

Eigenfunctions of Spin and Orbital Angular Momentum by the Projection Operator Technique*

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A computer program has been written in Fortran IV to produce eigenfunctions of spin and orbital angular momentum (LS functions) by the projection operator technique. The projection operator acts on a Slater determinant built up from symmetry-adapted spinorbitals. When degeneracies exist, it is easy to provide a set of determinants whose projections span the whole degenerate space. In such cases, the LS functions are Schmidt orthonormalized.

These functions provide natural partitions of degenerate LS spaces which are useful in the simplification and systematization of atomic calculations. Some representative examples are discussed.

I. INTRODUCTION

Atomic calculations of electronic states characterized by $\{\gamma; L, M_L, S, M_S\}$ can be greatly simplified by expanding an approximate solution in terms of eigenfunctions to $L^2, L_z, S^2,$ and S_z , with eigenvalues $L(L + 1), M_L, S(S + 1),$ and M_S , respectively [1]. In addition, Löwdin [2] has stressed the importance of using symmetric projection operators in constructing the LS functions, as such an alternative introduces simplifications in the evaluation of matrix elements of operators which commute with $L^2, L_z, S^2,$ and S_z . Rotenberg has developed an elegant algorithm [3] to implement Löwdin's formalism into a FAP computer code for the IBM 7090 [4]. Schaefer and Harris [5] have proposed a different kind of symmetric projection operator, although in practice they obtain and handle LS eigenfunctions without the help of projection operators. Recently, one of us [6] pointed out how to improve the convergence of the atomic configuration interaction (CI) expansion with the help of Löwdin's symmetric projection operators, by means of a suitable partition of the degenerate LS spaces. It is this latter develop-

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ment which prompts the present paper. A detailed study on the partition of degenerate LS spaces shall be the subject of another article [7].

We have written a computer program in FORTRAN IV [8] which produces Schmidt orthonormalized LS functions $\Phi_K^{(p)}$ expressed as

$$\Phi_K^{(p)} = O(L^2, S^2) \sum_{\alpha=1}^p D_{K\alpha} b_{K\alpha}^{(p)} \quad (1)$$

$$= \sum_{\alpha=1}^{n_K} D_{K\alpha} c_{K\alpha}^{(p)}, \quad (2)$$

where $O(L^2, S^2)$ is an idempotent projection operator for spin and orbital angular momentum [9]:

$$O(L^2, S^2) = O(\mathbf{L}^2; L, M_L) \times O(\mathbf{S}^2; S, M_S) \quad (3)$$

$$O(\mathbf{M}^2; k, m) = (2k + 1)! \frac{(k + m)!}{(k - m)!} \sum_{\nu=0}^{k_{\max} - k} \frac{(-1)^\nu \mathbf{M}_-^{(k-m+\nu)} \mathbf{M}_+^{(k-m+\nu)}}{\nu! (2k + \nu + 1)!}. \quad (4)$$

The symbol \mathbf{M} stands for either \mathbf{L} or \mathbf{S} , and $k(k + 1)$ is the eigenvalue of \mathbf{M}^2 to be projected; the function upon which $O(\mathbf{M}^2; k, m)$ acts must already be an eigenfunction of \mathbf{M}_z with eigenvalue m . In Eqs. (1) and (2), the function $\Phi_K^{(p)}$ represents the p -th degenerate element of configuration K , and $D_{K\alpha}$ denotes a normalized ordered Slater determinant.

In Section II we outline the computational scheme. Some of the new results on atomic LS eigenfunctions are presented in Section III, and a comparison with previous works is made in Section IV.

II. COMPUTATIONAL SCHEME

The computational scheme consists of two steps: the application of $O(L^2, S^2)$ to a single Slater determinant, and the calculation of the $b_{K\alpha}^{(p)}$ and $c_{K\alpha}^{(p)}$ coefficients of Eqs. (1) and (2).

A. Projection of a Single Determinant

Equation (4) is first applied with $\mathbf{M} = \mathbf{L}$ and then with $\mathbf{M} = \mathbf{S}$, because, in general, spin projections are much shorter. In order to apply the operator $O(\mathbf{M}^2; k, m)$ to a Slater determinant, it is convenient to write the powers of \mathbf{M}_+ in the form of a multinomial expansion:

$$\mathbf{M}_+^{(k-m+\nu)} = \left\{ \sum_{i=1}^N \mathbf{m}_+(i) \right\}^{(k-m+\nu)} = \sum_j \left\{ \prod_{i=1}^N (\mathbf{m}_+(i))^{\nu_i} \right\} d_j = \sum_j \mathbf{O}_j + d_j, \quad (5)$$

with

$$\sum_{i=1}^N \nu_i = k - m + \nu. \tag{6}$$

N is equal to the number of electrons, and the d_j 's are the coefficients of the multinomial expansion. The operator \mathbf{O}_j^+ acting on determinant D_{K_α} gives

