

有限系から無限系バンド構造構築法と含重原子分子集合系への応用

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Introduction: The standard crystal orbital (CO) method based on periodic boundary conditions (PBC) sometimes can meet difficulties to be applied for systems with big unit cells while the convergence and electron correlation treatment is easier for finite clusters. Furthermore, CO method is not completely adequate with a treatment of any single local perturbations those are straightforward for molecular types of calculations. Anyway, the complexity of calculations with PBC is limited by the number of interacting neighboring unit cells. For example, nontraditional supermolecular interactions between molecules with heavy main-group elements are matter of growing interest. The benzo-1,2,5-telluradiazole dimmers in solid are formed in plane ribbon with length of the Te - N SBI about 2.7Å [1]. However, in terms of reliable atomic orbital basis set the unit cell of such polymer is too big to make effective quantum chemical treatment within PBC.

The method to extract band structure (BS) from the finite cluster calculations of big periodic quasi one dimensional system has been developed [2]. The methodology is accommodated for elongation method (EM) [3] that intended to perform very efficient calculations for the electronic structure of molecular system big enough to be representative of infinite system. This development gives possibilities to get energy dispersion and related properties in good agreement with PBC calculations. The method has been successfully applied for different quasi periodic molecular systems including those containing heavy atoms.

Methodology: The main problem of cluster calculations is edge effects. The spectrum of molecular orbitals (MOs) has some states localized on near the chain ends. However states of periodic system must obey Bloch theorem i.e. MOs of an oligomer represented of infinite periodic system should be correspondingly delocalized along the chain. The localized states have no correspondence in reciprocal space and they should be discarded. The charge associated with the central units of the oligomer can provide a good criterion for localization. If the absolute value is close to zero it means that the MO is localized whether near the one end of the chain or the other.

Delocalized MOs could be projected on reciprocal space based on the assumption that crystal COs of a 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 eigenvalues of it are associated with wave vector. It becomes possible for every state of a linear chain to assign an appropriate wave vector as well. Thus, k -values for the states of the chain are defined by

$$k = \frac{q}{M+1} \frac{\pi}{a}, q=1,2,\dots,M, \quad 0 < k < \frac{\pi}{a} \dots\dots\dots (1)$$

where M is number of repeated units of the oligomer 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 model COs of degenerated energies.

Another problem is the correspondence between the MO and the band index or co-called band crossing problem. While we have finite set of eigenvalues distributed over Brillouin zone the question of connections between them appears. To assign the bands the procedure based on multiplication of CO

constructed from proper MO and respective wave vector in vicinity of possible crossing point have been developed.

Deriving BS from oligomer calculations is sensible only in the case when oligomer is big enough to represent the infinite chain. For this purpose our method have been accommodated to EM that mimics the mechanism of polymerization in experiment. For the every next elongation step the MOs of cluster are divided into frozen and active regions. It is the active region that actually provides necessary information of the system, for every 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. The number of available k-points in this case is limited by the number of units in active region. The other way to get BS from elongation calculations is to perform the back transformation firstly and get canonical MOs of the whole region for the last elongation step. The number of k-points in this case is determined by the total number of units of the oligomer.

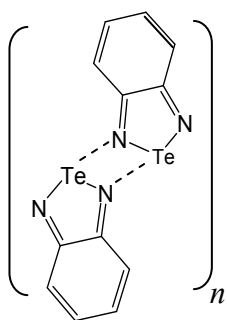


Figure 1. Unit cell of the benzo-2,1,3-telluradiazole ribbon polymer

with PBC calculated gaps. Even elongation active region, if it is long enough, can provide reliable BS. HF quantum chemical calculations of the benzo-1,2,5-telluradiazole oligomers (Fig.1) elongated up to 15 units of length with Effective Core Potential (ECP) and for Te atoms and 6-311G for the others have been performed. The BS and densities of states (LDOS) extracted from the oligomer calculations are presented on Fig. 2. Indirect energy gap is about 8.58 eV. It is formed by π states of the polymer. The energy dispersion of the bands is rather weak unlike the sigma bands formed by nitrogen localized MOs that means the leading role of the orbitals in the polymerization.

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[3] F. L. Gu, A. Imamura, and Y. Aoki, "Elongation Method for Polymers and its Application to Nonlinear Optics", in *Atoms, Molecules and Clusters in Electric Fields: Theoretical Approaches to the Calculation of Electric Polarizabilities*, edited by G. Maroulis, Imperial College Press, Vol. 1, 2006, pp. 97-177

Results: The method has been tested on the series of simple polymers [2] like water chain, trans-polyacetylene, polydiacetylene, polyethylene. It provides perfect coincidence of the band structure with one obtained under PBC for calculations performed both at the Hartree-Fock (HF) and Density Functional (DFT) levels. The difference between values of energy gap obtained with PBC and with 30 units' oligomer conventionally calculated bands for all these systems about only 0.01 eV.

EM also provided accurate computations for the BS. The band gaps derived from the whole set of MOs of 127 units' oligomers obtained with EM are in perfect agreement (about 10^{-3} eV)

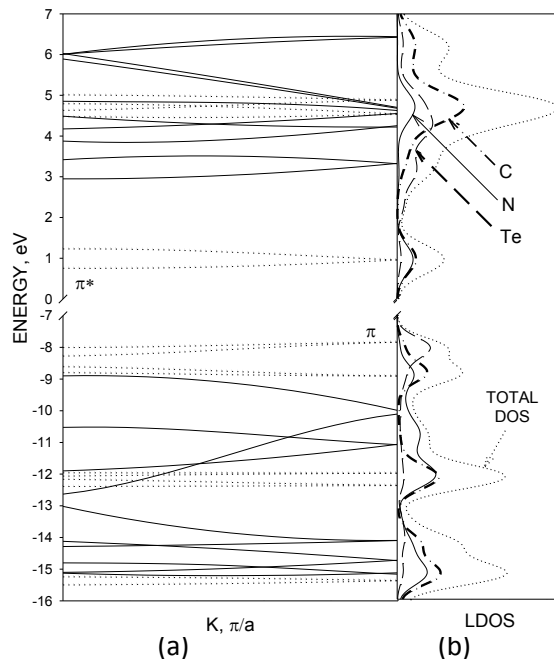


Figure 2. BS(a) and LDOS(b) of benzo-2,1,3-telluradiazole ribbon polymer extracted from 15 units' oligomer calculations at HF/ 6-311G level with ECP for Te