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A generic procedure for determining atomic LS spectral terms and their LS eigenfunctions*

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This paper develops a Fortran code which is capable to construct the simplest LS eigenfunctions for desired symmetry and determine all permitted atomic LS spectral terms under a given orbital occupancy by implementing and extending the Schaefer and Harris method. Examples (in some cases the most complete set to date) of multiple spectroscopic terms of LS coupling of atomic states for both non-equivalent and equivalent electronic configurations are given. It also corrects a few observed errors from the recent literature.

Keywords: LS coupling, multiples spectroscopic term
PACC: 3110, 3120A

1. Introduction

One of the central problems in quantum mechanics of atoms has been the construction and manipulation of electronic wave functions which completely characterizes the permutational and angular symmetry of an atomic state. For the central-field approximation, in general, the approximate wave functions and configuration state functions (CSFs) in the form of Slater determinants are not eigenfunctions of the total angular momentum operator, as the exact eigenfunctions are. However, by a linear combination of Slater determinants belonging to the same electron occupancy, eigenfunctions of the angular momentum operator can be formed. Since $[H, L^2] = 0$, $[H, S^2] = 0$, $[H, L_z] = 0$ and $[H, S_z] = 0$, these eigenfunctions are also the eigenfunctions of the Hamiltonian. This significantly simplifies the diagonalization of the Hamiltonian.

Following the Schaefer and Harris method,[1] we developed a computer code to calculate the coefficients of the Slater determinants which ensure that the wave functions are eigenfunctions of the appropriate angular momentum operators. This program is part of a series of our codes written for the calculation of atomic structure by using developed variational Laguerre-type orbitals in configuration interaction.[2,3] This code is presented separately because the method can be simply extended to calculate all spectral terms arising from many particle configurations, a basic but often laborious and complicated problem in the atomic and nuclear shell model. The current feasible methods usually make several steps of simplification, such as group theory method, Young patterns method, enumerate method etc. Often, these are difficult and complicated to implement, whereas the present method is conceptually clearest and simplest to implement.

In this work, we simply modified our initial code[2] for the construction of atomic wavefunctions, which completely characterizes the permutational and angular symmetry of an atomic state, to directly determine all LS terms for an arbitrary given electronic configuration, in the simplest, to our knowledge, clearest, and error-free way. This offers a basis for further calculations of energy levels for laser and soft x-rays. As an application, we calculate the most complete set of calculations to date (to our knowledge) of all spectral terms arising from non-equivalent electronic configurations of Co-like ions $3d^8 4p$, Np (Z=93) $5f^4 6d$, and

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Gd (Z=64) 4f^{7}5d. Also, for equivalent electron configurations, since the terms s^n, p^n, d^n, f^n can be found in text books, (e.g. Ref.[4]), we present the complete set of the multiple spectroscopic terms of LS coupling, g^n,($n = 1, ..., 9$), as well as d^5, f^7, compared with (and correcting) results partially appearing in the literature. To our knowledge, g^5, g^6, g^7, g^8 are given for the first time in the literature. In addition, as a small but nontrivial example for our code, directly usable for further atomic structure calculations, we give the LS eigenfunctions of Co-like ions 3d^{8}4p of ^6D symmetry type.

2. Algorithm

For an N-electron atom, according to Schaefer and Harris,[1] in order to find the LS eigenfunctions of a given symmetry type ^{2S+1}L and a given orbital occupancy we generate matrix elements of $L^2+\lambda S^2$ (λ is a small arbitrary number, enough to distinguish the two contributions) within the $n_{\rm det}$–dimensional Slater determinant basis obtained from the given orbital occupancy and chosen (see below) such that $M_L = L$, and $M_S = S$, where M_L and M_S are the sums of ml_i and ms_i of each given orbital (singly occupied), $i = 1, ..., N$.

