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Variational Discretization: A New Algorithm for the Generator Coordinate Method

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A new algorithm for discretization of the GCM eigenvalue problem is proposed. It is tested on the H-atom ground state with Gaussian basis. It is found that the new method, as compared with existing methods, gives a better compromise between accuracy and computational speed.

1. INTRODUCTION

The generator coordinate method (GCM) is a variational method [1] which is now well established and which has been used mainly in nuclear physics for the past 20 years [2]. Recently the method has also been proposed [3, 4] in connection with problems of atomic and molecular physics.

In the GCM the trial function ψ is formally written as a continuous superposition of generator basis functions $\Phi(\alpha)$, depending on the generator coordinates α,

$$\psi = \int d\alpha\, f(\alpha)\, \phi(\alpha). \tag{1}$$

The variational principle then leads to an integral equation (Hill–Wheeler equation) for the amplitude $f(\alpha)$,

$$\int d\alpha' \, [H(\alpha, \alpha') - EN(\alpha, \alpha')] f(\alpha') = 0 \tag{2}$$

with the overlap kernel

$$N(\alpha, \alpha') = \langle \phi(\alpha) | \phi(\alpha') \rangle \tag{3}$$

and the Hamiltonian kernel

$$H(\alpha, \alpha') = \langle \phi(\alpha) | H | \phi(\alpha') \rangle. \tag{4}$$

An analytic solution of the Hill–Wheeler equation (2) can be obtained only in a limited number of simple cases. In more realistic applications, the GCM problem has

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hitherto been treated through discretization of the continuous variable α, an approach which has been given a rigorous mathematical foundation in [5]. In actual numerical work the problem of choosing the discretization points α_i is a central one. Three criteria must be balanced against one another: convergence (i.e., the results should be quasi-exact within the GCM model space), compactness (i.e., the results should be represented by as few discretization points as possible), and computational speed. The methods of discretization used so far usually stress one of these criteria.

After an examination of existing methods, we propose an algorithm which strikes a balance between the above criteria. It is compared to existing techniques in a test case.

2. Discretization Techniques in GCM

Discretization techniques in GCM cannot be justified as straightforward approximations of the formal integral (1). Rather, these techniques should be based on a theorem [5] stating that the continuous variational basis

$$\Gamma = \{\phi(\alpha) | \alpha \in \mathbb{R}\} \tag{5}$$

of the model space

$$\mathscr{H}_{\mathrm{GCM}} = \overline{\mathrm{span}(\Gamma)} \tag{6}$$

can be replaced by a (not necessarily unique) countable basis

$$\Gamma_0 = \{\phi(\alpha_i) | i \in \mathbb{N}\} \tag{7}$$

such that

$$\mathscr{H}_{\mathrm{GCM}} = \overline{\mathrm{span}(\Gamma_0)}. \tag{8}$$

This implies that the ansatz (1) is equivalent to

$$\psi = \sum_{i=1}^{\infty} c_i \phi(\alpha_i) \tag{9}$$

which leads to

$$\sum_{j=1}^{\infty} (H_{ij} - E N_{ij}) c_j = 0 \tag{10}$$

with

$$N_{ij} = \langle \phi(\alpha_i) | \phi(\alpha_j) \rangle, \tag{11}$$

$$H_{ij} = \langle \phi(\alpha_i) | H | \phi(\alpha_j) \rangle \tag{12}$$

instead of (2)–(4).

The numerical problem therefore consists in approximating the series (9) by a finite sum

$$\psi = \sum_{i=1}^{n} c_i^{(n)} \phi(\alpha_i). \tag{13}$$

Whether the finite set of α's converges, with increasing n, to a basis Γ_0 depends on the algorithm for choosing the α's and on H and ϕ. Such a proof has not been found neither in general nor for the algorithm we will propose.

The variational principle suggests that the discrete values α_i should be chosen such that the energy $E^{(n)}$ given by

$$\sum_{j=1}^{n} (H_{ij} - EN_{ij})\, c_j^{(n)} = 0 \tag{14}$$

be minimum. This must, however, be balanced against the other criteria mentioned before.

