Predicting the Nodal Properties of Molecular Orbitals by Means of Signed Graphs

Ivan Gutman*, Shyi-Long Lee+,1, Jeng-Horng Sheu+ and Chiuping Li‡

*Institute of Physical Chemistry, Attila Jozsef University, P.O.Box 105, H-6701 Szeged, Hungary; on leave from Faculty of Science, University of Kragujevac, Yugoslavia
+Department of Chemistry, National Chung-Cheng University, Ming-Hsiung, Chiayi, Taiwan
‡Chinese Petroleum Corp. Refining and Manufacturing Research Institute, Chiayi, Taiwan

The method for predicting the signs of the MO coefficients by means of signed graphs, recently proposed by two of the present authors, is further elaborated. Special emphasis is given on the cases when the signed-graph approach fails to reproduce the nodal properties of the canonical MOs. The reasons for the occurrence of such difficulties are analyzed and procedures how to avoid them proposed.

Key Words: Signed graph, Net signs, Nodal properties of molecular orbitals

Introduction

Linear combination of atomic orbitals (LCAO) is one of the powerful tools in the arsenal of a theoretical chemist. The LCAO-MO scheme can, however, become clumsy in rationalizing the experimental observations made on systems containing a large number of atoms. Most of us, nevertheless, believe that the development of the computing speed of modern computer technology will hopefully, eventually overcome this difficulty one day. Before that day arrives, our daily research work is still inspired by intriguing concepts such as the absolute hardness,¹ graph-theoretic indices,²,⁴ net sign,⁵,⁶ and knotting pattern.⁷,⁸ In this article, we would like to report recent development of net sign approach.

Molecular orbitals are conventionally generated by solving Schrödinger equation variationally under certain physically reasonable approximations adopting a certain set of basis functions. Three frequently used computational schemes are approximate EHMO,⁹ semiempirical MOPAC¹⁰ and *ab initio* Gaussian.¹¹ No matter how sophisticated the computational scheme is, the relative sign of the contribution of each atom on the LCAO-MO does not change. This fact is seldom studied systematically until the appearance of the net sign approach in 1987.⁵

The crucial notion in the net-sign approach is the quantity $S_r$, associated with the $i$-th molecular orbitals. It is defined as

$$S_r = \Sigma_{\alpha} \text{sign}(C_r C_{\alpha})$$

where $C_{\alpha}$ is the coefficient of the $i$-th MO corresponding to the atom $r$, and the summation

¹To whom correspondence should be addressed.
goes over all pairs of adjacent atoms. The quantity $S$, is called the net sign of the respective MO. In a series of researches it was established and documented by numerous examples, that $S$, reflects the bonding capacity of the respective MO and that it provides a means to rationalize the scheme of chemical bonding in the respective molecule. The net sign can be understood as a quantification of the nodal properties of MOs.

A problem inherent in eq. (1) is that for the calculation of the net sign of a molecular orbital we need to know the MO itself. A challenging task is, therefore, to deduce the net signs without employing any information about the MOs, i.e., without using eq. (1). A few attempts along this line have been already made. In this paper we will further elaborate an approach recently put forward by two of the present authors. In order to do this we first define a few auxiliary notions and briefly repeat the method of ref. 14.

Let $G$ be a molecular graph possessing $N$ vertices. Denote these vertices by $1, 2, \ldots, N$. Let $s = (s(1), s(2), \ldots, s(N))$ be an ordered $N$-tuple, such that for $x = 1, 2, \ldots, N$, $s(x) \in \{-1, +1\}$. If we associate a sign $s(x)$ to each vertex $x$ of $G$, $x = 1, 2, \ldots, N$, then we obtain a graph with signed vertices, which we denote by $G[s]$. We call such a graph a sign-configuration. Evidently, the labeled graph $G$ possesses $2^N$ distinct sign-configurations.

Let $-s = (-s(1), -s(2), \ldots, -s(N))$. Because the sign-configurations $G[s]$ and $G[-s]$ reflect the same physical situation, we want to design a theory in which only one of the configurations $G[s]$ or $G[-s]$ will occur. This can be done in the following manner. Choose a vertex in the graph $G$ and refer to it as the root of $G$. Let the root vertex be labeled by $r$. Then we will consider only those sign-configurations of $G$ for which $s(r) = +1$.

To each sign-configuration we associate a net sign $\sigma(s)$, defined in analogy to eq. (1) as

$$\sigma(s) = \sum s(x) s(y)$$

in which the summation goes over pairs of adjacent vertices.

