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Preliminary Results on the Density Matrix Structure of the First Beryllium ^1S Excited State*

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The 1- and 2-matrix analyses of a trial configuration interaction wave function, constructed over an orthonormal basis set, for the first beryllium ^1S excited state are presented. The results are compared with those of the ground state (also reported) to clarify the changes undergone by the natural orbitals and geminals. The changes in the nature of the electron correlation effect are also examined.

Die Analyse der Dichtematrizen 1. und 2. Ordnung eines CI-Ansatzes mit orthonormierter Einteilchen-Basis wird für den ersten angeregten ^1S Zustand des Berylliums dargestellt. Die Resultate werden mit denen des ebenfalls angegebenen Grundzustands verglichen, um die Veränderungen, die sich für die natürlichen Orbitale und Geminale ergeben, zu verfolgen. Die Änderungen bezüglich der Korrelation werden gleichfalls untersucht.

On présente pour le premier état exité de beryllium ^1S l'analyse de matrices de densité de 1. et 2. ordre pour une évaluation IC sur une base orthonormée. Les résultats sont comparés avec celui de l'état fondamental (aussi donné) en vue de montrer les changements des orbitaux naturels et des geminaux. Les changements des la nature de la correlation électronique sont aussi examinés.

Introduction

In obtaining wave functions by means of the limited configuration interaction (CI) technique one is faced with the two-fold problem of chosing (a) orbital basis functions from which to build the wave function, and (b) configurations to be included in the CI expansion. While the inclusion of an extended set of basis functions and configurations is greatly desirable the attending methematical complications impose practical limitations on such an endeavor with the result that one's ingenuity to find a suitable compromise is seriously taxed. It is with the hope of clarifying this seemingly monumental task that the density matrix [1] study of a CI wave function is often pursed. The density matrix of order 1 and 2 (hereafter referred to as the 1- and 2-matrix, respectively) of some small fermion systems have been discussed [2]. However relatively little is known about excited state CI wave functions and their density matrix structure. Rothenberg and Davidson [3] reported the 1-matrix analysis of several hydrogen molecule excited states and concluded that electron correlation plays a decreasing role in these states. More recently, Brown and Shull [4] (hereafter referred to as BS) reported the 1-matrix eigenvalues of the first LiH excited state at various internuclear distances. This paper presents some preliminary results on the first (as far as this author is aware) 1- and 2-matrix study of the excited state of a 4-electron system. We also discuss in some detail the steps employed in generating the excited state wave function. Whenever possible the results will be compared with those of LiH.

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Theory and Method

In the formalism of second quantization [5] the reduced density matrix of order p is simply the expectation value of the p-particle density operator, $\boldsymbol{\Gamma}_p$ expressed in terms of local creation and annihilation operators, designated respectively by $\psi^+(1')$ and $\psi(1)$.

$$\begin{aligned}\Gamma^{(p)}(1'2'\ldots p'|12\ldots p) &= \langle\Psi|\boldsymbol{\Gamma}_p|\Psi\rangle \\ &= (p!)^{-1}\langle\Psi|\psi^+(1')\psi^+(2')\ldots\psi^+(p')\psi(p)\psi(p-1)\ldots\psi(1)|\Psi\rangle.\end{aligned} \tag{1}$$

The N-particle wave function is assumed normalized to unity so that the trace of the matrix is equal to the binomial factor $\binom{N}{p}$. For a CI wave function constructed out of Slater determinants, D_K, of orthonormal orbitals, i. e., $\Psi=\sum_K C_K D_K$ where the C_K's are variational coefficients, the pth-order matrix expressed by [Eq. (1) reduces to the form [6]

$$\Gamma^{(p)}(x'|x)=\sum_{ij}\Phi_i^*(x')\Delta_{ij}\Phi_j(x) \tag{2}$$

where the collective index $1'2'\ldots p'$ has been represented by the variable x' for brevity. The Φ_i's are normalized p-particle Slater determinants and $\Delta=\boldsymbol{C}\boldsymbol{C}^+$. Diagonalization of Eq. (2) transforms the Φ_i's into the natural p-states, P_i, with occupation numbers q_i.

$$\Gamma^{(p)}(x'|x)=\sum_i q_i P_i^*(x')P_i(x). \tag{3}$$

For $p=1$ or 2, which are the cases of common interest, the natural states, usually represented by χ_i and g_i, are known as natural orbitals (NO) and natural geminals (NG) or, if spin is included, natural spin orbital (NSO) and natural spin geminal (NSG).

