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Induced mapping in the n-electron space and a transformation of valence-bond structures to molecular-orbital functions

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A mathematical study of the problem of mappings on the n-electron configurations induced by one-electron orbital transformations is carried out. The main objective is to design a procedure that uses the chemical information of valence-bond functions in the determination of a limited number of significant orthogonal configurations for a molecular-orbital treatment. The example of the $He_2{}^+$ ion is given.

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I. INTRODUCTION

In quantum chemistry, the n-electron wave function is generally constructed from a finite set of one-electron functions, i.e., the spin orbitals, and expressed in the form of a linear combination of Slater determinants. The spin orbitals themselves are usually defined in terms of some basis sets of atomic orbitals, but they can be subjected in actual computations to various linear transformations. For instance, the standard molecular-orbital (MO) method starts with orthogonal spin orbitals, solutions of self-consistent-field (SCF) or multiconfiguration self-consistent-field (MCSCF) treatments, but possibly modified by means of transformations designed for improving both their physical meaning and the convergency of the subsequent configuration-interaction (CI) treatment (relocalized MO's, natural MO's, etc.). On the other hand, the valence-bond (VB) theory expresses the total wave function directly in terms of chemical components built from atomic orbitals and, consequently, significant from a structural point of view provided that their nonorthogonality properties are preserved [1] (note that computer algorithms dealing with Hamiltonian matrix elements between nonorthogonal basis functions have been recently presented [2]).

The connection of total wave functions expressed in terms of orthogonal MO's with those expressed in terms of VB formulas has been known for a long time. First, the complete equivalence of corresponding full configuration-interaction and full valence-bond developments, established by Slater in the case of a two-electron, two-orbital problem [3], has been generalized to more complicated systems [4–6]. Second, the study of the VB content of one (or several) Slater determinants built from orthogonal MO's has been made possible with the help of appropriate computer programs [7,8]. In contrast, information concerning the backward transformation from one (or several) given formulas to MO determinants is lacking.

We have tried to give an answer to the reverse problem mentioned above, using the exterior algebra as a fruitful alternative to more traditional formalisms [9]. This paper is organized as follows: the first part studies the general problem using exterior algebra concepts, the second gives some results for the test example of the $He_2{}^+$ ion. The choice of this three-electron system was first dictated by the fact that it is the simplest compound for which the transformation is not a trivial problem. Possible applications of the $He_2{}^+$ model for understanding more complicated situations are suggested in the last section.

II. THE GENERAL CASE

A. The backward transformation problem

Let E be the K-vector space of the one-electron spin orbitals (K denotes the field of real numbers or of complex numbers), $(\omega_i)_{1\le i\le 2m}$ a basis set of E consisting of atomic orbitals. The notation $\wedge^n E$ denotes the space spanned by the n-electron configurations:

$$(\Omega_I)_{I\in P_{2m,n}}=(\omega_{i_1}\wedge\cdots\wedge\omega_{i_n})_{i_1<\cdots<i_n}\ , \tag{2.1}$$

where $\wedge$ is the exterior product, and $P_{2m,n}$ is the set of n-element subsets of integers $\{1,\ldots,2m\}$. A valence-bond wave function can be expanded in the following way:

$$\Psi_{VB}=\sum_I \lambda_I\Omega_I\ . \tag{2.2}$$

(Ω_I is nothing but an antisymmetrized product of atomic orbitals as it is used by the usual quantum chemical theories.)

The problem we are concerned with is to reexpand Ψ_{VB} in a well-chosen basis set of orthogonal orbitals $(\phi_j)_{1\le j\le 2m}$.

B. Choice of the basis set of orthogonal spin orbitals

There are two requirements that one can think of to select an orthonormal basis set of spin orbitals. The first one is to use a basis set that gives an expansion of Ψ_{VB} as compact as possible. The second one is to use a basis set adapted to the (space and spin) symmetries of the molecule, since we know that this usually leads to more simple calculations.

