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Analysis of the ^2S Ground State of Lithium in Terms of Natural and Best Overlap (Brueckner) Spin Orbitals with Implications for the Fermi Contact Term*

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Some very accurate wave functions (containing explicitly r_{ij} terms) for the ^2S ground state of Lithium have been analyzed in terms of natural spin orbitals (NSO) and best overlap orbitals (BO). Comparison of BO's determined from a wave function giving 99.9% of the correlation energy with the spin-polarized Hartree-Fock orbitals (HF), revealed very small differences at least for the core orbitals. The difference between BO's and NSO's was significant but negligible. The BO's can be transformed unitarily among themselves and such a transformation was made before the comparison to make the orbitals fit as much as possible. The calculation of the Fermi contact term in the hyperfine structure of the spectrum has been discussed and it was found that the small difference between the HF value and the exact value could be accounted for, to a large extent, by the difference between HF and BO (or NSO). The pure correlation effects were found to be only about 0.5%. The separated valence orbital model has been analyzed on the basis of the NSO results and it has been shown that the eigenvalues (except the largest one) are degenerate in pairs for this model and that the corresponding NSO's have the same spatial factor, if orthogonality is assumed between the valence orbital and the singlet core. It has been shown that this orthogonality constraint has serious consequences for the Fermi contact term.

I. INTRODUCTION

Natural spin orbitals (NSO), introduced by Löwdin,[1] are the eigenfunctions of an integral operator γ_ψ with the kernel

$$\gamma_\psi(1,1')=N\int\psi(1,2,\ldots,N)$$
$$\times\psi^*(1',2,\ldots,N)d2\cdots dN. \tag{1}$$

The kernel or one-particle density matrix[2] can be expanded in terms of its eigenfunctions and eigenvalues

$$\gamma_\psi(1,1')=\sum_i\nu_i\chi_i(1)\chi_i^*(1'). \tag{2}$$

In this expansion, we order the terms so that $\nu_i \leqslant \nu_j$ for $i>j$. The eigenvalues ν_i are interpreted as occupation numbers[1] of the eigenfunctions (NSO) χ_i.

The antisymmetric wave function ψ can be expanded in terms of antisymmetrized products of NSO's.[3] This expansion, called the natural expansion of ψ is known to give a rapid convergence. Analysis of wave functions in terms of natural spin orbitals indicates the relative importance of various spin orbitals in the description of the state and provides a method of comparison among approximate wave functions which is more thorough than, for example, energy comparison.

In this paper we analyze some wave functions for the ^2S ground state of atomic lithium, all of which contain explicitly interelectronic distance coordinates r_{ij}. An accurate wave function of this kind was first given for Li (^2S) by James and Coolidge[4] and we examine a wave function which we have recalculated with the same basis as they used. Recently a number of wave functions of high accuracy have been given by one of us.[5] These wave functions and those of James and Coolidge are calculated from a basis of nonorthogonal Hylleraas functions

$$\psi=\mathfrak{A}_3\sum C(i,j,k,l,m,n,a,b,c)$$
$$\times r_1^{\,i}r_2^{\,j}r_3^{\,k}r_{23}^{\,l}r_{13}^{\,m}r_{12}^{\,n}e^{-ar_1-br_2-cr_3}$$
$$\times\{A_1[\alpha(\zeta_1)\beta(\zeta_2)\alpha(\zeta_3)-\beta(\zeta_1)\alpha(\zeta_2)\alpha(\zeta_3)$$
$$+A_2[2\,\alpha(\zeta_1)\alpha(\zeta_2)\beta(\zeta_3)-\alpha(\zeta_1)\beta(\zeta_2)\alpha(\zeta_3)$$
$$-\beta(\zeta_1)\alpha(\zeta_2)\alpha(\zeta_3)]\}. \tag{3}$$

$\mathfrak{A}_3$ is the three-particle antisymmetrizer

$$\mathfrak{A}_3=6^{-1/2}[e-(12)-(13)-(23)+(123)+(132)]. \tag{4}$$

A_1, A_2, and the C's are linear parameters varied to minimize the energy according to the variation principle. i, j, k, l, m, n are non-negative integers; a, b, c are real positive numbers; α and β are the usual one-electron spin functions. The wave functions are listed in Tables I–III, and data for them in Table IV.

The natural spin orbitals and natural p-states (eigenfunctions to the p-particle reduced density matrix) are closely connected to the problem of approximation of a function of a certain number of variables by functions of a fewer number of variables. Of special interest is the approximation by a single Slater determinant of an N-electron wave function. For two-electron wave functions, the best approximation in the sense of minimizing the distance in Hilbert space between the wave function and the Slater determinant is the determinant of the two NSO's with largest oc-

TABLE I. The James-Coolidge wave function $W2$ with spin function $S_1 = \alpha\beta\alpha - \beta\alpha\alpha$.

$ijklmn$	a	b	c	Coefficient × $(4\pi)^{3/2}$
001000	3.0	3.0	0.65	−10.643 710 407 9
101000	3.0	3.0	0.65	−1.113 528 244 9
201000	3.0	3.0	0.65	−9.200 421 354 0
111000	3.0	3.0	0.65	2.759 269 138 7
001001	3.0	3.0	0.65	−5.715 625 243 3
001002	3.0	3.0	0.65	0.744 322 515 6
000000	3.0	3.0	1.5	9.414 557 716 8
100000	3.0	3.0	1.5	4.335 242 272 9
000100	3.0	3.0	0.65	−4.315 610 138 5

cupation numbers.[6] For an N-electron system ($N > 2$), the best determinant of this kind is no longer formed from the first N NSO's.[7] The criterion of minimum distance between the true wave function and a determinantal wave function is equivalent to the criterion of best overlap with the true wave function. The spin orbitals with this property are called best overlap orbitals,[7] Brueckner orbitals,[8] or exact self-consistent field orbitals.[9] A review of the theory of approximation which is relevant in our case is given in Sec. II.

To simplify the calculation, γ_ψ has been expanded in terms of a finite set of one-electron functions. γ_ψ is then represented by an ordinary matrix which may be diagonalized in the usual manner to find its eigenvalues and eigenfunctions. The error made by employing the finite basis set will be quite small. When comparisons are made among the various types of spin orbitals (natural, best overlap, and Hartree-Fock) the same basis sets are employed. The method of calculation is further discussed in Sec. III.

In Secs. IV, V, and VI, we present the results of our calculations. It is evident that the correlation effect that contributes most to energy is from the core. For all the wave functions examined, core correlation has been taken into account. The occupation numbers of the core spin orbitals will decrease therefore below 1, their value in the independent particle model. Of more interest is the polarizing effect of the valence electron. The wave function of an alkali atom can be well approximated by the separated va-

TABLE II. The wave functions $W1$, $W3$, $W4$, with $a = 2.76$, $b = 2.76$, $c = 0.65$; and with spin functions $S_1 = \alpha\beta\alpha - \beta\alpha\alpha$, $S_2 = 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha$.

	Spin	Coefficients × $(4\pi)^{3/2}$		
$ijklmn$	function	$W1$	$W3$	$W4$
001000	S_1	14.543 994 149 9	19.020 268 940 8	19.016 331 912 0
101000	S_1	−4.165 412 922 5	−7.872 169 612 3	−7.678 122 742 0
111000	S_1	−3.282 812 933 4	−4.197 309 092 3	−4.220 996 386 4
201000	S_1	5.620 423 214 9	7.236 548 912 4	7.257 004 795 0
001001	S_1	5.095 292 737 1	6.014 347 888 2	6.009 603 266 1
001002	S_1	−1.027 971 227 6	−2.491 848 642 4	−2.494 337 068 9
000000	S_1		−9.569 075 147 4	−9.556 748 430 0
000100	S_1		3.313 694 775 7	3.225 448 096 1
002000	S_1		−0.931 115 368 5	−0.950 048 618 5
010100	S_1		3.552 982 565 5	3.353 122 272 4
001003	S_1		0.676 158 561 7	0.676 176 323 2
001100	S_1		−0.775 495 154 8	−0.720 836 970 3
003000	S_1		0.093 281 545 2	0.090 164 947 3
101001	S_1		−0.549 611 415 9	−0.542 928 688 7
301000	S_1		−0.819 529 852 6	−0.835 448 695 6
001004	S_1		−0.092 725 813 0	−0.092 717 266 5
221000	S_1		−0.590 020 574 9	−0.588 919 581 8
111001	S_1		1.240 066 456 6	1.250 014 760 0
101000	S_2			−0.434 196 656 3
201000	S_2			0.015 492 264 8
000100	S_2			0.151 170 974 1
010100	S_2			−0.353 822 498 0
001100	S_2			0.016 520 368 5
101001	S_2			0.028 842 545 9
301000	S_2			0.001 243 502 9

TABLE III. The wave function $W5$ with $a=b=2.76$, $c=0.65$, and with spin functions $S_1=\alpha\beta\alpha-\beta\alpha\alpha$, $S_2=2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha$.

