

## Random tempering of Gaussian-type geminals. I. Atomic systems

S. A. Alexander, H. J. Monkhorst, and K. Szalewicz

Citation: *J. Chem. Phys.* **85**, 5821 (1986); doi: 10.1063/1.451543

View online: <http://dx.doi.org/10.1063/1.451543>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v85/i10>

Published by the [American Institute of Physics](#).

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



Special Topic Section:  
**PHYSICS OF CANCER**

Why cancer? Why physics? [View Articles Now](#)

# Random tempering of Gaussian-type geminals. I. Atomic systems

S. A. Alexander, H. J. Monkhorst, and K. Szalewicz

*Quantum Theory Project, Departments of Physics and Chemistry, University of Florida, Gainesville, Florida 32611*

(Received 13 June 1986; accepted 12 August 1986)

We use a method inspired by Monte Carlo quadrature formulas to create a basis set of Gaussian-type geminals for the calculation of the second-order energy of the beryllium atom. This technique matches results obtained by the full optimization of all nonlinear parameters but requires considerably less computational effort. For calculations involving microhartree accuracy this reduction may be as much as a factor of 1000.

## I. INTRODUCTION

Application of explicitly correlated Gaussian-type geminals (GTG's) leads to highly accurate properties of atoms and molecules<sup>1-8</sup> (for a complete list of references before 1983 see Ref. 4). A nonlinear optimization of GTG parameters is usually employed to minimize some functional. Since such optimizations can require at least  $N^2$  function evaluations,<sup>9</sup> where  $N$  is the number of nonlinear parameters, the computational effort needed to straightforwardly minimize these parameters can be quite large. One alternative is to shift the burden of optimization from a large number of parameters to a small number of more sensitive "tempering" parameters. Some of these approaches involve generation of (pseudo)random numbers and can be called random tempered optimizations. Earlier calculations by Thakkar and Smith,<sup>10</sup> who referred to the process as an integral-transform method and showed its relation to the generator coordinate method, and Poshusta,<sup>11</sup> who referred to the process as Monte Carlo tempering, have illustrated both the accuracy and advantages of this technique. The former calculations were an unqualified success since the authors were able to obtain—with relatively short Slater–Hylleraas geminal expansions—energies of the helium atom and some two-electron ions which were competitive to those obtained with other methods. With a 66-term expansion, Thakkar and Smith were able to come within 14 nhartrees of the best computed helium energy.<sup>12</sup> Using this same technique and larger expansions, Frolov and Efros<sup>13</sup> calculated the most accurate dissociation energies to date for muonic molecular ions and reproduced the best helium energy to within 5 nhartrees. In contrast the 135-term Hylleraas expansion of Anderson and Weinhold<sup>14</sup> differs from the value in Ref. 12 by 11 nhartrees and the original 1078-term Pekeris function<sup>15</sup> differs by 2 nhartrees. In addition, Thakkar and Smith<sup>10</sup> using random tempering and expansions into products of spherically symmetric orbitals obtained results close to the radial correlation limit for Li atom.

Earlier applications of random tempering to GTG's appeared to be less successful: Poshusta's 100-term random tempered optimization gave a result which could be reached with only 16 fully optimized functions.<sup>8</sup> In this communication we examine the effect of random tempering on GTG calculations of the second-order correlation energy. Using the Be atom as an example, we show that this technique can

give accurate energies and substantially reduce the computational effort of GTG calculations.

## II. RANDOM TEMPERING

In atomic systems each GTG is a function of three unknown parameters:

$$g_k(r_1, r_2) = e^{-\alpha_k r_1^2 - \beta_k r_2^2 - \gamma_k r_1 r_2}. \quad (1)$$

Previous calculations<sup>4,5</sup> determined these parameters by optimizing a set of  $K$  geminals to some functional. In our random tempering scheme  $\alpha_k$ ,  $\beta_k$ , and  $\gamma_k$  are considered functions of a smaller set of nonlinear parameters:

$$\begin{aligned} \alpha_k &= a e^{\sum_{i=1}^I A_i \langle k, 3i-2 \rangle}, \\ \beta_k &= b e^{\sum_{i=1}^I B_i \langle k, 3i-1 \rangle}, \\ \gamma_k &= c e^{\sum_{i=1}^I C_i \langle k, 3i \rangle}, \end{aligned} \quad (2)$$

