

Reduced local energy as a criterion for the accuracy of Hartree-Fock wave functions

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The reduced local energy concept is applied to assess the local accuracy of Hartree-Fock wave functions. The method is illustrated by application to all the Clementi and Roetti's wave functions for the helium atom and to the first row of the helium isoelectronic series. The use of the reduced local energy as a means for improvement of expectation values is discussed. Application to the five term helium wave functions of Clementi and Clementi and Roetti is considered.

I. INTRODUCTION

The energy associated with a given wave function is the well-known criterion for assessing the quality of the wave function. Additional confirmation of the accuracy of the wave function can be gauged by the agreement of various computed expectation values with the appropriate experimental results. Subsidiary constraints such as the virial theorem also serve to test the quality of approximate wave functions.

The aforementioned criteria test the *global* accuracy of the wave function. While it is possible to assess the accuracy of a wave function in different regions of configuration space by computing expectation values of appropriately chosen operators, it is impossible to circumvent the major limitation of the global test. That is, inaccuracies in the wave function in one region of configuration space may offset inaccuracies in another region of configuration space, with the result that com-

puted expectation values may be fortuitously in close agreement with experimental values.

An alternative to the global accuracy critique is the local energy functional approach. The idea has been in the literature for a considerable time.¹⁻³ The Bartlett-Frost local energy functional (in position space) is given by (for an N electron system)

$$E_{BF}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{H\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)} \quad (1)$$

The local energy approach gives the severest test of the local accuracy of the wave function, however, its functional dependence on each configuration space coordinate does not lead to a simple means of presentation of the local accuracy. Thomas, Javor, and Rothstein^{4,5} bypassed the latter problem by introducing the notion of a reduced local energy, defined for a system of $N (\geq 2)$ electrons by

$$E_L(\mathbf{r}_1) = \frac{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) H \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 d\tau_3 \dots d\tau_N}{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 d\tau_3 \dots d\tau_N} \quad (2)$$

For the exact wave function, E_L defined by Eq. (2) is a constant for all points in configuration space. The reduced local energy functional represents a compromise; it examines the local accuracy in a less effective manner than does the Bartlett-Frost functional, but is a far more satisfactory approach for interpreting results.

II. REDUCED HARTREE-FOCK LOCAL ENERGY

The Bartlett-Frost and Thomas-Javor-Rothstein functionals are particularly relevant for testing ex-

tremely accurate wave functions. However, the latter functional can be generalized to incorporate one extremely important special case, that is, where Ψ in Eq. (2) is replaced by the Hartree-Fock wave function.

It was first recognized by Cohen and Frishberg,⁶ and independently by Nakatsuji⁷ that a local energy functional exists for the Hartree-Fock case. The reduced Hartree-Fock local energy functional is defined for an $N (\geq 2)$ electron system by

$$E_L^{HF}(\mathbf{r}_1) = \frac{\int \Psi_{HF}^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) H \Psi_{HF}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 d\tau_3 \dots d\tau_N}{\int \Psi_{HF}^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{HF}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 d\tau_3 \dots d\tau_N} \quad (3)$$

When Ψ_{HF} is the exact Hartree-Fock wave function, it can be rigorously shown that E_L^{HF} is a constant for all points in configuration space.⁸

Equation (3) is likely to have considerable practical applications, since accurate Hartree-Fock wave functions are of course much easier to generate than cor-

related wave functions for which Eq. (2) serves as a necessary accuracy constraint.

The reduced Hartree-Fock local energy functional is applied to examine the local accuracy of some standard atomic Hartree-Fock wave functions computed by Clementi and Roetti.⁹ In this paper we restrict our at-

attention to several different helium wave functions and we also examine the first row of the helium isoelectronic series. For the matrix element calculations reported in Sec. V, the five-term function for the helium atom reported by Clementi¹⁰ has also been examined. Our intention has not been to study every available helium wave function, but rather, to consider some simple though fairly accurate wave functions. Many other Hartree-Fock wave functions containing both fewer and greater number of expansion terms have been reported,^{11,12} and some of these are examined in a further investigation.¹³ The Clementi wave functions have special interest because they are fairly accurate in the global sense, have been extensively employed in the literature, and have a simple analytic form which is convenient to work with.

