Atomic Wave Function Forms

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ABSTRACT: Using variational Monte Carlo, we compare the features of 118 trial wave function forms for selected ground and excited states of helium, lithium, and beryllium in order to determine which characteristics give the most rapid convergence toward the exact nonrelativistic energy. We find that fully antisymmetric functions are more accurate than are those which use determinants, that exponential functions are more accurate than are linear function, and that the Padé function is anomalously accurate for the two-electron atom. We also find that the asymptotic and nodal behavior of the atomic wave function is best described by a minimal set of functions. © 1997 John Wiley & Sons, Inc. Int J Quant Chem **63**: 1001–1022, 1997

Introduction

Variational Monte Carlo is a method of computing the total energy

$$\langle H \rangle = \sum_i [\Psi_i H \Psi_i / w_i] \Big/ \sum_i [\Psi_i^2 / w_i] \qquad (1)$$

and its variance (i.e., statistical error)

$$\sigma^2 = \sum_i \left[(H\Psi_i - E_{in}\Psi_i)^2 \Psi_i^2 / w_i^2 \right] \Big/ \left\{ \sum_i [\Psi_i^2 / w_i] \right\}^2 \qquad (2)$$

using Monte Carlo integration [1–17]. Here, H is the Hamiltonian, $\Psi_i = \Psi_t(\mathbf{x}_i)$ is the value of the trial wave function at the Monte Carlo integration point $\mathbf{x}_i$, and $w_i = w(\mathbf{x}_i)$ is the relative probability of choosing this point (usually referred to as a configuration). The constant E_{in} is fixed at a value close to the desired state in order to start the optimization in the proper region. The exact wave function is known to give both the lowest value of $\langle H \rangle$ and a zero variance. If the adjustable parameters in the trial wave function are optimized so as to minimize the energy, an instability often occurs. This happens when a set of parameters causes $\langle H \rangle$ to be estimated a few sigma too low. Although such parameters will produce a large variance, they are favored by the minimization. This problem can be avoided only by using a very large number of configurations during the optimization of the wave function so as to distinguish between those wave functions for which $\langle H \rangle$ is truly low and those which are merely estimated to be low. In contrast, variance minimization favors those wave functions which have a constant local energy. Parameter values which do not produce this property will be eliminated by the optimization process. As a result, only a small fixed set of configurations is needed to accurately determine the variance.

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Previous studies have shown that the rate of convergence of a variational calculation can be tremendously accelerated by using basis functions which satisfy the two-electron cusp condition and which have the correct asymptotic behavior [18–24]. Unfortunately, the integrals of such functions can rarely be evaluated analytically. Because our method uses Monte Carlo integration, we can easily build into the trial wave function many features which will accelerate convergence. Although, in principle, this flexibility leads to an enormous number of possible forms, in practice, the ideal trial wave-function form must have a low variance, must add adjustable parameters in a straightforward manner, and must be easy to optimize.

In this article, we examine a variety of trial wave-function forms for the ground and first excited singlet states of helium, the triplet ground state of helium, the ground state of lithium, and the ground state of beryllium. We use the ratio of the variance and the number of adjustable parameters to determine which forms produce the most rapid convergence. When computed at several values, this quantity enables us to tell whether additional parameters will noticeably lower the variance of a particular wave-function form or if this form has saturated. All our energies and variances are computed using a set of 4000 biased-as-random configurations which were generated specifically for each atom [15]. In those forms which use a Hylleraas or Padé-type function, we add all possible combinations of variables which produce a given excitation level. The excitation level N denotes the sum of the exponents of the variables in each term of the Hylleraas function, e.g., r_{13}^2 and $r_1 r_{23}$ are $N = 2$. Unless otherwise indicated, all values in this article are in atomic units.

Helium Ground State

Table I presents the results of those trial wave-function forms which consist exclusively of a product of one-electron orbitals. These include a determinant which was optimized so as to minimize the total energy [25], a variance-optimized determinant, $\Psi_2 = \phi(r_1)\phi(r_2)$, and a variance-optimized different-orbitals-for-different-spins form, $\Psi_3 = (1 + P_{12})\phi(r_1)\eta(r_2)$. All three forms contain enough adjustable parameters to obtain a saturated result from their respective optimization functionals. Because Ψ_1 is the result of an energy minimization, it is not surprising that this form has the lowest energy and the largest variance. When variance minimization, Eq. (2), is used to optimize the adjustable parameters in Ψ_2 and Ψ_3, the energy of both forms increases by a significant amount while their variance decreases. Even though the energy of Ψ_3 is much higher than that of the Hartree–Fock determinant, its variance is almost a factor of 2 smaller. For this reason, Ψ_3 will turn out to be a better starting point for our next step which is the addition of correlation.

In Table II, the process of including electron correlation begins with a study of wave-function forms which consist of one-electron orbitals multiplied by a function of the interelectronic coordinate, i.e., $g(r_{12})$. When the orbitals from the Hartree–Fock determinant are used, e.g., Ψ_5, the variance drops by a factor of 2.9 compared to Ψ_1 and roughly 69% of the correlation energy is obtained before saturation occurs. Using a variance-optimized determinant, e.g., Ψ_{14}, or a different-orbitals-for-different-spins form, e.g., Ψ_{17}, lowers the variance by an additional factor of 2 and 2.8, respectively. Although we find that the form of

TABLE I
Helium ground-state wave functions: product form.[a]

Form	No. parameters	Energy (au)
$\Psi_1 = \text{det}$	0	$-2.8655059 \pm 0.130e\text{-}1$
$\Psi_2 = \phi(r_1)\phi(r_2)$	5	$-2.7948343 \pm 0.111e\text{-}1$
$\Psi_3 = (1 + P_{12})\phi(r_1)\eta(r_2)$	10	$-2.7617876 \pm 0.858e\text{-}2$
Literature		-2.903724375 [26]

[a] Here, $\text{det} = \phi(r_1)\phi(r_2)$ as computed by Clementi and Roetti [25] using an energy minimization. Elsewhere, $\phi(r_1) = [1 + \Sigma_{k=1}^{4} a_k r_1^k]e^{-\alpha r_1}$ and $\eta(r_2) = [1 + \Sigma_{k=1}^{4} b_k r_2^k]e^{-\beta r_2}$.

TABLE II

Helium ground-state wave functions: product form times function of r_{12}[a]; N is the excitation level.

Form	No. parameters	Energy (au)
$\Psi_4 = \det \exp(\Sigma_{k=0} a_k r_{12}^k)$	1 ($N = 1$)	$-2.8776681 \pm 0.633e\text{-}2$
	2 ($N = 2$)	$-2.8913797 \pm 0.471e\text{-}2$
	3 ($N = 3$)	$-2.8907489 \pm 0.445e\text{-}2$
$\Psi_5 = \det \Sigma_{k=0} a_k r_{12}^k$	1 ($N = 1$)	$-2.8820978 \pm 0.555e\text{-}2$
	2 ($N = 2$)	$-2.8923208 \pm 0.451e\text{-}2$
	3 ($N = 3$)	$-2.8919144 \pm 0.443e\text{-}2$
	Best form with Hartree-Fock determinant	
$\Psi_6 = \det \exp\left(\frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k}\right)$	2 ($N = 1$)	$-2.8911825 \pm 0.448e\text{-}2$
	4 ($N = 3$)	$-2.8916771 \pm 0.446e\text{-}2$
$\Psi_7 = \det \frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k}$	2 ($N = 1$)	$-2.8917250 \pm 0.448e\text{-}2$
	4 ($N = 2$)	$-2.8922225 \pm 0.443e\text{-}2$
$\Psi_8 = \det \exp(-a \exp(-br_{12}))$	2 ($N = 1$)	$-2.8922208 \pm 0.443e\text{-}2$
$\Psi_9 = \det \exp(-ar_{12} \exp(-br_{12}))$	2 ($N = 1$)	$-2.8924062 \pm 0.447e\text{-}2$
$\Psi_{10} = \det(1 + \Sigma_{k=1} a_k e^{-\gamma_k r_{12}})$	2	$-2.8921694 \pm 0.444e\text{-}2$
	4	$-2.8921900 \pm 0.443e\text{-}2$
$\Psi_{11} = \phi(r_1)\phi(r_2)\exp(\Sigma_{k=0} a_k r_{12}^k)$	6 ($N = 1$)	$-2.8894165 \pm 0.426e\text{-}2$
	7 ($N = 2$)	$-2.8963100 \pm 0.254e\text{-}2$
	8 ($N = 3$)	$-2.8979303 \pm 0.237e\text{-}2$
$\Psi_{12} = \phi(r_1)\phi(r_2)\Sigma_{k=0} a_k r_{12}^k$	6 ($N = 1$)	$-2.8948153 \pm 0.307e\text{-}2$
	7 ($N = 2$)	$-2.8979310 \pm 0.231e\text{-}2$
	8 ($N = 3$)	$-2.8981832 \pm 0.230e\text{-}2$
$\Psi_{13} = \phi(r_1)\phi(r_2)\exp\left(\frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k}\right)$	7 ($N = 1$)	$-2.8985944 \pm 0.230e\text{-}2$
	9 ($N = 2$)	$-2.8984142 \pm 0.229e\text{-}2$
$\Psi_{14} = \phi(r_1)\phi(r_2)\left(\frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k}\right)$	7 ($N = 1$)	$-2.8986614 \pm 0.230e\text{-}2$
	9 ($N = 1$)	$-2.8983958 \pm 0.229e\text{-}2$
	Best form with same orbitals	
$\Psi_{15} = (1 + P_{12})\phi(r_1)\eta(r_2)\exp(\Sigma_{k=0} a_k r_{12}^k)$	11 ($N = 1$)	$-2.8963143 \pm 0.368e\text{-}2$
	12 ($N = 2$)	$-2.8992829 \pm 0.210e\text{-}2$
	13 ($N = 3$)	$-2.9030682 \pm 0.173e\text{-}2$
$\Psi_{16} = (1 + P_{12})\phi(r_1)\eta(r_2)\Sigma_{k=0} a_k r_{12}^k$	11 ($N = 1$)	$-2.9009906 \pm 0.263e\text{-}2$
	12 ($N = 2$)	$-2.9023661 \pm 0.174e\text{-}2$
	13 ($N = 3$)	$-2.9041682 \pm 0.163e\text{-}2$
$\Psi_{17} = (1 + P_{12})\phi(r_1)\eta(r_2)\exp\left(\frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k}\right)$	12 ($N = 1$)	$-2.9038071 \pm 0.161e\text{-}2$
	14 ($N = 2$)	$-2.9043052 \pm 0.159e\text{-}2$
	Best form with different orbitals	

(Continued)

TABLE II
(Continued)

Form	No. parameters	Energy (au)
$\Psi_{18} = (1 + P_{12})\phi(r_1)\eta(r_2)\dfrac{\sum_{k=0} a_k r_{12}^k}{\sum_{k=0} b_k r_{12}^k}$	12 ($N = 1$)	$-2.9038865 \pm 0.161e\text{-}2$
	14 ($N = 2$)	$-2.9043037 \pm 0.159e\text{-}2$
Literature		-2.903724375 [26]

[a] Here, det $= \phi(r_1)\phi(r_2)$ as computed by Clementi and Roetti [25] using an energy minimization. Elsewhere, $\phi(r_1) = [1 + \sum_{k=1}^{4} a_k r_1^k]e^{-\alpha r_1}$ and $\eta(r_2) = [1 + \sum_{k=1}^{4} b_k r_2^k]e^{-\beta r_2}$.

$g(r_{12})$ has relatively little influence on the convergence of the variance, all these forms saturate at about the third excitation level; it should be noted that our best wave-function form in this group, Ψ_{17}, is able to obtain almost 100% of the correlation energy before this occurs.

