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Relationes

Physical Nature of the Chemical Bond

I. Approach to a Quasi-Optimized LCGTO-MO-SCF Wave Function for the Helium Hydride Ion

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The effect of such variables as size of basis set, number of S and P type functions in the basis set, size of initial exponent in the basis set, size of multiplicative factor in the geometrical progression of exponents, and interatomic distance has been examined by a self-consistent-field calculation with Gaussian orbitals on HeH^+. A quasi-optimized wave function has been obtained by allowing only the initial exponent and multiplicative factor to vary in the optimization process.

Introduction

Theoretical work in this laboratory has been concerned in part, with the physical nature of the chemical bond [10]. It seemed reasonable and appropriate, in connection with the studies, to initiate work on the bonds in simpler molecules, particularly those where the influence of increasingly better wave functions and size of basis set could conveniently be examined. The simplest molecule containing a heteronuclear two-electron bond is the molecule HeH^+, the helium hydride ion. In the process of performing preliminary calculations on this molecule using Gaussian basis functions, for later use in investigations on bonds, it became apparent that HeH^+, because of its heteronuclear nature, its small number of electrons, and its diatomic nature, was an interesting molecule on which to test various effects in Gaussian SCF calculations.

In any calculations with Gaussian functions, which of necessity will be in larger number than in a corresponding calculation with Slater orbitals, there are two important problems, one associated with methods of contraction of the basis set, and the other with optimization of exponents. Much of the recent work involving Gaussian functions has been directed toward extension to larger molecules [1, 2, 11, 15]. Although Clementi [2] has developed an interesting technique for the contraction of basis sets of Gaussian functions, much of this recent work on large molecules has been done by selecting a relatively small number of basis functions per atom. Although values for the electronic energies which are obtained in this latter way are usually not very good, calculated values of other molecular properties are often surprisingly close to the experimental ones. Hence, it seems apparent that this method of optimization and the effects of optimization on various sizes of basis sets is important in order to demonstrate to what extent the calculations using a small basis set can be conveniently improved by at least a partial optimization of exponents.

In addition, most of the work involving Gaussian functions has so far employed basis sets containing only *s* and *p* type functions, presumably since, with the smaller basis sets employed for the larger molecules, a larger decrease in energy would be obtained in general by the addition of one *s* or one *p* type function than by the addition of one *d* type function. It is likely that as attempts are made in the future to extend Gaussian calculations of wavefunction to larger molecules, much of the work will still be restricted to *s* and *p* type functions. Hence, for the present work it seemed reasonable and desirable to examine the results of optimization on a small molecule using basis sets of *s* and *p* type Gaussians only. It is hoped to show, among other things, to what extent one can approach the results obtained with large basis sets of Gaussian functions with or without optimization by using smaller basis sets with optimization. The advantage of using a small molecule such as the helium hydride ion for such calculations can then be seen. Good values of the electronic energy from calculations involving other than Gaussian functions are available for comparison. The number of electrons is small enough so that the ratio of Gaussian functions to electrons can be made quite large to provide data to compare with the results from smaller basis sets.

The present paper is concerned with the examination of the influence of certain variables on the results of the calculation, that is, on such quantities as the orbital energies, and the total electronic energy. The variables considered were (a) size of basis set of Gaussian functions, (b) number of *s* and *p* type functions in the basis set, (c) size of initial exponent for each of *s* and *p* types, while maintaining the exponents in a fixed geometrical progression, (d) size of multiplicative factor in geometrical progression for each of *s* and *p* types, and (e) interatomic distance (I.D.).