ijklmn	Spin function	Coefficient × $(4\pi)^{3/2}$
001000	S_1	18.399 076 696 0
101000	S_1	−10.990 201 721 9
101000	S_2	0.794 530 807 2
111000	S_1	−5.715 778 773 5
201000	S_1	10.028 857 193 9
201000	S_2	−0.786 612 639 3
001001	S_1	6.166 944 535 0
001002	S_1	−4.779 701 653 6
000000	S_1	−8.194 349 267 8
000100	S_1	2.774 509 982 1
000100	S_2	0.665 987 347 1
002000	S_1	−1.326 226 113 5
010100	S_1	3.853 265 813 7
010100	S_2	0.354 379 863 2
001003	S_1	2.606 582 249 2
001100	S_1	0.659 600 651 4
001100	S_2	−0.333 384 677 9
003000	S_1	0.105 294 288 0
101001	S_1	3.740 262 289 3
101001	S_2	0.225 662 178 5
301000	S_1	0.004 566 841 8
301000	S_2	0.234 346 117 4
001004	S_1	−0.685 698 632 3
221000	S_1	−0.194 497 298 2
111001	S_1	1.998 064 875 4
201001	S_1	−8.717 712 058 9
201001	S_2	−0.076 472 268 9
301001	S_1	2.745 674 540 5
301001	S_2	0.023 438 907 5
000200	S_1	−0.919 152 501 7
000200	S_2	−0.074 864 458 8
000110	S_1	0.220 034 065 1
020100	S_1	1.174 575 908 7
020100	S_2	−0.355 736 980 1
110100	S_1	−0.924 533 400 1
110100	S_2	0.141 720 279 2
004000	S_1	0.001 929 704 1
000001	S_1	−1.261 334 050 5
002001	S_1	−0.145 076 963 9
100000	S_1	4.001 783 191 6
100000	S_2	−0.979 872 733 9
102000	S_1	0.382 893 268 1
102000	S_2	−0.199 584 475 7
000101	S_1	0.771 383 346 5
000101	S_2	−0.038 067 071 5
010200	S_1	−0.581 325 295 7
010200	S_2	0.056 786 222 4
011100	S_1	0.472 935 788 2
011100	S_2	−0.229 326 528 4
000300	S_1	0.160 970 314 0
000300	S_2	−0.002 277 475 4
001200	S_1	−0.206 459 256 4
001200	S_2	0.057 621 814 5
001005	S_1	0.175 615 317 9
401000	S_1	−0.916 838 721 3
401000	S_2	−0.058 107 620 6
401001	S_1	−0.067 592 188 3
401001	S_2	0.000 388 306 9
501000	S_1	0.141 100 103 8
501000	S_2	0.010 721 539 4
101002	S_1	1.807 968 432 9
101002	S_2	0.022 375 551 2
201002	S_1	1.470 564 528 2
201002	S_2	−0.031 377 324 2
101003	S_1	−1.676 378 275 6
101003	S_2	−0.009 338 850 7
110000	S_1	0.280 985 449 1
112000	S_1	0.074 939 590 9
200000	S_1	−2.860 411 424 7
200000	S_2	0.996 194 949 4
202000	S_1	−0.234 365 137 3
202000	S_2	0.151 847 972 2
100001	S_1	0.138 284 729 8
100001	S_2	−0.644 949 770 9
102001	S_1	0.017 427 944 3
102001	S_2	−0.017 303 136 8
200001	S_1	−0.487 584 458 4
200001	S_2	0.409 385 595 8
021100	S_1	−0.058 805 122 0
021100	S_2	0.124 294 966 7
030100	S_1	−0.005 858 032 5
030100	S_2	−0.069 303 195 4
201003	S_1	0.454 313 197 6
201003	S_2	0.009 277 178 3
005000	S_1	−0.000 180 254 0
211000	S_1	0.261 131 201 8
211000	S_2	−0.022 676 708 1
001006	S_1	−0.015 616 119 3
302000	S_1	0.068 269 776 6
302000	S_2	−0.012 812 929 2
300000	S_1	0.974 231 786 8
300000	S_2	−0.658 987 997 0
000400	S_1	0.000 076 424 6
000400	S_2	−0.001 718 501 4
100100	S_1	−0.095 088 420 0
100100	S_2	−0.085 509 286 6
311000	S_1	−0.085 868 098 2
311000	S_2	0.012 109 573 3
301002	S_1	−0.757 605 003 8
301002	S_2	−0.005 301 396 0

TABLE IV. Properties of the wave functions examined.

Wave function	$W1^5$	$W2^4$	$W3^5$	$W4^5$	$W5^5$
Number of terms	6	9	18	25	100
$-$Energy[a] (a.u.)	7.473 999	7.476 098	7.477 665	7.477 683	7.478 025
Error, % of correlation energy	8.98	4.35	0.89	0.85	0.10
Fermi contact term[b]	3.516	2.812	3.155	2.911	2.906
Overlap between HF[c] and wave function	0.997 949	0.997 928	0.998 138	0.998 133	0.998 098

[a] The corresponding experimental value is $-7.478\,069$ a.u. (see Ref. 45).

[b] Experimental value 2.906 (see Ref. 5).

[c] Orbital basis $r^i \exp(-ar)$, $i=0,1,2,3$; $a=0.65$, 2.76.

lence-orbital model, where the core is described by a two-electron wave function $\phi(1,2)$ and the valence electron by a spin orbital $\varphi(3)$

$$\psi = \mathcal{A}_3[\phi(1,2)\varphi(3)]\,. \tag{5}$$

ϕ is assumed to be antisymmetrized and a spin singlet, i.e., ϕ can be a wave function for the two-electron ion Li$^+$. In Sec. IV, we study particularly how the behavior of the occupation numbers and the NSO's are related to the orthogonality condition between ϕ and φ.

Section V contains a numerical comparison among the first-three NSO's, the best overlap orbitals and the Hartree-Fock orbitals. The relationship between the latter and the first-three NSO's may be discussed[10, 11] on the basis of a theorem[10] which says that they are the same after a unitary transformation to the second order in a perturbation expansion.[12] This is true only for the spin-polarized Hartree-Fock orbitals (HF) for which the two core spin orbitals have different spatial functions.[13] The Brueckner orbitals play an important role in many-particle theories of atomic and molecular systems. They are usually assumed to be very similar to the Hartree-Fock orbitals.[14]

In Sec. VI, we discuss the calculation of the Fermi contact term f, which is responsible for the hyperfine structure of atomic S states.[15, 16]

$$f = \left\langle 4\pi \sum_{i=1}^{3} \delta(\vec{r}_i)\sigma_{z_i} \right\rangle, \tag{6}$$

where δ is the three-dimensional Dirac delta function and σ_{z_i} the usual Pauli spin operator with the properties

$$\sigma_{z_i}\alpha(\zeta_i) = \alpha(\zeta_i); \quad \sigma_{z_i}\beta(\zeta_i) = -\beta(\zeta_i)\,. \tag{7}$$

If the wave function describing the state is approximated by a Slater determinant of spin orbitals, $\det(\varphi_{1s}\alpha, \varphi_{1s'}\beta, \varphi_{2s}\alpha)$ the Fermi contact term f is

$$f = 4\pi[\varphi_{1s}{}^2(0) - \varphi_{1s'}{}^2(0) + \varphi_{2s}{}^2(0)]\,. \tag{8}$$

The energy of the Slater determinant can be minimized by solving the Hartree-Fock equations with or without the restriction $\varphi_{1s} = \varphi_{1s}'$. In the first case (restricted Hartree-Fock, RHF) we find an f value only 70% of the experimental value.[16] The contribution from the core orbitals $\varphi_{1s}\alpha$ and $\varphi_{1s}\beta$ cancel. In the second case the exchange term between the two α orbitals has been taken into account. We then have different equations for the spatial parts of the core orbitals, and a splitting or polarization of the core. The contribution to f from the valence orbital $\varphi_{2s}\alpha$ changes only slightly from RHF, but we get an additional contribution from the core, so that f now is 97% of the experimental value. We speak in this case of spin-polarized or exchange-polarized Hartree-Fock.[17]

Due to this splitting the determinantal wave function is not a pure ^2S state as is the true wave function. Various aspects of this problem have been discussed extensively in the literature. The validity of the exchange polarized Hartree-Fock method has been questioned. Of interest to us has been a paper by Berggren and Wood[18] who calculated f for a number of the wave functions of James and Coolidge. They found 98.8% of the exact value of f for a wave function which was incorrectly said to have a symmetric core. It will be evident from the analysis in Sec. IV that this wave function is not restricted in any sense with respect to symmetry of the core and thus should give good values. Our analysis in Sec. VI will also show that contributions to the Fermi contact term from pure correlation effects are small.