In Table III, we generalize the wave-function form used above to include electronic coordinates in the correlation function, i.e., $g(r_1, r_2, r_{12})$. This allows some of the restrictions which are imposed by the orbital function, $f(r_1, r_2)$, to be relaxed. Such forms have been examined by a number of earlier studies [5, 7, 8, 12, 27–30]. Our results show that the rapid saturation of the variance which occurred in Tables I and II has been eliminated and that it is now possible to obtain even lower variances and much better energies. When the orbitals from the Hartree–Fock determinant are used, the variance of our best form of this type, Ψ_{21}, is a factor of 23 lower than Ψ_5. Our best variance-optimized determinant form, Ψ_{23}, and best different-orbitals-for-different-spins form, Ψ_{26}, show an even more impressive decrease—a factor of 83 compared to Ψ_{14} and a factor of 49 compared to Ψ_{17}, respectively. When examined as a whole, we find a slight preference for the Padé-like functions over the Hylleraas-like functions as well as a slight preference for the exponential Padé forms over the linear Padé forms. On a per constant basis, we also find that the form $\phi(r_1)\phi(r_2)g(r_1, r_2, r_{12})$ converges more rapidly than does the $\phi(r_1)\eta(r_2)g(r_1, r_2, r_{12})$ form. This somewhat counterintuitive result is due to the eight constants required to saturate both ϕ and η compared to only four constants needed to saturate ϕ alone. These extra four constants are apparently much more effective when placed in the correlation function rather than in the orbital. This suggests that we could obtain even better convergence if we were to examine the form of our orbitals. This is done below.

In Table IV, we make no distinction between the orbital part of the wave function and the correlation function. The wave-function form $\Psi(r_1, r_2, r_{12})$ is parameterized as freely as we could imagine. When compared to the results in Table III, our results show that the best convergence is obtained when each orbital is reduced to a single exponential. This "minimal orbital" set satisfies the boundary conditions and gives the correlation part the maximum flexibility it needs to reproduce the rest of the wave function. In contrast to the wave-function forms in Table III, the forms in this group show an even more pronounced preference for the Padé-like functions over the Hylleraas-like functions and a still slight preference for the exponential Padé forms over the linear Padé forms. The variance of our best form, the exponential Padé Ψ_{43}, is almost a factor of 5 lower than its counterpart in Table III.

In Table IV, we also examine the convergence of some of the more widely used wave-function forms. The form popularized by Drake [31] is based on the use of two Hylleraas expansions in order to more rapidly reproduce the form of the wave function at different length scales. We find that for this system such a form, Ψ_{40}, is not substantially better than the original Hylleraas form, Ψ_{31}. In contrast, a wave function of Slater-type geminals [32, 33], Ψ_{46}, and two of its variants, Ψ_{47} and Ψ_{48}, converge much more rapidly. We found, however, that adding additional fully optimized functions to these wave functions became increasingly difficult. This greatly limits their usefulness. Morgan and co-workers obtained very accurate energies for two-electron atoms using Hylleraas-like expansions containing negative powers and logarithmic terms [26, 34]. The latter are designed to increase convergence by correctly modeling the three-particle cusp [23, 35]. We find that negative powers do not noticeably improve the convergence of our calculations (Ψ_{41} is actually worse than the

TABLE III

Helium ground-state wave functions: product form times a general function of r_1, r_2, and r_{12} [a]; N is the excitation level.[a]

Form	No. parameters	Energy (au)
$\Psi_{19} = \det \sum_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m$	2 ($N = 1$)	$-2.8942232 \pm 0.429e\text{-}2$
	6 ($N = 2$)	$-2.9001721 \pm 0.208e\text{-}2$
	12 ($N = 3$)	$-2.9028168 \pm 0.965e\text{-}3$
	21 ($N = 4$)	$-2.9036992 \pm 0.471e\text{-}3$
$\Psi_{20} = \det \exp\left(\frac{\sum_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}{\sum_{k=0} b_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m} \right)$	4 ($N = 1$)	$-2.8983108 \pm 0.320e\text{-}2$
	12 ($N = 2$)	$-2.9038436 \pm 0.890e\text{-}3$
	24 ($N = 3$)	$-2.9034622 \pm 0.196e\text{-}3$
$\Psi_{21} = \det \frac{\sum_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}{\sum_{k=0} b_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}$	4 ($N = 1$)	$-2.8982490 \pm 0.320e\text{-}2$
	12 ($N = 2$)	$-2.9038469 \pm 0.887e\text{-}3$
	24 ($N = 3$)	$-2.9034624 \pm 0.195e\text{-}3$
	Best form with Hartree-Fock determinant	
$\Psi_{22} = \phi(r_1)\phi(r_2) \sum_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m$	7 ($N = 1$)	$-2.8979704 \pm 0.282e\text{-}2$
	11 ($N = 2$)	$-2.9028438 \pm 0.108e\text{-}2$
	17 ($N = 3$)	$-2.9040016 \pm 0.371e\text{-}3$
	25 ($N = 4$)	$-2.9036601 \pm 0.206e\text{-}3$
$\Psi_{23} = \phi(r_1)\phi(r_2) \exp\left(\frac{\sum_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}{\sum_{k=0} b_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m} \right)$	9 ($N = 1$)	$-2.8978042 \pm 0.226e\text{-}2$
	17 ($N = 2$)	$-2.9037349 \pm 0.201e\text{-}3$
	29 ($N = 3$)	$-2.9037314 \pm 0.275e\text{-}4$
	Best form with same orbitals	
$\Psi_{24} = \phi(r_1)\phi(r_2) \frac{\sum_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}{\sum_{k=0} b_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}$	9 ($N = 1$)	$-2.8977419 \pm 0.226e\text{-}2$
	17 ($N = 2$)	$-2.9038225 \pm 0.208e\text{-}3$
	29 ($N = 3$)	$-2.9037383 \pm 0.209e\text{-}4$
$\Psi_{25} = (1 + P_{12}) \phi(r_1) \eta(r_2) \sum_{k=0} a_k r_1^n r_2^l r_{12}^m$	13 ($N = 1$)	$-2.9003935 \pm 0.224e\text{-}2$
	19 ($N = 2$)	$-2.9041190 \pm 0.767e\text{-}3$
$\Psi_{26} = (1 + P_{12}) \phi(r_1) \eta(r_2) \exp\left(\frac{\sum_{k=0} a_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^l r_{12}^m} \right)$	16 ($N = 1$)	$-2.9035825 \pm 0.278e\text{-}3$
	28 ($N = 2$)	$-2.9037524 \pm 0.322e\text{-}4$
	Best form with different orbitals	
$\Psi_{27} = (1 + P_{12}) \phi(r_1) \eta(r_2) \frac{\sum_{k=0} a_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^l r_{12}^m}$	16 ($N = 1$)	$-2.9036545 \pm 0.352e\text{-}3$
	28 ($N = 2$)	$-2.9037527 \pm 0.457e\text{-}4$
Literature		-2.903724375 [26]

[a] Here, $\det = \phi(r_1)\phi(r_2)$ as computed by Clementi and Roetti [25] using an energy minimization. Elsewhere, $\phi(r_1) = [1 + \sum_{k=1}^{4} a_k r_1^k] e^{-\alpha r_1}$ and $\eta(r_2) = [1 + \sum_{k=1}^{4} b_k r_2^k] e^{-\beta r_2}$.

functionally similar form Ψ_{39}). Similarly, we find that adding logarithmic terms to an exponential Padé, Ψ_{49}, decreased our variance only slightly. This result is probably due to the fact that our calculations have not reached the required level of accuracy needed for the three-particle cusp to play an important role.

In Table V, we examine whether the use of transformed variables can improve our rate of convergence. These variables enable one to separate

TABLE IV
Helium ground-state wave functions: general function in r_1, r_2, and r_{12}; N is the excitation level.

Form	No. parameters	Energy (au)
$\Psi_{28} = \exp(-\alpha(r_1 + r_2))$	1 ($N = 0$)	−2.8522779 ± 0.154e-1
$\Psi_{29} = \exp(\Sigma_{k=0} a_k r_{12}^k - \alpha(r_1 + r_2))$	2 ($N = 1$)	−2.8806861 ± 0.533e-2
	3 ($N = 2$)	−2.8759777 ± 0.493e-2
	4 ($N = 3$)	−2.8797514 ± 0.457e-2
$\Psi_{30} = \Sigma_{k=0} a_k r_{12}^k e^{-\alpha(r_1 + r_2)}$	2 ($N = 1$)	−2.8785526 ± 0.480e-2
	3 ($N = 2$)	−2.8770205 ± 0.474e-2
	4 ($N = 3$)	−2.8823565 ± 0.445e-2
$\Psi_{31} = \Sigma_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m e^{-\alpha(r_1 + r_2)}$	3 ($N = 1$)	−2.8798136 ± 0.468e-2
	7 ($N = 2$)	−2.9030741 ± 0.119e-2
	13 ($N = 3$)	−2.9042841 ± 0.470e-3
	21 ($N = 4$)	−2.9038214 ± 0.212e-3
$\Psi_{32} = \exp\left(\frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k} - \alpha(r_1 + r_2)\right)$	3 ($N = 1$)	−2.8764614 ± 0.473e-2
	5 ($N = 2$)	−2.8816835 ± 0.443e-2
$\Psi_{33} = \exp\left(\frac{\Sigma_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}{\Sigma_{k=0} b_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m} - \alpha(r_1 + r_2)\right)$	5 ($N = 1$)	−2.8822870 ± 0.367e-2
	13 ($N = 2$)	−2.9039788 ± 0.221e-3
	25 ($N = 3$)	−2.9037142 ± 0.392e-4
$\Psi_{34} = \frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k} e^{-\alpha(r_1 + r_2)}$	3 ($N = 1$)	−2.8767865 ± 0.471e-2
	5 ($N = 2$)	−2.8815663 ± 0.444e-2
$\Psi_{35} = \frac{\Sigma_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m}{\Sigma_{k=0} b_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m} e^{-\alpha(r_1 + r_2)}$	5 ($N = 1$)	−2.8822005 ± 0.367e-2
	13 ($N = 2$)	−2.9040320 ± 0.231e-3
	25 ($N = 3$)	−2.9037121 ± 0.369e-4
$\Psi_{36} = (1 + P_{12})\exp(-\alpha r_1 - \beta r_2)$	2 ($N = 0$)	−2.7836668 ± 0.898e-2
$\Psi_{37} = (1 + P_{12})\exp(\Sigma_{k=0} a_k r_{12}^k - \alpha r_1 - \beta r_2)$	3 ($N = 1$)	−2.8974720 ± 0.387e-2
	4 ($N = 2$)	−2.8978520 ± 0.278e-2
	5 ($N = 3$)	−2.8984970 ± 0.241e-2
$\Psi_{38} = (1 + P_{12})\Sigma_{k=0} a_k r_{12}^k e^{-\alpha r_1 - \beta r_2}$	3 ($N = 1$)	−2.8995372 ± 0.294e-2
	4 ($N = 2$)	−2.8991548 ± 0.246e-2
	5 ($N = 3$)	−2.8999454 ± 0.229e-2
$\Psi_{39} = (1 + P_{12})\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m e^{-\alpha r_1 - \beta r_2}$	5 ($N = 1$)	−2.9021813 ± 0.234e-2
	11 ($N = 2$)	−2.9027775 ± 0.883e-3
	21 ($N = 3$)	−2.9041953 ± 0.363e-3
	36 ($N = 4$)	−2.9038038 ± 0.172e-3
	57 ($N = 5$)	−2.9037496 ± 0.796e-4
$\Psi_{40} = (1 + P_{12})[\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m e^{\alpha r_1 - \beta r_2}$	11 ($N = 1$)	−2.9028785 ± 0.206e-2
$+\Sigma_{k=0} \hat{a}_k r_1^n r_2^l r_{12}^m e^{-\hat{\alpha} r_1 - \beta r_2}]$	23 ($N = 2$)	−2.9048122 ± 0.368e-3
	43 ($N = 3$)	−2.9038500 ± 0.104e-3

