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Direct determination of effective Hamiltonians by wave-operator methods. II. Application to effective-spin interactions in π-electron systems

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Starting from a Pariser-Parr-Pople Hamiltonian, exact effective-spin interactions are determined in a significant set of π molecules by the means of the wave-operator method presented in the preceding paper. Comparison with the quasidegenerate perturbation theory (QDPT) demonstrates the technical efficiency of the wave-operator formalism which exhibits regular convergence properties while the QDPT diverges for actual physical Hamiltonians. The determination of accurate spin-exchange interactions between bonded and nonbonded carbon atoms makes possible a careful study of their transferability. Then it is shown how effective-spin Hamiltonians of large systems can be constructed from Hamiltonians of small pattern molecules. Finally, the wave-operator formalism is applied to effective Hamiltonians arising from higher ionic atomic states which correspond to the lowest dipolar-allowed states and may be considered as an extension of the family of the Heisenberg-type effective Hamiltonians.

I. INTRODUCTION

In order to check the efficiency of the wave-operator formalism developed in part one of this series[1] we have applied it to the theoretical determination of Heisenberg-type Hamiltonians. The most popular effective Hamiltonians are actually the effective-spin Hamiltonians which have been proposed for the study of magnetism.[2] These Heisenberg Hamiltonians involve either positive or negative effective exchange interactions. These interactions are usually determined from experimental data and used for parametrizing phenomenological Heisenberg Hamiltonians.

The theoretical origin of these effective Hamiltonians has been well established from localized descriptions by Anderson[3] and has been later rationalized by Brandow.[4] If one considers for simplicity a system composed of N electrons and N orthogonal atomic orbitals on different centers, the effective exchange expresses both the direct exchange integral and the possible mixing of the neutral determinants (one electron per center) with the ionic determinants where one electron of α spin has jumped from the center A to the adjacent atom B which previously carried one electron of β spin. The effective exchange between $a\bar{b}$ and $\bar{a}b$ results from a mixing with ionic $b\bar{b}$ (or $a\bar{a}$) configurations. This superexchange theory[3] may be refined by a proper discussion of the orthogonality problems.[5] It is sure for instance that the antiferromagnetic terms which appear to result from ionic configurations when orthogonal atomic orbitals are used, result from overlap factors in nonorthogonal—valence-bond (VB) approaches, as shown very early by the Heitler-London treatment of the H_2 molecule.[6]

If one deals with a basis of orthogonal-VB—like determinants, the most efficient way to derive spin Hamiltonians is certainly the quasidegenerate perturbation theory (QDPT).[7] Such an approach has been followed by two authors of the present paper who constructed spin-effective Hamiltonians for the π systems of conjugated molecules choosing the subspace of the neutral determinants [in the sense of VB theory (one electron per center)] as the model space spanning the effective Hamiltonian.[8] The use of effective Heisenberg Hamiltonians for the treatment of the π system had been proposed before by Klein[9] and by Bulaewskii,[10] using two-body effective interactions only. The QDPT treatment of the full π configuration interaction (CI) built from the a Pariser-Parr-Pople (PPP) (Ref. 11) or a Hubbard[12] Hamiltonian has been pushed to higher orders and it has been shown that the indirect coupling with nonadjacent ionic or polyionic determinants results in effective two-body operators between nonadjacent atoms, and in many-body operators involving more than two spins. Four- and six-body operators are especially important in cyclic molecules. The appearance of many-body effective operators is the price to pay for the reduction of the Hamiltonian to a small subspace which has to deal with complex phenomena; this general conclusion has been illustrated by the attempts of Freed and co-workers[13] to build effective valence operators which would take into account the role of the core electrons in "heavy" atoms.

This QDPT deduction of the Heisenberg-type effective operators for π systems was shown to be poorly convergent; the authors[8] had to damp the high-order terms to reach a good agreement with the full—configuration-interaction results.

In the present contribution we again determine VB effective Hamiltonians for the neutral states of π-electron systems. However, instead of deriving these spin interactions through a perturbation expansion we determine exact solutions by solving the wave-operator equations presented in paper I. The paper is organized as follows: The parametrization of the PPP Hamiltonian is first recalled. Then exact effective-spin Hamiltonians are derived and compared with the results of the QDPT. The powerful convergence properties of our model are investigated particularly in the case of molecules containing ionic intruder states. Then a first quantitative study of the transferability of spin interactions is given and it is shown that in large molecules they can be deduced from effective Hamiltonians of smaller π fragments. Finally it is shown that our wave-operator methodology is not limited to the lowest neutral states and that it can also be applied to the first mainly ionic states which are responsible for the first dipole-allowed transitions from the lowest neutral states.

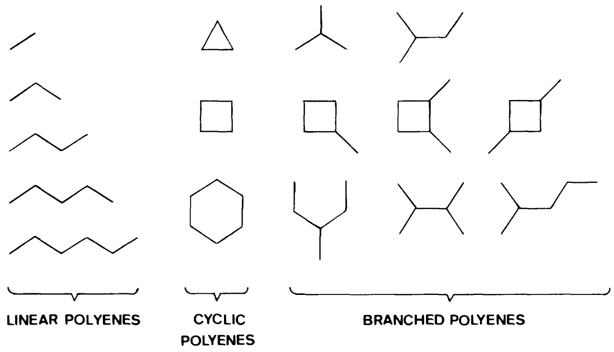


FIG. 1. Linear, cyclic, and branch polyenes investigated for the determination of effective-spin interactions.

II. FROM THE PARISER-PARR-POPLE HAMILTONIAN TO EFFECTIVE-SPIN HAMILTONIANS

The effective-spin Hamiltonians will be derived from a Pariser-Parr-Pople (PPP) (Ref. 11) Hamiltonian which is most easily written in second quantization as

$$H=\sum_{p=1}^{N}\sum_{\substack{q=1\\ q\neq p}}^{N}(a_p^\dagger a_q+a_{\bar p}^\dagger a_{\bar q})\beta_{pq} +\tfrac{1}{2}\sum_{p=1}^{N}\sum_{q=1}^{N}(\hat n_p-1)(\hat n_q-1)\gamma_{pq} \; . \tag{1}$$

$a_p^\dagger$ and $a_{\bar p}^\dagger$ are the creation operators of an electron with an atomic orbital $2p_z$ in site p with spin up and down, respectively. These atomic carbon orbitals are assumed to be orthonormal.

$\hat n_p = a_p^\dagger a_p + a_{\bar p}^\dagger a_{\bar p}$ is the occupation number on site p. The hopping integrals β_{pq} and the Coulomb bielectronic repulsion terms have been chosen (in atomic units) to obey the R dependence

$$\beta_{pq}=-29.74\exp(-2.206R_{pq})$$
$$=0 \quad \text{if } R_{pq}>3 \text{ a.u.} \; , \tag{2}$$
$$\gamma_{pq}=\frac{1}{\gamma_{pp}^{-1}+R_{pq}}, \quad \gamma_{pp}=0.588 \text{ a.u. } (16 \text{ eV}) \; . \tag{3}$$

R_{pq} is the distance between two atoms on sites p and q. The above parametrization gives the usual value $\beta_{pq}=-0.086$ a.u. (2.34 eV) for a distance $R_{pq}=2.65$ a.u. (1.4 Å) between two carbon atoms. The interpolation scheme for the bielectronic term γ_{pq} is the one first proposed by Mataga and Nishimoto.[14] The PPP Hamiltonian is known to predict correctly the elementary excitations of conjugated hydrocarbons. It is the simplest generalization of the Hubbard model[12] to which it reduces when one only considers the monocentric integrals γ_{pp} generally noted U. All calculations will be performed with standard geometries (C—C bonds equal 1.4 Å and C—C—C bond angles equal 120°). The molecules investigated are listed in Fig. 1.

