

H₂O) electrolyte mixture. An additional advantage of the present treatment is that it not only predicts the activity coefficient data of the components of a ternary electrolyte mixture but Glueckauf's relation and Harned and Owen's eq (14-5-7) also follow as a direct consequence of the cross-differentiation of the fundamental eq 6. Further only one adjustable parameter is needed unlike models which retain the Debye-Hückel term at all values of the ionic strength and for which more parameters are required to represent equally well the activity coefficient data. In view of the lack of any satisfactory theory of mixed electrolytes solution, the semiempirical eq 6 is a good representation of the activity coefficient data of the components A or B of a (A + B + H₂O) mixture over an appreciable concentration range.

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Topological Orbitals, Graph Theory, and Ionization Potentials of Saturated Hydrocarbons¹

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Abstract: Graph theory is used to obtain a complete set of degenerate orthonormal eigenvectors on a bond orbital basis for saturated hydrocarbons. After symmetry and topological analyses, the eigenvector coefficients are written by inspection. The obtained wave functions are used as zero-order functions to parametrize a bond orbital theory of molecular ionization potentials. The parametrization method uses experimental data and a novel reverse similarity transformation to generate all parameters in a single step. The final parameters, obtained after iteration, give calculated ionization potentials that compare favorably with experimental values (correlation coefficient 0.9995).

I. Introduction

At the simplest levels, the π electrons of unsaturated molecules are customarily treated by three different theoretical techniques. These are the Hückel² and perturbational molecular orbital³ methods (HMO and PMO), which give numerical results that can be compared with experimental values, and the use of orbital-symmetry principles^{4,5} (Woodward-Hoffmann rules), which lead to significant qualitative predictions concerning reactivity in pericyclic reactions. The quantitative results obtained by the PMO method³ are particularly noteworthy since their correlations with structure-reactivity data are as good as those obtained using more complex LCAO-MO-SCF calculations. An additional feature is that PMO calculations are very simple to carry out by hand making use of the mathematical properties of nonbonding molecular orbitals.

In saturated systems, several different levels of quantum-mechanical empirical approximations have been tested, with numerous published applications.⁶ Orbital symmetry principles have also been applied in discussions of reactivity problems involving σ electrons.⁵ However, a parallel development of a perturbational MO theory for σ systems has not materialized. This may be due to the fact that it is not generally realized that a complete set of orthonormal bond orbital coefficients can be

obtained for σ systems simply from a knowledge of the system topology. The situation is actually more advantageous than in the case of π systems, where usually only a single nonbonding orbital will have predetermined coefficients.

Some characteristics of these localized topological orbitals were first described by Platt in 1959 and 1961,^{7,8} and Herndon has outlined a single example of their use in predicting molecular ionization potentials.⁹ A similar treatment by Thompson has been used to predict MO symmetries from localized pair models.¹⁰ None of these works sufficiently illustrates the utility of this approach. Therefore, the objective of this article is first to show how topological wave functions are quickly and efficiently obtained for saturated systems. The exposition will make use of elementary concepts of group theory and graph theory where appropriate. In order to avoid an abstract presentation of necessary concepts, the procedures will be demonstrated by application to the simplest organic compounds, i.e., the saturated alkanes.

In a following section, the obtained orbitals will be used as starting points for parametrization of a highly correlative empirical MO theory of ionization potentials. The development will employ first-order perturbation theory and a novel averaging algorithm that is very effective for operations of this type. A large number of MO theories have been used to correlate ionization potentials.^{6,11-17} The present method gives quan-