(Continued)

TABLE IV
(Continued)

Form	No. parameters	Energy (au)
$\Psi_{41} = (1 + P_{12})\Sigma_{k=0} a_k (r_1 + r_2)^n (r_1 - r_2)^l r_{12}^m e^{-\alpha r_1 - \beta r_2}$		
	5 ($N = 1$)	−2.9021811 ± 0.234e-2
	11 ($N = 2$)	−2.9027419 ± 0.884e-3
	15 ($N = 2$, $n = -1$)	−2.9023392 ± 0.640e-3
	20 ($N = 2$, $n = -2$)	−2.9024091 ± 0.578e-3
	26 ($N = 2$, $n = -3$)	−2.9019591 ± 0.522e-3
$\Psi_{42} = (1 + P_{12})\exp\left(\dfrac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k} - \alpha r_1 - \beta r_2 \right)$	4 ($N = 1$)	−2.8996389 ± 0.235e-2
	6 ($N = 2$)	−2.9006769 ± 0.225e-2
$\Psi_{43} = (1 + P_{12})\exp\left(\dfrac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m} - \alpha r_1 - \beta r_2 \right)$	8 ($N = 1$)	−2.9035974 ± 0.408e-3
	20 ($N = 2$)	−2.9037434 ± 0.297e-4
	40 ($N = 3$)	−2.9037228 ± 0.558e-5
	Best form	
$\Psi_{44} = (1 + P_{12})\dfrac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k} e^{-\alpha r_1 - \beta r_2}$	4 ($N = 1$)	−2.8997302 ± 0.234e-2
	6 ($N = 2$)	−2.9006684 ± 0.225e-2
$\Psi_{45} = (1 + P_{12})\dfrac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m} e^{-\alpha r_1 - \beta r_2}$	8 ($N = 1$)	−2.9036625 ± 0.558e-3
	20 ($N = 2$)	−2.9036934 ± 0.380e-4
	40 ($N = 3$)	−2.9037201 ± 0.595e-5
$\Psi_{46} = (1 + P_{12})\Sigma_{k=1} a_k e^{-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}}$	8	−2.9016091 ± 0.123e-2
	16	−2.9037691 ± 0.426e-3
	24	−2.9036837 ± 0.151e-3
	32	−2.9037805 ± 0.603e-4
$\Psi_{47} = (1 + P_{12})\Sigma_{k=1} a_k (1 + \gamma_k r_{12}) e^{-\alpha_k r_1 - \beta_k r_2}$	8	−2.9020742 ± 0.201e-2
	16	−2.9032493 ± 0.152e-2
	24	−2.9036084 ± 0.147e-2
$\Psi_{48} = (1 + P_{12})\Sigma_{k=0} a_k (1 + \gamma_k r_{12} + \delta_k r_{12}^2) e^{-\alpha_k r_1 - \beta_k r_2}$	10	−2.9016281 ± 0.122e-2
	20	−2.9043933 ± 0.454e-3
	30	−2.9040674 ± 0.290e-3
$\Psi_{49} = (1 + P_{12})\exp\left(\dfrac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m} + c(r_1^2 + r_2^2 - r_{12}^2)\ln[r_1^2 + r_2^2] - \alpha r_1 - \beta r_2 \right)$	21 ($N = 2$)	−2.9037428 ± 0.297e-4
	41 ($N = 3$)	−2.9037235 ± 0.556e-5
Literature		−2.903724375 [26]

two major demands on the trial wave function—its need to satisfy the asymptotic boundary conditions of the system and its need to fill space in the appropriate regions. Transformed variables also allow us to consider some new wave-function forms, e.g., e^{hyll}, which might otherwise violate the boundary conditions at $r \to \infty$. For helium, one common transformation is $q_x = r_x/(1 + b_x r_x)$, where $x = 1, 2$, or 12. The value of b_x can be fixed at a constant, e.g., 1.0 as in [12], optimized as a

TABLE V
Helium ground-state wave functions: general form in transformed coordinates[a]; *N* is the excitation level.

Form	No. parameters	Energy (au)
$\Psi_{50} = \det \exp(\Sigma_{k=0} a_k (q_1 + q_2)^n (q_1 - q_2)^l q_{12}^m)$	3 ($N = 1$)	$-2.8989579 \pm 0.344e\text{-}2$
	7 ($N = 2$)	$-2.9022706 \pm 0.162e\text{-}2$
	13 ($N = 3$)	$-2.9039398 \pm 0.580e\text{-}3$
	22 ($N = 4$)	$-2.9035629 \pm 0.165e\text{-}3$
$\Psi_{51} = \phi(r_1)\phi(r_2)\exp(\Sigma_{k=0} a_k (q_1 + q_2)^n (q_1 - q_2)^l q_{12}^m)$	8 ($N = 1$)	$-2.8995703 \pm 0.230e\text{-}2$
	11 ($N = 2$)	$-2.9024948 \pm 0.161e\text{-}2$
$\Psi_{52} = \exp(\Sigma_{k=0} a_k (q_1 + q_2)^n (q_1 - q_2)^l q_{12}^m - \alpha(r_1 + r_2))$	4 ($N = 1$)	$-2.8799693 \pm 0.452e\text{-}2$
	8 ($N = 2$)	$-2.8984988 \pm 0.243e\text{-}2$
	14 ($N = 3$)	$-2.9037259 \pm 0.141e\text{-}2$
$\Psi_{53} = (1 + P_{12})\exp(\Sigma_{k=0} a_k q_1^n q_2^l q_{12}^m - \alpha r_1 - \beta r_2)$	6 ($N = 1$)	$-2.9001629 \pm 0.177e\text{-}2$
	12 ($N = 2$)	$-2.9029465 \pm 0.506e\text{-}3$
	21 ($N = 3$)	$-2.9037485 \pm 0.916e\text{-}4$
$\Psi_{54} = (1 + P_{12})\exp\left(\dfrac{\Sigma_{k=0} a_k \hat{q}_1^n \hat{q}_2^l \hat{q}_{12}^m}{\Sigma_{k=0} b_k \hat{q}_1^n \hat{q}_2^l \hat{q}_{12}^m} - \alpha r_1 - \beta r_2\right)$	8 ($N = 1$)	$-2.9024366 \pm 0.139e\text{-}2$
	20 ($N = 2$)	$-2.9035820 \pm 0.249e\text{-}3$
$\Psi_{55} = (1 + P_{12})\exp\left(\dfrac{\Sigma_{k=0} a_k q_1^n q_2^l q_{12}^m}{\Sigma_{k=0} b_k q_1^n q_2^l q_{12}^m} - \alpha r_1 - \beta r_2\right)$	9 ($N = 1$)	$-2.9035968 \pm 0.408e\text{-}3$
	21 ($N = 2$)	$-2.9037434 \pm 0.297e\text{-}4$
$\Psi_{56} = (1 + P_{12})\exp\left(\dfrac{\Sigma_{k=0} a_k \tilde{q}_1^n \tilde{q}_2^l \tilde{q}_{12}^m}{\Sigma_{k=0} b_k \tilde{q}_1^n \tilde{q}_2^l \tilde{q}_{12}^m} - \alpha r_1 - \beta r_2\right)$	11 ($N = 1$)	$-2.9035998 \pm 0.408e\text{-}3$
	23 ($N = 2$)	$-2.9037447 \pm 0.297e\text{-}4$
Literature		-2.903724375 [26]

[a] Here, $\det = \phi(r_1)\phi(r_2)$ as computed by Clementi and Roetti [25] using an energy minimization; $\hat{q}_i = r_i/(1 + r_i)$, $q_i = r_i/(1 + br_i)$ and $\tilde{q}_i = r_i/(1 + b_i r_i)$ $(i = 1, 2, 12)$. Elsewhere, $\phi(r_1) = [1 + \Sigma_{k=1}^{4} a_k r_1^k]e^{-\alpha r_1}$.

single parameter for all three variables or optimized as a separate parameter for each variable. For this system, none of these options, Ψ_{54}–Ψ_{56}, was found to significantly improve the convergence of our best form Ψ_{43}. We did find, however, that when we use transformed variables to create several of the exponential Hylleraas forms many of these wave functions converged faster than did the corresponding linear Hylleraas forms in Tables III and IV.

The relative convergence of many of our trial wave-function forms is shown in Figure 1. Although both the Hylleraas and the Padé forms are easily extendible, the former is much easier to optimize. For this system, however, any increase in difficulty due to the Padé form is more than offset by its superior convergence.

For comparison, we also evaluated the exponential Padé helium wave-function form in [7] with the same 4000 configurations used to determine the results in Tables I–V. This form is similar to Ψ_{33} in Table IV and gives comparable results, $-2.9037245 \pm 0.792e\text{-}5$, using 52 parameters which include terms up to the fourth power of the variables. In contrast, our best form, Ψ_{43}, has a lower variance, $-2.9037228 \pm 0.558e\text{-}5$, and uses only 40 adjustable parameters with terms only up to the third power. The major difference is that Ψ_{43} includes an explicit permutation of the electronic coordinates while the one in [7] (and Ψ_{33}) does not.

Helium Singlet Excited State

We have optimized several wave-function forms for this state using a functional which includes explicit orthogonality with the ground state (see Appendix 1). Table VI and Figure 2 show that the convergence of these forms is generally slower

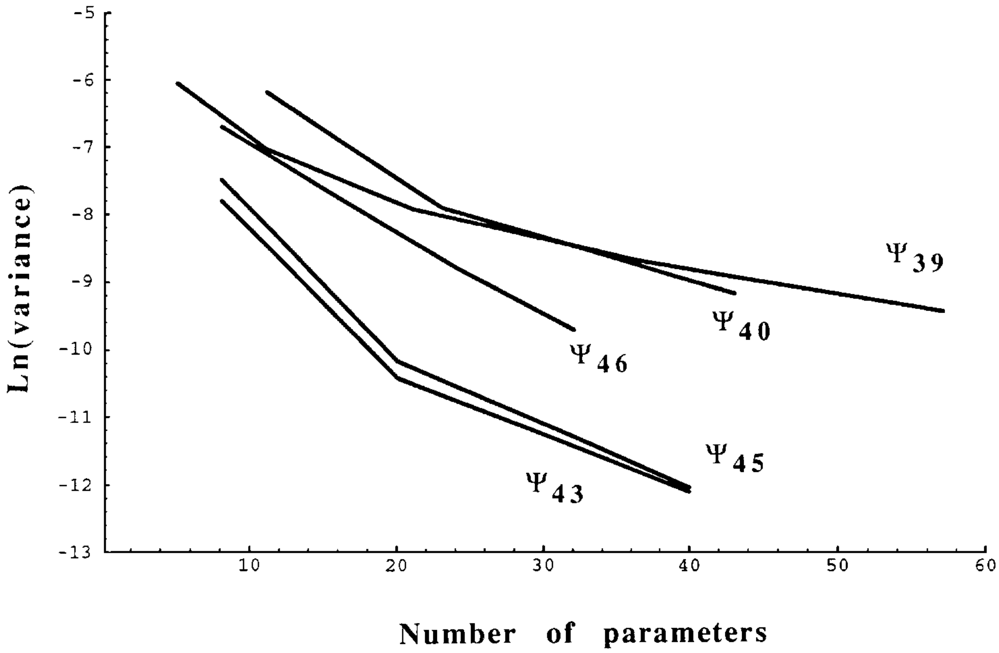

FIGURE 1. Convergence comparison of several helium ground-state wave functions. Variances from Table IV.

than are their ground-state counterparts. One exception, however, is the Drake form, Ψ_6, which is now noticeably better than either the Hylleraas or linear Padé forms. Although the values are not included in Table VI, we also investigated the effect of negative powers and logarithmic terms on the convergence of this state. As in the ground state, these features were found to have little influence on the variance. Our best form is once again an exponential Padé. The forms Ψ_{10}–Ψ_{14} show that the terms associated with r_1 (the unexcited electron) have little effect on the variance and can be eliminated without penalty. In contrast, the terms associated with r_2 describe the excited-state node and must be considered in some detail. Our results show that the maximum convergence per constant is given by Ψ_{13} which uses the polynomial $1 + cr_2 + dr_2^2$ to describe the single node in this system.

