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Spin-Adapted Vector Method: An Alternative to the Conventional Configuration Interaction Approach*

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A number of refinements have been incorporated in the vector method. The refinements include utilization of spin-adapted configurations, partitioning the steps in the calculation, and determining the connection of this spin-adapted vector method and standard configuration interaction techniques. To this end, the spin-adapted vector method can be used to generate an integral inverted formula tape commonly used by standard configuration interaction. Sample calculations on LiH are used to compare standard CI and the spin-adapted vector method.

INTRODUCTION

One method for determining accurate electronic structure information for atoms and molecules is the method of superposition of configurations; often called configuration interaction (CI). The wavefunction ψ is expanded as a linear combination of configurations, ϕ_i :

$$\psi = \sum c_i \phi_i \tag{1}$$

The energies and expansion coefficients (c_i's) are determined by diagonalization of the Hamiltonian interaction matrix,

$$\mathbf{Hc} = \lambda \mathbf{c}, \tag{2}$$

where the matrix elements of **H** are computed using the Hamiltonian operator,

$$(\mathbf{H})_{pq} = \langle \phi_p \mid H_{op} \mid \phi_q \rangle. \tag{3}$$

The traditional approach for calculating eigenvalues and eigenvectors involves construction and subsequent diagonalization of the Hamiltonian matrix [1]. Recently, an alternative approach for determining the eigenvalue and eigenvectors was introduced. [2, 3]. This technique, the vector method (VM), utilizes an iterative diagonali-

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zation procedure involving a second-quantized form of the Hamiltonian operator for solving Eq. (2) directly. The new method was shown to have a number of desirable features; particularly impressive was the near-linear relationship between the number of Slater determinants (subelements of the configurations) and computer times. The method was more general than previously introduced direct methods [4] which were developed to describe very specific symmetries, configurations, and states. The early VM papers did point out a major disadvantage of the method; Slater determinants rather than configurations (spin eigenfunctions) were used.

The purpose of this paper is to describe recent modifications of the vector method for direct utilization of the spin configurations. This spin-adapted vector method will be described, as will a number of the computational steps involved in its implementation.

THEORETICAL BACKGROUND

The standard form of the nonrelativistic Hamitlonain operator is

$$H_{op} = \sum_i \left(-\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}\right) + \sum_{i>j} \frac{1}{r_{ij}}, \tag{4}$$

where Z_A is the charge on atom A and i and j represent the electrons. The vector method uses a second-quantized or occupation number representation form of the Hamiltonian,

$$H_{op} = \sum_{\alpha\beta\gamma\delta} \langle\alpha\beta \mid H \mid \gamma\delta\rangle\, a_\alpha^+ a_\beta^+ a_\delta a_\gamma\,, \tag{5}$$

where a, β, δ, and γ denote spin orbitals. The a_k and a_k^+ are normal fermion annihilation and creation operators, respectively. Slater determinants ϕ, the expansion functions of the wavefunction, are very convenient because they can be expressed as a product of N single-particle operators

$$\phi_p = \mathscr{A}\{\alpha(1)\,\beta(2)\cdots\omega(N)\} = a_\alpha^+ a_\beta^+ \cdots a_\omega^+ \mid 0\rangle, \tag{6}$$

where $\mid 0\rangle$ is the vacuum state. The matrix elements in Eq. (5) are

$$\langle\alpha\beta \mid H \mid \gamma\delta\rangle = \frac{1}{N-1}\langle\alpha \mid -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \mid \gamma\rangle\langle\beta \mid \delta\rangle + \frac{1}{2}\langle\alpha\beta \mid \frac{1}{r_{12}} \mid \gamma\delta\rangle. \tag{7}$$

In the vector method, iterative diagonalization methods are used to solve the operator equation

$$H_{op}\boldsymbol{\phi}\mathbf{d}_E = E\boldsymbol{\phi}\mathbf{d}_E\,, \tag{8}$$

where $\mathbf{d}_E$ is a column of expansions coefficients and $\boldsymbol{\phi}$ is a list of Slater determinants arranged in a row vector. Iterative diagonalization methods are ideally suited because they can be applied to either matrices or operators. The diagonalization algorithm developed by Davidson [5] has proven to be very effective for the lowest few (5–10) eigenvalues, whereas the Lanczos [6] method is favored when larger (20–50) numbers or roots are required.

