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On the Use of $T_H[1s]$ and $1s$ Functions as Expansion Functions*

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It is shown by a numerical calculation that although a $T_H[1s]$ function (0s orbital) is a much better approximation to the exact Hartree-Fock 1s orbital than a usual 1s function, the set of $T_H[1s]$ functions does not have markable advantage over the set of 1s functions as expansion functions.

It has been shown that a Hulthèn transform 1s function $T_H[1s] = r^{-1}[\exp(-\alpha r) - \exp(-\beta r)]$ (0s orbital) is a much better approximation to the Hartree-Fock 1s orbital than a Slater 1s function [1–3], even an electron-nuclear cusp conditions forced $T_H[1s]$ function with only one-parameter is superior to the one-parameter Slater 1s function. For the ground state of the helium atom, wavefunctions constructed with single $T_H[1s]$ basis function give a cusp-free closed-shell energy -2.860842 a.u. and a cusp-free open-shell energy -2.876194 a.u. as compared to the corresponding Slater energies [4] -2.847656 a.u. and -2.875661 a.u., versus the Hartree-Fock energies -2.861680 a.u. [5] and -2.87800 a.u. [6]. Furthermore, the closed-shell Hulthèn wavefunction also gives more accurate expectation values than the corresponding Slater wavefunction as can be seen from Table 2. However, the $T_H[1s]$ function is too diffuse as compared to the exact Hartree-Fock orbital while the 1s function is too small at intermediate to large distances from the nucleus [2]. This is also reflected by the calculated expectation values shown in Table 2.

A substantial improvement in both the energy and expectation values is obtained (see Table 2) over a single 1s basis function when a linear combination of two 1s functions $C_1 1s + C_2 1s'$ is used to approximate the Hartree-Fock orbital [7, 8]. The improved energy is -2.861672 a.u. [9]. Nevertheless, this improved approximate orbital still differs appreciably from the exact Hartree-Fock orbital and is too small at large distances.

A further slightly improved approximate orbital is obtained when one of the 1s functions is replaced by a more diffuse $T_H[1s]$ function [8], i.e. $C_1 1s + C_2 T_H[1s']$. This improves the orbital at intermediate and large distances at the expense of decreasing the accuracy of the orbital at short distances. As a consequence, the calculated values of $\langle r_1 \rangle$, $\langle r_1^{+2} \rangle$, $\langle r_1^{+3} \rangle$ and $\langle r_1^{+4} \rangle$ are more accurate than the values of $\langle \delta(r_1) \rangle$, $\langle r_1^{-2} \rangle$ and $\langle r_1^{-1} \rangle$. The energy is improved to -2.861673 a.u. However, this improved orbital is smaller than the exact Hartree-Fock orbital almost at all distances and the calculated expectation values shown in Table 2 are smaller than the corresponding Hartree-Fock values.

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Since $T_H[1s]$ functions are more diffuse and they are able to revert to $1s$ functions [3] when the latter are more appropriate to describe the system, it is hoped that a linear combination of two $T_H[1s]$ functions as an approximation to the exact Hartree-Fock $1s$ orbital for the helium atom will lead to better results than all previously mentioned orbitals. At the same time, we can study and compare the usefulness of the set of $T_H[1s]$ functions and the set of $1s$ functions as expansion functions.

The results of calculation using $C_1 T_H[1s] + C_2 T_H[1s']$ are shown in Table 1 and Table 2. Although the energy obtained is essentially the same as the $C_1 1s + C_2 T_H[1s']$ orbital, there is a definite improvement in the calculated expectation values and hence $C_1 T_H[1s] + C_2 T_H[1s']$ represents a better approximate orbital as expected. The orbital exponents of the two $T_H[1s]$ functions are well separated at the minimum energy and none of them reverts to a $1s$ function.

