ON THE CHOICE OF \(S\)-FUNCTIONS

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Abstract

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ON THE CHOICE OF S-FUNCTIONS

IN THE METHOD OF CONTACT TRANSFORMATIONS

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1. The method of contact transformations (c.t.) was first applied by Van Vleck to the calculation of the multiplet structure of the levels of diatomic molecules ([1]), and subsequently by Jordahl in calculations of the paramagnetic susceptibility of a number of salts ([2]). Later this method was used mainly for the analysis of vibrational-rotational spectra of polyatomic molecules ([3]). In the works of Herman and Shaffer ([4]) and Amat, Nielsen, and Goldsmith ([5], [6]), S-functions of the first and second c.t. were found for diagonalizing the matrix of the vibrational-rotational energy of a polyatomic molecule. In the literature, S-functions are unknown for the subsequent transformations of the energy operator. Nor are there indications of general methods for finding them.

In the present work a general formula is derived for the c.t. of the operator of vibrational-rotational energy, and a method is proposed for finding S-functions for diagonalizing operators containing terms of the type $(p^m q^n + q^n p^m)$ with arbitrary m and n.

2. Let a Hermitian operator H be given in the form

$$H = \sum_{n=0}^{\infty} \lambda^n H_n,$$

where λ is a small parameter, and the orthonormal eigenbasis $H_0(\Psi_0)$ and commutators of the type

$$[H_m, H_n],\ [H_m, [H_n, H_k]], \dots,\ m, n, k = 0, \dots, \infty \tag{1}$$

are known.

Owing to the Hermiticity of the operator H, there exists some unitary transformation T that diagonalizes the matrix of the operator H given in the representation Ψ_0, i.e.

$$\Psi = \Psi_0 T, \qquad \Psi^+ = T^+ \Psi_0^+, \qquad E = \Psi_0 T H T^+ \Psi_0^+. \tag{2}$$

Thus, the problem of determining the elements of the diagonal matrix E of the operator H reduces to transforming it by means of T into the operator THT^+, diagonal in the representation Ψ_0.

In the c.t. method T is specified in the form of the product

$$T = T_\infty \cdots T_k T_{k-1} \cdots T_2 T_1, \tag{3}$$

and the individual T_k in the form

$$T_k = \exp(i\lambda^k S_k), \qquad T_k^+ = \exp(-i\lambda^k S_k), \tag{4}$$

which automatically ensures the orthonormality of the basis Ψ. Expanding T_k in a series in powers of λ, and restricting ourselves to the k-th term of (3), we obtain

$$T_k = \sum_{n=0}^{\infty} (n!)^{-1} (i\lambda^k S_k)^n, \qquad T_k^+ = \sum_{n=0}^{\infty} (n!)^{-1} (-i\lambda^k S_k)^n; \tag{5}$$

$$T^{(k)} = \prod_k T_k = \prod_k \sum_{n=0}^{\infty} (n!)^{-1} (i\lambda^k S_k)^n; \tag{6}$$

$$E^{(k)} = \Psi_0 \left[\prod_k \sum_{n=0}^{\infty} (n!)^{-1} (i\lambda^k S_k)^n H \prod_k \sum_{n=0}^{\infty} (n!)^{-1} (-i\lambda^k S_k)^n \right] \Psi_0^+. \tag{7}$$

where the expression in square brackets in (7) is the k-fold transformed operator ($H^{(k)}$). The functions S_k must be chosen so that the operator $H^{(k)}$ commutes with H_0. Then the operators $H^{(k)}$ and H_0 have a common orthonormal basis Ψ_0, and $E^{(k)}$ is a diagonal matrix. Assigning to k the values $1, 2, \dots, n, \dots$, one can successively obtain the corresponding $E^{(n)}$, diagonal to within terms of the $(n+1)$-st order of smallness.

