A New Look at Correlations in Atomic and Molecular Systems. I. Application of Fermion Monte Carlo Variational Method*

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Abstract

We are engaged in research directed toward the development of compact and accurate correlation functions for many-electron systems. Our computational tool is the variational method in which the many-electron integrals are calculated by Monte Carlo using the fermion Metropolis sampling algorithm. That is, a many-fermion system is simulated by sampling the square of a correlated antisymmetric wave function. The principal advantage of the method is that interelectronic distance r_{ij} may be included directly in the wave function without adding significant computational complexity. In addition, other quantities of physical and theoretical interest such as electron correlation functions and representations of Coulomb and Fermi "holes" are very easily obtained. Preliminary results are reported for He, H_2, and Li_2.

1. Introduction

Despite its many numerical successes and conceptual utility, the Hartree–Fock self-consistent-field approximation has proven unequal to the task of predicting accurate molecular excitation and dissociation energies [1]. The reason for this breakdown in the Hartree–Fock approximation arises from the fact that the independent particle model cannot adequately represent the correlation of the motion of electrons with opposite spins ("Coulomb hole") [2] and indeed the correlation of electrons with parallel spins is only partly accounted for ("Fermi hole") [3]. The proper description of electron correlation has thus been one of the central problems of quantum chemistry.

Correlated wave functions are most commonly constructed either by means of the configuration interaction method or by some variation of many-body perturbation theory [4]. An alternative approach is to use correlation factors which explicitly introduce the interelectronic coordinates r_{ij} into the wave function. For two electron systems it is possible to obtain wave functions of extraordinary accuracy by this method [5]. The rapid convergence of those wave functions is due both to the ease with which they can reproduce the Coulomb hole in the neighborhood of the cusp and to the fact that the Coulomb hole has

a rather simple structure when viewed relative to one of the electrons, while it has a rather complex structure when viewed relative to a fixed set of axes [6]. Thus a description in terms of a superposition of configurations is both complicated and slowly convergent as has been graphically illustrated by Rehmus, Roothaan, and Berry [7].

Although electron correlation calculations for atoms and molecules are usually based on the configuration interaction method, recently two attempts have been made to directly introduce interelectronic coordinates into the wave function of many electron systems. The first of these is the transcorrelated Hamiltonain approximation of Boys and Handy [8]. Although excellent estimates have been obtained for the correlation energy of Be [9], Ne [10], and LiH [11], the approximation leads to a non-Hermitian Hamiltonian and the resultant necessity of solving the transcorrelated equations in a nonvariational manner. The second approach is based on a combined configuration interaction Hylleraas method. Accurate energies and properties have been obtained in this way for three and four electron atoms and ions by Hagstrom and Sims [12], and more recently for the Ne atom [13] and several four electron diatomic molecules [14] by Clary and Handy. Unfortunately the extension of the method to more complex systems seems fraught with computational difficulty.

In this work we have applied the fermion Metropolis method [15] to the development of compact and accurate correlation functions for many electron atomic and molecular systems. The essence of the method is the Monte Carlo simulation of a many-fermion system by the proper sampling of the square of a correlated antisymmetric wave function. The advantages of applying this algorithm are manifold: (i) the interelectronic distance r_{ij} may be included directly in the wave function without adding significant computational complexity. (ii) Unlike the transcorrelated Hamiltonian approximation the energy is determined variationally. (iii) Unlike the configuration interaction Hylleraas technique the method can be applied quite generally to systems of any reasonable size, shape, or number of electrons. Computations have been recently carried out for an electron gas model [16] containing up to 162 correlated electrons in the unit cell. (iv) The computations may be performed on a minicomputer with modest storage and peripheral requirements. The algorithm is suitable for implementation on a vector machine, array or parallel processor. (v) Various observables and other interesting properties such as correlation functions, "coulomb" and "fermion" holes may be easily studied.

