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# Variational Method for Calculating Molecular Multipole Polarizabilities Using Atom Centered Extended Trial Functions

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An improvement of the variational method for calculating the electronic multipole polarizabilities is proposed. This modification allows the computation of the polarizabilities at any point and the results are compatible with the relations existing for a change of origin. It is applied to $H_2$, HF, CO and $N_2$ by using SCF wavefunctions developed on a limited basis. The computed polarizabilities are systematically too large but this discrepancy is attributed to the fact that the ground state is too far from the exact wavefunction.

**Key words:** Molecular multipole polarizabilities – Variational method for calculating polarizabilities.

## 1. Introduction

Recently [1], we described the application to molecules of a variational method for calculating the multipole electronic polarizabilities proposed earlier for atoms [2]. This procedure sometimes referred to as the Kirkwood–Pople–Schofield (KPS) method proved being quite easy to use, since it has the advantage of needing a good ground state wavefunction only. Recently Sadlej [3] has studied the accuracy of the method and shown that it is strongly dependent on the quality of this wavefunction. The components of the electric field and the appropriate linear combinations of their derivatives are treated as the components of a generalized field vector $[\mathscr{F}]$ of any dimension so that the hamiltonian operator for

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the molecule embedded in an electric field can be written

$$\mathcal{H} = \mathcal{H}_0 - [\boldsymbol{\mathcal{M}}][\boldsymbol{\mathcal{F}}] \tag{1}$$

where $\mathcal{H}_0$ denotes the hamiltonian operator of the free molecule and $[\boldsymbol{\mathcal{M}}]$ is the row matrix of the $\mathcal{M}$'s operators defined in [1] as the real linear combinations:

$$(\mathcal{M}_l^m + \mathcal{M}_l^{-m})/2 \text{ and } (\mathcal{M}_l^m - \mathcal{M}_l^{-m})/2i$$

of the spherical functions

$$\mathcal{M}_l^m = \sum_i r_i^l Y_l^m(\Theta_i, \chi_i) \tag{2}$$

where $i$ refers to electron $n°i$ and $r$, $\Theta$ and $\chi$ are the usual spherical coordinates, the origin being taken at the point where the polarizabilities are computed.

The number of elements in $[\boldsymbol{\mathcal{M}}]$ or $[\boldsymbol{\mathcal{F}}]$ is $\sum_{l=1}^{n}(2l+1)$ if $n$ is the order of the highest multipole taken in consideration.

The energy of the system is thus written in the form:

$$W = W_0 - [\boldsymbol{M}][\boldsymbol{\mathcal{F}}] - \tfrac{1}{2}[\boldsymbol{\mathcal{F}}][\boldsymbol{\mathcal{A}}][\boldsymbol{\mathcal{F}}] \tag{3}$$

where $[\boldsymbol{M}]$ is the row matrix of the expectation values of the moment operators $\mathcal{M}$ computed with the ground state eigenfunction $\psi_0$ of $\mathcal{H}_0$ and $[\boldsymbol{\mathcal{A}}]$ is a square matrix whose components are linear combinations of those of the polarizability tensor. The details of the transformation are given in Ref. [1]. The calculation of $[\boldsymbol{\mathcal{A}}]$ has been performed by a variational method making use of the trial wavefunction:

$$\psi = N(1 + [\boldsymbol{\mathcal{M}}][\boldsymbol{\lambda}])\psi_0 \tag{4}$$

in which $N$ is the normalization factor and $[\boldsymbol{\lambda}]$ a vector of variational coefficients.

The results obtained for HF and $CH_4$ appearing to be too small, especially in the case of the dipole-quadrupole polarizability $A_{x,yz}$, we tried to use [4], like Shukla and Easa [5] in the case of atoms, an improvement issued from the method proposed for calculating dipole polarizabilities of diatomic molecules by Kolker and Karplus [6] and multipole polarizabilities of atoms and ions by Langhoff, Karplus and Hurst [7–8].