Four main types of discretization techniques have appeared in the literature. They have their respective merits and shortcomings to be taken into account for the problem under consideration:

(a) those that choose a larger number of points α: e.g., by equidistant spacing around the minimum of the energy curve (or surface) $E(\alpha) = H(\alpha, \alpha)/N(\alpha, \alpha)$ [6] or some other way of parametrizing the sequence α_n [7];

(b) those that choose the α_i by some quadrature rule, e.g., as in [3], with a variationally optimized generator-coordinate domain;

(c) the iterative method originally proposed by Caurier [8], in which for a given $(\alpha_1 \cdots \alpha_{n-1})$ that point α_n is added for which the lowest ground state energy is obtained with (14);

(d) the optimum procedure, i.e., optimization [9] of all parameters involved.

3. Variational Discretization Algorithm

In this section we propose a new method for choosing the discretization points α_i which is iterative and variational. The first point α_1, is that for which $E^{(1)}(\alpha) = H(\alpha, \alpha)/N(\alpha, \alpha)$ is minimum.

The first approximation to the eigenvector is then $\psi^1 = \phi(\alpha_1)\, N_{11}^{-1/2}$. Now suppose that $n-1$ points $(\alpha_1 \cdots \alpha_{n-1})$ and the corresponding ground state $\psi^{(n-1)}$ have been determined. The nth discretization point α_n is chosen such that the energy obtained from the 2×2 matrix problem with $\psi^{(n-1)}$ and $\phi(\alpha)$ is minimum. Once α_n has been determined in this way, the nth approximation to the energy $E^{(n)}$ and wave function $\psi^{(n)}$ are given by the solution of the $n \times n$ GCM matrix problem (14).

Each candidate α_n examined during the nth iteration necessitates the calculation of

the matrix elements H_{nm} and N_{nm} $(m = 1, 2, ..., n)$. This has to be followed by the solution of a secular equation of dimension 2 in this method and of dimension n in Caurier's method. Thus our method is always faster, but the reduction in computer time will not be so significant in a problem in which the matrix element computation is rate-determining. The advantage of the final $n \times n$ diagonalization to obtain $E^{(n)}$ and $\psi^{(n)}$ is that the next value α_{n+1} will necessarily be different from all previously chosen α_i. Indeed the coefficients $c_i^{(n)}$ are already optimized through (14). One advantage of the iterative method is that one can estimate the stability of the results from a comparison of successive approximations. The numbers $\Delta E^{(n)} = E^{(n)} - E^{(n+1)}$ and $\Delta\psi^{(n)} = \|\psi^{(n)} - \psi^{(n+1)}\|$ should be significant in this respect. The algorithm carried through to n steps yields approximations to the lowest n eigenvalues and eigenvectors. In order to improve still on the excited states, the same algorithm can be used, now however with the generator basis function $\phi^1(\alpha)$, which is the component of $\phi(\alpha)$ orthogonal to the previously determined eigenvectors.

As in the other discretization methods, the well-known problem of numerical linear dependences, which is related to the ratio ε of the smallest to the largest eigenvalue of the overlap matrix N (calculated with normalized basis functions) can occur. Due to the fact that in our algorithm a judicious choice of a relatively small number of generator coordinate values is made, it is to be expected that these linear dependences will not occur before a large number of iterations. This is demonstrated in the test case reported in Section 4 (cf. Table I).

4. A Test of the New Method

As a test for the variational discretization we have considered the GCM description of the hydrogen atom ground state, using Gaussian generator basis function. This exactly soluble problem [10] has been investigated previously both as a test case for GCM [6] and in connection with "Gaussian orbitals" in atomic and molecular physics [7, 9, 11]. In Refs. [9, 11] the $1s$ ground state wave function $\exp(-r)$ is approximated by an expansion $\sum A_i \exp(-a_i r^2)$ and all parameters are optimized. In the context of GCM one would interpret this as a discretization corresponding to a generator basis of dilated Gaussians and using method (d) of Section 2.

