

# Nonlinear programming approach to locally constrained variational calculations: He and H<sup>-</sup> in the Hartree–Fock approximation

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Nonlinear programming procedures are employed to carry out constrained variational calculations on the helium atom and the hydride ion in the Hartree–Fock approximation. The inequality constraints imposed to improve the local behavior of the wave function are based on the reduced local energy, evaluated at selected points in configuration space. Improved moments  $\langle r^n \rangle$  are obtained for the helium atom and the hydride ion using this procedure. The calculations provide empirical support for the fact that the reduced local energy does reflect errors in the wave function.

## I. INTRODUCTION

It is well known that wave functions determined by the variational technique often lead to non-Hamiltonian expectation values of poorer quality, relative to the accuracy obtained for the energy. This is a direct reflection of the local inaccuracies in the wave function. An excellent illustrative example comes from the work of Pekeris.<sup>1</sup> In a classic paper he determined the ground-state energy of the helium atom to an estimated accuracy of one part in 10<sup>10</sup> (verified by later calculations to be correct), while the same 1078-term wave

function used to evaluate the energy gave a 5% error in the coefficient of the  $r_{12}$  term of the wave function.

The variational technique is a global procedure; there is no *explicit* functional dependence on any local configuration-space coordinate. The purpose of this paper is to extend the standard variational technique, by including an *indirect* dependence on local configuration-space coordinates. The constraint that is employed in this study is based on the reduced local energy.

The reduced local energy is defined for an  $N$ -electron system ( $N \geq 2$ ) by<sup>2–4</sup>

$$E_L(\mathbf{r}_1) = \frac{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) H \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 d\tau_3 \dots d\tau_N}{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\gamma_1 d\tau_2 d\tau_3 \dots d\tau_N} \quad (1)$$

An analogous result holds for the Hartree–Fock formalism, namely,<sup>5–8</sup>

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

The calculations in this paper will focus on the Hartree–Fock approximation, so it is Eq. (2) that will be utilized.

The reduced local energy represents a *necessary* but not sufficient condition that must be satisfied by the exact Hartree–Fock wave function. That is,

$$\text{as } \Psi_{\text{HF}} \rightarrow \Psi_{\text{HF}}^{\text{exact}}, \quad E_L^{\text{HF}}(\mathbf{r}) \rightarrow E^{\text{HF}}, \quad (3)$$

where  $E^{\text{HF}}$  denotes the exact Hartree–Fock energy corresponding to  $\Psi_{\text{HF}}^{\text{exact}}$ . A central issue is how does the quantity  $\Delta E_L^{\text{HF}}(\mathbf{r})$  defined by

$$\Delta E_L^{\text{HF}}(\mathbf{r}) = |E_L^{\text{HF}}(\mathbf{r}) - E^{\text{HF}}| \quad (4)$$

reflect errors in the density difference,  $\Delta\rho_{\text{HF}}(\mathbf{r})$ , defined via

$$\Delta\rho_{\text{HF}}(\mathbf{r}) = |\rho_{\text{HF}}(\mathbf{r}) - \rho_{\text{HF}}^{\text{exact}}(\mathbf{r})|, \quad (5)$$

where  $\rho_{\text{HF}}(\mathbf{r})$  and  $\rho_{\text{HF}}^{\text{exact}}(\mathbf{r})$  denote the electronic densities, determined from  $\Psi_{\text{HF}}$  and  $\Psi_{\text{HF}}^{\text{exact}}$ , respectively. There is no question that at particular points of configuration space,  $E_L^{\text{HF}}(\mathbf{r})$  may be inaccurate and  $\rho_{\text{HF}}(\mathbf{r})$  reasonably accurate. This situation often occurs (depending on the choice of basis functions) in the near-nuclear region of configuration space.<sup>9–11</sup> The converse may also occur. That is,  $E_L^{\text{HF}}(\mathbf{r})$  might be extremely accurate, but  $\rho_{\text{HF}}(\mathbf{r})$  is much less so, for

