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Method for locating errors in Hamiltonian matrices

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A method for locating errors in matrices representing Hermitian operators in Hilbert spaces is discussed. The method is based on invariance properties of the first two moments of the spectral density distribution of these operators with respect to unitary transformations of the basis. In particular, applications to eigenvalue problems of the N-electron Hamiltonians in finite-dimensional spin-adapted Hilbert spaces are studied in detail.

I. INTRODUCTION

Algorithms for constructing matrices representing Hermitian operators in finite-dimensional N-particle spin-adapted Hilbert spaces are, in general, very complex.[1-6] With no limitations imposed upon the N-particle basis, different matrix elements can be constructed according to many different and to a large extent mutually independent algorithms. Particularly important is the case of Hilbert spaces being antisymmetric subspaces of the N-fold Cartesian products of a one-particle space. In nuclear physics this formulation leads to the nuclear-shell model.[3] In the theory of N-electron systems the eigenvalue problem of the Hamiltonian in this space is known as the configuration-interaction (CI) method and the space is referred to as the full CI space.[7] During the past decade an unprecedented advancement in CI methodology has taken place. Several highly sophisticated and general methods for constructing CI matrices have been developed and implemented.[4-6] These new concepts combined with the developments in computer technology have resulted in new computer codes[8-15] designed to perform CI calculations using large sets of general N-electron basis functions. Developing new algorithms of high complexity creates a need for efficient tests of both the formal and numerical correctness of the associated programs and also for simple ways of locating errors. The most common way to prove the correctness of a CI program is to check the invariance of the eigenvalues against unitary transformations of the one-electron functions. This approach is certainly quite useful for globally checking the correctness of a CI program but it is of little or no help in locating the error. Recently, expressions have been derived for the first two moments of the spectral density distribution of the Hamiltonian matrix[16] and have been shown useful in locating the specific sections of a CI program containing errors.[17] The method consists of comparing dispersions of the Hamiltonian matrix calculated by different algorithms. The application of this method to debugging a direct CI program has demonstrated the high efficiency of this approach as well as difficulties associated with round-off errors.[17,18] It is recalled that the dispersion contains the expression $\mathrm{Tr}H^2$, which is a sum of D^2 terms where D is the dimension of the matrix H. Thus for larger matrices ($D \geq 10^3$) the contribution of the round-off error of the individual matrix elements to the sum may become comparable to the error of the specific matrix element to be located. The aim of this study is to check the loss of accuracy in calculating $\mathrm{Tr}H^2$ due to round-off errors in case of a matrix representing a real quantum-chemical system and to modify the method of locating errors in the Hamiltonian matrix such that the round-off errors do not affect the result or are avoided completely, respectively. It is demonstrated that accumulating $\mathrm{Tr}H^2$ in a double-precision variable improves the accuracy by several orders of magnitude. Further, it is shown how to avoid any round-off effects by choosing the interaction integrals entering the matrix elements and the transformation matrices such that the resulting dispersion has integer values. The table of dispersion values supplied may be used as standard reference against which dispersions calculated by a configuration interaction program may be compared. Certainly, the same approach can be used in nuclear-shell-model calculations.

II. METHOD

Let us consider the operator

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_1(i) + \sum_{\substack{i<j \\ i,j=1}}^{N} \hat{h}_2(i,j) , \tag{1}$$

where $\hat{h}_1(1)$ and $\hat{h}_2(1,2)$ describe, respectively, one- and two-body interactions. In order to focus attention it is assumed that $\hat{H}$ represents a Hamiltonian and that the particles are electrons. However, since the formalism does not depend upon the explicit form of $\hat{h}_1$ and $\hat{h}_2$, all considerations remain valid for an arbitrary operator containing one- and/or two-body interactions and for any system of N identical Fermions. In particular, either $\hat{h}_1$ or $\hat{h}_2$ may be set equal to zero. The operator $\hat{H}$ is represented in an antisymmetric and spin-adapted Hilbert space. The basis for this space is constructed from spin-adapted antisymmetrized products of orthonormal orbitals $\{\varphi_i\}_{i=1}^{K}$. The spin-adapted basis functions are the eigenfunctions of the total spin operators $\hat{S}^2$ and $\hat{S}_z$ with the eigenvalues $S(S+1)$ and M, respectively. The rather nontrivial methodology of constructing this basis and of calculating the matrix elements of $\hat{H}$ is discussed in several recent reviews.[1-6]

The form of the Hamiltonian matrix depends on the representation chosen. However, the Hamiltonian spectrum and the moments of the spectral density distribution are representation independent. Therefore the values of these invariants calculated by using the Hamiltonian matrix expressed in different representations may be used to check for both formal correctness and numerical accuracy of the algorithm. Different representations may be obtained through unitary transformations of the basis in the D-dimensional Hilbert space. All these transformations form the unitary group $U(D)$. The subgroup of $U(D)$ generated by unitary transformations of the orbitals $\{\varphi_i\}_{i=1}^{K}$ proves to be particularly useful for the present purpose.

