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A Comparison of Different Contractions for Molecular Calculations with Gaussian-Type Functions

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The effect of various possible contractions of a gaussian basis set is investigated for atomic and molecular calculations. The gaussian basis set used consists of 11*s*-type functions and 7*p*-type functions. Atomic calculations for the atoms Li to F are reported with fourteen different contractions of the *s* orbitals. The effect of the same contractions has also been investigated for molecular calculations of LiH, BH, CH_2, NH_2^-, H_2O, and FH, together with the effect of the contraction for the *p* orbitals and for the *s* orbitals of the hydrogen atom. It is shown that the contraction in itself does not affect seriously the quality of a molecular calculation, but that a wrong choice of the contraction can produce a poor result.

Der Einfluß der verschiedensten Kontraktionen einer Basis von Gauß-Funktionen bei Berechnung atomarer oder molekularer Systeme wird untersucht. Diese Basis besteht zunächst aus 11 *s*-Funktionen und 7 *p*-Funktionen. 14 verschiedene Kontraktionen werden für die Atome Li bis F sowie für die Moleküle LiH, BH, CH_2, NH_2^-, H_2O und FH getestet. Wie zu erwarten wird die Genauigkeit nicht wesentlich beeinflußt, solange man nur die „richtigen" Kontraktionen wählt.

On étudie l'effet des différentes contractions possibles d'une base de fonctions gaussiennes dans le cas d'atomes et de molécules. La base de fonctions gaussiennes comprend 11 fonctions du type *s* et 7 fonctions du type *p*. On donne les résultats de quatorze différentes contractions des orbitales *s* pour les atomes du Li à F ainsi que pour les molécules LiH, BH, CH_2, NH_2^-, H_2O et FH. L'effet de la contraction des orbitales *p* ainsi que des orbitales *s* des atomes d'hydrogène est également discuté pour les molécules CH_2 et H_2O. On montre que la contraction par elle-même n'affecte pas sensiblement les résultats obtenus a condition d'effectuer un choix judicieux parmi les contractions possibles.

1. Introduction

One of the bottlenecks in *ab-initio* quantum mechanical calculations has been the evaluation of many-center integrals. The use of Slater orbitals appeared restricted mainly to linear molecules [1] or to small molecules using a one-center expansion [2]. For large molecules of general geometry, the difficulty has been presently overcome mainly through the use of Gaussian orbitals instead of Slater orbitals. Unfortunately, one needs a much larger basis set to obtain a given energy, say the Hartree-Fock energy, by using Gaussian as compared with Slater-type orbitals [3]. This drawback can have some drastic consequences, since the number of two-electron integrals required for an SCF computation is proportional to the fourth power of the number of atomic functions. Between 9 to 11 *s*-type Gaussian functions, and 5 to 7 *p*-type Gaussian functions are needed to describe adequately an atom of the first period, i.e. to obtain an energy reasonably close to the Hartree-Fock [3]. This could turn untractable calculations even for very simple molecules.

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With a basis set of 11s and 7p functions, a first row diatomic molecule requires 64 functions, not including d-like polarization functions, and the total number of integrals over basis functions already exceeds two millions. In the computation scheme of the IBMOL program for molecular calculations [4], these integrals over the basis functions are transformed into integrals over the symmetry-adapted functions. The computational time required for this transformation is proportional to the size of the list. Let us emphasize that this transformation has to be done even in the case where there is no symmetry in the molecule. Indeed, the transformation sets up the proper combination of coulomb and exchange integrals, so that the integral list can be used in the more efficient way during the SCF section. This integral list is read repeatedly at each SCF iteration, and it can be said that the number of symmetry adapted integrals, hence the computation time, is proportional to the fourth power of the number of atomic functions. This would seem to rule out the use of Gaussian orbitals for large molecular systems.