For $k = 1$, for $H^{(1)}$ we obtain the expression

$$H^{(1)} = \sum_{n=0}^{\infty} \lambda^n H_n^{(1)} = \sum_{n=0}^{\infty} \lambda^n H_n + \sum_{l=1}^{\infty} (l!)^{-1} (i\lambda)^l \left[S_1, \underbrace{[\ldots[}_{l \text{ times}} S_1, \sum_{m=0}^{\infty} \lambda^m H_m] \ldots] \right]$$
$$= \sum_{n=0}^{\infty} \lambda^n H_n + \sum_{l=1}^{\infty} \sum_{m=0}^{\infty} (l!)^{-1} i^l \lambda^{l+m} K_{lm}^{(1)}, \tag{8}$$

where the commutators $K_{lm}^{(1)} = [S_1, \underbrace{[\ldots[}_{l \text{ times}} S_1, H_m] \ldots]]$ are expanded according to the usual rules.

For arbitrary k,

$$H^{(k)} = \sum_{n=0}^{\infty} \lambda^n H_n^{(k-1)} + \sum_{l=1}^{\infty} \sum_{m=0}^{\infty} (l!)^{-1} i^l \lambda^{lk+m} K_{lm}^{(k)}, \tag{9}$$

where $K_{lm}^{(k)} = [S_k, [\ldots [S_k, H_m^{(k-1)}] \ldots]]$. Expressions for the individual $H_n^{(k)}$ can be obtained by equating terms with identical powers λ^n in the right- and left-hand sides of (9). All S-functions, up to S_k, are chosen so that the operator $H^{(k)}$ is diagonal in the basis Ψ_0. The terms $H_n^{(k)}$ with $n > k$ are nondiagonal in this basis Ψ_0, but the nondiagonal elements $H_n^{(k)}$ (with $n > k$) give a correction to the eigenvalues of H_0 only in the $(n+1)$-st approximation. Therefore, to compute corrections to the eigenvalues of H_0 in the n-th approximation it is sufficient to make $n-1$ transformations, whereas to compute corrections to the eigenvectors in the same (n-th) approximation it is necessary to make n transformations of H.

3. Suppose all S-functions up to S_{k-1} have been found and all operators $H_n^{(k-1)}$ with $n \leq k$ have been constructed. It follows from equation (9) that the function S_k must satisfy the condition

$$H_k^{(k)} = H_k^{(k-1)} + iK_{10}^{(k)}, \tag{10}$$

where $H_k^{(k)}$ in the basis Ψ_0 is a diagonal matrix.

Finding a function S_k satisfying condition (10) is possible if the commutation laws are known for the operators of which H_k^{-1} is composed, with H_0. For the vibrational-rotational energy operator of a diatomic molecule [7], the problem is simplified by the fact that $H_k^{(k-1)}$ is expressed through combinations of operators of the dimensionless coordinate and momentum of the type $(p^m q^n + q^n p^m)$. Using the relation $[p, q] = -i$, one can obtain commutation relations for any combination $(p^m q^n + q^n p^m)$ with H_0.*

* The commutation relations for $(p^m q^n + q^n p^m)$ used below in the calculations are not given for lack of space.

