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Generalization of Heisenberg Hamiltonians to non half-filled bands : a magneto-angular effective Hamiltonian for boron clusters

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Résumé. — On propose un hamiltonien effectif pour l'étude des états neutres d'agrégats de Bore, en généralisant les hamiltoniens de Heisenberg au cas d'une bande remplie au $1/6^e$. L'espace modèle est porté par les produits des fonctions fondamentales $^2P(s^2p)$ des atomes. L'hamiltonien effectif implique, outre des termes d'échange de spin de type Heisenberg, des opérateurs d'échange du moment angulaire et des opérateurs changeant à la fois le spin et le moment angulaire des atomes. La logique de cet hamiltonien effectif est obtenue par développement au 3^e ordre de la théorie des perturbations quasi dégénérées. En pratique l'hamiltonien est obtenu directement par les équations de Bloch à partir de calculs précis des fonctions d'onde de B_2 . La transférabilité de cet hamiltonien effectif a été testée sur le système B_3 linéaire ; la partie basse du spectre est correctement reproduite. Ce modèle sera utilisé pour l'étude du ferromagnétisme possible de chaînes linéaires de Bore. L'article discute le rôle de l'hybridation et souligne la portée de cette approche, qui étend la rationalisation par Anderson des hamiltoniens de Heisenberg à des systèmes autres que les bandes $1/2$ remplies.

Abstract. — An effective Hamiltonian has been proposed for the study of the neutral states of boron clusters, i.e. for a $1/6$ th filled band. This generalization of Heisenberg Hamiltonians rests upon the definition of a model space spanned by products of ground state $^2P(s^2p)$ atomic wave-functions. The resulting effective Hamiltonian involves, besides Heisenberg-type effective spin exchange terms, angular-momentum exchange operators and spin-and-angular-momentum exchange operators. The logic of this effective Hamiltonian has been derived through 3d order quasi-degenerate perturbation theory. In practice the effective interactions are obtained from accurate MO-CI large basis set calculations on B_2 through the use of a spectral definition of H^{eff} . The transferability has been tested on the linear B_3 system, by comparing the H^{eff} predictions with accurate MO-CI results. The transferability proves to be satisfactory for the lower part of the spectrum. The model will be used for the treatment of the magnetic character of (possibly high spin) B_n linear chains. The role of hybridization processes has been discussed and the possible extension of this approach, derived from Anderson's rationalization of Heisenberg Hamiltonians, has been outlined.

1. Introduction.

The theoretical foundations of Heisenberg Hamiltonians [1] are known to be based on the theory of effective Hamiltonians and on the use of quasi-degenerate perturbation theory [2]. These effective Hamiltonians are easy to derive for systems involving one electron in one Atomic Orbital (AO) on each centre [2], and (although less evidently [3]) for systems

involving p electrons in p AO's per centre. In both cases the systems involve a half-filled-band (the other bands being full or empty). Besides their typical applications for Mott insulators and magnetic problems in coordination chemistry, the Heisenberg Hamiltonians have proved to be surprisingly efficient tools for problems where the electronics delocalization is far from being small, namely in organic chemistry for the study of conjugated molecules [4] and even for alkali atom clusters or solids [5].

The basic idea of the present work is to attempt an extension of this approach to non-half filled bands, for

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instance to 1/6-filled bands, as will occur in s^2p atoms (B or Al clusters). The motivation and the strategy are developed in section 2 ; the choice of the model space, spanned by the Valence Bond (VB) determinants built from ground state $^2P(s^2p)$ atomic wave-functions, is explained and discussed. The ferromagnetic character of the B_2 ground state suggests a possible ferromagnetic ordering of the linear B_n chains.

Section 3 derives the formal structure of the effective Hamiltonian from the application of the quasi-degenerate perturbation theory (to third order) to the B_2 problem. It is shown that, besides angular dependant repulsion terms and other first order terms, the effective Hamiltonian presents a large variety of operators, of second-and third-order origin. These operators act on local spins only, angular momenta only or on both spin and angular momenta, and imply 2 AO's only (of either the same or orthogonal subsystem) or 4 AO's. The effective Hamiltonian for this problem is thus a magneto-angular effective Hamiltonian since it acts on both the local (i.e. atomic) spin and angular momenta. Its formal structure is developed in second-quantization formalism. From accurate molecular orbital configuration interaction (MO-CI) and orthogonal V.B. calculations on B_2 numerical effective Hamiltonians are proposed, referring to a direct (non-perturbative) definition of the effective Hamiltonian, analogous to those of Bloch [6] and Des Cloiseaux [7].

In a fourth section the transferability of these effective Hamiltonians to heavier systems is tested on the linear B_3 problem. For this molecule accurate MO-CI calculations have been performed assessing the exact state ordering. It appears that in this system all the lowest neutral states essentially keep the s^2p character of the atoms. The effective Hamiltonian, extracted from the relevant lowest eigenstates of B_2 , gives surprisingly accurate energies for all the lowest states of B_3 of various spin multiplicities and symmetries. This implicit treatment of the hybridization problem is discussed and a further generalization of the approach to the simultaneous treatment of different bands is suggested. Applications to longer linear chains is planned for the near future.

2. Situation of the problem.

2.1 HALF-FILLED BANDS : THE HEISENBERG HAMILTONIANS. — For a system involving n electrons and n active AO's, the procedure to obtain Heisenberg Hamiltonians consists first in the definition of a model space ; this model space is spanned by the Valence Bond single determinants which occupy each of the n active AO's of the system once and only once. Then all the determinants of the model space have the same space part ; they only differ by the spin distribution, and the model space is composed of $C_n^{n/2}$ determinants. These determinants are all neutral in the sense of V.B.

theory, and they are the determinants of lowest energy in the V.B. matrix (at least in non-polar well-defined problems). The second step of the procedure consists in applying the QDPT [8] to this model space, i.e. to construct perturbatively the effective energies and effective coupling of the neutral determinants under the influence of the ionic determinants. For a two-electron, two-AO (a and b), two-centre system, Anderson shows that the effective exchange between the two neutral determinants $|ab\rangle$ and $|\bar{a}\bar{b}\rangle$ is

$$\langle |ab\rangle | H^{\text{eff}} | |\bar{a}\bar{b}\rangle \rangle = -K_{ab} + F_{ab}^2/\Delta E$$

where K_{ab} is the direct bicentric exchange, F_{ab} the hopping integral between the two centres and ΔE is the « transition » energy from the neutral to the ionic $|a\bar{a}\rangle$ or $|\bar{b}b\rangle$ determinants. The Heisenberg Hamiltonian treats the electronic delocalization (i.e. the mixture between neutral and ionic determinants) as effective spin operators between the neutral determinants.

This straight forward approach is not directly generalizable to the general half-filled band problems (p electrons in p AO's per centre), if one uses the well-known Bloch [6] or Des Cloiseaux [7] definitions of the effective Hamiltonian, as shown by Maynau *et al.* [3] recently ; new definitions of the effective Hamiltonian are to be proposed to obtain a good transferability of the effective couplings from the two-centre problem to larger systems. Nevertheless the general foundations of the Heisenberg Hamiltonians for half-filled band problems are clear.

The Heisenberg Hamiltonians have recently received new applications, far from the typical field of Mott insulators. They have been applied with surprising success to the π -systems of conjugated molecules in organic chemistry [4]. A precise MO-CI calculation on ethylene makes possible the accurate extraction of two operators (a spin-dependant σ potential + π repulsion and an effective exchange) which are functions of the interatomic distances. This Heisenberg Hamiltonian predicts very accurately the geometries, isomerization energies, rotational barriers, lowest excited states energies and conformations of conjugated molecules involving up to 10 carbon atoms [4].

A similar attempt has been performed on an isoelectronic problem, namely the alkali atom clusters. A Heisenberg Hamiltonian has been extracted from accurate MO-CI potential curves of Na_2 ; it proves to give realistic energies of small clusters and the cohesive energy of the bulk [5].

