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Atomic and Molecular Calculations Using Quasirandom Numbers

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We have calculated the total ground-state energy, kinetic energy, and potential energy of He, H_2, Li, and Be using explicitly correlated wavefunctions and two numerical integration procedures. The first integration procedure uses pseudorandom numbers and converges as $N^{-0.5}$. The second uses a set of quasirandom numbers generated by Halton's algorithm. Under some circumstances the convergence of this integration procedure can be as fast as N^{-1}. When a small to intermediate number of quasirandom numbers are used, most of our expectation values converge faster than those computed using pseudorandom numbers. When a large number of quasirandom numbers are used, however, we find that most of the expectation values converge at roughly the same rate as those computed using pseudorandom numbers. © 2001 Academic Press

INTRODUCTION

A number of studies have shown that the convergence of atomic and molecular calculations can be tremendously accelerated by using basis functions which satisfy the two-electron cusp condition and which have the correct asymptotic behavior (see, for example Ref. [1]). The integrals of such functions, however, can rarely be integrated analytically. Traditional numerical integration techniques (e.g., Gauss–Laguerre and Gauss–Legendre) can be used to evaluate the matrix elements of systems with just a few electrons [2]. For systems with many electrons, and thus many dimensions, Monte Carlo methods can perform the necessary numerical integrations much more efficiently.

In a variational Monte Carlo calculation, a trial wavefunction form is chosen and the adjustable parameters in this form are optimized so as to minimize the variance in the local energy [2, 3]. Since such optimizations normally require several iterations, this step is done with just enough Monte Carlo integration points to adequately sample the parameter space (typically a few thousand) but not too many to be computationally impractical. Once the trial wavefunction has been optimized, it is then used to evaluate one or more expectation

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values. This step is done with as many Monte Carlo integration points as possible (typically a few million) so as to minimize the statistical error.

The “random” numbers used in most Monte Carlo calculations are statistically uncorrelated values generated from some deterministic algorithm (e.g., a linear congruential generator) [4]. As such, they are more properly labeled pseudorandom numbers. When these numbers are used in any numerical integration they produce a statistical error that is proportional to $\mathbf{c}\ N^{-0.5}$. Here $\mathbf{c}$ is a constant that depends on the expectation value being evaluated and N is the number of Monte Carlo integration points used to evaluate it. In a variational Monte Carlo calculation the first step serves to make $\mathbf{c}$ as small as possible and the second step serves to make $N^{-0.5}$ as small as possible.

In many applications the convergence of a numerical integration can be significantly improved by using quasirandom numbers instead of pseudorandom numbers (see, for example, Ref. [5]). Both pseudorandom and quasirandom points are uniformly distributed in some n-dimensional space—typically the unit hypercube. Whereas the former are as uncorrelated as possible, the latter are quite correlated and are chosen in such a way that new numbers uniformly fill the gaps between the old ones. Because quasirandom methods can converge as fast as N^{-1} under some circumstances, we wish to determine whether they can be used to replace pseudorandom numbers in either step of a variational Monte Carlo calculation and, if so, to discover what their convergence will be.

In this paper we calculate the total ground-state energy, kinetic energy, and potential energy of He, H_2, Li, and Be using pseudorandom numbers and a type of quasirandom numbers proposed by Halton [6]. For our trial wavefunctions we use explicitly correlated Slater and Gaussian geminals. Although these forms converge relatively slowly for both atoms and molecules, they can be analytically integrated and this allows us to compare our numerical results to the exact analytic result and thus to conclusively compare these two integration methods. Unless otherwise indicated, all values in this paper are given in atomic units.

PSEUDORANDOM CONFIGURATIONS

For atoms with only a few electrons we have found that an effective set of numerical integration points can be generated using the “biased as random” method [2]. This algorithm determines the coordinates of the ith electron, $\mathbf{x}_i = (r_i,\ \theta_i,\ \phi_i)$, such that

$$R = \int_0^{r_i} g(s)\,ds, \quad \Theta = \theta_i, \quad \text{and} \quad \Phi = \phi_i, \tag{1}$$

where R, Θ, and Φ are pseudorandom numbers chosen from the range

$$R = \left(0, \int_0^{\infty} g(s)\,ds\right), \quad \Theta = (0, 2\pi) \quad \text{and} \quad \Phi = (-\pi, \pi), \tag{2}$$

and where $g(s)$ is a guiding function which depends on the electron–nuclear distance. The weight of this point is the relative probability of choosing these coordinates and is given by

$$w(\mathbf{x}_i) = g(r_i) \Bigg/ \left(4\pi r_i^2 \int_0^{\infty} g(s)\,ds\right). \tag{3}$$

The factor $4\pi r_i^2$ compensates for choosing this point in spherical coordinates in Eq. (1).

