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Self-Consistent-Field Calculation of the Energy of HeH $^+$

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The use of the exact solutions of the one-electron–two-nucleus problem as a basis set of functions for SCF calculations is investigated for the HeH+ ion. The calculations are made with both scaled and non-scaled functions. The best energy obtained here is −3.345 a.u. at an internuclear distance of 1.40 a.u. The conclusion is that these functions form an only moderately good basis set for such calculations. Their conditioning to the problem can only partially overcome their lack of completeness when continuum states are omitted.

INTRODUCTION

QUANTUM-mechanical calculations of the structures of diatomic molecules have been made using basis functions constructed both from one-center orbitals and from functions expressed in ellipsoidal coordinates directly. The latter are reasonably termed two-center functions. Calculations using as basis functions the exact solutions (henceforth, 2CMO's) of the one-electron–two-nucleus system are not common, however. Wallis and Hulbert[1a] and Matcha[1b] appear to have made the only published attempts at using 2CMO functions in their calculations of the energy of H_2. Wallis and Hulbert conclude that the complexity of the 2CMO functions makes their use too unwieldy, particularly for heteronuclear cases. This admitted complexity seems much less serious today, however, because of the incredible advances in computing machinery since 1954. This point is borne out by the very recent report by Matcha also.

The present article gives a report of a self-consistent-field calculation of the ground-state energy of the HeH+ ion using Roothaan's method[2] with 2CMO basis functions. Other calculations of the energy of HeH+ have been made.[3-7] The most ambitious of these is that of Conroy,[7] whose results we have used for comparison.

The primary disadvantage of the 2CMO's as basis functions is, of course, the incompleteness of the set unless continuum-state functions are included. However, to offset this disadvantage, the first few 2CMO functions are presumably better conditioned to the problem at hand than simpler forms. In addition, when these basis functions are scaled to minimize the calculated energy, one obtains a screening constant which can be compared with similar results from atomic calculations.

2CMO BASIS FUNCTIONS

The present calculation uses the form of 2CMO functions developed by Jaffe.[8] In terms of the ellipsoidal coordinates $\xi(1\leq\xi<\infty)$, $\eta(-1\leq\eta\leq1)$, and $\phi(0\leq\phi<2\pi)$, these functions have the form

$$U = S(\xi)T(\eta)\Phi(\phi), \tag{1}$$

with

$$S(\xi) = (\xi^2-1)^{|m|/2} \exp(-\alpha\xi)\left(\frac{2}{\xi+1}\right)^s \sum_{k=0}^{\infty} b_k \left(\frac{\xi-1}{\xi+1}\right)^k,$$

$$T(\eta) = \sum_{l=0}^{\infty} a_l \theta_l^m(\eta),$$

$$\Phi(\phi) = 1/(2\pi)^{1/2} \exp(im\phi),$$

where the θ_l^m are the associated Legendre functions. Wilson[9] has discussed these functions for the heteronuclear case and has shown that the 2CMO depend on the physical parameters of the two-nucleus system through the combinations

$$\rho' = (Z_a+Z_b)\rho \tag{2}$$

and

$$\gamma = (Z_a-Z_b)/(Z_a+Z_b), \tag{3}$$

where Z_a and Z_b are the atomic numbers of the two nuclei and ρ is the distance between them. The designation of the 2CMO of different energies as $1s\sigma$, $2p\sigma$, etc., follows the system of Bates, Ledsham, and Stewart[10] and is also discussed by Wilson.[9]

SCF CALCULATION

Roothaan's method[2] of solution of the restricted Hartree–Fock equations was used. In this two-electron problem with double occupancy in the ground state only σ-type 2CMO functions enter the calculation,

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[9] L. Y. Wilson, Ph.D. thesis, University of Nebraska, 1965.

