

Monte Carlo study of electron correlation functions for small molecules*

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A study is made of electron-electron correlation functions for use in trial wave functions for small molecules. New forms are proposed that have only a few variational parameters, and these parameters have physical meanings that are easily discerned. Total energies for H_2 , LiH and Li_2 computed using these correlation functions are presented, and comparison is made with previous forms, including the Jastrow-Pade form often used in Monte Carlo studies. We further treat the possibility that correlation depends not only on the separation of a pair of electrons but also on the location of the electron pair relative to the nuclei - indicative of a density-dependent or many body correlation effect. Our results indicate that such a many-body correlation effect is weakly present.

Key words: Correlation functions — Monte Carlo — Small molecules — Variational calculations — Trial wave functions

1. Introduction

In variational methods of obtaining the energy of a quantum system, one evaluates the expectation value $E_T = \langle \Psi_T | H | \Psi_T \rangle$ for a normalized trial wave function Ψ_T .

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Parameters in Ψ_T are varied and, by the variational theorem, E_T remains an upper bound to the true ground-state energy. The minimum energy Ψ_T thus provides the best upper bound to the energy, and in this sense is the “best” wave function. Variational Monte Carlo (VMC) methods [1-4] follow this same approach, with the exception that the necessary integrals are performed by a variety of Monte Carlo methods.

In the fixed-node quantum Monte Carlo (QMC) method [5-8], the trial function Ψ_T , plays a different role. It acts as a guiding function for importance sampling, speeding up the stochastic procedure which *solves* the Schrödinger equation. A better Ψ_T for fixed-node applications enables one to use less computer time to obtain the final result [8, 9].

A frequently used form of Ψ_T [4-30] in variational and, recently, QMC calculations is expressed as a product of two factors, namely,

$$\Psi_T = \phi S, \quad (1)$$

where ϕ is an independent-particle (generally self-consistent field or SCF) approximation to the exact wave function, and is antisymmetric in the electron coordinates. The function S , on the other hand, typically depends explicitly on interelectronic coordinates r_{ij} , and is symmetric in these coordinates. In reality, of course, many-body correlations also play a role, but we ignore these at present. Our goal will be to seek a form for the function $S(r_{ij})$ that may be readily optimized to yield lower variational energies.

We note that there are two different sources of electron correlation [10]. Due to the Pauli principle, electrons of like spin have an exchange correlation. This correlation is partially accounted for by the determinantal part of Ψ_T . Additional correlation derives from the Coulomb repulsion between electrons, independent of their spins. The correlation function S is primarily intended to describe the latter.

Correlation functions used previously in non Monte Carlo variational methods were limited by the difficulty in performing the necessary integrals over Slater-type basis functions [11]. Beyond two-electron systems Gaussian correlation functions are generally employed [12] for this reason. In VMC and QMC calculations, however, one may readily deal with *arbitrary* forms of correlation functions.

2. Correlation functions

As a starting point in discussing correlation functions, let us examine the general behavior that is often assumed to characterize such functions.

(i) $S(r_{ij})$ should satisfy the electron cusp condition [5-8, 10, 13]:

$$\left. \frac{1}{S} \frac{\partial S}{\partial r_{ij}} \right|_{r_{ij}=0} = a, \quad (2)$$

where $a = 0.5$ a.u. for electrons of opposite spin. For electrons of like spin, the electron cusp condition is partially satisfied by the Slater determinant. Thus S is only needed to satisfy the “remaining cusp”, which it does with $a = 0.25$ a.u.

(ii) As r_{ij} increases from zero, $S(r_{ij})$ should rise monotonically to provide for an increasing probability that two electrons are separated by r_{ij} , and to provide maximum inter-electronic repulsion at $r_{ij} = 0$.

(iii) By interpreting (2) as a pseudoforce, which we discuss below, it is argued that as r_{ij} increases, $S(r_{ij})$ should approach a non-zero constant. This provides a pseudoforce which decays as an electron pair is separated, and reflects the weakening of the Coulomb repulsion. Forms which explicitly consider this requirement were pioneered by Handy [14], though it is not clear that this condition is rigorously justified. An argument that supports this requirement is that when a molecule is separated into subsystems the wave function should factor. The correlation between two electrons which ultimately belong to different sub-systems should thus vanish, and so S approaches a constant. For the additional purpose that it limits the possible forms for S , we exploit this condition here. Without loss of generality we choose the constant $S(\infty)$ as unity.

A number of forms for the electron correlation function S have been used previously. For example, Hylleraas [15] considered the forms

$$S(r_{12}) = \exp(\alpha r_{12}) \quad (3)$$

and

$$S(r_{12}) = 1 + \alpha r_{12} \quad (4)$$

for He-like systems, where α is a variational parameter.

Using Eq. (1) with a minimum basis set for ϕ , Green et al. [16a] derived and solved numerically the differential equation for S . They found the exact solution in this case to be fit well by Eq. (4) out to several bohr, and to lead to only slight improvement in the energy over the use of (4). Frost and Braunstein [16b] also obtained quite satisfactory variational results with Eq. (4) in their treatment of H_2 . Nevertheless, neither (3) nor (4) satisfies (iii) above; both diverge as $r_{12} \rightarrow \infty$, and the correlation is too strong at large pair separations. In 1957 Roothaan [17] proposed a modified form for S that he applied to He, namely,

$$S(r_{12}) = 1 - \exp(-\alpha r_{12}) \sum_{\mu=0}^3 b_{\mu} r^{\mu}. \quad (5)$$

This function satisfies (i)–(iii), however, the presence of the electron-nuclear coordinate r limits it to monatomic systems.

