Theoret. Chim. Acta (Berl.) 47, 263–273 (1978)

THEORETICA CHIMICA ACTA

Original Investigations

Influence of Polarization Functions on Molecular Electrostatic Potentials

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We study the effects of *d*-polarization functions, centered on the heavy atoms, on the SCF molecular electrostatic potentials calculated for some molecules. The positions and energies of the minima found are very sensitive to the inclusion of polarization functions in the basis set used. The variations depend on the heavy atom involved and on the possible anisotropy of its charge distribution. These variations are particularly important for second-row atoms.

Key words: Polarization functions – Molecular electrostatic potentials

1. Introduction

It is well established that molecular electrostatic potentials provide a good first-order prediction of molecular reactivity, especially for reactions involving closed-shell molecules and ions [1–5]. Recently protonation of open-shell systems has been interpreted [6] in terms of electrostatic potentials, too. These studies made no special point of discussing the influence of the wave function accuracy on the shape of molecular electrostatic potentials and on the values of the minima [4, 5].

Ideally, this type of calculation should be carried out with a large basis set, but in practice this is only possible for very small molecules. Fortunately, qualitative conclusions, of interest from the reactivity point of view, can be drawn even when a small basis set is used [4]. Nevertheless, it has been proved that the value of the minima depends very strongly on the basis set used to obtain the SCF first-order density function.

In all these calculations only *s*- and *p*-type atomic functions, either STO or GTO, were used. *d*-type polarization functions centered on the heavy atoms have been included, but only for very few molecules. This is the case of the work done by

0040–5744/78/0047/0263/$02.20

Arrighini *et al.* [7] on the electrostatic potentials of the water molecule or that of Perahia *et al.* [8] on the phosphate group. But, to our knowledge, no one has yet attempted a systematic study of the influence of *d*-type polarization functions on molecular electrostatic potentials.

Such a study is the aim of this paper. We performed SCF calculations, with contracted GTO's for a series of molecules containing first row atoms and one molecule containing a second-row atom, where the polarization effects must be more important.

2. Basis Sets and Evaluation of Integrals

Two basis sets are used for molecules containing first-row atoms: 6-31G and 6-31G*. The 6-31G basis is a split-valence contracted Gaussian basis developed by Hehre *et al.* [9], and the 6-31G* basis set [10] includes six polarization functions $(x^2, y^2, z^2, xy, yz, xz) \exp(-\alpha r^2)$ added to the previous one, for each heavy atom.

For molecules containing second-row atoms the bases used are: STO-3G and STO-3G*. The first one is a minimal basis set of contracted Gaussians least square fitted to STO's. The star means again the addition of a set of six polarization functions on the heavy atom.

We have selected these bases for our study because in this way we can guarantee that all the differences observed in the electrostatic potentials calculated, will be due exclusively to the influence of the polarization functions.

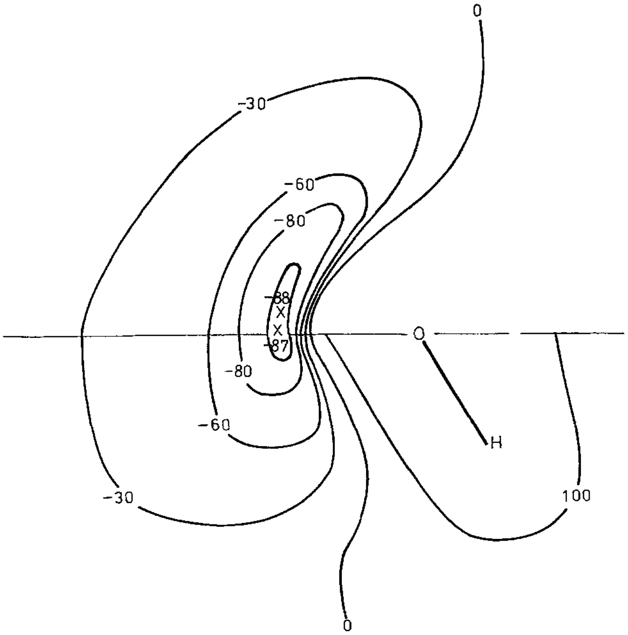

Fig. 1. Electrostatic potential map for H_2O (6-31G basis)