The application of *ab initio* extracted efficient Heisenberg-type Hamiltonian for the study of metal clusters may appear as a tempting challenge in view of the difficulty of usual *ab initio* MO-CI techniques for the treatment of such versatile systems, presenting certainly several nearly degenerate optimal conformations with possibly different spin multiplicities.

2.2. NON HALF-FILLED BAND : TOWARDS NEW TYPES OF EFFECTIVE HAMILTONIANS. — The basic purpose of the present paper is to establish the form of an effective Hamiltonian, inspired by the strategy leading to the Heisenberg Hamiltonians but dealing with non half-filled bands. The fundamental idea is that, as in Anderson's legitimization of the Heisenberg Hamiltonian, one may :

i) choose as model space the set of neutral determinants with maximum spread of the electrons in the concerned band,

ii) apply the quasi degenerate perturbation theory, or an alternative variational formalism [9], to build the effective Hamiltonian spanned by this model space, to treat the effect of ionic configurations on the neutral subspace.

As a model problem we consider a one-sixth (1/6)-filled band, i.e. a cluster of B (or Al) atoms in their s^2p (2P) ground state. The s band is supposed to be filled up, and the hybridization will be considered as a perturbation only. We choose the model space S_0 as built of all the determinants in which each atom A bears one (and only one) p -electron in a p_x , p_y or p_z AO. The projector P_0 on the model space is written as :

$$P_0 = \sum_{K \in S_0} |K\rangle \langle K|,$$

where

$$|K\rangle = \mathcal{A} \prod_A \left[\left(s_A^2 \right) p_{A,i_A} \right], \quad i_A = x, y, z. \quad (1)$$

Then it is clear that the model space determinants do not have the same space-part ; for each atom one has two degrees of freedom namely the orientation x , y or z of the occupied AO and its spin. The size of the effective matrix for a 2 n -atom problem is $3^{2n} C_{2n}^n$, larger than for a typical Heisenberg Hamiltonian, but tremendously smaller than the full V.B.-matrix size.

The logic of the effective Hamiltonian is of course different from that of a Heisenberg Hamiltonian since it deals with both the local spin and angular momentum. One may expect that the effective operators will be both bicentric spin exchange operators and l -exchange operators, as will be confirmed in the next section. The logical structure of the effective Hamiltonian has to be established from analytic perturbative developments using the quasi degenerate perturbation theory on a two centre problem in the spirit of the Anderson-Bradow approach to Heisenberg Hamiltonians.

Two types of problems may arise along this path :

— non-convergence of the quasi degenerate perturbation expression, especially at short distances ;

— mixing with hybridized structures in which the sp^2 excited atomic configuration becomes dominant.

These configurations may appear as intruder states in

the QDPT expansion, questioning the validity of the choice of the model space. This problem will be briefly discussed in the present paper but the perturbative difficulties will be avoided by a spectral definition of the effective Hamiltonian. The generalization of this approach to the simultaneous treatment of several bands is out of the scope of the present work.

2.3 INTEREST IN B CLUSTERS. — At least at long distances, the reduction of the model space to the determinants built from the s^2p (2P) ground state of the atoms is valid ; the lowest sp^2 (2P) atomic state is 3.5 eV above the ground state, and the corresponding sp^2 (2D) is 6 eV above the ground state. The ground state of B_2 is of $^3\Sigma_g^-$ symmetry, is essentially built from $A(s^2p_x) \times B(s^2p_y)$ atomic configurations, and is ferromagnetic :

This point is interesting since it suggests that :

i) the s^2p configuration may dominate the ground state of at least linear B clusters.

ii) the linear B chain may be a high spin compound since it may be viewed as dominated by a spin-angular

arrangement i.e. presenting a molecular magnet. Besides the formal problem treated here, the present work may then be of practical interest.

3. Structure of the B_2 effective Hamiltonian.

3.1 LOWER PART OF THE SPECTRUM FROM A MO-CI APPROACH. — The number of papers related to the B_2 molecule is rather limited. Among those concerning the order of the low-lying states, let us note first the calculations of Padgett and Griffing [10] at the SCF level and of Bender and Davidson [11] at the CI level. In the last, the CI was not sufficiently extended so that the $^5\Sigma_u^-$ is assigned to the ground state in both papers, instead of the true $^3\Sigma_g^-$ state [12]. At the same time, Bader, Henneker and Cade [13] focused their attention on the charge distributions and the chemical binding. More recently Dupuis and Liu [14] performed a more extended CI calculation and found a good agreement between their results and Douglas and Herzberg's experimental interpretation of the symmetry of the ground state ($^3\Sigma_g^-$) and of the first $^3\Sigma_u^- \leftrightarrow ^3\Sigma_g^-$

transition. The $^5\Sigma_u^-$ state was found 0.006 a.u. higher than the ground state. Becke [15] using a numerical Hartree-Fock-Slater method studied only the ground state $^3\Sigma_g^-$. He found a dissociation energy of 3.8 eV, slightly larger than the experimental value

Fig. 1. — MO-CI $[xy]$ -symmetry potential curves of B_2 .

Fig. 2. — MO-CI $[xx, yy, zz]$ -symmetry potential curves of B_2 . Δ states, degenerate with those of the $[xy]$ -symmetry have been removed from the figure.

(3.1 ± 0.2 eV [16]). All these calculations found an interatomic distance close to the experimental value 3.005 a.u. [17]. The most accurate results are those of Dupuis and Liu but unfortunately they only concern the $X^3\Sigma_g^-, a^5\Sigma_u^-$ and the two first $^3\Sigma_u^-$ states.

As will be seen in next sections, a series of potential curves of B_2 are required for the construction of the desired effective Hamiltonians. By the way, it is also interesting to test the validity of our MO-CI calculations for this simple case and in particular concerning the small difference separating the $^3\Sigma_g^-$ and $^5\Sigma_u^-$ states. At the SCF level we used the Pshondo program [18], an extension of Hondo [19]. From the basis evaluated for the B atom [20] we extracted a triple- ζ s (contracted [3, 1, 1]), a double- ζ p (contracted [3, 1]) and one single- ζ d basis set. The d -exponent parameter was chosen equal to 0.5. Correlation effects have been introduced by means of the CIPSI algorithm [21]. In this method, a multiconfigurational zero-order wave function is first obtained from a variational configuration interaction (CI) calculation in a restricted subspace built up from the most important determinants for the states being studied; then this wave function is perturbed up to second order in energy.

The $^3\Sigma_g^-$ state is clearly found to be the ground state. The spectroscopic characteristics ($r_e = 3.05$ a.u., $D_e = 3.10$ eV) are in good agreement with experiment ($r_e = 3.005$ a.u., $D_e = 3.10$ eV). As also predicted by Dupuis and Liu, the $^5\Sigma_u^-$ state is obtained at 0.01 a.u. above the ground state, with a slightly smaller equilib-

Fig. 3. — MO-CI $[xz]$ -symmetry potential curves of B_2 .

rium distance ($r_c = 3.00$ a.u.). One must immediately notice that this $^5\Sigma_u^-$ state is necessarily spanned by B $sp^2(^2D) \times B s^2p(^2P)$ V.B. structures, and it is necessarily outside of our model space (cf. Eq. (1)).