where  $\langle k, j \rangle$  is the fractional part of  $[k(k+1)/2 P(j)]^{1/2}$  and  $P(j)$  is the  $j$ th prime number in the sequence 2, 3, 5, 7, ... . Thus Eq. (2) reduces the number of nonlinear parameters from  $3K$  to  $3I + 3$ . The form of Eq. (2) is a combination of Poshusta's method<sup>11</sup> and Ruedenberg's formula for even tempered atomic orbitals.<sup>16</sup> Unlike Ruedenberg's method, however, the base is not varied because this would only lead to a rescaling of the parameters in the exponential. We also examined tempering schemes which eliminate the exponential (as in Thakkar and Smith<sup>10</sup> and Frolov and Efros<sup>13</sup>) but encountered severe problems with linear dependence. Including the exponential gives a much wider distributed spread of values and seems to lessen this problem. Since both large and small values of the  $3K$  nonlinear parameters are desired, the value of  $I$  must be greater than one. As in Refs. 4–6, the parameters  $\alpha$ ,  $\beta$ , and  $\gamma$  are positive. Our earlier experience showed that negative values complicate the optimization procedure and do not lead to significant improvements in the energy if the basis sets contain more than just a few geminals. Other parametrizations of Eq. (2) are possible<sup>10,11</sup>—in particular the  $\gamma$  parameter can be mapped into a finite domain—and we expect that they would give similar results. The advantage of our formulation, however, is that it treats all three parameters on an equal footing.

In Sec. III we examine the following variants of Eq. (2):

$$\text{Method 1: } \delta = e^{A\langle \rangle + B\langle \rangle},$$

$$\text{Method 2: } \delta = a e^{A\langle \rangle + B\langle \rangle},$$

$$\text{Method 3: } \delta = e^{A\langle \rangle + B\langle \rangle + C\langle \rangle}, \quad (3)$$

$$\text{Method 4: } \delta = e^{A\langle \rangle + B\langle \rangle + C\langle \rangle + D\langle \rangle},$$

where  $\delta$  is  $\alpha_k$ ,  $\beta_k$ , or  $\gamma_k$ ;  $a$ ,  $A$ , and  $B$  are nonlinear parameters, and  $\langle \rangle$  denotes a pseudorandom number as defined above.

### III. CALCULATIONS

In a previous study of the beryllium atom<sup>4,5</sup> we obtained highly accurate second-order pair energies by optimizing all 180 nonlinear parameters per pair ( $K = 60$  geminals) using eight SCF orbitals ( $M = 8$ ), a large value for the strong orthogonality (SO) parameter ( $\eta = 100$ ), and a small minimization tolerance. After this optimization the final second-order energy was calculated using  $M = 20$  and  $\eta = 0$ . On a  $\sim 1$  Mflop computer the entire calculation would need about 100 h of CPU time. Using random tempering we were able to match or exceed these values in significantly less time. In brief our method of calculation can be described as follows:

Step (1): Select a method for generating random tempered geminals.

Step (2): Optimize a set of such geminals ( $K = 50$  or  $100$ ) using a small SCF basis ( $M = 5$  or  $8$ ) and  $\eta = 1$ . Since the purpose of this optimization is only to approximately locate the minimum, a fairly loose tolerance can be used. We choose a smaller value of  $\eta$  than was used in Ref. 5 since later studies showed<sup>6</sup> that very large values of this parameter are not necessary to achieve stability of the coupled-pair calculations and may slow down the convergence in  $K$ .

Step (3): Take the optimized parameters from step (2) and perform a single calculation with  $M = 20$  and  $\eta = 0$ . Though small SCF expansions introduce some error into the pair energies, the resulting values of the nonlinear parameters are close to optimal.<sup>4,5</sup> To obtain an upper bound to the exact pair energies one must, however, perform a single calculation with a large SCF basis. In our earlier second-order energy calculations on the Be atom<sup>4,5</sup> we found that  $M = 20$  was essentially equivalent to using exact Hartree-Fock orbitals. Since the weak orthogonality (WO) functional provides an upper bound for all positive values of  $\eta$ , we set  $\eta$  to zero to obtain the lowest energy.

Step (4): Take the optimized nonlinear parameters from step 2 and calculate the energy using  $M = 20$ ,  $\eta = 0$ , and a large number of geminals ( $K = 200$  or  $400$ ). Since no optimization is done, the amount of CPU time required by this step is relatively small.