The basis functions used in this study were formed from a linear combination of Slater-type orbitals (STO), S_{jl}

$$R_{nl}(r)=\sum_j S_{jl}a_{jln} \tag{4}$$

where $R_{nl}(r)$ is the radial part of the basis orbitals with the usual quantum numbers as indices.

The Be problem is relatively simple because previous studies [7, 8] have shown good STO parameters and configurations for at least the Be ground state. Since the idea is to generate a compromise CI wave function that is equally good for describing the ground and excited state, we began by considering our 95 CI beryllium ground state function [6] which is a subset of Bunge's 180 CI [8]. Both functions were constructed with an orbital basis set of 7*s*, 7*p*, and 4*d* which were formed in turn from an STO set of 9*s*, 7*p*, and 5*d*. The initial CI calculation gave a ground state energy of -14.663552 a. u. accounting for about 96 per cent of the correlation energy [9] but the first ^1S excited state energy was rather poor, i. e., -14.296646 a. u., in contrast to the non-relativistic experimental energy of -14.41832 a. u. [10]. For a start we investigated the space spanned by the ground state-adapted STO basis while temporarily keeping the original 95 configurations. The NO iterations were employed to allow the 1-matrix to show us initially how the charge distribution looks like in the excited state. Such iterations on the excited state (second root of the secular equation) clearly increases the ground state energy while initially improving that of the excited state. Even the latter ceases at some stage (the energy may even worsen) and it is then necessary to (a) optimize some STO parameters, and (b) change and/or augment the configurations. Past experience in ground state CI calculations indicates that (b) is a cheaper and more effective way of reducing the total energy. However in this case, (a) may be done just as easily, if not more so, because only a few parameters play critical roles and need to be optimized (see below).

Several exploratory attempts to generate a reasonably good compromise wave function with the above procedure and set-up, coupled with trial changes in no more than four non-linear STO parameters brought the following considerations into focus: (1) Examination of the NO's during the first stages of the iteration revealed the synthesis of a new orbital presumably to describe the excited electron. The form of the wave function indicated that the excitation is described by $\chi_1^2\chi_2^2 \rightarrow \chi_1^2\chi_2\chi_3$ where all χ's are s-type NO's and χ_3 is the new orbital while χ_2 and χ_3 are very close to the Hartree-Fock basis orbitals. A plot of χ_3 showed a maximum radial probability distribution extending farther away from the nucleus than either χ_1 or χ_2. The goodness of the excited state function appeared to be greatly dependent on how well some STO parameters are chosen such that χ_3 is localized at the correct region of space. These few nonlinear STO parameters which principally determine the shape of χ_3 are referred to herein as the critical parameters. (2) The excited state energy could not be improved much below -14.360 a. u. if one persists with the 95 configurations which, we may recall, are predominantly ground state-adapted. A concerted effort for choosing the critical parameters must also be undertaken. Moreover, the density matrix analysis of these exploratory wave functions pointed to the relative ineffectiveness of many *p*- and *d*-type orbital basis.

In view of result (2) it was deemed advisable to restart with a full CI over a smaller orbital basis set, i. e., 4*s*, 2*p* and 1*d*, but conditionally keeping the same large STO basis set. The idea is to perform a computerized optimization search for the critical parameters and then augment the basis with orbitals that have proved useful in ground state calculations. A full CI is of course the most logical starting point in a non-linear parameter optimization search when one has only a vague notion as to which configurations are important to the state under consideration. The function obtained at the termination of the optimization procedure indicated that a number of configuration types, notably triple and quadruple excitations (with respect to the "ground state" configuration $s_1^2s_2^2$) such as sp^2d, p^2d^2, p^4, $p_x^3p_y (x \neq y)$, etc. may be discarded without any significant loss of accuracy.

In the next section we report the results obtained from a trial 74 CI function constructed over an orbital basis of 6*s*, 4*p*, and 1*d*. This wave function will serve as the prototype for the final, and hopefully much improved, function. The results, although preliminary in nature, reflect what we believe to be the essential features of the density matrix structure of the first Be ^1S excited state and clarify the changes undergone by the NO's and the NG's in going from the ground to the excited state. The results also lead to additional questions that must be resolved in the ultimate characterization of the excited state.

