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PHYSICAL REVIEW A VOLUME 7, NUMBER 3 MARCH 1973

Natural Analysis of the ^2S and ^2P States of the Lithiumlike Ions*

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(Received 13 September 1972)

Since two recent investigations revealed different structures for the one-electron reduced-density matrix (one matrix) of the Weiss wave function of the lowest (^2P) state of lithium, we have reanalyzed the Weiss wave functions for both the lowest ^2S and ^2P states of the three-electron ions. Although Weiss employed "^2S restrictions" in the construction of his ^2P wave functions, their natural spin orbitals are not as spatially symmetry adapted as they are for the ^2S states.

The natural analysis[1] of correlated wave functions has proved in recent years[2] to be a powerful tool for understanding of the correlation problem and the comparison of wave functions of apparently dissimilar form. This method involves the determination of the eigenfunctions χ_j [natural spin orbitals (NSO)] and eigenvalues ν_j (occupation numbers) of the one-electron reduced-density matrix (one matrix) $\gamma_\Psi(x_1, x_1')$. Here $\gamma_\Psi(x_1, x_1')$ is defined by

$$\gamma_\Psi(x_1, x_1') = N \int \Psi(x_1, x_2, \ldots, x_n) \times \Psi^*(x_1', x_2, \ldots, x_n)\, dx_2 \cdots dx_n , \qquad (1)$$

where N is the number of electrons and x_i denotes the space and spin coordinates of electron i. In terms of the $\chi_j(x)$ and ν_j,

$$\gamma_\Psi(x_1, x_1') = \sum_{j=1} \nu_j \chi_j(x_1) \chi_j^*(x_1') \qquad (2a)$$

and

$$\int \gamma_\Psi(x_1, x_1') \chi_j(x_1')\, dx_1' = \nu_j \chi_j(x_1) , \qquad (2b)$$

where

$$\sum_{j=1} \nu_j = N \qquad (2c)$$

and the ν_j's are ordered such that

$$0 \le \nu_{j+1} \le \nu_j \le 1 . \qquad (2d)$$

Natural analyses have been performed for a number of atomic systems of ^1S symmetry; in particular for two-,[3] four-,[4] six-,[5] and ten-electron[6] atomic ions. For atomic wave functions of ^1S symmetry, the NSO are eigenfunctions of the one-electron operators l^2, l_z, s^2, s_z, and i (the inversion operator). As a result, the eigenvalue spectrum possesses degeneracies of order $2(2l+1)$ between all NSO with the same quantum number l.[7]

In the construction of correlated wave functions for atomic states which are not of ^1S symmetry, one is faced with the additional problem of describing properly the orbital ($L \ne 0$) and spin ($S \ne 0$) polarization effects in addition to the normal correlation problem found in the more symmetric ^1S states. This polarization leads to a quite different structure of the one matrix. In particular, Larsson and Smith[8] have analyzed a number of wave functions for the Li (^2S) ground state and demonstrated the effects of spin polarization, the only type present for ^2S states. Here the NSO eigenvalue spectrum possesses degeneracies of order

TABLE I. The NSO occupation numbers of the Weiss wave functions for the three-electron ions (^2P).