A number of other finite series expressions for S were subsequently explored. Two examples are the Roothaan-Weiss form [18]:

$$S(r_{12}) = \sum_{\mu=0}^n c_{\mu} (\zeta r_{12})^{\mu}, \quad (6)$$

and the Gaussian form [12d]

$$S(r_{12}) = \sum_{\mu=0}^n b_{\mu} \exp(-\beta_{\mu} r_{12}^2). \quad (7)$$

Equation (6) derives its flexibility from the many terms that are possible in the sum. However, it is not succinct and generally contains so many parameters that optimization becomes quite difficult. Furthermore, no clear physical meaning is readily given to these parameters. Finally, (6) also fails condition (iii). On the other hand, the Gaussian expansion (7) was chosen primarily for mathematical convenience. Although it also yields lowered variational energies, this form does not satisfy the cusp condition, (i).

Pritchard [19] combined the Roothaan-Weiss form (6) with the Hylleraas form (3) in a product. He observed that the cusp condition was satisfied for his optimized parameters. However, the large r_{ij} behavior of his function remained problematic: For closed-shell systems he obtained $\alpha > 0$, for which $S \rightarrow \infty$; for open-shell systems $\alpha < 0$, leading to $S \rightarrow 0$. Furthermore, Pritchard's results indicate little improvement in the energy over the use of (6) alone.

In the 1960's, Conroy [20] investigated a number of correlation functions designed to satisfy the electron-cusp condition. Promising results were obtained, but his forms were complicated expansions entailing a product of powers of a number of two-electron variables in addition to r_{ij} . Later, Carlton [21] proposed a simpler form, also using auxiliary variables, namely,

$$S = (1 + r_{ij} + t^2 + r_{ij}^2/s)^{1/2}, \quad (8)$$

where $t \equiv r_2 - r_1$ and $s \equiv r_1 + r_2$. The latter variables were introduced by Hylleraas for He [15]. These forms are capable of high accuracy, and have been used recently by Umrigar *et al.* [22] in VMC trial wave functions for two- and four-electron systems. They have achieved excellent results for these systems, though relatively large expansions were required.

The goal of the present effort is to construct S with the correct asymptotic behavior and thereby perhaps achieve a more concise wave function, and concomitantly a local energy function having fewer fluctuations - a condition of particular significance in Monte Carlo calculations. Taking conditions (i)-(iii) as suitable criteria, we note that many functional forms *can* satisfy them. For example, there is the often-used Jastrow-Pade pair correlation factor [5-8, 23]

$$S(r_{ij}) = \exp\left(-\sum_{ij} U_{ij}\right), \quad (9)$$

with a pseudopotential U_{ij} given by

$$-U_{ij} = ar_{ij}/(1 + br_{ij}), \quad (10a)$$

and its quadratic extension [24],

$$-U_{ij} = \frac{a_1 r_{ij} + a_2 r_{ij}^2}{1 + b_1 r_{ij} + b_2 r_{ij}^2}. \quad (10b)$$

To satisfy the cusp condition (i), a in (10a) or a_1 in (10b) must be the constant a of Eq. (2). Handy [14] considered a further extension wherein

$$-U_{ij} = \frac{1}{2}[r_{ij}/(1 + b_1 r_{ij})] + \sum_k D_k G_k(r_i, r_j) + \sum_p d_p [g_p(r_i) + g_p(r_j)], \quad (11)$$

in which $g_p(r_i) = \bar{r}_i^p$, and $G_k(r_i, r_j)$ is an expansion in powers of u , t , and s , where

$$u^n \equiv (\bar{r}_i \cdot \bar{r}_j)^n \quad (12a)$$

$$t^n \equiv (\bar{r}_i \bar{r}_j)^n \quad (12b)$$

$$s^n \equiv \bar{r}_i^n + \bar{r}_j^n \quad (12c)$$

and

$$\bar{r}_i \equiv r_i / (1 + b_2 r_i). \quad (12d)$$

The use of the variable \bar{r}_i insures the desired behavior as $r_{ij} \rightarrow \infty$; furthermore, the cusp condition is satisfied (though only for unlike spins in Eq. (11)). Handy used a 19-term expansion of G_k in a study of Be. Using the transcorrelated method [25], a non-variational approach, he obtained 88% of the correlation energy. Unfortunately, a variational (Monte Carlo) calculation [4b] with the same wave function obtained none of the correlation energy. Though Handy's form may be useful if properly optimized, it appears to have too many parameters to be broadly applicable. In fact, the quadratic Jastrow-Pade form discussed above (cf., Eq. (10b)) is already difficult to optimize. In addition, care must be taken to ensure these functions are monotonic. The following quadratic pseudopotential partially addresses these concerns,

$$-U_{ij} = \frac{ar_{ij}}{1 + br_{ij}} + \beta \left(\frac{ar_{ij}}{1 + br_{ij}} \right)^2. \quad (13)$$

To a certain extent the parameter b is responsible for the correlation range and β governs the strength of the correlation. However, the roles of b and β are not independent. For example, $(b = 2.2, \beta = 2)$ and $(b = 1.9, \beta = 1)$ give almost identical curves. Use of large β provides some improvement in this regard, although (13) has led to only slight improvement in the variational energy [26] relative to the simpler one-parameter form Eq. (10a).