The improvements proposed previously [3] included use of "spinless" two-body matrix elements and spineigenfunctions (rather than single Slater determinants). The Hamiltonian operator in Eq. (4) can be rewritten as

$$H_{op} = \sum_{\substack{i \geqslant j \\ k \geqslant l \\ (ij) \geqslant (kl)}} A_{ijkl}[Q_{ijkl} + (1 - \delta(ij, kl))\, Q_{lkji}], \tag{9}$$

where

$$(ij) \equiv (i(i-1))\tfrac{1}{2} + j, \tag{10}$$

and i, j, k, and l refer to space (spinless) orthonormal orbitals. The spin dependence is included in the operator

$$Q_{ijkl} = \sum_{pq} a^{+}_{ip} a^{+}_{jq} a_{kq} a_{lp}\,, \tag{11}$$

where p and q run over both spin projections $(\pm\frac{1}{2})$. The two-body matrix elements take a more complicated form,

$$\begin{aligned} A_{ijkl} &= \langle ij \mid H \mid kl\rangle + (1 - \delta_{ij})(1 - \delta_{kl})\langle ji \mid H \mid lk\rangle \\ &\quad - (1 - \delta_{ij})\langle ji \mid H \mid kl\rangle - (1 - \delta_{lk})\langle ij \mid H \mid lk\rangle, \end{aligned} \tag{12}$$

where Eq. (7) is used to evaluate the components of A_{ijkl}. This form of the Hamiltonian operator preserves operator hermiticity and reduces the number of two-body matrix elements and operators by approximately a factor of 16, a factor of 8 coming from the spatial symmetry of the two-electron integral and a factor of 2 from the spin integration.

The list of Slater determinants can be partitioned by spatial orbital occupancy (electron configuration) which leads to increased efficiency, using the above form of the Hamiltonian. The Q_{ijkl} operator when operating on Slater determinants of one electron configuration will create Slater determinants of *only one* electron configuration.

Another improvement, use of linear combinations of Slater determinants (in particular spin eigenfunctions), will further increase computational efficiency. This increase is realized in two ways: first, the number of spin eigenfunctions is considerably less than the number of Slater determinants, and second, only wavefunctions of the desired spin symmetry are generated. Both effects reduce iterative diagonalization times which are proportional to the number (between N and N^2) of nonzero matrix elements times the required number of eigenvalues.

Equation (8) can be rewritten as

$$H_{op}\boldsymbol{\psi}\mathbf{C}_E = E\boldsymbol{\psi}\mathbf{C}_E\,, \tag{13}$$

where $\mathbf{C}_E$ is a column of expansion coefficients and $\boldsymbol{\psi}$ is a row vector of linear combinations of Slater determinants, ϕ_{kp}, i.e.,

$$(\boldsymbol{\psi})_p = \sum_k e_{kp}\phi_{kp}\,. \tag{14}$$

For an approximate wavefunction $\boldsymbol{\psi}\mathbf{C}_Q$ the energy is given by

$$E_Q = \langle \boldsymbol{\psi}\mathbf{C}_Q \mid H_{op} \mid \boldsymbol{\psi}\mathbf{C}_Q\rangle / \langle \boldsymbol{\psi}\mathbf{C}_Q \mid \boldsymbol{\psi}_Q\rangle, \tag{15}$$

$$H_{op}\boldsymbol{\psi}\mathbf{C}_Q = \boldsymbol{\psi}\mathbf{f} + R, \tag{16}$$

where $\mathbf{f}$ is a column vector of coefficients and R is a linear combination of Slater determinants not contained in $\boldsymbol{\psi}$ (or of combinations orthogonal to those in $\boldsymbol{\psi}$). Thus calculation of the approximate energy depends only on $\boldsymbol{\psi}$,

$$E_Q = \mathbf{C}_Q{}^{+}\langle \boldsymbol{\psi} \mid \boldsymbol{\psi}\rangle f = \mathbf{C}_Q{}^{+}\mathbf{f}. \tag{17}$$

Although not a restriction, an obvious choice of the vector $\boldsymbol{\psi}$ would be the linear combinations which define orthonormal spin eigenfunctions (or a subset of them).

COMPARISON WITH STANDARD CI TECHNIQUES

One standard CI method for determining potential energy surfaces involves the use of a formula tape. For a fixed list of configurations, $\boldsymbol{\psi}$, the geometry-independent coefficients of the one- and two-electron integrals are determined,

$$\langle \psi_p \mid H_{op} \mid \psi_q\rangle = \sum_{abcd} C^{pq}_{abcd}[ab \mid cd]. \tag{18}$$

The coefficients and symbolic representations of the one- and two-electron integrals, $[ab \mid cd]$, are stored compactly. Calculations for different geometric arrangements of atoms involve multiplying the value of the integral with the appropriate coefficient and forming the Hamiltonian matrix which is subsequently diagonlized. One problem arises with this technique: when forming a matrix element of the Hamiltonian, the integrals must be randomly (and rapidly) accessed. Many calculations involve millions of integrals which tend to amplify this problem. Yoshimine [7] has developed a sort-merge technique for "inverting" the formula tape. This inverted form connects all references to a particular integral. An integral can then be added to all matrix elements simultaneously. Clearly, the elements of the Hamiltonian matrix must be randomly accessed. Yoshimine has solved this problem with a merge of partial sums.

