Nonlinear programming approach to locally constrained variational calculations

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The standard variational problem is modified so that the local behavior of the wave function is indirectly incorporated into the optimum energy calculation. The minimum energy is determined subject to certain inequality constraints, formulated so that the reduced local energy is bounded above and below by a certain error, at different points in configuration space. This modified formulation of standard variational theory constitutes a problem in nonlinear programming. The gradient projection method has been employed to solve this problem. Calculations are carried out using the Hartree–Fock formalism for the ground state of the helium atom.

I. INTRODUCTION

There has been recent interest in applying the concept of the reduced local energy to examine the accuracy of wave functions.[1–6] The reduced local energy is defined for an N electron system ($N \geq 2$) by[1,2,7]

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

An analogous result holds for the Hartree–Fock formalism,[8–11] namely,

$$E_L^{\mathrm{HF}}(\mathbf{r}_1)=\frac{\int \Psi_{\mathrm{HF}}^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)H\Psi_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\gamma_1\,d\tau_2\,d\tau_3\cdots d\tau_N}{\int \Psi_{\mathrm{HF}}^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,\Psi_{\mathrm{HF}}^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\gamma_1\,d\tau_2\,d\tau_3\cdots d\tau_N}\,. \tag{2}$$

The MCSCF case has also been discussed.[12]

Equations (1) and (2) may be employed as fairly sensitive tests of the local accuracy of a wave function. For the case of an exact wave function, the right-hand side of Eq. (1) would be a constant, independent of the configuration space coordinate $\mathbf{r}_1$, and equal to the exact energy E. Equation (2) has a similar interpretation: employing the exact Hartree–Fock wave function for the expression on the right-hand side of the equation, yields a constant equal to the Hartree–Fock energy. The idea of reduced local energy is an extension of the local energy concept first discussed by Bartlett and Frost and co-workers many years ago.[13–16]

The standard variational approach examines the minimization of the quantity

$$\frac{\int \psi^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)H\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\tau_1\,d\tau_2\cdots d\tau_N}{\int \psi^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\tau_1\,d\tau_2\cdots d\tau_N}\,,$$

with respect to parameters which appear in the expansion of the trial wave function ψ. It is well known that while such a procedure may lead to good values for the energy, there is no guarantee that equally satisfactory results will be obtained for the expectation values of other operators, particularly those which depend on regions of configuration space different from that emphasized in the determination of the energy. One possible approach that has been discussed in the literature to circumvent the above problem, is the idea of using expectation values of one electron properties as constraints in the standard variational procedure.[17]

An alternative approach recently discussed for the case of Hartree–Fock wave functions, makes use of the idea of performing the standard variational calculation, with the additional constraint that $D[E_L^{\mathrm{HF}}]$, defined by[4]

$$D[E_L^{\mathrm{HF}}]=\int \{E^{\mathrm{HF}}-E_L^{\mathrm{HF}}(\mathbf{r})\}^2\rho_{\mathrm{HF}}(\mathbf{r})d\tau \tag{3}$$

be as small as possible. In Eq. (3), $\rho_{\mathrm{HF}}(\mathbf{r})$ is the Hartree–Fock electronic density and E^{HF} is the "exact" Hartree–Fock energy. The weight function $\rho_{\mathrm{HF}}(\mathbf{r})$ is included in the integrand to ensure convergence behavior for $D[E_L^{\mathrm{HF}}]$. In the limit that the exact Hartree–Fock wave function is obtained,

$$D[E_L^{\mathrm{HF}}]\to 0\,. \tag{4}$$

An analogous approach may be employed for a wave function approximating the exact eigenstate using $D[E_L]$ where E_L is given in Eq. (1).

Both the above approaches of utilizing expectation values, or employing the functional $D[E_L]$, are ideas that

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essentially emphasize the improvement of the local behavior of the wave function as interpreted in a *global* manner. It is of course possible by the careful selection of expectation values, or by modifying the weight function in Eq. (3), to emphasize a restricted region of configuration space.

In the present investigation, we utilize constraints which depend on *particular points* in configuration space. The reduced local energy is employed as the measure of local accuracy. Section II describes the approach, Sec. III gives the computational details, and Sec. IV presents the results of an application of the method for the ground state of the helium atom.

