

**Moments of the reduced local energy**  
**A convenient measure of the local accuracy of atomic**  
**Hartree-Fock wavefunctions**

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Compact measures of the local accuracy of a wavefunction are proposed. They are defined in terms of the reduced local energy. These compact measures are applied to examine the local accuracy in different regions of configuration space for some well known Hartree-Fock wavefunctions from helium through argon.

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1. INTRODUCTION

The accuracy of the computed energy is universally regarded as the first test of the quality of a wavefunction. The computation of a range of expectation values for observables emphasizing different regions of configuration space represents an additional means to test the overall quality of the wavefunction. Close agreement with experimental values for a variety of expectation values is an important necessary though not sufficient criterion for the accuracy of the wavefunction.

A problem to resolve for any energy optimized wavefunction is the *a priori* prediction of which expectation values are likely to be accurate, particularly when the expectation value emphasizes a region of configuration space different from that involved in the energy optimization. The situation becomes most critical if the experimental result for a particular quantity is not available for comparison with the computed expectation value.

The most desirable circumstance is to test the quality of the wavefunction in advance of comparison with experimental expectation values. Some tests are available, such as the virial theorem [1-4], cusp conditions [5, 6], Armstrong energy expression [7, 8] and local [9-13] and reduced local energy expressions [14-18]. These tests may be broadly categorized into three groups. The first are those tests giving an essentially global assessment of accuracy, although one region of configuration space may be more heavily emphasized than other regions, as, for example, with the virial theorem constraint. The second group includes those tests that provide an assessment of local accuracy which is limited to a narrow range of configuration space, for example, the cusp constraint. The third group comprises those tests that examine the local accuracy, either directly (the local energy functional [9, 10]), or indirectly (the reduced local energy functionals [14, 18]), for an unrestricted range of configuration space. The

importance of any particular test is keyed to which expectation value is of interest; for example, the satisfaction of the cusp constraint is obviously important for the calculation of accurate hyperfine coupling constants. Related information assessing the accuracy of the wavefunction in the near nuclear region may also be obtained from the local and reduced local energy functionals.

The purpose of this paper is to propose a convenient set of criteria to assess the local accuracy of the wavefunction, as measured in a global manner. These criteria are then employed to assess the accuracy of some standard Hartree–Fock wavefunctions.

## 2. THEORY

The reduced local energy is defined for an  $N$  electron system ( $N \geq 2$ ) by [14]

$$E_L(\mathbf{r}_1) = \frac{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) H \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) ds_1 d\tau_2 \dots d\tau_N}{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) ds_1 d\tau_2 d\tau_3 \dots d\tau_N}. \quad (1)$$

It has been recognized that a corresponding result holds for the Hartree–Fock formalism [16, 17],

$$E_L^{\text{HF}}(\mathbf{r}_1) = \frac{\int \Psi_{\text{HF}}^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) H \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) ds_1 d\tau_2 \dots d\tau_N}{\int \Psi_{\text{HF}}^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) ds_1 d\tau_2 \dots d\tau_N}. \quad (2)$$

Equation (1) represents a necessary condition on the wavefunction; in the limit that the exact eigenstate is available,

$$E_L(\mathbf{r}_1) \equiv E, \quad (3)$$

where  $E$  is the exact energy. A similar situation holds in the Hartree–Fock formalism; if the exact Hartree–Fock wavefunction is available,

$$E_L^{\text{HF}}(\mathbf{r}_1) \equiv E^{\text{HF}}, \quad (4)$$

where  $E^{\text{HF}}$  denotes the exact Hartree–Fock energy.

Equation (2) has recently received some attention, both as a means to assess the local accuracy, and as a constraint, or set of constraints, in a modified Hartree–Fock formalism [19–23].

