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VB Calculations with Orthogonal Basis Functions

I. Minimal Basis *ab initio* Calculations

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As a first step in the development of a semiempirical VB method, *ab initio* VB calculations were performed to obtain potential energy curves for the molecules HF and BeH_2 and the energy profile of the collinear exchange reaction $F+H_2 \rightarrow HF+H$. The applicability of the method is discussed with particular emphasis on the calculation of integrals over OAO's, the choice of valence structures to be included in the CI scheme and the interpretation of the wave function in terms of OAO's.

Key words: VB method

1. Introduction

Until recently, one of the main interests of quantum chemistry was the correct theoretical description of molecular structure and of the properties of isolated molecules. This has resulted in an almost exclusive application of the molecular orbital (MO) method, both on the *ab initio* as well as on the semiempirical level. This is not only due to the numerical advantages of the MO method, but also to its simple interpretation of electronic excitation energies and ionization potentials in terms of molecular orbitals. In fact, Hartree-Fock calculations are very well suited for the determination of equilibrium geometries and for conformational analysis [1].

Now that attention is more and more turning away from simple molecules towards chemical reactions, i.e. processes involving the making and breaking of bonds, the shortcomings of the Hartree-Fock method become more severe. Thus, for the calculation of processes in which the number of paired electrons changes as for the

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homolytic bond cleavage, the Hartree-Fock method is of no great use. Even reactions for which the electronic wave function has a closed shell structure along the entire reaction path, changes in correlation effects may be appreciable, thus demanding for methods which account for electron correlation effects [2].

It is for this reason that the valence bond (VB) method deserves further exploration. Its main disadvantages are essentially computational, due to the severe problems which arise from the non-orthogonality of the atomic orbitals (AO's). Its main advantage over the MO approach is its ability to deal with both excited states and non-equilibrium geometries, for it is a simple method to obtain correct dissociation results using VB methods, by including among the valence structures of the configuration interaction scheme those structures which at infinite nuclear separations represent the atoms in their ground states [3].

Although several methods are available for the evaluation of the cofactors appearing in the matrix elements between Slater determinants constructed from non-orthogonal spin orbitals [4], the number of *ab initio* VB calculations for polyatomic molecules is still very limited because of computational difficulties [5]. These difficulties, however, do not occur if the basis functions are orthogonal. The reformulation of the VB method, starting from a set of orthogonalized atomic orbitals (OAO's), was first put forward by McWeeny as early as in 1954 [6]. Although this approach seems to be particularly suited for the development of a semiempirical VB scheme, as already noted by McWeeny [7] and by van der Lugt and Oosterhoff [8, 9], it has been rarely used since. This is because essentially three problems remain to be solved within the framework of the VB method with orthogonal basis functions, namely the calculation of integrals over OAO's, the choice of valence structures to be included in the configuration interaction scheme, and the interpretation of the wave function expressed in terms of OAO's.

2. Method

This paper is concerned with some exploratory results of *ab initio* VB calculations using a minimal basis set of Löwdin-orthogonalized AO's. Such calculations are quite feasible for small molecules and were performed according to the following scheme: Integrals over a minimal basis of $1s$ STO's with orbital exponent $\zeta = 1.0$ expanded as described earlier [11] in terms of 3 GTO's for hydrogen and $1s$, $2s$ and $2p$ STO's with Slater exponents expanded in terms of 5, 2 and 3 GTO's respectively for second row elements were calculated using modified POLYATOM-1 subroutines [12] and transformed into integrals over OAO's. The transformation matrix V was obtained by Schmidt orthogonalization of all valence AO's with respect to the inner shell AO's (transformation by W), formation of hybrid orbitals or symmetry adapted orbitals (unitary transformation U) and finally Löwdin orthogonalization of all valence orbitals. The same transformation is obtained if the Löwdin orthogonalization is applied before the formation of hybrid or symmetry orbitals, i.e. the resulting orbitals may be termed either "orthogonalized hybrid or symmetry orbitals" or "symmetry adapted or hybridized OAO's".