The fermion Metropolis method is described in Section 2. In Section 3 are presented some preliminary results of computations on He, H_2, and Li_2 with various correlation functions. In Section 4 the results are discussed and some new directions for future research proposed.

2. Fermion Metropolis Method

In order to compute the total electronic energy of an N-electron system

$$\langle E \rangle = \int \psi^*(r) H \psi(r) \, dr \Big/ \int |\psi(r)|^2 \, dr, \tag{1}$$

we choose an antisymmetric trial wave function of the form

$$\psi(r) = \det |D_{ij}^{\alpha}| \det |D_{ij}^{\beta}| \exp\left(\sum_{i>j} U_{ij}\right), \qquad (2)$$

where the D_{ij}^{s} represent determinants of n_s one-electron spin orbitals for electrons of α and β spin, respectively,

$$D_{ij}^{s} = \phi_i(r_j, s) \qquad (3)$$

and the U_{ij} represent two particle correlation functions

$$U_{ij} = U(r_{ij}, r_i, r_j). \qquad (4)$$

In the closed shell case, $n_\alpha = n_\beta = \frac{1}{2}N$.

The method of sampling the wave function is based on the Monte Carlo algorithm of Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller [17] widely used for chemical ensembles and implemented for fermion systems by Ceperley et al. [15]. Initial coordinates are assigned to the particles. Each particle is then moved one after another to a new position uniformly distributed inside a cube of side Δ. That move is either accepted or rejected depending on the magnitude of the trial function at the new position compared with the old position. Suppose r is the old position and r' the new. Then if $|\psi(r')|^2 > |\psi(r)|^2$ the new point r' is accepted. Otherwise the new point is accepted with probability q, where

$$q = |\psi(r')|^2/|\psi(r)|^2. \qquad (5)$$

If the move is rejected the configuration is returned to its original state. This random walk is Markovian and the set of coordinates generated by a sufficiently long calculation is an unbiased sample drawn from the probability distribution

$$p(r) = |\psi(r)|^2 \Big/ \int |\psi(r)|^2 \, dr. \qquad (6)$$

The expectation value of the energy, Eq. (1), is simply the average value of the operator $H\psi/\psi$ evaluated at the N steps of the random walk:

$$\langle E \rangle \cong \frac{1}{N} \sum_{i=1}^{N} E(r_i),$$
$$E(r_i) = H\psi(r_i)/\psi(r_i). \qquad (7)$$

The variance σ^2 of the mean given by Eq. (7) may be estimated by dividing the random walk into blocks sufficiently large so that the average energy in one block is nearly independent of the others. Then the variance is obtained from the mean square deviation from the mean of the block energies.

The presence of the determinants in the trial function complicates the random walk somewhat since one must compute the ratio of two determinants at each step. Ceperley [15] has proposed an efficient method to handle this problem based on calculating the inverses of the matrices D_{ij}^{s} at the beginning of the random walk and then updating them as the particles are moved. This inverse

is needed to compute the Metropolis acceptance ratio q and the variational energy.

Several brief comments about Monte Carlo computations should be made at this point. First, the closer the trial wave function approaches the exact wave function, the closer $H\psi/\psi$ approaches a constant value leading in the limit to the possibility of a zero variance Monte Carlo computation. The practical consequence of this result is that a well chosen wavefunction can lead to a dramatic decrease in the variance for a given number of steps in the random walk. As one incorporates better orbitals and correlation factors, the calculation converges faster. A striking example is given below. Thus, the Metropolis Monte Carlo method readily permits a form of importance sampling. It is distinguished from other Monte Carlo algorithms in that $|\psi|^2$ is sampled directly rather than some function which although more easily sampled only somewhat resembles $|\psi|^2$. Finally, we mention two recent Monte Carlo calculations which bear on the present investigation. One by Coldwell and Lowther [18] of the inter-molecular potential for two He atoms exploited the possibility of a zero variance Monte Carlo computation by using an antisymmetric combination of Hylleraas type wave functions plus additional intermolecular correlation terms. The other computation by Whittington and Bersohn [19] employed the Metropolis algorithm for He with a rather crude two parameter trial function.

