BioChem Press

Inter*net* Electronic Journal of
𝔐𝔬𝔩𝔢𝔠𝔲𝔩𝔞𝔯 𝔇𝔢𝔰𝔦𝔤𝔫

Graph Theoretically Formulated Electronic–Structure Theory

Douglas J. Klein

Texas A & M University at Galveston, Galveston, Texas 77553, USA

Citation of the article:
D. J. Klein, Graph Theoretically Formulated Electronic–Structure Theory, *Internet Electron. J. Mol. Des.* **2003**, *2*, 814–834, http://www.biochempress.com.

Graph Theoretically Formulated Electronic–Structure Theory[#]

Douglas J. Klein*

Texas A & M University at Galveston, Galveston, Texas 77553, USA

Abstract

Possibilities are indicated for purely graph–theoretically defined model Hamiltonians for molecular electronic structure. It is emphasized that many of the models so described are chemically interesting, go substantively beyond the Hückel model, and are yet little explored from a mathematical point of view. Thence it seems that a rich diversity of further chemical graph–theoretic work awaits. It is noted for several models that there is a possibility of some theorems reminiscent of those for the Hückel model, and that wave–function *ansätze* for the eigenstates of these "refined" graph–theoretic models often naturally lead to novel graph invariants, which are mathematically little explored.

Keywords. Graph theory; Hückel model; quantum chemistry.

1 Historical Perspective and Nenad Trinajstić

In the early 1970s research in chemical graph theory rapidly developed, with a motivational recognition that formal mathematical graph theory makes especially close contact with chemistry. Indeed the mathematical field of "graph theory" apparently drew its name from chemistry when Sylvester [1] in 1878 became infatuated by molecular structural formulas then often termed "graphical formulas". Utilization of the connection languished for some time, so that often such a connection was not mentioned either in chemistry or graph theory texts. In any event Nenad Trinajstić was one of the researchers central to the reinvigoration of chemical graph–theoretical work in the 1970s. As a result there was a tremendous out–pouring of chemical graph–theoretic research. Nenad was interested cosmopolitanly in all of chemical graph theory, publishing a seminal book [2] in the field. He has worked on reframing Hückel theory, on enumerating molecular isomers, on enumerating resonance–theoretic quantities, on making graph–structure/property correlations, and similarly on making graph–structure/bio–activity correlations (QSAR), as well as

---

[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.
* Correspondence author; E–mail: kleind@tamug.edu.

numerous other chemical applications of graph theory. Indeed he has exhibited a very wide range of interests beyond chemical graph theory, with others including mathematical chemistry, the philosophy and history of science (particularly as relevant to chemistry and to Croatia), and literature. But especially in chemical graph theory Nenad managed to interest many other people in the area, and he ended up collaborating with many.

One of the first areas of chemical graph theory attracting Nenad's interest at Zagreb concerned the idea of merging formal graph theoretic ideas to electronic structure theory, so that in fact already in 1977 the group at Zagreb published [3] the survey *Topological Approach to the Chemistry of Conjugated Molecules*. In fact, graph–theoretic electronic–structure models were a main topic which Nenad and I along with Milan Randić discussed at a Sanibel meeting about 1981. There I emphasized that the Pauling–Wheland Valence–Bond (VB) model [4] could be expressed purely graph theoretically in an elegant mathematical form making it the same [5] as the standard (isotropic spin–1/2) Heisenberg spin Hamiltonian. It was understood that thence there was a prospect of proving graph–theoretic theorems for this VB model, perhaps paralleling the many already noted results for the Hückel model, as discussed in [2]. Indeed, I already had in hand some such theorematic results, most of which eventually appeared [6]. Further, Nenad and I met again at Sanibel, and we collaborated on an article [7] emphasizing that though the so–called "Hubbard" model went qualitatively beyond the Hückel model in including explicit electron–electron interaction, it still was fundamentally graph theoretical, so that one might also attempt graphical theorematic results for the Hubbard model as well. With this additional pair interaction though the problem seems to become more difficult, and various results which have been established [2,8,9] have been comparatively limited. Since then Nenad and I have continued our interest in novel electronic structure models expressed in a graph–theoretic framework. Later another collaborative work [10] developed a "Simpson–Herndon" model Hamiltonian, which is defined on a space of orthogonal Kekulé structures, and which gives rise to the conjugated–circuits resonance energy, of Herndon [11] and of Randić [12].

2 Preview

Thence it seems appropriate here to look further at the range of graph–theoretically formulatable models for molecular electronic structure, it being understood that the graph–theoretic relation offers promise of direct connection to classical chemical–bonding ideas. Or further one may view such models as various sorts of intermediates between the quantitative quantum–mechanical Schrödinger equation and classical chemical bonding ideas. It may be emphasized that here "model" is taken to entail an *effective Hamiltonian*, whose eigenvalue spectrum is to correlate to molecular energies, and whose eigenvectors are to correspond to molecular electronic structure. A molecular *graph* is denoted by G, which most simply is that of the π–network of a conjugated

hydrocarbon. Typically the number of vertices (or sites) of *G* is denoted by *N*, and the edges of *G* are between neighbor (bonded) pairs of sites. Here an attempt is made to make a relatively comprehensive identification of the various purely graph–theoretic models available for molecular graphs, with the focus primarily on the mathematical formulation of the models. Much of the discussion is framed in terms of conjugated π–networks, though especially later here there is attention to more general circumstances.

3 Simple Hückel MO Model

The most prominent example of a graph theoretically framed model Hamiltonian is that early on described by Hückel [13] for conjugated π–networks. Here the 1–electron Hamiltonian matrix is essentially just the graph–theoretic adjacency matrix A of the molecular π–network graph *G*, with matrix elements:

$$A_{ij} \equiv \begin{cases} 1, & i \sim j \\ 0, & \text{otherwise} \end{cases}$$

where *i* and *j* are sites of *G* and *i*~*j* indicates that *i* and *j* are neighbors in *G*. Significantly the model is relatively easy to numerically solve (just entailing the diagonalization of the *N*×*N* matrix *A*), and further there has been an immense amount of characterization of *A* in both the chemical and mathematical literature, so that we do not even attempt a listing of original results. A nice concise chemical graph–theoretic book [3] reviews this subject, while Nenad's broader book [2] devotes some space to this also. The chemical literature is enormous, there probably being more than a dozen other more chemically oriented works focused on the Hückel model, and also a few other books viewing it from a chemical graph–theoretic perspective. One recent book covering mathematical results fairly thoroughly (along with some chemical results deemed to be of a mathematical nature) is the up–dated edition of Cvetković, Doob, and Sachs [14].

An alternative so–called "second–quantized" way to represent the Hückel model may be mentioned, first because of its elegance and second because this sort of representation is especially convenient for several other models (which even may be purely graph–theoretic). This representation uses Fermion creation and annihilation operators $a_{i\sigma}^{+}$ and $a_{i\sigma}$ which create (if not already present) and annihilate (if already present) an orbital occupancy for a spin–σ electron at site *i*. Then the (many–electron) Hückel Hamiltonian is:

$$H_{\text{HMO}} = \sum_{i \sim j}^{G} \sum_{\sigma} (a_{i\sigma}^{+} a_{j\sigma} + a_{j\sigma}^{+} a_{i\sigma})$$

where the *i*~*j* sum is over neighbor pairs (*i.e.*, edges) of G, and the σ–sum is over spins (↑ and ↓). Here the operator $a_{i\sigma}^{+} a_{j\sigma}$ evidently simply moves a σ–spin electron from site *j* to site *i*. This model has not only 1–electron eigenfunctions, but also many–electron eigenfunctions, which are just

(antisymmetrized) products of the 1–electron functions. The eigenvalues of H_{HMO} are just corresponding sums of those of A.