Thus, the OAO's $\tilde{a}, \tilde{b}, \tilde{c}, \ldots$ are given in terms of the non-orthogonal AO's $a, b, c, \ldots$ by

$$(\tilde{a}, \tilde{b}, \tilde{c}, \ldots) = (a, b, c, \ldots)\boldsymbol{V},$$

with

$$\boldsymbol{V} = \boldsymbol{W}\boldsymbol{U}\boldsymbol{S}_c^{-1/2} = \boldsymbol{W}\boldsymbol{S}_b^{-1/2}\boldsymbol{U}$$

where $\boldsymbol{S}_b$ and $\boldsymbol{S}_c$ refers to the overlap matrix of the Schmidt orthogonalized orbitals before and after the unitary transformation $\boldsymbol{U}$ respectively.

As shown by Simonetta *et al.* [13] the loss of localization of the hydrogen AO's arising from the Schmidt orthogonalization, which is necessary within the frozen core approximation in order to keep the inner shells uncontaminated, does not seem to influence the convergence of the VB results. In fact, Garrett [5] showed that the orthogonalization of singly occupied AO's with respect to the core orbitals does not change the total wave function.

The transformation of the two-electron integrals is a rather time-consuming procedure, being a four index transformation, but computer time may be reduced considerably by taking into account the fact that only those integrals need to be transformed to the OAO basis which are needed in the subsequent calculation. In the case of BeH_2 with $n = 5$ basis orbitals, only 59 out of the $n^4 = 625$ integrals, from which 120 are essentially different, have to be transformed.

In order to make full use of the orthogonality of the basis orbitals, valence structures were constructed which are as well spin eigenfunctions as orthogonal. Starting from all possible orbital configurations which may be obtained from the minimal basis set within the frozen core approximation, i.e. excluding excitation from the inner shell $1s$ AO's, the valence structures were obtained by multiplication with the appropriate spin functions belonging to $S = M_S = 0$ for singlet and $S = M_S = \frac{1}{2}$ for doublet states, which were obtained by the spin-pairing method and subsequent Schmidt orthogonalization [14]. Thus, the total wave function is given by

$$\Psi(1, 2, \ldots, N) = \sum_{\kappa} C_\kappa \Phi_\kappa(1, 2, \ldots, N),$$

in which each VB structure Φ_κ is a linear combination of Slater determinants and has the form

$$\Phi_\kappa(1, 2, \ldots, N) = \mathscr{A}\Omega_\kappa(r_1, r_2, \ldots, r_N)\theta_\kappa(s_1, s_2, \ldots, s_N)$$

where $\mathscr{A}$ is the usual antisymmetrizer and the orbital factor Ω_κ is a product

$$\Omega_\kappa(r_1, r_2, \ldots, r_N) = \phi_1(r_1)\phi_2(r_2) \ldots \phi_N(r_N)$$

of N orbitals ϕ_i from the orthonormal basis set $\tilde{a}, \tilde{b}, \ldots$, and $\theta_\kappa(s_1, s_2, \ldots, s_N)$ is a normalized spin eigenfunction. In general more than one valence structure may be obtained from any one orbital configuration, i.e. the same orbital factor Ω may be combined with different spin functions, which are chosen to be orthogonal.

In building up the Hamiltonian matrix $\langle \Phi_\kappa | \mathscr{H} | \Phi_\lambda \rangle$, a list of labels is generated, indicating which integral appears in which matrix element. This list can be used for subsequent calculations of the same system at different geometries, making the VB part of computations on potential hypersurfaces considerably faster. Thus, once the label list is set up, each point of the potential hypersurface requires only the evaluation of the integrals of OAO's needed and the determination of just one or at most a few eigenvalues of the matrix $\boldsymbol{H}$, which may therefore be of rather large dimension.