In the case of Coldwell and Lowther, it is difficult to see how their extremely accurate results could be extended to molecular systems of increasing complexity. This is due primarily to the unavailability of Hylleraas type wave functions for atoms of higher atomic number.

3. Preliminary Results

Here are presented some preliminary results for three systems of increasing complexity, He, H_2, and Li_2. In the case of He and H_2 the spin variables may be eliminated at the outset and the wave function written in the form

$$\psi(1, 2) = N\phi(r_1)\phi(r_2)f(r_1, r_2, r_{12}).\tag{8}$$

Several different orbital functions and correlation factors were employed during the course of the investigation. The results of the computations are given in Tables I and II. The analytic results for He are taken from the work of Green et al. [20] and Banyard and Seddon [21], while the results for H_2 are due to Frost and Braunstein [22] and Kolos and Roothaan [5]. In order to study the size and shape of the Coulomb hole it is of interest to compute the distribution function for the interelectronic distance $f(r_{12})$ normalized so that

$$\int_0^\infty f(r_{12})\, dr_{12} = 1.\tag{9}$$

The Coulomb hole is then defined by Coulson and Neilson [2] as the difference between the values of $f(r_{12})$ when the function is derived from the true wave function, or our best approximation to it, and from the best uncorrelated wave

TABLE I. Electronic energy and $\langle r_{12} \rangle$ for He atom ground state by analytical and Monte Carlo integration. Number of integration points, $N = 10^6$. Energy in hartree a.u. and distance in bohr.

	Orbitals $\phi(r_i)$[a]	Correlation factors[a]	Analytical E[a]	$\langle r_{12} \rangle$[a]	Monte Carlo E	σ	$\langle r_{12} \rangle$
A	$\exp(-Z'r)$	$\cdots$	-2.8477	1.30	-2.8474	0.0025	1.30
B	$[\exp(-Z'r) + C\exp(-kZ'r)]$	$\cdots$	-2.86167	1.36	-2.86107	0.0017	1.36
C	$\exp(-Z'r)$	$(1+\alpha r_{12})$	-2.89112	1.37	-2.89283	0.0011	1.37
D	$[\exp(-Z'r) + C\exp(-kZ'r)]$	$(1+\alpha r_{12})$	-2.89807	1.42	-2.89818	0.00062	1.43
E	$[\exp(-Z'r) + C\exp(-kZ'r)]$	$[1+\alpha r_{12}+\beta(r_1-r_2)^2]$	-2.90262	1.43	-2.90243	0.00048	1.43
F	Hartree–Fock		-2.86168	1.36			
G	"Exact" Pekeris[b]		-2.90372	1.42			

[a] Energy and parameters of wave function taken from Refs. 20 and 21.
[b] Reference 5.

TABLE II. Electronic energy and $\langle r_{12} \rangle$ for H_2 molecule ground state by analytical and Monte Carlo integration. Number of integration point, $N = 10^6$. Energy in hartree a.u. and distance in bohr. Binding energy (BE) in eV.

	Orbitals $\phi(r_i)$	Correlation factor	R	Analytical E (BE)	$\langle r_{12} \rangle$	Monte Carlo E (BE)	σ	$\langle r_{12} \rangle$
A	$[\exp(-Zr_a) + \exp(-Zr_b)]$[a]	$\cdots$	1.40	-1.12808 (3.49)	$\cdots$	-1.12807 (3.48)	0.0013	2.03
B	$[\exp(-Zr_a) + \exp(-Zr_b)]$[b]	$(1+Cr_{12})$[b]	1.34	-1.151[b] (4.11)	$\cdots$	-1.15528 (4.23)	0.00089	2.23
C	$[\exp(-Zr_a) + \exp(-Zr_b)]$[b]	$(1+Cr_{12})$[b]	1.40	$\cdots$	$\cdots$	-1.15678 (4.27)	0.00053	2.24
D	Hartree–Fock (9 term)[c]		1.40	-1.13363 (3.64)	2.04			
E	Correlated (24 term)[c]		1.40	-1.17433 (4.74)	2.17			
	Experimental[c]		1.40	-1.1746 (4.75)				