The Hartree-Fock orbital is given by

$$\phi(\mathbf{r}) = \sum_i C_i \chi_i(\mathbf{r}), \quad (4)$$

where

$$\chi_i(\mathbf{r}) = N_i r_i^{\alpha_i-1} e^{-\alpha_i r} Y_{00}(\theta, \phi) \quad (5)$$

and N_i is the normalization factor. The coefficients C_i and orbital exponents α_i are tabulated by Clementi and Roetti. Evaluation of the reduced local energy functional for the many electron atomic case is straightforward though somewhat more tedious than the corresponding derivation of the expectation value of the energy. For the particular case of interest in this work, the reduced Hartree-Fock local energy is (atomic units are used throughout)

$$E_L^{\text{HF}}(\mathbf{r}) = \frac{-Z}{r} + \frac{\sum_i C_i \chi_i \left[(\alpha_i/r) - \frac{1}{2} \alpha_i^2 \right]}{\sum_i C_i \chi_i} - \sum_i \sum_j \frac{C_i C_j N_i N_j}{\xi_{ij}^3} \left[Z \xi_{ij} - \alpha_i \alpha_j - \frac{2}{r} + \left(\xi_{ij} + \frac{2}{r} \right) e^{-\xi_{ij} r} \right], \quad (6)$$

where $\xi_{ij} = \alpha_i + \alpha_j$. In Eq. (6) we have also carried out the angular integration over (θ_i, ϕ_i) .

III. ASYMPTOTIC LIMITS

The behavior of the reduced local energy in the limits $r \rightarrow \infty$ and $r \rightarrow 0$ is of particular interest. It is in these limits that the approximate Hartree-Fock wave functions tend to be rather poor, especially the limit $r \rightarrow 0$. The latter result should not be too surprising since the orbital basis function must satisfy the cusp constraint before an accurate reduced local energy as $r \rightarrow 0$ can be expected.

For the large r behavior we find

$$E_L^{\text{HF}}(\mathbf{r}) \underset{r \rightarrow \infty}{\sim} - \sum_i \sum_j C_i C_j N_i N_j \frac{(Z \xi_{ij} - \alpha_i \alpha_j)}{\xi_{ij}^3} - \frac{1}{2} \alpha_{\text{min}}^2, \quad (7)$$

where α_{min} denotes the smallest orbital exponent in the given basis set. It is obvious from Eq. (7) that the long-range behavior of $E_L^{\text{HF}}(\mathbf{r})$ does not asymptotically

approach the correct Hartree-Fock energy for the particular basis set employed.

The functional dependence of E_L^{HF} on r^{-1} displayed in Eq. (6) clearly indicates that for the region close to the nucleus, the wave function will very likely be extremely inaccurate. For the limit $r \rightarrow 0$,

$$E_L^{\text{HF}}(r=0) = \frac{-\frac{1}{2} \sum_i C_i N_i \alpha_i^2}{\sum_i C_i N_i} - \sum_i \sum_j \frac{C_i C_j N_i N_j}{\xi_{ij}^3} \times [(Z+1)\xi_{ij} - \alpha_i \alpha_j], \quad (8)$$

if

$$\frac{\sum_i C_i N_i \alpha_i}{\sum_i C_i N_i} - Z = 0, \quad (9)$$

otherwise

$$E_L^{\text{HF}}(r=0) \rightarrow \pm \infty. \quad (10)$$

The sign in Eq. (10) being determined by the sign of the left-hand side of Eq. (9). Of course, for practical computations, Eq. (9) will never be exactly satisfied, and so Eq. (10) determines the appropriate behavior in the region $r \rightarrow 0$. This result serves to point out that the reduced local energy functional near the nucleus represents an extremely severe necessary condition that the wave function must be forced to satisfy.

From the preceding comments it should be recognized that Eq. (3) becomes an extremely important test of the quality of the wave function, when expectation values of operators that weight the region close to the nucleus are to be evaluated. For expectation values such as the energy, inaccuracies in the wave function in the region $r \sim 0$ are substantially reduced by the r^2 factor from the volume element $d\tau$.