The spin-adapted vector method (SVM) is ideally suited for generating an "inverted" formula tape by noting that the operator Q_{ijkl} associated with the A_{ijkl} integral determines the coefficients to multiply each configuration in Eq. (16). That is,

$$f_q = \sum_{ijkl} \sum_{p} (\mathbf{c}_Q)_p \, A_{ijkl} \langle \psi_q \mid Q_{ijkl} \mid \psi_p \rangle. \tag{19}$$

Hence $(\mathbf{C}_Q)_p \, A_{ijkl}$ contributes to $(\mathbf{f})_q$ only if the k, l orbitals are occupied in ψ_q and the i, j orbitals are occupied in ψ_p (or vice versa). One important feature of SVM should be noted, the Hamiltonian matrix need not be accumulated if the operator form is used.

From the above discussion the equivalence of the standard CI (formation of Hamiltonian matrix) and the SVM is obvious because

$$(\mathbf{f})_p = \sum_{q} \langle \psi_p \mid H \mid \psi_q \rangle \, (\mathbf{C}_Q)_q \, , \tag{20}$$

and

$$H_{pq} = \langle \psi_p \mid H \mid \psi_q \rangle = \sum_{\substack{ij\\kl}}{}' \langle \psi_p \mid Q_{ijkl} \mid \psi_p \rangle \, A_{ijkl} \, , \tag{21}$$

where the prime on the sum indicates that i, j involves only occupied orbitals in ψ_p and that k, l involves only occupied orbitals in ψ_q. Thus, the SVM method can be used to generate directly the "inverted" formula tape used by the standard matrix diagonalization CI methods. (i.e., conventional formula tape contains $\langle p \mid Q_{ijkl} \mid q \rangle$ sorted on pq, "inverted" is sorted on $ijkl$.)

COMPUTATIONAL IMPLEMENTATION OF THE SVM

The improvements described above have been incorporated in a new section in the Livermore SCREEPER code. This code has been used extensively for calculating *ab initio* potential energy surfaces for small polyatomic molecules. Determination of potential energy surfaces requires hundreds to thousands of individual CI calculations, thus a SVM formula tape technique has been developed.

For all unique orbital (spatial) indices

$$Q_{ijkl} \boldsymbol{\psi} \rightarrow \boldsymbol{\psi} \mathbf{V}_{ijkl} \, , \tag{22}$$

where $\mathbf{V}_{ijkl}$ is a matrix which is very sparse if $ij \neq kl$. It can be stored compactly as a formula tape. The remaining operators generate a very dense matrix

$$Q_{ijij} \boldsymbol{\psi} = \boldsymbol{\psi} \mathbf{V}_{ijij} \, ; \tag{23}$$

however, combinations of these matrix elements are identically the diagonal spin blocks of the Hamiltonian matrix,

$$\sum_{ij} A_{ijij} Q_{ijij} \psi = \psi \mathbf{B}, \tag{24}$$

where

$$\begin{aligned} (\mathbf{B})_{kk} &= \langle \psi_k \mid H_{op} \mid \psi_k \rangle, \\ (\mathbf{B})_{kl} &= 0, \qquad k \neq l. \end{aligned} \tag{25}$$

Here ψ_k is small row vector of spin couplings for one electron configuration.

These matrix elements require a number of two electron matrix elements and geometry independent coefficients

$$(\mathbf{B})_{kk} = \sum_{ij} a_{ij} \langle ij \mid H \mid ij \rangle + b_{ij} \langle ij \mid H \mid ji \rangle. \tag{26}$$

The formulas for B are not saved but rather the numerical values are computed for each geometry. This is possible because there are only N matrix elements (N is the number of configurations) and the number of unique integrals is roughly $2n^2$ (n is the number of space orbitals).

A calculation on a particular molecular system proceeds in two steps. The geometry independent "formula tape" is first generated. For each unique Q_{ijkl}, corresponding to a nonzero A_{ijkl}, the $\mathbf{V}_{ijkl}$ matrix is determined. The nonzero blocks of $\mathbf{V}_{ijkl}$ can be determined by noting which electron-configuration spin-coupling block in the original configuration list can be generated from another electron configuration by replacement of space orbitals l, k by space orbitals i, k, e.g.,

$$Q_{ijkl} \psi_p \rightarrow \psi_q . \tag{27}$$

Then for each pair of blocks of configurations (ψ_p, ψ_q) giving a nonzero A_{ijkl}, the $\mathbf{V}_{ijkl}$ matrix is determined by representing the spin eigenfunctions as linear combinations of Slater determinants. In practice, since Slater determinants are the natural basis set for the annihilation and creation operations, all operations involving Q_{ijkl} are carried out on the Slater determinants followed by a transformation to the space defined by the spin eigenfunctions. The nonzero $\mathbf{V}_{ijkl}$ matrix elements are stored compactly for later use.

