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REDUCED LOCAL ENERGY FOR ATOMIC HARTREE–FOCK WAVEFUNCTIONS

Frederick W. KING, Michael K. KELLY, Mary A. LeGORE and Martin E. POITZSCH

Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54701, USA

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PROGRAM SUMMARY

Title of program: Reduced local energy for atoms

Catalogue number: ACCE

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Computer: Honeywell DPS 8/20; *Installation*: University of Wisconsin-Eau Claire

Operating system: GCOS

Programming language used: FORTRAN 77

High speed storage required: 85 Kwords

No. of bits in a word: 36

Peripherals used: disc (unit 25) for input

No. of lines in combined program and test deck: 1135

Keywords: reduced local energy, Hartree–Fock, local accuracy, atomic systems, wavefunctions

Nature of physical problem

The reduced local energy (diagonal elements of the reduced local energy 1-matrix) is defined in position space for an N electron system ($N \geq 2$) by [1]

$$E_{\mathrm{L}}(\boldsymbol{r}_1) = \frac{\int \Psi^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \mathrm{H} \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \mathrm{d}s_1 \mathrm{d}\tau_2 \ldots \mathrm{d}\tau_N}{\int \Psi^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \Psi(\boldsymbol{r}_1, \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \mathrm{d}s_1 \mathrm{d}\tau_2 \mathrm{d}\tau_3 \ldots \mathrm{d}\tau_N}. \tag{1}$$

An analogous definition holds in the Hartree–Fock approximation [2,3]. The program evaluates $E_{\mathrm{L}}^{\mathrm{HF}}(r_1)$, the Hartree–Fock reduced local energy, for atomic systems.

Method of solution

The reduced local energy is evaluated from analytic formulae for the 'reduced' matrix elements, as a function of the radial coordinate r_1. The 'reduced' matrix elements are evaluated using a basis involving Slater type orbitals. A Gaussian quadrature of $E_{\mathrm{L}}^{\mathrm{HF}}(r_1)$ is carried out to check the evaluation of this function.

Restrictions on the complexity of the program

The program is presently written to consider atoms with up to 18 electrons. A restriction to 8 basis functions for each s and p orbital has been employed. Both of these limits may be extended upwards with only very minor changes to the program.

Typical running time

Execution times depend on the number of electrons, and increase steeply as this factor becomes large. On the Honeywell DPS 8/20, the evaluation of $E_{\mathrm{L}}^{\mathrm{HF}}(r_1)$ at 100 configuration space points for Be requires 130 s; 200 points can be generated in 165 s. The Gaussian quadrature option to check the total energy and to compute certain moments involving $E_{\mathrm{L}}^{\mathrm{HF}}(r_1)$ requires approximately 390 s for Be.

Unusual features of the program

The program is written in FORTRAN 77 and has been checked to ensure that it satisfies ANSI standards.

References

[1] G.F. Thomas, F. Javor and S.M. Rothstein, J. Chem. Phys. 64 (1976) 1574.
[2] L. Cohen and C. Frishberg, Phys. Rev. A13 (1976) 927.
[3] H. Nakatsuji, Phys. Rev. A14 (1976) 41.

LONG WRITE-UP

1. Introduction

The reduced local energy is defined for an N electron system ($N \geqslant 2$) by [1,2]

$$E_{\mathrm{L}}(\boldsymbol{r}_1)=\frac{\int \Psi^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)_{\mathrm{H}}\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\mathrm{d}s_1\mathrm{d}\tau_2\ldots\mathrm{d}\tau_N}{\int \Psi^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\mathrm{d}s_1\mathrm{d}\tau_2\mathrm{d}\tau_3\ldots\mathrm{d}\tau_N}. \tag{1}$$

In the limit that the exact wavefunction is available,

$$E_{\mathrm{L}}(\boldsymbol{r}_1)\equiv E, \tag{2}$$

where E is the exact energy. Eq. (1) represents a stringent test of the local accuracy of the wavefunction. A similar result holds in the Hartree–Fock formalism [3,4]

$$E_{\mathrm{L}}^{\mathrm{HF}}(\boldsymbol{r}_1)=\frac{\int \Psi_{\mathrm{HF}}^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)_{\mathrm{H}}\Psi_{\mathrm{HF}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\mathrm{d}s_1\mathrm{d}\tau_2\ldots\mathrm{d}\tau_N}{\int \Psi_{\mathrm{HF}}^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\Psi_{\mathrm{HF}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\mathrm{d}s_1\mathrm{d}\tau_2\ldots\mathrm{d}\tau_N}, \tag{3}$$

and for the exact Hartree–Fock wavefunction,

$$E_{\mathrm{L}}^{\mathrm{HF}}(\boldsymbol{r}_1)\equiv E^{\mathrm{HF}}, \tag{4}$$

where E^{HF} is the exact Hartree–Fock energy.