In atomic units (a.u.) the hydrogen Hamiltonian is

$$H = -\frac{1}{2}\Delta - \frac{1}{r} \tag{15}$$

and with the generator basis functions

$$\phi(b) = \exp(-r^2/b^2). \tag{16}$$

TABLE I

Variational Discretization Results for the H-Atom Ground State

n^a	$E^{(n)\,b}$	$\Delta E^{(n)\,b}$	$\Delta E_x^{(n)\,b}$	$\Delta\psi^{(n)\,c}$	$\Delta\psi_x^{(n)\,c}$	ε^d
1	−0.42379089	5E-2	8E-2	2E-2	2E-1	1E-0
2	−0.47410269	2E-2	3E-2	2E-1	2E-1	3E-1
3	−0.49275755	4E-3	7E-3	1E-2	4E-2	8E-2
4	−0.49683577	9E-4	3E-3	2E-2	4E-2	4E-2
5	−0.49771000	7E-4	2E-3	8E-3	4E-2	6E-3
6	−0.49843110	4E-4	2E-3	3E-2	4E-2	3E-3
7	−0.49881342	2E-4	1E-3	8E-4	3E-2	2E-3
8	−0.49897151	1E-3	1E-3	3E-2	3E-2	2E-3
9	−0.49997875	4E-6	2E-5	3E-5	5E-4	4E-4
10	−0.49998238	1E-5	2E-5	3E-4	5E-4	1E-4
11	−0.49999552	2E-6	4E-6	4E-5	5E-4	1E-4
12	−0.49999795	1E-7	2E-6	2E-6	5E-4	1E-4
13	−0.49999806	5E-8	2E-6	3E-4	5E-4	1E-4
14	−0.49999811	7E-7	2E-6	2E-4	4E-4	1E-4
15	−0.49999885	1E-7	1E-6	1E-5	4E-4	1E-4
16	−0.49999895	3E-9	1E-6	1E-7	4E-4	1E-4
17	−0.49999895	1E-8	1E-6	2E-4	4E-4	1E-4
18	−0.49999896	4E-7	1E-6	2E-4	4E-4	1E-4
19	−0.49999934	1E-7	7E-7	4E-4	4E-4	2E-5
20	−0.49999947	5E-9	5E-7	5E-7	2E-4	2E-5
21	−0.49999947	3E-7	5E-7	2E-4	2E-4	2E-5
22	−0.49999974	9E-10	3E-7	1E-7	2E-4	3E-6
23	−0.49999974	2E-7	3E-7	2E-4	2E-4	3E-6
24	−0.49999989	3E-9	1E-7	7E-5	2E-4	4E-7
25	−0.49999989	5E-11	1E-7	1E-7	2E-4	3E-7
26	−0.49999989	8E-8	1E-7	2E-4	2E-4	3E-7
27	−0.49999998	2E-9	2E-8	4E-6	1E-4	2E-8
28	−0.49999998	7E-9	2E-8	5E-6	1E-4	1E-8
29	−0.49999998	2E-9	2E-8	7E-7	1E-4	1E-8
30	−0.49999999		1E-8		1E-4	1E-8

[a] Iteration number.
[b] Energy, energy gain, and energy error in atomic units.
[c] Wave function gain and wave function error.
[d] Indicator for numerical linear dependences.
(Last five columns in notation $xE-y = x \times 10^{-y}$.)

The kernels (3) and (4) are easily calculated [13]:

$$N(b, b') = \pi^{3/2}\left(\frac{1}{b^2}+\frac{1}{b'^2}\right)^{-3/2}, \tag{17}$$

$$H(b, b') = 3\pi^{3/2}\frac{1}{b^2+b'^2}\left(\frac{1}{b^2}+\frac{1}{b'^2}\right)^{5/2} - 2\pi\left(\frac{1}{b^2}+\frac{1}{b'^2}\right). \tag{18}$$

