Exact topological π-electron Hamiltonians from ab initio wavefunctions?*

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A general topological π-electron Hamiltonian is defined as an appropriate function of the adjacency matrix. It is shown that any electronic property of a planar benzenoid hydrocarbon, including its all-electron wavefunction, is entirely determined by the topological π-electron Hamiltonian describing the hydrocarbon. However, using electronic wavefunctions (calculated at the HF/6-31G** level) of several such hydrocarbons as examples, it is demonstrated that it is impossible to construct topological Hamiltonians with eigenvectors related by simple universal algebraic formulae to the corresponding occupied Hartree–Fock orbitals of π symmetry. This observation casts doubt on the usefulness of the Hückel π-electron orbitals in understanding the electronic structures of benzenoid systems.

1.   Topological π-electron Hamiltonians and their relation to the exact electronic properties of planar benzenoid hydrocarbons

Let M stand for a molecule of a planar benzenoid hydrocarbon with its ground-state equilibrium geometry specified by the charges and the Cartesian coordinates of its nuclei. Let $G(M)$ be the hydrogen-suppressed molecular graph of M possessing N vertices, and A(M) be the corresponding adjacency matrix [1]. Let H(M) be an $N \times N$ square symmetric matrix. We call H(M) a topological π-electron Hamiltonian describing M if

$$H_{ij} = A_{ij} f_{ij}(\mathbf{A}), \quad f_{ij}(\mathbf{A}) \neq 0, \quad \text{for } 1 \leq i, j \leq N, \tag{1}$$

where the functions f_{ij} defining H are such that H transforms with respect to the permutations of the vertices of G in the same way A does.

The two most common examples of topological π-electron Hamiltonians are the Hückel Hamiltonian and the "variable β" Hamiltonian. The Hückel Hamiltonian [2] is defined by the trivial choice of $f_{ij} \equiv 1$. To obtain the "variable β" Hamiltonian, one puts [3–5]

$$f_{ij}(\mathbf{A}) = 1 + f(P_{ij}), \tag{2}$$

where $f(x)$ is a nondecreasing function of x, and the bond order matrix $\mathbf{P}$ is related to $\mathbf{H}$ through the following relation, valid for bipartite $G(M)$ [6,7]:

$$\mathbf{P} = \mathbf{1} + (\mathbf{H}^2)^{1/2}\mathbf{H}^{-1}. \tag{3}$$

Such an implicitly defined "variable β" Hamiltonian is often regarded as an improvement over the Hückel Hamiltonian.

From the definition (2), it is obvious that, for a given choice of the functions f_{ij}, the adjacency matrix entirely defines the topological π-electron Hamiltonian. Conversely, $\mathbf{H}$ entirely defines $\mathbf{A}$, which can be simply obtained by replacing all the non-zero elements of $\mathbf{H}$ by ones. For obvious reasons, there is (ignoring the permutations of vertices) a one-to-one correspondence between the adjacency matrix and the molecular graph. Moreover, because cis/trans isomerism is impossible in planar benzenoid hydrocarbons, the molecular graph $G(M)$ uniquely determines the molecule M (including its ground-state geometry), and vice versa. This is so because the knowledge of $G(M)$ is sufficient to determine an approximate geometry of M (for example, by assuming standard bond lengths and angles) which can then be optimized by minimizing the total ground-state energy. For a given M, such minimization is always expected to converge to the same minimum, independent of the initial approximate geometry. Therefore, one may write down the following chain of bijective relationships:

$$M \leftrightarrow G(M) \leftrightarrow A(M) \leftrightarrow H(M). \tag{4}$$

On the other hand, the knowledge of M is sufficient to write down the corresponding electronic Hamiltonian (including the nucleus–nucleus repulsion terms) $\hat{h}(M)$. The Schrödinger equation

$$\hat{h}(M)\psi(M) = e(M)\psi(M) \tag{5}$$

yields the exact electronic ground-state wavefunction of M, $\psi(M)$, and the exact Born–Oppenheimer total ground-state energy $e(M)$. It is also easy to realize that $\psi(M)$ not only allows one to compute any electronic property of M, $Q(M)$, but also uniquely determines $\hat{h}(M)$. Therefore, one may extend the chain (4) and write:

$$Q(M) \leftarrow \psi(M) \leftrightarrow \hat{h}(M) \leftrightarrow M \leftrightarrow G(M) \leftrightarrow A(M) \leftrightarrow H(M). \tag{6}$$

