

VALENCE BOND THEORY FOR CONJUGATED HYDROCARBONS

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Abstract—Semiempirical valence bond theory for conjugated π -electron systems is reconsidered, with special attention being directed to common criticisms of the theory. Especially in light of recent results, flaws in the criticisms are revealed. Prospects for valence bond theory hence seem brightened.

INTRODUCTION

During the first decades of quantum mechanics valence bond (VB) theory for organic chemical purposes was presented (see, e.g., Refs. 1-4) and evidently widely accepted as the natural quantum mechanical extension of classical chemical bonding concepts. Localized bonds such as occur in alkanes were interpreted as singlet-coupled pairs of electrons on adjacent atoms, so that a single (spin-coupling) structure is determined. For delocalized bonds the system wavefunction was interpreted as a combination of several VB structures with singlet-coupled electron pairs occurring in different places for each structure. Pauling (Ref. 5) achieved many and diverse qualitative successes. At the same time molecular orbital (MO) theory seems to have been less appreciated despite significant contributions by Huckel (Ref. 6), as well as Coulson (Ref. 7) and others. Around 1950 the preference began to shift, and dramatically so. First, Longuet-Higgins, Coulson and Dewar developed (Refs. 7,8,9) simply stated general theorems and rules for Huckel MO theory such that qualitative agreement with and extension of chemical ideas was obtained; second, the ease of making precise Huckel MO calculations typically in semi-quantitative agreement with experiment became widely appreciated; and third, Woodward, Hoffman and others developed (Ref. 10) MO rules for organic reactions. Today one finds many supposedly general quantum chemistry and theoretical organic chemistry texts dealing almost exclusively with MO theory. Often they make only perfunctory mention of VB theory; brief criticisms may be made and VB theory alleged to be inadequate.

Still there are disadvantages of MO theory in comparison to VB theory. Some relevant evidence is found when Dewar and Lo (Ref. 11) remark that: "One of the problems which has arisen with the development of sophisticated MO treatments is the difficulty of relating such calculations to the traditional picture of molecules in terms of localized bonds, resonance energy, etc." Pauling (Ref. 12) more clearly espouses the advantages of a qualitative VB approach: "The valence bond treatment is much simpler than the molecular orbital treatment, and it is also more powerful, so far as elementary, non-mathematical discussions are concerned." Quantitative VB theory also has an advantage by association with the simple theory and its straight-forward chemical interpretation. It is of interest to note that VB theory explicitly includes electron correlation in contrast to simple MO theory but in agreement with both state-of-the-art *ab initio* calculations and with the practicing organic chemists' usage of Lewis electron-dot diagrams and "electron pushing" (or "arrow pushing") concepts.

The question then arises whether the disadvantages of quantitative VB theory outweigh the advantages. Here we shall review and analyze several criticisms of VB theory. Attention is directed primarily to π -electron networks of neutral conjugated hydrocarbons whence the simple VB model is limited to covalent structures. From our analysis we find that previous criticisms often: are exaggerated (being true only in part); or are incompletely validated at present; or are irrelevant; or are based upon misinterpretations; or finally are combinations of the preceding. Indeed upon consideration of a few example applications some of the supposed disadvantages appear more in the nature of advantages.

To begin let us be precise about the model considered. The *simple VB model* (Refs. 2,3,4,13,14) for neutral conjugated hydrocarbons assigns a singly-occupied π -orbital (spin-up or spin-down) to each C-atom of the π -network, so that we are dealing with the space of covalent VB structures. One assumes only a few nonzero integrals: a unit overlap for each spin-orbital, a geometry-independent one-site orbital energy, Coulomb interaction integrals between different sites, and finally nearest-neighbor exchange parameters $-J_{jj}$. The one-site orbital energies and Coulomb integrals will merely shift all the neutral (purely covalent) states by

a fixed amount, and so will be suppressed here. Since single occupancy of the spin-free π -orbitals remains unchanged by this implied "effective" Hamiltonian H acting on the covalent space, H can be represented as a transformation on spin space. The relevant spin-space operators are permutations exchanging pairs of spin indices, the one exchanging i and j being expressed (see, e.g., Refs. 3,14) in terms of the usual spin operators \vec{s}_i and \vec{s}_j as $2\vec{s}_i \cdot \vec{s}_j + \frac{1}{2}$. Then the effective VB Hamiltonian may be written as

