Obtaining microhartree accuracy for twoelectron systems with randomtempered Gaussiantype geminals

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Obtaining microhartree accuracy for two-electron systems with random-tempered Gaussian-type geminals

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The ground state energies of the helium atom, H_2 molecule, and the HeH$^+$ and H_3^+ molecular ions are calculated, using the variational method and basis sets of explicitly correlated Gaussian-type geminals. These energies are accurate to about 1 μhartree for He and H_2, about 27 μhartrees for HeH$^+$, and an estimated 10 μhartrees for H_3^+. This accuracy is comparable to that of the Hylleraas-CI method and for diatomics approaches that obtained with explicitly-correlated basis sets in elliptical coordinates.

I. INTRODUCTION

Gaussian-type geminals (GTGs) are two-electron functions that contain the factor $\exp(-\gamma r_{12}^2)$ where r_{12} is the interelectronic distance. These functions have been used in variational calculations on two-electron systems since the 1960's.[1,2] Although they were not particularly accurate, these early calculations highlighted the ease of use and versatility of this basis. The calculation of the total energy of H_2 to an accuracy of 60 μhartrees in 1979 first showed that GTGs could produce highly accurate results.[3] The wave functions resulting from this work have since been used to calculate such properties as Compton profiles,[3] electron scattering cross sections,[4] and electron densities.[5] GTGs have also been used in calculations on multielectronic systems using many-body perturbation theory (MBPT)[6-10] and coupled cluster (CC)[11-13] techniques. In the last few years, the accuracy achievable with GTGs has been significantly increased due to the use of random tempering methods. Random tempering is a computational technique that shifts the burden of optimizing a basis set from a large number of parameters to a smaller number of more sensitive tempering parameters. Since the optimization of all parameters can require N^2 function evaluations, where N is the total number of parameters, tempering methods can be much more efficient than those that optimize each parameter directly. In previous papers, we showed that random tempering formulas could be used to generate very accurate basis sets of GTGs for MBPT[14,15] and CC calculations.[16] In each case, the random tempering method was able to easily compute a number of accurate basis sets in a consistent and efficient manner.

Recently, Clementi, Lie, and co-workers[17-19] investigated the properties of another basis set which could also be called a GTG basis. This one, however, includes the r_{12} distance linearly rather than in the exponential as do the original GTGs. With these "linear GTGs" they obtained an excellent accuracy for several two-electron systems using the variational method. In Refs. 17–19 this approach is referred to as the Hylleraas-CI method. In this paper, we compare the accuracy of our random-tempered GTG approach with that obtained with linear GTGs. To facilitate this compari-

son, we have examined the same systems as in Ref. 17, i.e., the H_2 molecule and the HeH$^+$ and H_3^+ ions. In addition, we have considered the He atom as the simplest system on which our method may be tested and compared with other techniques. All the systems investigated were in their singlet ground states, and for molecules we assumed the Born–Oppenheimer approximation. With these restrictions, the electronic wavefunction of these states can be written as

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{K} c_k (1 + P_{12}) g_k(\mathbf{r}_1,\mathbf{r}_2;P_k), \qquad (1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the electron coordinates, g_k is a geminal dependant on a set of parameters P_k, P_{12} is the operator that interchanges electrons 1 and 2, and c_k is the linear coefficient obtained by diagonalizing the Hamiltonian in the above basis set. The precise definition of the functions g_k and in particular their dependence on the set of parameters P_k will be given in the following sections.

