

Local behavior of the Clementi–Roetti atomic Hartree–Fock wave functions. Improved local accuracy using global constraints

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The reduced local Hartree–Fock energy for the neutral atoms Li through to Al have been calculated using the Hartree–Fock wave functions of Clementi and Roetti. These wave functions were found to give rather accurate values of the reduced local energy in the medium range region (r values 1–12 a.u.), but inaccurate values close to the nucleus. The reduced local energy was found in each case to exhibit oscillations about the “exact” total Hartree–Fock energy as a function of the configuration space coordinate r , indicating some cancellation of opposing errors in the wave functions used for the calculation of the total energy. A method is outlined for determining Hartree–Fock wave functions which not only satisfy the customary condition that the total energy be minimized, but in addition, are locally accurate. The criterion which is used to monitor the local accuracy is the reduced local energy. The reduced local energy is incorporated into a global accuracy constraint on the wave function, and the energy is determined subject to the minimization of this additional constraint. Calculations are performed for various helium wave functions. The five-term Clementi–Roetti wave function is refined, maintaining essentially the same total energy, but with considerable improvement in local accuracy. The Clementi (1965) wave function for helium is also refined. A ten-term function for helium is devised which has improved accuracy at the local level. Comparison of expectation values of r_1^{-1} using the different wave functions is made, in order to assess the utility of the reduced local energy as a criterion for refinement of such values.

INTRODUCTION

Hartree–Fock wave functions are used extensively in a variety of applications in molecular quantum chemistry and other fields. The accuracy of the Hartree–Fock approach is almost invariably ascertained by how close a particular expectation value, most frequently the energy, agrees with the experimental value. This criterion examines two important effects. First of all, such calculations reveal basic defects in the Hartree–Fock formalism. These calculations also reveal inaccuracies in the Hartree–Fock wave function employed. The inaccuracies revealed are global in nature. In a situation where the formalism is likely to be applicable, a close correspondence between experimental results and computed expectation values says nothing about the accuracy of the wave function at the local level. Errors in one region of configuration space may cancel those of another region of configuration space, and hence the computed expectation value may be in fortuitous agreement with experimental results.

An indication of accidental cancellation of errors may be obtained when the same “good” wave function is used to compute expectation values of operators which emphasize different regions of configuration space. It is unlikely that accidental cancellation of errors will occur for *each* operator, and thus an estimate of the local accuracy is obtained. While global accuracy is obviously an important necessary criterion, it is not the most sensitive test of the molecular wave function.

In this work, our attention is centered on a much more stringent test of the accuracy of the Hartree–Fock wave function, the local reduced Hartree–Fock energy, which is defined as follows:

$$E_L^{\text{HF}} = \frac{\int \Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) H \Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 \dots d\tau_N}{\int \Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 \dots d\tau_N} \quad (1)$$

This is a special case of the reduced local energy introduced by Rothstein and co-workers.¹ Equation (1) represents a necessary condition to be satisfied by the exact Hartree–Fock wave function. When the exact Hartree–Fock wave function is employed, Eq. (1) yields $E_L^{\text{HF}} = E^{\text{HF}}$. For an approximate Hartree–Fock wave function, the local energy E_L^{HF} depends on \mathbf{r}_1 , and the deviation between $E_L^{\text{HF}}(\mathbf{r}_1)$ and E^{HF} is a measure of the accuracy of the wave function at the point \mathbf{r}_1 in configuration space. To make the presentation of the results as simple as possible, both the numerator and denominator of Eq. (1) have been integrated over the angles (Θ_1, ϕ_1).

Recently the present authors² have employed Eq. (1) to examine the local accuracy of several two-electron Hartree–Fock wave functions for the helium atom^{3,4,5} and several members of the helium isoelectronic series.⁴ In that study, we showed that the reduced local energy is a very useful criteria for examining the accuracy of Hartree–Fock wave functions.

In the present work, Eq. (1) is applied to test the accuracy of the Clementi–Roetti atomic Hartree–Fock wave functions.⁴ The number of atomic Hartree–Fock calculations in the literature is extremely large. Clementi and Roetti’s tables represent an extensive tabulation of atomic Hartree–Fock wave functions. We have chosen these Hartree–Fock wave functions for the following reasons. First, these wave functions have received wide usage in the chemical literature, and therefore, some knowledge of their local accuracy seems very desirable. Second, the atomic case requires only one center integrals, with the result that the com-

ations require only a modest amount of computer time. Finally, the Hartree-Fock wave functions are presented in analytic form with the coefficients and orbital exponents tabulated by Clementi and Roetti. Although the Clementi-Roetti wave functions are accurate in the energetic sense, these wave functions do not accurately satisfy the cusp constraints,^{6,7} and this fact is reflected in the poor accuracy found for $E^{\text{HF}}(r)$ at small

The most difficult region to construct an accurate Hartree-Fock wave function is close to the nucleus. Expectation values of operators which weight this region heavily, e.g., the spin density operator, are required, then it is the near-nuclear region where the wave function must be refined. Basis sets which do not satisfactorily satisfy the cusp constraint have been discussed in the literature.^{6,8} The use of such basis sets is obviously highly desirable, but is *not sufficient* to guarantee an accurate value for the reduced local energy as $r \rightarrow 0$.

Part of the purpose of the present work is to utilize the reduced local energy as a local accuracy constraint to improve the quality of the wave function. There are two basic approaches that may be employed to achieve this goal. The first approach is to determine the minimum energy subject to the additional constraint that the reduced local energy be as accurate as possible. This can be achieved by considering a constraint of the form

$$|E^{\text{HF}} - E_L^{\text{HF}}(\mathbf{r})| < a, \quad (2)$$

where a is some specified constant which should be chosen sufficiently small for an accurate Hartree-Fock wave function to be obtained. Since the left-hand side of Eq. (2) is dependent on the configuration space coordinate \mathbf{r} , this constraint provides a means to improve the wave function in any specified region of configuration space. This approach is under investigation. The sec-

ond scheme is to consider the local inaccuracies in the wave function in a global manner, and this is the approach taken in the present study.

COMPUTATIONAL PROCEDURE FOR LOCAL ENERGY

The wave function $\Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is a Slater determinant constructed from the orbitals ϕ_i :

$$\Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \mathcal{A}(\phi_1 \cdots \phi_N), \quad (3)$$

where \mathcal{A} is the antisymmetrizer and N is the total number of electrons. The orbitals are expanded in terms of a set of basis functions

$$\phi_i(\mathbf{r}) = \sum_j^{\alpha_i} C_{ij} \chi_{ij}(\mathbf{r}), \quad (4)$$

where the basis functions $\chi_{ij}(\mathbf{r})$ are Slater-type orbitals with integer quantum numbers. The expansion coefficients C_{ij} and the orbital exponents (denoted α_i) for each Slater-type orbital are provided in tables by Clementi and Roetti.