A number of recent studies have appeared in which eq. (3) has been employed to assess the local accuracy of Hartree–Fock wavefunctions [5–8]. The reduced local energy concept has also been incorporated into a constrained Hartree–Fock method [6,9].

A compact way to assess the local accuracy of a Hartree–Fock wavefunction utilizes the moments [10]

$$A_m=\frac{1}{N}\int |E^{\mathrm{HF}}-E_{\mathrm{L}}^{\mathrm{HF}}(\boldsymbol{r})|\, r^m\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}, \tag{5}$$

$$D_m=\frac{1}{N}\int \left(E^{\mathrm{HF}}-E_{\mathrm{L}}^{\mathrm{HF}}(\boldsymbol{r})\right)^2 r^m\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}, \tag{6}$$

where $\rho(\boldsymbol{r})$ is the Hartree–Fock electronic density. In the limit that the exact Hartree–Fock wavefunction is available,

$$A_m=0, \tag{7}$$

$$D_m=0. \tag{8}$$

By considering various values of m in eqs. (5) and (6), it is possible to assess the local accuracy of the wavefunction in different regions of configuration space.

2. Computational procedure

The program evaluates $E_{\mathrm{L}}^{\mathrm{HF}}(r_1)$ for atomic systems. All results are presented in atomic units. The

Hartree–Fock orbitals are expanded in terms of a set of basis functions,

$$\phi_i(\boldsymbol{r}) = \sum_j^{\mathcal{N}_i} C_{ij}\chi_{ij}(\boldsymbol{r}), \tag{9}$$

where the basis functions $\chi_{ij}(\boldsymbol{r})$ are Slater type orbitals with integer quantum numbers. To take advantage of spherical symmetry, the numerator and denominator of eq. (3) are integrated over the polar angles (θ_1, ϕ_1).

Eq. (3) can be written as

$$E_{\mathrm{L}}^{\mathrm{HF}}(r) = (K + E_{\mathrm{N}} + E_{\mathrm{E}})/\Gamma, \tag{10}$$

where K, E_{N} and E_{E} denote the 'reduced' kinetic energy, the 'reduced' electron–nuclear potential energy, and the 'reduced' electron–electron potential energy, respectively, Γ is N^{-1} times the angle averaged electronic density. The algebraic expressions for these reduced matrix elements are given in the appendix.

3. Program description

The detailed working of the program is described by comment cards throughout the deck. A description of variables is given in the comment cards at the start of the program. The program is structured in the following manner. The MAIN routine calculates all the necessary $3j$ symbols and evaluates all parts of the 'reduced' matrix elements (given in the appendix) which are independent of r. The most time consuming aspects of the calculation involves the matrix elements of r_{12}^{-1}. Because of the structure of eq. (A.16), the matrix elements of r_{12}^{-1} are conveniently compressed into a three-dimensional array. The final segment of the MAIN routine involves the Gaussian quadrature check on $E_{\mathrm{L}}^{\mathrm{HF}}(r)$ and the calculation of the moments A_m and D_m defined in eqs. (5) and (6) (if this option is required). The loop to obtain $E_{\mathrm{L}}^{\mathrm{HF}}(r)$ is the last calculation in MAIN.

Two subroutines are employed. Subroutine TRIANG performs a short calculation for the generation of the $3j$ symbols. Subroutine FUNCT is called to perform the calculation of all r dependent parts of the 'reduced' matrix elements given in the appendix.

The program has been written to handle up to 18 electrons. This limit can be expanded upward very easily by making appropriate adjustments to the dimensions of various arrays and some minor changes to certain summation limits. Comment cards have been included in the deck referring to these changes. A restriction to 8 basis functions for each s and p orbital has been employed (following the format of the early sections of the Clementi–Roetti tables of atomic Hartree–Fock wavefunctions [11]). This limit can be modified without difficulty.

Depending on the points at which $E_{\mathrm{L}}^{\mathrm{HF}}(r)$ is evaluated, the size of various orbital exponents and, in particular, the maximum allowable negative exponent, underflow may be encountered in subroutine FUNCT at lines 951, 971, 1013, 1014, 1052 and 1053. When these are set to zero no difficulties are encountered. This has been tested on the Honeywell DPS 8/20 using the extended HEX option.

4. Required input

The input has been arranged to follow the format of the information available in the Clementi–Roetti tables [11]. All input is read from a disc file (unit 25). Both of these arrangements can be readily modified to meet the user's own requirements.