IV. REDUCED LOCAL ENERGY PLOTS

In Fig. 1 the dependence of the reduced local energy on r is illustrated for each of the helium Hartree-Fock wave functions reported by Clementi and Roetti. The true Hartree-Fock wave function should yield a constant E_L^{HF} , and this is represented in Fig. 1 as the horizontal line at -2.8617 . Not surprisingly, the single zeta

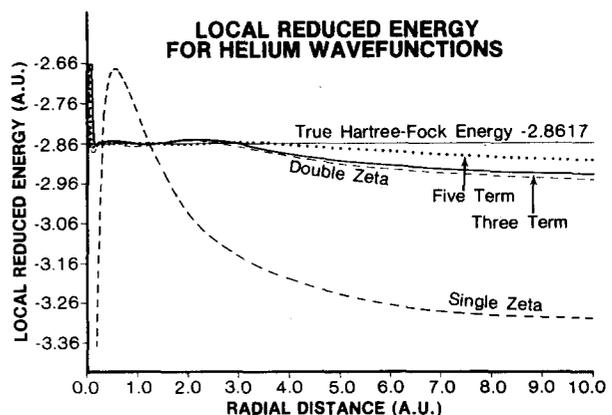


FIG. 1. The Hartree-Fock local reduced energy ($E_L^{\text{HF}}(\mathbf{r})$) as a function of r for the ground state helium wave functions of Clementi and Roetti (Ref. 9).

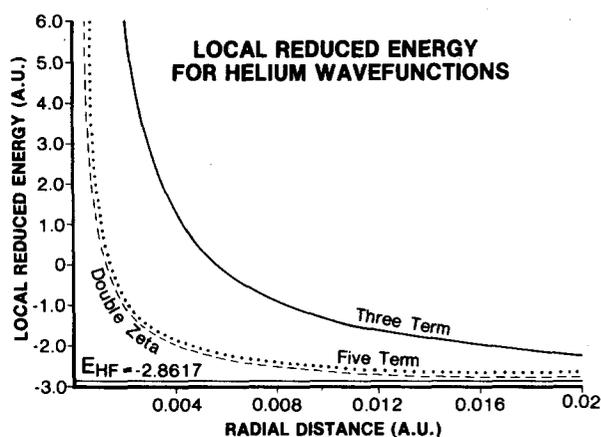


FIG. 2. $E_L^{\text{HF}}(r)$ as a function of r for the region near the nucleus.

basis function is rather poor over almost the entire range of r illustrated in Fig. 1. The double zeta, three-term and five-term wave functions are progressively in closer agreement to the local behavior for the exact Hartree-Fock wave function. All of the wave functions become rather inaccurate close to the nucleus.

The region close to the nucleus is illustrated in detail for the double zeta, three-term and five-term wave functions in Fig. 2. In each case, the deviation from the true Hartree-Fock result is extremely large, indicating that for the radial distances shown in Fig. 2, the wave functions are of extremely poor quality (in the local sense). From Fig. 2 it is observed that the three-term Clementi-Roetti wave function appears to be somewhat worse than the double zeta wave function. This result can probably be attributed to the fact that either one or more of the coefficients or orbital exponents (or perhaps both) reported by Clementi and Roetti must have a typographical error, since there is a small error of approximately 0.6% in the normalization integral. Small errors in C_i or α_i are likely to have pronounced effects on the accuracy of the wave function close to the nucleus.

Difficulties associated with producing wave functions which are accurate near the nucleus and which give accurate expectation values of molecular properties sensitive to the near nucleus region are well known. The necessary conditions for selecting basis sets which satisfy the cusp constraints have been discussed in the literature.^{14,15} More flexible expansions which satisfy the cusp constraint have also been discussed.¹⁶ The wave functions reported by Clementi do not satisfy the cusp constraint, so it is not surprising to find significant local inaccuracies for $E_L^{\text{HF}}(r)$ as $r \rightarrow 0$.

