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PHYSICAL REVIEW A VOLUME 1, NUMBER 6 JUNE 1970

Spin-Optimized Self-Consistent-Field Function. II. Hyperfine Structure of Atomic Nitrogen

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(Received 18 December 1969)

The spin-optimized self-consistent-field (SOSCF) method, based on optimizing the spin function in the whole (S, M_s) space simultaneously with spatial orbital optimization, is applied to the ^4S ground state of the nitrogen atom. The maximally paired Hartree-Fock (MPHF) function, where both $1s$ and $2s$ electron pairs are associated with the singlet factor $\alpha\beta-\beta\alpha$, is also calculated, as are functions in which either the $1s$ or the $2s$ electrons are thus paired. The SOSCF energy is $-54.421\,67$ Hartree, compared with $-54.400\,93$ by the restricted Hartree-Fock (RHF) and $-54.417\,22$ by the MPHF methods. The net spin density at the nucleus, responsible for the hfs of nitrogen, is 0.1200 a.u., compared with 0.1853 a.u. by the spin-extended Hartree-Fock method and the experimental value of 0.0972 a.u. (the RHF and MPHF methods give 0). The contributions of the $1s$ and $2s$ pairs, obtained from two separate calculations employing two-dimensional subspaces of the six-dimensional spin-function space, add very nearly to the full SOSCF results for the energy and spin density. The SOSCF orbitals are also described. Their most interesting feature is the nonexistence of radial nodes in any of them.

INTRODUCTION

The spin-optimized self-consistent-field (SOSCF) function described in a recent paper[1] is of the form

$$\Psi = \mathcal{A}\Xi\Theta \quad , \tag{1}$$

where Ξ is a product of one-electron spatial functions

$$\Xi = \chi_1(1)\chi_2(2)\cdots\chi_n(n) \quad , \tag{2}$$

and Θ is a linear combination of all independent spin functions θ_k spanning the space of appropriate S and M_s

$$\Theta = \textstyle\sum_k t_k \theta_k \ . \tag{3}$$

The orbitals χ_i and the coefficients t_k are optimized to obtain the SOSCF function. Similar methods have been recently described by other authors.[2] The SOGI function of Ladner and Goddard[2a] is equivalent to our SOSCF function, though obtained in a different way. The BRNO method[2b] is somewhat inferior, not involving reoptimization of the spatial orbitals for the best spin function.

In paper I,[1] we investigated three- and four-electron atoms. These systems have only two independent spin functions [$k=1,\ 2$ in Eq. (3)], and the optimal Θ is found to be very close to θ_1, the maximally paired Hartree-Fock function (MP HF, equivalent to Goddard's G1[3]), with a singlet factor of $\alpha\beta-\beta\alpha$ corresponding to the two $1s$ electrons (and to the $2s$ electrons in Be). The contribution of the other function t_2 is two orders of magnitude lower than t_1. The small admixture of θ_2, while hardly affecting the total energy, greatly improves the description of the wave function at the vicinity of the atomic nucleus, as shown by spin-density results. Thus, while the spin density at the lithium nucleus in the ^2S ground state as given by the MPHF function is 9% in error, the SOSCF result is within 2% of the experimental value. Even more significant improvement is achieved for Li (^2P). The deviation from experiment, which is 100% for the MPHF function, goes down to only 7% when the SOSCF method is used.[1]

While these results are encouraging, it is known that several methods utilizing independently optimized one-electron orbitals, one orbital per electron, such as the unrestricted Hartree-Fock[4] (UHF) and spin-extended Hartree-Fock[5] (SEHF, equivalent to Goddard's GF[3]), reproduce closely the experimental spin density at the lithium nucleus, but fail rather miserably for other first-row atoms, notably nitrogen.[4,6,7] Nitrogen is a good test case also because the electron spin density at its nucleus in the ^4S ground state is directly obtainable from hfs data and is therefore accurately known, which is not the case for the lighter atoms boron and carbon.[8] We therefore present in this paper an investigation of the ground state of atomic nitrogen by the SOSCF method.