In our attempt to construct improved correlation functions we considered three factors. First, how strong is the correlation? We can quantify this by the difference in $S(r_{ij})$ between $r_{ij} \rightarrow 0$ and $r_{ij} \rightarrow \infty$. Second, how long is the range of the correlation? We can adjust this by controlling how rapidly $S(r_{ij})$ approaches its asymptotic ($r_{ij} \rightarrow \infty$) constant value. Third, what is the functional form or shape of the curve $S(r_{ij})$? Is it linear, concave, or convex? As a minimum, one requires $\partial S / \partial r_{ij} \geq 0$ to ensure that the correlation between two electrons is repulsive.

For arbitrary S we define a pseudopotential $U \equiv -\ln S$ (cf. Eq. (9)). The corresponding pseudoforce $F_{ij} = -\partial U / \partial r_{ij}$ should be repulsive to physically keep electrons apart. If we rewrite F_{ij} as $F_{ij} = (1/S) \partial S / \partial r_{ij}$ we see that indeed one wants $\partial S / \partial r_{ij} \geq 0$. Furthermore, for $r_{ij} = 0$ the cusp condition sets the pseudoforce between two electrons at the value a (Eq. (2)). Also, F_{ij} should monotonically decrease as $r_{ij} \rightarrow \infty$. Specifically, with this interpretation of F_{ij} , one expects that $F_{ij} \rightarrow 0$ as $r_{ij} \rightarrow \infty$, and the only flexibility in choosing F_{ij} is how rapidly it drops to zero.

Let us consider how two electrons interact. Primarily, each responds to the Coulomb potential of the other; however, the presence of other electrons screens this two-particle interaction. In this case, the effective potential decays faster than that of a bare charge. Such a screened potential has the form

$$V(r) = \frac{b}{r} \exp(-r/\lambda_D) \quad (14)$$

where b is a positive constant, r is the distance between the two particles, and λ_D is the Debye screening length. Generally, the higher the density of charged particles, the smaller is the Debye length. Making use of the idea that a pair-product wave function can be expressed as an exponential of the negative of a pseudopotential (see, e.g. Eq. (9)), a natural form for $S(r_{ij})$ might be

$$S(r_{ij}) = \exp \left\{ -\frac{b}{r_{ij}} \exp(-r_{ij}/\lambda_D) \right\}. \quad (15)$$

This form, however, fails the cusp condition. Nevertheless, the simple modification

$$S(r_{ij}) = \exp \{-b \exp(-r_{ij}/\lambda_D)\} \quad (16a)$$

satisfies all the necessary conditions when $\lambda_D = b/a$, where a is defined following Eq. (2). This will be one of the forms we shall consider. A second form is obtained by noting that $\lambda_D > 0$, and thus for $b < 1$, $\exp(-r_{ij}/\lambda_D)$ will be small. In that case, the form (16a) may be expanded, and gives

$$S(r_{ij}) = 1 - b \exp(-r_{ij}/\lambda_D). \quad (16b)$$

In this form the cusp condition is satisfied for $\lambda_D = b/a(1-b)$. This function is reminiscent of Eq. (5) restricted to $\mu = 0$ with $\alpha = 1/\lambda_D$. It was previously considered by Hartree and Ingman [27] who chose it on physical grounds. In Eqs. (16a) and (16b) the variational parameters b and λ_D have physical meaning that is easily described: λ_D is a measure of the correlation range and b is a measure of its strength. However, as noted, to satisfy the cusp condition these parameters can not be chosen independently. Thus constrained, increasing b increases both the range and strength of the correlation in both forms. In fact, (16a) and (16b) differ only in the intermediate r_{ij} domain where (16a) is more repulsive. However, the repulsion should not have too long a range. Thus S should converge rapidly to unity when $r_{ij} \sim \rho$ (where ρ is a molecular distance scale).

In order to adjust the range and strength of the correlation *separately*, we consider the forms

$$S(r_{ij}) = \exp \{-b \exp(-r_{ij}/2b - r_{ij}^2/c)\}, \quad (17a)$$

and

$$S(r_{ij}) = 1 - b \exp \{-(1-b)r_{ij}/2b - r_{ij}^2/c\}, \quad (17b)$$

where b and c are independent. In (17a) and (17b), b essentially governs the strength and c the range of the correlation. For suitable c , $S(r_{ij})$ can be made to converge rapidly to unity at large r_{ij} . This gives (17) additional flexibility. Further flexibility can be introduced in (17) by allowing an arbitrary power n instead of the quadratic term. Adjusting n permits variation of the range at fixed strength without sacrificing the initial ($r_{ij} \sim 0$) repulsive pseudoforce F_{ij} .