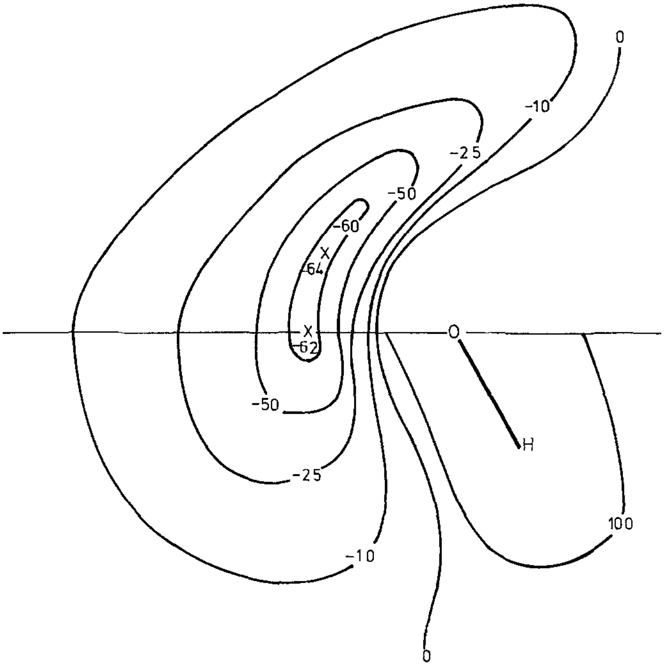

Fig. 2. Electrostatic potential map for H_2O (6-31G* basis)

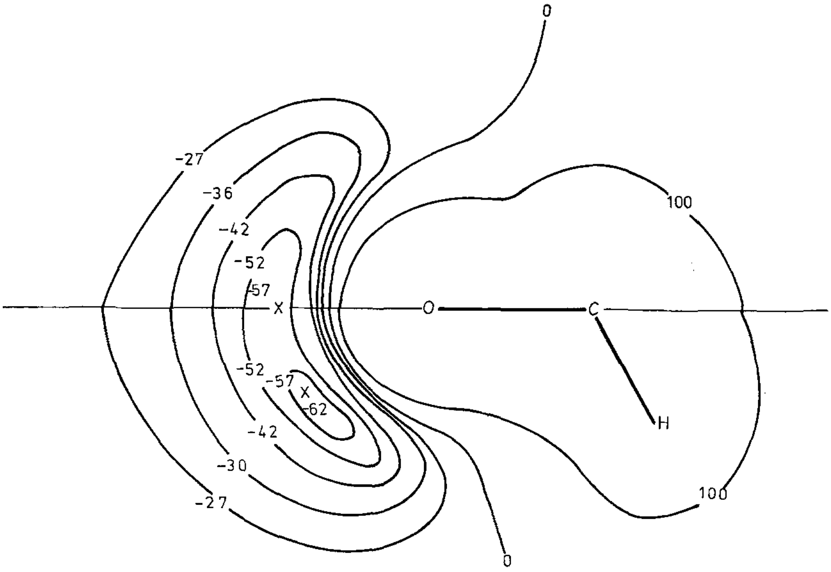

Fig. 3. Electrostatic potential map for H_2CO (6-31G basis)

The molecules we study are: water, ammonia, formaldehyde, hydrogen fluoride and hydrogen chloride.

The evaluation of the electrostatic potential, $\phi(r_i)$ at the point r_i, requires the evaluation of integrals of the form,

$$\phi(r_i)=\int\rho(r)|r_i-r|^{-1}\,d\tau \qquad (1)$$

where $\rho(r)$ is the electron first-order density function.