II. THE HELIUM ATOM

For the helium atom, the singlet spin-free electronic wavefunction can be expanded in a GTG basis set of the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{K} c_k (1 + P_{12}) e^{-\alpha_k r_1^2 - \beta_k r_2^2 - \gamma_k r_{12}^2}. \qquad (2)$$

To random temper the nonlinear parameters α_k, β_k, and γ_k we selected the following tempering formula:[14]

$$\alpha_k = e^{A_1 \langle k,j \rangle + A_2 \langle k,j+1 \rangle},$$
$$\beta_k = e^{B_1 \langle k,j+2 \rangle + B_2 \langle k,j+3 \rangle}, \qquad (3)$$
$$\gamma_k = e^{C_1 \langle k,j+4 \rangle + C_2 \langle k,j+5 \rangle},$$

where A_1, A_2, B_1, B_2, C_1, and C_2 are the tempering parameters, $\langle k,j \rangle$ is the fractional part of $[k(k+1)/2P(j)^{1/2}]$, and $P(j)$ is the jth prime number in the sequence 2,3,5,7,.... This formula is based on the earlier work of Thakkar and Smith[20] and of Poshusta.[21] Using a small number of geminals ($K = 100$), we optimized the tempering parameters so as to minimize the total energy. With these parameters, we then increased the number of geminals until convergence was

reached, linear dependence occurred or the calculation became computationally intractable. To diagonalize the matricies formed by this step, we used the inverse-iteration method. When the GTG basis is chosen purely by random tempering, Table I shows that the total energy converges slowly. Although the same tempering formula is able to produce accurate second-order energies,[14] its failure here is not surprising. The important difference between these two examples is that our earlier calculation of the second-order energy involved only the correlation energy, while our present variational calculation of the total energy has to also recover the much larger SCF energy. Because an SCF wavefunction needs very large exponents to properly describe the electron-nuclear cusps (exponents that play a much lesser role in correlation energy calculations), a single tempering function is not able to efficiently recover both the SCF energy and the correlation energy. One solution to this problem is to use separate sets of tempering parameters to describe these two very different parts of the wavefunction. Since accurate SCF functions are often available, however, it is much simpler to just add such functions to our basis set. We tested this idea by taking a small 10-term Gaussian type orbital (GTO) SCF wavefunction for helium from Ref. 22 and then converting it into a geminal basis. This was done by forming all $M*(M+1)/2$ (where $M = 10$) possible products of the orbitals and setting $\gamma_k = 0$. The optimization step was then repeated with this fixed "core" of $K_c = 55$ geminals and 45 random-tempered geminals. This simple procedure (Method 2) produced a considerable improvement in the convergence. Further improvements might be possible by using larger SCF basis sets but this leads to increasingly larger cores and thus to larger sets of geminals in the optimization step. Since most of the CPU time required by our random-tempered calculation is spent in the optimization step, it is more efficient to first optimize the tempering parameters with a small basis and then use a larger basis in the expansion step. Table I shows that with the 16-GTO SCF basis from Ref. 23, this procedure (Method 3) was able to determine the total energy of the helium atom to within one microhartree.

Although our best result for helium required a total of 600 geminals (136 of which were used to construct the core), the size of this calculation is not due to our use of GTGs but rather to our use of random-tempering. Recently, Rybak et al.[24] optimized a 100-term GTG variational wavefunction for He to be used in a symmetry-adapted perturbation theory calculation on He_2. This optimization, which involved all 300 nonlinear parameters, produced a total energy that was virtually the same as that obtained by our 600 geminal random-tempered basis. However, the total CPU time required to optimize the 300 nonlinear parameters was much larger than that needed to optimize the 6 tempering parameters.

The size of the error in our final energy, 0.8 μhartrees, is due in large part to the inaccuracy of the SCF orbitals we used to construct the core. When compared with an accurate evaluation of the SCF limit, we find that our 16-term GTO basis has an error of about 0.5 μhartrees. Any improvement in the accuracy of the total energy must thus depend on improvements in both the SCF part and the correlation part. Our accuracy of 10^{-6} hartrees for this system is, of course, much worse than that of recent calculations which use basis functions containing logarithmic terms (accurate to 10^{-16} hartrees),[25] Pekeris's classic result (accurate to about 10^{-9} hartrees)[26] or even calculations that use basis sets of Slater–Hylleraas geminals (accurate to 10^{-8} hartrees).[20] None of these other methods, however, can be applied to many-electron atoms or molecules.

TABLE I. Total energy of the helium atom (in hartrees).