As with any importance sampling technique, the use of a guiding function allows us to concentrate the placement of our points in the important regions of space. For this reason our convergence is increased tremendously compared to a simple sampling of the unit hypercube. In this paper our guiding function is taken to be

$$g(r) = e^{-\alpha r}, \tag{4}$$

where α is a parameter which can be adjusted so as to minimize the variance. This form was chosen because it provides a good approximation of Ψ^2 in the asymptotic region [3].

For molecular systems we compute the point $\mathbf{x}_i = (\hat{r}_i, \theta_i, \phi_i)$ in much the same way as we do for atoms. One important difference is that we now place each electron with respect to one of the atoms in the molecule, i.e., $\hat{r}_i = r_i + \mathbf{R}_j$. Here r_i is the electron–nuclear distance computed from Eq. 1 and $\mathbf{R}_j$ is the position of a randomly chosen atom. The weight of this configuration is found by averaging the electron–nuclear distance over all the atoms:

$$w(\mathbf{x}_i) = \frac{1}{\#\ \text{Atoms}} \sum_{k=1}^{\#\ \text{Atoms}} g(|\mathbf{r}_i - \mathbf{R}_k|) \Bigg/ \left(4\pi \,|\, \mathbf{r}_i - \mathbf{R}_k \,|^2 \int_0^\infty g(s)\, ds \right). \tag{5}$$

This averaging causes the weight to become infinite when an electron approaches any of the atoms. It is this feature that keeps the singularities in the electron–nuclear potential from dominating the variance [1, 3].

QUASIRANDOM CONFIGURATIONS

Altering the biased as random method to use quasirandom numbers instead of pseudorandom numbers is straightforward. We simply replace the pseudorandom numbers R, Θ, and Φ in Eq. (1) with three quasirandom numbers. No other changes are required. We generate our quasirandom numbers using the Halton program developed by Berblinger and Schlier [7]. In this program the quasirandom numbers h_i are produced by the recursive relation $h_{i+1} = (p+1)y - (1 - h_i)$, where p is the prime number used to generate this sequence and y is a function of p. In our program the quasirandom sequences used to sample each variable $(r_1, \theta_1, \phi_1, r_2, \ldots)$ are based on the primes chosen in ascending order $(2, 3, 5, 7, \ldots)$.

For molecular systems the deterministic nature of the quasirandom numbers means that we can no longer place each electron around a randomly chosen atom. Instead we pick the first half of our points such that electron 1 is on atom A and electron 2 is on atom B. For the second half of our points we place both electrons on atom A. Because of the symmetrization operator, this choice adequately covers the parameter space for H_2.

CALCULATIONS

The numerical evaluation of an expectation value can be written as

$$\langle A \rangle = \sum_i \left(\Psi_i A \Psi_i / w(\mathbf{x}_i) \right) \Bigg/ \sum_i \left(\Psi_i^2 / w(\mathbf{x}_i) \right), \tag{6}$$

where A is the operator to be determined and $\Psi_i = \Psi_T(\mathbf{x}_i)$ is the value of the trial wavefunction at the point $\mathbf{x}_i$. When pseudorandom numbers are used to compute this quantity we can define the statistical error in Eq. (6) as

$$\sigma^2 = \sum_i \left((A\Psi_i - \langle A\rangle\Psi_i)^2\Psi_i^2/w(\mathbf{x}_i)^2\right) \Bigg/ \sum_i \left(\Psi_i^2/w(\mathbf{x}_i)\right)^2. \tag{7}$$

When quasirandom numbers are used, however, the statistical error has no well-defined meaning and so is not computed.

