Study of Lone Pair Description in Molecules by the Modified Delocalized Floating Spherical Gaussian Orbital Method

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Abstract

This research has been carried out to study and find a rather general description for a lone pair orbital in molecules. Since the orbital parameters must be manageable in advance, and correct geometry of the molecule (bond lengths) is depend on the appropriate lone pair description; the FSGO method including optimization has been used to obtain orbital parameters and energy. The proposed models for lone pair description have been tested by two molecules: HF and NH.29 models for HF and 23 models for NH have been used to obtain simultaneously correct bond length and dipole momentum. We show that contribution of lone pair electrons in binding gives satisfactory results. An approach which we called "Modified Delocalized Floating spherical Gaussian orbital (MDFSGO)" method was performed for these molecules. The linear combination of p-type and s-type orbital are tested. They can predict only correct bond length or dipole momentum, but the contribution of lone pair electrons in binding can predict rather satisfactory results for both bond length and dipole momentum. By using this method, the error of dipole moment and bond length decrease from 229.75% to %9.72 and from 27.28% to 4.03% in HF molecule. For NH, the error of dipole momentum changes from 256.45% to 8.023% and for bond length from 32.84% to 1.92%.

Keywords: FSGO, MDFSGO, Orbital, Lone pair, Gaussian, Dipole moment

1. Introduction

This paper is a study of the description of lone pairs in molecules [1]. In this article attention was paid to obtaining a proper lone pair description by using the FSGO method [2]. The investigation into finding the correct geometries is extended by a new approach; the Modified Delocalized Floating Spherical Gaussian Orbital Method (MDFSGO).

In this research, all of the calculations have been performed through the ab initio approach [3]. The MDFSGO method has been used, which is a reconciliation of the FSGO and SCF methods. [4]

Two molecules HF and NH have been selected to test the proposed lone pair description models. [5]

For a large number of researchers, who use the SCF method, the problem of how to construct a basis set in order to obtain the correct geometry is very important. An attempt to find some type of rule for selecting a suitable basis set is therefore very important. [6]

However, a point of confusion which arises should be clarified, i. e. the goal of this research, and that our approach to describe the lone pair in molecules by using MDFSGO is quite different from Linnett's approach [7].

Linnett's approach is the spreading of the multi-gaussian description of lone pair around the atom (containing a lone pair) and using the original FSGO method. Therefore, Linnett's model [8] does not only use the localized FSGO method, but also is symmetry dependent, which is difficult to generalize for more than one lone pair on one atom.

The effect of a lone pair on inter-atomic distance (bond length) is a well-known phenomenon in chemistry. We will show in this paper how the lone pair description depends upon the bonding orbital description or vice versa. An inadequate lone pair description not only causes an incorrect geometry in a FSGO calculation, but also we believe that obtaining a wrong geometry by some SCF calculations can be affiliated to a wrong orbital description in molecules. Hence, the calculation of the correct geometry in the MDFSGO method is the result of a correct description of basis set, and consequently correct lone pair description.

2. Method and computational procedure

The FSGO method [9, 10], which was introduced by Frost in 1967[11] is quite ab initio, and is extensively used in the literatures [12, 13, 14]. The method is briefly described here. The spherical gaussian, which is the simplest gaussian function, has the following form:

$$G_i(r - R_i) = (2\alpha_i / \pi)^{3/4} \exp[-(r - R_i)^2 \alpha_i] \ (1)$$

Where the orbital exponent α and the components of the orbital centre vector R_i are variation parameters. The spherical gaussians, which are used to represent the orbital description, are positioned in the molecule in the same way as that of Lewis's concept of valence. The total electronic energy for a single determinant wave function is obtained by:

$$E_{el} = 2\sum_{j,k} (j \mid k)T_{jk} + \sum_{k,l} \sum_{p,q} (kl \mid pq)$$
$$\times (2T_{kl}T_{pq} - T_{kq}T_{lp}) \quad (2)$$

Where $T = s^{-1}$, and s is the overlap matrix. The total energy is obtained by:

$$E = E_{ed} + \sum_{i,j}^{N} Z_i Z_j / R_{ij} \quad (3)$$

and is optimized with respect to the nuclear coordinates and the orbital parameters in a molecule.