	Method 1[a]	Method 2[b]	Method 3[c]
$K = 100$	− 2.9036078	− 2.9036680	− 2.9036680
$K = 200$	− 2.9036855	− 2.9037168	− 2.9036758
$K = 300$	− 2.9036982	− 2.9037195	− 2.9037220
$K = 400$	− 2.9037027	− 2.9037198	− 2.9037230
$K = 500$	− 2.9037038	− 2.9037201	− 2.9037235
$K = 600$	− 2.9037097	− 2.9037203	− 2.9037236
Rybak et al.[d]			− 2.9037238
Thakkar and Smith[e]			− 2.903724363
Pekeris[f]			− 2.903724375
Baker et al.[g]			− 2.9037243770341184

[a] Random-tempered optimization and expansion of all geminals.
[b] Random-tempered optimization and expansion with a core built from a 10-GTO SCF basis[22] ($K_c = 55$), $E_{SCF} = − 2.8616729$ hartree.
[c] Random-tempered optimization with a core built from a 10-GTO SCF basis[22] ($K_c = 55$), $E_{SCF} = − 2.8616729$ hartree. Expansion with a core built from a 16-GTO SCF basis[23] ($K_c = 136$), $E_{SCF} = − 2.8616795$ hartree. The SCF limit is − 2.8616799 hartree.[27]
[d] 100 fully optimized GTGs (Ref. 24).
[e] 66 random-tempered Slater-type geminals (Ref. 20).
[f] 1078 functions in perimetric coordinates (Ref. 26).
[g] 476 Hylleraas functions with logarithmic terms (Ref. 25).

III. THE H₂ MOLECULE

The electronic wavefunction of H_2 can be expanded in a GTG basis set of the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{K} c_k(1 + P_{12})(1 + I_{AB})e^{-\alpha_k r_{1A}^2 - \beta_k r_{2B}^2 - \gamma_k r_{12}^2},$$

(4)

where

$$r_{1A}^2 = |\mathbf{r}_1 - \mathbf{A}_k|^2$$

(5)

and

$$r_{2B}^2 = |\mathbf{r}_2 - \mathbf{B}_k|^2,$$

(6)

and where $\mathbf{A}_k$ and $\mathbf{B}_b$ denote the two centers of the k th geminal. The operator I_{AB} replaces $\mathbf{A}_k$ with $-\mathbf{A}_k$ and $\mathbf{B}_k$ with $-\mathbf{B}_k$, and so it takes inversion symmetry into account. To evaluate the total energy of this system, we must thus optimize not only the nonlinear parameters α_k, β_k, and γ_k but also the positions $\mathbf{A}_k$ and $\mathbf{B}_k$. Because of axial symmetry, only those vectors $\mathbf{A}_k$ and $\mathbf{B}_k$ that lie on the internuclear axis of H_2 (assumed here to be the x axis) need to be considered. In Ref. 15 we showed that a relatively simple method of moving the geminal centers,

$$A_{xk} = A_0 + [X_1\langle k, j+6\rangle + X_2\langle k, j+7\rangle]/\alpha_k^{X},$$

$$B_{xk} = B_0 + [Y_1\langle k, j+8\rangle + Y_2\langle k, j+9\rangle]/\beta_k^{Y}, \quad (7)$$

gave good results. Here A_0 and B_0 are nuclear positions and X_1, X_2, X_3, Y_1, Y_2, and Y_3 are additional tempering parameters. This formula is based on the observation that fully optimized molecular geminals tend to be located somewhat closely to a nucleus and that this distance is inversely proportional to the exponent of the geminal. Because of the inversion symmetry, there are two possible choices for A_0 and B_0 (A_0 and B_0 on the same nucleus, A_0 and B_0 on different nuclei), and we calculate the optimal fraction of each using

one additional variable. The optimization of these 25 nonlinear parameters was performed with $K_c = 42$ (a 12-GTO SCF basis[28]) and 58 random tempered geminals i.e., a total of 100 geminals ($K = 100$).