Results and Discussion

The CI *Wavefunction*

The wave function was generated with a partly optimized STO basis whose non-linear parameters are shown in Table 1. We discarded many unimportant configurations from the full CI mentioned earlier, augmented the orbital basis with two *s* and two *p* giving rise to the present 6*s*, 4*p*, and 1*d* basis, and performed a limited search of configurations. We report here (Table 2) the functions associated

Table 1. *Non-linear* STO *parameters*[a]

j	n_j	Z_{j1}	Z_{j2}	Z_{j3}
1	0	6.00000	9.00000	12.00000
2	0	0.93710	1.30920	2.00000
3	1	5.99931	8.99994	12.00000
4	1	1.07320	1.50970	2.00000
5	2	5.99701	8.90002	12.00000
6	2	0.48153	1.50000	
7	3	6.00000	9.00000	
8	3	0.80300		
9	4	6.00000		

[a] The STO orbital is of the form: $S_{jl}(r) = N_{jl} r^{(n_j+l)} \exp(-rZ_{jl})$.

Table 2. *Ground and excited state wave functions of* Be

Energy (a. u.) K	Configuration[a, b]					Ground state (I) −14.6542837 Coefficient	Excited state (II) −14.4003881
1	01	01	02	03		0.0027117712	0.9765059533
2	01	01	11	11		−0.2657444409	0.1456055488
3	01	01	03	03		−0.0112654468	−0.1121047197
4	01	01	03	05		−0.0130273203	−0.0541203884
5	01	01	02	05		0.0014516116	0.0472608666
6	01	01	03	04		0.0109911739	0.0456622346
7	01	01	02	04		−0.0012902487	−0.0400702666
8	01	01	02	02		0.9571833139	0.0350098875
9	02	03	12	12		−0.0000782248	−0.0288636824
10	02	03	04	04		0.0000010735	−0.0238864856
11	01	02	02	03		0.0006669422	0.0183589316
12	01	01	13	13		−0.0223683542	−0.0155966332
13	02	03	11	12	(1)	−0.0000116966	−0.0088530414
14	01	01	12	13		−0.0098790781	−0.0077336043
15	02	02	03	04		0.0022553461	0.0074151784
16	01	03	11	11		0.0005332808	0.0073185816
17	01	03	11	12	(1)	0.0005400665	0.0064657389
18	01	03	04	04		−0.0002062941	−0.0063195218
19	02	03	14	14		−0.0000139763	−0.0053711157
20	02	03	11	12	(2)	0.0000065136	−0.0052258046
21	01	03	11	12	(2)	−0.0001862198	−0.0049422846
22	01	01	21	21		−0.0166471737	−0.0045575929
23	01	01	11	13		0.0924327518	−0.0044828054
24	01	01	11	12		0.0380008921	−0.0042435434
25	11	11	12	12	(1)	−0.0071745603	0.0039263495

Table 2. (continued)

Energy (a. u.)	Configuration[a,b]	Ground state (I)	Excited state (II)
		−14.6542837	−14.4003881
K		Coefficient	
26	01 03 12 12	−0.0001514461	−0.0037407931
27	04 04 11 11	0.0066145129	−0.0036050250
28	01 02 03 04 (1)	0.0010422870	0.0035456378
29	03 03 12 12	0.0003300210	0.0033076958
30	01 02 03 04 (2)	−0.0009766923	−0.0032871569
31	01 02 11 11	0.0012285933	0.0031852790
32	01 02 03 03	−0.0003835479	−0.0029704538
33	02 03 11 11	−0.0001868979	−0.0027449290
34	03 03 04 04	0.0002584256	0.0026972551
35	01 02 03 05 (1)	−0.0005343349	−0.0021326403
36	01 02 04 04	−0.0075489295	0.0015702668
37	02 04 11 11	0.0022725145	−0.0014197139
38	11 11 12 12 (2)	−0.0028835400	0.0014056263
39	11 11 11 12	−0.0021807159	0.0012329227
40	03 03 11 12	0.0001161045	0.0011816094
41	02 02 04 04	−0.0237010632	−0.0011348512
42	11 11 12 12 (3)	0.0019840918	−0.0011090764
43	01 01 04 04	−0.0100988886	0.0010050870
44	02 02 12 12	−0.0282980602	−0.0009988162
45	01 02 03 05 (2)	0.0002784606	0.0009808376
46	01 02 12 12	−0.0043031912	0.0009591452
47	01 02 11 12 (2)	−0.0065559400	0.0009319553
48	01 04 11 12 (1)	−0.0016248818	0.0009034274
49	01 03 21 21	0.0000068933	0.0007387696
50	11 11 14 14 (1)	−0.0013362325	0.0007297611
51	01 03 13 13	−0.0000102356	−0.0006732283
52	01 01 05 05	−0.0025657535	0.0006385123
53	02 02 03 03	−0.0001090973	−0.0006172765
54	01 02 02 05	−0.0002383699	0.0005546419
55	05 05 11 11	0.0010055204	−0.0005411003
56	02 02 11 11	−0.0021303824	−0.0004797384
57	01 02 11 12 (1)	0.0091390093	−0.0004639503
58	02 03 03 04	−0.0001083214	0.0004439640
59	06 06 11 11	0.0007628539	−0.0004145687
60	02 02 11 12	−0.0100988886	−0.0003656501
61	03 03 11 11	0.0000637921	0.0003624377
62	01 02 21 21	0.0005975510	−0.0002897119
63	01 02 11 14 (1)	−0.0033711311	0.0002204163
64	01 02 02 04	0.0001625332	−0.0002008584
65	02 02 14 14	−0.0052653385	−0.0001829950
66	01 02 11 14 (2)	0.0014911058	−0.0001656023
67	01 02 13 13	−0.0012396757	−0.0001441783
68	02 02 06 06	−0.0027457372	−0.0000944627
69	01 05 11 11	0.0004915673	−0.0000926136
70	01 01 02 06	0.0000130559	−0.0000743077
71	02 02 13 13	−0.0023179641	−0.0000515417
72	02 02 03 05	−0.0000483338	−0.0000470239
73	02 02 05 05	−0.0035659608	−0.0000261288
74	01 01 03 06	0.0000167171	−0.0000117779