Table 1

$(H_k^{(k-1)})_i$	$(S_k)_i \cdot \frac{\omega}{2}$	$(H_k^{(k)})_i$
p	$\frac{1}{2}q$	0
q	$-\frac{1}{2}p$	0
p^2	$\frac{1}{8}(pq+qp)$	$\frac{1}{2}(p^2+q^2)$
$pq+qp$	$-\frac{1}{2}p^2$	0
q^2	$-\frac{1}{8}(pq+qp)$	$\frac{1}{2}(p^2+q^2)$
p^3	$\frac{1}{4}(p^2q+qp^2)+\frac{1}{3}q^3$	0
p^2q+qp^2	$-\frac{1}{3}p^3$	0
pq^2+q^2p	$\frac{1}{3}q^3$	0
q^3	$-\frac{1}{4}(pq^2+q^2p)-\frac{1}{3}p^3$	0
p^4	$\frac{5}{32}(p^3q+qp^3)+\frac{3}{32}(pq^3+q^3p)$	$\frac{3}{8}(p^2+q^2)^2+\frac{3}{8}$
p^3q+qp^3	$-\frac{1}{4}p^4$	0
$p^2q^2+q^2p^2$	$-\frac{1}{16}(p^3q+qp^3)+\frac{1}{16}(pq^3+q^3p)$	$\frac{1}{4}(p^2+q^2)^2-\frac{3}{4}$
pq^3+q^3p	$\frac{1}{4}q^4$	0
q^4	$-\frac{3}{32}(p^3q+qp^3)-\frac{5}{32}(pq^3+q^3p)$	$\frac{3}{8}(p^2+q^2)^2+\frac{3}{8}$
p^5	$\frac{1}{4}(p^4q+qp^4)+\frac{1}{3}(p^2q^3+q^3p^2)+\frac{4}{15}q^5+q$	0
p^4q+qp^4	$-\frac{1}{5}p^5$	0
$p^3q^2+q^2p^3$	$\frac{1}{6}(p^2q^3+q^3p^2)+\frac{2}{15}q^4-q$	0
$p^2q^3+q^3p^2$	$-\frac{1}{6}(p^3q^2+q^2p^3)-\frac{2}{15}p^5+p$	0

$(H_k^{(k-1)})_i$	$(S_k)_i \cdot \frac{\omega}{2}$	$(H_k^{(k)})_i$
$pq^4 + q^4p$	$\frac{1}{5}q^5$	0
q^5	$-\frac{1}{4}(pq^4 + q^4p) - \frac{1}{3}(p^3q^2+q^2p^3) - \frac{4}{15}p^5 - p$	0
p^6	$\frac{11}{64}(p^5q+qp^5) + \frac{5}{64}(pq^5 + q^5p) + \frac{5}{24}(p^3q^3 + q^3p^3) + \frac{15}{16}(pq+qp)$	$\frac{5}{16}(p^2+q^2)^3 + \frac{25}{16}(p^2+q^2)$
$p^5q + qp^5$	$-\frac{1}{6}p^6$	0
$p^4q^2 + q^2p^4$	$-\frac{1}{32}(p^5q + qp^5) + \frac{1}{32}(pq^5 + q^5p) + \frac{1}{12}(p^3q^3 + q^3p^3) - \frac{3}{8}(pq+qp)$	$\frac{1}{8}(p^2+q^2)^3 - \frac{19}{8}(p^2+q^2)$
$p^3q^3 + q^3p^3$	$-\frac{1}{8}(p^2q^4 + q^4p^2) + \frac{1}{12}q^6 + \frac{3}{2}p^2$	0
$p^2q^4 + q^4p^2$	$-\frac{1}{32}(p^5q + qp^5) + \frac{1}{32}(pq^5 + q^5p) - \frac{1}{12}(p^3q^3 + q^3p^3) + \frac{3}{8}(pq+qp)$	$\frac{1}{8}(p^2+q^2)^3 - \frac{19}{8}(p^2+q^2)$
$pq^5 + q^5p$	$\frac{1}{6}q^6$	0
q^6	$-\frac{5}{64}(p^5q + qp^5) - \frac{11}{64}(pq^5 + q^5p) - \frac{5}{24}(p^3q^3 + q^3p^3) - \frac{15}{16}(pq+qp)$	$\frac{5}{16}(p^2+q^2)^3 + \frac{25}{16}(p^2+q^2)$

To choose the function S_k that diagonalizes $H_k^{(k-1)}$, we shall use the following device.