As shown recently by one of us [9] the algebraic concept of internal space may be used to answer the first requirement. The internal space $[\Psi]$ of a wave function Ψ is defined to be the space spanned by the least number of spin orbitals necessary to expand Ψ. It has been known for a long time in the field of exterior algebra, though it is not a trivial result, that such a space does exist and is unique. To determine the internal space it is convenient to begin with its orthogonal complement $[\Psi]^{\perp}$ given by

$$\psi \in [\Psi]^{\perp} \Longleftrightarrow \psi \leftharpoondown\!\lrcorner\, \Psi = 0 \ , \tag{2.3}$$

where $\leftharpoondown\!\lrcorner$ denotes the interior product, and ψ a one-electron spin orbital. The equation means, in terms of second quantization operators, that the annihilation of ψ in Ψ gives zero.

The above relation can be used to build a basis set of $[\Psi_{\text{VB}}]^{\perp}$, the latter is then completed to obtain an orthonormal basis set of E, and the complement is precisely a basis set of $[\Psi_{\text{VB}}]$. In the expansion of Ψ_{VB}, the elements of the basis set of $[\Psi_{\text{VB}}]^{\perp}$ (external spin orbitals) will not appear, since by definition Ψ_{VB} decomposes on the elements of the basis set of $[\Psi_{\text{VB}}]$ (internal spin orbitals) only. Note that if Ψ_{VB} is an eigenfunction of S^2 and S_z, as is normally the case, and if say, eigenvalue$(S_z) \geq 0$, then [10] the internal β-spin orbitals can be chosen to have the same spatial part as some of the internal α-spin orbitals. Note also that the occupied natural spin orbitals (the ones which diagonalize the one-electron density matrix with nonzero eigenvalues) are a particular case of internal spin orbitals, but it will appear (see Sec. III B) that this case is not worth considering, because precisely, the natural β-spin orbitals do not have necessarily the same spatial parts as the natural α-spin orbitals.

To fulfill the second requirement, we have to represent symmetry groups on the internal space, and the usual group theory can be applied to obtain symmetry-adapted internal spin orbitals.

Remark. It may be interesting in practical applications to swap the order in which the requirements are fulfilled.

C. Induced transformation by changing the one-electron spin orbitals

As a matter of fact, the choice of the orthonormal basis set corresponds to the choice of a linear transformation v such that

$$\phi_i = v(\omega_i) \quad \forall i \in \{1, \ldots, 2m\} \ . \tag{2.4}$$

This being done, we are left with a purely algebraic problem (in other words, the orthogonality of the basis set does not play any part); let u be the inverse of v:

$$\omega_i = u(\phi_i) \quad \forall i \in \{1, \ldots, 2m\} \ , \tag{2.5}$$

then setting, by analogy with Eq. (2.1),

$$(\Phi_I)_{I \in P_{2m,n}} = (\phi_{i_1} \wedge \cdots \wedge \phi_{i_n})_{i_1 < \cdots < i_n} \tag{2.6}$$

the linear mapping $\wedge^n u$ defined by

$$\wedge^n u(\Phi_I) = u(\phi_{i_1}) \wedge \cdots \wedge u(\phi_{i_n}) = \Omega_I \quad \forall I \in P_{2m,n} \tag{2.7}$$

is called the induced mapping [11,12] by u and must be made explicit in the basis set of the Φ_I's, if we want to obtain the desired expansion of Ψ_{VB} from Eq. (2.2):

$$\Psi_{\text{VB}} = \sum_I \lambda_I \wedge^n u(\Phi_I) = \sum_I a_I \Phi_I \ , \tag{2.8}$$

denoting by a_I the coefficients of the new expansion of the VB function.