There are several ways to evaluate these integrals. They can be even considered as a particular case of the nuclear potential integrals involved in any typical SCF calculation.

Srebrenik *et al.* [11] have proposed an analytical method for the calculation of these potentials, based on the solution of the Poisson's equations. They present the final expressions for potentials defined in terms of *s*- and *p*-type GTO atomic functions.

We have solved that equation for potentials including *d*-type Gaussian atomic functions. This derivation is almost trivial, but we have included the most important steps and the final expressions in the Appendix, because this derivation is independent on the approximations used to obtain the first-order density function. In semiempirical methods the inclusion of polarization functions [12, 13] implies only a small increase in calculation time. Most of these methods use a STO's basis set, but the expressions from the Appendix can be used if the STO's are expanded in terms of GTO's. In fact, some applications of Srebrenik's equations, using the results from semiempirical calculations, with *s*- and *p*-type atomic orbitals, have already been published [11, 14].

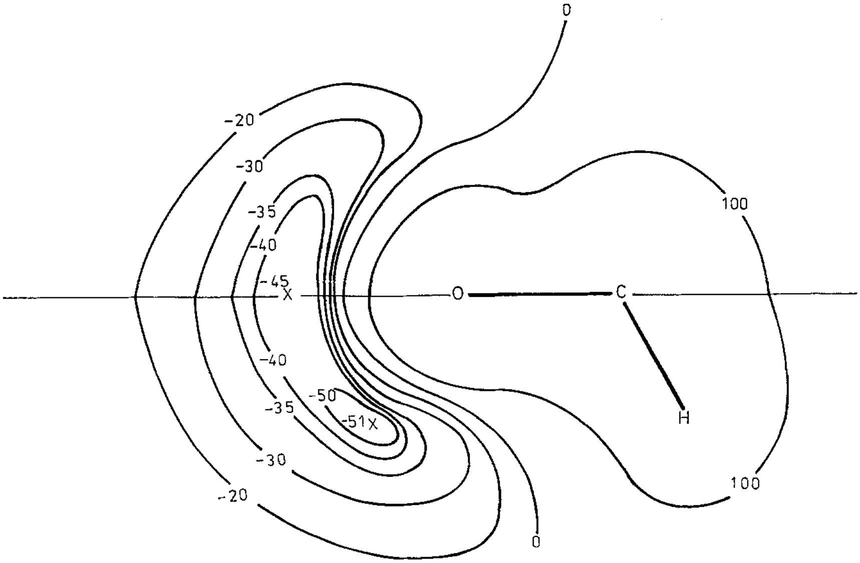

Fig. 4. Electrostatic potential map for H_2CO (6-31G* basis)

3. Results and Discussion

The molecular electrostatic potential maps for water and formaldehyde are presented in Figs. 1–4. Figs. 1 and 3 refer to results obtained with the 6-31G basis set and Figs. 2 and 4 to those using the 6-31G* basis. The lower part of the figures corresponds to the molecular plane (σ_v) and the upper part to a perpendicular plane (σ'_v) containing the molecular axis. Energies are always in kcal/mole.

For the ammonia molecule the molecular electrostatic potential was evaluated in one of the three symmetry planes. The results obtained with both basis sets (6-31G and 6-31G*) are plotted in Figs. 5 and 6 respectively. Figs. 7 and 8 show the results for hydrogen fluoride. For hydrogen chloride, the results obtained with the STO-3G and STO-3G* basis sets are presented in Figs. 9 and 10, respectively.

All the cases we have studied present some common features. The positions and energies of the minima are very dependent on the basis set used. The lower value is always the one obtained including polarization functions in the basis set. In general, these minima are further from the heavy atom when polarization functions are included. The shape of the iso-potential curves, with some exceptions that we will discuss later, does not change too much, but the attractive hole is much deeper when the basis without polarization features is used.