[a] $Z = 1.2$.
[b] Reference 22, $Z = 1.285$, $c = 0.28$.
[c] Reference 5.

function, i.e., the Hartree–Fock wave function:

$$\Delta(r_{12}) = f(r_{12})_{\text{corr}} - f(r_{12})_{\text{uncorr}}. \tag{10}$$

The interelectronic distribution function and the Coulomb hole for He and H_2 are shown in Figures 1 and 2.

Several conclusions may be drawn from the tabulated data. First and foremost, the fermion Metropolis method is capable of reproducing the results of the analytic computation to sufficient accuracy. Second, the standard deviation is reduced as expected as the quality of wave function is improved. Third, the Monte Carlo algorithm allows the simple computation of distribution functions such as $f(r_{12})$ and expectation values other than the energy.

For the Li_2 molecule in the $^1\Sigma_g$ ground state $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2)$ the properly antisymmetrized trial wave function was defined by Eq. (2) with spin orbitals

$$\phi_i = \sum_j C_{ij}\eta_j, \tag{11}$$

where η_j represents either $1s$, $2s$, or $2p$ nodeless Slater orbitals centered on the Li nuclei and with a correlation function

$$U_{ij} = Ar_{ij}/(1 + Br_{ij}). \tag{12}$$

The results for the Li_2 computation are given in Table III for both a single-zeta basis with spin orbitals