II. THEORY

We are interested in the approximation of an N-particle wave function ψ by a function ϕ which can be written in terms of functions ξ of a fewer number of particles.

$$\phi(1,2,\ldots,N)=\sum_{i=1}^{M} c_i\xi_{1i}(s_1)\xi_{2i}(s_2)\cdots\xi_{li}(s_l). \tag{9}$$

The N-particle coordinate space has been partitioned into subsets of $q_1, q_2, \ldots q_l$ particles ($\sum q_i = N$) with the coordinates $s_1, \ldots, s_l$, respectively. ϕ is a subset of the Hilbert space usually called the Grassman manifold $G_M{}^l$. The case $\phi\in G_1{}^N$ is thus the familiar approximation in the form of a Hartree product of one-particle functions (spin orbitals), i.e.,

$$\phi(1,2,\ldots,N)=\xi_1(1)\xi_2(2)\cdots\xi_N(N). \tag{10}$$

To choose the best approximating function, we shall minimize

$$\delta=\|\psi-x\phi\|, \tag{11}$$

where x is a real variable. The problem has been considered by Schmidt,[19] Golomb,[20] and others.[21] We consider the case $\phi\in G_1{}^l$. The minimum error δ is obtained when the functions ξ are solutions of the integral equation system

$$\int\psi(1,2,\ldots,N)\xi_1^*(s_1)\cdots\xi_{j-1}^*(s_{j-1})\xi_{j+1}^*(s_{j+1})\cdots \times\xi_l^*(s_l)ds_1\cdots ds_{j-1}ds_{j+1}\cdots ds_l=c\xi_j(s_j),\quad j=1,2,\ldots,l; \tag{12}$$

for the largest c for which such solutions exist. For the case $l=2$ we have the linear homogeneous equation system[22]

$$\int\psi(s_1,s_2)\xi_1^*(s_1)ds_1=c\xi_2(s_2),\quad \int\psi(s_1,s_2)\xi_2^*(s_2)ds_2=c\xi_1(s_1). \tag{13}$$

By eliminating ξ_2 we obtain

$$\int\psi(s_1,s_2)\psi^*(s_3,s_2)\xi_1(s_3)ds_3ds_2=c^2\xi_1(s_1). \tag{14}$$

Thus ξ_1 is an eigenfunction of the p particle reduced density matrix[23]

$$\Gamma^{(p)}(s_1,s_3)=\binom{N}{p}\int\psi(s_1,s_2)\psi^*(s_3,s_2)ds_2. \tag{15}$$

In the same way, ξ_2 is an eigenfunction of the $(N-p)$-particle reduced density matrix $\Gamma^{(N-p)}$. In both cases the eigenvalue is

$$c^2\binom{N}{p}=c^2\binom{N}{N-p}\ .$$

Thus to obtain the minimum error (11), we only need to solve the linear eigenvalue problem (14). In general ($l>2$) Eq. (11) has, however, to be solved by an iteration method with starting functions sufficiently close to the solutions.[20]

For a system of fermions, ψ is antisymmetric and we wish the approximation (9) to consist of antisymmetrized products. We consider the case $\phi\in G_1{}^N$. Equation (11) can be written

$$\delta^2=\|\psi\|^2+\|\phi\|^2(x-\langle\psi|\phi\rangle/\|\phi\|^2)^2-\langle\psi|\phi\rangle^2/\|\phi\|^2\,. \tag{16}$$

We can choose x independently of ϕ so that the second term vanishes. The minimum error is thus obtained when $\langle\psi|\phi\rangle^2/\|\phi\|^2$ is a maximum. The spin orbitals ξ in the Hartree product which gives the best overlap with ψ are thus the solutions of (12). Since ψ is antisymmetric it follows easily from (12) that the spin orbitals ξ are orthogonal.

We now antisymmetrize ϕ with the antisymmetrizer

$$\mathcal{A}_N=(N!)^{-1/2}\sum_P(-1)^pP, \tag{17}$$

where P is a permutation with parity p of the N particles. $\mathcal{A}_N$ satisfies

$$\mathcal{A}_N{}^2 = (N!)^{1/2}\mathcal{A}_N = (N!)^{1/2}\mathcal{A}_N{}^\dagger . \tag{18}$$

Instead of (11) we want to minimize the error

$$\delta^2 = \|\psi - x\mathcal{A}_N\phi\|^2 = \|\psi\|^2 + \|\mathcal{A}_N\phi\|^2(x - \langle\psi|\mathcal{A}_N\phi\rangle/\|\mathcal{A}_N\phi\|^2)^2 - \langle\psi|\mathcal{A}_N\phi\rangle^2/\|\mathcal{A}_N\phi\|^2 . \tag{19}$$

We choose x so that the second term is zero. The spin orbitals in the Slater determinant can be transformed linearly among themselves without changing the value of the third term and we can then assume that the spin orbitals are orthogonal. From (18) it follows for antisymmetric ψ that

$$\langle\psi|\mathcal{A}_N\phi\rangle = \sqrt{N!}\,\langle\psi|\phi\rangle\ ; \quad \|\mathcal{A}_N\phi\|^2 = \|\phi\|^2. \tag{20}$$

Therefore $\delta_{\min}{}^2 = \|\psi\|^2 - N!\,\langle\psi|\phi\rangle^2/\|\phi\|^2.$ (21)

The minimum error is thus obtained for the same ϕ as before, i.e., the N spin orbitals in the Slater determinant which gives best overlap with ψ are solutions of (12).[24] They are determined up to a unitary transformation among themselves.

We now assume that ψ, the Hartree product ϕ and the Slater determinant $\phi_0 \equiv \mathcal{A}_N\phi$ are all normalized to unity. Then the minimum error when we approximate ψ by the Hartree product ϕ is from Eq. (16)

$$\delta_{\min}{}^2 = 1 - \langle\psi|\phi\rangle^2. \tag{22}$$

If instead we approximate ψ with the Slater determinant ϕ_0 we obtain from Eq. (21)

$$\delta_{\min}{}^2 = 1 - \langle\psi|\phi\rangle^2 N! = 1 - \langle\psi|\phi_0\rangle^2, \tag{23}$$

which is a considerable improvement.

The best overlap determinant has the useful property when used in an expansion of the wave function ψ in Slater determinants that determinants which are singly substituted with respect to it are not present.[7,8,25] To see this we add orthogonal spin orbitals φ_a, φ_b, ... to the best overlap set $\{\xi_1, \xi_2, \cdots, \xi_N\}$ and substitute φ's in ϕ_0 for ξ's. The singly substituted determinants are then orthogonal to ψ, so that the expansion coefficient $c_i{}^a$ for such a determinant is zero. Using Eq. (12)

$$c_i{}^a = \int \psi(1,2,\ldots,N)\xi_1{}^*(1)\cdots\xi_{i-1}{}^*(i-1)\varphi_a{}^*(i)\xi_{i+1}{}^*(i+1)\cdots$$
$$\times\xi_N{}^*(N)d1\cdots dN = c\int\xi_i(i)\varphi_a{}^*(i)di = 0. \tag{24}$$

This necessary condition for the best overlap orbitals is sometimes called the Brueckner condition[8] and the determinant ϕ_0 the Brueckner determinant. Notice that this determinant is not always unique, i.e., there may be more than one determinant whose orbitals satisfy (12). The condition is not sufficient for we may construct a wave function containing a determinant with orbitals satisfying (24) but not (12) for the largest possible c. If certain conditions are satisfied the Brueckner determinant or, in case of degeneracy, the set of Brueckner determinants is uniquely determined.[26] The exact self-consistent-field orbitals of Löwdin[9] satisfy (24) and these additional conditions and are thus best overlap orbitals. In our case the best overlap determinant is uniquely determined. In the following we will use interchangeably the terms best overlap, Brueckner, and exact self-consistent-field orbitals. They are as was pointed out before determined only up to a unitary transformation among themselves.

For two particles the best overlap orbitals are obviously also natural spin orbitals and solutions to Eq. (14). They are in general not the same as the first N natural spin orbitals[7] although they can be very similar.

For three particles, the best approximation $\phi\in G_1{}^2$ is the product of the first natural spin orbital and the first natural spin geminal (eigenfunction of $\Gamma^{(2)}$). The natural spin geminals (NSG) and the NSO's have for $N=3$ the same eigenvalues. The occupation numbers given in Table V are thus occupation numbers both for NSO's and for NSG's.

III. METHOD OF CALCULATION

Since ψ is an eigenfunction of L^2 with eigenvalue zero and of L_z and S_z, the natural spin orbitals are or can be chosen to be of the form[27]

$$\chi_i(r,\Theta,\varphi,\zeta) = R_i(r)Y_{lm_l}(\Theta,\varphi)\begin{Bmatrix}\alpha(\zeta)\\ \beta(\zeta)\end{Bmatrix}, \tag{25}$$

TABLE V. Occupation numbers multiplied by $2l+1$.

