

GRAPH REPRESENTATION OF QUANTUM MECHANICAL OPERATORS AS MOLECULAR STRUCTURAL FORMULAS

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Abstract: A brief overview of the Valency Interaction Formula method, VIF, based on Sinanoğlu's covariant quantum mechanics and theory of structural covariance of graphs is made. The use of VIF pictures as one-electron density operators is emphasized. A simple formula for judging the significance of relative interaction strengths in σ -ring systems is presented and used. This applied toward understanding of the chemical bonding in ethene, cyclopropane, and cyclohexane.

AMS Subject Classification: 92E10, 81R15

Key Words: molecular structural formula, valency interaction formula, one-electron operators, molecular graph, non-unitary classification, applications in chemistry, quantum mechanics, operator research and algebraic analysis, graph theory

1. Introduction

Graph representation of quantum mechanical operators as molecular structural formulas allows for non-unitary classification of molecules in a way related simultaneously to the molecule's three dimensional structure and electronic properties.

The mathematical foundations for this method were formulated by Sinanoğlu and are the basis of the Valency Interaction Formula (VIF) method, see [5]. In the simplest application of the VIF method, graph representations of one-

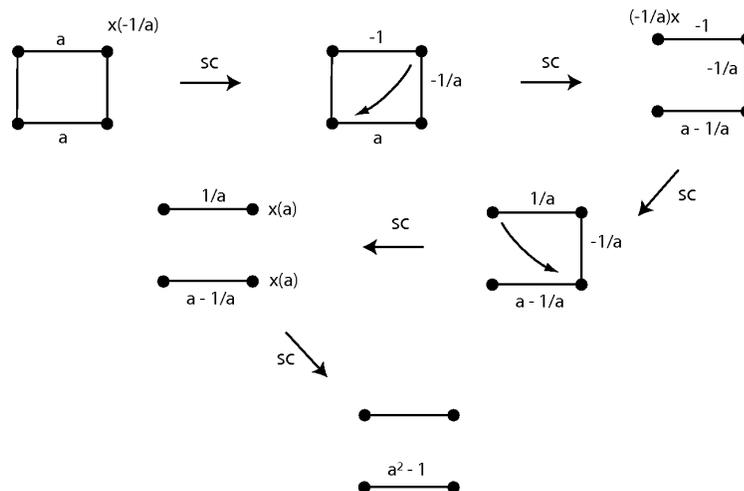


Figure 1:

electron density operators are molecular structural formulas, see [1]. This method has been used to understand the molecular geometries of singlet and triplet cyclobutadiene and the π -distortivity of the benzene molecule, see [2]. In this paper a simple formula for relating the electronic properties of ring systems to the number of carbon atoms in the ring is presented.

2. The VIF Method

A quantum operator, Ω projected into a valency vector space so that $\Omega = \sum \Omega_{\mu\nu} |\phi^\mu\rangle \langle \phi^\nu|$ is represented by a graph with each vertex, $A^{\mu\mu} = |\phi^\mu\rangle \langle \phi^\mu|$, and all $A^{\mu\nu} = (1/2)(|\phi^\mu\rangle \langle \phi^\nu| + |\phi^\nu\rangle \langle \phi^\mu|)$ implicit. $\Omega^{\mu\mu}/\beta_0 = \xi$, is the strength of a loop affixed to vertex $A^{\mu\mu}$ and $\Omega_{\mu\nu}/\beta_0 = \kappa$ is the strength of a line between vertex $A^{\mu\mu}$ and vertex $A^{\nu\nu}$. Vertices are called *valency* points and lines are called *valency interactions*. β_0 is a constant chosen to make κ equal to one if possible and unitless. One value of β_0 is used for a given graph (VIF picture) and as we will see later in this paper, relative interaction strengths designated by a constant, a , are sometimes crucial.