In order to perform the comparison with the QDPT and in order to study the convergence behavior of our algorithm, H will be divided into two parts

$$H=H_0+\lambda V \; , \tag{4}$$

where V is the monoelectronic operator.

$$V=\sum_{\substack{p,q\\ p\neq q}}(a_p^\dagger a_q+a_{\bar p}^\dagger a_{\bar q})\beta_{pq}$$

while H_0 is the bielectronic part of Eq. (1); VB determinants $|I\rangle$ may be ordered and classified according to their ionicity and energy

$$E_I^0=\langle I\,|H\,|I\rangle=\langle I\,|H_0\,|I\rangle \; .$$

The low-energy determinants are covalent or neutral (one electron per center), the monoionic determinants, which involve one positive and one negative charge, lie higher in energy, the di-ionic determinants (two positive and two negative charges) lie even higher and so on. This approach treats the delocalization of the electrons as a perturbation, while the usual treatments of the electronic correlation start from a delocalized zeroth-order treatment which diagonalizes a monoelectronic operator ($H_0=V$ in Hückel theory or H_0 is the Fock operator), the electron repulsion is then treated as a perturbation and reduces the weight of the ionic instantaneous situations which is overestimated by the independent particle approaches.

The connection between the two opposite perturbation treatments of the full Hamiltonian (H_0 is monoelectronic, V is the bielectronic repulsion or H_0 is the bielectronic repulsion, V is the monoelectronic delocalization) appears clearly in the model studies of Pellégatti, Čižek, and Paldus.[15]

For an N-atom π system, effective-spin Hamiltonians are defined within the subspace spanned by the 2^N neutral determinants in a one to one correspondence with the 2^N Ising configurations. The taking into account of the spin symmetries of the PPP Hamiltonian makes it possible to determine effective-spin Hamiltonians with definite quantum number $S_z=0, \pm\frac{1}{2}, \pm 1, \ldots$. Table I gives the spin basic states for ethylene ($S_z=0$), the allyl radical ($S_z=-\frac{1}{2}$), and butadiene ($S_z=0$).

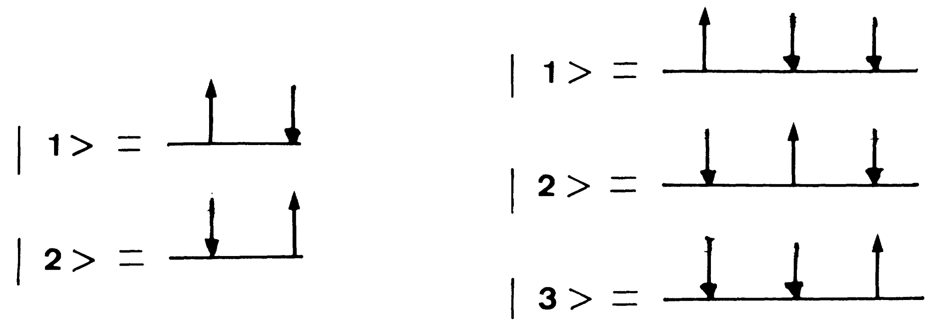
Beyond the usual two-body interactions the effective Hamiltonians contain four-spin, six-spin, . . . , N-spin interactions:

$$H_{\text{eff}}=C+\sum_{\substack{p,q\\ p<q}}H_{\text{eff},pq}+\sum_{\substack{p,q,r,s\\ p<q<r<s}}H_{\text{eff},pqrs}+\cdots \; . \tag{5}$$

C is a constant. It is to be expected that n-spin interac-

TABLE I. Matrix elements in a.u. of the effective-spin Hamiltonian for ethylene ($S_z=0$) and the allyl radical ($S_z=-\frac{1}{2}$). The spin distributions of the basic determinants are indicated by arrows.

Ethylene — Allyl radical



Ethylene

	$\vert 1\rangle$	$\vert 2\rangle$
$\langle 1 \vert$	$-0.034\,61$	
$\langle 2 \vert$	$+0.034\,61$	$-0.034\,61$

Allyl radical

	$\vert 1\rangle$	$\vert 2\rangle$	$\vert 3\rangle$
$\langle 1 \vert$	$-0.035\,785$		
$\langle 2 \vert$	$0.034\,174$	$-0.068\,348$	
$\langle 3 \vert$	$0.001\,611$	$0.034\,174$	$-0.035\,785$

tions will quickly decrease with n as will be discussed from perturbation corrections in Sec. VII. In fact they do and the two-body terms are by far the most important ones as will be shown below.

III. EXACT RESULTS FOR LINEAR AND CYCLIC MOLECULES

The methodology presented in paper I is used for exactly solving the wave-operator equation [Eq. (20)] starting from the full π-CI matrix. From the knowlege of the wave operator Ω we determine either the non-Hermitian Bloch effective Hamiltonian $H_{\text{eff},B}$ or the Hermitian des Cloizeaux effective Hamiltonian designated $H_{\text{eff,dC}}$. The details of the computational procedure are given in the Appendix. Tables I and II give the matrix elements of these Hamiltonians for ethylene, the allyl radical, and butadiene.

For the first two molecules, due to evident symmetry properties, $H_{\text{eff},B}$ is identical to $H_{\text{eff,dC}}$. For butadiene the two effective Hamiltonians have almost identical matrix elements. As expected the lowest diagonal matrix elements are those corresponding to the most alternant spin distributions: $|2\rangle$ for the allyl radical (Table I), $|2\rangle$ and $|5\rangle$ for butadiene (Table II). The most important extradiagonal terms are those associated with the exchange of two spins. Those arising from two bonded atoms are one order of magnitude greater than those proceeding from nonbonded atoms. For example, the values of the exchange terms between the pair of atoms (1-2) and (1-3) in butadiene are 0.034 and 0.002 a.u., respectively. As will be seen later, values of these spin interactions and the analysis of their transferability from a π system to another π system are more basically understood by the means of perturbation theory.

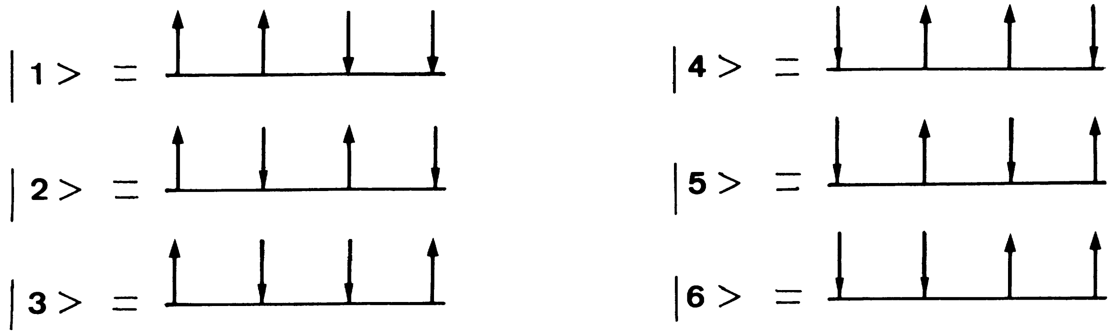
IV. COMPARISON WITH THE QUASIDEGENERATE PERTURBATION THEORY

In order to compare the convergence properties of our perturbation-iteration scheme with the QDPT, let us first consider the matrix element of $H_{\text{eff},B}$ for butadiene between the most alternant spin wave function. Figure 2 gives the values obtained at the successive iterative steps by our method as a function of the perturbation parameter λ [let us recall that the perturbation term is the monoelectronic hopping term of H in Eq. (1)]. The convergence toward the exact solution is regular up to $\lambda=2.5$. In agreement with a previous analysis[16] the convergence of the iterative procedure is almost quadratic for small values of λ and becomes linear beyond $\lambda=0.5$ including the value $\lambda=1$ which corresponds to the true physical Hamiltonian. Similarly Fig. 3 shows the values obtained by the QDPT at various orders of perturbation. The series converges very fast for small values of λ, very slowly near $\lambda=1$, and strongly diverges beyond $\lambda=1$. Note that the divergences occur in the physical region ($\lambda=1$) as was previously reported.[15] Similar results are shown in Figs. 4 and 5 for the two-body interaction term associated with the exchange of two spins on the central bond of butadiene. The comparison between our wave-operator formalism and the QDPT is similar for all molecules listed in Fig. 1.