$$\mathbf{O}_j^+ D_{K_\alpha}(m) = u_{j\alpha} D_{K_j}(k + \nu), \text{ or zero,} \tag{7}$$

and

$$\mathbf{M}_+^{(k-m+\nu)} D_{K_\alpha}(m) = \sum_j d_j u_{j\alpha} D_{K_j}(k + \nu), \tag{8}$$

where the quantity in parentheses denotes the eigenvalue of \mathbf{M}_z of the given determinant. The coefficients d_j and $u_{j\alpha}$, and the determinants $D_{K_j}(k + \nu)$ are generated as a result of operations carried out within ten nested *DO* loops (ten is the maximum number of electrons in the present version of the program); when $N < 10$, the N innermost loops are utilized. Only those values for which Eq. (6) is satisfied are considered. In this way, the right hand member of Eq. (8) is obtained for $\nu = 0$.

Equations analogous to (5) and (6) may be written for the operator $\mathbf{M}_-^{(k-m+\nu)}$, which is next applied on the set of determinants obtained above, for $\nu = 0$, giving a new set of determinants $\{D_{K_\alpha}(m)\}$ and coefficients. The process is repeated for all the running values of ν , the new coefficients being added to the old ones when they correspond to a determinant already present in $\{D_{K_\alpha}(m)\}$.

Let $\bar{\Phi}_K^{(p)}$ be a normalized function defined by

$$\bar{\Phi}_K^{(p)} = O(L^2, S^2) D_{K_p} \bar{f}_{K_p}^{(p)} = \sum_{\alpha=1}^{n_K} D_{K_\alpha} \bar{c}_{K_\alpha}^{(p)}. \tag{9}$$

In actual calculations, some of the $\bar{c}_{K_\alpha}^{(p)}$'s turn out to be very small numbers in instances where they should vanish identically (as it can be deduced from consideration of the possible internal couplings of angular momentum [7]). The zeroing of these small coefficients, although strictly unnecessary, minimizes the loss of significant figures in the final results, Eqs. (1) and (2). From our experience with thousands of projections with n_K up to 400, the magnitudes of the nonzero $\bar{c}_{K_\alpha}^{(p)}$'s are seldom as small as 10^{-3} . On the other hand, we have noticed instances where theoretically vanishing coefficients resulted as big as $10^{-(NSIGFG-3)}$, where *NSIGFG* is equal to the computer's precision. That is, as much as 3 significant figures could be lost in getting Eq. (9) while up to 5-cipher losses were noticed in the final results. On this account, we decided to make equal to zero all $\bar{c}_{K_\alpha}^{(p)}$'s smaller than

$10^{-(NSIGFG-5)}$. We also set $NSIGFG \gg 11$ in order to place a safe margin to avoid the unwanted zeroing of (theoretically nonvanishing) $\bar{c}_{K\alpha}^{(p)}$'s. The degenerate elements of doubly excited configurations of first-row atomic states are obtained with 13 or more significant figures, on an IBM 360/50 using double precision arithmetic.

B. Orthonormalization

Because of the properties of symmetric projection operators, the Schmidt orthonormalization turns out to be equivalent to a Gauss elimination procedure [2]. The only serious problem here is to establish linear dependencies. The function $\bar{\Phi}_K^{(p)}$ is linearly dependent on the previous $(p - 1)$ functions when the function $\Phi_K^{(p)}$, Eq. (2), obtained through the Schmidt process is identically zero. Since we are using floating point arithmetic, this test is open to criticism. It is easily seen, however, that a necessary and sufficient condition for linear independence is

$$c_{K\alpha}^{(p)} = 0, \quad \alpha = 1, \dots, p - 1, \quad (10a)$$

$$c_{K\alpha}^{(p)} \neq 0, \quad \text{for some } \alpha \geq p, \quad (10b)$$

or, in floating point arithmetic,

$$c_{K\alpha}^{(p)} = \text{very small}, \quad \alpha = 1, \dots, p - 1, \quad (11a)$$

$$c_{K\alpha}^{(p)} \neq \text{very small}, \quad \text{for some } \alpha \geq p. \quad (11b)$$

Thanks to the criterion [Eqs. (11)], the use of fixed-point arithmetic can be rigorously dispensed with, in connection with the detection of linear dependencies [10]. Moreover, in many applications it is possible to find *a priori* a sequence of determinants which give, after projection, a complete set of linearly independent *LS* functions associated with a given configuration [7].

