Theoret. chim. Acta (Berl.) 3, 241—253 (1965)

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On the Validity of the Electron Pair Approximation for the Beryllium Ground State

By

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The Watson-wave function for the Be ground state is used to check the necessary conditions – derived previously – for the validity of the antisymmetrized product of strongly orthogonal geminal (APSG) approximation. The agreement between the actual properties of the numerical 1st and 2nd order density matrices and those predicted from the APSG scheme is satisfactory, whereas the predictions made in the framework of the antisymmetrized product of identical geminals (APIG) scheme are not at all realized. "Correlation adapted" orbitals and "generating geminals" are "extracted" from the given numerical wave function. The former are compared with the Edmiston-Ruedenberg localized orbitals, the latter with the Be^{++} wave functions.

An Watsons Wellenfunktion für den Be Grundzustand werden die notwendigen Bedingungen für die Gültigkeit der APSG-Näherung getestet, die früher abgeleitet worden waren (APSG = Antisymmetrisiertes Produkt stark orthogonaler Geminale). Die Übereinstimmung zwischen dem tatsächlichen Verhalten der numerischen Dichtematrizen 1. und 2. Ordnung und demjenigen, das vom Standpunkt der APSG-Näherung vorausgesagt wird, ist zufriedenstellend. Überhaupt nicht erfüllt werden allerdings die Voraussagen der APIG-Näherung (APIG = Antisymmetrisiertes Produkt identischer Geminale). Die „korrelationsadaptierten Orbitale" sowie die „erzeugenden Geminale" werden, ausgehend von der gegebenen Funktion, konstruiert, und erstere mit den Edmiston-Ruedenbergschen lokalisierten Orbitalen verglichen, letztere mit der Wellenfunktion des Be^{++}.

On se sert de la fonction numérique de Watson pour l'état fondamental de l'atome de Beryllium pour examiner les conditions nécessaires dérivées antérieurement, qui doivent être satisfaites si l'approximation APSG est valable. Dans le cadre de cette approximation la fonction d'onde peut être représentée comme produit antisymmétrique de géminales fortement orthogonales. Les prédictions faites à partir de ce modèle et les propriétés des matrices densité numériques sont en bon accord. Il n'en est pas autant pour l'approximation APIG où l'on choisit les géminales identiques plutôt que fortement orthogonales. On «extrait» les «orbitales adaptées à la corrélation» aussi bien que les «géminales génératrices» de la fonction numérique. Les premières sont comparées aux «orbitales localisées» d'Edmiston et Ruedenberg, les secondes à la fonction d'onde de Be^{++}.

Introduction

The method [*14*] of describing a quantum mechanical state of a $2n$-electron system approximatively by an Antisymmetrized Product of Strongly orthogonal Geminals (APSG) has recently been formulated in terms of natural orbitals and natural geminals [*19*]. Several theorems have been obtained which are necessarily fulfilled by the first and second order density matrices of a given state provided that the APSG approximation is an exact description and which are supposed to be almost fulfilled if the APSG scheme is a good approximation.

It is therefore straightforward to test the validity of the APSG approximation by examinating in how far 1st and 2nd order density matrices obtained from good numerical wave functions have the properties which one would expect if the APSG approximation is valid. Unfortunately the only state of a $2n$ (> 2)-electron system for which sufficiently accurate wave functions are available is the Beryllium ground state [*30, 31*]. From the wave function computed by WATSON [*30*], FOGEL [*12*] has calculated the reduced density matrices and the natural orbitals and geminals for this state*. The first order density matrix of the same state has been calculated before from the somewhat simpler BOYS wave function [*6*] by SHULL and LINDERBERG [*28*]. These authors also calculated the natural expansion of the wave function.

In this paper both those theorems which have to be valid irrespective of any approximation [*3, 9, 18, 21, 22*] and those which are necessary conditions for the validity of the APSG approximation [*19*] will be checked for the numerical Beground state density matrices. The same test can be applied to any other case.

ALLEN and SHULL [*1*] have pointed out that in omitting those terms in the WATSON function which violate the strong orthogonality condition one can construct an APSG wave function which has an overlap of .99889 with the WATSON function. McWEENY and SUTCLIFFE [*23*] have published a variation calculation for the Be-ground state using an APSG type wave function. Although their trial geminals were somewhat too simple, they concluded that the APSG scheme should be a rather good approximation for the Be-ground state. The usefulness of the APSG approximation is hence not in doubt, a more precise analysis of both its merits and its limitations is however needed.

The APSG typ wave function belongs to a special class of wave functions, which are Antisymmetrized Products of Geminals (APG), but with the additional restriction of Strong orthogonality. There is evidence [*23*] that the appreciable increase in mathematical complication on relaxing the strong orthogonality constraint is not worth the very small gain of accuracy of the wave function and the energy. Another special class of APG functions has recently received interest in quantum chemistry, namely the Antisymmetrized Products of Identical Geminals (APIG). These have sometimes been called (N-projected) BCS-functions, because of their relation to the BARDEEN-COOPER-SCHRIEFFER theory [*2, 5, 10, 24*] of superconductivity**. The reduced-density-matrix formulation for functions of this type has been given by COLEMAN [*10*]. BRATOŽ [*7*] has suggested that APIG wave functions (they contain the independent model as a special case, so do — by the way — the APSG functions) might also be useful for atomic and molecular calculations, e.g. for the Be-ground state. We shall therefore test as well if the WATSON function has the properties which are necessary conditions for the fulfilment of the APIG approximation.

