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Analysis of the Natural Spin Orbitals of the Three-Electron System: Lithium Hydride Molecule Ion*

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Natural spin orbitals of LiH^+ were calculated from a 60-determinantal generalized valence-bond wave function which gives the total energy of -7.758855 a.u. at $R = 3.736$ a.u. Using the orbitals corresponding to the three highest occupation numbers, the electronic structure of this system is analyzed and the role of the Fermi and Coulomb correlations is studied. The electron density distribution along the nuclear axis and some one-electron properties of weakly occupied orbitals are also presented. A discussion, with regard to the electron correlation, of these natural spin orbitals is made and a brief mention is made of the spinadapted natural orbitals.

Die natürlichen Spinorbitale des LiH^+-Ions wurden aus einer verallgemeinerten VB-Wellenfunktion bestimmt, die aus 60 Determinanten besteht und mit der eine Gesamtenergie von $-7{,}758855$ a.E. bei $R = 3{,}736$ a.E. berechnet wurde. Mit Hilfe der Orbitale, die zu den drei größten Besetzungszahlen gehören, wurde die Elektronenstruktur dieses Systems analysiert und die Rolle der Fermi- und der Coulomb-Korrelation untersucht. Weiterhin wurde die Elektronenverteilung entlang der Kernverbindungslinie sowie einige Einelektronen-Eigenschaften der schwach besetzten Orbitale angegeben. Diese natürlichen Spinorbitale werden im Hinblick auf die Elektronenkorrelation diskutiert, während die Spin-adaptierten natürlicher Orbitale nur kurz erwähnt werden.

Des orbitales naturelles de LiH^+ sont calculées à partir d'une fonction généralisée de liaison de valence à 60 déterminants correspondant à une énergie totale de -7.758855 u. a. à $R = 3.736$ u.a. En utilisant les orbitales correspondant aux trois plus grands nombres d'occupation on analyse la structure électronique de ce système et l'on étudie le rôle des corrélations de Fermi et de Coulomb. On obtient aussi la distribution électronique le long de l'axe des noyaux et certaines propriétés monoélectroniques des orbitales faiblement occupées. Une discussion porte sur la corrélation électronique dans ces spin-orbitales naturelles et une brève mention est faite des orbitales naturelles adaptées au spin.

1. Introduction

The three-electron system in the ground state is the simplest case where both the intra-shell Coulomb correlation and the Fermi correlation are present. Two electrons in the inner-shell are governed by the Coulomb correlation while the two electrons of the same spin are subject to the Fermi correlation. How these two correlations [4] would influence each other in determining the overall electron density distribution is an interesting question. Being the simplest, the three-electron system is an ideal case for this study; for this purpose, the natural spin orbitals are undoubtedly most useful. Since the ground state of a three-electron system is doublet, a wave function which is also an eigenfunction of S_z necessarily leads to two sets of natural spin orbitals, one each for α- and β-spins, which are, in general, different. If the configuration constructed from the orbitals corresponding to the three highest occupation numbers[1] can be shown to very satisfactorily reproduce the original wave function, an analysis of these natural spin orbitals may cast some light on the above question.

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[1] Naturally, these three orbitals alone can not give a pure spin state. However, an analysis in Section III shows this to be a very good approximation.

In this report, the natural spin orbitals calculated from the 60-determinantal generalized valence-bond wave function of LiH$^+$, in terms of 13 elliptic orbitals [5], and the results of analysis based on the natural spin orbitals are presented.

2. Result

Since the calculation of the natural spin orbitals from a wave function expanded in terms of a non-orthogonal basis set has been reported [1], it will not be described here. The original wave function gives the total energy of -7.758855 a.u. at $R=3.736$ a.u. for this molecule ion.

The orbitals obtained are tabulated in Tables 1 and 2. For the sake of convenience, the orbitals in Table 1 are designated by $\alpha-1$, $\alpha-2$, *etc.*, in the decreasing order of the occupation number and those in Tables 2 by $\beta-1$, $\beta-2$, *etc.* The electron density distribution of $\alpha-1$, $\alpha-2$, and $\beta-1$ are computed. Fig. 1 shows the contour maps.

Let the axis passing through both nuclei be designated by x, with the origin at the lithium nucleus and $x=-1$ at the proton. It should be kept in mind that,

Table 1[a]. *Natural orbitals of* LiH$^+$. *α-spin*

Occupation No.	0.99996635 $E+0$	0.99817157 $E+0$	0.13081202 $E-2$	0.51902753 $E-3$
ϕ_1	−0.31309797 −2	0.39610148 +0	−0.26599337 +1	−0.10266631 +0
ϕ_2	−0.25760730 +0	0.77545928 +0	0.43194367 +1	−0.93194731 +0
ϕ_3	0.10005399 +0	−0.70807206 −2	0.20479383 −2	0.86399478 −2
ϕ_4	0.88519123 +0	−0.59401956 −1	−0.33444315 −1	0.75973004 −1
ϕ_5	0.56493881 −1	−0.22824942 +0	0.87599153 +0	−0.24196040 +0
ϕ_6	0.69395378 +0	−0.11200565 +1	0.44959715 +1	−0.22312223 +1
ϕ_7	0.10424192 −2	0.43834713 +0	−0.27832980 +1	−0.10189628 +1
ϕ_8	0.28882876 +0	0.15974070 +0	−0.15624195 +1	−0.35564672 +0
ϕ_9	0.30794349 +0	−0.51403224 +0	−0.31119477 +0	−0.11207334 +1
ϕ_{10}	0.21195440 +0	−0.18725083 +0	0.89249401 +0	−0.19938837 +1
ϕ_{11}	−0.17751666 −1	−0.11412514 −1	0.91995453 −1	0.29158659 +0
ϕ_{12}	0.24029832 −1	0.13737055 +0	0.53064867 +0	−0.34505122 +1
ϕ_{13}	−0.14254156 +0	−0.66219757 −1	−0.55091598 +0	0.21624124 +1
	0.38967661 $E-4$	0.11690016 $E-4$	0.65360871 $E-5$	0.36707790 $E-5$
ϕ_1	0.29403496 +0	0.53411453 +1	0.24576846 +1	0.14743178 +0
ϕ_2	0.21497858 +1	−0.17944578 +1	0.84532086 +1	−0.25538283 +1
ϕ_3	0.35209553 +0	−0.18149729 +0	0.54625374 +0	0.35212120 +0
ϕ_4	0.55222432 +0	0.27007348 +0	−0.41124046 +0	−0.43284858 +0
ϕ_5	0.21879031 +0	0.63473233 +1	0.35133873 +1	0.10042016 +1
ϕ_6	0.60087303 +0	−0.35168515 +1	0.36598443 +2	0.48230015 +0
ϕ_7	−0.72133606 +1	−0.18795749 +0	−0.16693143 +2	0.58717689 +0
ϕ_8	−0.58614554 +1	−0.51431145 +1	0.23226708 +0	0.13655841 +1
ϕ_9	−0.30890513 +1	−0.71477598 +1	0.18085022 +1	0.12568982 +1
ϕ_{10}	−0.12282165 +1	−0.10830838 +1	0.57094513 +1	0.60978367 +0
ϕ_{11}	−0.10952583 +1	0.34192572 +0	−0.23499642 +1	0.14160926 +0
ϕ_{12}	0.21537073 +1	0.14141144 +1	0.84164270 +1	−0.20001989 +0
ϕ_{13}	−0.38437173 +1	−0.15479865 +1	−0.85645763 +1	−0.44806814 −1