For the helium atom we used a Slater-type geminal for our trial wavefunction,

$$\Psi_T = (1 + P_{12}) \sum_k c_k \exp(-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}), \tag{8}$$

where P_{12} is the operator which interchanges the coordinates of the two electrons. For this system we optimized all of the parameters in two basis sets so as to minimize the total energy. The first consists of a single Slater geminal and the second consists of a set of eight Slater geminals. For the molecule H_2 (at an internuclear distance of 1.4 a.u.) we used a single Gaussian-type geminal for our trial wavefunction,

$$\Psi_T = (1 + P_{12}) \exp\left(-\alpha r_{1A}^2 - \beta r_{2B}^2 - \gamma r_{12}^2\right), \tag{9}$$

where

$$r_{1A}^2 = x_1^2 + y_1^2 + (z_1 - \delta)^2,$$
$$r_{2B}^2 = x_2^2 + y_2^2 + (z_2 - \varepsilon)^2.$$

Since the position of each Gaussian can be optimized along the z axis, a small number of basis functions can capture a large percentage of the total energy. For the lithium and beryllium atoms we used a single Gaussian-type geminal for our trial wavefunctions,

$$\Psi_T = A\left[\exp\left(-\sum_i \alpha_i r_i^2 + \sum_{i<j} \beta_{ij}\, r_{ij}^2\right)\right], \tag{10}$$

where A is an antisymmetrization operator which interchanges the appropriate electron coordinates. As before, the parameters α_i and β_{ij} are optimized so as to minimize the total energy of each system. The values of the adjustable parameters used in each of these wavefunctions are listed in Table I. Because each of these forms can be analytically integrated, we can compare our numerical results to the exact analytic result. These analytic values are given in Table II.

For the helium atom we computed the total ground-state energy, the kinetic energy, and the potential energy using both a low accuracy wavefunction and a moderately accurate one. As Tables III and IV show, the convergence of the total energy and the potential energy are significantly improved when a small to intermediate number of quasirandom points is used (up to about 100,000). When a larger number of points are used we found that the convergence of both types of points becomes roughly the same. In contrast, quasirandom points produce a better convergence for the kinetic energy even when a large number of points are used. This is true for both basis sets. For the H_2 molecule we see in Table V that, once again the total energy and the potential energy converge much faster when quasirandom numbers are used. This is true over the entire range of points considered. In the kinetic energy the error drops quickly when a small to intermediate number of quasirandom points are used. For a large number of points, however, the convergence is roughly the same using

TABLE I
Parameters Used to Define Each Wavefunction

c_k	α_k	β_k	γ_k						
Helium: 1 Slater geminal									
1.0	2.20658596	1.44056369	−0.20732642						
Helium: 8 Slater geminals									
−3726.515833	3.097945909	3.135143448	2.342072767						
3726.403051	3.116721432	3.116254663	2.342214235						
−12891.90405	2.325914812	2.325895569	0.5716645040						
16976.13932	2.280638104	2.366346238	0.5747828281						
−4181.953857	2.220935545	2.414945234	0.5829312757						
−46.76132610	1.576650155	1.833087597	0.04489740713						
97.81803086	2.121441948	2.679729163	0.5197587834						
42.82455069	1.696513290	1.698453234	0.06716685943						
H_2: 1 Gaussian geminal									
α	β	γ	δ	ε					
0.61173259	0.21243090	−0.04079273	−0.00000046	0.00002941					
Li: 1 Gaussian geminal									
α_1	α_2	α_2	β_{12}	β_{13}	β_{23}				
1.70345	1.70345	1.70345	−0.10052	−0.10052	−0.10052				
Be: 1 Gaussian geminal									
α_1	α_2	α_3	α_4	β_{12}	β_{13}	β_{14}	β_{23}	β_{24}	β_{34}
7.65577	2.14003	0.13359	0.14138	−0.14422	−0.00230	−0.00314	−0.00225	−0.00513	−0.02400

TABLE II

The Analytic Values of the Total Energy, Kinetic Energy, and Potential Energy (in a.u.) Produced by the Trial Wavefunctions of Each System Considered Here

System	$\langle H\rangle$	$2\langle KE\rangle$	$\langle PE\rangle$
Helium (1 geminal)	−2.899534	5.799068	−5.799090
Helium (8 geminals)	−2.903716	5.807433	−5.809411
H_2	−1.038862	1.984539	−2.031132
Lithium	−6.760903	13.521806	−13.521806
Beryllium	−14.799508	29.599018	−29.599017

TABLE III

The Total Energy, Kinetic Energy, and Potential Energy (in a.u.) of Helium Using a Single Slater Geminal and the Guiding Function $g(r) = e^{-0.8r}$