a particular point in configuration space. A working hypothesis of the present study is that, given a sufficiently large region of configuration space, the inaccuracies in  $E_L^{\text{HF}}(\mathbf{r})$  will be reflected in the inaccuracies in  $\rho_{\text{HF}}(\mathbf{r})$ . There is no known relationship connecting  $E_L^{\text{HF}}(\mathbf{r})$  with  $\rho_{\text{HF}}(\mathbf{r})$ , and it appears very unlikely that any simple connection can be found. The above conjecture does not imply any simple proportionality between  $\Delta E_L^{\text{HF}}(\mathbf{r})$  and  $\Delta\rho_{\text{HF}}(\mathbf{r})$ . There is some empirical evidence that  $\Delta E_L^{\text{HF}}(\mathbf{r})$  does reflect errors in  $\rho_{\text{HF}}(\mathbf{r})$  as assessed by monitoring various expectation values.<sup>9,10,12–16</sup> Similar empirical observations have been made for the post-Hartree–Fock case.<sup>2,3,11</sup> Further investigation of exactly soluble model problems might shed some light on the relationship between  $\Delta E_L(\mathbf{r})$  and  $\Delta\rho(\mathbf{r})$ .<sup>17</sup>

An alternative procedure that has been suggested is to utilize the global variance of the 1-reduced local energy matrix as a quantitative measure of the error in the wave function.<sup>18,19</sup> Unfortunately, numerical applications of this idea have not been made.

In this study, the He atom and the H<sup>-</sup> ion are examined. These were both selected because of the relative ease of carrying out the nonlinear optimizations described in the next section. Both species offer the advantage that there are fairly

accurate values for the moments  $\langle r^n \rangle$  (for a range of values of  $n$ ) available for comparison.  $H^-$  offers an interesting target. Despite the fact that the Hartree–Fock method does not yield a bound state for this system, the  $H^-$  ion has been well studied with this procedure. The  $H^-$  ion presents a situation where the energy-important region of configuration space is somewhat more diffuse, in comparison with the He atom. This provides an additional challenge in the constrained optimization task, since a much larger region of configuration space must be incorporated in the calculations.

## II. THEORY

The following optimization problem is the focus of this investigation. Minimize

$$E^{\text{HF}} = \frac{\int \Psi_{\text{HF}}^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) H \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\tau_1 d\tau_2 \dots d\tau_N}{\int \Psi_{\text{HF}}^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\tau_1 d\tau_2 \dots d\tau_N} \quad (6)$$

subject to the following constraints:

$$\begin{aligned} E^{\text{HF}} - E_L^{\text{HF}}(\mathbf{r}_1) &\leq a_1, \\ E^{\text{HF}} - E_L^{\text{HF}}(\mathbf{r}_2) &\leq a_2, \\ &\vdots \\ E^{\text{HF}} - E_L^{\text{HF}}(\mathbf{r}_i) &\geq a_i, \\ E^{\text{HF}} - E_L^{\text{HF}}(\mathbf{r}_j) &\geq a_j, \\ &\vdots \end{aligned} \quad (7)$$

by varying adjustable parameters appearing in the wave function  $\Psi_{\text{HF}}$ . The optimization task presented in Eqs. (6) and (7) is a nonlinear programming problem.

There is an extensive literature on nonlinear programming.<sup>20,21</sup> Nonlinear programming problems of fundamental importance arise in a diverse number of fields,<sup>22</sup> and for this reason, we may expect to see continued progress in the development of robust algorithms to solve such problems. In a previous work in this area,<sup>16</sup> the gradient projection method developed by Rosen<sup>23,24</sup> was employed. Rosen's method suffers the disadvantage of being inefficient when implemented with nonlinear inequality constraints of the type employed in Eq. (7). In the present work, the more recently developed generalized reduced gradient method as implemented by Lasdon *et al.*<sup>25</sup> is employed. Concisely, the strategy employed is to convert the inequality constraints to equalities (by the introduction of appropriate slack variables). For a problem with  $n$  variables, the algorithm solves for  $m$  basic variables satisfying equality constraints in terms of  $n - m$  independent (nonbasic) variables. The objective function [in the present calculation this is Eq. (6)] can then be transformed to a function of the nonbasic variables. The new objective function is called the reduced objective and its gradient the reduced gradient. The independent variables are varied so as to rapidly obtain the minimum of the objective function. Solution of the constraint equalities at each step is done using a variant of Newton's method. Lasdon *et al.*<sup>25</sup> should be consulted for details on the nonlinear programming technique as employed in this study. For those not familiar with nonlinear programming, Himmelblau's book<sup>21</sup> gives a very readable introduction.

