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Construction and Use of Atomic *L–S* Eigenfunctions[1]

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ABSTRACT

Explicit formulas are given for matrix elements of operators commuting with $\mathscr{L}^2$ and $\mathscr{S}^2$, using complete or partial sets of L–S eigenfunctions as a basis. A computer program is described for obtaining such eigenfunctions by direct diagonalization of $\mathscr{L}^2 + (1/20)\, \mathscr{S}^2$, and examples are given.

INTRODUCTION

One of the central problems in the quantum mechanics of atoms has been the construction and manipulation of electronic wave functions which completely characterize the permutational and angular symmetry of the atomic states. The earliest approach to this problem was by Slater [1], who introduced the determinantal wave function and the idea of constructing angular momentum eigenfunctions as linear combinations of Slater determinants. Because both orbital and spin angular momentum must be considered, the formation of appropriate combinations of determinants is not always a simple matter, particularly for systems with many electrons outside of closed shells.

For the majority of the atomic systems, it is most convenient to work with the angular eigenfunctions appropriate to Russell–Saunders coupling [2], i.e. with eigenfunctions of the operators $\mathscr{L}^2$, $\mathscr{L}_z$, $\mathscr{S}^2$, and $\mathscr{S}_z$. Diagonal matrix elements for these "L–S eigenfunctions" can be evaluated without the need of a prior explicit construction of the eigenfunctions themselves, following the elegant procedures described by Racah [3]. However, accurate studies of atoms require the simultaneous use of many L–S eigenfunctions, and it is therefore necessary to have means of evaluating the off-diagonal matrix elements connecting different eigenfunctions.

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These off-diagonal elements could be evaluated by an extension of Racah's methods, but it would then be necessary to have extremely large numbers of coefficients of fractional parentage and the convenience of the methods would be lost. It thus once again seems expedient to follow procedures based on the explicit construction of L–S eigenfunctions as linear combinations of Slater determinants.

The construction of matrix elements between L–S eigenfunctions can be much simplified by the use of projection operators and group theory. This application of projection operators has been discussed by Lowdin [4], and Nesbet [5] has made a detailed study of the most efficient ways to form matrix elements of symmetry-projected wavefunctions. Nesbet's procedures can be readily adapted to the present situation in which appropriate eigenfunctions are explicitly available. The specific approach which thereby results also permits a convenient handling of problems involving less than a complete set of L–S eigenfunctions of given quantum numbers. Such cases arise when certain vector couplings dominate others in their contributions to a particular energy level.

This paper reports a direct diagonalization procedure for generating L–S eigenfunctions and gives explicit formulas for the construction of matrix elements. A computer program for the eigenfunction generation is described, and typical results and computation times are cited.

MATRIX ELEMENTS

It is assumed that there are available complete orthonormal sets of L–S eigenfunctions corresponding to various orbital occupancies. The eigenfunctions of one such set, denoted θ_i, $i = 1,..., d$, are specified as linear combinations of orthonormal Slater determinants χ_μ, $\mu = 1,..., n$:

$$\theta_i = \sum_{\mu=1}^{n} c_{\mu i}\chi_\mu \qquad i = 1,..., d \tag{1}$$

It will occasionally be useful to think of the $c_{\mu i}$ as defining a $n \times d$ rectangular matrix denoted $\mathbf{c}$. When it is necessary to consider simultaneously two different orbital occupancies, let the second occupancy have L–S eigenfunctions θ'_i, $i = 1,..., d'$, formed as linear combinations of Slater determinants χ'_μ, $\mu = 1,..., n'$, with coefficient matrix $\mathbf{c}'$. The problem at issue here is simply the evaluation of the matrix elements $\langle\theta_i \mid H \mid \theta_j\rangle$ and $\langle\theta'_i \mid H \mid \theta_j\rangle$ in terms of the Slater-determinant elements $\langle\chi_\mu \mid H \mid \chi_\sigma\rangle$ or $\langle\chi'_\mu \mid H \mid \chi_\sigma\rangle$, for operators H which commute with $\mathscr{L}^2$ and $\mathscr{S}^2$ and are totally symmetric with respect to permutations of the particle numbering.