SOSCF FUNCTION OF ATOMIC NITROGEN

The branching diagrams method of Kotani *et al.*[9] shows that seven electrons can form 14 independent quartet spin functions. Not all these functions survive, however, the restrictions imposed on the spatial orbitals. The spatial orbitals are chosen to be eigenfunctions of the one-electron momentum operators L^2 and L_z, and the p orbitals are equivalent (i.e., connected by the angular momentum raising and lowering operators L^+ and L^-). It is this last-mentioned requirement in particular (l-equivalence restriction) that eliminates eight of the possible 14 spin functions (see Appendix). It should be noted that the spin-equivalence restriction is not applied, leading to four independent s orbitals in Ξ of Eq. (2). Lifting the l-equivalent restriction would yield an over-all function not representing a pure S state, or else necessitate the application of angular momentum projection operators, greatly complicating the calculations and taking us beyond the scope of the present SOSCF method.

The construction of the six allowed spin functions is described in the Appendix, where the resulting functions are given explicitly [Eq. (A4)]. Of these functions, θ_1 is referred to as "maximally paired," as it has factors of $\alpha\beta-\beta\alpha$ corresponding to both the 1s and 2s electron pairs. The same factor is connected with the 1s pair in θ_4, and functions of the form (1) which have only t_1 and t_4 [Eq. (3)] different from zero will therefore be called "1s-paired." Similarly, a "2s-paired" function will have all $t_k = 0$ except t_1 and t_3. If Θ is optimized in the whole six-function space, we obtain the SOSCF function. It should be emphasized that the spatial orbitals χ_i are separately optimized for each of these functions. The method of obtaining the optimal Θ and χ_i, using a generalized form of Brillouin's theorem, has been described in I.[1]

RESULTS

The basis sets used to expand the atomic orbitals are listed in Table I. They fall into two classes. Type-I sets are those satisfying (approximately) the cusp condition[10] for the s orbitals; other sets are denoted type II. Sets 1 and 2 are taken from Bagus and Gilbert,[11] set 3 from Clementi, Roothaan, and Yoshimine,[12] and sets 4–10 are those given by Goddard.[7] All these sets were optimized for the RHF function. The additional sets 1a and 2a were obtained from sets 1 and 2, respectively, by using the SEHF energy as a criterion for optimization.[6] Set 10a was arbitrarily chosen to test the sensitivity of the results to small variations in the basis functions (*vide infra*).

The MPHF and SOSCF energies and spin densities are presented in Table II. As in the SEHF case,[6,7] we find that the total energy is not particularly sensitive to the s-orbital cusps and varies fairly regularly with the size of the basis sets. The same is not true for the spin density at the nucleus. Type-II basis sets yield erratic values (note the big differences between sets 1 and 1a or 2 and 2a) which are of the wrong sign, whereas results obtained with type-I sets seem to have converged to two decimal places (compare sets 7–10, also 10 with 10a). A similar behavior was observed by Goddard in his GF calculations.[7] The final SOSCF result of 0.12 a.u.[13] is 23% higher than the experimental value of 0.0972 a.u.[14] Our method is compared in Table III with results calculated by other workers. We see that ours is the best value given by a method associating only one spin orbital with each electron. Better agreement with experiment has so far been obtained only by abandoning this conceptually pleasing one-to-one correspondence between electrons and orbitals.

The results reported above involved optimizing the spin part Θ in the whole six-dimensional function space (see Appendix). The dimensionality of this space increases rapidly with the number

TABLE I. Basis sets for nitrogen. (A) Not satisfying cusp condition (type II). (B) Approximately satisfying cusp condition for *s* orbitals (type I).