For the evaluation of the matrix elements of $L^2 + \lambda S^2$, for an N electron atom, we denote the Slater determinants by $D_a = D(n^1l^1ml_a^1ms_a^1; ...; n^Nl^Nml_a^Nms_a^N)$ [all determinants have the same n^i, l^i ($i = 1, ..., N$) - we use 2p2p in the example given below in the Appendix], $a = 1, ..., n_{\rm det}$, and similarly for $b = 1, ..., n_{\rm det}$. Since

$$L^2 = \sum_{i=1}^{N} (L^i)^2 + 2\sum_{i>j}^{N} L_z^i L_z^j + \sum_{i\neq j}^{N} L_+^i L_-^j, \quad (1)$$

$$L_\pm \equiv L_x \pm {\rm i}L_y, \quad (2)$$

and

$$L_\pm Y_{l,m} = \sqrt{(l(l+1) - m(m\pm 1))}Y_{l,m\pm 1}, \quad (3)$$

and similarly for S^2, we have

$$\begin{aligned}\langle D_a|\, L^2 + \lambda S^2 \,|D_b\rangle = &\left\{\sum_{i=1}^{N}[l^i(l^i+1) + \lambda s^i(s^i+1)] + 2\sum_{i>j}^{N}(ml_a^i ml_a^j + \lambda ms_a^i ms_a^j)\right\}\\ &\times \prod_{i=1}^{N}\delta(ml_a^i, ml_b^i)\delta(ms_a^i, ms_b^i)\\ &+ \sum_{i\neq j}^{N}\{[l^i(l^i+1) - ml_a^i(ml_a^i+1)]^{\frac{1}{2}}[l^j(l^j+1) - ml_a^j(ml_a^j-1)]^{\frac{1}{2}}\}\\ &\times\ \delta(ml_a^i+1, ml_b^i)\delta(ml_a^i-1, ml_b^i)\prod_{k\neq i,j}^{N}\delta(ml_a^k, ml_b^k)\delta(ml_a^k, ml_b^k)\\ &+ \lambda\sum_{i\neq j}^{N}\{[s^i(s^i+1) - ms_a^i(ms_a^i+1)]^{\frac{1}{2}}[s^j(s^j+1) - ms_a^j(ms_a^j-1)]^{\frac{1}{2}}\}\\ &\times\ \delta(ms_a^i+1, ms_b^i)\delta(ms_a^i-1, ms_b^i)\prod_{k\neq i,j}^{N}\delta(ms_a^k, ms_b^k)\delta(ms_a^k, ms_b^k). \quad (4)\end{aligned}$$

We find all matrix elements and simultaneously diagonalize L^2 and S^2 by diagonalizing the matrix $L^2 + \lambda S^2$. As seen from the diagonal basis, the eigenvalues of this matrix are of the form $L^k(L^k + 1) + \lambda S^k(S^k + 1)$, $k = 1, ..., n_{\rm det}$, where $n_{\rm det}$ is also the dimensionality of this matrix. In order to obtain distinct, well spaced eigenvalues for all possible L^k and S^k values, one should keep $\lambda S^k(S^k + 1) < 0.1$, in this work, we set λ =1/2000.

Since $|M_L| = L, L-1, ..., 0$, and $|M_S| = S, S-1, ..., 0$ or $1/2$, many LS terms can have a certain $M_L : L = M_L, M_L+1, ...$, and similarly for S. Thus, if we work only with all determinants having fixed $M_L = L$, and $M_S = S$, then the lowest eigenvalue is $L(L+1) + \lambda S(S+1)$ and the corresponding eigenvectors have symmetry type ^{2S+1}L. The higher eigenvalues are $L^k(L^k+1)+\lambda S^k(S^k+1)$, where $L^k = M_L + k = L + k$, $S^k = M_S + k = S + k$, $k = 1, ..., n_{\rm det} - n_{\rm lowest}$ ($n_{\rm lowest}$ is the degeneracy of the lowest eigenvalue), and the corresponding eigenvectors have symmetry $^{2S^k+1}L^k$.

Therefore, for a given orbital occupancy: (i) in order to produce the simplest LS eigenfunctions of ^{2S+1}L symmetry type, we diagonalize Eq.(4) with $M_L = L$ and $M_S = S$ and take all eigenvectors belonging to the lowest eigenvalue; (ii) on the other hand, in order to produce all LS terms for the given orbital occupancy, we take advantage of the Schaefer and Harris approach, starting from the lowest possible $|M_L| = L = 0$ and the lowest possible $|M_S| = S =$ (1/2 or 0)- depending on the number of electrons (odd or even, respectively).