The relevant potential curves of B_2 are pictured in figures 1-3. Curves corresponding to various irreducible representations of the $D_{\infty h}$ point group have been gathered into three reducible representations, which may be reached from the use of $p_x p_z$ and p_z AO's (z being the internuclear axis); this presentation is especially convenient for the forthcoming construction of the effective Hamiltonians. The figures only report the potential curves of the states having significant components in the model space (with the exception of the above mentioned $^5\Sigma_u^-$ state, which appears as a dotted line). The concerned states are always the lower ones of their symmetry, with three exceptions only: the highest in each symmetry. Other states, of redundant (spin or space) symmetry and/or of irrelevant V.B. character were found between the two reported $^3\Sigma_u^+$, $^3\Delta_u$ and $^1\Sigma_u^-$, $^3\Pi_g$ and $^1\Pi_g$ states. In particular, one notices irregular shapes of the $^3\Pi_g$ and $^1\Pi_g$ potential curves, which result from an avoided crossing with upper configurations. Since the corresponding eigenstates kept, at short interatomic distances, a non-negligible (although non-dominant) component in the model V.B. space, we decided to use these states in the definition of the «target» stable subspace defining H^{eff} . This may be called an adiabatic definition of the target space S (see below for a more detailed discussion).

3.2 DEFINITION OF THE EFFECTIVE HAMILTONIAN.

3.2.1 Model space, size and symmetry partitioning. — According to the basic choice of our treatment, the model space for B_2 reduces to the neutral $A(s^2p) \times B(s^2p)$ V.B. determinants (cf. Eq. (1)).

$$P_0 = \sum_{\substack{i,j \\ x,y,z}} \left| \left(s_A^2 \right) p_{A,i} \left(s_B^2 \right) p_{B,j} \right\rangle \times \\ \times \left\langle \left(s_A^2 \right) p_{A,i} \left(s_B^2 \right) p_{B,j} \right| \quad (2)$$

where $p_{A,i}$ is a spin orbital p_x, y or z on the atom A . The model space splits into $S_z = \pm 1, S_z = 0$ independent subspaces, the last one being the largest one and containing all the relevant information. Equations (1) and (2) implicitly assume the use of orthogonal valence AO's. This may be achieved by a preliminary $S^{-1/2}$ transformation, but, as noticed elsewhere [4, 5], the precise specification of this basis is not necessary. This orthogonality problem, connected with transferability to larger systems, will be discussed in the subsequent section. This model space may be split into three different symmetries $[x_a x_b, y_a y_b, z_a z_b]$,

$[x_a y_b, y_a x_b]$ and $[x_a z_b, z_a x_b]$ (and its degenerate $[y_a z_b, z_a y_b]$ counterpart) where the atoms are denoted a and b for convenience. The size of the effective matrices will be 6, 4 and 4 respectively for $S_z = 0$, and 3, 2, 2, for $S_z = \pm 1$. The u, g symmetry will be exploited later on.

Once the model space is defined the effective Hamiltonian may be obtained by two different routes:

— the perturbative approach, using quasidegenerate perturbation theory in one of its versions;

— the direct use of the Bloch or Des Cloiseaux equations, since in that precise problem, almost exact energies and wave functions are available from the MO-CI preliminary calculations. The latter solution is equivalent to an infinite order summation of the perturbative expansion, and is by far more precise, but the low-order perturbative approach gives the main structure of the effective Hamiltonian and the physical origin of the effective interactions.

3.2.2 Structure of the effective Hamiltonian from third order perturbative expansion. — Some details about the general structure were given in previous papers [3-5]. Let us recall that the perturbation operator is defined by:

$$H = H_0 + V$$

with

$$H_0 = \sum_{K \in S_0} E_K^0 |K\rangle \langle K| + \sum_{\alpha \notin S_0} E_\alpha^0 |\alpha\rangle \langle \alpha|$$

where S_0 is the model space. In an Epstein-Nesbet definition [22] of H_0 , the V operator is purely extradiagonal. Up to second order the effective Hamiltonian matrix elements take the form:

$$\langle I | H^{eff(2)} | J \rangle = \langle I | H | J \rangle - \sum_{\alpha \notin S_0} \frac{\langle I | H | \alpha \rangle \langle \alpha | H | J \rangle}{E_\alpha^0 - E_J^0}$$

and to third order

$$\langle I | H^{eff(3)} | J \rangle = \langle I | H^{eff(2)} | J \rangle + \sum_{\alpha, \beta \notin S_0} \frac{\langle I | H | \alpha \rangle \langle \alpha | H | \beta \rangle \langle \beta | H | J \rangle}{(E_\alpha^0 - E_J^0)(E_\beta^0 - E_J^0)} - \sum_{\alpha \notin S_0} \sum_{L \in S_0} \frac{\langle I | H | \alpha \rangle \langle \alpha | H | L \rangle \langle L | H | J \rangle}{(E_\alpha^0 - E_J^0)^2}$$

where α, β may be ionic or hybridized neutral determinants.

Since the ionic determinants are known to play the dominant role in the interpretation of the effective antiferromagnetic coupling in half-filled bands, we shall concentrate our attention on their effect in our problem. If one restricts the V.B. minimal set of determinants

ants to those which keep s^2 electron pairs on each atom, the V.B. matrix may be schematically pictured as in figure 4, for the $[xx, yy, zz]$ symmetry, which is the largest and most complex one. The zeroth order energies of the neutral determinants are repulsive, but to a larger extent for $z_a z_b$ spatial parts ($R_{zz} > R_{xx}$); the same differences appear among ionic states. The largest extradiagonal elements are hopping integrals F coupling the neutral $x_a \bar{x}_b$ (resp. $y_a \bar{y}_b$ or $z_a \bar{z}_b$) and ionic $x_a \bar{x}_a$ (resp. $y_a \bar{y}_a$ or $z_a \bar{z}_a$) determinants. One should also notice the occurrence of non-negligible monocentric exchange integrals K between ionic determinants. The h_{xy} (and h_{xz}) integrals represent electrostatic interactions between the atomic xy (or xz) quadrupoles; the other integrals involve bicentric overlap distributions and are much smaller.

To first order, the different symmetries involve 6 parameters

$$\begin{aligned} R_1 &= R_{xx} = R_{yy}; R'_1 = R_{zz} \\ R_2 &= R_{xy} \\ R_3 &= R_{xz} = R_{yz} \\ h &= (x_a y_a, x_b y_b) \\ h' &= (x_a z_a, x_b z_b) = (y_a z_a, y_b z_b). \end{aligned}$$

The identity of the Δ_{xy} and $\Delta_{x^2-y^2}$ solutions at first order leads to the following relation

$$R_1 = R_2 + 2h.$$

Starting from the neutral $x_a \bar{x}_b$ determinant one may go to an ionic $x_a \bar{x}_a$ or $x_b \bar{x}_b$ determinant. From it one may either move back to the $x_a \bar{x}_b$ original determinant (and obtain a diagonal second order correction) or reach the $x_b \bar{x}_a$ determinant; the effective coupling is then an interatomic exchange, shown in the following scheme where * and O stand for α and β spins respectively.

This back-and-forth second order process in the π_x subsystem repeats the well-known Anderson's mechanism of antiferromagnetic coupling. One may write diagonal $-g_{xx}|x_a \bar{x}_b\rangle\langle x_a \bar{x}_b|$ and off-diagonal $-g_{xx}|x_a \bar{x}_b\rangle\langle x_b \bar{x}_a|$ operators, with $g_1 = g_{xx} = 2F_{xx}^2/\Delta E_{xx}$, which give the amplitude of the negative effective exchange integral in the π_x system. Analogous contributions occur in the π_y ($g_{yy} = g_1$) and σ ($g_{zz} = g'_1$) systems.