II. THEORY

The basic problem addressed in this work is the following optimization task. Determine the minimum of the quantity

$$E^{\mathrm{HF}}=\frac{\int\psi^{*}_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)H\psi_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\tau_1\,d\tau_2\cdots d\tau_N}{\int\psi^{*}_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\psi_{\mathrm{HF}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)d\tau_1\,d\tau_2\cdots d\tau_N}, \tag{5}$$

subject to the following constraints:

$$\begin{aligned}
&E^{\mathrm{HF}}-E_L^{\mathrm{HF}}(\mathbf{r}_1)\le a_1\,,\\
&E^{\mathrm{HF}}-E_L^{\mathrm{HF}}(\mathbf{r}_2)\le a_2\,,\\
&\quad\vdots\\
&E^{\mathrm{HF}}-E_L^{\mathrm{HF}}(\mathbf{r}_i)\ge a_i\,,\\
&E^{\mathrm{HF}}-E_L^{\mathrm{HF}}(\mathbf{r}_j)\ge a_j\,,\\
&\quad\vdots
\end{aligned} \tag{6}$$

by varying adjustable parameters appearing in the wave function ψ_{HF}. The optimization task presented in Eqs. (5) and (6) is a nonlinear programming problem.[18,19]

The problem considered in Eqs. (5) and (6) is formulated for an approximate Hartree–Fock wave function, as this case is relatively straightforward to implement. However, a similar problem may be formulated using a trial approximation for the exact eigenstate, in which case E^{HF} and $E_L^{\mathrm{HF}}(\mathbf{r}_i)$ are replaced by the exact energy (or a very good approximation to it) and the reduced local energy at the point $\mathbf{r}_i$ determined from the trial wave function, respectively.

For the case involving an approximation to the exact eigenstate, the problem can be generalized to include constraints involving a more general local energy function, obtained by integration over $N-p$ $(p>1)$ particle coordinates. The resulting p-reduced local energy function will serve as a source of severe constraints on the local accuracy of the wave function. However, the complexity of the calculation would quickly escalate. For this reason, the reduced local energy represents a nice compromise; it is not as severe a criterion of accuracy as the Bartlett–Frost local energy, or the p-reduced local energy, but it is considerably easier to visualize and to handle in practical computations.

The objective function given in Eq. (5) depends on both orbital exponents and expansion coefficients. A general optimization can be carried out such that both of these are varied. In this work, we have concentrated our attention on the optimization of the orbital exponents in the nonlinear programming problem. The expansion coefficients have been determined directly from a variational calculation on the optimized objective function.

The number of constraints is unrestricted, but clearly the complexity of the computations increases very quickly if an excessive number are included in the calculation. From our calculations to date, a few well chosen constraints are more useful than a number of constraints with arbitrary selected points $\mathbf{r}_i$. The size of the error limits in Eq. (6) a_i are selected with two considerations in mind. The first is that the a_i are not selected so small that the computational method cannot find an optimum point, i.e., the algorithm employed fails to converge. Secondly, the a_i have been made rather small at a few selected points, in order to improve an existing wave function in a specific region of configuration space. For the small-term wave functions employed in this study, a large number of constraints with very small error limits does not allow an optimum point to be found.

The nonlinear programming technique employed in this work was a slightly modified version of Rosen's gradient projection method.[18-21] The principal idea behind the gradient projection solution of the nonlinear programming problem is as follows. A search from within the feasible region [i.e., the region bounded by the constraints in Eq. (6)] is made by taking steps in the direction of the negative gradient of the objective function $\mathbf{g}=\nabla f(\mathbf{r})$, i.e.,

$$-\mathbf{x}=-\mathbf{g}\,. \tag{7}$$

If a step takes the search point outside the feasible region, or the initial starting point does not lie in the feasible region, a return direction is constructed. The return direction is determined in a straightforward manner from the gradients of the active constraints. On the boundary of the feasible region, the negative gradient direction may not be the correct path to search, because of the possible resulting violation of one or more of the constraints. The basic idea is to search, so that the objective function decreases, in a direction that is tangential to the boundaries of the active constraints. The appropriate calculation is to find the projection on to the tangent hyperplane at the current boundary point. The required direction of search from this point is

$$-\mathbf{x}=-\mathbf{P}\mathbf{g}\,, \tag{8}$$

where $\mathbf{P}$ denotes the projection matrix, which depends on the gradients of the constraints. Rosen's papers may be consulted for further details on the gradient projection algorithm.[20,21]