Graph representation of quantum operators as molecular structural formulas (VIF pictures) are drawn according to a reference, α and simplified using two pictorial rules which are linear transformations and preserve the sign of the

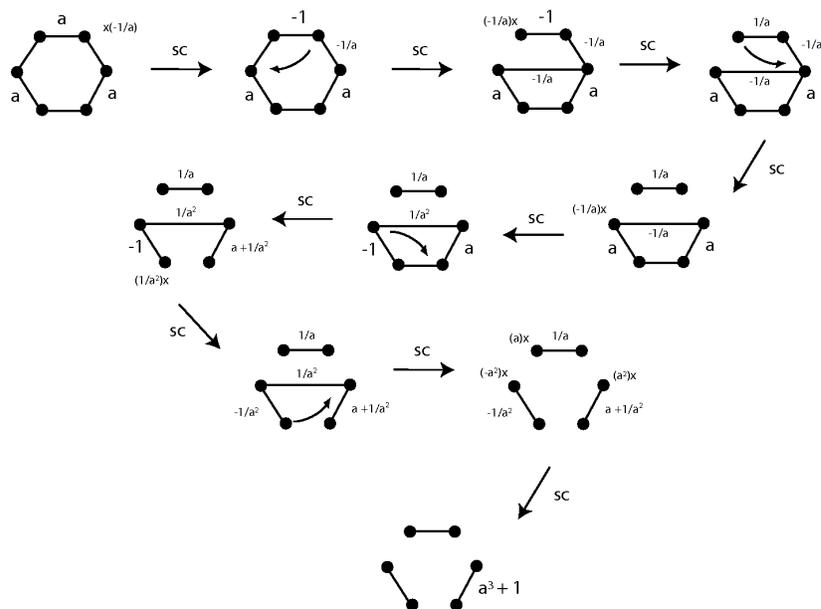


Figure 2:

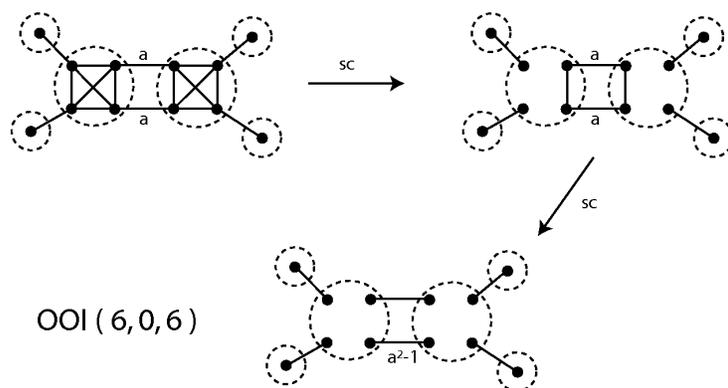


Figure 3:

eigenvalues of the operator. This invariance property is then used to classify graphs and/or molecules into equivalence classes. If the VIF picture represents a one-electron Hamiltonian operator the signs of the eigenvalues with respect to the reference energy are enumerated in the level pattern index, $LPI(n_+, n_0, n_-)$, with n_+ the number of eigenvalues lower in energy than the reference energy,