Equation (1) can be rewritten as

$$E_L^{\text{HF}} = \frac{K + E_N + E_E}{\Gamma}, \quad (5)$$

where K , E_N , and E_E denote the reduced "kinetic energy", the reduced "electron-nuclear potential energy" and the reduced "electron-electron potential energy" respectively; Γ is N times the angle averaged electronic density. The calculation of the appropriate expressions for K , E_N , and E_E is straightforward though more tedious than the standard expressions for the total energy. This arises due to the loss of symmetry because integration over all coordinates is not carried out. To save space, the expressions for K , E_N , and E_E are omitted. To check the computations of the local energy, the total energy was evaluated directly from the local energy by numerical quadrature, and was found to be

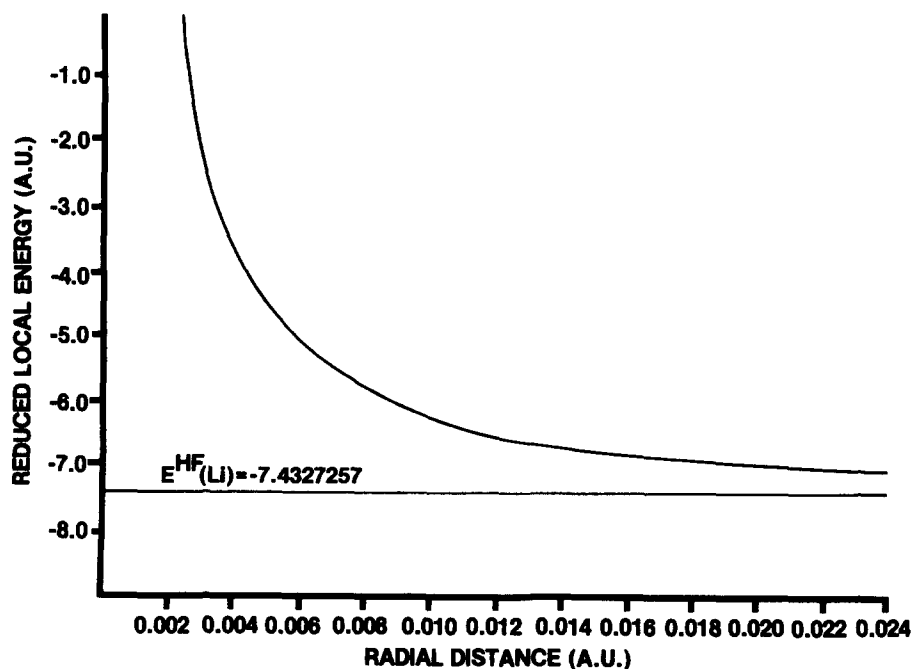


FIG. 1. The Hartree-Fock reduced local energy $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the Li atom for the short range region. The exact Hartree-Fock wave function should yield a reduced local energy which follows the horizontal line at -7.4327257 a.u.

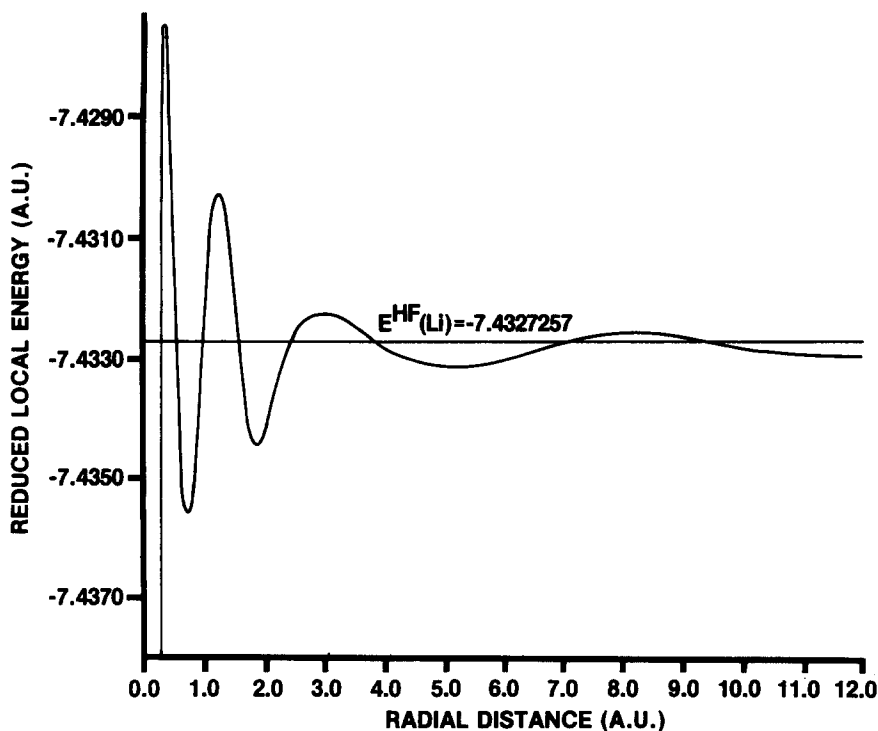


FIG. 2. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the Li atom for the medium range region.

in agreement with the results reported by Clementi and Roetti for each atom examined.

LOCAL ENERGY PLOTS FOR CLEMENTI-ROETTI FUNCTIONS

The results of our calculations of the reduced local energy are shown in Figs. 1-12. In all cases, the exact Hartree-Fock wave function would yield a reduced local energy that followed the horizontal line (r independent) indicated in each of the figures. All energies and radial distances are reported in atomic units.

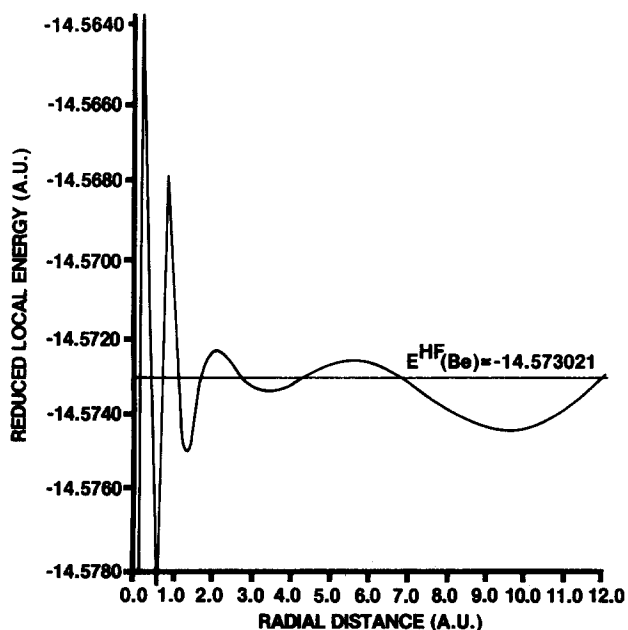


FIG. 3. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the Be atom.

For the Li atom, the short range behavior of the reduced local energy is shown in Fig. 1, and the medium range behavior is illustrated in Fig. 2. For the region close to the nucleus, the Hartree-Fock wave function for

TABLE I. Values of the reduced local energy at short range values of the configuration space coordinate r for the neutral atoms. The Hartree-Fock energies calculated by Clementi and Roetti are given for comparison. For the exact wave function, $E_L^{\text{HF}} = E^{\text{HF}}$.

Atom	Radial distance	Reduced local energy E_L^{HF}	Total energy
Li	2×10^{-4}	77.7518	-7.4327257
	2×10^{-2}	-6.9560	
Be	2×10^{-4}	81.4074	-14.573021
	2×10^{-2}	-14.1512	
B	2×10^{-4}	70.2849	-24.529057
	2×10^{-2}	-24.2229	
C (3P)	2×10^{-4}	60.6109	-37.688612
	2×10^{-2}	-37.4552	
N (4S)	2×10^{-4}	54.6937	-54.400924
	2×10^{-2}	-54.2011	
O (3P)	2×10^{-4}	69.9462	-74.809370
	2×10^{-2}	-74.5883	
F	2×10^{-4}	38.2799	-99.409300
	2×10^{-2}	-99.2728	
Ne	2×10^{-4}	-40.9906	-128.54705
	2×10^{-2}	-128.6030	
Na	2×10^{-4}	-101.9470	-161.85890
	2×10^{-2}	-161.9989	
Mg	2×10^{-4}	-144.3365	-199.61461
	2×10^{-2}	-199.7980	
Al	2×10^{-4}	-180.3364	-241.87668
	2×10^{-2}	-242.0590	