The programming problem must be convex, in order to ensure determination of the global minimum. When the problem is nonconvex, determination of the global minimum depends upon the probability of the starting point being selected on the face of the deepest valley. In the present work, the parameters which have been optimized satisfy $0\le\alpha_i<2$ (see Sec. III). We have cho-

TABLE I. Coefficients and parameters for energy optimized cosh wave functions.

Values of n_i	Coefficients C_i	α_i parameters	Energy (a.u.)	Figure on which $E_L^{HF}(r)$ is plotted
(0,0)	$0.252\,229\times10^{1}$, $-0.153\,218\times10^{1}$	0.394 13, 0	−2.861 6024	1
(0,3)	$0.103\,111\times10^{1}$, $-0.561\,848\times10^{-1}$	0.698 58, 0.240 38	−2.861 6763	2,3
(0,2,3)	0.971 083, $0.730\,016\times10^{-1}$	0.597 09, 0.265 07	−2.861 6773	4
	$-0.423\,724\times10^{-1}$	$0.176\,32\times10^{-1}$		

sen a wide selection of starting points for the α vector in order to ensure that the optimum set of α values was found. Such a procedure is of course not foolproof, since the global minimum of the programming problem may lie at the bottom of a very sharp spike.

III. COMPUTATIONAL DETAILS

The orbital basis functional form chosen was

$$\phi(r)=\sum_i C_i N_i r^{n_i} e^{-Zr}\cosh(\alpha_i r)Y_{00}\,, \tag{9}$$

where Z is the nuclear charge, N_i is a normalization factor, and α_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. (9) has the advantage that the cusp condition on the orbital function[22,23]

$$\left\{\frac{\partial\phi(r)}{\partial r}\right\}_{r\to0} = -Z\{\phi(r)\}_{r\to0} \tag{10}$$

is exactly satisfied. There is ample flexibility built into the basis function, particularly if one is interested in describing the region close to the nucleus. Several terms with $n_i = 0$ may be employed if the near nuclear region is of central importance. A closely related form has been discussed by Lunell.[24]

In this work, one of our goals is the determination of a Hartree–Fock wave function which is accurate in the region very close to the nucleus, as judged by the reduced local energy criterion. If the near nuclear region and cusp characteristics of the wave function are not of particular interest, the more conventional STO's have the advantage of simplifying the algebra required to implement the gradient projection computations.

The derivatives of E_L^{HF} and E^{HF} with respect to the parameters α_i were evaluated analytically and also checked by numerical computation. The numerical computation was found to be more efficient in terms of computer time required. All the computations were carried out on a Honeywell DPS 8/20 using double precision. All the results are reported in a. u.

To simplify the calculations, both the numerator and denominator of Eq. (5) have been integrated with respect to the polar angles (θ, ϕ). The resulting reduced local energy depends only on the radial coordinate.

IV. RESULTS

In this section we present the results of an application of the idea discussed in Sec. II to the ground state of the helium atom. Table I gives a summary of the coefficients and α_i values for some small-term energy optimized cosh-type wave functions [see Eq. (9)]. For reference, the Hartree–Fock ground state energy of the helium atom has been given as −2. 861 679 995 612 2 a. u.[25]

Table II lists coefficients, α_i values, and the constraints employed to obtain locally improved wave functions. No more than five constraints have been employed in any single constrained optimization calculation. The configuration space points adopted to impose

TABLE II. Coefficients and parameters for the locally improved cosh wave functions.