Methane (T_d)	Ethane (D_{3d})	Propane (C_{2v})	Isobutane (C_{3v})	Neopentane (T_d)
-2.00 (a_1)	-2.24 (a_{1g}) -1.73 (a_{2u})	-2.33 (a_1) -2.00 (b_1) -1.61 (a_1)	-2.39 (a_1) -2.00 (e) -1.50 (a_1)	-2.45 (a_1) -2.00 (t_2) -1.41 (a_1)
0.00 (t_2)	0.00 ($a_{1g} + e_u + e_g$)	0.00 ($2a_1 + a_2 + 2b_1 + 2b_2$)	0.00 ($2a_1 + a_2 + 3e$)	0.00 ($e + t_1 + 2t_2$)
+2.00 (a_1)	+1.73 (a_{2u}) +2.24 (a_{1g})	+1.61 (a_1) +2.00 (b_1) +2.33 (a_1)	+1.50 (a_1) +2.00 (e) +2.39 (a_1)	+1.41 (a_1) +2.00 (t_2) +2.45 (a_1)

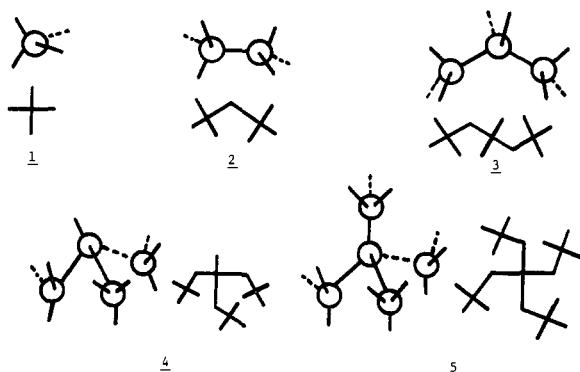
Figure 1. Eigenvalues and eigenvector symmetries of topological graphs.

titative results that compare favorably with previous treatments.

II. Topological Orbitals

The atoms in a molecular structure can be adequately described in terms of cores of nuclei and tightly bound inner shell electrons, and valence shells of electrons. The valence electrons of σ systems are usually depicted as covalent electron pair bonds and lone pairs. For our purposes a molecule will be represented by two different kinds of molecular graphs. The first is composed of circles and lines, corresponding to cores and σ bonds, respectively. These graphs resemble the molecular models often used to picture covalent molecules, so the molecular symmetry and conformation can be discerned.

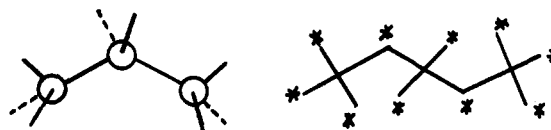
The molecular model graphs for the series of methylmethanes, $(CH_3)_nCH_{4-n}$, are given in 1-5. Also shown are less



conventional planar graphs which define the zero-order topology of the electronic system. The vertices of these graphs represent the loci of electrons. The tetravalent vertices correspond to core electrons; terminal vertices and the divalent vertices represent carbon-hydrogen and carbon-carbon bonds, respectively.

As defined in this way, the graphs of all electronic systems composed of σ bonds, lone pairs, and core electrons are bipartite or bicolorable.^{18,19} The vertices of any bipartite graph can be divided into two sets such that any given vertex is only attached to neighboring vertices of the opposite set. In π -electron theory, molecular graphs with this characteristic are called "alternant" systems,²⁰ and the process of dividing the vertices into two sets is called "starring". In σ systems and their graphs, the valence electron pairs are isomorphic with starred vertices and the inner cores are unstarred, as shown in 6 for propane.

The patterns of eigenvalues for the adjacency matrices of alternant graphs can be deduced by counting starred and unstarred vertices, and computing the difference. The "pairing



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theorem" of Coulson and Rushbrooke²¹ states that positive eigenvalues will be matched by complementary negative eigenvalues, and there will be a central group of zero eigenvalues, in number at least equal to the difference, starred minus unstarred vertices.²² In π systems with odd numbers of p orbitals the energy levels with zero eigenvalues are called nonbonding levels. Generally, only a single nonbonding level is obtained.²² This is not the case with the graphs given in 1-5, where the number of degenerate levels with zero eigenvalue always outnumbers the nonzero eigenvalue levels.