Investigations of this type are also useful if one wants to eliminate the wave function from quantum mechanics and to work with density matrices only.

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* The author is indebted to Prof. P. O. LÖWDIN for making him Dr. FOGEL's thesis available.

** BRATOŽ used the name "fonction biorbitale" and COLEMAN recently proposed "antisymmetrized geminal power" or AGP, which must not be mixed up with APG as used here.

1. General properties of the reduced density matrices

General properties of the reduced density matrices have been derived by various authors [*3, 4, 8, 9, 18, 21, 22*]. If $\Phi\,(1, \ldots n)$ is a wave function of an n-electron system, than the 1st order density matrix $\gamma\,(1, 1')$ and the 2nd order density matrix $\Gamma\,(1, 2; 1', 2')$ are defined by

$$\gamma\,(1, 1') = n \int \Phi\,(1, 2 \ldots n)\, \Phi^*\,(1', 2 \ldots n) d\tau_2 \ldots d\tau_n \tag{1}$$

$$\Gamma\,(1, 2; 1', 2') = \binom{n}{2} \int \Phi\,(1, 2, 3 \ldots n)\, \Phi^*\,(1', 2', 3 \ldots n)\, d\tau_3 \ldots d\tau_n\ . \tag{2}$$

The natural spin orbitals (NSO) $\chi_i\,(1)$ and their occupation numbers ν_i as well as the natural spin geminals (NSG) $\psi_i\,(1, 2)$ and their occupation numbers μ_i are the eigenfunctions and eigenvalues of the integral operators defined by the 1st and 2nd order density matrices respectively.

$$\int \gamma\,(1, 1')\, \chi_i\,(1')\, d\tau_{1'} = \nu_i\, \chi_i\,(1) \tag{3}$$

$$\int \Gamma\,(1, 2; 1', 2')\, \psi_i\,(1', 2')\, d\tau_{1'}\, d\tau_{2'} = \mu_i\, \psi_i\,(1, 2)\ . \tag{4}$$

We are especially interested in symmetry properties, degeneracies and bounds of the eigenvalues. If we limit ourselves to the ^1S-state of a 4-electron atom, we find:

1. Both the NSO and the NSG are pure spin state functions. They can be labelled with quantum numbers s and m_s [*3, 22*].

2. The eigenvalues ν_i of the first order density matrix are evenly degenerate. To any pair of equal eigenvalues corresponds the same space orbital, multiplied by α- and by β-spin [*3, 22*].

3. The trace of the 1st order density matrix is (in Löwdin normalization [*21*]) equal to the number of electrons, *i.e.* 4. Any eigenvalue ν_i is bounded above by 1.

4. The trace of the 2nd order density matrix is (again in Löwdin normalization) equal to $\binom{n}{2}$ *i.e.* $\binom{4}{2} = 6$. Any eigenvalue is bounded above by $n/2 = 2$ [*9, 26*].

5. The second order density matrix can be decomposed in the following way into space and spin factors [*18*]

$$\begin{aligned} \Gamma\,(1, 2; 1', 2') = {} & \Gamma_s\,(r_1\, r_2 \,|\, r_1'\, r_2')\, \theta_s\,(1, 2)\, \theta_s^*\,(1', 2') + \\ & + \Gamma_t\,(r_1\, r_2 \,|\, r_1'\, r_2') \sum_{i=-1}^{+1} \theta_t^i\,(1, 2) \cdot \theta_t^{i*}\,(1', 2') \end{aligned} \tag{5}$$

where $\theta_{s,t}^i$ are the normalized two-particle spin functions

$$\begin{aligned} \theta_s\,(1, 2) &= 2^{-\frac{1}{2}} \{\alpha\,(1)\, \beta\,(2) - \beta\,(1)\, \alpha\,(2)\} \\ \theta_t^{-1} &= \beta\,(1)\, \beta\,(2) \qquad\qquad \theta_t^1 = \alpha\,(1)\, \alpha\,(2) \\ \theta_t^0 &= 2^{-\frac{1}{2}} \{\alpha\,(1)\, \beta\,(2) + \beta\,(1)\, \alpha\,(2)\}\,. \end{aligned} \tag{6}$$

The trace of the singlet density matrix Γ_s is equal to 3, the trace of the triplet density matrix Γ_t is equal to 1. Any eigenvalue of Γ corresponding to a NSG of triplet type has degeneracy divisible by 3.

6. Both NSG and NSO are adapted to the point symmetry group, *i.e.* the threedimensional rotation group. They can therefore be labelled with angular quantum numbers l and m_l. Those NSG (or NSO) which have the same l, but different m_l have the same occupation number, which has consequently degeneracy divisible by $(2\,l + 1)$.

