J. Am. Chem. Soc. **1984**, *106*, 6496-6502

Valence Bond Theory of Aromaticity

Satoru Kuwajima*

Contribution from the Department of Physics, Faculty of Science, Kyoto University, Kyoto 606, Japan. *Received February 16, 1984*

Abstract: A valence bond (VB) treatment of aromaticity, including the treatment of what is called ring current, is presented. The essence of the treatment consists of full consideration of the ring permutation, which is a novel theoretical constituent of VB theory first introduced in 1970 by Mulder and Oosterhoff. It is shown that the ring permutation accounts for ring current and antiaromaticity (precisely, antiaromaticity of systems composed of even-membered rings). Close correlation between the novel ring-permutation effect and the classical resonance effect is discussed; in particular, the ring-permutation effect, when causing antiaromaticity, can be regarded as resonance destabilization. The treatment of ring current is a VB analogue of the MO Hückel–London theory. It is stressed that this treatment sometimes gives quite different results from the Hückel–London theory.

Aromaticity is one of the central concepts in organic chemistry. While molecular orbital (MO) theory has been playing the leading role in the theory of aromaticity, valence bond (VB) theory has long been seriously unsuccessful in this field. Basic failures of the classical VB theory, i.e., the simplified VB theory developed by Pauling and others,[1,2] are that it cannot account for antiaromaticity[3,4] and that it cannot treat magnetic effects such as exaltation of diamagnetic susceptibilities.[5] VB studies of aromaticity beyond the classical VB theory have so far been made in two ways. One way, which has been fairly successful, is to develop empirical treatments.[6-8] Such approaches have succeeded in treating antiaromaticity, but the theoretical basis is still uncertain.[6] The other way is to try to improve VB theory basically.[9-13] Such approaches have achieved an essential finding, but they are still of very limited success. In this paper we present a framework of theory that can account for both antiaromaticity and magnetic effects and is just an extension of the classical VB theory.

In 1970 Mulder and Oosterhoff[9] found a clue for resolving the failures of the classical VB theory. They found that, in the case of monocyclic systems, special terms in the VB energy expression bear the effect of destabilizing ($4n$)-membered rings while they stabilize ($4n + 2$)-membered rings. Their finding was recently given a sound and clear description by using the spin-Hamiltonian formalism of VB theory.[14] As has long been known, the VB theory which takes into account only covalent VB structures can be formulated by using the effective spin Hamiltonian. The spin Hamiltonian of the classical VB theory takes the form[1b,2]

$$\hat{H} = -\sum^{\mathrm{NN}} J_{ij}(ij) \tag{1}$$

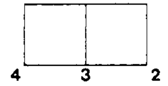
where (ij) are transpositions of spin variables, J_{ij} are exchange integrals, and the sum is taken over the nearest-neighbor (NN) transpositions. The recent finding is that in cyclic systems we should add permutations which permute electrons circularly around rings[12,14b]; it was found that such permutations often become the largest terms next to the nearest-neighbor transpositions.[14b] These permutations were named as the ring permutation.[15] The main subject of this paper is to investigate roles of the ring permutation in VB treatment of aromaticity.

Theoretical Framework

We study the spin Hamiltonian obtained by adding ring permutations to the classical Hamiltonian 1:

$$\hat{H} = -\sum^{\mathrm{NN}} J_{ij}(ij) + \sum_{P}^{\mathrm{R}} (-1)^P J_P P \tag{2}$$

where the second summation is taken over the ring (R) permutations and $(-1)^P$ denotes the parity of a permutation. A ring permutation is a cycle permutation which successively permutes electrons by their nearest-neighbor electrons. For instance, the Hamiltonian 2 for butalene, along with the numbering of electron positions, is as follows:



$$\hat{H} = -J[(12) + (23) + (34) + (45) + (56) + (16) + (36)] - J_{\mathrm{A}}[(1236) + (1632) + (3456) + (3654)] - J_{\mathrm{B}}[(123456) + (654321)]$$

where ring permutations are in the second and third brackets. We treat ring permutations as a perturbation. Then, the first-order energy of the Hamiltonian 2 is given by

$$E = E_0 + \sum_{P}^{\mathrm{R}} (-1)^P r_P J_P \tag{3}$$

where E_0 is the classical VB energy and r_P are the expectation values of ring permutations, i.e.,

$$r_{\mathrm{P}} = \langle\theta_0|P|\theta_0\rangle / \langle\theta_0|\theta_0\rangle \tag{4}$$

with θ_0 being the nonperturbed eigenfunction. Equation 3 is the basic formula of our treatment. Aside from the classical VB energy, eq 3 describes ring-permutation contribution to the energy. If a ring permutation lowers the energy then it is an aromatic agent, and if it raises the energy then it is an antiaromatic agent. In this way ring permutations are linked to the phenomena of

---

*Present address: Department of Chemistry, Princeton University, Princeton, New Jersey 08544.

(1) (a) Pauling, L.; Wheland, G. W. *J. Chem. Phys.* **1933**, *1*, 362. (b) Van Vleck, J. H.; Sherman, A. *Rev. Mod. Phys.* **1935**, *7*, 167.

(2) An up-to-date reconsideration of the classical VB theory is given by Klein: Klein, D. J. *Pure Appl. Chem.* **1983**, *55*, 299.

(3) Wheland, G. W. *J. Chem. Phys.* **1934**, *2*, 474.

(4) In ref 2 is given a vindication of the classical VB theory with respect to Hückel's $4n + 2$ rule, a prototype of the aromaticity problem. We have to say, however, that the classical VB theory is decisively unsuccessful concerning this rule. In the classical VB theory the resonance stabilization, as measured by the resonance energy[1a] per electron, becomes strongest in cyclobutadiene and weakens monotonously with increasing ring size. It is pointed out in ref 2 that the nontotally symmetric ground state of ($4n$)-membered rings may imply open-shell and, consequently, biradical nature of the system. This point, however, cannot save the situation since it is purely an MO notion.

(5) Brooks, H. *J. Chem. Phys.* **1940**, *8*, 939.

(6) Herndon, W. C.; Ellzey, M. L., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631.

(7) Herndon, W. C. *J. Mol. Struct.* **1983**, *103*, 219 and references therein.

(8) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444.

(9) Mulder, J. J. C.; Oosterhoff, L. J. *Chem. Commun.* **1970**, 305, 307.

(10) van der Hart, W. J.; Mulder, J. J. C.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 5724.

