



HAL
open science

Foundation of Heisenberg Hamiltonians for systems with several active electrons per centre: acetylene and polyines

Daniel Maynau, M.A. Garcia-Bach, Jean-Paul Malrieu

► To cite this version:

Daniel Maynau, M.A. Garcia-Bach, Jean-Paul Malrieu. Foundation of Heisenberg Hamiltonians for systems with several active electrons per centre: acetylene and polyines. *Journal de Physique*, 1986, 47 (2), pp.207-216. 10.1051/jphys:01986004702020700 . jpa-00210197

HAL Id: jpa-00210197

<https://hal.science/jpa-00210197>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

31.20G — 31.20R — 75.10 — 75.10J

Foundation of Heisenberg Hamiltonians for systems with several active electrons per centre : acetylene and polyines

D. Maynaud, M. A. Garcia-Bach (+) and J. P. Malrieu

Laboratoire de Physique Quantique, Université Paul Sabatier,
Unité Associée au C.N.R.S. n° 505, 118, route de Narbonne, 31062 Toulouse Cedex, France(+) Universitat de Barcelona, Facultat de Física,
Física de l'Estad Sòlid, Diagonal 645, Barcelona, 28 Spain

(Reçu le 27 mars 1985, accepté sous forme définitive le 4 octobre 1985)

Résumé. — Un Hamiltonien de Heisenberg non empirique, proposé pour des systèmes π conjugués à partir de calculs sur l'éthylène, s'était révélé très performant. Son fondement théorique découlait de façon évidente de l'Hamiltonien total, grâce à la Théorie des Perturbations Quasi Dégénérées (QDPT), comme l'a montré Anderson. Si on veut, de la même façon, définir un Hamiltonien de Heisenberg pour des systèmes comportant deux électrons actifs dans deux Orbitales Atomiques orthogonales par centre comme dans les polyines, on peut extraire l'information d'un calcul poussé sur l'acétylène. Le développement QDPT ne converge pas, et la simple application des définitions de Bloch et des Cloizeaux donne des Hamiltoniens effectifs mal conditionnés, très éloignés de la structure de Heisenberg ; leur transfert à l'homologue C_3H_2 donne de mauvais résultats. Nous définissons un autre Hamiltonien effectif qui a bien l'allure d'un Hamiltonien de Heisenberg et qui conduit à un spectre raisonnable pour C_3H_2 .

Abstract. — A non-empirical Heisenberg Hamiltonian had been proposed for conjugated π systems from *ab initio* calculations on ethylene, and proved to be very efficient. Its theoretical foundation from the full Hamiltonian was evident from the concept of effective Hamiltonian and the use of Quasi-Degenerate-Perturbation Theory (QDPT), as shown by Anderson. When one wants to define a Heisenberg Hamiltonian for systems bearing two active electrons in two orthogonal Atomic Orbitals per centre, as in polyines, one may try to derive it from an accurate calculation on acetylene. The QDPT procedure does not converge, and it is shown that the direct use of the Bloch and des Cloizeaux definitions lead to ill-behaved effective Hamiltonians, which deviate strongly from a Heisenberg structure, and give erroneous results on C_3H_2 . A modified definition of the effective Hamiltonian is proposed, which recovers the form of a Heisenberg Hamiltonian and proves to give a reasonable spectrum of C_3H_2 .

Introduction.

The Heisenberg Hamiltonians [1] have been essentially developed in solid state physics for Mott insulators. They have been applied in coordination chemistry to rationalize the lower part of the spectrum of molecules with several unpaired electrons. A series of previous papers [2-5] have shown however that the Heisenberg Hamiltonians might be successfully applied to the π systems of conjugated molecules usually described through Molecular Orbital Theory. The Heisenberg Hamiltonians are not only an elegant and correlated description of the rules governing the electronic distribution in the molecules, they are able to predict accurate geometries of ground and excited states, rotational barriers, spectroscopic features and photochemical behaviours [5]. An extension of this

approach to more general chemical systems seems an attractive idea.

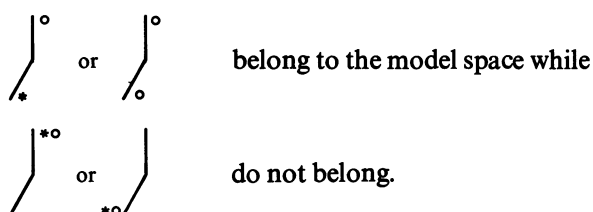
In the above mentioned studies the neutral configurations (with one π electron and one π AO per carbon atom) span a model space on which the magnetic Heisenberg Hamiltonian is expressed. This Hamiltonian is obtained perturbatively using the Quasi Degenerate Perturbation Theory [6] following the procedure proposed by Anderson [7] and Brandow [8]. It may also be obtained from the canonic definitions of effective Hamiltonians proposed by Bloch [9] or des Cloizeaux [10] from the knowledge of accurate wave functions and energies, obtained for instance from high quality molecular calculations, with large basis sets and extensive Configuration Interaction (CI). The practical successes mentioned above were obtained after extraction of such a Hei-

senberg Hamiltonian from accurate MO-CI calculation on ethylene.

When one wants to generalize this approach one must remember that the Heisenberg Hamiltonians are restricted to half filled-bands, i.e. systems where each atom brings p electrons in p Atomic Orbitals (AO). The purpose of this paper is to determine whether it is possible, following the way opened by Anderson, to obtain Heisenberg Hamiltonians for half-filled bands with several active electrons per atom. The simplest physical problem deals with the acetylene molecule and the polyynes treated as π systems. The σ core is kept frozen and each carbon atom brings two π electrons and two orthogonal p_x and p_y AO's. The conclusions obtained from this precise study will be general and valid for other half-filled bands.