A second type of coupling occurs at third order, pictured as follows

which couples $x_a \bar{x}_b$ and $y_a \bar{y}_b$ through

$$\varepsilon_{xy}|x_a \bar{x}_b\rangle\langle y_a \bar{y}_b| = 2 \frac{F_{xx} K_{xy} F_{yy}}{\Delta E_{xx} + \Delta E_{yy}} |x_a \bar{x}_b\rangle\langle y_a \bar{y}_b|$$

(the factor 2 reflects the possible travel through A^+A^- and A^-B^+ structures). This operator changes the angular part of the wave-function, and therefore cannot enter a Heisenberg Hamiltonian. Analogous operators occur between x and z or y and z spatial parts, with a different amplitude $\varepsilon_{xz} = \varepsilon_{yz}$. Table I summarizes the expected structure of the effective

$x_a \bar{x}_b$	$x_b \bar{x}_a$	$y_a \bar{y}_b$	$y_b \bar{y}_a$	$z_a \bar{z}_b$	$z_b \bar{z}_a$	$x_a \bar{x}_a$	$x_b \bar{x}_b$	$y_a \bar{y}_a$	$y_b \bar{y}_b$	$z_a \bar{z}_a$	$z_b \bar{z}_b$
R_{xx}		h_{xy}		h_{xz}		F_{xx}	F_{xx}				
	R_{xx}		h_{xy}		h_{xz}	F_{xx}	F_{xx}				
		R_{yy}		h_{yz}				F_{yy}	F_{yy}		
			R_{yy}		h_{yz}			F_{yy}	F_{yy}		
				R_{zz}						F_{zz}	F_{zz}
					R_{zz}					F_{zz}	F_{zz}
						$R_{xx} + \Delta E_{xx}$	K_{xy}			K_{xz}	
						$R_{xx} + \Delta E_{xx}$		K_{xy}			K_{xz}
							$R_{yy} + \Delta E_{yy}$		K_{yz}		
								$R_{yy} + \Delta E_{yy}$			K_{yz}
									$R_{zz} + \Delta E_{zz}$		
										$R_{zz} + \Delta E_{zz}$	

Fig. 4. — Structure of the V.B. matrix spanned by the non hybridized, $S_z = 0$, determinants in the $[xx, yy, zz]$ -symmetry. Bicentric exchange integrals are not taken into account. Identities between matrix elements, resulting from the degeneracy of π orbitals are explicitly given in table I.

Table I. — Schematic structure of the effective Hamiltonians for B_2 up to third order. The repulsive zeroth order interactions are written : $R_1 = R_{xx} = R_{yy}$, $R'_1 = R_{zz}$, $R_2 = R_{xy}$, $R_3 = R_{xz} = R_{yz}$. The elements : $h = h_{xy}$ and $h' = h_{xz} = h_{yz}$ represent quadrupole-quadrupole interactions. The second and third order corrections g and ε are defined in the text.

Space sym.	Spin sym.	V.B. déterminants	matrix elements	Spin sym.	V.B. déterminants	matrix éléments
Σ^+, Δ	$S_z = 0$	$\begin{bmatrix} * \\ ^0 \end{bmatrix}$	$ x_a \bar{x}_b \quad R_1 - g_1$	$S_z = 1$	$\begin{bmatrix} * \\ ^* \end{bmatrix}$	$ x_a x_b \quad R_1$
		$\begin{bmatrix} 0 \\ ^* \end{bmatrix}$	$ x_b \bar{x}_a \quad -g_1 \quad R_1 - g_1$		$\begin{bmatrix} / \\ ^* \end{bmatrix}$	$ y_a y_b \quad h \quad R_1$
		$\begin{bmatrix} / \\ ^* \end{bmatrix}$	$ y_a \bar{y}_b \quad h + \varepsilon_1 \quad \varepsilon_1 \quad R_1 - g_1$		$\begin{bmatrix} * \\ ^* \end{bmatrix}$	$ z_a z_b \quad h' \quad h' \quad R'_1$
		$\begin{bmatrix} / \\ ^0 \end{bmatrix}$	$ y_b \bar{y}_a \quad \varepsilon_1 \quad h + \varepsilon_1 \quad -g_1 \quad R_1 - g_1$			
		$\begin{bmatrix} * \\ ^0 \end{bmatrix}$	$ z_a \bar{z}_b \quad h' + \varepsilon'_1 \quad \varepsilon'_1 \quad h' + \varepsilon'_1 \quad \varepsilon'_1 \quad R'_1 - g'_1$			
		$\begin{bmatrix} 0 \\ ^* \end{bmatrix}$	$ z_b \bar{z}_a \quad \varepsilon'_1 \quad h' + \varepsilon'_1 \quad \varepsilon'_1 \quad h' + \varepsilon'_1 \quad -g'_1 \quad R'_1 - g'_1$			
		$\begin{bmatrix} * \\ ^0 \end{bmatrix}$	$ x_a \bar{y}_b \quad R_2 - g_2$		$\begin{bmatrix} * \\ ^* \end{bmatrix}$	$ x_a y_b \quad R_2 - \bar{g}_2 \quad (\bar{g}_2 = \bar{g}_2)$
		$\begin{bmatrix} / \\ ^0 \end{bmatrix}$	$ y_b \bar{x}_a \quad \varepsilon_2 \quad R_2 - g_2$		$\begin{bmatrix} / \\ ^* \end{bmatrix}$	$ y_a x_b \quad h + \bar{g}_2 \quad R_2 - \bar{g}_2$
		$\begin{bmatrix} / \\ ^0 \end{bmatrix}$	$ y_a \bar{x}_b \quad h + \varepsilon_2 \quad -\bar{g}_2 \quad R_2 - g_2$			
		$\begin{bmatrix} * \\ ^0 \end{bmatrix}$	$ x_b \bar{y}_a \quad -\bar{g}_2 \quad h + \varepsilon_2 \quad \varepsilon_2 \quad R_2 - g_2$			
Π	$S_z = 0$	$\begin{bmatrix} * \\ ^0 \end{bmatrix}$	$ x_a \bar{z}_b \quad R_3 - g_3$	$S_z = 1$	$\begin{bmatrix} * \\ ^* \end{bmatrix}$	$ x_a z_b \quad R_3 - \bar{g}_3$
		$\begin{bmatrix} 0 \\ ^* \end{bmatrix}$	$ z_b \bar{x}_a \quad \varepsilon_3 \quad R_3 - g_3$		$\begin{bmatrix} * \\ ^* \end{bmatrix}$	$ z_a x_b \quad h' + \bar{g}_3 \quad R_3 - \bar{g}_3$
		$\begin{bmatrix} * \\ ^0 \end{bmatrix}$	$ z_a \bar{x}_b \quad h' + \varepsilon_3 \quad -\bar{g}_3 \quad R_3 - g_3$			
		$\begin{bmatrix} 0 \\ ^* \end{bmatrix}$	$ x_b \bar{z}_a \quad -\bar{g}_3 \quad h' + \varepsilon_3 \quad \varepsilon_3 \quad R_3 - g_3$			

Hamiltonian in the $[xx, yy, zz]$ symmetry ($S_z = 0$ and 1).

In the $[xy]$ symmetry, analogous processes take place leading to second order diagonal and off-diagonal corrections,

with for example the corresponding off-diagonal operator

$$g_{xy} |x_a \bar{y}_b\rangle \langle x_b \bar{y}_a| = 2 \frac{F_{xx} F_{yy}}{\Delta E_{xy}} |x_a \bar{y}_b\rangle \langle x_b \bar{y}_a|$$

where one may notice that $\Delta E_{xy} = \Delta E_{xx} - 2 K_{xy}$, since one does not go through an ionic determinant with 2 electrons in the same AO, as occurred in the Anderson typical problem and in the $[xx, yy, zz]$ symmetry.