Table 1. (Continued)

Occupation No.	$0.85244280\,E-6$	$0.44029592\,E-6$	$0.25607625\,E-6$	$0.52724910\,E-7$
ϕ_1	0.68033456 +1	−0.13567020 +2	0.73207268 +0	−0.77022437 +1
ϕ_2	−0.82009911 +2	0.23918504 +2	−0.42641114 +2	0.30869787 +2
ϕ_3	−0.70896989 +0	0.12080315 +1	0.10596082 +1	−0.58663180 +0
ϕ_4	0.40210204 +0	−0.20019390 +1	−0.16206638 +1	0.16320490 +1
ϕ_5	−0.26648356 +2	0.31538345 +2	−0.35743519 +1	0.16290763 +2
ϕ_6	−0.45829752 +2	0.61635692 +2	0.49335481 +2	0.17941112 +3
ϕ_7	0.42567901 +1	−0.98969535 +1	−0.32935443 +1	−0.10970596 +3
ϕ_8	0.38537155 +2	−0.21751979 +2	0.30587512 +2	−0.33365880 +2
ϕ_9	0.25257453 +2	0.30601023 +2	0.20972758 +2	0.36111062 +2
ϕ_{10}	−0.36936016 +1	0.11999171 +1	0.30346680 +2	0.37080909 +2
ϕ_{11}	0.32137784 +1	−0.20648762 +1	−0.50212472 +1	0.40635550 +1
ϕ_{12}	−0.11873665 +2	−0.51253663 +1	−0.10796928 +2	−0.33991693 +2
ϕ_{13}	0.13361407 +2	0.32626905 +1	−0.62543785 +1	0.45608260 +2

	$0.28633511\,E-8$
ϕ_1	0.19849282 +2
ϕ_2	−0.36466627 +3
ϕ_3	0.13010116 +1
ϕ_4	−0.96237313 +0
ϕ_5	0.32189519 +2
ϕ_6	0.40329830 +3
ϕ_7	−0.18776054 +3
ϕ_8	0.32801976 +2
ϕ_9	0.22502071 +3
ϕ_{10}	0.17424722 +3
ϕ_{11}	0.30971893 +2
ϕ_{12}	0.10900269 +3
ϕ_{13}	−0.19290121 +3

[a] See Ref. [4] for the functions ϕ_i.

in this report, distances are always measured in unit of the internuclear distance, $R=3.736$ a.u. Two mutually perpendicular axes which are also perpendicular to the x-axis will be labeled y and z. Because of the axial symmetry of this molecule ion, the quantity $2\pi y_0|\phi^2|_{x=x_0, y=y_0}$ where ϕ is a normalized orbital, gives the total electron density on a circle of radius y_0 in the plane $x=x_0$. The distribution of this quantity along the y-axis is the only density distribution which has the physical meaning similar to the radial distribution of the spherically symmetric system and their general appearance is actually alike. Each of the orbitals $\alpha-1$, $\alpha-2$ and $\beta-1$, has, in any (y, z)-plane, a maximum close to the x-axis while $\alpha-2$ has, in some region of x, a second maximum, the order of 10^{-4} times the first one, at large value of y, usually $y \geqq 0.8$. The value of y corresponding to the absolute maximum of $2\pi y|\phi^2|_{x=x}$ in each (y, z)-plane will be denoted by $y_{\max}(x)$. In Fig. 2 are shown the plots of $y_{\max}(x)$ vs. x-axis for $\alpha-1$ and $\alpha-2$ while in Fig. 3 those of $\alpha-2$ and $\beta-1$ are presented.

When the quantity $2\pi y|\phi^2|_{x=x_0}$ is integrated over y, it gives the total density in the plane $x=x_0$, planar density. The plot of planar density against

Table 2. *Natural orbitals of* LiH$^+$. *β-spin*[a]