A demonstration is given in the Appendix for the orbital occupancy p^2.

For case (i) we developed the mode 'LS_config': Input: the desired configuration (orbital occupancy) and desired symmetry type ^{2S+1}L; output: the simplest corresponding LS eigenfunctions.

For case (ii) we developed the mode 'LS_terms': Input: only the desired configuration (orbital occupancy); output: all LS terms. According to the above discussion, in order to find all LS terms for a given configuration, we input the lowest possible L and S as input symmetry, i.e $L = 0$ and $S = 0$ when the number of electrons is even, or $L = 0$ and $S = 1/2$ when the number of electrons is odd. Then, by examining all eigenvalues of $L^2 + \lambda S^2$, we can find all possible L and S values by solving for L and S the equations

$$L(L+1) = \text{Integer_part (Eigenvalue)}, \qquad (5)$$

and

$$S(S+1) = (1/\lambda)(\text{Einenvalue} - \text{Integer_part (Eigenvalue)}). \qquad (6)$$

Both modes of the program, 'LS_terms' and 'LS_config', are divided into three distinct sections:

(a1-1) For the mode 'LS_terms', given (input) an orbital occupancy, we create and identify all Slater determinants D obtained from this occupancy and having symmetry either ^1S, when the number of electrons is even, or ^2S, when the number of electrons is odd.

(a1-2) For the mode 'LS_config', given (input) an orbital occupancy and a (desired) symmetry, chosen from (a1-1), we create and identify all Slater determinants D obtained from the given occupancy and having the desired symmetry.

(a2) In Subroutine /base/, from the desired [(a1-2)] or the lowest possible [(a1-1)] L, S symmetry (here L=0, S=0, or 1/2), we set $M_L = L$ and $M_S = S$, and for the given l_i and s_i of each i-orbital, i=1 to N, (N is the number of electrons), we produce all possible ml_i and ms_i, and all possible Slater determinants with $\sum m_{l_i} = M_L$ and $\sum m_{s_i} = M_S$.

In Subroutine /compa/, by checking all the above Slater determinants, we exclude the ones which are inconsistent with the Pauli principle and store all different Slater determinants, identified by quick (N log$N$) sort, in array wp.

(b) We evaluate the matrix elements $\langle D_i|L^2 + \lambda S^2|D_j\rangle$, i, j: 1 to $n_{\rm det}$, by Eq.(4), through subroutine /ls_matrix/. Through subroutines /ls_lap/ /sort_bu/ we take care of the δ-functions appearing in Eq.(4) and of the $\pm$sign of the resulting determinants, by writing them in a common order [e.g. $(1^+, -1^-)$ and $(-1^-, 1^+)$ are the same determinants, but $(1^+, -1^-) = -(-1^-, 1^+)$].

(c) We diagonalize this matrix in subroutine /jacobi/

3. Results and discussion

The notation of the spectral terms given below is proposed by Russell[5] and Russell and Saunders[6] is widely used: *S P D F G H I K L M N O Q R T U V W X Y Z*, for L=0 to 20 respectively. Owing to the length of the tables below, a compact format[7] of terms is given here: $^A(L_N, L'_{N'}....)$, in which the superscript A indicates the multiplicity of all terms included in the parentheses, and the subscripts N, N' indicate the number of terms. The default number is 1; for example, $^7P_2$ means that there are two ^7P terms and ^9D means that there is one ^9D term.

For each configuration, the last number is the total number of LS terms; for example, g^8 totally has 1070 LS terms.