The algorithm described in the previous section was applied. The minimization fixing the value of α_n was made simply by scanning an equidistant grid in the b-interval. We have found that the application of a more refined method of minimization in this step does not improve the overall performance of the method after a number of points α_n. This yielded a distribution of b-values which was highly peaked at small b ($b < 0.1$ a.u.). This indicated that many narrow Gaussians are needed to approximate the cusp of the true wave functions $\exp(-r)$, while a few broad Gaussians are required to fit the tail. We therefore changed our generator coordinate to $\alpha = b^{1/4}$, now scanning an equidistant grid of α-values, in the interval $[0.2, 2.2]$ so as to obtain a high density and resolution of b-values where it is needed. The distribution of α-values then becomes almost homogeneous. This change did indeed significantly improve our results. The results, for each iteration, are collected in Table I: the energy $E^{(n)}$, the energy gain $\Delta E^{(n)} = E^{(n)} - E^{(n+1)}$ and energy error w.r.t. the exact value of -0.5 a.u., $\Delta E_x^{(n)} = E^{(n)} + 0.5$, the wave function gain $\Delta\psi^{(n)} = \|\psi^{(n)} - \psi^{(n+1)}\|$, and wave function error w.r.t. the exact wave function $\Delta\psi_x^{(n)} = \|\exp(-r) - \psi^{(n)}\|$. In Table II the generator coordinate values are given. The calculation was stopped, arbitrarily, after 30 iterations.

An inspection of Table I shows that the convergence to the exact result is good, both for the energy and the wave function. Indeed, the resulting representation of the Slater 1s orbital be meanss of Gaussian orbitals is probably the best existing in the literature ($\Delta\psi_x^{(30)} = 0.96 \times 10^{-4}$). The table also shows that there exist strong positive correlations between the several gains and errors, demonstrating that $\Delta E^{(n)}$ and $\Delta\psi^{(n)}$ are meaningful indicators, not only for stability but also for convergence of energy and wave function. Finally we have plotted in Fig. 1 how the convergence proceeds as a function of n. One notes that the rate of convergence is not monotonic but slows down now and again.

We can compare these results with those obtained from the existing methods. In [6] method (a) was used with 50 points, yielding an energy of -0.4994 a.u. An

TABLE II

Generator Coordinate Values b_n Obtained by Variational Discretization for the H-Atom Ground State

n	b_n	n	b_n	n	b_n
1	1.16	11	0.6	21	0.316
2	0.92	12	0.42	22	0.9832
3	1.4	13	0.28	23	0.2356
4	0.68	14	1.98	24	1.1048
5	1.04	15	0.74	25	1.7956
6	0.8	16	0.461333333	26	0.231644444
7	1.64	17	0.204977778	27	1.22062222
8	0.52	18	2.2	28	0.641066667
9	1.28	19	0.857777778	29	0.553777778
10	0.36	20	1.51768889	30	0.388088889