Orbital	$W1$	$W2$	$W3$	$W4$
$s0\alpha$	1.000 000	0.999 744	0.999 515	0.999 504
$s1\alpha$	0.996 789	0.996 827	0.996 664	0.996 679
$s1\beta$	0.996 789	0.996 791	0.996 507	0.996 479
$p1\alpha$	0.001 739	0.001 791	0.001 819	0.001 816
$p1\beta$	0.001 739	0.001 789	0.001 861	0.001 871
$s2\alpha$	0.001 312	0.001 288	0.001 325	0.001 327
$s2\beta$	0.001 312	0.001 286	0.001 317	0.001 319
$d1\alpha$	0.000 095	0.000 061	0.000 099	0.000 100
$d1\beta$	0.000 095	0.000 061	0.000 100	0.000 100
$p2\alpha$	0.000 025	0.000 226	0.000 402	0.000 408
$p2\beta$	0.000 025	0.000 031	0.000 131	0.000 143
$s3\alpha$	0.000 012	0.000 012	0.000 030	0.000 031
$s3\beta$	0.000 012	0.000 012	0.000 032	0.000 033
$f1\alpha$	0.000 008	0.000 006	0.000 010	0.000 011
$f1\beta$	0.000 008	0.000 006	0.000 011	0.000 011
$d2\alpha$	0.000 006	0.000 005	0.000 010	0.000 010
$d2\beta$	0.000 006	0.000 004	0.000 009	0.000 009
$p3\alpha$	0.000 001	0.000 027	0.000 089	0.000 081
$p3\beta$	0.000 001	0.000 003	0.000 011	0.000 012
$s4\alpha$	0.000 001	0.000 001	0.000 003	0.000 003
$s4\beta$	0.000 001	0.000 001	0.000 002	0.000 002
$p4\alpha$	• • •	0.000 002	0.000 008	0.000 008
$p4\beta$	• • •	• • •	0.000 001	0.000 001
$d3\alpha$	• • •	0.000 001	0.000 003	0.000 003
$d3\beta$	• • •	• • •	0.000 001	0.000 001
$f2\alpha$	• • •	0.000 001	0.000 001	0.000 001
$f2\beta$	• • •	0.000 001	0.000 001	0.000 001
$s5\alpha$	• • •	• • •	0.000 002	0.000 002
$p5\alpha$	• • •	• • •	0.000 001	0.000 001
Sum	2.999 976	2.999 986	2.999 965	2.999 967

where the Y_{lm_l} are the usual spherical harmonics. The eigenvalue problem for γ_ψ is block diagonal with one α and one β block. These are further divided into blocks characterized by the value of l, and each l block into $(2l+1)$ m_l-blocks. Within each block we determine the radial function $R_i(r)$ by expansion in a finite set of basis functions

$$R_i(r) = \sum_{j=1}^{M} c_j r^{n_j} \exp(-a_j r). \tag{26}$$

This basis set is the same for all blocks with the same l value. The c_j are determined from the matrix eigenvalue problem

$$(\underline{\gamma} - \nu\underline{\Delta})\underline{c} = 0,$$

$$\gamma_{ij} = \int r_1^{\nu_i} e^{-a_i r_1} Y_{lm_l}(\Theta_1,\varphi_1) \begin{Bmatrix}\alpha(\zeta_1)\\ \beta(\zeta_1)\end{Bmatrix} \gamma(1,2) r_2^{\nu_j} e^{-a_j r_2} Y_{lm_l}(\Theta_2,\varphi_2) \begin{Bmatrix}\alpha(\zeta_2)\\ \beta(\zeta_2)\end{Bmatrix} d1d2, \tag{27}$$

$$\Delta_{ij} = \int r_1^{\nu_i+\nu_j} \exp[-(a_i+a_j)r_1] r_1^2 dr_1. \tag{28}$$

The eigenvalues and eigenvectors of the matrix $\underline{\gamma}$ obtained from (27) will tend to the true eigenvalues and eigenvectors of $\gamma(1,1')$ when we extend the basis towards completeness. The eigenvalues ν in (27) will always be lower bounds to the true eigenvalues.[28] The calculation of the matrix elements is described in an Appendix. The eigenvalue problem (27) was solved in double precision by well-known methods.[29] The basis in (26) was for *s*, *p*, and *d* orbitals of the dimension $M=8$ and for *f* orbitals of the dimension $M=6$. The exponents were the same as in the wave function from which $\underline{\gamma}$ was constructed, thus 0.65 and 3.0 for the James and Coolidge wave function and 0.65 and 2.76 for the others. The radial part of the NSO's behave like r^l for small r. Since the basis set used for *s* orbitals is not complete we cannot reproduce exactly the r^l behavior with this basis set. We therefore used the powers r^l, r^{l+1}, r^{l+2}, r^{l+3}. For comparison we used for the James and Coolidge wave function the *s* basis set also for $l>0$. This basis set is better in the sense that it gives eigenvalues that are closer to the exact ones. The sum of the eigenvalues is here 2.999 986 compared to 3.0 for the sum of the exact eigenvalues.

IV. BEHAVIOR OF OCCUPATION NUMBERS AND NSO'S FOR DIFFERENT MODEL WAVE FUNCTIONS

The calculated occupation numbers are given in Table V and some of the NSO's for the wave function *W*4 are given in Table VI and plotted in Figs. 1 and 2.

A. Separated Valence-Orbital Model

*W*1 can be written in the form

$$\psi=\mathfrak{A}_3\{\phi(\vec{r}_1,\vec{r}_2)[\alpha(\zeta_1)\beta(\zeta_2)-\beta(\zeta_1)\alpha(\zeta_2)]\varphi(\vec{r}_3)\alpha(\zeta_3)\}\,. \tag{29}$$

Thus it corresponds to a model with an electron moving independently in a valence orbital outside a core. Such a model can be expected to be a good description of an alkali atom. This has been verified by some calculations.[30,31] Our wave function *W*1 is of this kind but it has only a very simple description of the valence spin orbital, namely a single Slater-type 2*s* orbital. We expect that a better outer orbital as well as a better core would yield an improved energy. The core spatial function can be symmetrized in $\vec{r}_1$ and $\vec{r}_2$. This is no restriction since its antisymmetric part will vanish when the antisymmetrizer is applied.

A model function of this kind has a density matrix with one eigenvalue equal to one and the corresponding eigenfunction $\varphi(\vec{r}_3)\alpha(\zeta_3)$. The other eigenvalues are degenerate in pairs. The NSO's corresponding to one pair can be chosen as eigenfunctions to S_z. Their radial parts are the same if ϕ and φ are orthogonal, i.e.,

$$\int\phi(\vec{r}_1,\vec{r}_2)\varphi(\vec{r}_2)dv_2=0. \tag{30}$$

To prove the above we write (29) as

$$\psi=12^{-1/2}\mathfrak{A}_3[g(1,2)h(3)]\,, \tag{31}$$

where h and ψ are normalized to one. g is an antisymmetric singlet wave function, so that ψ is of type (29). g' is the part of g which is orthogonal to h

$$\begin{aligned}g'(1,2)&=g(1,2)-\int g(1,3)h^*(3)d3\,h(2)\\&\quad-\int g(3,2)h^*(3)d3\,h(1)\\&=g(1,2)-d(1)h(2)+d(2)h(1),\end{aligned} \tag{32}$$

$$\text{where}\quad d(1)=\int g(1,3)h^*(3)d3. \tag{33}$$

Since g is antisymmetric

$$\int d(1)h^*(1)d1=\int g(1,2)h^*(1)h^*(2)d1d2=0. \tag{34}$$

It follows that

$$\int g'(1,2)h^*(1)d1=0\,. \tag{35}$$

TABLE VI. Eigenvectors from *W*4 given in the basis $u_{ia}(r)=(4\pi)^{-1}r^{i+l}\exp(-ar)$, (coefficients truncated to six significant figures).