[10] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) **A246**, 215 (1953).

and only one space orbital is obtained as a result. Since the 2CMO are orthogonal, Roothaan's equations are somewhat simplified. The space orbital Ψ is defined as

$$\Psi = C_1(1s\sigma) + C_2(2s\sigma) + C_3(2p\sigma) + \cdots, \qquad (4)$$

which results in the eigenvalue problem,

$$HC - \lambda C = 0. \qquad (5)$$

The matrix H is defined by

$$H_{kl} = F_{kl} + \sum_{p,q} C_p{}^* C_q (2G_{klpq} - G_{kqpl}), \qquad (6)$$

and F_{kl} and G_{klpq} have their usual significance. The values of some of the integrals in (6) can be obtained directly from the corresponding one electron problem. If the Neumann[11] expansion is used for $1/r_{12}$, the remaining integrals can be calculated to sufficient accuracy by a technique combining an analytical integration over the ϕ- and η-type coordinates with a numerical integration over the ξ-type coordinates. The factor $e^{-\alpha\xi}$ in the 2CMO makes the "Laguerre" quadrature formulas[12] the most useful. The evaluation of the various integrals and the solution of Eqs. (5)
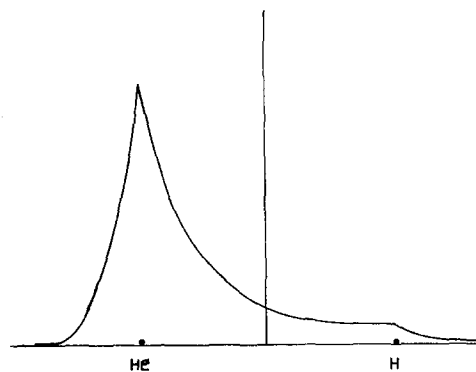

Fig. 1. Relative electron density of HeH$^+$ along internuclear axis for $\rho = 1.40$ a.u.

and (6) were performed on the IBM 1410 computer in the University of Nebraska Computing Center.

RESULTS AND DISCUSSION

Although as mentioned above the 2CMO functions depend upon the parameters ρ' and γ only, the Hamiltonian depends upon ρ also. Hence, to characterize the system completely, Z_a, Z_b, and ρ (or equivalently ρ', γ, and ρ) must be specified for the Hamiltonian and ρ' and γ for the 2CMO. The latter pair need not be the physical values, of course. Since we are interested in HeH$^+$ only, the values of ρ' and γ used in the Hamiltonian were always 3ρ and $\frac{1}{3}$, respectively (He is Nucleus a). Values other than these were used in the 2CMO in order to calculate the minimum in the total energy with respect to variation of these parameters.

The actual calculations are divided into two series. Table I shows the results of the first series. In this the actual physical values of ρ' and γ were used for the 2CMO functions, and the value of the calculated energy was tested with respect to the number of 2CMO retained in Ψ. In addition to the results shown in Table I the effect of including the $3p\sigma$ and $3d\sigma$ functions was investigated at $\rho = 1.40$ and was found to be negligible. Since the set is not complete, inclusion of a large number of 2CMO cannot be expected to result in the convergence of the calculated energy to the correct SCF value. It is evident, however, that a relatively few basis functions are required to yield essentially as good an answer as one can get with these functions.

The results of the other series of calculations are given in Table II. Since the more accurate treatment of HeH$^+$ by Conroy[7] yielded $\rho = 1.40$ a.u. for the equilibrium internuclear distance, all of this series of calculations used his value. The energy is given for different values of ρ' and γ for the 2CMO. The rows labeled ΔE give the amounts by which the calculated energy is increased if the $3s\sigma$ function is omitted from the basis set.

The best electronic energy obtained here for $\rho = 1.40$

TABLE I. Coefficients of basis functions in occupied SCF orbital and the orbital, electronic, and total energies.

Function	Coefficients of 2CMO's in SCF orbital		
	$\rho = 1.20$ a.u.	$\rho = 1.40$	$\rho = 2.00$
$1s\sigma$	0.9928	0.9924	0.9834
$2s\sigma$	0.1120	0.1231	0.1815
λ^a	-1.680 a.u.	-1.573	-1.363
$E_e{}^a$	-4.524 a.u.	-4.292	-3.837
$E_t{}^a$	-2.857 a.u.	-2.863	-2.837
$1s\sigma$	0.9889	0.9862	0.9774
$2s\sigma$	0.1158	0.1165	0.1230
$2p\sigma$	0.0926	0.1173	0.1700
λ^a	-1.715 a.u.	-1.623	-1.421
$E_e{}^a$	-4.548 a.u.	-4.326	-3.874
$E_t{}^a$	-2.881 a.u.	-2.898	-2.874
$1s\sigma$	0.9888	0.9856	0.9777
$2s\sigma$	0.1108	0.1139	0.1174
$2p\sigma$	0.0923	0.1157	0.1694
$3s\sigma$	-0.0397	-0.0472	-0.0401
λ^a	-1.722 a.u.	-1.633	-1.426
$E_e{}^a$	-4.553 a.u.	-4.332	-3.878
$E_t{}^a$	-2.886 a.u.	-2.903	-2.878