The reduced local energy can be incorporated into global measures of local accuracy. The following measures of local accuracy are defined:

$$D_m = \frac{1}{N} \int (E^{\text{HF}} - E_L^{\text{HF}}(r))^2 r^m \rho(\mathbf{r}) d\mathbf{r}, \quad (5)$$

$$A_m = \frac{1}{N} \int |E^{\text{HF}} - E_L^{\text{HF}}(r)| r^m \rho(\mathbf{r}) d\mathbf{r}, \quad (6)$$

for values of  $m$  which lead to convergent integrals, i.e.  $m \geq -2$ .  $\rho(\mathbf{r})$  is the Hartree–Fock electronic density. Equations (5) and (6) have been formulated specifically for atomic systems. To take advantage of spherical symmetry, the numerator and denominator of (2) have been integrated over the angular coordinates ( $\theta, \phi$ ), leading to the quantity  $E_L^{\text{HF}}(r)$ . The density weighting factor is inserted in the integrands in order to ensure convergence of the integrals in

(5) and (6). Generalization of (5) and (6) to deal with systems of general symmetry (including molecular systems) presents no new features. Analogous expressions may be defined for near exact wavefunctions.

$A_m$  and  $D_m$  measure the local accuracy in a global manner. In the limit that the exact Hartree–Fock wavefunction is available, the following results hold :

$$D_m = 0, \quad (7)$$

$$A_m = 0, \quad (8)$$

for  $m \geq -2$ . Equations (5) and (6) represent stringent *a priori* tests of the local accuracy of the wavefunction. No knowledge of any experimental expectation value other than the energy is required ; in practical applications, the computed energy from the energy optimized wavefunction is used. The moments  $A_m$  and  $D_m$  have the advantage that they offer the most compact means to express information on the local inaccuracies in the wavefunction.

Equations (5) and (6) represent necessary but not sufficient tests of the accuracy of the wavefunction. By performing the global integration over configuration space, it is possible for a particular moment, that errors in one region may offset errors in a different region. With this fact in mind, it is obviously advantageous to compute several moments. It is far less likely that a fortuitous cancellation of errors in different regions of configuration space will occur when several different powers of  $r$  are employed. For this reason, we believe the moments defined in (5) and (6) will represent a very useful means to assess local accuracy. Attention may be focused on different regions by examining different powers of  $r$  ; the short range behaviour can be studied using  $m = -2$  and  $-1$ , the long range inaccuracies can be studied using  $m = 8, 9$  and  $10$  and higher values.

### 3. CALCULATIONS

Equations (5) and (6) have been applied to study the local accuracy of the atomic Hartree–Fock wavefunctions of Clementi and Roetti [24]. These wavefunctions have been examined for three reasons. They are very widely used in the chemical literature, so some assessment of their local accuracy is of interest. They are accurate (in the energetic sense). They are compact ; the expansion coefficients and orbital exponents are presented in the Clementi–Roetti tables.

In tables 1 and 2, values of  $D_m$  and  $A_m$  are presented for several different helium wavefunctions. All results in tables 1 and 2 and throughout this work are expressed in atomic units. From the results given, an understanding of how basis size alters  $D_m$  and  $A_m$  can be obtained. The single zeta quality wavefunction, as expected, exhibits the largest errors. The  $D_m$  and  $A_m$  values indicate that this wavefunction is uniformly poor over a large range of configuration space. The double zeta quality wavefunction is observed to be a substantial improvement over the single zeta wavefunction, for essentially all of configuration space examined by the tabulated moments. It is already apparent from the single zeta and double zeta results, that the smallest moments,  $m = 0, 1$ , and  $2$ , directly reflect the quality of the wavefunction in the energy important region, i.e. at modest distances from the nucleus ;  $r \sim 1 - 3$  a.u. (for He).

Table 1.  $D_m$  moments (see (5)) for different helium wavefunctions.