In the original FSGO method [15] a molecular orbital is described by only a single gaussian. The above formalism can be used when the orbital description as a linear combination of gaussians (multi-gaussian description) is used. The linear coefficients of the multi- gaussians are determined by direct optimization, similar to the other parameters. The molecular orbital description in the original FSGO is limited by those gaussians that are allowed to contribute. This way of truncation, which is used in multi-gaussian FSGO calculations, makes us call it the localized FSGO method in contrast to what has already been applied in this paper and is explained below.

The DFSGO method is a reconciliation of the FSGO and SCF methods. The

procedure employs the FSGO method for multi-gaussian calculation of total energy, and the SCF method is used to find a set of orthonormal eigenvectors, which are the coefficients of multi – gaussian orbital description. Therefore, the gaussians for p and d orbitals are not used directly.

The orbitals with high angular momentum are built up by a linear combination of spherical gaussians with appropriate positioning of the centers of the gaussians and obtaining the proper coefficients by the SCF procedure. It has been shown in the literature [16, 17, 18], when the center of a 1S orbital (GTO or STO) is not at the nuclear center (bond function), this can be considered as applying a function of high angular momentum. The calculated energies by this procedure are identical to the SCF results. However, if the single gaussian is used for orbital description both of the delocalized and localized FSGO methods are the same.

Now, we contribute the lone pair electrons in bonding by using a common s-type gaussian in both orbitals. This approach which is called the "Modified Delocalized Floating Spherical Gaussian Orbital" (MDFSGO) method was utilized for these molecules.

3. Results and discussion

We would like to present briefly the results of some of fully optimized calculations and discuss them to find a proper basis set in order to give a fairly accurate bond length and dipole momentum by using a relatively correct lone pair description. In this research, different basis sets have been tested for the two molecules: HF and NH.

Before presentation of the models, it is best to mention how to make them. We try to make a model in such a way that it can be handled and generalized with ease.

If an atom containing one lone Pair in a molecule connected with only one bond (in a special case, the molecule is linear), positioning of the bonding and lone pair spherical gaussians are along the z-axis (sometimes this is the principal axis).

If there are two lone pairs on one atom, the spherical gaussians for one of the pairs are along the bond as before. One of the axes (x, or y) is considered for positioning of the spherical gaussians describing the second lone pair, depending upon the condition of the molecule, in such a way that there is minimum repulsion energy (in the case of a double bond connected to the atom, the spherical gaussians are positioned in the plane perpendicular to the plane which contains the center of the gaussians describing the Π-bond). If there are three lone pairs on the same atom, the spherical gaussians for describing the lone pairs are centered on three coordinate axes, if the Cartesian coordinate is set up on the atom.

This method of positioning the spherical gaussians is not the same as the Linnett's model.

The calculations are presented and discussed in this section. Some main models for describing electronic distribution have been tested for each molecule. These models are as follows:

A. One spherical gaussian is assumed for each lone pair, this is known as the 1S-type model for lone pair description.

B. Two identical exponent spherical gaussians, which are off-center from the origin in the two opposite directions but the same extent along the proposed axis, are assigned to the lone pairs. This is known as the 2p-type model for lone pair description.

C. One spherical gaussian is added to model B at about the origin. This is known as the single 2p-type plus 1s-type model.

D. Two concentric spherical gaussians with different exponents are added to model B at about the origin. This model is called the single 2p-type plus 2s-type model.

E. Four spherical gaussians which are off-center from the origin in two opposite directions but the same extent two by two along the proposed axes. This model is called the double 2p-type model.

F. One spherical gaussian is added to model E at about the origin. This model is called the double 2p-type plus 1s-type model.