Note that in order to derive theorems 1 and 2 it is necessary to assume that for the 4-electron state $M_s = 0$, for theorem 5 that $S = 0$ and for theorem 6 that $L = 0$. Hence they are, contrary to theorems 3 and 4 not generally valid for other than ^1S-states.

2. Special properties of the reduced density matrices in the APSG scheme

If the wave function of the 4-electron system can be written as an antisymmetrized product of strongly orthogonal normalized two-electron functions (geminals) [*14*]

$$\Phi = \mathscr{A}\, \psi_1(1,2)\, \psi_2(3,4) \tag{7}$$

$$\int \psi_1(1,2)\, \psi_2(1',2)\, d\tau_2 = 0 \tag{8}$$

then its reduced density matrices satisfy the following theorems [*19*] in addition to those outlined in section 1.

1. The natural spin orbitals can be classified into two sets, to be labelled with superscripts K and L referring to K and L-shell respectively, such that

$$\sum_i \nu_i^K = \sum_i \nu_i^L = 2 \tag{9}$$

and that *no* natural spin orbital belongs to both sets.

2. The NSO of the total wave function Φ are automatically natural spin orbitals of the generating spin geminals ψ_1 and ψ_2, and of all the natural spin geminals.

3. Exactly two natural spin geminals are of correlated type, i.e. when expanded in terms of their natural spin orbitals they have the form

$$\psi(1,2) = \sum_{i=1} c_i\, [\chi_{2i-1}(1)\, \chi_{2i}(2) - \chi_{2i}(1)\, \chi_{2i-1}(2)] \tag{10}$$

whereas all the other NSG are simple antisymmetric products of natural spin orbitals*. We call them "non-correlated".

$$\psi(1,2) = 2^{-\frac{1}{2}}\, [\chi_i(1)\, \chi_j(2) - \chi_j(1)\, \chi_i(2)]. \tag{11}$$

The two correlated NSG have the occupation numbers equal to one, the occupation numbers of the other NSG are bounded above by one.

4. Any triplet type natural spin geminal has the same occupation number as a singlet type geminal. The corresponding eigenvalue has hence degeneracy divisible by 3 + 1 = 4.

5. The two correlated natural spin geminals are (except for a unitary transformation, since they belong to the same eigenvalue) equal to the (strongly orthogonal) generating spin geminals.

6. The occupation numbers μ_{ij} of the non-correlated NSG are expressible as products of those of the NSO, belonging to *different* sets as defined in 1.

$$\mu_{ij} = \nu_i^K\, \nu_j^L\,. \tag{12}$$

Note that in this scheme the eigenvalues of the 2nd order density matrix are expressible in terms of those of the 1st order one. The fulfilment of this statement can be most easily tested.

3. Special properties of the reduced density matrices in the APIG approximation

We are here especially interested in relations between the eigenvalues of the 1st and 2nd order density matrices. These are less easily obtained than for the APSG

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* Or, if they belong to a degenerate eigenvalue, possibly linear combinations of "degenerate" antisymmetric products.

approximation. Since we shall see that the relations predicted from the APIG approximation are not at all realized by the actual density matrices of the Beryllium ground state, it is sufficient to derive these relations approximatively.

If a four electron wave function is expressible as an antisymmetric product of two identical geminals, the following theorems ought to hold. The proofs are given in the appendix. As to a formal treatment of this scheme see ref. 10.

1. There is no classification of the natural spin orbitals into two sets. Any of them belongs to the inner as well as to the outer pair.

2. The natural spin orbitals of the total wave function are also natural spin orbitals of the generating geminal and of all the natural spin geminals.

3. There are correlated NSG, *i.e.* they are of the form (10) and uncorrelated ones, *i.e.* they are simple antisymmetrized products of NSO (11). The sum of the occupation numbers of the correlated ones is equal to 2, of the uncorrelated ones to 4, the total sum being 6. The occupation number of any of the correlated NSG is bounded above by 2, of any uncorrelated one by 1. If one eigenvalue approaches the bound 2, all the other eigenvalues tend simultaneously to zero.

4. The occupation numbers of the correlated NSG may all be different, those of the non-correlated NSG have degeneracy divisible by 4.

5. The generating geminal is, in general, not equal to any of the natural spin geminals.

6. The eigenvalues μ_{ij} of the non-correlated NSG are related to the occupation numbers of the natural spin orbitals ν_i approximatively by the following relation

$$\mu_{ij} \approx a \cdot \nu_i \nu_j \tag{13}$$

where $a = \frac{1}{4}$ if both $\nu_i \ll 1$ and $\nu_j \ll 1$

$a = \frac{1}{2}$ if $\nu_i \sim 1, \nu_j \ll 1$ or vice versa

$a = 1$ if $\nu_i \sim 1, \nu_j \sim 1$.

This theorem is essentially different from the corresponding one in the APSG scheme. Note that here *all* possible products $a \cdot \nu_i \nu_j$ should appear as μ_{ij}.

4. Analysis of the Beryllium ground state

The highest eigenvalues of the 1st and 2nd order density matrices of the Be-ground state are collected in Tab. 1 and 2, together with their degeneracy and their label. The twofold degeneracy as stated by theorem 2 of section 1 obtains, so does theorem 6.