Values of n_i	Constraints employed	Coefficients C_i	α_i parameters	Energy (a.u.)	Figure on which $E_L^{HF}(r)$ is plotted
(0,0)	$E_L^{HF}(10^{-5}) \geq -2.861\,68$	$0.300\,918\times10^{1}$, $-0.200\,992\times10^{1}$	0.579 15, 0.549 15	−2.861 2439	1
(0,3)	$E_L^{HF}(2.0) \leq -2.856$	$0.102\,757\times10^{1}$, $-0.503\,480\times10^{-1}$	0.691 60, 0.262 43	−2.861 6726	2
	$E_L^{HF}(3.0) \leq -2.856$				
	$E_L^{HF}(3.0) \leq -2.845$				
	$E_L^{HF}(3.75) \geq -2.868$				
	$E_L^{HF}(4.9) \geq -2.868$				
(0,3)	$E_L^{HF}(5.0) \leq -2.85$	$0.100\,434\times10^{1}$, $-0.875\,276\times10^{-2}$	0.637 67, 0.371 29	−2.861 3051	3
	$E_L^{HF}(8.0) \leq -2.85$				
	$E_L^{HF}(10.0) \leq -2.85$				
	$E_L^{HF}(7.0) \geq -2.865$				
	$E_L^{HF}(10.0) \geq -2.865$				
(0,2,3)	$E_L^{HF}(5.7) \leq -2.861$	0.916 674, 0.178 272,	0.472 85, 0.387 82,	−2.861 6753	4
	$E_L^{HF}(7.0) \leq -2.861$	$-0.703\,675\times10^{-1}$	0.240 99		
	$E_L^{HF}(3.4) \geq -2.862$				
	$E_L^{HF}(7.0) \geq -2.862$				

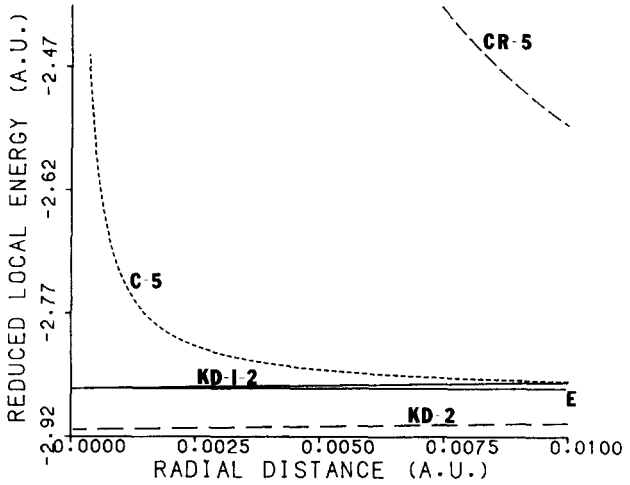

FIG. 1. Reduced local energy vs radial distance for the ground state of the helium atom for the near nuclear region. Curve CR-5 denotes the reduced local energy calculated from the five-term Clementi–Roetti wave function taken from Ref. 27. C-5 denotes E_L^{HF} calculated from the five-term Clementi wave function taken from Ref. 26. KD-2 represents E_L^{HF} determined using the energy optimized two-term cosh wave function with $n_i = 0, 0$. KD-I-2 is the locally improved version of the preceding function, using the constraint indicated in Table II. The horizontal line denoted by E is the result which would be obtained using the exact Hartree–Fock wave function.

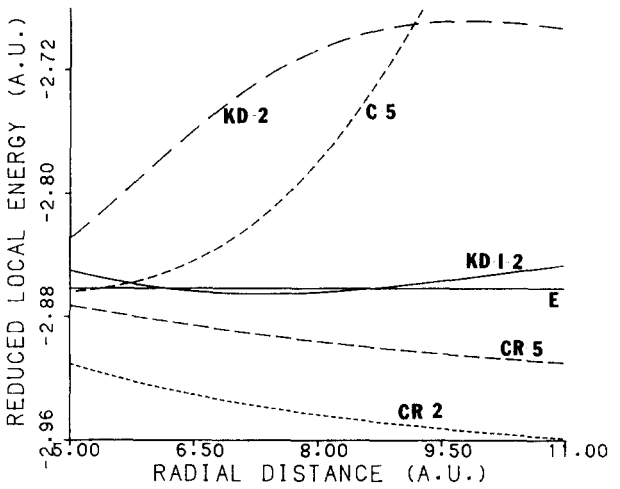

FIG. 3. Reduced local energy vs radial distance for the ground state of the helium atom for the long-range region. The two term cosh function (KD-2) employed has $n_i = 0, 3$. The improved version (KD-I-2) uses the constraints listed in Table II. The other symbols are defined in the captions to Figs. 1 and 2.

the constraints have been selected on the basis of the behavior of the reduced local energy for the energy optimized wave functions (presented in Table I). The optimized energy wave function was used as a starting point for improvement of the local behavior in a selected region.

