

GRAPH THEORY AND THE PPP METHOD

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Abstract

A graph theoretical formulation of the PPP method is presented. A weighted adjacency matrix of the PPP graph is given, wherein the off-diagonal elements are the bond orders. The automorphism group of the PPP graph is defined and shown to be isomorphic with the permutational subgroup of the permutation–inversion group of the molecule. It is demonstrated that the characteristic polynomial of the adjacency matrix of the PPP bond graph is invariant in every SCF iteration. It is shown that the PPP spectra discriminate isospectral graphs.

1. Introduction

It has been over thirty-five years since the Pariser–Parr–Pople method [1,2] has been formulated. Although the relationship between the Hückel theory of conjugated π -electronic systems and chemical graph theory has now been very well established, it seems that the relationship between the PPP method and graph theory has not been explored, possibly due to the numerical complexity of the PPP method introduced by the electron repulsion integrals which are neglected in the Hückel method. Yet there is an underlying graph-theoretical invariance in the PPP method. The author's attention was drawn to this topic as a result of a recent contribution he made to an issue of the International Journal of Quantum Chemistry dedicated to the PPP method [3].

The objective of the present article is to show that there are several possible graph-theoretical representations of the PPP method. It is shown that the characteristic polynomials of PPP bond graphs obtained from the PPP bond orders are invariant to the actual changes in the PPP Hamiltonian matrix itself in each SCF iteration. It is further established that isospectral graphs can be discriminated based on the PPP Hamiltonian. The spectra of the bond matrices are, however, shown to be the same for all conjugated π -electronic graphs with the same number of vertices. Possible topological indices based on the PPP spectra are briefly considered.

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2. Graph-theoretical formulations

2.1. PRELIMINARIES

The Pariser–Parr–Pople Hamiltonian [1,2] matrix element $F_{\mu\nu}$ is given by:

$$F_{\mu\mu} = \alpha_{\mu} + \frac{1}{2} q_{\mu} \gamma_{\mu\mu}, \quad (1)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \quad (\mu \neq \nu), \quad (2)$$

$$q_{\mu} = \sum_i C_{\mu i}^2 N_i, \quad (3)$$

$$P_{\mu\nu} = \sum_i C_{\mu i} C_{\nu i} N_i, \quad (4)$$

where N_i is the occupancy of the i th MO and $C_{\mu i}$ is the μ th coefficient of the i th MO. In the above expressions, $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$ are two-electron repulsion integrals, q_{μ} and $P_{\mu\nu}$ are the charge density on center μ and bond order between centers μ and ν , respectively. The α and β parameters are the well-known Hückel parameters. The γ integrals can be parameterized using a number of methods. One such common parameterization is the Nishimoto–Matanga parameterization.

As is well known, in the PPP method one starts with the Hückel matrix. The eigenvectors of the Hückel matrix are used to construct the charge densities (q_{μ}) and bond orders ($P_{\mu\nu}$). These quantities are then used to construct the matrix elements of the F matrix. The F matrix is then diagonalized to obtain a new set of eigenvectors. This process is repeated until the F matrix elements, eigenvalues and eigenvectors converge. Hence, it is clear that the PPP matrix is a geometry-dependent and parameter-dependent matrix. In each iteration, the PPP F matrix changes since q_{μ} s and $P_{\mu\nu}$ s change. Yet there is an underlying graph-theoretical invariance in the PPP method, as shown here.

There are a number of graph-theoretical representations of the PPP method. An obvious representation could use the PPP Hamiltonian matrix. This would generate a complete weighted graph on n vertices. The edges between centers i and j should be weighted by the matrix element F_{ij} . The diagonal elements could be incorporated as loops.

Since the electron repulsion integrals in the PPP method bring in the difference between ordinary topological matrices and the PPP matrices, a logical graph-theoretical representation of the PPP method would be to use the electron repulsion integrals (γ_{ij}). In fig. 1, we show such a graph for butadiene. Note that all electron repulsion integrals that are equal are given the same symbol.

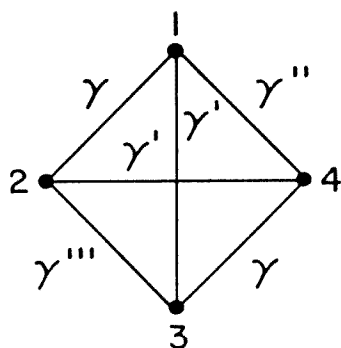


Fig. 1. The PPP graph of butadiene.