This improvement consisted in introducing in addition to the $\mathcal{M}$'s operators in the trial wavefunction those which have the form:

$$r\mathcal{M}_k = \sum_i r_i m_k(i) \tag{5}$$

and

$$r^2\mathcal{M}_k = \sum_i r_i^2 m_k(i) \tag{6}$$

where $m_k(i)$ is a one-electron moment operator and $\mathcal{M}_k$ one of the $\mathcal{M}$'s operators

$$\mathcal{M}_k = \sum_i m_k(i) \tag{7}$$

Shukla and Easa generalized, for the atomic multipole polarizabilities, a result which was known for atomic dipole polarizabilities [9–10]: the $r^2\mathcal{M}_k$ operators do not bring a noticeable improvement so that the convergence appeared to be almost reached after the introduction of the $r\mathcal{M}$ moment operators. Applied to $CH_4$ molecule this extension of the trial wavefunction increased the values of $\boldsymbol{\alpha}$, $\boldsymbol{A}$ and $\boldsymbol{C}$ but $\boldsymbol{\alpha}$ was the most strongly affected [4]. We also verified that the introduction of the third variational term did not affect noticeably the results. Nevertheless, some problems appeared when we applied this method to other molecules, due to non-linear dependence of the $r\mathcal{M}$ operators on the electrons coordinates: the value of the pure-dipole polarizabilities were dependent on the point origine where they had been computed and the dipole-quadrupole and pure quadrupole polarizabilities no-longer verified the well-known relations [11]:

$$A_{z',z'z'} = A_{z,zz} - 2\alpha_{zz}R \tag{8}$$

$$C_{z'z',z'z'} = C_{zz,zz} - \tfrac{4}{3}A_{z,zz}R + \tfrac{4}{3}\alpha_{zz}R^2 \tag{9}$$

where the origin of the primed system is $(0, 0, R)$ in the unprimed system. In Table 1 we give the values obtained for $H_2$, HF, CO and $N_2$ when computed with the center of mass and the center of each of the nuclei as origin. We can also notice that in the case of $N_2$, the convergence is not reached with the introduction of the $r\mathcal{M}$ moments. The values obtained with this modification to the variational method will be referred to as ref. [4] in the Tables 2 to 5.

## 2. Trial Wavefunction Including Moments Computed with the Nuclei of the Molecule as Origin

In order to avoid the difficulties due to the introduction into the trial wavefunction of the $r\mathcal{M}$ moments having their origin at the point where the polarizabilities are computed, we propose to replace them by a superposition of $r\mathcal{M}$ moments having fixed origins taken at the nuclei. We will expose this method in the case of diatomic molecules. The trial wavefunction can be written as

$$\psi = N(1 + [\boldsymbol{\mathcal{M}}][\boldsymbol{a}] + [\boldsymbol{r}_1\boldsymbol{\mathcal{M}}_1][\boldsymbol{b}_1] + [\boldsymbol{r}_2\boldsymbol{\mathcal{M}}_2][\boldsymbol{b}_2])\psi_0 \tag{10}$$

where $[\boldsymbol{r}_j\boldsymbol{\mathcal{M}}_j]$ is the row matrix of operators

$$r_j\mathcal{M}_{j,k} = \sum_i r_{j,i}m_{j,k}(i) \tag{11}$$

with $m_{j,k}(i)$ being a one-electron moment operator computed with $j$ as origin and applied to electron No. $i$. $[\boldsymbol{a}]$, $[\boldsymbol{b}_1]$ and $[\boldsymbol{b}_2]$ are three sets of variational parameters.