The qualitative problem may be formulated as follows : for systems with one electron and one AO per centre (for instance π conjugated molecules, or alkali clusters) the model space involves all the neutral determinants (in the sense of Valence Bond (VB) Theory). The effective Hamiltonian does not give any information on the predominantly ionic eigenstates, but delivers all the neutral valence eigenstates, which represent most of the lower part of the spectrum. In the case of $p e^-$, p AO per centre, the Heisenberg Hamiltonian does not exclude only the ionic determinants (and ionic eigenstates), it also excludes a whole category of neutral determinants ; the Heisenberg Hamiltonian model space is composed of determinants where each active AO bears one electron ; but other neutral determinants exist, where one AO bears 2 electrons, while another one on the same atom is empty.

Hereafter the stars represent α spins and the circles β spins ; these symbols are easier to read than the usual \uparrow and \downarrow arrows.



These situations will be called « pseudo-ionic ». The occurrence of such situations is general for systems having more than one electron per centre. These neutral situations are slightly higher in energy than those where each AO only bears one electron, because of the excess repulsion of the two electrons in the same AO, but they are much lower in energy than the ionic situations, and their proximity will result in practical and conceptual problems.

One may either

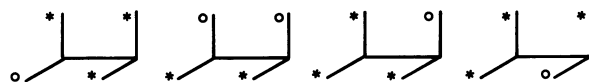
- i) keep a strong restriction of the model space to the configurations with one electron per AO ;
- ii) or enlarge the model space to all neutral configurations, including those with 0 or 2 e^- in the same AO.

The Heisenberg formalism necessarily belongs to the first case ; however the present paper demonstrates that the usual foundations of Heisenberg Hamiltonians based on the effective Hamiltonian concepts and Quasi Degenerate Perturbation Theory are not applicable and that a new type of effective Hamiltonians must be defined to obtain Heisenberg Hamiltonians in such problems.

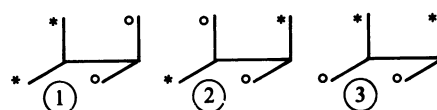
The second hypothesis (enlarged model space) which goes out of the Heisenberg formalism will be treated in paper II.

2. The second order Heisenberg Hamiltonian.

2.1 THE MODEL SPACE. — The effective Hamiltonian must satisfy some consistency rules. The basis set must involve all the determinants of the chosen type (here one electron per AO). When S_z has its maximum value $\pm n$ for n atoms, all spins are parallel, and there is only one determinant in the basis set. The energy of this determinant will be kept as the zero of energy in the rest of the paper. When S_z decreases, the dimension of the basis increases to reach the value C_{2n}^n when $S_z = 0$. For the acetylene molecule, there are four equivalent determinants for $S_z = \pm 1$.



For $S_z = 0$, there are six determinants of three different types



The other three are obtained by exchanging stars and circles. One may notice that the determinants of type ① and ② have $S_z = 0$ in both π bonds, allowing for electron delocalization in both bonds, while electron delocalization is forbidden in determinants of type ③. The determinants ① also respect the Hund's rule on both atoms, having $S_z = \pm 1$ on each atom, while $S_z = 0$ in determinants ② and ③.

2.2 THE HEISENBERG HAMILTONIAN AS A SECOND-ORDER EFFECTIVE HAMILTONIAN. — Figure 1 gives a schematic view of the full $S_z = 0$ π Hamiltonian. The σ core is supposed to be frozen (for instance at the SCF level), the π AO's x_a, y_a, x_b, y_b are supposed to be orthogonal(ized), and the π VB determinants are divided into neutral 1 e^- /AO determinants, neutral pseudo ionic determinants with 0 or 2 e^- /AO, singly ionic ($A^- B^+$) and doubly ionic ($A^{--} B^{++}$) determinants.

One should notice the occurrence of first order

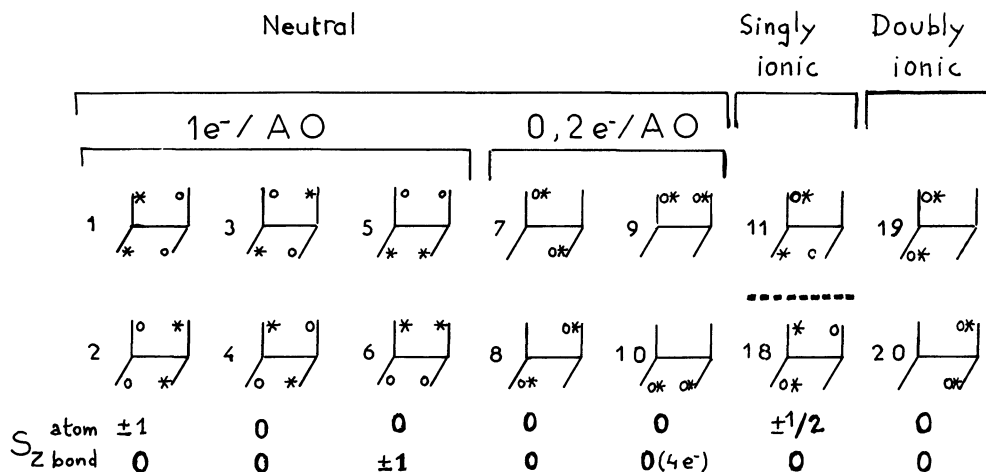


Fig. 1a. — Definition of the VB determinants.

Determ.	Neutrals			Pseudo-ionic		Singly ionic	Doubly ionic
	1-2	3-4	5-6	7-8	9-10		
	0	0	0	0	0	<i>F</i>	0
		2 <i>K</i>	- <i>K</i>	0	0	<i>F</i>	0
			2 <i>K</i>	0	0	0	0
				ΔE_1	<i>K</i>	<i>F</i>	0
					ΔE_2	0	0
						ΔE_i	<i>F</i>
							2 ΔE_i

Fig. 1b. — Schematic picture of the full π electron VB Hamiltonian matrix. *K* and *F* represent respectively the intra-atomic exchange and hopping integrals.