Combining the use of group theory with the topological analysis leads to the symmetry-assigned groups of eigenlevels summarized in Figure 1. The levels are divided into three sets. The symmetries of the levels in the lower groups alternate, gerade and ungerade, and the characters of the irreducible representations can be assigned from their required nodal properties as recently summarized by Wilson.²³ The upper levels have corresponding symmetries from the pairing theorem. The actual magnitudes of the eigenvalues are of no consequence and will not be used further.

The graphical model is unrealistic, the main problems being the assumptions that the core and σ bond electrons constitute a degenerate (isoenergetic) set of basis functions, and that there are no interactions between the σ bonds. The first problem can be alleviated by introducing a core electron potential, experimentally of the order of 300 eV,²⁴ as a perturbation. In the topological graph, if the potential at vertices corresponding to K shells is a large value, the group of K-shell vertices is essentially decoupled from the vertices corresponding to bonds. This gives a disconnected graph as shown in 7 for propane. The



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interactions between the bonds, also considered to be a perturbation, reassemble the graph of the bond functions into a connected graph. In graph theory terminology, the resulting connected graph is the complement of the decoupled central graph illustrated in 7 for nearest-neighbor interactions only.

In a more conventional description, bond orbitals and core electron pairs act as two independent groups. The lower group

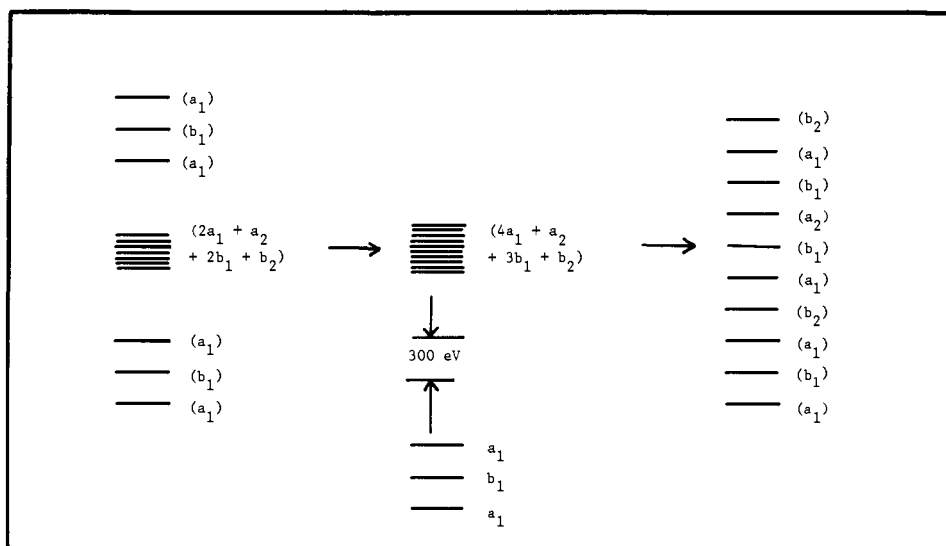


Figure 2. Energy level perturbation diagram for propane.

of core electronic levels are well separated from the valence levels as illustrated in Figure 2. The perturbation corresponding to the introduction of the K-shell potential factors out the three lower levels, and alters the three levels in the corresponding upper group so that they are practically degenerate with the original central group with zero eigenvalues. Anticipating the results of the next section, the final perturbation partitions the bond levels into two groups. The levels pictured as lower in energy would have predominant carbon 2s orbital character, and are referred to as inner valence levels. The orderings of the levels given in Figure 2 follow primarily from nodal characteristics.

The advantage of the foregoing analysis lies in the fact that the original central group of degenerate eigenlevels have associated eigenvectors whose coefficients can be obtained by inspection. These coefficients are required to obey the "zero sum rule",^{22,25} i.e., the coefficients must sum to zero around every vertex position in the topological graph. A facile assignment is possible when this requirement is combined with the constraint that a particular function must transform under symmetry operations according to a particular irreducible representation of the molecular point group. Finally, the remaining valence functions of each symmetry species have coefficients determined by orthogonalization.