We say that the sign-configurations having equal net signs are degenerate. Such sign-configurations form a degenerate class.

The main idea of the work is that the set of all degenerate sign-configurations determines the nodal structure of a canonical MO. This is realized by means of the numbers

$$S(x, \sigma) = \text{sign} \sum s(x)$$

where $s(x)$ is the sign associated with the vertex $x$ in the sign-configuration $G[s]$, and where the summation goes over all members of a degeneracy class (whose net-signs are equal to $\sigma$).

In many cases $S(x, \sigma)$ coincides with the sign of the MO coefficient $C_x$. Furthermore, the net sign of the $i$-th MO, eq. (1), happens often to be equal to $\sigma$.

The readers are reminded that the canonical MOs are just the eigenvectors of the respective molecular graph $G$. The number of (linearly independent) MOs is equal to the number of eigenvalues of $G$ (which, in turn, is equal to $N$). The number of mutually non-degenerate canonical MOs is therefore equal to the number of distinct graph eigenvalues.

The above theoretical concepts are illustrated on the example of the molecular graph $G_6$ of pentadienyl, Figure 1.

Consider first the case when the root of $G_6$ is the vertex 1, $r = 1$. Then the relevant sign-
configurations are 1-16. The configuration 1 has net sign 4. The configurations 2-5 are degenerate, all having net signs 2. The configurations 6-11 as well as 12-15 are also degenerate, having net signs 0 and -2, respectively. Finally the configuration 16 has net sign -4.

Hence there are 5 different s values, which is equal to the number of canonical MOs of pentadienyl. Applying eq. (3) we now immediately obtain:

\[
S(1,4) = +1 \quad S(2,4) = +1 \quad S(3,4) = +1 \quad S(4,4) = +1 \quad S(5,4) = +1 \\
S(1,2) = +1 \quad S(2,2) = +1 \quad S(3,2) = 0 \quad S(4,2) = -1 \quad S(5,2) = -1 \\
S(1,0) = +1 \quad S(2,0) = 0 \quad S(3,0) = -1 \quad S(4,0) = 0 \quad S(5,0) = +1 \\
S(1,-2) = +1 \quad S(2,-2) = -1 \quad S(3,-2) = 0 \quad S(4,-2) = +1 \quad S(5,-2) = -1 \\
S(1,-4) = +1 \quad S(2,-4) = -1 \quad S(3,-4) = +1 \quad S(4,-4) = -1 \quad S(5,-4) = +1
\]

which completely matches the coefficient-sign pattern of the five canonical MOs.\(^{14}\)

Consider next the choice \( r = 2 \). Now the sixteen relevant sign-configurations are 1-4, 6, 7, 9, 12, 17-24. Of them, configuration 1 has \( \sigma = 4 \), configurations 2,3,4 and 17 have \( \sigma = 2 \), configurations 6,7,9 and 18-20 have \( \sigma = 0 \), configurations 12 and 21-23 have \( \sigma = -2 \) and the
configuration 24 has $\sigma = -4$. Using eq. (3) we now calculate:

\[
\begin{align*}
S(1,4) &= +1 \quad S(2,4) = +1 \quad S(3,4) = +1 \quad S(4,4) = +1 \quad S(5,4) = +1 \\
S(1,2) &= +1 \quad S(2,2) = +1 \quad S(3,2) = +1 \quad S(4,2) = +1 \quad S(5,2) = -1 \\
S(1,0) &= 0 \quad S(2,0) = +1 \quad S(3,0) = 0 \quad S(4,0) = 0 \quad S(5,0) = 0 \\
S(1,-2) &= -1 \quad S(2,-2) = +1 \quad S(3,-2) = -1 \quad S(4,-2) = 0 \quad S(5,-2) = +1 \\
S(1,-4) &= -1 \quad S(2,-4) = +1 \quad S(3,-4) = -1 \quad S(4,-4) = +1 \quad S(5,-4) = -1
\end{align*}
\]

Contrary to the previous case, here only the first and last sequence of $S(x,\sigma)$ values coincides with the signs of the coefficients of the (highest and lowest) canonical MOs. The $S(x,2)$-, $S(x,0)$- and $S(x,-2)$- sequences are at variance with the respective MOs.