For fixed values of N, K, and S the dimension of the Hilbert space is equal to[1,19]

$$D(N,K,S)=\frac{2S+1}{K+1}\begin{bmatrix}K+1\\N/2-S\end{bmatrix}\begin{bmatrix}K+1\\N/2+S+1\end{bmatrix}\ . \tag{2}$$

The average value of $\hat{H}$ in the Hilbert space is defined as

$$E[\underline{H}(N,S)]=\frac{1}{D}\mathrm{Tr}\underline{H}(N,S)\ , \tag{3}$$

where $\underline{H}(N,S)$ is the matrix representation of $\hat{H}$. The nth moment of the spectral density distribution is defined as

$$M_n[\underline{H}(N,S)]=\frac{1}{D}\mathrm{Tr}\{\underline{H}(N,S)-E[\underline{H}(N,S)]\}^n\ . \tag{4}$$

In particular, the second moment, or dispersion, of the spectrum may be expressed in the form

$$\begin{aligned}\sigma^2(N,S)&\equiv M_2[\underline{H}(N,S)]\\&=\frac{1}{D}\mathrm{Tr}\underline{H}(N,S)^2-E[\underline{M}(N,S)]^2\\&=\frac{1}{D}\sum_{i,j=1}^{D}H_{ij}H_{ji}-\frac{1}{D^2}\sum_{i,j=1}^{D}H_{ii}H_{jj}\ .\end{aligned} \tag{5}$$

The moments are defined by Eqs. (3)—(5) in terms of the Hamiltonian matrix elements. On the other hand, the same quantities may be expressed directly in terms of one- and two-electron integrals involving $\hat{h}_1(1)$ and $\hat{h}_2(1,2)$ defined, respectively, as

$$(p|q)=\langle\varphi_p(1)|\hat{h}_1(1)|\varphi_q(1)\rangle\ , \tag{6}$$

$$(pq|rs)=\langle\varphi_p(1)|\langle\varphi_r(2)|\hat{h}_2(1,2)|\varphi_s(2)\rangle|\varphi_q(1)\rangle\ . \tag{7}$$

By comparing the values of the moments calculated by summation of the matrix elements of $\hat{H}$ with those calculated directly from the list of integrals, both the correctness and the numerical accuracy of the algorithms can be checked.

A. Two-electron case

In the two-electron case the average value of $\hat{H}$ becomes[16]

$$E[\underline{H}(2,S)]=2\langle\hat{h}_1\rangle+\frac{1}{K\pm1}(\langle\hat{\mathcal{J}}\rangle\pm\langle\hat{\mathcal{K}}\rangle)\ , \tag{8}$$

where the + (−) signs correspond to $S=0$ (1),

$$\langle\hat{h}_1\rangle=\frac{1}{K}\sum_{p=1}^{K}(p|p)\ , \tag{9}$$

$$\langle\hat{\mathcal{J}}\rangle=\frac{1}{K}\sum_{p,q=1}^{K}(pp|qq)\ , \tag{10}$$

$$\langle\hat{\mathcal{K}}\rangle=\frac{1}{K}\sum_{p,q=1}^{K}(pq|qp)\ , \tag{11}$$

and similarly

$$\mathrm{Tr}[\underline{H}(2,S)^2]=\tfrac{1}{4}\sum_{p,q,r,s=1}^{K}\left[(pq|rs)\pm(ps|rq)+\frac{1}{N-1}[(i|j)\delta_{kl}+(k|l)\delta_{ij}\pm(i|l)\delta_{kj}\pm(k|j)\delta_{il}]\right]^2\ , \tag{12}$$

where again the + (−) signs correspond to $S=0$ (1).