It should be emphasized, that an orbital function developed to satisfy the cusp constraint, in the present work given by Eq. (9), will not necessarily give an extremely close approximation to the exact reduced local energy as $r \rightarrow 0$. That is, Eq. (8) is not guaranteed to yield a close approximation to E_L^{HF} because Eq. (9) is satisfied. Although clearly, it is highly desirable to satisfy Eq. (9) if an accurate $E_L^{\text{HF}}(r)$ is to be obtained. We have examined the Roothaan-Sachs-Weiss helium wave function, which does obey the cusp con-

straint fairly closely, and found the reduced local energy only slightly improved over the results obtained for the Clementi-Roetti function. This means that while the cusp constraint on the orbital function is certainly a necessary condition to have an accurate reduced local energy, it is not a sufficient condition.

In Fig. 3 the various contributions to the reduced local energy for the different helium wave functions are reported. It is to be noted that there is no constant local energy interpretation for either the kinetic energy or the potential energy. Figure 3 does, however, illustrate which contribution is most affected by improvement of the wave function. For the case of helium, improvement on the local scale shows up most significantly in the "kinetic energy" contribution to the reduced local energy. Very minor changes are found in the "potential energy" contribution.

The Hartree-Fock wave functions for the helium isoelectronic series reported by Clementi and Roetti have also been analyzed and the results are shown in Fig. 4. Each $E_L^{\text{HF}}(r)$ exhibits a similar local behavior; rather inaccurate near the nucleus, reasonably accurate for a short region, and then each approaches an asymptotic value which is somewhat different from the behavior for the true Hartree-Fock wave function. The asymptotic values for the helium isoelectronic series along with the corresponding values for the different helium wave functions are tabulated in Table I. Also listed are the values of

$$\frac{\sum_i C_i N_i \alpha_i}{\sum_i C_i \alpha_i} - Z,$$

the sign of which dictates the behavior of $E_L^{\text{HF}}(r)$ near the nucleus. This factor is positive for all the wave functions examined except the single zeta, and this accounts for the behavior of the reduced local energy of the single zeta function near the nucleus as shown in Fig. 1. In none of the cases examined is Eq. (9) closely satisfied, and hence all the Clementi-Roetti wave functions studied are very inaccurate in the near-nucleus region. Even if this condition was satisfied, the values of $E_L^{\text{HF}}(r=0)$ are found to be in very poor

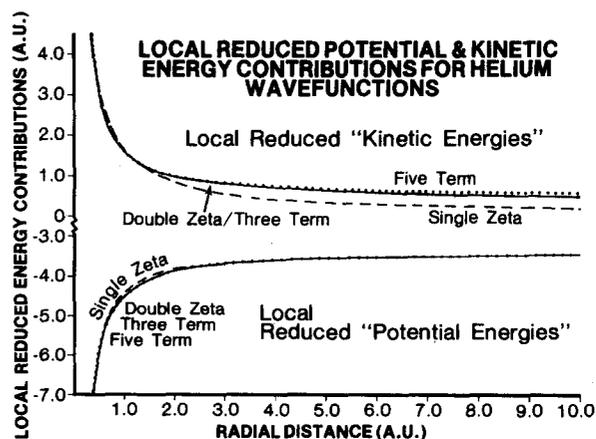


FIG. 3. Local behavior of the "kinetic" and "potential" energy contributions to the local reduced energy. The contributions shown in this plot combine to yield the results of Fig. 1.

TABLE I. Asymptotic limits for E_L^{HF} for various helium wave functions and for the helium isoelectronic series.

Atom	$E_L^{\text{HF}}(r=\infty)$	$E_L^{\text{HF}}(r=0)$	$\left(\frac{\sum_i C_i N_i \alpha_i}{\sum_i C_i N_i}\right) - Z$
He (single zeta)	-3.375 00	-5.062 50	-0.313
He (double zeta)	-3.000 25	-5.888 58	0.399×10^{-2}
He (three-term)	-2.998 82	-5.936 36	0.179×10^{-1}
He (five-term)	-2.947 91	-5.879 19	0.431×10^{-2}
Li ⁺	-7.446 74	-12.134 23	0.159×10^{-1}
Be ⁺²	-13.829 07	-20.396 97	0.229×10^{-1}
B ⁺³	-22.319 73	-30.566 56	0.199×10^{-1}
C ⁺⁴	-32.780 73	-42.690 98	0.155×10^{-1}
N ⁺⁵	-45.259 49	-56.759 71	0.106×10^{-1}
O ⁺⁶	-59.740 70	-72.846 75	0.748×10^{-2}
F ⁺⁷	-76.141 85	-91.087 73	0.991×10^{-2}
Ne ⁺⁸	-94.647 35	-111.060 86	0.388×10^{-2}

agreement with the corresponding values of E^{HF} .