The first step in solving this problem is to introduce a projection operator $\mathcal{O}$ which projects an arbitrary function onto the appropriate eigenspace of $\mathscr{L}^2$ and $\mathscr{S}^2$. A sufficiently general form of this projector can be written as

$$\mathcal{O} = \sum_{i=1}^{d} | \theta_i \rangle\langle \theta_i | + \sum_{i=1}^{d'} | \theta'_i \rangle\langle \theta'_i | \tag{2}$$

It is clear from Eq. (2) that $\mathcal{O}$ is idempotent and Hermitian, and the commutation of H with $\mathscr{L}^2$ and $\mathscr{S}^2$, plus the completeness of the sets θ_i and θ'_i, insure the commutation of H with $\mathcal{O}$ within all matrix elements to be considered here. It should be noted that the commutation of H with $\mathcal{O}$ depends upon the inclusion of the full sets of θ_i and θ'_i. By direct application of $\mathcal{O}$ to χ_ν followed by use of Eq. (1), one may obtain the relation

$$\mathcal{O}\chi_\nu = \sum_{i=1}^{d} c_{\nu i}^{*} \theta_i \qquad \nu = 1,\dots, n \tag{3}$$

where the asterisk indicates complex conjugation. From Eqs. (1) and (3), one may also obtain

$$\mathcal{O}\chi_\nu = \sum_{\mu=1}^{n} \sum_{i=1}^{d} c_{\nu i}^{*} c_{\mu i} \chi_\mu \tag{4}$$

It is also convenient to express θ_i as a linear combination of the $\mathcal{O}\chi_\nu$. Ordinarily n will be much greater than d, so that the n functions $\mathcal{O}\chi_\nu$ of Eq. (3) will be linearly dependent. However, there must exist exactly d linearly independent $\mathcal{O}\chi_\nu$, and it will be assumed that the χ_ν are ordered in such a way that the first d $\mathcal{O}\chi_\nu$ form a linearly independent set. It will then be possible to invert the first d of Eqs. (3), leading to

$$\theta_i = \sum_{\nu=1}^{d} (\bar{\mathbf{c}}^{*})^{-1}_{i\nu} \, \mathcal{O}\chi_\nu \qquad i = 1,\dots, d \tag{5}$$

Here $\bar{\mathbf{c}}$ stands for the square matrix consisting of the first d rows of $\mathbf{c}$. The linear independence of the first d $\mathcal{O}\chi_\nu$ assures the nonsingularity of $\bar{\mathbf{c}}$.

The matrix elements $\langle \theta'_i \mid H \mid \theta_j \rangle$ may now be expressed in terms of the $\mathcal{O}\chi_\nu$ with the aid of Eq. (5), following which the Hermiticity and commutation properties of $\mathcal{O}$ may be used to eliminate one of its occurrences. The remaining occurrence of

$\mathcal{O}$ may then be eliminated according to Eq. (4). These steps are illustrated in the following series of equations.

$$\begin{aligned}\langle\theta_i' \mid H \mid \theta_j\rangle &= \sum_{\mu=1}^{d'} \sum_{\nu=1}^{d} (\bar{c}')^{-1}_{i\mu} (\bar{c}^*)^{-1}_{j\nu} \langle \mathcal{O}\chi_\mu' \mid H \mid \mathcal{O}\chi_\nu\rangle \\ &= \sum_{\mu=1}^{d'} \sum_{\nu=1}^{d} (\bar{c}')^{-1}_{i\mu} (\bar{c}^*)^{-1}_{j\nu} \langle \chi_\mu' \mid H \mid \mathcal{O}\chi_\nu\rangle \qquad (6) \\ &= \sum_{\mu=1}^{d'} \sum_{\nu=1}^{d} \sum_{\sigma=1}^{n} \sum_{k=1}^{d} (\bar{c}')^{-1}_{i\mu} (\bar{c}^*)^{-1}_{j\nu}\, c^*_{\nu k} c_{\sigma k} \langle \chi_\mu' \mid H \mid \chi_\sigma\rangle\end{aligned}$$

Equation (6) may now be simplified by performing the summation over ν, taking note of the fact that $\sum_{\nu=1}^{d} (\bar{c}^*)^{-1}_{j\nu}\, c^*_{\nu k} = \delta_{jk}$. Summing then also over k,

$$\langle\theta_i' \mid H \mid \theta_j\rangle = \sum_{\mu=1}^{d'} \sum_{\sigma=1}^{n} (\bar{c}')^{-1}_{i\mu}\, c_{\sigma j} \langle \chi_\mu' \mid H \mid \chi_\sigma\rangle \qquad (7)$$

The matrix element $\langle\theta_i \mid H \mid \theta_j\rangle$ will have a corresponding form without the primes.