In this investigation our attention has been concentrated on improving the wave function (in the sense of improved reduced local energy) for only a limited region of configuration space. Figures 1–3 show the results for improvement in the near nuclear, medium, and long-range regions, respectively, based on a two-term cosh wave function. Figure 4 shows the reduced local energy based on a three-term cosh wave function, with constraints selected (see Table II) to improve the long-range behavior of E_L^{HF}.

In Fig. 1, the five-term wave functions of Clementi[26] and Clementi and Roetti[27] are shown for comparison. Neither of these wave functions obey the cusp condition, which is the reason for the poor behavior of the reduced local energy near the nucleus. The two-term optimum

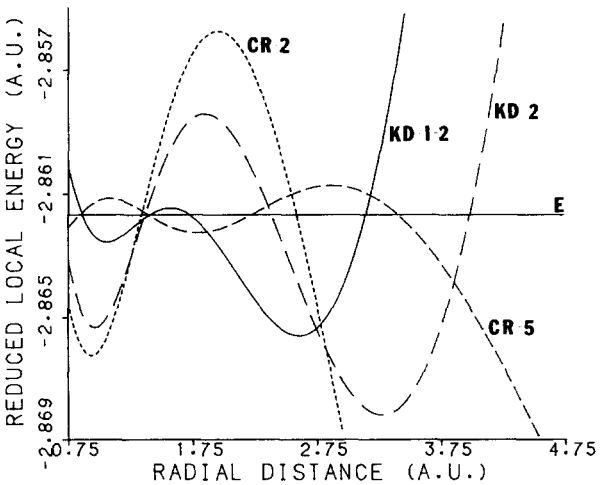

FIG. 2. Reduced local energy vs radial distance for the ground state of the helium atom for the medium r range. CR-2 denotes the reduced local energy calculated using the Clementi–Roetti double zeta wave function taken from Ref. 27. The two-term cosh function (KD-2) employed has $n_i = 0, 3$. The improved version (KD-I-2) uses the constraints listed in Table II. E denotes the exact result.

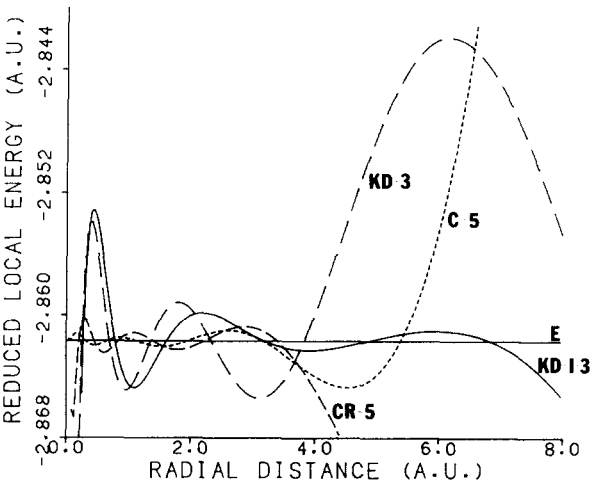

FIG. 4. Reduced local energy vs radial distance for the ground state of the helium atom for three-term cosh wave function (KD-3) with $n_i = 0, 2, 3$ and a long-range improved version (KD-I-3). The constraints employed for the nonlinear programming problem are listed in Table II.