(11) Epiotis, N. D. "Unified Valence Bond Theory of Electronic Structure"; Springer-Verlag: New York, 1982.

(12) Malrieu, J. P.; Maynau, D. *J. Am. Chem. Soc.* **1982**, *104*, 3021. Maynau, D.; Malrieu, J. P. *Ibid.* **1982**, *104*, 3029.

(13) Gründler, W. *Monatsh. Chem.* **1982**, *113*, 15.

(14) (a) Kuwajima, S. *J. Chem. Phys.* **1981**, *74*, 6342. (b) Kuwajima, S. *Ibid.* **1982**, *77*, 1930.

(15) We adopt this designation though Mulder and Oosterhoff[9] used the term cyclic permutation.

0002-7863/84/1506-6496$01.50/0 © 1984 American Chemical Society

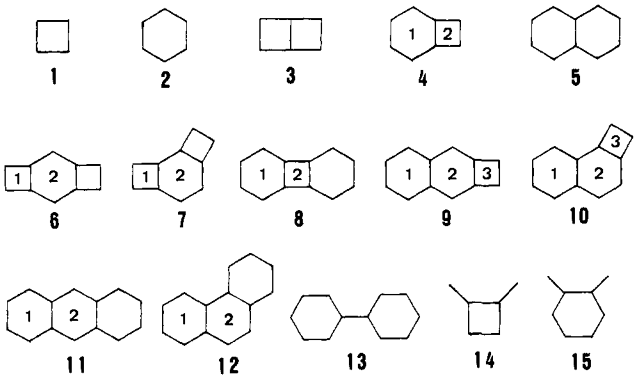


Figure 1. Systems treated: even-ring systems.

aromaticity. The classical VB energy in eq 3 should also play a part in our treatment. We, however, focus our attention on the ring permutations in this section and in the next two sections; the effect involved in the classical VB energy will be examined in the later sections. Returning to the ring permutation, J_P is usually negative, and the sign of r_P determines whether a ring permutation stabilizes or destabilizes the system. We call the quantity r_P ring permutation (RP) index. The quantity J_P, which we refer to as the RP coefficient, also is important. While the RP index is defined with no ambiguity, how to evaluate RP coefficients is rather ambiguous. In this paper we calculate them theoretically by using the Pariser–Parr–Pople (PPP) model and by means of a self-consistent-field (SCF) type VB method[14] that was shown to provide a theoretical basis of the spin Hamiltonian 2.[16] However, RP coefficients thus obtained are more or less preliminary in nature. Though they are suited for examination of fundamental aspects of the treatment, it is preferable to treat them as adjustable parameters in further studies. As for the exchange integrals J_{ij} in eq 2, we set them equal throughout this paper:

$$J_{ij} = J \tag{5}$$

We should also note that eq 5 is unsuitable for quantitative comparison with experiments when we deal with compounds exhibiting strong variation of bond lengths.

Examples

We first touch on monocyclic systems, which are essentially the case treated by Mulder and Oosterhoff.[9] In this case the ring permutation stabilizes $(4n + 2)$-membered rings and destabilizes $(4n)$-membered rings: the RP index is -1 in the former case and $+1$ in the latter case. This result is obtained by considering only the two Kekulé structures, but it is also the correct result derived from the exact solution of the corresponding classical Hamiltonian 1.[17] As for the RP coefficient, the calculated value was found to decrease fairly rapidly with increasing ring size.[18] Table I shows calculated RP indices and coefficients of the systems depicted in Figure 1. Let us mention a few examples. In butalene (**3**) ring permutations around a four-membered ring destabilize the system and those around the periphery work oppositely. In benzocyclobutadiene (**4**) ring permutations around the four-membered ring and around periphery destabilize the system while those around the benzene ring stabilize the system. In naphthalene (**5**) all the ring permutations stabilize the system; and so forth. Ring permutations encircling only one fused ring have fairly large RP coefficients as compared with those encircling more than one fused ring. Consequently, the former permutations mainly govern the effect, though the latter ones are never negligible. In all the systems containing a four-membered ring, ring permutations around the four-membered ring, and also those making an eight-membered cycle when they appear, destabilize the system. Hence it is concluded that these systems have antiaromatic character around the four-membered ring. Ring permutations thus enable VB theory to explain antiaromaticity of these systems. In Table I are also shown the total ring-permutation energies. Their magnitude would be reasonable for explaining actual aromaticity or antiaromaticity. (The antiaromatic energies in Table I are probably an underestimate, as referred to later.) We should notice that the total ring-permutation energy is not a proper index of aromaticity to systems composed of both aromatic and antiaromatic moieties; systems which have a stabilizing total ring-permutation energy can be unstable if they contain a moiety around which strong local antiaromaticity exists. Therefore, although the total ring-permutation energy becomes stabilizing in systems **9** and **10**, this does not contradict with the unstableness of actual compounds[19] because their local antiaromaticity is fairly

Table I. RP Indices and Coefficients of Even-Ring Systems

system[a]	cycle[b]	r_P	$-J_P$[c]	total[d]
1	A	1	0.50	1.01
2	A	-1	0.52	-1.04
3	A	0.66	0.43	0.64
	B	-0.95	0.26	
4	A1	-0.63	0.47	0.31
	A2	0.63	0.45	
	B	0.94	0.18	
5	A	-0.59	0.48	-1.35
	B	-0.94	0.12	
6	A1	0.53	0.43	0.85
	A2	-0.42	0.42	
	B	0.62	0.16	
	C	-0.93	0.06	
7	A1	0.72	0.43 (2.0)	1.20
	A2	-0.37	0.42	
	B	0.56	0.16 (4.1)	
	C	-0.85	0.06	
8	A1	-0.69	0.46	-0.70
	A2	0.36	0.38	
	B	0.55	0.16	
	C	0.89	0.04	
9	A1	-0.47	0.47	-0.17
	A2	-0.39	0.43	
	A3	0.55	0.44	
	B12	-0.61	0.11	
	B23	0.58	0.17	
	C	0.91	0.04	
10	A1	-0.68	0.47 (0.8)	-0.22
	A2	-0.34	0.43 (0.6)	
	A3	0.70	0.43 (1.4)	
	B12	-0.56	0.11 (5.8)	
	B23	0.52	0.16 (2.9)	
	C	0.86	0.04 (2.5)	
11	A1	-0.49	0.47	-1.54
	A2	-0.36	0.44	
	B	-0.57	0.11	
	C	-0.90	0.03	
12	A1	-0.66	0.47 (0.5)	-1.79
	A2	-0.32	0.44	
	B	-0.52	0.11 (4.6)	
	C	-0.87	0.02	
13	A	-0.90	0.50	-1.78
14	A	0.24	0.49	0.23
15	A	-0.17	0.51	-0.17

[a] Figure 1. [b] A, B, and C represent ring permutations which encircle one, two, and three fused rings, respectively. Different permutations belonging to the same class are distinguished by the ring numbers shown in Figure 1. For instance, B12 of **9** denotes the ring permutation around the naphthalene moiety. [c] In eV. If calculated values are different between P and P^{-1}, the mean value of them is shown with the difference of them given in parentheses (ratio to the mean value in percent). [d] Total ring-permutation energy in eV.