In the case of water and formaldehyde, both basis sets predict two minima in the σ'_v plane, one above and one below the molecular plane; they are due to the two lone pairs on the oxygen. For both systems the attractive zone changes considerably with the basis set. When polarization functions are included the attractive area "encloses" the oxygen atom to a considerable degree, which is not the case with the 6-31G basis set. At the same time the minima move away from the molecular

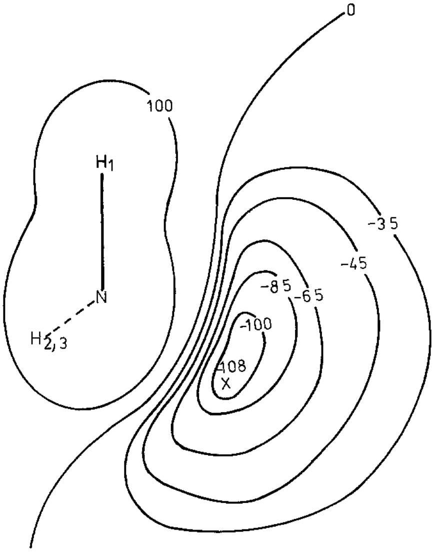

Fig. 5. Electrostatic potential map for NH_3 (6-31G basis)

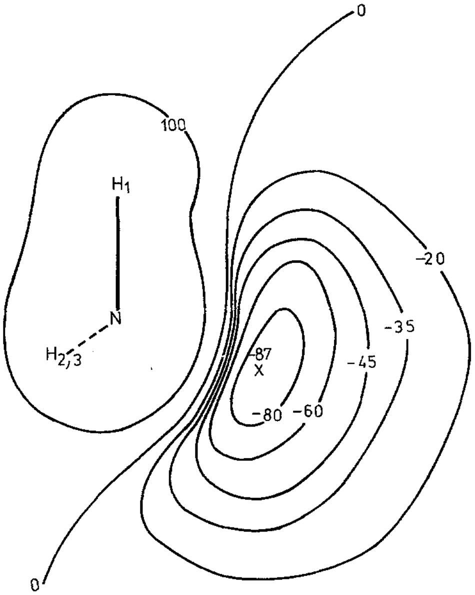

Fig. 6. Electrostatic potential map for NH_3 (6-31G* basis)

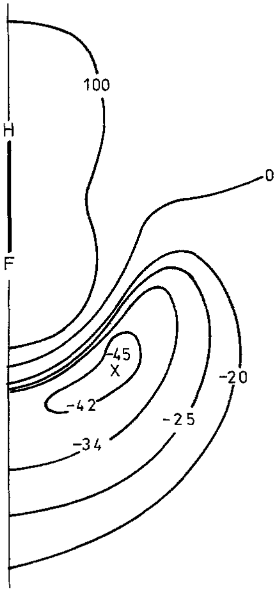

Fig. 7. Electrostatic potential map for FH (6-31G basis)

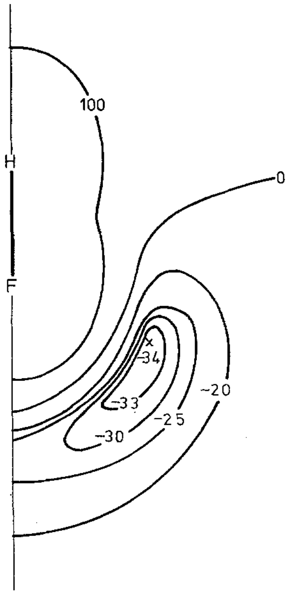

Fig. 8. Electrostatic potential map for FH (6-31G* basis)