Equation (7) shows the key result of the present discussion, namely that a $d' \times n$ block of Slater-determinant matrix elements is required to generate the entire $d' \times d$ matrix for the L–S eigenfunctions. Moreover, the necessary coefficients are directly given from the representation of the eigenfunctions as linear combinations of Slater determinants. The present formulation becomes equivalent to that of Nesbet if the eigenfunctions θ_i and θ_i' are transformed to bases in which the matrices $\bar{c}$ and $\bar{c}'$ are triangular. Imposition of this condition would reduce still further the extents of the summations in Eq. (7), but would interfere with the procedures about to be discussed.

There is one practical observation to be made with respect to Eq. (7). Because H is Hermitian, $\langle\theta_i' \mid H \mid \theta_j\rangle$ can alternatively be computed as $\langle\theta_j \mid H \mid \theta_i'\rangle^*$, which according to Eq. (7), would involve summations of extents d and n'. If dn' is smaller than $d'n$, the alternative formulation will be computationally more efficient.

PARTIAL EIGENFUNCTION SETS

It is well known that d, the number of linearly independent θ_i, is rather large for many orbital occupancies of interest. However, it is often possible to restrict consideration to relatively few of the full set of θ_i. For example, consider the ^3P terms corresponding to the orbital occupancy $1s^2d_1{}^22p^4$. These configurations must be added to the Hartree-Fock function $1s^22s^22p^4$ to obtain an accurate configuration-interaction wavefunction for the ground state of oxygen. There are six electrons of these terms outside of closed shells, namely $d_1{}^2 2p^4$, and these six electrons give rise to six linearly independent ^3P eigenfunctions, which are expressible as linear combinations of 27 Slater determinants. But in a particular basis, only one of these ^3P eigenfunctions contributes significantly to the oxygen wavefunction, namely the function usually denoted $1s^2(d_1{}^2)^1S\,2p^4$. (This state of affairs is not purely fortuitous; the other five eigenfunctions involve triple or higher excitations from the spinorbitals of the Hartree-Fock function. [6]) The single significant ^3P eigenfunction uses only five of the 27 Slater determinants needed to describe the full eigenfunction set, and it is highly desirable to take advantage of the computational savings afforded by the restriction of both the θ_i and the χ_ν.

Another, more striking example of the savings possible by using only the significant θ_i is illustrated by the orbital occupancy $1s2sp_1p_2 2p^4$ for oxygen. This eight-electron configuration involves 27 ^3P eigenfunctions formed from 106 Slater determinants. However, only the eigenfunctions of the form $(1s2sp_1p_2)^1S\,2p^4$ are important, and there are only two such functions, involving 18 Slater determinants.

The formulation given in Eq. (7) is of precisely the form needed to take advantage of the above described situations. It is only necessary to make appropriate restriction of the values of i and j, dropping also any μ or σ values which have vanishing contributions for all retained i and j. This means that the calculations will only use certain *rows* of $\bar{\mathbf{c}}'^{-1}$ and certain *columns* of $\bar{\mathbf{c}}$, and the presence of suitable zeroes in the retained portions of $\bar{\mathbf{c}}'^{-1}$ and $\mathbf{c}$ may obviate the need for certain $\langle \chi'_\mu \mid H \mid \chi_\sigma \rangle$.

COMPUTATION OF EIGENFUNCTIONS

The earliest attempt at systematic generation of more complicated L–S eigenfunctions was by Johnson [7], who generated matrices of $\mathscr{L}^2$ and $\mathscr{S}^2$ with a Slater-determinant basis, and then simultaneously diagonalized these matrices to obtain eigenfunctions. More recently Rotenberg [8] developed and programmed an approach corresponding to the explicit application of a projection operator to convert a Slater determinant into an L–S eigenfunction.

It seemed to the authors that the direct diagonalization approach was more suitable for actual computation on larger systems, and it was elected to achieve a simultaneous diagonalization of $\mathscr{L}^2$ and $\mathscr{S}^2$ by diagonalizing the matrix of $\mathscr{L}^2 + k\mathscr{S}^2$, where k is in principle arbitrary. The eigenvalues of this matrix are of the form $L(L+1) + kS(S+1)$, and a suitable choice of k can cause all the possible values of L and S to lead to distinct, well-spaced eigenvalues. In this work k was set at 1/20.