Wavefunction	$D_m$ moments										
	$m =$	-2	-1	0	1	2	3	4	6	8	10
Single Zeta†	0.384 + 4	0.950 + 1	0.156	0.240 - 1	0.239 - 1	0.473 - 1	0.115	0.927	0.101 + 2	0.144 + 3	
Double Zeta†	0.638	0.121 - 2	0.310 - 4	0.229 - 4	0.500 - 4	0.162 - 3	0.621 - 3	0.116 - 1	0.263	0.716 + 1	
Three-term†	0.140 + 2	0.283 - 1	0.213 - 3	0.345 - 4	0.451 - 4	0.112 - 3	0.383 - 3	0.694 - 2	0.164	0.466 + 1	
Three-term‡	0.201 + 2	0.407 - 1	0.276 - 3	0.217 - 4	0.454 - 4	0.168 - 3	0.672 - 3	0.123 - 1	0.272	0.719 + 1	
Five-term§	0.814 - 3	0.148 - 5	0.721 - 7	0.113 - 6	0.366 - 6	0.176 - 5	0.107 - 4	0.581 - 3	0.411 - 1	0.344 + 1	
Five-term†	0.773	0.141 - 2	0.663 - 5	0.503 - 6	0.103 - 5	0.427 - 5	0.207 - 4	0.578 - 3	0.187 - 1	0.691	
Five-term	0.178 - 1	0.310 - 4	0.782 - 6	0.720 - 6	0.149 - 5	0.503 - 5	0.222 - 4	0.591 - 3	0.190 - 1	0.697	

† Wavefunctions from [24].

‡ Recalculated wavefunction using same orbital exponents given in [24].

§ Wavefunction from [25].

|| Refined Clementi-Roetti wavefunction from [20].

The notation employed in the table is illustrated by  $0.384 + 4 \equiv 0.384 \times 10^4$ .

Table 2.  $A_m$  moments (see (6)) for different helium wavefunctions.

Wavefunction $m =$	$A_m$ moments									
	-2	-1	0	1	2	3	4	6	8	10
Single Zeta†	0.329 + 2	0.786	0.157	0.106	0.132	0.232	0.499	0.334 + 1	0.320 + 2	0.418 + 3
Double Zeta†	0.377	0.113 - 1	0.405 - 2	0.352 - 2	0.521 - 2	0.111 - 1	0.305 - 1	0.371	0.654 + 1	0.147 + 1
Three-term†	0.181 + 1	0.250 - 1	0.595 - 2	0.477 - 2	0.604 - 2	0.109 - 1	0.263 - 1	0.283	0.495 + 1	0.114 + 3
Three-term‡	0.218 + 1	0.262 - 1	0.302 - 2	0.178 - 2	0.306 - 2	0.848 - 2	0.280 - 1	0.386	0.679 + 1	0.149 + 3
Five-term §	0.126 - 1	0.418 - 3	0.209 - 3	0.220 - 3	0.362 - 3	0.808 - 3	0.229 - 2	0.324 - 1	0.857	0.367 + 2
Five-term†	0.390	0.386 - 2	0.619 - 3	0.434 - 3	0.588 - 3	0.125 - 2	0.371 - 2	0.581 - 1	0.135 + 1	0.392 + 2
Five-term	0.585 - 1	0.163 - 2	0.712 - 3	0.658 - 3	0.901 - 3	0.169 - 2	0.434 - 2	0.593 - 1	0.136 + 1	0.394 + 2

† Wavefunctions from [24].

‡ Recalculated wavefunction using same orbital exponents given in [24].

§ Wavefunction from [25].

|| Refined Clementi-Roetti wavefunction from [20].

The notation employed in the table is illustrated by  $0.585 - 1 \equiv 0.585 \times 10^{-1}$ .

The first three-term entry in tables 1 and 2 is not an improvement over the double zeta results, and in the energy important region, the values of  $A_m$  and  $D_m$  are worse than the corresponding double zeta values. This wavefunction from the Clementi–Roetti table is not properly normalized. The energy and expansion coefficients have been recomputed using the same exponents reported by Clementi and Roetti. The  $A_m$  and  $D_m$  values obtained from this new three term wavefunction are given as the second three term entry in tables 1 and 2. Both the energy obtained from the recomputed wavefunction, and the observation that the  $A_m$  and  $D_m$  moments for the energy important region are not substantially better than the first three term results, and in fact for a number of moments, poorer than the double zeta values, indicates that the quoted three term orbital exponents are far from optimum.