The first identification of the singly charged helium hydride molecular ion apparently occurred about 1925 [6] at which time it was found in mass-spectrometric experiments. Since that time many quantum-mechanical calculations have been done. Table 1 records the equilibrium interatomic distance, the total electronic energy, for that distance, and the associated orbital energy, from some of the more recent of these calculations. Michels [8] has compiled an excellent and apparently complete bibliography of calculations on HeH^+ prior to those given in Table 1. It should be mentioned here that the work of Schwartz and

Table 1. *Recent calculations on the ground* $^1\Sigma$ *state of* HeH^+

Equilibrium Interatomic Distance (a.u.)	Total Electronic Energy (a.u.)	Orbital Energy (a.u.)	Reference
1.4	−2.93043	−1.65934	Schwartz and Schaad [16]
1.44	−2.9433	—	Harris [5]
1.4	−2.93251	—	Hoyland [7]
1.40	−2.903	−1.633	Gallup and McKnight [4]
1.44	−2.94321	—	Michels [8]
1.455	−2.933126	−1.63748	Peyerimhoff [12]
1.455	−2.930206	−1.6358	Moffat (this work)

Table 2. *Helium atom exponents*

s exponents			*p* exponents		
Exponent Set Number	Initial Exponent	Multiplying Factor	Exponent Set Number	Initial Exponent	Multiplying Factor
*HeS*1	0.0100	3.16	*HeP*1	0.0160	3.00
*HeS*2	0.0280	2.50	*HeP*2	0.0160	3.44
*HeS*3	0.0280	3.14	*HeP*3	0.0160	4.00
*HeS*4	0.0280	3.86	*HeP*4	0.0160	4.50
*HeS*41	0.0280	3.20	*HeP*5	0.0160	5.00
*HeS*42	0.0280	3.30	*HeP*51	0.0320	4.00
*HeS*43	0.0300	3.00	*HeP*6	0.0030	3.46
*HeS*44	0.0300	3.10	*HeP*7	0.0041	3.41
*HeS*45	0.0300	3.20	*HeP*8	0.0050	3.48
*HeS*6	0.0200	3.16	*HeP*9	0.0100	3.47
*HeS*7	0.0312	3.16	*HeP*91	0.0150	3.47
*HeS*8	0.0400	3.16	*HeP*12	0.3300	3.45
*HeS*9	0.1000	3.16			
*HeS*91	0.1300	3.16			
*HeS*92	0.1000	4.00			
*HeS*14	0.4400	3.18			

Schaad [16] is of particular interest in connection with the present study. Their results, which appeared when the present work was nearly completed, have all been obtained at an I.D. of 1.4 a.u. for HeH^+ using basis sets consisting only of *s* type Gaussian functions.

Method

The Gaussian orbital calculations have been performed using the Roothaan self-consistent-field method [14] as described previously [9]. A brief survey of earlier work using Gaussian orbitals has already been given [9] and will not be repeated here. The basis set was restricted to *s*- and p_q-type Gaussians, of the form $N \cdot \exp(-\alpha r^2)$ and $Nq \exp(-\alpha r^2)$, respectively, where q may be x, y, or z. The bond in HeH^+ was considered to be directed along the X-axis with the helium atom at the origin and internuclear distances between 1.30 and 1.50 a.u. were employed. In the labelling of the basis sets as found in the tables, the first four figures indicate the number of s, p_x, p_y, and p_z type functions of helium, the second four figures those on hydrogen, respectively. The largest set contained 37 functions. The quasi-optimization technique which was used in the present work involved two variables, the value of the smallest exponent in either or both of the *s* and *p* type functions, and the multiplicative factor which operated to generate the remainder of the particular set of exponents. The various sets of exponents employed are summarized in Table 2.

Results and Discussion

Over two hundred separate calculations were performed on the helium hydride molecular ion. A portion of the results are given here. Full details may be obtained from the author. All calculations have been iterated to an accuracy of 10^{-4} a.u., except those marked by an asterisk, which have been iterated to 10^{-6} a.u.

Table 3. *Total energy of* HeH^+ *(in a.u.) at various interatomic distances and for various basis sets*

Gaussian Set Number	Exponent Set Number	Number of basis functions	Elements of set	Interatomic Distance (a.u.)			
				1.35	1.40	1.4632	1.50
1	1	2	(1000/1000)	−2.2168	−2.2343	−2.2523	−2.2609
2	2	4	(2000/2000)	−2.7975	−2.8015	−2.8048	−2.8061
3	3	6	(3000/3000)	−2.8843	−2.8863	−2.8876	−2.8878
4	4	9	(3100/3200)	−2.8856	−2.8876	−2.8887	−2.8888
5	5	11	(3300/3200)	−2.8980	−2.9002	−2.9015	—
6	6	13	(3300/4300)	−2.8994	−2.9013	−2.9023	−2.9023
7	7, *H*1	17	(7300/4300)	—	−2.9187	−2.9202	−2.9204