N	$\langle H\rangle$	ΔE	$2\langle KE\rangle$	ΔKE	$\langle PE\rangle$	ΔPE
Pseudorandom						
4000	−2.8969686 ± 0.00613	2.5e−3	5.7993802 ± 0.02653	2.6e−4	−5.8029533 ± 0.1238	3.8e−3
16,000	−2.9001522 ± 0.00245	6.1e−4	5.7949044 ± 0.01310	4.2e−3	−5.7624505 ± 0.0612	3.6e−2
64,000	−2.9000623 ± 0.00137	5.2e−4	5.7979472 ± 0.00656	1.1e−3	−5.7835529 ± 0.0307	1.5e−2
256,000	−2.9004921 ± 0.00071	9.5e−4	5.8000703 ± 0.00329	9.5e−4	−5.7916157 ± 0.0153	7.4e−3
1,024,000	−2.8996931 ± 0.00038	1.5e−4	5.7991047 ± 0.00165	6.6e−6	−5.7971412 ± 0.0076	1.9e−3
4,096,000	−2.8996216 ± 0.00017	8.7e−5	5.7988927 ± 0.00082	2.1e−4	−5.7986339 ± 0.0038	4.5e−4
Quasirandom						
4000	−2.9008601	1.3e−3	5.8005677	1.4e−3	−5.8027595	3.6e−3
16,000	−2.8963012	3.2e−3	5.7992245	1.1e−4	−5.7932060	5.8e−3
64,000	−2.8994216	1.1e−4	5.7991489	3.7e−5	−5.7990082	8.1e−5
256,000	−2.8993191	2.1e−4	5.7991324	2.1e−5	−5.7986535	4.3e−4
1,024,000	−2.8994594	7.5e−5	5.7990974	1.3e−5	−5.7989853	1.0e−4
4,096,000	−2.8994745	5.9e−5	5.7991110	3.0e−7	−5.7989810	1.0e−4

Note. N is the number of integration points. The difference in each quantity is with respect to the analytic result.

TABLE IV

The Total Energy, Kinetic Energy, and Potential Energy (in a.u.) of Helium Using 8 Slater Geminals and the Guiding Function $g(r) = e^{-0.8r}$

N	$\langle H\rangle$	ΔE	$2\langle KE\rangle$	ΔKE	$\langle PE\rangle$	ΔPE
Pseudorandom						
4000	−2.9038559 ± 0.0000645	1.3e−4	5.8126059 ± 0.1075	1.2e−3	−5.8097089 ± 0.1242	2.9e−4
16,000	−2.9037747 ± 0.0000311	5.7e−5	5.8096016 ± 0.0531	1.7e−3	−5.7717103 ± 0.0615	3.7e−2
64,000	−2.9037438 ± 0.0000156	2.7e−5	5.8105506 ± 0.0265	8.3e−4	−5.7938968 ± 0.0308	1.5e−2
256,000	−2.9037214 ± 0.0000079	4.6e−6	5.8122366 ± 0.0133	8.4e−4	−5.8018206 ± 0.0154	7.5e−3
1,024,000	−2.9037221 ± 0.0000041	5.3e−6	5.8114981 ± 0.0066	1.0e−4	−5.8075083 ± 0.0077	1.9e−3
4,096,000	−2.9037177 ± 0.0000020	9.0e−7	5.8112073 ± 0.0033	1.8e−4	−5.8089816 ± 0.0038	4.2e−4
Quasirandom						
4000	−2.9036954	2.1e−5	5.8135036	2.1e−3	−5.8128954	3.4e−3
16,000	−2.9037191	2.3e−6	5.8121461	7.5e−4	−5.8044305	4.9e−3
64,000	−2.9037119	4.9e−6	5.8115490	1.6e−4	−5.8093714	3.9e−5
256,000	−2.9037185	1.7e−6	5.8114222	3.3e−5	−5.8090399	3.7e−4
1,024,000	−2.9037185	1.7e−6	5.8113725	1.6e−5	−5.8093314	7.9e−5
4,096,000	−2.9037181	1.3e−6	5.8113882	5.0e−7	−5.8093156	9.5e−5

Note. N is the number of integration points. The difference in each quantity is with respect to the analytic result.