3. Results

Results of VB calculations obtained by including all valence structures which may be constructed from a minimal basis of OAO's within the frozen core approximation, i.e. by solving the full CI problem are given in Figs. 1 and 2, where the calculated potential energy curves for the $X^1\Sigma^+$ state of HF and the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states of BeH_2 are shown and compared to the SCF results. Within the frozen core approximation, the full CI for configurations constructed from a minimal basis of OAO's is equivalent to a full CI for configurations constructed from the corresponding non-orthogonal AO's as well as to the complete MO-CI. Therefore, the ground state minimum energy is lower than the SCF result obtained with the same basis set by 0.037 a.u. = 97 kJ mol^{-1} in the case of HF and by 0.022 a.u. = 59 kJ mol^{-1} in the case of BeH_2, as may be seen from the data collected in Tables 1 and 2. A comparison with the highly sophisticated calculations of Ahlrichs *et al.* [15] shows that this corresponds approximately to the inclusion of 27% of the total pair correlation energy, although one should remember that a minimal basis SCF calculation is far from the HF limit and does not take into account any intraatomic correlation energy. With increasing internuclear distances the differences between VB and SCF results increase due to the correct asymptotical behaviour of the VB potential energy curve. As a consequence the minimum energy

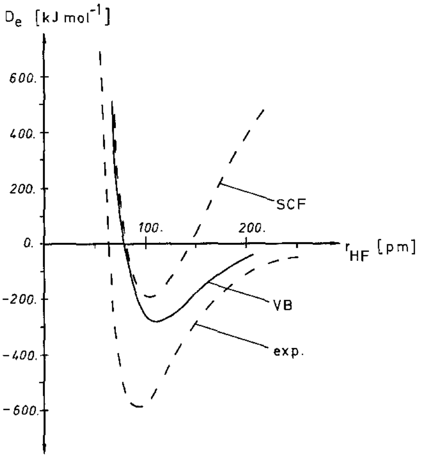

Fig. 1. Potential energy curve for HF ($X^1\Sigma^+$) as calculated by the OAO-VB approach, as well as SCF and experimental curves (broken line, Ref. see Table 1)

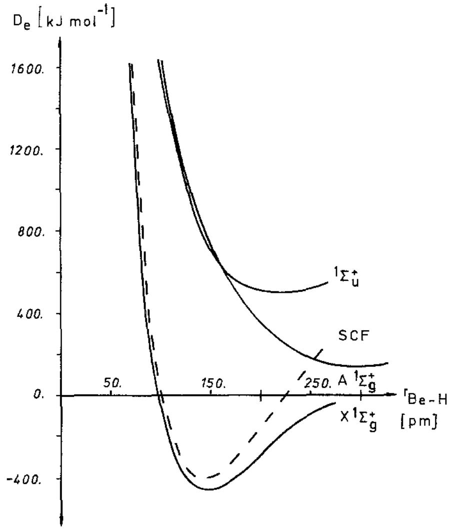

Fig. 2. Potential energy curves for the lowest states of linear BeH_2 as calculated by the OAO-VB approach, and SCF ground state curve (broken line)

Table 1. Computational results and experimental data for HF ($X^1\Sigma^+$)

	SCF[a]	OAO-VB[a]	SCF[b]	Exp.[c]
E_e [a.u.]	− 99.29614	− 99.33270	−100.07084	—
D_e [kJ mol^{-1}]	−193	−289	−424	−590
r_e [pm]	103.8	110.2	89.7	91.7

[a] Minimal STO-H(3)F(5-2-3)G basis with Slater exponents.
[b] Cade, P. E., Huo, W. M.: J. Chem. Phys. **47**, 614 (1967).
[c] Johns, J. W. C., Barrow, R. F.: Proc. Roy. Soc. **A251**, 504 (1959).

Table 2. Results of different calculations for linear BeH_2 ($^1\Sigma_g^+$)

	SCF[a]	OAO-VB[a]	SCF[b]
E_e [a.u.]	− 15.70400	− 15.72647	− 15.94243
D_e [kJ mol^{-1}]	−400	−459	−721
r_e [pm]	142	146	134

[a] Minimal STO-H(3)Be(5-2-3)G basis; exponents were taken from Clementi, E., Raimondi, D. L.: J. Chem. Phys. **38**, 2686 (1963).
[b] Kaufman, J. J., Sachs, L. M., Geller, M.: J. Chem. Phys. **49**, 4369 (1968).

internuclear distances obtained from the VB calculation are larger than those obtained from the SCF calculations.