---

(16) RP coefficients were calculated by a method called HTR truncation in ref 14b. A brief explanation of how to calculate RP coefficients is given in the Appendix. The PPP parametrization employed is the following: the resonance integral of −2.6 eV, the Ohno formula of electron-repulsion integrals with the one-center value of 11.13 eV, and equal bond lengths of 1.397 Å.

(17) Hulthén, L. *Ark. Mat. Astron. Fys.* **1938**, *26A*, 1.

(18) We calculated RP coefficients of hypothetical monocyclic systems which have the shape of a regular polygon with a bond length of 1.397 Å. The values obtained were, in eV, −0.34 (C_8H_8), −0.21 ($C_{10}H_{10}$), −0.12 ($C_{12}H_{12}$), −0.07 ($C_{14}H_{14}$), −0.04 ($C_{16}H_{16}$), and −0.02 ($C_{18}H_{18}$).

(19) Cava, M. P.; Mitchell, M. J. "Cyclobutadiene and Related Compounds"; Academic Press: New York, 1967.

Table II. Ring-Current Susceptibilities[a] of Benzenoid Hydrocarbons

			exptl	
system	VB[b]	Hückel	*A*[c]	*B*[d]
naphthalene	1.95	2.19	2.23	2.00
anthracene	2.59	3.45	3.55	3.09
phenanthrene	2.73	3.25	3.37	2.92
biphenyl	1.71	1.87	1.91	1.83

[a] Ratio to the benzene susceptibility. [b] Calculated from the quantities given in Table I. Areas of the hexagons were taken to be equal. [c] Reference 25. [d] Modification of ref 25. Estimated from Haberditzl's increment system without using annelation and phenylation increments, which were used by Dauben et al.[25] but appear not to be well-founded; see ref 25.

strong.[20] In order to make a detailed analysis of actual compounds we should lift the restriction of eq 5 and use more carefully determined RP coefficients. The former point is important to antiaromatic systems because these systems should change bond lengths so that the antiaromatic destabilization is reduced.

Magnetic Effects

Anomaly of magnetic properties such as observed in diamagnetic susceptibilities and ^{1}H NMR shifts is an important phenomenon associated with aromaticity. A VB treatment of diamagnetic susceptibility was given by Brooks[5] in 1940, but it was not successful. We present here a treatment in which magnetic effects are caused by the ring permutation. The treatment is simply a VB analogue of the well-known MO Hückel–London theory.[21] The essence of the treatment is that in a magnetic field perpendicular to the molecular plane RP coefficients are replaced by

$$J_P' = J_P \exp(ie\sigma_P S_P H/\hbar c) \qquad (6)$$

where J_P is the RP coefficient of zero magnetic field, σ_P ($=\pm1$) is a sign factor[22] that satisfies $\sigma_{P^{-1}} = -\sigma_P$, S_P is the area encircled by the ring permutation (the area of hexagon in the case of benzene), H is the magnitude of the magnetic field, and other notations are the usual ones. Equation 6 is derived from similar assumptions to the Hückel–London theory. We discuss the derivation in the Appendix. We here only note that the exchange integrals J_{ij} in eq 2 are not affected by the magnetic field on the assumptions we employ. Replacing J_P in eq 3 with J_P' and assuming that RP coefficients satisfy the equation $J_P = J_{P^{-1}}$, we obtain the energy in the magnetic field as

$$E = E_0 + \sum_{P}^{R} (-1)^P r_P J_P \cos(eS_P H/\hbar c) \qquad (7)$$

(Note that RP indices satisfy $r_P = r_{P^{-1}}$, as readily shown from eq 4.) This expression provides basic formulas of magnetic effects. The RP coefficients we have been using slightly break the assumed equality (for instance, **7**, **10**, and **12** in Table I), and in such cases the resulting energy becomes imaginary. We settle this trouble simply by dropping the resultant imaginary part, and the final energy expression we use is the same as eq 7 in such cases, too.[23] From eq 7 we readily obtain the magnetic susceptibility as

$$\chi = (e/\hbar c)^2 \sum_{P}^{R} (-1)^P r_P S_P^2 J_P \qquad (8)$$

Table III. ^{1}H NMR Shifts of Benzenoid Hydrocarbons (τ value)

system	proton	VB[a]	Hückel[b]	exptl[c]
benzene	1	2.73	2.79	2.73
naphthalene	1	2.21	2.31	2.27
	2	2.55	2.52	2.62
anthracene	1	2.34	2.18	2.07
	2	2.73	2.48	2.61
	9	1.88	1.68	1.64
phenanthrene	1	2.23	2.22	2.20
	2	2.56	2.43	2.49
	3	2.52	2.41	2.43
	4	1.88	2.01	1.38
	9	2.22	2.35	2.35

[a] RP coefficients scaled from the values in Table I were used, see ref 24. The olefinic shift was taken to be 4.23 ppm following early works. The current was split into two currents flowing above and below the molecular plane. The distance between the current and the molecular plane, 0.506 Å, was determined by fitting the benzene shift to the experimental value. The current of the polyhexagon form was used. The C–C and the C–H distances were taken to be 1.397 and 1.084 Å, respectively. [b] Haigh, C. W.; Mallion, R. B.; Armour, E. A. G. *Mol. Phys.* **1970**, *18*, 751. [c] Haigh, C. W.; Mallion, R. B. *Mol. Phys.* **1970**, *18*, 737.