Helium Triplet Ground State

A Hartree–Fock description of the triplet ground state is usually written as $\Phi_{1s}(r_1)\Phi_{2s}(r_2) - \Phi_{2s}(r_1)\Phi_{1s}(r_2)$. The question that we wish to examine here is whether the nodal structure of this state requires an explicit node (like the one provided by Φ_{2s} above or by r_2 in the singlet excited state). We show in Table VII that the extra boundary condition $(1 + cr_2)$ does not speed the convergence of the exponential Padé form as a function of the number of adjustable parameters. Thus, we conclude that the antisymmetry operator alone is capable of introducing the proper symmetry.

Lithium Ground State

In Table VIII and Figure 3, we compare the results of several trial wave-function forms for the ground state of lithium. Those forms which most accurately describe this state are different in several respects from those which best described the various helium states in the second to fourth sections. Transformed coordinates, e.g., were of minor importance for helium but are essential for all of the good lithium forms. Although, in principle, any wave function can be expanded in a polynomial basis, in practice, the higher-power terms of such expansions have an increasing tendency to violate the asymptotic boundary condition of systems with more than two electrons. Coordinate transformation remove this problems by making the variables local. The form that we have chosen, $r_x/(1 + b_x r_x)$, is especially well suited for this job. It has no maximum for $r_x > 0$ and is very smooth.

TABLE VI

Helium excited-state wave functions of general form[a]; *N* is the excitation level.

Form	No. parameters	Energy (au)
$\Psi_1 = (1 + P_{12})\phi(r_1)\eta(r_2)$	12 ($N = 0$)	$-2.1226698 \pm 0.141e\text{-}2$
$\Psi_2 = (1 + P_{12})\phi(r_1)\eta(r_2)\exp(\Sigma_{k=0} a_k r_{12}^k)$	13 ($N = 1$)	$-2.1269442 \pm 0.756e\text{-}3$
	14 ($N = 2$)	$-2.1296726 \pm 0.657e\text{-}3$
$\Psi_3 = (1 + P_{12})\phi(r_1)\eta(r_2)\Sigma_{k=0} a_k r_{12}^k$	13 ($N = 1$)	$-2.1271674 \pm 0.749e\text{-}3$
	14 ($N = 2$)	$-2.1274805 \pm 0.539e\text{-}3$
$\Psi_4 = (1 + P_{12})\phi(r_1)\eta(r_2)\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m$	15 ($N = 1$)	$-2.1269762 \pm 0.724e\text{-}3$
	21 ($N = 2$)	$-2.1393280 \pm 0.465e\text{-}3$
$\Psi_5 = (1 + P_{12})\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m e^{-\alpha r_1 - \beta r_2}$	5 ($N = 1$)	$-2.1462072 \pm 0.743e\text{-}3$
	11 ($N = 2$)	$-2.1453213 \pm 0.569e\text{-}3$
	21 ($N = 3$)	$-2.1456610 \pm 0.327e\text{-}3$
	36 ($N = 4$)	$-2.1465248 \pm 0.161e\text{-}3$
$\Psi_6 = (1 + P_{12})[\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m e^{-\alpha r_1 - \beta r_2} + \Sigma_{k=0} \hat{a}_k r_1^n r_2^l r_{12}^m e^{-\hat{\alpha} r_1 - \hat{\beta} r_2}]$	11 ($N = 1$)	$-2.1370713 \pm 0.832e\text{-}3$
	23 ($N = 2$)	$-2.1459418 \pm 0.940e\text{-}4$
	43 ($N = 3$)	$-2.1459938 \pm 0.298e\text{-}4$
$\Psi_7 = (1 + P_{12})\phi(r_1)\eta(r_2)\exp\left(\frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k}\right)$	12 ($N = 1$)	$-2.1454987 \pm 0.349e\text{-}3$
	14 ($N = 2$)	$-2.1457859 \pm 0.322e\text{-}3$
$\Psi_8 = (1 + P_{12})\phi(r_1)\eta(r_2)\exp\left(\frac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m}\right)$	18 ($N = 1$)	$-2.1457433 \pm 0.312e\text{-}3$
	30 ($N = 2$)	$-2.1459725 \pm 0.254e\text{-}4$
$\Psi_9 = (1 + P_{12})(1 + cr_2)\exp\left(\frac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m} - \alpha r_1 - \beta r_2\right)$	9 ($N = 1$)	$-2.1440458 \pm 0.429e\text{-}3$
	21 ($N = 2$)	$-2.1459913 \pm 0.492e\text{-}4$
	41 ($N = 3$)	$-2.1459722 \pm 0.963e\text{-}5$
$\Psi_{10} = (1 + P_{12})(1 + cr_2 + \mathrm{d}r_2^3)\exp\left(\frac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m} - \alpha r_1 - \beta r_2\right)$	10 ($N = 1$)	$-2.1439478 \pm 0.426e\text{-}3$
	22 ($N = 2$)	$-2.1459590 \pm 0.353e\text{-}4$
	42 ($N = 3$)	$-2.1459755 \pm 0.722e\text{-}5$
	Best form	
$\Psi_{11} = (1 + P_{12})(1 + cr_2 + dr_{12})\exp\left(\frac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m} - \alpha r_1 - \beta r_2\right)$	10 ($N = 1$)	$-2.1440997 \pm 0.429e\text{-}3$
	22 ($N = 2$)	$-2.1459770 \pm 0.489e\text{-}4$
	42 ($N = 3$)	$-2.1459632 \pm 0.944e\text{-}5$
$\Psi_{12} = (1 + P_{12})\phi(r_1)\eta(r_2)\frac{\Sigma_{k=0} a_k r_{12}^k}{\Sigma_{k=0} b_k r_{12}^k}$	12 ($N = 1$)	$-2.1381185 \pm 0.528e\text{-}3$
	14 ($N = 2$)	$-2.1457857 \pm 0.322e\text{-}3$
$\Psi_{13} = (1 + P_{12})\phi(r_1)\eta(r_2)\frac{\Sigma_{k=0} a_k r_1^n r_2^l r_{12}^m}{\Sigma_{k=0} b_k r_1^n r_2^l r_{12}^m}$	18 ($N = 1$)	$-2.1439512 \pm 0.442e\text{-}3$
	30 ($N = 2$)	$-2.1458232 \pm 0.163e\text{-}3$

(Continued)

TABLE VI
(Continued)

Form	No. parameters	Energy (au)
$\Psi_{14} = (1 + P_{12})\dfrac{\sum_{k=0} a_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^l r_{12}^m} e^{-\alpha r_1 - \beta r_2}$	8 ($N = 1$)	$-2.1424814 \pm 0.734e\text{-}3$
	20 ($N = 2$)	$-2.1457626 \pm 0.210e\text{-}3$
	40 ($N = 3$)	$-2.1459045 \pm 0.633e\text{-}4$
$\Psi_{15} = (1 + P_{12})(1 + cr_2)\dfrac{\sum_{k=0} a_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^l r_{12}^m} e^{-\alpha r_1 - \beta r_2}$	9 ($N = 1$)	$-2.1440590 \pm 0.615e\text{-}3$
	21 ($N = 2$)	$-2.1457518 \pm 0.209e\text{-}3$
	41 ($N = 3$)	$-2.1459049 \pm 0.632e\text{-}4$
$\Psi_{16} = (1 + P_{12})\sum_{k=1} a_k e^{-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}}$	16	$-2.1389128 \pm 0.795e\text{-}3$
	24	$-2.1458506 \pm 0.143e\text{-}3$
	32	$-2.1460007 \pm 0.425e\text{-}4$
Literature		-2.145974046 [31]

[a] Here, $\phi(r_1) = [1 + \sum_{k=1}^{4} a_k r_1^k]e^{-\alpha r_1}$ and $\eta(r_2) = [1 + \sum_{k=1}^{4} b_k r_2^k]e^{-\beta r_2}$.

This makes the task of parameterizing the wave function relatively straightforward. We examined the difference between scaling all variables independently and scaling all variables using a single parameters. For this system, we find that there is little difference between these two approaches.

Another major difference is that all our lithium wave functions have a variance which is much larger than their helium counterparts. This is due almost entirely to the presence of the third electron (the lithium cation can be computed to the same relative error as helium). The variance of just the Hartree–Fock determinant, Ψ_1, is 0.042 Hartrees (compared to 0.013 for the helium ground state). Multiplying the lithium determinant by an exponential Padé, Ψ_3, lowers the variance by a factor of 28 to 0.0015 Hartrees. Optimizing the parameters in the determinant, however, had little influence on this number. On a per constant basis, the variance also seems to be relatively insensitive to the form of the correlation functional. The Padé form which was by an order of magnitude more accurate than any other trial wave function for the helium ground state is *not significantly better* on a

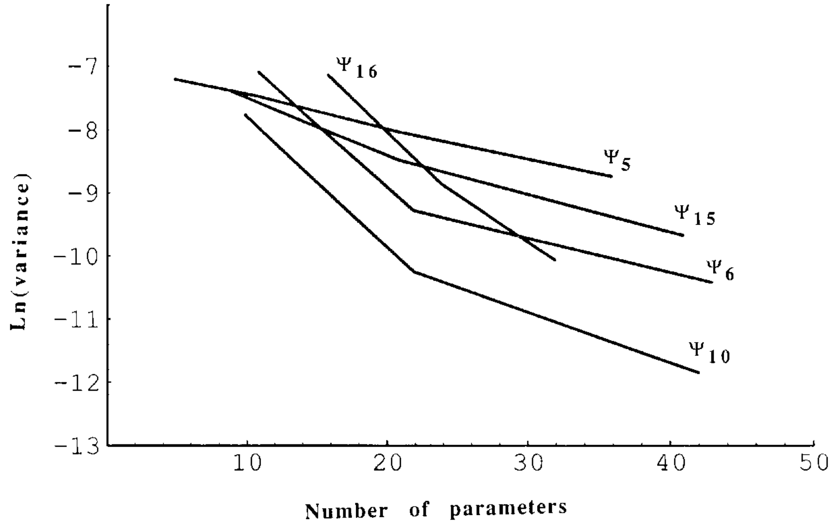

FIGURE 2. Convergence comparison of several helium ^2S wave functions. Variances from Table VI.

TABLE VII
Helium triplet ground-state wave functions of general form; *N* is the excitation level.