Of particular interest are the results of Table 3 which illustrate the dependence of VB results for BeH_2 on the choice of valence structures. From the work of Slater [16] and McWeeny [17] it has been known for a long time that the VB method based on OAO's does not predict stable ground states of molecules and therefore gives no explanation of chemical bonding if merely covalent structures are taken into account, but that the inclusion of larger numbers of ionic structures becomes necessary. This is verified from the results in columns 8 and 9: the calculated energy is 1114 kJ mol^{-1} or even 2373 kJ mol^{-1} respectively above that of the separated atoms, if only non-polar structures or only the most important configuration are considered. If all structures with formal charge zero at the Be atom ($q_{Be}=0$) are taken into account the VB calculation converges towards a different state (column 5).

Table 3. Study on the importance of valence structures in the OAO-VB-CI for linear BeH_2 ($^1\Sigma_g^+$) at $r_{BeH}=134$ pm

Column	2	3	4	5	6	7	8	9
			Valence structure coefficient in the OAO-wavefunction					
No.	q_{Be}	Config.	C_{VB}	C_{VB}	C_{VB}	C_{VB}	C_{VB}	C_{VB}
1	0	$szhh'$	0.207	−0.066	0.215	0.240	0.184	0.015
2	0		0.499	−0.002	0.505	0.582	0.754	0.999
3	0	$(s)^2(h')^2$	−0.218	−0.427	−0.201	−0.225	−0.292	—
4	0	$(z)^2(h)^2$	−0.275	−0.081	−0.272	−0.282	−0.559	—
5	−1	$(s)^2zh'$	−0.265	—	−0.259	−0.253	—	—
6	−1	$s(z)^2h$	−0.320	—	−0.326	−0.365	—	—
7	+1	$sh(h')^2$	−0.380	—	−0.379	−0.390	—	—
8	+1	$z(h)^2h'$	−0.411	—	−0.417	−0.351	—	—
9	−2	$(s)^2(z)^2$	−0.144	—	−0.142	—	—	—
10	+2	$(h)^2(h')^2$	−0.266	—	−0.269	—	—	—
11	0	$(s)^2(h)^2$	0.073	0.897	—	—	—	—
12	0	$(z)^2(h')^2$	0.029	0.050	—	—	—	—
D_e [kJ mol^{-1}]			−441	+1641	−428	−87	+1114	+2373

These results may be compared with the finding of MacLagan and Schnuelle [18] that in the case of BeH_2 a VB function neglecting ionic structures is a very good approximation and that even the resonance function based on a single configuration is only slightly worse than the MO function and still bonding if the valence structures are constructed from the non-orthogonal AO's.

A comparison of columns 6 and 7 emphasizes the importance of doubly excited structures; from columns 4 and 6 on the other hand it is seen that the last two structures, which correspond to charge shifts between different bonds, contribute very little to the ground state energy.

Results for calculations on the hypersurface of the reaction $F+H_2 \rightarrow HF+H$ are collected in Table 4 and Figs. 3 and 4. Again, the VB results are obtained by including all structures which may be obtained from a minimal basis of OAO's within the frozen core approximation, whereas the SCF results are based on the unrestricted Hartree-Fock method, a collinear arrangement of the three atoms being assumed for all calculations. The left hand part of the energy profile given in Fig. 3 was obtained by choosing suitable values for r_{FH} and minimizing the total energy with respect to r_{HH}, whereas in calculating the right hand part the energy was optimized with respect to r_{HF} for given values of r_{HH}.