Clementi suggested to overcome this difficulty through the use of a "contraction" [4, 5], i.e. to replace the individual Gaussian basis functions with some appropriate linear combinations of Gaussians (called "contracted" functions). This would reduce the number of stored integrals, hence the time needed for the symmetry transformation and for each SCF iteration. Practically the contracted orbitals are chosen through a careful analysis of the atomic expansion coefficients, by trying to find appropriate linear combinations of the atomic functions. Examples for the Ne atom and the N_2 molecule were given by Clementi in the description of the IBMOL program [4]. Since that time, the process of the contraction has been used through numerous molecular calculations. The most striking example of the usefullness of the contraction was probably a set of SCF calculations by Clementi for large aromatic compounds (pyrrole, pyridine, etc.) [6]. For instance, contraction brought down the number of integrals for pyridine from twenty millions to two hundred thousands.

Our purpose in this paper is to reascertain the choice of the contracted orbitals. Given a definite basis set of atomic Gaussian orbitals and a preassigned size for the contracted basis set, what would be the best choice of contracted orbitals, i.e. how should we group together the basis orbitals to build the contracted orbitals. The answer can be straightforward only in a few cases. For instance, Clementi used a basis set of 7s atomic orbitals for the C and N atoms of pyridine, which he contracted to two orbitals representative of the 1s and the 2s atomic orbitals [6]. The choice of the linear combinations of Gaussians is determined in this case by the fact that, out of the 7s basis functions, only the first five contribute to the 1s atomic orbital, while only the last two contribute to the 2s atomic orbital (apart for the orthogonalization of the 2s orbital to the 1s). However, such an unambiguous determination of the contracted orbitals should occur in only very few cases, namely when using only one contracted orbital per shell. In the other cases, there will always be some arbitrariness in the choice of the linear combinations, even if the set of Gaussian basis functions is well divided into subsets, with each of the subset contributing to a different atomic shell (up to now, this has been found approximately true for first-row atoms). One might hope that some small differences in the choice of the linear combinations will not affect seriously the total energy (in what follows, we shall restrict ourselves to a discussion of the best possible contraction in terms of the total energy). Unfortunately, this is not true as it will be shown from the calculations reported in this paper.

To illustrate this point, let us give an example where the choice of the linear combinations for the contracted orbitals turned out to be a poor one. We performed two calculations for the CH_3F molecule. In the first one, we used the basis set obtained by Huzinaga [3] and consisting of 9 Gaussian functions of *s*-type with 5 Gaussian functions of *p*-type (and 4*s*-type Gaussian functions for the hydrogen atoms). This basis set was contracted to a set of 5*s* orbitals and 3*p* orbitals (with 3*s* orbitals for the hydrogen atoms). The energy turned out to be − 139.032 a.u. In the second calculation, we used a larger basis set (see further) consisting of 11*s* functions and 7*p* functions for the C and F atoms, together with 6*s* functions for the H atoms. As expected, the energies of the C and F atoms in their ground states are lower with this 11*s*, 7*p* set than with the 9*s*, 5*p*. The same number of contracted functions (5*s*, 3*p*/3*s*) was built from this large basis set. However, this calculation produced a higher energy of − 139.004 a.u., despite the use of a larger basis set and of the same number of contracted functions. Comparison with atomic calculations using contracted basis sets showed us that the poor result of the second calculation could be traced to a poor choice of the linear combinations.

This led us to examine the effect of the different possible contractions on atomic and molecular calculations, energy speaking. Atomic calculations have been included from a comparison point of view, since the contraction is of practical interest only for molecular calculations. We shall discuss first the results obtained for the atomic calculations and next the one for the molecular calculations. To make the discussion easier, the detail of the calculations and the bulk of the numerical results is given in the Appendix.

2. Effect of Different Contractions on Atomic Calculations for First-Row Atoms

The Gaussian basis set used is an unpublished one due to Huzinaga *et al.* [7] consisting of 11*s*-type functions and 7*p*-type functions. So far it is the best optimal basis set presently obtained with Gaussian orbitals for the atoms of the first row. Exponents, coefficients of the atomic orbital expansions and the corresponding total energies are reported in the Appendix.