Assume that u is represented by the matrix $U = (u_{i,j})_{1 \leq i,j \leq 2m}$ in the basis set $(\phi_i)_i$, then $\wedge^n u$ is represented in the induced basis set $(\Phi_I)_I$ by the matrix

$$\wedge^n U = (\det U_{I,J})_{I,J \in P_{2m,n}} \ , \tag{2.9}$$

where $\det U_{I,J}$ is the determinant of the minor $U_{I,J} = (u_{i,j})_{i \in I, j \in J}$ of dimension $(n \times n)$ associated to the n indices (i and j) defining Φ_I and Φ_J, which is to be extracted from the U matrix of dimension $(2m \times 2m)$. *A priori*, we have to compute C_{2m}^n determinants per configuration Ω_I in Eq. (2.2). However, use of internal spin orbitals reduces this number to C_p^n where p is the dimension of $[\Psi_{\text{VB}}]$. Now we will show that, as expected, symmetry properties simplify the problem further.

1. Induced mapping and point group symmetry

Let ρ: $G \rightarrow GL(E)$ be a linear representation of group [13] G in E, i.e.,

$$\forall t,s \in G, \quad \rho(t), \rho(s) \in GL(E) \ ,$$

and

$$\rho(st) = \rho(s)\rho(t) \ .$$

Then the mapping $\wedge^n \rho$: $G \rightarrow GL(\wedge^n E)$ defined by

$$\forall s \in G, \quad (\wedge^n \rho)(s) = \wedge^n \rho(s) \tag{2.10}$$

is a linear representation of G in $\wedge^n E$. We call it the induced representation of ρ.

Remark. $\wedge^n \rho$ is not in general irreducible, even if ρ is so. It decomposes into a direct sum of irreducible representations which can be determined by means of character theory. Care must be taken, however, of the antisymmetry of the exterior product; for example in D_{2d} symmetry with z as principal axis, the exterior product of degenerate p orbitals (centered at the symmetry center) $p_x \wedge p_y$ transforms as the B_1 irreducible representation (i.e., like a $d_{x^2-y^2}$ orbital) whereas the tensorial product $p_x \otimes p_y$ transforms as the B_2 irreducible representation (i.e., like a d_{xy} orbital). In other words, the character of $\wedge^n \rho$ is not n times the character of ρ as it would be in the case of the tensorial product.

If ρ and ρ' are conjugate representations in E then $\wedge^n \rho$ and $\wedge^n \rho'$ are conjugate representations in $\wedge^n E$, since for all $s \in G$

$$\rho'(s) = u\rho(s)u^{-1} \tag{2.11}$$

implies

$$\wedge^n \rho'(s) = \wedge^n u \wedge^n \rho(s) (\wedge^n u)^{-1} \ . \tag{2.12}$$

In practice that means that if a multiconfiguration Φ transforms a certain way under the mappings $\wedge^n \rho(s)$ (typically as a basis vector of an irreducible subrepresentation which can be degenerate or not), then $\Omega=\wedge^n u(\Phi)$ transforms the same way under the mappings $\wedge^n\rho'(s)$. Consequently, if we start with a valence-bond function Ψ_{VB} which transforms like a given irreducible representation (irrep.), the Φ_I's which transform like the other irreps. of the group will not appear in the expansion and there is no need to compute the corresponding determinants.

2. *Induced mapping and spin symmetry*

We now investigate some properties of the mappings $\wedge^n u$ induced by mappings u which act on the spatial part of the spin orbitals only.

Assume there are n electrons, m α-spin orbitals $(\phi_i)_i$, and m β spin orbitals $(\bar{\phi}_i)_i$ with the same spatial part as the $(\phi_i)_i$. The most general transformation of orbitals will be a mapping which decomposes into an α-spin and a β-spin part,

$$u=u^{\alpha}+u^{\beta}\ , \qquad (2.13)$$

and satisfies the relationship

$$u(\bar{\phi}_i)=\overline{u(\phi)_i}\ , \qquad (2.14)$$

meaning that u commutes with the operation of α-β spin exchange. As a result, u^{α} and u^{β} have the same matrix representation in the basis $(\phi_i)_i$ and $(\bar{\phi}_i)_i$, respectively. Denote by U the matrix of u in the basis $(\phi_i)_i,(\bar{\phi}_i)_i$; then U has the form