We present complete results and critically compare with results partially appearing in the literature

for the following cases:

(a) For non-equivalent electron configurations, we present all LS terms for d^8p, f^4d, f^7d, corresponding to Co-like ions $3d^84p$, Np (Z=93) $5f^46d$, and Gd (Z=64) $4f^75d$ states, respectively.

$$
\begin{aligned}
d^8p \quad & {}^2(SP_3D_3F_3G_2H) && 19,\\
& {}^4(SPD_2FG)
\end{aligned}
$$

$$
\begin{aligned}
f^4d \quad & {}^2(S_6P_{14}D_{23}F_{27}G_{29}H_{26}I_{24}K_{18}L_{13}M_8N_5O_2Q) && 342,\\
& {}^4(S_3P_{11}D_{16}F_{19}G_{19}H_{18}I_{14}K_{11}L_7M_4N_{20})\\
& {}^6(SP_2D_4F_3G_4H_3I_2KL)
\end{aligned}
$$

$$
\begin{aligned}
f^7d \quad & {}^1(S_7P_{22}D_{34}F_{41}G_{45}H_{45}I_{40}K_{34}L_{27}M_{19}N_{13}O_8Q_4R_2T) && 1118.\\
& {}^3(S_{13}P_{35}D_{56}F_{66}G_{73}H_{70}I_{63}K_{51}L_{40}M_{27}N_{18}O_{10}Q_5R_2T)\\
& {}^5(S_7P_{16}D_{26}F_{30}G_{33}H_{29}I_{26}K_{19}L_{14}M_8N_5O_2Q)\\
& {}^7(SP_3D_5F_5G_5H_4I_3K_2L)\\
& {}^9(D)
\end{aligned}
$$

As a relatively small but nontrivial example, we present the LS eigenfunctions of excited Co-like ions of $3d^84p$ ^2F symmetry type. The number of independent LS eigenfunctions is 3, consistent with the above result of the d^8p configuration. The simplest LS eigenfunctions are

$$
\begin{aligned}
\Psi_1(^2F) = & -0.14407481\ D_1 + 0.46845184\ D_2\\
& - 0.32437703\ D_3 + 0.40458495\ D_4\\
& + 0.32262463\ D_5 + 0.23921287\ D_6\\
& - 0.56183750\ D_7 + 0.11796204\ D_8,\\
\Psi_2(^2F) = & -0.30632076\ D_1 - 0.39206730\ D_2\\
& + 0.69838806\ D_3 + 0.07001176\ D_4\\
& + 0.27586595\ D_5 + 0.12734859\ D_6\\
& - 0.40321454\ D_7 - 0.07001176\ D_8,\\
\Psi_3(^2F) = & +0.18221078\ D_1 - 0.18729121\ D_2\\
& + 0.0050804303\ D_3 - 0.01046392\ D_4\\
& + 0.30080012\ D_5 - 0.30959968\ D_6\\
& + 0.0087995634\ D_7 + 0.86323567\ D_8,
\end{aligned}
$$

where $n(i) = 3$, $l(i) = 2$, $(i = 1, ..., 7)$, $n(8) = 4$, $l(8) = 1$ in all the following Slater determinants and

$$
\begin{aligned}
D_1 &= (2^+, 2^-, 1^+, 1^-, 0^-, -1^+, -1^-, -2^+, 1^+),\\
D_2 &= (2^+, 2^-, 1^+, 1^-, 0^+, -1^+, -1^-, -2^-, 1^+),\\
D_3 &= (2^+, 2^-, 1^+, 1^-, 0^+, -1^+, -1^-, -2^+, 1^-),\\
D_4 &= (2^+, 2^-, 1^+, 1^-, 0^+, 0^-, -2^+, -2^-, 1^+),\\
D_5 &= (2^+, 2^-, 1^+, 1^-, 0^+, 0^-, -1^-, -2^+, 0^+),\\
D_6 &= (2^+, 2^-, 1^+, 1^-, 0^+, 0^-, -1^+, -2^-, 0^+),\\
D_7 &= (2^+, 2^-, 1^+, 1^-, 0^+, 0^-, -1^+, -2^+, 0^-),\\
D_8 &= (2^+, 2^-, 1^+, 1^-, 0^+, 0^-, -1^+, -1^-, -1^+).
\end{aligned}
$$

As demonstrated in the Appendix, instead of linear combinations of 19 Slater determinants of the d^8p orbital occupancy (see above), they are constructed by 8 Slater determinants.