In order to check the correctness of an algorithm and the associated computer code the values of σ^2 or of $\mathrm{Tr}\underline{H}^2$ calculated from Eqs. (8)–(12) are compared with those obtained directly from the matrix according to Eq. (5). Since $\mathrm{Tr}\underline{H}^2$ is a sum of non-negative contributions, no fortuitous cancellation of errors can occur. If the values computed in both ways differ from each other, the error can be located easily by a proper choice of the values of the $(p|q)$ and/or $(pq|rs)$ integrals. There are three main classes of matrix elements of $\underline{H}$ depending on the kind of integrals being involved:[4,6] (I) the matrix elements depending on $(p|p)$, $(pp|qq)$, and $(pq|qp)$; (II) the matrix elements depending on $(p|q)$, $(pq|rr)$, $(pr|rq)$, and $(pq|qq)$, $p\neq q$; (III) the matrix elements depending on $(pq|rs)$, $p\neq q\neq r\neq s$. For details concerning this classification see, e.g., Ref. 6. Assuming that only integrals of one selected class are different from zero at a time, each of the three main sections of the program may be checked separately. Finally, taking, for example, just one integral to be different from zero at a time, specific parts of the algorithm and/or associated computer code may be checked.

It is worthwhile to point out a useful consequence of the invariance properties of the moments. If two sets of orbitals, $\{\psi\}$ and $\{\varphi\}$, are connected by a unitary transformation, i.e., if

$$\psi_m(1) = \sum_{p=1}^{K} U_{mp}\varphi_p(1) \ , \tag{13}$$

where

$$\sum_{p=1}^{K} U_{mp}U_{np} = \delta_{mn} \ , \tag{14}$$

then also the resulting two sets of N-electron basis functions (the one derived from $\{\psi_m\}_{m=1}^{K}$ and the other derived from $\{\varphi_p\}_{p=1}^{K}$) are connected by a unitary transformation. In consequence, the moments calculated in the two bases are the same. If $(\tilde{k}\,\tilde{l}|\tilde{m}\,\tilde{n})$ is a two-electron integral (7) calculated in the basis $\{\Psi\}$, then

$$(\tilde{k}\,\tilde{l}|\tilde{m}\,\tilde{n}) = \sum_{p,q,r,s=1}^{K} U_{kp}U_{lq}U_{mr}U_{ns}(pq|rs) \ . \tag{15}$$

In particular, if all integrals in the basis $\{\varphi_p\}_{p=1}^{K}$ are set equal to 0 except for one, say $(11|11)$, which is set equal to 1, then

$$(\tilde{k}\,\tilde{l}|\tilde{m}\,\tilde{n}) = U_{k1}U_{l1}U_{m1}U_{n1} \tag{16}$$

and $\mathrm{Tr}\underline{H}^2 = \frac{1}{4}(11|11)^2 = 1$ in both the bases. The U_{m1}, $m = 1, 2, \ldots, K$, have to fulfil only the normalization condition

$$\sum_{m=1}^{K} U_{m1}^2 = 1 \ . \tag{17}$$

Independently of the choice of U_{1m}, integrals (17) must always lead to an $\underline{H}$ matrix for which $\mathrm{Tr}H^2 = 1$. Obviously, applying different variations of this idea, specific parts of the algorithm and of the associated computer code can be checked.

B. N-electron case

When checking a CI program for correctness it is wise to start from a two-electron case. Then the spin part is trivial and checking is limited essentially to the orbital part only. More types of elements appear in the matrix if the number of electrons N is increased (consult Refs. 6 and 20 for details). All different types of matrix elements appear in the matrix only if $N \geq 6$.[20] However, a complete check of the program is possible only for $N \geq 9$. This is true because the formula for a matrix element depends not only on the distribution of the occupation numbers over the orbitals but also on the relative arrangement of the orbitals in the two N-electron basis functions involved.

The average value of $\hat{H}$ in the N-electron case is[16]

$$E[\underline{H}(N,S)] = a^{+}E[\underline{H}(2,0)] + a^{-}E[\underline{H}(2,1)] - N(N-2)\langle \hat{h}_1 \rangle \ , \tag{18}$$

where

$$a^{+} = \frac{1}{2}\left[\frac{N}{2}\left[\frac{N}{2}+1\right] - S(S+1)\right] \ , \tag{19}$$

$$a^{-} = \frac{N(N-1)}{2} - a^{+} \ . \tag{20}$$

The general expressions for $\mathrm{Tr}\underline{H}(N,S)^2$ and for the dispersion $\sigma^2(N,S)$ have been published elsewhere.[16] For the present purpose it is convenient to use separate expressions for the dispersions of the one-body and of the two-body parts of $\hat{H}$ (i.e., assuming that either $\hat{h}_1 = 0$ or $\hat{h}_2 = 0$). Then, according to Ref. 16, in the case of $\hat{h}_2 = 0$, the dispersion is given by

$$\sigma_1^2(N,S) = A_1\sigma_1^2(1,\tfrac{1}{2}) \ , \tag{21}$$

where

$$A_1 = \frac{2K}{(K+1)(K-1)}\left[\frac{N}{2}\left[1-\frac{N}{2K}\right](K+2) - S(S+1)\right] \ , \tag{22}$$

$$\sigma_1^2(1,\tfrac{1}{2}) = \frac{1}{K}\sum_{p,q=1}^{K}(p|q)^2 - \langle \hat{h}_1 \rangle^2 \ . \tag{23}$$