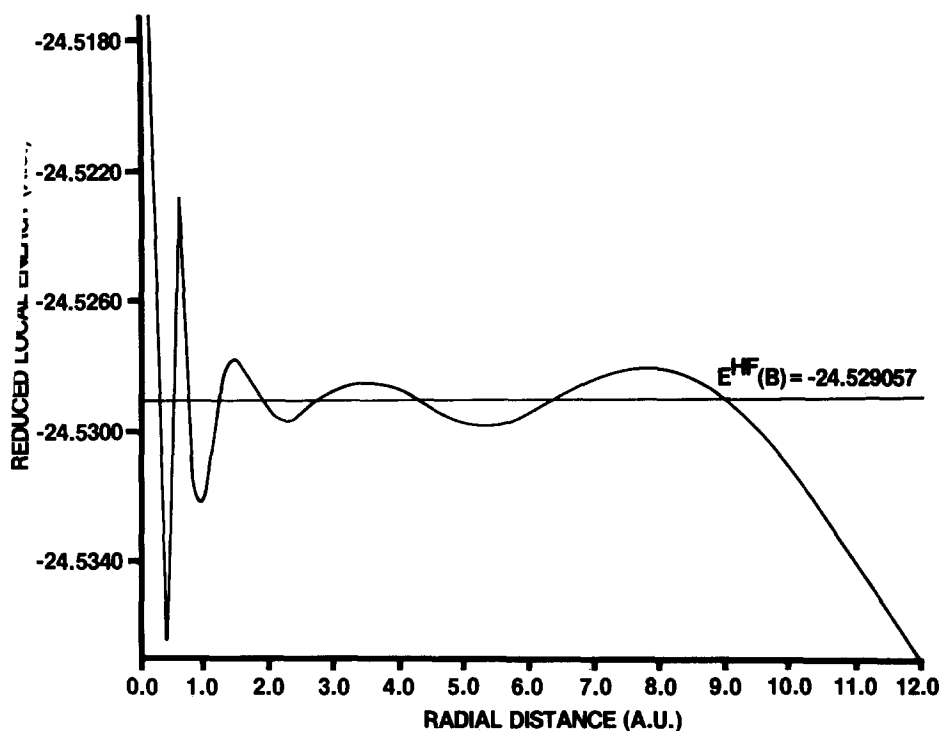


FIG. 4. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the B atom.

Li is of rather poor quality, as indicated by the fact that the reduced local energy becomes positive! All the neutral atoms examined gave curves of similar shapes for the reduced local energy as a function of r in the near-nuclear region.

An indication of the quality of the atomic Hartree-Fock wave functions of Clementi and Roetti at short range can be obtained from Table I, where the reduced local energy is given for two values of r close to the nucleus. For extremely accurate Hartree-Fock wave

functions, the reduced local energy should be close to the "exact" total Hartree-Fock energy which is reported in column 4 of Table I. In all cases, the Hartree-Fock wave functions are very inaccurate at distances close to the nucleus. Similar results were found in a study of two-electron systems.² With increasing Z , the inaccuracies in the wave functions for the neutral atoms are smaller, as can be observed from Table I.

The plots of the reduced local energy as a function of the radial distance for the neutral atoms, exhibit the

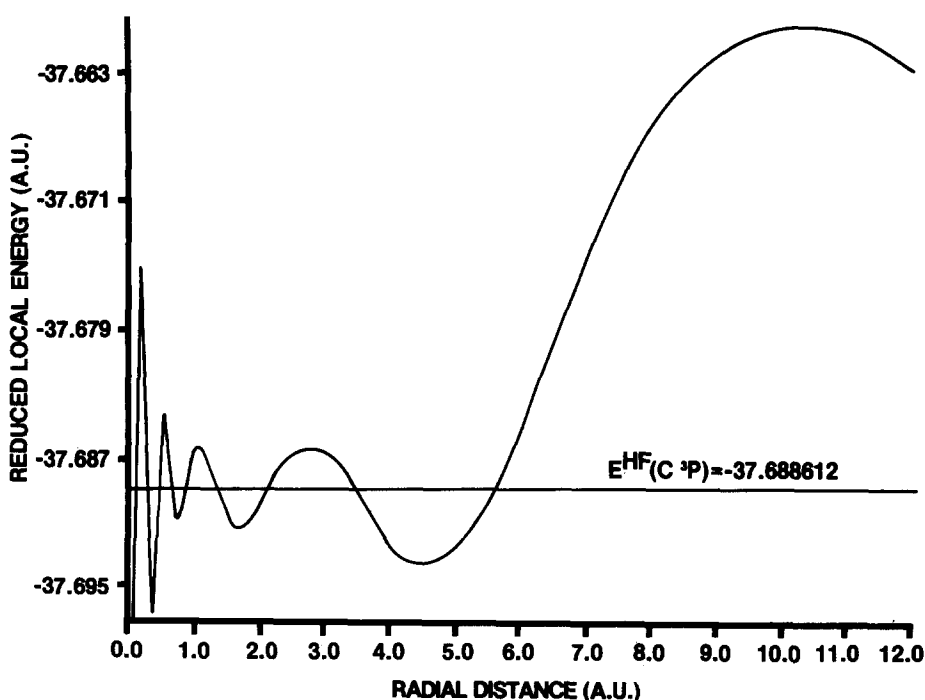


FIG. 5. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the C atom.

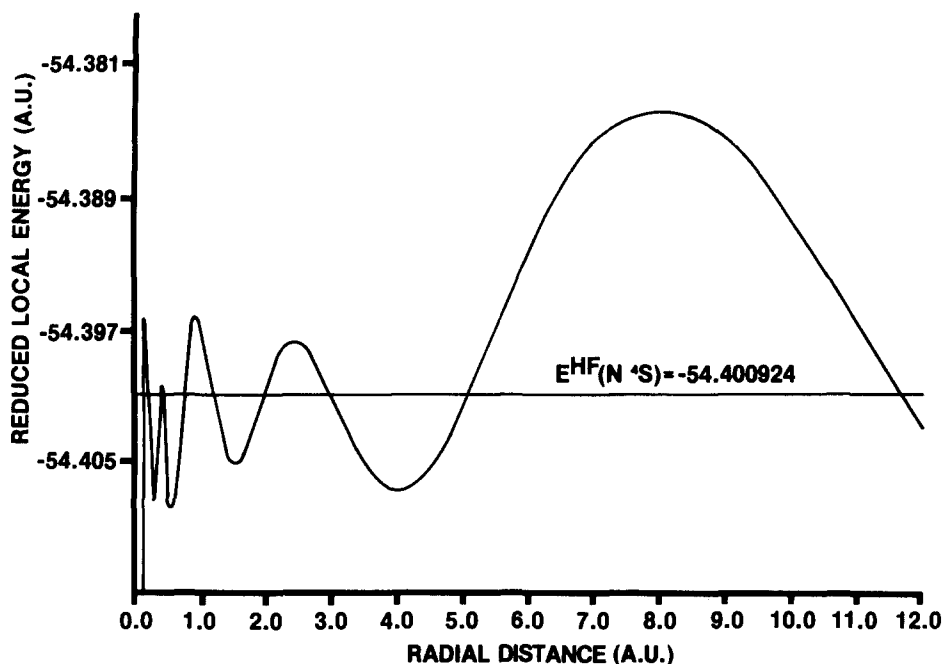


FIG. 6. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the N atom.

following general features for the region of configuration space $r \sim 0.1-12$ a.u. All the systems considered show sharp oscillations in the reduced local energy about the exact Hartree-Fock energy at r values near the nucleus ($r \sim 0.1-1$ a.u.). The reduced energy also oscillates at larger values of r . Two important observations must be noted from the figures. The Clementi-Roetti Hartree-Fock wave functions are fairly accurate for medium distances from the nucleus; typically $r \sim 1-10$ a.u. Since the Hartree-Fock reduced local energy determined from the Clementi-Roetti wave

functions oscillates about the exact Hartree-Fock energy, cancellation of inaccuracies in the wave function will result when the total Hartree-Fock energy is computed.