In each of these forms, F_{ij} decays as $r_{ij} \rightarrow \infty$. On the other hand, the Hylleraas form (3) maintains maximum repulsion at all r_{ij} , i.e., F_{ij} remains constant. Since we expect F_{ij} to vanish at sufficiently large r_{ij} , we have attempted using this form with a cut-off at $r_{ij} = \Lambda$, with Λ on the scale of the molecular system. Our calculations show that this form is substantially worse than any of the forms we have discussed above, i.e. Eqs. (10), (16) and (17), although it is better than no correlation function at all. Obviously, a physically motivated pseudoforce should not drop abruptly to zero. On the other hand, F_{ij} should also not remain constant. The linear form (4) with $\alpha = a$ is thus more reasonable, because the force decays as r_{ij} increase, though relative to the other forms we propose it decays too slowly. We have performed VMC calculations of H_2 using (4) (cf. Table 2). The results confirm that this form is superior to $S(r_{ij}) = \exp(ar_{ij})$, though poorer than (10), and (16)–(17).

Table 1. Basis sets used in this study. The Slater determinants of molecular orbitals (MO's) are constructed from linear combinations of the Slater type orbitals (STO's) presented here. The orbital exponents (ζ) and MO coefficients are also listed

Molecule	Basis set	STO	ζ	MO coefficients		
				ψ_1	ψ_2	ψ_3
H_2	$\Phi_{H_2}^{(1)}$	1s	1.285	1.0		
	$\Phi_{H_2}^{(2)}$	1s ₁	1.64	0.0662849		
		1s ₂	1.12	0.4741826		
		2p _z	2.00	0.0250578		
	$\Phi_{H_2}^{(3)}$	1s	1.19	0.48610		
1s _{Bond}		1.19	0.11089			
LiH	Φ_{LiH}	1s _{1,Li}	2.521	0.91404	-0.16422	
		1a _{2,Li}	4.699	0.09375	0.00957	
		2s _{Li}	0.797	0.00737	0.25797	
		2p _{z1,Li}	0.737	-0.01061	-0.12394	
		2p _{z2,Li}	1.200	0.02020	-0.06485	
		1s _{1,H}	0.888	0.00367	0.69595	
		1s _{2,H}	1.566	0.00212	0.06224	
		2p _{z,H}	1.376	0.00617	0.02057	
Li_2	Φ_{Li_2}	1s _a	2.69	1.0	1.0	0
		1s _b	2.69	1.0	-1.0	0
		2s _a	0.694	0	0	1.0
		2s _b	0.694	0	0	1.0

Table 2. Comparison of total ground-state energies of H_2 obtained with variational and fixed-node QMC using various correlation functions. (Hartree-Fock energy = -1.1336 ; Exact energy = -1.17447) Energies are in hartrees

Basis set	e-e correlation function	e-n correlation function	Variational		Fixed-node	
			Energy	%ce	Energy	%ce
$\Phi_{H_2}^{(1)}$	—	—	-1.118	<0	—	—
	exp ^a	—	-1.134 (3)	0 (8)	—	—
	linear ^b	—	-1.148 (1)	35 (3)	—	—
	linear ^b	$J-P^{r,s}$	-1.154 (2)	50 (5)	—	—
	$J-P^{c,d}$	—	-1.1566 (15)	56 (4)	-1.173 (3)	96 (8)
	$QJ-P^{e,f}$	—	-1.1569 (6)	57 (1)	-1.174 (4)	99 (9)
	exp exp ^{g,h}	—	-1.1579 (6)	59 (2)	-1.172 (4)	94 (10)
	$(1-\exp)^{i,j}$	—	-1.1581 (14)	60 (3)	-1.175 (3)	101 (8)
	$Q \exp \exp^{k,l}$	—	-1.1581 (9)	60 (2)	-1.175 (2)	101 (5)
$Q (1-\exp)^{m,n}$	—	-1.1583 (4)	60 (1)	-1.174 (2)	99 (5)	
$\Phi_{H_2}^{(2)}$	—	—	-1.134 (1)	0 (3)	—	—
	$J-P^{e,a}$	—	-1.1587 (5)	61 (1)	-1.1735 (26)	98 (6)
	$J-P^{c,o}$	$J-P^{r,t}$	-1.1652 (9)	77 (2)	-1.1729 (14)	96 (3)
	$(1-\exp)^{i,p}$	—	-1.1595 (7)	63 (2)	-1.1748 (20)	101 (5)
	$(1-\exp)^{i,p}$	$J-P^{r,t}$	-1.1662 (9)	80 (2)	-1.1744 (16)	100 (4)
$\Phi_{H_2}^{(3)}$	—	—	-1.129 (3)	<0	—	—
	$J-P^{e,o}$	$J-P^{r,u}$	-1.165 (1)	77 (2)	-1.174 (3)	99 (7)
	$(1-\exp)^{i,q}$	$J-P^{r,u}$	-1.1657 (5)	79 (1)	-1.176 (2)	104 (5)

^a $e^{\alpha r}$, Eq. (3)

^b $1 + \alpha r$, Eq. (4)

^c Jastrow-Pade form, Eqs. (9), (10a)

^d $b = 0.35$

^e Quadratic Jastrow-Pade, Eqs. (9), (10b)

^f $b_1 = 0.38$, $a_2 = 0.088$, $b_2 = 0.144$

^g double exponential, Eq. (16a)