For the isoelectronic series, there is no completely systematic trend for the local accuracy of the wave function as the nuclear charge increases. This is illustrated by the results shown in Table II. The error in E_L^{HF} does not simply increase or decrease with increasing nuclear charge, and furthermore, the changes from one member of the series to the next depend on the particular value in position space being examined.

V. LOCALLY IMPROVED WAVE FUNCTIONS

In this section, the question of how the reduced local energy can be used as a constraint to improve Hartree-Fock wave functions is examined. An expanded treatment with detailed applications is in progress.¹³

Standard Hartree-Fock calculations have been carried out with the additional Lagrange constraint that the quantity $D[E^{\text{HF}}]$ defined by

$$D = \frac{1}{N} \int [E^{\text{HF}} - E_L^{\text{HF}}(\mathbf{r})]^2 \rho(\mathbf{r}) d\mathbf{r} \quad (11)$$

is minimized. In Eq. (11), $\rho(\mathbf{r})$ is the Hartree-Fock electronic density, N is the number of electrons and E^{HF} is the Hartree-Fock energy. The quantity D satisfies the following condition:

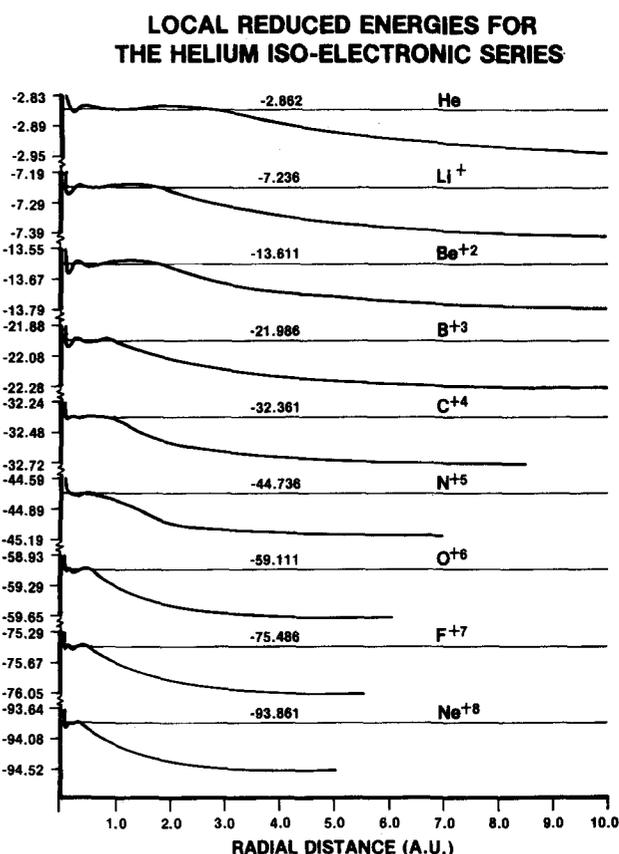


FIG. 4. $E_L^{\text{HF}}(r)$ as a function of r for the helium isoelectronic series wave functions reported by Clementi and Roetti (Ref. 9).

ifies the following condition:

$$D \rightarrow 0 \text{ as } E_L^{\text{HF}}(\mathbf{r}) - E^{\text{HF}}. \quad (12)$$

The idea of using additional constraints to improve the wave function is well known. Fraga and Birss have for example, considered using expectation values of one electron properties as constraints in the standard variational procedure.¹⁷ This scheme requires preassigned values for the matrix elements. The additional constraint used in the present study is more flexible in that one attempts to minimize E^{HF} subject to the constraint that D be a minimum. It should be noted that with the additional constraint, the energy does not reach the minimum achieved in the unconstrained calculation, though the differences are very minor for the cases

TABLE II. Values of $E_L^{\text{HF}}(r)$ at the distances $r=0.5, 1.0$ and 5.0 and associated errors for the helium isoelectronic series wave functions of Clementi and Roetti.