Determ.	1	2	3	4	5	6
	-2 <i>g</i>	0	<i>g</i>	<i>g</i>	0	0
		-2 <i>g</i>	<i>g</i>	<i>g</i>	0	0
			-2 <i>g</i> +2 <i>K</i>	0	- <i>K</i>	- <i>K</i>
				-2 <i>g</i> +2 <i>K</i>	- <i>K</i>	- <i>K</i>
					2 <i>K</i>	0
						2 <i>K</i>

Fig. 1c. — Structure of the Heisenberg Hamiltonian for the acetylene molecule.

intra atomic exchange operators between orthogonal AO's,

$$K = K_{x_a y_a}$$

which are far from negligible, and will contribute in first order to the Heisenberg Hamiltonian. The model space (1 e/AO) determinants have the lower energy, they are coupled through *F* hopping bicentric integrals to the singly ionic determinants, of higher energy. Among the pseudo ionic determinants (0, 2 e⁻/AO) the determinants $x_a^2 y_b^2$ are very low in energy, they are not directly coupled with the model space, but they are obtained from the singly ionic determinants through a second interatomic electron jump.

Following the way which led to a rationalization of

the Heisenberg Hamiltonian for 1 e⁻/AO per atom problems, one may establish the structure of a second order effective Hamiltonian built in the model space through the Quasi Degenerate Perturbation Theory. The perturbation operator is defined by

$$H = H_0 + V$$

$$H_0 = \sum_{K \in S} E_K^0 |K\rangle \langle K| + \sum_{\alpha \notin S} E_\alpha^0 |\alpha\rangle \langle \alpha|$$

and in practice

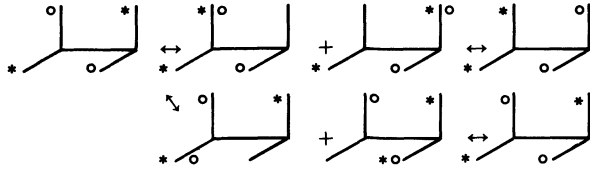
$$E_K^0 = E^0 = 0.$$

The second order expression of the effective Hamiltonian matrix elements is

$$\langle I | \bar{H}^{(2)} | J \rangle = \langle I | H | J \rangle - \sum_{\alpha \notin S} \frac{\langle I | H | \alpha \rangle \langle \alpha | H | J \rangle}{E_\alpha^0 - E_J^0}$$

I, J \in S.

The singly ionic determinants α will perturb the diagonal energy of the determinants presenting two electrons of opposite spins in each π bond (i.e. the first four determinants) and they will couple them two by two. The coupling is for instance



Calling $g = 2F^2/\Delta E$, where ΔE is the energy difference between the neutral and singly ionic determinants, one obtains the Heisenberg Hamiltonian pictured in figure 1b, and expressed as

$$\bar{H} = \sum_A \sum_{i_a j_a} K |i_a \bar{j}_a - \bar{i}_a j_a\rangle \langle \bar{i}_a j_a - i_a \bar{j}_a| + \sum_A \sum_B \sum_{i_a j_b} (-g) |i_a \bar{i}_b - \bar{i}_a i_b\rangle \langle i_a \bar{i}_b - \bar{i}_a i_b|$$

where i and j represent p_x or p_y AO's, a and b symbolizing the A and B atoms respectively. The interatomic effective exchange $-g$ only couples p_x or p_y AO's, but the coupling is the same in both π subsystems.

To this stage, the derivation leads to a Heisenberg Hamiltonian. However two problems will evidently occur

i) The third order expression

$$\langle I | \bar{H}^{(3)} | J \rangle = \langle I | \bar{H}^{(2)} | J \rangle + \sum_{\alpha, \beta \notin S} \frac{\langle I | H | \alpha \rangle \langle \alpha | H | \beta \rangle \langle \beta | H | J \rangle}{(E_\alpha^0 - E_J^0)(E_\beta^0 - E_J^0)} - \sum_{\alpha \notin S} \sum_{L \in S} \frac{\langle I | H | \alpha \rangle \langle \alpha | H | L \rangle \langle L | V | J \rangle}{(E_\alpha^0 - E_J^0)^2}$$

is non Hermitian if there exist some matrix elements of the perturbation operator V in the model space, as occurs for the K matrix elements in the model space.

ii) The fourth order expression of $\langle I | \bar{H}^{(4)} | J \rangle$ involves terms of the type

$$- \sum_{\alpha, \beta, \gamma \notin S} \frac{\langle I | V | \alpha \rangle \langle \alpha | V | \beta \rangle \langle \beta | V | \gamma \rangle \langle \gamma | V | J \rangle}{(E_\alpha^0 - E_J^0)(E_\beta^0 - E_J^0)(E_\gamma^0 - E_J^0)}$$

where the β determinants may be the pseudo-ionic neutral states which have a very low energy. They will lead to a divergent behaviour of the perturbation series.

This is a major problem and one must refer to the basic definitions of the effective Hamiltonians which the QDPT is supposed to obtain.

3. Features of exact effective Hamiltonians

3.1 DEGREES OF FREEDOM IN THE DEFINITION OF EXACT EFFECTIVE HAMILTONIANS.

3.1.1 *The Bloch non-Hermitian effective Hamiltonian.* — The Quasi Degenerate Perturbation Theory leads, when it converges, to an effective Hamiltonian built on the model space. If P_0 is the projector on the

model space S , of dimension n_S

$$P_0 = \sum_{K \in S=1, n_S} |K\rangle \langle K|$$

the effective Hamiltonian \bar{H} has n_S exact eigenvalues ε_m equal to eigenvalues of the exact Hamiltonian H , and the corresponding eigenvectors $\bar{\psi}_m$ of \bar{H} are the projections of the exact eigenvectors into the model space. There exist n_S roots of H such that

$$\bar{H} | \bar{\psi}_m \rangle = \varepsilon_m | \bar{\psi}_m \rangle \\ | \bar{\psi}_m \rangle = P_0 | \psi_m \rangle.$$

This is the Bloch definition of the effective Hamiltonian, and the usual QDPT series expansion leads to this effective Hamiltonian

$$\bar{H}^B = \sum_{m=1}^{n_S} | \bar{\psi}_m \rangle \varepsilon_m \langle \bar{\psi}_m^\perp | \quad (1)$$

where the vector $\bar{\psi}_m^\perp$ is the biorthogonal transform of ψ_m in S

$$| \bar{\psi}_m^\perp \rangle = S^{-1} | \bar{\psi}_m \rangle$$

where S is the overlap matrix of the $\bar{\psi}_m$'s ($S_{mn} = \langle \bar{\psi}_m | \bar{\psi}_n \rangle$).