[a] The numbers 1−6 refer to the basis orbitals s_1-s_6; 11 − 14 to p_1-p_4; 21 to d_1.

[b] Numbers in parenthesis refer to degenerate elements (see Ref. [8]).

with the first and second of a 74 × 74 secular equation spanning a unique determinantal space of order 355 and which will be referred to hereafter as I (ground state) and II (excited state), respectively. Although we attempted to include in the 74 CI all configurations that the limited configuration search showed to be good for both states, the energy of I (cf. non-relativistic experimental energy of -14.667 a. u.) indicates that ground-state adapted configurations and basis orbitals need eventually to be added. The first s-type orbital basis used here resembles Watson's 1s Hartree-Fock basis for the ground state [7]. In later discussions it will be evident that a good s-orbital basis is required in describing the excited state and it is furthermore helpful to notice that in II, configurations such as $s_1^2d_1^2$, and $s_2^2p_2^2$ play relatively minor roles. Note also that singly excited configurations involving s-orbitals (excitation with respect to $s_1^2s_2s_3$) and doubly excited configurations involving p-orbitals are particularly weighty. The wave functions would be characterized more thoroughly by examining their density matrices.

The 1-*Matrix*

In Table 3 are shown the 1-matrices of I and II and those of the independent particle model (IPM). It is well-known that in I the depression of the two 1-matrix occupation numbers below unity results from the correlation effect and the significant population of one p-type NO may be attributed to the importance of the $2s-2p$ degeneracy [11] in the Be ground state. The latter is shown to play a diminished role in the excited state, a fact that is already evident in Table 2. There we observe that the configuration $s_1^2p_1^2$ appears in the excited state wave function with a coefficient slightly more than half of its ground state value.

The 1-matrix of II indicates an open-shell function described largely by $\chi_1^2\chi_2^{1.09}\chi_3^{0.86}$. The second NO's of I and II bear some resemblance to each other but χ_3 of II is a new orbital having no counterpart in the ground state NO's. Since the 3 electrons of the excited state thus appear to be in a Li-like core it is not surprising that the 1-matrix of II resembles somewhat that of LiH (ground state) in the limit of large internuclear distances. Our results should be contrasted with those of BS [4] for the first LiH excited state. They reported the NSO occu-

Table 3. 1-*matrix eigenvalues of* Be *ground and excited states*

Ground State			Excited State		
Degeneracy[a]	IPM	I	Degeneracy	IPM	II
2	1.0	0.9982391663	2	1.0	0.9982491361
2	1.0	0.9178520378	2	0.5	0.5472143038
6		0.0271226588	2	0.5	0.4310650561
2		0.0008025168	6		0.0071417344
6		0.0003485612	2		0.0006843444
2		0.0002808601	6		0.0003385722
10		0.0000554971	6		0.0000883181
2		0.0000371008	2		0.0000302499
6		0.0000177303	6		0.0000098176
6		0.0000119533	10		0.0000042802
2		0.0000081210	2		0.0000001808