In Table I we compare the energies given by our four methods of generating geminal sets. All the optimizations have been performed with  $K = 50$ ,  $M = 5$ , and  $\eta = 1$ . The methods described by Eq. (3) differ both in the number of tempering parameters (6 for method 1, 9 for methods 2 and 3, and 12 for method 4) and in the positions of these parameters (which are not always equivalent). In this variational

TABLE I. Comparison of various random tempered optimizations of second-order pair energies. Optimizations were performed with  $K = 50$ ,  $M = 5$ , and  $\eta = 1$ . Values are in mhartrees with signs reversed.

Method	Pair <sup>b</sup>	$K = 50$ $M = 5$ $\eta = 1$	$K = 50$ $M = 20$ $\eta = 0$	$K = 100$ $M = 20$ $\eta = 0$	$K = 200$ $M = 20$ $\eta = 0$	$K = 400$ $M = 20$ $\eta = 0$	$K = 60^a$ $M = 20$ $\eta = 0$
		$\eta = 1$	$\eta = 0$	$\eta = 0$	$\eta = 0$	$\eta = 0$	$\eta = 0$
1	11	40.199	40.148	40.258	40.301	40.319 <sup>c</sup>	40.341
	12	2.136	2.205	2.214	2.217	2.218	2.219
	21	2.962	3.187	3.222	3.242	3.248	3.252
	22	<u>31.510</u>	<u>30.357</u>	<u>30.477</u>	<u>30.517</u>	<u>30.530</u>	<u>30.536</u>
	total	76.807	75.897	76.171	76.277	76.315	76.348
2	11	40.245	40.171	40.258	40.296	40.313 <sup>c</sup>	
	12	2.144	2.213	2.218	2.219	2.219	
	21	2.983	3.207	3.227	3.248	3.251	
	22	<u>31.524</u>	<u>30.347</u>	<u>30.474</u>	<u>30.518</u>	<u>30.531</u>	
	total	76.896	75.938	76.171	76.281	76.314	
3	11	40.279	40.199	40.279	40.305	40.321 <sup>c</sup>	
	12	2.145	2.214	2.218	2.219	2.219	
	21	2.983	3.213	3.229	3.247	3.252	
	22	<u>31.542</u>	<u>30.354</u>	<u>30.490</u>	<u>30.526</u>	<u>30.536</u>	
	total	76.949	75.980	76.216	76.297	76.328	
4	11	40.284	40.204	40.278	40.304	40.321 <sup>c</sup>	
	12	2.146	2.214	2.218	2.219	2.219	
	21	2.988	3.217	3.234	3.247	3.252	
	22	<u>31.555</u>	<u>30.330</u>	<u>30.485</u>	<u>30.523</u>	<u>30.534</u>	
	total	76.973	75.965	76.215	76.293	76.326	

<sup>a</sup> Fully optimized result from Ref. 5.

<sup>b</sup> The "12" and "21" pairs are triplet and singlet-coupled 1s-2s electron pairs, respectively.

<sup>c</sup> Linear dependence observed.

calculation an increase in the number of tempering parameters always leads to a lowering of the energy (for a given  $K$ ,  $M$ , and  $\eta$ ) but only if the parameters are equivalent.

Our first observation concerns the surprisingly small difference in the optimized energies between different methods. This closeness of energies suggests that even the simplest functional form, method 1, is nearly optimal. Table I also shows that an additional parameter in the exponential is more effective than a multiplicative parameter: method 3 (nine parameters) gives a slightly better result than method 2 (nine parameters). The differences between all these methods, however, are so small that one method should not yet be preferred over the other.

When the optimized values are recomputed with  $M = 20$  and  $\eta = 0$ , the best results are given by method 3. The energy given by this method is even better than the energy given by method 4 which employs one more parameter. With  $M = 5$  and  $\eta = 1$  the order of these two methods was, as expected, reversed. Thus, the parameters optimized with  $M = 5$  and  $\eta = 1$  are not quite optimal for  $M = 20$  and  $\eta = 0$ . Such a possibility cannot be excluded. The two methods are, however, very close and the above behavior has no significant effect on the final outcome of our work.