(A)	
1	1*s* − 10.507, 6.346; 3*s* − 3.715; 2*s* − 1.697; 2*p* − 5.573, 2.555, 1.352.
1a	1*s* − 10.5064, 6.3463; 3*s* − 3.6667; 2*s* − 1.6545; 2*p* − 5.5743, 2.5409, 1.3488.
2	1*s* − 10.586, 6.037; 3*s* − 7.334; 2*s* − 2.539, 1.588; 2*p* − 7.677, 3.270, 1.890, 1.222.
2a	1*s* − 10.5873, 6.0403; 3*s* − 7.3232; 2*s* − 2.4419, 1.4838; 2*p* − 7.6785, 3.2676, 1.8946, 1.210.
3	1*s* − 6.4595, 10.8389; 2*s* − 1.4699, 1.9161, 3.156, 5.0338; 2*p* − 1.1937, 1.7124, 3.0012, 7.101.
(B)	
4	1*s* − 6.98; 3*s* − 7.45, 3.690, 2.012; 2*p* − 1.4948, 3.236.
5	1*s* − 7.01; 3*s* − 8.06, 5.58, 3.34, 1.921; 2*p* − 1.495, 3.236.
6	1*s* − 7.011; 3*s* − 8.07, 5.53, 3.326, 1.920; 2*p* − 1.3527, 2.56, 5.6.
7	1*s* − 7.015; 3*s* − 8.1, 5.48, 3.302, 1.938, 1.0; 2*p* − 1.353, 2.56, 5.6.
8	1*s* − 7.0; 3*s* − 8.1, 5.48, 3.327, 1.935, 0.93; 2*p* − 7.677, 3.270, 1.890, 1.222.
9	1*s* − 7.02; 3*s* − 8.2, 5.49, 3.438, 2.054, 1.03; 4*s* − 1.13; 2*p* − 1.353, 2.56, 5.6.
10	1*s* − 7.02; 3*s* − 8.2, 5.49, 3.438, 2.054, 1.03; 4*s* − 1.13; 2*p* − 7.677, 3.270, 1.890, 1.222.
10a	1*s* − 7.00; 3*s* − 8.1, 5.4, 3.5, 2.0, 1.0; 4*s* − 1.2; 2*p* − 7.7, 3.3, 1.8, 1.2.

of electrons, and it will therefore be necessary to work with a smaller subspace if we hope to tackle larger systems. We carried out several calculations in which not all of the spin functions of Eq. (A4) were allowed to contribute to Θ, in order to investigate the feasibility of eliminating them from future work. The spin functions optimized under these limitations are shown in Table IV together with the SOSCF spin parts, and the energies and spin densities are collected in Table V. We find that the energy of the 1*s*-paired function is very close (within $1–2\times10^{-4}$ hartree) to the full SOSCF result, meaning that practically all the energy reduction with respect to the MPHF value is due to unpairing the 2*s* shell. Moreover, most of the difference may be obtained by separately estimating the effect of unpairing the 1*s* shell, using the 2*s*-paired function. The spin-density results are even more encouraging. Here the contributions of the 1*s* and 2*s* electrons, as given by the 2*s*- and 1*s*-paired functions, respectively, are much larger in absolute value than the SOSCF value and of opposite signs, yet their sum is very close to the SOSCF result (the difference is 2–4%, except for set 4 which is very small and gives poor results). We may therefore be able to carry out two two-dimensional calculations instead of a six-dimensional one. This result,

TABLE II. Energies and spin densities with different basis sets (a.u.).

				Energy[a]				Spin density at nucleus[a]	
Basis set[b]		RHF	UHF	SEHF	MPHF	SOSCF	UHF	SEHF	SOSCF
1	(4/3)	−54.400 80	−54.403 08	−54.404 39	−54.416 17	−54.419 50	0.0263	0.0118	−0.0498
1a				−54.404 55	−54.416 08	−54.419 67		0.0381	−0.0233
2	(5/4)	−54.400 93	−54.403 85		−54.416 89	−54.421 02	0.3187		−0.0666
2a				−54.405 84	−54.416 67	−54.421 27		0.3208	−0.0438
3	(6/4)	−54.400 91	−54.404 51		−54.416 84	−54.421 26	0.2127		−0.0341
4	(4/2)		−54.400 84		−54.412 38	−54.415 85	−0.0313		−0.0852
5	(5/2)		−54.401 74		−54.414 79	−54.418 81	0.1611		0.0663
6	(5/3)		−54.403 92	−54.405 62	−54.416 85	−54.421 03	0.1751	0.1461	0.0847
7	(6/3)		−54.404 37	−54.406 21	−54.416 93	−54.421 35	0.1922	0.1629	0.1135
8	(6/4)		−54.404 44		−54.416 97	−54.421 38	0.1940		0.1149
9	(7/3)		−54.404 46		−54.417 15	−54.421 59	0.1835		0.1177
10	(7/4)		−54.404 56	−54.406 42	−54.417 22	−54.421 67	0.1853	0.1579	0.1200
10a						−54.421 29			0.1165