$$H = \sum_{i \sim j} J_{ij} (2\vec{s}_i \cdot \vec{s}_j + \frac{1}{2}) \quad (1)$$

where the sum is over "bonded" pairs of atoms. The representation of H in this form has an advantage in that it is basis-independent; that is, the canonical Rumer basis of VB structures (although important for many chemical interpretations) need not be used. Moreover, the Hamiltonian of (1) is recognized as being of the same mathematical form as the physicist's Heisenberg spin model (see, e.g., Ref. 15), so one might expect to be able to utilize some of their results for this model. (Conversely ideas developed in chemistry for the treatment of H can be expected to be of use to physicists.) Finally note that if all the J_{ij} for bonded atoms are taken to be equal, then H is entirely determined by the topological graph of the π -network; as such graph-theoretic ideas may be relevant here, just as has already been revealed (see, e.g., Ref. 16) to be the case for Huckel MO theory.

CRITICISMS AND RESPONSES

We turn now to an explicit listing and discussion of various criticisms of VB theory:

Criticism 1. The lack of inclusion of ionic states limits VB theory to small systems. The essence of the argument behind this criticism begins with the assumption of a nonzero probability, say $p > 0$, for the admixture of an excited structure with a (+ and -) *ionic pair* for a given typical pair of sites. Then the probability P that none of the, say N , different π -orbitals of the molecule are involved anywhere in an *ionic pair* is roughly something like

$$P \sim (1 - p)^{N/2} \quad (2)$$

Thus the probability $1 - P$ of an *ionic pair* occurring someplace approaches certainty as the number N of sites becomes large. Moreover the overlap between the two (say ground-state) wavefunctions calculated with and without the inclusion of multiple *ionic pairs* then should approach $\sim P \rightarrow 0$ for very large molecules. The argument concludes with the assertion that the *VB theory* wavefunction limited to *covalent structures* is exceedingly poor for large systems. This same type of criticism is often given of resonance theory too; the argument is made with the terms *resonance theory*, *long-bond pair*, and *Kekulé structure* replacing the terms *VB theory*, *ionic pair* and *covalent structure*.

Response. Actually the same type of argument applies to MO theory, with the terms *MO theory*, *pair excitation*, *unexcited wavefunction*, and "orbital" replacing the terms *VB theory*, *ionic pair*, *covalent structure*, and "site". In fact we are dealing with a standard type of many-body paradox, which is properly understood (Refs. 17,18). The argument of the criticism is largely valid up till the final assertion of wavefunction inadequacy; the reliability of a wavefunction for computing few-particle properties (such as are virtually always of interest) depends not on global overlap accuracy but rather on local wavefunction accuracy, in the VB case this accuracy being the likelihood of a typical ionic pair occurring. For instance, a local (say bond or ring) energy depends not upon a global wavefunction property (as measured by P) but rather upon the local accuracy of the wavefunction (as measured by p). That is, the practical utility for many properties depends not on the similarity of P of (2) to 1 but rather on the similarity of $1 - p$ to 1.

Criticism 2. The VB model of (1) lacks a theoretical justification and derivation. The argument in this case notes that if one uses orthogonalized atomic orbitals ϕ_i and ϕ_j on sites i and j and takes

$$-J_{ij} = K_{ij} \equiv \iint \phi_i^*(1) \phi_j(1) \frac{1}{r_{12}} \phi_i(2) \phi_j^*(2) d\tau_1 d\tau_2 \quad (3)$$

then $-J_{ij}$ may be viewed as an electrostatic self-repulsion of an "exchange charge density". Consequently J_{ij} is negative, opposite in sign to that required in (1) for agreement with experiment. Further, calculations of J_{ij} via (3) with orthogonalized orbitals give (see, e.g., Ref. 19) a value smaller than the corresponding neglected electron-hopping (or resonance) integral.