2.2. THE AUTOMORPHISM GROUP OF THE PPP GRAPH

The automorphism group of a graph in general is defined [4–7] as a group consisting of permutations of vertices whose permutation matrices P satisfy

$$P^{-1}AP = A,$$

where A is the adjacency matrix of the graph. The topic of symmetry of graphs has received considerable attention for many years [5–8]. This can be extended to the PPP graph itself. The automorphism group of the weighted graph in fig. 1 can easily be seen to be $S_2 = \{(1)(2)(3)(4), (14)(23)\}$. The result of the permutation $(14)(23)$ on the graph in fig. 1 is shown in fig. 2. It is evident that the automorphism group

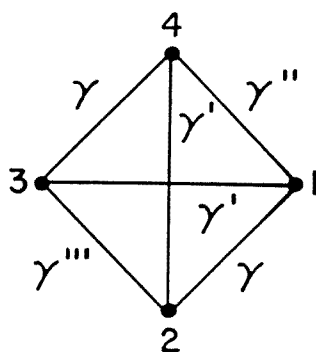


Fig. 2. The effect of a permutation in the automorphism group of the PPP graph.

of the PPP γ graph must contain only those permutations which are present in the permutation–inversion group representation of the molecular symmetry group of

the molecule [9–12]. This follows from the definition of the γ integrals which depend on the interatomic distances between the various centers of the molecule under consideration. Since the interatomic distance matrix is invariant to the PI group of the molecule, the PPP γ matrix is also invariant to the permutations in the PI group since there is a one-to-one correspondence between the PPP γ integral matrix and the interatomic distance matrix.

2.3. THE BOND MATRIX REPRESENTATION OF THE PPP HAMILTONIAN

There is another interesting graph-theoretical representation of the PPP method. Two important quantities, namely, charge densities (q_i) and bond order matrix elements (p_{ij}) emerge from the PPP method. Define a matrix

$$P_{ij} = \begin{cases} 0 & \text{if } i = j, \\ p_{ij} & \text{if } i \neq j, \end{cases}$$

where p_{ij} is the bond-order between centers i and j . Note that the above matrix can be extended to heteronuclear compounds as well as by setting the diagonal elements to $1 - q_i$ for the heteroatoms.

Figure 3 shows the bond matrix graph of butadiene at the first PPP iteration, the second iteration and the final iteration using the Matanga–Nishimoto parameterization with $\alpha = -11.16$ and $\beta = -2.39$ values. All diagonal elements of the P matrix are set to zero for butadiene and hence not shown.

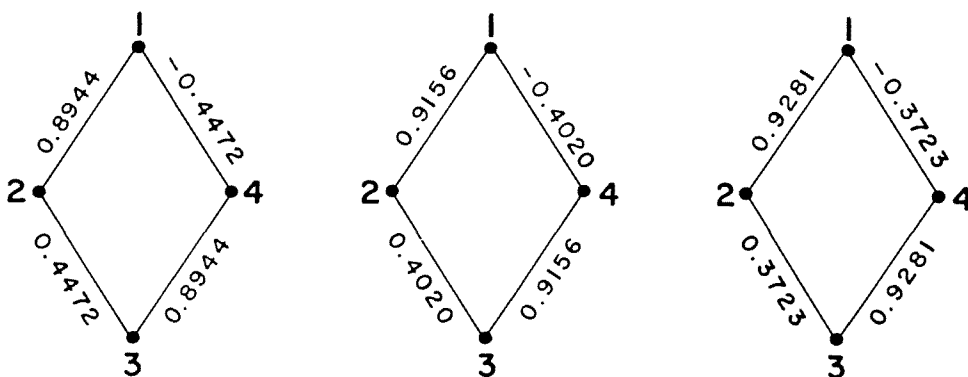


Fig. 3. The PPP bond matrix graph in the first, second and last iterations of the PPP method applied to butadiene.

As seen from fig. 3, the PPP bond matrix graph is a weighted cyclic graph. The weights of edges (1, 2) and (3, 4) are the same due to symmetry, but the weights of (2, 3) and (1, 4) are equal in magnitude but opposite in sign. The PPP

method introduces negative bond orders between non-bonded atoms 1 and 4 to compensate for the delocalization between 2 and 3. This structure is preserved in every iteration, but the actual magnitudes change.

In general, the PPP bond matrix is represented by a complete weighted graph. The edge weights are in general real numbers which numerically change in each step of the PPP method. Hence, it may appear as if this representation is not useful. However, in the next section we show that the characteristic polynomial of the PPP bond matrix is the same in every iteration.

3. Characteristic polynomials of PPP bond matrix graphs

The characteristic polynomial of the bond matrix P is defined as

$$|P - \lambda I|,$$

where P is the bond matrix defined before, and I is the $n \times n$ identity matrix if there are n vertices in the PPP graph. It may be recalled that the ordinary characteristic polynomial of a graph is given by

$$|A - \lambda I|,$$

where A is the adjacency matrix of the graph.