	$a=0.65$				$a=2.76$			
i	0	1	2	3	0	1	2	3
$s0\alpha$	−0.221 668	0.581 420 6	−0.039 547 9	0.002 135 68	−0.258 32	0.160 29	−0.340 61	0.066 11
$s1\alpha$	−0.096 115	0.093 421	−0.008 403 5	0.000 408 93	−9.251 95	2.038 18	−2.900 73	0.706 98
$s1\beta$	0.083 565	−0.036 879	0.005 214 5	−0.000 233 40	9.120 54	−2.013 08	2.900 59	−0.699 44
$p1\alpha$	0.049 373	−0.020 703 1	0.002 738 39	−0.000 111 926	−29.462 13	25.777 10	−9.684 36	1.095 55
$p1\beta$	0.048 013	−0.020 832 7	0.002 738 35	−0.000 111 527	−28.741 25	24.551 31	−9.291 33	1.054 47
$s2\alpha$	2.080 837	−1.076 161	0.140 901 2	−0.006 488 83	−18.731 19	24.725 71	6.044 54	−7.850 02
$s2\beta$	1.852 332	−0.828 751	0.118 168 7	−0.005 337 02	−18.444 04	24.657 55	5.015 52	−7.248 59
$d1\alpha$	−0.204 258 8	0.067 631 50	−0.007 127 182	0.000 238 217 3	−85.913 75	128.486 59	−66.758 60	12.419 446
$d1\beta$	−0.203 584 2	0.067 347 03	−0.007 093 056	0.000 236 983 9	−85.259 48	127.280 07	−66.145 03	12.299 392
$p2\alpha$	0.711 549	−0.171 211 0	0.013 941 67	−0.000 410 829	−19.488 64	27.094 07	−11.505 32	3.103 28
$p2\beta$	−0.531 052	0.203 468 4	−0.024 430 30	0.000 925 366	−57.847 34	124.413 74	−67.301 60	14.885 31
$s3\alpha$	−3.341 896	1.639 654	−0.212 297 0	0.009 566 43	−26.118 35	135.323 04	−126.978 46	32.910 13
$s3\beta$	2.137 931	−0.852 738	0.107 790 2	−0.004 381 96	25.992 21	−124.779 91	114.299 80	−27.452 70
$f1\alpha$	0.030 449 76	−0.006 602 942	0.000 336 184 4	• • •	−71.178 53	69.024 148	−16.513 81	• • •
$f1\beta$	0.030 261 54	−0.006 552 73	0.000 333 661 0	• • •	−70.884 98	68.638 08	−16.421 69	• • •
$d2\alpha$	−0.736 857 0	0.247 597 09	−0.026 404 914	0.000 891 071 3	−123.266 81	272.493 76	−170.251 86	36.595 989
$d2\beta$	−0.910 353 0	0.304 307 34	−0.032 333 636	0.001 088 400 7	−139.218 58	313.446 18	−198.961 56	42.783 053
$p3\alpha$	1.729 403	−0.555 453 4	0.061 010 16	−0.002 214 901	67.883 98	−170.698 80	103.634 70	−23.930 24
$p3\beta$	5.171 043	−1.945 553 3	0.234 545 09	−0.008 974 204	93.442 88	−331.923 98	285.819 24	−84.804 92

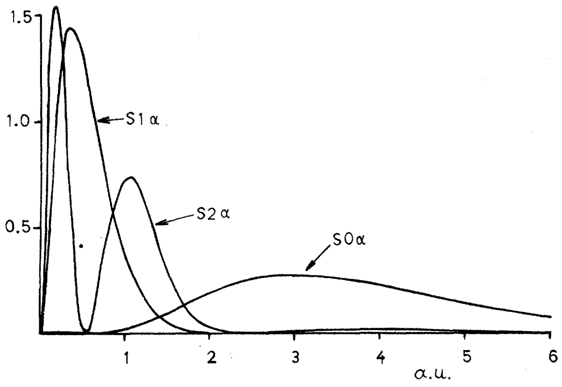

FIG. 1. Radial density distribution $4\pi r^2\chi^2(r)$ for the first NSO's of s type. The curve for $s1\beta$ and $s2\beta$ are similar to $s1\alpha$ and $s2\alpha$, respectively, but the latter orbitals have one more node and are nonzero ($s1\alpha$ curve ≈ 0.002, $s2\alpha$ curve ≈ 0.02) in the valence region.

We note that g' is antisymmetric but not a spin singlet. If we substitute the expression (32) for g in (31), we obtain

$$\psi(1,2,3)=12^{-1/2}\mathfrak{A}_3[g'(1,2)h(3)], \tag{36}$$

and

$$\gamma_\psi(1,1')=3\int\psi(1,2,3)\psi^*(1',2,3)d2d3$$
$$=2\int g'(1,2)g'^*(1',2)d2+h(1)h^*(1')$$
$$=\gamma_{g'}(1,1')+\gamma_h(1,1'). \tag{37}$$

It follows that h is an NSO of γ_ψ with the eigenvalue one.

To show the degeneracy of the eigenvalues of $\gamma_{g'}$ we use a theorem by Coleman.[3] Suppose a is an eigenfunction to $\gamma_{g'}$ with the eigenvalue λ, then the function b, defined by

$$b(1)=\int g'(1,2)a^*(2)d2, \tag{38}$$

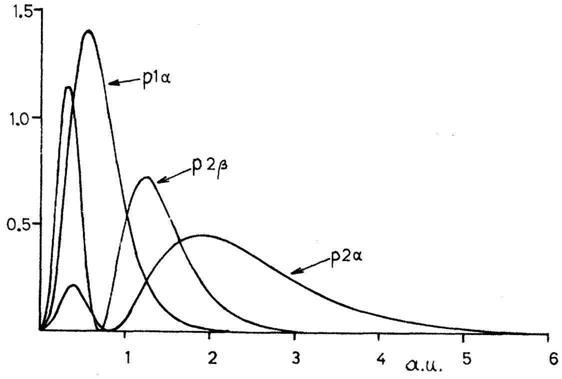

FIG. 2. Radial density distribution $4\pi r^2\chi^2(r)$ for the first NSO's of p type. The curve for $p1\beta$ is similar to $p1\alpha$, $p3\alpha$ is similar to $p2\beta$ but has one more node.

is also an eigenfunction to $\gamma_{g'}$ with the same eigenvalue λ:

$$\int\gamma_{g'}(1,1')b(1')d1'$$
$$=\int g'(1,3)g'^*(1',3)g'(1',2)a^*(2)d2d3d1'$$
$$=\int g'(1,3)\gamma_{g'}^*(3,2)a^*(2)d2d3$$
$$=\lambda\int g'(1,3)a^*(3)d3=\lambda b(1), \tag{39}$$

where we have used the antisymmetry of g'. Since $\gamma_{g'}$ and γ_ψ are both block diagonal with one α and one β block, we can choose a as an α spinfunction. It follows from (38) that b has β spin. Then a and b are two orthogonal eigenvectors for the degenerate eigenvalue λ.

If ϕ and φ are orthogonal as defined in (30) we have

$$g'=g$$

and
$$\gamma_{g'}=\gamma_g=\int\phi(\vec{r}_1,\vec{r}_2)\phi^*(\vec{r}_{1'},\vec{r}_2)dv_2$$
$$\times[\alpha(\zeta_1)\alpha(\zeta_{1'})+\beta(\zeta_1)\beta(\zeta_{1'})]. \tag{40}$$

Then both a and b have the spatial function $u(\vec{r})$, which is an eigenfunction to γ_ϕ

$$\int\phi(\vec{r}_1,\vec{r}_2)\phi^*(\vec{r}_{1'},\vec{r}_2)dv_2u(\vec{r}_{1'})dv_{1'}$$
$$=\lambda u(\vec{r}_1). \tag{41}$$

The theorem is illustrated by the results in Table IV. φ and ϕ are nonorthogonal for $W1$. The eigenvalues are degenerate in pairs but the NSO's corresponding to a degenerate eigenvalue have nonidentical spatial parts, which will be evident when we discuss the Fermi contact term in Sec. VI.

We want to examine in greater detail the importance of the overlap between the core function and the valence orbital. The function d defined by (33) can be written

$$d(1)=\int g'(1,2)h^*(2)d2$$
$$=-\int\phi(\vec{r}_1,\vec{r}_2)\varphi^*(\vec{r}_2)dv_2\beta(\zeta_1)$$
$$=-\tau(\vec{r}_1)\beta(\zeta_1). \tag{42}$$

The core function can be made orthogonal to the valence orbital φ

$$\phi'(\vec{r}_1,\vec{r}_2)=\phi(\vec{r}_1,\vec{r}_2)-\tau(\vec{r}_1)\varphi(\vec{r}_2)$$
$$-\varphi(\vec{r}_1)\tau(\vec{r}_2)+\langle\varphi|\tau\rangle\varphi(\vec{r}_1)\varphi(\vec{r}_2) \tag{43}$$

ϕ and ϕ' are symmetric in $\vec{r}_1$ and $\vec{r}_2$. The separated valence orbital wave function can now be written

$$\psi=\mathfrak{A}_3[\phi(\vec{r}_1,\vec{r}_2)(\alpha\beta-\beta\alpha)\varphi(\vec{r}_3)\alpha(\zeta_3)]$$
$$=\mathfrak{A}_3[\phi'(\vec{r}_1,\vec{r}_2)(\alpha\beta-\beta\alpha)\varphi(\vec{r}_3)\alpha(\zeta_3)]$$

$$-2\mathcal{A}_3[\varphi(\vec{r}_1)\alpha(\zeta_1)\varphi(\vec{r}_2)\beta(\zeta_2)\tau(\vec{r}_3)\alpha(\zeta_3)]. \quad (44)$$

The first term is a separated valence-orbital wave function with the orthogonality constraint and the second term is a correction term consisting of a single determinant which can be written approximately as[32]

$$\mathcal{A}_3(\varphi\alpha\varphi\beta\tau\alpha)\approx\mathcal{A}_3(\varphi\alpha\varphi\beta\chi_{1s}\alpha)\langle\chi_{1s}|\varphi\rangle, \quad (45)$$

where χ_{1s} is the natural orbital of ϕ with highest occupation number.