Occupation No.	0.99831811 +0	0.12936916 −2	0.51702711 −3	0.16185534 −4
ϕ_1	0.39117913 +0	−0.26852289 +1	−0.14315570 +0	0.32920470 +1
ϕ_2	0.77075137 +0	0.46506232 +1	−0.55659801 +0	−0.11306210 +2
ϕ_4	−0.11787116 −2	0.16694090 −2	0.60889430 −1	0.46187412 +0
ϕ_5	−0.20740048 +0	0.10095290 +1	−0.14801900 +0	0.54192808 +0
ϕ_6	−0.10705966 +1	0.47334122 +1	−0.21013158 +1	−0.14513214 +2
ϕ_7	0.45493624 +0	−0.26348967 +1	−0.10238304 +1	−0.12449875 +1
ϕ_8	0.17033254 +0	−0.15845216 +1	−0.51279374 +0	−0.31661559 +1
ϕ_9	−0.49353346 +0	−0.36313990 +0	−0.12270345 +1	−0.32429656 +1
ϕ_{10}	−0.17450167 +0	0.92606767 +0	−0.20080553 +1	−0.30325393 +1
ϕ_{11}	−0.13690895 −1	0.69510682 −1	0.28096200 +0	0.50037217 +0
ϕ_{12}	0.31960272 +0	0.59767911 +0	−0.34389174 +1	−0.22057063 +1
ϕ_{13}	−0.80178561 −1	−0.61933284 +0	0.21739255 +1	0.21733840 +1

	0.97989758 −5	0.44124165 −5	0.17096463 −5	0.24322888 −6
ϕ_1	0.51122993 +1	0.89357814 −1	0.19081368 +0	−0.11245787 +2
ϕ_2	0.38414032 +1	−0.72363855 +1	0.10320563 +2	−0.11359275 +2
ϕ_4	−0.16566002 +0	0.88996819 +0	−0.56246714 +0	−0.72640745 +0
ϕ_5	0.70199343 +1	−0.21691710 +1	0.31319879 +0	0.25671744 +2
ϕ_6	0.14482310 +2	−0.56888736 +1	−0.30753134 +2	0.96333236 +2
ϕ_7	−0.36100829 +1	0.35969116 +1	0.17462504 +2	−0.33446416 +2
ϕ_8	−0.22541004 +1	0.29855779 +1	−0.65064199 +1	−0.13154484 +2
ϕ_9	−0.53499143 +1	0.47991202 −1	−0.14749919 +2	0.48748212 +2
ϕ_{10}	0.32747092 +1	0.22910633 +1	−0.44784438 +1	0.19390203 +2
ϕ_{11}	−0.29027049 +0	0.47999971 +0	0.28106641 +1	0.82899401 +0
ϕ_{12}	0.48337618 +1	−0.40211009 +1	0.12612854 +1	−0.11095742 +2
ϕ_{13}	−0.48474869 +1	0.23652393 +1	0.13341421 +0	0.52942557 +1

	0.12102378 −6	0.23741011 −7	0.11020804 −8	0.16118949 −9
ϕ_1	0.81950229 +0	0.64071076 +1	−0.88554309 +1	−0.20004580 +2
ϕ_2	−0.14784717 +2	−0.59216655 +2	0.20464077 +3	0.27012320 +3
ϕ_4	0.51411506 −1	−0.52333387 +0	−0.12562999 +1	0.37926595 +0
ϕ_5	−0.34986801 +1	−0.30455974 +2	−0.30128147 +2	−0.22910971 +0
ϕ_6	0.74954120 +2	−0.50720326 +2	−0.36852052 +3	−0.12666892 +3
ϕ_7	−0.27671060 +2	0.69690170 +1	0.19678638 +3	0.47288398 +2
ϕ_8	0.15289223 +2	0.39439541 +2	0.79817438 +1	−0.52980778 +2
ϕ_9	0.10535652 +2	0.11345786 +2	−0.16130071 +3	−0.12062611 +3
ϕ_{10}	0.33943751 +2	−0.50289277 +1	−0.13160221 +3	−0.87818375 +2
ϕ_{11}	−0.38761948 +1	0.19583698 +1	−0.24038754 +2	−0.17222145 +2
ϕ_{12}	−0.15107058 +2	−0.25444879 +2	−0.51548879 +2	−0.87095043 +2
ϕ_{13}	0.42902857 +1	0.32527404 +2	0.93893612 +2	0.14857683 +3

[a] See Ref. [4] for the functions ϕ_i.

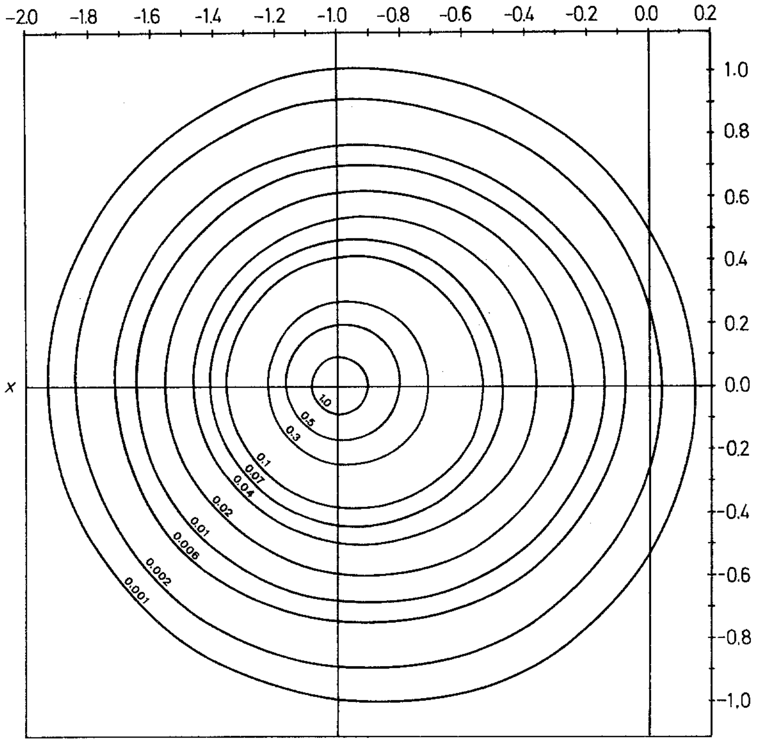

Fig. 1a

Fig. 1a—c. Contour maps of the first three natural orbitals $\alpha - 1$, $\alpha - 2$, and $\beta - 1$. Coordinates are in unit of $R(=3.736$ a.u.) while the density is in unit of 2π a.u. The internuclear axis is taken as X-axis, with the lithium nucleus at $X=0$ and the proton at $X=-1$

x-axis is the planar density distrubution. The planar density distribution of $\alpha - 1$ is almost identical to the left-half of Fig. 2 of a previous paper [5], that of $\alpha - 2$ has a prominent peak at the lithium nucleus and a much smaller one, about 1/650 of the former, at the proton and finally that of $\beta - 1$ is very similar to the distribution of $\alpha - 2$ except that the small peak at the proton is absent. These are not shown. Let the space between the planes $x=0$ and $x=-1$ be donated by II, the one on its right, i.e., $x<0$, by I and the space where $x<-1$ by III. In Table 3 are shown the breakdown of the electron density of each orbital in these regions. The total density in each region and the corresponding values computed from the original wave function are also included for comparison.