There is a degree of arbitrariness in the final valence functions obtained using this topological approach. This is to be expected when one is dealing with an analysis of degenerate eigenfunctions. The main problems arise in assigning the coefficients to the eigenvectors of the totally symmetric type (a , a_1 , a' , and a_2 type orbitals). In general, these a type orbitals are most numerous, and their assigned coefficients have significant effects on subsequent perturbational calculations. Empirically, one finds that the best functions are delocalized as much as possible, and that a convenient starting point for one of the inner valence functions is a nodeless function with unnormalized coefficients of +1 the C-H bonds and +2 at the C-C bonds. The a type orbitals that obey the zero sum rule are then easily obtained orthogonal to this first function.

The topological functions for the methylmethanes are given in the supplementary material. Using propane as an example, the unnormalized coefficients are illustrated in Figure 3. The number of nodal regions is also given for each function. The core electrons are not considered, and the lowest function, therefore, turns out to be nodeless. The justification for ignoring the inner shell electrons is summarized by Wilson.²³

A set of functions of this type can be obtained for the valence electrons of any σ system. The problem is first simplified by

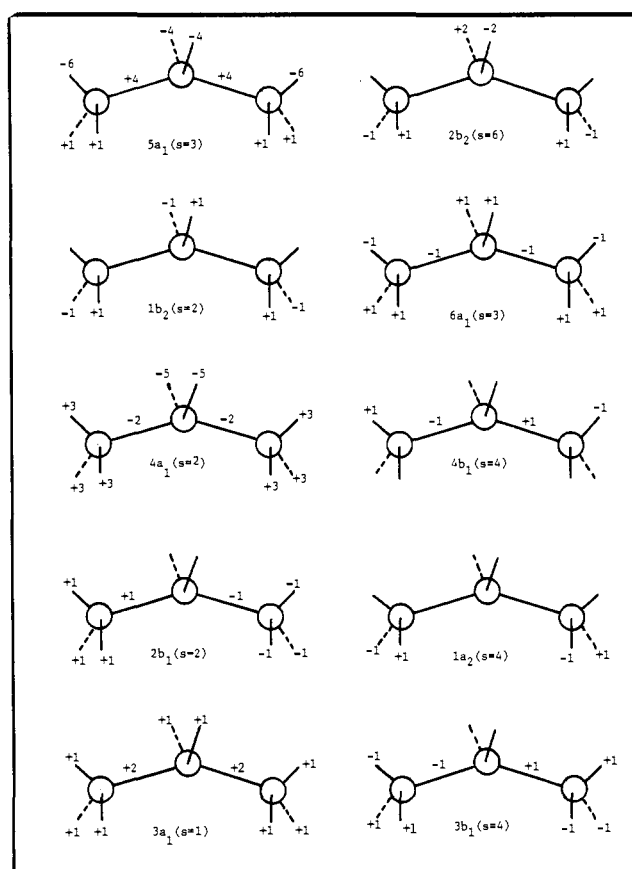


Figure 3. Propane topological eigenvectors on a bond orbital basis.

including K electrons so that the topological graph for the system possesses alternant character. Then the K electrons and the valence electrons are assumed to act independently, and the valence electron degenerate functions are written subject to the constraints of symmetry.

The functions obtained in this way have a one-to-one correspondence to symmetry combinations of localized CH and CC bond orbitals, where no interactions between the bonds have been permitted. They, therefore, also correspond to molecular orbitals on a bond orbital basis. The functions given in Figure 3 can now be referred to as orbitals rather than as eigenfunctions of the topological molecular graph. A comparison with molecular orbital drawings listed by Jorgensen

and Salem²⁶ demonstrates a close correspondence of nodal characteristics and eigenvectors for the topological orbitals and molecular orbitals obtained from semiempirical calculations.