III. RESULTS

As a first example, let us consider the *LS* eigenfunctions arising from the 3P state of configuration $(s_1)^2 (p_1)^2 (p_2)^2$ which participates in the expansion of the ground state wave function of the *C* atom. The five degenerate set may be expressed in terms of the five possible internal couplings compatible with a 3P state, as shown in Table I. The association of the different functions with the inner couplings can be made *a priori*, by inspection of the sequence of determinants to be projected [7],

TABLE I
Five Degenerate Set From The 3P of $(s_1)^2(p_1)^2(p_2)^2$

Determinants ^a	$b_{K\alpha}^{(1)b}$	$b_{K\alpha}^{(2)c}$	$b_{K\alpha}^{(3)d}$	$b_{K\alpha}^{(4)e}$	$b_{K\alpha}^{(5)f}$
11 12 16 116	$\sqrt{15}/3^g$	$-\sqrt{3}/3$	$\sqrt{2}$	0	0
12 13 15 115		$\sqrt{3}$	0	0	0
11 13 15 116			$\sqrt{8}$	0	0
13 14 15 113				$\sqrt{15}/3$	$-\sqrt{3}/3$
12 15 16 112					$\sqrt{3}$

^a A determinant is written in terms of its spinorbitals. A spinorbital with quantum numbers (i, l, m_l, m_s) is denoted by $N(i, l, m_l, m_s)$:

$$N(i, l, m_l, m_s) = I(l) + (i - 1) \times (2l + 1) + m_l + l + 1 + (\frac{1}{2} - m_s) \times 100,$$

where $I(l) = 0, 10, 30,$ and 70 , for $l = 0, 1, 2,$ and 3 , respectively. The s_1 orbitals are omitted for brevity.

^b Inner coupling: ${}^3P(p_1)^2 {}^1D(p_2)^2$.

^c Inner coupling: ${}^3P(p_1)^2 {}^1S(p_2)^2$.

^d Inner coupling: ${}^3P(p_1)^2 {}^3P(p_2)^2$.

^e Inner coupling: ${}^1D(p_1)^2 {}^3P(p_2)^2$.

^f Inner coupling: ${}^1S(p_1)^2 {}^3P(p_2)^2$.

^g Computer output is in decimal form. Conversion to the form $\sqrt{a/b}$ where a and b are integers was achieved by squaring the numbers in decimal form and approximating to the nearest ratio a/b . In this and the following table the precision is of 14 significant figures.

or *a posteriori*, by examining the $c_{K\alpha}^{(p)}$ coefficients, which we do not reproduce here for lack of space. There are three interesting things to say about these functions:

(i) The second function, exhibited in the third column of Table I, is the only one which has a nonvanishing Hamiltonian matrix element with the ground state configuration $(s_1)^2(s_2)^2(p_1)^2$, since the other functions are expressed as linear combinations of projections of three-excited determinants. In a previous paper [6], it was pointed out that these "Hartree-Fock interacting" spaces make out for the largest contributions to the correlation energy and to the wave function. This sort of simplification is typical in atomic calculations and it provides, in conjunction with natural spinorbital techniques [11], the most rapidly convergent set for expressing the CI series.

(ii) Each one of these functions belongs to different invariant subspaces which are useful in connection with convergence properties and related matters [6].

(iii) The number of $b_{K\alpha}^{(p)}$ coefficients in the Hartree-Fock interacting function is as small as possible; it is impossible to project a different sequence of determinants yielding the same function with a smaller number of $b_{K\alpha}^{(p)}$ coefficients. Hence, this gives the most efficient representation of N -electron functions with regard to the computation of the Hamiltonian matrix elements [2].

TABLE II
Relevant Couplings from the 3P of $s_2d_1(p_1)^2(p_2)^2$

Determinants ^a	$b_{K\alpha}^{(11)}$	$b_{K\alpha}^{(12)}$	$b_{K\alpha}^{(13)}$	Sequence of couplings ^b $s_2d_1(p_1)^2(p_2)^2$
2 13 14 44 113 114	$\sqrt{15}/3^c$	$\sqrt{10}$	$-\sqrt{5}$	${}^3F \{ {}^3D \ 1D \} \ 1D$
2 12 14 45 113 114	0	0	0	${}^3F \{ {}^3D \ 3P \} \ 1D$
2 12 13 14 114 145	0	0	0	${}^3F \{ 1D \ 3P \} \ 1D$
2 12 16 41 113 116	$-\sqrt{30}/6$	$-\sqrt{5}$	$\sqrt{10}/2$	$\left[\begin{array}{l} {}^3D \{ {}^3D \ 1D \} \ 1D \\ {}^3P \{ {}^3D \ 1D \} \ 1D \\ {}^3D \{ {}^3D \ 3P \} \ 1D \end{array} \right]$
2 13 16 41 112 116	$-\sqrt{30}/6$	$-\sqrt{5}$	$\sqrt{10}/2$	
2 11 16 43 112 116	$-\sqrt{5}$	$-\sqrt{30}/3$	$\sqrt{15}/3$	
2 12 16 43 111 116	$-\sqrt{5}$	$\sqrt{30}/3$	$-\sqrt{15}/3$	${}^3P \{ {}^3D \ 3P \} \ 1D$
2 12 16 42 112 116	$-\sqrt{15}$	$-\sqrt{10}$	$\sqrt{5}$	${}^3D \{ {}^3D \ 1S \} \ 1D$
2 11 12 16 116 143	0	0	$-\sqrt{60}/3$	$\left[\begin{array}{l} {}^3D \{ 1D \ 3P \} \ 1D \\ {}^3P \{ 1D \ 3P \} \ 1D \end{array} \right]$
2 11 13 16 116 142	0	0	0	
2 12 15 44 112 115	$\sqrt{15}$	$\sqrt{10}$	$-\sqrt{5}$	${}^3P \{ {}^3D \ 1D \} \ 1S$
2 11 15 45 112 115		$\sqrt{20}$	$-\sqrt{10}$	${}^3P \{ {}^3D \ 3P \} \ 1S$
2 11 12 15 115 145			$\sqrt{10}$	${}^3P \{ 1D \ 3P \} \ 1S$