This determinant will contribute very little to the energy.[33] It contains, however, an unpaired spin orbital with large amplitude at the origin and will therefore be of importance for the Fermi contact term. The orthogonality constraint can therefore be expected to be serious for the hyperfine structure but not for the energy.

We may apply the variation principle to find a good wave function of type (29) without orthogonality constraints. For a limited basis set, as that for $W1$, we will get a core function which approximates the "exact" ϕ best in the core region and a valence orbital which approximates the exact φ for this model in the valence region. The function τ will be well determined only after many terms have been introduced, which are localized both in the core and valence region. It is probably good to include a Hartree-Fock type wave function in the basis.

B. Correlation Between Core and Valence Orbital

When correlation between the core and the valence electron is taken into account in the wave function, the occupation number of the valence orbital is depressed below one. The square root of this number is equal to the best overlap between ψ and a function of type (29), as shown in Sec. II. We also find a splitting of the core eigenvalues, from 0.36×10^{-4} for $W2$ to 1.57 for $W3$ and 2.0×10^{-4} for $W4$ for the largest s eigenvalues. For $W4$ all terms with the spin function $2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha$ contribute to this splitting. The $s1\alpha$ and $s2\alpha$ orbitals for $W4$ are localized partly in the valence region. This holds true also for the corresponding orbitals from $W1$, $W2$, and $W3$. The Hartree-Fock $1s\alpha$ orbital is, however, localized only in the core region.

The splitting of the next-two largest p orbitals is still larger 1.95×10^{-4} for $W2$, 2.71×10^{-4} for $W3$, and 2.65×10^{-4} for $W4$. The terms in the wave functions contributing to this angular correlation can only be those with r_{ij} factors between core and valence orbital, thus number 9 for $W2$, 8, 10, and 12 for $W3$, 8, 10, 12, 21–24 for $W4$. We also see from Fig. 2 that the $p2\alpha$ orbital is localized around 2 a.u. from the nucleus in the neighborhood of the valence orbital which has its maximum probability density at about 3 a.u. An orbital of this kind is thus very important for the description of the correlation between the shells. For the rest of the p orbitals there seems to be a pairing $p2\beta\approx p3\alpha$, $p3\beta\approx p4\alpha$, etc. The occupation numbers of these pairs also tend to be similar.

The term "symmetric core" should according to the discussion above, be reserved for functions of type (29) with (strong) orthogonality between the core function ϕ and the valence orbital φ. To this group belong the restricted Hartree-Fock wave function[34] and the wave function of Ahlrichs.[35] This group has been examined in some detail by Öhrn and McWeeny.[36] We may expect a good energy but a bad Fermi contact term for these models. The contributions from the core cancels, and the contribution from the valence orbital will probably be not very different from Hartree-Fock.

We may relax the orthogonality restriction or the restriction to a core singlet as in (36) but still keep the valence orbital as in (31). This group is represented by the spin polarized Hartree-Fock model,[37] $W1$, the wave functions by Öhrn and Nordling,[30] Arai and Onishi,[31] and wave functions given by Ritter, Pauncz, and Appel,[38] Lunell,[39] Goddard III,[40] the "closed-shell" wave functions of Burke and Mulligan[41] and the "open-shell" wave functions of Hurst, Gray, Brigman, and Matsen.[42]

V. COMPARISON BETWEEN DIFFERENT INDEPENDENT-PARTICLE MODELS

The best overlap orbitals were calculated by the iteration procedure described in Sec. II. We used the same basis set to expand the orbitals as for the NSO's of s type.

$$\sqrt{6}\int\psi(1,2,3)\varphi_1{}^{(0)}(1)\varphi_2{}^{(0)}(2)d1d2$$

$$=\lambda^{(1)}\varphi_3{}^{(1)}(3)=\lambda^{(1)}\sum_{i=1}^{M}c_i{}^{(1)}u_i(3). \quad (46)$$

We multiply by $u_j(3)$, integrate over 3 and get the linear equation system

$$\underline{b}^{(0)}=\lambda^{(1)}\underline{\Delta}\,\underline{c}^{(1)},$$

$$\Delta_{ij}=\langle u_i|u_j\rangle,$$

$$b_j=\sqrt{6}\int\psi\varphi_1{}^{(0)}\varphi_2{}^{(0)}u_j\,d1d2d3, \quad (47)$$

from which we obtain

$$\lambda^{(1)}\underline{c}^{(1)}=\underline{\Delta}^{-1}\underline{b}^{(0)}. \quad (48)$$

$\lambda^{(1)}$ is determined when we require

$$\varphi_3{}^{(1)}=\sum_{i=1}^{M}c_i{}^{(1)}u_i$$

to be normalized. In the same way $\varphi_2{}^{(1)}$ and $\varphi_1{}^{(1)}$ are calculated. These new orbitals are then the input in the next iteration step. NSO orbitals were used as starting orbitals and the procedure converged rapidly. Since ψ is an eigenfunction of S_z, it follows from (46) that the iteration procedure will lead to orbitals which are spin eigenfunctions if the starting orbitals are spin eigenfunctions. The pure s character of the orbitals is obviously also "self-consistent."

The difference between the NSO's and the best overlap orbitals was negligible. The overlap with the original wave function ($W4$) was 0.998 164 368 for the NSO determinant and 0.998 164 372 for best overlap determinant. Since we have calculated all integrals with 10 significant figures and solved the eigenvalue problem for the NSO in double precision, this difference signifies that they are different. In Table VIII we see that the differences for energy and orbital overlaps are indeed very small.

Notice that for $W1$ the NSO's are best overlap orbitals. This follows from (36). The NSO's of g' are best overlap orbitals for $g'(1, 2)$ since g' is a two electron function.

The spin-polarized Hartree-Fock orbitals were calculated with the same basis as the NSO's and the best overlap orbitals. The energy $-7.432\,722$ a.u. and the Fermi contact term 2.826 were obtained in comparison to the exact HF values $-7.432\,751$ and 2.823,[37] respectively.

The relationship between HF orbitals and NSO's is that they are the same after a unitary transformation up to second order in a perturbation expansion, where HF is the zero-order solution.[10–12] The unitary transformation is in our case a two dimensional rotation of the two α orbitals and no change of the β orbital. The overlap between the HF and NSO β orbital was 0.999 998. The overlap between the corresponding α orbitals was maximized for the rotation angle 6.20° and was then 0.999 998 for the core α orbital and 0.999 973 for the valence orbital. The amplitude of the valence orbital at the origin was considerably larger for HF than for the corresponding NSO, and the first orbital was therefore more delocalized. On the other hand the $1s\alpha$ and $1s\beta$ HF orbitals are nodeless, whereas the NSO $s1\alpha$ has a node at about 0.6 a.u. and is nonzero in the valence region.

The first NSO determinants of the different wave functions are compared in Table VII. None of our wave functions are constructed with the help of the HF function. It is therefore easy to understand that the simple wave function $W1$ has a quite small overlap with HF, and that this overlap in general increases the more complicated the wave function. It is also obvious that the overlap between the wave function and its first natural determinant decreases from one its value for an independent particle model, becoming smaller as the wave function becomes more detailed. From Tables IV and VII we also see that the values of the overlap between HF and the wave function and between the NSO determinant and the wave function come closer and closer to each other. It might seem to be an open question if there really is a difference for the exact wave function. We therefore needed an NSO determinant for a better wave function than $W4$, and also a better orbital basis. We know that the NSO's are very near to the best overlap orbitals, so near that we can consider the NSO's to be best overlap orbitals. The number of integrals of type (28) required to calculate NSO's for the 100 term wave function ($W5$) with the orbital basis of dimension 10 is about 30 times as many as for the 25 term wave function and orbital basis of dimension 8. We therefore calculated only the best overlap orbitals according to the iteration scheme with HF orbitals as starting orbitals. The integrals required here are fewer and considerably simpler. The iteration process converged rapidly. The $1s'\beta$ orbital will be the same as when NSO's are used as starting orbitals but the α orbitals come out with the above mentioned transformation, 6.20°. The results are given in Table VIII. Notice that the augmented orbital basis gives an HF energy very close to the exact HF energy. The BO-determinant energy decreased much when the orbital basis was improved. It also decreases as expected when the wave function is improved. However the difference in overlap with $W5$ for HF and BO determinants has increased instead of decreasing and we therefore think that this difference is significant and typical for the state in question. The difference between the HF and BO-density distribution is given in Fig. 3. The BO density comes somewhat closer to the nucleus than the

TABLE VII. Properties of the first natural determinants.