In Table II, we give the result of the optimization and of subsequent expansions up to $K = 900$. A 30-GTO SCF basis was optimized by us and used as the core in the expansion step. We set the internuclear distance to be 1.4011 a.u. so as to most closely compare with the calculations in Refs. 17 and 19. Our best total energy is 0.2 μhartrees more accurate than the value obtained by Frye *et al.*[19] with the linear GTG basis. Our value also compares favorably with the results of very accurate calculations using explicitly correlated basis sets in elliptical coordinates.[29-31] In fact, our result is more accurate than Kolos and Wolniewicz's 1965 value that was obtained with an 80-term basis[29] and only 0.1 μhartrees worse than their 1968 value that was obtained with a 100-term basis.[30] Compared to the energy limit established in Ref. 31, our result is in error by almost 1 μhartree. As before, the major part of our error can be traced to the inaccuracy of the SCF orbitals.

IV. THE HeH⁺ ION

For this ion, the electronic wavefunction can be expanded in a GTG basis set of the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{K} c_k(1 + P_{12})e^{-\alpha_k r_{1A}^2 - \beta_k r_{2B}^2 - \gamma_k r_{12}^2}. \quad (8)$$

As in Ref. 15, there are three possible choices for A_0 and B_0 (A_0 and B_0 on He, A_0 and B_0 on H, A_0 on He and B_0 on H), and we calculate the optimal fraction of each using two additional variables. The optimization of these 38 nonlinear parameters was performed using a set of 45 random-tempered geminals and a core of $K_c = 55$ geminals generated by a 10-GTO SCF basis optimized by us. For the expansion

TABLE II. Total energy of H_2 (in hartrees). Unless otherwise indicated, the internuclear distance is 1.4011 a.u.

This work	$K = 100$	− 1.17438165[a]	
	$K = 300$	− 1.17446061	
	$K = 400$	− 1.17447234	
	$K = 500$	− 1.17447370	
	$K = 600$	− 1.17447416	
	$K = 700$	− 1.17447452	
	$K = 800$	− 1.17447473	
	$K = 900$	− 1.17447485	
Jeziorski and Szalewicz[3]	101 GTGs	− 1.17442	$R = 1.4$
Kolos *et al.*[4]	36 GTGs	− 1.174435	$R = 1.4009$
Moszynski and Szalewicz[5]	292 GTGs	− 1.174458	$R = 1.4$
Urdaneta *et al.*[17]	Linear GTGs[b]	− 1.174467	
Frye *et al.*[19]	Linear GTGs[c]	− 1.17447467	
Kolos and Wolniewicz[29]	80 terms[d]	− 1.1744746	
Kolos and Wolniewicz[30]	100 terms[d]	− 1.17447498	
Kolos *et al.*[31]	249 terms[d]	− 1.17447588[e]	

[a]Random-tempered optimization with a core built from a 12-GTO SCF basis ($K_c = 42$),[28] E_{SCF} = − 1.1334711 hartrees. Expansion with a core built from a 30-GTO SCF basis optimized by us ($K_c = 240$), E_{SCF} = − 1.133622 hartrees. The SCF limit is − 1.133623 hartrees.[32]
[b]Basis constructed from 80 GTOs.
[c]Basis constructed from 116 GTOs.
[d]Explicitly correlated functions in elliptical coordinates.
[e]Interpolated to $R = 1.4011$ a.u. The closest value in Ref. 31 is at $R = 1.4$ a.u. with $E = $ − 1.174475668 hartrees.

TABLE III. Total energy of the HeH$^+$ ion (in hartrees). The internuclear distance is 1.46324 a.u.