^a See footnote *a* of Table I.

^b The p -th function $\Phi_K^{(p)}$ corresponds to the coupling (or linear combinations of the couplings comprised between the brackets) under this column.

^c See footnote *g* of Table I.

A second example should give an idea of how well the CI series can be simplified by performing an appropriate partition of degenerate LS spaces, by means of the present method. Let us consider the 3P functions of $(p_j)^2 s_2 d_1 (p_1)^2$, which define a 29-degenerate manifold corresponding to the leading three-excited configurations of the ground state of the carbon atom [6]. The $(p_j)^2$ represents a K shell excitation and hence it has a strong tendency to preserve its spherical symmetry, i.e., a 1S coupling. It is found that the relevant terms correspond to the three couplings shown in Table II. Because of the "projection separability" [7] between the 13 functions in which $(p_j)^2$ is coupled to a 1D or a 1S , and the remaining 16 functions in which $(p_j)^2$ is coupled to a 3P , it is possible to write the three couplings of Table II in terms of 13 or less projected determinants. Finally the three-degenerate subset can be simplified into an effective two-degenerate subset, as shown in the discussion following Eqs. (12)–(14) of Ref. 6 [12]. Not only the original 29-fold degeneracy is reduced to two, but also the number of $b_{K\alpha}^{(p)}$ and $c_{K\alpha}^{(p)}$ coefficients is considerably diminished. This one and related results are not trivial; they can only be deduced after a detailed analysis of each particular case [7]. It should also be pointed out that, for most configurations, not all the types of internal couplings can be written as successively orthonormalized projected determinants. Fortunately, however, those instances turn out to be of no practical importance in atomic calculations.

IV. DISCUSSION

The purpose of the present computer program is to produce LS eigenfunctions *suitable for atomic calculations*, as illustrated in the previous section.

The present version of the program is limited to handle up to 10 electrons, but is general otherwise, and hence it should be useful in first- and second-row atomic calculations. Also, the method described in Section II can be extended to a larger number of particles without any substantial loss of efficiency, as we have incidentally found out while extending our original 6-electron program into the present one. The program can be extended in a routine manner up to, say, 20 electrons, which is all that should be needed in practical problems.

The main advantage of our program over Rotenberg's is that ours is written in FORTRAN IV, and hence it is effectively available to a wider audience (Rotenberg's algorithm is suitable for FAP but not for FORTRAN). The automatic generation of the full degenerate spaces is not carried out in our program, as it is of more interest to use particular sequences of projected determinants, in order to determine the partitions appropriate for atomic calculations (Section III). It is apparently very difficult to write a computer code to generate such sequences.

For comparison with Schaefer's program, the 27 functions corresponding to

the 3P of the configuration $1s2sp_1p_2(2p)^4$ can be obtained in 2.8 minutes, in an IBM 360/50, FORTRAN IV level *G*, as compared with the 1.4 minutes for Schaefer program on an IBM 360/67 FORTRAN IV, level *H*. In other words, both programs are comparable with regard to efficiency in the generation of the *LS* functions. However, Schaefer's program does not permit a controlled partition of degenerate spaces, neither does it compute the $b_{K\alpha}^{(p)}$ coefficients, important for the simplification of the matrix elements. The partial eigenfunction sets (we call them internal couplings) mentioned by Schaefer and Harris are particular cases of *LS* functions which can be expressed by means of Eq. (1) [7, 11]. Also, ours is the only computer code to date which can produce such partial eigenfunction sets [13].

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12. At the time of writing [6], the possibility of expressing the desired internal couplings of this particular configuration in terms of Eqs. (1) and (2) was not known.
13. We are grateful to Dr. F. Schaefer for information regarding this point.