The figures also provide a guide as to where the Clementi-Roetti functions are likely to be useful for the computation of expectation values. For the calculation of expectation values of operators which place emphasis on the medium range of r (such as the energy), then the Clementi-Roetti wave functions are likely to

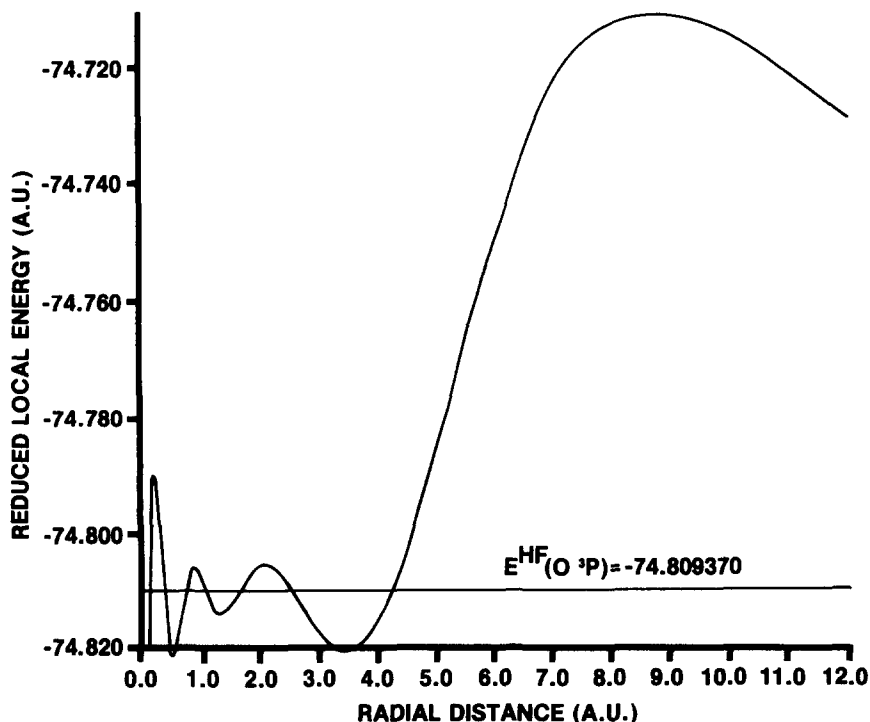


FIG. 7. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the O atom.

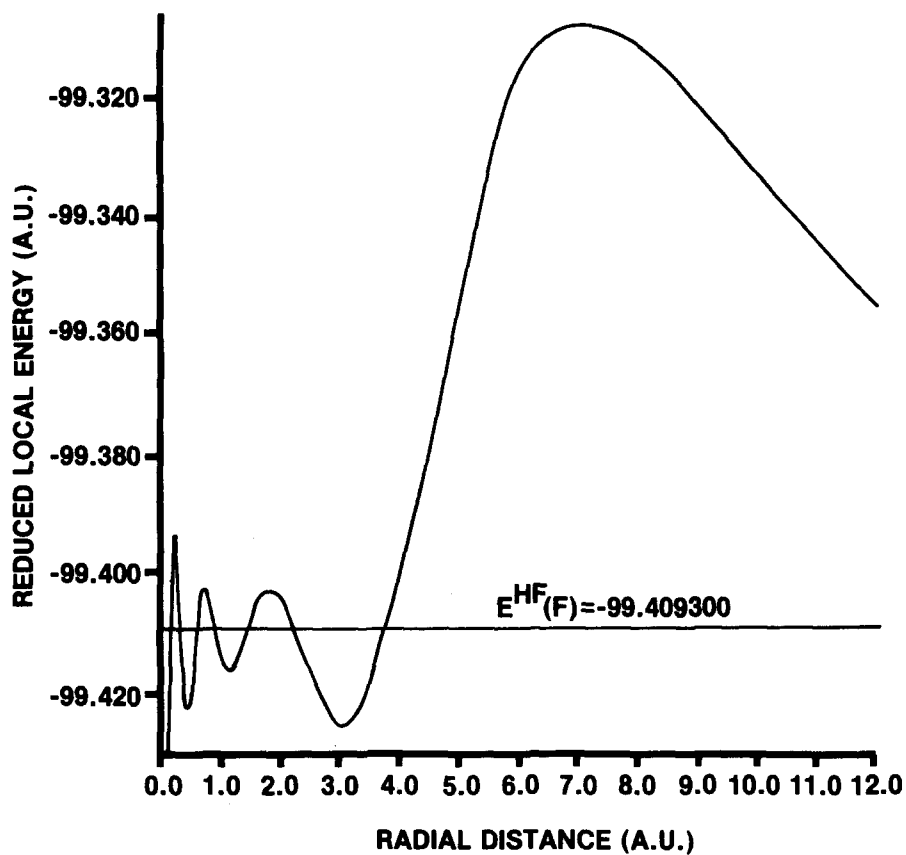


FIG. 8. $E_L^{HF}(\tau)$ as a function of τ for the ground state of the F atom.

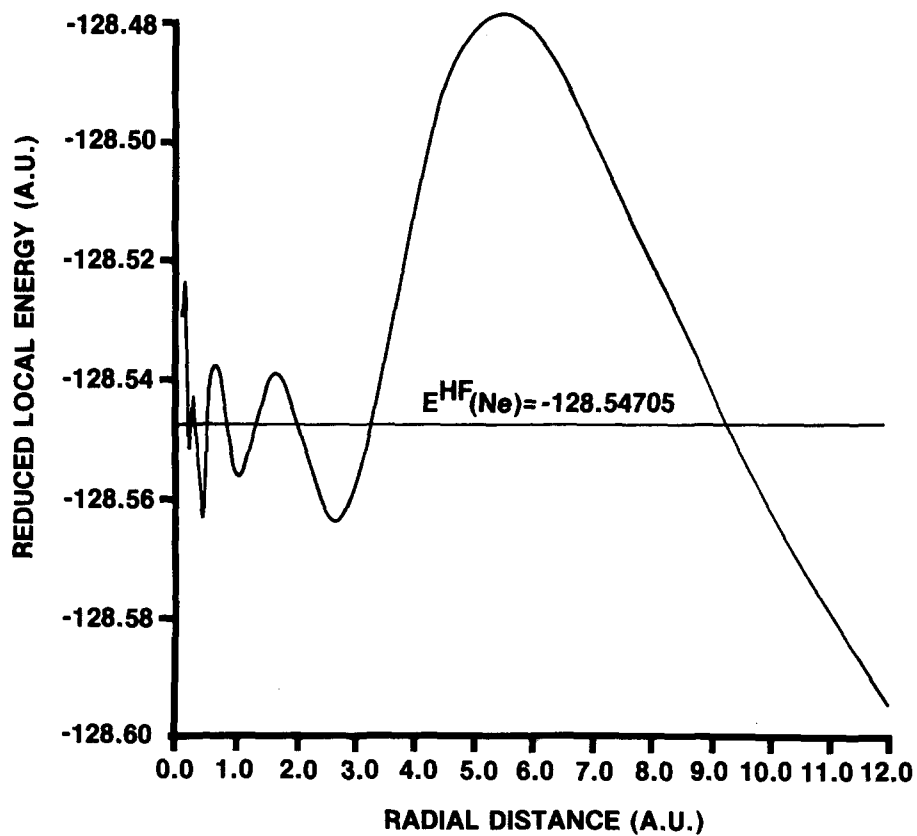


FIG. 9. $E_L^{HF}(\tau)$ as a function of τ for the ground state of the Ne atom.