Response. Actually, this argument merely indicates that this is not the appropriate route to the derivation of (1). Pauling (as well as Heisenberg for magnetic problems) was

apparently led to the equivalent of (1) by the commendably straight-forward and size-consistent expedient of summing over the simplest feasible neighbor-site interactions. Without further theoretical development it can be argued that the appropriate view to take would be to let empirical comparison to experiment provide evidence for or against the model. But, in addition, Van Vleck and others (Refs. 3,20,21,22) have given different derivations yielding corrected formulas for the J_{ij} through the leading order in intersite differential overlap,

$$J_{ij} = S_{ij}^2 C_{ij} - K_{ij} \quad (4)$$

where now nonorthogonal atomic orbitals are used in computing K_{ij} , S_{ij} is the intersite overlap integral, and C_{ij} is a combination of Coulomb-type integrals. Still there were objections concerning a large-system nonorthogonality catastrophe, but these were answered (Refs. 20,21,22) in an essentially correct manner. Further J_{ij} so computed is (Ref. 19) larger than the corresponding electron-hopping integral over nonorthogonal orbitals. In a derivation of (4) one first considers Hamiltonian and overlap matrices \mathbf{H} and \mathbf{S} over a basis of Slater determinants composed from nonorthogonal atomic orbitals; second the eigenvalue problem for \mathbf{H} and \mathbf{S} is transformed to the equivalent problem with matrices

$$\mathcal{H} \equiv \mathbf{S}^{-\frac{1}{2}} \mathbf{H} \mathbf{S}^{-\frac{1}{2}} \text{ and } \mathbf{1} \quad (5)$$

then third one expands matrix elements in powers of intersite differential overlap to obtain an effective exchange parameter for \mathcal{H} , as given in (4). Another derivation (Refs. 23,24,25) of the basic model (1) proceeds through orthogonalized atomic orbitals and a correlated Parisier-Parr-Pople (PPP) model which is transformed via a degenerate perturbation expansion to (1); in this case one finds

$$J_{ij} = \frac{\beta_{ij} \beta_{ji}}{\gamma_{ii} - \gamma_{ij}} + \frac{\beta_{ji} \beta_{ij}}{\gamma_{jj} - \gamma_{ji}} \quad (6)$$

where β_{ij} and γ_{ij} are the usual resonance and Coulomb integrals appearing in the PPP model. In fact when Bulevski (Ref. 26) derived H of (1) in this manner, he evidently did not realize that (1) was simply the chemist's VB model, and he independently suggested (Ref. 26) that (1) could be used as a model for conjugated hydrocarbons. Higher-order perturbative corrections for both (4) and (6) have been given (Refs. 22,23,25) and apparently are important. Other derivations transcending perturbation theory are available (Refs. 23,27,28). Finally let us note that ionic structures (or configurations) play a role in VB theory different than in MO or PPP models; that is, various configurations should occur with different weights since different transformations (in addition to different truncations) have been made in deriving the effective Hamiltonians.

Criticism 3. Since MO and VB theory are qualitatively different and since MO theory is qualitatively correct, VB theory must be wrong.

Response. Actually when such a disagreement occurs between simple MO and VB theories, it may be that the VB predictions are superior. Just such a situation occurs with the prediction of negative spin densities (Ref. 29) as well as of negative NMR spin-spin coupling constants (Refs. 29,30). Additional such examples are found in criticisms 5 and 6. Generally it might be that whether simple MO or VB theory is more reliable will depend upon the particular property and type of molecule considered.

Criticism 4. VB theory is inadequate for excited states. The basis of this criticism is that simple VB theory excludes ionic structures which are supposed to contribute strongly to excited states. For example if one compares the eigenvalues for the covalent VB model to those for a (more complete) full configuration interaction solution to a Parisier-Parr-Pople model, one finds that some of the (low spin) excited states are missing.

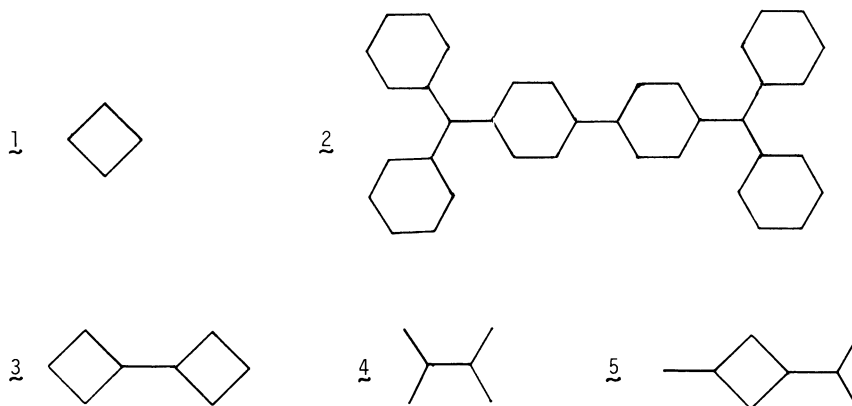
Response. These missing lower-lying excited states are evidently ionic in nature and can be recovered in a VB treatment of the lowest excited ionic manifold. Although such calculations increase the complexity of the VB model, they should still be simpler than a full configuration interaction treatment of a PPP model in the sense that fewer states (and smaller matrices) arise in this VB approach. Still the simple covalent VB model locates some excited states accurately, particularly those of higher spin multiplicities. Finally we note that MO theory generally does a poor job with excited states too, here because of electron correlation as manifested through configuration interaction between various single excitations of similar overall energies.