$$U=\begin{bmatrix} A & 0\\ 0 & A\end{bmatrix} \qquad (2.15)$$

with

$$A=(a_{i,j})_{1\le i,j\le m}\ , \qquad (2.16)$$

i.e.,

$$u(\phi_i)=\sum_j a_{i,j}\phi_j\ . \qquad (2.17)$$

Equation (2.13) implies that $\wedge^n u$ (and so does the matrix $\wedge^n U$) decomposes on the eigenspaces of S_z:

$$\wedge^n u=\sum_{n^{\alpha}+n^{\beta}=n}\wedge^{n^{\alpha}}u^{\alpha}\otimes\wedge^{n^{\beta}}u^{\beta}\ , \qquad (2.18)$$

which means that $\wedge^n u$ commutes with S_z and that $\wedge^n U$ is block diagonal. In fact, it also commutes with S_x and S_y. Let γ denote x, y, or z, S_γ and s_γ the components of the spin operator in $\wedge^n E$ and E, respectively,

$$S_\gamma(\phi_1\wedge\cdots\wedge\phi_n)=\sum_i\phi_1\wedge\cdots\wedge s_\gamma(\phi_i)\wedge\cdots\wedge\phi_n\ .$$

Setting

$$\Phi=\phi_1\wedge\cdots\wedge\phi_n\ ,$$

we get

$$\wedge^n u(S_\gamma(\Phi))=\sum_i u(\phi_1)\wedge\cdots\wedge u(s_\gamma(\phi_i))\wedge\cdots\wedge u(\phi_n)\ ,$$

$$S_\gamma(\wedge^n u(\Phi))=\sum_i u(\phi_1)\wedge\cdots\wedge s_\gamma(u(\phi_i))\wedge\cdots\wedge u(\phi_n)\ .$$

Therefore $\wedge^n u$ and S_γ commute if and only if u and s_γ commute.

Notice that a matrix of the form given in Eq. (2.15) commutes with all matrices of the form

$$U=\begin{bmatrix} aI & bI\\ cI & dI\end{bmatrix}\ ,$$

where I is the $m\times m$ identity submatrix. Thus u commutes with s_x,s_y,s_z, whose matrix representations are, respectively ($\hbar=1$),

$$\begin{bmatrix} 0 & \frac{1}{2}I\\ \frac{1}{2}I & 0\end{bmatrix},\quad \begin{bmatrix} 0 & -\frac{1}{2}iI\\ +\frac{1}{2}iI & 0\end{bmatrix},\quad \begin{bmatrix} \frac{1}{2}I & 0\\ 0 & -\frac{1}{2}I\end{bmatrix}.$$

Consequently $\wedge^n u$ commute with S_x, S_y, and S_z and since

$$S^2=S_x^2+S_y^2+S_z^2\ ,$$

with S^2 as well. In practice this means that only the Φ_I's or linear combinations of the Φ_I's which are eigenfunctions of S_z and S^2 with the same eigenvalues as Ψ_{VB} will appear in the expansion of the latter. As a result, only the matrix elements (2.9) belonging to a given block of $\wedge^n U$ are of interest and in addition it is not necessary to calculate all of them. In fact, regardless of the point group symmetry, the number of matrix elements to be computed is given by the Weyl's dimension formula [14], nevertheless, as in the case of an MCSCF calculation, the number of orbitals is not the dimension of the orbital basis set m, but the number of internal orbitals [provided that we have chosen the internal β-spin orbitals with the same spatial part as internal α-spin orbitals for eigenvalue$(S_z)\ge 0$]. This is what makes the transformation computationally feasible.

