1977

Spin-orbit parameters by the Gelfand-Harter method-a test calculation

J. Drake

Gordon W. F. Drake
University of Windsor

M. Schlesinger

Spin-orbit parameters by the Gelfand-Harter method—a test calculation

Judith Drake, G. W. F. Drake, and M. Schlesinger

Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4

(Received 27 September 1976)

The spin-orbit parameters for the sextet states of the f^5 configuration are computed using the Young-tableau techniques developed by Harter. The conceptual and computational advantages over traditional methods are discussed.
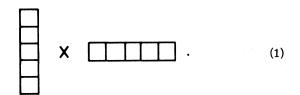
I. INTRODUCTION

The traditional Racah approach to atomic structure calculations becomes very cumbersome for systems involving many equivalent electrons. In particular, the seniority scheme eventually fails to label uniquely all the states for equivalent f electrons and beyond. In recent papers[1,2] Harter and co-workers have developed the Young-tableau representation of atomic states into a complete computational scheme for the evaluation of any matrix element such that one need never refer to the detailed angular and spin structure of the wave functions. Since the scheme is equivalent to the unitary group representation of Gelfand and Zetlin,[3] one is always assured of a complete one-to-one correspondence between the Young tableaus and the correctly antisymmetrized Russel-Saunders coupled states $|^{2S+1}L\rangle$ which they represent. Further improvements were suggested by the present authors,[4] and applications to molecular orbitals have been made by Paldus.[5] The main advantages of the Young-tableau representation are that the techniques are easily grasped and any example, however complicated, is a straightforward, unambiguous extension of the simplest cases.

Despite the power and versatility of Harter's methods, they have not yet been widely accepted as a practical scheme for performing calculations. The purpose of this Comment is to report that the entire scheme has been programmed for an arbitrary configuration of equivalent electrons, and to give as sample output the spin-orbit parameters for the sextet states of the f^5 configuration.

II. THEORY

As described previously,[1,2,4] the basis states are represented by products of orbital and spin tableaus, which for the f^5 sextet states have the form

$$ \tag{1} $$

The orbital part of the wave function is represented by the column tableau on the left. Each box represents an f electron and is labeled lexically by an integer $\mu = 1, 2, \ldots, 7$ corresponding to the one-electron orbital magnetic quantum numbers $3, 2, \ldots, -3$, such that no label appears more than once. Each such a column tableau corresponds to an antisymmetrized wave function with definite total spin $\frac{5}{2}$ and component of total angular momentum M_L in the z direction, but is a mixture of all possible values of L. The value of M_L for a particular column is

$$ M_L = n(l+1) - \sum_{i=1}^{n} \mu_i \tag{2} $$

where, for this case, $n = 5$ is the number of boxes and $l = 3$ is the one-electron angular momentum.

The linear combinations of column tableaus which diagonalize L^2 can easily be found by the combination of lowering- and projection-operator techniques described previously.[6] In addition to its computational efficiency, the lowering-operator method guarantees the conventional phase relationship among states in the same L family with different M_L's. The states generated in this way are ^6H, ^6F and ^6P. The wave functions for the states of highest M_L are given in Table I.

The symmetrized spin part of the wave function is represented by the row tableau in (1). The boxes are labeled lexically by the values of $m_S = \pm\frac{1}{2}$ for the individual electrons such that the total spin magnetic quantum number M_S is the sum of the labels. The labeling can be done in six distinct ways corresponding to the sextet structure. The linear combinations of orbital and spin products of the form (1) then correspond to

TABLE I. Tableau eigenvectors of L^2 with largest M_L.

State	Eigenvector
$^6H\,(M_L=5)$	$\boxed{\begin{smallmatrix}1\\2\\3\\4\\5\end{smallmatrix}}$
$^6F\,(M_L=3)$	$\sqrt{\tfrac{1}{3}}\,\boxed{\begin{smallmatrix}1\\2\\3\\5\\6\end{smallmatrix}} - \sqrt{\tfrac{2}{3}}\,\boxed{\begin{smallmatrix}1\\2\\3\\4\\7\end{smallmatrix}}$
$^6P\,(M_L=1)$	$\sqrt{\tfrac{37}{42}}\,\boxed{\begin{smallmatrix}1\\3\\4\\5\\6\end{smallmatrix}} - \sqrt{\tfrac{135}{42\times37}}\,\boxed{\begin{smallmatrix}1\\2\\4\\5\\7\end{smallmatrix}} - \sqrt{\tfrac{25}{21\times37}}\,\boxed{\begin{smallmatrix}1\\2\\3\\6\\7\end{smallmatrix}}$

TABLE II. Reduced spin-orbit matrix elements for the f^5 sextet states.