One should notice that this effective Hamiltonian exists even when the QDPT expansion diverges, if the n_S vectors ψ_m 's and energies ε_m are known. When one has solved the problem $H\psi = \varepsilon\psi$, it is always possible to select the n_S eigenvectors having the largest components in the model space i.e. the n_S vectors ψ_m such that

$$\sum_{m=1}^{n_S} \langle P_0 \psi_m | P_0 \psi_m \rangle = \max.$$

The existence of the effective Hamiltonian is independent on the convergence properties of the series expansion. One may thus pick up all the eigenfunctions of H having the largest components in S and build \bar{H} from equation (1). In our problem these states are a part of the so-called neutral states of VB theory, those which are essentially spanned by neutral determinants with one electron per AO.

As apparent from equation (1), due to the non-orthogonality of the projected functions $\bar{\psi}_m$, the Bloch effective operator is not Hermitian. From a practical point of view, obtaining an effective Hamiltonian for the acetylene molecule may proceed as follows.

— Perform accurate MO-CI calculations of the lowest part of the acetylene molecule spectrum. One should obtain all the neutral states of interest. The highest of them is the quintuplet with one active electron per AO, since no delocalization takes place in this state. The other relevant states are selected from evident symmetry considerations and in view of their components in the model space.

— The corresponding wave functions are projected onto the model space; one has thus the n_S ε_m and $\bar{\psi}_m$,

and applying equation (1) gives the Bloch effective Hamiltonian to which the usual QDPT expansion converges within the radius of convergence.

Of course this procedure is only interesting for transferability purposes; one hopes that the operators so obtained may be transferred to larger molecular systems, as occurred for the one-electron one AO per centre problems (alkali and π conjugated molecules).

3.1.2 The des Cloizeaux Hermitian effective Hamiltonian. — To have a Hermitian effective Hamiltonian one may simply orthogonalize in a symmetric way, through an $S^{-1/2}$ transform, the n_s vectors $|\bar{\psi}_m\rangle$, as proposed by des Cloizeaux [10]

$$\{\bar{\psi}'_m\} = S^{-1/2} \{\bar{\psi}_m\}.$$

Then one defines an Hermitian effective Hamiltonian \bar{H}^{dC} such that

$$\bar{H}^{dC} |\bar{\psi}'_m\rangle = \varepsilon_m |\bar{\psi}'_m\rangle$$

admitting the n_s orthogonalized projected eigenvectors $\bar{\psi}'_m$ as eigenvectors.

$$\bar{H}^{dC} = \sum_{m=1}^{n_s} |\bar{\psi}'_m\rangle \varepsilon_m \langle \bar{\psi}'_m|.$$

The construction of a Bloch effective Hamiltonian represents the smallest loss of information. Going to the des Cloizeaux definition one introduces a further distortion of the eigenvectors.

This effective Hamiltonian may be obtained through a variant of the QDP Theory, proposed by Brandow. This variant is not supposed to have better convergence properties than the usual one.

3.1.3 New proposal: a hierarchically Hermitized effective Hamiltonian. — The des Cloizeaux procedure alters equally the lowest vectors $|\bar{\psi}_m\rangle$, which are of main physical importance, and the highest vectors. As will be shown on the acetylene problem, the ground state vector may be strongly distorted by the $S^{-1/2}$ transform, losing much of its physical significance. One may propose, a hierarchized orthogonalization procedure of the $|\bar{\psi}_m\rangle$, dividing them into two classes. The first class M (of dimension n_M) defines a projector,

$$P_M = \sum_{m=1}^{n_M} |\bar{\psi}_m\rangle S_M^{-1} \langle \bar{\psi}_m|$$

where S_M is the overlap matrix of the n_M vectors of the first class. The complementary part (class I) is defined by the projector

$$P_I = P_0 - P_M.$$

In practice the procedure consists in a projection of the $|\bar{\psi}_i\rangle$ which do not belong to the first class into P_I by subtracting their components in the first class vectors

$$|\bar{\psi}''_i\rangle = |\bar{\psi}_i\rangle - \sum_m |\bar{\psi}_m\rangle \langle \bar{\psi}_m | \bar{\psi}_i \rangle.$$

The $|\bar{\psi}''_i\rangle$ are then orthogonal to the $|\bar{\psi}_m\rangle$; if the (major) elements of the S matrix between the $\bar{\psi}_m$ are of the type $\langle \bar{\psi}_m | \bar{\psi}_i \rangle$, the operator built on the set $\psi'' = \{\bar{\psi}_m, \bar{\psi}''_i\}$ is (nearly) Hermitian.

$$\bar{H}^{HH} = \sum_{m=1}^{n_M} |\bar{\psi}_m\rangle \varepsilon_m \langle \bar{\psi}_m| + \sum_{i=n_M+1}^{n_s} |\bar{\psi}''_i\rangle \varepsilon_i \langle \bar{\psi}''_i|.$$

If the $|\bar{\psi}_m\rangle$'s are not orthogonal, an $S_M^{-1/2}$ symmetrical orthogonalization within the class M may be applied, and $S_I^{-1/2}$ symmetrical orthogonalization may also be applied in the class I to obtain perfect hermiticity.