[a] The RHF results are from Refs. 11 and 12, the UHF from Ref. 7, and the SEHF values from Refs. 6 and 7.

[b] (*n*/*m*) denotes a set consisting of *n s* orbitals and *m p* orbitals.

should it be confirmed in other cases, will greatly facilitate investigations of larger systems.

SPATIAL ORBITALS

Each spatial orbital in the SOSCF function is varied independently, thus "splitting" the doubly occupied RHF orbitals. The same is true for the SEHF function,[6,7] but the splitting produced in that case is very small whereas it is considerable in the functions described in this work (see Tables VI and VII). This does not apply to the $2p$ orbitals, which are not split, and are virtually identical with their RHF counterparts. The SOSCF orbitals are shown in Fig. 1. The $1s$ orbitals are of the same general shape as the corresponding RHF function. The splitting at the origin is somewhat larger for MPHF orbitals than for SOSCF ones, and considerably larger with type-II than with type-I basis sets (Table VII); the total overlap of corresponding α and β orbitals does not however change much with basis sets or spin functions (Table VI).

The greatest departure from RHF character is offered by the $2s$ orbitals. The over-all RHF

TABLE III. Comparison of different methods.

	Energy	Spin density at nucleus
Methods involving one spin orbital per electron		
RHF (Ref. 11)	−54.400 93	0
UHF (Ref. 7)	−54.404 53	0.1853
SEHF (Refs. 6 and 7)	−54.406 42	0.1579
MPHF	−54.417 22	0
SOSCF	−54.421 29	0.120
Other Methods		
CI (Ref. 8)	−54.451 76	0.0730
CI[a]	−54.456 63	0.0722
Bethe-Goldstone[b]		0.101
Many-body[c]		0.098
Experiment	−54.614 2[d]	0.0972 (Ref. 14)

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TABLE IV. Coefficients of spin functions for nitrogen.

	SOSCF						$1s$ paired		$2s$ paired	
Basis set	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_1	θ_4	θ_1	θ_3
3	0.5551	−0.0124	0.0054	−0.1308	−0.0010	−0.0008				
4	0.5638	−0.0190	0.0082	−0.0993	−0.0051	−0.0009	0.5684	−0.0999	0.5800	0.0078
5	0.5561	−0.0153	0.0060	−0.1139	−0.0018	−0.0008	0.5595	−0.1146	0.5734	0.0059
8	0.5572	−0.0144	0.0059	−0.1277	−0.0013	−0.0009	0.5601	−0.1286	0.5734	0.0058
10	0.5569	−0.0139	0.0058	−0.1312	−0.0011	−0.0009	0.5595	−0.1320	0.5728	0.0057

TABLE V. Results with paired functions.