4 Simple Covalent–Space VB Model

Another important early example of a graph theoretically framed model Hamiltonian is the covalent–space *valence–bond* (or *VB*) model of Pauling and Wheland [4] for neutral conjugated π–networks. Though again the model is specified by the graph, there has been little study of it in the mathematical literature. However there has been extensive study in the physics literature, traditionally viewed as describing the magnetic character of inorganic networks, and called the (isotropic spin–1/2) Heisenberg model. This model is conveniently defined on a 2^N–dimensional space of N–fold spin products $\sigma_1 \times \sigma_2 \times \sigma_3 \times ... \times \sigma_N$, with each $\sigma_i = \pm 1$ and N the number of sites of the molecular graph G. For each site i there are site–spin operators s_i^x, s_i^y, s_i^z, in terms of which the model Hamiltonian may be presented as

$$H_{\text{VB}} = \sum_{i \sim j}^{G} 2\vec{s}_i \cdot \vec{s}_j$$

If one wishes to avoid these spin operators (with preference to permutations), it may be noted that $2\vec{s}_i \cdot \vec{s}_j + 1/2 \equiv (ij)_{spin}$ may be viewed as the operator which transposes spins σ_i and σ_j. Though the model is purely graph–theoretic, an exact solution is generally a challenge, with the possibility of the need to diagonalize a matrix with dimension increasing exponentially with system size, so that Pauling and Wheland [5] advocated as a reasonable simplifying ground–state approximation: the diagonalization in a sub–space of dominant resonance structures, often the so–called Kekulé structures with nearest–neighbor pairings only (in which case we might interpret this restriction to be a new model $H_{\text{P-W-ResTh}}$). Rather amusingly the fairly extensive physics literature before the mid–1980s seldom made reference to Pauling and Wheland [4] or to the associated resonance–theoretic ideas they advocated. Indeed the solid–state solution techniques *via* Neel states, or Neel–state perturbation theory, or antiferromagnetic spin waves were so different than Pauling and Wheland's ideas about resonance that one might wonder whether they were dealing with the same model. As it turns out the two different approaches are most [15] adequate for rather different structural circumstances:

(*a*) Neel–state based approaches work best for bipartite (or alternant) graphs with higher vertex degrees (>3), such as occur for many of the studied solid–state species in physics; and

(*b*) resonance–theoretic based approaches work best for graphs G with low vertex degrees (≤ 3) and with G having many Kekulé structures, such as for the more stable benzenoids of chemistry.

And yet further it was emphasized first by Hartmann [16] and then especially by Malrieu and Maynau [17] that the Neel–state based ideas even worked fairly well for (alternant) chemical

species. Reviews [18] of work relating to this model are found in a recent general overview of VB theory, and a comparable number of reviews mostly by different authors are found in an earlier book [19] (with Nenad as co–editor).

5 Spin–Free VB Model

The covalent–space VB model may be represented in other manners, which may seem more natural to a graph theoretician. In a "spin–free" representation one may presume a basis $\varphi_{i_1}(1) \times \varphi_{i_2}(2) \times ... \times \varphi_{i_N}(N)$, with $\varphi_i(a)$ being an orbital for electron a at a site i, these orbitals most conveniently being identified as orthonormal. Then a simplest graph–theoretic Hamiltonian may be represented as

$$H_{\text{sf-Heis}} = -\sum_{i \sim j}^{G} (ij)$$

where the (*ij*) are transposition permutations for the (spin–free) orbital indices. Evidently there are $N!$ ways of permuting electrons around amongst the N different π–centers, so that this gives an $N! \times N!$ matrix representation, which may be blocked according to the symmetries of the symmetric group of permutations on the electron coordinates. The eigenvalues associated to the relevant symmetric–group symmetries are shifted by $N/2$ from those of H_{VB} above, and have different degeneracies. *E.g.*, these correspondences have been discussed [20,21]. In fact the spin–free representation is essentially that as originally given by Heisenberg [22], with the representation as in H_{VB} above being due to Dirac [23] and the utility of Dirac's representation being elucidated (and thereby promulgated) by Van Vleck [24]. The representation of Pauling and Wheland [4] was yet different than either as in H_{VB} or $H_{\text{sf-Heis}}$ above.

6 Free–Electron Model

Another interesting purely graph–theoretic model developed most seriously in the decade around 1950 is the so–called *free–electron* model, again originally formulated for conjugated π–networks. This entails one–dimensional unit–length line segments between adjacent vertices, with the line segments joined at the vertices. Then on this piecewise 1–dimensional network one takes the model Hamiltonian to be the Schrödinger equation for non–interacting electrons. That is the Hamiltonian up to proportionality is just

$$H_{\text{free-e}} = -\sum_{i \sim j}^{G} \frac{\partial^2}{\partial x_{ij}^2}$$

with x_{ij} the length along the line segment between adjacent sites i and j. Further there is a question of boundary conditions: one typically demands solutions vanishing at degree–1 vertices, and at

higher degree vertices there is continuity and a condition on derivative sums for the solutions on the incident line segments. Though very simple and elegant with many of the same features as the simple Hückel model, this free–electron model has been relatively little studied in chemistry in recent years, though earlier there was a fair amount of interest in the model. See *e.g.*, Platt's group's reprint collection [25]. The solution of the model is reduced to the diagonalization of an $N \times N$ matrix much like the adjacency matrix (*i.e.*, more like the Laplacian matrix), so that it seems that many deemed the model to be a sort of Hückel–like. Sometimes this model has been termed the "chemical network model", though a better name in this regard would be "non–interacting–electron chemical–network model" or "free–electron chemical–network model".

7 Digression on Parametrics

The Hückel, the free–electron, and VB models are interesting in that they appear parameter–free, though to fit experimental spectra a multiplicative constant dependent on the units for measuring energy may be included. The constant for the Hückel model is in chemistry usually denoted as β (or sometimes t especially in physics). The constant for H_{VB} is denoted as J (or sometimes $-J$), and termed the exchange parameter. Sometimes the various models are shifted by an additive constant.

The graph–theoretic models to be described next here incorporate parameters beyond a simple scale factor, though these models still may be categorized as purely graph–theoretic. That is, the parameters can be introduced in a manner dependent solely on graph–theoretic information, *e.g.*, so that ground–state eigenvalues and eigenspectra may be viewed as graph invariants, possibly as a function of the parameters introduced. Many of these ensuing models have found interest for inorganic networks – to make the model purely graph–theoretic the sites are best viewed as all of the same chemical type of site.

8 Slightly Extended Hückel Model

A simple parametric graph–theoretic model is just a slightly extended Hückel model. See, *e.g.*, Streitweiser [26] for a nice discussion. One may introduce an overlap matrix $I + sA$, with I the identity matrix, A the adjacency matrix, and s an "overlap" parameter. Then the model is defined *via* the generalized eigenvalue equation

$$\beta A \vec{c} = \varepsilon (I + sA) \vec{c}$$

with $\vec{c}$ the (column) eigenvector with eigenvalue ε. This model is well–known to have the same eigenvectors as A, with the eigenvalues ε given in terms of the corresponding eigenvalues λ of A as $\varepsilon = \beta \lambda /(1 + s\lambda)$. Then much of the theory for the simple Hückel model carries over to this slightly extended version.