$$\phi_1 = N[\exp(-z_{1s}r_a) + \exp(-z_{1s}r_b)],$$

$$\phi_2 = N[\exp(-z_{1s}r_a) - \exp(-z_{1s}r_b)], \tag{13}$$

$$\phi_3 = N[r_a \exp(-z_{2s}r_a) + r_b \exp(-z_{2s}r_b)],$$

and for a double-zeta plus polarization basis where the coefficients C_{ij} of the spin orbitals ϕ_i were determined by a Hartree–Fock computation. Two sets of results are tabulated for the correlated wave function for each basis. The first set is computed with the identical spin orbitals used for the uncorrelated basis while for the second set the screening constants of the valence spin orbital were uniformly scaled by a factor of 1.2. This contraction of the valence charge density was determined variationally in the case of the double-zeta plus polarization basis and results in a significant lowering of the electronic energy. In the case of the single-zeta basis the electronic energy of the scaled and unscaled computations are virtually identical within the statistical error. The distribution function $f(r_{12})$ and the coulomb hole for the scaled double-zeta plus polarization basis are plotted in Figure 3. The results are compared in Table III to a Hartree–Fock and a Moller–Plesset perturbation theory (RMP3) [23] computation with both a minimal and double-zeta plus polarization STO-6G basis as well as with a more elaborate 4-31G^{**} Gaussian basis including $3d$ polarization functions. It should be noted that an exact comparison with the Hartree–Fock results is only possible for the double-zeta plus polarization basis as the ϕ_i of Eq. (13) are not orthogonal.
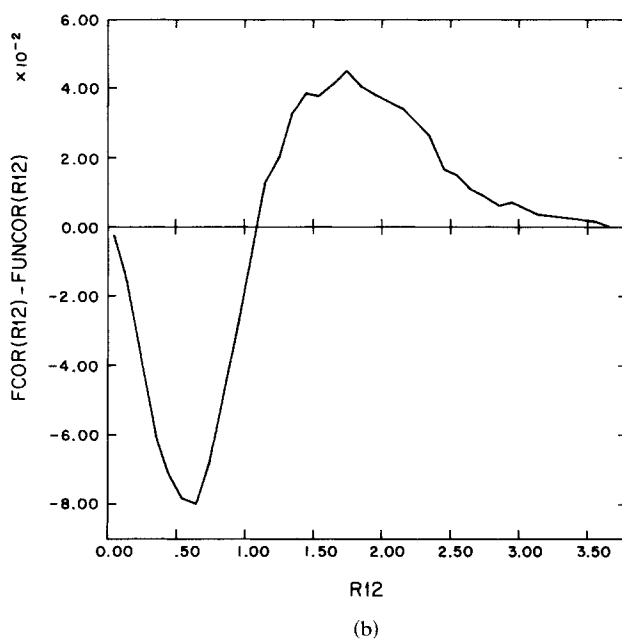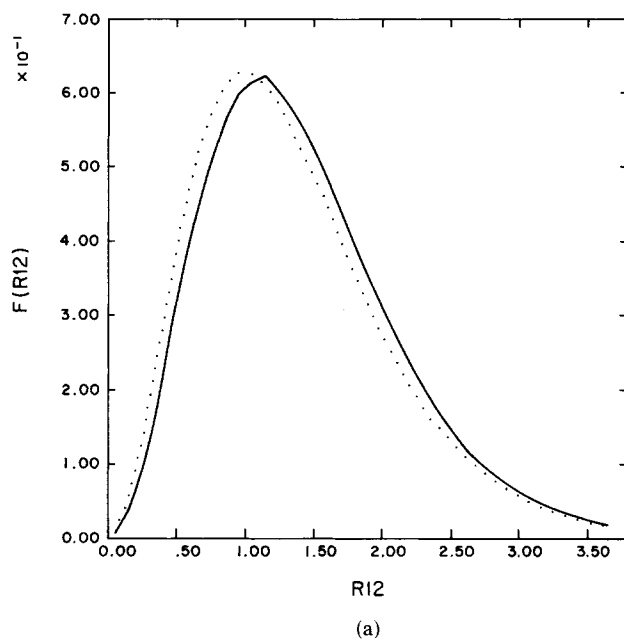
(a)

(b)

Figure 1. (a) He atom pair distribution function for wave function B [uncorrelated (· · ·)] and wave function E [correlated (——)] of Table I. (b) He atom Coulomb hole from Eq. (10).
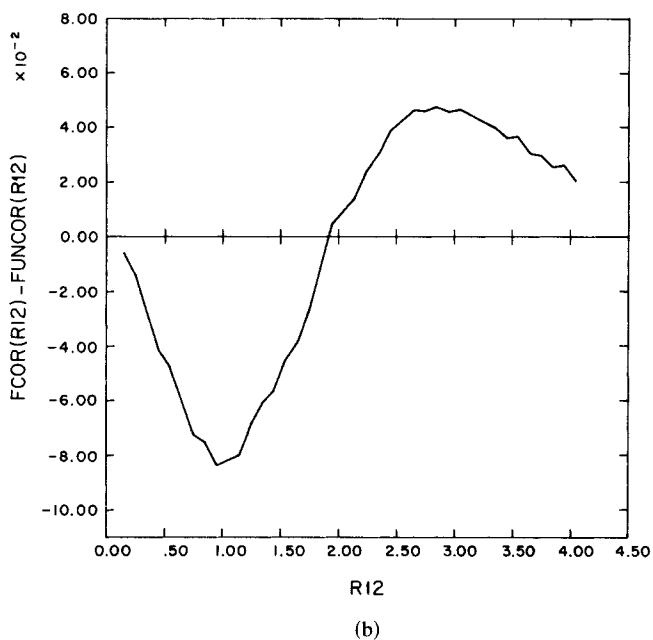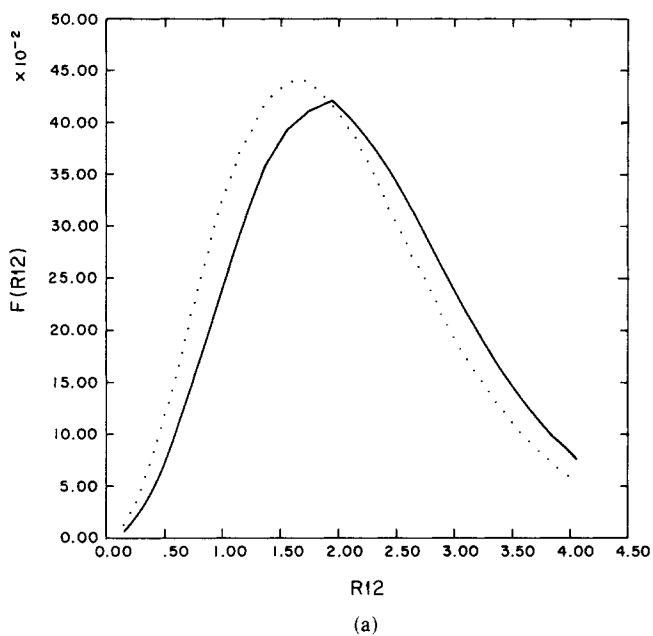
(a)