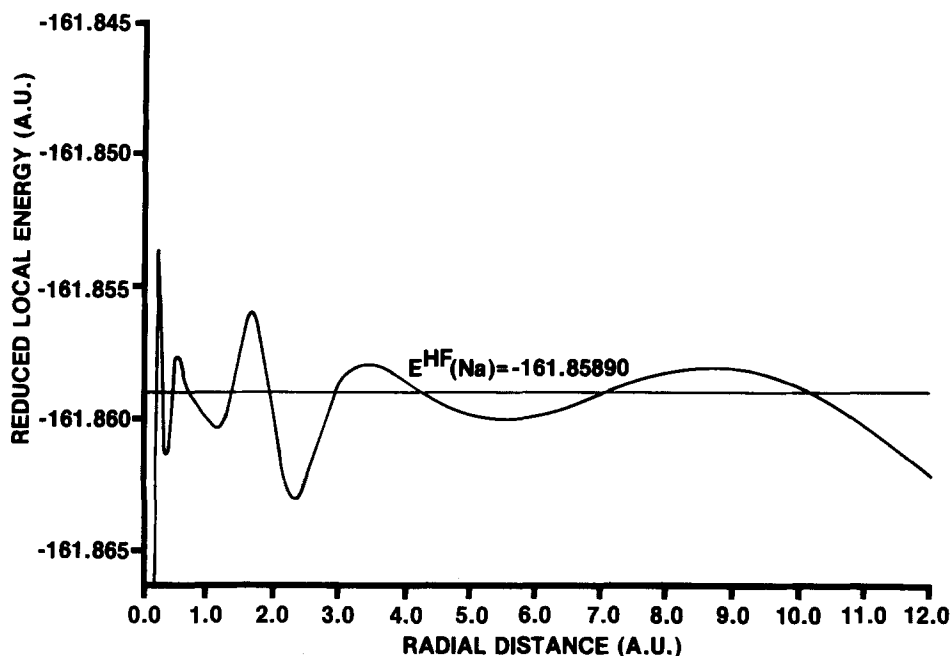


FIG. 10. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the Na atom.

give satisfactory results. The computation of expectation values of operators that place emphasis on the short range behavior of the wave function, for example hyperfine interactions, will lead to fairly poor values in such cases. A glance at Fig. 1 and the values listed in Table I should convince the reader of this fact. For the region r less than approximately 0.01 a.u., there are no oscillations in the reduced local energy, and there is no reason to expect cancellation of inaccuracies in the wave function when expectation values of operators that weight this region heavily are considered.

The poor behavior of the reduced local energy at small r values is a direct consequence of the fact that the Clementi-Roetti wave functions do not accurately satis-

fy the cusp constraint. It is to be noted that a wave function which obeys the cusp constraint will not *automatically* yield an accurate E_L^{HF} as $r \rightarrow 0$. It should also be remarked that the reduced local energy criterion tests not only the small r region of configuration space (i.e., the cusp quality of the wave function), but also examines *all* other points in configuration space. For this reason the Hartree-Fock reduced local energy criterion is a particularly useful test of the accuracy of the wave function.

GLOBAL CONSTRAINTS

A global measure of the local accuracy of the Hartree-Fock wave function is defined by the equation

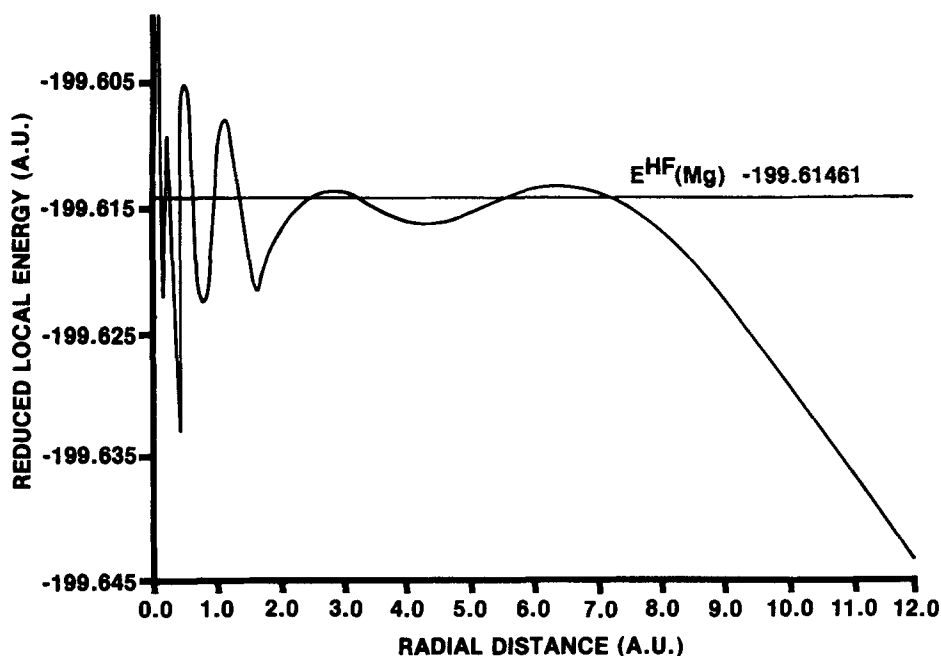


FIG. 11. $E_L^{\text{HF}}(r)$ as a function of r for the ground state of the Mg atom.

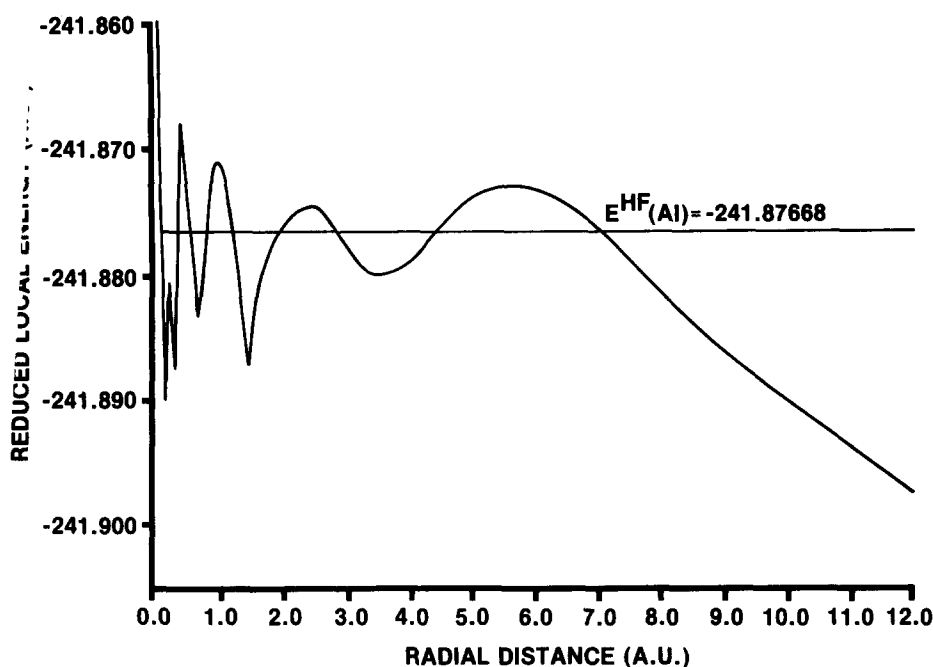


FIG. 12. $E_L^{HF}(r)$ as a function of r for the ground state of the Al atom.

$$D = \frac{1}{N} \int (E^{HF} - E_L^{HF}(r))^2 \rho(r) dr, \quad (6)$$

where $\rho(r)$ is the Hartree-Fock electronic density, which satisfies

$$\int \rho(r) dr = N. \quad (7)$$

The quantity D satisfies the following important condition:

$$D \rightarrow 0 \text{ as } E_L^{HF}(r) \rightarrow E^{HF}. \quad (8)$$

We call D a global measure of the local accuracy because it's independent of configuration space coordinates. This is to be contrasted with a constraint like the one described by Eq. (2), which provides a local measure of the accuracy of the wave function. Note that D is always positive. The global functional $D[C]$ is used as an additional Lagrange constraint in the standard energy minimization procedure. The problem is then reduced to finding the coefficients C such that the energy is a minimum, subject to the constraints that the orbitals are orthonormal and that D is a minimum. The minimization equation for the energy takes the form

$$\delta E[C] + \lambda \delta D[C] + \mu \delta S[C] = 0, \quad (9)$$

where λ and μ are Lagrange multipliers and S is the normalization integral.