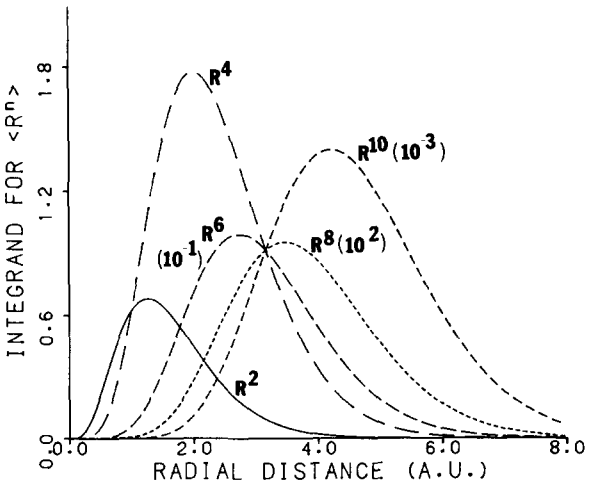

FIG. 5. Integrands for expectation values of r^n. The curves were calculated using the Clementi–Roetti five-term wave function taken from Ref. 27. To bring all curves onto the same scale, the integrands for r^6, r^8, and r^{10} have been multiplied by 10^{-1}, 10^{-2}, and 10^{-3}, respectively.

energy cosh function does obey the cusp condition. E_L^{HF} derived from this function is denoted KD-2 in Fig. 1. This wave function has been improved with a single constraint $E_L^{HF}(10^{-5}) \geq -2.861\,68$, and the corresponding E_L^{HF} is denoted by KD-I-2 in Fig. 1. The horizontal line denoted by E represents the reduced local energy to be expected using the exact Hartree–Fock wave function. Clearly, the two-term improved wave function given in Table II is very satisfactory (as measured by the accuracy of the reduced local energy) for the region close to the nucleus. Both of the Clementi wave functions yield excellent values for the energy; the inaccuracies in these wave functions near the nucleus are offset by the r^2 factor in the volume element employed when calculating the expectation value of the energy.

Figure 2 shows our present efforts at improving the wave function in the medium r range. For comparison the Clementi–Roetti five-term (CR-5) and Clementi–Roetti two-term (CR-2) reduced local energies are also displayed. The improved two-term cosh function (KD-I-2) is locally better than the Clementi-Roetti two-term function, but the Clementi–Roetti five-term wave function leads to a better E_L^{HF}, particularly around $r \sim 2.7$ a.u.

For the long-range region displayed in Fig. 3, the improved two-term function is observed to be superior to the Clementi–Roetti two-term and five-term functions and the Clementi[26] five-term function. For the three-term function investigated, the constraints were selected to improve the long-range behavior. The resulting E_L^{HF}(KD-I-3) is presented in Fig. 4. The E_L^{HF} determined from the locally improved wave function is observed to be better than the Clementi and Clementi and Roetti wave functions for the approximate range $r \sim 4.0$–8.0 a.u. However, both the Clementi functions are observed to be superior at short range $r \sim 0.5$–2.5 a.u.

Figure 5 gives an idea of the importance of the various regions of configuration space for calculating expectation values of r^n for the helium atom. This plot has been constructed using the five-term wave function of Clementi and Roetti. For the higher moments, the long-range region becomes increasingly important as expected, however, there is increased emphasis on a wider range of values for the radial coordinate due to the increased broadening of the integrands.

V. DISCUSSION

When the wave function is improved locally in a specific region of configuration space, there is a slight increase in energy. In some cases, the increase is rather small, which reflects the fact that the local improvement has been made in a region which is important for the computation of the energy expectation value. A second possibility, is that the improvement is made in a region which is not of central importance for the determination of the energy, and the wave function remains essentially unperturbed in the region important for the energy calculation. The latter situation was not found for the situations examined in this work. In principle, it should be possible to offset the increase in energy obtained in the local optimization calculation, by the addition of extra basis functions. Work in this direction is in progress.

The most difficult region to obtain improvement at the local level with small-term basis expansions is around $r \sim 1$ a.u. In this region, the reduced local energy exhibits sharp oscillatory character, which cannot be readily flattened, without leading to larger deviations at nearby locations. If the imposed constraints are made too severe, the gradient projection alogrithm does not converge.

Three measures of the local behavior of the wave functions that can be usefully tabulated are $E_L^{HF}(r=0)$, $E_L^{HF}(r=\infty)$, and $D[E_L^{HF}]$ [see Eq. (3)]. Values for the wave functions discussed above are presented in Table III. Except for the two-term cosh wave function with $n_i = 0, 0$, the values of $E_L^{HF}(r=0)$ are not very close to E^{HF}. The Clementi[26] and Clementi–Roetti[27] $E_L^{HF}(r=0)$

TABLE III. Reduced local energy $r=0$ and $r=\infty$ limits and the D values for different wave functions.