We see that aromatic ring permutations cause diamagnetic susceptibilities and antiaromatic ring permutations cause paramagnetic susceptibilities. Our treatment thus succeeds in explaining the fundamental correspondence between aromaticity and magnetic character. Susceptibilities calculated by eq 8 from the values listed in Table I are shown in Table II for benzenoid hydrocarbons. The VB results are roughly as successful as the Hückel (–London) results if we compare them with the experimental estimates of the last column.[24] It is noteworthy that, in contrast to the case of energy, ring permutations encircling more than one fused ring now make a contribution comparable to those encircling only one fused ring; this is due to the factor S_P^2 appearing in eq 8. We can also calculate the ring-current portion of ^{1}H NMR shifts by assuming that the magnetic susceptibility represented by eq 8 comes from currents flowing on the molecular frame. Noting that a ring permutation causes a dipole moment $\chi_P H = (e/\hbar c)^2 H (-1)^P r_P S_P^2 J_P$ and that current I flowing around an area S makes a magnetic dipole IS/c, we obtain the current associated with a ring permutation as

$$I_P = (e^2 H/\hbar^2 c)(-1)^P r_P S_P J_P \qquad (9)$$

We have assumed that the current of a ring permutation flows around the area encircled by the ring permutation. Adding up eq 9 for all the ring permutations and using Biot-Savart's law, we obtain the secondary field H' induced at a proton position, the final ring-current shift being $(1/3)(H'/H)$.[21] Table III shows ^{1}H NMR shifts thus calculated for benzenoid hydrocarbons. The VB results are fairly successful.[26]

The present VB treatment sometimes yields quite different results from the Hückel theory. As an important example, we discuss here the ring current of large monocyclic systems. When monocyclic systems, $(4n + 2)$-membered ones, do not take on bond alternation, the Hückel theory predicts that the ring current increases unboundedly with increasing ring size. (Rigorously speaking, this is correct only when the area of the ring increases

---

(20) In light of the fact that RP coefficients used here involve some uncertainty, it is possible for the total ring-permutation energies of 9 and 10 to become positive. Note that these values come out as a small sum of fairly large quantities of different signs.

(21) See, e.g.: Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin: New York, 1966; Chapter 4.

(22) This factor is defined as follows. Let us suppose an x–y plane on the molecule with the z axis parallel to the magnetic field. A ring permutation draws a circle on the plane as it successively permutes its elements. If this circular motion is clockwise (from y to x), $\sigma_P = 1$, and otherwise, $\sigma_P = -1$.

(23) This trouble stems from the approximate nature of the spin Hamiltonian 2. Though it implies that results we obtain involve an error of the order of the ignored imaginary part, the error is adequately small, as shown in Table I.

(24) It should be remarked that absolute values of the calculated VB susceptibilities are considerably larger than experimental estimates of Dauben et al.[25] For example, the VB value of benzene (using 1.397 Å for the bond length) becomes 59 in units of 10^{-6} cm^3/mol while Dauben et al. gave 41. For this reason, in the further calculation of magnetic properties we use RP coefficients scaled from the values in Table I. The scaling factor is 0.692 adapted to benzene.

(25) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991.

(26) In Table III Hückel results are somewhat better than VB results. However, an inconsistency underlying the Hückel results should be remarked: the resonance integral used to obtain them, ca. −1.5 eV, is in gross discrepancy with the resonance integral adapted to the susceptibility data of Dauben et al.[25] (Table II), the latter being about −3 eV. The VB results do not suffer from such inconsistency.

more rapidly than the ring size.[27]) In the VB treatment the ring-current intensity is expressed as

$$I = (2e^2H/\hbar^2c)S|J_R| \tag{10}$$

where S is the area of the ring and J_R denotes the RP coefficient. In the VB case the current intensity goes to zero in very large systems since the RP coefficient decreases roughly exponentially with increasing ring size.[18] (See eq A3 and the discussion in the Appendix.) We should note that the Hückel theory[28] had to assume bond alternation in [18]annulene to explain ^{1}H NMR shifts of this compound though X-ray analysis[29] did not show such bond alternation. The above VB result is interesting in that it shows that ring current of large annulenes can decrease without bond alternation. (RP coefficients employed in this paper themselves are presumably too small for large annulenes.[30])

Resonance Effect

In the classical VB theory aromaticity is explained from the resonance effect (resonance between Kekulé structures). We here examine the relationship between this classical effect and the novel ring-permutation effect. We first treat the two effects in a qualitative scheme used in the structure-resonance theory of Herndon.[6] We approximate the spin function, θ_0 in eq 4, by a sum, not linear combination, of Kekulé structures:

$$\theta_0 = \sum_{k=1}^{K} f_k \tag{11}$$

where f_k represents the Kekulé structures and K denotes the number of them. We neglect overlaps between different Kekulé structures. Resonance stabilization is then given by

$$E_{RS}' = (2/K) \sum_{k<k'} H_{kk'} \tag{12}$$

where $H_{kk'}$ are Hamiltonian (eq 1) matrix elements between Kekulé structures. Equation 12, however, contains fallacious terms, and we should instead employ

$$E_{RS} = (2/K) \sum_{(k,k')}^{R} H_{kk'} \tag{13}$$

where the summation is taken over the pairs of Kekulé structures which are transformed to each other by a ring permutation.[31] Equation 13 means that $H_{kk'}$ are mainly negative. We can show further that $H_{kk'}$ are all negative and the Kekulé structures in eq 11 fulfill

$$\langle f_k | f_{k'} \rangle > 0 \tag{14}$$

where f_k and $f_{k'}$ are the Kekulé structures connected by a ring permutation.[32] Noting that $H_{kk'}$ are equal for all the pairs of Kekulé structures connected by a common ring permutation, we regroup the terms in eq 13 to obtain the final expression[6]

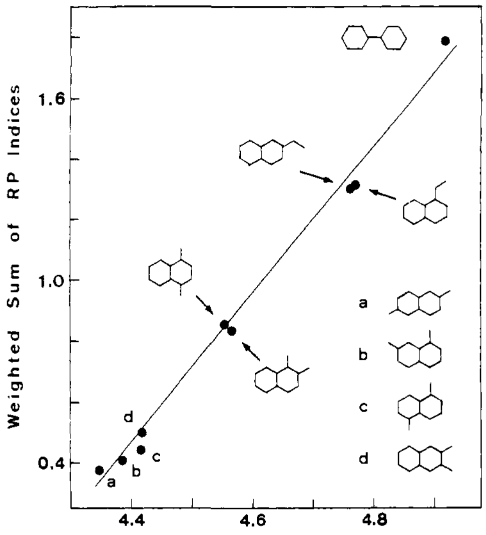


Figure 2. Plot of a weighted sum of RP indices vs. the classical VB energy, the former being $\sum_{\mathrm{P}}^{\mathrm{R}} a_{\mathrm{P}} r_{\mathrm{P}}$ with $a_{\mathrm{P}} = -1$ and -0.25 for six- and ten-membered ring permutations, respectively.

