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Geometry Optimization in *ab initio* SCF Calculations

III. Floating Orbital Geometry Optimization (FOGO) with Floating Outer-shell Basis Functions

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The floating orbital geometry optimization (FOGO) described previously [1, 2] for atoms without polarized inner-shell electrons, is extended to the general case. Instead of the Hellmann–Feynman force a special gradient is calculated analytically and utilized in a variable metric procedure simultaneously with the ordinary energy gradient. Test calculations on a sample of 12 molecules were performed to check the efficiency of the method. The geometries obtained are better than those obtained with the corresponding double-zeta basis set. The most striking results, however, are excellent dipole moments.

Key words: Geometry optimization – Floating orbital ~ – Floating outer-shell basis functions – SCF calculations – Geometry optimization in *ab initio* ~.

1. Introduction

In recent years methods became available which allow geometry optimizations in *ab initio* SCF calculations for relatively large molecules [3]. However, these calculations are still very time-consuming. In a first paper [1] we investigated, how the Hellmann–Feynman force can help to make geometry optimizations more efficient.

The FOGO method applies the Hellmann–Feynman force and the energy gradient (both calculated analytically) in a variable metric method. The orbitals are no longer fixed on the corresponding nuclei but their position is optimized simultaneously with the nuclear geometry. This procedure yields energies similar to the ones obtained with a basis set including polarization functions. In the previous paper [1] all basis functions corresponding to a certain nucleus were

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floating on a dummy nucleus in the same way. This method was applied to molecules having no atoms with polarized inner-shells. Good results were obtained for hydrogen-ion-clusters investigated in a second paper [2].

Here the method is generalized, using a special energy gradient instead of the Hellmann–Feynman force.

2. Method

Double-zeta basis sets usually yield a much improved energy compared to minimal basis sets. To calculate many molecular properties in a quantiative way, however, the basis set should allow for some polarization.

If a Gaussian lobe function (at the origin) is attracted (polarized) by another nucleus on the x-axis and therefore shifted along the x-axis by a distance R, the function can be developed in a series around the origin as

$$f = e^{-\alpha[(x-R)^2+y^2+z^2]} = e^{-\alpha r^2}\, e^{-\alpha R^2}\left[1+(2\alpha R)x+\frac{(2\alpha R)}{2!}\cdot x^2+\cdots\right] \tag{1}$$

with α being the exponent, r the distance from the origin and x, y, z the corresponding Cartesian coordinates.

If the shift R is small, f is equivalent to a Gaussian lobe and a Cartesian Gaussian p-orbital in the origin. The parameter R is related to the coefficient of the p-orbital. If R is larger, in addition to the p-function, d, f, and higher orbitals are mixed by in a fixed ratio.

To account for polarization one can follow therefore two different procedures, which, though similar, are however not identical. The classical way is to add polarization functions on a nucleus, i.e. p-functions on a hydrogen or d-functions on the first row elements. Our approach, using the FOGO method, is to shift some of the orbitals in the existing basis set to an optimal polarized position. If no geometry optimization is performed, the classical procedure is probably more efficient. However, if a geometry optimization is performed, the optimal polarization can be obtained in the same variable metric procedure utilizing an additional gradient (with different coefficients of following, see Ref. [4]) if consuming relatively little additional computer time.

2.1. Geometry optimization

Complete floating of all orbitals increases the number of independent variational parameters so much as to make a real problem untractable. Therefore we have compromised by assigning to each nucleus a single dummy center. Functions originally assigned to the nucleus are divided into two groups: those which are still moving rigidly with the nucleus (e.g. inner-shell functions) and those which are floating, i.e. assigned to the dummy centers. The latter are mostly the functions in the outermost shell. The positions of the nuclei and of the dummy centers are optimized simultaneously with a variable metric method [5]. This way only $3N$

additional variational parameters, the positions of the dummies, are introduced, and we can account for a polarization of the atom e.g. in a uniform electric field. Note that if the function assigned to the dummy center is of s-type (in hydrogen) then the optimization of the dummy is equivalent (to first order) to a complete set of p-type polarization functions. However, if the floating functions are of p-type, this is not equivalent to a situation where a set of $5d$-functions is applied, as already seen from the fact that there are only three additional parameters instead of five. Thus, no improvement is obtained if the outermost p-shell of the carbon atom is allowed to float in the equilibrium geometry of methane. Nevertheless, as our results show, the most important polarization effects are quite well accounted for.