Similarly, in the case of $\hat{h}_1 = 0$, the dispersion is given by

$$\begin{aligned}\sigma_2^2(N,S) = {} & A_2^{+}\sigma_2^2(2,0) + A_2^{-}\sigma_2^2(2,1) + B^{+}\sigma_2^2(\mathcal{J}+\mathcal{K}) \\ & + B^{-}\sigma_2^2(\mathcal{J}-\mathcal{K}) + C^{+}\sigma_2^2(\mathcal{K}) \ ,\end{aligned} \tag{24}$$

where

$$A_2^{+} = \frac{a^{+}}{K(K-1)}\left[\left[K-\frac{N}{2}\right]\left[K-\frac{N}{2}+1\right] - S(S+1)\right] \ , \tag{25}$$

$$\begin{aligned}A_2^{-} = {} & \left\{\frac{N}{2}\left[K-\frac{N}{2}\right]\left[N\left[K-\frac{N}{2}\right]F(1,1,3) - (K+1)F(1,4,-6)\right]\right. \\ & - S(S+1)\left[2N\left[K-\frac{N}{2}\right]F(1,3,-3) - KF(5,-1,-6)\right] \\ & \left. + 2[S(S+1)]^2F(1,-3,3)\right\}\Big/ K(K+1) - \frac{K-1}{K+1}A_2^{+} \ ,\end{aligned} \tag{26}$$

$$B^{+} = \frac{2Ka^{+}}{(K+1)(K-1)(K-2)}\left[\left[K-\frac{N}{2}\right]\left[\frac{N}{2}-1\right](2K-1) - S(S+1)\right] \ , \tag{27}$$

$$B^- = \frac{K^2}{(K+1)(K-1)} \left[N \left[K - \frac{N}{2} \right] \left[\frac{N}{2} - 1 \right] [NF(0,2,-1) - 2F(0,1,7)] - 2S(S+1)[N^2F(0,1,2) - 2NF(0,4,3) + 12F(0,1,0)] - [S(S+1)]^2 F(0,0,4) \right] - B^+ , \quad (28)$$

$$F(p,q,r) = \frac{pK^2 + qK + r}{(K-2)(K-3)} , \quad (29)$$

$$C^+ = -\frac{2K^2 a^+}{(K+1)(K-1)(K-2)} \left[6 \left[K - \frac{N}{2} \right] \left[\frac{N}{2} - 1 \right] - S(S+1) \right] , \quad (30)$$

$$\sigma_2^2(2,s) = \frac{1}{2K(K \pm 1)} \sum_{p,q,r,s=1}^{K} [(pq|rs) \pm (ps|rq)]^2 - \{E[\underline{H}(2,s)]\}^2 , \quad (31)$$

where + (−) corresponds to $s = 0$ (1),

$$\sigma_2^2(a\mathcal{J} + b\mathcal{K}) = \frac{1}{K} \sum_{p,q=1}^{K} (a\mathcal{J}_{pq} + b\mathcal{K}_{pq})^2 - \left[\frac{1}{K} \sum_{p=1}^{K} (a\mathcal{J}_{pp} + b\mathcal{K}_{pp}) \right]^2 , \quad (32)$$

$$\mathcal{J}_{pq} = \frac{1}{K} \sum_{k=1}^{K} (pq|kk) , \qquad \mathcal{K}_{pq} = \frac{1}{K} \sum_{k=1}^{K} (pk|kq) . \quad (33)$$

Thus, for a given set of orbitals, the dispersions are expressed as fourth-order polynomials in N and S. Using the same techniques as described for systems of two electrons, the correctness of a program can be checked rather easily by comparing the dispersions calculated directly from the Hamiltonian matrix with those derived from Eqs. (21) and (24).

III. IMPLEMENTATIONS

In this section two sets of calculations of dispersions of spectra of many-electron Hamiltonians are presented. In the first case different states of the H_2O molecule in its ground-state equilibrium geometry are considered. This case has been set by several authors as a benchmark for studying different approaches to solving the Schrödinger equation for molecules.[21,22] In the second case all spin states of a model system of spin-$\frac{1}{2}$ particles ($2 \leq N \leq 9$) in a regular nonogonal potential are considered.