Basis set	Energy relative to MPHF value				Spin density at nucleus			
	$1s$ paired	$2s$ paired	sum	SOSCF	$1s$ paired	$2s$ paired	sum	SOSCF
4	−0.003 28	−0.000 13	−0.003 41	−0.003 47	0.4966	−0.5689	−0.0723	−0.0852
5	−0.003 88	−0.000 09	−0.003 97	−0.00402	0.5999	−0.5352	0.0647	0.0663
8	−0.004 27	−0.000 09	−0.004 36	−0.004 45	0.6409	−0.5302	0.1107	0.1149
10	−0.004 32	−0.000 08	−0.004 40	−0.00445	0.6467	−0.5302	0.1165	0.1200

TABLE VI. Orbital overlaps.[a]

		$(1s \mid 1s')$	$(2s \mid 2s')$	$(1s \mid 2s)$	$(1s' \mid 2s')$	$(1s \mid 2s')$	$(1s' \mid 2s)$
MPHF	Set 3	0.9728	0.9346	0.3036	0.2462	0.1759	0.4015
	Set 10	0.9683	0.9307	0.3039	0.2484	0.1540	0.4253
SOSCF	Set 3	0.9745	0.9336	0.2392	0.2220	0.1830	0.3035
	Set 10	0.9724	0.9335	0.2414	0.2267	0.1838	0.3105
$1s$ paired	Set 10	0.9732	0.9351	0.2497	0.2393	0.2117	0.3044
$2s$ paired	Set 10	0.9697	0.9344	0.2978	0.2523	0.1713	0.4072

[a] For RHF $1s \equiv 1s'$, $2s \equiv 2s'$. For SEHF (Ref. 6), $(1s \mid 1s') = 1.0000$, $(2s \mid 2s') = 0.9934$.

TABLE VII. Orbital densities at nucleus.

		$1s$	$1s'$	$2s$	$2s'$
MPHF	Set 3	12.2276	7.4018	0.7557	0.2457
	Set 10	11.5474	8.0737	0.9428	0.1731
SOSCF	Set 3	12.2709	7.5462	0.4696	0.5548
	Set 10	11.5759	8.2277	0.5339	0.5834
$2s$ paired	Set 10	11.5306	8.0899	0.8077	0.2808
$1s$ paired	Set 10	11.5657	8.2432	0.5675	0.8071
RHF[a]	Set 3	9.9100		−2.1837[b]	
SEHF[c]	Set 2a	10.0163	10.0480	−1.6291[b]	−1.4036[b]

[a] Reference 12.

[b] Sign is chosen so that the asymptotic behavior of all $2s$ orbitals will be similar (see Fig. 1).

[c] Reference 6.

function is invariant under any linear transformation among its orbitals, which may therefore be made orthogonal. Similarly, the SEHF orbitals associated with the same spin factor may be chosen orthogonal to one another. The orthogonality introduces radial nodes into all atomic orbitals but the lowest one of each l value. Such transformations are not allowed in the SOSCF (and MPHF) case, and the $2s$ orbitals need not, and indeed do not, have nodes (see Fig. 1). A nodeless $2s$ was first encountered in Goddard's G1[15] (equivalent to our MPHF) calculations for atomic lithium,[3] and more recently in SOSCF functions for the same atom.[1,2] This is probably the most striking feature of SOSCF orbitals. It is of interest to note that the details of the $2s$ orbitals near the origin depend strongly on the spin function used (Fig. 2). The dependence on the type of basis set is smaller, but still significant (Fig. 3). All these differences die rapidly away from the origin.

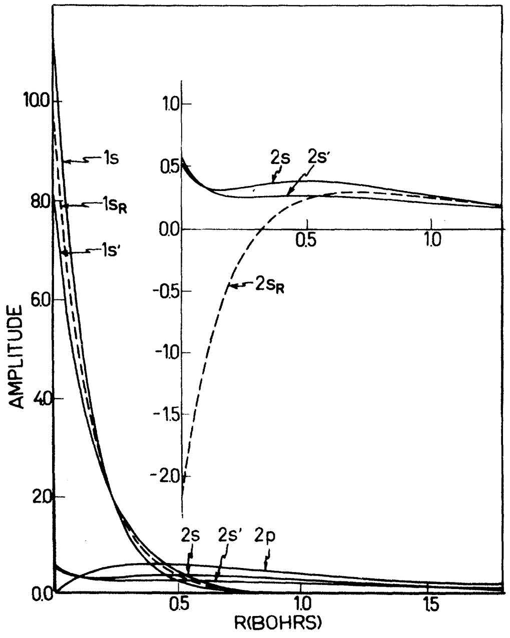

FIG. 1. SOSCF orbitals (basis set 10). Dashed lines are RHF orbitals, shown for comparison. The RHF $2p$ orbital falls on the SOSCF one.