Next we consider the effect of simply "expanding" the basis set with respect to  $K$  without reoptimizing the tempering parameters. For all practical purposes methods 1 and 2 give the same results for all the expanded basis sets. The same is also true of methods 3 and 4. Furthermore, as  $K$

increases the differences between all the methods become smaller. This fact, that the expanded results are so insensitive to the specific form of the tempering function and to the values of the tempering parameters, could have been anticipated since in a complete basis set the values of parameters are irrelevant as long as they do not cause linear dependencies.

Since method 1 with only six parameters gives practically the same energies as methods with more parameters, computational considerations favor this method. There is, however, some unpredictability in the expansion procedure. Although the best energies for  $M = 20$  and all values of  $K$  are given by method 3, we found one set of tempering parameters for method 2 which gave, compared to the results in Table I, worse energies for the  $K = 50$  optimization but better energies for the  $K = 400$  expansion. The total energy of this  $K = 400$  expansion ( $-76.327$  mhartrees) was as good as the value obtained with methods 3 and 4. Again this shows that parameters optimized for a given  $K$ ,  $M$ , and  $\eta$  may not be optimal with changed  $K$ ,  $M$ , and  $\eta$ .

The best values in Table I are in good agreement (within  $20 \mu$ hartrees) with the full optimization  $K = 60$  values. The only problem with the expansions is that at some point linear dependencies in the geminal set occur. This prohibited larger than  $K = 400$  expansions in our investigation and thus even further improvement of the energy.

Finally we wanted to determine whether our energies could be improved by performing optimizations with a larger  $K$ . Since method 2 is closely related to the Ruedenberg even tempered formula,<sup>16</sup> we decided to use this method and method 1 in an optimization with 100 geminals per pair,  $\eta = 1$ , and five SCF orbitals. The results presented in Table II are in excellent agreement with the full optimization values. In addition, the earlier linear dependence problems seem to have lessened. The  $K = 400$  value of method 2 constitutes the new best second-order energy for the Be atom.

The final optimized values of the tempering parameters for method 2 are given in Table III. As one may see,  $a$  values

TABLE III. Random tempered optimized parameters. Method 2,  $K = 100$ ,  $M = 5$ , and  $\eta = 1$ .

	Pair 11	Pair <sup>a</sup> 12	Pair <sup>a</sup> 21	Pair 22
$\alpha$ parameters				
$a$	1.0289	1.1274	1.0000	1.3586
$A$	-3.8469	-9.7241	-1.4831	-6.3381
$B$	5.0900	7.4833	3.5474	6.1450
$\beta$ parameters				
$a$	3.8843	1.0981	1.0000	0.3832
$A$	-5.7195	-5.3702	-9.2273	-5.6736
$B$	5.6390	4.8915	10.1219	2.4801
$\gamma$ parameters				
$a$	0.5436	0.3292	1.0000	0.1874
$A$	-13.5290	-6.5313	-9.3928	-8.8961
$B$	13.7859	4.1139	6.6235	6.7724

<sup>a</sup> See Table I, footnote b.

are of the order one. The variation is, however, much larger than one would expect from the closeness of energies of methods 1 and 2 in Table II.

In Table IV we examine what effect the number of SCF functions has on our energies. Using method 1 we performed a  $K = 50$ ,  $\eta = 1$  optimization with  $M = 8$ . These results should be compared with the earlier energies optimized with  $M = 5$ . Interestingly, although at  $K = 50$ ,  $M = 20$ , and  $\eta = 0$  all the pair energies calculated with parameters optimized with  $M = 8$  are lower than those obtained with parameters optimized with  $M = 5$ , the same is not true when the basis sets are expanded to  $K = 400$ . Again we wish to emphasize that because of the inherent randomness of this technique, such behavior cannot be excluded. For all practical purposes though, Table IV shows that the energies calculated with  $M = 20$  are independent of the choice of  $M$  in the

TABLE II. Effect of optimization size on pair energies with  $K = 100$  initial optimization. Values in mhartrees with signs reversed.