^{a} λ is the orbital energy, E_e is the electronic binding energy, and E_t is the total energy including nuclear repulsion.

[11] F. Neumann, *Theorie des Potentials* (B. G. Tuebner, Leipzig, Germany, 1887).

[12] V. I. Krylov, *Approximate Calculation of Integrals* (The MacMillan Co., New York, 1962).

TABLE II. Coefficients of scaled basis functions in occupied SCF orbital and the corresponding energies.[a]

	Function	Coefficients in occupied SCF orbital			
		$\rho'=3.3$	$\rho'=3.6$	$\rho'=3.75$	$\rho'=3.9$
$\gamma=0.30$	$1s\sigma$	0.9995	0.9998		0.9970
	$2s\sigma$	−0.0215	0.0191		0.0628
	$2p\sigma$	−0.0235	0.0065		0.0427
	$3s\sigma$	0.0064	−0.0050		−0.0212
	λ	−1.657 a.u.	−1.650		−1.642
	E_e	−4.316 a.u.	−4.338		−4.345
	ΔE	(0.0001)	(0.0001)		0.001
$\gamma=0.33$	$1s\sigma$	0.9998	0.9991	0.9973	0.9946
	$2s\sigma$	−0.0163	0.0253	0.0468	0.0685
	$2p\sigma$	0.0009	0.0347	0.0538	0.0739
	$3s\sigma$	0.0095	−0.0075	−0.0159	−0.0241
	λ	−1.654 a.u.	−1.647	−1.643	−1.638
	E_e	−4.324 a.u.	−4.342	−4.344	−4.343
	ΔE	(0.0003)	(0.0002)	0.001	0.002
$\gamma=3.6$	$1s\sigma$		0.9979	0.9955	0.9921
	$2s\sigma$		0.0308	0.0529	0.0752
	$2p\sigma$		0.0558	0.0760	0.0971
	$3s\sigma$		−0.0097	−0.0183	−0.0266
	λ		−1.644 a.u.	−1.639	−1.635
	E_e		−4.343 a.u.	−4.343	−4.340
	ΔE		(0.0003)	0.001	0.001

[a] In all cases $E_t = (E_e + 1.428)$ a.u.

a.u. is 1.3% higher than the lowest energy reported.[7] However, it is only 0.27% higher than the SCF energy calculated by Anex,[4] which is a more comparable result. The conclusion is that the 2CMO functions form only a moderately good basis set for this problem. The principal difficulty is the lack of completeness.

Analysis of the data given in Tables I and II yields the result that for $\rho=1.40$ a.u., $\rho'=3.9$ a.u., and $\gamma=0.30$ are the best values of the parameters for the 2CMO functions. These correspond to apparent nuclear atomic numbers of $Z_{He}'=1.81$ and $Z_H'=0.97$. It is seen that the shielding of the helium nucleus is considerably greater than the shielding of the proton, and also, that the effective Z_{He}' is larger than the value of 1.69 obtained in the simple screening-constant calculation of the helium atom itself.[13] There are two reasons the

present value of Z_{He}' is the larger. First, the inclusion of $2s\sigma$, $2p\sigma$, etc., orbitals with the $1s\sigma$ contributes to the screening. Second, the percent of shielding should increase with increasing electron density near the nucleus. In the case of HeH⁺, the presence of the proton dilutes the electronic charge density near the helium nucleus compared to its value for the lone He atom.

Figure 1 shows a graph of the relative electronic density along the internuclear line for the equilibrium internuclear distance. As can be seen, the value of the electronic density is considerably greater at the helium nucleus than at the proton.

ACKNOWLEDGMENTS

[13] See, e.g., L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., Inc., New York, 1935), pp. 221ff.