III. Ionization Potentials of Saturated Hydrocarbons

The photoelectron spectra (PES) of saturated hydrocarbons give bands in the range 11–25 eV that can be assigned to ionizations from valence molecular orbitals,²⁷ assuming the validity of Koopmans' theorem.²⁸ Several investigators have interpreted these spectra within highly parametrized bond orbital or localized orbital models, implicitly assuming an orthonormal basis.^{11–17} The parameters which need to be chosen or calculated are the CC and CH diagonal matrix elements and the off-diagonal interaction terms of the effective molecular Hamiltonian matrix.

One approach is to use selected ionization potentials for highly symmetrical molecules to establish parameter values. For example, each of the hydrocarbons methane through neopentane has at least one symmetry adapted MO for which the eigenvalue is linearly related to some of the parameters. Murrell and Schmidt¹⁴ used this procedure, combined with judicious guesswork and ab initio calculations, and were reasonably successful in analyzing the PES of saturated hydrocarbons. Others have discussed the PES of one or two of the molecules within the same framework.¹³ One purpose of these studies was to assign the symmetry character of the energy levels, and where the molecular symmetry is high there is general agreement.

Brailsford and Ford¹¹ used a standard computer search procedure where all parameters were varied simultaneously to find optimum values. The criterion used was the sum of the squares of the differences between selected calculated and experimental vertical ionization potentials. The resulting parameters were used to correlate the PES of the *n*-alkanes through hexane, and a very good fit was obtained. The Murrell and Schmidt and the Brailsford and Ford parameters do differ by as much as 0.5 eV in some cases, but the calculated eigenvalues are very similar.

Our procedure for obtaining the parameters makes use of all of the experimental data, in contrast to the previous treatments. In addition, we do not employ time-consuming search techniques, nor do we set the values of any parameter by recourse to theory or arbitrary choice. Instead, in a single step for each molecule, we simply use matrix algebra to generate all of the elements of the Hamiltonian matrix on the bond orbital basis. This leads, via an averaging process, to a set of parameters which can be used in further calculations to correlate ionization potentials. As will be seen, the process is very efficient and gives excellent results.

The starting point for the calculation is the set of topological symmetry-adapted eigenvectors ordered as obtained in the previous section, and a knowledge of the eigenvalues of the Hamiltonian matrix. These eigenvalues are taken as the negative of the experimental ionization potentials from the PES. We carry out a similarity transform by the matrix of the eigenvectors on the diagonal matrix of the ionization potentials, according to

$$H^b = T[IPs]\tilde{T} \quad (1)$$

This reverse transformation generates a completely parametrized Hamiltonian matrix for each molecule. The eigenvalues of each molecular H^b matrix are required to be numerically identical with the respective ionization potentials.

Examination of the elements of the H^b matrices for transferability²⁹ shows that there is a correspondence where elements in two different molecular matrices refer to the same kind of bond-bond interaction or diagonal Coulomb-type bond term. The results are quite similar to those obtained in studies

Table I. Parameters for Bond Orbital Calculations

Matrix element	Description	Value, eV
α_1 (CH)	Diagonal term	-16.03
α_2 (CC)	Diagonal term	-16.11
β_1 (CH-CH)	Geminal interaction	-2.29
β_2 (CH-CC)	Geminal interaction	-2.02
β_3 (CC-CC)	Geminal interaction	-1.77
γ_1 (CH-CH)	Vicinal gauche interaction	-0.63
γ_2 (CH-CH)	Vicinal trans interaction	+1.01
γ_3 (CH-CC)	Vicinal gauche interaction	-0.44
γ_4 (CH-CC)	Vicinal trans interaction	+0.66
δ_1 (CH-CH)	1,4 interaction (w type)	-0.54
δ_2 (CH-CH)	1,4 interaction (cis)	-0.12
δ_3 (CH-CH)	1,4 interaction (skew)	+0.07

of transferability of ab initio Fock matrix elements over localized orbitals.^{30,31} In analogy to that work, we then use the mean values of matrix elements for similar environments to construct a set of parameters for this bond orbital method.