$$E_{RS} = \sum_{P}^{R'} H_{kk'}(K_P/K) \tag{15}$$

where the summation is taken over half of the ring permutations, i.e., additions are made only once between P and P^{-1}, $H_{kk'}$ is the common Hamiltonian matrix element of each ring permutation, and K_P is the number of the Kekulé structures which are transformed to another Kekulé structure by the ring permutation P. Now, the fact that $H_{kk'}$ in eq 15 are all negative means that the resonance effect is always stabilizing; this describes the failure of the classical VB theory in treating antiaromaticity. In the structure–resonance theory of Herndon[6,33] the concept of parity of Kekulé structures is utilized and, as is theoretically unjustifiable, $H_{kk'}$ are taken to be positive if the two Kekulé structures have opposite parities.[34] The ring permutation provides a sound solution to this puzzling problem. Let us calculate RP indices in the present scheme. Substituting eq 11 into eq 4 and neglecting also non-Kekulé structures, we obtain

$$r_P = (-1)^{n_P/2}(K_P/K) \tag{16}$$

where n_P is the number of the members forming the cycle of P. The sign factor $(-1)^{n_P/2}$ has come from condition 14. Noting that $(-1)^P = (-1)^{n_P-1} = -1$, the total ring-permutation energy becomes

$$E_{RP} = \sum_{P}^{R} (-1)^{n_P/2+1} J_P(K_P/K) \tag{17}$$

This expression is very similar to eq 15, and its terms become positive when $n_P = 4n$ (recall $J_P < 0$), i.e., when the ring permutation connects Kekulé structures of opposite parities. Thus the ring permutation provides a theoretical basis to the treatment of Herndon: his treatment implicitly deals with ring permutations by eq 17, which just becomes the source of the destabilizing interaction. Now, eq 15 and 17 clearly show parallelism between the resonance and the ring-permutation effects. This would explain why the classical VB theory was successful in benzenoid systems without considering ring permutations. The parallelism also enables us to regard the ring-permutation effect, when causing antiaromaticity, as resonance destabilization (or destabilization

---

[27] The current intensity of the N-membered ring is expressed as $I = (4e^2\beta H/\hbar^2c)SN^{-2} \csc(\pi/N)$ (S is area of the ring).[21]

[28] Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1960**, *257*, 445. See also ref 21, pp 511–513.

[29] Bregman, J.; Hirshfeld, F. L.; Rabinovich, D.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *19*, 227. Hirshfeld, F. L.; Rabinovich, D. *Ibid.* **1965**, *19*, 235.

[30] As a preliminary analysis of experimental ^{1}H shifts, we tried to estimate the ratio of the ring current of [18]annulene to that of benzene. By using the model of ref 28, the ratio was calculated to be 1.2. The split current model (0.506 Å separation, see footnote *a* of Table III) reduced the ratio to 0.95. The calculated RP coefficient of [18]annulene was –0.024 eV, and the VB ratio became 0.32. This value is too small, but an RP coefficient of [18]annulene adjusted to the present analysis would still be acceptably small. The Hückel theory (equal β's) yields the ratio of 2.24.

[31] We have eliminated from eq 12 interactions between Kekulé structures which are connected by a product of independent ring permutations. Such interactions are fallacious because their energy has wrong (quadratic or higher) dependence on the size of the system. This point is clear if we consider a set of noninteracting, say, benzenes.

[32] We first note that $H_{kk'}$ (eq 1 and 5) is proportional to $\langle f_k | f_{k'} \rangle$ with a negative proportionality constant. Then, eq 13 means that $\langle f_k | f_{k'} \rangle$ are mainly positive for the Kekulé structures connected by a ring permutation. We can easily show that if $\langle f_k | f_l \rangle$ and $\langle f_l | f_m \rangle$ are positive and every two of the three Kekulé structures are connected by a ring permutation, $\langle f_k | f_m \rangle$ also becomes positive. The consequences stated in the text then readily result.

[33] Gutman, I.; Herndon, W. C. *Chem. Phys. Lett.* **1975**, *34*, 387.

[34] Partities of Kekulé structures are defined only in alternant hydrocarbons (cf. systems 19 and 20 in Figure 3). The precise elucidation of Herndon's treatment is that $H_{kk'}$ are taken to be positive if the two Kekulé structures are connected by a (4n)-membered ring permutation.

Table IV. Dewar-Type VB Resonance Energies^{a} (in eV)

system^{b}	RE	system^{c}	RE
2	0.48	**1**	0.71
5	0.71	**3**	1.07
11	0.92	**4**	0.88
12	1.01	**6**	1.22
13	0.89	**7**	1.37
15	0.11	**14**	0.20

^{a}When the additive energy was not unique, the lowest one was adopted. ^{b}Benzenoid systems (except 15). ^{c}Antiaromatic systems.

attending resonance); this becomes the theoretical basis of the notion of resonance destabilization,[35] which has so far been an empirical postulate. Although the above discussion is only qualitative, the parallelism between the two effects can be a quantitative one. Figure 2 shows this point. The systems dealt with in the figure have different numbers of Kekulé structures, and their classical VB energy exhibits the resonance effect. The correlation between the two effects is very good. (In Figure 2 the ring-permutation effect is represented by a simplified ring-permutation energy in which RP coefficients are replaced by weight factors that are fixed with respect to the cycle size. The weight factors are taken from the RP coefficients of naphthalene.)

We next attempt to assess the relative magnitude of the two effects. For this purpose we need a quantity to measure the resonance effect. The classical resonance energy, defined as the energy lowering from the energy of a Kekulé structure, is inappropriate because it assigns rather large values to acyclic systems. We employ here so called Dewar-type resonance energy.[36] Following Hess and Schaad,[36b] we determined a set of bond energies so that they could additively reproduce classical VB energies of acyclic systems.[37] The Dewar-type resonance energy is defined as the difference between the actual VB energy (the classical one) and the energy obtained by applying the additive bond energies to a Kekulé structure of the system.[38] We further need the value of the exchange integral J. We use here $J = -1.5$ eV, which is a typical value obtained in the procedure of calculating RP coefficients. (This value is the same as Pauling and Wheland's estimate,[1a] and it is in rough accordance with a recent nonempirical study of Said et al.[39]) Resonance energies thus obtained are shown in Table IV. Comparing Table IV with Table I (the last column), we see that the resonance effect in benzenoid systems is about half of the ring-permutation effect in magnitude. Thus the present analysis strongly suggests that the ring-permutation effect dominates over the resonance effect even in benzenoid systems. Unfortunately, the results of antiaromatic systems are erroneous since the resonance stabilization in most cases exceeds the ring-permutation destabilization. We remember that total effect may become stabilizing in antiaromatic systems if they contain aromatic moieties but this argument does not apply to **3**, and also to **6** and **7**, presumably. We point out two factors that may cause such erroneous results. One is an underestimate of RP coefficients around four-membered rings.[40] The other is the next-nearest-neighbor transpositions that are not included in Hamiltonian 2.[41] Further investigation is necessary to establish relative magnitude of the two effects as driving forces of aromaticity.