Let us specify S^k in the form of a linear combination of the operators $(p^lq^j + q^jp^l)$

$$S_k = \sum_{lj} y_{lj}(p^l q^j + q^j p^l), \qquad l + j \leqslant m + n, \tag{11}$$

and $H_k^{(k)}$ in the form of the series

$$H_k^{(k)} = \sum_i x_i (p^2 + q^2)^i, \qquad i \leqslant (m+n)/2, \tag{12}$$

where the operator $(p^2 + q^2)$, and hence all its powers, are diagonal in the vibrational quantum number v. Substituting (11) and (12) into (10) and equating the coefficients of identical combinations $(p^m q^n + q^n p^m)$ on the right- and left-hand sides of (10), one can find all y_{lj} and x_i, and consequently the function S_k and, at the same time, the diagonal correction $H_k^{(k)}$.

If $H_k^{(k-1)}$ contains many terms, they can be diagonalized separately: the complete function S_k will be equal to the sum of the $(S_k)_i$ that diagonalize the separate terms $(H_k^{(k-1)})_i$ in $H_k^{(k-1)}$, and the diagonal correction $H_k^{(k)}$ will be the sum of the diagonal corrections $(H_k^{(k)})_i$.

As an example, let us find the function $(S_k)_i$ for diagonalizing $(H_k^{(k-1)})_i = c_i q^6$, where c_i is a constant coefficient. We represent $(S_k)_i$ and $(H_k^{(k)})_i$ in the following form

$$(S_k)_i = y_{51}(p^5 q + q p^5) + y_{15}(p q^5 + q^5 p) + y_{33}(p^3 q^3 + q^3 p^3) + y_{11}(pq + qp),$$

$$(H_k^{(k)})_i = x_1 (p^2 + q^2) + x_3 (p^2 + q^2)^3. \tag{13}$$

The remaining coefficients y_{lj} and x_i are equal to zero.*

Substituting (13) and $(H_k^{(k-1)})_i = c_{iq}^6$ into (10) and taking into account that

$$[(p^5 q + q p^5), (p^2 + q^2)] = 4ip^6 - 10i(p^4 q^2 + q^2 p^4) - 60ip^2,$$

$$[(p q^5 + q^5 p), (p^2 + q^2)] = -4iq^6 + 10i(p^2 q^4 + q^4 p^2) + 60iq^2,$$

$$[(p^3 q^3 + q^3 p^3), (p^2 + q^2)] = 6i(p^4 q^2 + q^2 p^4) - 6i(p^2 q^4 + q^4 p^2) + 18i(p^2 - q^2),$$

$$x_3 (p^2 + q^2)^3 = x_3 (p^6 + q^6) + \frac{3}{2} x_3 (p^4 q^2 + q^2 p^4 + p^2 q^4 + q^4 p^2) +$$

$$+4x_3(p^2+q^2),$$

we obtain the following values for the coefficients y_{lj} and x_i:

$$y_{51}=-\frac{5}{64}\frac{2c_i}{\omega};\qquad y_{15}=-\frac{11}{64}\frac{2c_i}{\omega};\qquad y_{33}=-\frac{5}{24}\frac{2c_i}{\omega};$$

$$y_{11}=-\frac{15}{16}\frac{2c_i}{\omega};\qquad x_3=\frac{5}{16}c_i;\qquad x_1=\frac{25}{16}c_i.$$

In this way the S-functions given in the table have been found for diagonalizing the operators $(p^mq^n+q^np^m)$ for values $m+n\leqslant 6$. The first column of the table contains the various $(p^mq^n+q^np^m)$ entering as separate terms in $H_k^{(k-1)}$, the second contains the function $(S_k)_i$, and the third contains the diagonal correction $(H_k^{(k)})_i$. We note that the diagonal correction from $(p^mq^n+q^np^m)$ is equal to zero if at least one of the exponents (m or n) is odd. For even m and n in (12), only the terms with $i=(m+n)/2,\ (m+n)/2-2$, etc., are nonzero.

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* The coefficients y_{lj} that are different from zero are chosen with the aid of the table of commutators $[(p^mq^n+q^np^m),(p^2+q^2)]$.