If one assumes that the inner pair of the Be-atom resembles to the Be^{++}-ion in its ground state [*17*], at least as much that the corresponding eigenvalues of the respective density matrices are of the same order of magnitude, then one can make a first guess which of the orbitals of the Be-atom probably belong to the inner and which to the outer shell. The division of the ν_i into two sets is then achieved by trying to satisfy theorem 1 of section 2. In fact one finds

$$\Sigma \nu^K = 1.99997 \qquad \Sigma \nu^L = 2.00002$$

for the Watson wave function and

$$\Sigma \nu^K = 2.00004 \qquad \Sigma \nu^L = 1.99996$$

for the Boys wave function.

Table 1. *The first eigenvalues of the* 1st *order density matrix*

Nr.	degeneracy	shell	label	ν (Watson)	ν (Boys)	ν (Be^{2+})
1, 2	2	K	$1s$	.998306	.998877	.99838
3, 4	2	L	$2s$	.918574	.912102	
5 – 10	6	L	$2p$	.027034	.029299	
11, 12	2	K	$3s$	.000721	.000571	.000633
13 – 18	6	K	$3p$	.000281	.000182	.000297
19 – 28	10	L	$3d$	.000066		
29 – 30	2	K	$4s$	.000034		
31 – 32	2	K	$5s$	.000009		.000009
33 – 42	10	K	$4d$	.000008		.000009
43 – 48	6	K	$4p$	.000008		.000007
49 – 50	2	K	$6s$	.000007		
51 – 60	10	K	$5d$	.000001		
Σ				3.99999	3.99999	1.99996

This division into two sets is checked by forming the possible products of the ν_i and comparing them with the eigenvalues of the 2nd order density matrix (Tab. 2). The agreement between the actual eigenvalues and those predicted by the APSG approximation is excellent, and only those products are found which are in agreement with theorem 6 of section 2.

That theorems 5 and 6 of section 1 are fulfilled, is not at all trivial. When Fogel did his calculations no general theorems on the symmetry properties of natural spin geminals were known, and he was surprised to find the NSG symmetry adapted and pure spin state functions. According to theorem 5 of section 1 the NSG 4 – 6 must have the same occupation numbers. The actual values are .917100, .916971, .916971. The small differences are a measure of the accuracy of the whole calculation; in Tab. 2 the mean value .91701 is given, it is, however, equal to the occupation number of geminal 3. This coincidence is not expected for general wave functions, but for those of APSG-type (theorem 4 of section 2).

We come back later to theorems 3 and 5 of section 2 and state that so far the prediction made for the APSG scheme are well fulfilled. On the other hand the theorems which should be expected if the state could be described by an APIG wave function are not at all verified.

Table 2. *The first eigenvalues of the* 2nd *order density matrix*

Nr.	degeneracy	label	eigenvalue	assignmentby APSG	predicted by APSG
1	1	^1S	1.00085	generating	1.00000
2	1	^1S	.99893		
3	1	^1S	.91701	$1s \times 2s$	.91702
4 – 6	3	^3S	.91700		
7 – 9	3	^1P	.02700	$1s \times 2p$	.02699
10 – 18	9	^3P	.02700		
19	1	^1S	.00069	$2s \times 3s$	.00066
20 – 22	3	^3S	.00069		
23 – 25	3	^1P	.00026	$2s \times 3p$	.00026
26 – 34	9	^3P	.00026		
35 – 39	5	^1D	.000065	$1s \times 3d$	.000066
40 – 54	15	^3D	.000065		

This is clearly seen if we compare the eigenvalues of the second order density matrices calculated from those of the v_i by use of eq. (13) with the actual ones. Instead of 12 NSG with occupation number $\sim .027$ as predicted from the APSG type wave function we should *e.g.* expect 24 NSG with occupation numbers $\sim .013$.

The only fact which is better predicted from the APIG scheme is that the occupation numbers of the first two NSG may be different and are not bounded by one. It is a serious drawback of the APSG approximation in that it cannot account for a geminal occupation number bigger than one, which evidently occurs, although the deviation from unity is rather small.

5. The correlation adapted orbitals

It has been recognized quite early that for two electron systems the first natural orbitals are very close to the HARTREE-FOCK-orbitals [*29*]. The question whether or not the two types of orbitals should be identical can now be regarded as settled in the sense that they are essentially different [*16*, *25*]. That they are not very different is demonstrated by the fact that for atoms their $1/Z$-expansions coincide up to the $1/Z$ term and their expectation values with respect to the Hamiltonian even up to the $1/Z^3$-term [*25*].