The coefficient vector C has been determined so that the variation of C , denoted δC , satisfies

$$E[C - \delta C] < E[C]. \quad (10)$$

In the calculations, the global constraint D has first been minimized with respect to variations in the coefficient vector C to yield the value D_m . The energy is then minimized by adjustment of C subject to the orthogonality constraint and the additional constraint

$$D[C] - D_m = 0. \quad (11)$$

The whole process can be repeated to yield a value of D_m and a lower energy E .

In the present work, we have concentrated our attention on the helium atom. The Clementi-Roetti⁴ five term Hartree-Fock wave function has been examined, and we have obtained substantial improvement in the local sense, without any loss in the energy minimum. A similar refinement has also been carried out for the Clementi³ five term function, however, in this case, only slight improvement in local accuracy is achieved. A ten term wave function has been devised and this gives the best local accuracy of all the wave functions considered (smallest D_m).

TABLE II. Local accuracy of various helium wave functions indicated by the global measure of local accuracy D .

Wave function	Energy(a. u.)	D
Single zeta ^a	-2.8476562	0.156
Double zeta ^a	-2.8616726	0.310×10^{-4}
Three term ^a	-2.8616784	0.194×10^{-3}
Clementi-Roetti ^a five term	-2.8616799	0.663×10^{-5}
Refined Clementi-Roetti five term	-2.8616798	0.781×10^{-6}
Clementi ^b five term	-2.8616799	0.721×10^{-7}
Refined Clementi five term	-2.861680	0.642×10^{-7}
Roothaan-Sachs-Weiss ^c twelve term	-2.861680	0.127×10^{-5}
Ten term	-2.861680	0.165×10^{-7}

^aWave functions from Ref. 4. ^cWave function from Ref. 5.

^bWave function from Ref. 3.

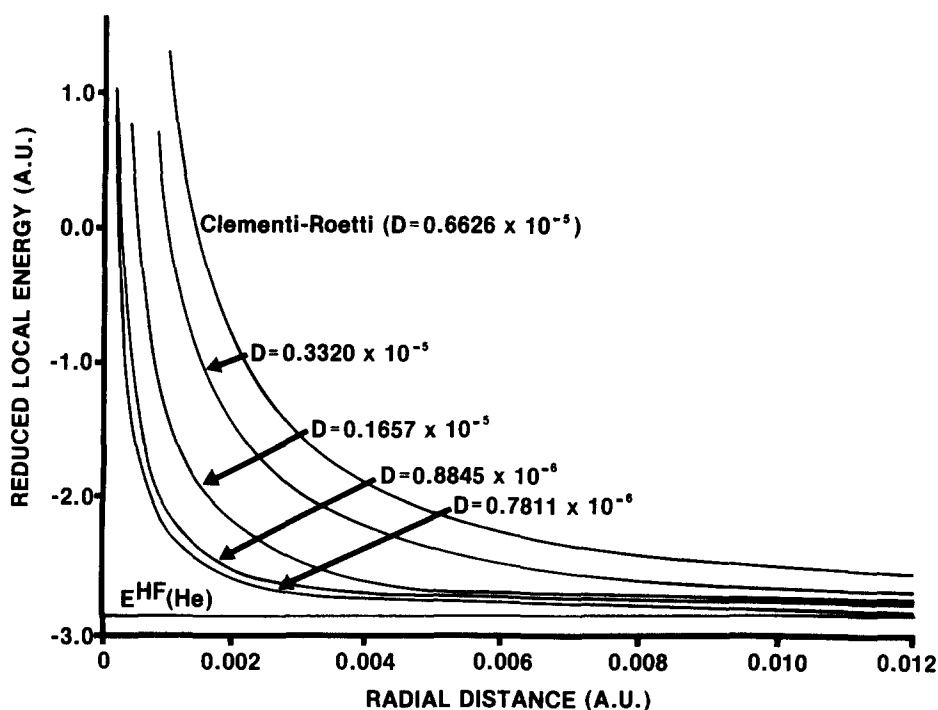


FIG. 13. Hartree-Fock reduced local energy in the near nuclear region for the five term Clementi-Roetti ground state helium wave function for progressive refinements to this wave function. In the near nuclear region the D values reflect the improvement in the reduced local energy.

CONSTRAINED CALCULATIONS

To give some idea of how D varies with different wave functions, we have calculated this quantity for the four ground state helium wave functions reported by Clementi and Roetti,⁴ the five term function of Clementi,³ the refined Clementi-Roetti and refined Clementi functions calculated in this work, the twelve term function of Roothaan-Sachs and Weiss,⁵ and also the ten term function devised in this work (see Table II). It is not too surprising to find that the single zeta function gives a rather large D value. The fact that the three term wave function gives a D value larger than the D value for the double zeta function can be probably traced to the fact that one of the coefficients or orbital exponents (or both) reported by Clementi and Roetti must be a typographical error, a fact noted in our earlier calculations.² To get some idea of how accurate each of the Clementi-Roetti wave functions is on the local level, the reader should consult the plots of the reduced local energy versus r in our previous paper.²

The refined five term entries in Table II were determined in the following manner. The Clementi-Roetti five term wave function was used as input into the scheme discussed in the Global Constraints section, and D minimized. The Clementi-Roetti starting point is not

essential, it just saves some additional computations. The same procedure was used for the refinement of the Clementi function. Because of the slow convergence, the values reported for D are possibly uncertain by approximately 1-3 in the last quoted figure for the refined and ten term functions reported in Table II.

Figure 13 illustrates how the reduced local energy as a function of r changes for different values of D . All the curves shown in Fig. 13 are for five term wave functions employing the orbital exponents given by Clementi and Roetti.⁴ It is the short range r region ($r < 0.1$ a. u.) where the factor $[E^{\text{HF}} - E_L^{\text{HF}}(\mathbf{r})]^2$ is largest and this is where considerable improvement is obtained for the reduced local energy as D becomes progressively smaller.

There are two points to note with respect to the refinement of the Clementi-Roetti five term wave function. First, the *additional* constraint that D be a minimum no longer guarantees that the energy minimum reached by Clementi and Roetti can be achieved. Second, only minor changes in the expansion coefficients can result in appreciable improvements in the reduced local energy. This is indicated by the results tabulated in Table III where it is observed that small changes in the expansion coefficients have resulted in a marked

TABLE III. Variation of the global measure of the total accuracy D , for changes in the expansion coefficients of the five term helium wave function of Clementi and Roetti.

D	Expansion coefficients					Energy
	C_1	C_2	C_3	C_4	C_5	
0.663×10^{-5}	0.76838	0.22346	0.04082	-0.00994	0.00230	-2.86167990
0.332×10^{-5}	0.768393	0.223426	0.040823	-0.009865	0.002233	-2.86167990
0.166×10^{-5}	0.768475	0.223357	0.040660	-0.009508	0.002033	-2.86167988
0.885×10^{-6}	0.767965	0.224383	0.039497	-0.008468	0.001609	-2.86167986
0.781×10^{-6}	0.767553	0.225091	0.038904	-0.008024	0.001443	-2.86167979

TABLE IV. Asymptotic limits for the local energy E_L^{HF} and cusp factors for the Clementi, Clementi-Roetti, and refined versions of these wave functions.

Wave function	$E_L^{\text{HF}}(r=\infty)$	$E_L^{\text{HF}}(r=0)$	$\frac{\sum_i C_i \alpha_i N_i}{\sum_i C_i N_i} - Z$
Single Zeta ^a	-3.3750	-1.6875	-0.313
Double Zeta ^a	-3.0002	-3.0132	0.399×10^{-2}
Three Term ^a	-2.9888	-3.1478	0.179×10^{-2}
Clementi-Roetti ^a five term	-2.9479	-2.9834	0.431×10^{-2}
Refined Clementi-Roetti five term	-2.9479	-2.8978	0.648×10^{-3}
Clementi five term ^b	-2.2620	-2.8682	0.144×10^{-3}
Refined Clementi five term	-2.2620	-2.8684	0.103×10^{-3}
Ten term	-1.9858	-2.8662	0.848×10^{-4}

^aWave functions from Ref. 4.