If $\psi_0$ is the exact eigenfunction of hamiltonian $\mathcal{H}_0$, the lemma established in [1] and which has been expressed in the form:

$$\langle\psi_0\mathcal{M}_n|\mathcal{H}_0|\psi_0\mathcal{M}_k\rangle = W_0\langle\psi_0|\mathcal{M}_n\mathcal{M}_k|\psi_0\rangle + \tfrac{1}{4}\langle\psi_0|\nabla^2\mathcal{M}_n\mathcal{M}_k|\psi_0\rangle \tag{12}$$

is easily generalized when $\mathcal{M}$'s operators are replaced by their product with $r$, so that:

$$\langle\psi_0\mathcal{M}_n|\mathcal{H}_0|\psi_0 r_j\mathcal{M}_{j,k}\rangle = \langle\psi_0|\mathcal{M}_n r_j\mathcal{M}_{j,k}|\psi_0\rangle + \tfrac{1}{2}\langle\psi_0|\nabla\mathcal{M}_n \cdot \nabla r_j\mathcal{M}_{j,k}|\psi_0\rangle \tag{13}$$

**Table 1.** Results obtained for the multipole polarizabilities of $H_2$, HF, CO and $N_2$ using the trial function described in Ref. [4] taking different points as origin. ($N$ being the number of variational terms in $\psi$)

| Molecule | Origin | $z$ coordin. of the point ($a_0$) | $\alpha_{zz}(a_0^3)$ | | | $A_{z,zz}(a_0^4)$ | | | $C_{zz,zz}(a_0^5)$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $N=1$ | $N=2$ | $N=3$ | $N=1$ | $N=2$ | $N=3$ | $N=1$ | $N=2$ | $N=3$ |
| $H_2$ | H1 | 0.000000 | 9.027 | 9.098 | 9.125 | 12.652 | 12.727 | 12.761 | 10.585 | 10.770 | 10.787 |
| | H2 | 1.40165 | 9.027 | 9.098 | 9.125 | −12.652 | −12.727 | −12.761 | 10.585 | 10.770 | 10.787 |
| | CM [a] | 0.700825 | 9.027 | 9.107 | 9.143 | 0.000 | 0.000 | 0.000 | 4.673 | 4.867 | 4.872 |
| HF | H | 1.733000 | 4.748 | 5.835 | 6.331 | −12.006 | −15.351 | −16.559 | 14.530 | 17.977 | 19.047 |
| | F | 0.000000 | 4.761 | 6.760 | 6.813 | 4.472 | 5.401 | 5.459 | 5.811 | 6.381 | 6.431 |
| | CM [a] | 0.08729876 | 4.761 | 6.696 | 6.745 | 3.640 | 4.185 | 4.222 | 5.340 | 5.807 | 5.846 |
| CO | C | 0.000000 | 16.278 | 16.623 | 18.930 | 29.762 | 28.393 | 34.148 | 44.997 | 47.022 | 51.940 |
| | O | 2.132000 | 16.276 | 17.352 | 18.871 | −39.642 | −38.994 | −42.111 | 59.040 | 63.102 | 65.434 |
| | CM [a] | 1.21811953 | 16.276 | 16.339 | 18.312 | −9.892 | −10.052 | −10.505 | 28.861 | 34.280 | 35.531 |
| $N_2$ | N1 | −1.03704999 | 19.990 | 20.742 | 23.125 | 41.460 | 40.100 | 45.386 | 51.177 | 52.096 | 56.174 |
| | N2 | 1.03704999 | 19.990 | 20.742 | 23.125 | −41.460 | −40.100 | −45.386 | 51.177 | 52.096 | 56.174 |
| | CM [a] | 0.000000 | 19.990 | 19.990 | 22.475 | 0.000 | 0.000 | 0.000 | 22.513 | 26.096 | 27.158 |

[a] CM: Center of Mass

and

$$\langle\psi_0 r_i\mathcal{M}_{i,n}|\mathcal{H}_0|\psi_0 r_j\mathcal{M}_{j,k}\rangle = W_0\langle\psi_0|r_i\mathcal{M}_{i,n}r_j\mathcal{M}_{j,k}|\psi_0\rangle + \tfrac{1}{2}\langle\psi_0|\nabla r_i\mathcal{M}_{i,n}\cdot\nabla r_j\mathcal{M}_{j,k}|\psi_0\rangle \tag{13b}$$

By using the identities (12) and (13), the normalization condition of the trial wavefunction and the extremum conditions $\partial W/\partial a_j = \partial W/\partial b_{1j} = \partial W/\partial b_{2j} = 0$ for all $j$, the components of the polarizability tensor $[\mathscr{A}]$ are easily found. Doing that we make an approximation whose effects are unpredictable [3], $\psi_0$ not being the exact eigenfunction of hamiltonian $\mathcal{H}_0$. This will be discussed over numerical results.