Pair <sup>b</sup>	$K = 100$ $M = 5$ $\eta = 1$	$K = 100$ $M = 20$ $\eta = 0$	$K = 200$ $M = 20$ $\eta = 0$	$K = 400$ $M = 20$ $\eta = 0$	Ref. 5
Method 1					
11	40.343	40.270	40.317	40.339 <sup>a</sup>	40.341
12	2.146	2.217	2.219	2.219	2.219
21	3.009	3.239	3.249	3.251	3.252
22	31.564	30.458	30.507	30.531	30.536
	77.062	76.184	76.292	76.340	76.348
Method 2					
11	40.365	40.284	40.325	40.340	
12	2.146	2.217	2.219	2.219	
21	3.009	3.239	3.249	3.251	
22	31.590	30.489	30.536	30.540	
	77.120	76.229	76.329	76.350	

<sup>a</sup> Linear dependence observed.

<sup>b</sup> See Table I, footnote b.

TABLE IV. Effect of SCF basis size on pair energies. Optimizations were performed with method 1,  $K = 50$ ,  $\eta = 1$ , and  $M = 5$  or  $M = 8$ . Values are in mhartrees with signs reversed.

Pair <sup>b</sup>	$K = 50$ $\eta = 1$	$K = 50$ $\eta = 0$	$K = 100$ $\eta = 0$	$K = 200$ $\eta = 0$	$K = 400$ $\eta = 0$	Ref. 5
	$M = 5$	$M = 20$	$M = 20$	$M = 20$	$M = 20$	
11	40.199	40.148	40.258	40.301	40.319 <sup>a</sup>	40.341
12	2.136	2.205	2.214	2.217	2.218	2.219
21	2.962	3.187	3.222	3.242	3.248	3.252
22	31.510	30.357	30.477	30.517	30.530	30.536
	76.807	75.897	76.171	76.277	76.315	76.348
	$M = 8$	$M = 20$	$M = 20$	$M = 20$	$M = 20$	
11	40.131	40.151	40.256	40.302	40.318 <sup>a</sup>	
12	2.204	2.206	2.214	2.216	2.218	
21	3.178	3.189	3.223	3.242	3.248 <sup>a</sup>	
22	30.355	30.369	30.476	30.510	30.526	
	75.868	75.915	76.169	76.270	76.310	

<sup>a</sup> Linear dependence observed.

<sup>b</sup> See Table I, footnote b.

optimization step. Since the computational effort of a single calculation is proportional to  $aM^2K^2 + bM^4K$ , the savings in using a small orbital basis set can be considerable.

#### IV. COMPUTATIONAL PERFORMANCE

Comparing the results in Tables I and II with the values from Refs. 4 and 5 we see that one needs about three to four times more random tempered geminals to get the same accuracy as with fully optimized geminals. This is a much better ratio than obtained by Poshusta<sup>11</sup> whose helium atom energy with 100 tempered geminals was higher than a 16-term fully optimized result.<sup>8</sup> Thus, Poshusta's calculation gave a ratio which is at least equal to 6. A precise estimate of this ratio is not possible because fully optimized values with less than 16 geminals are not available. A crude extrapolation using the Regier and Thakkar<sup>8</sup> fully optimized energies with 16, 20, 25, 30, and 35 geminals suggests that Poshusta's 100-term tempered result could be obtained with 11 fully optimized geminals. This would give a ratio of 9. We believe that the problems encountered by Poshusta<sup>11</sup> were either due to linear dependencies in his basis sets or to a premature termination of his optimization in a local minimum.

Although a random tempered optimization needs three to four times more geminals to obtain the same accuracy as a full optimization, it requires much less computer time. For large  $K$  and small  $M$  a single second-order energy calculation takes about nine times longer if the geminal basis set is three times larger. This increase is more than compensated by the smaller number of the functional evaluations in the random tempered optimization. Assuming  $N^2$  functional evaluations per optimization,<sup>9</sup> we need  $0.25 K^2$  (i.e.,  $3^2 K^2/6^2$ ) more points in a full optimization than in a six-parameter random tempered one. This value is equal to 900 for  $K = 60$  and leads to an overall reduction factor of 100. This factor, however, underestimates the true savings. In an actual optimization we would not use a  $K = 180$  random tempered basis but rather a smaller one and then expand the results without reoptimizing the parameters. If the initial random tempered optimization was performed with 60 geminals, it would give a factor of 900 and larger savings would result from even smaller basis sets.