Diagonalization of the parametrized bond orbital matrix B for each molecule gives eigenvalues $\lambda(B)$ that differ from the experimental ionization potentials by small amounts. A new set of eigenvectors is also obtained for each system, according to

$$\tilde{T}|B|T = \lambda(B) \quad (2)$$

Another similarity transform by the eigenvectors of B on the IPs gives a new completely parametrized effective Hamiltonian matrix for each molecule. A second set of bond orbital parameters is obtained according to the averaging algorithm as outlined above. Several cycles through eq 1 and 2 lead to final parameters that give a minimum value for the absolute value of the sum of the deviations of experimental and calculated ionization potentials.

The parameters, obtained after 29 iterations (94 s, IBM 360-65), are listed in Table I. We chose to make the initial test of the procedure using what we consider to be the minimum number of parameters based on bond type. Thus, in this group, primary, secondary, and tertiary bonds are not distinguished, since each molecule would have at least one unique parameter if dissections of this type were to be made.

Table II gives the calculated and experimental ionization potentials. The number of nodal regions and the symmetries assigned are deduced from an examination of the coefficients of the eigenvectors. A plot of the IPs is given in Figure 4. The theory-experiment line has unit slope, and the correlation coefficient of calculated and experiment values is 0.9995. The average deviation is ± 0.1 eV, of the order of the estimates of experimental error.

IV. Discussion

The topological analysis which is used to obtain the zero-order orbitals of the saturated hydrocarbons has several advantages. The computations are simple, and nonobservable parameters are largely avoided. The employment of these topological functions as first approximations to bond orbitals is a first step in developing a perturbational MO theory for saturated systems. The reverse transformation, eq 1, using the experimental ionization potentials to find transferable parameters, constitutes a use of first-order perturbation theory in this context. The iterative procedure is novel, but it is so much faster and easier to apply than previous computer search methods that we do not believe extended comments are necessary. However, this section does contain several explicatory remarks regarding the ionization potential calculations, and finally, some brief statements on potential applications to other systems.

Table II. Ionization Potentials of Methylmethanes

Compd	Symmetry species	Nodal regions	IPs, eV calcd	IPs, eV PES ^a
Methane	1 t ₂	2	13.73	14.0
	2 a ₁	1	22.90	22.9
Ethane	1 e _g	4	12.09	12.1
	3 a _{1g}	3	12.99	13.0
	1 e _u	2	15.38	15.4
	2 a _{2u}	2	20.37	20.4
	2 a _{1g}	1	23.96	23.9
Propane	2 b ₂	6	11.50	11.5
	6 a ₁	3	12.08	12.1
	4 b ₁	4	12.13	12.5
	1 a ₂	4	13.54	13.5
	3 b ₁	4	13.98	14.1
	5 a ₁	3	15.22	15.3
	1 b ₂	2	16.16	16.0
	4 a ₁	2	19.39	19.4
	2 b ₁	2	21.97	22.1
	3 a ₁	1	24.44	24.5
Isobutane	6 a ₁	3	11.40	11.2
	5 e	4	11.84	11.8
	1 a ₂	6	12.94	12.8
	4 e	4	13.62	13.4
	3 e	4	14.98	14.9
	5 a ₁	2	16.04	16.0
	4 a ₁	2	18.54	18.4
	2 e	2	21.98	21.9
	3 a ₁	1	24.80	24.8
	Neopentane	4 t ₂	4	11.61
1 t ₁		8	12.94	12.7
1 e		3	14.15	14.1
3 t ₂		3	15.47	15.4
4 a ₁		2	17.32	17.6
2 t ₂		2	21.99	21.9
3 a ₁		1	25.08	25.1

^a References 14, 17, and 32.