Form	No. parameters	Energy (au)
$\Psi_1 = (1 - P_{12})\exp\left(\frac{\sum_{k=0} a_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^l r_{12}^m} - \alpha r_1 - \beta r_2\right)$	8 ($N = 1$)	$-2.1742064 \pm 0.390e\text{-}3$
	20 ($N = 2$)	$-2.1752449 \pm 0.174e\text{-}4$
	Best form	
$\Psi_2 = (1 - P_{12})(1 + cr_2)\exp\left(\frac{\sum_{k=0} a_k r_1^n r_2^l r_{12}^m}{\sum_{k=0} b_k r_1^n r_2^l r_{12}^m} - \alpha r_1 - \beta r_2\right)$	9 ($N = 1$)	$-2.1751780 \pm 0.331e\text{-}3$
	21 ($N = 2$)	$-2.1752392 \pm 0.155e\text{-}4$
Literature		-2.175229378 [31]

per constant basis than is the simpler Hylleraas form for the lithium ground state. The only advantage of the Padé in this system is that it provides a straightforward way to double the number of parameters.

Our examination of the asymptotic form of the wave function shows that the "minimal orbitals" for this system are given by $e^{-\alpha r_1}$ and $e^{-\beta r_2}$ for the first two (1*s*-type) electrons and $(r_3 - c)e^{-\gamma r_3}$ for the third (2*s*-type) electron. This is entirely consistent with what one would expect from a single-particle description. While a decrease in the variance can be gained by making the 1*s* orbital more flexible, setting the correct nodal behavior of the 2*s* orbital is ultimately more important.

For a system with multiple electrons, the antisymmetric nature of the wave function can be described using either a determinant or by explicitly permuting all electrons (see Appendix 2). When compared with our best determinant-based wave function, Ψ_6, the variance of our best fully antisymmetric wave function, Ψ_{18}, is smaller by a factor of 5.6.

Beryllium Ground State

In Table IX and Figure 4, we compare the results of several trial wave-function forms for the ground state of beryllium. For the most part, we find that the behavior of this system is similar to that of the lithium ground state. The major difference is that an accurate orbital description requires that we now take into account the near degeneracy of the $2s$–$2p$ levels. In a determinant-based wave function, this can be done most simply by using the four-determinant form $\det(\phi_{1s}, \phi_{2s}) + \text{constant}[\det(\phi_{1s'}, \phi_{px}) + \det(\phi_{1s'}, \phi_{py}) + \det(\phi_{1s'}, \phi_{pz})]$. In a purely antisymmetric wave function, this degeneracy can be included by using the term $(x_3 x_4 + y_3 y_4 + z_3 z_4)$ to reproduce the close-in behavior of the p states [36].

For this system, the variance of the Hartree–Fock determinant, Ψ_1, is 0.035 Hartrees. Multiplying this form by an exponential Padé, Ψ_3, lowers the variance by a factor of 8 to 0.0044 Hartrees. As in lithium, optimizing the parameters inside the determinant does not significantly lower the variance—in fact, the value for Ψ_{13} is slightly worse than for Ψ_3. On a per constant basis, the form of the correlation functional again seems to have little effect. Although the variances of our four determinant forms, e.g., Ψ_{14}, have only a slightly smaller variance than those of our single-determinant forms, e.g., Ψ_{12}, their energy is noticeably better. This behavior was also seen by Umrigar et al. in [7].

Our examination of the asymptotic form of the wave function again shows that the "minimal orbitals" for this system are given by $e^{-\alpha r_1}$ and $e^{-\beta r_2}$ for the first two (1*s*-type) electrons and $(r_3 - c)e^{-\gamma r_3}$ for the third (2*s*-type) electron. We still see, however, some lingering desire to make the 1*s* orbital more flexible.

If we choose to explicitly permute the electronic coordinates in the wave function rather than to use determinants, both our variance and our energy show a significant improvement. When compared

TABLE VIII
Lithium ground wave functions of general form[a]; *N* is the excitation level.

Form	No. parameters	Energy (au)
$\Psi_1 = \det$	0 ($N = 0$)	−7.377666 ± 0.426e-1
$\Psi_2 = \det e^{\text{hyll1}}$	7 ($N = 1$)	−7.469512 ± 0.101e-1
	28 ($N = 2$)	−7.479467 ± 0.416e-2
$\Psi_3 = \det e^{\text{padé1}}$	13 ($N = 1$)	−7.466850 ± 0.979e-2
	55 ($N = 2$)	−7.475383 ± 0.151e-2
$\Psi_4 = \text{opt} \det(a) e^{\text{hyll1}}$	2 ($N = 0$)	−7.270501 ± 0.361e-1
	9 ($N = 1$)	−7.468003 ± 0.706e-2
	30 ($N = 2$)	−7.474828 ± 0.410e-2
$\Psi_5 = \text{opt} \det(b) e^{\text{hyll1}}$	4 ($N = 0$)	−7.301724 ± 0.311e-1
	11 ($N = 1$)	−7.467400 ± 0.689e-2
	32 ($N = 2$)	−7.475041 ± 0.403e-2
$\Psi_6 = \text{opt} \det(c) e^{\text{hyll1}}$	3 ($N = 0$)	−7.233649 ± 0.357e-1
	10 ($N = 1$)	−7.454445 ± 0.682e-2
	31 ($N = 2$)	−7.477295 ± 0.407e-2
	87 ($N = 3$)	−7.477064 ± 0.152e-2
	Best form with minimal orbital determinant	
$\Psi_7 = \text{opt} \det(a) e^{\text{padé1}}$	2 ($N = 0$)	−7.274083 ± 0.361e-1
	15 ($N = 1$)	−7.470297 ± 0.525e-2
	57 ($N = 2$)	−7.473268 ± 0.261e-2
$\Psi_8 = \text{opt} \det(b) e^{\text{padé1}}$	4 ($N = 0$)	−7.305709 ± 0.311e-1
	17 ($N = 1$)	−7.473371 ± 0.398e-2
	59 ($N = 2$)	−7.473565 ± 0.150e-2
$\Psi_9 = \text{opt} \det(c) e^{\text{padé1}}$	3 ($N = 0$)	−7.233649 ± 0.357e-1
	16 ($N = 1$)	−7.465996 ± 0.521e-2
	58 ($N = 2$)	−7.474210 ± 0.259e-2
$\Psi_{10} = A[e^{\text{hyll1} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	3 ($N = 0$)	−7.275161 ± 0.345e-1
	10 ($N = 1$)	−7.470221 ± 0.473e-2
	31 ($N = 2$)	−7.477487 ± 0.124e-2
$\Psi_{11} = A[\text{hyll1}\, e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	10 ($N = 1$)	−7.463641 ± 0.589e-2
	31 ($N = 2$)	−7.476566 ± 0.165e-2
$\Psi_{12} = A[e^{\text{padé1} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	16 ($N = 1$)	−7.463701 ± 0.446e-2
	58 ($N = 2$)	−7.477765 ± 0.577e-3
$\Psi_{13} = A[\text{padé1}\, e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	16 ($N = 1$)	−7.471567 ± 0.458e-2
	58 ($N = 2$)	−7.477468 ± 0.433e-3
$\Psi_{14} = A[r_3 e^{\text{hyll1} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	3 ($N = 0$)	−7.287719 ± 0.362e-1
	10 ($N = 1$)	−7.471244 ± 0.476e-2
	31 ($N = 2$)	−7.477611 ± 0.123e-2
$\Psi_{15} = A[r_3 \text{hyll1}\, e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	10 ($N = 1$)	−7.472713 ± 0.378e-2
	31 ($N = 2$)	−7.477633 ± 0.148e-2

(Continued)

TABLE VIII
(Continued)

Form	No. parameters	Energy (au)
$\Psi_{16} = A[r_3 e^{\text{padé1} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	16 ($N = 1$)	$-7.470518 \pm 0.435e\text{-}2$
	58 ($N = 2$)	$-7.477935 \pm 0.330e\text{-}3$
$\Psi_{17} = A[r_3 \text{padé1} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	16 ($N = 1$)	$-7.470874 \pm 0.218e\text{-}2$
	58 ($N = 2$)	$-7.477702 \pm 0.438e\text{-}3$
$\Psi_{18} = A[(r_3 - c) e^{\text{hyll1} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	4 ($N = 0$)	$-7.275045 \pm 0.345e\text{-}1$
	11 ($N = 1$)	$-7.470166 \pm 0.473e\text{-}2$
	32 ($N = 2$)	$-7.477765 \pm 0.123e\text{-}2$
	88 ($N = 3$)	$-7.478281 \pm 0.276e\text{-}3$
	Best form	
$\Psi_{19} = A[(r_3 - c) \text{hyll1} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	11 ($N = 1$)	$-7.473313 \pm 0.375e\text{-}2$
	32 ($N = 2$)	$-7.477858 \pm 0.146e\text{-}2$
$\Psi_{20} = A[(r_3 - c) e^{\text{padé1} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	17 ($N = 1$)	$-7.470957 \pm 0.199e\text{-}2$
	59 ($N = 2$)	$-7.478069 \pm 0.319e\text{-}3$
$\Psi_{21} = A[(r_3 - c) \text{padé1} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	17 ($N = 1$)	$-7.471629 \pm 0.213e\text{-}2$
	59 ($N = 2$)	$-7.477793 \pm 0.352e\text{-}3$
$\Psi_{22} = A[(r_3 - c) e^{\text{hyll2} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	16 ($N = 1$)	$-7.472168 \pm 0.457e\text{-}2$
	37 ($N = 2$)	$-7.477795 \pm 0.119e\text{-}2$
$\Psi_{23} = A[(r_3 - c) \text{hyll2} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	16 ($N = 1$)	$-7.474202 \pm 0.369e\text{-}2$
	37 ($N = 2$)	$-7.477785 \pm 0.146e\text{-}2$
$\Psi_{24} = A[(r_3 - c) e^{\text{padé2} - \alpha r_1 - \beta r_2 - \gamma r_3}]$	22 ($N = 1$)	$-7.475782 \pm 0.165e\text{-}2$
	64 ($N = 2$)	$-7.478067 \pm 0.316e\text{-}3$
$\Psi_{25} = A[(r_3 - c) \text{padé2} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}]$	22 ($N = 1$)	$-7.469480 \pm 0.192e\text{-}2$
	64 ($N = 2$)	$-7.477967 \pm 0.327e\text{-}3$
Exact		-7.478060326 [37]

[a] Here, det is the Hartree–Fock determinant computed by Clementi and Roetti [25] using an energy minimization;

$$\text{hyll1} = \sum_{k=0} a_k q_1^c q_2^d q_3^e q_{12}^f q_{13}^g q_{23}^h, \qquad \text{where } q_i = r_i / (1 + b r_i),$$

$$\text{hyll2} = \sum_{k=0} a_k q_1^c q_2^d q_3^e q_{12}^f q_{13}^g q_{23}^h, \qquad \text{where } q_i = r_i / (1 + b_i r_i),$$

$$\text{padé1} = \frac{\sum_{k=0} a_k q_1^c q_2^d q_3^e q_{12}^f q_{13}^g q_{23}^h}{\sum_{k=0} b_k q_1^c q_2^d q_3^e q_{12}^f q_{13}^g q_{23}^h}, \qquad \text{where } q_i = r_i / (1 + b r_i),$$

$$\text{padé2} = \frac{\sum_{k=0} a_k q_1^c q_2^d q_3^e q_{12}^f q_{13}^g q_{23}^h}{\sum_{k=0} b_k q_1^c q_2^d q_3^e q_{12}^f q_{13}^g q_{23}^h}, \qquad \text{where } q_i = r_i / (1 + b_i r_i).$$

The orbitals which define det(a) are $\phi_1 = e^{-\alpha_1 r}$ and $\phi_2 = r e^{-\alpha_2 r}$. The orbitals which define det(b) are $\phi_1 = e^{-\alpha_1 r} + c e^{-\alpha_2 r}$ and $\phi_2 = r e^{-\alpha_3 r}$. The orbitals which define det(c) are $\phi_1 = e^{-\alpha_1 r}$ and $\phi_2 = (r + c) e^{-\alpha_2 r}$.