The speed of parameter optimization depends on how the independent variables are chosen in the $6N$-dimensional space. We found that with the method we used before [1] convergence in some cases was very poor, due to a strong coupling term between the nuclear coordinates and the coordinates of the dummy assigned to the nucleus. This coupling can be much diminished by using an alternative set of coordinates, consisting of the $3N$ coordinates of the nuclei and the $3N$ coordinates of the dummies relative to the corresponding nuclei. In this set of coordinates, the gradient formulas are:

$$g_{\mathrm{A}} = \sum_{i \in \mathrm{A}} g_i + \sum_{j \in D_{\mathrm{A}}} g_j - f_{\mathrm{A}}^{\mathrm{HF}} \tag{2}$$

$$g_{\mathrm{D}} = \sum_{j \in \mathrm{D}} g_j$$

where A and D stand for the atoms and dummies, respectively. $g_i = (\partial E / \partial \xi_i)$ denotes the negative force on the basis function i [4]. The summation extends to those functions which move rigidly with the nucleus or dummy, respectively. $f_{\mathrm{A}}^{\mathrm{HF}}$ is the Hellmann–Feynman force on nucleus A. The formula for the forces on the nuclei is now the same as in the non-floating case.

3. Calculations

Full geometry optimizations were done for all molecules in two ways, once in the classical way and once with FOGO. We applied the double-zeta $(7s3p/4s2p)$ basis set described by Roos and Siegbahn [6], except for hydrogen, where we used the $(4s/2s)$ basis set of Dunning [7], the exponents increased by a factor of 1.2. This basis set used in the conventional way will be referred to as DZ throughout this paper. The same basis set was used with the FOGO method. All hydrogen basis functions were allowed to float relative to the nucleus. For all other atoms only the most diffuse p-orbital was allowed to float. The results dicussed in the rest of this paper as obtained by FOGO refer to this basis set.

For H_2O, in addition, a geometry optimization with polarization functions was performed. This basis set will be called DZ+P. The polarization functions were p-functions with exponent one on the hydrogen and d-functions with exponent two on the oxygen.

The calculations were performed on a Univac U-1100/81 computer using single precision (36 bit) with a program utilizing Gaussian lobe functions. The *k*-parameter [8] was chosen as 0.01.

4. Results and Discussion

To check the efficiency of FOGO we decided to optimize the geometries of the nine molecules which Ditchfield et al. [9] had chosen to test the 4-31G basis set. In the course of the calculations three more molecules were added for special reasons to be discussed later.

Our program needs about 50% more time for one geometry iteration due to the calculation of the additional gradient g_D. Further we found, that it required about twice as many iterations compared to the standard gradient geometry optimization. This means that it took about three times as much CPU-time with FOGO as with the standard method. As FOGO provides for some polarization this time may also be compared to standard calculations with the DZ+P basis set, which typically needs about ten times longer than the same optimizations with the DZ basis set. For H_2O the total CPU-time needed in the DZ, FOGO, and DZ+P case, were 235*s*, 570*s*, and 3000*s*, respectively. The energies obtained were $-75.8829\ E_h$, $-75.9094\ E_h$, and $-75.9277\ E_h$, respectively, i.e. FOGO yields in this case about 60% of the "polarization energy" $[E(\mathrm{DZ+P})-E(\mathrm{DZ})]$ and needs about 12% of the "polarization time" $[t(\mathrm{DZ+P})-t(\mathrm{DZ})]$. The time saving would probably be smaller with a Cartesian Gaussian function program, which usually handles polarization functions more efficiently, or if bond functions were applied for polarization purposes.

The number of geometry iterations depends much on the quality of the starting position of the floating orbitals. With experience the number of iterations will therefore decrease. Furthermore the calculation of the additional gradient can be programmed more efficiently, following Pulay's scheme [4]. Its calculation should need virtually no additional time. Therefore, we estimate, that it will be possible to decrease the time to a factor of less than 2 for FOGO compared to the classical DZ optimization.