Wave function	$E_L^{HF}(r=0)$	$E_L^{HF}(r=\infty)$	$D[E_L^{HF}]$
KD-2($n=0,0$)[a]	−2.912 01	−3.233 07	0.196×10^{-3}
KD-2($n=0,3$)	−2.988 49	−2.988 70	0.558×10^{-4}
KD-3($n=0,2,3$)	−2.985 87	−2.927 80	0.511×10^{-4}
KD-I-2($n=0,0$)[b]	−2.861 69	−2.952 02	0.886×10^{-3}
KD-I-2($n=0,3$)[c]	−2.973 32	−2.799 82	0.572×10^{-4}
KD-I-2($n=0,3$)[d]	−2.857 24	−2.873 57	0.954×10^{-3}
KD-I-3($n=0,2,3$)[d]	−3.004 21	−3.109 81	0.782×10^{-4}
CR-5	...	−2.947 91	0.663×10^{-5}

[a]KD-n denotes an n-term cosh wave function of the authors.
[b]I denotes an improved wave function using the constraints listed in Table II.
[c]Wave function improved at medium range.
[d]Wave function improved at long range.

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

Wave function	$\langle r_1^{-2}\rangle$	$\langle r_1^{-1}\rangle$	$\langle r_1^{2}\rangle$	$\langle r_1^{4}\rangle$	$\langle r_1^{6}\rangle$	$\langle r_1^{10}\rangle$
KD-2($n=0,0$)[a]	6.012	1.689	1.183	3.814	2.357×10^{1}	3.348×10^{3}
KD-2($n=0,3$)	5.991	1.687	1.185	3.894	2.552×10^{1}	4.862×10^{3}
KD-3($n=0,2,3$)	5.991	1.687	1.185	3.889	2.534×10^{1}	4.537×10^{3}
KD-I-2($n=0,0$)[b]	6.045	1.691	1.209	4.172	2.887×10^{1}	5.691×10^{3}
KD-I-2($n=0,3$)[c]	6.000	1.688	1.185	3.895	2.543×10^{1}	4.709×10^{3}
KD-I-2($n=0,3$)[d]	6.085	1.698	1.190	4.008	2.695×10^{1}	5.002×10^{3}
KD-I-3($n=0,2,3$)	5.988	1.687	1.185	3.891	2.531×10^{1}	4.458×10^{3}
Clementi–Roetti five-term (CR-5)	5.996	1.687	1.185	3.884	2.517×10^{1}	4.350×10^{3}
20-term Hylleraas[e]	6.018	1.688	1.193	3.969	2.614×10^{1}	4.677×10^{3}

[a]KD-n denotes an n-term cosh wave function of the authors.
[b]I denotes wave function improved using constrained variational calculation.
[c]Wave function optimized for medium range region.
[d]Wave function optimized for long-range region.
[e]Based on the density calculation by Benesch using the Hart–Herzberg Hylleraas wave function, Refs. 28 and 29.

values are both infinite, a direct consequence of the fact that neither wave function satisfies the cusp condition. All of the values reported for $E_L^{\mathrm{HF}}(r=\infty)$ tend to be slightly higher than E^{HF}.

The quantity $D[E_L^{\mathrm{HF}}]$ is a sensitive measure of local accuracy as measured in a global sense.[3,4] $D[E_L^{\mathrm{HF}}]$ is very sensitive to both small changes in the coefficients and in the exponents. The value of $D[E_L^{\mathrm{HF}}]$ reported for the Clementi–Roetti five-term wave function is based on the reported coefficients (and exponents) from Ref. 27. Recomputation of the coefficients (with the same exponents) leads to a value of $D[E_L^{\mathrm{HF}}]$ about 10% lower than the number reported in Table III. In all cases, refinement of the wave function in a restricted region of configuration space, leads to slight modifications of the wave function elsewhere, which leads to a slightly poorer overall local accuracy as measured by $D[E_L^{\mathrm{HF}}]$. When the improvement was made in the energy important region $r\sim2$ a.u. for the two-term cosh wave function with $n_i=0,3$, the change in the value of $D[E_L^{\mathrm{HF}}]$ was observed to be quite small, compared with the typical kind of change observed in $D[E_L^{\mathrm{HF}}]$ (see Table III). This in part is tied to the important dependence of $D[E_L^{\mathrm{HF}}]$ on the region $r\sim2$ for helium.