A double-precision FORTRAN IV computer program to construct L–S eigenfunctions by direct diagonalization was written for the IBM 360/67 computer.

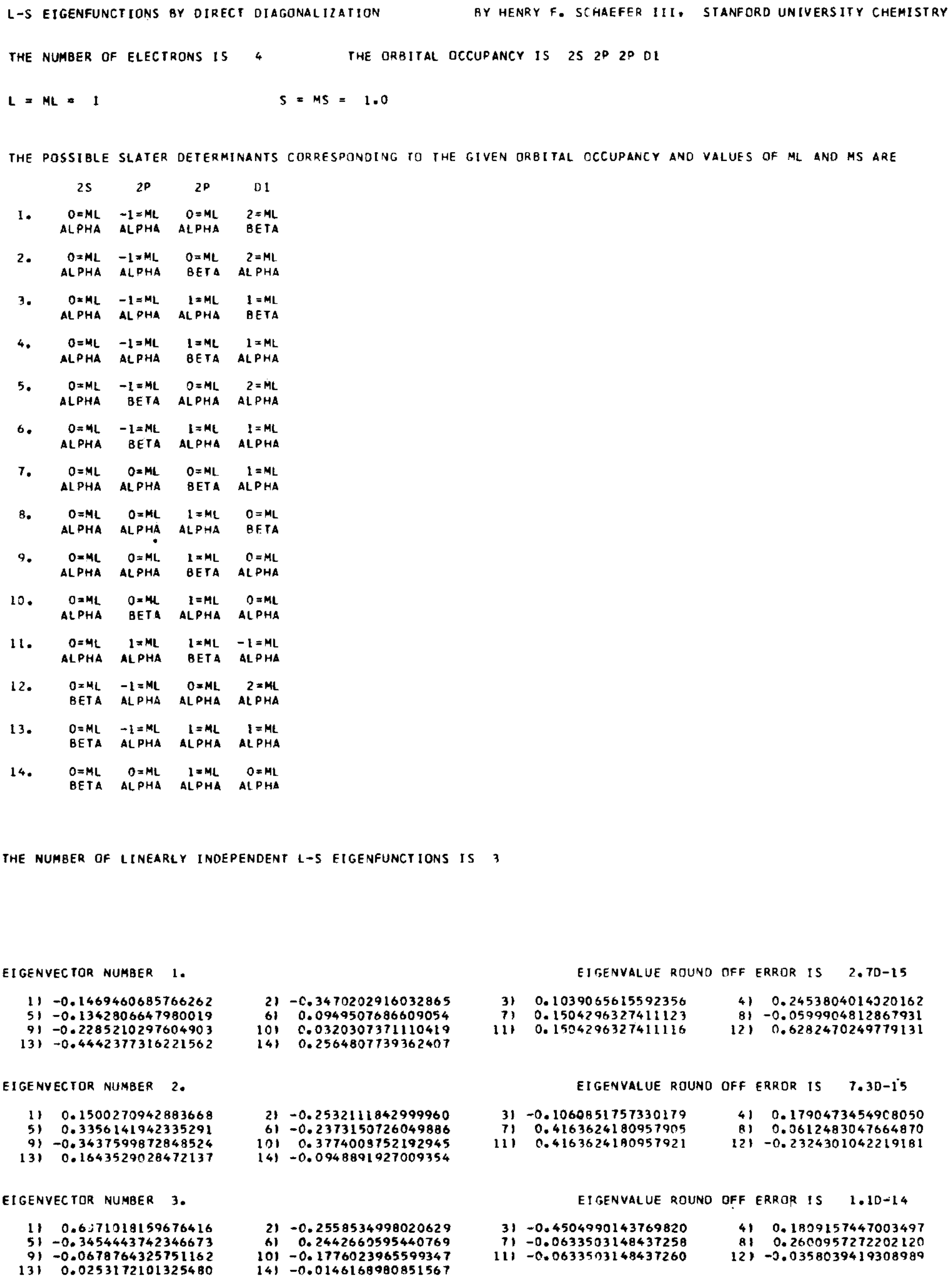
This program, designated LSDIAG, has been placed in the Quantum Chemistry Program Exchange [9] and is available to FORTRAN users. The program is divided into three distinct sections. The first section identifies all Slater determinants χ_μ which can arise from a given orbital occupancy and values $M_L = L$, $M_S = S$. The second section evaluates $\langle\chi_\mu \mid \mathscr{L}^2 + (1/20)\, \mathscr{S}^2 \mid \chi_\nu\rangle$ by standard techniques. The third section of the program finds an orthonormal set of eigenvectors of $\mathscr{L}^2 + (1/20)\, \mathscr{S}^2$ corresponding to the eigenvalue $L(L+1) + (1/20)\, S(S+1)$, using a modification of the computer program GIVENS written by Prosser [10]. To avoid the necessity of prior knowledge of the number of L–S eigenfunctions, the program finds all the matrix eigenvalues near to the required value. Because of the choice $M_L = L$, $M_S = S$, the smallest matrix eigenvalues are those required.