4.1. Energies

Table 1 shows the energies we obtained and for comparison the 4-31G energies obtained by Ditchfield et al. [9].

The FOGO energies are 0.007 to 0.027 E_h (20 to 70 kJ/mol) lower than the DZ energies. This improvement is fully due to polarization, as the number of basis functions, the exponents and the contraction coefficients, are the same. The 4-31G energies are sometimes worse and sometimes better than the DZ energies; in two cases (CH_3F and HF) they are even better than the FOGO energies. We think that these differences between the 4-31G and the DZ basis set are mainly the result of the quality of the inner-shell orbitals, which in the 4-31G basis set seem to be better for H, O, and F, and worse for C and N. An analysis of the

Table 1. Energies (E/E_h)

Molecule	4-31G[a]	DZ	FOGO
H_2O	−75.9084	−75.8829	−75.9094
NH_3	−56.1045	−56.0987	−56.1208
CH_4	−40.1396	−40.1501	−40.1608
CHCH	−76.7111	−76.7386	−76.7452
CH_2CH_2	−77.9205	−77.9464	−77.9592
CH_3CH_3	−79.1148	−79.1354	−79.1524
CH_3F	−138.856	−138.830	−138.852
H_2CO	−113.692	−113.693	−113.717
HCN	−92.7308	−92.7540	−92.7687
CH_2CHF		−176.638	−176.664
HF	−99.8873[b]	−99.8382	−99.8548
CO		−112.565	−112.592

[a] From Ref. [9].
[b] From Ref. [10].

energies shows, that the energy differences between the 4-31G and DZ basis sets can approximately be explained in an additive scheme with parameters −0.0029, 0.0192, −0.0161, 0.0049, and −0.0414 E_h for H, C, O, N, and F, respectively. Therefore, we expect no major differences in the molecular properties predicted by the 4-31G and the DZ basis set, but hope for an improvement with FOGO.

4.2. Geometries

A significant improvement with FOGO was found for the bond angles, especially for H_2O and NH_3. This shows that FOGO accounts for the main polarization effects. The improvement for the bond-length, however, seems rather fortuitous, as it is well known, that SCF bond-lengths tend to be too short near the Hartree–Fock limit.

Table 2. Angles (Θ/Degrees)

Molecule	Angle	4-31G[a]	DZ	FOGO	Exp.	Ref.[b]
H_2O	H-O-H	111.2	107.3	104.2	104.5	[11]
NH_3	H-N-H	115.9	111.5	106.6	106.7	[12]
CH_2CH_2	H-C-H	116.0	115.9	116.5	116.6	[13]
CH_3CH_3	H-C-H	107.7	108.0	108.2	(107.8)[c]	[14]
CH_3F	H-C-H	110.7	110.2	109.7	(110.3)[c]	[15]
H_2CO	H-C-H	116.4	116.0	116.1	116.5	[16]
	RMS[d]	4.7	2.3	0.4		

[a] From Ref. [9].
[b] References for the experimental values.
[c] r_0-structure.
[d] $\mathrm{RMS} = \sqrt{(1/n)\sum_{i=1}^{n}(\Theta_{i,\mathrm{exp}}-\Theta_{i,\mathrm{calc}})^2}$, including r_0-structures, which usually deviate only little from r_e-structures for angles.

For H_2O angles of 112.2°, 107.3°, 104.2°, and 102.9° were found with the 4-31G, DZ, FOGO, and DZ+P basis sets. The O–H bond lengths were 0.951 Å, 0.971 Å, 0.958 Å, and 0.945 Å, respectively ($1\ \text{Å} = 10^{-10}\ \text{m}$), compared to an experimental angle of 104.5° and a bond length of 0.957 Å.

Table 2 shows the calculated and experimental angles.

One immediately can see a strong improvement in the H_2O and NH_3 angles. The other angles being already in good agreement with experiment were hardly improved.

Table 3 gives calculated and experimental bond lengths.