Before going through the results of the calculations, let us first discuss how an atomic calculation can depend, energy speaking, on the choice of the contracted basis set. Since we always choose the coefficients of the contraction from the expansion coefficients of the uncontracted atomic calculation, it is clear that for the first row atoms the energy will not depend on the contraction used for the *p* orbitals. Contraction for the *p* orbitals is then merely equivalent to a unitary transformation, which will leave the energy invariant. The same is not true for the *s* orbitals: taking the contraction coefficients equal to the expansion coefficients of the 1*s* atomic orbital distorts the representation of the 2*s* atomic orbital and vice-versa. The contraction for the *s* orbitals decreases the flexibility of the wave function, hence raising slightly the value of the total energy.

Table 4 in the Appendix reports the energies obtained for some fourteen different contractions of the *s* orbitals for the atoms Li to F. As already said, the contraction used for the *p* orbitals is irrelevant. In all the cases the number of contracted s orbitals was kept equal to 5. This number has been more or less chosen through some analogy with the number of Slater orbitals needed to get accurate Hartree-Fock atomic energies [8] and extensively used for molecular calculations [1]. It is small enough to keep molecular calculations tractable and large enough to provide much flexibility for an atomic or molecular wavefunction. In fact, it is found that the best energy for each atom, using this number of contracted s functions, is very close to the energy obtained for the uncontracted atomic calculation. For instance, for the carbon atom, the energy reported for the $11s$, $7p$ basis set is -37.6874 a.u. and the best energy from the calculations with contraction is -37.6849 a.u. The difference is small enough if one remembers that, for molecules other than linear or diatomics, there are few calculations with energy values less than 0.1 a.u. from the Hartree-Fock value.

The important conclusion which comes out from Table 4 is that, for a given number of contracted orbitals, the energy value can be very sensitive to the choice of the linear combinations. For instance, the energy values for the fourteen calculations relative to the carbon atom will range from -37.659 a.u. to -37.6849. The difference is large enough to affect sizely the energy value for a molecular calculation. We have already reached one major conclusion, namely that, while the contraction in itself does not seem to affect seriously the quality of a molecular calculation, a wrong choice of the contraction can indeed bring a poor result. That is what happened in the previously reported calculation of CH_3F, which used the contraction reported as No. 1 in Table 4. Examination of Table 4 shows that this contraction yields a poor atomic energy for the carbon and fluorine atoms.

Although there is some variation from one atom to another, some contractions are definitely better than the others. However, it seems rather difficult, from an examination of Table 4, to make any prediction in advance concerning the best possible contractions. Relatively minor changes in the linear combinations can have a marked effect on the total energy. For instance, the two contractions labelled No. 7 and No. 8 in Table 3 differ only in the way the sixth basis orbital is associated with the others, either with the first five orbitals or with the seventh one. Yet this change has a pronounced effect on the total energy as can be seen from Table 4.

Up to now, we have been looking for the best contracted set, given the number of contracted orbitals and the contraction coefficients which were taken equal to the expansion coefficients of the atomic calculation. A further possibility is to optimize the contraction coefficients in a way analogous to the one used for the orbital exponents [9]. This has been done for each atom by choosing the best set of contracted orbitals from Table 4 and by optimizing the coefficients of the linear combinations. So far, the improvement obtained (see Table 5) is only very slight. In one sense, this is very reassuring, since it means that the contraction coefficients taken from the atomic expansion are nearly optimal. In what follows, we used the atomic expansion coefficients.

3. Effect of Different Contractions on Molecular Calculations for First-Row Atoms

Although the best contracted sets for the atoms will be a useful starting point for molecular calculations, it seems probable that they will no longer be the best ones. As it is well-known, the inner-shell orbitals are the more important ones for atomic calculations, since the main contribution to the energy comes from the 1*s* electrons. While this is still true for the atomic components of the molecular energy, the bond energy associated with the bond formation is sensitive mainly to the shape of the outer orbitals. While some contractions with more flexibility for the inner shells should give the best atomic results, the best molecular energies will be probably obtained when some freedom is left to the orbitals with the lower exponents. This led us to reinvestigate what are the best contracted sets for molecular calculations. Again we tried the effect of the fourteen different contractions of the *s* orbitals, and this has been done for a series of molecules including LiH, BH, CH_2, NH_2^-, H_2O and FH. The results are reported in Table 7 of the Appendix.