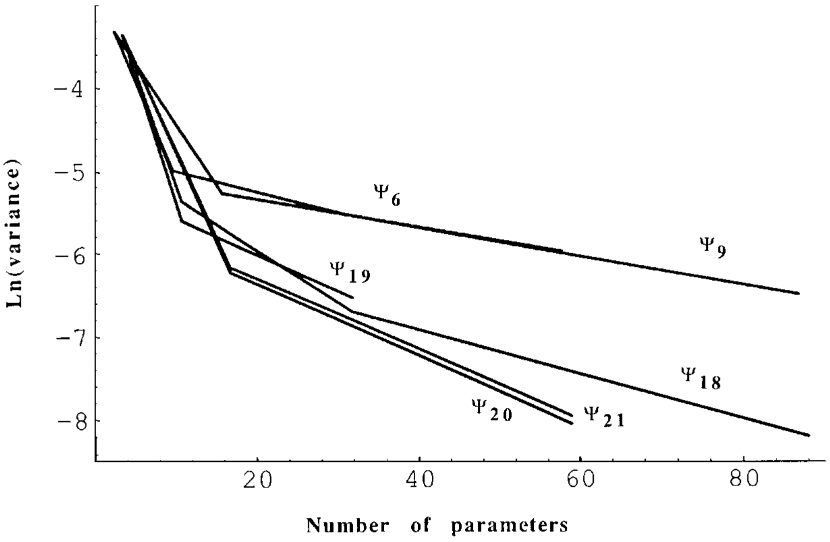

FIGURE 3. Convergence comparison of several lithium ground-state wave functions. Variances from Table VIII.

with the best determinantal form, Ψ_{14}, the variance of our best fully antisymmetric form, Ψ_{16}, is smaller by a factor of 2.7.

For comparison, we have also examined the four-determinant exponential Padé form described in [17]. This form has 110 parameters and includes terms up to the fourth power of the variables but has a single parameter for each type of term (e.g., the coefficient of $r_i r_{ij}$ is the same for all values of i and j). When evaluated with the same 4000 configurations used to determine the results in Table IX, this wave function has a value of $-14.66642 \pm 0.175e\text{-}2$. In contrast, our most similar form, Ψ_{15}, has 137 parameters and includes terms up to the second power of the variables but uses separate parameters for all terms (e.g., the coefficient of $r_1 r_{12}$ is allowed to be different from that of $r_3 r_{34}$). Because our value, $-14.66261 \pm 0.265e\text{-}2$, is slightly worse than the one in [17], we conclude that our rate of convergence could be improved by combining some types of terms in the Hylleraas and Padé expansions rather than using separate parameters for each one.

Antisymmetry Considerations

A number of calculations have recently been able to obtain highly accurate energies of atoms and molecules by using a fully antisymmetric wave function (see, e.g., [38–40]). For this reason, it is of interest to compare the convergence of the forms $\det f(r_1, \ldots, r_n)$ and $A[f(r_1, \ldots, r_n)]$ in some detail. It should be noted that on the order of $N!$ evaluations of the complete trial wave function are required to antisymmetrize N same-spin coordinates (see Appendix 2). In contrast, only about N^3 arithmetic operations are required to evaluate a determinant. This is a substantial difference and a large drop in the variance will be needed to justify the extra time required.

For the helium ground state, our best single-determinant form, Ψ_{24}, produced an energy of $-2.90374(2)$ with 29 adjustable constants. In contrast, our best form, Ψ_{43}, gives $-2.903723(6)$ with 40 constants, i.e., a factor of 4 decrease in the variance. A similar improvement was found for the lithium ground state. There our best single-determinant form, Ψ_6, produced an energy of $-7.477(1)$ with 87 adjustable constants, while our best form, Ψ_{18}, gives 7.4783(3) with 32 constants, i.e., a factor of 5.4 improvement in the variance. In the case of the beryllium ground state, our best single-determinant form, Ψ_{12}, produced an energy of $-14.640(4)$ with 69 adjustable constants while our best four-determinant form, Ψ_{14}, gives $-14.661(4)$ with 72 constants. Our best form for this system, Ψ_{16}, was designed to include the degeneracy between the $2s$ and $2p$ orbitals [36]. Compared to either of the single determinant or the multideterminant form, the variance of the full antisymmetrized wave function, $-14.663(1)$ with 72 constants, is lower by almost a factor of 3.

TABLE IX

Beryllium ground wave functions of general form[a]; *N* is the excitation level.

Form	No. parameters	Energy (au)
$\Psi_1 = \det$	0 ($N = 0$)	−14.521009 ± 0.350e-1
$\Psi_2 = \det e^{\mathrm{hyll1}}$	11 ($N = 1$)	−14.631914 ± 0.674e-2
	66 ($N = 2$)	−14.638787 ± 0.438e-2
$\Psi_3 = \det e^{\text{padé1}}$	21 ($N = 1$)	−14.632676 ± 0.491e-2
	131 ($N = 2$)	−14.662865 ± 0.305e-2
$\Psi_4 = \mathrm{opt}\,\det(a) e^{\mathrm{hyll1}}$	2 ($N = 0$)	−14.531015 ± 0.329e-1
	13 ($N = 1$)	−14.628944 ± 0.708e-2
	68 ($N = 2$)	−14.641285 ± 0.468e-2
$\Psi_5 = \mathrm{opt}\,\det(a) e^{\text{padé1}}$	23 ($N = 1$)	−14.633346 ± 0.526e-2
	133 ($N = 2$)	−14.639388 ± 0.384e-2
$\Psi_6 = [\Sigma_{i=1}^{4} \mathrm{opt}\,\det_i(b)] e^{\mathrm{hyll1}}$	5 ($N = 0$)	−14.512123 ± 0.326e-1
	16 ($N = 1$)	−14.643356 ± 0.693e-2
	71 ($N = 2$)	−14.660304 ± 0.444e-2
$\Psi_7 = [\Sigma_{i=1}^{4} \mathrm{opt}\,\det_i(b)] e^{\text{padé1}}$	26 ($N = 1$)	−14.654809 ± 0.491e-2
	136 ($N = 2$)	−14.658009 ± 0.321e-2
$\Psi_8 = \mathrm{opt}\,\det(c) e^{\mathrm{hyll1}}$	4 ($N = 0$)	−14.563531 ± 0.290e-1
	15 ($N = 1$)	−14.628784 ± 0.696e-2
	70 ($N = 2$)	−14.641373 ± 0.468e-2
$\Psi_9 = \mathrm{opt}\,\det(c) e^{\text{padé1}}$	25 ($N = 1$)	−14.633497 ± 0.522e-2
	135 ($N = 2$)	−14.643355 ± 0.350e-2
$\Psi_{10} = [\Sigma_{i=1}^{4} \mathrm{opt}\,\det_i(d)] e^{\mathrm{hyll1}}$	9 ($N = 0$)	−14.536849 ± 0.277e-1
	20 ($N = 1$)	−14.631374 ± 0.686e-2
	75 ($N = 2$)	−14.660843 ± 0.441e-2
$\Psi_{11} = [\Sigma_{i=1}^{4} \mathrm{opt}\,\det_i(d)] e^{\text{padé1}}$	30 ($N = 1$)	−14.653399 ± 0.490e-2
	140 ($N = 2$)	−14.662517 ± 0.277e-2
$\Psi_{12} = \mathrm{opt}\,\det(e) e^{\mathrm{hyll1}}$	3 ($N = 0$)	−14.520258 ± 0.323e-1
	14 ($N = 1$)	−14.629705 ± 0.686e-2
	69 ($N = 2$)	−14.640387 ± 0.431e-2
	Best single determinant form	
$\Psi_{13} = \mathrm{opt}\,\det(e) e^{\text{padé1}}$	24 ($N = 1$)	−14.634530 ± 0.490e-2
	134 ($N = 2$)	−14.642677 ± 0.325e-2
$\Psi_{14} = [\Sigma_{i=1}^{4} \mathrm{opt}\,\det_i(f)] e^{\mathrm{hyll1}}$	6 ($N = 0$)	−14.491088 ± 0.316e-1
	17 ($N = 1$)	−14.644169 ± 0.670e-2
	72 ($N = 2$)	−14.661215 ± 0.403e-2
	Best multiple determinant form	
$\Psi_{15} = [\Sigma_{i=1}^{4} \mathrm{opt}\,\det_i(f)] e^{\text{padé1}}$	27 ($N = 1$)	−14.658263 ± 0.444e-2
	137 ($N = 2$)	−14.662610 ± 0.266e-2

(Continued)

TABLE IX
(Continued)

Form	No. parameters	Energy (au)
$\Psi_{16} = A[((r_3 - d)(r_4 - d) + c(x_3x_4 + y_3y_4 + z_3z_4))e^{\text{hyll1} - \alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}]$	5 ($N = 0$)	$-14.670208 \pm 0.314e\text{-}1$
	17 ($N = 1$)	$-14.669376 \pm 0.694e\text{-}2$
	72 ($N = 2$)	$-14.663186 \pm 0.150e\text{-}2$
	Best form	
$\Psi_{17} = A[((r_3 - d)(r_4 - d)) + c(x_3x_4 + y_3y_4 + z_3z_4))\text{hyll1}e^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}]$	17 ($N = 1$)	$-14.662252 \pm 0.621e\text{-}2$
	72 ($N = 2$)	$-14.663404 \pm 0.191e\text{-}2$
$\Psi_{18} = A[((r_3 - d)(r_4 - d) + c(x_3x_4 + y_3y_4 + z_3z_4))e^{\text{padé1} - \alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}]$	27 ($N = 1$)	$-14.665581 \pm 0.472e\text{-}2$
	137 ($N = 2$)	$-14.667133 \pm 0.745e\text{-}3$
$\Psi_{19} = A[((r_3 - d)(r_4 - d) + c(x_3x_4 + y_3y_4 + z_3z_4))\text{padé1}e^{-\alpha r_1 - \beta r_2 - \gamma r_3 - \delta r_4}]$	27 ($N = 1$)	$-14.661077 \pm 0.468e\text{-}2$
	137 ($N = 2$)	$-14.665984 \pm 0.735e\text{-}3$
Literature		$-14.66737(3)$ [41]

[a] Here, det is the Hartree–Fock determinant computed by Clementi and Roetti [25] using an energy minimization;

$$\text{hyll1} = \sum_{k=0} a_k q_1^c q_2^d q_3^e q_4^f q_{12}^g q_{13}^h q_{14}^m q_{23}^n q_{24}^o q_{34}^p, \qquad \text{where } q_i = r_i/(1+br_i) \text{ and } q_{ij} = r_{ij}/(1+br_{ij}),$$

$$\text{padé1} = \frac{\sum_{k=0} a_k q_1^c q_2^d q_3^e q_4^f q_{12}^g q_{13}^h q_{14}^m q_{23}^n q_{24}^o q_{34}^p}{\sum_{k=0} b_k q_1^c q_2^d q_3^e q_4^f q_{12}^g q_{13}^h q_{14}^m q_{23}^n q_{24}^o q_{34}^p}, \qquad \text{where } q_i = r_i/(1+br_i) \text{ and } q_{ij} = r_{ij}/(1+br_{ij}).$$

The orbitals which define det(a) are $\phi_1 = e^{-\alpha_1 r}$ and $\phi_2 = re^{-\alpha_2 r}$. $[\sum_{i=1}^4 \text{opt}\det_i(b)] = \det(\phi_1, \phi_2) + \text{const}[\det(\phi_3, \phi_4(x)) + \det(\phi_3, \phi_4(y)) + \det(\phi_3, \phi_4(z))]$, where $\phi_1 = e^{-\alpha_1 r}$, $\phi_2 = re^{-\alpha_2 r}$, $\phi_3 = e^{-\alpha_3 r}$, and $\phi_4(x) = xe^{-\alpha_4 r}$. The orbitals which define det(c) are $\phi_1 = e^{-\alpha_1 r} + ce^{-\alpha_2 r}$ and $\phi_2 = re^{-\alpha_3 r}$. $[\sum_{i=1}^4 \text{opt}\det_i(d)] = \det(\phi_1, \phi_2) + \text{const}[\det(\phi_3, \phi_4(x)) + \det(\phi_3, \phi_4(y)) + \det(\phi_3, \phi_4(z))]$, where $\phi_1 = e^{-\alpha_1 r} + ce^{-\alpha_2 r}$, $\phi_2 = re^{-\alpha_3 r}$, $\phi_3 = e^{-\alpha_4 r} + \bar{c}e^{-\alpha_5 r}$, and $\phi_4(x) = xe^{-\alpha_6 r}$. The orbitals which define det(e) are $\phi_1 = e^{-\alpha_1 r}$ and $\phi_2 = (r + c)e^{-\alpha_2 r}$. $[\sum_{i=1}^4 \text{opt}\det_i(f)] = \det(\phi_1, \phi_2) + \text{const}[\det(\phi_3, \phi_4(x)) + \det(\phi_3, \phi_4(y)) + \det(\phi_3, \phi_4(z))]$, where $\phi_1 = e^{-\alpha_1 r}$, $\phi_2 = (r + c)e^{-\alpha_2 r}$, $\phi_3 = e^{-\alpha_3 r}$, and $\phi_4(x) = xe^{-\alpha_4 r}$.