The number of constraints imposed in Eq. (7) is not restricted; however, practical limitations dictate using a few well-selected constraints. The choice of constraints, that is, their location  $\mathbf{r}_i$  and the values for the bounds  $a_i$ , were initially made on the basis of trial calculations. For a  $\Psi_{\text{HF}}$  with few expansion terms, it is very easy to impose constraints in such a way that no feasible solution can be found. This can be done by choosing a few constraints with small values for the bounds  $a_i$ .

If the programming problem presented by Eqs. (6) and (7) were convex, determination of a global minimum would be relatively straightforward. However, it is expected that Eqs. (6) and (7) will present a nonconvex optimization problem, and determination of a global minimum depends on choosing a starting search point on the face of the deepest valley.

## III. COMPUTATIONAL APPROACH

The orbital basis functional form chosen was

$$\phi(r) = \sum_i C_i N_i r^{n_i} e^{-Zr} \cosh(\alpha_i r) Y_{00}, \quad (8)$$

where  $Z$  is the nuclear charge,  $N_i$  is a normalization factor, and  $\alpha_i$  are the parameters determined in the nonlinear optimization problem. If the restriction  $n_i \neq 1$  ( $n_i \geq 0$ ) is employed, then the functional form given in Eq. (8) has the advantage that the cusp condition on the orbital function<sup>26,27</sup>

$$\left. \frac{\partial \phi(r)}{\partial r} \right|_{r=0} = -Z\phi(0) \quad (9)$$

is exactly satisfied. The  $\alpha_i$  parameters satisfy

$$|\alpha_i| < Z. \quad (10)$$

This range restriction on the  $\alpha_i$  parameters allows the nonconvexity of the problem to be addressed in part by carrying out trial calculations with different starting sets for the  $\alpha_i$ .

The basis functions in Eq. (8) were selected with the expectation that they would be particularly advantageous in minimizing errors in the region of configuration space close to the nucleus. In the large  $r$  limit, the choice of basis functions given in Eq. (8) would be less suitable. However, this is likely to be a problem only for the very diffuse region of configuration space. Support for this assertion is based on our ability to produce wave functions in the nonlinear programming calculations for the long-range region, which lead to accurate moments  $\langle r^n \rangle$  for large values of  $n$ .

To simplify the calculations, the numerator and denominator of Eq. (6) were integrated with respect to the polar angles ( $\theta_1, \phi_1$ ). This leads to a reduced local energy depending only on the radial coordinate.

The nonlinear programming aspect of the problem was solved using GRG2 (generalized reduced gradient)—a software package commercially available from L. S. Lasdon, University of Texas, Austin, Texas. The GRG2 code appeared to be rather robust in applications, and is well documented.

All the calculations were carried out in double precision. The final results are all reported in atomic units.

TABLE I. Expectation values  $\langle \Psi | r^m | \Psi \rangle$  for He.<sup>a</sup>

$n$	Fischer numerical HF	Clementi-Roetti	Energy optimized	Short-range optimized	Intermediate-range optimized	Long-range optimized
-2	5.995 50	5.995 92	5.995 05	5.993 62	5.994 95	5.994 88
-1	1.687 28	1.687 33	1.687 27	1.687 10	1.687 26	1.687 26
1	9.272 73[-1]	9.272 51[-1]	9.272 73[-1]	9.275 75[-1]	9.272 73[-1]	9.272 73[-1]
2	1.184 83	1.184 66	1.184 83	1.187 91	1.184 83	1.184 83
3	1.940 64	1.939 80	1.940 64	1.971 86	1.940 64	1.940 64
4	3.887 95	3.883 84	3.887 94	4.212 56	3.887 98	3.887 98
5	9.221 20	9.200 75	9.221 04	1.267 62[1]	9.221 50	9.221 53
6	2.527 84[1]	2.517 37[1]	2.527 64[1]	6.287 40[1]	2.528 10[1]	2.528 12[1]
7	7.865 25[1]	7.809 76[1]	7.863 00[1]	4.966 59[2]	7.867 13[1]	7.867 34[1]
8	2.738 45[2]	2.707 95[2]	2.736 16[2]	5.023 47[3]	2.739 72[2]	2.739 98[2]
9	1.054 83[3]	1.037 40[3]	1.052 65[3]	5.623 94[4]	1.055 58[3]	1.055 89[3]
10	4.453 56[3]	4.349 79[4]	4.433 73[3]	6.605 76[5]	4.457 19[3]	4.460 68[3]
11	2.045 10[4]	1.980 70[4]	2.027 76[4]	8.009 60[6]	2.046 04[4]	2.049 92[4]
12	1.014 76[5]	9.730 90[4]	1.000 14[5]	9.979 93[7]	1.013 97[5]	1.018 13[5]
13	5.410 43[5]	5.129 15[5]	5.292 62[5]	1.276 51[9]	5.392 33[5]	5.435 30[5]
14	3.084 70[6]	2.886 76[6]	2.996 30[6]	1.676 15[10]	3.061 90[6]	3.104 85[6]
15	1.872 72[7]	1.727 58[7]	1.815 31[7]	2.260 23[11]	1.849 60[7]	1.891 20[7]