The order of input to the program is as follows. The first two cards contain the TITLE information. The next card indicates the number of electrons (NE), the number of expansions terms for an s-orbital (NS), the number of expansion terms for a p-orbital (NP) and program options required (NITEST) (the latter is fully explained in the lead comment cards in the program). The next card gives the nuclear charge (Z). The next card gives the Hartree–Fock energy (EHF) used for the calculation of A_m and D_m. The next NS cards give the expansion coefficients, orbital exponents and principal quantum numbers for the 1s orbitals. The next set of data cards read in the expansion coefficients for the 2s orbitals. The following NP cards contain expansion coefficients, orbital exponents and principal quantum numbers for the 2p orbitals. The next card gives the magnetic quantum numbers for the 2p orbitals (MY). The next NS cards give expansion coefficients for the 3s orbitals. The following set of cards give the expansion coefficients for the 3p orbitals. The next card gives the magnetic quantum number for the 3p orbitals. The spin quantum numbes (MS) are given on the next card; α spin is 1, β spin is 0. The following card gives the number of points in each range (NR1) for which $E_L^{HF}(r)$ is to be calculated. The next four cards specify the increment in the radial distance for the evaluation of $E_L^{HF}(r)$ for each range (FR1).

5. Test run

The first test run calculates the reduced local energy for the Be atom using the wavefunction given by Clementi–Roetti [11]. A plot of $E_L^{HF}(r)$ versus r is given elsewhere [6]. The principal output consists of the D_m and A_m values (called DINT(M) and ABSINT(M), respectively) for values of $m = -2$ to 10. The program also prints out the intermediate segments in the Gaussian quadrature to provide a guide to the convergence of these moments. The reader should be alert to the fact that the number of meaningful significant figures for D_m and A_m is critically tied to the number of significant figures for the input expansion coefficients and orbital exponents. This results directly from taking the difference $E^{HF} - E_L^{HF}(r)$ in eqs. (5) and (6). The final Be output consists of the radial distance, the 'reduced' matrix elements and $E_L^{HF}(r)$. All results are in atomic units.

The second test run shows the input data and a partial output for the Ne atom. The wavefunction employed for Ne has been taken from the Clementi–Roetti table [11].

Acknowledgement

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Appendix

The details necessary to calculate the reduced local energy for the atomic Hartree–Fock wavefunctions are given in this appendix. In the following, $\rho(\mathbf{r})$ and $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ denote the electronic density and the diagonal part of the 2-particle density matrix, respectively; $\rho_1(\mathbf{r}_1; \mathbf{r}_1')$ and $\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2')$ denote the 1-particle and 2-particle density matrices, respectively. It is most convenient to develop separate expressions for the kinetic energy, electron–nuclear potential energy and the electron–electron potential energy.

A.1. Denominator of eq. (10)

The denominator of eq. (10) is simply evaluated to yield

$$\Gamma = \langle \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \mid \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \rangle_{2 \ldots N} = \frac{1}{N} \int \rho(\mathbf{r}_1) \mathrm{d}\Omega_1, \tag{A.1}$$

where the subscript $2\ldots N$ indicates integration over all coordinates $2-N$ and integration over the angular variables (θ_1, ϕ_1). Making use of the expansion

$$\rho_1(\boldsymbol{r}_1; \boldsymbol{r}_1') = \sum_i \phi_i(\boldsymbol{r}_1)\phi_i^*(\boldsymbol{r}_1') \tag{A.2}$$

and employing eq. (9) yields

$$\Gamma = \frac{1}{N}\sum_{i=1}^{N}\sum_{k=1}^{\mathcal{N}_i}\sum_{l=1}^{\mathcal{N}_i} X_{ik}X_{il} = \frac{1}{N}\sum_{i=1}^{N}\sum_{k=1}^{\mathcal{N}_i}\sum_{l=1}^{\mathcal{N}_i} C_{ik}C_{il}N_{ik}N_{il}r_1^{n_{ik}+n_{il}-2}\mathrm{e}^{-\zeta_{iikl}r_1}, \tag{A.3}$$

where

$$\zeta_{ijrs} = \alpha_{ir} + \alpha_{js}, \quad X_{ik} = \chi_{ik}C_{ik}, \tag{A.4}$$

α_{ir} denotes an orbital exponent.

A.2. Electron–nuclear potential energy

$$\begin{aligned} E_\mathrm{N} &= \left\langle \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \left| \sum_{i=1}^{N} \frac{-Z}{r_i} \right| \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \right\rangle_{2\ldots N} \\ &= \frac{1}{N}\int\left[\frac{-Z}{r_1}\rho(\boldsymbol{r}_1) - 2Z\int\frac{\rho(\boldsymbol{r}_1, \boldsymbol{r}_2)}{r_2}\mathrm{d}\boldsymbol{r}_2\right]\mathrm{d}\Omega_1. \end{aligned} \tag{A.5}$$