[a] Degeneracies of 2,6 and 10 refer to s-, p- and d-type NSO's, respectively.

pation numbers of χ_2 and χ_3 to be 0.717491 and 0.280041, respectively at the equilibrium distance of 4.90 bohrs. Their tabulated values further indicate a widening of the occupation number gap between these two NO's not only at large internuclear distances but also in the united atom limit. Thus, the first excited states of LiH and Be are dissimilar in this respect and further we observe that in the excited state Be exists in a more open-shell form. In II the unequal population of χ_2 and χ_3, indicative of some sort of incomplete excitation process, may be attributed partly to electron correlation and is influenced to some extent by the non-negligible weight of the "ground state" configuration $s_1^2 s_2^2$. It would be desirable to examine whether a more improved wave function would exhibit a narrowing of the occupation number gap between χ_2 and χ_3.

The apparent reduction in the occupation number of the first p-type NO in going from I to II was hinted at earlier. An examination of Table 3 reveals that the same situation holds for the d-type NO. Note now that these orbitals are primarily localized in the outer shell so that the difference in angular character between I and II is almost exclusively outer-shell in nature. Hence, for the excited state we expect a rather drastic reduction in angular correlation. This appears to clarify our earlier findings that the goodness of the excited function greatly depends on the choice of outer-shell s-basis and for present purposes an extended basis set over p- and d-orbitals are not necessary. Finally, it is of interest to observe that BS reported total π correlation energies of 0.0263 and 0.0164 Hartrees for the LiH ground and excited state, respectively. The difference in the two values is due primarily to the contributions from the outer shell, these being 0.0116 H for the ground state and 0.0015 H for the excited state.

The 2-Matrix

The important terms of the 2-matrix expansion for both I and II are presented in Table 4. Also, it is shown there that the IPM excited 2-matrix consits of a set of doubly degenerate singlet NSG's with occupation numbers of 1.0 and a set of 8-fold degenerate NSG's, including 6 triplets and 2 singlets, with eigenvalues of 0.5. It is well-known that the presence of additional configurations in the CI function destroys the simplicity of the degenerate Be IPM NSG's. Hence it is not surprising to note that the principal NSG's of II, like their counterparts in I, are delocalized geminals in the sense that they are essentially linear combinations of inner- and outer-shell Slater geminals. Since the only atomic system whose 2-matrix has been reported is the Be ground state (as far as we know) one has become somewhat accustomed to seeing an NSG that is very strongly occupied (in this case, with an eigenvalue greater than the IPM limit of 1.0). Therefore it may seem unexpected to notice that the first excited state NSG has an occupation number below unity. It has been shown [12] that the theoretical upper bound for a 2-matrix eigenvalue of an N-particle system is $N/2$ for N even [13]. However, the underlying reasons for the existence of what we prefer to call "supereigenvalue" in the Be ground state still remain to be satisfactorily explored. Is the Be ground state a special case in this respect by virtue of its rather unique outer-shell correlation characteristic, i. e., of its abnormally large outer-shell angular correlation which in turn is influenced greatly by the $2s$-$2p$ splitting? If indeed

Table 4. *2-matrix eigenvalues of* Be *ground and excited states*[a]