For closed-shell states with more than two electrons one finds essentially the same behaviour [*13*, *20*]. The corresponding theorem cannot, however, be quoted in the simple form that the "strongly occupied" natural orbitals *i.e.* those which have occupation numbers ≈ 1 coincide with the HARTREE-FOCK orbitals up to linear terms in a perturbation parameter. By HARTREE-FOCK-*orbitals* we mean in general those solutions of the HARTREE-FOCK equations which diagonalize the HARTREE-FOCK operator, although any orthogonal linear combinations of them satisfy the HARTREE-FOCK equations as well. The integro-differential equations satisfied by the strongly occupied natural orbitals — which differ from the HARTREE-FOCK equations by a small correlation potential [*16*, *17*, *19*] are no longer invariant with respect to unitary transformations. The presence of the (non-local) correlation potential removes (at least partially) the arbitrariness in the choice of the HARTREE-FOCK orbitals and allows us to define *correlation adapted* orbitals which are linear combinations of the canonical HARTREE-FOCK orbitals. These correlation adapted orbitals are then slightly modified by the correlation potential to yield the strongly occupied natural orbitals.

The WATSON wave function has been built up from the HARTREE-FOCK wave function and "excited configurations". Singly excited configurations were not incorporated since they do not much effect the energy, although it is not justified to neglect them completely. Due to the neglect of singly excited configurations the strongly occupied natural orbitals obtained from this particular wave function span the same vector space as the HARTREE-FOCK orbitals. The effect of the correlation potential is hence just to rotate the coordinate system of this space and to specify correlation adapted linear combinations of the HARTREE-FOCK orbitals. If we call the canonical HARTREE-FOCK orbitals $1s_{HF}$ and $2s_{HF}$ we obtain from the WATSON wave function the correlation adapted orbitals

$$1s_{ca} = 0.999898 \cdot 1s_{HF} - 0.014259 \cdot 2s_{HF},$$

$$2s_{ca} = 0.014259 \cdot 1s_{HF} + 0.999898 \cdot 2s_{HF}.$$

It has been suggested that the correlation adapted orbitals should be close to the "localized orbitals" as defined by EDMISTON and RUEDENBERG [*11*]. Using their localization criterion we obtain the EDMISTON-RUEDENBERG orbitals for the Be ground state:

$$1s_{ER} = 0.993849 \cdot 1s_{HF} - 0.110741 \cdot 2s_{HF},$$

$$2s_{ER} = 0.110741 \cdot 1s_{HF} + 0.993849 \cdot 2s_{HF}.$$

It is somewhat surprising that the correlation adapted orbitals are so much closer to the canonical HARTREE-FOCK orbitals than to the EDMISTON-RUEDENBERG localized orbitals. This may in part be due to the fact that the WATSON wave function contains arbitrary assumptions which anticipate this result. It should therefore be checked on more refined wave functions. On the other hand KLESSINGER's [*15*] calculations on water support the evidence that, in what concerns $1s$ and $2s$ orbitals, the canonical HARTREE-FOCK solutions are closer to the correlation adapted orbitals than the RUEDENBERG-EDMISTON localized orbitals. This is probably connected with the very big difference in orbital energy between $1s$ and $2s$ and with the almost degeneracy between $2s$ and $2p$ orbitals. For more "normal" cases the correlation adapted orbitals may nevertheless be localized rather than canonical HARTREE-FOCK orbitals.

6. The natural form of the natural geminals

Since in the APSG approximation the natural spin orbitals of the total wave function are automatically natural spin orbitals of the natural spin geminals it is straightforward to expand the natural geminals in terms of the natural orbitals. These expansions should then have the simple form

$$\psi = \sum_i c_i \, \varphi_i(1) \, \varphi_i^*(2) \, \theta_s(1,2) \tag{14}$$

(where the φ_i are the spinless natural orbitals) for the first two natural spin geminals and

$$\psi_{ij} = \frac{1}{\sqrt{2}} \left[\varphi_i(1)\,\varphi_j(2) \pm \varphi_j(1)\,\varphi_i(2)\right] \begin{cases} \theta_s(1,2) \\ \theta_t^{-1,0,+1}(1,2) \end{cases} \tag{15}$$

for all the other natural geminals. Expansions of this type are in fact obtained within the limits of accuracy in agreement with theorem 2 of section 2. Of special

Table 3. *Natural expansion of the first two natural spin geminals and the "generating" geminals*

χ_i	degeneracy	$c_i(1)$	$c_i(2)$	$2^{-\frac{1}{2}}[c_i(1)+c_i(2)]$	$2^{-\frac{1}{2}}[c_i(1)-c_i(2)]$	Be^{2+}
$1s$	1	.7045	.7086	.9992	.0029	.9992
$2s$	1	.6794	−.6760	.0024	.9185	—
$3s$	1	−.0184	−.0187	−.0262	—	−.0252
$4s$	1	.0038	.0038	.0054	—	−.0030
$5s$	1	−.0010	.0010	−.0014	—	−.0007
$2p$	3	−.1171	.1153	−.0013	.2699	—
$3p$	3	−.0114	−.0114	−.0161	—	−.0173
$4p$	3	−.0018	−.0017	−.0025	—	−.0028
$4d$	5	−.0058	.0058	—	.0082	—
$5d$	5	−.0019	−.0019	−.0027	—	−.0030

interest are the first two natural spin geminals. Their expansion coefficients c_i are tabulated in Tab. 3*, together with the corresponding coefficients of both the normalized sum and difference of ψ_1 and ψ_2. As will be demonstrated in the following section the latter are, in so far as the APSG approximation is valid, to be identified with the generating spin geminals of the wave function.