	He	Li ⁺	Be ⁺²	B ⁺³	C ⁺⁴	N ⁺⁵	O ⁺⁶	F ⁺⁷	Ne ⁺⁸
E^{HF}	-2.861 678	-7.236 405	-13.61130	-21.986 15	-32.361 28	-44.736 17	-59.111 36	-75.486 57	-93.861 43
$r=0.5$	-2.852 108	-7.236 599	-13.615 62	-21.990 63	-32.355 68	-44.723 19	-59.105 16	-75.479 22	-93.895 23
error ^a	3.34×10^{-1}	-2.68×10^{-3}	-3.17×10^{-2}	-2.04×10^{-2}	1.73×10^{-2}	2.90×10^{-2}	1.05×10^{-2}	9.74×10^{-3}	-3.60×10^{-2}
$r=1.0$	-2.858 589	-7.234 354	-13.605 45	-21.987 27	-32.393 77	-44.837 16	-59.298 40	-75.701 20	-94.195 20
error	1.08×10^{-1}	2.83×10^{-2}	4.30×10^{-2}	-5.09×10^{-3}	-1.00×10^{-1}	-2.26×10^{-1}	-3.16×10^{-1}	-2.84×10^{-1}	-3.56×10^{-1}
$r=5.0$	-2.901 388	-7.356 689	-13.742 96	-22.230 89	-32.691 73	-45.169 35	-59.664 50	-76.066 10	-94.568 24
error	-1.39	-1.66	-9.67×10^{-1}	-1.11	-1.02	-9.68×10^{-1}	-9.36×10^{-1}	-7.68×10^{-1}	-7.53×10^{-1}

^aComputed as $100(E^{\text{HF}} - E_L^{\text{HF}}(r))/E^{\text{HF}}$.

TABLE III. Values of the global accuracy measure $D[E^{\text{HF}}]$ and 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	D	$\langle r_1^{-2} \rangle$	$\langle r_1^k \rangle$	$\langle r_1^0 \rangle$	$\langle r_1^{10} \rangle$
Clementi-Roetti five term ^a	0.663×10^{-5}	5.996	2.517×10^1	2.708×10^2	4.350×10^3
Refined Clementi-Roetti	0.781×10^{-6}	5.996	2.522×10^1	2.717×10^2	4.373×10^3
Clementi five term ^b	0.721×10^{-7}	5.996	2.528×10^1	2.744×10^2	4.506×10^3
Refined Clementi ^c	0.642×10^{-7}	5.996	2.528×10^1	2.745×10^2	4.508×10^3
Hylleraas ^d	...	6.018	2.614×10^1	2.858×10^2	4.677×10^3

^aWave function from Ref. 9.

^bWave function from Ref. 10.

^cNew coefficients are 0.784964, 0.202905, 0.368919×10^{-1} , -0.292446×10^{-2} , 0.327139×10^{-2} , $E = -2.86167997$.

^dWave function from Refs. 18 and 19.

studied in this work. In principle the aforementioned consideration can be overcome by increasing flexibility in the basis set.

In the present study we restrict our considerations to just a couple of wave functions given by Clementi.^{9,10} Other wave functions reported by Clementi and by Roothaan *et al.*¹¹ are considered elsewhere.¹³ Table III lists values of D calculated for the five-term helium wave functions of Clementi¹⁰ and Clementi and Roetti.⁹ The entries listed as "refined" were calculated by employing the appropriate Clementi wave functions as a first approximation in the modified Hartree-Fock calculation with the D constraint. In the present calculations only the expansion coefficients have been recalculated. It should not be too surprising to learn that the orbital exponents do have an important bearing on the local accuracy. Some idea of how much the exponents affect D can be obtained from Table III by comparing the Clementi and Clementi-Roetti five-term functions. We intend to expand our present studies to investigate the reoptimization of orbital exponents in the D -constrained calculations. Listed in Table III are some matrix elements

$$\langle \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) | r_1^k | \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \rangle.$$