The one-electron basis for H_2O is formed by 14 orbitals obtained as solutions of the Hartree-Fock equations in the Gaussian double-ζ Huzinaga-Dunning O(9s5p/4s2p), H(4s/2s) basis.[23,24] Since the Hamiltonian transforms according to C_{2v} point-group symmetry, the ten-electron full CI space may be factorized into four subspaces corresponding to the four irreducible representations: A_1, A_2, B_1, and B_2. However, the moments for the subspaces have been calculated directly from the Hamiltonian matrix [Eqs. (2)–(5)] because Eqs. (18)–(33) in which the moments are expressed directly in terms of the one- and two-electron integrals are valid for complete spaces only.

Values of the dispersions in the complete (i.e., including both one- and two-electron interactions) Hamiltonian spectrum, $\sigma^2(N,S)$, are collected in Table I. The expression for $\sigma^2(N,S)$ may be easily obtained from that for $\sigma_2^2(N,S)$ [Eq. (24)] by replacing all $(pq|rs)$ integrals with[18]

$$(pq|rs) + [\delta_{pq}(r|s) + \delta_{rs}(p|q)]/(N-1) .$$

In the consecutive columns of Table I are displayed the total dispersion $\sigma^2(N,S)$ and the dispersions $[\sigma^2(N,S)]_C$, $C =$ I,II,III obtained assumming that only integrals entering class C of matrix elements (see Sec. II) are different from zero. In all cases the same orbitals are used to construct the Hilbert space. Calculations have been performed for all possible values of the total spin. The entries in Table I marked by an asterisk correspond to dispersions calculated using the expressions in terms of the one- and two-electron integrals. All other dispersions have been obtained by summing the Hamiltonian matrix elements. The corresponding numbers calculated in both ways agree up to 11–14 significant figures for $S=5$ ($D = 10^3$), up to 8–10 figures for $S=4$ ($D = 3\times10^4$), and up to 7–8 figures for $S=0$ ($D=10^6$). The matrix elements have been computed in the CRAY single precision, i.e., they are accurate to at most 14 significant figures. Since the main contribution to $\mathrm{Tr}\underline{H}^2$, and to the cumulative error, is due to the diagonal elements of $\underline{H}$, the minimum error resulting from the round-off contributions is $10^{-14}D$. This estimate leads to the minimum relative error of σ^2 equal to 10^{-11}, 3×10^{-10}, and 10^{-8} for $S=5$, $S=4$, and $S=0$, respectively. It agrees with the data in Table I and proves that there is virtually no loss of accuracy in the procedure for determining the values of H_{ij}. To check this result independently, the sum of H_{ij}^2 is accumulated in the CRAY double precision, with all other variables in single precision. Then the results are accurate up to at least 14 figures. In Table II the contributions to σ_1^2 and to σ_2^2 (the dispersions due to the one- and two-electron parts of the Hamiltonian, respectively) are displayed. These data are considered to be useful as a reference for locating errors in CI programs.

TABLE I. Dispersions of the H_2O Hamiltonian matrix. The positions marked 1 (2) indicate precision of the dispersion achieved within CRAY single (double) precision accuracy. See text for details. All quantities are in a.u.