Type	Li	Be^+	B^{2+}	C^{3+}	N^{4+}	O^{5+}
$p_+\alpha$	0.999 834 5	0.999 761 6	0.999 813 1	0.999 863 2	0.999 900 3	0.999 934 0
	0.000 646 2	0.000 428 7	0.000 289 6	0.000 203 2	0.000 147 6	0.000 099 5
	0.000 040 8	0.000 039 6	0.000 023 9	0.000 014 5	0.000 009 2	0.000 005 4
	0.000 007 1	0.000 004 4	0.000 002 7	0.000 001 7	0.000 001 2	0.000 000 7
	0.000 000 6	0.000 000 5	0.000 000 4	0.000 000 3	0.000 000 2	0.000 000 2
	0.000 000 1					
$s\alpha$	0.996 620 3	0.998 093 7	0.998 796 2	0.999 177 2	0.999 404 4	0.999 607 6
	0.001 455 0	0.000 847 2	0.000 543 8	0.000 373 0	0.000 269 1	0.000 169 2
	0.000 084 2	0.000 083 1	0.000 056 0	0.000 037 6	0.000 025 9	0.000 013 2
	0.000 016 5	0.000 008 8	0.000 005 3	0.000 003 6	0.000 002 5	0.000 002 9
	0.000 000 7	0.000 000 4	0.000 000 2	0.000 000 1	0.000 000 1	0.000 000 1
	0.000 000 1	0.000 000 1				
$s\beta$	0.996 656 0	0.998 130 9	0.998 814 3	0.999 184 8	0.999 406 9	0.999 607 2
	0.001 375 7	0.000 716 9	0.000 440 6	0.000 298 1	0.000 214 5	0.000 128 6
	0.000 029 4	0.000 020 8	0.000 015 1	0.000 010 8	0.000 007 8	0.000 006 2
	0.000 004 6	0.000 004 8	0.000 003 3	0.000 002 2	0.000 001 6	0.000 001 1
	0.000 000 6	0.000 000 3	0.000 000 2	0.000 000 1	0.000 000 1	0.000 000 1
	0.000 000 1	0.000 000 1				
$p_+\beta$	0.000 609 7	0.000 375 1	0.000 250 0	0.000 176 6	0.000 130 8	0.000 091 6
	0.000 033 0	0.000 034 0	0.000 024 0	0.000 016 4	0.000 011 5	0.000 007 6
	0.000 006 9	0.000 005 1	0.000 003 6	0.000 002 7	0.000 002 0	0.000 001 5
	0.000 000 6	0.000 000 6	0.000 000 4	0.000 000 3	0.000 000 3	0.000 000 2
$p_0\alpha$, $p_-\alpha$, $p_0\beta$	0.000 573 0	0.000 322 3	0.000 205 7	0.000 142 5	0.000 104 7	0.000 073 0
	0.000 020 2	0.000 011 8	0.000 007 7	0.000 005 4	0.000 004 0	0.000 002 8
	0.000 001 8	0.000 001 0	0.000 000 7	0.000 000 5	0.000 000 3	0.000 000 2
	0.000 000 1	0.000 000 1				
$p_-\beta$	0.000 562 9	0.000 302 6	0.000 186 1	0.000 125 4	0.000 090 3	0.000 062 0
	0.000 019 8	0.000 011 0	0.000 006 9	0.000 004 7	0.000 003 4	0.000 002 4
	0.000 001 7	0.000 001 0	0.000 000 6	0.000 000 4	0.000 000 3	0.000 000 2
	0.000 000 1	0.000 000 1				
$d_{-2}\alpha$, ... $d_{+2}\alpha$	0.000 016 3	0.000 009 7	0.000 006 4	0.000 004 6	0.000 003 4	0.000 002 4
	0.000 001 6	0.000 000 9	0.000 000 6	0.000 000 4	0.000 000 3	0.000 000 2
	0.000 000 2	0.000 000 1	0.000 000 1			
$d_{-2}\beta$, ... $d_{+2}\beta$	0.000 016 3	0.000 009 7	0.000 006 4	0.000 004 6	0.000 003 4	0.000 002 4
	0.000 001 6	0.000 000 9	0.000 000 6	0.000 000 4	0.000 000 3	0.000 000 2
	0.000 000 2	0.000 000 1	0.000 000 1			
$f_{-3}\alpha$, ..., $f_{+3}\beta$	0.000 001 5	0.000 000 9	0.000 000 6	0.000 000 4	0.000 000 3	0.000 000 2
	0.000 000 2	0.000 000 1	0.000 000 1			
$g_{-4}\alpha$, ..., $g_{+4}\beta$	0.000 000 2	0.000 000 1	0.000 000 1	0.000 000 1		

$(2l+1)$ between all NSO of the same l and m_s quantum number.

For ^2P states, all such degeneracies should disappear in general and the NSO are eigenfunctions of only l_z, s^2, s_z, and i due to the polarization by the unfilled shells. This behavior was demonstrated by the natural analysis by Brown and Smith[9] (BS) of some B (^2P) wave functions due to Schaeffer, Klemm, and Harris.[10]

In their analysis[9] of the Weiss 45-term wave function for the Li (^2P) state,[11(a)] BS observed that the Weiss one matrix does not show much of the

TABLE II. First three NSO occupation numbers of the Weiss wave functions for the three-electron ions (^2S).