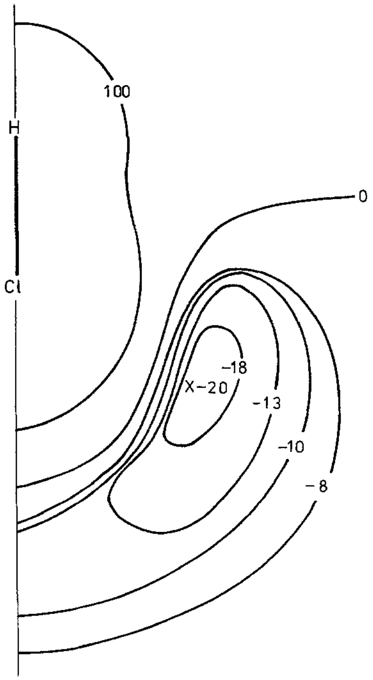

Fig. 9. Electrostatic potential map for ClH (STO-3G basis)

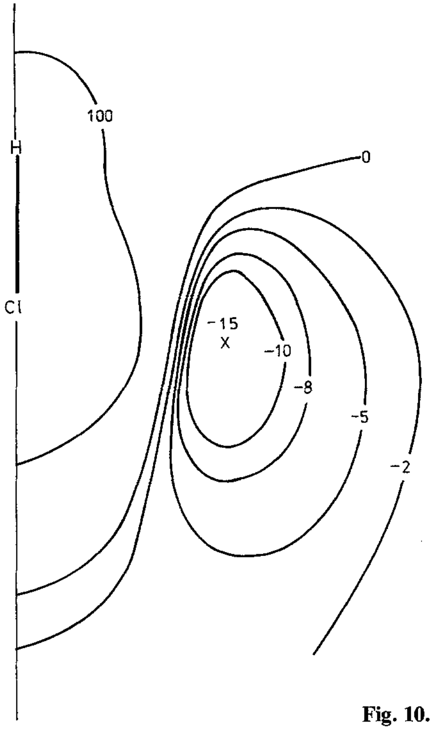

Fig. 10. Electrostatic potential map for ClH (STO-3G* basis)

plane when the 6-31G* basis set is used. In the case of ammonia, both basis sets predict a single minimum, since the nitrogen atom has only one lone pair.

For hydrogen fluoride, both bases predict a minimum zone of energy in the shape of a ring whose axis is the molecular axis.

In hydrogen chloride the changes produced by the inclusion of polarization basis are more important than in the other molecules studied, where the repulsive areas are not very affected by the polarization effects. In the case of hydrogen chloride the repulsive area around the chlorine atom increases, while that around the hydrogen atom is virtually unchanged. The zero potential line cuts the molecular axis at 4.2 a.u. or at 2.8 a.u. from the chlorine atom when STO-3G* or STO-3G bases are used, respectively. A similar effect to that described for water and formaldehyde is detected in the attractive zone. The displacement of the minimum is, in this case, particularly large.

The relative decrease in the energy value of the minima when we include polarization functions in the basis set varies for the different molecules and is presented in Table 1.

This decrease depends not only on the heavy atom involved (O, N, F, Cl) but also on the possible anisotropy caused by its environment. For water the energy lowering

Table 1. Energy lowerings (%) due to addition of *d*-functions

Molecule	Energy lowering
H_2O	27
H_2CO	17
NH_3	20
FH	24
ClH	25

is larger than for formaldehyde. This can be explained by a greater anisotropy of the charge distribution on the oxygen atom which requires stronger polarization effects to adequately describe the system. For this reason the influence of polarization functions must be greater in this case.

The inclusion of polarization functions centered on the heavy atoms allows the charge distribution to move away from the nucleus on which they are centered [15]. This may explain why the minima move away from the heavy atom, in all the cases presented here. It seems that the center of the charges may be somewhere in the bond and not on the nuclei. This may explain why the potential curves try to "enclose" the heavy atom, decreasing the depth of the attractive area.

From our results we conclude that it is necessary to incorporate polarization functions in the basis set used to calculate the molecular electrostatic potentials. It is also clear that their contribution is particularly important in the area of the minimum. Good results could probably be obtained if the general map is calculated without polarization functions and they are used to study in detail the area of the minima.