If the expansion

$$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') = \tfrac{1}{2}\left[\rho_1(\boldsymbol{r}_1; \boldsymbol{r}_1')\rho_1(\boldsymbol{r}_2; \boldsymbol{r}_2') - \rho_1(\boldsymbol{r}_2; \boldsymbol{r}_1')\rho_1(\boldsymbol{r}_1; \boldsymbol{r}_2')\right] \tag{A.6}$$

and Eq. (A.2) are substituted into eq. (A.5), then

$$E_\mathrm{N} = \frac{-Z}{N}\left[\frac{\Gamma'}{r_1} + \Gamma'\sum_{i=1}^{N} R_{ii} - \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{\mathcal{N}_i}\sum_{l=1}^{\mathcal{N}_j} X_{ik}X_{jl}R_{ij}\right], \tag{A.7}$$

where $\Gamma' = N\Gamma$ and

$$R_{ij} = \left\langle \phi_i(\boldsymbol{r}_2) \left| \frac{1}{r_2} \right| \phi_j(\boldsymbol{r}_2) \right\rangle = \sum_{r=1}^{\mathcal{N}_i}\sum_{s=1}^{\mathcal{N}_j} \frac{C_{ir}C_{js}N_{ir}N_{js}(n_{ir}+n_{js}-1)!}{\zeta_{ijrs}^{n_{ir}+n_{js}}}\delta_{L_i,L_j}\delta_{M_{Li},M_{Lj}}\delta_{M_{si},M_{sj}}. \tag{A.8}$$

In eq. (A.8), the Kronecker deltas test the three quantum numbers L, M_L and M_s.

A.3. Kinetic energy

$$\begin{aligned} K &= \left\langle \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \left| \sum_{i=1}^{N} -\tfrac{1}{2}\nabla_i^2 \right| \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \right\rangle_{2\ldots N} \\ &= \frac{1}{N}\int\left\{\left[-\tfrac{1}{2}\nabla_1^2\rho_1(\boldsymbol{r}_1; \boldsymbol{r}_1')\right]_{\boldsymbol{r}_1'=\boldsymbol{r}_1} - \int_{\boldsymbol{r}_2'=\boldsymbol{r}_2}\nabla_2^2\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2')\mathrm{d}\boldsymbol{r}_2\right\}\mathrm{d}\Omega_1. \end{aligned} \tag{A.9}$$

Employing eqs. (A.2) and (A.6), eq. (A.9) may be written as

$$K=\frac{-1}{2N}\left\{\sum_{i=1}^{N}\sum_{k=1}^{\mathcal{N}_i}\sum_{l=1}^{\mathcal{N}_i}X_{ik}X_{il}\left[r_1^{-2}\left(n_{il}[n_{il}-1]-L_i[L_i+1]\right)-2\alpha_{il}n_{il}r_1^{-1}+\alpha_{il}^2\right]+\Gamma'\sum_{i=1}^{N}T_{ii}\right.$$
$$\left.-\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{\mathcal{N}_i}\sum_{l=1}^{\mathcal{N}_j}X_{ik}X_{jl}T_{ji}\right\}, \tag{A.10}$$

where

$$T_{ij}=\langle\phi_i(\boldsymbol{r}_2)|\nabla_2^2|\phi_j(\boldsymbol{r}_2)\rangle=\sum_{k=1}^{\mathcal{N}_i}\sum_{l=1}^{\mathcal{N}_j}\delta_{M_{s_i},M_{s_j}}\delta_{L_i,L_j}\delta_{M_{L_i},M_{L_j}}C_{ik}C_{jl}N_{ik}N_{jl}$$
$$\times\left\{\frac{(n_{ik}+n_{jl})!\alpha_{jl}^2}{\zeta_{ijkl}}-2\alpha_{jl}n_{jl}(n_{ik}+n_{jl}-1)!+(n_{ik}+n_{jl}-2)!\zeta_{ijkl}\right.$$
$$\left.\times\left[n_{jl}(n_{jl}-1)-L_j(L_j+1)\right]\right\}/\zeta_{ijkl}^{n_{ik}+n_{jl}}. \tag{A.11}$$

A.4. Electron–electron potential energy

$$E_{\mathrm{E}}=\left\langle\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\left|\sum_{i<j}\frac{1}{r_{ij}}\right|\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\right\rangle_{2\ldots N}$$
$$=\frac{1}{N}\int\mathrm{d}\Omega_1\left\{2\int\frac{\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{r_{12}}\mathrm{d}\boldsymbol{r}_2+3\int\frac{\rho_3(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)}{r_{23}}\mathrm{d}\boldsymbol{r}_2\mathrm{d}\boldsymbol{r}_3\right\}. \tag{A.12}$$