The fact that the radius of convergence of the series occurs approximately for $\lambda=1$ which corresponds to the true physical parameter of the PPP model explains why precise results are difficult to obtain within the standard QDPT (without infinite summation). However, the QDPT is very illuminating for understanding the origin of the spin-coupling mechanisms and for obtaining their orders of magnitude which are closely related to the first appearance of a nonzero contribution in the perturbation series. For example, the QDPT explains immediately why in Table III the two-spin interaction terms of two bonded

TABLE II. Matrix elements (in a.u.) of the effective-spin Hamiltonian for butadiene ($S_z=0$). The spin distribution of the basic determinants are indicated by arrows. Numerical arrays (a) and (b) correspond to the non-Hermitian Bloch $H_{\text{eff},B}$ and Hermitian des Cloizeaux $H_{\text{eff,dC}}$ effective Hamiltonian, respectively.

(a)



	$\vert 1\rangle$	$\vert 2\rangle$	$\vert 3\rangle$	$\vert 4\rangle$	$\vert 5\rangle$	$\vert 6\rangle$
$\langle 1\vert$	−0.037 167	0.033 750	0.001 613	0.001 613	0.000 174	0.000 016
$\langle 2\vert$	0.033 782	−0.102 175	0.034 248	0.034 248	0.000 055	−0.000 157
$\langle 3\vert$	0.001 763	0.034 098	−0.071 529	−0.000 192	0.034 098	0.001 763
$\langle 4\vert$	0.001 763	0.034 098	−0.000 192	−0.071 529	0.034 098	0.001 763
$\langle 5\vert$	−0.000 157	0.000 055	0.034 248	0.034 248	−0.102 175	0.033 782
$\langle 6\vert$	0.000 016	0.000 174	0.001 613	0.001 613	0.033 750	−0.037 167

(b)

	−0.037 168					
	0.033 764	−0.102 169				
	0.001 691	0.034 175	−0.071 534			
	0.001 691	0.034 175	−0.000 197	−0.071 534		
	0.000 001	0.000 054	0.034 175	0.034 175	−0.102 169	
	0.000 022	0.000 001	0.001 691	0.001 691	0.033 764	−0.037 168

atoms are much greater than those associated with two nonbonded atoms. The former ones appear at second order in the perturbation series while the latter ones make their first appearance at fourth order. Similarly it can be seen in Table IV that four-spin interactions can be compared with (1-3) two-spin exchange terms between nonbonded atoms both bonded to an intermediate carbon atom. The difference in the order of magnitude of the six-spin interaction terms in hexatriene and benzene given in Table IV is also easily explained by perturbation. However, for benzene the QDPT gives at sixth order a very large six-body contribution between the two most alternant spin distributions. In a Hubbard model its expression, in atomic units, is

$$-504\left[\frac{\beta_{pq}}{\gamma_{pp}-\gamma_{pq}}\right]^5 \beta_{pq}=-0.035$$

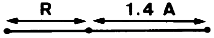
which is much greater than the exact value −0.004 489 quoted in Table IV.

The conclusion of the above discussion is that if the QDPT is the natural framework for understanding and giving the right order of magnitude of spin interactions, precise values of these terms can only be obtained beyond perturbation theory by using nonperturbative approaches. Moreover it will also be shown that exact results are necessary for studying in a precise way the transferability of spin interactions.

V. MORE ABOUT THE CONVERGENCE PROPERTIES (INTRUDER STATES)

The convergence properties of our method are now pursued a step further in investigating effective-spin Hamiltonians in the presence of intruder states. The problem of intruder states is well known especially in nuclear physics[17] where, despite some progress, all basic convergence and stability difficulties do not seem to have been overcome.

As an illustrative example we consider the unsymmetrical linear allyl radical



for which the distance between the second and the third carbon atom is maintained equal to 2.65 a.u. (1.4 Å) and we vary the distance R between the two first atoms. The variation of the three eigenenergies of the effective-spin Hamiltonian ($S_z=-\frac{1}{2}$) corresponding to the three neutral states (see Table I) are given in Fig. 6. Note the discontinuity of the second eigenvalue at the distance $R\cong 1.8$ a.u. corresponding to an avoided crossing occurring at small distance between the second neutral doublet and the

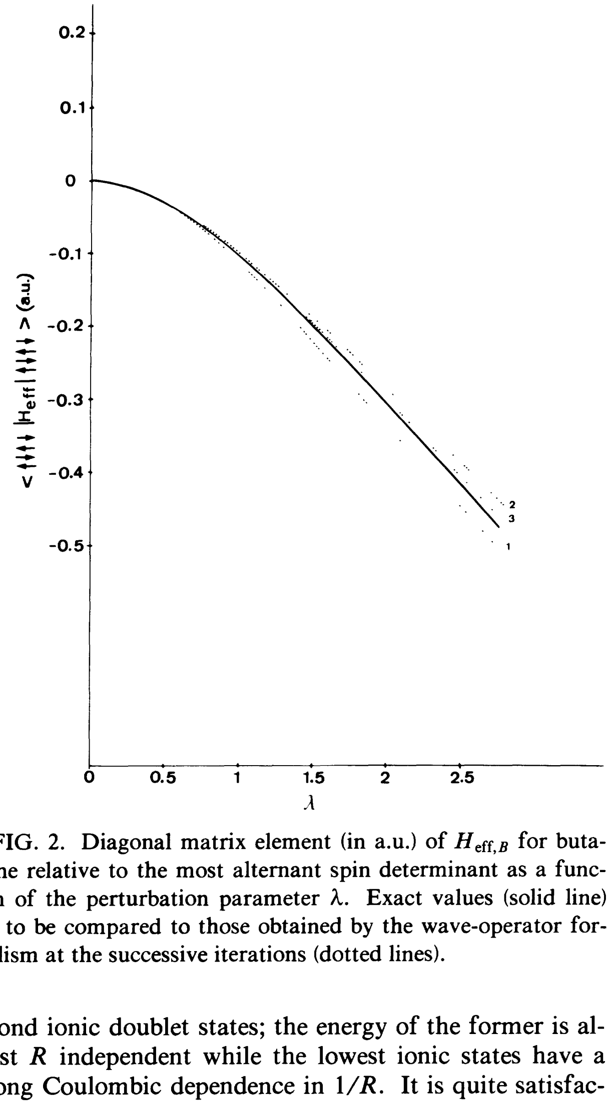


FIG. 2. Diagonal matrix element (in a.u.) of $H_{{\rm eff},B}$ for butadiene relative to the most alternant spin determinant as a function of the perturbation parameter λ. Exact values (solid line) are to be compared to those obtained by the wave-operator formalism at the successive iterations (dotted lines).

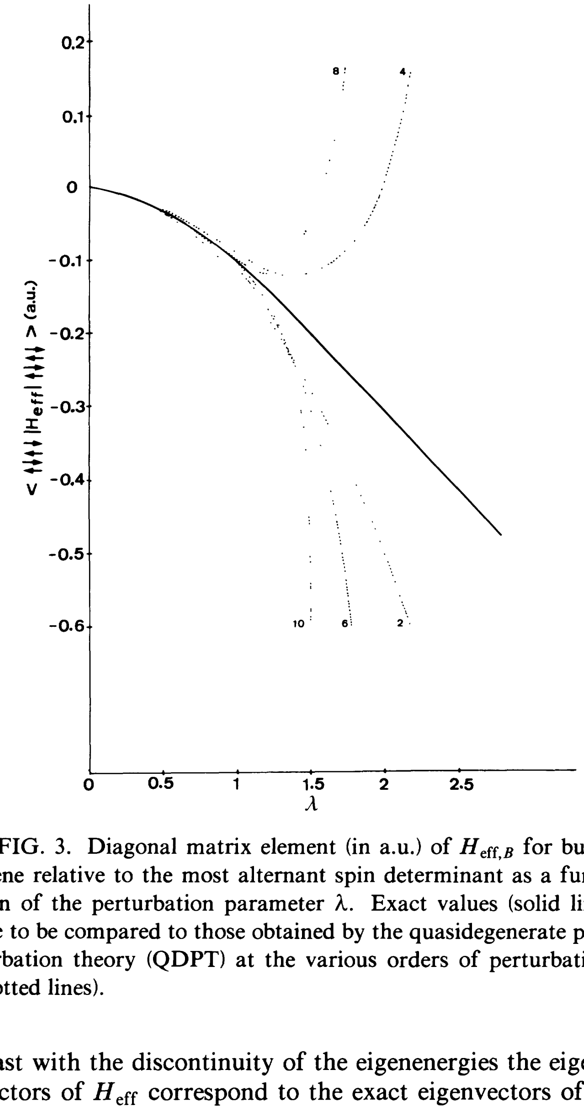


FIG. 3. Diagonal matrix element (in a.u.) of $H_{{\rm eff},B}$ for butadiene relative to the most alternant spin determinant as a function of the perturbation parameter λ. Exact values (solid line) are to be compared to those obtained by the quasidegenerate perturbation theory (QDPT) at the various orders of perturbation (dotted lines).

second ionic doublet states; the energy of the former is almost R independent while the lowest ionic states have a strong Coulombic dependence in $1/R$. It is quite satisfactory to note that our iterative procedure converges in the region of the avoided crossing. However, as expected, the convergence is slower in this region (38 iterations at $R = 1.85$ a.u. instead of 11 at $R = 2.4$ a.u.).