In Table 4 are tabulated some one-electron properties of the first 15 natural spin orbitals. From this table, one can readily see that $\beta - 1$, $\beta - 2$, and $\beta - 3$ are very similar to $\alpha - 2$, $\alpha - 3$, and $\alpha - 4$, in the same order. As a matter of fact, the electron density distribution of any one of the three pairs, $(\beta - 1) - (\alpha - 2)$, $(\beta - 2) - (\alpha - 3)$, and $(\beta - 3) - (\alpha - 4)$, are indiscernible using a practicable scale of plotting. For the purpose of discussion, the electron density distributions, along the nuclear axis, of these six orbitals are collected in Table 5. Finally, the same quantities of seven α-orbitals are shown in Fig. 4.

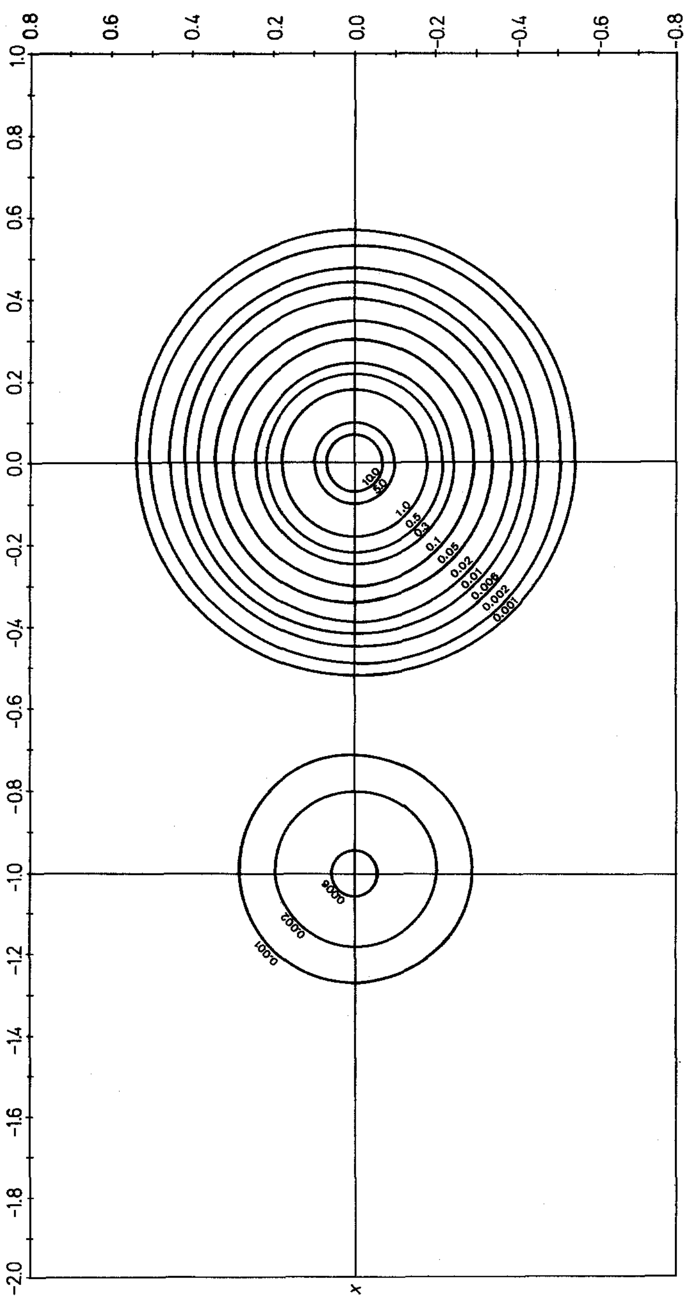

Fig. 1b

3. Discussion

For a two-electron system, the natural spin orbital expansion gives the most rapid convergence [6]. The most important term in the expansion is the one involving the natural spin orbital of the highest occupation number. For systems with more than two electrons it is also generally true that the configuration con-