The first term on the right-hand side of eq. (A.12) (denoted $E_{1\mathrm{E}}$) can be evaluated using eqs. (A.2) and (A.5) to yield

$$E_{1\mathrm{E}}=\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{\mathcal{N}_i}\sum_{s=1}^{\mathcal{N}_j}\sum_{n=0}^{2}(-1)^{M_{L_i}+M_{L_j}}(2L_i+1)(2L_j+1)X_{ik}C_{js}N_{js}$$
$$\times\left\{\sum_{l=1}^{\mathcal{N}_i}\sum_{r=1}^{\mathcal{N}_j}F_{jjrs}X_{il}C_{jr}N_{jr}\begin{pmatrix}L_i & L_i & n\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L_j & L_j & n\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L_i & L_i & n\\ -M_{L_i} & M_{L_i} & 0\end{pmatrix}\begin{pmatrix}L_j & L_j & n\\ -M_{L_j} & M_{L_j} & 0\end{pmatrix}\right.$$
$$\left.-\sum_{l=1}^{\mathcal{N}_j}\sum_{r=1}^{\mathcal{N}_i}\sum_{m=-n}^{n}F_{ijrs}X_{jl}C_{ir}N_{ir}(-1)^m\begin{pmatrix}L_i & L_j & n\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}L_i & L_j & n\\ -M_{L_i} & M_{L_j} & -m\end{pmatrix}\begin{pmatrix}L_i & L_j & n\\ M_{L_i} & -M_{L_j} & m\end{pmatrix}\right\}$$
$$\tag{A.13}$$

where $\begin{pmatrix}l_1 & l_2 & l_3\\ m_1 & m_2 & m_3\end{pmatrix}$ denotes a $3j$ symbol and

$$F_{ijrs}=\delta_{M_{s_i},M_{s_j}}\left\{\frac{(n_{ir}+n_{js}-n-1)!}{\zeta_{ijrs}^{n_{ir}+n_{js}-n}}r_1^n\mathrm{e}^{-\zeta_{ijrs}r_1}\sum_{w=0}^{n_{ir}+n_{js}-n-1}\frac{\zeta_{ijrs}^w r_1^w}{w!}\right.$$
$$\left.+\frac{(n_{ir}+n_{js}+n)!}{r_1^{n+1}\zeta_{ijrs}^{n_{ir}+n_{js}+n+1}}\left[1-\mathrm{e}^{-\zeta_{ijrs}r_1}\sum_{w=0}^{n_{ir}+n_{js}+n}\frac{\zeta_{ijrs}^w r_1^w}{w!}\right]\right\}. \tag{A.14}$$

Eq. (A.13) has been written explicitly to handle the wavefunctions provided by Clementi and Roetti through to Ar. To extend the formulae for atoms beyond Ar, the only modification required is to extend the summation over n (arising from the expansion of r_{12}^{-1}) to the required value. This comment also applies to eq. (A.17) given below.

The second factor in eq. (A.12), denoted $E_{2\mathrm{E}}$, can be simplified by employing

$$\rho_3(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = \tfrac{1}{6}\begin{vmatrix} \rho_1(\boldsymbol{r}_1, \boldsymbol{r}_1) & \rho_1(\boldsymbol{r}_1, \boldsymbol{r}_2) & \rho_1(\boldsymbol{r}_1, \boldsymbol{r}_3) \\ \rho_1(\boldsymbol{r}_2, \boldsymbol{r}_1) & \rho_1(\boldsymbol{r}_2, \boldsymbol{r}_2) & \rho_1(\boldsymbol{r}_2, \boldsymbol{r}_3) \\ \rho_1(\boldsymbol{r}_3, \boldsymbol{r}_1) & \rho_1(\boldsymbol{r}_3, \boldsymbol{r}_2) & \rho_1(\boldsymbol{r}_3, \boldsymbol{r}_3) \end{vmatrix} \tag{A.15}$$

and eq. (A.2) to yield

$$E_{2\mathrm{E}} = \frac{1}{2N} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ \Gamma'\left(J_{ijij} - J_{ijji}\right) + 2 \sum_{k=1}^{N} \sum_{r=1}^{\mathcal{N}_i} \sum_{s=1}^{\mathcal{N}_j} X_{ir} X_{js}\left(J_{kjik} - J_{kjki}\right) \delta_{L_i, L_j} \delta_{M_{L_i}, M_{L_j}} \delta_{M_{s_i}, M_{s_j}} \right\}, \tag{A.16}$$