To conclude this section we note that the transformation of several VB functions to an expansion over the same Φ_I's is possible; it is only necessary to consider the internal space of the set of the VB functions defined as the sum of the internal spaces of each function. This might increase the size of the internal space, but in the case of degenerate VB functions the internal spaces will only differ by some degenerate spin orbitals, since $\psi\in[\Psi]$ implies $\rho(s)\psi\in[(\wedge^n\rho)(s)\Psi]$.

III. APPLICATION: He$_2^+$

As an application we consider the He$_2^+$ ion and transform a chemically significant VB wave function constructed with atomic orbitals to a multiconfiguration formed of well-chosen orthogonal molecular orbitals.

This multiconfiguration is compared to the full configuration-interaction (FCI) wave function and used to construct a limited configuration interaction (LCI).

A. Weinbaum's wave function

The $He_2{}^+$ ion has $D_{\infty h}$ symmetry and the ground state transforms as the Σ_u^+ irreducible representation. Weinbaum [15] has found that the wave function

$$\Psi_w=\frac{1}{N}(1_{s_A}\wedge 1_{s'_B}\wedge \bar{1}_{s_A}-1_{s_B}\wedge 1_{s'_A}\wedge \bar{1}_{s_B}) ,$$

with

$$N=[2(1-S'^2_{AB}-S(SS''-S'^2_{AA}))]^{1/2} ,$$

$$S=\langle 1_{s_A}|1_{s_B}\rangle,\quad S''=\langle 1_{s'_A}|1_{s'_B}\rangle ,$$

$$S'_{AA}=\langle 1_{s_A}|1_{s'_A}\rangle,\quad S'_{AB}=\langle 1_{s_A}|1_{s'_B}\rangle ,$$

is a good approximation of this state when 1_{s_A} ($1_{s'_A}$) is a Slater orbital centered on atom A with exponent $z=1.734$ ($z'=2.029$). We use this wave function as a starting point for the induced transformation (where the Slater orbitals have been replaced by their STO-6G [16] counterparts). The orbital $1_{s'}$ can be seen as the orbital 1_s of the He^+ ion.

B. Choice of the orthogonal basis set and simplifications

In the case of the Weinbaum wave function it is easy to check that the only atomic spin orbitals satisfying Eq. (2.3) are $\bar{1}_{s'_A},\bar{1}_{s'_B}$, and that the internal space is spanned by the remaining spin orbitals $\bar{1}_{s_A},\bar{1}_{s_B},1_{s_A},1_{s_B},1_{s'_A},1_{s'_B}$.

Now making use of the symmetry properties of the molecule, only one choice for β-spin orbitals is relevant, namely,

$$\bar{\sigma}_g=\frac{(\bar{1}_{s_A}+\bar{1}_{s_B})}{\sqrt{2(1+S)}} , \tag{3.1}$$

$$\bar{\sigma}_u=\frac{(\bar{1}_{s_A}-\bar{1}_{s_B})}{\sqrt{2(1-S)}} , \tag{3.2}$$

which belong to the internal space, and

$$\bar{\sigma}'_g=\frac{-(S'_{AA}+S'_{AB})(\bar{1}_{s_A}+\bar{1}_{s_B})+(1+S)(\bar{1}_{s'_A}+\bar{1}_{s'_B})}{\sqrt{2(1+S)[(1+S)(1+S'')-(S'_{AA}+S'_{AB})^2]}} , \tag{3.3}$$

$$\bar{\sigma}'_u=\frac{-(S^{-}_{AA}-S'_{AB})(\bar{1}_{s_A}-\bar{1}_{s_B})+(1-S)(\bar{1}_{s'_A}-\bar{1}_{s'_B})}{\sqrt{2(1-S)[(1-S)(1-S'')-(S'_{AA}-S'_{AB})^2]}} , \tag{3.4}$$

which span the orthogonal complement. Since we are dealing with an orbital transformation, we must choose $\sigma_u,\sigma_g,\sigma'_u,\sigma'_g$ as the α-spin orbitals (note that σ_g and σ'_g are not natural α-spin orbitals). The functions $\bar{\sigma}'_g$ and $\bar{\sigma}'_u$ cannot appear in the configurations of the expansion of Ψ_w, because they do not belong to its internal space.