#### V. SELECTION OF COMPACT GEMINAL BASIS SETS

One of the reasons for optimizing the second-order energy is to obtain a geminal basis set which can subsequently be used in a more complete treatment of the correlation energy. One such treatment is the coupled-pair method.<sup>6</sup> In general, coupled-pair calculations are more time consuming than a single second-order calculation and moreover, their computational cost depends strongly on  $K$ . Such a calculation with a basis set of 400 geminals would be quite expensive. One method of generating a small yet accurate basis set is to first do a random tempered minimization and expansion as outlined above and, next, sort from the others the  $L$  geminals ( $L < K$ ) which contribute most significantly to the energy. The smaller set obtained after sorting can then be used in higher-level correlation energy calculations. To obtain an even more compact basis, the sorted geminals can be used as the starting point for a full optimization where all  $3L$  nonlin-

ear parameters are to be varied. With such a good initial guess, this optimization should require substantially fewer functional evaluations to reach convergence. In addition, there should be a much smaller risk of ending up in a local minimum with a much higher energy than the global minimum.

We tried one simple sorting procedure which calculates the pair energies for all subsets such that the  $L$  th subset contains the  $L$  first geminals of the full basis set for  $L = 1, 2, \dots, K$ . This procedure determines the improvement in energy produced by a given geminal. The geminals are then reordered such that those geminals which lower the energy most are moved to the top of the basis set. The whole process is then repeated several times. In subsequent steps however, the sum of the increments from the previous steps is taken into account. We found that the first few iterations lead to a substantial improvement in the energies calculated with the  $L$  th subset. After about five to ten iterations no further improvement was observed and the  $L$  th energy slightly oscillated around some value.

The energies obtained from the sorting procedure are presented in Table V. Comparison of these results with the values in Tables I and II shows the effectiveness of this technique. For small  $K$ , the errors of the sorted energies (relative to the limit value of the second-order energy) are about two times smaller than the errors of energies obtained by direct random tempered optimization. For large  $K$ , the improvement is even better. For example the 100-term sorted energy is almost as good as the 200-term direct result and the 200-term sorted energy is only  $2\mu$  hartrees above the limit value. Comparison of the sorted geminals with the fully optimized geminals is also quite impressive. We need 24, 46, 71, 100, and 189 sorted random tempered geminals to obtain the same accuracy as with 10, 20, 30, 40, and 60 fully optimized

TABLE V. Comparison of sorted pair energies with fully optimized values. Random tempered values were initially optimized with method 2,  $K = 100$ ,  $M = 5$ , and  $\eta = 1$  then expanded to  $K = 400$ ,  $M = 20$ , and  $\eta = 0$ . Values in  $\mu$ hartrees with signs reversed.

$K$	Pair 11	Pair 12	Pair 21	Pair 22	Energy
Random tempered optimized + sorting					
10	37.143	2.069	2.752	28.599	70.563
20	39.488	2.190	3.058	29.786	74.522
30	40.014	2.207	3.174	30.265	75.660
40	40.206	2.213	3.204	30.359	75.982
50	40.258	2.216	3.228	30.445	76.147
75	40.313	2.218	3.242	30.511	76.284
100	40.329	2.219	3.249	30.527	76.324
200	40.339	2.219	3.251	30.539	76.348
300	40.340	2.219	3.251	30.539	76.349
400	30.340	2.219	3.251	30.540	76.350
Fully optimized (Refs. 4 and 5)					
10	39.663	2.199	3.087	30.166	75.115
20	40.252	2.210	3.225	30.404	76.091
30	40.321	2.216	3.245	30.494	76.276
40	40.333	2.218	3.250	30.523	76.324
60	40.341	2.219	3.252	30.536	76.348

\* See Table I, footnote b.

geminals, respectively. This factor of 2–3 is an important improvement over the earlier ratio of 3–4 and makes the present method even more advantageous from a computational perspective. Finally we wish to point out that our sorting procedure is a very simple one. Other methods may produce even more compact basis sets. In an unpublished work,<sup>17</sup> Regier and Thakkar describe a more complicated method of expansion based on importance sampling which may avoid the need for sorting. Using this method they have calculated the energy of the helium atom with a 50-term basis.<sup>8</sup> Their result is very similar to the 20 geminal fully optimized energy and thus their ratio ( $\sim 2.5$ ) is about the same as ours.