Criticism 5. The VB model yields no simple yet general theorems such as the Huckel MO model does, particularly for alternant systems.

Response. In fact there are several simple to use theorems for the ground states of VB models for alternant systems. Lieb and Mattis (Ref. 31) proved the ground-state spin to be

$$S = \frac{1}{2} ||A| - |B|| \quad (7)$$

where $|A|$ and $|B|$ are the orders of the sets A and B of starred and unstarred sites. This value always is (Ref. 32) less than or equal to the predicted value from Huckel MO theory, so that differences in this qualitative prediction can occur only for systems predicted to have high-spin ground states by Huckel MO theory. For instance, this theorem predicts that species 1, 2, 3, 4, and 5 all have singlet $S = 0$ ground states, while MO theory predicts a spin just half the number of nonbonding MO's, the spin prediction $S = 1, 0, 1, 1, \text{ and } 1$ for



these same species. In all cases investigated so far the VB prediction appears to be correct when compared: with full configuration interaction calculations on PPP models (Refs. 32,33); with accurate *ab initio* configuration interaction calculations (Refs. 33,34,35); or with experiment (Refs. 36-39). A second theorem identifies (Ref. 40) the ground-state point group symmetry for a group operation G which does not include a reflection in the molecular plane to have a character

$$\chi(G) = \begin{cases} (-1)^{|G|} & , \text{ if } GA = A \text{ and } GB = B \\ (-1)^{|G| + N/2} & , \text{ if } GA = B \text{ and } GB = A \end{cases} \quad (8)$$

where $(-1)^{|G|}$ is the parity of the site-permutation corresponding to G, i.e., G is the (minimal) number of transpositions into which G may be factored when viewed as a permutation of π -orbital sites. Again these predictions appear to be correct when gauged against full configuration interaction calculations on PPP models. In the case that G is a reflection (vertical to the molecular plane) leaving some π -centers fixed the top line of (8) is equivalent to a specialization to alternants of a rule proposed sometime ago by Craig (Ref. 41). At least for alternants (8) then verifies and extends Craig's rule. Moreover (8) is applicable to the "extended" point group which (if J_{ij} on corresponding bonds are equal) is isomorphic to the automorphism group of the π -network graph. For example, this "extended" symmetry (which also arises for the Huckel MO model (Ref. 42)) includes operations exchanging the π -centers on the forked ends of the species 4 and 5 above while leaving the rest of the molecule fixed; in these two cases G corresponds to a single transposition so that $\chi(G) = -1$. A third theorem says (Ref. 40) that if ψ is the ground-state wavefunction, then

$$\langle \psi | \vec{s}_i \cdot \vec{s}_j | \psi \rangle \begin{cases} > 0 & , \text{ if } i, j \in A \text{ or if } i, j \in B \\ < 0 & , \text{ otherwise} \end{cases} \quad (9)$$

This result makes interesting predictions (Refs. 29,30) for signs of NMR spin-spin coupling constants and of spin densities. Also there are extensions of these various theorems to the lowest energy states of any spin multiplicity, and there is (Ref. 31) a theorem concerning signs of wavefunction expansion coefficients.

Criticism 6. Huckel's $4n+2$ rule is contrary to VB theory. Evidently this criticism refers to the prediction of VB theory that the ground-states are spin singlets for both $N=4n$ and $N=4n+2$ and that there is little alternation in "resonance energies".