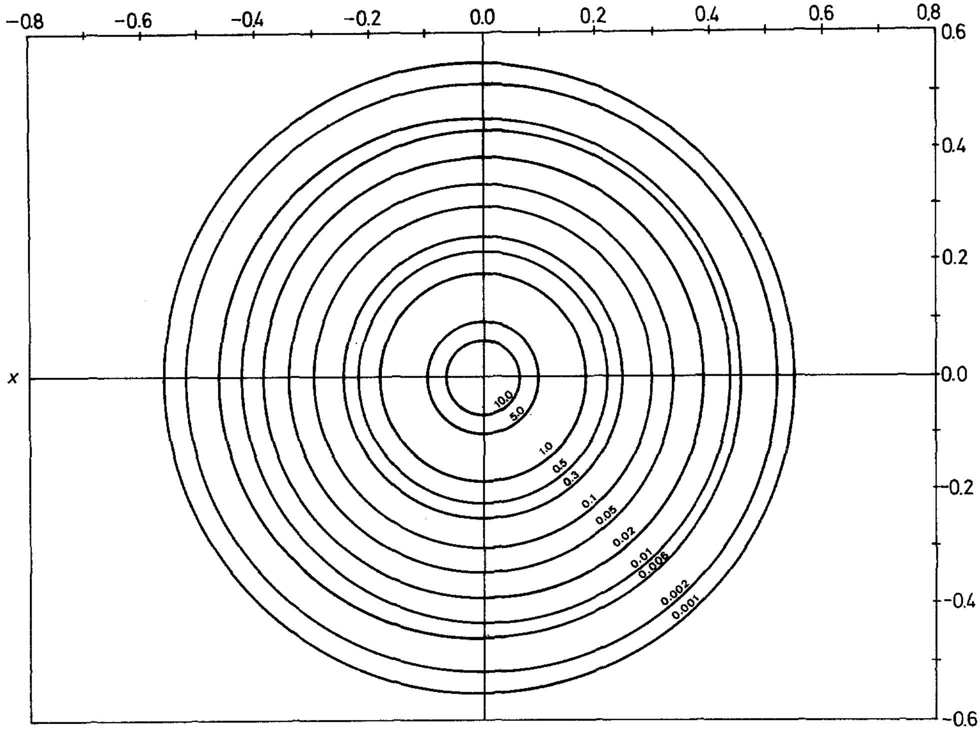

Fig. 1c

structed from the orbitals of the highest occupation numbers is very prominent. However, to test how closely the configuration involving $\alpha-1$, $\alpha-2$, and $\beta-1$ would reproduce the original wave function, the following steps were taken. The electron densities of $\alpha-1$, $\alpha-2$, and $\beta-1$ were summed up at various specific

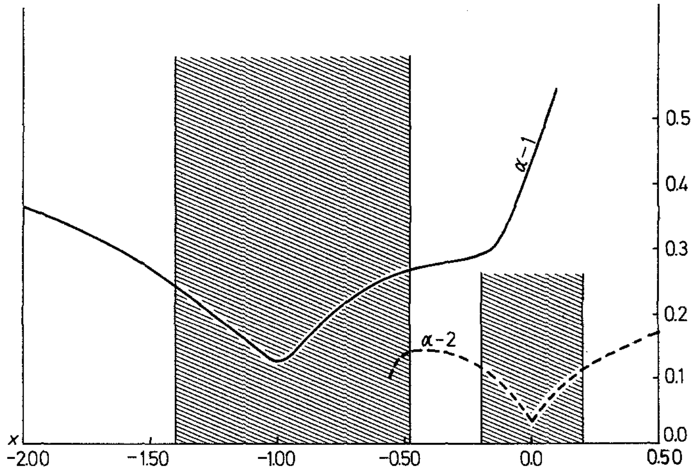

Fig. 2. Plots of $y_{\max}(x)$ of the orbitals $\alpha-1$ and $\alpha-2$ vs. internuclear distance. The shaded areas contain over 90% of electron density in each orbital. The strong separation of these two shaded areas indicates a very high localization of electron density around nuclei. Solid line, $\alpha-1$; Broken line, $\alpha-2$

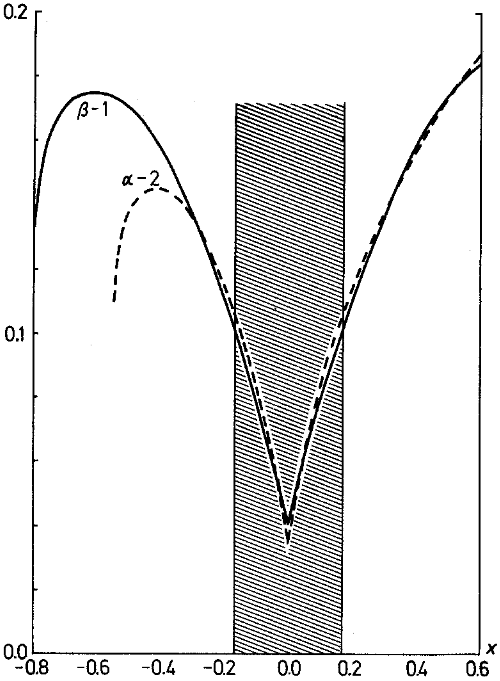

Fig. 3. Plots of $y_{\max}(x)$ of the orbitals $\alpha-2$ and $\beta-1$ vs. internuclear distance. The splitting of their loci in the shaded area has an average width of approximately 100 times the diameter of the proton. Solid line, $\beta-1$; broken line, $\alpha-2$

points on the internuclear axis and compared with the corresponding value obtained from the original wave function. Similarly, the planar density distribution from both sources were compared. In each case, these two sets of values are very close; the ratio, sum/original, of the electron density on the internuclear axis lies between 0.994 and 0.999 at twenty points in the range $0.5 \geqq x \geqq -0.6$ and 1.0000 for the entire range $-1.5 \leqq x \leqq -0.6$. At two points, $x=0.1$ and $x=-0.1$, this ratio was 1.0011 and 1.0004, respectively. Since the ratio is everywhere very close to unity, it is assumed that this system can be very satisfactorily described by the single-configurational wave function involving $\alpha-1$, $\alpha-2$, and $\beta-1$.

From Fig. 1 it is obvious that the electron density in the orbital $\alpha-1$ is strongly drawn towards the lithium nucleus. As compared to the neutral hydrogen

Table 3. *Breakdown of electron density distribution of natural orbitals*

	I[a]	II[a]	III[a]
$\alpha-1$	0.0001	0.5878	0.4121
$\alpha-2$	0.5047	0.4915	0.0038
$\beta-1$	0.5005	0.4995	0.0000
sum	1.0053	1.5788	0.4159
original[b]	0.993	1.595	0.412

[a] II refers to the space between two planes $x=0$ and $x=-1$ with the proton at $x=-1$ and lithium nucleus at $x=0$. I is on the right, $x>0$, of II while III is the remainder.

[b] From the 60-determinantal wave function of Ref. [4].