The present author [13–16] has shown that characteristic polynomials of weighted graphs, directed graphs and signed graphs can be obtained easily using computer codes [14] developed based on Frame's method [13]. A computer code was developed to construct the PPP Hamiltonian matrix from the neighborhood table and the coordinates of the atoms in the graph. This was interfaced with the matrix diagonalization subroutines based on the Givens–Householder diagonalization procedure. From the eigenvectors thus obtained, the bond matrix was constructed. This was then fed to the codes developed by the author to compute the characteristic polynomials of weighted graphs. The bond matrices thus constructed were then used to obtain the new PPP Hamiltonian matrix. This process was iterated until convergence is obtained in the PPP Hamiltonian matrix and the PPP bond matrix. Finally, the code computes the characteristic polynomial of the converged PPP bond matrix. The codes thus assembled were tested on many graphs. The results obtained are discussed below.

The ordinary characteristic polynomial of butadiene is given by

$$Ch(A) = \lambda^4 - 3\lambda^2 + 1.$$

The characteristic polynomials of all three graphs in fig. 3 can be easily verified to be

$$Ch(P) = \lambda^4 - 2\lambda^2 + 1 = (\lambda^2 - 1)^2.$$

Similarly, the ordinary characteristic polynomial and the PPP polynomial of octatetraene are given by

$$Ch(A) = \lambda^8 - 7\lambda^6 + 15\lambda^4 + 1,$$

$$Ch(P) = \lambda^8 - 4\lambda^6 + 6\lambda^4 - 4\lambda^2 + 1 = (\lambda^2 - 1)^4.$$

The ordinary and PPP characteristic polynomials of naphthalene are given by

$$Ch(A) = \lambda^{10} - 11\lambda^8 + 41\lambda^6 - 65\lambda^4 + 43\lambda^2 - 9,$$

$$Ch(P) = \lambda^{10} - 5\lambda^8 + 10\lambda^6 - 10\lambda^4 + 5\lambda^2 - 1 = (\lambda^2 - 1)^5.$$

The ordinary and PPP polynomials of benzene are given by

$$Ch(A) = \lambda^6 - 6\lambda^4 + 9\lambda^2 - 4,$$

$$Ch(P) = \lambda^6 - 3\lambda^4 + 3\lambda^2 - 1 = (\lambda^2 - 1)^3.$$

The PPP polynomials of numerous other conjugated molecules were calculated, including graphs containing heteroatoms. The characteristic polynomial of the PPP bond matrix was always found to be

$$Ch(P) = (\lambda^2 - 1)^{n/2},$$

where n is the number of π -electronic orbitals. Thus, it is evident that although the PPP matrix itself changes and is numerically complex in each iteration, the characteristic polynomial of the associated PPP bond matrix is invariant to each SCF iteration.

It is evident from the characteristic polynomial of the PPP (bond matrix) graph that the eigenvalues of the bond matrix are ± 1 . A proof that the eigenvalues of the PPP bond matrix should always be ± 1 can be easily found from the associated eigenvalues of the density matrix. The density matrix (D) of the PPP Hamiltonian can be defined as:

$$D = \begin{cases} q_i & \text{if } i = j, \\ p_{ij} & \text{if } i \neq j. \end{cases}$$

The eigenvalues of the density matrix (also known as the occupancies) are 0 or 2 for closed-shell electronic states. The zero eigenvalues are for unoccupied orbitals, while occupied orbitals have density matrix eigenvalues of 2. Suppose d_i is the i th eigenvalue of the D matrix. If p_i is the i th eigenvalue of the bond matrix, then it can be easily seen that for non-heteronuclear molecules

$$p_i = 1 - d_i.$$

This relation follows from the fact that the diagonal elements q_i are all unities for the D matrix of conjugated hydrocarbons containing no heteroatoms. Thus, the eigenvalues of the P matrix for which diagonal elements are zero are shifted by unity relative to the eigenvalues of the D matrix. Hence, the characteristic polynomial of the P matrix is $(\lambda^2 - 1)^{n/2}$ for an alternant hydrocarbon containing n atoms.

4. Isospectral graphs and the PPP method

There is considerable discussion in the literature on isospectral graphs [17–19]. Two graphs are said to be isospectral if they give rise to the same spectra and characteristic polynomials. It is also well recognized that the presence of isospectral points in the graphs results in special problems in automorphism partitioning of vertices, chemical coding, and canonical labelling of vertices [20–22]. Thus, it would be interesting to see how far the PPP method discriminates isospectral graphs.

Figure 4 shows two isospectral graphs. These two graphs have the same set of Hückel eigenvalues. The PPP method was used to obtain their spectra. The converged orbital energies are shown in table 1 for the two graphs in fig. 4. As seen

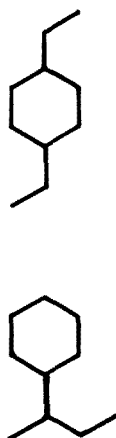


Fig. 4. Two isospectral graphs. Their PPP spectra are shown in table 1.