Ground state				Excited state			
Symmetry	IPM	I	NSG[b]	Symmetry	IPM	II	NSG[b]
^1S	1.0	1.0003675173	$s_1^2+s_2^2$	^1S	1.0	0.9999063418	$s_1^2+s_2s_3$
^1S	1.0	0.9991352141	$s_1^2-s_2^2$	^1S	1.0	0.9995873123	$s_1^2-s_2s_3$
^1S	1.0	0.9164240318	s_1s_2	^1S	0.5	0.5464451889	$s_1s_3-s_1s_2$
^3S	1.0	0.9162875277	s_1s_2	^3S	0.5	0.5462723626	$s_1s_2-s_1s_3$
^1P		0.0270831197	s_1p_1	^1S	0.5	0.4303803789	$s_1s_3+s_1s_2$
^3P		0.0270798885	s_1p_1	^3S	0.5	0.4302981496	$s_1s_2+s_1s_3$
^1S		0.0006812556	s_2s_4	^1P		0.0071167750	s_1p_1
^3S		0.0006653646	s_2s_4	^3P		0.0071101289	s_1p_1
^3S		0.0003525421	s_1s_3	^1S		0.0004420587	$s_3s_4-s_2s_4$
^1S		0.0003482385	s_1s_3	^3S		0.0003841104	$s_3s_4-s_2s_4$
^3P		0.0003055976	s_2p_2	^1S		0.0003217008	$s_3s_4+s_2s_4$
^1P		0.0003025231	s_2p_2	^3S		0.0003071117	$s_3s_4+s_2s_4$
^1P		0.0000608047	s_1p_2	^3P		0.0001802287	s_3p_2
$^{1,3}D$		0.0000554971	s_1d_1	^1P		0.0001764742	s_3p_2
^1P		0.0000449571	s_2p_1	^3P		0.0001443909	s_2p_2
^1S		0.0000380228	s_1s_5	^1P		0.0001423122	s_2p_2
^3S		0.0000369204	s_1s_5	^1P		0.0001074037	s_1p_3
^1S		0.0000178514	p_2p_2	^3P		0.0001011165	s_1p_3
^1S		0.0000164722	s_4s_4	^1S		0.0000415062	$s_1s_4-s_1s_5$
^3P		0.0000163606	s_4p_1	^3S		0.0000401032	$s_1s_5-s_1s_4$

[a] The complete 2-matrix expansion is extensive but for brevity only the first 20 terms are listed.

[b] NSG's refer to CI only. Listed are the 2 × 2 Slater determinants formed from the original basis (s_1, p_2, etc.) which are the leading terms in the expression for the particular NSG. The determinant xy is understood to be a singlet or triplet Slater determinant depending on whether the NSG is a singlet or triplet.

the splitting plays a key role in the formation of a geminal supereigenvalue, or more correctly, a "supergeminal", we would expect a principal NSG eigenvalue less than 1.0, not only for the Be ^1S excited state but also for example for the Ne ground state despite the fact that in principle, the latter can have a 2-matrix occupation number as large as 5.0. This question would be examined in detail when final computations on the excited state are completed. As to what this all means, it is helpful to remark that physically, the presence of a supereigenvalue in an electronic system has been taken to imply superconductivity [14]. Coleman [15] proposed the existence of macroscopic or infinite range correlation in such a case which apparently is manifested as superconductivity if the supergeminal is a singlet, and magnetic ordering if it is a triplet.

From Table 4 we observe that the 8-fold degenerate NSG's of the excited state IPM split into two distinguishable sets in the CI function, each consisting of a singlet-triplet pair with one set having eigenvalues greater, and the other lower, than the IPM limit of 0.5. This rearrangement is predictable from the 1-matrix result and the magnitude of the pair occupation number gap between the two sets is dependent on the completeness of the excitation $\chi_1^2\chi_2^2 \rightarrow \chi_1^2\chi_2\chi_3$ mentioned earlier. The singlet-triplet pairs are further split in II by the presence of mixing configurations. Generally, the relative importance, in the eigenvector sense, of various mixing configurations determines whether the splitting would proceed in such a way that the pair occupation number of the singlet would exceed that of the triplet, or vice-versa.

Of the first 70 NSG's representing better than 5.9991 of the 2-matrix trace of 6.0 for both I and II, the eigenvalues associated with *S*-, *P*- and *D*-geminals are 5.6690556681, 0.3289435887 and 0.0011099420, respectively for the ground state. These should be compared with the excited state values of 5.9090300001, 0.0904516803 and 0.0. The rather drastic de-population of *P*- and *D*-geminals in the excited state reflects perhaps more dramatically the reduction in angular correlation in going from I to II. In view of earlier discussions we note that it also stresses the importance of having a good *s*-basis for the outer shell.

Conclusions

It would seem, at least preliminarily, that for describing the excited state no great effort should be spent in searching for basis orbitals of high angular momentum symmetry. Our findings indicate that configuration types representing triple and quadruple excitations with the aforementioned orbitals contribute negligibly to the wave function. From a comparison of their 1-matrices, Be and LiH appear to be somewhat dissimilar in their excited states although both systems exhibit a remarkable reduction of outer-shell angular correlation over their ground states. In the Be case this conclusion is reflected in the substantial de-population of the important *p*- and *d*-type NO's (all outer-shell) and *P*- and *D*-type NSG's. This was attributed largely to the diminished role played by the $2s-2p$ degeneracy effect in the excited state. The $2s-2p$ splitting may also play a key role in the noted absence of a supergeminal in the excited state.

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