Present limitations on the program are: (1) no more than 16 electrons outside of closed shells; (2) no more than 200 determinants arising from the specified orbital occupancy; (3) no more than 50 L–S eigenfunctions arising from the specified orbital occupancy and the specified L and S values. These restrictions are necessitated by the memory size of the IBM 360/67 computer on which the program was tested. The only problems of potential interest to the authors which exceed these limitations are some of the terms least important according to Hund's rules (those with the lowest L and S values) arising from configurations g^n, when $n > 4$.

The above methods, which lead to complete sets of L–S eigenfunctions, can also be used to generate partial sets of the types illustrated in an earlier section. For example, the ^3P functions of the form $(1s2s\, p_1\, p_2)^1S\, 2p^4$ can be constructed as the product of a four-electron ^1S function for occupancy $1s2s\, p_1\, p_2$ and a ^3P function for occupancy $2p^4$. These functions can be generated by applying the LSDIAG program to occupancies $1s2s\, p_1\, p_2$ and $2p^4$. However, note that to obtain the matrix $\bar{c}^{-1}$ for the eight-electron orbital occupancy $1s2s\, p_1\, p_2\, 2p^4$, the remaining ^3P functions must also be generated by coupling all other $1s2s\, p_1\, p_2$ and $2p^4$ states leading to ^3P.

RESULTS

Since the amount of space required to tabulate the L–S eigenfunctions can be enormous, only one relatively simple but nonetheless nontrivial example is displayed here. Figure 1 shows the ^3P functions arising from the orbital occupancy $2s2p^2\, d_1$. All three of these functions are needed as single excitations ($2s \rightarrow d_1$) in an accurate wavefunction for the ground state of the carbon atom, for which the Hartree–Fock function has the form $1s^2 2s^2 2p^2$. The entries in Figure 1 called "Eigenvalue Round Off Error" give a good indication of the accuracy of the eigenfunctions produced. In all cases tested so far, the eigenfunctions have proved exact to at least 13 decimal digits.



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L-S EIGENFUNCTIONS BY DIRECT DIAGONALIZATION            BY HENRY F. SCHAEFER III, STANFORD UNIVERSITY CHEMISTRY