Choice of Experimental Data. The PES of saturated hydrocarbons are characteristically diffuse, and the vertical IPs are difficult to establish. In methane³² the band due to the triply degenerate Jahn-Teller ²T state of CH₄⁺ extends from 12.6 to 16.0 eV. The band is asymmetric in shape, and 14.0 eV (Table II) corresponds to the line which divides the band area equally. The other values in Table II generally correspond to band maxima. For consistency, all IPs below 20 eV came largely from the work of Murrell and Schmidt,¹⁴ and all values above 20 eV were taken from Potts and Streets.¹⁷ In agreement with others, we deduce that the shoulder in the propane spectrum, 12.7 eV according to Murrell and Schmidt, should be located at 12.5 eV,¹¹ and the first band in the isobutane spectrum is taken as the maximum of an a₁ type band (11.2 eV), with the second band an e-type Jahn-Teller doublet with a center at 11.8 eV.¹⁶

Assignment of the Irreducible Representations. The accurate use of the similarity transform, eq 1, requires that an accurate assignment of the symmetry-adapted eigenvectors be made for each experimental IP. Many of the orbitals can be assigned without ambiguity according to their nodal characteristics. This includes all of the orbitals for methane and ethane, all of the inner valence orbitals for the remaining molecules, and one or two of the outer valence orbitals in each set. The remaining assignments in the outer valence set were made by assuming that the more delocalized an orbital, the lower its energy, and that the splittings between orbitals of the same symmetry classification would be symmetrical, above and below those orbitals with nonrepeated irreducible representations.

The higher orbital sequences for ethane (... [3 a_{1g}][1 e_g]), propane (... [4 b₁][6 a₁][2 b₂]), and isobutane (... [5 e][6 a₁]) given by these qualitative rules are inverted from assignments

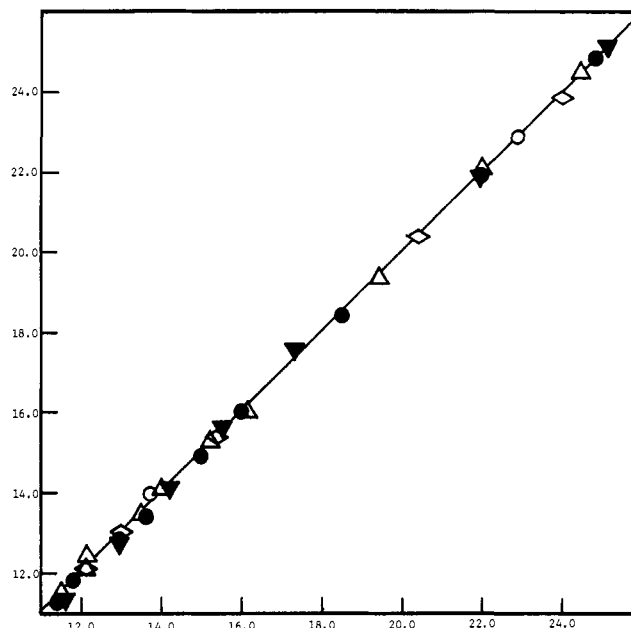


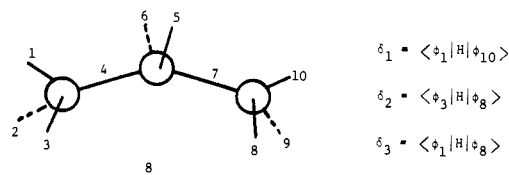
Figure 4. Ionization potentials (eV) for saturated hydrocarbons: methane, O; ethane, ◇; propane, Δ; isobutane, ●; neopentane, ▼. Horizontal axis, calculated; vertical axis, experimental.

