Theoret. Chim. Acta (Berl.) 60, 1–10 (1981)

THEORETICA CHIMICA ACTA

A Simple Comparative Test of Multiple Versus Single-Centered Spherical Gaussians

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HeH^{++} was selected as a simple model for the comparison of relative efficiencies of single and multi-centered Gaussian functions in computing molecular orbitals and their corresponding energies. One-, two-, and three-center linear combinations of twelve basis functions were applied to the calculation of potential curves for the ground state and lowest two excited sigma states of HeH^{++}. A point-by-point comparison was made with the same states generated by an exact solution calculation. This comparison demonstrated that the multi-centered functions were capable of reproducing energy minima, potential curve crossings and dissociation modes in agreement with the exact calculation. The single center functions were not capable of duplicating this behavior.

Key words: Spherical Gaussians, HeH^{++}.

1. Introduction

The work of Butscher et al. [1], and Rothenberg and Schaefer [2] has indicated the usefulness of bond-centered orbitals in both SCF and extensive CI calculations. These orbitals seem to have more flexibility than the usual atom-centered polarization basis functions. One- and two-center spherical Gaussian models have been used by Katriel and Adam for the H_2^+ molecule [3–5]; Hoyland [6] and Schwartz and Schaad [7] have used multiple-centered floating Gaussians on H_2^+. Rouse and Frost [8] demonstrated an improvement in energy in a wide variety of molecules when two Gaussians per center were employed in the calculation. In the present work we have explored the possibility of combining features of all of these approaches in a model which is simple enough both to display the advantages of the bond-centered approach and to facilitate comparison with the exact solution calculation.

We have adopted a one-electron molecule (HeH^{++}) with as many as three independently floating centers, using a sufficient number of Gaussians per center to overcome inherent deficiencies in this function. Optimization of wave functions was performed with various combinations of Gaussians having fixed and floating centers in order to compare the relative merit of single and multiple centers, both for excited and ground states.

In most molecules the basis functions involved in the bonding orbitals are not of 1*s* type, but have a combination of *s*-, *p*-, and *d*-character. Therefore we have extended the calculations to include the first two excited states as well as the ground state, in order to incorporate this type of bonding characteristic. Accurate electronic energies are available for the one-electron, two-center problem, enabling a comparison between the results of our model and those of the exact solution. In addition, the work of Bates [9], illustrating the exact wave function of the molecule, makes possible a graphic comparison with the wave functions obtained in this investigation. The heteronuclear HeH^{++} was chosen since the general effects of unequal charge distribution are considered to be more typical of a real chemical bond. Its known dissociation properties – leading to He^{++} and H in one case and to He^{+} and H^{+} in another provide a good test of the model.

2. The Model

The wave functions used in these calculations were linear combinations of floating spherical Gaussians of the form $\Psi = \exp[-AB^n(r-C)^2]$. This particular form is that used by Katriel and Adam [4], who showed, in calculatons of the 2-center spherical limits for H_2^+, that this parameter choice is essentially equivalent to a completely optimized set of orbital exponent coefficients. For $n = 8$ they noticed no change in the fifth decimal place in the energy corresponding to the wave function in calculations performed on the H atom. A, B, and C are adjustable parameters. The wave function used in each calculation was a 1-, 2-, or 3-center linear combination of twelve functions of the above form. The exponent n was stepped integrally from 1 to 12 for the 1-center functions, from 1 to 6 for each center of the 2-center functions, from 1 to 4 for each center of the 3-center functions. The total number of orbitals was fixed at twelve so that a judgement might be made as to the relative effectiveness of the number of centers – fixed or floating – in providing a reliable energy, and for the practical consideration that this choice fit the time and space limitations of our computing facility. In the case of the 1-center functions, our results showed that no improvement could be obtained by adding more Gaussians; four Gaussians per center on the 3-center function was probably not sufficient to give maximum reliability for this type of function, however.

Potential energy curves were calculated for the three lowest energy states of HeH^{++} at internuclear separations of 0.1, 0.5, 2.0, 4.0, 6.0 and 12.0 a.u.. Complete optimization of the non-linear parameters was carried out at each point to give a minimization of the energy.