3.2 STRUCTURES OF THREE « EXACT » EFFECTIVE HAMILTONIANS FOR THE ACETYLENE MOLECULE. — Table I gives the eigenvalues, the truncated eigenvectors and the symmetry of the six $S_z = 0$ neutral states having the largest components on the model space of the six determinants with 1 e⁻ per π AO. The energies are obtained using a double-zeta valence basis set and extensive CI's. The zero of energy has been taken equal to the energy of the quintet ${}^5\Sigma_g^+$ state. The table also gives the two states lying in the same energy range which have weak or zero components in the model space, and the components of the eigenvectors on the neutral determinants with zero or two electrons in the π AO's (i.e. pseudo-ionic determinants). The two ${}^1\Sigma_g^+$ vectors which must be given by the effective Hamiltonian have large components on these pseudo-ionic determinants, and these large components will be responsible for some major problems.

The overlap of the 1 and 6 (${}^1\Sigma_g^+$) eigenvectors when projected in the model space is very large: $\langle \bar{\psi}_1 | \bar{\psi}_6 \rangle = 0.47$. The Bloch, des Cloizeaux and Hierarchically Hermitized effective Hamiltonians will therefore be very different.

One should notice that the ground state determinant has its largest coefficients on the determinants $|x_a y_a \bar{x}_b \bar{y}_b|$ or $|\bar{x}_a \bar{y}_a x_b y_b|$ which satisfy both the atomic Hund's rule and the interatomic ferromagnetic coupling. The $S^{-1/2}$ transformed $\bar{\psi}'_1$ vector is deeply modified, having coefficients of 0.45 and 0.54 on the determinants $|x_a y_a \bar{x}_b \bar{y}_b|$ (Hund) and $|x_a \bar{y}_a \bar{x}_b y_b|$ (non Hund) instead of 0.52 and 0.47 respectively in $\bar{\psi}_1$.

There are four $S_z = 1$ neutral determinants of equal energy. The four corresponding eigenstates (${}^3\Sigma_u^+$, ${}^3\Delta_u$, ${}^5\Sigma_g^+$ and ${}^3\Delta_g$) have equal components on these four determinants and different phases; being of different symmetries, they are orthogonal; the $S_z = 1$ effective Hamiltonians are therefore identical for the Bloch, des Cloizeaux and hierarchic Hermitization definitions (and of course Hermitian). This effective Hamiltonian is given in table II; it is clear that it does not deviate much from a Heisenberg Hamiltonian structure. The intraatomic ferromagnetic exchange integral K is + 0.029 a.u., the antiferromagnetic coupling $-g$ between two AO's belonging to the same π system is - 0.098 a.u. In a Heisenberg scheme

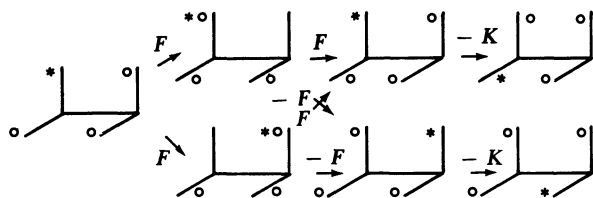
Table I. — Neutral eigenvectors in the basis set of neutral and pseudo ionic determinants. There is one line for two determinants differing by a full spin inversion. The symbol \pm means that the two coefficients of the two spin-inverse determinants have opposite signs. The starred ${}^1\Delta_u$ state is neutral but essentially pseudo ionic (0 or 2 e^- per AO). Notice the occurrence of an ionic ${}^1\Sigma_u^+$ state among the neutral eigenstates.

Symmetry	Determinants	${}^1\Sigma_g^+$	${}^3\Sigma_u^+$	${}^3\Delta_u$	${}^1\Delta_u^*$	${}^5\Sigma_g^+$	${}^1\Sigma_u^{+*}$	${}^1\Sigma_g^+$	${}^3\Delta_g$
Eigen-values		- 0.367	- 0.189	- 0.138	- 0.083	0.	0.059	0.064	0.064
Eigen-vectors	1-2	0.346	± 0.595	0.	0.	0.397		0.365	0.
	3-4	- 0.310	0.	± 0.580	0.	0.397		0.130	0.
	5-6	- 0.036	0.	0.	0.	0.397		0.485	± 0.678
	7-8	0.254	0.	0.	± 0.530	0.		- 0.251	0.
	9-10	- 0.021	0.	0.	0.	0.		0.088	0.

Table II. — $S_z = 1$ effective Hamiltonian for acetylene molecule resulting from an ab initio MO-CI calculation. The symbols between parenthesis represent the matrix elements of a Heisenberg Hamiltonian.

- 0.066			
(-g + K)			
- 0.029	- 0.066		
(-K)	(-g + K)		
0.098	- 0.003	- 0.066	
(g)	(0)	(-g + K)	
- 0.003	0.098	- 0.029	- 0.066
(0)	(g)	(-K)	(-g + K)

the diagonal matrix element should be $-g + K = -0.069$ instead of the exact value -0.066 . The difference is due to terms which involve more than two AO's. One may notice the existence of a small non-diagonal term (-0.003 a.u.) representing an exchange between the p_x^A and p_y^B AO's; this term appears through third order contributions in QDPT, through the sequences



corresponding to the third order contributions to the $\langle I | \bar{H} | I \rangle$ term

$$-\sum_{J,\alpha} \frac{\langle L | V | \alpha \rangle \langle \alpha | V | J \rangle \langle J | V | I \rangle}{\Delta\alpha^2}$$

where L, J, I belong to the model space, α belonging to the outer space. This third order contribution ($-2KF^2/\Delta E^2$) is negative. A third order correction to the monocentric exchange has an opposite value, as seen in the above scheme (i.e. 0.003 a.u.), so that the proper two-body exchange is $K = 0.032$ a.u. The third order corrections are three-electron three-AO contributions which might be written in second quantization or symbolically

$$-0.003 |\bar{x}_a y_a y_b \rangle \langle x_a y_a \bar{y}_b | + \text{equivalent terms} \\ + 0.003 |\bar{x}_a y_a y_b \rangle \langle x_a \bar{y}_a y_b | + \text{equivalent terms}.$$

Notice that in the first operator the $|y_a \rangle \langle y_a |$ (i.e. $a_{y_a}^+ a_{y_a}$) product is a simple counter. The same is true for the product $|y_b \rangle \langle y_b |$ in the second term.

