

Ground-State Eigenvectors for Many Configuration Wavefunctions

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An n -th order steep descent technique for determining the lowest eigenvector of the matrix equation,

$$[\mathbf{H} - E\mathbf{S}] \mathbf{c} = 0,$$

is investigated. The convergence is suited to the molecular wavefunction configuration interaction problem, in particular where bases are used which may be nearly overcomplete in certain regions of the vector space. The algorithm is also suited to computer solutions for large matrices, since it can be broken down to apply to blocks of convenient dimensions which may be treated iteratively and separately.

The solution for the lowest eigenvector \mathbf{c} and eigenvalue E of the matrix equation,

$$[H_{ij} - ES_{ij}][c_j] = 0, \quad (1)$$

is of considerable practical importance in many branches of physics, and has been the subject of much study [1, 2]. It arises in the calculation of molecular wavefunctions by configuration interaction where

$$H_{ij} = \int \psi_i H \psi_j d\tau$$

and

$$S_{ij} = \int \psi_i \psi_j d\tau$$

are the matrix elements of the Hamiltonian and unity for the many electron basis functions ψ_i , E is the total electronic Energy of the molecule, and the integral is taken over all space and spin variables.

Very efficient procedures, such as those of Lowdin [3] and Nesbet [4] can be used for large matrices of this type. Generally effective methods for computer solution of Eq. (1) with large matrices, (which may have orders of several thousands) involve an iterative approach. An infinite sequence of operations, which can be

performed separately on different parts of the matrix, is truncated after a certain degree of self-consistency has been achieved.

When near-linear dependences exist among the matrix elements,

$$H_{jk} \approx \sum_{i \neq k} \alpha_i H_{ij}$$

and

$$S_{jk} \approx \sum_{i \neq k} \alpha_i S_{ij},$$

the convergence of iterative procedures usually becomes extremely slow. Such approximate equalities arise from the use of "nearly over-complete" bases [3] which may be derived from integral transform wavefunctions [5], high-order different orbitals for different spins wavefunctions, complete multi-configuration interaction [6] and so on. Indeed all calculations of molecular wavefunctions using combinations of atomic bases centered at different points in space are liable to such over-complete behaviour.

Any method which relies on linear variation of the vector components will converge slowly when the approximate equalities [Eqs. (2)] hold. The characteristic flatness of such surfaces is not suited to a first-order steep descent such as that of McWeeny [7], and Hestenes and Karush [8], though these can be efficient in other contexts. The present technique which relies on higher-order derivatives of the energy with respect to variation in the components of the vector may sometimes be of use in speeding convergence. It is an iterative procedure based on an integral variational principle whose more general application is considered elsewhere [9]. The present approach has points of contact with previous work [3, 4, 7, 8].

METHOD

The expectation value E of the energy for vector \mathbf{c} with components c_i defines a smooth, n -dimensional surface:

$$E = \sum_{i,j=1}^n c_i c_j H_{ij} / \sum_{i,j=1}^n c_i c_j S_{ij}. \quad (3)$$

The components $c_i^{(f)}$ of the ground-state eigenvector $\mathbf{c}^{(f)}$ of Eq. (1) give the coordinates of the minimum of this surface. Let $\mathbf{c}^{(0)}$ be some crude zero-order approximation to the eigenvector. Consider all possible smooth paths which may pass through the surface at $\mathbf{c}^{(0)}$. The one which descends the most steeply at each point from $\mathbf{c}^{(0)}$ to $\mathbf{c}^{(f)}$ may be defined by a functional relationship. *For an element of the path of any arbitrary length the line integral of the energy is stationary and a minimum.*

A smooth path through $\mathbf{c}^{(0)}$ may be expanded in terms of its derivatives with respect to a scalar progress variable s :

$$\mathbf{c}(s) = \mathbf{c}^{(0)} + \mathbf{c}^{(1)}s + \mathbf{c}^{(2)}s^2/2 + \dots \quad (4)$$

The energy expectation value along any such path can also be expanded in terms of its derivatives at the origin:

$$E(s) = E^{(0)} + E^{(1)}s + E^{(2)}s^2/2 + \dots \quad (5)$$

If an element of such a path extending to equal distances Δs on *either side* of the origin is defined, the line integral may be expanded in terms of the *even* derivatives $E^{(2t)}$ alone. For an infinitesimal Δs the value of the line integral is dominated by $E^{(0)}$. For larger Δs there are adjacent ranges whose contributions to the line integral are dominated by $E^{(2)}$, $E^{(4)}$ and so on. Since the functional relationship is true for any arbitrary length separate minimum principles must govern *successive* even-order energy derivatives at the origin.