The equilibrium structure of CH_2CHF has not yet been reported. Several experimental r_0 and r_g structures from microwave and electron diffraction studies were published. However, these structures show considerable differences for most parameters. For a discussion of the experimental results and the controversy going on, see the paper of Huisman et al. [23].

We think, that (except for the C=C double bond) the calculated r_e-structure we obtain with FOGO has at least the accuracy of the experimental values at this

Table 3. Bond lengths (r/Å)

Molecule	Bond	4-31G[a]	DZ	FOGO	Exp.	Ref.[b]
H_2O	O–H	0.951	0.971	0.958	0.957	[11]
NH_3	N–H	0.991	1.007	1.012	1.011	[12]
CH_4	C–H	1.081	1.084	1.087	1.085	[17]
CHCH	C–H	1.051	1.054	1.055	1.061	[18]
CH_2CH_2	C–H	1.073	1.074	1.078	1.076	[13]
CH_3CH_3	C–H	1.083	1.084	1.087	(1.095)[c]	[14]
CH_3F	C–H	1.076	1.080	1.085	(1.095)[c]	[15]
H_2CO	C–H	1.081	1.084	1.093	1.099	[16]
HCN	C–H	1.051	1.054	1.058	1.066	[19]
HF	F–H	0.922[d]	0.943	0.919	0.917	[20]
	RMS[f]	0.012	0.013	0.004		
CH_3CH_3	C–C	1.529	1.538	1.543	(1.534)[c]	[14]
CH_3F	C–F	1.412	1.409	1.389	(1.389)[c]	[15]
CH_2CH_2	C=C	1.316	1.315	1.317	1.330	[13]
H_2CO	C=O	1.206	1.208	1.209	1.203	[16]
CHCH	C≡C	1.190	1.190	1.190	1.203	[18]
HCN	C≡N	1.140	1.139	1.143	1.153	[19]
CO	C≡O	1.128[e]	1.128	1.136	1.128	[21]

[a] From Ref. [9].
[b] References for the experimental values.
[c] r_0-structure.
[d] From Ref. [10].
[e] From Ref. [22].
[f] $\text{RMS} = \sqrt{(1/n) \sum_{i=1}^{en} (r_{i,\text{exp}} - r_{i,\text{calc}})^2}$, r_0-structures (being quite different from r_e for C–H bonds) not included.

Table 4. Structure of CH_2CHF (r/Å, Θ/Degrees)

Parameter	MW[a]	ED[b]	ED[c]	DZ	FOGO
$r_{C=C}$	1.332	1.333	1.330	1.304	1.310
$r_{C\text{-}F}$	1.348	1.348	1.351	1.376	1.352
$r_{C\text{-}H}$(gem.)	1.071	1.076	1.107	1.068	1.074
$r_{C\text{-}H}$(cis)	1.086	1.090	1.108	1.066	1.072
$r_{C\text{-}H}$(trans)	1.079	1.085	1.097	1.068	1.072
Θ_{CCF}	121.2	121.0	121.5	121.3	122.5
Θ_{CCH}(gem.)	120.9	127.7	130.8	124.9	125.2
Θ_{CCH}(cis)	118.8	121.4	120.4	121.0	121.5
Θ_{CCH}(trans)	120.7	123.9	118.7	118.8	119.5

[a] From Ref. [24].
[b] From Ref. [25].
[c] From Ref. [23].

stage. In Table 4 we compare the DZ and the FOGO structures with the most recent microwave and electron diffraction results. The angles and bond lengths other than X–H should be very similar in the different structures.

A geometry optimization will be the faster the better the starting position is. For FOGO this also includes the starting position of the floating orbitals. We may hope, that the polarization for similar bonds is always approximately the same and, therefore, that with growing experience we are able to estimate the starting positions for the floating orbitals quite accurately.

In the molecules we investigated, the polarization is always along a line, which is nearly identical with the direction of the classical bond. For the following we therefore define the polarization as the distance between the position of the floating orbitals and the corresponding nucleus given in Å. These polarizations are listed in Table 5. The entry 0.063 for O–H e.g. means, that the orbitals of the hydrogen are shifted 0.063 Å towards the oxygen. The negative entry for F–C means that the outermost *p*-orbitals of the carbon are shifted 0.095 Å *away* from the fluorine.