where

$$\begin{aligned} J_{abcd} &= \langle \phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) \left| \frac{1}{r_{12}} \right| \phi_c(\boldsymbol{r}_1)\phi_d(\boldsymbol{r}_2) \rangle \\ &= \delta_{M_{s_a}, M_{s_c}} \delta_{M_{s_b}, M_{s_d}} \sum_{n=0}^{2} \sum_{m=-n}^{n} \sum_{w=1}^{\mathcal{N}_a} \sum_{x=1}^{\mathcal{N}_b} \sum_{y=1}^{\mathcal{N}_c} \sum_{z=1}^{\mathcal{N}_d} C_{aw} C_{bx} C_{cy} C_{dz} N_{aw} N_{bx} N_{cy} N_{dz} \\ &\quad \times (-1)^{M_{L_a} + M_{L_b} + m} \left[(2L_a + 1)(2L_b + 1)(2L_c + 1)(2L_d + 1)\right]^{1/2} \\ &\quad \times \begin{pmatrix} L_a & L_c & n \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_b & L_d & n \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_a & L_c & n \\ -M_{L_a} & M_{L_c} & -m \end{pmatrix} \begin{pmatrix} L_b & L_d & n \\ -M_{L_b} & M_{L_d} & m \end{pmatrix} \\ &\quad \times \left\{ \frac{(n_{bx} + n_{dz} + n)!}{\zeta_{bdxz}^{n_{bx} + n_{dz} + n + 1}} \left[\frac{(n_{aw} + n_{cy} - n - 1)!}{\zeta_{acwy}^{n_{aw} + n_{cy} - n}} - \sum_{g=0}^{n_{bx} + n_{dz} + n} \frac{(n_{aw} + n_{cy} - n - 1 + g)!\,\zeta_{bdxz}^{g}}{g!\left(\zeta_{abwx} + \zeta_{cdyz}\right)^{n_{aw} + n_{cy} - n + g}} \right] \right. \\ &\quad \left. + \frac{(n_{bx} + n_{dz} - n - 1)!}{\zeta_{bdxz}^{n_{bx} + n_{dz} - n}} \sum_{g=0}^{n_{bx} + n_{dz} - n - 1} \frac{(n_{aw} + n_{cy} + n + g)!\,\zeta_{bdxz}^{g}}{g!\left(\zeta_{abwx} + \zeta_{cdyz}\right)^{n_{aw} + n_{cy} + n + g + 1}} \right\}. \end{aligned} \tag{A.17}$$

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TEST RUN INPUT AND OUTPUT

Run 1. Sample input for Be atom

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                      REDUCED LOCAL ENERGY FOR BERYLLIUM ATOM.  VALUES FR      1117
OM CLEMENTI PAGE 185.  DATE 8/15/83.                                           1118
  4   6   0   0                                                                1119
  4.D+00                                                                       1120
 -0.14573021D+02                                                               1121
   0.91796D+00    3.47116D+00 1                                                1122
   0.08724D+00    6.36861D+00 1                                                1123
   0.00103D+00    0.77820D+00 2                                                1124
  -0.00199D+00    0.94067D+00 2                                                1125
   0.00176D+00    1.48725D+00 2                                                1126
   0.00628D+00    2.71830D+00 2                                                1127
  -0.17092D+00   -0.01455D+00     0.21186D+00     0.62499D+00                  1128
   0.26662D+00   -0.09919D+00                                                  1129
  1   0   1   0                                                                1130
   9                                                                           1131
  0.000100D+00                                                                 1132
  0.010000D+00                                                                 1133
  0.100000D+00                                                                 1134
  0.100000D+01                                                                 1135
```

Run 1. Partial output: D_m and A_m moments

```
 M                   DINT(M)                          ABSINT(M)
-2               0.73978371D+002                    0.79516353D+001
-1               0.12911030D+000                    0.55593545D-001
 0               0.49543616D-003                    0.39531712D-002
 1               0.12119228D-004                    0.15206399D-002
 2               0.33225986D-005                    0.19995105D-002
 3               0.41051972D-005                    0.58022195D-002
 4               0.14038105D-004                    0.24836617D-001
 5               0.80999089D-004                    0.13262439D+000
 6               0.59323001D-003                    0.82687377D+000
 7               0.50363872D-002                    0.58263449D+001
 8               0.48300010D-001                    0.45533967D+002
 9               0.51934535D+000                    0.39021092D+003
10               0.62310711D+001                    0.36442417D+004
```

Run 1. Reduced local energy output for the Be atom

```
 DISTANCE      OVERLAP        KINETIC       ELECTRON-NUCLEUS  ELECTRON-ELECTRON  K.E.DIVIDED   TOTAL P.E. DIVIDED  REDUCED LOCAL
  (A.U.)       INTEGRAL       ENERGY        POTENTIAL ENERGY  POTENTIAL ENERGY   BY OVERLAP       BY OVERLAP          ENERGY