For the third possible choice of the root vertex of $G_0$, namely $r=3$, the sign-configurations are 1-3, 6, 8, 13, 15, 16-19, 22, 25-28. A reasoning analogous to what is described above leads to:

\[
\begin{align*}
S(1,4) &= +1 \quad S(2,4) = +1 \quad S(3,4) = +1 \quad S(4,4) = +1 \quad S(5,4) = +1 \\
S(1,2) &= 0 \quad S(2,2) = +1 \quad S(3,2) = +1 \quad S(4,2) = +1 \quad S(5,2) = 0 \\
S(1,0) &= -1 \quad S(2,0) = 0 \quad S(3,0) = +1 \quad S(4,0) = 0 \quad S(5,0) = -1 \\
S(1,-2) &= 0 \quad S(2,-2) = -1 \quad S(3,-2) = +1 \quad S(4,-2) = -1 \quad S(5,-2) = 0 \\
S(1,-4) &= +1 \quad S(2,-4) = -1 \quad S(3,-4) = +1 \quad S(4,-4) = -1 \quad S(5,-4) = +1
\end{align*}
\]

This time $S(x,4)$, $S(x,0)$ and $S(x,-4)$ correctly reproduce the nodal structures of the respective MOs, but $S(x,2)$ and $S(x,-2)$ do not.

**Cases When the Signed-Graph Approach Fails**

In the example just considered we encounter some difficulties in the application of the signed-graph approach. In this section we wish to point out a few other cases where the method proposed in ref. 14 does not yield satisfactory results. In the subsequent section we discuss the possible causes of these discrepancies and propose some remedies.

From the above example we see the following.

1. **The choice of the root vertex is essential for the success of the signed-graph approach; the method gives different results for different choices of the root.**

   In the above example the number of degeneracy classes (i.e., the number of distinct $\sigma$-values) coincided with the number of canonical MOs. This, however, needs not always be the case.

2. **The number of degeneracy classes may be smaller or greater than the number of (non-degenerate) canonical MOs.**

   Rule (2) is illustrated by the molecular graph depicted in Figure 2. The system represented by the graph $G_0$ has four mutually non-degenerate canonical MOs (and a total of 5 linearly independent MOs), but only 3 distinct $\sigma$-values. On the other hand, the system $G_1$ has five mutually non-degenerate canonical MOs, six linearly independent MOs, but seven distinct $\sigma$ values.

3. **It may happen that the number of degeneracy classes is equal to the number of canonical MOs, but not to the number of non-degenerate MOs.**
Rule (3) is illustrated by the example of graph $G_3$, depicted in Figure 3.

(4) **The graph whose vertices are signed by $S(x, \sigma)$, eq. (3), needs not have the net sign $\sigma$.**

Rule (4) is illustrated by an example given in Figure 4. Here the entire degeneracy class
of the [4]-radialene graph G₄, with σ = 6, is depicted. When performing the summation (3) over this degeneracy class, a sign-configuration with σ = 8 is obtained.

(5) The sequence S(x, σ) needs not reflect the symmetry of the respective molecular graph.

Examples supporting Rule (5) are found in the preceding section.

Discussion

To our opinion there are two basic reasons causing the difficulties in the previous section and formulated as Rules (1)-(5). First, the MO coefficients may sometimes assume zero value (e.g.; as a consequence of symmetry). To properly emulate this fact one would have to start with sign-configurations in which both +1, -1 and 0 are associated to the vertices. Second, the choice between the sign-configurations G[s] and G[-s] is trivial only is the respective degeneracy class contains a single element. If there are several degenerate sign-configurations, then it is essential to make a justified decision whether to pick G[s] or G[-s]. This delicate selection procedure must not be made “automatically” by choosing a root r and requiring that s(r) = 1 holds for all degenerate sign-configurations.

From the above follows that the difficulties with the signed-graph approach proposed in Ref. 14 can be overcome by introducing two additional requirements:

(a) The starting point in the examination of the nodal structure of MOs should be sign-configurations in which the vertices have signs either +1 or -1 or 0.

(b) A more careful recipe for choosing of the sign-configurations (i.e., deciding whether to employ G[s] or G[-s]) should be elaborated; the choice put forward in Ref. 14, in which one vertex has the same sign in all sign-configurations, has to be abandoned.

With amendments (a) and (b) the signed-graph approach can be made efficient and complete. Work along these lines is in progress.
Acknowledgment

One of the authors (SLL) thanks the National Science Council, Taiwan for financial support.

Received January 6, 1995.
Accepted February 13, 1995.

References

利用符號圖預測分子軌域的節點特質

I. Gutman  李錫隆  許正宏  李秋萍

摘   要

我們對最近發表的符號圖學理論做更深入的探討，尤其是一些符號圖學理論無法再現分子軌域節點特徵的情況及例子，文中也會探討這些例子。文中也會探討這些例外產生的原因並提出避免這些困難的可能性及解決辦法。