7. The generating geminals

It has been stated [*19*] that if the APSG approximation is valid, the generating spin geminals are automatically natural spin geminals. It would be more correct to say that the vector space spanned by the generating geminals of a $2n$-electron system is identical with the one spanned by the first n natural spin geminals (which all have the occupation number 1) — or, if more than n natural spin geminals have the occupation number 1, is contained in the vector space spanned by the natural spin geminals with occupation number 1. The second order density matrix is of course invariant with respect to a unitary transformation among spin geminals with the same occupation number.

We now ask, how will this theorem be changed, if the actual wave function deviates slightly from an APSG typ one. The first n natural spin geminals will have occupation numbers slightly different from unity and the density matrix will no longer be invariant with respect to a unitary transformation among the first n natural spin geminals. Which linear combinations of the generating geminals will then be adapted to the perturbation ? This problem will be discussed in detail elsewhere. We limit ourselves here to the special case of a closed shell state of a four-electron system.

Suppose the actual wave function can be written in the form

$$\Phi\,(1,2,3,4) = \mathscr{A}\,\tilde{\psi}_1\,(1,2)\,\tilde{\psi}_2\,(3,4) + \omega\,(1,2,3,4) \qquad (16)$$
$$\|\omega\| \ll 1$$

where ω is a very small correction which represents the deviation from the APSG scheme. The generating geminals can be written:

$$\begin{aligned} \tilde{\psi}_1\,(1,2) &= [c_1\,\varphi_1\,(1)\,\varphi_1\,(2) + \sigma_1\,(1,2)]\;\theta_s\,(1,2) \qquad (17)\\ \tilde{\psi}_2\,(1,2) &= [c_2\,\varphi_2\,(1)\,\varphi_2\,(2) + \sigma_2\,(1,2)]\;\theta_s\,(1,2)\\ &\|\sigma_1\| \ll 1\\ &\|\sigma_2\| \ll 1 \end{aligned}$$

where φ_1 and φ_2 are the strongly occupied (spinfree) natural orbitals, and σ stands for the contribution of the weakly occupied natural orbitals.

Then

$$\begin{aligned} \Phi\,(1,2,3,4) = {} & 6^{-\frac{1}{2}}\,[\tilde{\psi}_1\,(1,2)\,\tilde{\psi}_2\,(3,4) + \tilde{\psi}_2\,(1,2)\,\tilde{\psi}_1\,(3,4)] + \\ & + c_1\,c_2\,6^{-\frac{1}{2}}\,[\tilde{\psi}_3\,(1,2)\,\tilde{\psi}_3\,(3,4) + \tilde{\psi}_4\,(1,2)\,\tilde{\psi}_6\,(3,4) + \qquad (18)\\ & + \tilde{\psi}_5\,(1,2)\,\tilde{\psi}_5\,(3,4) + \tilde{\psi}_6\,(1,2)\,\tilde{\psi}_4\,(3,4)] + \\ & + \text{terms containing } \sigma_1 \text{ and/or } \sigma_2 + \omega\,(1,2,3,4) \end{aligned}$$

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* Off-diagonal terms in the expansion are not completely removed by the transformation to the natural basis. They are however small and may even result from numerical inaccuracy. The most appreciable ones refer to configurations $1s\,(1)\;2s\,(2)$.

where

$$\tilde{\psi}_3(1, 2) = 2^{-\frac{1}{2}} [\varphi_1(1)\, \varphi_2(2) + \varphi_2(1)\, \varphi_1(2)]\; \theta_s(1, 2) \tag{19}$$

$$\tilde{\psi}_{4, 5, 6}(1, 2) = 2^{-\frac{1}{2}} [\varphi_1(1)\, \varphi_2(2) - \varphi_2(1)\, \varphi_1(2)]\; \theta_t^{-1,0,1}(1, 2)\,.$$

The natural spin geminals of Φ are called ψ_i and their occupation numbers μ_i. We can then expand Φ using the CARLSON-KELLER theorem [*8*, *9*].

$$\Phi(1, 2, 3, 4) = 6^{-\frac{1}{2}} \sum_i a_i\, \psi_i(1, 2)\, \psi_i'(3, 4) \tag{20}$$

$$|\, a_i\, |^2 = \mu_i$$

where ψ_i and ψ_i' are NSG belonging to the same eigenvalue μ_i. If μ_i is not degenerate they are necessarily identical. Suppose that in our wave function (16) the correction ω vanishes, then the $\tilde{\psi}_i$ are essentially equal to the strongly occupied ψ_i [*19*], further $|\, a_1\, | = 1$, $a_i = c_1 \cdot c_2$, $i = 3, 4, 5, 6$. Since then $|\, a_1\, | = |\, a_2\, |$ we have the choice to write the first two terms of the CARLSON-KELLER expansion in either of the following ways

$$\psi_1 = \tilde{\psi}_1;\; \psi_1' = \tilde{\psi}_2;\; \psi_2 = \tilde{\psi}_2;\; \psi_2' = \tilde{\psi}_1;\; a_1 = a_2, \tag{21}$$

$$\psi_1 = \psi_1' = 2^{-\frac{1}{2}} [\tilde{\psi}_1 + \tilde{\psi}_2];\; \psi_2 = \psi_2' = 2^{-\frac{1}{2}} [\tilde{\psi}_1 - \tilde{\psi}_2];\; a_1 = -a_2. \tag{22}$$