<sup>a</sup>The notation [ $m$ ] designates  $\times 10^m$ .

## IV. RESULTS

An initial set of calculations were made to determine an energy-optimized wave function for both the He atom and the H<sup>-</sup> ion. For both systems, a seven-term basis set was employed. The resulting energies were  $-2.861\ 679\ 921$  a.u. for He and  $-0.487\ 929\ 69$  a.u. for H<sup>-</sup>. For comparison, the Hartree-Fock ground-state energy for He is  $-2.861\ 679\ 995\ 61$  a.u.,<sup>28</sup> and a result due to Silverstone quoted in Ref. 29 gives  $-0.487\ 929\ 734\ 35$  a.u. for the H<sup>-</sup> ion. Roothaan and Soukup have published similar values.<sup>30</sup> The Hartree-Fock wave functions employed are at least in the energetic sense of fairly high quality. The energy optimized wave functions determined in this study are available from the Physics Auxiliary Publication Service (PAPS).<sup>31</sup>

Since a principal objective of the present investigation was to explore the effect of the nonlinear programming technique on computed expectation values, optimizations were carried out on three separate regions of configuration space: the short-range near-nuclear region of configuration space, the intermediate region of configuration space, and the long-range region. The tabulated wave functions and the nonlinear constraints employed are available from PAPS.<sup>31</sup>

For each wave function, expectation values of  $\langle \Psi_{\text{HF}} | r^m | \Psi_{\text{HF}} \rangle$  have been determined, and these are presented in Tables I and II. For comparison purposes, the moments for the helium atom calculated from the Clementi-Roetti wave function<sup>32</sup> and from the numerical Hartree-Fock wave function of Fischer<sup>33</sup> are also included in Table I. For the hydride ion, the wave functions of Gupta and Boyd<sup>29</sup>

TABLE II. Expectation values  $\langle \Psi | r^m | \Psi \rangle$  for H<sup>-</sup>.

$n$	Gupta and Boyd <sup>a</sup>	Curl and Coulson <sup>b</sup>	Energy optimized	Short-range optimized	Intermediate-range optimized	Long-range optimized	Fischer <sup>c</sup> numerical HF
-2	1.081 51	1.081 49	1.081 34	1.081 38	1.081 37	1.081 22	1.081 49
-1	6.856 71[-1]	6.857 85[-1]	6.856 63[-1]	6.856 54[-1]	6.856 62[-1]	6.856 53[-1]	6.856 72[-1]
1	2.503 96	2.526 08	2.503 96	2.504 07	2.504 03	2.503 96	2.503 96
2	9.411 07	9.712 22	9.411 05	9.413 61	9.412 94	9.411 10	9.411 10
3	4.870 06[1]	5.286 77[1]	4.869 90[1]	4.875 34[1]	4.874 35[1]	4.870 07[1]	4.870 10[1]
4	3.261 39[2]	3.861 93[2]	3.260 75[2]	3.272 62[2]	3.271 15[2]	3.261 38[2]	3.261 44[2]
5	2.700 38[3]	3.615 71[3]	2.698 12[3]	2.725 02[3]	2.722 55[3]	2.700 19[3]	2.700 30[3]
6	2.672 53[4]	4.160 73[4]	2.665 03[4]	2.728 39[4]	2.723 03[4]	2.671 46[4]	2.671 64[4]
7	3.083 99[5]	5.674 17[5]	3.059 32[5]	3.213 75[5]	3.198 82[5]	3.078 49[5]	3.078 81[5]
8	4.082 96[6]	8.904 58[6]	3.995 61[6]	4.383 57[6]	4.336 27[6]	4.051 54[6]	4.052 26[6]
9	6.207 34[7]	1.572 37[8]	5.834 66[7]	6.836 00[7]	6.681 14[7]	5.996 33[7]	5.998 60[7]
10	1.149 27[9]	3.072 48[9]	9.389 35[8]	1.203 84[9]	1.153 36[9]	9.856 50[8]	9.865 36[8]
11	3.192 64[10]	6.562 17[10]	1.645 12[10]	2.362 44[10]	2.199 75[10]	1.780 93[10]	1.784 63[10]
12	1.672 44[12]	1.517 67[12]	3.107 05[12]	5.093 95[11]	4.573 87[11]	3.506 24[11]	3.521 80[11]
13	1.401 30[14]	3.773 52[13]	6.273 48[13]	1.190 26[13]	1.024 42[13]	7.463 94[12]	7.529 04[12]
14	1.435 63[16]	1.002 88[15]	1.345 12[14]	2.976 70[14]	2.446 33[14]	1.706 27[14]	1.733 40[14]
15	1.614 06[18]	2.835 60[16]	3.046 10[15]	7.886 03[15]	6.177 12[15]	4.162 74[15]	4.275 81[15]