Acknowledgments. Part of the results presented here were obtained at the Carnegie-Mellon University Computation Center, Pittsburgh, Pa. (U.S.A.)

M.Y. and O.M. wish to thank The Program of Cultural Interchange between The United States of America and Spain and Ministerio de Educación y Ciencia of Spain, respectively, for grants.

4. Appendix

Analytic solution of the Possion equation for potentials involving *d*-type Gaussian functions.

We use the equations of Srebrenik *et al.* [11] for *s*- and *p*-GTO's: The Poisson equations and its solutions are:

a) For "*s*-*s*" type potential

$$\nabla^2\phi_0(r) = -4\pi \exp(-\alpha r^2) \tag{1}$$

and

$$\phi_0(r) = (\pi/\alpha)^{3/2} r^{-1} \operatorname{erf}(\alpha^{1/2} r) \tag{2}$$

b) For a "*s-p*" type potential:

$$\nabla^2\phi_1(r) = -4\pi X_i \exp(-\alpha r^2) \tag{3}$$

$$\phi_1(r) = \pi x/\alpha^2 r^2(-g+f) \tag{4}$$

where

$$g = \exp(-\alpha r^2) \tag{5}$$

and

$$f = 1/r \int_0^r \exp(-\alpha t^2)\,\mathrm{d}t \tag{6}$$

c) For a "*p-p*" type potential there are two possibilities:

1) $$\nabla^2\phi_2(r) = -4\pi X_i X_j \exp(-\alpha r^2) \tag{7}$$

where

$$\phi_2(r) = \pi xy/2\alpha^3 r^4[3f-(2\alpha r^2+3)g] \tag{8}$$

for $X_i = x$ and $X_j = y$.

2) $$\nabla^2\phi_3(r) = -4\pi X_i^2 \exp(-\alpha r^2) \tag{9}$$

where

$$\phi_3(r) = \pi/2\alpha^3 r^4[(3x^2-r^2+2\alpha r^4)f-(3x^2+2\alpha r^2x^2-r^2)g] \tag{10}$$

for the particular case $X_i = x$.

Our equations for "*p-d*" potentials are:

a) $$\nabla^2\phi_4(r) = -4\pi X_i^2 X_j \exp(-\alpha r^2) \tag{11}$$

which can be obtained by deriving Eq. (9) with respect to X_j:

$$\nabla^2(-1/2\alpha\cdot\partial\phi_3/\partial X_j) = -4\pi X_i^2 X_j \exp(-\alpha r^2) \tag{12}$$

Using (11) and (12):

$$\phi_4(r) = -1/2\alpha\cdot\partial\phi_3/\partial X_j \tag{13}$$

and for $X_j = y$,

$$\phi_4(r) = -y/2\alpha r\cdot\partial\phi_3/\partial r \tag{14}$$

Using now Eq. (10) we obtain:

$$\phi_4(r) = \pi y/4\alpha^4 r^6[(15x^2-3r^2+2\alpha r^4)f-(15x^2-3r^2+10\alpha x^2r^2+4\alpha^2x^2r^4)g] \tag{15}$$

The same result can be obtained by differentiating Eq. (7) with respect to X_i.

b) $$\nabla^2\phi_5(r) = -4\pi X_i X_j X_k \exp(-\alpha r^2) \tag{16}$$

By differentiating Eq. (7) with respect to X_k we obtain:

$$\phi_5(r) = \pi xyz/4\alpha^4 r^6[15f-(15+10\alpha r^2+4\alpha^2 r^4)g] \tag{17}$$

c) $\nabla^2\phi_6(r) = -4\pi X_i \exp(-\alpha r^2)$ (18)