This work	$K = 100$	$- 2.9782755$[a]
	$K = 400$	$- 2.9785283$
	$K = 500$	$- 2.9786419$
	$K = 600$	$- 2.9786639$
	$K = 700$	$- 2.9786697$
	$K = 800$	$- 2.9786728$
	$K = 900$	$- 2.9786756$
	$K = 1000$	$- 2.9786771$
	$K = 1100$	$- 2.9786783$
	$K = 1200$	$- 2.9786792$
Urdaneta et al.[17]	Linear GTGs[b]	$- 2.978668$
Kolos and Peek[33]	83 terms[c]	$- 2.9786907$[d]
Bishop and Cheung[34]	255 terms[c]	$- 2.978706$[e]

[a] Random-tempered optimization with a core built from a 10-GTO SCF basis optimized by us ($K_c = 55$), $E_{SCF} = - 2.932499$ hartrees. Expansion with a core built from a 26-GTO SCF basis optimized by us ($K_c = 351$), $E_{SCF} = - 2.933085$ hartrees. The SCF limit is $- 2.933094$ hartrees.[32]
[b] Basis constructed from 25 GTOs.
[c] Explicitly correlated functions in elliptical coordinates.
[d] Interpolated.
[e] This energy was obtained by starting with the value calculated at $R = 1.46$ a.u., $E = - 2.97870262$ hartrees,[34] interpolating to $R = 1.46324$ a.u. and then adding the estimated $- 2$ μhartree basis set convergence error.[34]

step, we used a 26-GTO SCF basis optimized by us. Following the choice of Urdaneta et al.,[17] we have performed these calculations at the internuclear distance $R = 1.46324$ a.u. Table III shows that our best energy is 11 μhartrees lower than the value obtained with linear GTGs[17] and that it is 10 μhartrees above the result obtained by Kolos and Peek with 83 explicitly correlated elliptical basis functions.[33] Our energy is also about 27 μhartrees above the limit energy estimated by Bishop and Cheung.[34]

Our result for HeH$^+$ is of a lower accuracy than that obtained for H$_2$ because of three reasons. First, we have used a comparatively smaller number of geminals in the expansion phase, since our H$_2$ wavefunction contained the inversion symmetry operator. Thus, a 1200-term basis set for HeH$^+$ is equivalent to only a 600-term basis set for H$_2$. Second, a larger number of nonlinear parameters had to be optimized for HeH$^+$. This may have led to a less precise

tempering function. Third, the SCF orbitals for this system were much less accurate than those obtained for H$_2$. A comparison of the SCF energy from our 26-term SCF basis with the limit value,[34] shows that our total energy could be improved by at least 9 μhartrees by simply using a better set of SCF orbitals to form the core of the expansion.

V. THE H$_3^+$ ION

The geometry of this system is taken to be an equilateral triangle whose sides are 1.65 a.u. in length. The electronic wavefunction can thus be written as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=1}^{K} c_k (1 + P_{12})(1 + I_{ABC}) e^{- \alpha_k r_{1A}^2 - \beta_k r_{2B}^2 - \gamma_k r_{12}^2}, \quad (9)$$

where I_{ABC} is the the operator (containing 5 terms) that interchanges the positions of geminals about each of the three nuclei and so takes into account D_{3h} symmetry. Because this system is planar rather than linear, its tempering formula must also include the parameters A_{yk} and B_{yk}. These are tempered exactly like the ones in Eq. (7). In all, 36 tempering parameters were used. Since no compact SCF basis containing only s-type orbitals was available, our basis set does not contain a "core" set of geminals. This omission, however, has not prevented us from obtaining the most accurate value available for this system. From the convergence patterns shown in Table IV one might expect an inaccuracy of about 5 μhartrees in our final result. Our experience with the helium atom (see Table I) shows that such an estimate may be somewhat too low if no core is used. We do not expect, however, the error to be much larger than about 10 μhartrees.

As Table IV shows, the H$_3^+$ ion has been examined by a number of different methods. Anderson et al.[36,38,39] used a Green's function Monte Carlo method; all the others use various explicitly correlated basis sets and the variational method.[17,35,37,40] Our result is significantly lower—by 322 μhartrees—than the value obtained by Urdaneta et al.[17] with linear GTGs. Note, however, that the geometry used in this study is slightly different than ours. The calculations which come the closest to ours are the Monte Carlo calculation of

TABLE IV. Total energy of the H$_3^+$ ion (in hartrees). Unless otherwise indicated, this system is in an equilateral triangle configuration with $R = 1.65$ a.u. No core was used in these calculations.

