On the helium ground-state Hartree–Fock energy

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The Hartree–Fock limit for the ground state of the He atom is rediscussed on the basis of the generator-coordinate Hartree–Fock method and the Laplace transform. A numerical solution is implemented which leads to a value of 73×10^{-12} hartree below the commonly accepted limit.

Between 1973 and 1981, three different calculations produced the same value for the ground-state Hartree–Fock (HF) energy of the He atom, $E_0=-2.861679995612$ au: the even-tempered 1s functions by Raffenetti [1], the polynomial functions by Gasquez and Silverstone [2] and the superposition of 1s and 0s orbitals by Szalewicz and Monkhorst [3]. This coincidence led the authors of ref. [3] to claim that the HF limit had been reached and to dismiss the result of Roothaan and Soukup [4], 12×10^{-12} hartree lower, as being in error. Nevertheless, the point in error is not signaled, the calculation of ref. [4] being analytical for low and large values of r and numerical in the intermediate region.

The value obtained for E_0 in refs. [1–3] may well be the limit for the type of functions employed. But more flexible functions (or algorithms) may produce lower values for E_0. In what follows, we show that an integral transform technique indeed leads to lower values than the claimed limit.

In 1986, a generator-coordinate version of the HF (GCHF) method was introduced [5]. In the GCHF method, the one-electron function is represented by the Ansatz

$$\psi_i(r)=\int_0^\infty \phi_i(r;\alpha)f_i(\alpha)\,\mathrm{d}\alpha\,, \tag{1}$$

where ϕ_i is the generator function, f_i the weight function and α the generator coordinate. The minimization of the energy expectation value built with the one-electron functions ψ_i leads to the Griffin–Wheeler HF (GWHF) equations,

$$\int [F(\alpha,\beta)-\epsilon_i S(\alpha,\beta)]f_i(\beta)\,\mathrm{d}\beta=0\,,$$

$$i=1,2,\ldots,M\,. \tag{2}$$

The explicit forms of the Fock, $F(\alpha,\beta)$, and overlap, $S(\alpha,\beta)$, kernels in eq. (2) have been reported in recent literature [5–7] and shall not be repeated in this Letter.

If the generator function ϕ_i is a Slater-type 1s orbital, eq. (1) becomes

$$\psi(r)=\int \exp(\alpha r)f(\alpha)\,\mathrm{d}\alpha\,. \tag{3}$$

One can now interpret $\psi(r)$ as a Laplace transform of the unknown weight function f. Moreover, for major flexibility, f may be a distribution. For instance, fig. 1 shows one possible weight function which is reminiscent of the distribution,

$$f(\alpha)=0 \qquad \text{for } 0<\alpha<a\,,$$

$$f(\alpha)=\exp[-b(\alpha-a)] \quad \text{for } \alpha>a\,, \tag{4}$$

a, b being constants. The Laplace transform of (4) leads to [8]

$$\psi(r)=\frac{\exp(-ar)}{r+b}\,. \tag{5}$$

Form (5) has already been reported in the literature

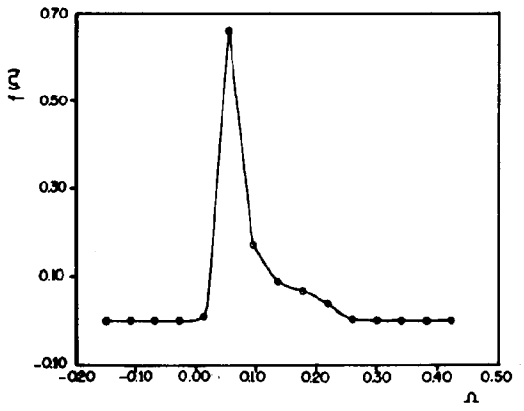

Fig. 1. The weight function $f(\Omega)$ for a mesh generated by $\Omega_{min}=-0.149$, $\Delta\Omega=0.0409012$ and $N=15$.

[9] but having only two parameters, it cannot compete with larger basis expansions.

In fact, the actual distribution which could approach the HF limit should be certainly more complicated than (4). We attempt here to attain this distribution numerically. As in previous applications for numerical integration, we replace the generator-coordinate space α for Ω through

$$\Omega=\frac{\ln\alpha}{A}, \tag{6}$$

where A ($A=6.0$) is a scaling parameter. The integration interval changes from $(0, +\infty)$ to $(-\infty, +\infty)$ but the weight functions become narrow. Then the GWHF equations (2) are discretized with an even-spaced mesh $\{\Omega_i\}$ so that

$$\Omega_{max}=\Omega_{min}+(N-1)\Delta\Omega, \tag{7}$$

where Ω_{max} and Ω_{min} are the upper and lower integration limits, respectively, $\Delta\Omega$ is the constant increment and N the number of discretization points. In this manner, the integral (2) becomes a linear problem; for details of the numerical solution, see refs. [5,10].

To ensure that the relevant digits are free from numerical noise, our program was run in quadrupole precision on a VAX 6420 machine. The convergence criterion for the energy was 10^{-20} hartree.

Table 1 shows the E_0 values obtained for a given choice of discretization parameters Ω_{min} and $\Delta\Omega$ and increasing values of N. The lowest value of E_0 is obtained for $N=21$. The E_0 values vary smoothly and seem to approach an asymptotic behaviour. We did not obtain lower values of E_0 with higher values of N. Although our result shows that the value of ref. [3] is clearly not the HF limit, we do not claim to have reached it necessarily. Indeed, a different choice of discretization parameters or a more sophisticated integration technique of eq. (2) could produce even lower values.

Table 1
He atom ground-state Hartree–Fock energy

This work		Literature $-E_0$ (au)
N [a]	$-E_0$ (au) [b]	
15	2.861679978227894	2.861679995612 [a]
16	2.861679992554325	2.861679995624 [d]
17	2.861679994082243	2.8616800 [e]
18	2.861679995501622	
19	2.861679995629078	
20	2.861679995636161	
21	2.861679995685207	

[a] Discretization points.
[b] $\Omega_{min}=-0.0927209$ and $\Delta\Omega=0.0215466$.
[c] Value from refs. [1–3].
[d] Value from [4].
[e] Numerical HF value from ref. [11].

In ref. 35], we used the He and Be atoms as test cases for the presentation of the GCHF method. For He with the set of discretization parameters $\Omega_{min}=-0.15$, $\Delta\Omega=0.04$ and $N=13$, we reached the same value for E_0 as in refs. [1–3]; at that time, we did not pursue the possibility of a lower value for the HF energy. In the present investigation, we span the generator coordinate Ω space in the same relevant region but with almost double the number of points N ($N=21$) and a more dense mesh ($\Delta\Omega\approx0.02$). In this manner, we believe that we have induced numerically a distribution – like behaviour of the weight function leading to the new HF value presented. The use of quadrupole precision and the 10^{-20} hartree convergence criterion provide support for our result.

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