<sup>a</sup> Evaluated from the wave function given in Ref. 29.<sup>b</sup> Evaluated from the wave function given in Ref. 34.<sup>c</sup> Reference 33.

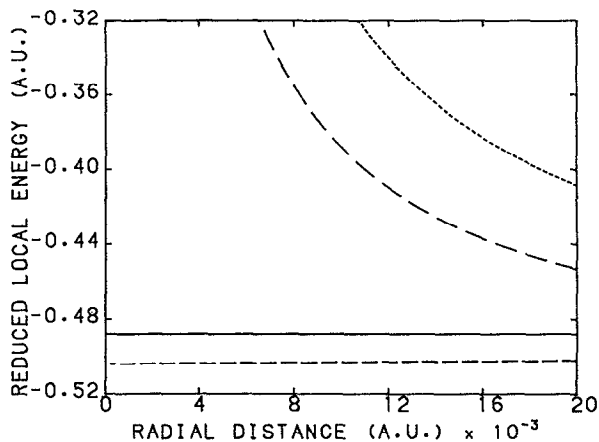


FIG. 1. Reduced local energy vs the radial coordinate for the short-range optimized wave function for the  $H^-$  ion. The Gupta-Boyd function is shown as ---. The Curl-Coulson function is shown as ——. The energy optimized function is shown as - · - ·. The short-range optimized function lies directly over the exact local energy (they agree to four significant figures).

and of Curl and Coulson<sup>34</sup> (see footnotes 32 and 33 of Ref. 29) have been utilized to calculate moments, and the numerical Hartree-Fock (HF) results of Fischer<sup>33</sup> are also included.

The reduced local energies calculated from the wave functions optimized for the short-, intermediate-, and long-range regions for  $H^-$  are shown in Figs. 1-3. Graphical results for He are available from the authors. For comparison, the reduced local energy calculated using the energy optimized wave function (no constraints imposed), as well as the Gupta-Boyd and Curl-Coulson wave functions, are also displayed.

## V. DISCUSSION

When carrying out the nonlinear programming phase of the calculations, it is tempting to make the bounds on the inequality constraints as tight as possible. The drawback is

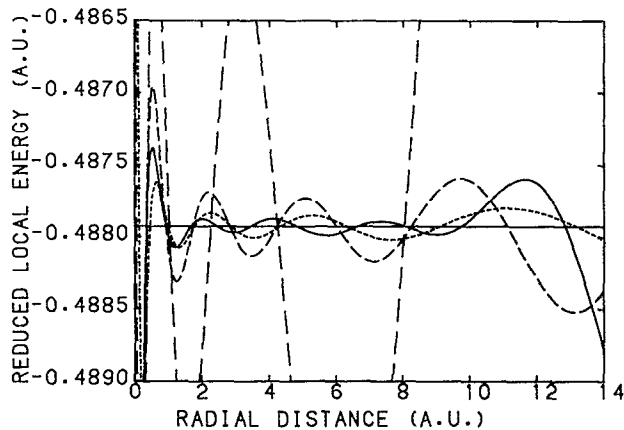


FIG. 2. Reduced local energy vs the radial coordinate for the intermediate-range optimized wave function for the  $H^-$  ion. The intermediate-range optimized function is shown as the solid curve. The other functions are defined in Fig. 1.