TABLE I. This scheme lists for $He_2{}^+$ how the properties of the induced transformation can simplify its computation.

Number of coefficients to be calculated:

$C_8^3=56$

$S_z\ \wedge^n u=\wedge^n u\ S_z$ ↓

$C_4^2C_4^1=24$

use of internal orbitals ↓

$C_4^2C_2^1=12$

$\rho'=u\rho u^{-1}\Longrightarrow \wedge^n\rho'=\wedge^n u\wedge^n\rho\wedge^n u^{-1}$ ↓

$\frac{1}{2}C_4^2C_2^1=6$

$S^2\ \wedge^n u=\wedge^n u\ S^2$ ↓

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Moreover, since Ψ_w transforms as Σ_u^+ in the representation in the basis set induced by the atomic orbitals, it must transform as Σ_u^+ for the conjugate representation in the basis set induced by the orthogonal orbitals. Taking into account that eigenvalue$(S_z)=\frac{1}{2}$, only the six following Σ_u^+ configurations will appear in the expansion:

$$\Phi_1=\sigma_g\wedge\bar{\sigma}_g\wedge\sigma_u ,$$

$$\Phi_2=\sigma_g\wedge\bar{\sigma}_g\wedge\sigma'_u ,$$

$$\Phi_3=\sigma_u\wedge\bar{\sigma}_u\wedge\sigma'_u ,$$

$$\Phi_4=\bar{\sigma}_g\wedge\sigma_u\wedge\sigma'_g ,$$

$$\Phi_5=\sigma_g\wedge\bar{\sigma}_u\wedge\sigma'_g ,$$

$$\Phi_6=\bar{\sigma}_g\wedge\sigma'_g\wedge\sigma'_u .$$

Finally since Ψ_w is an eigenfunction of S^2, and S^2 commutes with the induced mapping, the configurations in the expansion must form some eigenfunctions of S^2 (see Sec. II C 2). Φ_1,Φ_2,Φ_3 are already such eigenfunctions, but it can be seen that the three remaining functions will constitute an eigenfunction of S^2 if and only if Φ_4 and Φ_5 have coefficients of opposite sign in the expansion and the coefficient of Φ_6 is 0. This further reduces to four the number of coefficients to be determined. Table I summarizes the process followed to simplify the calculation of the induced mapping.

C. Results

1. *Analytical result*

The inversion of Eqs. (3.1)–(3.4) gives the matrix U of the transformation. The submatrix A of Eq. (2.15) is

$$A=\begin{bmatrix} b_1 & b_{-1} & 0 & 0\\ b_1 & -b_{-1} & 0 & 0\\ -c_1 & c_{-1} & d_1 & d_{-1}\\ -c_1 & -c_{-1} & d_1 & -d_{-1}\end{bmatrix}$$

with

$$b_\epsilon = \left[\frac{1+\epsilon S}{2}\right]^{1/2},$$

$$c_\epsilon = \frac{S'_{AA} + \epsilon S'_{AB}}{\sqrt{2(1+\epsilon S)}},$$

$$d_\epsilon = \frac{[(1+\epsilon S)(1+\epsilon S'') - (S'_{AA} + \epsilon S'_{AB})^2]^{1/2}}{\sqrt{2(1+\epsilon S)}},$$

where $\epsilon \in \{-1, +1\}$.