Wave function	$W1$	$W2$	$W3$	$W4$
–Energy (a.u.)	7.431 178	7.432 460	7.432 629	7.432 636
Fermi contact term % difference from value from density matrix	0.28	0.0	–0.26	–0.47
Overlap between NSO-determinant and wave function	0.998 393	0.998 340	0.998 170	0.998 164

TABLE VIII. Comparison between different independent particle models.

Determinant	Dimen. of wave function basis	Dimen. of orbital basis	−Energy (a.u.)	Fermi contact term	Overlap with wave function $W4$	Overlap with wave function $W5$	Overlap with HF orbitals (from the same orbital basis[a, b]) $1s\alpha$	$1s\beta$	$2s\alpha$
BO	100	10	7.432717	2.893	...	0.998145	0.9999997	0.9999995	0.9999564
BO	25	10	7.432693	2.899	0.998165	...	0.9999994	0.9999991	0.9999709
BO	25	8	7.4326367	2.901	0.998164	...	0.9999985	0.9999980	0.9999726
NSO	25	8	7.4326362	2.901	0.998164	...	0.9999983	0.9999980	0.9999728
HF	...	10	7.432750	2.825	0.998134	0.998101	1.0	1.0	1.0
HF	...	8	7.432722	2.826	0.998133	0.998098	1.0	1.0	1.0
HF	...	∞[37]	7.432751	2.8235	...	...	1.0	1.0	1.0

[a] For NSO after a 6.20° rotation of α orbitals.

[b] For BO with HF as starting orbitals in iteration procedure.

HF density. This has been found also for He.[14] The overlap between corresponding core orbitals was surprisingly large, even larger than was obtained for He.[11] The overlap between the valence orbitals is considerably lower and decreasing when the wave function was improved. Notice also that we have the following checking relation for the values in Table VIII.

$$\begin{aligned}\sqrt{6}\Big(\int\psi\varphi_1^{\mathrm{BO}}\varphi_2^{\mathrm{BO}}\varphi_3^{\mathrm{BO}} - \int\psi\varphi_1^{\mathrm{HF}}\varphi_2^{\mathrm{HF}}\varphi_3^{\mathrm{HF}}\Big) &= \sqrt{6}\Big[\int\psi\varphi_1^{\mathrm{BO}}\varphi_2^{\mathrm{BO}}(\varphi_3^{\mathrm{BO}} - \varphi_3^{\mathrm{HF}}) \\ &\quad + \int\psi\varphi_1^{\mathrm{BO}}(\varphi_2^{\mathrm{BO}} - \varphi_2^{\mathrm{HF}})\varphi_3^{\mathrm{BO}} \\ &\quad + \int\psi(\varphi_1^{\mathrm{BO}} - \varphi_1^{\mathrm{HF}})\varphi_2^{\mathrm{BO}}\varphi_3^{\mathrm{BO}}\Big] \\ &= \lambda\big[3 - (\varphi_3^{\mathrm{BO}}, \varphi_3^{\mathrm{HF}}) - (\varphi_2^{\mathrm{BO}}, \varphi_2^{\mathrm{HF}}) \\ &\quad - (\varphi_1^{\mathrm{BO}}, \varphi_1^{\mathrm{HF}})\big], \end{aligned} \tag{49}$$

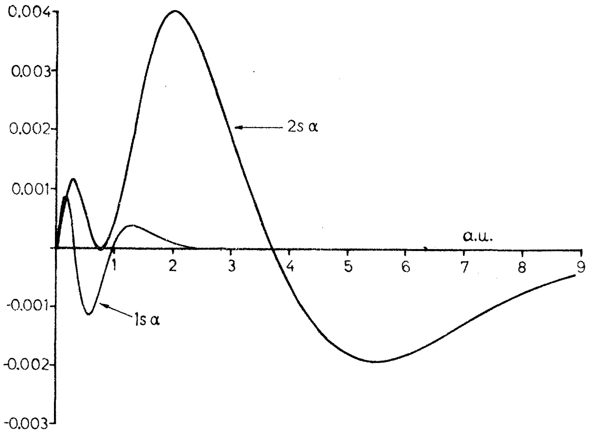

FIG. 3 Difference in radial density distribution between corresponding Brueckner and spin-polarized Hartree-Fock orbitals $4\pi r^2\chi_{\mathrm{BO}}^2(r) - 4\pi r^2\chi_{\mathrm{HF}}^2(r)$. The curve for $1s\beta$ is very similar to the $1s\alpha$ curve.

where only terms to first order in $(\varphi_\nu^{\mathrm{BO}} - \varphi_\nu^{\mathrm{HF}})$ have been retained. λ can be taken to be unity in the right side.

VI. THE FERMI CONTACT TERM

The Fermi contact term f can be calculated from the expansion of the one-particle density matrix in NSO's

$$f = 4\pi[\nu_{0\alpha}\chi_{0\alpha}^2(0) + \nu_{1\alpha}\chi_{1\alpha}^2(0) + \nu_{2\alpha}\chi_{2\alpha}^2(0) + \cdots - \nu_{1\beta}\chi_{1\beta}^2(0) - \nu_{2\beta}\chi_{2\beta}^2(0)\cdots]. \tag{50}$$

We have now numbered the α and β orbitals separately after magnitude of occupation numbers. Only the s orbitals contribute to the Fermi contact term. It can be seen from Table IX that the series is rapidly converging and the contribution from all but the three first orbitals $s0\alpha$, $s1\alpha$, and $s1\beta$, is only about 2 parts per thousand of f.

An interesting point is that the main contribution for the NSO determinant comes from the splitting of the core orbitals and less than 10% from the valence orbital. This is caused by the 6.2° rotation of the α orbitals discussed in the last section. This is most striking for $W1$, where we have no contribution at all from the valence orbital.

In Sec. II, it was shown that the best overlap orbitals are the same as Brueckner orbitals and exact self-consistent-field orbitals. They can be said to represent the effect of "dynamical correlation" on the HF orbitals and play an important role in many electron theory.[43] As can be seen in Tables VII–IX the main part of the remaining error in the spin-polarized HF method can be ascribed to this effect.

The error which is then left can be divided up into effects of core correlation and effects of correlation between the core and the valence electron in the following way. We write (50) as

TABLE IX. Contributions to Fermi contact term obtained from density matrix expansion.

	$W1$	$W2$	$W3$	$W4$
$-4\pi\chi_{1\beta}^2(0)$	-84.311	-85.797	-84.581	-84.715
$4\pi\chi_{0\alpha}^2(0)$	0.000	0.001	0.221	0.230
$4\pi\chi_{1\alpha}^2(0)$	87.845	88.601	87.518	87.386
Fermi contact term of determinant f_0	3.534	2.805	3.158	2.901
$A=4\pi(\nu_{1\alpha}-1)\,[\chi_{1\alpha}^2(0)-\chi_{1\beta}^2(0)]$	-0.011	-0.009	-0.010	-0.009
$B=4\pi(\nu_{0\alpha}-1)\chi_{0\alpha}^2(0)+(\nu_{1\alpha}-\nu_{1\beta})\chi_{1\beta}^2(0)$	0	0.003	0.013	0.017
f_0+A+B[a]	3.523	2.799	3.161	2.909
$C=4\pi\sum_{i=2}^{8}\nu_{i\alpha}[\chi_{i\alpha}^2(0)-\chi_{i\beta}(0)]$	0.001	0.006	0.004	0.004
$D=4\pi\sum_{i=2}^{8}(\nu_{i\alpha}-\nu_{i\beta})\chi_{i\beta}^2(0)$	0	0.000	0.001	0.002
Total value obtained from density matrix expansion $f_0+A+B+C+D$	3.524	2.805	3.166	2.915

[a] Contributions from strongly occupied orbitals in density matrix expansion, $\nu_{0\alpha}\chi_{0\alpha}^2(0)+\nu_{1\alpha}\chi_{1\alpha}^2(0)-\nu_{1\beta}\chi_{1\beta}^2(0)$.

$$\begin{aligned}(f/4\pi)-[\chi_{0\alpha}^2(0)+\chi_{1\alpha}^2(0)-\chi_{1\beta}^2(0)]&=(\nu_{1\alpha}-1)[\chi_{1\alpha}^2(0)-\chi_{1\beta}^2(0)]\\&+\nu_{2\alpha}[\chi_{2\alpha}^2(0)-\chi_{2\beta}^2(0)]\\&+\nu_{3\alpha}[\chi_{3\alpha}^2(0)-\chi_{3\beta}^2(0)]+\cdots\\&+(\nu_{0\alpha}-1)\chi_{0\alpha}^2(0)+(\nu_{1\alpha}-\nu_{1\beta})\chi_{1\beta}^2(0)\\&+(\nu_{2\alpha}-\nu_{2\beta})\chi_{2\beta}^2(0)\\&+(\nu_{3\alpha}-\nu_{3\beta})\chi_{3\beta}^2(0)+\cdots\,.\end{aligned}\tag{51}$$

The last terms are all zero for a separated valence orbital model. The first terms are probably not very much changed when correlations between the core and the valence electron are taken into account. The value of the different terms are listed in Table IX. The first terms in (51) are denoted by A and C and represent the effect of correlation in the core. In all the wave functions, that we examine, correlation in the core has been well taken into account. We see that the effect on f of $A+C$ is very small between -0.1 and -0.3%. When correlation between the valence electron and the core is introduced we get a positive contribution ranging from $+0.1\%$ for $W2$ to 0.7% for $W4$. The sum of the correlation contributions is 0.5% both for $W4$ and $W5$.