$2S+1$		D	$\sigma^2(10,S)$	$[\sigma^2(10,S)]_{\mathrm{I}}$	$[\sigma^2(10,S)]_{\mathrm{II}}$	$[\sigma^2(10,S)]_{\mathrm{III}}$
11	$A1$	273	$0.443\,597\,761\,290\,63\times 10^{3}$	$0.441\,354\,947\,184\,30\times 10^{3}$	$0.222\,545\,789\,097\,14\times 10^{1}$	$0.173\,562\,153\,682\,54\times 10^{-1}$
	$A2$	232	$0.403\,837\,163\,941\,37\times 10^{3}$	$0.401\,237\,856\,311\,26\times 10^{3}$	$0.256\,887\,044\,953\,52\times 10^{1}$	$0.304\,371\,805\,784\,93\times 10^{-1}$
	$B1$	208	$0.395\,187\,618\,045\,43\times 10^{3}$	$0.392\,784\,482\,404\,09\times 10^{3}$	$0.237\,938\,250\,746\,12\times 10^{1}$	$0.237\,531\,338\,828\,91\times 10^{-1}$
	$B2$	288	$0.460\,955\,788\,316\,64\times 10^{3}$	$0.458\,428\,173\,386\,16\times 10^{3}$	$0.250\,804\,753\,969\,53\times 10^{1}$	$0.195\,673\,907\,947\,54\times 10^{-1}$
		1 001	$0.429\,683\,255\,686\,24\times 10^{3}$	$0.427\,242\,563\,443\,88\times 10^{3}$	$0.241\,833\,886\,264\,89\times 10^{1}$	$0.223\,533\,797\,065\,68\times 10^{-1}$
	*	1 001	$0.429\,683\,255\,686\,24\times 10^{3}$	$0.427\,242\,563\,443\,87\times 10^{3}$	$0.241\,833\,886\,265\,78\times 10^{1}$	$0.223\,533\,797\,069\,91\times 10^{-1}$
			1↑	1↑	1↑	1↑
9	$A1$	6 747	$0.642\,040\,538\,257\,14\times 10^{3}$	$0.638\,911\,959\,645\,52\times 10^{3}$	$0.306\,471\,831\,226\,63\times 10^{1}$	$0.638\,602\,993\,588\,73\times 10^{-1}$
	$A2$	6 792	$0.637\,601\,970\,544\,83\times 10^{3}$	$0.634\,156\,569\,032\,28\times 10^{3}$	$0.336\,385\,698\,518\,19\times 10^{1}$	$0.815\,445\,273\,655\,93\times 10^{-1}$
	$B1$	6 672	$0.622\,332\,956\,109\,55\times 10^{3}$	$0.618\,958\,267\,961\,57\times 10^{3}$	$0.329\,430\,198\,620\,12\times 10^{1}$	$0.803\,861\,617\,834\,34\times 10^{-1}$
	$B2$	6 816	$0.645\,068\,803\,086\,78\times 10^{3}$	$0.641\,861\,964\,166\,28\times 10^{3}$	$0.314\,227\,837\,493\,34\times 10^{1}$	$0.645\,605\,455\,813\,42\times 10^{-1}$
		27 027	$0.636\,930\,968\,716\,61\times 10^{3}$	$0.633\,642\,278\,874\,18\times 10^{3}$	$0.321\,612\,918\,014\,19\times 10^{1}$	$0.725\,606\,622\,911\,51\times 10^{-1}$
	*	27 027	$0.636\,930\,968\,775\,24\times 10^{3}$	$0.633\,642\,278\,929\,60\times 10^{3}$	$0.321\,612\,918\,323\,78\times 10^{1}$	$0.725\,606\,624\,049\,61\times 10^{-1}$
			1↑ 2↑	1↑ 2↑	1↑ 2↑	1↑ 2↑
7	*	245 245	$0.802\,762\,173\,171\,82\times 10^{3}$	$0.798\,783\,602\,993\,11\times 10^{3}$	$0.385\,193\,879\,409\,78\times 10^{1}$	$0.126\,631\,384\,614\,32\times 10$
5	*	975 975	$0.927\,154\,846\,259\,07\times 10^{3}$	$0.922\,652\,167\,851\,13\times 10^{3}$	$0.432\,738\,279\,230\,73\times 10^{1}$	$0.175\,295\,615\,634\,42\times 10$
3	*	1 756 755	$0.101\,009\,247\,107\,43\times 10^{3}$	$0.100\,523\,719\,766\,62\times 10^{4}$	$0.464\,367\,250\,066\,81\times 10^{1}$	$0.211\,600\,907\,439\,76\times 10$
1	$A1$	256 473	$0.105\,897\,170\,263\,47\times 10^{4}$	$0.105\,388\,947\,747\,28\times 10^{4}$	$0.484\,676\,787\,880\,04\times 10^{1}$	$0.235\,457\,283\,070\,46\times 10^{0}$
	$A2$	245 000	$0.104\,543\,165\,005\,37\times 10^{4}$	$0.104\,044\,562\,648\,68\times 10^{4}$	$0.475\,913\,842\,114\,26\times 10^{1}$	$0.226\,885\,145\,790\,99\times 10^{0}$
	$B1$	245 776	$0.104\,644\,945\,325\,95\times 10^{4}$	$0.104\,145\,821\,820\,50\times 10^{4}$	$0.476\,350\,716\,232\,89\times 10^{1}$	$0.227\,727\,892\,239\,72\times 10^{0}$
	$B2$	254 752	$0.105\,491\,104\,932\,34\times 10^{4}$	$0.104\,984\,399\,496\,74\times 10^{4}$	$0.483\,377\,266\,064\,99\times 10^{1}$	$0.233\,281\,695\,336\,26\times 10^{0}$
		1 002 001	$0.105\,156\,402\,240\,05\times 10^{4}$	$0.104\,653\,149\,516\,17\times 10^{4}$	$0.480\,161\,496\,898\,10\times 10^{1}$	$0.230\,912\,269\,921\,02\times 10^{0}$
	*	1 002 001	$0.105\,156\,403\,630\,90\times 10^{4}$	$0.104\,563\,150\,854\,66\times 10^{4}$	$0.480\,161\,546\,771\,48\times 10^{1}$	$0.230\,912\,294\,680\,02\times 10$
			1↑ 2↑	1↑ 2↑	1↑ 2↑	1↑ 2↑