(b)

Figure 2. (a) H_2 molecule pair distribution function for wave function A [uncorrelated ($\cdots$)] and wave function C [correlated (——)] of Table II. (b) H_2 molecule Coulomb hole from Eq. (10).

Once again the data indicate that the fermion metropolis method is capable of producing results of reasonable accuracy for a many electron system despite the somewhat crude spin orbitals and correlation factor employed in the computation. In fact the correlation factor picks up approximately half the correlation energy ($E_{uncor} - E_{corr} = 0.125$ a.u.) and does substantially better than the analytical results in the RMP3 approximation even for an extended basis ($E_{HF} - E_{RMP3} = 0.047$ a.u. for the double zeta plus polarization basis and 0.025 a.u. for the $4\text{-}31G^{**}$ basis). The need for a more flexible correlation function is indicated by the more complex shell structure of $f(r_{12})$ and the coulomb hole shown in Figure 3 compared to the simple structure for the two electron systems He and H_2. In addition the difference between $\langle r_{12} \rangle$ parallel and $\langle r_{12} \rangle$ antiparallel for the uncorrelated wave function shows the strong effect of the Fermi hole. The coulomb hole is a small perturbation on this effect. This may be seen clearly when the same orbital functions (unscaled) are used for both the correlated and uncorrelated computations in Table III. In this case $\langle r_{12} \rangle$ increases uniformly for electrons with both the same and opposite spins.

4. Discussion

The purpose of this investigation has been to show the possibility of developing correlated wavefunctions for atomic and molecular systems which are at once reasonably accurate, compact, and relatively easy to understand. The fermion metropolis method has been shown in our preliminary results to be an appropriate technique for the investigation of this important problem. Unlike the conventional configuration interaction and many body perturbation methods the magnitude of the computational effort increases approximately linearly with the complexity of the wave function and as the square of the number of electrons. Moreover, for a Monte Carlo calculation, as our results clearly demonstrate the more sophisticated the wave function the less the effort required for a given accuracy. It is evident however that more complex correlation functions than those employed above are required to approach chemical accuracy.

Previous investigations of the two electron systems provide some guidance to the proper choice of a correlation function. Many workers have pointed out the desirability of accurate spin orbitals in order not to distort the effect of the correlation function. The proper balance, however, is certainly not clear as can be seen by the excellent result of including radial correlation $\beta(r_1 - r_2)^2$ in wave function E for the He atom in Table I. Recently, several authors [24] have demonstrated the necessity of including three-body effects in order to attain the most accurate results. These three-body effects manifest themselves in logarithmic terms in the wave function.