In practice, the ground-state eigenvalue and eigenfunction of $\hat{h}(M)$ can be computed only in an approximate manner. However, when a well-defined level of approximation, such as the Hartree–Fock method, is used, the above chain of

relationships remains valid even when the exact $\psi(M)$ and $Q(M)$ are replaced by the approximate ones. One concludes that *the knowledge of the adjacency matrix (or the topological π-electron Hamiltonian in general) describing a planar benzenoid hydrocarbon is sufficient to determine any of its exact or approximate electronic properties*. This does not necessarily imply, however, that the corresponding functions $\psi_A[A]$ and $Q_A[A]$ (or $\psi_H[H]$ and $Q_H[H]$),

$$Q(M) = \langle \psi_A[A(M)] | \hat{Q} | \psi_A[A(M)] \rangle = Q_A[A(M)]$$

$$= \langle \psi_H[H(M)] | \hat{Q} | \psi_H[H(M)] \rangle = Q_H[H(M)] \tag{7}$$

should be expected to have simple forms. This is in some sense reminiscent of density functional theory [8] in which the total energy of M, $e(M)$, is a unique functional of the electron density of M, $\rho(M, r)$, but only approximations to the exact functional are mathematically tractable.

The fact that the relationships between the adjacency matrix (or the quantities derived directly from it) and some of the electronic properties of M can be accurately approximated by simple algebraic functions is often viewed as an indication that the methods of chemical graph theory are capable of explaining some aspects of the electronic structures of planar benzenoid hydrocarbons. In particular, even the unsophisticated Hückel Hamiltonian is known to yield total π-electron energies that correlate reasonably well with the total Hartree–Fock energies [9, 10] or with the π-electron kinetic energies [10]. On the other hand, the bond lengths (as correlated with the bond orders, eq. (3)) [3] and the ionization potentials (as correlated with the eigenvalues of H(M)) [11] are calculated more accurately when a "variable β" Hamiltonian is used instead of the Hückel one. This observation demonstrates that, although the properties are functions of the adjacency matrix itself, use of the more general topological π-electron Hamiltonians is expected to either simplify the functional dependencies needed to calculate the properties or improve the accuracy of approximate relationships.

Although the existence of simple, yet reasonably accurate, correlations between the topological π-electron Hamiltonians and the electronic properties of planar benzenoid hydrocarbons is gratifying, the importance of the all-electron wavefunction (either exact or approximate) in interpreting the electronic structure of any molecule cannot be ignored. Since a one-to-one mapping between the topological π-electron Hamiltonian H(M) and the corresponding all-electron wavefunction $\psi(M)$ is provided by the chain (8), one may inquire whether it is possible to construct topological Hamiltonians with eigenvectors $C(M)$ that are related to $\psi(M)$ (or quantities derived from it) through simple functional dependencies. Specifically, the question of the relations between the ith eigenvector of H(M), $C_i(M)$, and the corresponding occupied Hartree–Fock molecular orbital of π symmetry, $\phi_i(M, r)$, is of particular importance. Should such a construction be possible, the resulting topological Hamiltonians could be regarded as "exact".

2. The possible relationships between eigenvectors of the topological Hamiltonians and the occupied Hartree–Fock molecular orbitals of π symmetry

Before the aforementioned relationships can be considered, an approach allowing one to map $\phi_i(M, r)$ onto a finite space of the vertices of $G(M)$ has to be specified. Although, in practical calculations, the Hartree–Fock orbitals are expanded into a finite set of basis functions usually centered at nuclei, the mapping has to be free from the arbitrariness imposed by such an expansion. This means that the coefficients of the basis functions *cannot* be used for the mapping. However, it is possible to employ Bader's topological theory of atoms in molecules [12] for this purpose.

Within the scope of Bader's theory, the knowledge of electron density $\rho(M, r)$, which is directly derivable from the electronic wavefunction $\psi(M)$, allows one to partition the entire Cartesian space into so-called atomic basins. When carried out over atomic basins, integration of quantities related to $\psi(M)$ affords atomic properties. In particular, the atomic overlap matrices are given by [12]

$$\langle i | j \rangle_A (M) = \int_{\Omega_A} \phi_i^*(M, r) \phi_j(M, r) \, dr, \tag{8}$$

where Ω_A is the atomic basin of the atom A belonging to M. The above definition can be directly extended to provide vertex overlap matrices by replacing the atomic basins by the vertex basins. A vertex basin is defined as the union of the atomic basins of the carbon atom associated with the vertex and the atomic basins of any hydrogen atoms linked to it.