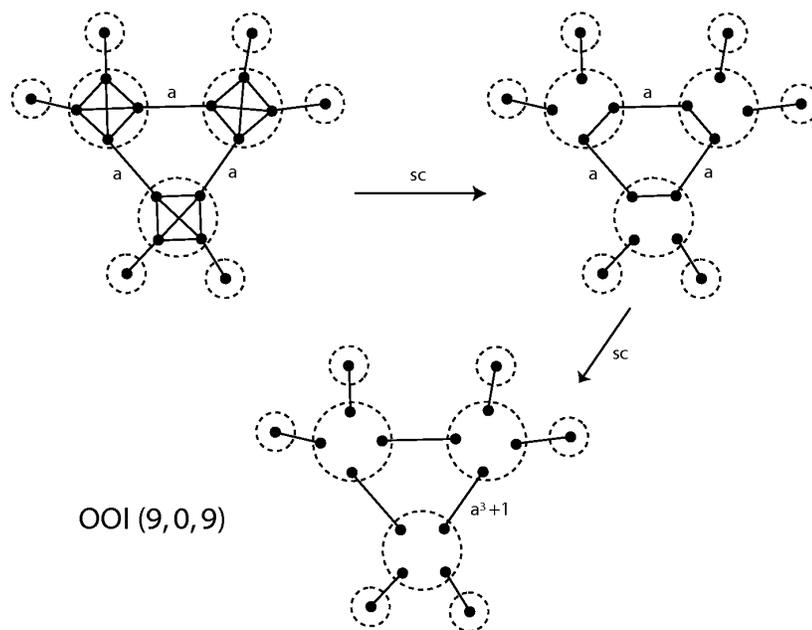


Figure 4:

n_0 the number of eigenvalues at the reference energy, and n_- is the number of eigenvalues higher than the reference energy, see [10]. If the VIF picture is a one-electron density operator the sign of the eigenvalues with respect to a reference electron density of one electron per orbital is listed in the orbital occupancy index, $OOI(n_2, n_1, n_0)$ with n_2 the number of doubly occupied orbitals, n_1 the number of singly occupied orbitals and n_0 the number of unoccupied orbitals, see [1]. The linear transformations carried out on the graph using the pictorial rules and sequences of these transformations are in general non-unitary and allow for transformation between all linearly related basis frames. The VIF picture is fully reduced when all of the lines between valency points have been cancelled. The two pictorial rules are given below.

Multiplication Rule: A vertex, $A^{\mu\mu}$, may be multiplied by a nonzero constant. All constants, κ of lines attached to $A_{\mu\mu}$, are then multiplied by this nonzero constant. If vertex $A^{\mu\mu}$ has a loop, its constant, ξ , is multiplied by the square of the nonzero constant.

Addition Rule: A vertex, $A^{\mu\mu}$, may be “lifted” and superimposed on another vertex, $A^{\nu\nu}$. All lines and loops attached to $A^{\mu\mu}$ are carried along. Constants, ξ and κ , of superimposed loops and lines respectively add. If $A^{\mu\mu}$