Table IIIa gives the Bloch Hamiltonian for the $S_z = 0$ model space. The structure which one would expect from a Heisenberg Hamiltonian appears in terms of g and K matrix elements, together with the deviations of the Bloch effective Hamiltonian from the Heisenberg structure assuming the values of the g and K integrals extracted from the $S_z = 1$ effective Hamiltonian. The results deserve the following comments :

i) the non-hermiticity of the Bloch effective Hamiltonian is remarkable, the difference between transposed elements $|\bar{H}_{ij} - \bar{H}_{ji}|$ is about $+0.06$ a.u. i.e. larger than $+2K$!

ii) very large matrix elements appear between determinants which are not coupled by a Heisenberg Hamiltonian, for instance

$$\left\langle \begin{array}{c} * \\ \circ \\ * \end{array} \middle| \bar{H}^B \middle| \begin{array}{c} * \\ \circ \\ * \end{array} \right\rangle = -0.068 \text{ a.u.}$$

Table III. — $S_z = 0$ effective Hamiltonians for acetylene in a.u. The g and K integrals are those deduced from the $S_z = 1$ matrix (0.098 and 0.032 a.u. respectively) and the numbers represent the deviations from the Heisenberg structure (0 symbolizes a zero matrix element in the Heisenberg formalism). The second number on the diagonals concern the 1-2, 3-4 or 5-6 matrix element.

Bloch		
1	$-2g + 0.034, 0 - 0.026$	$g + 0.038$
3	$0 - 0.029$	$-2g + 2K - 0.046, 0 - 0.042$
5	$0 - 0.001$	$-K + 0.006$
des Cloizeaux		
1	$-2g + 0.036, 0 + 0.026$	$g - 0.004$
3		$-2g + 2K - 0.040, 0 - 0.034$
5		$2K - 0.014, 0 - 0.014$
Hierarchic Hermitization		
1	$-2g + 0.003, 0 - 0.003$	$g - 0.002$
3		$-2g + 2K - 0.011, 0 - 0.005$
5		$0 + 0.002$ $-K + 0.010$ $2K - 0.012, -0.012$

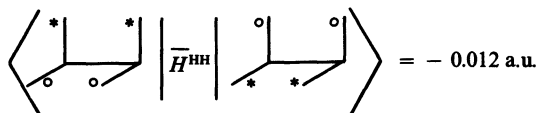
iii) the diagonal energy of the determinants $|x_a y_a \bar{x}_b \bar{y}_b|$ which satisfy the Hund's rule on both atoms and take benefit of the antiferromagnetic interatomic coupling are almost degenerate with those of the determinants $|x_a \bar{y}_a \bar{x}_b y_b|$ which lose the benefit of Hund's rule.

Table IIIb gives the des Cloizeaux effective Hamiltonian, according to the same conventions; one may notice that

$$2 \bar{H}_{ij}^{ac} = \bar{H}_{ij}^B + \bar{H}_{ji}^B.$$

The deviation from a Heisenberg structure is very large and the preceding comments ii) and iii) remain valid. The near degeneracy between the diagonal terms concerning the determinants $x_a y_a \bar{x}_b \bar{y}_b$ and $x_a \bar{y}_a \bar{x}_b y_b$ reflects the fact that the $S^{-1/2}$ transformed vector $\bar{\psi}'_1$ has equal weights on these two types of determinants.

Our proposal of an Hierarchic Hermitization leads to an effective Hamiltonian which weakly deviates from a Heisenberg structure. The largest deviation concerns the four-body operators



One may notice that the determinants $|x_a y_a \bar{x}_b \bar{y}_b|$ are now significantly lower in energy than the $|x_a \bar{y}_a \bar{x}_b y_b|$ ones, as one would expect.

This analysis demonstrates clearly that for systems having more than one active electron per atom, Heisenberg Hamiltonians cannot be considered as effective Hamiltonians derived from the full Hamiltonian by a natural choice of the model space (as the neutral determinants with one electron per π AO) and one of the canonic definition of effective Hamiltonians. Heisenberg Hamiltonians can only be obtained through new definitions of effective Hamiltonians,

one of them being the above defined hierarchically Hermitized definition; this point will be briefly discussed in the conclusion. This problem is related to the convergence problem, since the large effect of the pseudo-ionic neutral determinants is responsible for both the divergence of QDPT and for the large overlaps between the $^1\Sigma_g^+$ projected eigenvectors, resulting in strong non-hermiticity. But the divergence of the QDPT expansion is a minor problem in front of the structural defects of the Bloch and des Cloizeaux effective Hamiltonians.

4. Test of transferability to larger systems.

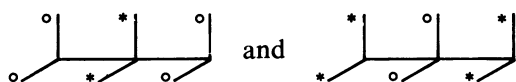
The three effective Hamiltonians obtained in the previous section may be used to treat larger systems, such as polyines. The smallest larger molecule is the linear three-centre analog of acetylene C_3H_2 . Our present purpose is essentially methodological, and we simply want to see the ability of the effective Hamiltonians to predict the ground state nature and the excited state ordering of this model molecule, for which accurate MO-CI calculations have been performed by us, using the same basis set as for acetylene. These MO-CI calculations are used as benchmarks.

The fact that the Bloch and des Cloizeaux effective operators strongly deviate from a Heisenberg structure does not invalidate them; they might be as efficient as the Hierarchically Hermitized effective operator, which keeps a Heisenberg structure and has smaller four-body operators.

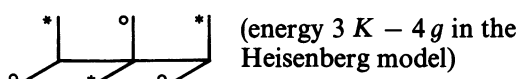
The matrix for the three-centre problem involves 20 vectors. The operators assume a tight-binding approximation, i.e. all determinants presenting spin exchanges between atoms 1 and 3 are supposed to have a zero interaction.