The most interesting point to be noted is that in contrast with the discontinuity of the eigenenergies the eigenvectors of $H_{\rm eff}$ correspond to the exact eigenvectors of H which have the largest components within the subspace of the neutral states. This is of fundamental importance for keeping the same physical meaning of the spin interactions and warranting their transferability. The main reason why the solutions remain stable within the sub-

TABLE III. Two-spin interactions in hexatriene involving one, two, and three bonds between the two atoms exchanging their spins. Exchanged spins are represented by filled arrows. Order of perturbation gives the first order of perturbation providing a nonzero contribution.

Matrix element	Number of bonds between the two atoms exchanging their spin	Order of perturbation	Energies (a.u.)
$< \Uparrow\Downarrow\uparrow\downarrow\uparrow\downarrow \mid H_{\rm eff} \mid \Downarrow\Uparrow\uparrow\downarrow\uparrow\downarrow >$	1	2	0.034 250
$< \Uparrow\uparrow\Downarrow\downarrow\uparrow\downarrow \mid H_{\rm eff} \mid \Downarrow\uparrow\Uparrow\downarrow\uparrow\downarrow >$	2	4	0.001 607
$< \Uparrow\uparrow\downarrow\Downarrow\uparrow\downarrow \mid H_{\rm eff} \mid \Downarrow\uparrow\downarrow\Uparrow\uparrow\downarrow >$	3	6	−0.000 194

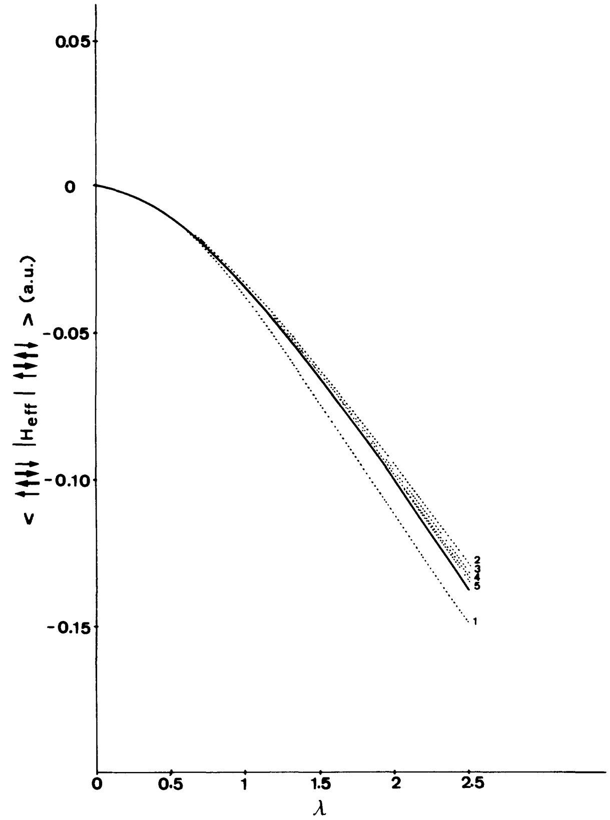


FIG. 4. Matrix element (in a.u.) of $H_{\mathrm{eff},B}$ corresponding to the exchange of two spins represented by thick arrows on the central bond of butadiene. Values are given as a function of the perturbation parameter λ. Exact values (solid line) are to be compared to those obtained by the wave-operator formalism at the successive iterations (dotted lines).

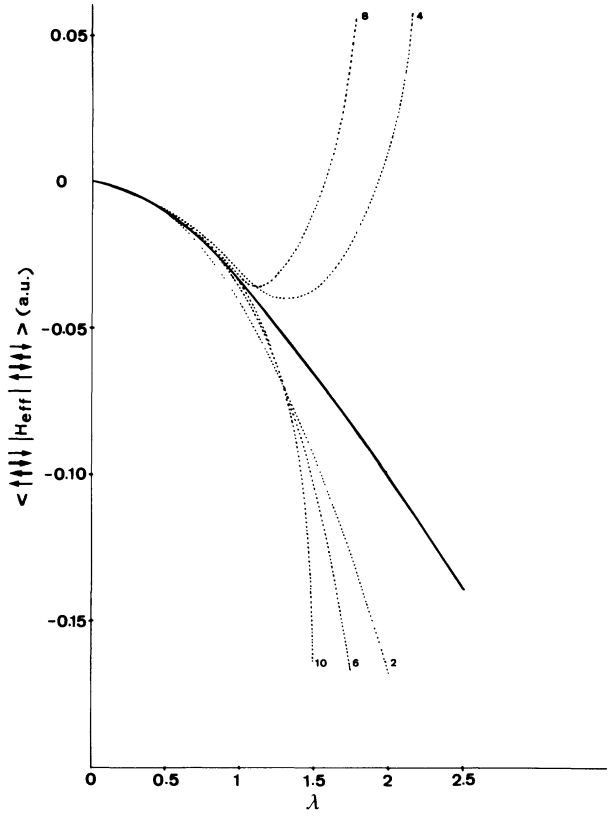
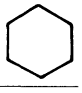


FIG. 5. Matrix element (in a.u.) of $H_{\mathrm{eff},B}$ corresponding to the exchange of two spins represented by thick arrows on the central bond of butadiene. Values are given as a function of the perturbation parameter λ. Exact values (solid line) are to be compared to those obtained by the QDPT at the various orders of perturbation (dotted lines).

space of neutral states (or equivalently the Ising configurations) in the presence of intruder states is that instead of using a variational principle on the energies our procedure is implicitly based on a variational principle for the wave functions. However, one should notice that the discontinuity in the eigenvalues of H_{eff} occurs at $R = 1.85$ a.u. while the weight of the fourth exact eigenvector on the neutral space is larger than the corresponding one of the second eigenvector between $R = 1.95$ and 1.85 a.u. This kind of hysteresis is a good illustration of the nonobvious correspondence between the approximate model space S_0 and the exact subspace S matched through the wave

TABLE IV. Two- four-, and six-spin interactions in hexatriene and benzene. Exchanged spins are represented by filled arrows. Order of perturbation gives the first order of perturbation providing a nonzero contribution.

Matrix element	n-spin interaction	Order of perturbation	Energies (a.u.)	
				