If Eqs. (4) and (5) are substituted into Eq. (3) and the denominator is expanded as a power series the equations for $E^{(t)}$ for successive orders t can be separated. Applying the conditions:

$$dE^{(2t)}/dc_k^{(t)} = 0, \quad k = 1, 2, \dots, n$$

yields sets of linear inhomogeneous simultaneous equations which appear in matrix form,

$$\mathbf{B}\mathbf{c}^{(t)} = \boldsymbol{\beta}^{(t)}. \quad (6)$$

These may be solved successively for $t = 1, 2, \dots$. The elements of \mathbf{B} are

$$\begin{aligned} B_{ik} = & (H_{ik} - E^{(0)}S_{ik}) - \left(2 \sum_{j=1}^n c_j^{(0)} S_{jk}\right) \left(\sum_{j=1}^n c_j^{(0)} (H_{ji} - E^{(0)}S_{ji})\right) \\ & - \left(2 \sum_{j=1}^n c_j^{(0)} S_{ji}\right) \left(\sum_{j=1}^n c_j^{(0)} (H_{jk} - E^{(0)}S_{jk})\right). \end{aligned} \quad (7)$$

The elements of the first- and second-order $\beta_k^{(t)}$ are¹

$$\beta_k^{(1)} = 0 \quad (8)$$

¹ The higher order $\beta^{(t)}$ can be derived from the general expressions given in reference [9], Eq. (20) by setting $H_{ik}^{(t)} = S_{ik}^{(t)} = 0$, $t > 1$.

and

$$\begin{aligned}
\beta_k^{(2)} = & 2 \left\{ 2 \left(\sum_i \sum_j c_i^{(1)} c_j^{(0)} S_{ij} \right) \left(\sum_j c_j^{(1)} (H_{jk} - E^{(0)} S_{jk}) \right) \right. \\
& + \left(\sum_j c_j^{(0)} S_{jk} \right) \left(\sum_i \sum_j c_i^{(1)} c_j^{(1)} (H_{ij} - E^{(0)} S_{ij}) \right) \\
& + \left(\sum_i \sum_j c_i^{(1)} c_j^{(1)} S_{ij} \right) \left(\sum_j c_j^{(0)} (H_{jk} - E^{(0)} S_{jk}) \right) \\
& + 2 \left(\sum_j c_j^{(1)} S_{jk} \right) \left(\sum_i \sum_j c_i^{(1)} c_j^{(0)} (H_{ij} - E^{(0)} S_{ij}) \right) \\
& - 8 \left(\sum_j c_j^{(0)} S_{jk} \right) \left(\sum_i \sum_j c_i^{(0)} c_j^{(1)} S_{ij} \right) \left(\sum_i \sum_j c_i^{(0)} c_j^{(1)} (H_{ij} - E^{(0)} S_{ij}) \right) \\
& \left. - 4 \left(\sum_i \sum_j c_i^{(0)} c_j^{(1)} S_{ij} \right)^2 \left(\sum_j c_j^{(0)} (H_{jk} - E^{(0)} S_{jk}) \right) \right\}. \quad (9)
\end{aligned}$$

The rank of the matrix B is one greater than its order. One coefficient, preferably the coefficient of the most important component, can be arbitrarily set equal to 1 as an alternative to the normalization condition. The solutions \mathbf{c} are then obtained by inverting a $(n - 1)$ -dimensional matrix in the usual manner [10], (or by using any other suitable technique). The same inverted matrix can be used to obtain $\mathbf{c}^{(t)}$ for all orders.

The vectors $\mathbf{c}^{(0)}$, $\mathbf{c}^{(1)}$... $\mathbf{c}^{(v)}$ to some low-order v , which might conveniently be 1 or 2, provide the basis of the form of Eq. (4) which converges most rapidly on the eigenvalue of Eq. (1).

All that is needed now is the solution to the $(v + 1)$ -order eigenvalue equation:

$$\det | K_{ij} - \mathcal{E} L_{ij} | = 0, \quad (10)$$

where

$$K_{ij} = \mathbf{c}^{(i)} \mathbf{H} \mathbf{c}^{(j)}$$

and

$$L_{ij} = \mathbf{c}^{(i)} \mathbf{S} \mathbf{c}^{(j)}.$$

Let the $(v + 1)$ -component eigenvector of Eq. (10) be α . Then the new trial vector in Eq. (3) is

$$\mathbf{c}^{(0)} = \sum_{t=0}^v \alpha_{t+1} \mathbf{c}^{(t)} \quad (11)$$

with expectation value \mathcal{E} . That is the eigenvector of Eq. (10) provides the new trial vector for the next iteration with Eq. (3).