A next higher order model which still is purely graph–theoretic uses a further generalized eigenvalue equation:

$$(\beta A + \beta' A')\vec{c} = \varepsilon(I + sA)\vec{c}$$

where A' is a next–neighbor matrix (*i.e.*, with non–zero elements A'_{ij}, all =1, for $i \sim\sim j$), and β' is a next–neighbor electron–transfer parameter. From a graph–theoretic view β' is a general parameter, though for chemical purposes the values of interest are when it is but a fraction of β (and further s is but a fraction of 1). Here the eigenvector $\vec{c}$ and eigen–energy ε are generally different than in the preceding generalized eigenvalue equation, and are not typically simply related to those of the usual simple Hückel model. More generally more distant electron–transfers and overlaps are incorporated, though usually in a geometry–dependent manner, even with s, β, and β' typically also geometry dependent, whence we do not term such a fully extended Hückel model to be purely graph theoretical.

9 Nonorthogonal–Orbital Covalent–Space VB Model

The covalent–space VB model may be somewhat analogously extended to include intersite overlap. That is, one may consider the atomic orbitals on the different centers to be non–orthogonal, most simply with the sole correction being an overlap of s between orbitals on adjacent sites. This model has seldom been written down in any elegant form. But we still might try, first for the overlap operator for a graph G',

$$S(G') \equiv I + \sum_{k \geq 1} s^{2k} \sum_{P}^{k-\text{edges}} P$$

where I is the identity, and the P sum is over all sets of k disjoint edges of G' with P being the corresponding k–fold transposition interchanging the pairs of sites in each of these edges. Then the Hamiltonian operator is

$$H_{\text{non-orth.VB}}(G) = J \sum_{i \sim j}^{G} (ij) S(G - \{i, j\})$$

where $G - \{i, j\}$ represents the graph obtained from G by deletion of sites i and j (and the edges incident thereon). The generalized eigen–problem to be considered is

$$H_{\text{non-orth.VB}}(G)|\Psi\rangle = E \cdot S(G)|\Psi\rangle$$

with $|\Psi\rangle$ the wave–function (or eigenfunction), and E the energy. This model underlies the ordinary VB model H_{VB} (or $H_{\text{sf–Heis}}$), as early emphasized by Van Vleck [27] with the derivation from one to the other historically engendering a good deal of confusion. This history and a relatively straightforward derivation (from $H_{\text{non–orth.VB}}$ to H_{VB}) may be found elsewhere [28]. There

have been rather few studies of this model on its own, one notable exception being in the work of Mulder and Oosterhoff [29] in their VB exposition of the Hückel rule and Woodward–Hoffmann rules, though in their (still graph–theoretic) model they include additional cyclic permutations. A significant point is that for greatest precision the orbitals should be "anti–orthogonalized" (so as to have more intersite overlap than bare atomic orbitals) – though there were several recognitions of this, by Mueller and Eyring [30, 31], by Wheland [32], and by Epiotis [33], the point seems not to have been generally well recognized till the seminal *ab initio* computation on benzene by Cooper *et al* [34], whence many *ab initio* VB works have followed [35].

10 Hubbard Model

An elegant purely graph–theoretic model with explicit electron–electron interaction is that of Hubbard [36] (who viewed it as a simple model interpolating between separated–atoms and metal). This model may be defined on a 4^N dimensional space with a basis of Slater determinants built from $2N$ orthonormal spin orbitals, one spin–up and one spin–down orbital for each site. That is, each site has either 0 electrons, 1 spin–up electron, 1 spin–down electron, or 2 electrons of opposite spins. Then with the use of Fermion creation and annihilation operators $a_{i\sigma}^{+}$ and $a_{i\sigma}$ for spin σ on site *i*, the Hamiltonian is concisely given as:

$$H_{\text{Hubbard}} = t \sum_{i \sim j}^{G} \sum_{\sigma} (a_{i\sigma}^{+} a_{j\sigma} + a_{j\sigma}^{+} a_{i\sigma}) + \gamma_0' \sum_{i}^{G} a_{i\alpha}^{+} a_{i\beta}^{+} a_{j\beta} a_{j\alpha}$$

where *t* and γ_0' are parameters (respectively, representing electron hopping and electron repulsion). Here the first *t*–term may be viewed just as a many–electron representation of the Hückel Hamiltonian, and the second γ_0'–term is a simple form for electron–electron repulsion. For *t*=0 one obtains a simple model for separated atoms, while instead with $\gamma_0' = 0$ one has a simple model for a metal. With the γ_0'–term, exact solutions become very challenging, and nice theorematic results seem even harder to come by than for the Heisenberg model, though we should mention results of Lieb [37] for the half–filled case, as is of interest for neutral conjugated π–network hydrocarbons. The Hubbard model is especially popular in some more theoretically oriented areas of solid–state physics.

11 Hubbard/PPP and PPP/Hubbard Models

Yet two more related graph–theoretic models are what we term the Hubbard/PPP and PPP/Hubbard models. These are intermediate between the Hubbard model and a full geometry–dependent PPP model [38,39] which would then supercede graph theory. These models are all defined on the same space as the Hubbard model, and the resultant Hamiltonians are again neatly

expressible in terms of Fermion creation and annihilation operators. The Hamiltonians contain terms like those of the Hubbard model with an additional one or two terms,

$$H_{\text{Hubbard/PPP}} = t\sum_{i\sim j}^{G}\sum_{\sigma}(a_{i\sigma}^{+}a_{j\sigma} + a_{j\sigma}^{+}a_{i\sigma}) + \gamma_{0}''\sum_{i}^{G}a_{i\alpha}^{+}a_{i\beta}^{+}a_{j\beta}a_{j\alpha} + \gamma_{1}''\sum_{i\sim j}^{G}(1-n_{i})(1-n_{j})$$

$$H_{\text{PPP/Hubbard}} = t\sum_{i\sim j}^{G}\sum_{\sigma}(a_{i\sigma}^{+}a_{j\sigma} + a_{j\sigma}^{+}a_{i\sigma}) + \gamma_{0}'''\sum_{i}^{G}a_{i\alpha}^{+}a_{i\beta}^{+}a_{j\beta}a_{j\alpha} + \gamma_{1}'''\sum_{i\sim j}^{G}(1-n_{i})(1-n_{j}) + \gamma_{2}'''\sum_{i\sim\sim j}^{G}(1-n_{i})(1-n_{j})$$

where $n_{i} \equiv a_{i\alpha}^{+}a_{i\alpha} + a_{i\beta}^{+}a_{i\beta}$ is a number operator, the $i\sim\sim j$ sum is over next–nearest neighbor pairs of sites in G, and γ_{m}'' and γ_{m}''' are additional parameters, having to do with Coulombic interactions between nearest–neighbor and next–nearest neighbor pairs of sites. The appropriate values of γ_{m}', γ_{m}'', and γ_{m}''' to use in the Hubbard, Hubbard/PPP, and PPP/Hubbard models are different, since they appropriately measure [40,41] nearer electron–electron interactions relative to the first neglected inter–site Coulomb interactions. That is, if γ_{m} denotes the typical mth neighbor interaction (asymptotically usually taken to be of the Coulombic form e^{2}/r_{m}) for the full PPP model, then $\gamma_{0}' \cong \gamma_{0} - \gamma_{1}$, $\gamma_{0}'' \cong \gamma_{0} - \gamma_{2}$, $\gamma_{1}'' \cong \gamma_{1} - \gamma_{2}$, $\gamma_{0}''' \cong \gamma_{0} - \gamma_{3}$, $\gamma_{1}''' \cong \gamma_{1} - \gamma_{3}$, and $\gamma_{2}''' \cong \gamma_{2} - \gamma_{3}$. These models seem to be even more difficult to treat than the Hubbard model. Perhaps the bulk of the applications of these various models (Hubbard/PPP) have been by way of SCF solutions, which of course are just a (well–defined) approximation. But we emphasize the graph–theoretic nature, such as does not occur for the usual full Parisier–Parr–Pople (PPP) model which contains Coulombic interactions between every pair of sites at particular geometric locations. The point is that usually the interaction parameter γ_{ij} between vertices i and j is taken to depend (beyond graph theory) on the geometric distance between vertices i and j. In the Hubbard/PPP and PPP/Hubbard models above we have chosen the various Coulombic interaction strengths to depend solely upon the (shortest–path) graph–theoretic distances d_{ij} between pairs of sites i and j. Especially for the nearest and next–nearest–neighbor cases the geometric distances are reasonably correlated with the graph–theoretic distances, at least in benzenoids. In principle one could introduce yet further distant Coulombic interaction terms still depending solely upon graph–theoretic distance. There are several texts making significant discussion of the PPP model (and particularly its SCF solutions) from a quantum–chemical viewpoint. One nice discussion and reprint collection is that of Parr [42].