< ↑↓↑↓↑↓ | H_{eff} | ↓↑↑↓↑↓ >	2	2	0.034 250	0.034 321
< ↑↓↑↓↑↓ | H_{eff} | ↓↑↓↑↑↓ >	4	4	−0.000 058	0.000 083
< ↑↓↑↓↑↓ | H_{eff} | ↓↑↓↑↓↑ >	6	6	0.000 001	−0.004 489

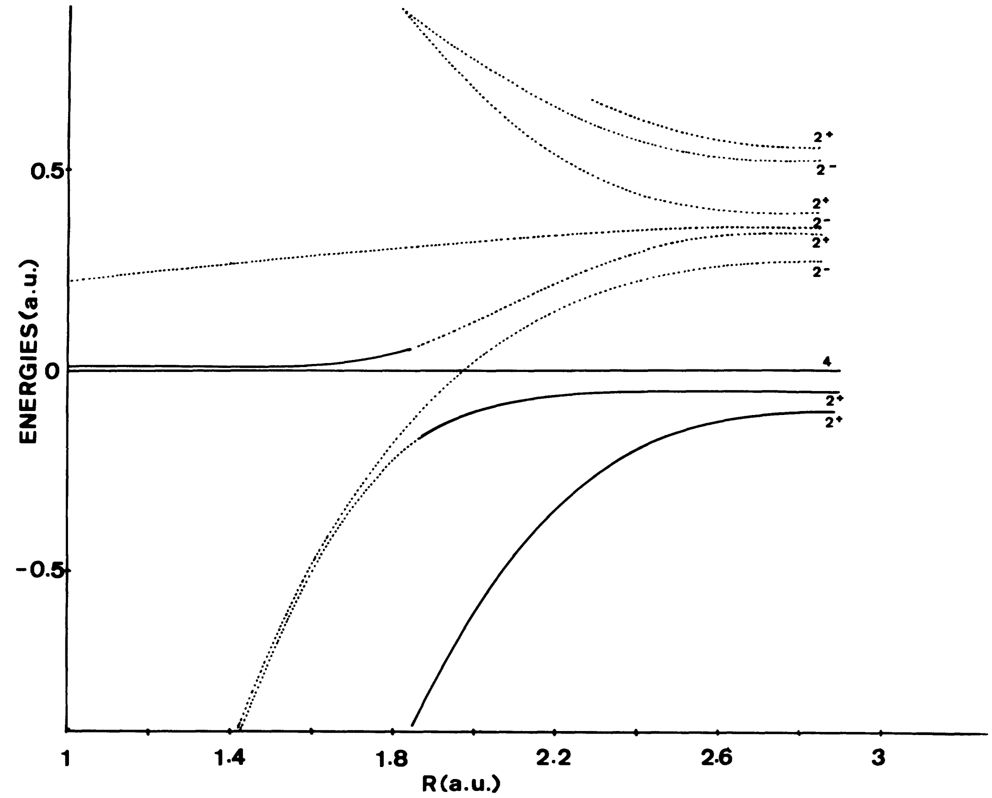
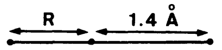


FIG. 6. Dependence of the eigenvalues of $H_{\mathrm{eff},B}$ (solid lines) of a linear unsymmetrical allyl radical



on the distance R between the two first carbon atoms. Complementary spectrum is represented by dotted lines. Each energy level is characterized by its spin degeneracy $(2S+1)$ and an inner symmetry index (+ or −).

operator Ω (see the first section of paper I).

Good convergence has also been obtained for other molecules including more compact structures than those listed in Fig. 1, for example, a formal tetrahedron which stabilizes the ionic configurations by the means of the Madelung field.

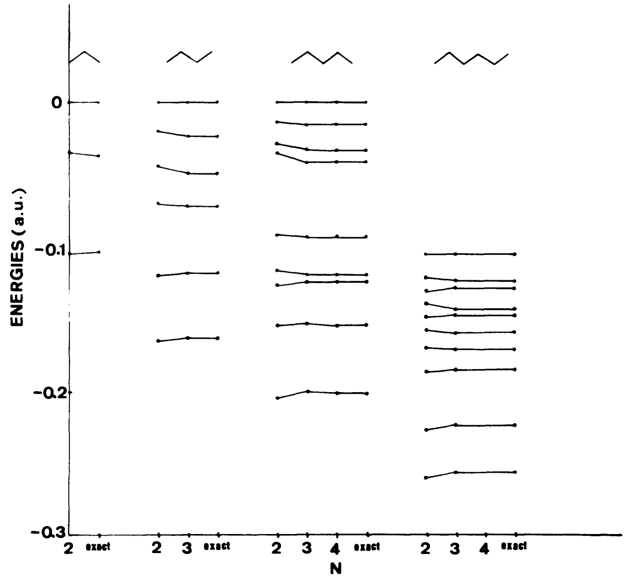
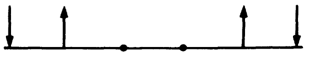


FIG. 7. Convergence of the eigenvalues of H_{eff} of linear π molecules with respect to the number N of atoms involved in the construction of H_{eff}.

VI. TRANSFERABILITY OF SPIN INTERACTIONS

The determination of exact effective-spin interactions allows for a careful analysis of the transferability of spin interactions in a molecule and from one molecule to another molecule. In this section and the next one we will only consider Hermitian des Cloizeaux effective Hamiltonians $(H_{\mathrm{eff,dC}})$. Table V gives an idea of the variability

TABLE V. Dependence of the two-spin exchange interactions on the central double bond of hexatriene on the spin distribution on the other carbon atoms. Values of the adjoint matrix elements are given in parentheses; they give an idea of the non-Hermitian character of $H_{\mathrm{eff},B}$.

Spin distribution	Exchange interaction (a.u.)	
	0.339 59	(0.336 26)
	0.339 00	(0.339 00)
	0.337 85	(0.334 25)

of the two-spin exchange interactions on the central bond of hexatriene as a function of the distribution of the spins on the other carbon atoms. The mean value is 0.0337 a.u. and the dispersion 0.002 a.u. Table VI gives the values of this same two-spin exchange term for two bonded carbon atoms for a large set of linear and cyclic π molecules. The mean value is 0.0335 and the dispersion 0.002 a.u. is identical to the intramolecular dispersion (the discrepancy for the four-membered ring is due to a large cyclic contribution as will be discussed below). The above results show that, as expected, the effective interaction exchanging two spins on two neighbor atoms is almost transferable in the whole series of π systems within a relative fluctuation of about 1%. For very accurate calculations one can take into account increments of interactions associated with π fragments containing a small number of carbon atoms as will be shown in the next section.

VII. BUILDING UP EFFECTIVE-SPIN HAMILTONIANS FOR LARGE SYSTEMS FROM SMALL FRAGMENTS

Let us again consider the two-spin interaction corresponding to the exchange of two spins on two bonded atoms. Let us first define n-atom increments associated with n-atom fragments. Consider, for example, the allyl radical where the three-atom increment to the two-body exchange operator in the difference between the exact two-spin exchange term of the allyl radical and the corresponding two-body operator in the two-atom problem (ethylene):

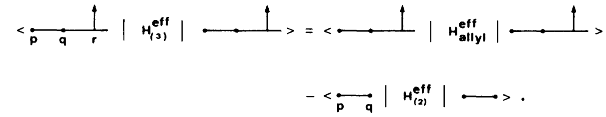
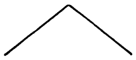
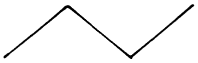
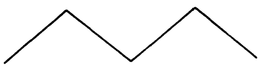
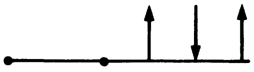
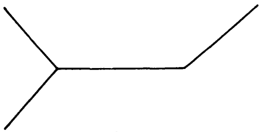
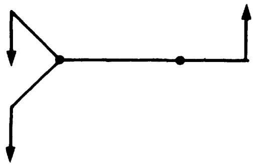
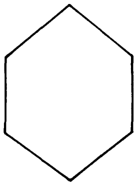
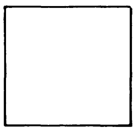


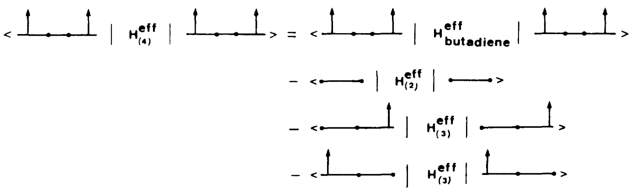
TABLE VI. Two-spin exchange interactions between bonded carbon atoms in a series of linear, branched, and cyclic conjugated molecules. Dots indicate the two sites exchanging their spins. Values of the adjoint matrix elements are given in parentheses; they give an idea of the non-Hermitian character of $H_{\text{eff},B}$.