0.10000D-003  0.884982D+001  0.355681D+006  -.354158D+006      0.526552D+002     0.401908D+005    -.400128D+005     0.1780680D+003
0.20000D-003  0.884271D+001  0.177687D+006  -.177020D+006      0.526129D+002     0.200942D+005    -.200128D+005     0.8140735D+002
0.30000D-003  0.883560D+001  0.118355D+006  -.117973D+006      0.525706D+002     0.133953D+005    -.133461D+005     0.4918766D+002
0.40000D-003  0.882850D+001  0.886897D+005  -.884502D+005      0.525283D+002     0.100458D+005    -.100128D+005     0.3307820D+002
0.50000D-003  0.882141D+001  0.708904D+005  -.707363D+005      0.524861D+002     0.803617D+004    -.801276D+004     0.2341283D+002
0.60000D-003  0.881432D+001  0.590242D+005  -.589270D+005      0.524439D+002     0.669640D+004    -.667943D+004     0.1696950D+002
0.70000D-003  0.880724D+001  0.505484D+005  -.504919D+005      0.524017D+002     0.573941D+004    -.572704D+004     0.1236734D+002
0.80000D-003  0.880016D+001  0.441916D+005  -.441655D+005      0.523596D+002     0.502167D+004    -.501276D+004     0.8915915D+001
0.90000D-003  0.879310D+001  0.392474D+005  -.392449D+005      0.523174D+002     0.446344D+004    -.445720D+004     0.6231639D+001
0.10000D-001  0.817383D+001  0.326555D+004  -.342246D+004      0.486037D+002     0.399513D+003    -.412763D+003     -.1324957D+002
0.20000D-001  0.754526D+001  0.149865D+004  -.165021D+004      0.447890D+002     0.198621D+003    -.212773D+003     -.1415118D+002
0.30000D-001  0.696669D+001  0.917558D+003  -.105923D+004      0.412429D+002     0.131706D+003    -.146122D+003     -.1441536D+002
0.40000D-001  0.643399D+001  0.632362D+003  -.763767D+003      0.379531D+002     0.982846D+002    -.112809D+003     -.1452473D+002
0.50000D-001  0.594337D+001  0.465125D+003  -.586658D+003      0.349064D+002     0.782595D+002    -.928348D+002     -.1457530D+002
0.60000D-001  0.549140D+001  0.356567D+003  -.468824D+003      0.320893D+002     0.649320D+002    -.795307D+002     -.1459874D+002

0.70000D-001  0.507490D+001  0.281308D+003  -.384931D+003      0.294877D+002     0.554312D+002    -.700395D+002     -.1460833D+002
0.80000D-001  0.469099D+001  0.226677D+003  -.322302D+003      0.270881D+002     0.483217D+002    -.629322D+002     -.1461050D+002
0.90000D-001  0.433702D+001  0.185650D+003  -.273885D+003      0.248768D+002     0.428060D+002    -.574147D+002     -.1460868D+002
0.10000D+000  0.401057D+001  0.154028D+003  -.235443D+003      0.228410D+002     0.384056D+002    -.530104D+002     -.1460478D+002
0.20000D+000  0.185228D+001  0.350108D+002  -.716766D+002      0.968351D+001     0.189014D+002    -.334684D+002     -.1456704D+002
0.30000D+000  0.868429D+000  0.110210D+002  -.278042D+002      0.413374D+001     0.126907D+002    -.272567D+002     -.1456595D+002
0.40000D+000  0.411835D+000  0.401541D+001  -.118118D+002      0.179428D+001     0.975004D+001    -.243241D+002     -.1457403D+002
0.50000D+000  0.197308D+000  0.160185D+001  -.527441D+001      0.796155D+000     0.811849D+001    -.226968D+002     -.1457827D+002
0.60000D+000  0.958533D-001  0.692529D+000  -.245467D+001      0.364865D+000     0.722488D+001    -.218022D+002     -.1457727D+002
0.70000D+000  0.478542D-001  0.333580D+000  -.120803D+001      0.177058D+000     0.697076D+001    -.215441D+002     -.1457331D+002
0.80000D+000  0.252862D-001  0.189630D+000  -.653284D+000      0.952512D-001     0.749933D+001    -.220687D+002     -.1456934D+002
0.90000D+000  0.148118D-001  0.132419D+000  -.408035D+000      0.598421D-001     0.894010D+001    -.235079D+002     -.1456781D+002
0.10000D+001  0.100364D-001  0.110178D+000  -.300994D+000      0.445925D-001     0.109778D+002    -.255471D+002     -.1456930D+002
0.20000D+001  0.393983D-002  0.570331D-001  -.132618D+000      0.181725D-001     0.144760D+002    -.290484D+002     -.1457233D+002
0.30000D+001  0.123233D-002  0.174092D-001  -.405276D-001      0.515950D-002     0.141271D+002    -.287003D+002     -.1457318D+002
0.40000D+001  0.317553D-003  0.445137D-002  -.103348D-001      0.125569D-002     0.140177D+002    -.285909D+002     -.1457317D+002
0.50000D+001  0.765322D-004  0.106867D-002  -.247539D-002      0.291452D-003     0.139636D+002    -.285362D+002     -.1457257D+002
```

Run 2. Sample input for Ne atom