A third order contribution also appears through processes such as

leading to non-Heisenberg operators

$$\varepsilon_2 |x_a \bar{y}_b\rangle \langle y_b \bar{x}_a| = 2 \frac{F_{xx}^2 K_{xy}}{\Delta E_{xy}^2} |x_a \bar{y}_b\rangle \langle y_b \bar{x}_a|.$$

Table I gives the structure of the third order effective Hamiltonian in the $[xy]$ symmetry for $S_z = 0$ and $S_z = 1$. The identity of the $S_z = 0$ and $S_z = 1$ triplet eigenvalues requires that

$$\bar{g}_2 = g_2 + \varepsilon_2. \quad (3)$$

This relation is easily understood from the difference in the energy denominators

$$\Delta E(S_z = 1) \simeq \Delta E(S_z = 0) - K$$

so that

$$\begin{aligned} \bar{g}_2 &= g_2 + \frac{2 K F^2}{\Delta E^2} + \dots \\ &= g_2 + \varepsilon_2. \end{aligned}$$

Similar derivations are possible for the $[xz]$ (and $[yz]$) symmetry and are also shown in table I. However one should notice that :

i) the diagonal second order corrections are

$$-\left(\frac{F_{xx}^2}{\Delta E} + \frac{F_{zz}^2}{\Delta E}\right) = -g_3$$

while the off-diagonal second-order correction obtained from the operator

$$-\tilde{g}_3 |x_a \bar{z}_b\rangle \langle x_b \bar{z}_a| = -2 \frac{F_{xx} F_{zz}}{\Delta E} |x_a \bar{z}_b\rangle \langle x_b \bar{z}_a|$$

is of different amplitude than the diagonal correction and

ii) the F_{zz} hopping integral is positive, resulting in apparent changes in sign, also active in the ε_3 third order terms.

The identity of the $^3(S_z = 0)$ and $^3(S_z = 1)$ solutions for the $[xz]$ symmetry leads to the following relations

$$\begin{aligned} \bar{g}_3 &= g_3 + \varepsilon_3 \\ \tilde{g}_3 &= \tilde{g}_3 + \varepsilon_3 \end{aligned} \quad (4)$$

analogous to equation (3).

3.2.3 Physical typology of the effective operators. —

One may summarize the various types of operators according to several criteria :

- diagonal/non-diagonal character ;
- order of perturbation concerned ;
- number of AO's involved ;
- action on the local spin and angular momenta.

On the diagonal one first has purely (l_a, l_b) dependent terms R which are independent of the spin. One also has $-g$ stabilization second order contributions. The terms

$$-g_1 |x_a \bar{x}_b\rangle \langle x_a \bar{x}_b|, \quad -g'_1 |z_a \bar{z}_b\rangle \langle z_a \bar{z}_b|$$

only involve two AO's of the same subsystem, and appear when these two AO's bear electrons of different spins.

The $-g_2 |x_a \bar{y}_b\rangle \langle x_a \bar{y}_b|, -g_3 |x_a \bar{z}_b\rangle \langle x_a \bar{z}_b|$ terms imply two AO's belonging to two orthogonal subsystems.

The

$$-\bar{g}_2 |x_a y_b\rangle \langle x_a y_b|, \quad -\bar{g}_3 |x_a z_b\rangle \langle x_a z_b|$$

operators appear in the $S_z = 1$ (or -1) subspaces. They involve two AO's of two orthogonal subsystems bearing parallel spins.

Off the diagonal one finds typical second order spin exchange integrals involving only two AO's of the same subsystem, as in all Heisenberg Hamiltonians

$$-g_1 |x_a \bar{x}_b\rangle \langle x_b \bar{x}_a|$$

and analogous operators for $y\bar{y}$ ($-g_1$) and $z\bar{z}$ ($-g'_1$) determinants.

Other second order operators of the type

$$-\tilde{g}_2 |x_a \bar{y}_b\rangle \langle x_b \bar{y}_a|, \quad -\tilde{g}_3 |x_a \bar{z}_b\rangle \langle x_b \bar{z}_a|$$

change both the spin of the atom and its angular

Table II. — *Characters of the various off-diagonal effective operators.*

H^{eff} matrix element	action on atom-spin	action on atom-1	no. of A.O.'s involved	perturb. order.
g_1, g'_1	+	—	2	2
$\tilde{g}_2, \tilde{g}_3$	+	+	4	2
$(h + \tilde{g}_2), (h' + \tilde{g}_3)$	—	+	4	1 + 2
$\varepsilon_1, \varepsilon'_1$	+	+	4	3
$\varepsilon_2, \varepsilon_3$	+	—	2	3
$(h + \varepsilon_1), (h' + \varepsilon'_1)$	—	+	4	1 + 3
$(h + \varepsilon_2), (h' + \varepsilon_3)$				

momentum. These operators involve four AO's belonging to two orthogonal subsystems.

The second order off-diagonal

$$\begin{aligned} & (h + \tilde{g}_2) |x_a y_b\rangle \langle y_a x_b|, \\ & (h' + \tilde{g}_3) |x_a z_b\rangle \langle z_a x_b|, \end{aligned}$$

operators change the angular momenta of the atoms without changing their spins. One should notice that due to the identity of the π_x and π_y systems $\tilde{g}_2 = g_2$ and $\tilde{g} = \bar{g}_2$.

The third order operators

$$\varepsilon_2 |x_a y_b\rangle \langle y_b x_a|, \quad \varepsilon_3 |x_a z_b\rangle \langle z_b x_a|$$

change the spins of two spin-orbitals of different spins belonging to two orthogonal subsystems, without acting on the space part.

The third-order operators

$$\begin{aligned} & (h + \varepsilon_1) |x_a \bar{x}_b\rangle \langle y_a \bar{y}_b|, \\ & (h' + \varepsilon'_1) |x_a \bar{x}_b\rangle \langle z_a \bar{z}_b|, \\ & (h + \varepsilon_2) |x_a \bar{y}_b\rangle \langle y_a \bar{x}_b|, \\ & (h' + \varepsilon_3) |x_a \bar{z}_b\rangle \langle z_a \bar{x}_b| \end{aligned}$$

change the angular momentum on the atom without changing the local spin; they involve four atomic orbitals belonging to two orthogonal subsystems.

Finally the third-order operators

$$\varepsilon_1 |x_a \bar{x}_b\rangle \langle y_b \bar{y}_a|, \quad \varepsilon'_1 |x_a \bar{x}_b\rangle \langle z_b \bar{z}_a|$$

change both the angular and spin momenta on the atom, involving therefore four AO's on two orthogonal subsystems. This typology is clearly pictured in table II.

3.3 AB INITIO DERIVATION OF THE EFFECTIVE HAMILTONIANS FROM THE BLOCH EQUATION. — Since the effective Hamiltonian satisfies the Bloch

equation for n roots

$$H^{\text{eff}} |P_0 \psi_i\rangle = E_i |P_0 \psi_i\rangle \quad i = 1, \dots, n$$

with

$$H |\psi_i\rangle = E_i |\psi_i\rangle,$$

a spectral definition of H^{eff} is given by

$$H^{\text{eff}} = \sum_{i=1}^n |P_0 \psi_i\rangle E_i \langle P_0 \psi_i| \quad (5)$$

where $P_0 \psi_i^+$ is the biorthogonal vector associated with the projection $P_0 \psi_i$ of the eigenstate ψ_i of H into S_0 .

If the exact spectrum of H and its eigenvectors are known, a selection of n eigenvalues and eigenvectors ψ_i defines

$$P_s = \sum_{i=1}^n |\psi_i\rangle \langle \psi_i|,$$

the stable subspace, which we call « target space », and H^{eff} is entirely defined by P_0 , P_s and the exact eigenenergies, without any reference to a possibly divergent perturbation expansion. If one uses the wave operator Ω , then :

$$P_s = \Omega P_0.$$

Since for the B_2 molecule, accurate energies and wave functions are available from the MO-CI calculations, it is tempting to use equation (5) to obtain directly the H^{eff} matrix, in a purely numerical form : in this section the target space is defined as spanned by the eigenvectors of the correct symmetry, lowest energy and having significant components on the model space. Another definition of the target space might pick up the eigenvectors having the *largest* components onto the model space. From symmetry considerations, the following correspondence between model subspaces and eigenstates is expected :

$[xx, yy, zz]$ $S_z = 0$ corresponds to one $^1\Delta_g$, two $(^1\Sigma_g^+)$, one $(^3\Delta_u)$, two $(^3\Sigma_u^+)$ eigenstates, ($S_z = 1$ generates the triplets : one $(^3\Delta_u)$, two $(^3\Sigma_u^+)$).