Table V. Results of Odd-Ring Systems

			$\chi/\chi_{\text{benzene}}$^{d}	
system^{a}	RE^{b}	−RPE^{c}	VB	Hückel
16	−0.30	0.32	−0.31	−2.83
17	−0.26	0.33	0.66	2.26
18	−0.18	−0.54	−1.84	−8.34
19	−0.76	0.70	0.20	*e*
20	−0.74	0.67	0.71	2.25
20′^{f}	−0.59	0.06	−0.86	
21	−0.48	0.73	0.95	3.59
22	0.37	1.54	1.89	1.92
23	−0.72	−0.20	−0.01	0.01
24	−0.37	0.37	0.16	0.08
25	−0.23	−0.22	−0.42	0.16
26	−1.56	−0.38	−0.01	−0.20
27	−1.21	0.16	0.14	0.71
28	−0.82	0.70	0.30	−2.09
29	−0.67	0.14	−0.25	1.74
30	−0.50	−0.41	−0.77	−6.87

^{a}Figure 3. ^{b}Dewar-type VB resonance energy in eV. Positive value means stabilization. ^{c}Total ring-permutation energy with reversed sign, in eV. Positive value means stabilization. ^{d}Ring-current susceptibility. Ratio to the benzene value. Areas of constituent rings were taken to be those of regular polygons having the same bond length. Equal resonance integrals were used in the Hückel calculation. ^{e}Open-shell system. ^{f}Excited state of **20**. This state becomes the ground state in the classical VB theory, see text.

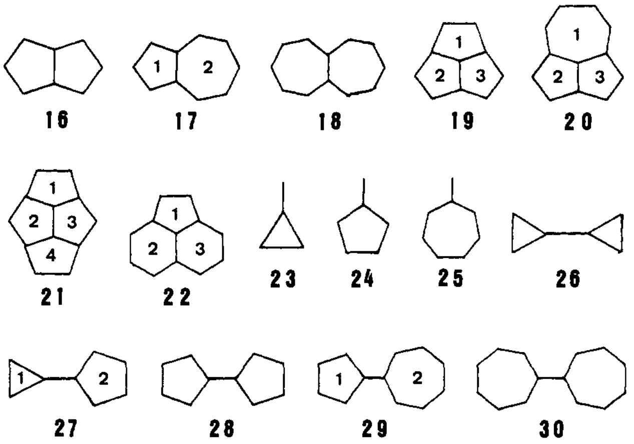


Figure 3. Systems treated: odd-ring systems.

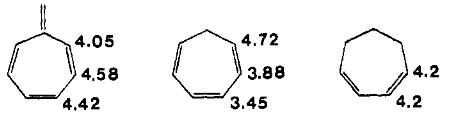


Figure 4. ^{1}H NMR shifts (τ values) of heptafulvene,[45] cycloheptatriene,[46] and 1,3-cycloheptadiene.[47]

Odd-Ring Systems

We have so far treated only systems composed of even-membered rings. When we deal with systems composed of odd-membered rings, features of aromaticity are considerably different from those so far examined and we meet with some problematic

---

(35) Platt, J. R. In "Handbuch der Physik"; Flügge, S., Ed.; Springer-Verlag: Berlin, 1961; Vol. XXXVII/2, pp 202–203.

(36) (a) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. (b) Hess, B. A., Jr.; Schaad, L. J. *Ibid.* **1971**, *93*, 305. (c) Aihara, J. *Ibid.* **1976**, *98*, 2750. (d) Gutman, I.; Milun, M.; Trinajstić, N. *Ibid.* **1977**, *99*, 1692.

(37) The bond energies we obtained are as follows. The energies of double bonds are, in J units: 0.991 for the bond type $C_1{=}C_2$, 1.018 for $C_2{=}C_2$, 0.973 for $C_1{=}C_3$, 1.017 for $C_2{=}C_3$, and 1.027 for $C_3{=}C_3$, where the subscripts of carbons denote the number of carbon atoms linked to the carbon in question. We did not distinguish types of bonds for the single bond and the energy is −0.255. The above values were determined somewhat arbitrarily from a small number of representative systems. Though they are not adapted to large systems, they accurately reproduce energies of small acyclic systems. The maximum, not mean, error is 0.016 J among all 48 systems that consist of up to 12 carbon sites.

(38) For example, the additive energy of benzene is 3(1.018−0.255) = 2.29 J. The actual energy is 2.61 J, and the resonance energy becomes 0.32 J. This value is much smaller than the classical resonance energy, 1.11 J.

(39) Said, M.; Maynau, D.; Malrieu, J. P.; Bach, M. A. G. *J. Am. Chem. Soc.* **1984**, *106*, 571.

(40) The RP coefficients we have been using (or HTR truncation[14b]) give a too low energy to cyclobutadiene; it is 1.0 eV lower than the full CI energy while similar errors are 0.06 and 0.05 eV in cyclopentadienyl and benzene, respectively.

(41) The next-nearest-neighbor terms, whose effect is destabilization, usually have coefficients of a few tenths of an electron volt. Since cyclic systems have a greater number of next-nearest-neighbor pairs than acyclic systems, these terms destabilize cyclic systems more strongly than acyclic systems. This argument does not apply to four-membered rings, but we have found that in this case the coefficients of the terms become exceptionally large, the size about twice as large as the size of other cases.