The first of the five term wavefunctions is taken from Clementi's older tables [25], the second is from the Clementi–Roetti tables. The former wavefunction is known to satisfy the cusp condition more closely than the Clementi–Roetti wavefunction. This is directly evident from the values of  $A_m$  and  $D_m$  appropriate to a description of the near nuclear region, i.e.  $m = -2$  and  $-1$ . The first of the two five term wavefunctions is also more accurate for most other regions of configuration space, except the very long range region. The values of  $A_m$  and  $D_m$  for the energy important region are very small, and this is consistent with the fact that both the Clementi and Clementi–Roetti wavefunctions for helium lead to an error of less than one in the eighth significant figure for the energy [26].

It is possible to modify the standard Hartree–Fock calculation by imposing additional constraints. One version of the constrained Hartree–Fock method imposes the requirement that the wavefunction satisfy certain expectation value constraints. For a recent discussion, containing relevant references to earlier studies, the work of Zeiss and Whitehead [27] may be consulted.

In a recent work from our group [20], a modified Hartree–Fock calculation for helium was carried out using as an additional imposed constraint, the requirement that the moment  $D_0$  be as small as possible. The starting input for the calculation was the Clementi–Roetti, five term Hartree–Fock wavefunction. The same orbital exponents were retained, and the expansion coefficients recalculated using the constrained Hartree–Fock procedure. The resulting wavefunction was employed to calculate the  $A_m$  and  $D_m$  moments recorded as the last entries in tables 1 and 2. The constrained Hartree–Fock calculation tended to refine the small  $r$  region. Graphs of  $E_L^{\text{HF}}(r)$  illustrating the observed changes can be found in [20]. This improvement in the near nuclear region is to be expected, because the imposed constraint emphasizes the shorter range behaviour of the wavefunction, and the Clementi–Roetti five term wavefunction does not satisfy the cusp condition. This improvement in the local accuracy of the wavefunction at short range is directly reflected by the values of  $D_{-2}$ ,  $D_{-1}$ ,  $D_0$  and  $A_{-2}$ ,  $A_{-1}$  for the refined five term wavefunction, which are all improved compared to the corresponding values obtained from the Clementi–Roetti wavefunction.

Tables 3 and 4 present values of  $D_m$  and  $A_m$  for the ground states of Li through Ar, derived from the wavefunctions in the Clementi–Roetti tables. Sulphur has not been studied because there is an error in the tables for this atom. In general, the values of  $A_m$  and  $D_m$  for  $m = -2$  and  $-1$  for all the

Table 3.  $D_m$  moments for ground state atoms(see (5)).