Since the most favorable electronic distribution is ferromagnetic on each atom and antiferromagnetic between adjacent atoms, one may expect

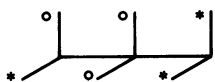
that the lowest energy determinant in C_3H_2 are



which the Heisenberg model predict to lie at $-4g$ below the septuplet; they belong to the $S_z = \pm 1$ subspace. One may thus expect that the ground state is triplet in nature, and its symmetry would then be $^3\Sigma_g^-$. This is actually verified by MO-CI calculation. The $S_z = 0$ $^1\Delta_u$ state lies 1.2 eV above the $^3\Sigma_u^-$. Its components necessarily violate Hund's rule on the three atoms if one wants to maintain the antiferromagnetic



ordering in all bonds. If one introduces a ferromagnetic coupling on two atoms, such as in



one destroys one antiferromagnetic bond stabilization at least, the energy becoming $K - 3g$ in the Heisenberg model. As noticed previously, the diagonal four-body terms in the Bloch or des Cloizeaux effective Hamiltonians destroy the stabilization of the structures having parallel spins on the same atom with respect to those having antiparallel spins. When transferred in the C_3H_2 problem, the Bloch and des Cloizeaux Hamiltonians result in a *major failure* (Fig. 2) : they predict a $^1\Delta_u$ ground state, the $^3\Sigma_g^-$ state being 0.65 eV above; the above remarks explain this failure as a consequence of the underestimation of the ferro-

magnetic intraatomic coupling in these effective operators.

On the contrary the Hierarchically Hermitized effective Hamiltonian gives a correct prediction of the ground state symmetry and of the $^1\Delta_u/{}^3\Sigma_g^-$ energy splitting (Fig. 2). We also calculated upper states of this molecule. One may notice that the Bloch and des Cloizeaux Hamiltonians also reverse the ${}^1\Sigma_u^-/{}^3\Sigma_u$ ordering of the third and fourth excited states and a ${}^5\Sigma_g^-/{}^3\Sigma_g^-$ ordering in an upper part of the spectrum. The Heisenberg type Hamiltonian does not present such misorderings. It is true that the transition energies to these excited states are not quantitatively correct (deviations of about 0.5 eV), but one should remember that some low lying neutral excited states have their largest components on Valence Bond structures with doubly occupied AO's; in C_3H_2 two such states (${}^1\Sigma_u$ and ${}^3\Delta_u$) appear in figure 2. Their specific interactions with the low-lying states spanned by the singly occupied AO structures may result in an energy lowering of the latter states. Notice that the ${}^5\Sigma_g^-$ does not interact with states involving doubly occupied AO's (since they necessarily involve two closed shell atoms and are therefore at most of triplet spin symmetry) and is correctly positioned by the Heisenberg Hamiltonian. For larger molecules the part of the spectrum correctly treated by the Heisenberg Hamiltonian should involve more and more states.

5. Conclusion.

The present paper shows that the theoretical derivation of a Heisenberg Hamiltonian from the exact Hamiltonian is not straightforward for half-filled band systems where some atoms bring $p(> 1)$ electrons in p AO. The derivation proposed by Anderson [7] of effective exchange operators reflecting the coupling through ionic determinants in a Quasi Degenerate Perturbation Theory works perfectly well for one electron/one AO systems. For $p e^-/p$ AO per atom systems, the second order approximation leads to a Heisenberg formalism, but its third order development breaks the hermiticity and the fourth order perturbation would diverge. The Quasi Degenerate Perturbation Theory is unable to produce Heisenberg-type Hamiltonians for systems like acetylene since the $s^2 p_x^2$ determinant of the carbon atom is not much higher in energy than the $s^2 p_x p_y$ determinant.

The lack of convergence of the Quasi Degenerate Perturbation Theory is not a major problem since the effective Hamiltonians that it should prove are well defined, either in the Bloch or in the des Cloizeaux versions; the knowledge of accurate variational wave functions and energies is sufficient to define the effective Hamiltonian spanned by a given model space. The present work has shown that the deviation from hermiticity of the Bloch effective Hamiltonian is very large; its structure largely deviates from that of a Heisenberg Hamiltonian. The des Cloizeaux effective

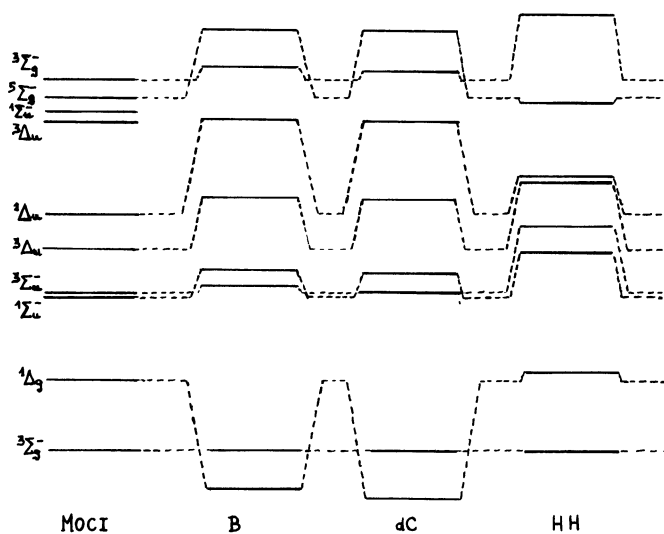


Fig. 2. — Lower part of the spectrum of C_3H_2 obtained from the fragment operators of C_2H_2 in the three cases : B : Bloch operator ; dC : des Cloizeaux Hermitization ; HH : Hierarchical Hermitization, compared with an MO-CI calculation. Note the similarity of B and dC results.

Hamiltonian is of course Hermitian but it also deviates strongly from the structure of a Heisenberg Hamiltonian. These deviations, which are large four-body terms, destroy the benefit of the expected ferromagnetic intraatomic coupling. The consequence is a complete failure of the simplest attempt to transfer these Hamiltonians, namely in the prediction of the ground state of the C_3H_2 linear molecule.