In spite of the improvement of $C_1 T_H[1s] + C_2 T_H[1s']$ over $C_1 1s + C_2 T_H[1s']$, the former orbital with five variational parameters is not much better than the orbital $C_1 1s + C_2 1s'$ with only three variational parameters which gives more accurate values of $\langle\delta(r_1)\rangle$, $\langle r_1^{-2}\rangle$ and $\langle r_1^{-1}\rangle$. A much inferior orbital is obtained

Table 1. *Approximate Hartree-Fock orbitals for the ground state of the helium atom*

Orbital	α	β	γ	δ	C_1	C_2	E(a.u.)[a]
$1s_\alpha$	1.687500						−2.847656
$T_H[1s]_{\alpha\beta}$	0.959771	3.040299					−2.859585[b]
$C_1 T_H[1s]_{\alpha\beta} + C_2 T_H[1s]_{\gamma\delta}$	1.071166	2.928834	1.998508	2.001492	1.297123	−0.301257	−2.860624[c]
$T_H[1s]_{\alpha\beta}$	1.016771	2.813653					−2.860842[d]
$C_1 1s_\alpha + C_2 1s_\gamma$	1.454799		2.916588		0.844974	0.179435	−2.861672[e]
$C_1 1s_\alpha + C_2 T_H[1s]_{\gamma\delta}$	1.454799		2.812000	3.024000	0.844994	0.179374	−2.861673[f]
$C_1 T_H[1s]_{\alpha\beta} + C_2 T_H[1s]_{\gamma\delta}$	1.406232	1.502637	2.813729	3.000397	0.843184	0.181212	−2.861673

[a] Hartree-Fock energy −2.861680 a.u., see Ref. [5].
[b] Cusp-forced orbital, see also Ref. [2].
[c] Cusp-forced orbital.
[d] Reference [1–3].
[e] Reference [9].
[f] Reference [8].

Table 2. *Comparison of expectation values for various helium orbitals in atomic units*

Orbital	cusp	$\langle\delta(r_1)\rangle$	$\langle r_1^{-2}\rangle$	$\langle r_1^{-1}\rangle$	$\langle r_1\rangle$	$\langle r_1^{+2}\rangle$	$\langle r_1^{+3}\rangle$	$\langle r_1^{+4}\rangle$
$1s_\alpha$	−1.6875	1.5296	5.6953	1.6875	0.8889	1.0535	1.5607	2.7746
$T_H[1s]_{\alpha\beta}$[a]	−2	1.8576	6.1324	1.7011	0.9354	1.2360	2.1543	4.7295
$C_1 T_H[1s]_{\alpha\beta} + C_2 T_H[1s]_{\gamma\delta}$[a]	−2	1.8290	6.0592	1.6913	0.9373	1.2312	2.1105	4.4993
$T_H[1s]_{\alpha\beta}$	−1.9152	1.7441	5.9525	1.6871	0.9305	1.2074	2.0438	4.3184
$C_1 1s_\alpha + C_2 1s_\gamma$	−2.0046	1.7976	5.9951	1.6874	0.9269	1.1828	1.9312	3.8466
$C_1 1s_\alpha + C_2 T_H[1s]_{\gamma\delta}$	−2.0050	1.7973	5.9939	1.6872	0.9270	1.1830	1.9317	3.8476
$C_1 T_H[1s]_{\alpha\beta} + C_2 T_H[1s]_{\gamma\delta}$	−2.0033	1.7968	5.9942	1.6873	0.9271	1.1835	1.9337	3.8557
Hartree-Fock[b]	−2.0019	1.7982	5.9956	1.6873	0.9273	1.1848	1.9406	3.8879

[a] Cusp-forced orbital.
[b] The expectation values are taken from: Ten Hoor, M. J.: Int. J. quant. Chem. **2**, 109 (1968) with the Hartree-Fock wavefunction of Ref. [5].

when the cusp constraint is imposed on $C_1 T_{\mathrm{H}}[1s] + C_2 T_{\mathrm{H}}[1s']$ to reduce the number of variational parameter to three. At the minimum energy -2.860624 a.u., one of the $T_{\mathrm{H}}[1s]$ functions becomes essentially a 1s function with a negative coefficient of linear combination.

Considering the number of variational parameters, the rate of convergence and the efforts in integrals evaluation and computation, the results of the present study indicate that although a $T_{\mathrm{H}}[1s]$ function (even with the cusp constraint imposed) is a much better approximation to the exact Hartree-Fock 1s orbital than a 1s function, the set of $T_{\mathrm{H}}[1s]$ functions does not have markable advantage over the set of 1s functions as expansion functions.

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9. See footnote b of Table 1 in Ref. [8].

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