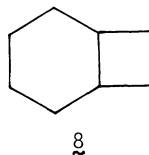
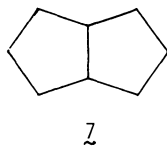
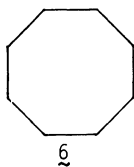
Response. In fact, the extent of alternation of these resonance energies is (Ref. 43) predicted by more sophisticated MO theories to be intermediate between that predicted by simple MO and VB theories. Moreover, as pointed out in the response to criticism 5 the VB predictions of the ground-state spin symmetries are evidently correct, in contrast to MO theory. Further VB theory makes an interesting prediction based on a consideration of the point group symmetry theorem of equation (8): for a reflection σ fixing two C atoms of an even N -annulene, say atoms 1 and $N/2 + 1$, one sees that σ is a product of $N/2 - 1$ transpositions, so that

$$\chi(\sigma) = (-1)^{|\sigma|} = (-1)^{N/2-1} = \begin{cases} +1 & , N = 4n+2 \\ -1 & , N = 4n \end{cases} \quad (10)$$

Hence the VB ground states of $N=4n$ cycles are predicted to exhibit nonsymmetric point group symmetries; but this in turn implies an open-shell species, presumably radicaloid in nature, in agreement with Craig's ideas (Ref. 41) from 1951. Thus VB theory indicates $4n$ -annulenes to be singlet biradical species. (Similar arguments apply for species 3, 4 and 5 mentioned previously.) We mention in passing that for charged annulenes VB theory can exhibit (Ref. 44) triplet ground-states when the number of π -electrons is a multiple of 4. The theorem of equation (5) may also be used to indicate relative π -electron stabilities of certain hydrocarbon species. For instance, models for species 7 and 8 may be viewed as being formed from that for 6 by the introduction of a single additional bond; then letting this additional bond be ij and letting ψ_0 denote the (zero-order) ground-state wavefunction for 6 we compute a first-order perturbation correction to the energies of 7 and 8 via

$$\Delta E_{\pi} = J_{ij} \langle \psi_0 | (2\vec{s}_i \cdot \vec{s}_j + \frac{1}{2}) | \psi_0 \rangle \quad (11)$$

but from (9) we see that ΔE_{π} for 7 is more destabilizing than it is for 8 (ΔE_{π} being $> J_{ij}/2$ or $< J_{ij}/2$ respectively).



Criticism 7. VB theory does not yield simple analogs of the Woodward-Hoffman rules.

Response. Here too there is evidence contrary to the claim of the criticism. We note the work of Yamaguchi et al (Refs. 45,46), though in this case the authors do not refer to the VB model by name but rather to the Heisenberg model. Also there are the important papers by Osterhoff and co-workers (Refs. 47,48), though they use a slight extension of the simple model of (1); in fact the model they use with nearest-neighbor overlap entering explicitly exhibits behavior which suggests that this modified model might account for a greater alternation in resonance energies mentioned in criticism 6. There is yet further work (Refs. 49-53) using VB models to treat organic reactivity. In Matsen's (Ref. 50) approach correlation diagrams between MO and separated atom limits are used to make qualitative corrections for electron correlation, such as is included in (1).

Criticism 8. VB theory does not predict bond-alternation for long polyene chains. Evidently this criticism has arisen because of the successful VB resonance-structure treatment of benzene, where there is no bond alternation.

Response. In fact Coulson and Dixon (Ref. 54) noted that if only Kekule structures are used, then bond alternation results. The two possible Kekule structures have an overlap of $2^{-N/2}$ and a corresponding interaction $\sim JN2^{-N/2}$. Hence in the limit of very large N chains the interaction (or resonance energy) between these two Kekule structures is vanishingly small; consequently each structure responds independently and linearly to bond-alternation perturbations, so that bond alternation should occur. Moreover such arguments have been extended (Refs. 55,56): first to avoid the need for explicit matrix element evaluation, via Pauling's (Ref. 57) "island counting" technique, if only a qualitative result is desired; second to cast the explanation in terms of "long-range-order" concepts; and third to account for the effect of the inclusion of additional VB structures, both qualitatively and quantitatively. These arguments indicate that inclusion of excited (long-bond or ionic) structures does not spoil large- N bond alternation for the ground state. Further this picture suggests (Ref. 58) the occurrence of low-lying charge-carrying "soliton" excitations,

Criticism 9. Calculations on the VB model are too difficult to carry out. Here the criticism refers to the dimension of the covalent structure basis which increases in size exponentially with N . Thus ordinary configuration interaction techniques rapidly exceed feasibility (with ~ 59000 singlet and ~ 149000 triplet structures at $N=22$). Moreover techniques developed by physicists for dealing with Heisenberg models for magnetic systems are of little direct aid in general; their methods (see, e.g., Ref. 15) are typically limited either to the linear chain case or to the treatment of "high-temperature" thermodynamic properties (where "high-temperature" here means $\sim J/k \sim 10^4$ °K).