TABLE V

The Total Energy, Kinetic Energy, and Potential Energy (in a.u.) of H_2 Using a Single Gaussian Geminal and the Guiding Function $g(r) = e^{-0.6r}$

N	$\langle H\rangle$	ΔE	$2\langle KE\rangle$	ΔKE	$\langle PE\rangle$	ΔPE
Pseudorandom						
4000	−1.0353102 ± 0.01619	3.5e–3	1.9812651 ± 0.02326	3.2e–3	−2.0260992 ± 0.0550	5.0e–3
16,000	−1.0256257 ± 0.00814	1.3e–2	1.9798107 ± 0.01169	4.7e–3	−2.0207030 ± 0.0272	1.0e–2
64,000	−1.0339303 ± 0.00424	4.9e–3	1.9761876 ± 0.00586	8.3e–3	−2.0311847 ± 0.0137	5.2e–5
256,000	−1.0412451 ± 0.00217	2.3e–3	1.9824086 ± 0.00293	2.1e–3	−2.0343312 ± 0.0068	3.1e–3
1,024,000	−1.0380460 ± 0.00106	8.1e–4	1.9849070 ± 0.00147	3.6e–4	−2.0298204 ± 0.0034	1.3e–3
4,096,000	−1.0383317 ± 0.00053	5.3e–4	1.9844853 ± 0.00073	5.4e–5	−2.0305376 ± 0.0017	5.9e–4
Quasirandom						
4000	−1.0300890	8.7e–3	1.9904178	5.8e–3	–2.0176825	1.3e–2
16,000	−1.0395744	7.1e–4	1.9846175	7.8e–5	−2.0318663	7.3e–4
64,000	−1.0397140	8.5e–4	1.9851255	5.8e–4	−2.0316088	4.7e–4
256,000	−1.0392290	3.6e–4	1.9847784	2.3e–4	−2.0313272	1.9e–4
1,024,000	−1.0386156	2.4e–4	1.9844087	1.3e–4	–2.0309801	1.5e–4
4,096,000	−1.0388429	1.9e–5	1.9845074	3.2e–5	–2.0311348	2.3e–6

Note. N is the number of integration points. The difference in each quantity is with respect to the analytic result.

TABLE VI

The Total Energy, Kinetic Energy, and Potential Energy (in a.u.) of Lithium Using a Single Gaussian Geminal and the Guiding Function $g(r) = e^{-0.6r}$

N	$\langle H\rangle$	ΔE	$2\langle KE\rangle$	ΔKE	$\langle PE\rangle$	ΔPE
Pseudorandom						
4000	−6.9742738 ± 0.2319	2.1e–1	13.832081 ± 0.1050	3.1e–1	–13.579923 ± 0.794	5.8e–2
16,000	−6.8280482 ± 0.1156	6.7e – 2	13.469668 ± 0.0534	5.2e – 2	–13.614904 ± 0.398	9.3e – 2
64,000	−6.7634122 ± 0.0563	2.5e – 3	13.439153 ± 0.0264	8.2e – 2	–13.565526 ± 0.196	4.3e – 2
256,000	−6.7755747 ± 0.0287	1.4e – 2	13.455804 ± 0.0132	6.6e–2	–13.569363 ± 0.098	4.7e–2
1,024,000	−6.7367849 ± 0.0146	2.4e–2	13.525391 ± 0.0066	3.5e–3	–13.495779 ± 0.049	2.6e–2
4,096,000	−6.7581585 ± 0.0072	2.7e–3	13.524475 ± 0.0033	2.6e–3	–13.517611 ± 0.024	4.1e–3
Quasirandom						
4000	−6.8217285	6.0e–2	13.464788	5.7e–2	−13.611025	8.9e–2
16,000	−6.7434073	1.7e–2	13.477887	4.3e–2	−13.526154	4.3e–3
64,000	−6.7790491	1.8e–2	13.518475	3.3e–3	−13.541502	1.9e–2
256,000	−6.7609826	7.9e–5	13.517605	4.2e–3	−13.523870	2.0e–3
1,024,000	−6.7640591	3.1e–3	13.519925	1.8e–3	−13.525786	3.9e–3
4,096,000	−6.7612530	3.4e–4	13.521617	1.8e–4	−13.522135	3.2e–4

Note. N is the number of integration points. The difference in each quantity is with respect to the analytic result.

