \left(Y_q^{m,r}\right)^2} \tag{3}$$

q value fitted with the maximum of Eq. (3) is accounted for wave vector k, Eq. (1), conformed to the energy state.

The critical problem of finite oligomer approximation is nonequivalence of atom's environment and as a result there are 'end effects'. States of any periodic system must obey Bloch theorem i.e. MOs of the oligomer representing infinite periodic system should be correspondingly delocalized along the chain. However, the spectrum of MOs has some states localized near the chain ends, especially if there are

terminated hydrogen atoms. These states have no correspondence in reciprocal space and they should be discarded before looking for the projection.

Furthermore, if MOs associated with the same band are degenerated then these MOs appear to be localized even without undergoing of end effects. These kinds of MOs also should be neglected when looking for accordance to COs.

The finite chain can not provide states associated with the edges of Brillouin zone (BZ). But still we can get accurate gaps in the Gamma point of BZ by taking into account the fact that the derivatives of energy band with respect to k are zero at the edge of the BZ

In the elongation method MOs of the oligomer are unitary transformed to regionally localized MOs (LMOs): active LMOs (ALMOs), those interact with the elongated units in the next step and frozen (FLMOs), those are far away from the ones so that the interaction between them is negligibly small. Thus, for the every next step the cluster is divided on frozen (FLMOs) and active regions: (ALMOs + elongated units). That is the active region that actually provides necessary information of the system, for every elongation step eigenvalue problem is solved for this reduced region only. The frozen part is disregarded during the calculations step by step.

Thus, canonical MOs of the active region projected on model COs of infinite chain, can provide energy dispersion in reciprocal space.
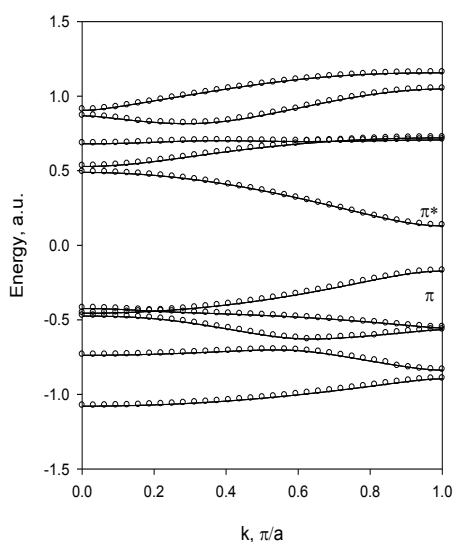
Results. The method was tested on the model oligomers such as water chain and trans-polyacetylene (PA) elongated up to 127 units of length.

The extracted band structures of these oligomers for HF level with sto-3g basis set perfectly coincide with ones calculated under PBC.

For the water chain the fundamental gap of the band structure extracted from elongation calculations of oligomer differs by 0.0006 a.u. from ones calculated with PBC. The total energy per unit is estimated as a difference between the total energy of N+1 and N units' oligomer. The difference between oligomer and polymer calculated values, is only 2.9×10^{-6} a.u.

In spite of the presence of terminated hydrogens the band structure of trans-PA obtained from oligomer calculations is indistinguishable from one computed with periodic band calculations. The fundamental gap is located in the edge of BZ (k=π/a) and differs from calculated under PBC by 0.0009 a.u. The difference for the total energy is 8.7×10^{-7} a.u..

Figure 1. Band structure of trans-polyacetylene, HF/STO-3G. Solid lines refer to calculations with PBC, circles to elongation oligomer calculations.

Conclusion. The developed method gives the energy dispersion of molecular orbitals over Brillion zone and displays the evidence of intrinsic relationship between oligomer and polymer systems. Elongation method is proved to provide correct information not only of total energy, density of states etc. but also of the actual form of MOs those reflect Bloch character of states of periodic system.

It can be a powerful tool to analyze the influence of periodicity on electronic states of long molecular chains. On the other hand without applying PBC it can naturally take into account any nonperiodic effects also.