The vertex overlap matrices satisfy the sum rules

$$\sum_{V \in G(M)} \langle i | j \rangle_V (M) = \delta_{ij}, \tag{9}$$

where the summation runs over all the vertices of the molecular graph $G(M)$. The calculation of the vertex overlap matrices constitutes a reduction process in which the Hartree–Fock wavefunction $\psi(M)$ is mapped onto a set of $(N/2) \times (N/2)$ ($N/2$ is the number of occupied molecular orbitals of π symmetry) symmetric matrices, with each vertex assigned one matrix.

In order to investigate the possible relationships between $\psi(M)$ and the eigenvectors of $H(M)$, the necessary (but not sufficient) conditions that the basis functions used in the construction of $H(M)$ must satisfy should first be studied. To do that, one has to understand the meaning of these basis functions. In its original formulation, the Hückel Hamiltonian acts upon the Hilbert space spanned by one p_z atomic orbital per each of the carbon atoms comprising the molecule in question. However, such basis functions are not mutually orthogonal and, unlike their ab initio counterparts, the Hückel Hamiltonian matrix elements do not have any clear physical

meaning. We prefer a more abstract interpretation of the topological π-electron Hamiltonian in which the N-dimensional vector of basis functions ω is not explicitly specified, provided its components satisfy the following conditions:

(1) Orthonormality:

$$\langle \omega_A | \omega_B \rangle = \delta_{AB}, \tag{10}$$

where A and B are any two vertices of $G(M)$.

(2) Compactness: The values of vertex overlap matrices for the basis functions $\langle \omega_A | \omega_B \rangle_V$ have to be close to zero unless the topological distances between the vertices A, B and $V \in G(M)$ are small enough. This condition arises from the notion that, in order to be (at least approximately) transferable between different molecules, the basis functions must resemble well-localized atomic orbitals.

Let $C_{iA}(M)$ stand for the component of the ith eigenvector of $H(M)$ at the vertex A. The topological vertex overlap matrix can then be defined as

$$\langle i | j \rangle_V(M) = \sum_{A,B \in G(M)} [iA | jB](M) \langle \omega_A | \omega_B \rangle_V(M), \tag{11}$$

where

$$[iA | jB](M) = C_{iA}^*(M) C_{jB}(M). \tag{12}$$

Note that the trivial relations

$$[iA | jB](M)[kC | lD](M) - [iA | lD](M)[kC | jB](M) = 0 \tag{13}$$

hold for all $A, B, C, D \in G(M)$, and $1 \leq i, j, k, l \leq N/2$.

The issue of the existence of simple relationships between the all-electron wavefunction and the eigenvectors of the topological π-electron Hamiltonian reduces now to the question of whether it is possible to find a set of basis functions for $H(M)$ yielding the corresponding overlap matrices $\langle \omega_A | \omega_B \rangle_V(M)$ such that, when used in conjunction with eq. (11) and the vertex overlap matrices *calculated from the occupied Hartree–Fock orbitals*, the resulting products $[iA | jB](M)$ satisfy the relations given by eq. (13). From the mathematical point of view, the problem of finding the aforementioned quantities is underdetermined. However, the orthogonality and compactness conditions impose severe restrictions on the possible solutions.

3. π-electron vertex overlap matrices from the HF/6-31G** electronic wavefunctions

In order to determine whether simple relationships exist between $\phi_i(M, r)$ and $C_i(M)$, Hartree–Fock calculations were carried out for five planar benzenoid hydrocarbons, namely naphthalene, anthracene, phenanthrene, benzanthracene, and

chrysene. All molecular geometries were fully optimized at the HF/6-31G** level. The Hartree–Fock wavefunctions were used in turn to compute the vertex overlap matrices for the occupied molecular orbitals of π symmetry.

The first hypothesis tested is that the basis functions of H(M) are strictly localized within the respective vertex basins. This means that the conditions

$$\langle \omega_A | \omega_B \rangle_V (M) = \delta_{AB} \delta_{AV} \tag{14}$$

are assumed to hold. This results in the simple relationship

$$\langle i | j \rangle_V (M) = [iV | jV](M) \tag{15}$$

between the π-electron vertex overlap matrices and the eigenvectors of the topological π-electron Hamiltonian. In order to asses the validity of eq. (15), the RMS error for a subset of the relations (13) was computed as

$$\Delta = \{N(N/2)[(N/2)-1]\}^{-1/4}$$

$$\times \left(\sum_{V \in G(M)} \sum_{i,j=1}^{N/2} \{[iV|iV](M)[jV|jV](M) - [iV|jV](M)[jV|iV](M)\}^2 \right)^{1/4}. \tag{16}$$

Δ is an estimate of the average deviation of each term $[iV|jV](M)$ from the value that would satisfy eq. (13). The square root of Δ provides a measure of the deviation of the individual component of the eigenvector of H(M), $C_{iV}(M)$.