Molecule	Spin distribution	Interaction (a.u.)	
		0.034 611	(0.034 611)
		0.034 176	(0.034 176)
		0.034 248	(0.034 098)
		0.034 255	(0.034 080)
		0.034 250	(0.034 101)
		0.033 247	(0.033 196)
	most alternant	0.034 321	(0.033 924)
	most alternant	0.029 340	(0.029 340)

Dots in the above matrix elements indicate the two sites exchanging their spins. One may write the operator corresponding to $H_{(3)}^{\text{eff}}$ in second quantization as

$$h_{p\bar{q},r}a_p^{\dagger}a_{\bar{q}}^{\dagger}a_q a_{\bar{p}}\hat{n}_r \ ,$$

where $\hat{n}_r = a_r^{\dagger}a_r$ is the occupation number of the α spin orbital on the r atom and $h_{p\bar{q},r}$ is the amplitude of the increment. In such a three-atom operator, the two atoms on sites p and q are active in the sense that their spins are exchanged while the electron on site r is apparently passive but plays a role in the intermediate ionic states resulting in the final contribution. Similarly for linear fragments, four-atom increments to the two-body exchange are obtained through



Let us now consider a numerical example that will give the order of magnitude of the many-atom fragments. Suppose that we are interested in evaluating the two-body matrix element

of the pentadienyl radical (sites exchanging their spins are represented by dots). Let us now consider smaller two-, three-, and four-atom fragments with (eventually) the same spin distributions in the neighborhood of the sites exchanging their spins. These fragments, the spin distributions and the values of the corresponding matrix elements, are given in Table VII. Thus we are able to write down the value of the above exchange term in the pentadienyl radical as the sum of the two-atom exchange integrals of ethylene and of two-, three-, four-, and five-atom increments (Table VIII). Note that these increments quickly decrease with the number of atoms of the fragment. In fact for evaluating this matrix element with a precision of 10^{-4} a.u. one needs only to get information from the effective-spin Hamiltonian of ethylene and the allyl radical.

The above results are general for any diagonal or extradiagonal spin matrix element. This means that from the knowledge of exact spin Hamiltonians of a small set of pattern molecules we are able to reproduce to any required precision the effective-spin Hamiltonian of large π systems. The procedure has been made entirely automatic on a computer. The improvement of the eigenvalues of the H_{eff}'s as a function of the number of atoms involved in their construction is given for hexatriene and benzene in Table IX and illustrated by Figs. 7–9 for a set of linear, branched, and cyclic conjugated molecules. Table IX shows that almost exact results for hexatriene (six atoms) are obtained from information contained in two- and four-atom fragments.

A comparison between linear and cyclic molecules clearly indicates the need for introducing four- and six-atom cyclic fragments in order to take into account the ring currents as previously discussed.[8] The conclusion of the above analysis is that accurate many-body effective-spin interactions can be derived for large π systems by picking up information from exact effective-spin Hamiltonians of small pattern molecules that can easily be determined once and for all.

The additivity of the effective operators in terms of 2-, 3-, . . . , n-atom contributions is easy to understand in the framework of perturbation theory. A generalized linked cluster theorem has been established for the Rayleigh

TABLE VII. Two-spin exchange interactions in a series of linear π fragments with an increasing number of carbon atoms (from 2 to 5). Dots indicate the two sites exchanging their spins.

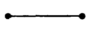
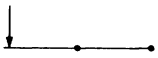
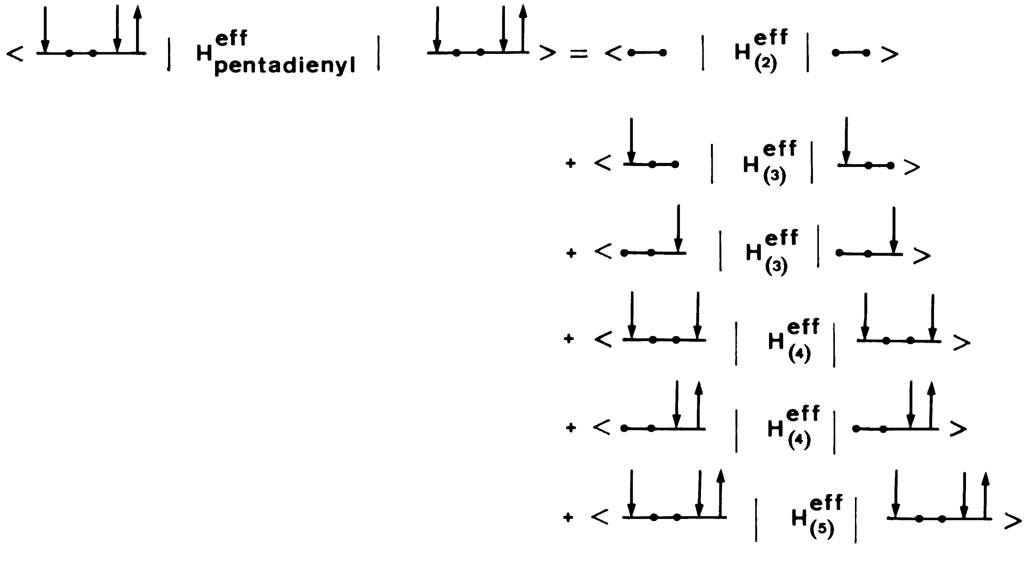
Spin distribution	S_z	Number of carbon atoms	Interactions (a.u.)
	0	2	0.034 611
	$-\frac{1}{2}$	3	0.034 174
	$-\frac{1}{2}$	3	0.034 174
	-1	4	0.034 337
	0	4	0.034 175
	$-\frac{1}{2}$	5	0.033 902

TABLE VIII. Two-spin exchange interaction in the pentadienyl obtained by the addition of increments associated with two-, three-, four-, and five-atom fragments. Dots indicate the two sites exchanging their spins. All energies are given in a.u.



	0.034 611	
	−0.000 437	three-atom increment
	−0.000 437	
	0.000 163	four-atom increment
	0.000 001	
	0.000 001	five-atom increment
exact value	0.033 902	

Schrödinger quasidegenerate perturbation theory for the case of complete model space by Brandow.[7(h)]. It has been generalized later on to any kind of model space by Hose and Kaldor[7(l)] and by Levy[7(i)]; the effective operators coupling two configurations of the model space are the sum of connected contributions which may be represented by linked diagrams. Since in our problem the perturbation V operator is the monoelectronic operator

$$V=\sum_{p,q\ \text{bonded}} \beta_{pq}(a_p^{\dagger}a_q+a_{\bar{p}}^{\dagger}a_{\bar{q}})$$

reduced to the hopping integrals between adjacent atoms, any nth order linked diagram (which involves n interaction lines) can only imply n connected bonds, i.e., a connected subfragment of n bonds in the molecular graph. Connected means that one may go from any bond of the subfragment to any other bond of it without going out of the subfragment. It may be shown[8] that for noncyclic molecular structures a $2n$th-order diagram can only imply n connected bonds. The linked cluster theorem therefore ensures that

(i) the effective operators may be considered as sums of contributions involving connected subfragments of the molecular graph, and

(ii) the contributions involving a subfragment of n bonds can only appear at the nth order of perturbation.

Therefore, the p-center contributions to a given effective operator should be greater than the contributions involving a $(p+q)$ subfragment. The n many-body terms should decrease in amplitude with n.

These conclusions are valid from the perturbative approach within the radius of convergence of the perturbative series. Since the effective Hamiltonian is unique once the model space is chosen, the same conclusions hold for the perturbation-iteration procedure presented here; the contributions of a given n-atom subfragment to an effective operator are the sum of all the QDPT diagrams which contribute to this operator and which imply all the n atoms of the subfragment at least once. These diagrams are of order n and larger than n and the increments which are presented there imply infinite summations in terms of perturbation theory; this logical structure of H_{eff} in terms

TABLE IX. For hexatriene (a) and benzene (b), convergence of the six lowest eigenvalues of H_{eff}'s constructed from fragments with an increasing number N of atoms. All energies are given in a.u.