Table 4. *Effect of changes of exponents on the total energy (in −a.u.) of* HeH^+ *at various interatomic distances for a basis set of 21 Gaussian functions (9500/4300)*

Exponent Set	Interatomic *distance*										
Numbers	1.450	1.453	1.455	1.457	1.4601	1.465	1.470	1.475	1.480	1.485	1.490
*HeS*3, *HeP*2, *H*1	2.929727	2.929733	2.929736	2.929737	2.929738						
*HeS*1, *HeP*2, *H*1	2.929011	2.929017	2.929021	2.929021	2.929021						
*HeS*2, *HeP*2, *H*1	2.927136	2.927144	2.927149	2.927151	2.927152		2.927139	2.927121	2.927096	2.927064	2.927025
*HeS*4, *HeP*2, *H*1	2.929115	2.929119	2.929122	2.929130	2.929121		2.929099	2.929075	2.929047	2.929018	2.928967
*HeS*3, *HeP*1, *H*1	2.930068	2.930069	2.930072	2.930070	2.930067		2.930036	2.930009	2.929975	2.929933	2.929885
*HeS*3, *HeP*3, *H*1	2.930184[a]	2.930188[a]	2.930192[a]	2.930192[a]	2.930192[a]	2.930184[a]	2.930169[a]	2.930147[a]	2.930118[a]	2.930080[a]	2.930036[a]
*HeS*3, *HeP*4, *H*1	2.929899	2.929900	2.929899	2.929896	2.929891	2.929875	2.929852	2.929821	2.929784	2.929738	2.929686
*HeS*3, *HeP*5, *H*1	2.928989	2.928990	2.928990	2.928989	2.928986	2.928972	2.928953	2.928926	2.928892	2.928752	2.928804
*HeS*3, *HeP*51, *H*1			2.929381	2.929382	2.929381						

[a] Interated to 10^{-6}.

Table 5. *Effect of changes of exponents on the total energy (in −a.u.) of* HeH^+ *at various interatomic distances for a basis set of 31 Gaussian functions (9555/4300)*

Exponent Set	Interatomic Distance												
Numbers	1.40	1.450	1.452	1.455	1.460	1.465	1.470	1.475	1.480	1.485	1.490	1.50	1.55
*HeS*6, *HeP*7, *H*1	2.926471	2.927426	2.927445	2.927473	2.927511		2.927515		2.927591		2.927585	2.927553	2.927019
*HeS*7, *HeP*7, *H*1	2.805029	2.807075	2.807142	2.807243	2.807406		2.807713	2.807859	2.807998	2.808132			
*HeS*7, *HeP*6, *H*1	2.923697	2.924774	2.924799	2.924835	2.924886		2.924966			2.925032	2.925039		
*HeS*8, *HeP*7, *H*1	2.926773	2.927677	2.927693	2.927719			2.927797	2.927807	2.927811	2.927807	2.927796		
*HeS*7, *HeP*8, *H*1	2.927951	2.928761	2.928774	2.928793	2.928816		2.928839	2.928839	2.928832				
*HeS*5, *HeP*7, *H*1	2.920655	2.920731	2.926852	2.926878	2.920621								
*HeS*9, *HeP*9, *H*1	2.929520		2.930002	2.930002									
*HeS*91, *HeP*9, *H*1	2.929317	2.929804	2.929805	2.929806	2.929800	2.929785							
*HeS*9, *HeP*91, *H*1		2.929805	2.929807	2.929813									
*HeS*92, *HeP*9, *H*1	2.926917	2.927396		2.927399	2.927392								

Table 6. *Effect of changes of exponents on the total energy (in −a.u.) of* HeH^+ *at various interatomic distances for a basis set of 37 Gaussian functions (9555/4333)*