made by Murrell and Schmidt.¹⁴ In essence, they find that the highest filled molecular orbitals are predominantly associated with C-C bond character, whereas our calculations lead to the conclusion that the first IP involves C-H bonding electrons for all five molecules. Experimentally, for ethane, studies of the vibrational splitting of the first Rydberg band³³ and a very thorough analysis of Jahn-Teller splitting in the PES³⁴ leave no doubt that the highest MO is a doubly degenerate e_g orbital. The other cases are not so clear-cut, but our assignments are in agreement with most semiempirical³⁵ and ab initio^{36,37} calculations and with comparisons of experimental PES of alkyl iodides and alkanes.¹⁶

It is interesting and important to note that an initial incorrect assignment of symmetry does not have any effect upon the final results obtained using our procedures. For example, if one chooses the orbital sequence for isobutane, 5 e above 6 a₁ for the two highest filled orbitals, this orbital sequence is inverted after the very first reverse transformation and averaging of matrix elements. Evidently, the internal consistency of this large set of ionization potentials is high, and incorrect assumptions are rectified during the iterative process. This observation, coupled with the excellent correlation of the eigenvalues and IPs, strongly supports the assignments listed in Table II.

Parameters. The choice of parameters has already been discussed. In general, the magnitudes determined in this work are similar to those previously reported.¹¹⁻¹⁷ The positive signs for the trans 1,3 interactions are understandable in terms of the Slater overlap integrals for hybrid bond orbitals. Pople and Santry³⁸ have shown that these integrals are negative, leading to a positive interaction term if one assumes the usual negative dependence on overlap.

Earlier work^{11,14} neglected the long-range interactions δ_1 , δ_2 , and δ_3 , defined for propane in **8**. Consequently, this neglect



was compensated for automatically by an increase in the magnitude of other interactions. Except for δ_1 , the values of these integrals are small and may not be significant. However, some type of 1,4 interaction must be introduced; otherwise, certain accidental degeneracies in isobutane (1 a₂ and 4 e) and neopentane (1 t₁ and 1 e) cannot be lifted. The inclusion of a single parameter δ_1 resolves this difficulty.

Eigenvectors of Topological and Bond Orbitals. The coefficients of the eigenvectors of the starting topological orbitals only differ by small amounts (usually less than 10%) from the final bond orbital coefficients (see paragraph at end of paper regarding supplementary material). Also, we remarked previously on the close correspondence of the topological functions to those obtained by Jorgensen and Salem²⁶ using the LCAO-MO method. This significant result indicates that the molecular connectedness is the main factor determining the molecular wave function, at least for these saturated hydrocarbons.

Applications. We plan to extend the calculations on saturated hydrocarbons to larger acyclic and cyclic alkanes. Calculations on substituted saturated compounds are being carried out, and questions regarding through-bond or through-space interactions between heteroatom or unsaturated moieties are under investigation.

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Supplementary Material Available: Listings of topological eigenvector coefficients and the bond orbital wave functions for methane, ethane, propane, isobutane, and neopentane (9 pages). Ordering information is given on any current masthead page.

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Ionization Potentials of H₂O from Valence Bond and Molecular Orbital Wave Functions¹

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Abstract: A comparison is presented of the H₂O ionization potentials calculated from molecular orbital wave functions using Koopmans' theorem with those calculated from valence bond wave functions using the extended Koopmans' theorem. It is found that the two methods give closely comparable results for the main peaks in the photoelectron spectrum. In addition, the valence bond calculation predicts two additional weak, closely spaced, shake up states which may correspond to a previously unassigned feature near 48 eV in the experimental photoionization spectrum.

I. Introduction

The recent revival of the valence bond (VB) model, both in its traditional form² and in various self-consistent-field (SCF) versions either with³ or without^{4,5} artificial orthogonality constraints, has provided a useful alternative to the molecular orbital (MO) model for the interpretation of many

molecular properties from ab initio calculations. However, ionization potentials, which are easily obtained from MO wave functions by means of Koopmans' theorem,⁶ have not hitherto been obtained as directly from VB calculations. The recently proposed extended Koopmans' theorem⁷ (EKT) appears to provide a simple and appealing procedure to extract ionization