A number of expectation values of r^k have been calculated. The results are reported in Table IV. In general, the results for moments with $k=-2$, -1, and 2 are all quite close. For the larger moments $k=6$ and $k=10$, the long-range improved three-term cosh wave function leads to expectation values in closer agreement with the Clementi–Roetti five-term result, than are the expectation values determined from the energy optimized three-term cosh wave function. A similar trend is not however noted for the two-term cosh wave function. This is probably due to the fact that as the two-term function is improved at long range, the wave function is perturbed at shorter range ($r\sim2$–4 a.u.) in such a way as to offset the advantage gained at large distances. The width of the integrand for r^{10} shown in Fig. 5 points to the necessity for obtaining good local behavior over a wide range, if satisfactory matrix elements are to be obtained.

In the present study, it has been demonstrated that the wave function can be improved (as measured by E_L^{HF}) in a restricted region of configuration space using nonlinear programming techniques. Under investigation is the possibility of improving the local behavior over an extended range of configuration space, using larger basis set expansions.

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[1]G. F. Thomas, F. Javor, and S. M. Rothstein, J. Chem. Phys. **64**, 1574 (1976).
[2]F. Javor, G. F. Thomas, and S. M. Rothstein, Int. J. Quantum Chem. **11**, 59 (1977).
[3]F. W. King, M. A. LeGore, and M. K. Kelly, J. Chem. Phys. **75**, 809 (1981).
[4]F. W. King, M. K. Kelly, and M. A. LeGore, J. Chem. Phys. **76**, 574 (1982).
[5]F. W. King, L. G. Nemec, and M. K. Kelly (Submitted for publication).
[6]H. H. Grelland and J. Almlöf, Int. J. Quantum Chem. **21**, 885 (1982).
[7]H. H. Grelland, Int. J. Quantum Chem. **19**, 847 (1981).
[8]L. Cohen and C. Frishberg, Phys. Rev. A **13**, 927 (1976).
[9]H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).
[10]L. J. Massa and L. Cohen, Int. J. Quantum Chem. Symp. **14**, 167 (1980).
[11]C. Frishberg, L. Cohen, and P. Blumenau, Int. J. Quantum Chem. Symp. **14**, 161 (1980).
[12]H. Schlosser, Phys. Rev. A **15**, 1349 (1977).
[13]J. H. Bartlett, Phys. Rev. **51**, 661 (1937).
[14]A. A. Frost, J. Chem. Phys. **10**, 240 (1942).
[15]J. H. Bartlett, Phys. Rev. **98**, 1067 (1955).
[16]A. A. Frost, R. E. Kellogg, and E. C. Curtiss, Rev. Mod. Phys. **32**, 313 (1960).
[17]S. Fraga and F. W. Birss, Theor. Chim. Acta **5**, 398 (1966).
[18]G. Hadley, *Nonlinear and Dynamic Programming* (Addison–Wesley, Reading, Mass. 1964).

[19]G. R. Walsh, *Methods of Optimization* (Wiley, London, 1975).
[20]J. B. Rosen, J. Soc. Indust. Appl. Math. **8**, 181 (1960).
[21]J. B. Rosen, J. Soc. Indust. Appl. Math. **9**, 514 (1961).
[22]C. C. J. Roothaan and P. S. Kelly, Phys. Rev. **131**, 1177 (1963).
[23]G. Malli and S. Fraga, Can. J. Phys. **44**, 3131 (1966).
[24]S. Lunell, Chem. Phys. Lett. **15**, 31 (1972).
[25]J. L. Bázquez and H. J. Silverstone, J. Chem. Phys. **67**, 1887 (1977).
[26]E. Clementi, IBM J. Res. Dev. Supp. **9**, 2 (1965).
[27]E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).
[28]J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).
[29]R. Benesch, J. Phys. B **4**, 1403 (1971).