In the case of many electron systems far less information is available. Early work by Lennard-Jones and Pople [25] emphasized the importance of angular correlation for the $2s$–$2p$ shell of first row atoms. More recently Boys and Handy obtained excellent results for Be [9], Ne [10], and LiH [11] with an exponential
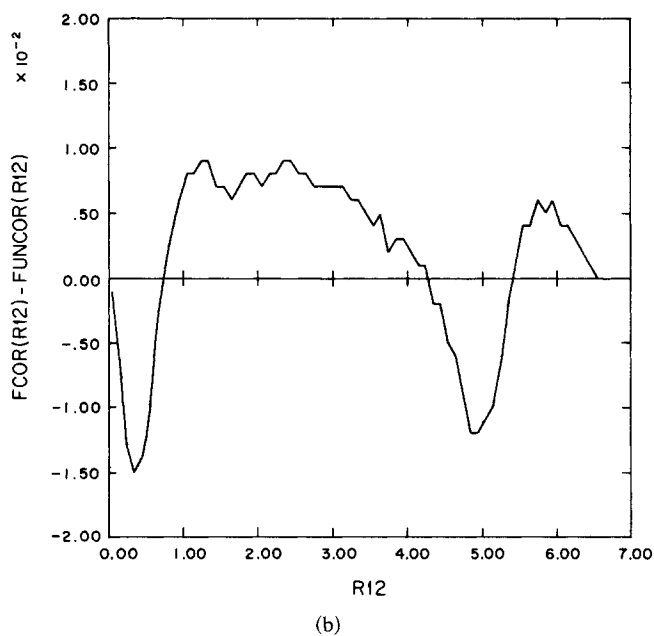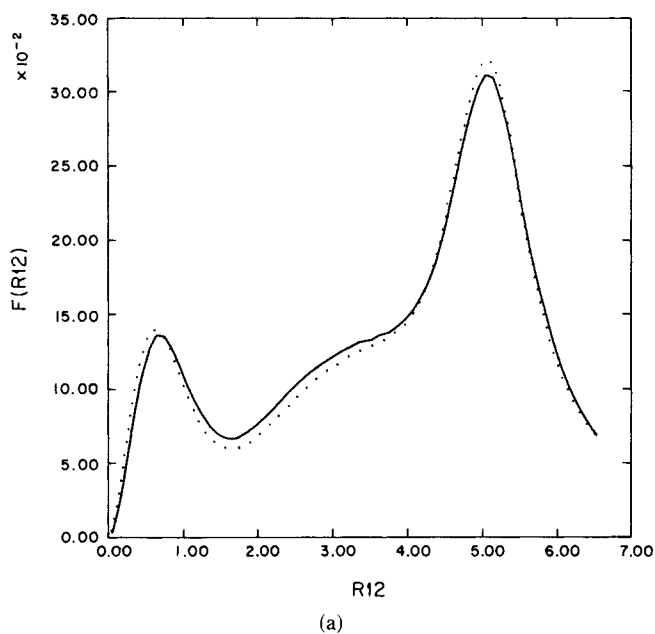
Figure 3. (a) Li$_2$ molecule pair distribution function for double-ξ plus polarization basis [uncorrelated ($\cdots$)] and scaled double-ξ plus polarization basis [correlated (——)] of Table III. (b) Li$_2$ molecule Coulomb hole from Eq. (10).

TABLE III Electronic energy and $\langle r_{12}\rangle$ for the ground $^1\Sigma_g$ state of the Li_2 molecule by analytical and Monte Carlo integration. The number of integration points $N = 8 \times 10^6$. Energy in hartree a.u. and distance in bohr. $R(Li–Li) = 5.05$ bohr.