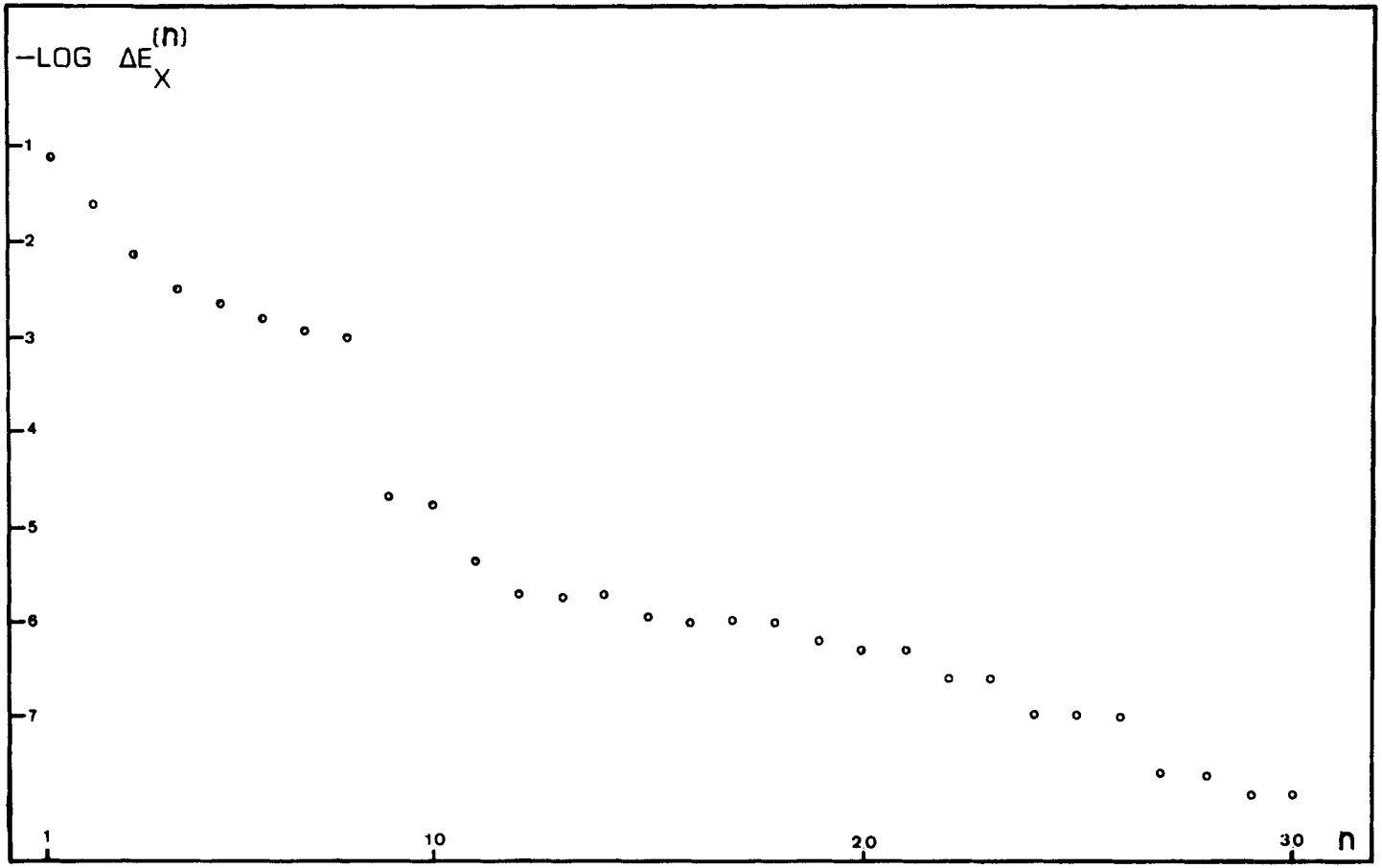

FIG. 1. Convergence of the variational discretization result for the H-atom ground state: Energy error vs. iteration number.