The results obtained in the case of the model Hamiltonian are intended exclusively as a set of numbers for checking the correctness of arbitrary programs evaluating matrix elements of one- and/or two-electron operators in N-electron spin-adapted Hilbert spaces. All spin states of a model system with $K=9$ and $N=2,3,\ldots,9$ are considered. The dispersions are calculated using for the one- and two-electron integrals the values

$$(p|q)=\begin{cases}1 & \text{if } |p-q|=1 \text{ or } |p-q|=8\\ 0 & \text{otherwise}\end{cases} \tag{34}$$

and

$$(pq|rs)=\delta_{pq}\delta_{rs}[3-\min(|p-q|,9-|p-q|)]\ , \tag{35}$$

and for the orbital transformation [according to Eq. (13)] the following matrix:

$$U=\begin{bmatrix} a & b & c & 0 & 0 & 0 & d & 0 & e\\ a & b & -c & 0 & 0 & 0 & d & 0 & e\\ a & b & 0 & c & 0 & 0 & -d & 0 & e\\ a & b & 0 & -c & 0 & 0 & -d & 0 & e\\ a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -f\\ a & -b & 0 & 0 & c & 0 & 0 & -d & e\\ a & -b & 0 & 0 & -c & 0 & 0 & -d & e\\ a & -b & 0 & 0 & 0 & c & 0 & d & e\\ a & -b & 0 & 0 & 0 & -c & 0 & d & e \end{bmatrix}$$

where $a=\frac{1}{3}$, $b=\frac{1}{2}\sqrt{2}$, $c=1/\sqrt{2}$, $d=\frac{1}{2}$, $e=\frac{1}{6}\sqrt{2}$, and $f=\frac{4}{3}\sqrt{2}$.

In Table III values for the dispersions in the transformed basis are displayed. The dispersions are multiplied by factors assuring that the resulting numbers are integers. The dispersions σ_1^2 and σ_2^2 are invariant with respect to unitary transformations of the orbitals. However, this is not the case for $\sigma_1^2(N,S)_C$ and $\sigma_2^2(N,S)_C$. In particular, in the original basis the following equations hold: $\sigma_1^2(N,S)=\sigma_1^2(N,S)_{\rm II}$, $\sigma_2^2(N,S)=\sigma_2^2(N,S)_{\rm I}$, and $\sigma_1^2(N,S)_{\rm I}=\sigma_2^2(N,S)_{\rm II}=\sigma_2^2(N,S)_{\rm III}=0$. In general, the following relations hold independently of the unitary transformation:

$$\sigma_1^2(N,S)=\sigma_1^2(N,S)_{\rm I}+\sigma_1^2(N,S)_{\rm II}$$

and

$$\sigma_2^2(N,S)=\sigma_2^2(N,S)_{\rm I}+\sigma_2^2(N,S)_{\rm II}+\sigma_2^2(N,S)_{\rm III}\ .$$

The data displayed in Table III are independent of the nature of the interaction. They may be used equally well in atomic physics and in the theory of nuclear structure. In these cases there are other constants of motion than

TABLE II. Dispersion for the one- and two-electron parts of the H_2O Hamiltonian matrix calculated directly from the list of integrals. All quantities are in a.u.

$2S+1$	D	$[\sigma_1^2(10,S)]_{\rm I}$	$[\sigma_1^2(10,S)]_{\rm II}$	$[\sigma_2^2(10,S)]_{\rm I}$	$[\sigma_2^2(10,S)]_{\rm II}$
11	1 001	$0.414\,068\,931\,308\,14\times10^3$	$0.123\,859\,711\,154\,13\times10^2$	$0.979\,032\,746\,595\,11\times10^1$	$0.501\,416\,403\,840\,66\times10^1$
9	27 027	$0.607\,301\,099\,251\,91\times10^3$	$0.181\,660\,909\,692\,73\times10^2$	$0.201\,584\,399\,939\,24\times10^2$	$0.905\,173\,252\,975\,62\times10^1$
7	245 245	$0.761\,886\,833\,606\,93\times10^3$	$0.227\,901\,868\,523\,60\times10^2$	$0.284\,744\,816\,912\,32\times10^2$	$0.122\,793\,646\,772\,32\times10^2$
5	975 975	$0.877\,826\,134\,373\,22\times10^3$	$0.262\,582\,587\,646\,76\times10^2$	$0.347\,240\,847\,745\,96\times10^2$	$0.146\,986\,755\,779\,03\times10^2$
3	1 756 755	$0.955\,119\,001\,550\,75\times10^3$	$0.285\,703\,067\,062\,19\times10^2$	$0.388\,964\,734\,065\,52\times10^2$	$0.163\,108\,765\,545\,72\times10^2$
1	1 002 001	$0.993\,765\,435\,139\,49\times10^3$	$0.297\,263\,306\,769\,91\times10^2$	$0.409\,844\,636\,954\,37\times10^2$	$0.171\,167\,751\,557\,72\times10^2$

TABLE III. Scaled dispersions for the model system described in the text; $G = 1944 \times 10^2$.