12 tJ and tJV Models

There also are VB graph–theoretic models applicable for ions of conjugated π–networks. Such models are conveniently expressed on a basis of atomic configurations of minimal ionicity, here viewed as (±) the number of sites with other than a single π–electron. Thence there is a charge–transfer matrix element t for moving an electron around, while not changing the ionicity. And further there may be a matrix element V for the Coulomb interaction of two adjacent charged sites,

and in fact one might incorporate even further distant Coulomb interactions, though beyond next–nearest neighbors, geometry conventionally becomes relevant (thereby superceding ordinary graph theory). Such models may be neatly represented in terms of creation and annihilation operators thusly

$$H_{tJ} = t \sum_{i\sim j}^{G} \sum_{\sigma} (a_{i\sigma}^{+} a_{j\sigma} n_{j\bar{\sigma}} h_{i\bar{\sigma}} + a_{j\sigma}^{+} a_{i\sigma} n_{i\bar{\sigma}} h_{j\bar{\sigma}}) + J \sum_{i\sim j}^{G} 2 \vec{s}_i \cdot \vec{s}_j + V \sum_{i\sim j}^{G} (1-n_i)(1-n_j)$$

where for the case with electrons fewer in number than the sites, $n_{i\tau} \equiv a_{i\tau}^{+} a_{j\tau}$ and $h_{j\tau} \equiv a_{j\tau} a_{j\tau}^{+} = 1 - n_{j\tau}$ are "particle" and "hole" projection operators, and $n_i \equiv n_{i\alpha} + n_{i\beta}$. When the number of electrons exceeds the number of sites, then the occurrences of $n_{i\tau}$ and $h_{i\tau}$ in the t–term are interchanged. This model was formulated [43] without the *V*–term, though the *t*–part of this model was earlier considered by Fisher and Murrell [44], where it was noted that cycles with 4*n*–electron cycles prefer triplet spin multiplicity while 4*n*+2–electron cycles prefer singlet spin multiplicity (when the number of electrons and sites are different). The model without the *V*–term has been much studied in the physics literature in recent years, under the name of the *tJ* model – see, *e.g.*, a relevant review [45] (on the theory of high–T superconductivity). The inclusion of the nearest neighbor Coulomb interaction *V* has been suggested by Schlottmann [46]. Without the *V*–term this may be viewed as a VB analogue of the Hubbard model, while with the *V*–term it may be viewed as a VB analogue of the Hubbard/PPP model *H*Hubbard–PPP, and if a next–nearest neighbor Coulomb term were added one would obtain a VB analogue of the PPP/Hubbard model.

13 Simpson–Herndon Model

The Simpson–Herndon model is also purely graph–theoretic. It is defined on a space of neighbor–paired resonance structures, also called Kekulé structures. For this model the Kekulé structures are taken as orthonormal. The Hamiltonian involves operators $\Lambda_{C,d}$ and Λ_C for a cycle *C* in *G* such that in application to a Kekulé–structure state $|\kappa)$ they give 0 if the Kekulé structure κ does not exhibit conjugation around *C*. When such a $|\kappa)$ does exhibit conjugation around *C*, these operators give back a Kekulé structure which is the same as $|\kappa)$ except possibly on the *C* portion of *G*: $\Lambda_{C,d}|\kappa) = |\kappa)$ and $\Lambda_C|\kappa)$ give the same result except that in $\Lambda_C|\kappa)$ the pattern of conjugation around *C* is reversed. It can be proved [47] that for benzenoid structures only conjugated circuits of sizes 4*n*+2 occur. Then the Simpson–Herndon model may be written as:

$$H_{\text{S-H}} = \sum_{C}^{6-\text{cycle}} (R_{1,o} \Lambda_C + R_{1,d} \Lambda_{C,d}) + R_2 \sum_{C}^{10-\text{cycle}} \Lambda_C$$

where $R_{1,0}$, $R_{1,d}$, and R_2 are parameters, and the two sums are over cycles of *G* of the indicated sizes. In the earlier work of Simpson [48] and Herndon [11] the "diagonal" term $\Lambda_{C,d}$ was not considered

(*i.e.*, $R_{1,d} = 0$). But as later seen [10] from quantum–chemical derivation this extra term occurs, though with a simple ground–state wave–function *ansätz* this does not influence the overall form for the so–called "conjugated–circuits" resonance energy [11, 12]. The diagonal term makes some difference in higher order refinements for the ground–state energy, and likely it makes more important differences for excited states. Higher order terms for larger conjugated–circuits are also sometimes suggested [10,12], though the associated parameters are smaller. Some review of the field has in fact been made by Nenad and co–workers [49,50], and also see other reviews [51,52].

14 Herndon–Hosoya Model

Another possibility for graph–theoretic models is to define them on an even smaller space, of so–called "Clar structures". A Clar structure S of G is a spanning subgraph consisting of 6–cycles and isolated edges, such that no triple of edges of S circumscribe a 6–cycle of G. That is, each S may be constructed from a Kekulé structure κ by identifying different conjugated 6–circuits (identified as triples of edges spanning a 6–cycle of G) in κ, and replacing disjoint ones by 6–cycles till no conjugated 6–circuits remain. (When two conjugated 6–circuits of κ occur in adjacent hexagons, then only one becomes replaced by a 6–cycle, so that one κ may give rise to more than one Clar structure γ. Also evidently one γ with m 6–cycles results from 2^m different Kekulé structures, each with different conjugation patterns around the m 6–cycles.) One might view each Clar–structure state as a linear combination of Kekulé states, each 6–cycle being resolvable into two patterns of edges around the 6–cycle. A first model Hamiltonian would then simply view a new model to be but a restriction of the Simpson–Herndon model to the sub–space of Clar structures. In this interpretation the Clar structures would be non–orthogonal to one another, though this non–orthogonal model seems so far to be completely uninvestigated. But a yet simpler form of model results if one considers orthonormal Clar–structure states $|\gamma)$, and one may imagine two simple operators $\Lambda(C)$ and $\Lambda(C;C')$ for C and C' being adjacent 6–cycles of G such that these operators act on $|\gamma)$ to give 0 unless $C \subseteq S$ whence $\Lambda(C)|\gamma) = |\gamma)$ and $\Lambda(C',C)|\gamma)$ gives back $|\gamma')$ with γ' the same 6–cycles as γ except having C' instead of C, whereas if no such γ' exists, the result is 0. Then a plausible Hamiltonian as first suggested by Herndon and Hosoya [53] is

$$H_{\text{Herndon-Hosoya}} = \alpha \sum_{C}^{6-cycles} \Lambda(C) + \beta \sum_{C \sim C'}^{6-cycles} \Lambda(C';C)$$

where α and β are parameters. Though the initial work is quite favorable, little further work has been done with this model. In chemical graph theory there has been much use of Clar structures (*sans* an explicit Hamiltonian model), and the success further recommends the exploration of such models. Randić gives a seminal review [52] on aromaticity with much focus on Clar structures, and this thence further supports the likely relevance of $H_{\text{Herndon–Hosoya}}$.