This work	$K = 100$	$- 1.3436371$	
	$K = 200$	$- 1.3437563$	
	$K = 300$	$- 1.3437892$	
	$K = 400$	$- 1.3438093$	
	$K = 500$	$- 1.3438154$	
	$K = 600$	$- 1.3438195$	
	$K = 700$	$- 1.3438220$	
Salmon and Poshusta[35]	18 GTGs	$- 1.34335$	
Mentch and Anderson[36]	Monte Carlo	$- 1.3439 \pm 0.0002$	
Preiskorn and Woznicki[37]	24 Linear GTGs	$- 1.343422$	$R = 1.6504$
Anderson[38]	Monte Carlo	$- 1.34376 \pm 0.00003$	
Traynor and Anderson[39]	Monte Carlo	$- 1.34387 \pm 0.00005$	
Urdaneta et al.[17]	Linear GTGs[a]	$- 1.343500$	$R = 1.6504$[b]
Wenzel[40]	4974 GTOs	$- 1.343814$	

[a] Basis constructed from 49 GTOs.
[b] Ref. 17 incorrectly gives $R = 1.6405$ (private information from the authors).

Traynor and Anderson[39] and the unpublished work of Wenzel (who contructed a set of GTGs from 132 Gaussian-type orbitals and used a kind of tempering method to determine only the correlation exponents).[40]

VI. CONCLUSIONS

Using basis sets of random-tempered GTGs and the variational method, we have obtained the total energies of the helium atom, the H_2 molecule, and the HeH$^+$ and H_3^+ ions with accuracies of 0.8, 1.0, 27, and about 10 μhartrees, respectively. For linear diatomics, our results are of comparable accuracy to the results of calculations obtained prior to 1976 with explicitly correlated basis sets in elliptical coordinates.[29,30,33] For H_3^+, our method has produced the best total energy to date.

If microhartree accuracy is desired in a variational calculation, our results show that the wavefunction must properly describe the electron-nuclear cusps. One way to do this is to perform an optimization with two sets of tempering parameters: the first describing the electron–electron correlation and the second describing the electron-nuclear interaction. Since the latter interactions are properly accounted for at the SCF level, we found that it is easier to simply include a core of products of SCF orbitals in our basis. Note, however, that to achieve an accuracy of 1 μhartree in the SCF energy, a large number of GTO basis functions are often needed.

Our current molecular integral package is limited to only S-type geminals. It seems likely that the convergence of our calculations could be improved by using P and D-type functions. These functions should also make it possible to fix the geminals on the atoms and thus eliminate the large number of tempering parameters that are now needed to move them. Such a simplification would be crucial when working with systems containing large numbers of nuclei.

When compared to linear GTGs, Gaussian-type Geminals have a number of advantages. Not only did this basis produce lower energies for each of the systems studied here (showing that they are at least of comparable quality for two-electron systems), but it has already been successfully applied to a number of many-electron systems using high levels of MBPT and CC techniques.[9–16] All of the multi-electron, multicenter integrals over the GTG functions reduce to algebraic expressions involving the error function. In contrast, the difficulty of evaluating integrals over linear-GTGs prevents this method from being straightforwardly applied in general many-electron correlation energy calculations. If more than two-electron integrals are involved, they must be evaluated by a numerical integration over at least two dimensions, which is very time consuming. In a recent second-order energy calculation for Ne and H_2O, Klopper and Kutzelnigg[41] avoided the calculation of such integrals by using an approximate resolution of the identity to separate multi-electron integrals into products of one and two-electron integrals. Klopper and Kutzelnigg argue that the error introduced by this rather drastic approximation is smaller than the error caused by the overall incompleteness of the basis set. It does not seem likely, however, that this will be true beyond third-order theory.

Note added in proof: Using a basis of linear GTGs, constructed from 138 GTOs, an improved value for the total energy of the H_3^+ ground state, -1.3438279 hartrees, has just been published by D. Frye, A. Preiskorn, G. C. Lie, and E. Clementi [J. Chem. Phys. **92**, 4948 (1990)]. This result is 6 μhartrees lower than ours and was performed at the same geometry.

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