As already said, the contraction of the *p* orbitals was irrelevant for the atomic calculations. This is no longer true in a molecular calculation, since the *p* functions will appear in different molecular orbitals with different expansion coefficients. This led us to investigate also the effect on the molecular energy of the number of contracted *p* orbitals and, given this number, of the different possible contractions. The coefficients of the linear combinations have been taken from the atomic expansion. Two sets of calculations for the H_2O and the CH_2 molecules are reported in Table 8. The two sets differ in the number of *p* contracted orbitals, three for the first one and four for the second one.

Since the molecules under study are hydrides, we turned also to the problem of the contraction of the *s* orbitals for the hydrogen atom. Again two sets of calculations are reported in Table 9 for the H_2O and the CH_2 molecules. Two contracted orbitals were used for the hydrogen atom in the first set and three in the second set. The coefficients of the contraction are taken from the expansion coefficients given by Huzinaga [3].

A comparison of Tables 4 and 7 brings immediately that the best contracted sets for the molecules are not the same as for the atoms. For instance, the best set of contracted *s* orbitals for the carbon atom was the set No. 6, while for the molecule CH_2 it is the set No. 10. Of the fourteen sets, the first six have the last two *s* orbitals (of low exponents) No. 10 and 11 contracted together, while the last eight sets leave orbital No. 11 (which has the lowest exponent) free. One will notice that without exception the best atomic set always belongs to the first six sets, while usually the best molecular set is one of the last eight sets. This emphasizes what we said above about the importance of leaving more flexibility for the building of the outer shell in molecular calculations.

Examination of Table 7 shows that the best set of contracted *s* orbitals is different for each molecular calculation. This opens the question of which set to use for further calculations. There are two possibilities, namely to pick for each atom the best set from Table 7 or to use a given set for all the atoms. In this case, it seems that the set No. 10 or No. 12 would probably give the best results. One should notice that, although they are not the best ones, these sets give for each molecule studied an energy very close to the best one. We believe that the results obtained by the two procedures will probably be very close.

From Table 8, it is clear that the use of four *p* contracted orbitals instead of three brings only a very slight improvement. The energy decrease is only 0.0013 a.u. for the CH_2 molecule and 0.0025 a.u. for the H_2O molecule. It seems that 3 contracted *p* orbitals will be satisfactory for most calculations, mainly if one thinks that a small increase in the number of contracted *p* orbitals will make any calculation considerably more bulky. In this case, the set No. 5 from Table 8 would seem the better.

Turning now to the number of *s* contracted orbitals for the hydrogen atom, one can see from Table 9 that the use of three *s* contracted orbitals instead of two brings only a very small energy gain (0.0013 a.u. for the CH_2 molecule and 0.0003 a.u. for the H_2O molecule). This seems to support the use of two *s* contracted orbitals for the hydrogen atom unless some very refined calculation is required. From the different sets of two *s* contracted orbitals for the H atom, set No. 3 (as given in Table 9) seems the better.

Let us now summarize what would seem the best possible choice of contracted orbitals for any molecule (with only first-row atoms), assuming that the number of contracted orbitals is 5 for the *s*-type orbitals, 3 for the *p*-type and 2 for the *s*-type of the hydrogen atoms:

for the *s* contracted orbitals, referring to Tables 3 and 7, either use the set No. 10 or No. 12 for every atom or the set marked in Table 7 with an asterisk for each atom,

for the *p* contracted orbitals, use the set No. 5 of Table 8,

for the *s* contracted orbitals of the hydrogen atom, use the set No. 3 of Table 9.

To fully test these choices, we reported in Table 10 the results of four different calculations for the CH_2 and the H_2O molecules:

the first calculation is an uncontracted one, using the 11*s*, 7*p* basis set for the carbon or oxygen atoms, together with 6*s* functions for the hydrogen atom,

the second calculation uses the same basis set which is now contracted according to the above rules (choosing the set No. 10 for the contracted *s* orbitals of the C and O atoms rather than the optimal set),

the third calculation is similar to the second one, but some *d*-type polarization functions have been added on the carbon or oxygen atoms, together with some *p*-type functions on the hydrogen atoms,

the fourth result corresponds to the best Hartree-Fock calculation presently available [10].