Also shown for reference are the corresponding values obtained from a 20-term correlated Hylleraas function¹⁸ using the density calculation of Benesch.¹⁹ For small k values, there are no significant differences for the matrix elements using the different wave functions. This reflects the fact that the Clementi five-term wave functions are very good for the calculation of matrix elements that emphasize the region not too distant from the nucleus. For larger k values, small improvements (as judged against the Hylleraas values) were obtained for the Clementi-Roetti function, but only very minor changes were recorded for the Clementi function. The function E_L^{HF} is however, a more sensitive measure of accuracy than the matrix elements, since it tests accuracy on a local scale.

The answer to the question of how large a deviation between $E_L^{\text{HF}}(\mathbf{r})$ and E^{HF} can be accepted and still have a reasonable wave function is governed by two principal factors. First, it depends how the deviation is mea-

sured. If it is determined by a global measure, as in Eq. (11), the error can be either uniformly spread out (as a function of \mathbf{r}) or peaked in certain locations, and similar values of D may result. The possibility also exists for partial cancellation of inaccuracies in different regions of configuration space. For the latter reason graphical presentation of results is very useful. The second factor concerns which particular matrix elements are of interest. If the expectation value to be calculated is sensitive to a particular region of configuration space, and the reduced local energy is very inaccurate in this region, then poor matrix elements are likely to be obtained. It must be stressed that the functional $D[E^{\text{HF}}]$ contains an electronic density weight function, so the global measure of inaccuracy given by D is less sensitive to the region distant from the nucleus.

A quantitative idea of how some matrix elements are affected can be obtained from Table III. The difference between the D values for the Clementi-Roetti and Clementi five-term functions is approximately a factor of 10^2 , and for the matrix elements of r_1^k for large k , an observed change of $\sim 0.4\%$ to 3% is found. Much more dramatic changes have been obtained for less accurate wave functions. For example, the Clementi-Roetti single zeta function for the helium atom has a D value approximately 2.4×10^4 larger than the Clementi-Roetti five-term function, and for the matrix elements of r_1^k , there are sizable differences ranging from a few percent at small values of k ($k = -2$) to approximately 70% at large k ($k = 10$). There is not a simple correspondence between the value of D for a particular wave function and the accuracy of any given expectation value computed with the same wave function. This is directly connected to the global nature of the accuracy measure D . For wave functions with large D values it can be expected that expectation values emphasizing *some* region of configuration space will be poor. Accuracy criteria which are not global in nature, and hence likely to give a better indication of errors in given expectation values, are presently under consideration.

VI. CONCLUSION

The results presented in this paper demonstrate conclusively the severity of Eq. (3) as a test of the local

accuracy of an approximate Hartree-Fock wave function. Equation (3) represents a *necessary* condition that must be satisfied by the Hartree-Fock wave function and clearly it is superior to any accuracy test based on global behavior. It should be emphasized that the reduced local energy does not simply measure inaccuracies due to poor cusp properties of the orbital basis functions, but examines inaccuracies for *all* points of configuration space. For this reason, it is a sensitive test of the accuracy of the wave function.

The analysis of the reduced local energy for an approximate wave function can serve as a means to improve the wave function in particular regions of configuration space. The minimization of the functional $D[E]$ discussed in Sec. V is such a procedure. Further work in this direction is currently in progress.

The important implication of this work is that Eq. (3) can be employed to test and improve the local accuracy of the wave function and hence to improve expectation values of any operator of interest, rather than simply relying upon the minimum energy criterion. When D is fairly large, (e.g., single zeta function) the resulting expectation values of r_1^k for a wide range of k were poor. For a large improvement in the quality of the wave function (e.g., the Clementi-Roetti five-term function), D decreases dramatically and the matrix elements of the r_1^k were much improved. Further refinements in the wave function (e.g., the Clementi (1965) five-term function), while giving significant improvement in D , gave only minor improvement in the expectation values. As a final point we note that the reduced local energy near the nucleus does reflect how well the orbital functions satisfy the cusp conditions.

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