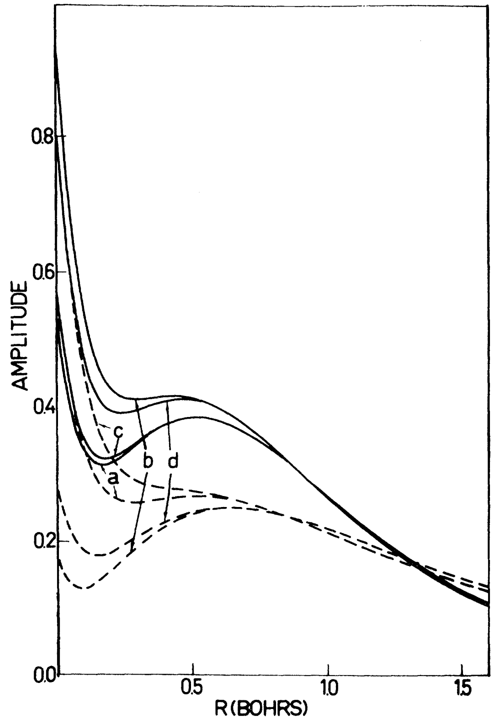

FIG. 2. $2s$ orbitals for different spin functions (basis set 10). Solid lines are $2s$ and dashed lines are $2s'$ orbitals. Spin functions (see Table IV) are (a) SOSCF, (b) MPHF, (c) paired $1s$, and (d) paired $2s$.

CONCLUSION

The SOSCF method yields considerable energy reduction with respect to the RHF value, while not abandoning the concept of one orbital per electron. More important, it gives a much better agreement with experiment for the rather sensitive spin density at the nitrogen nucleus than other methods based on this concept. It may be possible to forego the use of the whole spin function space in favor of separate calculations with appropriately chosen subspaces, followed by summation of the individual contributions. Other systems are now being investigated in order to check the generality of these results.

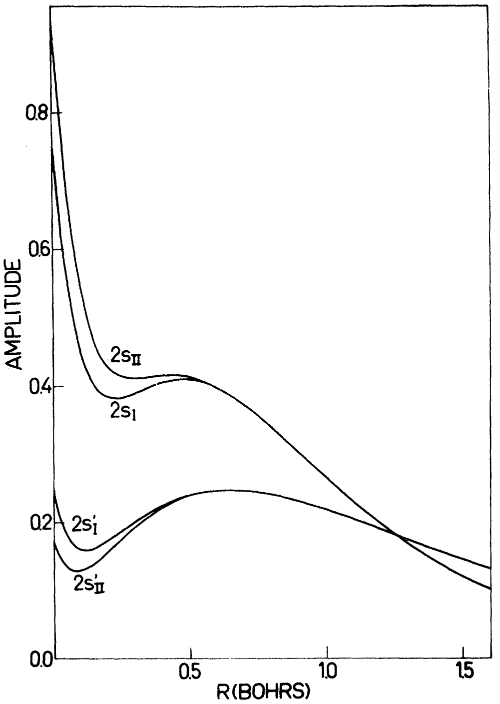

FIG. 3. Effect of basis set type on 2*s* orbitals. Shown are MPHF 2*s* orbitals with basis sets 10 ($2s_{II}$) and 3 ($2s_I$).

APPENDIX: SPIN FUNCTIONS FOR $N(^4S)$

The spin functions for the ^4S ground state of atomic nitrogen may be constructed in various ways. We choose to do it by first writing down all possible states of four nonequivalent *s* electrons, and then combining them with the functions of three equivalent *p* electrons.