Notably this model may be viewed [28,53] as the "last" of a sequence of systematically related VB–based models:

$$... \succ H_{\text{nonorth.VB}} \succ H_{\text{VB}} \succ H_{\text{P-W-ResTh}} \succ H_{\text{S-H}} \succ H_{\text{nonorth-Clar-str}} \succ H_{\text{Herndon-Hosoya}}$$

and the manner of derivation from one to the other has been discussed [28]. Further relations to a sequence of MO–based models have also been indicated [54].

15 Interacting–Electron Chemical–Network Model

The free–electron model might be extended in a purely graph–theoretic manner to include electron–electron interaction. Here to retain a purely graph–theoretic framework, the trick is to invoke a meaningful electron–electron interaction which does not incorporate geometric information. Perhaps the simplest such interaction is a delta–function interaction $\delta(m,n)$ understood to be non–zero (and integrating to 1) only when the coordinates of electrons m and n are at the same position in the network. Then

$$H_{\text{int}-\text{network}} = -\kappa \sum_{i \sim j}^{G} \sum_{m} \frac{\partial^2}{\partial x_{ij}(m)^2} + \gamma \sum_{m<n} \delta(m,n)$$

where κ and γ are parameters, and $x_{ij}(m)$ is understood to refer to a position for the mth electron along the (i,j)th edge. This model seems both non–trivial to solve and little studied, though one might view it as related to the free–electron model $H_{\text{free}-\text{e}}$ in a manner analogous to the way in which the Hubbard model H_{Hubbard} is related to the simple Hückel model H_{HMO}. Of course one can imagine longer–range Coulomb repulsions, say falling off as a function of the distance measured along the bonds.

16 Multi–orbital Models

Especially in proceeding beyond conjugated π–networks the vertices of a graph might be naturally chosen to identify localized orbitals in place of individual atomic centers. That is, for saturated hydrocarbons one might identify 4 different tetrahedral hybrid orbitals to each carbon and 1 atomic orbital to each hydrogen. Thus letting M denote the molecular graph with A the set of atomic centers and B the set of bonds, one understands that $a \sim b$ for $a \in A$ and $b \in B$ means that bond b of M is incident on atom a of M. The graph G_+ then is defined with vertex set

$$V \equiv \{(a,b) | a \in A, b \in B, \& a \sim b\}$$

and an edge set E which is partitioned into intra–atomic and inter–atomic pieces E_{intra} and E_{inter} given as

$$E_{\text{intra}} \equiv \left\{ \{(a,b),(a,b')\} \Big| a \in A \ , b \in B \ , b' \in B \ , a \sim b \ , a \sim b' \ , \& \ b \neq b' \right\}$$

$$E_{\text{inter}} \equiv \left\{ \{(a,b),(a',b)\} \Big| a \in A \ , b \in B \ , a' \in A \ , a \sim b \ , a' \sim b \ , \& \ a \neq a' \right\}$$

Then (to describe such σ–bonded hydrocarbon systems) a very simple model Hamiltonian matrix which might be considered is a weighted adjacency matrix, with elements

$$(H_\sigma)_{(a,b),(a',b')} \equiv \begin{cases} \alpha & , \ \{(a,b),(a',b')\} \in E_{\text{intra}} \\ \beta & , \ \{(a,b),(a',b')\} \in E_{\text{inter}} \\ 0 & , \ \text{otherwise} \end{cases}$$

where α and β are parameters. From a quantum chemical perspective one might naturally invoke further parameters, with different β values for CC and CH bonds, though recommended [55] values are in fact quite similar (to <10%). Also different site energies for C and H atoms could be introduced. H–atom site energies may perhaps [56] be as great as $\approx 0.5|\beta|$ with reference to that for a C–atom, though others have used [57] a value as little as $\approx 0.2|\beta|$ Indeed with such additional parameters the model has been much studied by way of empirical computations, as has been reviewed [58]. Sometimes even then the result can be considered purely graph–theoretic, with different parameters associated with sites of different degrees. Here the above first–mentioned model is somewhat simplified, though one might hope for a degree of chemical relevance while also achieving a little greater mathematical simplicity, which might aid in the development of elegant mathematical (graph–theoretic) theorems. Of course, even further "decorations" could be entertained, *e.g.*, with electron–electron interactions introduced much as for the Hubbard or Hubbard/PPP models. And presumably even chemical–network versions of these models could be considered. Most of the work to date goes beyond graph theory to involve geometry–dependence, there being very extensive use of different sorts of multi–orbital models, typically described as various "extended Hückel" models and as various "NDO" models.

Deserving special attention is an article by Pople and Santry [59], who develop a model of the sort in the previous paragraph. In their 0–order model they take α=0 (in our above notation), noting that this amounts to an assumption that 2s and 2p orbitals are degenerate. But they also allow additional (smaller) secondary β–parameters between (a,b) and (a',b') orbitals for atomic centers a and a' which are bonded while $b \neq b'$. Further first–order perturbation–theoretic corrections to this 0–order model are obtained, to reveal a nice bond–energy additivity. The overall paper could be viewed as "chemical graph–theoretic" though the work pre–dates the growth of this field. Overall Pople and Santry's work [59] indicates that indeed there is much further graph–theoretic development that should be possible.

Another related sort of graph–theoretic model attends just to bond orbitals. There results something like a Hückel model for a what is sometimes called the "line graph" of the molecular graph. One could also include electron–electron interactions. But for neutral species the number of

electrons is double the number of (spin–free) orbitals, so that all that results is a single energy, which we do not here view as a model Hamiltonian. If on the other hand ionized species are considered then a non–trivial line–graph based model results, or alternatively the graph could represent local excitations of bond orbitals (to anti–bonding orbitals) with the adjacency matrix of this line graph representing the interactions between these local excitations. Albeit quite natural, this sort of modeling seems to have been little explored, though one may note the success found in Simpson's work [60,61,62]. This sort of model may be viewed as analogous to standard "molecular exciton theory" for molecular crystals (see, *e.g.*, Davydov [63]).

17 On–Site Interactions

On–site interactions lead to a purely graph–theoretic model if all sites are treated in the same way. For the Hückel, Hubbard, and Hubbard/PPP type models one may add an on–site 1–electron interaction. For the Hückel model this amounts to adding a scalar, say α, to every element of the diagonal of the adjacency matrix, whence the MO eigenvalues are all rather trivially shifted by α and the MO eigenvectors remain unchanged. For the Hubbard and PPP type models this amounts to adding $\alpha \sum_i n_i$ to the Hamiltonians, and this simply shifts all M–electron energies by αM and again leaves the (electron–number–conserving) eigenvectors unchanged. But note that these shifts are different for different numbers of electrons (even when M–electron energies are made up from the 1–electron Hückel MO energies), whence this can be important in understanding ionization energies.

For the chemical network models the on–site interactions are rather naturally represented by delta–function interactions $\alpha \sum_m \delta(i,m)$ at the sites i of G. For the free–electron case, this leads to relatively straightforward modifications (of boundary conditions at nodes) as was noted when such a model was proposed [64,65] for hetero–atom species with different on–site interactions for different hetero–atoms. But even for homo–atomic systems such on–site interactions are quite reasonable (treating the atoms as different than bonds), and though "uniform", this does not simply shift the energies. What this would do for the interacting chemical network model seems not to have been considered at all.