^h $b = 0.8$

ⁱ $(1 - \exp)$ form, Eq. (16b)

^j $b = 0.6$

^k Quadratic double exponential, Eq. (17a)

^l $b = 0.8$, $c = 14$

^m Quadratic $(1 - \exp)$, Eq. (17b)

ⁿ $b = 0.55$, $a = 18$

^o $b = 0.5$

^p $b = 0.55$

^q $b = 0.72$

^r Jastrow-Pade form, Eq. (19)

^s $\lambda = 0.1$, $\nu = 1.0$

^t $\lambda = 0.16$, $\nu = 1.0$

^u $\lambda = 0.15$, $\nu = 1.0$

When ϕ is not re-optimized in the presence of S , electron-nuclear (e-n) “correlation” functions often provide considerable additional reduction in the variational energy when used in conjunction with electron-electron correlation functions. The reason is that electron correlation is repulsive, pushing electrons away from each other, and thus on average pushing them too far away from the nuclei. (This is particularly true for the core electrons in large- Z atoms.) Because ϕ is obtained from a mean-field calculation in which the charge radius (a “global” or average property) is roughly correct, the introduction of an electron correlation function $S(r_{ij})$ without corresponding adjustment to ϕ incorrectly expands the electron cloud, thereby increasing the charge radius. Adding an electron-nuclear “correlation” factor in effect reoptimizes ϕ globally. Our simulations show the importance of the e-n term in energy and variance reduction. Only for H_2 have we found the situation not so critical, because there the two electrons can both find space

near the nucleus and yet avoid each other. For the e-n term one can use a form similar to (16a), namely

$$S(r_{i\alpha}) = \exp \{ B \exp (r_{i\alpha} / \Lambda) \} \quad (18)$$

or a Jastrow-Pade form

$$S(r_{i\alpha}) = \exp \left(- \frac{\lambda r_{i\alpha}}{1 + \nu r_{i\alpha}} \right). \quad (19)$$

In (19), ν should be large enough to make $S(r_{i\alpha})$ saturate rapidly at large $r_{i\alpha}$, i.e., the range of the compensating attractive force must also be short.

3. Additional correlation effects

The above discussion has been based on the assumption that electron correlation is functionally the same everywhere in space, i.e. independent of the location of the electron pair. However, as alluded to earlier, the correlation may change as a function of the surrounding charge density, since the Coulomb screening varies. Thus, we can reasonably suppose that electron correlation depends not only on the separation of two electrons, but also on the location of the electron pair.

One way of introducing such many-body effects is by making the correlation function, S , dependent on the density ρ . A form which does this was introduced by Colle and Salvetti (CS) [28], who used

$$S = \prod_{i>j} [1 - \phi(r_i, r_j)] \quad (20)$$

where

$$\phi(r_i, r_j) = \exp(-\beta^2 r_{ij}^2) [1 - \Phi(R)(1 + ar_{ij})] \quad (21)$$

with $R \equiv |\mathbf{r}_i + \mathbf{r}_j|/2$, $\Phi(R) \equiv \pi^{1/2} \beta(R) / (1 + \pi^{1/2} \beta(R))$, and $\beta(R) \equiv \alpha \rho^{1/3}(R)$. CS choose $a = 0.5$ a.u. to satisfy the cusp condition for unlike spins. Using perturbation theory with a trial wave function containing this correlation factor, CS obtained 98% of the correlation energy of Be. Again, a variational (Monte Carlo) calculation [4b] with the same trial wave function showed this to be an artifact - it gave only 3% of the correlation energy. In another variational study of the CS factor [29], good results were obtained for He (81% of the correlation energy) after optimization of the parameter α , though a simple Jastrow factor proved better for Be. However, it was noted that results were strongly dependent on α , and that the poor results obtained with the CS form in [4b] are probably attributable to using a non-optimum value for α . Overall, the CS form has proved to have some merit, but to be less satisfactory and more complex than a Jastrow factor. However, a density dependence in the correlation factor remains a reasonable goal. For this reason it is perhaps better to introduce a density dependence into the Jastrow form, or better yet, into (16) and (17).

In (16a) and (16b), for example, b is taken as a constant for a particular molecule. Alternatively, by making b a function of the electron density through the location of the electron pairs, one in effect produces a many-body correlation. In order to test such a many-body term we have performed calculations on Li_2 using two

Table 3. Comparison of total ground-state energies of LiH obtained with variational and fixed-node QMC using various correlation functions. (Hartree-Fock energy = -7.987; Exact energy = -8.070.) More precise fixed-node calculations of LiH have been performed in [31]. Energies are in hartrees

Basis set	e-e correlation function	e-n correlation function	Variational		Fixed-node	
			Energy	%ce	Energy	%ce
Φ_{LiH}	$J - P^{a,b}$	$J - P^{g,h}$	-8.035 (2)	58 (2)	-8.069 (1)	99 (1)
	$(1 - \exp)^{c,d}$	$J - P^{g,i}$	-8.055 (3)	82 (3)	-8.067 (3)	96 (3)
	$Q (1 - \exp)^{e,f}$	$J - P^{g,j}$	-8.056 (3)	83 (3)	-8.071 (2)	101 (2)
	$Q \exp \exp^{k,l}$	$J - P^{g,i}$	-8.055 (2)	82 (2)	-8.072 (2)	102 (2)