If we now add a very small "perturbation" ω continuously then the a_i are slightly modified as well as the vector spaces spanned by ψ_i belonging to the same μ_i. The degeneracy between μ_3 to μ_6 will not be removed because it is due to symmetry, μ_1 and μ_2 may however be affected differently. Of the two alternatives (21) and (22) only the second one is "adapted" to this kind of "perturbation". In other words, even if there is only a very slight deviation from the APSG scheme, the "correlated" natural spin geminals will no longer be (approximatively) equal to the generating spin geminals, but rather to their normalized sum and difference.

Note that in this demonstration no assumptions were made as to the nature of ω, except that it removes the degeneracy among the first two eigenvalues.

In the Be ground state $\mu_1 > 1$ and $\mu_2 < 1$, their mean value is equal to 1 within the limits of error. This is a typical case of "removal of degeneracy".

The natural expansion of the generating geminals "extracted" from the wave function is given in Tab. 3. One sees definitely which NSO belongs to the inner and which to the outer pair, in agreement with the results of section 4. The expansion coefficients of the "inner" pair may be compared with those of the natural expansion of Be^{++} [*17*].

It is interesting to check *inhowfar* the generating geminals extracted from the Watson wave function are strongly orthogonal. As a measure of the deviation from strong orthogonality one may define

$$N = \left\| \int \psi_1(1, 2)\, \psi_2(1, 2)\, d\tau_2 \right\|. \tag{23}$$

We obtain $N = 0.007$, this means, the deviation from strong orthogonality is less then 1%. One may, of course, "purify" the geminals by omitting terms which violate the strong orthogonality. On the other hand the fact that an orbital strongly occupied by one geminal may be simultaneously, but weakly occupied by the other geminal, may be a hint how to refine the theory.

Conclusions

The fact that the results of this paper are in favour of the APSG approximation is not much astonishing since ALLEN and SHULL have shown before in a much simpler way that the WATSON wave function for the Beryllium ground state can be approximated rather well by an APSG wave function. The method used in this paper to test the validity of the APSG approximation, is, however, more generally applicable and furnishes some interesting extra results. It is possible to calculate the correlation-adapted-orbitals from a given wave function and to "extract" the generating spin geminals from it. One might, as SINANOGLU [*27*] would say, "purify" the original wave function from "spurious" terms which violate the APSG conditions, by constructing a new wave function from the extracted generating geminals. Whether or not one might thus get a better energy, *i.e.* whether or not the terms violating the APSG conditions are "spurious" is questionable. The fact that a given numerical wave function contains such terms does not necessarily mean that they have a physical meaning.

The results obtained here have to be checked on more refined wave functions of the Be ground state and on other systems. Since the electron pair approximation as represented by the APSG scheme is relatively simple and quite visualizable, it is important to know how good it is and what it implies.

It seems to be quite clear that the APIG scheme is not a good approximation for the Be ground state — although it is necessarily better than the HARTREE-FOCK approximation —, because it implies wrong relation between the first and second order density matrices. Whether it is superior to the APSG scheme for other atomic or molecular systems is an open question.

The APSG scheme cannot account for geminal occupation numbers bigger than one, the APIG scheme however can. If eigenvalues bigger than one are relevant in quantum chemistry, then it seems straight-forward to work with a generalized electron pair scheme which contains both APSG and APIG as special cases [*19*].

One may recall that the WATSON wave function has also been used by SINANOGLU [*27*], namely to test some implications of his limited cluster expansion method. That the results were positive is not surprising, if one considers that the APSG approximation is obviously a good approximation and that the relations between this scheme and the limited cluster expansion methods are closer than is often believed.

Appendix

Relation between the eigenvalues of the first and second-order density matrices in the antisymmetric product of identical geminals (APIG-) approximation

In the framework of this approximation the wave function for a 4-electron system can be written

$$\Phi = N' \mathscr{A} \psi(1,2) \psi(3,4) \tag{A 1}$$

The generating geminal ψ can be expanded in terms of its natural spin orbitals χ_i which are as well the natural spin orbitals of the total wave function. It has then the form

$$\psi(1,2) = \sum_{i=1}^{s} a_i [\chi_{2i-1}(1)\chi_{2i}(2) - \chi_{2i}(1)\chi_{2i-1}(2)] \; . \qquad \text{A (2)}$$

Inserting this expansion into (A 1) we obtain

$$\Phi = N \sum_{i<j} a_i a_j \det [\chi_{2i-1}(1)\chi_{2i}(2)\chi_{2j-1}(3)\chi_{2j}(4)] \; . \tag{A 3}$$

The occupation number of χ_i in the 1st order density matrix of the total wave function is, as usual, called ν_i. We define further the occupation number of χ_i in the 1st order density matrix associated with the geminal ψ.