Differentiating Eq. (9) with respect to X_i yields, for $X_i = x$:

$$\phi_6(r) = \pi/4\alpha^4 r^6[(15x^3 - 9xr^2 + 6\alpha xr^4)f - (15x^3 - 9xr^2 + 10\alpha x^3 r^2 + 4\alpha^2 x^3 r^4)g] \tag{19}$$

When the potential is given by the product of two *d*-functions there are four possibilities:

a) $\nabla^2\phi_7(r) = -4\pi X_i^2 X_j X_k \exp(-\alpha r^2)$ (20)

The solution can be found by differentiating Eq. (11) with respect to X_k (or by differentiating Eq. (16) with respect to X_i):

$$\begin{aligned}\phi_7(r) = \pi yz/8\alpha^5 r^8[&(105x^2 - 15r^2 + 6\alpha r^4)f - (105x^2 - 15r^2 - 4\alpha r^4 + 70\alpha x^2 r^2\\ &+ 28\alpha^2 x^2 r^4 + 8\alpha^3 x^3 r^6)g]\end{aligned} \tag{21}$$

b) $\nabla^2\phi_8(r) = -4\pi X_i^3 X_j \exp(-\alpha r^2)$ (22)

By differentiating Eq. (18) with respect to X_j (or Eq. (11) with respect to X_i) and for $X_i = x$ and $X_j = y$, we obtain:

$$\begin{aligned}\phi_8(r) = \pi y/8\alpha^5 r^8[&(105x^3 - 45xr^2 + 18\alpha xr^4 f) - (105x^3 - 45xr^2 - 12\alpha xr^4\\ &+ 70\alpha x^3 r^2 + 28\alpha^2 x^3 r^4 + 8\alpha^3 x^3 r^6)g]\end{aligned} \tag{23}$$

c) $\nabla^2\phi_9(r) = -4\pi X_i^2 X_j^2 \exp(-\alpha r^2)$ (24)

Differentiation of Eq. (11) with respect to X_j (for $X_i = x$ and $X_j = y$) yields

$$\begin{aligned}\phi_9(r) = \pi/8\alpha^5 r^8[&(105x^2y^2 - 15r^2y^2 + 6\alpha r^4 y^2 - 15r^2x^2 + 6\alpha r^4 x^2 + 3r^4\\ &- 4\alpha r^6 + 4\alpha^2 r^8)f - (105x^2y^2 - 15r^2y^2 - 4\alpha r^4 y^2 - 15r^2x^2\\ &- 4\alpha r^4 x^2 + 70\alpha x^2 y^2 r^2 + 28\alpha^2 x^2 y^2 r^4 + 8\alpha^3 x^2 y^2 r^6 + 3r^4 - 2\alpha r^6)g]\end{aligned} \tag{25}$$

d) $\nabla^2\phi_{10}(r) = -4\pi X_i^4 \exp(-\alpha r^2)$ (26)

Differentiation of Eq. (18) with respect to X_i (for $X_i = x$) leads to:

$$\begin{aligned}\phi_{10}(r) = \pi/8\alpha^5 r^8[&(105x^4 - 90x^2r^2 + 36\alpha x^2 r^4 + 9r^4 - 12\alpha r^6 + 12\alpha^2 r^8)f\\ &- (105x^4 - 90x^2r^2 + 70\alpha x^4 r^2 - 24\alpha x^2 r^4 + 9r^4 + 28\alpha^2 x^4 r^4\\ &+ 8\alpha^3 x^4 r^6 - 6\alpha r^6)g].\end{aligned} \tag{27}$$

We have not presented the solutions for potentials involving "*s-d*" products, because the corresponding equations are entirely similar to those for "*p-p*" products. We want to point out that the expressions presented here correspond to the six polarization functions mentioned in Sect. 2 of this paper. These expressions can be easily transformed to those in terms of the given *d*-functions: $(3z^2 - r^2$, $xz, yz, xy, x^2 - y^2) \exp(-\alpha r^2)$.

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Received April 1, 1977/September 16, 1977