			(a)			
$N=2$	−0.2592	−0.2551	−0.1849	−0.1686	−0.1567	−0.1470
$N=3$	−0.2551	−0.2216	−0.1840	−0.1699	−0.1586	−0.1464
exact value	−0.2554	−0.2219	−0.1842	−0.1704	−0.1584	−0.1468
			(b)			
$N=2$	−0.2978	−0.2504	−0.2077	−0.1925	−0.1731	−0.1384
$N=3$	−0.2912	−0.2454	−0.2121	−0.1939	−0.1745	−0.1446
exact value	−0.3012	−0.2404	−0.2087	−0.1981	−0.1728	−0.1448

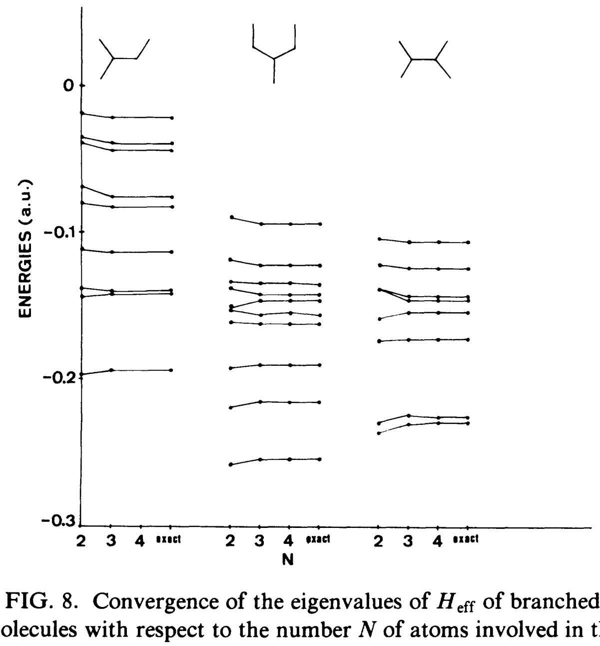


FIG. 8. Convergence of the eigenvalues of H_{eff} of branched π molecules with respect to the number N of atoms involved in the construction of H_{eff}.

of transferable increments is of course valid outside the radius of convergence of the perturbation series.

VIII. EXTENSION OF THE METHOD TO HIGHER IONIC STATES

The methodology presented in this paper is not limited to the subspace of the 2^N Ising configurations corresponding to the lowest neutral states of π systems. It is also efficient for determining the first dipole-allowed states which are the solution of intermediate effective Hamiltonians defined in the subspace of ionic states (always in the sense of the valence-bond theory). The two effective Hamiltonians spanned by the neutral and monoexcited states, respectively, have been investigated for butadiene. Figure 10 gives the spectrum as a function of the perturbation parameter λ. Good convergence properties are observed for $\lambda \in [0,2.5]$ (let us recall that the value $\lambda = 1$ corresponds to the actual physical situation). The good convergence properties of H^*_{eff} defined in the space of monoionic states is quite noticeable since these states are almost degenerate with the di-ionic states, resulting in a strong mixing of all these ionic states in the exact solutions.

The analysis of the physical structure of these effective Hamiltonians for excited states is beyond the scope of the present paper. One should only mention here that their operators translate both spin ordering effects and delocalization of the charges (holes and particles), as has been illustrated previously in the construction of effective Hamiltonian of π-systems cations.[18] This new example confirms that the Heisenberg Hamiltonians appear as a special case of a larger family of effective Hamiltonians.

It is also of value to notice that for large values of λ some eigenvectors corresponding to eigenvectors of H^*_{eff}

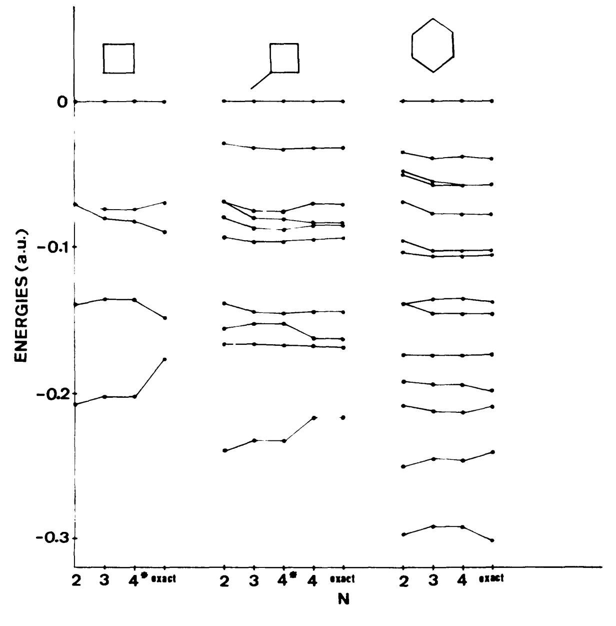


FIG. 9. Convergence of the eigenvalues of H_{eff} of cyclic π molecules with respect to the number N of atoms involved in the construction of H_{eff}. The star in 4^* means that the cyclic 4-atom contribution has been omitted.

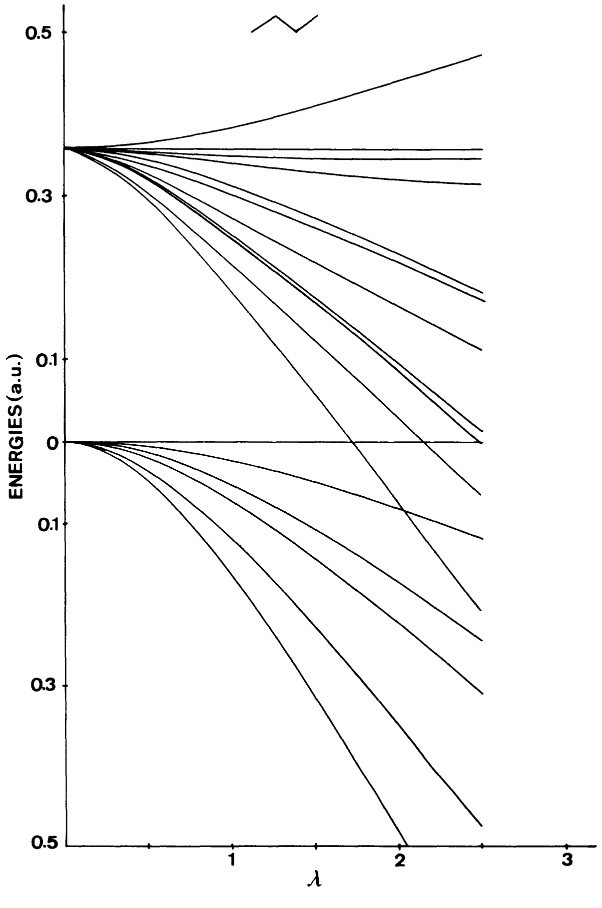


FIG. 10. Eigenenergies of butadiene arising from the neutral and monoionic states as a function of the perturbation parameter λ.

have a lower weight in the monoionic determinants (spanning H^{*}_{eff}) than the ground state which is attained through the Heisenberg effective Hamiltonian for neutral states. This remark illustrates again the nonobvious correspondence between the model subspace S_0 and the eigensubspace S to which one arrives through the wave-operator formalism: This example shows that the arrival subspace S is not defined by the eigenvectors of H which have the largest components on S_0. This behavior points out once again the problem of the one-to-one correspondence between S_0 and S. From a physical point of view it is satisfactory that H_{eff} and H^{*}_{eff} spanned by orthogonal S_0's, lead to orthogonal arrival S subspaces. This point is necessary to assure the transferability of the effective interactions.

IX. CONCLUSION

The comparison between the QDPT and the wave-operator formalism for the precise problem of constructing Heisenberg Hamiltonians from full π-CI matrices for conjugated molecules shows the technical efficiency of the second approach since the perturbative approach begins to diverge for the physically meaningful Hamiltonian ($\lambda \cong 1$), while the wave-operator treatment gives a regular convergence even for a very strong perturbation (λ up to 2.5).

Besides this technical efficiency for the lowest states of the spectrum one may notice that the wave-operator approach, when S_0 is chosen as the monoionic determinants, is able to lead to the lowest dipolar allowed "ionic" states.

With respect to the difficult problem of the one-to-one correspondence between the model space S_0 and the exact subspace S, illuminating results have been obtained showing that the eigenstates of S are not necessarily those having the largest components on the model space S_0. Starting from orthogonal model spaces, we however have always obtained orthogonal exact arrival subspaces.