Table 4. *Some one-electron properties of the first* 15 NSO's[a,b]

χ	$-\langle\chi\vert\frac{1}{2}\Delta\vert\chi\rangle$	$-\langle\chi\vert\mathrm{Li}^{3+}\vert\chi\rangle$	$-\langle\chi\vert\mathrm{H}^{+}\vert\chi\rangle$	$\langle\chi\vert r\vert\chi\rangle$
$\alpha-1$	0.4982 23	0.8630 54	0.9880 86	1.6304 01
$\beta-1$	3.6104 33	8.0528 10	0.2677 13	−1.8680 75
$\alpha-2$	3.6313 87	8.0609 75	0.2703 59	−1.8588 80
$\alpha-3$	10.6345 91	9.5299 76	0.2736 80	−1.8414 13
$\beta-2$	10.6127 28	9.5320 16	0.2707 94	−1.8424 73
$\alpha-4$	4.0166 04	4.1064 21	0.3054 76	−1.6142 66
$\beta-3$	3.9974 08	4.0885 59	0.3094 57	−1.6019 76
$\alpha-5$	1.4770 20	1.3856 51	0.6424 78	0.5534 82
$\beta-4$	4.0865 26	6.7171 56	0.5788 21	−2.8794 39
$\alpha-6$	9.3950 53	6.9035 85	0.2611 17	−2.5194 07
$\beta-5$	8.4821 17	5.3836 67	0.3323 77	−1.2449 80
$\alpha-7$	4.6798 40	3.1217 19	0.3134 77	−1.6447 60
$\beta-6$	1.0769 04	1.1462 95	0.8783 38	1.2726 29
$\alpha-8$	1.3043 79	4.7657 40	0.2742 44	−1.9107 16
$\beta-7$	2.0575 80	1.8417 30	0.3694 53	−1.1875 32

[a] NSO's are arranged in decreasing order of occupation numbers.

[b] All quantities in a.u.

atom, the electron density distribution of $\alpha-1$ is, in general, considerably elongated along the internuclear axis, approximately 10% in average, but is more contracted, by about 3%, along (y, z)-plane. Overall, it resembles a slightly asymmetric ellipsoid, with its center of mass shifted away from the proton towards the lithium nucleus. In fact, Table 3 shows that 58.8% of the density is in the region II, with the remaining 41.2% in III and less than 0.01% in region I. The numbers in the first row of Table 4 also reflect the same observation. A pure hydrogen 1*s* orbital placed at the same position would experience a nuclear attraction, from the lithium

Table 5. *Electron density distribution along the nuclear axis of six* NSO's[a]

ξ	η	$\alpha-2$	$\beta-1$	$\alpha-3$	$\beta-2$	$\alpha-4$	$\beta-3$
2.0	−1.0	0.3018 −2	0.3017 −2	0.1713 −1	0.1656 −1	0.1717 −1	0.1707 −1
1.8	−1.0	0.1723 −1	0.1714 −1	0.7767 −1	0.7567 −1	0.9498 −1	0.9458 −1
1.6	−1.0	0.1045	0.1038	0.2706	0.2668	0.4672	0.4639
1.4	−1.0	0.6884	0.6842	0.4044	0.4072	0.1878 +1	0.1856 +1
1.2	−1.0	0.5062 +1	0.5038 +1	0.9941	0.9584	0.4454 +1	0.4398 +1
1.0	−1.0	0.4257 +2	0.4239 +2	0.1643 +3	0.1643 +3	0.1709 −2	0.2441 −2
1.0	−0.8	0.4997 +1	0.5006 +1	0.2715 +1	0.2795 +1	0.6717 +1	0.6674 +1
1.0	−0.6	0.6638	0.6759	0.1823	0.1764	0.4854 +1	0.4855 +1
1.0	−0.4	0.9559 −1	0.1027	0.2708	0.2843	0.1610 +1	0.1615 +1
1.0	−0.2	0.1306 −1	0.1681 −1	0.9136 −1	0.1073	0.2497	0.2505
1.0	0.0	0.1060 −2	0.2787 −2	0.1314 −1	0.2122 −1	0.4315 −3	0.3460 −3
1.0	0.2	0.3162 −4	0.4377 −3	0.3717 −5	0.9811 −3	0.4798 −1	0.5064 −1
1.0	0.4	0.7538 −3	0.6149 −4	0.4139 −2	0.8800 −3	0.9019 −1	0.9671 −1
1.0	0.6	0.2036 −2		0.8691 −2	0.3160 −2	0.8341 −1	0.9346 −1
1.0	0.8	0.4281 −2		0.1081 −1	0.3927 −2	0.5170 −1	0.6436 −1
1.0	1.0	0.8806 −2		0.1133 −1	0.3419 −2	0.1932 −1	0.3269 −1
1.2	1.0	0.3954 −2		0.4402 −2	0.1227 −2	0.9795 −5	0.9160 −3
1.4	1.0	0.1734 −2		0.1472 −2	0.3131 −3	0.4365 −3	0.1133 −4

[a] $\xi=(r_{\mathrm{Li}}+r_{\mathrm{H}})/R$, $\eta=(r_{\mathrm{Li}}-r_{\mathrm{H}})/R$. Density in 2π a.u.