State	$\sum_i \langle L\|\vec{l}_i\|L\rangle\langle S\|\vec{s}_i\|S\rangle$
^6H	$\sqrt{11\times63}$
^6F	$\sqrt{14\times63/5}$
^6P	$\sqrt{63/5}$

Russel-Saunders coupled states $|LM_LSM_S\rangle$.
The spin-orbit operator is defined by

$$H_{\text{so}} = \xi \sum_{i=1}^{n} \vec{l}_i \cdot \vec{s}_i ,$$

where ξ is a radial function and the sum is over the n electrons in the system. For purposes of calculating the matrix elements of the spin-orbit operator, it is convenient to transform to states of definite total angular momentum $\vec{J} = \vec{L} + \vec{S}$ defined by

$$|LSJM_J\rangle = \sum_{M_L, M_S} \langle LSM_LM_S|JM_J\rangle\,|LM_LSM_S\rangle. \quad (3)$$

The results can then be compactly expressed in terms of reduced matrix elements through the relation[7]

$$\xi \sum_i \langle L'S'J'M_J'|\vec{l}_i \cdot \vec{s}_i|LSJM_J\rangle$$

$$= \xi(-1)^{L+S'+J}\delta_{J,J'}\delta_{M_J,M_J'}\begin{Bmatrix}J & S' & L'\\1 & L & S\end{Bmatrix}$$

$$\times \sum_i \langle L'\|\vec{l}_i\|L\rangle\langle S'\|\vec{s}_i\|S\rangle. \quad (4)$$

The reduced matrix element can easily be evaluated in general by expressing H_{so} in terms of Racah's double tensor operators and using the "assembly" formula given by Harter and Patterson.[2]

Our example is particularly simple since the tableaus are already in single-column form. Since the matrix element for a single J, M_J state is sufficient to determine the reduced matrix element, it is simplest to choose the "stretched" state with $J = L + S$, $M_J = J$. For this case, the only wave functions needed are those given in Table I. The results shown in Table II are in complete agreement with the decimal expansions given by Karwowski et al.[8]

III. DISCUSSION

This simple example is intended to demonstrate the practical computational power of the Young-tableau techniques and to stimulate further interest in their use. We consider it to be conceptually and computationally superior to the spin-adapted antisymmetrized product (SAAP) expansion method of Salmon and Ruedenberg[9] extensively used by Karwowski, Saxena, and Fraga.[10] It is also computationally simpler than the older Racah methods employing coefficients of fractional parentage (see Ref. 11 and earlier references therein). The example chosen does not illustrate all the features of the tableau method since in general the tableaus consist of two columns. However, the number of states is small enough to allow compact presentation of the results, and experimental data have been obtained by Nara and Schlesinger[12] for some of these states.

Agreement with the results of Karwowski et al.[8] has also been obtained for the quartet and doublet states of the f^5 configuration. However, here the situation is more complicated because several Russel-Saunders states with the same L, S quantum numbers can occur. The degeneracy is only partially resolved by transforming to states of definite seniority. Since our lowering- and projection-operator technique[6] already defines a unique self-consistent set of states with the proper phase relationships, and since the ultimate aim is to diagonalize other quantities such as electrostatic or crystal-field interactions, the transformation to states of definite seniority is probably not worthwhile.

[1]W. G. Harter, Phys. Rev. A <u>8</u>, 2819 (1973).

[2]W. G. Harter and C. W. Patterson, Phys. Rev. A <u>13</u>, 1067 (1976).

[3]I. M. Gelfand and M. Zetlin, Dokl. Akad. Nauk. SSR <u>71</u>, 825 (1950). The Gelfand pattern approach is further developed by L. C. Biedenharn, A. Giovannini, and J. D. Louck, J. Math. Phys. <u>8</u>, 691 (1967); J. D. Louck, Am. J. Phys. <u>38</u>, 3 (1970); and M. Moshinsky, in *Physics of Many Particle Systems,* edited by E. Meeron (Gordon and Breach, New York, 1966). Other related work is reviewed by G. A. Gallup, Adv. Quant. Chem. <u>7</u>, 113 (1973).

[4]J. Drake, G. W. F. Drake, and M. Schlesinger, J. Phys. <u>B8</u>, 1009 (1975).

[5]J. Paldus, in *Theoretical Chemistry: Advances and Perspectives,* edited by H. Eyring and D. J. Henderson (Academic, New York, 1976), Vol. 2, p. 131; Phys. Rev. A <u>14</u>, 1620 (1976).

[6]Reference 4. The lowering matrices in Eqs. (6), (7), and (8) of this reference all have the wrong sign. The overall signs of the wave functions obtained by an odd number of lowerings should therefore also be reversed.

[7]A. R. Edmunds, *Angular Momentum in Quantum Mechanics* (Princeton U.P., Princeton, N.J., 1960), p. 111.

[8]J. Karwowski, K. M. S. Saxena, and S. Fraga, Technical Report TC-ME-IV-75, Department of Chemistry, University of Alberta, unpublished.

[9]W. I. Salmon and K. Ruedenberg, J. Chem. Phys. <u>57</u>, 2776 (1972); <u>57</u>, 2791 (1972).

[10]J. Karwowski, K. M. S. Saxena, and S. Fraga, Can. J. Phys. <u>53</u>, 2421 (1975), and earlier references therein.

[11]K. M. S. Saxena and G. Malli, Can. J. Phys. <u>47</u>, 2805 (1969).

[12]H. Nara and M. Schlesinger, Phys. Rev. B <u>3</u>, 58 (1971).