Much elaborated 1–electron–like models are also conceivable which in effect include electron–electron interaction. More explicitly one may imagine a discrete analog of the Hohenberg–Kohn theorem [66]. That is, one considers a range of Hubbard/PPP–type Hamiltonians with fixed t–term and fixed (purely graph–theoretic) 2–electron part but variable on–site 1–electron interactions. Letting H_0 be the fixed part, the Hamiltonians then to be considered are of the form

$$H(\vec{\alpha}) \equiv H(\alpha_1, \alpha_2, ..., \alpha_N) \equiv H_0 + \sum_i^G \alpha_i n_i$$

http://www.biochempress.com

(with the n_i site number operators as in the Hubbard/PPP–type models). The electron density for an arbitrary normalized wave–function (whether it be an eigenfunction or not) is $\rho_i \equiv \langle \Psi | n_i | \Psi \rangle \geq 0$ with $\sum_i \rho_i$ the total number of electrons. Then the considered analog of the Hohenberg–Kohn theorem would say that there exists a function $F(\vec{\rho})$ such that the ground–state energy is given as

$$E(\vec{\alpha}) = \frac{\min}{\vec{\rho}} \{ F(\vec{\rho}) + \vec{\alpha}^\dagger \vec{\rho} \}$$

where the superscript † indicates a transpose of a vector and $\vec{\alpha}^\dagger \vec{\rho} = \sum_i^G \alpha_i \rho_i$ gives the expectation over $\sum_i^G \alpha_i n_i$. Indeed this result for $E(\vec{\alpha})$ may be neatly proved closely following Levy's proof [67], dealing with the standard (geometry–dependent) Schrödinger equation. Of course for a purely graph–theoretic problem the α_i all are 0, but still the same function $F(\vec{\rho})$ applies. The real trick is to find this $F(\vec{\rho})$, or at least a reasonable approximation thereto. But *e.g.*, Kohn and Sham [68] indicate an approach to do this for the ordinary Schrödinger equation, with $1/r_{ij}$ electron–electron interaction. And also there has been much work since then on this consequent "density functional theory", even with many texts, *e.g.* by Parr and Yang [69]. Moreover, Schindlmayr and Godby [70] fact indicate some beginning toward the estimation of $F(\vec{\rho})$ for the Hubbard model. Thus one might surmise that there could be a comparable theory for graph models, say of the Hubbard/PPP type.

18 Hetero–Atomic Models

It is of general chemical interest to consider models with hetero–atoms. However these generally are not of a purely graph–theoretic nature though involving different atomic labels for different types of atoms. In some cases these may still be considered as purely graph–theoretic – most simply when all the atoms are the same (hetero–) atom. *E.g.*, one circumstance for this with all sites boron atoms is considered in a graph–theoretic framework by King and Rouvray [71, 72]. More generally the model remains purely graph–theoretic when each type of atom is associated to a different degree. That is, on–site interactions $\sum_i^G \alpha(d_i) n_i$ (with d_i the degree of site i and α a function, of these degrees) could be incorporated in the Hückel, slightly extended Hückel, Hubbard, Hubbard/PPP, or PPP/Hubbard models and still retain the purely graph–theoretic nature. When incorporated in the Hückel model with the site energy further dependent on the electron density at a site, the model is often termed [26] the ω model, though in a more general way this may be viewed as naught but an SCF approximation to a Hubbard–type model. Still these models are not addressed here in any detail. Many aspects of the general (non–graph–theoretic) case are discussed in more chemically oriented texts, as that of Streiweiser [26] on the Hückel MO side, while Epiotis [73] presents results on the VB side. Theorematic results of a somewhat graph–theoretic nature arise in Dewar and Dougherty's text [74].

19 Miscellaneous Models

Another possible graph–theoretic model is that of a higher spin Heisenberg spin Hamiltonian, which in its simplest form is "parameterless". These have notable application for describing the exchange coupling amongst high–spin atomic ions. In solid–state physics this is a traditional model for the study of magnetism, with G which often are simple crystal lattices. Further (especially in chemistry) there is increasing interest in high–spin molecules or ions in place of simple atomic ions, and of finite molecular clusters in place of crystal lattices. See, *e.g.*, Kahn's text [75] and a collection [76] of reviews.

There has also been notable activity especially in the physics literature on a variety of other "many–body" models, which are devised so as to be exactly soluble. These may involve higher spins on the sites of the system or have unusually strong next–neighbor interactions or some other artifice which happens to facilitate an exact solution. Often these models are not so well motivated as to potential chemical application, though likely some may describe suitable inorganic materials. An opening to the rather extensive literature is found in the clear review of Ovchinnikov *et al* [77].

20 Overview and Relation to Graph Invariants

It is seen that there are a great variety of purely graph theoretic chemically interesting electronic–structure models and that for many of these a systematic development has been little attempted. Beyond chemistry to mathematical graph theory, one may wonder why some of models should not be of fundamental interest. As a general conclusion it then seems that there awaits a great deal more of chemical graph theory which can be studied in this electronic–structure realm (aside from isomer enumeration, structure–property correlations, reaction–graph characterization, and related graph theory). True, some of the models seem significantly more intransigent than the simple Hückel model, especially when electron–electron interaction is allowed. But this intransigence may be but a signal of greater chemical relevance, and already there are several fundamental theorems for the exact solutions for some of these models. *E.g.*, for the simple VB model [6,78,79,80], and a few for the Hubbard model [7,8,9,37], some of which even extend further to the Hubbard/PPP or PPP/Hubbard models.

Exact but quite complicated "analytic" solutions are available for the Heisenberg [81] and Hubbard [82] models for both the linear chain and the simple cycle, though these seem not to be readily extendable either to other geometries or to the Hubbard/PPP or PPP/Hubbard models. Still there is a whole host of other models. Sometimes exact results (short of an exact solution) are even rather readily possible. For instance, an application of the Frobenius–Perron theorem (*e.g.*, as reviewed by Gantmacher [83]) rather readily leads to the result that for the Simpson–Herndon model the exact ground state consists of a positive linear combination of all the Kekulé structures.

Granted the representation in terms of Kekulé structures there are then theorems [84,85] describing a consequent long–range order. And likewise, for the Herndon–Hosoya model the exact ground state consists of a positive linear combination of all the Clar structures. These results should in turn lead to signs of selected ground–state expectation values for these models, all somewhat paralleling theorems [6,80] for signs of selected expectation values for the simple Heisenberg model as follow from a consideration of its representation on the spin–product basis. Of the various models without electron–electron interaction it is surmised that there is even more promise of various exact results. Thus it seems likely that much can be done as regards exact theorematic results for a great variety of purely graph–theoretic model Hamiltonians.

Beyond the theorematic results for exact solutions, theorems for various approximate solutions are conceivable. With purely graph–theoretic models, reasonable wave–function *ansätze* should be describable in a purely graph–theoretic manner. A fairly well–known example of this involves a suite of neat "particle–hole" theorems [86,87] for the "restricted Hartree–Fock" approximations for the Hubbard and Hubbard/PPP models. And for the simple covalent–space VB model there are neat results for various different approximate solutions, *e.g.*, as for the Néel–state and perturbative corrections thereto [16,17,88].