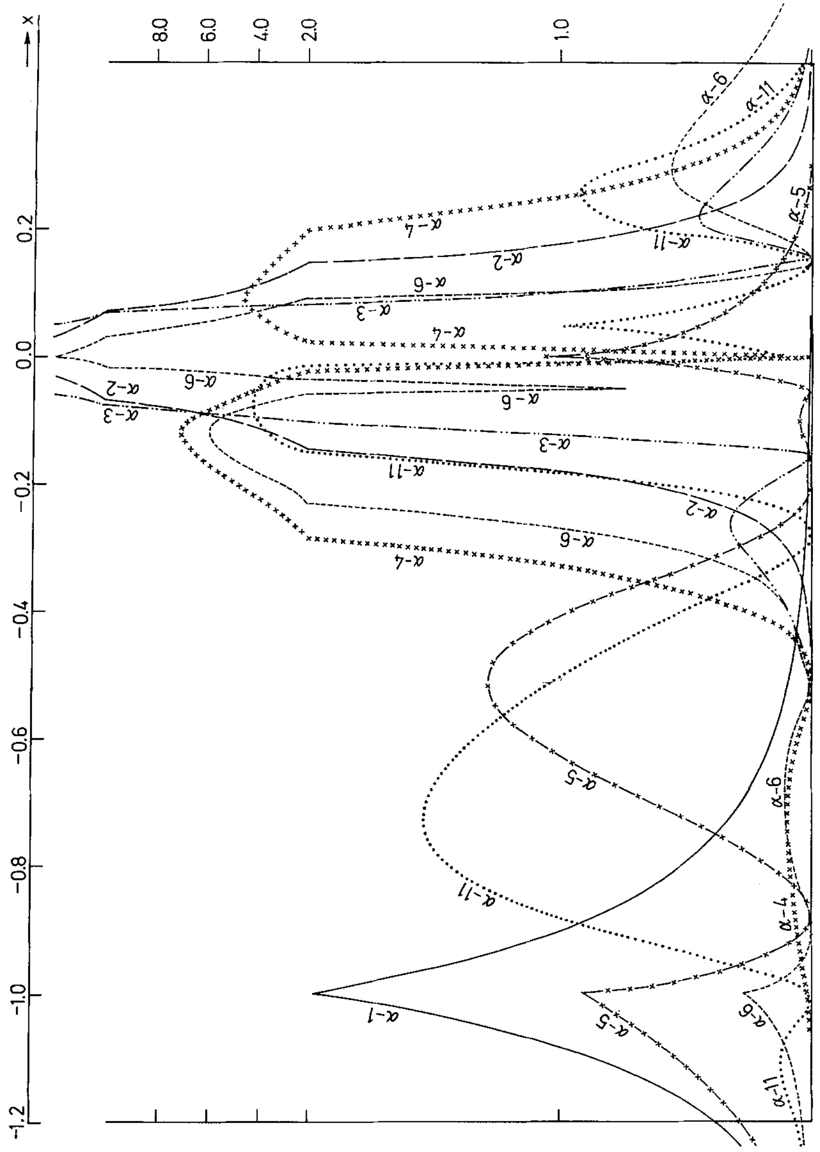

Fig. 4. Electron density distribution, along the nuclear axis, of several orbitals. Same legend and unit as in Fig. 1

nucleus, of −0.801044 a.u. instead of −0.863054 a.u. for $\alpha-1$. Because of the shift of the center, the nuclear attraction due to the proton decreases by −0.0119 a.u. in the $\alpha-1$ orbital and the change in the geometry of the orbital is shown in the kinetic energy which is about 0.0018 a.u. less than that of the neutral hydrogen atom.

The density distribution of $\alpha-2$ is quite different. There are two peaks, one on each nucleus. The ratio of the peak at the lithium nucleus to that at the proton is about 5000 to 1. The entire density distribution is also drawn towards the right of the lithium nucleus. However, the polarization is generally very slight and, except for the contour lines $\varrho \leqq 0.002$, this effect is negligible. In the orbital $\beta-1$

the polarization is even smaller. It is surprising that, in $\alpha-2$ and $\beta-1$, a very small amount of electron density is pushed away from the internuclear region. Whereas the polarization of $\alpha-1$ is due to the residual positive charge on the lithium nucleus, the very slight "adverse" polarization of $\alpha-2$ and $\beta-1$ is probably caused by the build-up of electron density in the region II by $\alpha-1$. Orthogonality between $\alpha-1$ and $\alpha-2$ may also partly account for this effect. From Table 3, one can also see that for this molecule ion the electron density distribution obtained from these three orbitals is in a good agreement with the one computed from the original wave function.

It is interesting to observe that 90% of electron density in $\alpha-2$ is contained in the space between $x=0.17$ and $x=-0.17$ while that of $\beta-1$ between $x=0.15$ and $x=-0.17$, approximately equal to 0.6 a.u. In both orbitals, 90% of the density in this space is within the region between $y=0$ and $y=0.2$. Therefore, the electron density in $\alpha-2$ and $\beta-1$ is very tightly packed around the lithium nucleus, closely resembling the K-shell of the lithium ion. For comparison, some one-electron properties of Li^+ ion deduced from the Hartree-Fock wave function of Roothaan *et al.* [8] are shown in Table 6 along with the corresponding values for $\alpha-2$ and $\beta-1$. From this table, one cannot fail to notice the striking similarity among these three orbitals and it should not be a mistake to consider, for all purposes, these orbitals as equivalent. Whereas the Hartree-Fock kinetic energy falls between those of $\alpha-2$ and $\beta-1$, with the average value of the latter two in close agreement with the former, which is a very desirable trait, the term $-\langle\chi|\mathrm{Li}^{3+}|\chi\rangle$ for both $\alpha-2$ and $\beta-1$ are lower than the Hartree-Fock value. This is due to the small shift of electron density in $\alpha-2$ to the proton, as mentioned earlier, and the result can be seen in the last column of Table 6. As can be expected, the orbital $\alpha-1$ is much more diffuse. The 90% boundaries of this orbital are at $x=-0.48$ and $x=-1.40$. This is approximately 6% longer than the neutral hydrogen atom. General feature of the planar density distribution of this orbital is very well described by Fig. 3 of Ref. [5]. The small increase in the electron density in the region II is almost entirely attributable to $\alpha-1$. Since it is well-established that the formation of a bond is invariably accompanied by a build-up of the electron density in the internuclear region [9], it seems safe to conclude that any bonding that may exist in this system is for the most part due to $\alpha-1$. The orbital $\alpha-1$, being bonding, occupancy by two electrons of this orbital would stabilize the system more than does occupancy by one electron. This may explain why LiH is more stable than its molecule ion. From these observations, one can

Table 6. *Comparison of the Hartree-Fock results, $\alpha-2$ and $\beta-1$*

	$-\langle\chi\|\frac{1}{2}\Delta\|\chi\rangle$	$-\langle\chi\|\mathrm{Li}^{3+}\|\chi\rangle$	$-\langle\chi\|\mathrm{H}^{+}\|\chi\rangle$
Hartree-Fock	3.6182 06	8.0622 57	~0.2677[a]
$\alpha-2$	3.6313 87	8.0609 75	0.2703 59
$\beta-1$	3.6104 33	8.0528 10	0.2677 13