```
                        REDUCED LOCAL ENERGY FOR NEON ATOM.  VALUES FROM
CLEMENTI PAGE 187.  DATE 8/15/83.
 10   6   4   0
 10.D+00
 -0.12854705D+03
   0.93717D+00    9.48486D+00 1
   0.04899D+00   15.56590D+00 1
   0.00058D+00    1.96184D+00 2
  -0.00064D+00    2.86423D+00 2
   0.00551D+00    4.82530D+00 2
   0.01999D+00    7.79242D+00 2
  -0.23093D+00   -0.00635D+00    0.18620D+00    0.66899D+00
   0.30910D+00   -0.13871D+00
   0.21799D+00    1.45208D+00 2
   0.53338D+00    2.38168D+00 2
   0.32933D+00    4.48489D+00 2
   0.01872D+00    9.13464D+00 2
  0   1  -1   0   1  -1
  1   0   1   0   1   1   1   0   0   0
   6
  0.000200D+00
  0.010000D+00
  0.100000D+00
  0.800000D+00
```

Run 2. Reduced local energy output for the Ne atom

```
 DISTANCE      OVERLAP        KINETIC      ELECTRON-NUCLEUS  ELECTRON-ELECTRON  K.E.DIVIDED   TOTAL P.E. DIVIDED  REDUCED LOCAL
  (A.U.)       INTEGRAL        ENERGY      POTENTIAL ENERGY  POTENTIAL ENERGY   BY OVERLAP         BY OVERLAP         ENERGY

0.2000D-003  0.617666D+002  0.309535D+007  -.310148D+007     0.359457D+004     0.501137D+005    -.501547D+005    -.409906D+002
0.4000D-003  0.615196D+002  0.154224D+007  -.155109D+007     0.358019D+004     0.250691D+005    -.251547D+005    -.856241D+002
0.6000D-003  0.612737D+002  0.102455D+007  -.103427D+007     0.356587D+004     0.167209D+005    -.168213D+005    -.104950D+003
0.8000D-003  0.610287D+002  0.765712D+006  -.775850D+006     0.355160D+004     0.125468D+005    -.126547D+005    -.107925D+003
0.1000D-002  0.607847D+002  0.610418D+006  -.620786D+006     0.353738D+004     0.100423D+005    -.101547D+005    -.112379D+003
0.1200D-002  0.605417D+002  0.506895D+006  -.517402D+006     0.352323D+004     0.837267D+004    -.848801D+004    -.115345D+003
0.1000D-001  0.507716D+002  0.521269D+005  -.615798D+005     0.295170D+004     0.102569D+004    -.115474D+004    -.128047D+003
0.2000D-001  0.415936D+002  0.218909D+005  -.296517D+005     0.241165D+004     0.526306D+003    -.654909D+003    -.128603D+003
0.3000D-001  0.340966D+002  0.122692D+005  -.186252D+005     0.196932D+004     0.359837D+003    -.488490D+003    -.128653D+003
0.4000D-001  0.279691D+002  0.774316D+004  -.129485D+005     0.160782D+004     0.276847D+003    -.405470D+003    -.128622D+003
0.5000D-001  0.229584D+002  0.521733D+004  -.948228D+004     0.131286D+004     0.227251D+003    -.355836D+003    -.128584D+003
0.6000D-001  0.188590D+002  0.366548D+004  -.716232D+004     0.107243D+004     0.194362D+003    -.322917D+003    -.128554D+003
0.1000D+000  0.866412D+001  0.112547D+004  -.272080D+004     0.481785D+003     0.129900D+003    -.258424D+003    -.128524D+003
0.2000D+000  0.144385D+001  0.136965D+003  -.401070D+003     0.784981D+002     0.948607D+002    -.223410D+003    -.128549D+003
0.3000D+000  0.456315D+000  0.530596D+002  -.137672D+003     0.259526D+002     0.116278D+003    -.244830D+003    -.128551D+003
0.4000D+000  0.295019D+000  0.386254D+002  -.936144D+002     0.170608D+002     0.130925D+003    -.259487D+003    -.128562D+003
0.5000D+000  0.228955D+000  0.300294D+002  -.724996D+002     0.130391D+002     0.131159D+003    -.259704D+003    -.128545D+003
0.6000D+000  0.174473D+000  0.225281D+002  -.546997D+002     0.974543D+001     0.129121D+003    -.257658D+003    -.128536D+003
0.8000D+000  0.923028D-001  0.116607D+002  -.285137D+002     0.498772D+001     0.126331D+003    -.254879D+003    -.128547D+003
0.1600D+001  0.576620D-002  0.714852D+000  -.174510D+001     0.289072D+000     0.123973D+003    -.252511D+003    -.128538D+003
0.2400D+001  0.434131D-003  0.537137D-001  -.130566D+000     0.210402D-001     0.123727D+003    -.252287D+003    -.128560D+003
0.3200D+001  0.395210D-004  0.488831D-002  -.118491D-001     0.188035D-002     0.123689D+003    -.252239D+003    -.128549D+003
0.4000D+001  0.417039D-005  0.515863D-003  -.124795D-002     0.196148D-003     0.123697D+003    -.252208D+003    -.128510D+003
0.4800D+001  0.482481D-006  0.596808D-004  -.144188D-003     0.225155D-004     0.123596D+003    -.252180D+003    -.128484D+003
```