G. Two concentric spherical Gaussians with different exponents are added to model E at about the origin .This is called the double 2p-type plus 2s-type model

Our calculations are performed for each of the models (B-G) of each molecule by using the above models .The specifications of these calculations are as follows:

I) the position of the k-shell gaussian is fixed at the origin.

II) Different exponents are imposed for free optimization and the other parameters are fixed.

III) The exponents are fixed at specific values and the position of the k-shell gaussian is fixed at the origin but the position of concentric spherical gaussians, which are called 1S-2S- and 3S- type orbitals, respectively, are free to float on the given axes. So, bonding gaussians are optimized at first on x-axes

IV) The position of the k-shell gaussian is fixed at the origin and the exponents are fixed at specific values and the position of landing gaussians are fixed but the spherical gaussians representing a-lp type orbital or 2p-type orbital for each set of lone pairs are not off-center from the origin to the same extent and must be optimized.(at first on x-axes).

V) Like IV but all of the positions of bonding gaussians and lone pare gaussians optimize.

VI) At first as III, then IV and finally as V but on y-axes.

VII) Like VI, but on z-axes.

VIII) The value of exponents is fixed, the position of the k-shell is on the origin and the position of bonding and lone pair gaussians are fixed after optimization on the x, y and z axes. Now the coefficients of the gaussians must the optimized. ix) After optimization of exponent, positing and coefficients, the nuclear coordinates are optimized.

An important point must be stated here that by 2S-type and 1S-type orbitals, we mean two concentric spherical gaussians with opposite signs of the coefficient and spherical gaussians respectively, concerned at the origin.

The selected results of the total energies, bond length and dipole momentum are illustrated in tables 1, 2. The results were calculated according to the minimum value in energy and reached to the maximum stability. According to the visual theorem, total energy and kinetic energy must the equal

Table 1 shows the percentages of error in bond length and dipole momentum calculations for HF and Table 2 shows this information for NH. The cases discussed below illustrate some of the points drawn from the results in table.

Increasing the number of gaussians to the bonding orbital, finally leads to a decrease in percentages of error in bond length and-dipole momentum for exponent in the first three models till 3 spherical gaussians, but HF bond length des not let that 4 gaussians used for bonding electrons and the coefficient of it negate the other bonding gaussions.

Putting gaussians on H leads to increasing the error. It is because of the high electro negativity of F that lowers the electronic density on H.

Modifying the linear combination of gaussians for lone pairs can predict other accurate and satisfactory results for bond length.

Putting 2p-type orbital on F decrease error value in dipole momentum from 240% to 10% and in bond length from 24.38% to 4/03%.

Increasing the number of gaussians for bonding orbital leads to lowering the error percentages error for bond length and dipole momentum, for example a decrease in the error of bond length from 159.36% to 30.6% or dipole momentum decrease from 11.42D to 4.47D.

Table1. Calculated energy and bond length and dipole moment and corresponding errors for different models for HF molecule.