^bWave function from Ref. 3.

improvement in D . The loss in the energy minimum is found to be almost negligible (a fraction of a cm^{-1}).

A stringent test of how accurate the wave functions can be obtained by examination of the asymptotic limits. For the two-electron case, the formula for $E_L^{\text{HF}}(\infty)$ was given in Ref. 2. For the limit $r \rightarrow 0$,

$$E_L^{\text{HF}}(r=0) = -\frac{3}{2} \frac{\sum_i C_i N_i \alpha_i^2}{\sum_i C_i N_i} - \sum_i \sum_j \frac{C_i C_j N_i N_j}{\zeta_{ij}^3} \times [(Z-1)\zeta_{ij} - \alpha_i \alpha_j] + \left(\frac{\sum_i C_i N_i \alpha_i}{\sum_i C_i N_i} \right)^2, \quad (12)$$

if

$$\frac{\sum_i C_i N_i \alpha_i}{\sum_i C_i N_i} = Z, \quad (13)$$

otherwise

$$E_L^{\text{HF}}(r=0) \rightarrow \pm \infty. \quad (14)$$

In Eq. (12), $\zeta_{ij} = \alpha_i + \alpha_j$ and N_i are the appropriate normalization factors. Equation (12) was stated incorrectly in Ref. 2. Corrected values of $E_L^{\text{HF}}(r=0)$ for the helium wave functions are given in Table IV; corrected values for Li^+ through Ne^{8+} are respectively -7.6681, -14.369, -22.862, -33.247, -45.492, -59.781, -76.445, and -94.466. The asymptotic results for the various wave functions considered in this work are summarized in Table IV. For none of the wave functions considered is Eq. (13) exactly satisfied, and so Eq. (14) determines the limit $r \rightarrow 0$. Column 3 in Table IV reports the values of $E_L^{\text{HF}}(r=0)$ ignoring the $1/r$ Coulomb singularity [that is, assuming Eq. (13) is exactly satisfied]. It is to be noted that the condition given above, Eq. (13), that the local energy be nonsingular at $r=0$, is equivalent to the constraint that the basis function satisfies the standard cusp condition.

The following observations can be made from Table IV: (i) Not too surprising is the fact that the values of $E_L^{\text{HF}}(r=0)$ are fairly poor except for the Clementi five

term and the ten term functions. The values of $E_L^{\text{HF}}(r \rightarrow \infty)$ show a systematic increase as the local accuracy (as measured by D) is improved. It might be expected that much better values of $E_L^{\text{HF}}(r \rightarrow \infty)$ should be readily obtained. However, this cannot be achieved easily with a global measure of accuracy like the one considered in this work. The majority of the error in the wave function arises in the region near the nucleus. The minimization process for D gains maximum improvement (in D_m) by making adjustments to the coefficients which directly affect the near-nuclear region. Since there is only small improvement to be gained at large r , and because of the long-range behavior of the weight function $\rho(r)$ improvement of the reduced local energy at large r is not dramatic. It is reasonable to conjecture that once the near-nuclear region has been considerably refined, then improvements in the reduced local energy at large r could be achieved, as these would become a major contribution to D once the short range deviations have been corrected. (ii) The cusp factor becomes smaller as the quality of the wave function improves (as measured by the values of D).

In the refined calculations based on the wave functions of Clementi and Clementi and Roetti, the orbital exponents have not been changed. Additional refinements in the reduced local energy can be obtained by an iterative scheme in which the orbital exponents are optimized following the energy and D minimizations.

The ten term function indicated in Tables II and IV was constructed from the Clementi five term function. The first five orbital exponents were those given by Clementi, the next five, chosen by stepwise minimization of D , have the values: $\alpha_6 = 3.97$, $\alpha_7 = 1.46$, $\alpha_8 = 0.29$, $\alpha_9 = 4.61$, and $\alpha_{10} = 0.53$. The coefficients obtained from the D constrained minimization are

$$\begin{aligned} C_1 &= 0.206\,911\,46, & C_2 &= 0.162\,010\,50, \\ C_3 &= -0.446\,389\,21, & C_4 &= -0.404\,946\,47 \times 10^{-2}, \\ C_5 &= 0.187\,529\,13 \times 10^{-1}, & C_6 &= 0.432\,142\,89, \end{aligned}$$

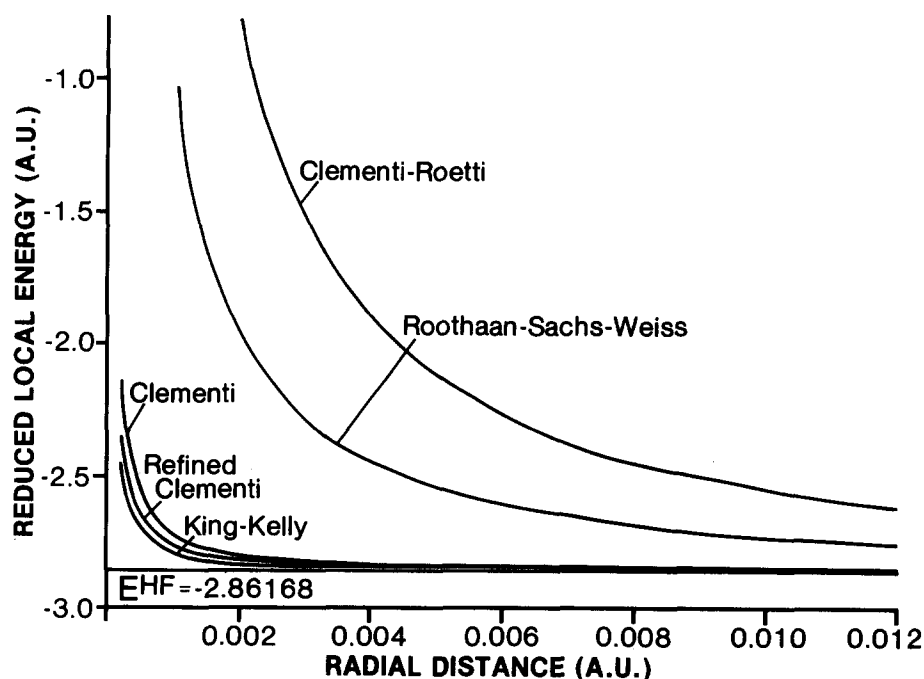


FIG. 14. Reduced local energy as a function of the configuration space coordinate in the near nuclear region for various helium ground state Hartree-Fock wave functions.

$$C_7 = 0.588\,931\,77, \quad C_8 = -0.629\,631\,30 \times 10^{-3},$$

$$C_9 = 0.715\,589\,40 \times 10^{-1}, \quad C_{10} = -0.538\,748\,19 \times 10^{-2}.$$

A reoptimization of all of these exponents would result in additional refinements to the reduced local energy. The importance of examining the orbital exponents can be gauged from the results for the two five-term functions reported by Clementi and Clementi and Roetti. From Table II it is observed that there is no difference in total energy for these two functions; however, the local accuracy of the former is considerably improved (as measured by D). This improvement is due principally to the better cusp quality of the basis function (see Table IV).

In Figs. 14 and 15, the reduced local energy calculated from several different wave functions is shown for the near nucleus region and the medium r range respectively. The most accurate reduced local energy for the small r region is obtained from the ten term function indicated in Fig. 14 as "King-Kelly". Figure 14 obviously reflects the cusp characteristics of the various wave functions; the better the cusp factors (see Table IV), the closer the reduced local energy lies to the exact Hartree-Fock result. It is to be noted however, as indicated in the introduction, that a cusp factor of zero is *not sufficient* to ensure the reduced local energy will asymptotically approach the exact Hartree-Fock total energy as $r \rightarrow 0$.