Novel graph invariants often may be associated with the different graph–theoretic models. The SCF Hartree–Fock ground–state energies for the Hubbard and PPP type models as discussed in the previous paragraph provide a simple such example. More generally a reasonable wave–function *ansätze* $|\Psi\rangle$, for the ground–state wave–function for any of the graph–theoretic models may be expected to give rise to interesting graph invariants $\langle\Psi|\Psi\rangle$, $\langle\Psi|H|\Psi\rangle$, and other expectation values. For instance for the Simpson–Herndon model already mentioned, a rather natural wave–function *ansatz* $|\Psi)$ is just a sum over all the Kekulé structures, in which case $(\Psi|\Psi)$ is the number of Kekulé structures and $\sum_{C}^{n-cyc}(\Psi|\Lambda_{C}|\Psi) = \sum_{C}^{n-cyc}(\Psi|\Lambda_{C,\mathrm{d}}|\Psi)$ (such as appear in $(\Psi|H|\Psi)$ is the overall conjugated n–circuit count K_n (*i.e.*, the number of conjugated n–circuits summed over all Kekulé structures). This leads [10,11] to the conjugated–circuits standard [11,12] resonance–energy expression.

Further *ansätze* with Kekulé–structure weights depending on the number of conjugated 6–circuits in each Kekulé structure have been investigated [89], and lead to further graph invariants. The weight choice $x^{\#(6,\kappa)}$ with $\#(6,\kappa)$ the number of conjugated 6–circuits in κ is size–consistent and leads to a conjugated–circuits polynomial also motivated otherwise [90]. Another *ansätze* takes weights which are products of edge weights for each edge in κ, and leads to exact solutions [91] in certain circumstances. In the context of the VB model there are various Néel–State–based energies and Kekulé–structure–based energies, thereby leading to novel graph invariants. Further there are several other models we have noted for which comparatively little seems to have been seriously attempted.

Indeed, it is intended in a future paper to address in a general manner approximate many–body graph–theoretic solutions for these models with electron–electron interaction. Such a general discussion for a general class of quasi–1–dimensional structures is presented elsewhere [92], and a discussion of a few such many–body solutions for the Heisenberg and Simpson–Herndon model has been indicated [93]. In any event there certainly seems much that can be done, especially for several of the very little studied models.

21 Conclusion and General Outlook

Evidently there are a great many purely graph–theoretic electronic–structure models, which though of fundamental relevance have been little studied graph theoretically. Some "extended Hückel" and "NDO" models are very widely used in "canned" packages with the underlying formulation going beyond graph theory, while other models with explicit electron–correlation have been less widely used. But both types are seen to have substantive purely graph–theoretic representations (though perhaps simplified). Of the chemical graph–theoretic work on electronic structure most of it is focused on the simple Hückel model, while a smaller portion attends to simple VB–based resonance–theoretic ideas (typically short of a model Hamiltonian). It seems that there is a substantive prospect for much new chemical graph theory. Indeed it is perhaps surprising that more of the plausible models have not been followed up to any great extent.

Further it may be surmised that there is an extended theory of "colored" graphs so as to correlate more completely with classical molecular structures. That is, one might define a *colored* or *chemical graph* as an ordinary graph with an additional "type labelling" or *coloring* for the vertices. For chemical relevance the different "types" or *colors* may be identified to different elements. Perhaps with no more than a dozen such atoms there results a description of the great bulk of organic chemistry, where such chemical graphs are most useful – correlating most closely with what is chemically realizable. Still these chemical graphs are rather modest (well–defined) extensions of ordinary graphs, so that much interesting mathematical theory might be surmised. That such is not only possible but likely is indicated in the systematics indicated in Dewar and Doughtery's text [74] on "Perturbed Molecular Orbital Theory". This is still far from geometry–dependence, and relatively little graph theoretically studied, though there seems to be a potential for a neat mathematical theory inter–relating classical valence theory and quantum–chemical molecular electronic structure.

Finally it may be argued that these possibilities for graph–theoretic models are not diminished by success of *ab–initio* quantum–chemical computation. As long ago emphasized by Coulson [94] such computations might like experimental observations be viewed as another means by which to generate numerical data, so that such reliable computations might be deemed "computer experiments", which need interpretation, rationalization, and understanding just as much as

traditional laboratory experiments. Thence the success of *ab initio* theory should in reality only provide more data to be handled by a simpler theory. At the same time with interest in ever larger nano–structures, where *ab initio* work becomes ever more demanding of computer time, there remains a need for simple models to deal not only qualitatively but also quantitatively (albeit approximately) with electronic structure. The overall outlook should please Nenad in indicating a large body of further relevant chemical graph theory to study.

Acknowledgment

22 REFERENCES

[1]   A. J. Sylvester, Am. J. Math. **1** (1878) 64.
[2]   N. Trinajstić, *Chemical Graph Theory* (CRC, Boca Raton, FL, 1983).
[3]   A. Graovac, I. Gutman, and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules* (Springer Verlag, Berlin, 1977).
[4]   L. Pauling and G. W. Wheland, J. Chem. Phys. **1** (1933) 362.
[5]   J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7** (1935) 167.
[6]   D. J. Klein, J. Chem. Phys. **77** (1982) 3098.
[7]   D. J. Klein and N. Trinajstić, J. Am. Chem. Soc. **106** (1984) 8050.
[8]   E. H. Lieb and D. C. Mattis, Phys. Rev. **125** (1962) 164.
[9]   S. Lee, J. Chem. Phys. **90** (1989) 2732.
[10]   D. J. Klein and N. Trinajstić, Pure and Appl. Chem. **61** (1989) 2107.
[11]   W. C. Herndon, Thermochimica Acta **8** (1974) 225.
[12]   M. Randić, Tetrahedron **33** (1977) 1905.
[13]   E. Hückel, Zeit. Physik **60** (1930) 423; **72** (1932) 310.
[14]   D. M. Cvetković, M. Doob, and H. Sachs, *Spectra of Graphs* (Johann Ambrosius Barth, Heidelberg, 1995)
[15]   D. J. Klein, S. A. Alexander, W. A. Seitz, T. G. Schmalz, and G. E. Hite, Theor. Chimica Acta **69** (1986) 393.
[16]   H. Hartmann, Zeit. Naturforschung A **2** (1947) 259.
[17]   J. P. Malrieu and D. Maynau, J. Am. Chem. Soc. **104** (1982) 3021 and 3029.
[18]   See chapters by D. J. Klein (pp.447–502), by T. G. Schmalz (pp. 635–698), by Y. Jiang and S. Li (pp. 565–602), by N. Flocke and J. Karwowski (603–634), by S. Ramasesha and Z. G. Soos (pp. 635–698), by V. O. Cheranovskii (pp. 699–728), and by M. A. Garcia–Bach (pp. 729–768) in *Valence–Bond Theory*, ed. D. Cooper (Elsevier, Amsterdam, 2001).
[19]   See chapters by Z. G. Soos and S. Ramasesha (pp. 81–110), by J.–P. Malrieu (pp. 135–176), by J. J. C. Mulder (pp. 355–364), by N. D. Epiotis (pp. 377–412), by R. Janoschek (pp. 413–436), by T. P. Zivkovi□ (pp. 437–468), by O. Kahn and M. F. Chariot (pp. 489–522), by D. C. Mattis (pp525–552), by L. Pauling and Z. S. Herman (pp. 569–610) in *Valence–Bond Theory and Chemical Structure*, ed. D. J. Klein and N. Trinajstić (Elsevier, Amsterdam, 1990).
[20]   W. A. Seitz and D. J. Klein, Intl. J. Quantum Chem. **7** (1973) 647.
[21]   F. A. Matsen and T. L. Welsher, Intl. J. Quantum Chem. **12** (1977) 985 and 1001.
[22]   W. Heisenberg, Zeit. Physik **49** (1928) 619.
[23]   P. A. M. Dirac, Proc. Royal Soc. (London) A **123** (1929) 714.
[24]   J. H. Van Vleck, esp. chap. 12, *Electric and Magnetic Susceptibilities* (Oxford U. Press, Oxford, 1931).
[25]   *Free–Electron Theory of Conjugated Molecules*, ed. J. R. Platt (John Wiley and Sons, NY, 1964).
[26]   A. Streitweiser, *Molecular Orbital Theory for Organic Chemists* (John Wiley and Sons, NY, 1961).
[27]   J. H. Van Vleck, Phys. Rev. **49** (1936) 232.
[28]   D. J. Klein, Topics Curr. Chem. **153** (1990) 57.
[29]   J. J. C. Mulder and L. J. Oosterhoff, Chem. Commun. (1970) 305 and 307.
[30]   C. R. Mueller and H. Eyring, J. Chem. Phys. **19** (1951) 1495 and 1498.
[31]   C. R. Mueller, J. Chem. Phys. **22** (1954) 1950.
[32]   G. W. Wheland, J. Chem. Phys. **23** (1955) 79.