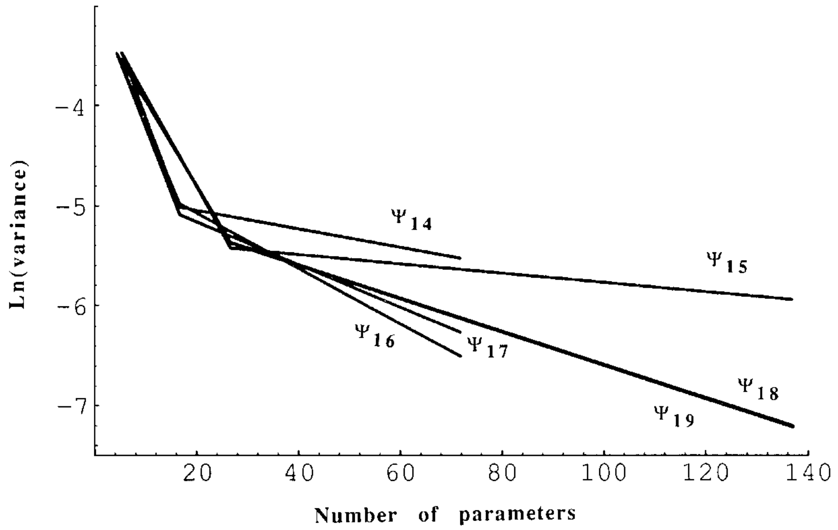

FIGURE 4. Convergence comparison of several beryllium ground-state wave functions. Variances from Table IX.

Expanding the Wave Function

Although our comparison of wave-function forms has heretofore been done using a relatively small number of configurations, we also calculated the energies of our best wave functions using 1,024,000 configurations. As discussed in [13], the variances of such expansions may be distorted because of the influence of the electron–electron singularities in the Hamiltonian. In the present work, we eliminated this problem by modifying our algorithm for generating Monte Carlo integration points so as to explicitly sample these singularities. This is done by selecting 10% of the electron locations with respect to other electrons and averaging over the various ways of selecting an electron as first discussed in [2], rather than only with respect to the nucleus.

As shown in Table X, with our best wave functions, we are able to obtain both a low variance and a large percentage of the correlation energy for all of the states considered. These values are also in excellent agreement with those computed using other methods.

In addition to the wave-function forms listed in Table X, we also expanded a few of the Padé forms for lithium and beryllium. These calculations exhibited clear signs of numerical instability. In each case, either the energy and/or the variance were found to be anomalously large. We traced this problem to the presence of nodes in the denomina-

TABLE X

Comparison of our best energies evaluated with 1,024,000 biased-as-random configurations with those in the literature. The number in parentheses is the variance.

System	Method	Energy (au)	
$1\,^1S$ He	Variational Monte Carlo (Ψ_{43})	−2.9037243(4)	This work
	Hylleraas expansion	−2.903724375	[42]
	Gaussian geminal expansion	−2.9037238	[43]
	Slater geminal expansion	−2.903724363	[32]
	Hylleraas expansion with log terms	−2.9037243770341184	[26]
	VMC	−2.903722(2)	[7]
	QMC	−2.90374(5)	[44]
$2\,^3S$ He	Variational Monte Carlo (Ψ_{13})	−2.175228(1)	This work
	Hylleraas expansion	−2.175229378237	[42]
	Slater geminal expansion	−2.175229376	[33]
	Double Hylleraas expansion	−2.1752293782367907	[31]
	VMC	−2.175226(2)	[7]
	QMC	−2.175243(66)	[45]
$2\,^1S$ He	Variational Monte Carlo (Ψ_1)	−2.1459737(5)	This work
	Hylleraas expansion	−2.145974037	[46]
	Slater geminal expansion	−2.145973824	[33]
	Double Hylleraas expansion	−2.145974046054143	[31]
	QMC	−2.14493(7)	[47]
$1\,^2S$ Li	Variational Monte Carlo (Ψ_{18})	−7.47800(3)	This work
	Hylleraas expansion	−7.478060326	[37]
	MBPT(2)	−7.4743	[48]
	CI	−7.477906662	[49]
	VMC	−7.4768(3)	[12]
	QMC	−7.47809(24)	[50]
$1\,^1S$ Be	Variational Monte Carlo (Ψ_{16})	−14.6667(2)	This work
	Hylleraas expansion	−14.66654	[51]
	Numerical MCSCF	−14.66737(3)	[41]
	Numerical CCSD	−14.666690	[52]
	CCSD(T)	−14.667264	[53]
	VMC	−14.66648(1)	[17]
	QMC	−14.66718(3)	[17]

tor of the Padé. During the optimization step, these nodes were placed in poorly sampled regions. If a configuration happens to sample this region during the expansion, a singularity is produced. We were able to eliminate this problem by making the coefficients in the denominator of the Padé positive definite, i.e., changing b_k to b_k^2 but this significantly increased the variances of these functions.

Conclusions

In this article, we examined the relationship between wave-function form and the rate of convergence for several atomic systems. Our calculations reveal a number of trends:

There is often a tradeoff one must make between the complexity of a wave-function form and its computational cost. Although the convergence of the Slater-geminal forms was quite good for helium, its structure makes it difficult to add additional functions. In contrast, both Hylleraas and Padé forms allow additional terms to be added in a straightforward manner. Because the Padé and Slater-geminal forms contain a number of nonlinear parameters per basis function, they take much longer to optimize than a Hylleraas form (in fact, our Padé optimizations were almost always started from the corresponding Hylleraas result). Once all parameters are optimized, however, the computational time needed to evaluate a trial wave function scales as the number of basis functions.

We find that of use of minimal orbitals to describe the boundary conditions (a concept not explicitly described in [7] but which is used there and in [17]) leads to an especially compact wave-function form. Because information about the Hartree–Fock determinant is available for many systems, a large number of trial wave functions incorporate this function. Hartree–Fock orbitals, however, contain a number of parameters which do not provide any information about the asymptotic or nodal behavior of the system but exist only to maintain orthogonality with the other orbitals. In a Monte Carlo calculation, this orthogonality requirement is unnecessary and may slow convergence.

We have found that explicit permutation of the electrons leads to even more flexible wave-function forms and more rapid convergence than do similar forms which are based on determinants. Explicit permutation of the wave function can probably be used in systems with up to about six electrons before the computational cost becomes prohibitive. The latter, however, give good results and will be much cheaper for systems with large number of electrons.

Transformed coordinates allow us to create exponential Hylleraas-type wave functions which do not violate the boundary conditions at large distances. Our calculations show that after a trial wave function reaches a certain level of accuracy these exponential forms are more accurate than are the corresponding linear forms. This can probably be attributed to the fact that an exponential form is able to adjust more rapidly to changes in the wave function. Because it is also a positive definite function, the exponential form cannot introduce extraneous nodes.

In general, we have found that the form of our trial wave function does not need to explicitly satisfy the cusp condition at the origin in order to obtain highly accurate results. The error associated with this omission is easily corrected by having the optimized guiding function put more configurations in this region. We have examined several wave-function forms which do explicitly satisfy this cusp condition and found that for a fixed number of constants they raised the total energy and/or the variance. We recommend that such terms not be used.

Our calculations confirm that the Padé form introduced by Umrigar et al. [7] is capable of producing low variances (and most of the correlation energy) with few parameters for the ground and excited states of helium. Although we have presented the results from only $[m, m]$-type Padés, we have explored the use of $[m, n]$-type Padés and found without exception that they performed slightly worse. Unfortunately, the rapid convergence of the Padé form seems to be restricted only to the helium atom. For larger systems, we find that the energies and variances produced by Hylleraas and Padé forms are not substantially different when examined on a per constant basis. This, together with the problems we had expanding the Padé forms for lithium and beryllium, led us to recommend that Hylleraas forms with transformed coordinates be used as the basis for future atomic calculations.

ACKNOWLEDGMENTS

We wish to thank Dr. Cyrus Umrigar with generously sharing with us the details of his helium and beryllium wave functions. We also wish to thank Drs. J. D. Morgan III, H. J. Monkhorst, R. D. Poshusta, B. Jezorzski, and K. Szalewicz for many useful discussions and the staff of the Northeast Regional Data Center for their support in running our program on the University of Florida IBM NERSP.

Appendix 1: Excited-state Calculations

The procedure used to optimize the wave functions of excited states is basically the same as the one used for ground states. For the first excited state, the optimization functional of the wave function must be changed from Eq. (2) to

$$\frac{\sum_i [H\Psi_t(\mathbf{x}_i) - E_{in}\Psi_t(\mathbf{x}_i)]^2 \frac{\Psi_t(\mathbf{x}_i)^2}{w(\mathbf{x}_i)}}{\left\{\sum_i \frac{\Psi_t(\mathbf{x}_i)^2}{w(\mathbf{x}_i)}\right\}^2} + \lambda \frac{\left\{\sum_i \frac{\Phi_t(\mathbf{x}_i)\Psi_t(\mathbf{x}_i)}{w(\mathbf{x}_i)}\right\}^2}{\sum_i \frac{\Phi_t(\mathbf{x}_i)^2}{w(\mathbf{x}_i)} \sum_i \frac{\Psi_t(\mathbf{x}_i)^2}{w(\mathbf{x}_i)}}. \tag{A1}$$

Here, Φ_t is the optimized wave function for the ground state and Ψ_t is the trial wave function for the first excited state. The second term approximately orthogonalizes the first excited state to the ground state. Higher excited states can be generated in similar manner. While this procedure has proved to be quite accurate [15], the only way to be certain that an excited state is rigorously orthogonal to all lower-state approximate wave functions is to perform a Rayleigh–Ritz calculation [13].

In [15], we reported that the mixing parameter $\lambda = 0.001$ was adequate for most applications. During the current calculations, we noticed that when the variance is smaller than 10^{-3} the optimization was frequently dominated by the orthogonality rather than by the variance. Setting $\lambda = 0.1\sigma$ removes this problem. As both Table XI and Figure 5 illustrate, this value produces a low variance and sufficient orthogonality with the ground state for accurate optimization.