^a Jastrow-Pade form, Eqs. (9), (10a)

^b $b = 1.0$

^c $(1 - \exp)$ form, Eq. (16b)

^d $b = 0.37$

^e Quadratic $(1 - \exp)$ form, Eq. (17b)

^f $b = 0.38, c = 3.33$

^g Jastrow-Pade form Eq. (19)

^h $\lambda_{\text{Li}} = 0.031, \lambda_{\text{H}} = 0.103, \nu_{\text{Li}} = \nu_{\text{H}} = 0.5$

ⁱ $\lambda_{\text{Li}} = 0.30, \lambda_{\text{H}} = 0.10, \nu_{\text{Li}} = \nu_{\text{H}} = 0.8$

^j $\lambda_{\text{Li}} = 0.33, \lambda_{\text{H}} = 0.10, \nu_{\text{Li}} = \nu_{\text{H}} = 0.8$

^k Quadratic double exponential form Eq. (17a)

^l $b = 0.48, c = 3.33$

forms for b . For the first one space is divided into two parts: a sphere of radius η whose origin is the mid-point of the two nuclei, and the rest of space. The value of b switches smoothly from b_2 inside the sphere to b_1 outside. Explicitly, b is the following function of the rms distance r_0 of the electron pair from the origin (see Fig. 1):

$$b(r_0) = b_1 + N(b_2 - b_1)[e^{\alpha(r_0^2 - \eta^2)} + 1]^{-1}, \quad (22)$$

where $N = e^{-\alpha\eta^2} + 1$, and $r_0^2 = r_i^2 + r_j^2$. The “diffuseness” and the location of the boundary between the two regions are controlled respectively by α and η .

Calculations performed using this correlation function lead to lower variational energies than with a fixed value of b (see Table 4, line 4; compare with line 2).

Table 4. Comparison of total ground-state energies of Li₂ obtained with variational and fixed-node QMC using various correlation functions. (Hartree-Fock energy = -14.872; Exact energy = -14.994 [32].) Energies are in hartrees

Basis set	e-e correlation function	e-n correlation function	Variational		Fixed-node	
			Energy	%ce	Energy	%ce
Φ_{Li_2}	$J - P^{a,b}$	$J - P^{k,l}$	-14.911 (2)	32 (2)	-14.984 (3)	92 (3)
	$(1 - \exp)^{c,d}$	$J - P^{k,m}$	-14.939 (2)	55 (1)	-14.983 (3)	91 (2)
	$Q (1 - \exp)^{e,f}$	$J - P^{k,n}$	-14.939 (5)	55 (4)	-14.989 (5)	96 (4)
	$D^{(1)} (1 - \exp)^{g,h}$	$J - P^{k,o}$	-14.943 (2)	58 (1)	-14.985 (3)	93 (2)
	$D^{(2)} (1 - \exp)^{g,i,j}$	$J - P^{k,m}$	-14.941 (1)	57 (1)	-14.987 (3)	94 (2)

^a Jastrow-Pade, Eqs. (9), (10a)

^b $b = 0.5$

^c $(1 - \exp)$ form, Eq. (16b)

^d $b = 0.36$

^e Quadratic $(1 - \exp)$ form, Eq. (17b)

^f $b = 0.35, c = 6.5$

^g density dependence through Eq. (22)

^h $\eta = 1.5, b_1 = 0.38, b_2 = 0.26, \alpha = 4.0$

ⁱ Density dependence through Eq. (23)

^j $b = 0.38, c = 0.38, d = 0.60$

^k Jastrow-Pade form, Eq. (19)

^l $\lambda = 0.3, \nu = 0.5$

^m $\lambda = 0.3, \nu = 0.8$

ⁿ $\lambda = 0.25, \nu = 0.8$

^o $\lambda = 0.28, \nu = 0.8$

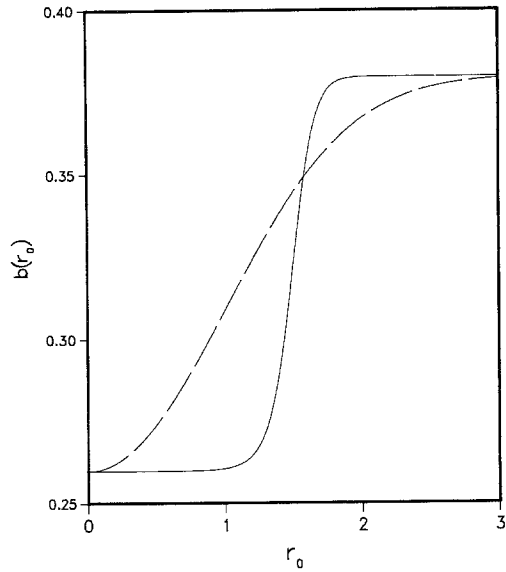


Fig. 1. Position-dependent correlation parameter $b(r_0)$. The *solid line* is Eq. (22) while the *dashed* one is Eq. (23)

Even though this model is crude, it demonstrates that the location of the electron pair influences the degree of correlation. One might argue that this results simply from the addition of more variational parameters. However, the degree to which a parameter lowers the energy reflects the underlying physics. In this case it indicates that to a certain extent the correlation does depend on the charge density.

