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**Hulthén Orbital and Hulthén  
Correlation Factor for the Ground  
State of Heliumlike Systems\***

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Several authors have found indications that it may be advantageous to include in approximate analytical atomic wavefunctions Hulthén or "0s" orbitals, functions<sup>1)</sup>

$$0s_{\alpha\beta}(r) = N(1/r) [\exp(-\alpha r) - \exp(-\beta r)],$$

$$N^2 = \alpha\beta(\alpha + \beta) / 2\pi(\alpha - \beta)^2. \quad (1)$$

Thus Cohen and Dalgarno<sup>2)</sup> noticed 0s orbitals appearing in their perturbation-theory determination of the Hartree-Fock orbital for helium starting from the hydrogen-like orbital  $1s_{\zeta}(r) = (\zeta^3/\pi)^{1/2} \exp(-\zeta r)$ . Variational mixing of  $0s_{\alpha\beta}$  with  $1s_{\zeta}$  for He was carried out by Zung and Parr.<sup>3)</sup> Very recently, Robinson<sup>4)</sup> has discovered 0s orbitals entering the first iterand of an iterative solution of the Hartree-Fock integral equation for He.

What seems to have been undiscovered heretofore is that 0s orbitals, *without mixing in of other orbitals*, are generally excellent approximations to Hartree-Fock 1s orbitals. Green et al.<sup>5)</sup> showed this for  $H^-$ , but the result is in fact universal. Namely, for heliumlike systems with any nuclear charge whatever, the wavefunction

$$\psi(r_1, r_2) = 0s_{\alpha\beta}(r_1) 0s_{\alpha\beta}(r_2) \quad (2)$$

is a much better approximation to the Hartree-Fock function than is the hydrogen-

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like product  $1s_\zeta(r_1) 1s_\zeta(r_2)$ . This is shown in Table I.

Table I. Hulthén orbitals for  $(1s)^2$  configurations of heliumlike systems.

Z	Slater energy <sup>a)</sup>	Hulthén energy <sup>b)</sup>	Hartree-Fock energy <sup>c)</sup>
1(H <sup>-</sup> )	-0.4727	-0.4879	-0.4879
2(He)	-2.8477	-2.8608	-2.8618
4(Be <sup>2+</sup> )	-13.5977	-13.6100	-13.6113
10(Ne <sup>8+</sup> )	-93.8477	-93.8596	-93.8611

- a) Best description  $1s_\zeta(r_1) 1i_\zeta(r_2)$  with  $\zeta=Z-0.3125$ .  
 b) Best description  $0s_{\alpha\beta}(r_1) 0s_{\alpha\beta}(r_2)$ . Parameter values  $Z(\alpha, \beta)$  as follows:  
 1(0.292949, 1.67052), 2(1.01657, 2.81522),  
 4(2.65187, 5.13516), 10(7.93951, 11.8228).  
 c) From C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32** (1960), 194.

For handling  $0s$  functions, the identity

$$0s_{\alpha\beta}(r) = N \int_{\alpha}^{\beta} \exp(-xr) dx \quad (3)$$

is useful.<sup>6)</sup> To illustrate the formulas one obtains, following is the expectation value of the energy,  $E(Z)$ , for a two-electron atom of nuclear charge  $Z$ , for the wavefunction of Eq. (2), with  $\alpha=kZ(1-q)$ ,  $\beta=kZ(1+q)$ :

$$\begin{aligned} Z^{-2}E(Z) &= k^2 \langle T \rangle + k [\langle V_{ne} \rangle + (1/Z) \langle V_{ee} \rangle], \\ \langle T \rangle &= 1 - q^2, \\ \langle V_{ne} \rangle &= (2/q^2) (1 - q^2) \ln(1 - q^2), \\ \langle V_{ee} \rangle &= (1/q^4) (1 - q^2) [f(q) - 4f(q/2)], \\ f(q) &= (1+q) (1-2q) \ln(1+q) \\ &\quad + (1-q) (1+2q) \ln(1-q). \end{aligned} \quad (4)$$

The  $0s$  functional form also is natural for describing electron correlation. For He the best wavefunction of the form

$$\psi(r_1, r_2, r_{12}) = 1s_\zeta(r_1) 1s_\zeta(r_2) \chi(r_{12}) \quad (5)$$

is known to give an energy  $-2.89126$  au, with  $\zeta=1.849$ .<sup>7)</sup> If one sets

$$\chi(r_{12}) = 1 + (A/\gamma r_{12}) [1 - \exp(-\gamma r_{12})] \quad (6)$$

and determines  $A$ ,  $\gamma$  and  $\zeta$  variationally, one obtains  $-2.89113$  au for  $A=-0.96196$ ,  $\gamma=0.02954$ ,  $\zeta=1.8484$ . This is as good an energy as is associated with any two-parameter approximation to  $\chi(r_{12})$  in the literature.<sup>8)</sup>

Zero- $s$  orbitals may be simply expressed in terms of Kotani  $B$  functions,  $B_k(r) = \int_{-1}^1 x^k \exp(-rx) dx$ .<sup>6)</sup> It is with particular pleasure, therefore that we dedicate this communication to Professor Masao Kotani, on the occasion of his 60th birthday.

- 1) L. Hulthén, Arkiv Fysik **28A** (1942), 5. The function of Eq. (1) is an eigenfunction of the potential  $V_{\alpha\beta}(r) = \frac{1}{2}(\alpha^2 - \beta^2) \exp(-\beta r) / [\exp(-\alpha r) - \exp(-\beta r)]$ .
- 2) M. Cohen and A. Dalgarno, Proc. Phys. Soc. (London) **77** (1961), 165.
- 3) J. T. Zung and R. G. Parr, J. Chem. Phys. **41** (1964), 2888.
- 4) P. D. Robinson, J. Chem. Phys. **45** (1966), in press. We are indebted to Dr. Robinson for a preprint of this paper.
- 5) L. C. Green, S. Matsushima, C. Stephens, E. K. Kolchin, M. M. Kohler, Y. Wang, B. B. Baldwin and R. J. Wiener, Phys. Rev. **112** (1958), 1187.
- 6) Remark of Professor Harrison Shull.
- 7) L. C. Green, C. Stephens, C. C. Chen, P. R. Rush and C. W. Ufford, J. Chem. Phys. **30** (1959), 1061.
- 8) The function  $\chi(r_{12}) = 1 - C \exp(-\eta r_{12})$ , due to D. R. Hartree and A. L. Ingman, Mem. Proc. Manchester Lit. and Phil. Soc. **77** (1933), 79, gives an energy  $-2.89111$  au, for  $\eta=0.04590$ ,  $C=-0.89312$ ,  $\zeta=1.84658$  (recalculation by D. D. Konowalow and J. L. J. Rosenfeld, private communication).