Then making use of Eq. (2.9) the following expansion is obtained:

$$\Psi_w = a_1\Phi_1 + a_2\Phi_2 + a_3\Phi_3 + a_4\frac{\Phi_4 - \Phi_5}{\sqrt{2}},$$

$$a_1 = \frac{S'_{AA} - SS'_{AB}}{\{(1-S)[1 - S'^2_{AB} - S(SS'' - S'^2_{AA})]\}^{1/2}},$$

$$a_2 = \left[\frac{1+S}{2}\right]\left[\frac{(1-S)(1-S'') - (S'_{AA} - S'_{AB})^2}{(1-S)[1 - S'^2_{AB} - S(SS'' - S'^2_{AA})]}\right]^{1/2},$$

$$a_3 = \frac{1}{2}\left[\frac{(1-S)[(1-S)(1-S'') - (S'_{AA} - S'_{AB})^2]}{1 - S'^2_{AB} - S(SS'' - S'^2_{AA})}\right]^{1/2},$$

$$a_4 = \left[\frac{(1-S)[(1+S)(1+S'') - (S'_{AA} + S'_{AB})^2]}{2[1 - S'^2_{AB} - S(SS'' - S'^2_{AA})]}\right]^{1/2}.$$

2. *Numerical result*

In order to evaluate the quality of the wave function Ψ_w, a FCI calculation using the GAMESS [17] computer program has been performed in the same one-electron orthogonal basis set. The FCI involves the ten following multiconfigurations:

$$\Psi_1 = \Phi_1,$$

$$\Psi_2 = \Phi_2,$$

$$\Psi_3 = \Phi_3,$$

$$\Psi_4 = \frac{\Phi_4 - \Phi_5}{\sqrt{2}},$$

$$\Psi_5 = \frac{1}{\sqrt{6}}(2\sigma_g \wedge \sigma_u \wedge \bar{\sigma}'_g - \bar{\sigma}_g \wedge \sigma_u \wedge \sigma'_g - \sigma_g \wedge \bar{\sigma}_u \wedge \sigma'_g),$$

$$\Psi_6 = \sigma_u \wedge \sigma'_u \wedge \bar{\sigma}'_u,$$

$$\Psi_7 = \sigma_u \wedge \sigma'_g \wedge \bar{\sigma}'_g,$$

$$\Psi_8 = \sigma'_g \wedge \bar{\sigma}'_g \wedge \sigma'_u,$$

$$\Psi_9 = \sigma_g \wedge \frac{\sigma'_g \wedge \bar{\sigma}'_u - \bar{\sigma}'_g \wedge \sigma'_u}{\sqrt{2}},$$

$$\Psi_{10} = \frac{1}{\sqrt{6}}(2\bar{\sigma}_g \wedge \sigma'_g \wedge \sigma'_u - \sigma_g \wedge \bar{\sigma}'_g \wedge \sigma'_u - \sigma_g \wedge \sigma'_g \wedge \bar{\sigma}'_u).$$

The optimization of geometry gives $r_e = 1.112$ Å and $E = 4.94$ a.u. (see Table II), and the corresponding coefficients of the FCI wave function are listed in Table III. In parallel, we give the coefficients of the expansion of Ψ_w at the same geometry. It is striking that the expansion of Ψ_w contains and only contains the four most important configuration state functions of the FCI wave function with the right order for their relative weights. A LCI using Ψ_1, Ψ_2, Ψ_3, Ψ_4, and Ψ_5 (the latter being simply the other eigenfunction of S^2 that can be built with the orbitals of Ψ_4) has also been performed. The LCI wave function turns out to be very similar to Ψ_w (see Table III), its energy is -4.93 a.u. as for the Weinbaum original wave function, and this is close to the FCI result.

TABLE II. Equilibrium geometries and energies.

Quantity	FCI	Weinbaum	Derived from experiment
r_e (Å)	1.112	1.097	1.081,[a] 1.090[b]
E (a.u.)	−4.94	−4.93	−5.00[b]

[a] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[b] W. Weizel, *Bandenspektren* (Akademische Verlagsgesellschaft, Leipzig, 1931), pp. 255 and 270.