Appendix 2: Electron Permutation

A fermion wave function must be antisymmetric with respect to all electrons. In many textbooks, this requirement is usually expressed as a summation over all $N!$ permutations (see, e.g., [54]):

$$\Psi(1,2\ldots N) = \frac{1}{\sqrt{N!}} \sum_v (-1)^v P_v \Phi(1,2\ldots N), \tag{A2}$$

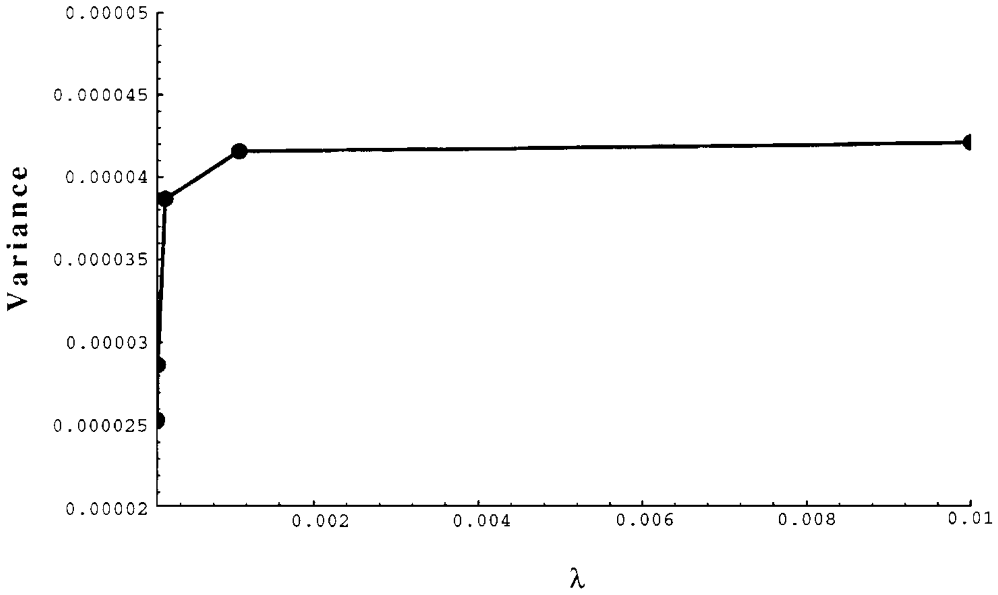

FIGURE 5. Convergence of a helium ^2S wave function as a function of the orthogonality parameter λ.

TABLE XI
Energy of the helium singlet excited state and its overlap with the helium ground state as a function of the orthogonality parameter λ in Eq. (A1).

λ	Energy	Overlap
10^{-2}	$-2.1459924 \pm 0.4188e\text{-}4$	$0.114e\text{-}4$
10^{-3}	$-2.1459901 \pm 0.4154e\text{-}4$	$0.124e\text{-}3$
10^{-4}	$-2.1459836 \pm 0.3866e\text{-}4$	$0.110e\text{-}2$
10^{-5}	$-2.1459684 \pm 0.2865e\text{-}4$	$0.522e\text{-}2$
10^{-6}	$-2.1459721 \pm 0.2536e\text{-}4$	$0.815e\text{-}2$
10^{-7}	$-2.1459740 \pm 0.2528e\text{-}4$	$0.862e\text{-}2$

The excited state wave function is Φ_8 ($N = 2$) as described in Table VI and the ground-state wave function is Ψ_{26} ($N = 2$) as described in Table III. All values are in atomic units.

where $P_v\Phi(1, 2 \ldots N)$ denotes the function obtained from $\Phi(1, 2 \ldots N)$ by the vth permutation of the N electrons in the system. If Φ contains only single-particle functions, Ψ can be written simply as a Slater determinant (which may not be an eigenfunction of the spin). If Φ contains interparticle coordinates, however, one must explicitly permute the electrons in the wave function in order to properly incorporate antisymmetry. The symmetric group approach is perhaps the most straightforward method of determining which of the possible $N!$ operations will contribute to a particular spin state [55]. In this procedure, one first writes down the Young diagram for the desired spin state, antisymmetrizes with respect to the columns, and then symmetrizes with respect to the rows. For the lithium doublet ground state, this leads to

$$\begin{aligned} \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}\ \Phi &= [I + (12)][I - (13)]\Phi \\ &= [I + (12) - (13) - (12)(13)]\Phi. \end{aligned} \tag{A3}$$

Here, I is the unit operator (no permutation) and (ij) interchanges electrons i and j in Φ. For the beryllium singlet ground state, the symmetric group approach yields

$$\begin{aligned} \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline\end{array}\ \Phi &= [I + (12)][I + (34)][I - (13)] \\ &\quad \times [I - (24)]\Phi \\ &= [I + (12) + (34) - (13) - (24) \\ &\quad + (12)(34) - (12)(13) - (12)(24) \\ &\quad - (34)(13) - (34)(24) - (13)(24) \\ &\quad - (12)(34)(13) - (12)(34)(24) \\ &\quad + (12)(13)(24) + (34)(13)(24) \\ &\quad + (12)(34)(13)(24)]\Phi. \end{aligned}$$

With such wave functions, the computation of the total energy [Eq. (1)] and the variance [Eq. (2)] is straightforward. For each configuration, one simply evaluates the trial wave function Φ as well as the quantity $H\Phi$ at each set of permuted electronic coordinates specified by the symmetric group approach. These values are then summed with the proper signs to produce Ψ and $H\Psi$, respectively. In our lithium calculation, this method requires four evaluations of the trial wave function for each configuration, and for beryllium, 16 evaluations. Although the computational cost of an explicitly permuted wave function is larger than that required by a wave function which uses a determinant to permute the electrons, the large reduction in the variance which we obtain does justify the additional expense.

References

1. R. L. Coldwell, Int. J. Quantum Chem. **S11**, 215 (1977).
2. R. L. Coldwell and R. E. Lowther, Int. J. Quantum Chem. **S12**, 329 (1978).
3. R. L. Coldwell, Int. J. Quantum Chem. **S13**, 705 (1979).
4. R. E. Lowther and R. L. Coldwell, Phys. Rev. A **22**, 14 (1980).
5. J. W. Moskowitz and M. H. Kalos, Int. J. Quantum Chem. **20**, 1107 (1981).
6. J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, J. Chem. Phys. **76**, 1064 (1982).
7. C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, Phys. Rev. Lett. **60**, 1719 (1988).
8. C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, in *Computer Simulation Studies in Condensed Matter Physics* D. P. Landau and H. B. Schuttler, Eds. (Springer, New York, 1988).
9. Z. Sun, P. J. Reynolds, R. K. Owens, and W. A. Lester, Jr., Theor. Chim. Acta **75**, 353 (1989).
10. S. Huang, Z. Sun, and W. A. Lester, Jr., J. Chem. Phys. **92**, 597 (1990).
11. Z. Sun, S. Y. Huang, R. N. Barnett, and W. A. Lester, Jr., J. Chem. Phys. **93**, 3326 (1990).
12. K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **93**, 4172 (1990); *Ibid*. **97**, 3382 (1992).
13. S. A. Alexander, R. L. Coldwell, H. J. Monkhorst, and J. D. Morgan III, J. Chem. Phys. **95**, 6622 (1991).
14. S. A. Alexander, R. L. Coldwell, G. Aissing, and A. J. Thakkar, Int. J. Quantum Chem. **S26**, 213 (1992).
15. S. A. Alexander, R. L. Coldwell, and J. D. Morgan III, J. Chem. Phys. **97**, 8407 (1992).

16. Z. Sun, W. A. Lester, Jr., and B. L. Hammond, J. Chem. Phys. **97**, 7585 (1992).
17. C. J. Umrigar, M. P. Nightingale, and K. J. Runge, J. Chem. Phys. **99**, 2865 (1993).
18. T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
19. C. Schwarz, Meth. Comp. Phys. **2**, 241 (1963).
20. B. Klahn and W. A. Bingel, Theor. Chim. Acta **44**, 9, 27 (1977).
21. B. Klahn and J. D. Morgan III, J. Chem. Phys. **81**, 410 (1984).
22. R. N. Hill, J. Chem. Phys. **83**, 1173 (1985).
23. J. D. Morgan III, in *Numerical Determination of the Electronic Structure of Atoms, Diatomics and Polyatomic Molecules*, NATO ASI Series #271, M. Defranceschi and J. Delhalle, Eds., (Kluwer, Boston, 1989).
24. W. Kutzelnigg and J. D. Morgan III, J. Chem. Phys. **96**, 4484 (1992).
25. E. Clementi and C. Roetti, At. Data Nucl. Data Tab. **14**, 177 (1974).
26. J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, Phys. Rev. A **41**, 1247 (1990).
27. L. C. Green, S. Matsushima, C. Stephens, E. K. Kolchin, M. M. Kholer, Y. Wang, B. B. Baldwin, and R. J. Wisner, Phys. Rev. **112**, 1187 (1958).
28. H. O. Prichard, J. Chem. Phys. **40**, 1496 (1964).
29. T. S. Carlton, J. Chem. Phys. **53**, 4234 (1970).
30. K. E. Banyard and G. J. Seddon, J. Chem. Phys. **58**, 1132 (1973).
31. G. W. F. Drake, Nucl. Inst. Methods B **31**, 7 (1988).
32. A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 1 (1977).
33. A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 16 (1977).
34. D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).
35. P. C. Abbot and E. N. Maslen, J. Phys. B **19**, 1595 (1986).
36. H. Eyring, J. Walter, and G. E. Kimble, *Quantum Chemistry* (Wiley, New York, 1944), pp. 135–151.
37. D. K. McKenzie and G. W. F. Drake, Phys. Rev. A **44**, R6973 (1991).
38. D. B. Kinghorn and R. D. Poshusta, Phys. Rev. A **47**, 367 (1993).
39. E. Schwegler, P. M. Kozlowski, and L. Adamowicz, J. Comp. Chem. **14**, 566 (1993).
40. W. Cencek and J. Rychlewski, J. Chem. Phys. **102**, 2533 (1995).
41. A. M. Martensson-Pendrill, S. A. Alexander, L. Adamowicz, N. Oliphant, J. Olsen, P. Oster, H. M. Quiney, S. Salomonson, and D. Sundholm, Phys. Rev. A **43**, 3355 (1991).
42. C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).
43. S. Rybak, K. Szalewicz, and B. Jeziorski, J. Chem. Phys. **91**, 4779 (1989).
44. R. J. Harrison and N. C. Handy, Chem. Phys. Lett. **113**, 257 (1985).
45. S. Zhang and M. H. Kalos, Phys. Rev. Lett. **67**, 3074 (1991).
46. C. L. Pekeris, Phys. Rev. **127**, 509 (1962).
47. P. J. Reynolds, R. N. Barnett, B. L. Hammond, R. M. Grimes, and W. A. Lester, Jr., Int. J. Quantum Chem. **29**, 589 (1986).
48. E. Eggarter and T. P. Eggarter, J. Phys. B **11**, 1157 (1978).
49. O. Jitrik and C. F. Bunge, Phys. Rev. A **43**, 5804 (1991).
50. W. A. Lester, Jr. and B. L. Hammond, Annu. Rev. Phys. Chem. **41**, 283 (1990).
51. J. S. Sims and S. A. Hagstrom, Phys. Rev. A **4**, 908 (1971).
52. S. Salomonson and P. Oster, Phys. Rev. A **41**, 4670 (1990).
53. J. Noga, Chem. Phys. Lett. **199**, 497 (1992).
54. A. S. Davydov, *Quantum Mechanics*, 2nd ed. (Pergamon, Oxford, 1976), p. 296.
55. C. D. H. Chisholm, *Group Theoretical Techniques in Quantum Chemistry* (Academic Press, London, 1976), Chaps. 6 and 7.