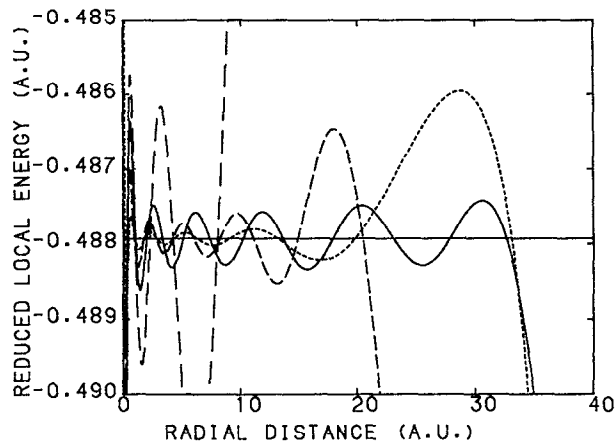


FIG. 3. Reduced local energy vs the radial coordinate for the long-range optimized wave function for the  $H^-$  ion. The long-range optimized function is shown as the solid curve. The other functions are defined in Fig. 1.

that such a strategy is not likely to lead to a solution of the programming problem. Some experimentation is required in the selection of appropriate bounds. Some violations of constraints were found, but these were rather minor. It is of course entirely feasible to adopt a procedure where the bounds for the inequality constraints are set rather tight, and the number of terms in the basis set progressively expanded, until a solution of the nonlinear programming problem is obtained. Since the principal objective of the present investigation was to see what improvements could be achieved for a fixed-size basis set, the aforementioned strategy was not utilized.

The nonlinear optimization calculations lead to a slight increase in the energy for each of the six wave functions determined in the present work. However, the changes compared with the energy optimized results are very minor.

The expectation values  $\langle \Psi_{HF} | r^n | \Psi_{HF} \rangle$  give an indication of how the nonlinear optimization has affected the local behavior of the radial density, and indirectly, the wave function. The higher moments depend on the more diffuse part of the electronic charge cloud. To get a good idea just what region is sampled for the evaluation of a particular moment, we have examined plots of the integrand  $\rho(r)r^{2+n}$  as a function of  $r$ , where  $\rho(r)$  is the electronic density. For the He atom, some functions are shown elsewhere.<sup>16</sup> For the larger moments there is, as expected, a significant contribution to the integrands from the long-range region, but there is also a rather significant contribution from the intermediate-range region. For the moments with smaller values of  $n$ , it is the near-nuclear and intermediate-range regions of configuration space that make the largest contributions to the integrands for the moments. The function  $E_L^{HF}(r)\rho(r)r^2$  vs the radial coordinate has also been examined. This gives direct information on the energy important region for use in the nonlinear programming calculations. It should be clear from the preceding remarks that the constrained optimization calculations may lead to changed values of  $\langle r^n \rangle$  by altering the structure of the wave function in one or more regions of configuration space. It is also possible that changes in one region of configuration space may offset changes in another

TABLE III. Values of  $D$  [see Eq. (11)] and the limits  $E_L^{\text{HF}}(r \rightarrow \infty)$  and  $E_L^{\text{HF}}(r \rightarrow 0)$ .

Wave function	He			H <sup>-</sup>		
	$D$	$E_L^{\text{HF}}(r \rightarrow 0)$	$E_L^{\text{HF}}(r \rightarrow \infty)$	$D$	$E_L^{\text{HF}}(r \rightarrow 0)$	$E_L^{\text{HF}}(r \rightarrow \infty)$
Energy optimized (unconstrained)	$2.27 \times 10^{-6}$	-2.901 31	-2.799 40	$2.64 \times 10^{-7}$	-0.503 850	-0.526 089
Short range	$7.06 \times 10^{-5}$	-2.861 69	-2.247 72	$3.13 \times 10^{-7}$	-0.487 939	-0.512 888
Intermediate range	$2.64 \times 10^{-6}$	-2.903 90	-2.799 40	$1.01 \times 10^{-7}$	-0.499 075	-0.516 522
Long range	$3.33 \times 10^{-6}$	-2.907 76	-2.799 43	$8.37 \times 10^{-7}$	-0.512 115	-0.545 334
Clementi and Roetti	$6.63 \times 10^{-6}$		-2.947 91			
Gupta and Boyd				$2.87 \times 10^{-7}$		-0.444 519

region, leading to only a small change in the computed value of  $\langle r^n \rangle$ .