[33] See, *e.g.*, N. D. Epiotis, *Unified Valence–Bond Theory of Electronic Structure* (Springer Verlag, Berlin, 1982).

[34] D. Cooper, J. Gerrat, and M. Raimondi, Nature (London) **323** (1986) 699.

[35] See, *e.g.*, several chapters in *Valence–Bond Theory and Chemical Structure*, ed. D. J. Klein and N. Trinajstić (Elsevier, Amsterdam, 1990), and even more of the chapters in *Valence–Bond Theory*, ed. D. Cooper (Elsevier, Amsterdam, 2001).

[36] J. Hubbard, Proc. Royal Soc. (London) A **276** (1963) 238; **281** (1964) 401.

[37] E. H. Lieb, Phys. Rev. Lett. **62** (1989) 1209.

[38] R. Parisier and R. G. Parr, J. Chem. Phys. **21** (1953) 466 and 767.

[39] J. A. Pople, Trans. Faraday Soc. **42** (1953) 1375.

[40] H. C. Longuet–Higgins and L. Salem, Proc. Royal Soc. (London) A **257** (1960) 445.

[41] J. N. Murrell and L. Salem, J. Chem. Phys. **34** (1961) 1914.

[42] R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, NY, 1964).

[43] D. J. Klein and W. A. Seitz, Phys. Rev. B **10** (1974) 3217.

[44] H. Fisher and J. N. Murrell, Theor. Chim. Acta **1** (1963) 463.

[45] E. Dagotto, Rev. Mod. Phys. **66** (1994) 763.

[46] P. Schlottmann, Phys. Rev. B **36** (1987) 5177.

[47] D. Cvetković, I. Gutman, and N. Trinajstić, J. Chem. Phys. **61** (1974) 2708.

[48] W. T. Simpson, J. Am. Chem. Soc. **75** (1953) 597.

[49] S. Nikolić, N. Trinajstić, and D. J. Klein, Comp. Chem. **14** (1990) 313.

[50] S. Nikolić, M. Randić, and D. J. Klein, D. Plavsić, and N. Trinajstić, J. Mol. Struct. **198** (1989) 223.

[51] D. J. Klein, J. Chem. Ed. **69** (1993) 691.

[52] M. Randić, Chem. Rev. (to appear 2003).

[53] W. C. Herndon and H. Hosoya, Tetrahedron **40** (1984) 3987.

[54] D. J. Klein, pp. 33–48 in *Theoretical Organic Chemistry* vol. **5**, ed. C. Parkanyi (Elsevier, Amsterdam, 1998).

[55] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. **17** (1949) 1248.

[56] C. Sandorfy, Can. J. Chem. **33** (1955) 1337.

[57] K. Fukui, H. Kato, and T. Yonezawa, Bull. Chem. Soc. Japan **34** (1961) 442 and 1111.

[58] *Sigma Molecular Orbital Theory*, ed. O. Sinanoglu and K. B. Wiberg (Yale University Press, New Haven, 1970)

[59] J. A. Pople and D. P. Santry, Mol. Phys. **7** (1963/64) 269.

[60] W. T. Simpson, J. Am. Chem. Soc. **77** (1955) 6164 and **78** (1956) 3585.

[61] J. W. Raymonda and W. T. Simpson, J. Chem. Phys. **47** (1967) 430.

[62] W. T. Simpson, Theor. Chim. Acta **18** (1970) 854.

[63] A. S. Davydov, *Theory of Molecular Excitations* (McGraw–Hill, NY, 1962).

[64] A. A. Frost, J. Chem. Phys. **23** (1955) 985.

[65] K. Ruedenberg, paper # 8 in ref. 24 above.

[66] P. Hohenberg and W. Kohn, Phys. Rev. B **136** (1964) 864.

[67] M. L. Levy, Proc. Natl. Acad. Sci. USA **76** (1979) 6062.

[68] W. Kohn and L. J. Sham, Phys. Rev. A **140** (1965) 1133.

[69] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[70] A. Schindlmayr and R. W. Godby, Phys. Rev. B **51** (1995) 10427.

[71] R. B. King and D. H. Rouvray, J. Am. Chem. Soc. **99** (1977) 7834.

[72] R. B. King, Inorg. Chim. Acta **57** (1982) 79.

[73] N. D. Epiotis, *Deciphering the Chemical Bond* (Springer Verlag, Berlin, 1995).

[74] M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry* (Plenum Press, NY, 1975).

[75] O. Kahn, *Molecular Magnetism* (VCH Pub.,NY, 1993).

[76] *Magnetic Properties of Organic Materials*, ed. P. Lahti (Marcel Dekker, NY, 1999).

[77] A. A. Ovchinnikov, V. Ya. Krivnov, and D. V. Dmitriev, pages 769–810 in *Valence Bond Theory*, ed. D. Cooper (Elsevier, Amsterdam, 2001).

[78] E. H. Lieb and D. C. Mattis, J. Math. Phys. **3** (1962) 749.

[79] V. O. Cheranovskii, Teor. and Eksp. Kh. **16** (1980) 147.

[80] D. J. Klein and S. Alexander, pages 404–419 in *Graph Theory and Topology in Chemistry*, ed. R. B. King and D. H. Rouvray (Elsevier, Amsterdam, 1987).

[81] L. Hulthen, Arkiv Mat. Astron. and Fys. A **26** (1938) 1.

[82] E. H. Lieb and F. Y. Wu, Phys. Rev. Lett. **20** (1968) 1445.

[83] F. Gantmacher, chap. 13 of *The Theory of Matrices* (Chelsea, NY, 1963).

[84] D. J. Klein and M. A. Garcia–Bach, Phys. Rev. B **19** (1979) 877.

[85] D. J. Klein, R. Valenti, and T. P. Zivković, Phys. Rev. B **43** (1991) 723.

[86] A. D. McLachlan, Mol. Phys. **4** (1961) 49.

[87] J. Koutecky, J. Chem. Phys. **44** (1966) 3702.

[88] D. Maynau, Ph. Durand, J. P. Dauday, and J.–P. Malreiu, Phys. Rev. A **28** (1983) 3193.

[89] M. Randić, D. J. Klein, S. El–Basil, and P. Calkins, Croat. Chem. Acta **69** (1996) 1639.

[90] D. J. Klein, M. Randić, D. Babić, and N. Trinajstić, Intl. J. Quantum Chem. **50** (1994) 369–384.

[91] D. J. Klein and T. G. Schmalz, Intl. J. Quantum Chem. **35** (1989) 373.

[92] D. J. Klein, G. E. Hite, and T. G. Schmalz, J. Comp. Chem. **7** (1986) 443.

[93] D. J. Klein, H. Zhu, R. Valenti, and M. A. Garcia–Bach, Intl. J. Quantum Chem. **65** (1997) 421.

[94] C. A. Coulson, Rev. Mod. Phys. **32** (1960) 170.