The difference between the values of the Fermi contact term from the wave functions given in Table IV and the values given by the density matrix expansions in Table IX are slightly different. This depends on the limited basis set that we have used. The absolute values of the electronic density at the nucleus are most in error. The errors will however cancel each other to a large extent, and the values in Table VIII are reliable except perhaps for the values of C and D. When the orbital basis was augmented to 10 terms, the error was considerably decreased as can be understood from the tables.

The differences between the HF and the Brueckner orbitals thus accounted for the major part (2.39%) of the difference (2.84%) in the Fermi contact term between HF (97.16%) and the exact value.

By Brueckner orbitals or best overlap orbitals we have in general meant those for an exact wave function. We can also define them for a model wave function like, for example, the separated-valence-orbital model. Since no sufficiently accurate wave function of this kind has been published in the literature, it is difficult to know how close these Brueckner orbitals are to the true ones. If they are assumed to be the same as the true Brueckner orbitals, we get with the help of Tables IX and X the Fermi contact term for the separated-valence-orbital model, $2.893-0.005=2.888$. This is under the assumption that the wave function $W5$ gives the correct values. The function for the separated-valence-orbital model must be obtained from the variation principle and, as in the Hartree-Fock case, we may get a wave function which is not of pure ^2S symmetry, but has ^4S admixture. It is then not strictly of the same type as the model discussed in Sec. IV, where ^2S symmetry was assumed.

In Sec. IV we found that the function d was of great importance for the Fermi contact term, and in order to get a good approximation of d, we must add terms to the basis set which have the valence part localized also in the core region and vice versa. This holds true also when we have left the separated valence-orbital model and introduced valence-core correlation terms. The James and Coolidge wave function has such terms, Nos. 7 and 8, whereas they are missing in $W1$ and $W3$. In $W4$ they are present, namely those with the spin function $S_2 = 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha$. The James and Coolidge wave functions and wave functions with the spin function S_2 give good values of f, whereas wave functions of the kind $W1$ and $W3$ give bad values. However, other effects may be of importance here.

CONCLUSION

The natural orbital analysis revealed the nature of correlation and particularly the nature of the correlation between the valence orbital and the core. Correlation of this kind is introduced when we leave the separated valence-orbital approximation and introduce for instance terms number 7 and 8 in the James and Coolidge wave function, or when we introduce r_{ij} terms between core and valence orbital as term No. 9. A third way of doing this is to use the spin function $S_2 = 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha$ which is equivalent to making a permutation of the coordinates for the valence electron and a core electron in the spatial part of the basis function and not change the spin function $S_1 = \alpha\beta\alpha - \beta\alpha\alpha$.[5] It was found that the introduction of r_{ij} terms splits the second pair of p orbitals very much, or corresponds to the introduction of a new p orbital localized in the region between the core and valence orbital. The effect of introducing terms with the spin function S_2 on the other hand increased the splitting of the occupation numbers of the strongly occupied core orbitals.

TABLE X. Orbital contributions to Fermi contact term from best overlap determinant compared to HF. Orbital basis $r^i \exp(-ar)$, $i=0,1,2,3,4$, $a=0.65$, 2.76.

Wave function	$W4$	$W5$	Spin-polarized Hartree Fock[37]
$-4\pi\chi_{1\beta}^2(0)$	-85.328	-85.627	-85.389
$4\pi\chi_{1\alpha}^2(0)$	2.228	2.153	2.058
$4\pi\chi_{1\alpha}^2(0)$	85.999	86.367	86.154
Total Fermi contact term from determinant	2.899	2.893	2.823

In the comparison of different independent-particle models we found that the spin-polarized Hartree-Fock wave function is very similar to the Brueckner determinant. The difference is largest for the valence orbital. All the Brueckner orbitals are more piled up at the nucleus and therefore the difference is noticeable for the Fermi contact term. The difference between NSO's and the corresponding best overlap orbitals was found to be negligible.

The analysis of the contributions to the Fermi contact term shows that the already good HF value is improved when we go over to the best overlap determinant. The Hartree-Fock result can therefore not be considered as fortuitous as has been done. Among the pure correlation effects the $1s-2s$ correlation is most important, about $+0.7\%$.

The separated valence-orbital model was studied in some detail. The eigenvalues are doubly degenerate (at least) for this model, excepting one eigenvalue which is one. The corresponding NSO's can be chosen as spin eigenfunctions. The spatial parts are then the same only when we have the orthogonality constraint between the valence orbital and the spin-singlet core function. The energy will probably be only slightly improved when the orthogonality constraint is relaxed but the Fermi contact term will be much improved.

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APPENDIX

The integrals required are of the following type

$$\int r_1^{p_1} r_2^{p_2} r_3^{p_3} r_{1'}^{p_{1'}} r_{gh}^{q_1} r_{ij}^{q_2} e^{-(a_1 r_1 + a_2 r_2 + a_3 r_3 + a_{1'} r_{1'})}$$

$$\times Y_{lm}(\vartheta_1, \varphi_1) Y_{lm}^*(\vartheta_{1'}, \varphi_{1'}) d\tau_1 d\tau_2 d\tau_3 d\tau_{1'} , \qquad \text{(A1)}$$

where p_i and q_i are non-negative integers. The volume elements are

$$d\tau_i = r_i^2 \sin\vartheta_i dr_i d\vartheta_i d\varphi_i . \tag{A2}$$

We expand $r_{ij}{}^q$ according to a formula of Sack.[44]

$$r_{ij}{}^q = \sum_\lambda R_{q\lambda}(r_i, r_j) P_\lambda(\cos\vartheta_{ij}), \tag{A3}$$

$$R_{q\lambda}(r_i, r_j) = [(-\tfrac{1}{2}q)^\lambda/(\tfrac{1}{2})^\lambda]\, r_>{}^q (r_</r_>)^\lambda F(\lambda - \tfrac{1}{2}q, -\tfrac{1}{2} - \tfrac{1}{2}q, \lambda + \tfrac{3}{2}; r_<{}^2/r_>{}^2), \tag{A4}$$

$$F(\alpha, \beta, \gamma; x) = 1 + \sum_{s=1}^{\infty} \frac{(\alpha)_s(\beta)_s}{(\gamma)_s s!} x^s; \quad (\alpha)_0 = 1; \quad (\alpha)_s = \alpha(\alpha+1)\cdots(\alpha+s-1), \tag{A5}$$

$$r_< = \min(r_i, r_j); \quad r_> = \max(r_i, r_j).$$

The Legendre polynomials $P_\lambda(\cos\vartheta_{ij})$ are expanded according to the well-known formula

$$P_\lambda(\cos\vartheta_{ij}) = \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}{}^*(\vartheta_i, \varphi_i) Y_{\lambda\mu}(\vartheta_j, \varphi_j). \tag{A6}$$

Since all our wave functions contain only one r_{ij} at a time we get at most two in the integrals, and none of them are $r_{1\,1'}$. This simplifies the angular integration, which then results in Kronecker deltas $\delta_{\lambda_1 l}$, $\delta_{\lambda_1\lambda_2}$, $\delta_{\mu_1 m}$, $\delta_{\mu_1\mu_2}$. Furthermore the total integral is independent of the value of m.

There remains to be done the integration over r_1, r_2, r_3 and $r_{1'}$. Since only two interelectronic separation coordinates are present the most difficult case is a triple integral. Because of (A4) we divide the region of integration into six parts, each of which is characterized by $r_i > r_j > r_k$; $\{ijk\}$ is a permutation of $\{123\}$. The resulting integrals are of the type

$$W(k, l, m, \alpha, \beta, \gamma) = \iiint_{0<x<y<z<\infty} x^k e^{-\alpha x} y^l e^{-\beta y} z^m e^{-\gamma z} dz dy dx, \tag{A7}$$

$$V(k, l, \alpha, \beta) = \iint_{0<x<y<\infty} x^k e^{-\alpha x} y^l e^{-\beta y} dy dx, \tag{A8}$$

$$A(k, \alpha) = \int_0^\infty e^{-\alpha x} x^k dx. \tag{A9}$$

The calculation of these integrals is discussed elsewhere[5] and will not be further treated here. We have made the calculation with 10 significant figures except for the d and f orbitals where a smaller number was sufficient.

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