no	MODEL	E_K	$-E_t$	μ	%e	r	%e
1	$(1G)_b(1p)_{L.P}$	84.630	84.636	2.007	109.7	2.2327	28.78
2	$(2G)_b (1P)_{L.P}$	84.687	84.688	2.077	116.9	2.2448	29.48
3	$(3G)_b (1P)_{L.P}$	84.693	84.693	1.948	103.5	2.2147	27.75
4	$(4G)_b (1P)_{L.P}$	84.693	84.694	3.156	229.7	2.2238	27.28
5	$(1G)_b (1G)_H (1P)_{L.P}$	84.681	84.682	2.256	135.7	2.8703	31.92
6	$(2G)_b (1G)_H (1P)_{L.P}$	84.693	84.693	1.950	103.7	2.2112	27.62
7	$(3G)_b (1G)_H (1P)_{L.P}$	84.693	84.694	1.939	102.6	2.2130	27.65
8	$[(3G)_b (1G)_H (1G)_F]_b (1P)_{L.P}$	84.695	84.696	1.941	102.8	2.2221	28.17
9	$(1G)_b (1P1S)_{L.P}$	84.553	84.522	3.343	249.1	1.6885	-2.56
10	$(1G)_b (1G)_H (1P1S)_{L.P}$	85.002	84.940	8.559	7.94.0	3.8383	122.4
11	$((1G)_{HF}(1S)_F(1G)_H)_b(1P1S)_{L.P}$	85.021	84.939	8.587	7.970	3.8383	121.4
12	$(2G)_b(1P1S)_{L.P}$	84.896	84.982	3.260	240.5	2.1563	24.38
13	$((2G)_{HF}(1S)_F)_b(1P1S)_{L.P}$	85.436	85.694	2.945	207.6	1.8506	6.746
14	$(2G)_b(2P)_{L.P}$	86.888	86.880	1.596	66.71	2.3416	35.07
15	$((2G)_{HF}(2P)_F)_b(2P)_{L.P}$	87.060	86.863	.8979	6.206	1.9512	12.55
16	$(1P)_F(2G)_b(1P1S)_{L.P}$	85.129	85.216	1.057	10.48	1.8036	4.037
17	$[(1P)_F(2G)_{HF}(1S)_F]_b(1P1S)_{L.P}$	85.131	85.216	1.050	9.721	1.8035	4.031
18	$(1P)_F(1G)_b(1P1S)_{L.P} (1P)_H$	84.551	84.662	11.42	1092.	4.4964	159.3
19	$(1P)_F(2G)_b (1P1S)_{L.P} (1P)_H$	86.188	85.494	4.478	367.8	2.2642	30.60
20	$(1P)_F (1G)_b (2P1S)_{L.P}$	87.053	87.076	3.103	224.1	1.6707	-3.62
21	$(1P)_F(2G)_b(2P1S)_{L.P}$	86.908	87.092	2.086	117.9	1.7940	-3.48
22	$[(1P)_F(2G)_{HF}(1S)_F]_b(2P1S)_{L.P}$	86.832	87.087	1.974	10.62	1.7902	3.266
23	$(1P)_F(1G)_b(2P1S)_{L.P}(1P)_H$	87.223	87.070	.0142	98.51	2.1006	21.17
24	$(1P)_F(1G)_b(2P1S)_{L.P}$	87.274	87.269	1.704	78.00	1.8547	6.984
25	$((1P)_F(1G)_{HF}(2S)_F)_b(2P2S)_{L.P}$	87.297	87.397	2.305	140.8	1.8638	7.512
26	$(1P)_F(2G)_b(2P2S)_{L.P}$	87.293	87.324	1.830	88.34	.03629	3.855
27	$(1P)_F(2G)_b(1P)_H(2P2S)_{L.P}$	87.444	87.292	1.696	77.23	1.7336	173.0
28	$(2G)_b(2P2S)_{L.P}$	87.272	87.280	1.755	83.40	1.8159	4.746
29	$((2G)_{HF}(2S)_F)_b(2P2S)_{L.P}$	87.286	87.283	1.903	83.30	1.8157	4.755

Table2. Calculated energy and bond length and dipole moment and corresponding errors for different models for NH molecule.