To obtain the elements of $[\mathscr{A}]$ we only need to compute the integrals:

$$\langle\psi_0|\nabla^2(\mathcal{M}_k\mathcal{M}_n)|\psi_0\rangle$$

$$\langle\psi_0|\nabla r_1\mathcal{M}_{1,k}\cdot\nabla r_1\mathcal{M}_{1,n}|\psi_0\rangle$$

$$\langle\psi_0|\mathcal{M}_k\mathcal{M}_n|\psi_0\rangle - \langle\psi_0|\mathcal{M}_k|\psi_0\rangle\langle\psi_0|\mathcal{M}_n|\psi_0\rangle$$

$$\langle\psi_0|r_1\mathcal{M}_{1,k}\mathcal{M}_n|\psi_0\rangle - \langle\psi_0|r_1\mathcal{M}_{1,k}|\psi_0\rangle\langle\psi_0|\mathcal{M}_n|\psi_0\rangle$$

$$\langle\psi_0|\nabla r_1\mathcal{M}_{1,k}\cdot\nabla\mathcal{M}_n|\psi_0\rangle$$

$$\langle\psi_0|\nabla r_1\mathcal{M}_{1,k} : \nabla r_2\mathcal{M}_{2,n}|\psi_0\rangle$$

## 3. Results

In Table 2–5 we give the results obtained for the pure dipole, dipole–quadrupole and pure quadrupole polarizabilities in the case of $H_2$, CO, HF and $N_2$.

The quantum mechanical averages of the operators needed to determine the components of the matrices written above are computed using an extension of the program Polyatom [12]. The subroutines allowing the computation of the fifth and sixth moments, likewise the $rx^ly^mz^n$ and $(x^{l1}y^{m1}z^{n1}/r)$ moments up to degree $l+m+n=4$ and $l_1+m_1+n_1=6$ and the $x_1^{l1}y_1^{m1}z_1^{n1}x_2^{l2}y_2^{m2}z_2^{n2}/r_1r_2$ moments upto degree $l_1+m_1+n_1+l_2+m_2+n_2=12$, were added to the original program.

The bases used are the "Double-zeta" gaussian basis set provided by Snyder and Basch [13] for which the results of the SCF calculation are tabulated. The values are computed with the center of mass as origin of the $\mathcal{M}$ moments and we have verified that, now, the relations (8) and (9) are satisfied.

## 4. Discussion

The better agreement with experimental values is reached for $\alpha_\perp$, and for HF we find a value of dipole-quadrupole polarizabilities in good agreement with these obtained by other authors. Nevertheless we can point out that in most of the results the increase of the values obtained for $\boldsymbol{\alpha}$, $\boldsymbol{A}$ and $\boldsymbol{C}$ is too large especially in the case of $\alpha_\parallel$. This is in agreement with the conclusions of Sadlej [3] who shows that the good results obtained with the (KPS) method depends on the quality of the ground state wavefunction of the molecule.