Atom	$D_m$ moments										
	$m =$	-2	-1	0	1	2	3	4	6	8	10
Li		0.314+2	0.578-1	0.269-3	0.776-5	0.242-5	0.424-5	0.256-4	0.586-2	0.248+1	0.123+4
Be		0.740+2	0.129	0.495-3	0.121-4	0.332-5	0.411-5	0.140-4	0.593-3	0.483-1	0.623+1
B		0.113+3	0.189	0.618-3	0.127-4	0.327-5	0.373-5	0.118-4	0.653-3	0.816-1	0.129+1
C		0.174+3	0.283	0.818-3	0.160-4	0.142-4	0.524-4	0.274-3	0.122-1	0.740	0.527+2
N		0.291+3	0.462	0.123-2	0.221-4	0.170-4	0.384-4	0.124-3	0.256-2	0.901-1	0.417+1
O		0.669+3	0.105+1	0.270-2	0.470-4	0.531-4	0.206-3	0.105-2	0.370-1	0.160+1	0.802+2
F		0.753+3	0.116+1	0.278-2	0.609-4	0.885-4	0.300-3	0.130-2	0.345-1	0.114+1	0.436+2
Ne		0.351+3	0.521	0.114-2	0.563-4	0.803-4	0.213-3	0.748-3	0.134-1	0.305	0.793+1
Na		0.183+3	0.264	0.586-3	0.112-4	0.439-5	0.178-4	0.162-3	0.282-1	0.633+1	0.160+4
Mg		0.175+3	0.252	0.629-3	0.304-4	0.238-4	0.938-4	0.816-3	0.946-1	0.127+2	0.191+4
Al		0.254+3	0.362	0.792-3	0.240-4	0.261-4	0.127-3	0.968-3	0.922-1	0.119+2	0.187+4
Si		0.367+3	0.519	0.103-2	0.239-4	0.478-4	0.281-3	0.230-2	0.244	0.336+2	0.533+4
P		0.235+3	0.333	0.787-3	0.512-4	0.131-3	0.736-3	0.569-2	0.542	0.690+2	0.103+5
Cl		0.163+2	0.119	0.145-2	0.151-3	0.295-3	0.110-2	0.579-2	0.307	0.256+2	0.267+4
Ar		0.742+3	0.103+1	0.184-2	0.940-4	0.189-3	0.772-3	0.442-2	0.234	0.164+2	0.134+4

Table 4.  $A_m$  moments for ground state atoms (see (6)).

Atom	$A_m$ moments										
	$m =$	-2	-1	0	1	2	3	4	6	8	10
Li	0.396 + 1	0.342 - 1	0.292 - 2	0.134 - 2	0.213 - 2	0.765 - 2	0.394 - 1	0.211 + 1	0.295 + 3	0.787 + 5	
Be	0.795 + 1	0.556 - 1	0.395 - 2	0.152 - 2	0.200 - 2	0.580 - 2	0.248 - 1	0.827	0.455 + 2	0.364 + 4	
B	0.120 + 2	0.714 - 1	0.425 - 2	0.153 - 2	0.184 - 2	0.437 - 2	0.150 - 1	0.371	0.201 + 2	0.190 + 4	
C	0.173 + 2	0.877 - 1	0.472 - 2	0.249 - 2	0.451 - 2	0.126 - 1	0.457 - 1	0.108 + 1	0.446 + 2	0.258 + 4	
N	0.257 + 2	0.118	0.557 - 2	0.310 - 2	0.465 - 2	0.998 - 2	0.275 - 1	0.377	0.927 + 1	0.342 + 3	
O	0.443 + 2	0.196	0.826 - 2	0.393 - 2	0.580 - 2	0.136 - 1	0.433 - 1	0.824	0.259 + 2	0.108 + 4	
F	0.519 + 2	0.212	0.907 - 2	0.497 - 2	0.716 - 2	0.153 - 1	0.436 - 1	0.652	0.162 + 2	0.533 + 3	
Ne	0.373 + 2	0.141	0.859 - 2	0.526 - 2	0.671 - 2	0.124 - 1	0.306 - 1	0.338	0.608 + 1	0.143 + 3	
Na	0.295 + 2	0.126	0.476 - 2	0.128 - 2	0.222 - 2	0.934 - 2	0.611 - 1	0.542 + 1	0.811 + 3	0.157 + 6	
Mg	0.313 + 2	0.145	0.812 - 2	0.345 - 2	0.460 - 2	0.153 - 1	0.903 - 1	0.619 + 1	0.620 + 3	0.752 + 5	
Al	0.403 + 2	0.168	0.759 - 2	0.334 - 2	0.654 - 2	0.261 - 1	0.145	0.805 + 1	0.727 + 3	0.887 + 5	
Si	0.515 + 2	0.190	0.625 - 2	0.312 - 2	0.780 - 2	0.296 - 1	0.147	0.698 + 1	0.616 + 3	0.778 + 5	
P	0.426 + 2	0.171	0.857 - 2	0.518 - 2	0.116 - 1	0.392 - 1	0.173	0.664 + 1	0.517 + 3	0.622 + 5	
Cl	0.250 + 2	0.283	0.144 - 1	0.939 - 2	0.176 - 1	0.474 - 1	0.163	0.368 + 1	0.173 + 3	0.136 + 5	
Ar	0.893 + 2	0.255	0.110 - 1	0.708 - 2	0.120 - 1	0.304 - 1	0.101	0.222 + 1	0.968 + 2	0.635 + 4	