[a] The repulsion between two protons 3.736 a.u. apart. Since the 1*s* atomic orbitals of the Li^+ ion is very small in dimension, this figure should be a reasonably good approximation.

conclude that the electronic configuration of the lithium hydride molecule ion can be very well written as $K_{\mathrm{Li}^+})^2\,\sigma)^1$ in a sharp contrast to the isoelectronic system He_2^+ which has the configuration [2], $1\sigma)^2\,1\sigma^*)^1$. In He_2^+ the nuclear field is symmetric with respect to the center of the internuclear distance while in LiH^+ it has only an axial symmetry. Therefore, the change in the nuclear field due to redistributing the four positive charges from a symmetric case as in He_2^+ to an uneven configuration as in LiH^+ is sufficient to make the bonding 1σ orbital of He_2^+ to recede into a practically pure atomic orbital and $1\sigma^*$ transmuted into a weakly bonding orbital.

Each of the three electrons of this molecule ion has different physical environment. The two electrons in the orbitals $\alpha-1$ and $\alpha-2$ are subject to the Fermi correlation while electrons in $\alpha-2$ and $\beta-1$ are separated by the Coulomb holes. Although the Coulomb correlation also works between the electrons in $\alpha-1$ and $\alpha-2$, the so-called inter-shell correlation, it is very small in comparison with the intra-shell correlation, the one between $\alpha-2$ and $\beta-1$, as will become clear later. In Fig. 2, over 90% of the electron density in each orbital is contained in the shaded area. The two shaded areas are separated by approximately 1.16 a.u. Since the electrons in these two orbitals are of the same spin they cannot have identical electron distribution. This figure very clearly conveys this fact. Not only that these two orbitals are orthogonal and that they have very different density distribution, but even their density distributions have only extremely small overlap. This indicates a very high localization of electron densities around nuclei. Combined with Fig. 3 of Ref. [5] this also indicates that although the orbital $\alpha-1$ is a weakly bonding molecular orbital with some covalent character, it is an intermediate case at the verge of receding into a strongly polarized atomic orbital centered on proton. This is in general accord with Browne's observation that the binding is entirely attributable to the polarization of the hydrogen atom by the lithium ion but not to the traditional chemical mechanism although it does not appear right to categorically rule out the contribution from the latter.

Fig. 3 shows the plots of $y_{\max}$ of $\alpha-2$ and $\beta-1$ against x-axis. The shaded area also contains over 90% of the electron density in each orbital. Electrons in these two orbitals are separated by Coulomb holes and it is remarkable the way the loci of $y_{\max}$ are split in the region of high electron density. This splitting of $y_{\max}$, which is the characteristics of the Different-Orbital-for-Different-Spin method, lowers the electronic interaction term without much changing the total nuclear attraction and thus enables recovery of the Coulomb correlation energy. It might be of interest to point out that the average width of the splitting in the shaded area is approximately equal to 4×10^{-11} cm, or about 100 times the diameter of the proton.

Finally if we compare Figs. 2 and 3, it is seen that in the shaded areas, the distance between the loci of $\alpha-1$ and $\alpha-2$ is in general slightly greater than that between $\alpha-1$ and $\beta<1$. Two electrons of the same spin are kept apart by the Fermi hole and also by the Coulomb interaction. It is not surprising that the pattern of the splitting suggests that, on the average, these two factors appear to work in the same direction.

Taking into account the binding energy, 0.0037 a.u., obtained by Browne [2], the Hartree-Fock energy of this system would be equal to -7.7401 a.u. From the above discussion on the orbitals $\alpha-1$, $\alpha-2$, and $\beta-1$, one could reasonably assume that the first configuration would give an energy very close to, but not worse than, the Hartree-Fock value. How the remaining weakly-occupied natural spin orbitals contribute to the recovery of the correlation energy should become evident from Fig. 4. Whereas $\alpha-3$ is enveloped, in most part, by $\alpha-2$, other orbitals shown have very different distribution. One should observe the number and position of nodal points of various orbitals. It should be pointed out, in particular, that $\alpha-4$ and $\alpha-11$ have a nodal point at the lithium nucleus. It would appear that $\alpha-4$, $\alpha-6$, and $\alpha-11$ would be most instrumental in accounting for the inner-shell correlation while $\alpha-5$ and $\alpha-11$ would be important for the binding of this system. Since the occupation numbers of these orbitals are very small compared to those of the first three orbitals, their weight in the original wave function should be quite small. Furthermore, since all basis functions used are of the σ-type, these natural orbitals would be able to effectively account for only the right-left correlation, leaving most part of the angular correlation unrecovered.

It was mentioned earlier that the orbitals $\alpha-1$, $\alpha-2$, and $\beta-1$ alone cannot give the proper spin symmetry. However, examination of Tables 4 and 5 unmistakably indicates that, as long as the practical purpose is concerned, the orbitals $\beta-1$ and $\alpha-2$ are equivalent and so are the pair $\alpha-3$ with $\beta-2$ and that between $\alpha-4$ and $\beta-3$ in spite of the fact that ϕ_3 is entirely absent from β-orbitals. The detail of the electron density distribution of these orbitals shows discrepancies to certain extent, of course. Especially where the density is low, *e.g.*, the lower part of $\alpha-3$ and $\beta-2$, one set can be twice or three times as large as the other. However, these discrepancies are practically insignificant as can be seen from Table 4, especially the last column. If the original wave function were constructed such as to include ϕ_3 also in the β-orbitals, one would be able to expect an even closer similarity for these pairs. Therefore, it should not be unreasonable to expect that at least the first two spin-adapted natural orbitals [7] would be very similar to the $\alpha-2$ (or equivalently $\beta-1$) and $\alpha-1$ of this report. Spin properties set aside, it should be a sufficiently good approximation to use the first configuration formed of the spin-polarized natural orbitals in analysis of the electronic structure.

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