During the geometry-dependent portion of the calculation the two-body matrix elements, A_{ijkl}, are computed. The $\mathbf{B}$ matrix is computed using the Q_{ijij} operator and the small set of A_{ijij} integrals. An "operator tape" is constructed by merging the numerical values of A_{ijkl} with the corresponding $\mathbf{V}_{ijkl}$ matrices. Two options then exist, the Hamiltonian matrix can be constructed by accumulating partial sums followed by matrix diagonalization, or the operator form of the eigenvalue problem can be solved directly. As will be seen later, if a number of eigenvalues are required, formation of the Hamiltonian matrix reduces computer time for eigenvalue extraction. This is because the sparse Hamiltonian matrix can be stored more compactly than the formulas.

SAMPLE CALCULATION

For the purpose of checking and timing, a calculation on LiH described in earlier studies [3, 8] has been repeated. Four wavefunctions were constructed, the SCF function

$$\psi_{\text{SCF}} = 1\sigma^2 2\sigma^2 \tag{28}$$

plus (1) all single and double excitations from the 2σ orbital, (2) all single and double excitations from both 1σ and 2σ, (3) the previous (2) plus triple excitations of 1σ and 2σ, and (4) full configuration interaction. Table I gives the number of electron configurations (Space), the number of spin eigenfunctions (Spin), and the number of Slater determinants (SD). One of the motivations for moving to the spin-adapted vector method is observed; as the number of unpaired electrons (related to the excitation level) grows, the number of Slater determinants grows much faster than the number of spin and space configurations. The number of terms vary over two orders of magnitude and should give reasonable timing comparisons.

TABLE I

Numbers of Terms in Example Calculation

Wavefunction[a]	Space	Spin	SD
1	48	48	82
2	135	162	357
3	457	638	1611
4	1002	1353	3033

[a] See text for description of wavefunction.

Computer times for standard configuration interaction (CI), the vector method (VM), and the spin-adapted vector method (SVM) are compared in Table II. For standard CI and VM, times are given for generation of the formula tape and extraction of the lowest eigenvalue (diagonalization). Timing for SVM is given for generation of the formula tape (V_{ijkl}), generation of the B matrix and insertion of the numerical matrix elements (prepare), direct diagonalization, and formation of the Hamiltonian matrix, followed by diagonalization.

Comparing formula tape generation times, VM appears considerably faster, followed by SVM. This comparison is not completely legitimate since the VM formula tape involves geometry-dependent information which must be regenerated for each geometry. In addition, the VM code was carefully optimized [9]. Clearly, the SVM formula tape generation is superior to the standard CI. It should be noted that the CI formula tape generation used in this analysis did not involve inversion which

TABLE II

Timing for Various Methods (in CDC 7600 sec)

	1	2	3	4
Standard CI				
Formula	1.3	7.9	86.3	278.1
Diagonalize (extract lowest root)	0.5	1.2	8.4	19.2
Vector method				
Formula	1.5	6.2	33.1	78.1
Diagonalize	0.4	1.4	6.2	13.1
Spin adapted				
Formula	0.9	5.4	42.0	117.8
Prepare	0.3	0.5	1.3	2.0
Diagonalize	0.4	1.6	11.6	27.1
Form Matrix	0.1	0.4	3.4	10.1
Diagonalize	0.2	0.8	9.9	16.3

would have further increased the generation time, but presumably decreased the H formation time.

Variation in diagonalization times reflect slightly different algorithms and convergence criteria. For this comparison the first, second, and fourth diagonalization times are equivalent. As noted earlier, diagonalization using the operator form is somewhat slower (roughly a factor of 2) than diagonalization of the matrix. It appears from Table II that the operator form should be used if only the lowest eigenvalue is required; however, if a number of eigenvalues are required the matrix should be formed for subsequent diagonalization.

CONCLUSION

Theoretical and computation improvements in the recently developed vector method have lead to the spin-adapted vector method. Calculations on numerous polyatomic systems indicate SVM can be used to generate an inverted formula tap directly and considerably faster than standard CI methods. The operator form can be used directly to extract the lowest eigenvalue or higher eigenvalues if storage limitations prevent formation of the Hamiltonian matrix (e.g., minicomputer facilities). Improvements in iterative diagonalization and formula tape storage may lead to further increased efficiencies.

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