From Fig. 3 it is seen that our results compare rather unfavourably with the SCF-CI results of Schaeffer III *et al.* [19] in so far as in contrast to the experimental data we calculated the reaction to be endothermic by $+24$ kJ mol^{-1}, whereas Schaeffer III *et al.* obtained a value of -144 kJ mol^{-1} for the heat of reaction to be compared with the experimental value of -131 kJ mol^{-1}. This is due to the fact that our basis set is rather poor as far as the description of the HF molecule is concerned. As is well known the description of chemical bonds involving the F atom requires a careful choice of the basis set including polarization functions [20].

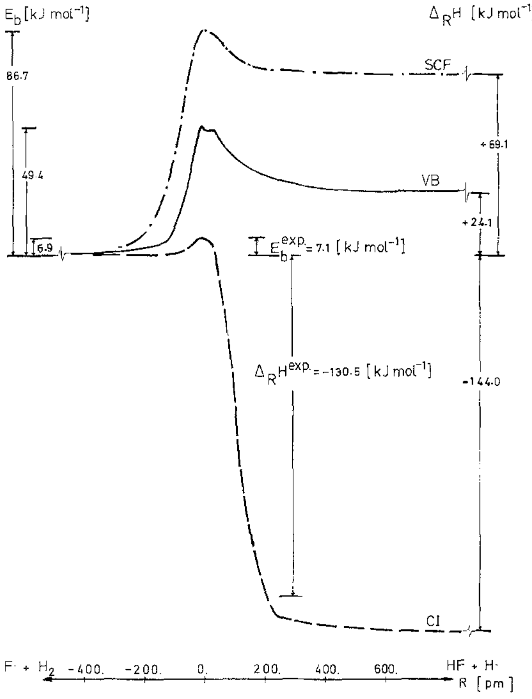

Fig. 3. Energy profile along the reaction path for the linear reaction $F + H_2 \rightarrow HF + H$, as calculated by the OAO-VB and SCF approach (present results), as well as SCF and SCF-CI results of Schaeffer III *et al.* [19] and experimental values for the barrier height and heat of reaction (Ref. see Table 4)

Thus, taking into account polarization functions improved the SCF value for the heat of reaction as calculated by Schaeffer III *et al.* from $+2.5$ kJ mol^{-1} to -55 kJ mol^{-1}. At the same time the barrier height with respect to $F + H_2$ changed from 14.4 kJ mol^{-1} to 123 kJ mol^{-1}; only by extensive CI a value of 6.9 kJ mol^{-1} could be reached, which is in close agreement with experiment.

Our results in Table 4 show that the VB treatment leads to an improvement over the SCF value for the description of both the reactants and products as well as the transition state, although the calculated barrier height of 49.4 kJ mol^{-1} is still fairly large. This value may improve considerably if a basis set flexible enough to describe the exothermicity of the reaction is used. This can be achieved in a particularly simple way by adjusting semiempirical parameters such as to give a good description of reactants and products, although a satisfactory description of the transition state may need some additional flexibility. This is seen from calculations on the linear H_3 system. Using fixed H(1*s*) orbital exponents $\zeta = 1.0$ the OAO-VB method leads to a value of 58.4 kJ mol^{-1} for the energy barrier of the exchange reaction, which is a slight improvement over the SCF value of 63.4 kJ mol^{-1}, the best value being 41 kJ mol^{-1} [21]. As noted already by Hirschfelder *et al.* [22], simultaneous variation of all three orbital exponents does not improve the results at all, but gives a barrier height of 105 kJ mol^{-1}; this is because in the transition state the central and outer atoms ought to have different orbital exponents. Obviously, $\zeta = 1.0$ is equally bad for $H+H_2$ as for H . . . H . . . H, the fairly low barrier height thus being merely fortuitous. It will be of particular interest to see whether semiempirical calculations with adjustable parameters can give a good description of the whole reaction. Calculations which hopefully confirm the applicability of semiempirical valence electron methods to problems of chemical reactivity are in progress and will be reported in a forthcoming paper.