Table 1

The calculated values of RMS error for the relations (13).

Molecule	Δ	
	strict localization	first neighbor included
naphthalene	0.0375	0.0130
anthracene	0.0270	0.0099
phenanthrene	0.0271	0.0094
benzanthracene	0.0215	0.0075
chrysene	0.0213	0.0074

The values of Δ, calculated for five planar benzenoid hydrocarbons, are given in the second column of table 1. They span the range of 0.021–0.038, which corresponds to an average error for $C_{iV}(M)$ of 0.15–0.19. It is obvious that these are unacceptably large errors. Therefore, the simple relationship given by eq. (15) does not hold and the hypothesis of basis functions localized strictly within the vertex basins has to be abandoned.

Another possibility worth investigating is that the basis functions are not confined to their respective vertex basins. The simplest approximation compatible with this assumption is provided by the overlap matrices satisfying the equation

$$\langle \omega_A | \omega_B \rangle_V(M) = \delta_{AB} \kappa_{AV}(M), \tag{17}$$

where the weights $\kappa_{AV}(M)$ are positive numbers for all pairs of vertices $A-V$ that share an edge, and equal to zero otherwise. This means that, for a given vertex, the corresponding basis function is assumed to stretch only over all of its first neighbors. Note that the weights have to satisfy the constraints

$$\sum_{V \in G(M)} \kappa_{AV}(M) = 1, \tag{18}$$

for all $A \in G(M)$, and that in general $\kappa_{AV}(M) \neq \kappa_{VA}(M)$. For obvious reasons, one expects the diagonal elements to dominate the matrix $\kappa(M)$.

The weights $\kappa_{AV}(M)$ are obtained by minimizing the values of Δ, eq. (16), with the terms $[iA|jA]_V(M)$ resulting from solving the system of linear equations, eq. (11), for each pair (i,j). The so minimized values of Δ are listed in the third column of table 1. It is apparent that relaxing the strict localization constraint reduces the Δs by about a factor of three. As in the previous case, the values of Δ decrease with increasing size of the hydrocarbons. However, this does not mean that the relations (13) are satisfied with better accuracy as the number of vertices in $G(M)$ increases; the absolute values of $C_{iA}(M)$ also decrease with the size of molecules, resulting in a relative error that is almost constant.

Even with the localization constraint relaxed, the values of Δ are too large to justify the existence of simple relationships between the Hartree−Fock orbitals and the eigenvectors of the topological π-electron Hamiltonians. Even worse, as found by further numerical testing, relaxing the localization constraint to include distant neighbors and nonzero overlap matrix elements between the basis functions does not decrease the Δs by a significant amount.

4. Conclusions

Although the existence of one-to-one relationships between all-electron wavefunctions of planar benzenoid hydrocarbons and the corresponding topological π-electron Hamiltonians can be rigorously proven, these relationships are of a complicated and implicit nature. This is well demonstrated by the failure of attempts to correlate the π-electron vertex overlap matrices with the eigenvectors of the corresponding topological π-electron Hamiltonians. The failure stems from the fact that it is impossible to find a set of localized (and therefore universal) basis functions for the topological Hamiltonians that would be capable of delivering the terms $[iA|jB]_V(M)$ satisfying the necessary relations given by eq. (13). What this means

is that *no set of basis functions composed of one function per vertex of the molecular graph can yield simple relationships between* $\phi_i(M, r)$ *and* C_i. This general negative conclusion has important consequences for the understanding of the mathematical structures of topological π-electron Hamiltonians, and the Hückel Hamiltonian in particular. The Hückel π-electron orbitals bear no simple relation to their Hartree–Fock counterparts except for sharing the same irreducible symmetry representations imposed by the symmetry of the molecular framework. This means that although quantities derived from the Hückel Hamiltonians, such as π-orbital energies, total π-electron energies, and bond orders can be successfully employed in correlations involving exact electronic properties, the Hückel π-electron orbitals themselves are of little importance in understanding the electronic structures of conjugated molecules.

Acknowledgement

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