In the case of the 2- and 3-center wave functions, various combinations of fixed and floating centers were compared. The 2-center functions were formed either with centers which were allowed to "float" in the minimization of energy routine, or with centers which were fixed at the locations of the nuclei. The 3-center functions were formed either by allowing all three centers to float or with two centers fixed at the nuclear sites, the third center being permitted to float. We will refer to these as three-center floating and three-center fixed/floating, respectively. This scheme led to the variation of three non-linear parameters for the 1-center functions; viz., A, B, and C; four non-linear parameters for the 2-center fixed center functions (A_1, B_1, A_2, B_2); six non-linear parameters for the 2-center floating center functions; seven for the 3-center functions with two fixed and one floating center; and nine for the 3-center floating center functions.

The non-linear optimization was performed on the individual ground and excited state functions, resulting in a more accurate, but non-orthogonal set. In order to obtain an orthogonal set, minimization of the sum of the ground state and first two excited state energies was performed. The optimization was terminated when there was no longer any change in the seventh decimal place (sixth place for the sum minimization). The computer program which accomplished the minimization of energy employed the STEPIT subroutine authored by Chandler [10] and furnished through the Quantum Chemistry Program Exchange. The routine performs a point-by-point direct search and does not use the method of steepest descents. To reduce the possibility of locating spurious local minima, the parameter search was begun at a number of different points. The program was executed on the University's CDC 3200 System. Each point on the potential curve calculated by the above method was compared with the result obtained for the exact solution obtained from the OEDM routine of Power [11].

3. Results and Discussion

It should be noted from Table 4 that all of the wave functions at 0.5 a.u. internuclear separation are qualitatively in agreement except for the one-center function, positioned at 0.407 a.u., which gives a reasonable value in the internuclear region at the expense of low values at the nuclear positions. The two-center, fixed position function is adequate at the nuclear positions but gives too low a value in the internuclear region. This deficiency in the wave function is also reflected in the energy (Table 1). The two-center floating-position function shows only minor variation in either energy or wave function when compared to the three-center functions and the three center fixed/floating function is almost identical with the three-center floating function (Fig. 1 and Table 4).

The first excited state, Ψ_1, ($2p\sigma$), at 0.1 a.u. internuclear separation, which should show a pronounced "p" character, cannot be represented by the one-center function which resembles a $2s$ function (Table 5) and gives much too high an energy. The two-center functions give energies which differ from the exact

Table 1. Ground state energy values, E_0, for selected internuclear separations. All energies and distances are in atomic units

R	0.1	0.5	2.0	4.0	6.0	12.0
Exact Value	15.58868	0.33446	−1.51219	−1.75061	−1.83345	−1.91667
E_0 minimized						
1 center, floating	15.59205	0.39613	−1.50070	−1.75009	−1.83335	−1.91666
2 center, fixed	15.58911	0.34230	−1.50542	−1.74944	−1.83270	−1.91603
2 center, floating	15.58901	0.33654	−1.51043	−1.75049	−1.83334	−1.91667
3 center, 2 fixed 1 floating	15.58892	0.33533	−1.51097	−1.75023	−1.83333	−1.91662
3 center, floating	15.58883	0.33498	−1.51150	−1.75053	−1.83340	−1.91666
$E_0+E_1+E_2$ minimized						
1 center, floating	15.59206	0.39625	−1.50063	−1.74990	−1.83328	−1.91658
2 center, fixed	15.59862	0.34627	−1.50333	−1.74794	−1.83110	−1.91429
2 center, floating	15.59525	0.34096	−1.50673	−1.74803	−1.83111	−1.91429
3 center, 2 fixed, 1 floating	15.59251	0.33874	−1.50618	−1.74294	−1.82891	−1.91275
3 center, floating	15.59204	0.33945	−1.50684	−1.74298	−1.82876	−1.91256