Type	Li	Be^+	B^{++}	C^{3+}	N^{4+}	O^{5+}
$s\alpha$	0.999 564 2	0.999 614 4	0.999 706 2	0.999 773 0	0.999 823 7	0.999 859 2
$s\alpha$	0.996 643 2	0.998 182 4	0.998 864 1	0.999 222 7	0.999 437 6	0.999 574 3
$s\beta$	0.996 495 0	0.998 019 5	0.998 730 6	0.999 114 6	0.999 352 1	0.999 504 7

TABLE III. NSO occupation numbers of the Weiss O^{5+} (^2S) wave function.

$s\alpha$	$s\beta$	$p_+\beta$, $p_0\beta$, $p_-\beta$
0.999 859 2	0.999 504 7	0.000 099 4
0.999 574 3	0.000 143 2	0.000 008 4
0.000 145 1	0.000 004 2	0.000 001 2
0.000 004 5	0.000 000 3	0.000 000 2
0.000 000 5		
$p_+\alpha$, $p_0\alpha$, $p_-\alpha$	$d_{++}\beta$, ..., $d_{--}\beta$	$d_{++}\alpha$, ..., $d_{--}\alpha$
0.000 092 4	0.000 003 0	0.000 002 7
0.000 035 5	0.000 000 5	0.000 000 9
0.000 003 3	0.000 000 1	0.000 000 2
0.000 000 5		
$f_{+++}\alpha$, ..., $f_{---}\beta$	$g_{++++}\alpha$, ..., $g_{----}\beta$	
0.000 000 2	0.000 000 0	

TABLE IV. Comparison of leading NSO occupation numbers (multiplied by $2l+1$) for Li (^2S).

Number	Type	Weiss	Larsson 25 term	Larsson 100 term
1	$s\alpha$	0.999 564	0.999 504	0.999 494
2	$s\alpha$	0.996 643	0.996 679	0.996 632
3	$s\beta$	0.996 495	0.996 479	0.996 447
4	$p\beta$	0.001 878	0.001 871	0.001 892
5	$p\alpha$	0.001 844	0.001 816	0.001 837
6	$s\alpha$	0.001 325	0.001 327	0.001 335
7	$s\beta$	0.001 325	0.001 319	0.001 329
8	$p\alpha$	0.000 388	0.000 408	0.000 421
9	$p\beta$	0.000 132	0.000 143	0.000 143
10	$d\beta$	0.000 086	0.000 100	0.000 087
11	$d\alpha$	0.000 083	0.000 100	0.000 085
12	$p\alpha$	0.000 075	0.000 081	0.000 084
13	$s\beta$	0.000 027$_1$	0.000 033	0.000 029
14	$s\alpha$	0.000 027$_4$	0.000 031	0.000 028
15	$p\beta$	0.000 023	0.000 012	0.000 021

expected structure as was found for the B (^2P) wave functions. In particular, there was no mixing of the basis orbitals of different symmetry, i.e., $s+d_0+g_0$, p_0+f_0, $d_+ + g_+$, etc. In addition, there were some partial degeneracies among those with the same l quantum number. Thus the $p_0\alpha$, $p_-\alpha$, and $p_0\beta$ NSO's were degenerate with the same radial parts. Similarly, the d-type NSO's were degenerate with the $d\alpha$'s all having the same radial part and the $d\beta$'s all having the same radial parts, but different from the $d\alpha$'s. The f-type NSO's were degenerate with the same radial part for both the $f\alpha$'s and $f\beta$'s. A similar statement is true for the g-type NSO's.

As BS pointed out, the Weiss ^2P wave function was constructed in a similar manner to the Weiss ^2S wave function[11(b)] (i.e., "^2S-type restrictions") and hence left out configurations of the form sdp, sdf, etc. which would allow coupling of the s, d, and g orbitals and also of the p and f orbitals in the one matrix. It is just configurations of this type which are necessary to properly describe the atomic hyperfine structure of the Li (^2P) state.[9,12]

Subsequently, Banyard, Dixon, and Tait (BDT) analyzed[13] the Weiss functions for the (^2P) three-electron isoelectronic series (Li-N^{4+}). They reported a structure of the one matrix which disagrees with that of Brown and Smith in that the α and β p-type NSO's were each $(2l+1)=$ threefold degenerate. Because of this disagreement, we have reanalyzed the one matrices of the Weiss (^2P) wave functions. As presented in Table I, we confirm the structure reported by BS for Li (^2P) and have extended the analysis through O^{5+}.[14]

For the purpose of comparison, we have analyzed again the Weiss (^2S) functions and report these eigenvalues for Li-N^{4+} in Table II, which differ from those reported by BDT.[15] In Table III, the entire eigenvalue spectrum for O^{5+} (^2S) is presented. In Table IV, the leading NSO for Li (^2S) are compared for the Weiss wave function ($E = -7.47710$ a.u.), the Larsson[16] 100-term wave function[8(b)] ($E = -7.478025$ a.u.), and the Larsson[16] 25-term[8(a)] wave function ($E = -7.471683$ a.u.). By comparison, the restricted Hartree-Fock energy is -7.4327 a.u.

