Elongation 法による有限鎖からの超効率的バンド構造抽出と
共役分子ワイヤ系への応用

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Introduction:

Metalloporphyrins (MPs) play an important role in biological systems where they serve as active species with the ability to bind ligands, facilitate light-harvesting photosynthetic reactions, transfer electrons, and catalyze enzymatic reactions. MP oligomers such as zinc(II) complexes are especially versatile, as coordination of pyridine and imidazole ligands to the zinc atom facilitates the self assembly of supramolecular structures. The *meso-meso*-linked porphyrin arrays have now reached a discrete 128-mer with a molecular length of approximately 108 nm.[1] Although the π-electron delocalization is disrupted in *meso-meso*-linked porphyrin because of the orthogonal arrangement of neighboring porphyrin units, electronic structure of excited states exhibits remarkable features for such periodic arrays.[2] As the first step to investigate phenomena connected with elongated MP chains, the ground state properties of periodic MPs chains with Mg, Zn, and Ni metals are focused on in the present study.

However, even for ground state, the *ab initio* study applying periodic boundary conditions (PBC) is rather difficult for systems with big unit cells. Nevertheless, recently developed method allows extracting band structure of polymers from quantum-chemical calculations of arrays with limited number of units[3]. In the present research Hartree-Fock (HF) electronic band structures were built for MPs polymers with Mg, Zn, and Ni metals from GAMMESS calculations of 22 units corresponding oligomers.

Methodology:

Method of building band structure of polymers from finite cluster calculations[3] is based on the projection technique which allows assigning a value for the wave vector k to each molecular orbital (MO) of an oligomer. In this method, delocalized MOs of a chain with M repeated units, written as LCAOs are projected on real linear combinations of model Bloch functions

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

Here C_{jr} are MO's expansion coefficients over a set of atomic orbitals (AO) χ_j^r where r is the AO in the jth unit. Then, maximum of the value R_q

$$R_q = \sum_r \sqrt{(X_q^r)^2 + (Y_q^r)^2} \tag{2}$$

defines integer number q which refers to the wave vector k

$$k = \frac{q}{M+1}\frac{\pi}{a}, q=1,2,...M, \quad 0 < k < \frac{\pi}{a} \tag{3}$$

The proposed methodology also involves the systematic elimination of strongly localized states from wave-vector assignment procedure, which is done by calculating the charge distribution over the chain and treatment of band crossing. After assignment states of energy bands in reciprocal space, the interpolation/extrapolation is used to eliminate weakly localized states and continue the bands across the entire Brillouin zone (BZ). Additionally, the method is accommodated for the elongation method[4] which is developed for accurate calculations of huge molecular systems with time and memory advantages compared to conventional calculations.

Results and discussion:

The investigated structures are schematically illustrated in Figure 1. Herein, the dihedral angle between adjacent porphyrin units is 90º, and the central metals are Mg, Zn, and Ni, respectively. These MP chains were elongated up to 22 MPs rings that correspond to 11 translated unit cells. In our HF calculations, 6-31G basis set is used to describe the C, N, and H atoms. To take into account the relativistic effect, the effective core potential (ECP) with corresponding valence double zeta (VDZ) basis set is employed for the metals.

Band structures and local density of states (LDOSs) of these MP polymers were calculated with our method based on finite oligomer calculations. In Figure 2 three valence and three conductive bands of Zn-P are presented in the first BZ as an example. Points refer to MOs of the MP array. One can see the ambiguity of the k-assignment procedure (double points). The fitted lines on the diagram refer to continues bands. All these bands have a clear p nature and mainly formed by contributions from C and N atoms. The metals give the significant contributions for upper unoccupied bands. The analysis of bands nature is in agreement with the investigations of electronic structure of monomers and dimers.

The behaviors of Mg-P and Ni-P are very similar to that of Zn-P. From Mg-P, Zn-P to Ni-P, the degenerate linear valence band shifts down. The fundamental energy gaps of Mg-P, Zn-P, and Ni-P are 5.76, 5.79, and 5.81 eV, respectively.
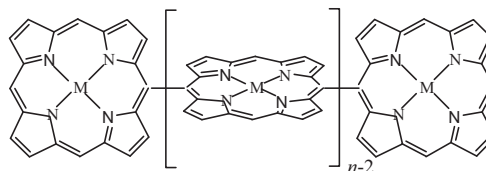

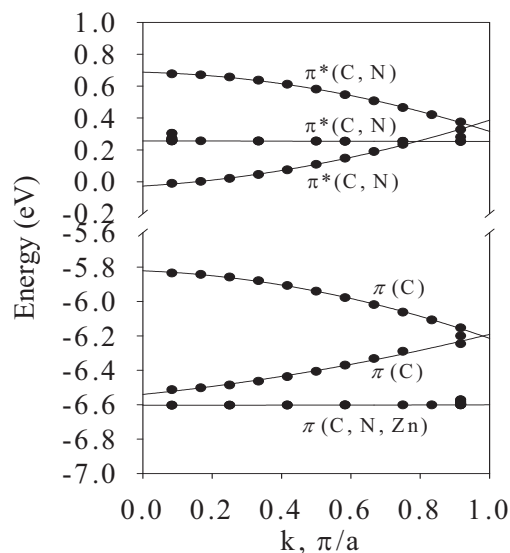Figure 1   Molecular structure for MPs (M=Mg, Zn, and Ni) arrays

Figure 2   Band structure of MP (Zn-P) polymers extracted from elongation HF/6-31 (ECP/DVZ for metals) calculations of 11 unit cells.

References:

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