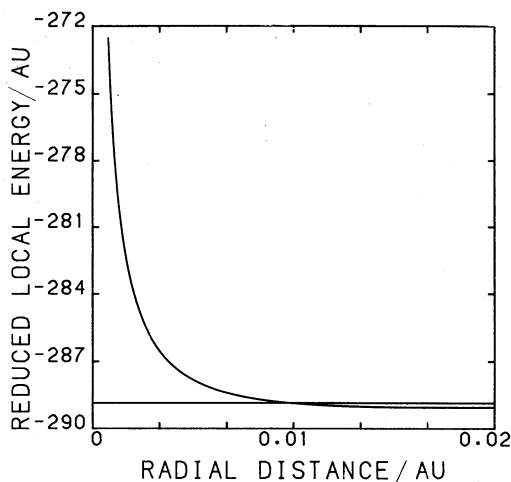


Figure 1. Hartree-Fock reduced local energy  $E_L^{\text{HF}}(r)$  as a function of  $r$  for the ground state of Si for the short range region. The 'exact' Hartree-Fock wavefunction should yield a reduced local energy which follows the horizontal line at  $E_L^{\text{HF}}(r) \equiv E^{\text{HF}} = -288.85431$  a.u.

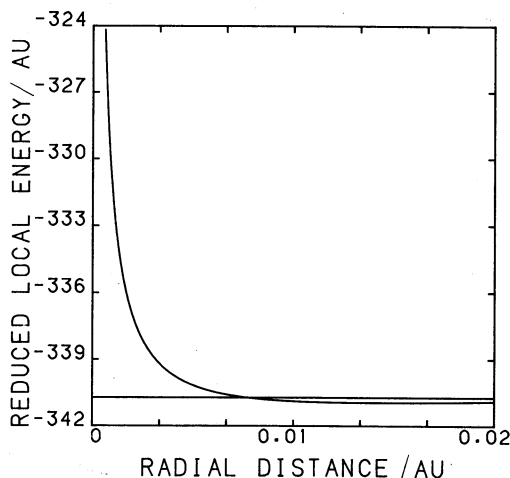


Figure 2.  $E_L^{\text{HF}}(r)$  as a function of  $r$  for the ground state of P for the short range region. The 'exact' Hartree-Fock wavefunction should yield a reduced local energy which follows the horizontal line at  $E_L^{\text{HF}}(r) \equiv E^{\text{HF}} = -340.71869$  a.u.

atoms indicate poor behaviour for the wavefunctions in the region near the nucleus. An indication of the poor behaviour of the wavefunctions in the near nuclear region is illustrated for the case of Si and P in figures 1 and 2 respectively, where  $E_L^{\text{HF}}(r)$  is plotted versus the radial coordinate  $r$ . The 'exact' Hartree-Fock wavefunctions would yield the horizontal line indicated in the figures. Similar behaviour is observed for other atoms in the near nuclear region. The low order moments ( $m = -2$ ,  $m = -1$ ) thus serve to quantify in a compact fashion the information represented by results such as those displayed in figures 1 and 2.