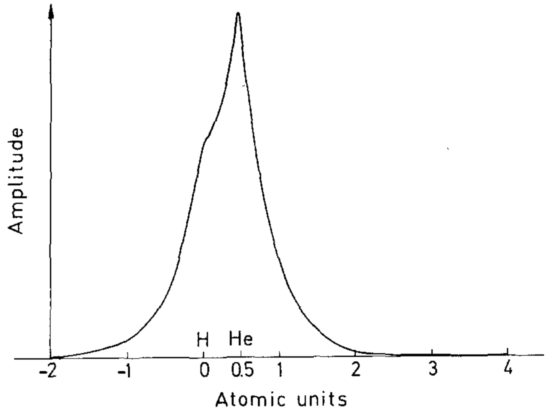

Fig. 1. Variation of amplitude of wave function along line joining nuclei. Ψ_0, 3-center, floating, at 0.5 a.u. internuclear separation

values in the fourth decimal place and do show the requisite "p" nature of the function (Fig. 2a and Table 5). In this instance the two-center functions give slightly lower energies than the three-center ones. The function is quite symmetric with respect to the nuclear positions and shows a node in the internuclear region, eliminating the need for a third independent center.

Whereas the ground state ($1s\sigma$) dissociates into H^+ and He^+, the $2p\sigma$ state dissociates into H and He^{++} [9]. The one-center function shows the correct dissociation pattern for the ground state and gives an energy essentially equal to the exact value at 12 a.u. (Table 1). However the one-center function also

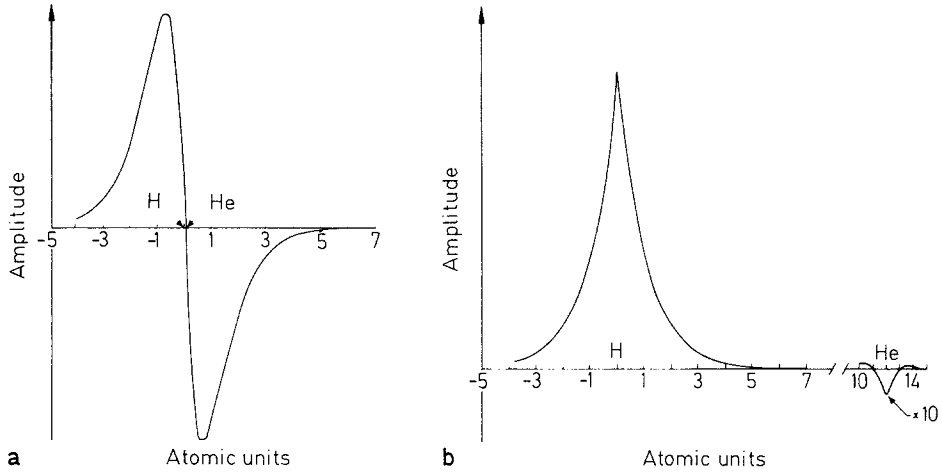

Fig. 2. Variation of amplitude of wave function along line joining nuclei. (a) Ψ_1, 2-center, floating, at 0.1 a.u. internuclear separation. (b) Ψ_1, 2-center, floating, at 12.0 a.u. internuclear separation

Table 2. First excited Sigma state energy values, E_1, for selected internuclear separations. All energies and distances are in atomic units

R	0.1	0.5	2.0	4.0	6.0	12.0
Exact Values	18.87200	2.80225	−0.34519	−0.53108	−0.51251	−0.50046
E_1 minimized						
1 center, floating	18.88658	2.99118	0.12419	−0.24421	−0.33322	−0.41666
2 center, fixed	18.87262	2.80941	−0.30252	−0.50069	−0.50167	−0.49984
2 center, floating	18.87223	2.80343	−0.32304	−0.50577	−0.50294	−0.49992
3 center, 2 fixed 1 floating	18.87351	2.80351	−0.34193	−0.52702	−0.50949	−0.49876
3 center, floating	18.87300	2.80338	−0.34291	−0.52836	−0.50990	−0.49886
$E_0+E_1+E_2$ minimized						
1 center, floating	18.88658	2.99159	0.12425	−0.24386	−0.33314	−0.41664
2 center, fixed	18.87791	2.81068	−0.30238	−0.50005	−0.50138	−0.49984
2 center, floating	18.87678	2.80589	−0.31488	−0.50479	−0.50269	−0.49992
3 center, 2 fixed 1 floating	18.87376	2.80761	−0.33994	−0.52394	−0.50560	−0.49876
3 center, floating	18.87322	2.80543	−0.34026	−0.52564	−0.50673	−0.49886