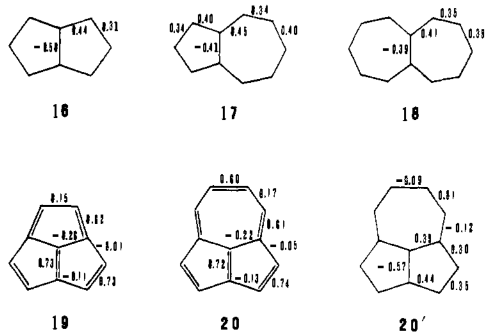


Figure 5. Decomposition of the classical VB energy to bond contributions (J unit). The dominant bonding structure, derived from the values shown, is drawn in **19** and **20**. **19**, which is doubly degenerate, represents the state having the symmetry shown here. **20′** is the ground state of the classical VB theory while **20** is the first singlet excited state.

cases. Table V shows calculated results of the systems shown in Figure 3. Let us see the VB resonance energy defined in the last section. We notice that all the systems, excluding **22** that contains even-membered rings, have negative (destabilizing) resonance energies in sharp contrast to systems composed of even-membered rings. Hence it is concluded that the classical effect, i.e., the effect arising from the classical part of Hamiltonian 2, is generally a destabilizing factor in systems composed of odd-membered rings. (This effect occurs also in **22**, as we see by comparing its resonance energy with that of naphthalene.) We hereafter refer to this classical effect as the odd-ring destabilization.[42] We next see from Table V that the ring-permutation effect is stabilizing in pentalene (**16**), which is highly reactive,[43] and in **19** and **21**, which are unknown and considered to be unstable. Therefore, we have to explain the unstableness of these compounds from the odd-ring destabilization. This explanation seems to be valid, but it is a problem that the destabilization energy given in Table V is nearly the same in magnitude as the ring-permutation stabilization. Azulene (**17**) is also a problem: the present results do not account for its stableness. We do not research these problems further; we only note that uncertainties involved in the present analysis, RP coefficients, eq 5, and how to treat the classical effect may have affected the results. We should also mention favorable cases. Some of them are in fact very interesting. An example is the unstableness of calicene (**27**). Although the Hückel MO theory[36b–d] predicts that this system is strongly aromatic, the unsubstituted calicene has not yet been synthesized.[44] The present VB result indicates that **27**, as well as **23** and **26**, is unstable owing to the odd-ring destabilization. Another example is the magnetic property of heptafulvene (**25**). As shown in Table V, the VB treatment predicts that the ring current of **25** is paramagnetic while the Hückel prediction is diamagnetism. Observed ^{1}H NMR shifts,[45–47] shown in Figure 4, appear to be in better accord with the VB prediction. As for the susceptibility results in Table V, we should remark the gross discrepancy between the two theories.

We present detailed VB results in the rest of this section. In Table VI are listed RP indices and coefficients of **16**–**30**. A general feature is that ring permutations encircling a five-membered ring have stabilizing (and diamagnetic) RP indices and those encircling a three- or seven-membered ring have destabilizing (and paramagnetic) RP indices. Figure 5 shows decomposition of the classical VB energy to bond contributions. Values given in Figure 5 are the quantity expressed by eq 4 (sign inverted) with P being the nearest-neighbor transpositions; this quantity correlates with bond length because it has a linear relationship to Penney's VB bond order.[48] There are bonds making a strong destabilizing contribution, and this seems to be a typical way in which the odd-ring destabilization exhibits itself. This observation also implies that variation of bond lengths is strong in odd-ring systems and removal of eq 5 becomes important. System **20** is a warning case: within the classical VB theory this system has a singlet excited state nearly degenerate (0.10$|J|$ separation) with the ground state, and the actual compound corresponds to the excited state. This is concluded from the comparison of the experimental geometry[49] with the theoretical bonding structure derived from the quantity shown in Figure 5. Theory also justifies this assignment: results in Table V indicate that the ring-permutation effect reverses the order of the states in question.

Table VI. RP Indices and Coefficients of Odd-Ring Systems

system	cycle	r_P	$-J_P$	cycle	r_P	$-J_P$
16	A	0.33	0.50	B	0.98	0.18
17	A1	0.31	0.52	A2	−0.27	0.40
	B	−0.98	0.12			
18	A	−0.25	0.41	B	0.98	0.07
19[a]	A1	0.32	0.47	A2	0.31	0.47
	B12	0.60	0.15	B23	−0.42	0.15
	C	0.26	0.12			
20[b]	A1	−0.27	0.37	A2	0.30	0.48[d]
	B12	−0.57	0.10[d]	B23	−0.32	0.16
	C	−0.26	0.07			
20′[c]	A1	−0.23	0.37	A2	0.30	0.48[d]
	B12	0.06	0.10[d]	B23	0.85	0.16
	C	−0.20	0.07			
21	A1	0.21	0.44	A2	0.29	0.43
	B12	0.37	0.14[d]	B23	−0.30	0.13
	C123	0.17	0.11	C124	−0.25	0.03
	D	−0.87	0.08			
22	A1	0.22	0.47	A2	−0.61	0.44[d]
	B12	0.19	0.13[d]	B23	−0.82	0.10
	C	−0.17	0.07			
23	A	−0.5	0.20			
24	A	0.33	0.56			
25	A	−0.26	0.43			
26	A	−0.5	0.19			
27	A1	−0.5	0.19	A2	0.33	0.53
28	A	0.33	0.53			
29	A1	0.33	0.53	A2	−0.25	0.42
30	A	−0.25	0.42			

[a] This system becomes doubly degenerate. Results are shown with respect to the state which has the symmetry (right-left symmetry) depicted in Figure 5. [b] The first singlet excited state of the classical VB theory. [c] The ground state of the classical VB theory. [d] Mean value of P and P^{-1}. The ratio of the difference to the mean value is 2.3% for **20**-A2, 6.1% for **20**-B12, 1.1% for **21**-B12, 1.1% for **22**-A2, and 3.8% for **22**-B12.

Conclusion

We have shown how a VB theory of aromaticity is constructed from spin Hamiltonian 2, placing emphasis on the role of ring permutations. It is shown that magnetic effects and antiaromaticity (antiaromaticity of systems composed of even-membered rings) are accounted for by the ring permutation; basic failures of the classical VB theory are thus removed. Classical effects, i.e., effects caused by the classical part of Hamiltonian 2, are also investigated. First, parallelism between the ring-permutation effect and the resonance effect is discussed. Second, the classical effect is shown to become a destabilizing factor in systems composed of odd-membered rings. It is also shown that the ring permutation provides a theoretical basis to the structure–resonance theory of Herndon.[6,7]

The framework of theory proposed in this paper, i.e., spin Hamiltonian 2 combined with eq 6 for magnetic effects, is a

---

(42) This effect is intuitively understood if we employ the usual Heisenberg form of eq 1 and regard the spin operators as classical vectors. We then see that perfect antiparallel arrangement of the spin vectors is impossible in systems containing odd-membered rings while it is always possible in even-ring systems.