Comparison of the first and second result indicates that the contraction does not bring any significant loss on the energy value if the linear combinations of the contracted orbitals are carefully chosen. This is substantiated by a comparison of the third and fourth results.

Appendix

Detail of the Calculations and Numerical Results

The orbital exponents of the Gaussian basis set are given in Table 1 and the corresponding expansion coefficients in Table 2. They are taken from unpublished results by Huzinaga, Coiro, Rusconi and Clementi. Exponents for the hydrogen atom are taken from Huzinaga's work [3].

Table 1. *Orbital exponents of the Gaussian basis set:* $11-(1s_g)$, $7-(2p_g)$

	Li(^2S)	Be(^1S)	B(^2P)	C(^3P)	N(^4S)	O(^3P)	F(^2P)
1*s*	1782.9	3630.38	6249.59	9470.52	13515.3	18045.3	23342.2
1*s*	267.096	532.280	916.065	1397.56	1998.96	2660.12	3431.25
1*s*	60.0718	117.799	202.205	307.539	439.998	585.663	757.667
1*s*	16.7798	32.6562	55.8340	84.5419	120.899	160.920	209.192
1*s*	5.40327	10.4801	17.8587	26.9117	38.4711	51.1637	66.7261
1*s*	1.90603	3.66826	6.25286	9.40900	13.4578	17.8966	23.3705
1*s*	0.717910	1.35431	2.31177	3.50002	4.99299	6.63901	8.62372
1*s*	0.266971	0.417501	0.682360	1.23220	1.65981	2.09625	2.70001
1*s*	0.081858	0.172393	0.260350	0.423084	0.736372	0.842082	1.08750
1*s*	0.032383	0.063445	0.096592	0.147699	0.293648	0.307280	0.396536
1*s*	0.014224	0.026239	0.036107	0.048957	0.123902	0.132539	0.172324
2*p*			15.4594	25.3655	35.9111	49.8279	65.6593
2*p*			3.48347	5.77636	8.48042	11.4887	15.2187
2*p*			1.06577	1.78730	2.70563	3.60924	4.78819
2*p*			0.392780	0.655774	1.00199	1.31104	1.72755
2*p*			0.150330	0.252790	0.400617	0.502347	0.648123
2*p*			0.059321	0.096693	0.168433	0.195677	0.244965
2*p*			0.021028	0.027189	0.076081	0.072412	0.091537

Table 2. *Orbital expansion coefficients of the Gaussian basis set* $11-(1s_g)$, $7-(2p_g)$

	Li(^2S)	Be(^1S)	B(^2P)	C(^3P)	N(^4S)	O(^3P)	F(^2P)
1*s*	0.00060	0.00052	0.00047	0.00044	0.00042	0.00041	0.00040
	0.00467	0.00422	0.00380	0.00358	0.00339	0.00333	0.00327
	0.02424	0.02238	0.02037	0.01932	0.01832	0.01800	0.01754
	0.09237	0.08694	0.08051	0.07746	0.07395	0.07286	0.07082
	0.24630	0.24128	0.23083	0.22631	0.21921	0.21796	0.21290
	0.42016	0.43291	0.42884	0.42862	0.42475	0.42426	0.42213
	0.32959	0.33723	0.35341	0.35277	0.36400	0.36745	0.37480
	0.04584	0.03794	0.04488	0.04816	0.05576	0.05629	0.05866
	−0.00168	−0.00719	−0.00988	−0.00200	−0.00711	−0.00905	−0.00944
	0.00119	0.00237	0.00416	0.00105	0.00297	0.00440	0.00468
	−0.00021	−0.00069	−0.00115	−0.00021	−0.00061	−0.00128	−0.00136
2*s*	−0.00009	−0.00009	−0.00009	−0.00009	−0.00009	−0.00009	−0.00009
	−0.00073	−0.00077	−0.00076	−0.00076	−0.00075	−0.00075	−0.00075
	−0.00384	−0.00412	−0.00417	−0.00417	−0.00407	−0.00412	−0.00409
	−0.01476	−0.01635	−0.01672	−0.01699	−0.01690	−0.01713	−0.01699
	−0.04256	−0.04874	−0.05213	−0.05406	−0.05354	−0.05502	−0.05476
	−0.08141	−0.10401	−0.11395	−0.12089	−0.12622	−0.13004	−0.13195
	−0.12976	−0.15319	−0.17130	−0.17757	−0.17467	−0.18090	−0.18473
	−0.05287	0.01518	0.07975	0.06488	0.03413	0.07658	0.08175
	0.50312	0.51157	0.58291	0.58880	0.44284	0.54881	0.55115
	0.56293	0.52751	0.43375	0.45624	0.50597	0.45224	0.44502
	0.05019	0.05609	0.03060	0.02467	0.14831	0.06010	0.06182
2*p*			0.00894	0.00876	0.00907	0.00894	0.00882
			0.05370	0.05464	0.05474	0.05768	0.05778
			0.17904	0.18365	0.18143	0.19213	0.19341
			0.35846	0.35652	0.34632	0.35535	0.35671
			0.43200	0.41977	0.38814	0.39094	0.39296
			0.19486	0.21158	0.22602	0.22918	0.22990
			0.00843	0.00869	0.04275	0.02925	0.03143