and incorrectly dissociates to H^+ and He^+ for the $2p\sigma$ state, and exhibits a large error in energy at 12 a.u. (Table 2). Even though the optimization search at 12.0 a.u. internuclear separation was initiated by placing the center at the H position, the function quickly migrated, centering itself near the He. The other four functions exhibit the correct dissociation behavior for the $2p\sigma$ state (Fig. 2b and Table 6). The two-center functions again give slightly lower energies than the three-center ones. This behavior can be attributed to the difficulty of obtaining complete optimization when the floating centers tend to coalesce.

Table 3. Second excited Sigma state energy values, E_2, for selected internuclear separations. All energies and distances are in atomic units

R	0.1	0.5	2.0	4.0	6.0	12.0
Exact Values	18.88617	2.98805	0.21291	−0.20685	−0.36484	−0.42850
E_2 minimized						
1 center, floating	19.50346	3.53499	0.57671	0.10973	−0.03464	−0.13877
2 center, fixed	18.88765	2.99227	0.24338	−0.18656	−0.32445	−0.41546
2 center, floating	18.88684	2.98932	0.21482	−0.18703	−0.32465	−0.41547
3 center, 2 fixed, 1 floating	18.88681	2.98933	0.21549	−0.20165	−0.35972	−0.42404
3 center, floating	18.88680	2.98873	0.21455	−0.20329	−0.36120	−0.42519
$E_0+E_1+E_2$ minimized						
1 center, floating	19.50348	3.53518	0.57679	0.10983	−0.03444	−0.13870
2 center, fixed	18.88972	2.99449	0.24425	−0.18629	−0.32424	−0.41506
2 center, floating	18.88820	2.99120	0.23652	−0.18518	−0.32395	−0.41506
3 center, 2 fixed 1 floating	18.88707	2.99015	0.21811	−0.19850	−0.34830	−0.42072
3 center, floating	18.88733	2.99006	0.21836	−0.19757	−0.34820	−0.42091

Table 4. Comparison of Ψ_0 at various positions along internuclear axis, at 0.5 a.u. internuclear separation. (Hydrogen at 0.0 a.u.) All positions and energies are in atomic units

	1 center, floating	2 center, fixed	2 center, floating	3 center, fixed/floating	3 center, floating
E_0	0.39613	0.34230	0.33654	0.33533	0.33498
Center 1	0.40748	0.0	0.05906	0.0	0.01917
Center 2		0.5	0.48918	0.36188	0.41999
Center 3				0.5	0.50008
Ψ_0					
Position			Amplitude of wave function		
−0.5	0.23950	0.32750	0.31046	0.30328	0.30471
0.0	0.80536	1.04030	1.01755	1.05732	1.04234
0.25	1.33979	1.26875	1.32153	1.31334	1.31769
0.5	1.48489	1.75632	1.74860	1.74451	1.77100
1.0	0.52282	0.54019	0.52125	0.50464	0.50803

The exact $2p\sigma$ function exhibits an energy minimum at approximately 3.9 a.u. [11]. The one-center function fails to show a minimum, whereas the two-center functions show a shallow minimum in the region of 4.0 to 6.0 a.u. (Table 2). The three-center functions show a minimum comparable in depth to the exact function at 4.0 a.u. [11].

The second excited state, Ψ_2, obtained in our studies from energy variation, is actually a composite of two states, a $2s\sigma$ which has lower energy from 0.0 a.u.