IV. CONCLUSION

The transformation of valence-bond structures into molecular-orbital functions amenable to large-scale configuration-interaction treatments has been addressed. Among the various choices of MO, the internal orbitals of the VB function are the most relevant since they lead to the most compact expansion. The symmetry properties of the induced mapping prove to have some practical interest for its effective calculation, since they allow considerable reduction of the computational effort. The present development can be seen, so to speak, as the reciprocal transformation of the decomposition of electronic configurations (determinants) in terms of products of atomic functions usually assimilated to valence-bond structures.

TABLE III. Expansion coefficients of different wave functions.

Coefficient of	FCI[a]	LCI[b]	Ψ_w[c]
Ψ_1	+0.991 599	+0.992 526	+0.993 054
Ψ_2	+0.041 991	+0.042 222	+0.061 806
Ψ_3	+0.038 819	+0.038 940	+0.038 106
Ψ_4	+0.105 811	+0.106 229	+0.092 582
Ψ_5	−0.016 982	−0.017 566	0
Ψ_6	−0.017 585	0	0
Ψ_7	−0.024 873	0	0
Ψ_8	−0.005 646	0	0
Ψ_9	−0.031 892	0	0
Ψ_{10}	−0.000 428	0	0

[a] Full configuration interaction.

[b] Limited configuration interaction.

[c] Weinbaum wave function at FCI geometry with STO-6G orbitals.

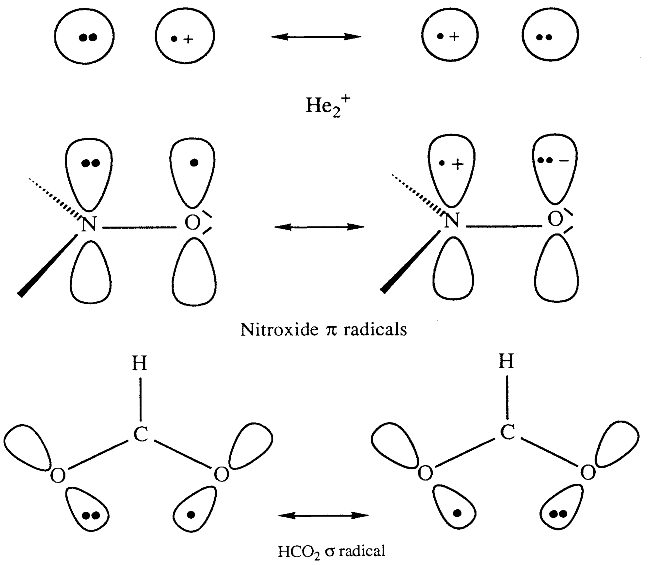

FIG. 1. Examples of 3-electron–2-center valence-bond structures.

The case of He_2^+ shows that such a transformation is feasible and worth being considered. Now, He_2^+ is much more than a case example. It is the simplest illustration of a widespread situation where three electrons share two atoms. Consider for example a homonuclear diatomic molecule with a hole in the 1*s* shell. This problem of core ionization has been studied first with the unrestricted Hartree-Fock (UHF) method [18] localizing a hole on a nucleus, then with CI methods [19], which do not exhibit the same feature but fit the experimental results in a satisfactory way as well, and give eigenfunctions of S^2. Similar situations indeed can be found in a number of free radicals of either σ or π symmetry. Among others, we would like to mention the nitroxide π radicals *RNOR'* where three π electrons are delocalized over nitrogen and oxygen. For these systems two dominant VB structures can be drawn, one covalent, another ionic (Fig. 1), and a correct balance between these structures is necessary to account for the spatial distribution of the spin density [20]. For σ radicals, a puzzling example is HCO_2, where the three σ electrons are shared between the two oxygen lone pairs (Fig. 1), and large MCSCF CI treatments are needed for a correct description of this system [21].

From a general point of view, the transformation of VB functions is of primary importance since it ensures that, at least, the subsequent MO treatment takes into account the main VB structures and this is true for the ground as for excited states, degenerate or not. Starting with intuitively important VB functions one can obtain in this way the basic orthogonal configurations to be used as a multireference space for extensive CI calculations.

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