TABLE VII

The Total Energy, Kinetic Energy and Potential Energy (in a.u.) of Beryllium Using a Single Gaussian Geminal and the Guiding Function $g(r) = e^{-0.7r}$

N	$\langle H\rangle$	ΔE	$2\langle KE\rangle$	ΔKE	$\langle PE\rangle$	ΔPE
Pseudorandom						
4000	−13.262923 ± 0.353	3.4e–2	25.994015 ± 0.350	4.6 –1	−26.688828 ± 1.557	2.3e–1
16,000	−13.054152 ± 0.187	1.7e–1	25.824068 ± 0.170	6.3e–1	−26.599055 ± 0.765	1.4e–1
64,000	−13.126207 ± 0.093	1.0e–1	26.390848 ± 0.085	6.6e–2	−26.354957 ± 0.384	1.0e–1
256,000	−13.160167 ± 0.047	6.8e–2	26.374199 ± 0.042	8.2e–2	−26.429454 ± 0.192	2.7e–2
1024000	−13.203534 ± 0.024	2.5e–2	26.423505 ± 0.021	3.3e–2	−26.448025 ± 0.097	9.1e–3
4,096,000	−13.228044 ± 0.012	5.2e–4	26.434565 ± 0.010	2.2e–2	−26.469177 ± 0.048	1.2e–2
Quasirandom						
4000	−13.019213	2.0e–1	26.523701	6.6e–2	−26.200488	2.5e–1
16,000	−12.955537	2.7e–1	26.416804	4.0e–2	−26.184675	2.7e–1
64,000	−13.056496	1.7e–1	26.402834	5.4e–2	−26.287416	1.6e–1
256,000	−13.176898	5.1e–2	26.414650	4.2e–2	−26.425275	3.1e–2
1,024,000	−13.218655	9.9e–3	26.460597	3.4e–3	−26.442934	1.4e–2
4,096,000	−13.226048	2.5e–3	26.455717	1.4e–3	−26.455973	1.1e–3

Note. N is the number of integration points. The difference in each quantity is with respect to the analytic result.

both quasirandom and pseudorandom numbers. In Table VI we list the results obtained for the lithium atom. We find that the convergence of the total energy, kinetic energy, and potential energy are very similar to those in helium, i.e., a small to intermediate number of quasirandom points produces a noticeable improvement. For the beryllium atom both the quasirandom and the pseudorandom numbers give a similar rate of convergence for the total energy and the potential energy. As Table VII shows this is true over the entire range of points considered. When we examine the kinetic energy we find that both types of points again produce a similar rate of convergence except when a large number of points is used. In this situation the quasirandom points converge noticeably faster.

CONCLUSIONS

All quasirandom sequences are defined by their discrepancy—the average distance between the points. To achieve an N^{-1} convergence using quasirandom numbers, the integrand must be relatively smooth and slowly changing (compared to the size of the discrepancy). If the integrand is not continuous or is quickly changing, then the error in a quasirandom integration drops to $N^{-0.5}$. Wilson and Coldwell [8] were able to show that the error in the kinetic energy and potential energy at the Monte Carlo points could be "paired" so that the fluctuations tend to cancel. Using this method they were able to obtain convergence of $N^{-0.72}$ for systems similar to those here. Because of the complexity of this method, it was never widely used. In this paper we have shown that expectation values can be easily computed using quasirandom numbers.

Our calculations show that the convergence of most expectation values is significantly faster when a small to intermediate number of quasirandom numbers are used. For this reason we believe that quasirandom numbers would be very effective in the first step in a variational Monte Carlo calculation. Here a single small set of configurations ($N \sim 4000$) is used to minimize the statistical error, Eq. (7) with $A = H$, with respect to the parameters in the trial wavefunction. In addition, the exact meaning of the minimization functional is not important in this step and so no confusion would exist as to what was being calculated. Because of their superior convergence, quasirandom numbers would enable us to use fewer integration points and thus substantially reduce the amount of computer time required by these calculations.

For most of the expectation values examined here we found that both pseudorandom and quasirandom numbers converge at approximately the same rate when a large number of integration points are used. This result has been seen before (see, for example, Ref. [9]). For this reason we believe that quasirandom numbers should not be used in the last step in a variational Monte Carlo calculation. Not only is there no savings in computer time but when pseudorandom numbers are used the variance has a well-tested meaning in terms of an expectation value. This definition is important when making the final comparison between the computed result and the established answer.

In other studies quasirandom numbers have also been shown to converge slowly in integrals with a large number of dimensions. We do not see any clear evidence of that here. Our largest system, beryllium ($N = 12$), does converge somewhat more slowly than our smallest system, helium ($N = 6$), but the wavefunction is also significantly poorer. A closer examination of this question is currently being investigated.

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