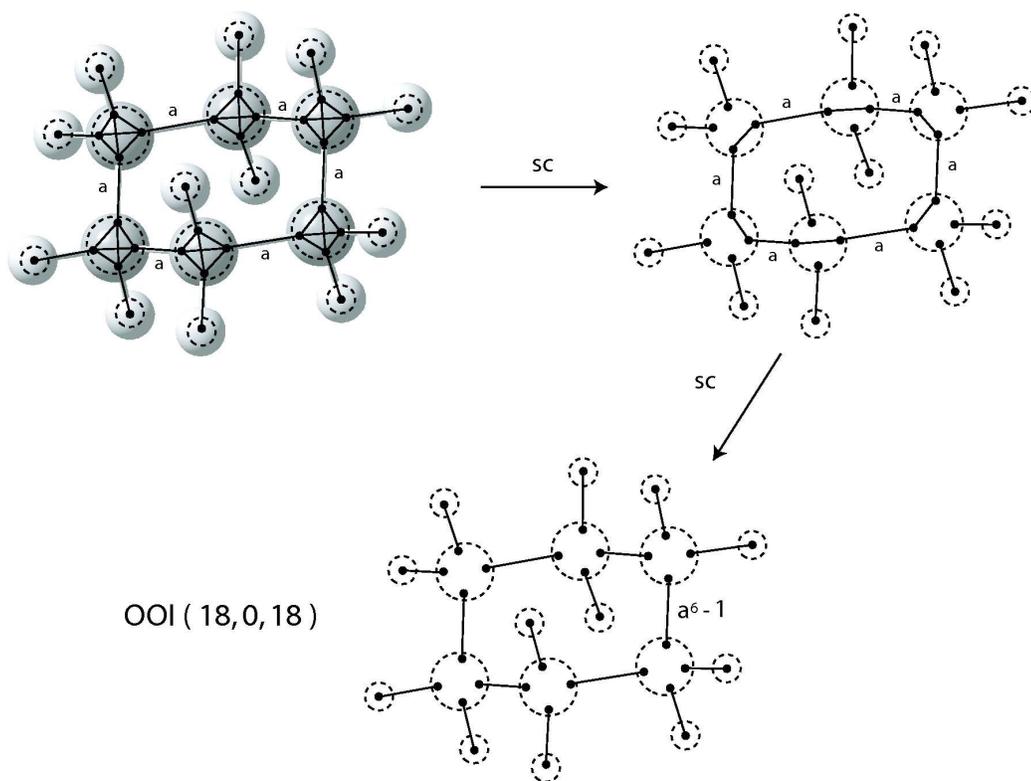


Figure 5:

and $A^{\nu\nu}$ are connected by a line of strength κ , this line curls up to form a loop with strength 2κ on $A^{\nu\nu}$. If $A^{\nu\nu}$ already had a loop, the curled up loop superimposes this original loop and the value 2κ is added to the original loop constant, ξ , on $A^{\nu\nu}$. $A^{\mu\mu}$, the line(s) attached to it unless cancelled, and loop if it has one, are not removed, they remain as if “chalk marks” left behind.

To summarize, quantum operators projected into a valency vector space are given graphical representation. Non-unitary classification of the molecular graph is then made by the use of two pictorial rules. The signs of the operator’s eigenvalues, are read from the graph and used to classify the molecule in a way based simultaneously on the molecule’s three dimensional geometry and electronic properties.

3. Relative Interaction Strengths in Ring Systems

Relative interaction strengths, a , can sometimes be important, particularly for ring systems. For the four-center/four-electron bond in the cyclobutadiene π -system, relative interaction strengths around the ring distinguish between the square triplet state and rectangular singlet state. The benzene π -system is not as sensitive to relative interaction strengths around the ring. The orbital occupancy index remains the same as long as a $a > -1$. This result is consistent with the ease of deformation of benzene between D_{3h} and D_{6h} symmetries [3]. Figure 1 and Figure 2 respectively show how four and six membered rings are reduced to two-center/two-electron bonds the last having a line strength of $\kappa = a^2 - 1$ or $\kappa = a^3 + 1$ respectively. The relationship between the geometries of singlet and triplet states is therefore found according to the two pictorial rules and theory of structural covariance. Figure 3 and Figure 4 show how this method applies to ethene and cyclopropane molecules respectively. Notice that the double bond in ethene is described by two sets overlapping sp^3 hybrid orbitals, “banana” bonds. The usual sp^2 carbon picture of ethene can also be drawn as a VIF picture, see [1].

A general rule applies for saturated ring hydrocarbons. Relative interaction strengths exist around the ring in these cases because the strength of valency interactions between hybrid orbitals centered on different carbon atoms around the ring are different than those between hybrid orbitals centered on the same carbon atom. The rings that result have an even number of valency points and can be reduced to sets of two-center/two-electron bonds with $\kappa = 1$ except for the last one. The last valency interaction in the reduction of a carbon ring system is $\kappa = a^n + (-1)^{(n-1)}$, where a is the relative interaction strength and n is the number of carbon atoms in the ring. The last interaction strength for the cyclohexane VIF is therefore $\kappa = a^6 - 1$, see Figure 5. Correct depiction of the cyclohexane singlet ground state therefore requires the use of relative interaction strengths, $|a| \neq 1$. Notice that results are different based on whether the ring has an odd or even number of carbon atoms. We are currently studying the implications of this result for vibrational force constants and charge distribution in electronic excited states.

Acknowledgements

The author is grateful to the conference and scientific committees of the Fifth International Conference of Applied Mathematics and Computing (Plovdiv, Bulgaria, August 12-18, 2008) for inviting him to present this work and to the University of Minnesota in supporting this research and travel from Minnesota to Bulgaria and to Mark Logan and Amanda Matson for help with L^AT_EX. The author also thanks Oktay Sinanoğlu for the VIF method and its mathematical foundations.

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