- [xy] $S_z = 0$ corresponds to one $^3\Sigma_g^-$, one $^1\Delta_g$, one $^1\Sigma_u^-$ and one $^3\Delta_u$ states,
($S_z = 1$ generates the corresponding triplet states).
- [xz] $S_z = 0$ corresponds to one $^3\Pi_u$, one $^1\Pi_u$, one $^3\Pi_g$ and one $^1\Pi_g$ states,
($S_z = 1$ generates the corresponding triplet states).

The Δ states obtained from $[xx, yy, zz]$ and $[xy]$ model subspaces are of course degenerate.

All the vectors which are the only ones of their symmetry in the concerned model subspace have their components in the model space entirely defined by symmetry. This means that the components of $P_0 \psi_i$ are immediately obtained. For instance for $^3\Sigma_g^-$ one necessarily has $+-+$ components on the $|x_a \bar{y}_b|$, $|y_b \bar{x}_a|$, $|y_a \bar{x}_b|$ and $|x_b \bar{y}_a|$ model determinants. The only exception concerns the pairs of $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states belonging to the $[xx, yy, zz]$ symmetry. The degree of freedom concerns of course the ratio of $|x_a \bar{x}_b|$ ($= |y_a \bar{y}_b|$) over $|z_a \bar{z}_b|$ components.

In principle the projected eigenvectors of the same symmetry are not orthogonal

$$\langle P_0 \psi_i | P_0 \psi_j \rangle \neq 0.$$

This results in a non-Hermitian structure of the Bloch effective Hamiltonian. For the sake of simplicity, we preferred to use Hermitian structure. One possible solution refers to an $S^{-1/2}$ transformation of the projections, and is known as the des Cloizeaux [7] effective Hamiltonian definition. This solution symmetrically distorts projections; previous work [3] on Heisenberg Hamiltonians for a half-filled band with $2e^-/2$ AO per centre has shown that this distortion may result in important deviations from the expected structure and difficulties in the transfer of effective operators to larger systems. A better solution consists of a Schmidt-type orthogonalization keeping the lowest projected eigenvector unchanged, and orthogonalizing the second one (of higher energy) to the first one. This solution has been applied for $^1\Sigma_g^+$ and $^3\Sigma_u^+$ symmetries.

The ratios of $|x_a \bar{x}_b|$ ($= |y_a \bar{y}_b|$) over $|z_a \bar{z}_b|$ projected components are given in table III, other pro-

jected eigenvectors on the model space being trivially obtained by symmetry. In this table, the first state of each symmetry corresponds to the lowest in energy. The changes of the order of magnitude (for $^1\Sigma_g^+$ states) and of the signs (for $^3\Sigma_u^+$ states), between the two states of each symmetry, occurring between 3.3 and 4.5 a.u., both correspond to avoided crossings. For 3.3 a.u., the two ratios smaller than 1.0 found for $^1\Sigma_g^+$ states do not mean that the states are both « z^2 -dominant » states, since the $[xx]$ -component has to be counted twice ($|xx|$ and $|yy|$ determinants). The first $^1\Sigma_g^+$ state is a $[|xx|, |yy|]$ -dominant state. The corresponding effective Hamiltonians are given in table IV, where the energy of the two separated atoms (5.18 a.u.) has been taken as zero of energy.

3.4 COMPARISON BETWEEN THE PERTURBATIVELY DERIVED AND NUMERICALLY OBTAINED EFFECTIVE HAMILTONIANS. — For the diagonal R « repulsive » matrix elements one should notice (cf. $S_z = 1$, $[xx, yy, zz]$ symmetry) that $R_{zz} (= R_i')$ is the most repulsive, as expected. The large off-diagonal matrix elements correspond to the effective exchanges g . Since the overlap (and hopping integrals) are of larger amplitude in the σ -system than in the π ones, one should have

$$g_{\sigma\sigma}(g_1') > |g_{\sigma\pi}| (|g_3|) > g_{\pi\pi}(g_1) = g_{\pi\pi'}(g_2).$$

The numerical values actually show the large $g_{\sigma\sigma}$ value (0.115 a.u.) at $r = 3$ a.u., but the three other integrals are of the same order of magnitude (-0.03 to 0.02 a.u.). One should not forget that our third-order perturbative development did not involve hybridized configurations, and deviations are logically expected. Nevertheless the numerical effective Hamiltonian keeps the predicted structure.

Table III. — Ratio of the projected components of $|x_a \bar{x}_b|$ over $|z_a \bar{z}_b|$ for the states in the $[xx, yy, zz]$ -symmetry, appearing necessary for the construction of the corresponding H^{eff} .

States	2.7	3.0	R (a.u.) 3.3	4.5	6.0
$^1\Sigma_g^+$	6.32833	2.56768	0.87945	0.18740	0.26010
$^1\Sigma_u^+$	— 0.07901	— 0.19473	— 0.56854	— 2.66809	— 1.92231
$^3\Sigma_g^+$	— 13.02096	— 9.58453	— 10.43056	28.95102	8.68067
$^3\Sigma_u^+$	0.03840	0.05217	0.04794	— 0.01727	— 0.05760

Table IV. — « Exact » numerical H^{eff} matrix elements at various B-B distances. Deviations from the theoretical third order structure are clearly outlined by a direct comparison to the second column.

Space symmetry	Third order corrected H^{eff} matrix elements	R (a.u.)				
		2.7	3.0	3.3	4.5	6.0
Σ^+, Δ	R_1	− 0.02880	− 0.04350	− 0.03301	− 0.00327	− 0.00790
	R'_1	0.24224	0.18655	0.15526	0.06182	0.00650
	$R_1 - g_1$	− 0.04500	− 0.06340	− 0.05634	− 0.01703	− 0.00991
	$R'_1 - g'_1$	0.12850	0.07155	0.04352	0.00580	− 0.00703
	g_1	0.01620	0.01990	0.02333	0.01376	0.00201
	g'_1	0.11374	0.11500	0.11174	0.05603	0.01353
	h	0.00883	0.00750	0.00606	0.00104	− 0.00030
	h'	0.01010	0.01167	0.00877	− 0.00111	− 0.00085
	ε_1	− 0.00076	0.00010	0.00099	0.00042	0.00009
	ε'_1	− 0.00780	− 0.00922	− 0.00713	− 0.00159	− 0.00086
	$h + \varepsilon_1$	0.00807	0.00760	0.00705	0.00145	− 0.00021
	$h' + \varepsilon'_1$	0.00230	0.00245	0.00165	− 0.00270	− 0.00171
Σ^-, Δ	$R_2 - g_2$	− 0.05169	− 0.06955	− 0.06323	− 0.02208	− 0.01005
	$R_2 - \bar{g}_2$	− 0.06552	− 0.08243	− 0.07376	− 0.02340	− 0.01030
	$\tilde{g}_2 \equiv g_2$	0.02927	0.03288	0.03484	0.01550	0.00235
	$h + \tilde{g}_2$	0.02789	0.03143	0.03469	0.01009	0.00270
	ε_2	0.01383	0.01288	0.01053	0.00132	0.00025
	$h + \varepsilon_2$	− 0.00138	− 0.00145	− 0.00015	0.00360	0.00035
Π	$R_3 - g_3$	− 0.02277	− 0.04314	− 0.03823	− 0.02032	− 0.01170
	$R_3 - \bar{g}_3$	− 0.04019	− 0.05787	− 0.05989	− 0.02879	− 0.01335
	$\tilde{g}_3$	− 0.00980	− 0.03188	− 0.04759	− 0.02856	− 0.00555
	$h' + \tilde{g}_3$	− 0.00853	− 0.03155	− 0.03955	− 0.02899	− 0.00715
	ε_3	0.01742	0.01472	0.02167	0.00847	0.00165
	$h' + \varepsilon_3$	0.00126	0.00033	0.00803	− 0.00043	− 0.00160

The effective Hamiltonians have been calculated for five interatomic distances. All matrix elements R , g , ε decrease exponentially with the interatomic distance, since they involve interatomic overlap distributions. The quadrupole-quadrupole interactions h decrease as r^{-8} . Analytic fittings of the matrix elements are easy and may be used for geometry optimizations in larger clusters.