no	MODEL	E_K	$-E_t$	μ	%e	r	%e
1	$(3G)_b (1P)_{L.P}$	47.125320	47.138565	3.26186	246.84	2.65263	35.193
2	$(2G)_b (1G)_H (1P)_{L.P}$	47.13074	47.137554	3.35180	256.45	2.60646	32.840
3	$(3G)_b (1G)_H (1P)_{L.P}$	47.129375	47.147154	3.03648	222.87	2.50135	27.475
4	$[(3G)_b (1G)_H (1G)_F]_b (1P)_{L.P}$	47.538826	47.551191	1.74368	79.095	2.03446	3.6883
5	$(1G)_b (1P1S)_{L.P}$	47.031963	47.041514	.630073	-1.312	1.93669	33.002
6	$(1G)_b (1G)_H (1P1S)_{L.P}$	47.177147	47.185897	.298218	-68.28	2.09958	7.0072
7	$(2G)_b (2P)_{L.P}$	47.203079	47.224053	1.01459	7.8843	2.01990	2.9461
8	$(2G)_b (1P1S)_{L.P}$	47.210001	47.217644	1.14768	22.066	2.01255	2.5712
9	$((2G)_{HF}(1S)_F)_b (1P1S)_{L.P}$	47.218493	47.226203	1.16224	23.584	2.00824	2.3515
10	$(1P)_F (2G)_b (1P1S)_{L.P}$	47.218912	47.223820	1.01590	80.233	1.99990	1.9261
11	$[(1P)_F (2G)_{HF}(1S)_F]_b (1P1S)_{L.P}$	46.924352	46.908447	1.40657	49.564	1.95709	-.2553
12	$(1P)_F (1G)_b (1P1S)_{L.P}$	47.328751	47.337135	1.80358	91.808	1.96785	.29331
13	$(1P)_F (1G)_b (1P1S)_{L.P}(1P)_H$	47.390134	47.386867	1.44758	33.631	1.95187	-.5211
14	$(1P)_F (2G)_b (1P1S)_{L.P}(1P)_H$	47.405796	47.401546	.370025	60.654	2.08526	6.2772
15	$(1P)_F (1G)_b (2P1S)_{L.P}$	46.833573	47.343289	1.56867	66.808	2.3103	18.131
16	$(1P)_F (2G)_b (2P1S)_{L.P}$	47.341432	47.345547	1.71058	81.890	1.85492	-5.468
17	$[(1P)_F (2G)_{HF}(1S)_F]_b (2P1S)_{L.P}$	47.284687	47.291913	1.86419	98.224	1.90234	-3.045
18	$(1P)_F (1G)_b (2P1S)_{L.P}(1P)_H$	47.504325	47.535447	.794392	-15.53	2.00863	2.3717
19	$(1P)_F (2G)_b (2P1S)_{L.P}(1P)_H$	47.537005	47.564648	.26189	-71.69	1.99823	1.8418
20	$(2G)_b (2P2S)_{L.P}$	47.218791	47.224127	1.01218	7.6279	2.03998	3.9665
21	$(1P)_F (1G)_{HF}(2S)_F)_b (2P2S)_{L.P}$	47.443527	47.462817	1.45775	55.001	2.0867	6.3542
22	$(1P)_F (2G)_b (2P2S)_{L.P}$	47.159792	47.223854	1.00216	6.5629	2.37990	6.0037
23	$(1P)_F (2G)_b (1P)_H (2P2S)_{L.P}$	47.575658	47.594616	.452229	-51.91	2.00499	2.1860

The same procedure for NH leads to the lowering of percentages of errors in bond length and dipole momentum.

Finally the error of dipole momentum in HF becomes 9.72% and for bond length 4.03% and for NH there are 8.023% and 1.92%.

Increasing the number of gaussians for lone pair orbitals leads to the lowering of the percentages of error. So, the effect of an appropriate description for lone pairs on lowering the earners must not be ignored.

The contribution of bonding electrons to the lone pair and vice versa, improve the electronic distribution and obtains a relatively better bond length and dipole momentum simultaneously. This approach which is called the "Modified Decolorized Floating Spherical Gaussian Orbital (MDFSGO)" method, was the method used for this cause. In fact, the mutual effect of lone pairs bonding orbitals is a well-known phenomenon in chemistry.

4. Conclusion

The purpose of this paper is to find a simple method of description of lone pairs in order to generalize and apply it to a chemical system.

The original FSGO method is used in some basis sets of these series.

Also, MDFSGO is employed in some of these basis sets in order to study the lone pair description in a molecule. It has been demonstrated that the lone pair description is

dependent on the k-shell and bonding description as expected chemically.

From the calculated results from the different parts we conclude that a significant contribution of lone pair orbitals in bonding one leads to a lower percentage of error.

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