Response. There are tentative indications that other computational methods can be used. First, cluster expansions utilizing chemical interpretations of VB structures are possible (Ref. 56); a long polyene chain calculation has been carried out with more than $4^{N/3}$ of the more important structures, where $N \rightarrow \infty$. Second, ground-state Monte Carlo calculations are in principle (Ref. 40) possible on alternants. Third, derivation techniques such as referred to in the response to criticism 3 can often be used in an iterative renormalization group manner to estimate low-lying eigenstates of (1). Fourth, and perhaps most importantly, degenerate perturbation treatments and such based upon the subspace of Kekule structures only could be made. The successful calculations of Gomes (Ref. 59) for resonance energies are effectively just such a first-order degenerate perturbation treatment. A model of the form of (1) but with next-nearest-neighbor interactions included has (Refs. 60,61) been identified such that the Kekule states are the ground states; these auxiliary interactions are in the direction required for corrections to the simple VB model, so that the use of this new model as a zero-order description appears promising. Finally high-order treatments should have much in common with "quantitative resonance theories" such as developed by Herndon and others (Refs. 62-69).

PROSPECTS

Our analysis of these various criticisms of VB theory renders a clearer view. These criticisms range from being unjustified to being partially true; in most cases additional work would be of value. Evidence indicates the possibility of fully derived VB theorems, rules and quantitative computational schemes which are clear and practical to use. If success in such an endeavor is achieved, then classical chemical ideas will have a more complete and useful natural quantum mechanical extension explicitly including electron correlation effects.

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REFERENCES

1. G. Rumer, Nachr. Ges. Wiss. Göttingen, 1932, 337-341(1932).
2. L. Pauling and G. W. Wheland, J. Chem. Phys. 1, 362-374(1933).
3. J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. 7, 167-228(1935).
4. H. Eyring, J. Walter, and G. E. Kimball, Quantum Chemistry, chap. 13 (John Wiley and Sons, New York, 1944).
5. L. Pauling, The Nature of the Chemical Bond, (Cornell University Press, Ithaca, 1940).
6. E. Huckel, Z. Physik 70, 204-286(1931); 76, 628-648(1932).
7. C. A. Coulson and G. S. Rushbrooke, Proc. Camb. Phil. Soc. 36, 193-199(1940).
8. H. C. Longuet-Higgins, J. Chem. Phys. 18, 265-291(1950).
9. M.J.S. Dewar, J. Am. Chem. Soc. 74, 3341-3359(1952).
10. Orbital Symmetry Papers, ed. H. E. Simmons and J. F. Bunnett (American Chemical Society, Washington D.C., 1974).
11. M.J.S. Dewar and D. H. Lo, J. Am. Chem. Soc. 93, 7201-7209(1971).
12. L. Pauling, J. Chem. Ed. 57, 38-40(1980).
13. G. W. Wheland, Resonance in Organic Chemistry (John Wiley and Sons, New York, 1955).
14. W. T. Simpson, Theories of Electrons in Molecules (Prentice-Hall, Englewood Cliffs, 1955).