4. Transferability to the linear B_3 system.

Transferability of the effective Hamiltonian has been tested on the simplest larger problem, namely the B_3 linear system keeping $D_{\infty h}$ symmetry.

4.1 QUALITATIVE CONSIDERATIONS. — Close to the equilibrium geometry, the lowest states of B_2 are, in increasing order : $^3\Sigma_g^-$ and $^1\Delta_g$ ($[xy]$ -symmetry $\hookrightarrow$) and $^3\Pi_u$ ($[xz]$ -symmetry : $\hookrightarrow$). Starting from two B interactions to form the linear B_3 molecule, we may predict to find, as lowest states for B_3 , a structure

resulting from the junction of two such $[xy]$ -structures $\hookrightarrow$ or one $[xy]$ - and one $[xz]$ -structure : $\hookrightarrow$. Moreover, as also outlined in the introduction, the distribution corresponding to all spins parallel, i.e. a quartet symmetry in that case, should be low in energy.

4.2 AB INITIO MO-CI CALCULATIONS. — Accurate MO-CI calculations have been performed on B_3 . The symmetry of the B_3 ground state was investigated first. Keeping in mind that d -functions were of fundamental importance in the determination of the right symmetry for the ground state of B_2 , we used the same triple- ζ_s , double- ζ_p and single- ζ_d valence basis set as for B_2 . According to the CIPSI algorithm, a great part of the valence correlation energy has been treated variationally and the remaining part perturbatively. Figure 5 shows the three lowest states close to the equilibrium internuclear distance which is found of the same order as that of B_2 . The $^2\Pi_u$ state is the ground state. The quartets $^4\Pi_g$ and $^4\Sigma_u^-$, suggested by our qualitative considerations, are only about 0.006 a.u. above the

Fig. 5. — MO-CI potential curves for the three lowest states of B_3 .

ground state, the $^4\Pi_g$ state being slightly more stable than the $^4\Sigma_u^-$ state.

In a second step, in order to lighten the calculations, we eliminated the d-functions from the basis set. Figures 6a and 7a show the lowest states for the three subsymmetries. These three subsymmetries are denoted here: $[xxx]$ (which also includes $|xyy|$ and $|xzz|$ determinants and the degenerate ones), $[zzz]$ (with also $|xxz|$ and $|yyz|$ determinants) and $[xyz]$. The u and g characters are then assigned appropriately to each MO in MOCI calculations while a, b and c subscripts characterize the atoms to each A.O. in the V.B. formalism. The three lowest states are still found to be: $^2\Pi_u$, $^4\Pi_g$ and $^4\Sigma_u^-$ in the same order.

4.3 COMPARISON BETWEEN *AB INITIO* AND EFFECTIVE HAMILTONIAN RESULTS FOR B_3 . — Malrieu *et al.* [5] discussed in detail the problem of the orthogonality between A.O.'s. The orthogonalized A.O.'s. for a two-atom system and those for a three-atom system are not the same. We must keep in mind that this could affect the transferability to some extent. Their calculations on alkali metals also have shown that, as expected, three-body increments $\delta g_{ab(c)}$ are small, at least in linear chains.

The B_3 effective Hamiltonian splits into three blocks of dimensions 18, 21 and 21 for the $[xyz]$, $[xxx]$ and $[zzz]$ pseudo-symmetries respectively. The long-distance (A-C)-interactions have been checked to have negligible effects. The ground state is correctly predicted to be of $^2\Pi_u$ symmetry by our model, and the

Fig. 6a. — MO-CI $[xxx]$ -symmetry lowest potential curves of B_3 .

Fig. 6b. — H^{eff} $[xxx]$ -symmetry lowest potential curves of B_3 .

Fig. 7a. — MO-CI $[xyz]$ - and $[zzz]$ -symmetry lowest potential curves of B_3 .

Fig. 7b. — H^{eff} $[xyz]$ - and $[zzz]$ -symmetry lowest potential curves of B_3 .

equilibrium distance is correct (3.08 a.u. to be compared to 3.01 in the *ab initio* calculations). From a V.B. point of view it may be analysed as a resonance between

The two upper states are very close in energy ; they are quartets of $^4\Pi_g$ and $^4\Sigma_u^-$ symmetries. The best MO-CI calculation predicts them at $T_c = 0.14$ eV and 0.19 eV above the ground state minimum, while the effective Hamiltonian predicts 0.22 and 0.03 eV respectively : this inversion corresponds to an error of ≈ 0.2 eV, which is not too bad. Deleting the d A.O.'s in the MO-CI calculation leads to $T_c = 0.11$ and 0.24 eV respectively for $^4\Pi_g$ and $^4\Sigma_u^-$. The important feature is the differential effect on the interatomic distances (cf. Figs. 6-7 and Table V) which are correctly reproduced by the effective Hamiltonian. The V.B. content of these wave functions may be pictured as

A direct comparison between the potential curves of upper states may be obtained by comparing figures 6a and 6b for the states of Π and Φ symmetries, and figures 7a and 7b for the states of Σ^- , Δ and Σ^+ symmetries.

The results are also summarized in table V. There is a significant gap (≈ 0.5 eV) between the three lowest states and a group of five states which lie in a narrow energy range of 0.4 eV. These states are of $^2\Pi_g$, $^2\Sigma_u^-$, $^4\Sigma_g^-$, $^2\Delta_u$ and $^2\Sigma_u^+$ character, in order of increasing energy in the MO-CI calculation. The effective Hamiltonian only permutes the position of the $^2\Pi_g$ and $^2\Delta_u$ states in this group. The largest equilibrium distances concern the $^2\Sigma_u^-$ and $^2\Delta_u$ states in both approaches.

The two next states are $^6\Pi_u$ and $^2\Sigma_g^+$ in the MO-CI calculation. The former cannot be reached from a three-open-shell model space and the second one is essentially hybridized ; from that region important discrepancies begin to appear between the MO-CI and effective Hamiltonian spectra.

5. Conclusion.

The major conceptual interest of the present derivation concerns the logical possibility and cost of an extension of the Heisenberg Hamiltonian to a non half-filled band problem. The basic philosophy is again the choice of a model space spanned by the neutral V.B. determinants,

Table V. — *Lowest spectroscopic states of B₃. The values in parentheses are relative to the largest basis set.*

States	T_e (eV)		ΔE (vert.) (eV)		r_e (a.u.)	
	MOCI	H^{eff}	MOCI	H^{eff}	MOCI	H^{eff}
$^2\Pi_u$	1.52	0.90	2.20	1.41	3.34	3.40
$^2\Sigma_g^+$	1.36	—	1.39	—	2.94	—
$^6\Pi_u$	1.14	—	1.14	—	3.00	—
$^2\Sigma_u^+$	1.09	0.87	1.25	1.03	3.12	3.24
$^2\Delta_u$	1.06	0.60	1.22	0.82	3.20	3.26
$^4\Sigma_g^-$	1.03	0.87	1.09	0.90	3.10	3.12
$^2\Sigma_u^-$	1.01	0.65	1.20	0.79	3.20	3.26
$^2\Pi_g$	0.68	0.92	0.68	0.92	3.00	3.06
$^4\Sigma_u^-$	0.24	0.03	0.41	0.14	3.15	3.30
	(0.19)		(0.30)		(3.14)	
$^4\Pi_g$	0.11	0.22	0.11	0.24	3.00	3.06
	(0.14)		(0.19)		(2.95)	
$^2\Pi_u$	0	0	0		3.00	3.08
					(3.00)	

and the use of quasi degenerate perturbation theory or spectral definition of the effective Hamiltonian. The use of the perturbative expansion has the advantage of putting in place the logical structure of H^{eff} , showing which are the leading terms and their physical origin. The use of the spectral definition of H^{eff} permits avoidance of divergence problems of the perturbative expansion and introduces high-quality (infinite order) information.