Four nonequivalent *s* electrons give rise to one ^5S, three ^3S, and two ^1S states. The corresponding spin functions (with $M_S = S$) are [16]

$$\begin{aligned} &{}^5S_2(4) && \alpha\alpha\alpha\alpha\,; \\ &{}^3S_1(4) && (\alpha\alpha\alpha\beta-\alpha\alpha\beta\alpha)\,/\,\sqrt{2}\,, \\ & && (\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha)\,/\,\sqrt{2}\,, \\ & && \tfrac{1}{2}\,(\alpha\alpha\alpha\beta+\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha)\,; \\ &{}^1S_0(4) && \tfrac{1}{2}\,(\alpha\beta\alpha\beta-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha+\beta\alpha\beta\alpha)\,, \\ & && (2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha-\alpha\beta\alpha\beta-\beta\alpha\alpha\beta \\ & && -\alpha\beta\beta\alpha-\beta\alpha\beta\alpha)\,/\,\sqrt{12}\,; \end{aligned} \qquad \text{(A1)}$$

where in $^{2S+1}S_M(n)$ the superscript indicates the spin multiplicity, the subscript is M_S and *n* is the number of electrons. Of the three terms that may be built of three equivalent *p* electrons, namely ^4S, ^2P, and ^2D, only the first, the spin part of which is

$$^4S_{3/2}(3) \quad \alpha\alpha\alpha, \qquad \text{(A2)}$$

can combine with the four-electron states of (A1) to yield ^4S functions for the whole atom. Six such functions may be obtained, one for each entry in (A1), by the relations

$$\begin{aligned} ^4S_{3/2}(7) &= {}^1S_0(4)\times{}^4S_{3/2}(3)\,, \\ ^4S_{3/2}(7) &= \sum_{m=0,\,1} {}^3S_m(4)\times{}^4S_{3/2-m}(3)\,(1\tfrac{3}{2}m\tfrac{3}{2}-m\,|\,1\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2})\,, \\ ^4S_{3/2}(7) &= \sum_{m=0,\,1,\,2} {}^5S_m(4)\times{}^4S_{3/2-m}(3)\,(2\tfrac{3}{2}m\tfrac{3}{2}-m\,|\,2\tfrac{3}{2}\tfrac{3}{2}\tfrac{3}{2})\,, \end{aligned} \qquad \text{(A3)}$$

where $(j_1j_2m_1m_2\,|j_1j_2jm)$ are the usual Clebsch-Gordan coefficients. The resulting spin functions are as follows:

$$\begin{aligned} \theta_1 &= \tfrac{1}{2}(\alpha\beta\alpha\beta-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha+\beta\alpha\beta\alpha)\alpha\alpha\alpha\,, \\ \theta_2 &= (2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha-\alpha\beta\alpha\beta-\beta\alpha\alpha\beta \\ &\quad -\alpha\beta\beta\alpha-\beta\alpha\beta\alpha)\alpha\alpha\alpha/\sqrt{12}\,, \\ \theta_3 &= [2(\alpha\alpha\alpha\beta-\alpha\alpha\beta\alpha)(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha) \\ &\quad -3(\alpha\beta\alpha\beta-\alpha\beta\beta\alpha+\beta\alpha\alpha\beta-\beta\alpha\beta\alpha)\alpha\alpha\alpha]/\sqrt{60}\,, \\ \theta_4 &= [2(\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha)(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha) \qquad \text{(A4)} \\ &\quad -3(\alpha\beta\alpha\beta+\alpha\beta\beta\alpha-\beta\alpha\alpha\beta-\beta\alpha\beta\alpha)\alpha\alpha\alpha]/\sqrt{60}\,, \\ \theta_5 &= [(\alpha\alpha\alpha\beta+\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha)(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha) \\ &\quad -3(\alpha\alpha\beta\beta-\beta\beta\alpha\alpha)\alpha\alpha\alpha]/\sqrt{30}\,, \\ \theta_6 &= [2\alpha\alpha\alpha\alpha(\alpha\beta\beta+\beta\alpha\beta+\beta\beta\alpha) \\ &\quad -(\alpha\alpha\alpha\beta+\alpha\alpha\beta\alpha+\alpha\beta\alpha\alpha+\beta\alpha\alpha\alpha) \\ &\quad \times(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)+(\alpha\alpha\beta\beta+\alpha\beta\alpha\beta+\beta\alpha\alpha\beta+\alpha\beta\beta\alpha \\ &\quad +\beta\alpha\beta\alpha+\beta\beta\alpha\alpha)\alpha\alpha\alpha]/\sqrt{30}\,. \end{aligned}$$