$$\tilde{\nu}_{2i} = 2 \mid a_i \mid^2 = \tilde{\nu}_{2i-1} \tag{A 4}$$

The normalization integral is then given by

$$N = (\sum_{i<j} \mid a_i \mid^2 \mid a_j \mid^2)^{-\frac{1}{2}} = 4\,(2 - \sum_i \tilde{\nu}_i^2)^{-\frac{1}{2}}\,. \tag{A 5}$$

In order for the wave function Φ not to vanish the rank (summation limit) s must be at least equal to 4. If $s = 4$, Φ represents one slater determinant. We obtain the bounds

$$0 \leq \tilde{\nu}_i \leq \tfrac{1}{2} \tag{A 6}$$

$$0 \leq \sum_i \tilde{\nu}_i^2 \leq 1 \tag{A 7}$$

$$\sqrt{8} \leq N \leq 4\ . \tag{A 8}$$

$N = 4$ corresponds to the HARTREE-FOCK case, where Φ is a single determinant, $N = 8$ corresponds to COLEMAN's "extreme type functions", where $s \gg 4$ and all a_i are equal. For closed shell atomic and molecular states we can assume $N \sim 4$. If we calculate the 1st order density matrix of Φ using (A 3) we obtain the ν_i in terms of the $\tilde{\nu}_i$

$$\nu_i = \tfrac{1}{4} N^2 (1 - \tilde{\nu}_i)\, \tilde{\nu}_i\ . \tag{A 9}$$

If we know N we can solve this equation for $\tilde{\nu}_i$

$$\tilde{\nu}_i = \tfrac{1}{2} - \tfrac{1}{2}\sqrt{1 - 16\,\nu_i N^{-2}} = \tfrac{1}{2}\,(1 - 1 + 8\,\nu_i N^{-2} - 2\,\nu^2 N^{-4} + \ldots) \tag{A 10}$$

$$16\,\nu_i N^{-2} \leq 1$$

Of the two roots of the 2nd order equation only the one with the minus-sign is valid, by virtue of (A 6).

For weakly occupied natural spin orbitals $\nu_i \ll 1$, and we get

$$\tilde{\nu}_i = 4\,\nu_i N^{-2} - \nu^2 N^{-4} + \ldots \tag{A 11}$$

If we assume that the state is of closed shell type and therefore $N \approx 4$, we get the approximate relation for weakly occupied orbitals

$$\tilde{\nu}_i \approx \tfrac{1}{4}\nu_i \text{ if } \nu_i \ll 1\ . \tag{A 12}$$

For strongly occupied natural spin orbitals, however, $\nu_i \approx 1$ and $\tilde{\nu}_i \approx \frac{1}{2}$, this means

$$\tilde{\nu}_i \approx \tfrac{1}{2}\nu_i \text{ if } \nu_i \sim 1\ . \tag{A 13}$$

The eigenvalues of the second order density matrix can be expressed in terms of the $\tilde{\nu}_i$ and by virtue of (A 12) and (A 13) in terms of the ν_i.

The 2nd order density matrix has s "correlated" eigenfunctions, *i.e.* natural spin geminals of the form (A 2), any of the corresponding eigenvalues is bounded above by 2, their sum is bounded by 2 as well. The bound 2 is approached by one occupation number, only if simultaneously all the other eigenvalues approach zero. In the limiting case of the independent-particle model two eigenvalues become equal to 1, and the occupation numbers of the other correlated geminals vanish.

The other $2s\,(s-1)$ natural spin geminals are simple antisymmetrized products of natural spin orbitals and their occupation numbers are given by

$$\mu_{ij} = \tfrac{1}{4} N^2\, \tilde{\nu}_i\, \tilde{\nu}_j\ . \tag{A 14}$$

Because of the even degeneracy of the $\tilde{\nu}_i$, any μ_{ij} has a degeneracy divisible by 4 — just as one finds for the APSG approximation.

By virtue of (A 12) and (A 13) and putting $N^2 \sim 16$ we can now predict that if the APIG approximation is valid for a 4-electron closed shell state the eigenvalues of the non-correlated natural spin geminals μ_{ij} should be related to the occupation numbers of the natural spin orbitals by one of the approximate formulas

$$\mu_{ij} \approx \tfrac{1}{4}\nu_i \nu_j \tag{A 15}$$

$$\mu_{ij} \approx \tfrac{1}{2}\nu_i \nu_j \tag{A 16}$$

$$\mu_{ij} \approx \nu_i \nu_j \tag{A 17}$$

where (A 15) holds if both χ_i and χ_j are weakly occupied, (A 16) if either χ_i or χ_j is weakly and the other strongly occupied and (A 17) if both χ_i and χ_j are strongly occupied.

One may mention that for COLEMAN's extreme type wave functions [*9*, *10*] (A 13) and (A 16) hold generally, but the Be ground state is anyway far from being describable by a wave function of that type.

Acknowledgements. The idea to test the APSG approximation on FOGEL's numerical density matrices originated from discussions with Dr. VEDENE H. SMITH in the "Quantum Chemistry Group" Uppsala in Summer 1964.

The present article is essentially identical with a talk which the author was kindly invited to give at the "Laboratoire de Chimie Quantique" in Paris in December 1964.

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(Received April 28, 1965)