Another form with variable b was also constructed. It has one less variational parameter than (22), and thus the diffuseness and the crossover point cannot be separately controlled. This form is

$$b(r_0) = \hat{b} \exp[-c \exp(-dr_0^2)]. \quad (23)$$

For a comparison of these two forms see Fig. 1. Results obtained using (23) show a lowering of the variational energy similar to (22) (cf. Table 4).

A form that contains *explicit* density dependence, might be superior to those proposed above. For example, such a form may have b vary as

$$b(r_0) = b_0 \exp(-d\rho^\lambda) \quad (24)$$

with $\rho(r_0)$ calculated from the SCF part of the trial wave function, i.e. $\rho = |\phi|^2$; λ would be empirically determined.

4. Results and discussion

The variational energy obtained with the wave function of Eq. (1) provides a good criterion for judging the quality of a correlation function, especially when

the function ϕ is held fixed. A better correlation function should result in a lower variational energy, once its parameters are optimized. Another related indicator of the quality of a wave function [9] is the smallness of the statistical error for a given amount of sampling in the QMC method. The variational energy, however, gives a clearer picture of the quality of the correlation function, because the variance itself – particularly in QMC calculations – usually has a considerable statistical uncertainty associated with it.

To construct ϕ , molecular orbitals (MO's) ψ_k were formed from linear combinations of Slater-type orbitals, and were used to form a Slater determinant with the symmetry of the ground state. The MO linear coefficients were optimized using the SCF method. The basis sets used in the present calculations are listed in Table 1. The full trial function has the form of (1) – a product of an SCF part and a correlation function. In the correlation function we have used $a = 0.5$ a.u. throughout, on the assumption that the electron–electron cusp for unlike spins is the more important to satisfy. Little difference has been found numerically when like spins are treated separately – with $a = 0.25$ a.u. [8, 30]. Tables 2–4 present the results of our calculations. Some comments on our findings follow.

4.1. Hydrogen molecule

We have used three different basis sets for H_2 : $\phi_{H_2}^{(1)}$ (single zeta), $\phi_{H_2}^{(2)}$ (double zeta + polarization), and $\phi_{H_2}^{(3)}$ (single zeta + bond function). For basis set $\phi_{H_2}^{(1)}$ we investigated many forms of correlation function (see Table 2).

For $\phi_{H_2}^{(1)}$ we note that the variational energy for the basis set without a correlation function is approximately -1.118 h. The correlation functions (3) and (4) lower the energy to -1.134 h and -1.148 h, respectively, without an e–n correlation

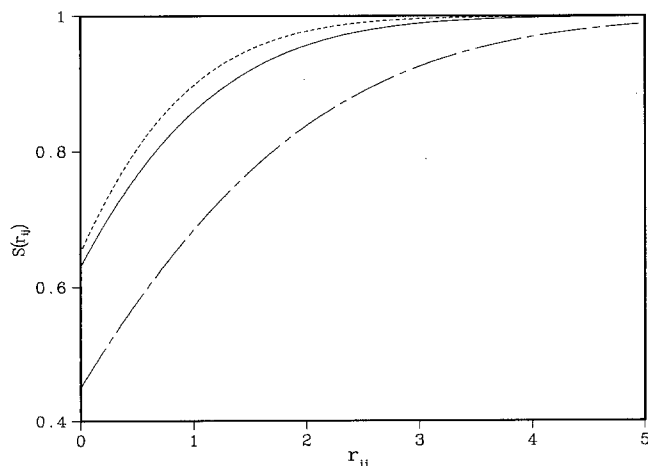


Fig. 2. Comparison of the optimized correlation functions, for H_2 (---), LiH (—) and Li_2 (-.-). The form used is Eq. (17b)

factor. Adding an e-n factor lowers the energy further to -1.154 h. On the other hand, using the physically motivated functions of (16) and (17) or the Jastrow functions (10) (even *without* e-n factors) gives variational energies lower than -1.154 h. However, we found that with this basis set, combining an e-n factor with these correlation functions did *not* lead to significant variational energy lowering. Results obtained using (16) and (17) were improved over those using (10), though the difference was smaller than that obtained comparing (3) to (4). The poorer behavior of the Jastrow-Pade functions relative to those proposed here probably results from their weaker and longer range pseudo-force.

Unlike $\phi_{H_2}^{(1)}$, calculations using basis sets $\phi_{H_2}^{(2)}$ and $\phi_{H_2}^{(3)}$ show lowering of the variational energy with inclusion of an e-n factor. This is likely due to the polarization component (or bond function in the case of $\phi_{H_2}^{(3)}$) which enriches electron density in the bonding region. Though this improves the charge distribution over $\phi_{H_2}^{(1)}$, this distribution is modified by the e-e correlation function, because the strong electron repulsion tends to offset this higher density in the bonding region. The pseudo-force resulting from the e-n factors compensates by pulling the electrons toward the nuclei, effectively again increasing the density in the bonding region. On the other hand, for basis set $\phi_{H_2}^{(1)}$ the density in the bonding region is lower initially, and so the electron-electron correlation factor appears to cause little change in the density for the e-n factor to correct.