15. D. C. Mattis, The Theory of Magnetism (Harper and Row, New York, 1965).
16. A. Graovac, I. Gutman, and N. Trinajstić, Topological Approach to the Chemistry of Conjugated Molecules (Springer-Verlag, Berlin, 1977).
17. H. Bethe, Phys. Rev. 103, 1353-1390(1965).
18. R. Peierls, Surprises in Theoretical Physics, section 6.2 (Princeton University Press, Princeton, 1979).
19. I. Fischer-Hjalmers, J. Chem. Phys. 42, 1962-1972(1965).
20. J. H. Van Vleck, Phys. Rev. 49, 232-240(1936).
21. W. J. Carr, Jr., Phys. Rev. 92, 28-35(1953).
22. W. C. Mullin, Phys. Rev. 136A, 1126-1130(1964).
23. L. N. Buleavski, Zh. Eksp. Teor. Fiz. 51, 230-239(1966).
24. J. Linderberg and Y. Ohrne, Propagators in Quantum Chemistry, chap. 10 (Academic Press, New York, 1973).
25. D. J. Klein and W. A. Seitz, Phys. Rev. 8B, 2236-2247(1973).
26. L. N. Buleavski, Teor. Eksp. Khim. 4, 12-21(1968).
27. D. J. Klein and D. C. Foyt, Phys. Rev. 8A, 2280-2287(1973).
28. R. D. Poshusta and D. J. Klein, Phys. Rev. Lett. (to appear, 1982).
29. H. M. McConnell and H. H. Dearman, J. Chem. Phys. 28, 51-53(1958).
30. H. M. McConnell, J. Chem. Phys. 30, 126-128(1959).
31. E. H. Lieb and D. C. Mattis, J. Math. Phys. 3, 749-751(1962).
32. D. J. Klein, C. J. Nelin, S. Alexander and F. A. Matsen, J. Chem. Phys. (to appear, 1982).
33. D. Dohnert and J. Koutecky, J. Am. Chem. Soc. 102, 1789-1796(1979).
34. R. J. Buenker and J. L. Whitten, J. Chem. Phys. 49, 5381-5387(1968).
35. W. T. Borden and E. R. Davidson, J. Am. Chem. Soc. 99, 4587-4594(1977).
36. A. Efraty, Chem. Rev. 77, 691-744(1976).
37. O. L. Chapman, C. L. McIntosh, and J. Paconsky, J. Am. Chem. Soc. 95, 614-617(1973).
38. C. A. Huthinson, Jr., A. Kowalsky, R. C. Pastor, and G. W. Wheland, J. Chem. Phys. 20, 1485-1486(1952).
39. R. K. Waring and G. J. Sloan, J. Chem. Phys. 40, 772-777(1962).
40. D. J. Klein, J. Chem. Phys. (to appear, 1982)
41. D. P. Craig, J. Chem. Soc. 1951, 3175-3182(1951).
42. V. Wild, J. Keller, and Hs. H. Gunthard, Theor. Chim. Acta 14, 383-395(1969).
43. A.L.H. Chung and M.J.S. Dewar, J. Chem. Phys. 42, 756-766(1965).
44. H. Fischer and J. N. Murrell, Theor. Chim. Acta 1, 463-467(1963).
45. K. Yamaguchi, Chem. Phys. Lett. 28, 93-97(1974).
46. Y. Yoshioka, K. Yamaguchi, and T. Fuens, Theor. Chim. Acta 45, 1-20(1977).
47. J.J.C. Mulder and L. J. Osterhoff, Chem. Comm. 1970, 305-309(1970).
48. W. J. van der Hart, J.J.C. Mulder, and L. J. Osterhoff, J. Am. Chem. Soc. 94, 5724-5730(1972).

49. D. M. Silver and M. Karplus, J. Am. Chem. Soc. 97, 2645-2654(1975).
50. F. A. Matsen, Acc. Chem. Res. 11, 387-392(1978).
51. S. S. Shaik, J. Am. Chem. Soc. 103, 3692-3701(1981).
52. A. Pross and S. S. Shaik, J. Am. Chem. Soc. 103, 187-195(1982).
53. V. O. Cheranovskii, Teor. Eksp. Khim. 17, 21-27(1981).
54. C. A. Coulsen and W. T. Dixon, Tetrahedron 17, 215-228(1962).
55. D. J. Klein and M. A. Garcia-Bach, Phys. Rev. 19B, 877-886(1979).
56. D. J. Klein, Intl. J. Quantum Chem. 13, 294-303(1979).
57. L. Pauling, J. Chem. Phys. 1, 280-283(1933).
58. W. P. Su and J. R. Schreiffer, Proc. Natl. Acad. Sci. U.S.A. 77, 5626-5629(1980).
59. J.A.N.F. Gomes, Theor. Chim. Acta. 59, 333-356(1981).
60. C. K. Majumdar, J. Phys. 3C, 911-915(1970).
61. D. J. Klein, J. Phys. 15A, 661-671(1982).
62. W. C. Herndon, J. Am. Chem. Soc. 95, 2404-2406(1973).
63. W. C. Herndon and M. L. Ellzey, Jr., J. Am. Chem. Soc. 16, 6631-6642(1974).
64. I. Gutman and W. C. Herndon, Chem. Phys. Lett. 34, 387-391(1975).
65. M. Randic, Tetrahedron 31, 1477-1481(1975).
66. J. Aihara, Bull. Chem. Soc. Japan 49, 1429-1430(1976).
67. M. Randic, J. Am. Chem. Soc. 99, 44-450(1977).
68. P. Illic and N. Trinajstic, J. Org. Chem. 45, 1738-1748(1980).
69. M. Aida and H. Hosoya, Tetrahedron 36, 1317-1326(1980).