**Table 2.** Multipole polarizabilities of H2

| Number of variational terms in $\psi$ | This work and Ref. [4] 1 | This work 2 | Ref. [4] 3 | Other Results | Experiment |
|---|---|---|---|---|---|
| $\alpha_{\parallel}(a_0^3)$ | 9.027 | 9.191 | 9.143 | 6.502 [b] | 6.381 [a] |
| $\alpha_{\perp}(a_0^3)$ | 4.284 | 4.640 | 4.624 | 4.595 [b] | 4.578 [a] |
| $\alpha(a_0^3)$ | 5.866 | 6.157 | 6.130 | 5.231 [b] | 5.179 |
| $\Delta\alpha(a_0^3)$ | 4.743 | 4.551 | 4.519 | 1.908 [b] | 1.803 |
| $C_{zz,zz}(a_0^5)$ | 4.673 | 4.872 | 4.872 | 5.927 [d] | |
| $C_{xx,xx}(a_0^5)$ | 3.448 | 3.611 | 3.618 | 4.944 [d] | |
| $C_{xz,xz}(a_0^5)$ | 3.126 | 3.276 | 3.275 | 4.242 [d] | |
| $C_{xy,xy}(a_0^5)$ | 2.280 | 2.393 | 2.400 | 3.463 [d] | |
| Bond $L(a_0)$ | | 1.40165 | | | |
| Energy | | −1.1266 Hartree | | | −1.17447 [c] |
| $\Theta_{zz}(ea_0^2)$ | | 0.3214 | | | 0.523 [c] |

[a] taken from Ref. [15]: accurate value
[b] see Ref. [16]
[c] taken from Ref. [17]
[d] see Ref. [18]

**Table 3.** Multipole polarizabilities of HF

| Number of variational terms in $\psi$ | This work and Ref. [4] | This work | Ref. [4] | Other results | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | HF SCF | Other meth. | Experiment |
| $\alpha_{\parallel(zz)}(a_0^3)$ | 4.761 | 6.807 | 6.745 | | | 6.593 [a] |
| $\alpha_{\perp(xx)}(a_0^3)$ | 3.004 | 4.496 | 4.488 | | | 5.103 [a] |
| $A_{z,zz}(a_0^4)$ | 3.640 | 4.292 | 4.222 | | 4.042 [19]<br>4.055 [11] | |
| $A_{x,xz}(a_0^4)$ | 0.494 | 0.415 | 0.415 | | 0.625 [19] | |
| $C_{zz,zz}(a_0^5)$ | 5.340 | 5.870 | 5.846 | | 5.470 [11] | |
| $C_{xx,xx}(a_0^5)$ | 3.571 | 4.024 | 4.038 | | | |
| $C_{xz,xz}(a_0^5)$ | 2.698 | 3.029 | 3.040 | | | |
| $C_{xy,xy}(a_0^5)$ | 2.236 | 2.557 | 2.557 | | | |
| $\alpha(a_0^3)$ | 3.589 | 5.266 | 5.240 | 4.90 [14]<br>4.04 [24]<br>4.74 [25] | 5.59 [14]<br>4.33 [26] | 5.60 [a] |
| $\Delta\alpha(a_0^3)$ | 1.757 | 2.311 | 2.257 | 1.28 [14]<br>1.91 [24]<br>1.59 [25] | 1.27 [14]<br>1.65 [26] | 1.49 [a] |
| Bond length $(a_0)$ | | 1.733 | | | | 1.733 [20] |
| Energy (Hartree) | | −100.0150 | | −100.0705 [11] | | |
| $\mu(ea_0)$ | | 0.9349 | | 0.7608 [11] | | 0.7156 [21]<br>0.707 [22] |
| $\Theta_{zz}(ea_0^2)$ | | 1.6535 | | 1.747 [11] | | 1.933 [23] |

[a] Taken from Ref. [14]