Table 3. *Contraction of the s-type basis orbitals*

Contraction No.	Grouping of the Gaussian basis orbitals
1	(1 2 3) (4 5) (6 7) (8 9) (10 11)
2	(1 2 3 4) (5 6) (7 8) (9) (10 11)
3	(1 2 3) (4 5 6) (7 8) (9) (10 11)
4	(1 2 3 4 5) (6) (7 8) (9) (10 11)
5	(1 2 3 4 5) (6 7) (8) (9) (10 11)
6	(1 2 3 4 5 6) (7) (8) (9) (10 11)
7	(1 2 3 4 5 6) (7) (8 9) (10) (11)
8	(1 2 3 4 5) (6 7) (8 9) (10) (11)
9	(1 2 3 4 5 6) (7 8) (9) (10) (11)
10	(1 2 3 4 5) (6 7 8) (9) (10) (11)
11	(1 2 3 4 5 6 7) (8) (9) (10) (11)
12	(1 2 3 4 5 6) (7) (8) (9 10) (11)
13	(1 2 3 4 5) (6 7) (8) (9 10) (11)
14	(1 2 3 4 5) (6) (7 8) (9 10) (11)

Table 4. *Total atomic energy (in a.u.) for the* Li *to* F *atoms. Comparison of uncontracted and contracted calculations*

Contraction No.	Li(^2S)	Be(^1S)	B(^2P)	C(^3P)	N(^4S)	O(^3P)	F(^2P)
0	−7.432513	−14.57262	−24.52833	−37.68741	−54.40007	−74.80675	−99.40559
1	−7.428621	−14.56739	−24.52053	−37.67399	−54.38342	−74.78531	−99.37728
2	−7.432464*	−14.57216	−24.52446	−37.68216	−54.39588	−74.79257	−99.38904
3	−7.432438	−14.57170	−24.52300	−37.67971	−54.39290	−74.78699	−99.38206
4	−7.432440	−14.57233*	−24.52575	−37.68431	−54.39787*	−74.79804	−99.39560
5	−7.432273	−14.57102	−24.52557	−37.68402	−54.39584	−74.80145*	−99.39880*
6	−7.432423	−14.57163	−24.52680*	−37.68493*	−54.39527	−74.80096	−99.39796
7	−7.431478	−14.57156	−24.52497	−37.68140	−54.39227	−74.79453	−99.38916
8	−7.429045	−14.56979	−24.52106	−37.67482	−54.38605	−74.78798	−99.38101
9	−7.432408	−14.57157	−24.52249	−37.67855	−54.39152	−74.78575	−99.38009
10	−7.431283	−14.57059	−24.52537	−37.68387	−54.39579	−74.79820	−99.39664
11	−7.430917	−14.56494	−24.50760	−37.65919	−54.36394	−74.75310	−99.33630
12	−7.432421	−14.57159	−24.52674	−37.68488	−54.39513	−74.80078	−99.39773
13	−7.432251	−14.57085	−24.52531	−37.68368	−54.39533	−74.80087	−99.39807
14	−7.432416	−14.57198	−24.52431	−37.68291	−54.39675	−74.79258	−99.39014

* Denotes the best result for each atom.