N	$2S+1$	D	$D\sigma_1^2$	$D\sigma_2^2$	$G(\sigma_1^2)_{\text{I}}$	$G(\sigma_1^2)_{\text{II}}$	$G(\sigma_2^2)_{\text{I}}$	$G(\sigma_2^2)_{\text{II}}$	$G(\sigma_2^2)_{\text{III}}$
2	3	36	126	45	707 616	8 110 368	125 550	1 679 292	1 344 438
	1	45	198	90	1 389 960	15 931 080	2 174 760	2 911 905	2 786 535
3	4	84	378	225	4 953 312	56 772 576	1 464 750	19 591 740	15 685 110
	2	240	1 404	1 125	52 565 760	602 484 480	90 398 040	231 859 200	202 622 760
4	5	126	630	450	12 383 280	141 931 440	4 394 250	58 775 220	47 055 330
	3	630	4 284	4 410	421 031 520	4 825 668 960	762 418 440	2 501 806 230	2 136 790 530
	1	540	4 158	4 995	350 269 920	4 014 632 160	834 298 110	2 363 815 980	2 045 437 110
5	6	126	630	450	12 383 280	141 931 440	4 394 250	58 775 220	47 055 330
	4	1 008	7 308	8 325	1 149 168 384	13 171 237 632	2 109 282 840	7 690 253 760	6 513 733 800
	2	1 890	16 254	22 950	4 792 329 360	54 927 467 280	12 115 204 290	38 912 170 500	33 294 597 210
6	7	84	378	225	4 953 312	56 772 576	1 464 750	19 591 740	15 685 110
	5	1 050	7 560	8 550	1 238 328 000	14 193 144 000	2 215 479 000	8 255 577 750	6 981 203 250
	3	3 402	30 618	46 170	16 249 340 016	186 242 435 568	41 716 361 610	142 397 418 744	121 230 960 606
	1	2 520	24 948	42 390	9 807 557 760	112 409 700 480	28 703 840 760	96 613 811 280	82 345 871 160
7	8	36	126	45	707 616	8 110 368	125 550	1 679 292	1 344 438
	6	720	4 788	4 815	537 788 160	6 163 879 680	893 934 360	3 161 479 680	2 684 045 160
	4	3 780	33 642	50 085	19 838 014 560	227 374 166 880	49 686 812 910	172 046 968 380	146 306 825 910
	2	6 048	61 992	110 430	58 488 708 096	670 370 577 408	174 311 192 160	607 612 852 224	516 435 919 776
8	9	9	18	0	25 272	289 656	0	0	0
	7	315	1 764	1 350	86 682 960	993 520 080	124 140 240	377 784 225	324 761 535
	5	2 700	22 410	30 375	9 439 092 000	108 186 516 000	21 987 402 750	74 209 027 500	63 235 869 750
	3	7 560	76 356	133 650	90 051 212 160	1 032 125 431 680	262 131 198 840	920 306 091 600	781 768 645 560
	1	5 292	58 212	113 400	48 057 033 024	550 807 532 352	153 740 379 240	547 953 736 680	464 925 167 280
9	10	1	0	0	0	0	0	0	0
	8	80	324	135	4 043 520	46 344 960	4 145 240	8 908 480	7 941 480
	6	1 215	8 748	9 720	1 658 095 920	19 004 330 160	3 326 966 460	10 574 961 480	9 056 323 260
	4	5 760	54 432	87 480	48 910 417 920	560 588 636 160	132 422 837 760	457 784 340 480	389 344 872 960
	2	8 820	95 256	181 440	131 064 635 520	1 502 202 360 960	409 974 344 640	1 461 209 964 480	1 239 800 446 080

spin, such as the total angular momentum, orbital angular momentum, or isospin. Unfortunately, formulas for dispersions in subspaces adapted to these constants of motion are not known. However, in each case $\sigma^2(N,S)$ may be calculated combining contributions from different subspaces in the appropriate way.

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