Table 1
The PPP spectra of the isospectral graphs (fig. 4)

Graph	Eigenvalues
Fig. 4 (I)	-14.0261, -12.4768, -10.7452, -10.5760, -9.2437, -2.5463, -1.2140, -1.0448, 0.6868, 2.2361
Fig. 4 (II)	-14.0061, -12.5646, -10.6244, -10.5654, -9.2973, -2.4926, -1.2246, -1.1656, 0.7746, 2.2162

from table 1, the converged spectra of the two isospectral graphs are sufficiently different to discriminate these graphs. Hence, Heilbronner's objection [23] that two isospectral graphs have sufficiently different photoelectron spectra is a result of the deficiency of the Hückel theory, since it neglects the electron repulsive integrals. However, more realistic PPP spectra of these graphs are sufficiently different to correlate with the differences in the He(I) photoelectron spectra of the two molecules in fig. 4. Consequently, Heilbronner's criticism is not due to a defect in chemical graph theory, but to the neglect of important terms in the Hamiltonian on which ordinary graphs are based.

It is interesting to note that the characteristic polynomials of the PPP bond matrices of both the graphs in fig. 4 are given by

$$\lambda^{10} - 5\lambda^8 + 10\lambda^6 - 10\lambda^4 + 5\lambda^2 - 1 = (\lambda^2 - 1)^5.$$

Although the bond order matrix elements of the two isospectral graphs in fig. 4 differ considerably, the bond matrix characteristic polynomials are the same.

5. Structural discriminators based on the PPP method

The PPP method could not only discriminate isospectral graphs but geometrical isomers as well, although the difference is somewhat subtle for the latter case. Figure 5 shows two geometrical isomers which are topologically identical. That is, their Hückel spectra and ordinary polynomials do not differ since, as ordinary graphs, the two structures in fig. 5 are the same. Table 2 shows the spectra of these

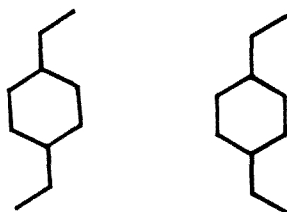


Fig. 5. Geometrical isomers of two conjugated hydrocarbons.

Table 2

The PPP eigenvalues of two geometrical isomers (fig. 5)

Isomer	Eigenvalues
Fig. 5 I (cis)	-14.0260, -12.4773, -10.7487, -10.5705, -9.2460, -2.5440, -1.2195, -1.0413, 0.6873, 2.2360
Fig. 5 II (trans)	-14.0261, -12.4768, -10.7452, -10.5760, -9.2437, -2.55463, -1.2140, -1.0448, 0.6868, 2.2361

two structures. As seen from table 2, although the difference in the spectra is subtle, it corresponds to the "molecular similarity" of the two isomers. Hence, more realistic molecular similarity indices can be derived from PPP results. A few such possibilities are discussed below.

A spectral difference index between two structures containing the same number of atoms can be defined as

$$\Delta = \sum_i |\lambda_i^I - \lambda_i^{II}|.$$

The smaller the value of Δ , the more similar the two structures. On this basis then, Δ is 0.5854 for the two graphs in fig. 4, while it is 0.0238 for the two isomers in fig. 5. Consequently, Δ discriminates isospectral graphs, while it is small for geometrical isomers which are similar to each other (cis and trans).

Other possible indices could be derived from the elements of the bond matrix and spectra. For example, indices P_1 , P_2 and λ can be derived as follows:

$$P_1 = \left(\sum_{\mu, \nu} P_{\mu\nu} / N \right),$$

$$P_2 = \left(\sum'_{\mu, \nu} P_{\mu\nu} / N \right),$$

$$\lambda = \sum_i \left| \frac{\lambda_i - \alpha - \gamma/2}{\beta} \right|,$$

where N is the number of atoms and the prime in the second sum is restricted to nearest-neighbors only. In the third expression, λ_i is the i th eigenvalue, α and β are the Hückel parameters, while γ is the $\gamma_{\mu\mu}$ integral in the PPP method. This expression is for graphs containing no heteroatoms, although this can be easily modified for such graphs. The P_2 indices for the two isospectral graphs in fig. 4 are the same (0.6422). Thus, the two isospectral graphs are not discriminated by both P_1 and P_2 . Hence, indices based on the actual spectra (for example, the λ index) are better discriminators than the ones based on bond matrices. Many variations of such indices could be formulated, but the underlying philosophy is that the PPP method takes into account the actual geometry of a structure and is computationally inexpensive. Perhaps the PPP method and other semiempirical techniques should be suitably adapted to formulate more realistic topological indices.

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