The first two electrons in θ_4 are paired to a singlet by the factor $\alpha(1)\beta(2)-\beta(1)\alpha(2)$. The same holds for electrons 3 and 4 in θ_3, while θ_1 has two such pairs and is, therefore, the "maximally paired" function.

The appearance of only six of the 14 seven-electron quartet spin functions can be traced to the nonexistence of a ^2S state for the p^3 configuration. This state does exist (with two independent spin functions) if the *p* electrons are nonequivalent, and can then combine with the ^5S and ^3S states of the four *s* electrons. As there are two $^2S(3)$ functions and four $^5S(4)$ and $^3S(4)$ ones, eight additional $^4S(7)$ functions would then appear, bringing the total to 14.

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Molecular-Orbital Calculation of the Shape Resonance in N_2^-†

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(Received 12 December 1969)

The 2-eV shape resonance in N_2-electron scattering is calculated by a self-consistent-field energy-variational procedure. The resonance state corresponds to the attachment of an incident d-wave electron to the $1\pi_g$ valence orbital of the metastable $^2\Pi_g$ state of N_2^-. The resonant behavior is due to the tunnelling of the electron through a $2(2+1)/r^2$ centrifugal barrier and temporary trapping in an attractive field. This tunnelling is reflected in the bimodal behavior of the calculated $1\pi_g$ orbitals; the inner portion of the orbital defines the resonance state. The "potential" curve for N_2^- is calculated in the Hartree-Fock approximation; a resonance threshold of 2.5 eV is predicted, with $R_e = 2.27$ a.u. and $\omega_e \approx 2000\ \text{cm}^{-1}$. Expected correlation-energy corrections would improve the agreement with experiment. A local potential for electron scattering is generated by inverting the $1\pi_g$ orbital, and resonance widths are calculated. The widths vary from 0.13 eV at the equilibrium distance of N_2^- to 0.8 eV at the N_2 equilibrium distance.

I. INTRODUCTION

The resonance structure in electron scattering from N_2 is due to "attachment" of the d wave of the incident electron to the first unoccupied π_g valence orbital. In terms of a "local" potential, the incident electron penetrates or tunnels through a barrier that can be represented asymptotically as

$$V_{r\to\infty} \sim -\alpha_0/2r^4 + 2(2+1)/r^2 \quad . \tag{1}$$

At short range, of the order of the size of the molecule (~ 1.5 a.u.), the potential is attractive and, for $E \sim 2$ eV, sufficient to support a metastable "bound" state. This picture was developed by Bardsley, Mandl, and Wood.[1] A $^2\Pi_g$ configuration for the N_2^- had been proposed earlier by Gilmore[2] on the basis of molecular-orbital theory and an estimate of a real N_2^- potential energy curve was made. Chen[3] has deduced a similar curve semi-empirically and the angular dependence of the scattered electron[4] is consistent with the $^2\Pi_g$ resonant state of N_2^-. Although the qualitative structure of the resonance state now appears to be understood, *a priori* calculations based on the molecule itself are lacking.

In this paper, we calculate the resonance state of N_2^- from molecular-orbital theory and use this to develop a local potential for electron scattering. The scattering wave function is assumed to be expanded in terms of a tight resonance state with decaying boundary conditions and appropriate phase-shifted continuum functions. Since we are concerned only about resonant scattering, where the electron penetrates into a well of the size of the molecule, we assume that a knowledge of the resonance function alone can be used to determine the "local" potential that supports the resonance state. This potential includes both exchange effects and the electrostatic polarization of the target mole-