The effective operators involve, beside the classical Heisenberg type spin exchange operators between A.O.'s of the same subsystem :

- spin-exchange operators between A.O.'s of two orthogonal subsystems ;
 - angular momenta-exchange operators ;
 - spin- and angular momenta-exchange operators ;
- the two last types implying necessarily *four* A.O.'s belonging to two orthogonal subsystems.

The generalization of the Heisenberg effective Hamiltonian approach to (p/n)-filled bands is thus in principle possible although some supplementary difficulties may arise from the existence of p electrons per atom. This approach may be useful for the study of the d^n systems of clusters of transition metals.

Concerning the precise case studied here, the main problem concerned of course the restriction of our model to a single band through the choice of a model space spanned by products of atomic s^2p configurations. The hybridization (i.e. the involment of sp^2 atomic configurations) should play a very important role, and this is clear from the existence of a low lying quintet state $^5\Sigma_u^-$ of B_2 , which cannot enter our model. The fact that we used the exact eigenenergies of B_2 for the spectral definition of H^{eff} has taken implicitly into account most of the hybridization mixing. One might have defined the target space S as spanned by the

eigenvectors of H having the *largest* components on the model space S_0 , some of them being higher in energy. Attempts along this line failed to give reliable results except for a few almost non-hybridized states (the ground state was correctly predicted to be $^2\Pi_u$). The success of our model for B_3 is certainly linked to the fact that the strongly hybridized states go to higher energies on linear chains at least, since the lowest essentially hybrid state $^6\Pi_u$ appears only in 9th position in the MO-CI calculation.

Such success would be unlikely for bi- and tridimensional clusters. We intend to apply our effective Hamiltonians to the prediction of the magnetic character of linear B_n chains.

It is clear that the main further step in the construction of effective Hamiltonians spanned by all *neutral* V.B. structures would consist in explicitly treating the hybridization, i.e. several bands, spanning the model space by all the possible products of neutral ground and excited valence atomic configurations. This strategy, now under study, faces three types of problem ;

- the large size of the model space makes the *ab initio* extraction difficult ; the use of the recently proposed intermediate Hamiltonians [23] may solve some intruder state problems, necessarily occurring in such situations ;

- effective integrals will be numerous, and their handling in larger problems may become tedious. Some analytic fittings of effective integrals (in terms of overlap for instance) may become necessary ;

- the number of neutral V.B. determinants for a moderate-size cluster or molecule will be large and the diagonalization of the generalized Heisenberg Hamiltonian matrix may become rather expensive. Sanchez *et al.* [24] recently proposed a procedure to truncate

and dress these large matrices insuring numerical accuracy and size-consistence. Despite these practical difficulties it is worthwhile knowing that the effect of electronic delocalization may be treated through

« effective » interatomic exchange operators acting on neutral V.B. structures only, and that this philosophy usually limited to half-filled bands, is completely general.

References

- [1] HERRING, C., in *Magnetism*, edited by C. T. Rado and M. Suhl (Academic Press, New York) 1966, Vol. II B.
- [2] ANDERSON, P. W., *Phys. Rev.* **115** (1959) 1 ; in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, New York) 1963, Vol. 14, p. 99 ;
BRANDOW, B. H., *Adv. Phys.* **26** (1977) 651.
- [3] MAYNAU, D., GARCIA-BACH, M. A. and MALRIEU, J. P., *J. Physique* **47** (1986) 207.
- [4] MALRIEU, J. P. and MAYNAU, D., *J. Am. Chem. Soc.* **104** (1982) 3021 ;
MAYNAU, D. and MALRIEU, J. P., *J. Am. Chem. Soc.* **104** (1982) 3029.
- [5] MALRIEU, J. P., MAYNAU, D. and DAUDEY, J. P., *Phys. Rev. B* **30** (1984) 1817.
- [6] BLOCH, C., *Nucl. Phys.* **6** (1958) 329.
- [7] DES CLOIZEAUX, J., *Nucl. Phys.* **20** (1960) 321.
- [8] VAN VLECK, J. H., *Phys. Rev.* **33** (1929) 467 ;
DES CLOIZEAUX, J., *Nucl. Phys.* **20** (1960) 321 ;
BRANDOW, B. H., *Rev. Mod. Phys.* **39** (1967) 771 ;
KIRTMAN, B., *J. Chem. Phys.* **49** (1968) 3890 ;
CERTAIN, P. R. and HIRSCHFELDER, O., *ibid.* **52** (1970) 5977 ;
HOSE, G. and KALDOR, U., *J. Phys. B* **12** (1979) 3827 ;
SHAVITT, I. and REDMON, L. T., *J. Chem. Phys.* **73** (1980) 5711.
- [9] DURAND, Ph., *Phys. Rev. A* **28** (1983) 3184.
- [10] PADGETT, A. A. and GRIFFING, V., *J. Chem. Phys.* **30** (1959) 1286.
- [11] BENDER, C. F. and DAVIDSON, E. R., *J. Chem. Phys.* **46** (1967) 3313.
- [12] DOUGLAS, A. F. and HERZBERG, G., *Can. J. Res. A* **18** (1940) 165.
- [13] BADER, R. F. W., HENNEKER, W. H. and CADE, P. E., *J. Chem. Phys.* **46** (1967) 3341.
- [14] DUPUIS, M. and LIU, B., *J. Chem. Phys.* **68** (1978) 2902.
- [15] BECKE, A. D., *J. Chem. Phys.* **76** (1982) 6037 ;
DUNLAP, B. I., *Ibid* **78** (1983) 4787 ;
BECKE, A. D., *Ibid* **78** (1983) 4787.
- [16] DE B. DARWENT, B., *Bond dissociation energies in simple molecules*, NSRDS-NBS 31 (Nat. Bur. Stand., Washington D.C.) 1970 ;
- HUBER, K. P., *American Institute of Physics Handbook*, edited by D. C. Gray (McGraw-Hill, New York) 1972, Sec. 7g ;
- HUBER, K. P. and HERZBERG, G., *Molecular spectra and molecular structure. Constants of diatomic molecules* (Van Nostrand Reinhold Cy, New York) 1979, p. 64.
- [17] *Handbook of Chemistry and Physics*, Ed. by R. C. Weast, 64th ed. (C.R.C. Press Inc.) 1983-1984.
- [18] DAUDEY, J. P., private communication.
- [19] DUPUIS, M., RYS, J. and KING, H. F., *J. Chem. Phys.* **65** (1976) 111 ;
DUPUIS, M. and KING, H. F., *Int. Quant. Chem.* **11** (1977) 613.
- [20] *Calculs atomiques et moléculaires ab initio* : Technical report, U.A. 505, Lab. Phys. Quant. Univ. Paul Sabatier, Toulouse, 1981.
- [21] HURON, B., MALRIEU, J. P. and RANCUREL, P., *J. Chem. Phys.* **58** (1973) 5745.
- [22] EPSTEIN, P. S., *Phys. Rev.* **28** (1926) 695 ;
NESBET, R. K., *Proc. R. Soc. London A* **230** (1955) 312, 322.
- [23] MALRIEU, J. P., DURAND, Ph. and DAUDEY, J. P., *J. Physics A Math. Gen.* **18** (1985) 809.
- [24] SANCHEZ-MARIN, J., MALRIEU, J. P. and MAYNAU, D., *Int. J. Quant. Chem.* in press.