Provided that the initial trial vector $\mathbf{c}^{(0)}$ has an expectation value of the energy at least as low as that for any of the n vectors with components

$$c_i^{(0)} = \delta_{ik},$$

the result will converge on the ground state eigenvalue. Some care may occasionally be necessary in the selection of the initial trial vector $\mathbf{c}^{(0)}$. In particular the eigenvector of the submatrix of order $n - 1$ would lead to a singularity.

The scheme can be applied equally well to a subspace of order m of the original n -dimensional space in order to break up the solution to a large eigenvalue equation. In particular setting $m = 2$ and $v = 1$ leads to the same convergence as Nesbet's method; indeed the same equations are solved. For larger values of m and v a faster convergence would be expected, since the trial vector responds to groups of elements simultaneously and to higher order derivatives of E with respect to change in the vector.

SPECIMEN RESULTS

The method was tested on a system where progressive stages leading in the limit to 100% over-completeness can be compared. A wavefunction for the H_2^+ molecule ion was set up using Gaussian orbitals. Huzinaga's optimal 10-term set of orbitals [11] was based at each atomic centre and also at the centre of the bond. Complete configuration interaction among all ${}^1\Sigma_g^+$ functions formed from the 30 orbital basis leads to 20 different configurations. In the limit where the internuclear distance $R \rightarrow 0$ obviously only 10 of these are independent. Table I compares the results of treatments using Nesbet's and McWeeny's methods with the present algorithm using the full vector space in each case.

Convergence was assumed to have been achieved only when three criteria had been satisfied:

1. $\delta\mathbf{c}$ the length of the vector joining the normalized vector from the present iteration to that for the previous one was less than ϵ_1 .
2. The magnitude of the residual \mathbf{r}

$$\mathbf{r} = \mathbf{H}\mathbf{c} - E\mathbf{S}\mathbf{c}$$

for the final normalized vector \mathbf{c} was less than ϵ_2 .

3. The energy change between cycles was less than ϵ_3 .

It is clear from the figures that even for the largest internuclear distances studied McWeeny and Nesbet's methods are not well suited to this nonorthogonal, overcomplete problem. For each internuclear distance substantial savings in time

TABLE I

Number of Iterations for Convergence of 20 Configuration "Overcomplete" Wavefunction for H_2^+
 The convergence criteria used were $\epsilon_1 = \epsilon_2 = 5 \times 10^{-8}$, $\epsilon_3 = 5 \times 10^{-9}$. (N.B. There are certainly
 more sophisticated ways than those used here of applying McWeeny and Nesbet's algorithms
 using steep descent partans.)

R	Electronic Energy ($t = 1, 2, \text{ or } 3$) a.u.	Proposed Method				Nesbet ^c
		$t = 1$	$t = 2$	$t = 3$	McWeeny	
8.0	-0.627365	71	4	4	>4000 ($E = -0.626$)	304
4.0	-0.795706	45	6	6	>4000 ($E = -0.792$)	1049
2.0	-1.102434	62	3 ^a	3 ^a	>2000 ($E = -1.097$)	>2000 ($E = -1.102433$)
1.5	-1.248869	61	3 ^a	3 ^a	>3000 ($E = -1.246$)	>3000 ($E = -1.248869$)
1.0	-1.451732	66	3 ^a	3 ^a	>2000 ($E = -1.449$)	>2000 ($E = -1.451731$)
0.5 ^b	-1.734971	52	3 ^a	3 ^a	>3000 ($E = -1.733$)	>3000 ($E = -1.734971$)
0.25 ^b	-1.898541	50	5	5		
0.15 ^d	-1.955701			5		

^a Actually converged after two iterations, the third merely ensured convergence of c and E .

^b Convergence criteria reduced to $\epsilon_1 = \epsilon_2 = 5 \times 10^{-6}$, $\epsilon_3 = 5 \times 10^{-7}$.

^c Where convergence was not achieved it was most apparent in the residual r .

^d Convergence criteria reduced to $\epsilon_1 = \epsilon_2 = 5 \times 10^{-4}$, $\epsilon_3 = 5 \times 10^{-6}$. Convergence of the vector was not certain here.

were obtained using the present algorithm though no direct comparison is possible since no care was taken to program with optimal efficiency. The time saving seems to be by a factor of at least 100 for $R < 2$ a.u. however. Prior orthogonalisation of the basis however would certainly have improved the performance of these alternative methods, but at the expense of a cumbersome and time consuming step.

It seems considerably more care is necessary to ensure convergence of the residual to the accuracy used than that needed to converge the vector and energy.

The figures of Table I indicate that little is to be gained by using a third-order steep descent over that achieved using a second-order descent. It is possible that the range of validity of the inverse expansion was exceeded. For $t = 1$ however a considerably larger number of iterations were required.

Application to the more difficult problem of the optimisation of many nonlinear parameters is in progress.

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