From the results of Table I, the impact of the constrained optimization on the energy (unconstrained) optimized wave function is readily apparent. The availability of the numerical HF values of Fisher certainly helps clarify the situation. The short-range, intermediate-range, and long-range constrained optimized functions all give fairly accurate values for  $\langle r^n \rangle$  for  $n = -2$  to 2. For higher values of  $n$ , the short-range function gives poor values for the moments, a fact not entirely unexpected. For the highest values of  $n$ , both the intermediate-range and the long-range optimized functions give better results than the energy-optimized function, and much superior results to the Clementi-Roetti function. The values for  $\langle r^n \rangle$  for the intermediate-range and long-range optimized functions are in good agreement with the results of other Hartree-Fock calculations.<sup>35</sup>

For the case of H<sup>-</sup> the changes are more dramatic, undoubtedly this is tied to the much more diffuse nature of the charge cloud. For the smallest values of  $n$  ( $n = -2$  to 3) all the cosh-type wave functions give similar values for the moments  $\langle r^n \rangle$ . As  $n$  increases, the intermediate-range, long-range, and energy-optimized functions all lead to moments that are now significantly different from one another. After the optimization calculations for H<sup>-</sup> were completed, Fischer<sup>33</sup> sent us the results of her numerical Hartree-Fock work on this system. It is apparent from the results presented in Table II that the long-range optimized results show significant improvements over the results obtained from the energy- (unconstrained) optimized wave function, particularly for the larger moments. The agreement with the numerical Hartree-Fock results is gratifying. The Gupta-Boyd moments for large  $n$  deviate significantly from those obtained with the cosh-type wave functions.

The functional form for the basis set allows a rather accurate  $E_L^{\text{HF}}(r)$  to be calculated in the near-nucleus region (see Fig. 1). For both He and H<sup>-</sup>, the unconstrained optimized function does not lead to a particularly accurate  $E_L^{\text{HF}}(r)$  in this region, though it is much more accurate than the other results presented based on Slater-type orbital basis

sets. It can be noted from Tables I and II that these inaccuracies do not have any significant impact on the expectation values of  $\langle r^n \rangle$  for small  $n$ . An important consideration in these cases is that the  $r^2$  factor from the volume element tends to iron out any inaccuracies in the wave function near the nucleus.

For the intermediate-range and for the long-range constrained optimizations, the computed  $E_L^{\text{HF}}(r)$  generally approaches the exact  $E_L^{\text{HF}}$  more closely than the other functions indicated in Figs. 2 and 3. In these cases, expectation value of  $\langle r^n \rangle$  apparently reflect these differences.

One way to assess the closeness of  $E_L^{\text{HF}}(r)$  to the exact value of  $E_L^{\text{HF}}$  is to use a global measure defined by<sup>16</sup>

$$D = \int_0^\infty [E_{\text{exact}}^{\text{HF}} - E_L^{\text{HF}}(r)]^2 \rho(r) r^2 dr. \quad (11)$$

In the limit that the exact Hartree-Fock wave function is obtained,  $D \rightarrow 0$ . Values of  $D$  for the different wave functions employed are tabulated in Table III. The values of  $D$  give an indication that the wave functions are all rather accurate, at least in the intermediate region of configuration space. Since the integrand of  $D$  is weighted by  $r^2$  at small  $r$ , and the density  $\rho(r)$  has a "leveling" effect at large  $r$ , the value of  $D$  will not strongly reflect errors in each of these regions of configuration space. A better way to examine these regions is to look at the asymptotic behavior  $E_L^{\text{HF}}(r \rightarrow \infty)$  and the limit  $E_L^{\text{HF}}(r \rightarrow 0)$ . These values are also reported in Table III. None of the values  $E_L^{\text{HF}}(r \rightarrow \infty)$  are particularly accurate, and only the short-range constrained values of  $E_L^{\text{HF}}(r \rightarrow 0)$  are accurate.

## VI. CONCLUSIONS

The results of the present study provide support for the hypothesis that the reduced local energy does reflect the local inaccuracies in the wave function, and indirectly, in the electronic density. The constrained variational calculations are shown for the case of He and H<sup>-</sup> to lead to improved values for the moments  $\langle r^n \rangle$ , in comparison with the results from unconstrained optimization calculations.

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<sup>31</sup>See AIP document No. PAPS JCPA-96-2889-7 for 7 pages of tables reporting wave functions employed in the present investigation. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for each microfiche (60 pages) or \$5.00 for photocopies of up to 30 pages, and \$0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.

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