(43) Hafner, K.; Dönges, R.; Goedecke, E.; Kaiser, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 337. Hafner, K.; Süss, H. U. *Ibid.* **1973**, *12*, 575.

(44) See, e.g.: Hess, B. A., Jr.; Schaad, L. J.; Ewig, C. S.; Čársky, P. *J. Comput. Chem.* **1983**, *4*, 53 and references therein.

(45) Zimmerman, H. E.; Sousa, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 834.

(46) Jackman, L. M.; Sternhell, S. "Applications of NMR Spectroscopy in Organic Chemistry"; 2nd ed.; Pergamon Press: New York, 1969; p 188.

(47) Read from a chart given in Pouchert and Campbell: Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: 1974; Vol. I.

(48) Penney, W. G. *Proc. R. Soc. London, Ser. A* **1937**, *158*, 306.

(49) Lindner, H. J. *J. Chem. Soc. B* **1970**, 907.

natural extension of the classical VB theory. This treatment appears to work, at least to a certain extent, as a theoretical model to analyze actual problems of aromaticity. Though there remain problems requiring further investigation, such as the relative position of the classical effect and the problem of odd-ring systems, it is of much interest to apply this treatment further and make detailed comparison with experiments and MO theory. Especially interesting will be the study of magnetic properties since the present treatment sometimes gives quite different predictions from the Hückel–London theory. We should recall that VB theory incorporates effects of electron correlation. In this respect we may expect that the present VB treatment will cast a new light on the understanding of aromaticity.

Acknowledgment. The author thanks Professor H. Fukutome for valuable discussions. He also thanks Professor H. Hosoya for stimulating lectures.

Appendix

We first elucidate how to calculate RP coefficients[14b] and then discuss the derivation of eq 6. Let $\{\psi_k\}$ be the basic (atomic) orbitals from which VB wave functions are constructed. We make a product of them as

$$\Psi_0 = \prod_{k=1}^{N} \psi_k(k) \tag{A1}$$

where N is the number of electrons and we assume for simplicity that all the orbitals are singly occupied. We use the symbol A to denote the set of the permutations constituting spin Hamiltonian 2. (The identity permutation is included in this set though it is omitted in eq 2.) We use the symbol J_{P} commonly to denote RP coefficients and exchange integrals, both of which are coefficients appearing in eq 2. Then, J_{P}, exchange coefficients, are defined through the linear equations

$$\sum_{P \in A} \langle Q\Psi_0 | \mathrm{P}^{-1}\Psi_0 \rangle J_P = \langle Q\Psi_0 | \hat{H}_{\mathrm{e}} | \Psi_0 \rangle \tag{A2}$$

where $\hat{H}_{\mathrm{e}}$ is the nonrelativistic electron Hamiltonian and Q takes all the elements of A. (The RP coefficients shown in the text were obtained in a somewhat different manner. They were calculated by including the next-nearest-neighbor transpositions in the set A.[14b]) If we neglect overlaps between different orbitals, we obtain an approximate expression of the exchange coefficients:

$$J_P = \langle P^{-1}\Psi_0 | \hat{H}_{\mathrm{e}} | \Psi_0 \rangle \tag{A3}$$

Equation A3 shows that RP coefficients are roughly proportional to s^n, where s is the overlap between the neareast-neighbor orbitals and n is the cycle size. This is why the RP coefficient decreases with increasing cycle size. We now elucidate assumptions to derive eq 6. Following the way of the Hückel–London theory,[21] we assume

$$\psi_k'(\mathbf{r}) = \psi_k(\mathbf{r}) \exp(-ieA_k \cdot \mathbf{r}/\hbar c) \tag{A4}$$

where ψ_k' are the orbitals in the magnetic field, ψ_k are identified with the zero-field orbitals, and $\mathbf{A}_k = (1/2)\mathbf{H} \times \mathbf{R}_k$, in which $\mathbf{H}$ is the magnetic field perpendicular to the molecular plane and $\mathbf{R}_k$ denotes the position vector of the kth atomic site. We approximate the integrals over ψ_k' by using the integrals over ψ_k. This is done by removing the phase factor in eq A4 outside the integral with the variable $\mathbf{r}$ replaced by a certain mean value; i.e.,

$$\langle ...\psi_k'(\mathbf{r})...|\hat{F}|...\psi_l'(\mathbf{r})...\rangle = \langle ...\psi_k...|\hat{F}|...\psi_l...\rangle \exp[(ie/\hbar c)(\mathbf{A}_k - \mathbf{A}_l)\cdot\mathbf{R}_{kl}] \tag{A5}$$

where $\hat{F} = \hat{H}_{\mathrm{e}}$ or 1 and $\mathbf{R}_{kl}$ denotes the mean position. In the case that ψ_k' and ψ_l' are nearest-neighbor orbicals, we set

$$\mathbf{R}_{kl} = (\mathbf{R}_k + \mathbf{R}_l)/2 \tag{A6}$$

If we employ eq A3 as the expression of exchange coefficients, eq 6 and the field independence of exchange integrals readily result from eq A5 and A6. A more rigorous derivation is possible if we use eq A5 in the case that ψ_k' and ψ_l' are the next-nearest-neighbor orbitals; the mean position is taken as

$$\mathbf{R}_{kl} = \mathbf{R}_m \tag{A7}$$

where $\mathbf{R}_m$ represents the site intervening between the kth and lth sites. Equation A7 is reasonable from the standpoint of SCF VB theory because the overlap between ψ_k and ψ_l in that theory stems mainly from their delocalization to the mth site. Equation A7, however, suffers from trouble in that it is inapplicable to the case that the kth and lth sites are on a common four-membered ring. Accordingly, we have to exclude from consideration the systems containing four-membered rings. Using eq A5, A6, and A7, we can prove

$$\langle Q\Psi_0' | \hat{F} | P\Psi_0' \rangle = \langle Q\Psi_0 | \hat{F} | P\Psi_0 \rangle \exp[ie(\sigma_{\mathrm{P}} S_{\mathrm{P}} - \sigma_Q S_Q)H/\hbar c] \tag{A8}$$

where Ψ_0' is the product of ψ_k', Q and P are elements of A, and S_P (S_Q) is set to be zero when P (Q) is not a ring permutation. Using eq A8, we readily see that eq A2, with Ψ_0 replaced by Ψ_0', has the solution expressed by eq 6. Since eq 6 now applies to the exchange integrals, their field independent readily results from the convention $S_{\mathrm{P}} = 0$.