| | Monte Carlo | | |
	Uncorrelated		Correlated
A	0.0		0.5
B	0.0		1.0
		Single-ξ[a]	
E	14.8324	−14.8998	−14.8947[b]
σ	0.0067	0.0041	0.0033
$\langle r_{12}\rangle$	4.41	4.64	4.34
$\langle r_{12}\rangle$ parallel	4.89	5.13	4.81
$\langle r_{12}\rangle$ antiparallel	4.10	4.33	4.04
		Double-ξ plus polarization[c]	
E	−14.8666	−14.9178	−14.9318[d]
σ	0.0034	0.0028	0.0025
$\langle r_{12}\rangle$	4.32	4.57	4.25
$\langle r_{12}\rangle$ parallel	4.80	5.05	4.72
$\langle r_{12}\rangle$ antiparallel	4.01	4.26	3.95
		Analytical	
	Hartree–Fock		RMP3[e]
E(single-ξ)[f]	−14.82242		−14.83265
E(double-ξ plus polarization)[g]	−14.86708		−14.91413
E(4-31G**)[h]	−14.86053		−14.88590
E(Hartree–Fock limit)[i]	−14.8719		
E(exact)[i]	−14.9967		

[a] The orbital exponents are $Z_{1S} = 2.69$ and $Z_{2S} = 0.694$.
[b] Z_{2S} scaled by 1.2.
[c] The orbital exponents are $Z_{1S} = 2.44$, $Z'_{1S} = 4.52$, $Z_{2S} = 0.671$, $Z'_{2S} = 1.98$, $Z_{2P} = 0.76$.
[d] Z_{2S}, Z'_{2S}, Z_{2P} scaled by 1.2.
[e] Reference 23.
[f] STO-6G with $Z_{1S} = 2.69$ and $Z_{2S} = 0.694$.
[g] STO-6G exponents from footnote c.
[h] Standard exponents from GAUSS 78.
[i] G. C. Lie and E. Clementi, J. Chem. Phys. **60**, 1288 (1974).

correlation function. In the case of Ne, for example, U_{ij} had the form

$$U_{ij} = \frac{0.5 r_{ij}}{1 + 0.5 r_{ij}} + \sum_k D_k G_k(r_i, r_j) \tag{14}$$

and $G_k(r_i, r_j)$ represents powers of the variables u, t, s, where

$$u^n = (\mathbf{r}_i \cdot \mathbf{r}_j)^n, \qquad t^n = (r_i r_j)^n, \qquad s^n = r_i^n + r_j^n \tag{15}$$

and

$$r_i^n = [r_i/(1 + 0.5 r_i)]^n, \tag{16}$$

where u^n is the vector and t^n is the scalar product. It should be noted that the expansion in G_k is roughly equivalent to a term in r_{ij}^2. Using accurate Hartree–Fock spin orbitals, a 19 term function in G_k obtained 92.2% of the Be atom correlation energy. In an attempt to simplify these results, Handy [26] proposed, for the atomic series Be, O, C, and Ne, the correlation function

$$U_{ij} = 0.5r_{ij}/[1 + f(r_i, r_j)r_{ij}]. \tag{17}$$

The switching function $f(r_i, r_j)$ goes smoothly to a constant when electron i and j are both in either the $1s$ or $2s$–$2p$ shell. Handy recovered 95% of the correlation energy of Be and 103% of the correlation energy of C in this manner. In addition, in the case of Be the accidental $2s$–$2p$ degeneracy was first removed by performing a simple two state configuration interaction computation and thus shifting some of the correlation effect to the orbital factor. Due to the nonvariational character of the transcorrelated Hamiltonian method, it is impossible to distinguish between the two approaches within the accuracy of the reported results.

Although Boys and Handy give some tantalizing clues as to the form of the correlation function the problem has not been satisfactorily resolved. Their choice was greatly influenced by technical considerations of integral evaluation. In this laboratory we are in the process of reinvestigating the correlation functions proposed above as well as the possibility that a simple power series expansion in r_{ij} would be more rapidly convergent. We believe that the fermion Metropolis method represents a powerful and efficient technique for the testing of simple models for the understanding and computation of the correlation energy of many electron atoms and molecules. This goal has never seemed approachable by the conventional methods of quantum chemistry.

Acknowledgments

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