ACKNOWLEDGMENTS

We wish to thank Dr. A. W. Weiss for furnishing a list of misprints in the published wave functions. One of us (V. H. S.) expresses his appreciation to Professor G. L. Hofacker for his hospitality in Munich and the Deutsche Forschungsgemeinschaft for the Richard-Merton Professorship.

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[*] Research supported in part by grants from the National Research Council of Canada.

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[15] We have corrected some misprints in the published Weiss wave functions. Furthermore, we renormalized the wave functions so that we may report the eigenvalues to the indicated number of significant figures. Thus our eigenvalues differ somewhat from those reported by BDT for the (^2S) series Li-N^{4+}. However, to the number of significant figures given by BDT, only the results for the first three NSO differ and only these are reported in Table II. NSO with occupation numbers smaller than 1×10^{-7} are not listed in the tables.

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Rotating-Wave Approximation and Spontaneous Emission

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(Received 31 July 1972)

This is an addendum to the author's previous paper [Phys. Rev. A 4, 1778 (1971)], where master equations describing the spontaneous emission from a collection of identical two-level atoms and oscillators were derived without the use of rotating-wave approximation. However, the terms corresponding to the *frequency shifts* were not adequately included. Here such terms are properly treated and the appropriate master equation is given. Explicit form of the frequency-shift terms is also given.

In a previous paper,[1] which appeared under the same title as the present one, we considered spontaneous emission from a collection of identical two-level atoms and a system of oscillators without the use of rotating-wave approximation (R. W. A.). The master equation describing the spontaneous emission from a system of two-level atoms (which were assumed to be confined to a region whose linear dimensions were small compared to the wavelength of emitted radiation) was found to be

$$\frac{\partial\rho}{\partial t}=-i\omega_0\sum_i[S_i^z,\ \rho]$$

$$-\gamma\sum_{ij}(S_i^+S_j^-\rho-S_j^-\rho S_i^++S_i^-S_j^-\rho-S_i^-\rho S_j^-+\text{H. c.}),\quad(1)$$

where ω_0 is the energy separation between two atomic levels and γ is equal to $\frac{1}{2}$(natural lifetime)$^{-1}$. In (1) ρ is the reduced-density operator corresponding to the atomic system alone and $S_i^\pm$ are the components of the spin-angular-momentum operator corresponding to spin-$\frac{1}{2}$ value. In the derivation of (1), we ignored the frequency-shift terms.[2] The purpose of this addendum is to include such terms in the master equation and to give the explicit form of these terms. We will also make a few comments on the use of R. W. A. We will consider, for the sake of simplicity, only the case of a single two-level atom.

The Hamiltonian of a single two-level atom interacting with a quantized radiation field can be, in the dipole approximation, written as

$$H=\omega_0S^z+\sum_{kS}\omega_{kS}a_{kS}^\dagger a_{kS}+\sum_{kS}[g_{kS}a_{kS}(S^++S^-)+\text{H. c.}],\quad(2)$$

where the coupling coefficient g_{kS} is given by[3]

$$g_{kS}=-i\left(\frac{2\pi c}{L^3}\right)^{1/2}k^{1/2}(\vec{d}_{12}\cdot\vec{\epsilon}_{kS}).\quad(3)$$

All the symbols have the same meaning as in Ref. 1. The master equation for the reduced-density operator ρ, in Born and Markovian approximations, may be written as

$$\frac{\partial\rho}{\partial t}+\int_0^\infty\text{Tr}_R[H(t),\ [H(t-\tau),\ \rho_R(0)\rho(t)]]d\tau=0,\quad(4)$$

where all the operators are in the interaction picture and Tr_R indicates the trace over the radiation-field variables. In (4) $\rho_R(0)$ is the initial vacuum state of the radiation field, i.e.,

$$\rho_R(0)=|\{0_{kS}\}\rangle\langle\{0_{kS}\}|.\quad(5)$$