In the atomic or molecular calculations, we have considered fourteen different possible contractions of the *s* orbitals, which are reported in Table 3. Of course, we have not considered all the possible contractions, and the fourteen reported here appear as the most plausible from an energy point of view. To illustrate the use of Table 3, let us go into the detail of the contraction No. 14 for the carbon atom, remembering that the coefficients of the linear combinations are taken equal to the expansion coefficients of Table 2. Let us denote by χ' the contracted orbitals and by χ the Gaussian basis functions. The information given in Table 3 can be rewritten more explicitly:

$$\chi'_1 = 0.00044\,\chi_1 + 0.00358\,\chi_2 + 0.01932\,\chi_3 + 0.07746\,\chi_4 + 0.22631\,\chi_5$$
$$\chi'_2 = \chi_6$$
$$\chi'_3 = 0.35277\,\chi_7 + 0.04816\,\chi_8$$
$$\chi'_4 = 0.58880\,\chi_9 + 0.45624\,\chi_{10}$$
$$\chi'_5 = \chi_{11}\,.$$

The energies obtained with the different contractions for the atoms Li to F are reported in Table 4, together with the energy obtained without contraction [7]. Calculations were performed using a program written for atomic calculations [11], which in his main lines is similar to the one described by Roothaan and Bagus [9]. For each atom, the best energy has been denoted in Table 4 by an asterisk. Using the same program, the contraction coefficients have been optimized for the best sets of Table 4 and the corresponding energies are given in Table 5.

Molecular calculations were done for the states ${}^1\Sigma^+$ of LiH, BH and FH, and ${}^1A_1$ of CH_2, NH_2^-, H_2O, using the program IBMOL [4]. Molecular geometries are reported in Table 6. Values of the energy for the fourteen calculations with different contractions of the *s* orbitals are given in Table 7. Values of the energy with different contractions of the *p* orbitals are given in Table 8 for the CH_2 and H_2O molecules. Values of the energy with different contractions of the *s* orbitals of the hydrogen atoms are given in Table 9 for the CH_2 and H_2O molecules.

Additional calculations were done for the CH_2 and H_2O molecules. The first one uses no contraction at all. The second one uses the contraction No. 10 from

Table 5. *Energies with the contraction coefficients from the atomic expansion (Energy A) and with optimized coefficients (Energy B)*

	Contraction No.	Energy *A*	Energy *B*
Li(${}^2S$)	2	− 7.432464	− 7.432469
Be(${}^1S$)	4	−14.57233	−14.57237
B(${}^2P$)	6	−24.52680	−24.52686
C(${}^3P$)	6	−37.68493	−37.68504
N(${}^4S$)	4	−54.39787	−54.39820
O(${}^3P$)	5	−74.80145	−74.80198
F(${}^2P$)	5	−99.39880	−99.39929

Table 6. *Molecular geometry*

	Bond Length (in Å)	Bond Angle (in degrees)
LiH	1.595	
BH	1.236	
CH_2	1.071	140°
NH_2^-	1.03	104°
OH_2	0.9572	104.52°
FH	0.9170	

Table 3 for the *s* orbitals of the C and O atoms, the contraction No. 5 from Table 8 for the *p* orbitals and the contraction No. 3 from Table 9 for the *s* orbitals of the hydrogen atoms. The third uses the same contracted set as the second one, with additional 3*d* polarization functions on the C and O atoms and 2*p* functions on the H atoms. Exponents of the 3*d* functions were set equal to 0.7 for the oxygen atom and 0.3 for the carbon atom. Exponents of the 2*p* functions on the hydrogen atoms were set equal to 0.4. These values are taken from a study of these molecules by Clementi *et al.* [12]. The corresponding energies are reported in Table 10.