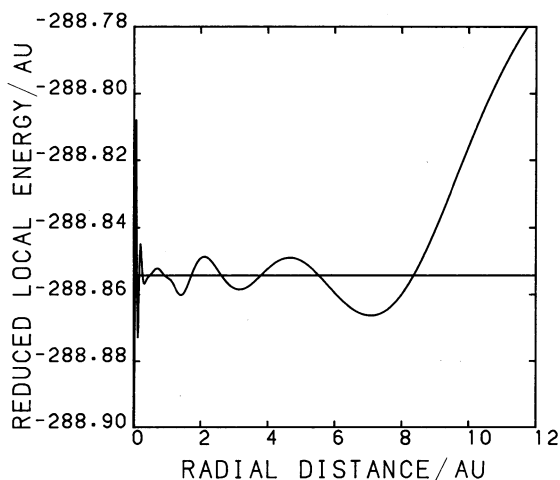


Figure 3.  $E_L^{\text{HF}}(r)$  as a function of  $r$ , for the ground state of Si for the medium range region. The 'exact' Hartree-Fock wavefunction should follow the horizontal line at  $E^{\text{HF}} = -288.85431$  a.u.

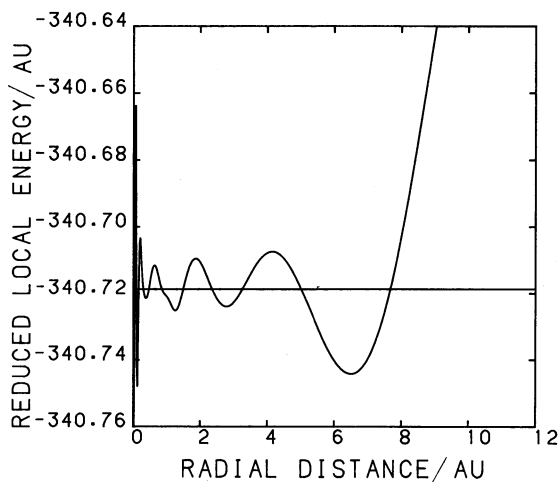


Figure 4.  $E_L^{\text{HF}}(r)$  as a function of  $r$ , for the ground state of P for the medium range region. The 'exact' Hartree-Fock wavefunction should follow the horizontal line at  $E^{\text{HF}} = -340.71869$  a.u.

For the energy important region, all values of  $A_m$  and  $D_m$  ( $m=1-3$ ) are reasonably small for each atom. This is an expected result, since the Clementi-Roetti wavefunctions are known to be fairly good in the energetic sense.

The results obtained for  $A_m$  and  $D_m$  for high values of  $m$  indicate poor behaviour for the wavefunctions at large distances from the nucleus. Figures 3-6 illustrate results for  $E_L^{\text{HF}}(r)$  for the atoms Si, P, Cl and Ar, which includes the longer range region. The reduced local energy for atoms Li through Al have been presented elsewhere [20]. The general trend observed in figures 3-6 (and also supported by results for the other atoms) is that the deviations of

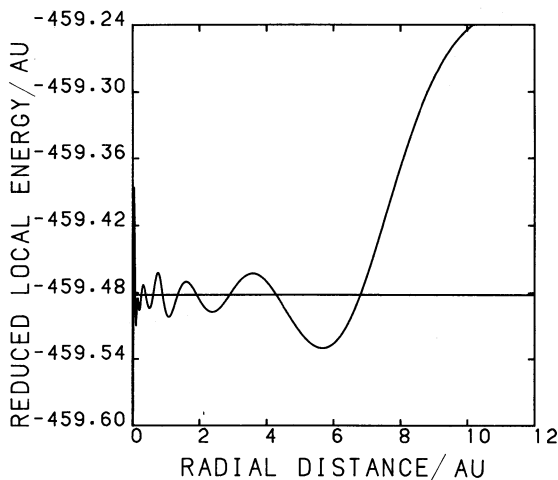


Figure 5.  $E_L^{\text{HF}}(r)$  as a function of  $r$ , for the ground state of Cl for the medium range region. The 'exact' Hartree-Fock wavefunction should follow the horizontal line at  $E^{\text{HF}} = -459.48187$  a.u.