**Table 4.** Multipole polarizabilities of CO

| Number of variational terms in $\psi$ | This work and Ref. [4] | This work | Ref. [4] | Other results | | Experiment |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | HF SCF | Other meth. | |
| $\alpha_{\parallel(zz)}(a_0^3)$ | 16.276 | 19.960 | 18.312 | 14.52 [28] | 15.85 [28] | 15.727 [a] |
| $\alpha_{\perp}(a_0^3)$ | 8.384 | 12.149 | 11.457 | 11.10 [28] | 11.66 [28] | 12.147 [a] |
| $\alpha(a_0^3)$ | 11.014 | 14.752 | 13.742 | 12.40 [14] | 13.13 [14]<br>11.34 [26] | 13.340 [a] |
| $\Delta\alpha(a_0^3)$ | 7.892 | 7.811 | 6.855 | 3.19 [14] | 3.91 [14]<br>3.20 [26] | 3.580 [a] |
| $A_{z,zz}(a_0^4)$ | -9.893 | -9.410 | -10.505 | | | |
| $A_{x,xz}(a_0^4)$ | -8.383 | -10.491 | -10.413 | | | |
| $C_{zz,zz}(a_0^5)$ | 28.861 | 34.531 | 34.315 | | | |
| $C_{xx,xx}(a_0^5)$ | 15.696 | 18.506 | 18.133 | | | |
| $C_{xz,xz}(a_0^5)$ | 21.822 | 26.760 | 26.326 | | | |
| $C_{xy,xy}(a_0^5)$ | 8.481 | 9.623 | 9.555 | | | |
| Bond length $(a_0)$ | | 2.132 | | | | 2.1323 [b] |
| Energy (Hartree) | | −112.6763 | | −112.7769 [28] | −112.8344 [28] | |
| $\mu(a_0e)$ | | 0.155 | | | | 0.044 [a] |
| $\Theta_{zz}(ea_0^2)$ | | −2.27325 | | | | |

[a] Taken from Ref. [27]
[b] Taken from Ref. [28]

**Table 5.** Multipole polarizabilities of $N_2$

| Number of variational terms in $\psi$ | This work and Ref. [4] | This work | Ref. [4] | Other results | | Experiment |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | HF SCF | Other meth. | |
| $\alpha_{\parallel(zz)}(a_0^3)$ | 19.989 | 24.679 | 22.475 | 14.78 [29] | 13.64 [29] | 14.854 [a] |
| $\alpha_{\perp}(a_0^3)$ | 7.764 | 11.266 | 10.558 | 9.74 [29] | 9.81 [29] | 10.184 [a] |
| $\alpha(a_0^3)$ | 11.839 | 15.737 | 14.530 | | 10.90 [26] | 11.741 [a] |
| $\Delta\alpha(a_0^3)$ | 12.225 | 13.413 | 11.917 | | 6.23 [26] | 4.640 [a] |
| $C_{zz,zz}(a_0^5)$ | 22.513 | 27.158 | 26.097 | | | |
| $C_{xx,xx}(a_0^5)$ | 13.690 | 15.889 | 15.602 | | | |
| $C_{xz,xz}(a_0^5)$ | 16.212 | 19.478 | 19.188 | | | |
| $C_{xy,xy}(a_0^5)$ | 8.055 | 9.097 | 9.076 | | | |
| Bond length $(a_0)$ | | 2.0741 | | | | 2.068 |
| Energy (Hartree) | | −108.8695 | | −108.9823 [28] | −109.0573 [28] | |
| $\Theta_{zz}(ea_0^2)$ | | −1.8427 | | | | −0.52<br>±0.04 [20] |

[a] Taken from Ref. [27]
[b] Taken from Ref. [29]

We already pointed out [4] that this method mimics for the trial wavefunctions, some features of the basis set extension effects. Since the polarizabilities are defined as the coefficients of the variation of energy when a field is applied, the use of an extended trial function with a limited initial basis set gives rise to an energy gap which is exagerated and, therefore, to values of polarizabilities which are too large. But, on the other hand, if we use a basis set including a great number of gaussian functions, the computation of the integrals over $\nabla r_1 \mathcal{M}_{1,k} \cdot \nabla r_2 \mathcal{M}_{2,n}$ becomes prohibitively time-consuming.

Therefore, it appears that reasonable values of polarizabilities can be obtained with a ground state wavefunction expanded on a medium basis set provided that the variational method is limited to the first term.

When the ground state wavefunction has been obtained with large basis sets the extension of the trial wavefunction proposed here can also be used, but previous method [4] is able to give good results too, provided that the problems arising from the choice of the origin are solved. This is easily done when the molecule is symmetric enough ($N_2$, $CO_2$, $CH_4$ . . .).

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