Table 5. Comparison of Ψ_1 at various positions along internuclear axis, at 0.1 a.u. internuclear separation. (Hydrogen at 0.0 a.u.) All positions and energies are in atomic units

	1 center, floating	2 center, fixed	2 center, floating	3 center, fixed/floating	3 center, floating
E_1	18.88658	18.87262	18.87223	18.87351	18.87300
Center 1	0.06886	0.0	−0.01907	0.0	−0.03232
Center 2		0.1	0.15248	0.02945	−0.02232
Center 3				0.1	0.16118
Ψ_1 Position			Amplitude of wave function		
−0.5	−0.07168	0.38296	0.37653	0.37875	0.37761
0.0	−0.80209	0.05295	0.04990	0.02665	0.03667
0.05	−0.88444	−0.01247	−0.01700	−0.03208	−0.02376
0.1	−0.87062	−0.07639	−0.08316	−0.08900	−0.08329
0.6	−0.10176	−0.37294	−0.38078	−0.38224	−0.38409

Table 6. Comparison of Ψ_1 at various positions along internuclear axis, at 12.0 a.u. internuclear separation. (Hydrogen at 0.0 a.u.) All positions and energies are in atomic units

	1 center, floating	2 center, fixed	2 center, floating	3 center, fixed/floating	3 center, floating
E_1	−0.41666	−0.49984	−0.49992	−0.49876	−0.49886
Center 1	11.99717	0.0	0.01163	0.0	0.01298
Center 2		12.0	12.00000	11.27894	11.26331
Center 3				12.0	12.00158
Ψ_1 Position			Amplitude of wave function		
0.0	0.00004	0.53585	0.53497	0.50578	−0.50515
12.0	−0.54752	−0.00001	−0.00001	−0.00178	0.00172

to the crossing point at approximately 3.6 a.u., and a $3d\sigma$ state which has the lower energy from the crossing point to the dissociation limit [11]. Thus the calculated function should have a $2s\sigma$ character at 2.0 a.u. and a $3d\sigma$ character at 4.0 a.u.. The one-center function shows a $3s\sigma$-type behavior and a correspondingly poor energy. The two-center fixed center wave function has a pronounced peak at the H position rather than the smooth curve given by the two-center floating and the three-center functions, and consequently too high an energy. The three-center functions have energies comparable to the exact value and a qualitatively similar functional form of $2s\sigma$ type (Fig. 3a and Table 7).

At 4.0 a.u. the one-center continues to exhibit a $3s\sigma$-type behavior and too high an energy. Both two-center functions approximate a $3d\sigma$ function but are too

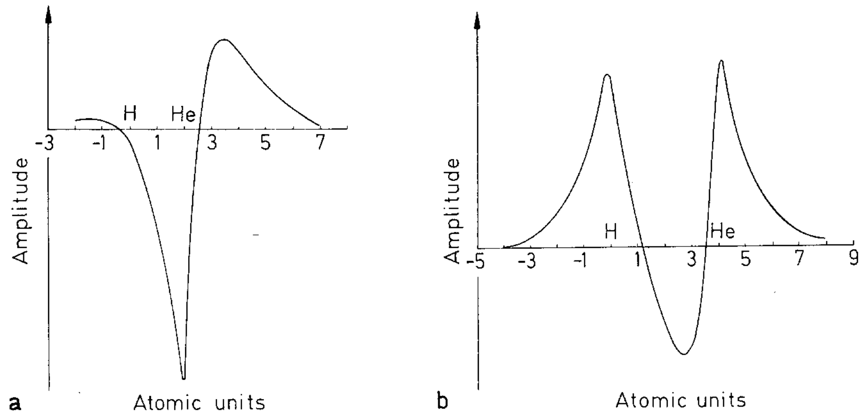

Fig. 3. Variation of amplitude of wave function along line joining nuclei. (a) Ψ_2, 3-center, floating, at 2.0 a.u. internuclear separation. (b) Ψ_2, 3-center, floating, at 4.0 a.u. internuclear separation

Table 7 Comparison of Ψ_2 at various positions along internuclear axis, at 2.0 a.u. internuclear separation. (Hydrogen at 0.0 a.u.) All positions and energies are in atomic units