Table 7. *Total energy (in a.u.) for the* LiH, BH, CH_2, NH_2^-, H_2O *and* FH, *molecules, as a function of the contraction for the s orbitals*

Contraction No.[a]	LiH	BH	CH_2	NH_2^-	H_2O	FH
1	−7.97600	−25.11173	−38.82252	−55.48528	−75.97067	− 99.99229
2	−7.97811	−25.11486	−38.83177	−55.49766	−75.98271	−100.00549
3	−7.97805	−25.11354	−38.83003	−55.49536	−75.97810	− 99.99900
4	−7.97811	−25.11601	−38.83310	−55.49902	−75.98685	−100.01137
5	−7.97780	−25.11590	−38.83223	−55.49771	−75.98823	−100.01359
6	−7.97814*	−25.11745*	−38.83264	−55.49638	−75.98626	−100.01210
7	−7.97748	−25.11594	−38.83148	−55.49486	−75.98260	−100.00719
8	−7.97623	−25.11210	−38.82448	−55.48958	−75.97647	−100.00002
9	−7.97801	−25.11386	−38.83121	−55.49533	−75.97719	− 99.99909
10	−7.97761	−25.11632	−38.83445*	−55.49821	−75.98739	−100.01459
11	−7.97623	−25.10000	−38.81575	−55.47351	−75.94789	− 99.95727
12	−7.97814*	−25.11585	−38.83269	−55.49737	−75.98782	−100.01470
13	−7.97775	−25.11407	−38.83041	−55.49805	−75.98923*	−100.01629*
14	−7.97809	−25.11228	−38.82922	−55.49964*	−75.98509	−100.01138

[a] The contraction no. refers to Table 3.

* Denotes the best result for each molecule.

Note: Above calculations use the contraction no. 1 of Table 8 for the *p* orbitals and the contraction no. 1 of Table 9 for the *s* orbitals of the hydrogen atoms.

Table 8. *Total energy (in a.u.) for the* CH_2 *and* H_2O *molecules, as a function of the contraction for the p orbitals*

Contraction No.	Number of contracted *p* orbitals	Grouping of the gaussian basis orbitals	CH_2	H_2O
1	3	(1 2 3 4) (5 6) (7)	−38.83445	−75.98739
2	3	(1 2 3) (4 5) (6 7)	−38.83190	−75.99898
3	3	(1 2 3) (4 5 6) (7)	−38.82484	−75.98261
4	3	(1 2 3 4 5) (6) (7)	−38.83213	−75.99948
5	3	(1 2 3 4) (5) (6 7)	−38.83521	−75.99977
6	4	(1 2 3) (4 5) (6) (7)	−38.83292	−76.00100
7	4	(1 2 3) (4) (5) (6 7)	−38.83657	−75.99999
8	4	(1 2 3 4) (5) (6) (7)	−38.83596	−76.00222
9	4	(1 2) (3 4) (5 6) (7)	−38.83488	−75.98794

Note: Above calculations use the contraction no. 10 of Table 3 for the *s* orbitals of the C and O atoms and the contraction no. 1 of Table 9 for the *s* orbitals of the hydrogen atoms.

Table 9. *Total energy (in a.u.) for the* CH_2 *and* H_2O *molecules, as a function of the contraction for the s orbitals of the hydrogen atoms*

Contraction No.	Number of contracted *s*-orbitals	Grouping of the gaussian basis orbitals	CH_2	H_2O
1	2	(1 2 3 4 5) (6)	−38.83445	−75.98739
2	2	(1 2 3) (4 5 6)	−38.82641	−75.99896
3	2	(1 2 3 4) (5 6)	−38.84138	−76.01286
4	3	(1 2 3) (4 5) (6)	−38.83879	−76.00276
5	3	(1 2 3 4) (5) (6)	−38.84263	−76.01314
6	3	(1 2) (3 4) (5 6)	−38.84139	−76.01310

Note: Above calculations use the contraction no. 10 of Table 3 for the *s* orbitals of the C and O atoms and the contraction no. 1 of Table 8 for their *p* orbitals.

Table 10. *Comparison of different calculations for the* CH_2 *and* H_2O *molecules*

	CH_2	H_2O
No contraction	−38.84784	−76.02273
With contraction	−38.84440	−76.01485
With contraction + polarization functions	−38.85662	−76.04673
Best available	−38.8026[a]	−76.0421[b]

[a] Ref. [13].

[b] Ref. [14].

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