As previously established by perturbation theory our calculations confirm that the two-spin exchange interactions between bonded atoms, which are generally considered in phenomenological Heisenberg Hamiltonians, are by far the most important ones. However, N-spin interactions play an important role in molecules involving N-membered rings. Although the right order of magnitude of these many-body interactions was previously reported, our results indicate that exact values, especially those appearing at a high order of perturbation, may be quite different and generally smaller than the perturbation values. From exact effective-spin Hamiltonians we were able to produce a careful study of their transferability. Finally we indicated a method for constructing accurate effective-spin Hamiltonians for large systems from a hierarchy of exact spin Hamiltonians of small molecules.

Another conclusion of this work is that one has to clearly recognize the domains of applicability of the QDPT and of the wave-operator techniques. QDPT provides the basic understanding of the origin and structural dependence of the spin interaction and of their order of magnitude. However, for obtaining exact solutions the iterative resolution of wave-operator equations seems to be much more efficient, since the limit of convergence of perturbation theories corresponds approximately to the true actual physical parameters of the original electrostatic Hamiltonian.

Finally it could be objected that we have derived spin interactions from an approximate electrostatic Hamiltonian, but it can be conjectured that similar convergence and transferability properties could be found from the exact electronic Hamiltonian. Very promising the results have already been obtained in this way for π systems in our laboratory.[19] We believe that the next step should be to apply the methods presented in this paper to highly degenerate systems such as alkaline and transition metals in order to extend Hund's rules for atoms and to get a better qualitative and quantitative understanding of spin interactions in condensed matter.

ACKNOWLEDGMENT

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APPENDIX: COMPUTATIONAL PROCEDURE AND APPLICATION TO BUTADIENE

The general method presented in paper I is applied to butadiene which is given as an example for explaining how the calculations were actually done. In a first step the full configuration interaction matrix is constructed using the atomic orbitals as monoelectronic wave functions. Then the effective-spin Hamiltonian is obtained by solving the reduced wave-operator equation.

1. Structure of the configuration interaction (CI) matrix

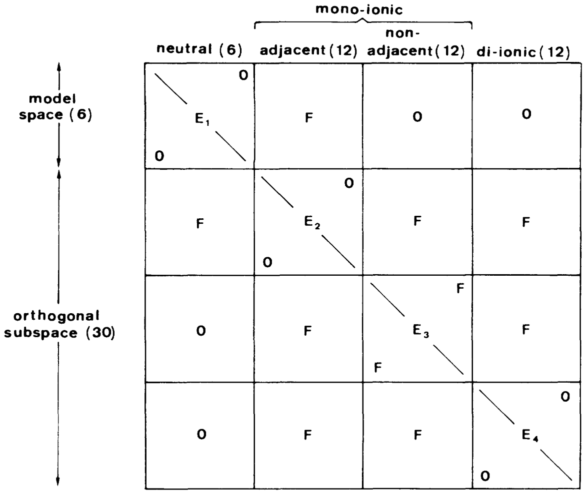
Butadiene is a four-electron four—π-orbital problem. In the minimal basis set the Hilbert space is spanned by the $C_8^4 = 70$ four-electron determinants. However, the spin symmetry $[S_z, H] = 0$ allows us to derive independently effective Hamiltonians for the various S_z values which run from $S_z = 0$ to 2. Therefore, we have only considered the subspace spanned by the 36, $S_z = 0$ determinants. The six neutral determinants with one electron per carbon atom are

$$|1\rangle = |ab\bar{c}\,\bar{d}|\,,\quad |2\rangle = |a\bar{b}c\bar{d}|\,,\quad |3\rangle = |a\bar{b}\,\bar{c}d|\ ,$$

$$|4\rangle = |\bar{a}bc\bar{d}|\,,\quad |5\rangle = |\bar{a}b\bar{c}d|\,,\quad |6\rangle = |\bar{a}\,\bar{b}cd|\ .$$

In these determinants the atomic orbitals appear in the natural linear sequence $a-b-c-d$ of the molecule. These determinants which span a six-dimensional model space S_0 are also in a one-to-one correspondence with the six spin configurations given in Table II. The orthogonal subspace $S_0^{\perp}$ is made up of 30 ionic determinants. For example, the determinant $|a\bar{a}b\bar{c}|$ belongs to $S_0^{\perp}$. These ionic determinants which have higher energies than the neutral ones are classified according to their increasing energies; there are 12 adjacent monoionic determinants, 12 nonadjacent monoionic determinants, and 6 di-ionic determinants which have the highest energies.

The matrix elements of the PPP Hamiltonian [Eq. (1)] are easily calculated and the schematic structure of the full CI matrix is given below,



F indicates the existence of charge transfer (i.e., β_{pq}) integrals outside the diagonal of the matrix.

2. Resolution of the wave-operator equation

The reduced wave-operator equation is solved by the perturbation-iteration method given in paper I of this series. The first order of the QDPT provides the initial values of the matrix elements of X

$$\langle i \mid X^{(1)} \mid a \rangle = \frac{\langle i \mid V \mid a \rangle}{E_a^0 - E_i^0} \; . \tag{A1}$$

$E_a^0 = \langle a \mid H \mid a \rangle$ and $E_i^0 = \langle i \mid H \mid i \rangle$ are the unperturbed energies corresponding to the model space S_0 and its orthogonal complement $S_0^{\perp}$. Later the labels a and i will always characterize the subspaces S_0 and $S_0^{\perp}$, respectively.

At the nth iteration ($n \geq 3$) the increments of the matrix elements of X are a linear combination of three increments

$$\begin{aligned}\langle i \mid \Delta X^{(n)} \mid a \rangle = {} & C_1 \langle i \mid -F^{(n-1)}(X) \mid a \rangle \\ & + C_2 \langle i \mid \Delta X^{(n-1)} \mid a \rangle \\ & + C_3 \langle i \mid \Delta X^{(n-2)} \mid a \rangle \; .\end{aligned} \tag{A2}$$

The operator F is defined by Eq. (46) of paper I. $\langle i \mid \Delta X^{(n-1)} \mid a \rangle$ and $\langle i \mid \Delta X^{(n-2)} \mid a \rangle$ are the increments of the matrix elements calculated at the $(n-1)$th and $(n-2)$th iterations. At each iteration the C_k coefficients are obtained by solving a system of linear equations

$$\sum_{l=1}^{3} a_{kl} C_l = -f_k , \quad k = 1,2,3 \tag{A3}$$

where

$$\begin{aligned} a_{kl} = \sum_{a,i} & \langle i \mid A \, \Delta X^{(n+1-k)} \mid a \rangle \\ & \times \langle i \mid A \, \Delta X^{(n+1-l)} \mid a \rangle , \quad k,l = 1,2,3 \end{aligned} \tag{A4}$$

and

$$\begin{aligned} f_k = \sum_{a,i} & \langle i \mid A \, \Delta X^{(n+1-k)} \mid a \rangle \\ & \times \langle i \mid F(X^{n-1}) \mid a \rangle , \quad k = 1,2,3 \; . \end{aligned} \tag{A5}$$

The operator A is defined by Eq. (47) of paper I. At each iteration the distance to the exact solution is estimated through the norm of F:

$$\epsilon = \left[\frac{1}{dD} \sum_{a,i} (\langle i \mid F^{(n)} \mid a \rangle)^2 \right]^{1/2} . \tag{A6}$$

d is the dimension of the model space S_0 and D is the dimension of $S_0^{\perp}$ (for butadiene $d = 6$ and $D = 30$). When the norm becomes smaller than a given threshold $\epsilon = 10^{-m}$, where m is a positive integer, the iterative procedure is stopped. Thus the matrix elements of X are determined with approximatively m exact figures. Finally the matrix elements of the effective Hamiltonian are obtained by a simple matrix multiplication

$$\langle a \mid H_{\text{eff}} \mid b \rangle = \langle a \mid H \mid b \rangle + \sum_i \langle a \mid V \mid i \rangle \langle i \mid X \mid b \rangle \; . \tag{A7}$$

For all the conjugated molecules investigated in this paper the iterative procedure generally converged in less than 20 iterations for a threshold $\epsilon = 10^{-6}$. Butadiene needed only 8 iterations.

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