Table 4. Summary of results on the linear reaction $H_2+F \rightarrow HF+H$ calculated in different ways

		SCF[a]	OAO-VB[a]	CI[b]	Exp.
E_1 (H_2+F)	[a.u.]	−99.81949	−99.83889	−100.56202	—
E_2 (HF+H)	[a.u.]	−99.793183	−99.829747	−100.61691	—
Heat of reaction:					
$E_1 - E_2$	[kJ mol^{-1}]	69.1	24.1	−144.0	−130.5[c]
r_e (HF)	[pm]	103.8	110.2	92.0	91.7
r_e (H_2)	[pm]	85.2	88.1	74.2	74.1
Saddle-point					
E (HFH)$-E_1$	[kJ mol^{-1}]	86.7	49.4	6.9	7.1[d]
r (HF)	[pm]	110.3	119.1	153.5	—
r (H_2)	[pm]	132.6	124.4	76.7	—

[a] OAO-VB calculation and DODS-SCF calculation with minimal STO-H(3)F(5-2-3)G basis with Slater exponents.

[b] Bender, C. F., O'Neil, S. V., Pearson, P. K., Schaefer III, H. F.: Science **176**, 1412 (1972).

[c] Trotman-Dickenson, A. F. *et al.*: J. Chem. Soc. **1960**, 1064.

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4. Discussion

The results reported in the present paper show that the use of Löwdin orthogonalized atomic orbitals in VB calculations is quite feasible for small molecules. Calculation of integrals may be achieved by the methods described earlier in connection with self consistent group calculations where the separability of groups of electrons is based on the strong orthogonality relation [23]. The four index transformation is a time-consuming process, but it should be remembered that the electron interaction integrals over MO's needed in an SCF-CI calculation are obtained by the same procedure.

Of course, the use of a minimal basis set imposes serious limitations in the reliability of the results. Thus, atomic polarization is missing as well as intraatomic correlation. This makes the description of H^- and F^- particularly poor, as may be seen from the calculated heat of reaction for $F + H_2 \rightarrow HF + H$. Furthermore, neither H and H^- nor F^- have any excited states in this approximation.

These minimal basis set calculations were undertaken with a semiempirical development of the method in mind, for it is well known that the zero differential overlap approximation, which serves as a starting-point for nearly all such schemes, may be justified on the basis of Löwdin OAO's [24]. A semiempirical development of the method used in this paper seems to be particularly promising, as most deficiencies of the minimal basis set may be overcome by a judicious choice of empirical parameters, although our results for the triatomic exchange reactions suggest that parameters optimized for the description of stable molecules may not be equally suited for geometries near the transition state.

One may conclude that the evaluation of integrals over OAO's is no problem, particularly within a semiempirical scheme based on the zero differential overlap approximation. Due to the orthogonality of the basis functions the evaluation of the matrix elements for the CI problem is thus very easy, although the CI problem may be of rather large dimension. For an N electron system with total spin S

$$\frac{N+1}{2S+1}(f_S^N)^2$$

VB structures can be constructed [25], where

$$f_S^N = \frac{(2S+1)N!}{(\frac{1}{2}N+S+1)!(\frac{1}{2}N-S)!}$$

is the number of spin eigenfunctions. For CH_4 with 8 valence electrons these are 1764 VB structures, and for C_2H_6 with 14 valence electrons already 2,760,615. Certainly, not all of these structures have to be taken into account. Van der Lugt and Oosterhoff [9], who applied the VB approach in connection with the approximations of Pariser, Parr and Pople to π-systems, showed that ground state energies and particularly the sequence of excited states very much depend on the inclusion of doubly and higher excited configurations. But the analysis of our results for BeH_2 suggests that in the case of molecules with localized bonds it is not necessary to include all doubly and higher excited configurations: those structures which correspond to charge shifts between different bonds contribute very little to the ground state energy. This is in agreement with the results from separated pair function calculations which suggest that a good approximation to the wave function may be obtained by including just those polar structures which correspond to charge shifts between bonded atoms [23].