(b) For equivalent electron configurations, we present all LS terms for d^5, f^7, and the complete g^n configuration series. To our knowledge, g^5, g^6, g^7, g^8 are given for the first time in the literature.

d^5	$^2(SPD_3F_2G_2HI)$ $^4(PDFG)$ $^6(S)$	16
f^7	$^2(S_2P_5D_7F_{10}G_{10}H_9I_9K_7L_5M_4N_2OQ)$ $^4(S_2P_2D_6F_5G_7H_5I_5K_3L_3MN)$ $^6(PDFGHI)$ $^8(S)$	119
g^1	$^2(G)$	1
g^2	$^1(SDGIL)$ $^3(PFHK)$	9
g^3	$^2(PD_2F_2G_3H_3I_2K_2L_2MNO)$ $^4(PF_2GHIKM)$	28
g^4	$^1(S_3D_5F_2G_6H_3I_6K_3L_5M_2N_3OQ_2T)$ $^3(P_4D_3F_6G_5H_7I_5K_6L_4M_4N_2O_2QR)$ $^5(SD_2FG_2HI_2KLN)$	104
g^5	$^2(S_3P_5D_{10}F_{11}G_{15}H_{14}I_{15}K_{13}L_{13}M_{10}N_9O_6Q_5R_3T_2UV)$ $^4(SP_4D_6F_8G_9H_9I_9K_8L_7M_6N_4O_3Q_2RT)$ $^6(SD_2FG_2HI_2KLN)$	226
g^6	$^1(S_7P_3D_{13}F_{11}G_{19}H_{13}I_{21}K_{13}L_{17}M_{12}N_{13}O_7Q_9R_4T_4U_2V_2X)$ $^3(SP_{13}D_{13}F_{23}G_{21}H_{28}I_{23}K_{26}L_{20}M_{20}N_{14}O_{13}Q_8R_7T_3U_3VW)$ $^5(S_2P_3D_8F_7G_{10}H_9I_{10}K_8L_8M_5N_5O_3Q_2RT)$ $^7(PF_2GHIKM)$	500
g^7	$^2(S_5P_{15}D_{24}F_{31}G_{37}H_{39}I_{40}K_{39}L_{36}M_{32}N_{27}O_{22}Q_{17}R_{13}T_9U_6V_4W_2XY)$ $^4(S_2P_{13}D_{16}F_{25}G_{25}H_{30}I_{27}K_{28}L_{23}M_{22}N_{16}O_{14}Q_9R_7T_4U_3VW)$ $^6(SP_3D_5F_6G_7H_7I_7K_6L_5M_4N_3O_2QR)$ $^8(PFHK)$	728
g^8	$^1(S_{10}P_7D_{24}F_{20}G_{34}H_{28}I_{37}K_{28}L_{34}M_{24}N_{26}O_{17}Q_{18}R_{10}T_{10}U_5V_5W_2X_2Z)$ $^3(S_3P_{23}D_{27}F_{43}G_{43}H_{53}I_{48}K_{52}L_{43}M_{42}N_{32}O_{29}Q_{20}R_{17}T_{10}U_8V_4W_3XY)$ $^5(S_5P_7D_{16}F_{16}G_{22}H_{20}I_{23}K_{19}L_{19}M_{14}N_{13}O_8Q_7R_4T_3UV)$ $^7(P_2D_2F_4G_3H_4I_3K_3L_2M_2NO)$ $^9(G)$	1070
g^9	$^2(S_8P_{19}D_{35}F_{40}G_{52}H_{54}I_{56}K_{53}L_{53}M_{44}N_{40}O_{32}Q_{26}R_{19}T_{15}U_9V_7W_4X_2YZ)$ $^4(S_6P_{16}D_{24}F_{34}G_{38}H_{40}I_{42}K_{39}L_{35}M_{32}N_{26}O_{20}Q_{16}R_{11}T_7U_5V_3WX)$ $^6(S_3P_3D_9F_8G_{12}H_{10}I_{12}K_9L_9M_6N_6O_3Q_3RT)$ $^8(PDFGHIKL)$ $^{10}(S)$	1070.