Exponent Set	Interatomic Distance											
Numbers	1.40	1.450	1.452	1.455	1.460	1.470	1.475	1.480	1.485	1.490	1.50	1.55
*HeS*7, *HeP*7, *H*1	2.926553		2.927497	2.927524	2.927559	2.927606	2.927619	2.927624	2.927621	2.927611	2.927572	2.926997
*HeS*8, *HeP*7, *H*1			2.927693	2.927719	2.927752	2.927797		2.927811				
*HeS*6, *HeP*7, *H*1			2.927445	2.927473	2.927511	2.927566		2.927590				
*HeS*14, *HeP*12, *H*1	2.929419		2.929947		2.929946							
*HeS*9, *HeP*9, *H*1	2.929520	2.930001	2.930001	2.930002	2.929993							

Table 7. *Orbital energy and dipole moment for the 21 basis function set at* $R = 1.455$ *a.u. for different sets of exponents*

Exponent Set Numbers	−Total energy (a.u.)	μ_x (Debye)	−Orbital energy (a.u.)
HeS2, HeP2, H1	2.927151	2.512087	1.6348
HeS3, HeP5, H1	2.928989	2.516825	1.6357
HeS1, HeP2, H1	2.929021	2.512736	1.6364
HeS4, HeP2, H1	2.929122	2.515126	1.6360
HeS3, HeP2, H1	2.929736	2.512707	1.6367
HeS3, HeP4, H1	2.929899	2.516333	1.6357
HeS42, HeP3, H1	2.930054	2.514477	1.6358
HeS3, HeP1, H1	2.930072	2.515155	1.6357
HeS45, HeP3, H1	2.930131	2.514618	1.6358
HeS43, HeP3, H1	2.930173	2.514756	1.6357
HeS3, HeP3, H1	2.930192	2.513466	1.6366
HeS41, HeP3, H1	2.930193	2.513491	1.6366
HeS44, HeP3, H1	2.930206	2.514672	1.6358

Tables 3 to 6 list the energies found for various basis sets and various internuclear distances. Table 7 gives a representative number of values of dipole moment and orbital energy.

From the energy values found, it appears that a multiplicative factor of approximately 4 yields the lowest energy of those sets of exponents considered. The set of exponents which gave the "best" energies with the 21 functions can be seen to yield a minimum energy of -2.93019 a.u. in the range from 1.455 to 1.460 bohr. This energy value is in reasonable agreement with the results of previous workers. However, the energy value obtained here for the minimum is about $3 \cdot 10^{-3}$ a.u. higher than that of Peyerimhoff [12] and $1.3 \cdot 10^{-2}$ a.u. higher than the values of Harris [5] and Michels [8], the latter two values being obtained at 1.44 bohr.

Table 5 illustrates the results of a 31 basis set obtained from the 21 basis set by addition of p functions to the helium atom in the Y and Z directions. Table 6 indicates that the addition of p functions in the Y and Z direction to the hydrogen atom of helium hydride in order to pass from the 31 basis function set provides no great advantage from an energy point of view. Only a limited examination of exponents was done for the 37 basis function set when it appeared that little benefit could be gained by so doing.

It should be mentioned that, considering the method employed in the present work for varying the exponents, it is not impossible that only relative minima have been found. However, it is believed that this is unlikely. Further, in a calculation in which only the optimized wave function was sought, it is probable that the optimization tests would be made at one fixed interatomic distance, at least until the exponents fell close to the optimum ones. In the present work, more emphasis has been placed on the path to the optimum wave function than on the optimized function itself. Hence, a number of different interatomic distances have been considered at each step.

In Table 7, the orbital energy and dipole moment for helium hydride (with the previously mentioned coordinates) obtained for $R = 1.455$ a.u., with 21 basis functions and the exponents given in Table 4, are shown. In addition the results of some calculations which were performed only at 1.455 a.u. are also shown. These have helium *s* exponents labelled *HeS*41 to *HeS*45. The lowest energy obtained with the 21 basis function sets, and in fact in all the calculations, is -2.930206 a.u. which was found at $R = 1.455$ a.u.

Hopefully the present study has provided some indication of the manner in which wave functions constructed from Gaussian functions are altered with change in the size of basis set, and particularly with the values of exponents used. Further, it is hoped that this work, in connection with future studies already in progress, may furnish sufficient information for the establishment of simple empirical rules for finding near-optimum exponents.

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