These difficulties are linked to the non-orthogonality of the projections in the model space of the first and second $^1\Sigma_g^+$ states of acetylene. This is due to the strong mixing of the second $^1\Sigma_g^+$ with a third $^1\Sigma_g^+$ state, which is essentially built on closed shell atoms $p_x^{A^2} p_y^{B^2}$, and which acts as an intruder state in the perturbation expansion. The symmetrical treatment of the overlap between the projected $^1\Sigma_g^+$ vectors, as managed by the des Cloizeaux $S^{-1/2}$ transform, results in a strong distortion of the lowest $^1\Sigma_g^+$ projected vector, and this lack of information on the lowest eigenvector destroys the transferability. It might seem astonishing that the Bloch effective Hamiltonian suffers the same defect, since its eigenvectors $|\bar{\psi}_m\rangle$ are not orthogonalized. But one should remember that in the spectral definition of the Bloch effective Hamiltonian

$$\bar{H}^B = \sum_m |\bar{\psi}_m\rangle \varepsilon_m \langle \bar{\psi}_m^\perp|$$

the $\langle \text{bra} |$ vectors are biorthogonal (i.e. S^{-1} transforms of the $|\bar{\psi}_m\rangle$) and strongly modified by the S overlap. It seems reasonable to say that when the projections of the eigenvectors in the model space are far from orthogonality, the transferability of the Bloch and des Cloizeaux effective Hamiltonians to larger systems is questionable.

A solution to this dilemma has been proposed. It consists in a non-symmetrical treatment of the projected eigenvector (or of the model space). Two classes of projected eigenvectors are defined, the lowest ones are kept unchanged, while the second class is projected in the complementary subspace (and eventually symmetrically orthogonalized in a later step). If the lowest vectors are orthogonal by symmetry the final eigenvectors are orthogonal and this new hierarchically hermitized effective Hamiltonian has only destroyed some information concerning the eigenvectors of the second class, i.e. excited eigenvectors; when applied to acetylene this effective Hamiltonian turns out to give a satisfactory Heisenberg structure, with

very small four-body terms. It reproduces nicely the lowest part of the C—H spectrum, presenting a good transferability.

This partition of the eigenvectors in two classes (or more than two) may be shown to correspond to a partition of the model space into a main subspace and intermediate model subspace. The above described hierarchic Hermitization does not lead to an analytic perturbative expansion as did the Bloch and des Cloizeaux definitions. However an analytic expansion has been recently proposed by one of us and coworkers [11], and it will be applied to the same problem. If one had only one vector in each class, the hierarchic Hermitization would simply consist in a Schmidt orthogonalization of the projected eigenvectors (instead of an $S^{-1/2}$ orthogonalization). In our precise problem the two procedures are identical.

Our hierarchic Hermitization is certainly one member of a large class of generalized effective Hamiltonians which accept to sacrifice some information on the highest eigenvectors and eventually on the highest eigenenergies.

The presently proposed Heisenberg Hamiltonian for triple bonds will be extracted for various $C\equiv C$ distances. It will allow the treatment of polyynes in their ground and lowest excited states. By combining it with the previously proposed Heisenberg Hamiltonians for conjugated molecules, it will be possible to treat cumulenes and mixed systems with double (or aromatic) and triple bonds. As—C=N— double bonds have been treated in the same formalism [12], —C≡N triple bonds might be studied in a similar fashion. Of course the Heisenberg Hamiltonians increase rapidly in size when the number of centres increases but some size-consistent approximate treatments have been recently proposed and tested with success [13], opening the way to the treatment of rather large molecules.

It is quite clear that this work must also be considered as a step on the way to a magnetic treatment of transition metals. The ground state of Cr atom for instance is sd^5 , i.e. with s and d half filled bands, and one might be tempted to define a Heisenberg Hamiltonian for Cr clusters. Heisenberg Hamiltonians are also very important for the study of magnetic properties of transition metal complexes. In both cases the neutral states where some d orbitals are doubly occupied will act as intruder states with respect to a model space where each active orbital is only occupied once.

References

- [1] For a review, see HERRING, C., *Magnetism* Vol. IIB, G. T. Rado and H. Suhl, Eds. (Academic Press, New York) 1966.
- [2] KLEIN, D. J., *Int. J. Quantum Chem.* **12** (1977) 255; KLEIN, D. J. and GARCIA-BACH, M. A., *Phys. Rev. B* **19** (1979) 877.
- [3] OVCHINIKOV, A. O., *Theor. Chim. Acta* **47** (1978) 297; BULAEVSKII, L. N., *Zh. Eksp. Teor. Fis.* **51** (1966) 230; Engl. Ed., **24** (1967) 154.
- [4] MALRIEU, J. P. and MAYNAU, D., *J. Am. Chem. Soc.* **104** (1982) 3021; MAYNAU, D. and MALRIEU, J. P., *ibid.* **104** (1982) 3029.

- [5] SAID, M., MAYNAU, D., MALRIEU, J. P. and GARCIA-BACH, M. A., *J. Am. Chem. Soc.* **106** (1984) 571 ; SAID, M., MAYNAU, D. and MALRIEU, J. P., *ibid.* **106** (1984) 580.
- [6] SHAVITT, I. and REDMON, L. T., *J. Chem. Phys.* **73** (1980) 5711.
- [7] ANDERSON, P. W., *Phys. Rev.* **115** (1959) 1 ; *Solid State Phys.* **14** (1963) 99.
- [8] BRANDOW, B. H., *Rev. Mod. Phys.* **39** (1967) 771 ;
- Adv. Quantum Chem.* **10** (1977) 187 ; *Int. J. Quantum Chem.* **15** (1979) 207.
- [9] BLOCH, C., *Nucl. Phys.* **6** (1958) 329.
- [10] DES CLOIZEAUX, J., *Nucl. Phys.* **20** (1960) 321.
- [11] MALRIEU, J. P., DURAND, Ph., DAUDEY, J. P., *J. Phys. A* **18** (1985) 809.
- [12] SANCHEZ-MARIN, J. and MALRIEU, J. P., *J. Phys. Chem.*
- [13] SANCHEZ-MARIN, J., MALRIEU, J. P. and MAYNAU, D., *Phys. Rev.* submitted for publication.
-