At medium range values of the configuration space coordinate, the reduced local energy oscillates about the exact Hartree-Fock energy. In fact Fig. 15 illustrates why all the wave functions used to construct this figure are very accurate in the usual sense of the term (i.e., total energy). The calculation of an expectation value such as the energy emphasizes the region within a few angstroms of the nucleus, and it is in this region that all the reduced local energies illustrated in

Fig. 15 show only very minor deviations from the exact Hartree-Fock energy. Also, because of the slight oscillations, there is partial cancellation of errors, and hence the total energy comes out rather accurate.

We now turn our attention to the calculation of expectation values. Our interest here is to see if it is possible to obtain more accurate expectation values by improving the local accuracy of the wave function.

Table V provides a tabulation of several expectation

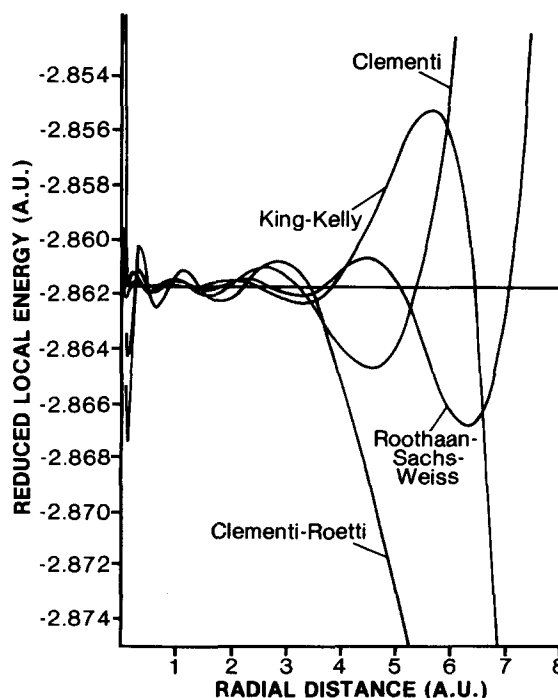


FIG. 15. Reduced local energy for the medium r range for various helium ground state Hartree-Fock wave functions.

TABLE V. Expectation values $\langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | r_1^k | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle$ for different wave functions.

Wave function	$\langle r_1^{-2} \rangle$	$\langle r_1^{-1} \rangle$	$\langle r_1 \rangle$	$\langle r_1^2 \rangle$	$\langle r_1^4 \rangle$	$\langle r_1^5 \rangle$	$\langle r_1^6 \rangle$	$\langle r_1^8 \rangle$
Single Zeta ^a	5.695	1.688	0.889	1.053	2.775	5.755	13.641	1.078×10^2
Double Zeta ^a	5.995	1.687	0.927	1.183	3.851	9.057	24.533	2.567×10^2
Clementi–Roetti ^a five term	5.996	1.687	0.927	1.185	3.884	9.201	25.174	2.708×10^2
Refined Clementi Roetti five term	5.996	1.687	0.927	1.185	3.886	9.211	25.215	2.717×10^2
Clementi five term ^b	5.996	1.687	0.927	1.185	3.888	9.220	25.279	2.744×10^2
Refined Clementi five term	5.996	1.687	0.927	1.185	3.888	9.220	25.280	2.745×10^2
Ten term	5.996	1.687	0.927	1.185	3.888	9.227	25.354	3.031×10^2
Roothaan ^c 12 term	5.996	1.687	0.927	1.185	3.888	9.221	25.279	2.739×10^2
20 term Hylleraas ^d	6.018	1.688	0.929	1.193	3.969	9.478	26.141	2.858×10^2

^aWave functions from Ref. 4.

^bWave function from Ref. 3.

^cWave function from Ref. 5.

^dBased on the density calculation by Benesch using the Hart–Herzberg Hylleraas function, Refs. 9 and 10.

values of r_1^k for different k values using a selection of Hartree–Fock wave functions. Also included for reference are expectation values of r_1^k calculated from the 20-term Hylleraas wave function of Hart and Herzberg⁹ using the density calculation of Benesch.¹⁰

The following general features emerge. For the expectation values $\langle r_1^k \rangle$ for small k values ($-2, -1, 1, 2, 3, 4$) all the wave functions examined (except the single zeta) yield essentially the same values for each expectation value. The volume element factor $d\tau$ has a significant effect on cancellation of inaccuracies in the near nuclear region. For expectation values $\langle r_1^k \rangle$ with larger k values, differences start to appear for the various wave functions. For the moments with $k=5, 6, 8$ we find that our refinement of the Clementi–Roetti five term function has led to small improvements of approximately 0.1%–1% (as judged against the Hylleraas values). For the five term Clementi function we have not gained any significant improvement.

It is clear that all the Hartree–Fock wave functions beyond the double zeta function are extremely accurate (in the global sense) and hence it is difficult to refine these functions any further. It is obviously a much easier problem to improve upon the single and double zeta functions than the multiterm functions of Clementi–Roetti and Clementi.

The ten term function listed in Table V gives better results for $\langle r_1^5 \rangle$ and $\langle r_1^6 \rangle$ relative to the other Hartree–Fock wave functions listed. However, for higher moments, the ten term function yields poorer results. Although this wave function is excellent in the sense of total energy and local accuracy as measured by D , its clearly poor at very large r (the region important for the calculation of large k moments). An indication of this inaccurate long range behavior is obtained from the poor asymptotic limit listed in Table IV. This defect in the ten term function emerges in large part from

its mode of construction. The two requirements were that the total energy and the local accuracy as measured by D were both minimized. However, the weight factor $\rho(\mathbf{r})$ in the definition of D essentially “irons out” inaccuracies in the long range behavior of the wave function. For this reason the D condition is best confined to improvement of wave functions for short and medium range values of r . Clearly, a local criterion such as the one introduced in Eq. (2) offers the possibility to overcome this problem at large r values.

The influence of different orbital exponents on the various expectation values can be observed in a limited way by comparison of the Clementi and Clementi–Roetti five term wave functions. Not surprisingly, larger changes in expectation values are achieved by modification of the orbital exponents, then by refinements of the expansion coefficients. Ideally, both factors need to be considered together.

The following general observations can be made concerning the quality of the various expectation values of $\langle r_1^k \rangle$ and the local accuracy of the different wave functions as measured by the D values. For less accurate wave functions, D is large (~ 0.1) and the corresponding expectation values are poor. An improvement of the local accuracy by a factor of 10^3 – 10^4 (i. e., $D \sim 10^{-4}$ – 10^{-5}) leads to substantial improvements in the expectation values. Further improvement in D by a factor of 10^2 (i. e., $D \sim 10^{-6}$ – 10^{-7}) leads to only minor improvements. An additional refinement of approximately a factor of ten in D , leads to negligible improvement in expectation values.

Since D is a global measure of accuracy, it is necessary to exercise caution when predicting whether a particular expectation value will turn out to be accurate. For wave functions with large D values, expectation values will in general be poor. For wave functions with small D values, it would be expected that *most* expecta-

tion values will be satisfactory. It is to be noted however, that an expectation value may be rather poor, because it emphasizes a particular region of configuration space where the wave function is inaccurate, but the D value computed from the same wave function may be very small. This may occur because of cancellation of errors of different sign, or because the function $\rho(\mathbf{r})$ deemphasizes the long range r region.

In this work we have discussed a stringent necessary accuracy test on the Hartree-Fock wave function. Because the reduced local energy criterion is able to examine the accuracy of *all* points in configuration space, and not just the near-nuclear region, this condition represents an important general test of the quality of the Hartree-Fock wave function.

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