For equivalent electron configurations, our results for g^2, g^3, g^4 are consistent with those of Rotenberg.[8] For d^5, f^7 and g^9, they are consistent with R. Xu's results.[9] For f^7, compared with Y. Xu's results,[10] the only difference is that their quadruple series for f^7 has H_{10} terms both in their Table 4 and in their final results. We and R. Xu[9] find H_5 and F_5 terms instead of H_{10}.

For non-equivalent electron configurations, our results for f^7d agree with those in Gong's *et al.*[11] Our results for f^4d differ from Yue *et al*,[12] with those in the Np (Z=93) ground state. We believe that Yue *et al* have omitted some of LS terms in their analysis of the problem.

4. Conclusion

We developed a code in two modes to directly determine all LS spectral terms and the simplest LS eigenfunctions for desired symmetry for arbitrary given atomic electronic configuration (orbital occupancy). This makes the calculation of coupled states of excited high energy electrons possible, and offers a basis for further calculations of energy levels for laser and soft x-rays. Compared to other computational methods, recently reported in the literature,[9–12] this method is simple in theory and concept, and, in particular, offers a systematic direct method of calculation, therefore, it has provided more reliable results.

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Appendix A

For some given orbital occupancy and for each possible (for this occupancy) symmetry type, ${}^{2S+1}L$, let us create a table by identifying all ($n_{\rm det}$) Slater determinants D_i with $M_L = \sum_k ml^k = L$, and $M_S = \sum_k ms^k = S$, $k = 1, ..., N$ (number of electrons), $i = 1, ..., n_{\rm det}$.

Next we show essentially, using p^2 as example, the reason why we need LS eigenvectors, in order to diagonalize H in the simplest way, and how to decompose it.

For p^2 configuration, the possible determinants are

	M_S		
M_L	1	0	–1
2		$D_5 = (1^+, 1^-)$	
1	$D_4 = (1^+, 0^+)$	$D_7 = (1^+, 0^-)$ $D_8 = (1^-, 0^+)$	$(1^-, 0^-)$
0	$D_6 = (1^+, -1^+)$	$D_1 = (0^+, 0^-)$ $D_2 = (1^-, -1^+)$ $D_3 = (1^+, -1^-)$	$(1^-, -1^-)$
–1	$(0^+, -1^+)$	$(0^+, -1^-)$ $(0^-, -1^+)$	$(0^-, -1^-)$
–2		$(-1^+, -1^-)$	

Since there are no matrix elements (of L^2, S^2 and H) between states of different M_L or M_S, inspection of this table shows that our 15×15 secular equation will factor down to one 3×3 $[(1^+, -1^-)(1^-, -1^+)(0^+, 0^-)]$, two 2×2 $[(1^+, 0^-)(1^-, 0^+)$ and $(0^+, -1^-)(0^-, -1^+)]$, and eight 1×1 determinant submatrices by M_L, M_S factorization alone. We shall demonstrate that: (i) in order to find all possible LS/H terms, i.e. ${}^1S$, ${}^3P$ and ${}^1D$, instead of solving a 15×15 secular equation, we simply need to solve one 3×3 $[(1^+, -1^-)(1^-, -1^+)(0^+, 0^-)]$; (ii) if we are only interested in a specific symmetry type, e.g. ${}^1D$, we can, even simpler, solve one 1×1 $[(1^+, 1^-)]$. The $L^2 + \lambda S^2$ eigenfunction with the lowest eigenvalue, in each case, has symmetry ${}^{2S+1}L$.

Evidently, for both tasks (i) and (ii), only the upper left quadrant of the above table needs to be considered to determine LS terms since the others can be obtained by suitable systematic sign changes.

Now we demonstrate the reason why, if we work on the subspace of determinants having $M_L = \sum_k ml^k = L$ and $M_S = \sum_k ms^k = S$, the eigenfunctions with the lowest eigenvalues have symmetry ${}^{2S+1}L$, and therefore, by calculating the central block of the ta-

ble, we obtain all LS terms of the orbital occupancy 2p 2p.