THE NUMBER OF ELECTRONS IS    4            THE ORBITAL OCCUPANCY IS  2S 2P 2P D1

L = ML =  1                        S = MS =  1.0


THE POSSIBLE SLATER DETERMINANTS CORRESPONDING TO THE GIVEN ORBITAL OCCUPANCY AND VALUES OF ML AND MS ARE

         2S     2P     2P     D1

 1.     0=ML  -1=ML   0=ML   2=ML
       ALPHA  ALPHA  ALPHA   BETA

 2.     0=ML  -1=ML   0=ML   2=ML
       ALPHA  ALPHA   BETA  ALPHA

 3.     0=ML  -1=ML   1=ML   1=ML
       ALPHA  ALPHA  ALPHA   BETA

 4.     0=ML  -1=ML   1=ML   1=ML
       ALPHA  ALPHA   BETA  ALPHA

 5.     0=ML  -1=ML   0=ML   2=ML
       ALPHA   BETA  ALPHA  ALPHA

 6.     0=ML  -1=ML   1=ML   1=ML
       ALPHA   BETA  ALPHA  ALPHA

 7.     0=ML   0=ML   0=ML   1=ML
       ALPHA  ALPHA   BETA  ALPHA

 8.     0=ML   0=ML   1=ML   0=ML
       ALPHA  ALPHA  ALPHA   BETA

 9.     0=ML   0=ML   1=ML   0=ML
       ALPHA  ALPHA   BETA  ALPHA

10.     0=ML   0=ML   1=ML   0=ML
       ALPHA   BETA  ALPHA  ALPHA

11.     0=ML   1=ML   1=ML  -1=ML
       ALPHA  ALPHA   BETA  ALPHA

12.     0=ML  -1=ML   0=ML   2=ML
        BETA  ALPHA  ALPHA  ALPHA

13.     0=ML  -1=ML   1=ML   1=ML
        BETA  ALPHA  ALPHA  ALPHA

14.     0=ML   0=ML   1=ML   0=ML
        BETA  ALPHA  ALPHA  ALPHA


THE NUMBER OF LINEARLY INDEPENDENT L-S EIGENFUNCTIONS IS  3



EIGENVECTOR NUMBER  1.                                                        EIGENVALUE ROUND OFF ERROR IS   2.7D-15

   1) -0.1469460685766262      2) -0.3470202916032865      3)  0.1039065615592356      4)  0.2453804014020162
   5) -0.1342806647980019      6)  0.0949507686609054      7)  0.1504296327411123      8) -0.0599904812867931
   9) -0.2285210297604903     10)  0.0320307371110419     11)  0.1504296327411116     12)  0.6282470249779131
  13) -0.4442377316221562     14)  0.2564807739362407

EIGENVECTOR NUMBER  2.                                                        EIGENVALUE ROUND OFF ERROR IS   7.3D-15

   1)  0.1500270942883668      2) -0.2532111842999960      3) -0.1060851757330179      4)  0.1790473454908050
   5)  0.3356141942335291      6) -0.2373150726049886      7)  0.4163624180957905      8)  0.0612483047664870
   9) -0.3437599872848524     10)  0.3774008752192945     11)  0.4163624180957921     12) -0.2324301042219181
  13)  0.1643529028472137     14) -0.0948891927009354

EIGENVECTOR NUMBER  3.                                                        EIGENVALUE ROUND OFF ERROR IS   1.1D-14

   1)  0.6371018159676416      2) -0.2558534998020629      3) -0.4504990143769820      4)  0.1809157447003497
   5) -0.3454443742346673      6)  0.2442660595440769      7) -0.0633503148437258      8)  0.2600957272202120
   9) -0.0678764325751162     10) -0.1776023965599347     11) -0.0633503148437260     12) -0.0358039419308989
  13)  0.0253172101325480     14) -0.0146168980851567
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FIG. 1. Computer output of the three ^3P eigenfunctions for the orbital occupancy $2s2p^2d_1$.

A summary of several other examples is given in Table I. For comparison with the projection operator program of Rotenberg [8], one of the examples consits of the five ^2P eigenfunctions corresponding to the orbital occupancy f^7. Rotenberg's time to calculate these five functions was at least 25 minutes on the IBM 7090, while the present program took 2.1 minutes on the IBM 360/67 (believed equivalent to about 8 minutes on the 7090).

TABLE I

EXAMPLES OF L–S EIGENFUNCTIONS BY DIRECT DIAGONALIZATION

Orbital occupancy	Symmetry	Number of Slater determinants	Number of linearly independent L–S eigenfunctions	IBM 360/67 execution time, minutes
$1s2sp_1p_2$	^1S	18	2	0.02
$1s2sp_1p_22p^4$	^3P	106	27	1.44
$1s2sp_1p_22p^4$	^1D	84	14	0.98
$2sd_12p^2$	^3P	14	3	0.01
$2s2p^2p_1d_1$	^4S	52	4	0.24
$2s2p^3d_1f_1$	^3P	179	18	3.53
f^7	^2P	114	5	2.10
g^9	^6D	96	9	2.79

Karayianis [11] has determined the number and types of terms which arise from the configurations g^n. Wybourne [12] has further classified the g^n terms according to the irreducible representations of the higher groups R_9 and U_9. During the testing of the present computer program, certain discrepancies were found between the results of Karayianis and those of Wybourne. In particular, the numbers of sextet ($S = 5/2$) terms arising from g^9 are in disagreement. The present results, which were obtained by a procedure completely different from that of Karayianis or Wybourne, agree with those of Karayianis. The present authors believe that Wybourne has omitted some of the g^9 sextet terms in his analysis of the problem.

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