	1 center, floating	2 center, fixed	2 center, floating	3 center, fixed/floating	3 center, floating
E_2	0.57671	0.24338	0.21482	0.21549	0.21455
Center 1	1.98102	0.0	1.58289	0.0	1.56409
Center 2		2.0	1.97417	1.71827	1.97574
Center 3				2.0	2.00950
Ψ_2					
Position			Amplitude of wave function		
−0.5	−0.02299	−0.09669	0.00451	−0.01862	0.00395
0.0	−0.04546	−0.13224	−0.02597	−0.05359	−0.02532
0.5	−0.05162	−0.07720	−0.08093	−0.08564	−0.08143
1.0	−0.01211	−0.07411	−0.16547	−0.15765	−0.16605
1.5	0.11979	−0.18907	−0.28135	−0.28199	−0.27945
2.0	0.37364	−0.46013	−0.43265	−0.42551	−0.45178
2.5	0.10512	−0.13206	−0.03050	−0.03403	−0.03116

low at the H position and too high at the He position. They also decrease rapidly beyond the He position. The three-center functions have the qualitatively correct $3d\sigma$ appearance although the three-center fixed/floating has too high a value at the He position (Fig. 3b and Table 8).

Minimization of the sum of the energies of the ground and first two excited states raises the energy of the one-center function only in the fourth or fifth decimal place, leaving the energies equally good for the ground state and equally poor for the excited states. In general, the energy increase is in the third decimal

Table 8 Comparison of Ψ_2 at various positions along internuclear axis, at 4.0 a.u. internuclear separation. (Hydrogen at 0.0 a.u.) All positions and energies are in atomic units

	1 center, floating	2 center, fixed	2 center, floating	3 center, fixed/floating	3 center, floating
E_2	0.10973	−0.18656	−0.18703	−0.20165	−0.20329
Center 1	3.99011	0.0	−0.06580	0.0	−0.04967
Center 2		4.0	3.98824	3.73719	3.65725
Center 3				4.0	4.07086
Ψ_2					
Position			Amplitude of wave function		
−0.5	0.02292	0.12812	0.13843	0.22320	0.23628
0.0	0.01637	0.19314	0.18518	0.30965	0.30803
0.5	0.00472	0.10475	0.09745	0.17078	0.16225
1.0	−0.01209	0.03477	0.03011	0.04195	0.03683
2.0	−0.04791	−0.04913	0.05078	−0.13716	−0.14322
3.0	−0.00797	0.00535	0.00765	−0.16476	−0.17380
3.5	0.11514	0.18116	0.18713	0.00657	−0.02021
4.0	0.36082	0.52650	0.52228	0.34909	0.29873
4.5	0.10795	0.17641	0.17008	0.23381	0.24726

place for the two-center and three-center functions. Minimization of the sum of energies with respect to the non-linear parameters seems to provide an attractive method of obtaining a flexible set of orthogonal basis functions.

Conclusion

The one-center floating function is capable of reproducing *sσ*-type behavior, but is incapable of reproducing the excited state wave functions for HeH^{++}, irrespective of the number of Gaussians used at the single center. Thus it would not seem to be the most appropriate choice for valence state orbitals which involve *p*- and *d*-basis functions.

The two-center functions seem reasonably capable of reproducing *sσ*- and *pσ*-type behavior, although floating centers are certainly preferable at certain values of internuclear separation.

In the case of *dσ*-type functions, when the wave function has extrema at three positions, only the three-center functions are capable of reproducing the behavior and there seems to be relatively little reason to prefer the three-center floating to the three-center fixed/floating function. Economic considerations would then seem to favor the three-center fixed/floating function as a possible alternative to *d*- and *f*-type atomic polarization functions in various types of many-electron calculations. Admittedly this simple model gives only an indication of such behavior and further testing with many-electron wave functions should be carried out.

The method of obtaining sets of orthogonal functions through optimization of the sum of state energies instead of individual optimization of states may also lend itself to many-electron calculations, since in this particular model there seemed to be no great loss in accuracy of energy or wave function.

One perhaps obvious but reassuring conclusion reached in this study is that obtaining an energy close to the exact value leads to a wave function also qualitatively similar to the exact one, even though the basis functions employed have a restricted flexibility.

Acknowledgements. The authors are grateful to Dr. Walter J. Smith for generously furnishing us with the plotting routine, to Mr. Mitchell Burke for the art work and to the staff of the Duquesne University Systems Center for their assistance and unflagging cooperation.

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Received January 29, 1981