In the case of VB calculations based on non-orthogonal AO's the extensive work of Simonetta [13, 26], Balint-Kurti [20] and others suggests that it is possible, to a large extent, to identify the most important configurations on the basis of chemical intuition. In order to carry over these results to the case of OAO's, one could expand these structures in terms of Slater determinants over OAO's; Moffitt [27] has shown that if the OAO's λ_μ are given in terms of the non-orthogonal AO's ϕ_i by

$$\lambda_\mu=\sum_i V_{i\mu}\phi_i \quad \text{or} \quad \phi_i=\sum_\mu Y_{\mu i}\lambda_\mu, \quad \text{with } Y_{\mu i}=(V^{-1})_{\mu i}$$

the Slater determinant $\Phi_i(i_1, i_2, \ldots, i_N)$ constructed from a selection $i_1, i_2, \ldots, i_N$ of N of the ϕ_i may be expressed in terms of Slater determinants $\Lambda_\mu(\mu_1, \mu_2, \ldots, \mu_N)$ constructed each from N OAO's λ_μ by the equation

$$\Phi_i(i_1, i_2, \ldots, i_N)=\sum_{\mu_1,\ldots,\mu_N} Y(\mu_1\mu_2\ldots\mu_N \mid i_1 i_2\ldots i_N)\Lambda_\mu(\mu_1, \mu_2, \ldots, \mu_N),$$

where the sum is over the $n!/N!(n-N)!$ cofactors of order $(n-N)$ of the matrix $\boldsymbol{Y}$ where $n>N$ is the number of basis spin orbitals. But in fact, the number and nature of the structures involved to represent one particular valence structure constructed from non-orthogonal AO's may easily be obtained without the tedious evaluation of cofactors just by replacing each AO in turn by those which mix due to the orthogonalization procedure. At the same time this method has the additional advantage that the resulting wave function is more flexible than one obtained by Moffitt's expansion. Thus the perfect pairing wave function for HF $\Phi(sz\bar{s}\bar{h})$ may be expanded in terms of $[3!/2!(3-2)!]\cdot[3!/2!(3-2)!]=9$ determinants over OAO's which correspond to the following 6 configurations: $(\tilde{s}\tilde{s}\tilde{z}\tilde{z})$, $(\tilde{s}\tilde{s}\tilde{h}\tilde{h})$, $(\tilde{z}\tilde{z}\tilde{h}\tilde{h})$, $(\tilde{s}\tilde{s}\tilde{z}\tilde{h})$, $(\tilde{z}\tilde{z}\tilde{s}\tilde{h})$, and $(\tilde{s}\tilde{z}\tilde{h}\tilde{h})$, i.e. to what has been referred to as full CI in the last paragraph. If on the other hand, the perfect pairing ground state configuration of BeH_2 is expressed in terms of determinants constructed from OAO's, the two structures which correspond to charge shifts between different bonds and which contribute only very little to the ground state energy, do not occur.

Finally, we should like to make a few comments on the interpretation of the VB functions constructed from OAO's. From the fact that only comparatively few valence structures are needed if the VB functions are constructed from non-orthogonal AO's whereas a large number of structures is necessary if OAO's are used instead, one may conclude that it might be advisable to express the valence structures over OAO's in terms of determinants over non-orthogonal AO's. This requires the inverse of the transformation given above, i.e. the evaluation of all cofactors $V(i_1 i_2\ldots i_N \mid \mu_1\mu_2\ldots\mu_N)$ of the matrix $\boldsymbol{V}$ and therefore involves the same amount of computing as would be required for evaluating the matrix elements over non-orthogonal AO's.

Fortunately it is not only very laborious but also very little informative to perform this transformation. For it is meaningless to interpret a given wave function in terms of the coefficients with which each structure appears and which indicate for instance the amount of ionic character of a particular bond etc. unless the structures concerned are strictly orthogonal and therefore mutually exclusive. An interpretation of the wave function should therefore be based on the wave function over OAO's. The large number of structures involved suggests that a kind of population analysis should be applied. A forthcoming paper of this series will be concerned with the use of spinless density matrixes [28], i.e. the charge density function $P_1(1)$ and the pair function $P_2(1, 2)$ for the interpretation of VB wave functions constructed from OAO's.

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