The given occupancy is p^2. If we want to find the LS eigenfunction with ^1S symmetry, $M_L = L = 0$, $M_S = S = 0$, then $n_{\rm det} = 3$, $D_1 = (0^+, 0^-)$, $D^2 = (1^-, -1^+)$, and $D_3 = (1^+, -1^-)$. By using the LS matrix elements formula of Eq.(4), (if $\lambda = 1/2000 = 0.0005$) we have

$$LS \text{ matrix} = \begin{pmatrix} 4 & -2 & 2 \\ -2 & 2.0005 & 0.0005 \\ 2 & 0.0005 & 2.0005 \end{pmatrix}.$$

The eigenvalues are 0.00, 2.001, 6.00, the corresponding eigenfunctions are

$$\Psi(^1S) = \frac{1}{\sqrt{3}}(D_1 + D_2 - D_3), \qquad \text{(A1)}$$

$$\Psi(^3P) = \frac{1}{\sqrt{2}}(D_2 + D_3), \qquad \text{(A2)}$$

$$\Psi(^1D) = \frac{1}{\sqrt{6}}(2D_1 - D_2 + D_3), \qquad \text{(A3)}$$

In this case the lowest eigenvalue is 0.00, and the corresponding eigenfunction, $\Psi(^1S) = \frac{1}{\sqrt{3}}(D_1 + D_2 - D_3)$, has symmetry ^1S. The eigenfunctions with higher eigenvalues 2.001, 6.00 are just the other possible eigenfunctions of p^2 configuration with higher L and S symmetry, which belong to the ^3P and ^1D terms. Our eigenfunctions (LS terms) coincide with those of Slater obtained via step-up, step-down and projection operators.[13]

However, if we want to find one LS eigenfunction with ^3P symmetry, and if we set $M_L = L = 1$, $M_S = S = 1$, then, from the above table, $n_{\rm det} = 1$, $D_4 = (1^+0^+)$. There is only one determinant, the LS matrix is 1×1. Indeed, from Eq.(4) we have LS matrix = 2.001 (if λ=0.0005). Therefore, $\Psi(^3P) = D_4 = (1^+, 0^+)$. Similarly, if we want to find one LS eigenfunction with ^1D symmetry, and if we set $M_L = L = 2$, $M_S = S = 0$, then $n_{\rm det} = 1$, $D_5 = (1^+, 1^-)$, LS matrix = 6.000. Therefore, $\Psi(^1D) = D_5$.

One can see at least two possible LS functions of ^1D symmetry for the configuration p^2, for $L = 2$ and $S = 0$: the simplest, $\Psi(^1D) = D_5$, obtained by setting $M_L = L = 1$ and $M_S = S = 0$, and by finding the eigenfunction with the lowest eigenvalue of $L^2 + \lambda S^2$ secular equation, (which, in this case is just one), and one more complicate, obtained by setting $M_L = L - 2 = 0$ and $M_S = S = 0$, and by finding the eigenfunctions with the highest eigenvalue of the $L^2 + \lambda S^2$ secular equation. Therefore if one was interested only in finding the simplest LS eigenfunctions for a given electronic orbital occupancy and symmetry type ^{2S+1}L, then, by working with all determinants having $M_L = L$, $M_S = S$, the lowest eigenvalue of $L^2 + \lambda S^2$ would be $L(L+1) + \lambda S(S+1)$, and the corresponding eigenvectors would be those required.

Furthermore, as mentioned before, only the upper left quadrant of the above table needs to be considered to determine all LS terms, i.e. $|M_L| = L, L-1, ..., 0$, and $|M_S| = S, S-1, ..., 0$ (if the number of electron is even), or 1/2 (if the number of electron is odd). In other words, all the L, S of the given configuration (orbital occupancy) will pass through $M_L = 0$, $M_S = 0$ (even) or $M_S = 1/2$ (odd). So, if we require the lowest possible $|M_L|(= 0)$ and the lowest possible $|M_S|$ (= 0 or 1/2, depending on the number of electrons—even or odd), the number of Slater determinants, the dimensionality, i.e. the number of eigenvalues of the $L^2 + \lambda S^2$ secular equation will be the number of LS terms, and the corresponding eigenvectors will be all possible LS terms for the given orbital occupancy.

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