A complete coupled-pair (CCP) method contains time consuming nonfactorizable terms which scale like  $K^3$ . Therefore, an increase of 2.5 in the size of the geminal basis set leads to an increase of 16 in CPU costs of a CCP calculation. The nonfactorizable terms are, however, rather small and may be neglected in most calculations. This approximation leads to the factorizable coupled-pair (FCP) method.<sup>6</sup> The FCP method contains only terms which scale as  $K^2$  and therefore we would get only a six times longer calculation. Additionally, it was shown in Ref. 6 that the FCP energies can be reliably calculated within the so-called super weak orthogonality plus approximate projection (SWOP) scheme. Such calculation is only a few times longer than a single second-order calculation. In conclusion the factor 6 increase in computer time for a SWOP FCP calculation is meaningless compared to the time of optimization.

## VI. CONCLUSIONS

We have shown that random tempering is a method of generating systematic sets of geminals which can match results obtained by the full optimization of all nonlinear parameters but with drastically reduced computational effort. We also showed that if a small set of geminals is desired, those geminals which contribute most significantly to the energy can be sorted from the others. Given these advantages we are convinced that random tempering should be the

method of choice when performing GTG calculations on atomic systems. A generalization to molecules is in progress.

## ACKNOWLEDGMENTS

We wish to thank Dr. B. Jeziorski and Dr. A. J. Thakkar for a critical reading of our manuscript and Florida State University for providing us with time on their Cyber 205. This work has been supported by NSF Grant No. CHE-8505733.

<sup>1</sup>S. F. Boys, Proc. R. Soc. London Ser. A **258**, 402 (1960); K. Singer, *ibid.* **258**, 412 (1960); W. A. Lester and M. Krauss, J. Chem. Phys. **41**, 1407 (1964); **42**, 2990(E) (1965).

<sup>2</sup>K. C. Pan and H. F. King, J. Chem. Phys. **53**, 4397 (1970); **56**, 4667 (1972).

<sup>3</sup>G. Chalasinski, B. Jeziorski, J. Andzelm, and K. Szalewicz, Mol. Phys. **33**, 971 (1977); K. Szalewicz and B. Jeziorski, *ibid.* **38**, 191 (1979); B. Jeziorski and K. Szalewicz, Phys. Rev. A **19**, 2360 (1979).

<sup>4</sup>K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983).

<sup>5</sup>K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **79**, 5543 (1983).

<sup>6</sup>B. Jeziorski, H. J. Monkhorst, K. Szalewicz, and J. G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984); K. Szalewicz, J. G. Zabolitzky, B. Jeziorski, and H. J. Monkhorst, *ibid.* **81**, 2723 (1984); K. B. Wenzel, J. G. Zabolitzky, K. Szalewicz, B. Jeziorski, and H. J. Monkhorst, *ibid.* **85**, 3964 (1986).

<sup>7</sup>B. S. Sharma and A. J. Thakkar, J. Phys. B **17**, 3405 (1984).

<sup>8</sup>P. E. Regier and A. J. Thakkar, Phys. Rev. A **30**, 30 (1984), J. Phys. B **18**, 3061 (1985).

<sup>9</sup>G. R. Walsh, in *Methods of Optimization* (Wiley, New York, 1975), Chap. 3.

<sup>10</sup>A. J. Thakkar and V. H. Smith Jr., Phys. Rev. A **15**, 1, 16, 2143 (1977).

<sup>11</sup>R. D. Poshusta, Int. J. Quantum Chem. Symp. **13**, 59 (1979).

<sup>12</sup>K. Frankowski and C. L. Pekeris, Phys. Rev. A **146**, 46 (1966); D. E. Freund, B. D. Huxtable, and J. D. Morgan III, *ibid.* **29**, 980 (1984).

<sup>13</sup>A. M. Frolov and V. D. Efros, JETP Lett. **39**, 544 (1984) [Pis. Zh. Eksp. Teor. Fiz. **39**, 449 (1984)]; J. Phys. B **18**, L265 (1985).

<sup>14</sup>M. T. Anderson and F. Weinhold, Phys. Rev. **9**, 118 (1974).

<sup>15</sup>C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

<sup>16</sup>K. Ruedenberg, R. C. Raffanetti, and R. D. Bardo, in *Energy, Structure, and Reactivity* (Wiley, New York, 1973), p. 164; M. W. Schmidt and K. Ruedenberg, J. Chem. Phys. **71**, 3951 (1979).

<sup>17</sup>P. E. Regier, M. Math. thesis, University of Waterloo, 1983; P. E. Regier and A. J. Thakkar (unpublished).