Table 5. Polarizations of the bonds[a] (r/Å)

Bond	Molecule	Polarization	Bond	Molecule	Polarization
C–H	(average)	0.035	C=C	CH_2CH_2	0.075
N–H	NH_3	0.049	O=C	H_2CO	0.025
O–H	H_2O	0.063	C=O	H_2CO	0.093
F–H	HF	0.067	C=C	CHCH	0.049
C–C	CH_3CH_3	0.043	N=C	HCN	0.030
F–C	CH_3F	−0.095	O≡C	CO	0.056
C–F	CH_3F	0.048	C≡N	HCN	0.128
H_3–N	NH_3	0.071	C≡O	CO	0.113
H_2–O	H_2O	0.064			

[a] See text.

It should be pointed out, that these polarizations are only meaningful in connection with the basis set used here, because the polarizations are related to the exponents (see Eq. (1)) and depend on which orbitals are allowed to float.

4.3. Dipole Moments

Table 6 shows the calculated and the experimental non-zero dipole moments. The experimental values are mostly accurate to at least 0.01 D, the calculated ones, may have rounding errors of about 0.01 D. As the difference between μ_e and μ_0 is usually less than 0.01 D and μ_e values are often not available, we did not specify the type of dipole moment.

The 4-31G basis set gives dipole moments typically 0.6 D or 30% too large. The dipole moments calculated with the DZ basis set are, as expected, only slightly better. It is well known [34] that calculated dipole moments are improved, if polarization functions are used. But even extended basis sets close to the Hartree–Fock limit yield dipole moments still 10 to 20% too large. The FOGO method with a double-zeta basis set corresponds to a standard calculation with a basis set somewhere between double-zeta and double-zeta-plus-polarization. We therefore expected an improvement in the calculated dipole moments. However, we were surprised, to obtain dipole moments typically with an error of less than 0.1 D or 5%.

For H_2O the 4-31G, DZ, FOGO and DZ+P dipole moments were 2.52 D, 2.37 D, 1.86 D, and 2.09 D, respectively, compared to an experimental value of 1.85 D. Evidently the sequence of the dipole moments is different from the one for the energies.

The dipole moment of HF was calculated in addition, to check, whether the relatively bad values for CH_3F and CH_2CHF (8% too small) were typically for fluorine compounds, what however was not confirmed.

Table 6. Dipole moments (μ/D)

Molecule	4-31G[a]	DZ	FOGO	Exp.	Ref.[b]
H_2O	2.52	2.37	1.86	1.85	[26]
NH_3	2.11	1.79	1.49	1.48	[27]
CH_3F	2.41	2.42	1.70	1.86	[28]
H_2CO	3.07	2.78	2.40	2.34	[29]
HCN	3.24	3.08	2.96	2.99	[30]
RMS[c]	0.60	0.42	0.08		
CH_2CHF		1.99	1.32	1.43	[31]
HF		2.16	1.80	1.83	[32]
CO		0.40	0.04	−0.12	[33]

[a] From Ref. [9].
[b] References for the experimental values.
[c] $\mathrm{RMS} = \sqrt{(1/n)\sum_{i=1}^{n}(u_{i,\mathrm{exp}} - u_{i,\mathrm{calc}})^2}$ for the molecules H_2O through HCN.

As a further test for the quality of FOGO dipole moments, the molecule CO was included. Reasonable values for the CO dipole moment were obtained previously only in very extensive CI calculations including single excitations (for a detailed discussion see Ref. [34]).

The excellent values for the calculated dipole moments may just be fortuitous, especially as it is known, that even calculations near the Hartree–Fock limit still give too high values. However, there is also the possibility, that basis sets which yield energies very close to the Hartree–Fock limit are still not flexible enough for accurate dipole moments. This would mean, that the special way, we allow for polarization in FOGO (including higher powers in Eq. (1)) is more suited to obtain accurate dipole moments. Further investigations will be needed to answer this question.

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