4.2. Lithium diatomics

As shown in Tables 3 and 4, function (17b) leads to lower variational and fixed-node energies than the Jastrow-Pade function. As expected, for these slightly larger molecules the range of electron correlation is shortened due to screening. As the molecule becomes larger the strength of the pair correlation also becomes weaker (see Fig. 2). In addition, the electron-nuclear factor becomes more important for larger Z atoms. The denser electron charge cloud near atomic centers - in the absence of an attractive e-n pseudo-force - becomes overly extended because of the e-e factor.

Calculations for Li_2 using the implicit density dependence of (22) and (23) are reported in Table 4. These variational results are lower than those obtained with (10), (16) or (17) alone. From these results we conclude that the location of electron pairs does play a role in their correlation. When we ignore this effect, only average correlation over the space is considered. In effect, Eqs. (22) and (23) introduce many-body effects into the correlation function. Our calculations using variable b take about 20% more computer time (for the same number of Monte Carlo iterations) than for fixed b . To compute the cost effectiveness, Ceperley [9] gives the following expression connecting the variational energy with the minimum variance of the fixed-node energy for a trial function

$$\sigma^2 \propto E_v - E_0. \quad (26)$$

Here E_v is the variational energy of the trial function, and E_0 is the exact energy. Noting that $E_0 = -14.994$ h, and that $E_v = -14.939$ h with (16b), while combined

with (22) $E_v = -14.943$ h, it is expected that (22) should reduce the fixed-node variance, and hence computing time, by about 10%. Since this is at a cost of roughly 20% more computer time consumed evaluating a more complex S and its derivative, together with optimization of parameters for (22), the benefit of this function in a fixed-node calculation appears marginal. In VMC, however, where (22) lowers the energy, a benefit is achieved. Improvements modeled on (22)–(24) may lead to further energy lowering and variance reduction for VMC and QMC.

5. Conclusions

It is reasonable to suppose that when two electrons are close, they feel a strong correlation “force,” and when their separation approaches the order of the size of the molecule under consideration, the “force” should quickly decay to zero. The correlation functions considered here have this behavior. Figure 3 compares the Jastrow-Pade form (10a) (properly normalized) to the double exponential form of (16a). One sees that the double exponential form has a more rapid cut off at large r_{ij} , and meets the above physical condition better than the Jastrow-Pade form. In the two parameter forms, the additional quadratic factor allows for the independent tuning of the range and strength of the correlation, so that in general these are more flexible. Unlike the quadratic Jastrow-Pade factors, however, the roles of the parameters in (17a) and (17b) are much clearer. The parameter b fixes $S(r_{ij}=0)$ and controls the “depth” of the pseudopotential well – while c determines the range of the pseudopotential. Our calculations show, however, that the parameter c generally does little to improve results over the one-parameter forms. Since the one-parameter forms are much easier to optimize and use less computer time to evaluate, (16a) and (16b) are satisfactory for many applications.

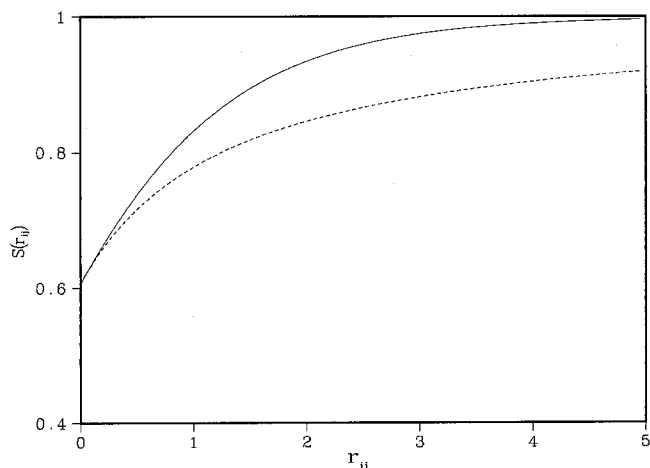


Fig. 3. Comparison of Jastrow-Pade form, S_1 (---), with the double exponential form S_2 (—), for fixed correlation strength

On the other hand, (16a) and (17a) are especially easy to implement, as their derivatives are particularly simple.

In conclusion, it is clear that adding even simple electron–electron correlation factors can improve the variational energy significantly. Using more complex forms often leads to only modest improvement in variational energies but carries considerably greater cpu-time requirements. This indicates the advantages of using simple, compact functional forms for S for use in VMC. For QMC, using the product form (1) and the forms of S we have discussed, the trial wave function has the same nodes with or without correlation. This means that fixed-node energies are independent of S , and that the role of S in QMC is solely for variance reduction. Thus a simple form is especially desirable. Our goal here was to test forms of S that are compact, and to ascertain their efficacy for describing electron correlation.

6. Summary

In this paper we have introduced a set of related forms for the electron correlation function which, based on Monte Carlo study, appear to be superior to the usual Jastrow–Pade forms. We have discussed the behavior of the various electron correlation functions, their ease of optimization, their interplay with electron–nuclear factors, and the characteristics of the associated pseudoforce. Monte Carlo calculations show the relative quality of these functions. Finally, we have presented an electron correlation function whose correlation strength changes with position, and implicitly with the electron density. This form, which implicitly contains many-body correlation effects, lowers the variational energy. Thus we conclude that such many-body effects play a role in correctly describing the molecular wave function.

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