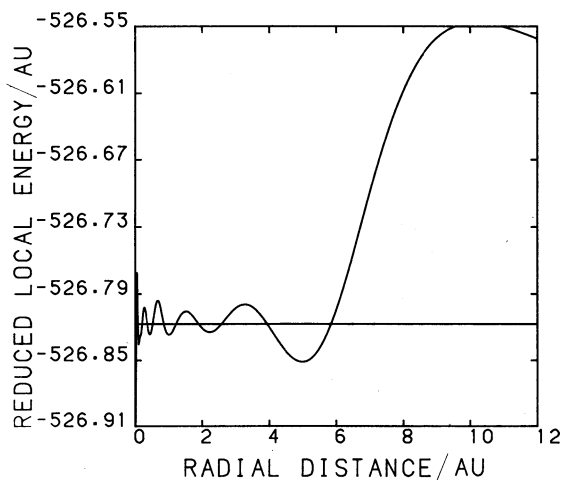


Figure 6.  $E_L^{\text{HF}}(r)$  as a function of  $r$ , for the ground state of Ar for the medium range region. The 'exact' Hartree-Fock wavefunction should follow the horizontal line at  $E^{\text{HF}} = -527.81739$  a.u.

$E_L^{\text{HF}}(r)$  from  $E^{\text{HF}}$  increase at long range  $r$ , reflecting inaccuracies in the wavefunctions in this region. Since the Hartree-Fock electronic density being used to compute  $D_m$  and  $A_m$  is derived from the energy optimized wavefunctions, both sets of moments will reflect in part, inaccuracies in  $\rho(r)$ . This is going to be particularly true at long range. In any case, the deviation of  $E_L^{\text{HF}}(r)$  from  $E^{\text{HF}}$ , and the deviation of the electronic density derived from the energy optimized wavefunction from the exact Hartree-Fock density, both reflect the local quality of the wavefunction.

All of the results reported in this work, except the modified 3-term and the refined 5-term Clementi–Roetti wavefunctions for helium reported in tables 1 and 2, have employed the wavefunctions exactly as presented in the Clementi tables. The definitions given in (5) and (6) involve the difference between  $E^{\text{HF}}$  and  $E_L^{\text{HF}}(r)$ , which for high quality wavefunctions, may involve the potential for considerable reduction in the number of significant figures for the resulting values of  $A_m$  and  $D_m$ . An indication of the nature of this problem has been ascertained from the following calculation. Using the orbital exponents for the Clementi–Roetti 5-term function, the wavefunction was recalculated yielding slightly more accurate expansion coefficients and then the  $D_m$  and  $A_m$  moments recalculated. For  $D_m$ , the observed changes were small at large  $m$ , approximately  $\pm 1$  in the third significant figure (i.e. 0.3 per cent change). This holds down to the energy important region where the change was  $\sim 0.6$  per cent. However, for the smallest values of  $m$ ,  $m = -2$  and  $m = -1$ , the results changed by approximately 13 per cent.  $A_m$  values are less sensitive to small changes in the expansion coefficients. Except for  $m = -2$ ,  $m = -1$  and  $m = 0$ , where the observed changes were approximately 7, 3 and 0.8 per cent respectively, higher moments did not change by more than  $\pm 2$  in the third significant figure.

A description of the program has been given elsewhere [28]. The algebraic details necessary for the evaluation of  $E_L^{\text{HF}}(r)$  may also be found in [28].

As the results in the tables of this paper clearly show, the moments  $A_m$  and  $D_m$  serve as very useful compact measures of the local accuracy of wavefunctions. Since these represent *a priori* constraints, it should be possible to construct better wavefunctions, and hence calculate improved expectation values, by using several moments, for a range of  $m$  covering the short, medium and long-range regions, as constraints in a modified Hartree–Fock calculation. Plans are underway to implement such a calculation.

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