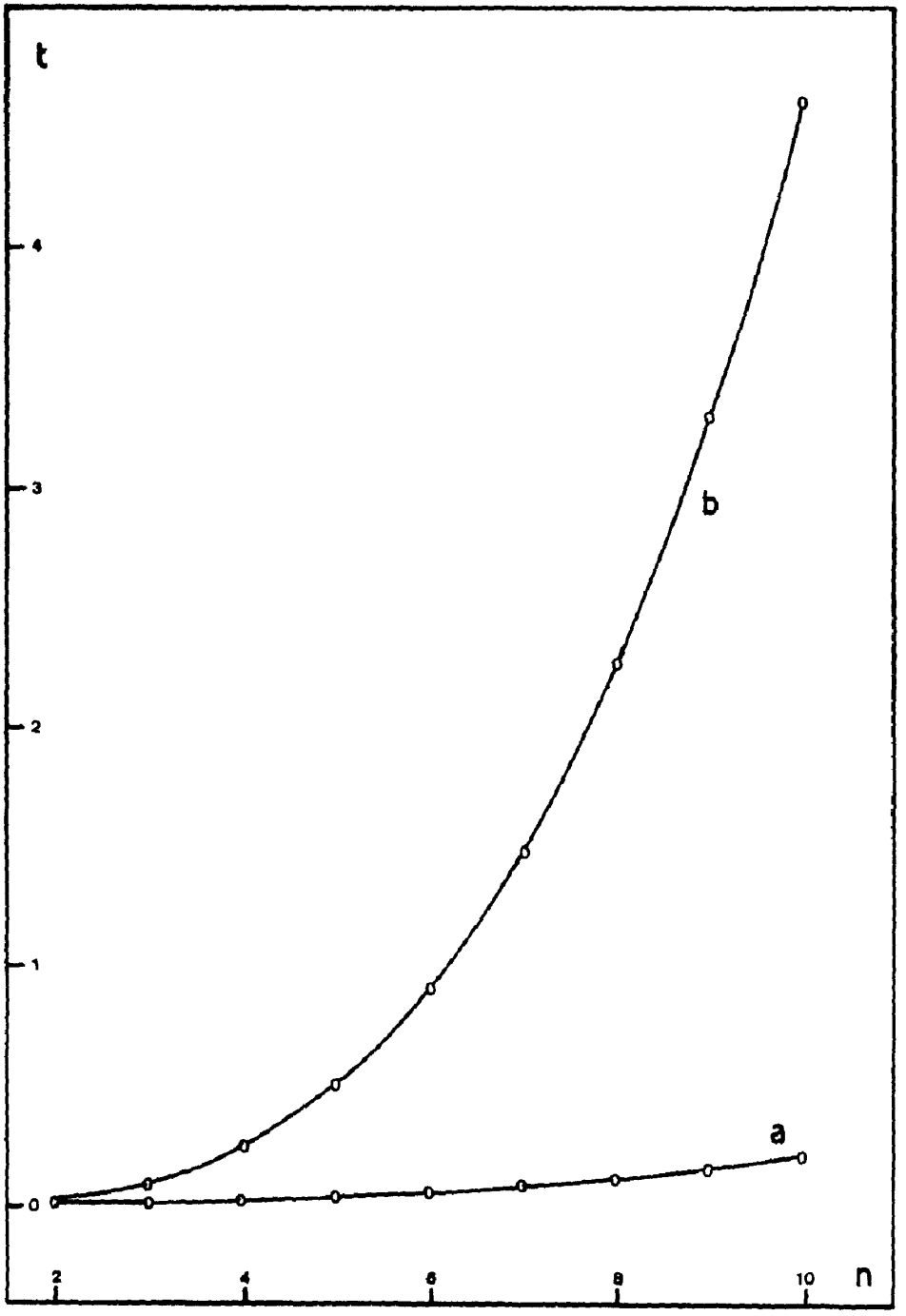

FIG. 2. Cumulative computation time vs. iteration number in arbitrary units. (a) Variational discretization; (b) Caurier's method.

increase of the number of points did not improve the energy, which shows that this method is not suitable to obtain high accuracy. We have, ourselves, applied method (c) to this problem, and obtained (with identical scanning as for Table I) an energy of -0.499166 a.u. at $n = 5$ and -0.499990 a.u. at $n = 10$. In [7] Raffenetti parametrized the Gaussian width parameter by a geometric progression $b_n^{-2} = \alpha\beta^n$ and minimized the energy with respect to α and β. This method is more economical and yields slightly better results but, of course, it is an ad hoc procedure not generalizable to other GCM problem. In [9], which also covers the results of [11], Sambe used method (d) to obtain an energy of -0.499805 a.u. at $n = 5$ and -0.499999 a.u. at $n = 10$. Comparison with the numbers in Table I shows that the new method needs roughly twice as many points to have an energy of the same quality.

There is, however, an important gain in computation time w.r.t. methods (c) and (d). In Fig. 2 we plot the cumulative computation times of the new method and method (c) in arbitrary units (both were run on a Tektronix 4051 desk computer with identical scanning procedure).

5. Conclusion

In this paper we have examined the discretization techniques used in the GCM. In view of the need for a method which combines high accuracy with low computation time, we have proposed a new method. From an application of this method to the hydrogen problem with a Gaussian basis, we conclude that it is indeed satisfactory. Its accuracy and compactness compare favourably with full optimization, while its computation time is orders of magnitude shorter. As far as accuracy, as a function of time, is concerned this new variational discretization method is superior to the existing methods.

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