

Semi-empirical calculation of static molecular polarizability using CHFT: some benzene derivatives and aromatic heterocycles

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Abstract. The static polarizability of fifteen organic molecules (point group symmetry: C_{2v} ; number of electrons ≥ 26) have been theoretically calculated using the CNDO/S-CHFT scheme and the results have been compared with other available data.

Keywords. Static polarisability; CNDO/S; CHFT.

1. Introduction

Calculation of electric polarizability, both static and dynamic, of large molecular systems have drawn considerable attention in recent times (Marchese and Jaffe 1977; Zamani-Khamiri and Hameka 1979; Waite and Papadopoulos 1983; Gupta and Bhattacharyya 1984a). In this context, the CNDO/S-CI method (Delbene and Jaffe 1968) coupled with second order perturbation theory (Marchese and Jaffe 1974) has been found to be quite promising insofar as inclusion of electron correlation and computational ease are concerned. In view of the facts that (i) the CNDO/S-CI method (Delbene and Jaffe 1968) is actually equivalent to working in the Tamm Dancoff approximation (TDA) (Dunning and McKoy 1967) of the equations of motion (EOM) (McCurdy *et al* 1977) approach and (ii) the TDA involves only the correlated excited states and not the ground state, it is natural, therefore, to seek a theory which incorporates the effect of electron correlation in both the ground and excited states. The coupled-Hartree-Fock-theory (CHFT) is one that provides a satisfactory route to this end.

So, here, we report a few exploratory calculations of static molecular polarizability by the CNDO/S-CHFT scheme, i.e., where the basis functions are generated by the CNDO/S approximation and the static polarizability is computed using the CHFT.

2. Theory

The theoretical aspects have been discussed in detail elsewhere (Gupta and Bhattacharyya 1984b). However, for convenience, the essential points are outlined

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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below. From the basic equation

$$(H_0 + V)|\psi\rangle = E|\psi\rangle, \tag{1}$$

we extract the Rayleigh-Schrodinger perturbation equations as

$$(H_0 - E_0)|0\rangle = 0, \tag{2}$$

$$(H_0 - E_0)|\psi^{(1)}\rangle + (V - E^{(1)})|0\rangle = 0, \tag{3}$$

etc., where the terms have their usual significance. The second-order correction to energy is given by

$$E^{(2)} = \langle 0|V|\psi^{(1)}\rangle. \tag{4}$$

By defining the excitation (de-excitation) operator $S^\dagger(S)$ as

$$S^\dagger|0\rangle = |\psi^{(1)}\rangle \tag{5a}$$

and

$$S|0\rangle = 0, \tag{5b}$$

we can proceed through (3) to obtain

$$[H_0, S^\dagger]|0\rangle + (V - E^{(1)})|0\rangle = 0. \tag{6}$$

$E^{(2)}$ may then be written in a commutator form as

$$E^{(2)} = \langle 0|[V, S^\dagger]|0\rangle, \tag{7}$$

and the polarizability (α) is given by

$$\alpha = 2E^{(2)}. \tag{8}$$

Now (6) may be rearranged to yield

$$[S, [H_0, S^\dagger]]|0\rangle + [S, V]|0\rangle = 0 \tag{9}$$

and the use of the triple commutator $[S, H_0, S^\dagger]$, (McCurdy *et al* 1977) yields

$$\langle 0|[S, H_0, S^\dagger]|0\rangle + \frac{1}{2}\langle 0|[V, S^\dagger]|0\rangle + \frac{1}{2}\langle 0|[S, V]|0\rangle = 0 \tag{10}$$

from (9).

At this point the ground state wavefunction $|0\rangle$ is approximated as $|\phi_{HF}\rangle$, S^\dagger is considered a linear combination of $(1h - 1p)$ excitation and de-excitation operators:

$$S^\dagger = \sum_{am} \langle m|g|\alpha\rangle a_m^\dagger a_\alpha - \sum_{n\beta} \langle \beta|h|n\rangle a_\beta^\dagger a_n,$$

and V is taken as

$$V = \sum_{ij} \langle i|v|j\rangle a_i^\dagger a_j$$

where m, n , etc denote particle orbitals, α, β, \dots the hole orbitals and i, j, \dots any orbital. These are precisely the approximations used in deriving the RPA (McCurdy *et al* 1977) and we can proceed in the same way to arrive at (11):

$$\sum_{n\beta} A_{m\alpha, n\beta} \langle n|g|\beta\rangle + B_{m\alpha, n\beta} \langle \beta|h|n\rangle + \frac{1}{2}\langle m|V|\alpha\rangle = 0. \tag{11}$$

The matrix elements are given by

$$A_{m\alpha, n\beta} = (\varepsilon_m - \varepsilon_\alpha) \delta_{mn} \delta_{\alpha\beta} + \{1 + (-1)^s\} \langle m\beta | v | \alpha n \rangle - \langle m\beta | v | n\alpha \rangle, \quad (12a)$$

$$B_{m\alpha, n\beta} = \{1 + (-1)^s\} \langle mn | v | \alpha\beta \rangle - \langle mn | v | \beta\alpha \rangle, \quad (12b)$$

with s representing the spin state.

Equation (11), along with (6), is identical with the CHFT equation deduced by Langhoff *et al* (1966). We have used here these very equations to evaluate different principal components of α .

3. Results and discussion

In table 1 we report the results of ground-state calculations of the polarizability components ($\alpha_{\mu\mu}$) and the mean polarizability ($\bar{\alpha}$) for 15 molecules, all having at least 8 atoms, 26 electrons and C_{2v} point group symmetry. Our results are also compared with the CNDO/S-CI values (Marchese and Jaffe 1977) and experimental data wherever available. In all these calculations $\{\alpha\}$ and $\{m\}$ have 10 orbitals each.

It is interesting to note that usually $\alpha_{\mu\mu}$ ($\mu = x, y$ or z) values calculated by the CNDO/S-CHFT scheme are *lower* than those obtained via the CNDO/S-CI scheme. However, we should mention that whereas the CNDO/S-CI describes correlated excited

Table 1. Ground-state polarizability components (α_{xx} , α_{yy} , α_{zz}) and average polarizability ($\bar{\alpha}$) of some planar molecules with C_{2v} symmetry (in units of 10^{-24} cm³), calculated by the CNDO/S-CHFT method.

Molecule	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
Benzene	9.377 (13.19) ^a [11.1] ^b	9.387 (13.50) [11.1]	1.008 (0.90) [7.4]	6.591 (9.20) [9.87]
Pyridine	9.200 (12.16)	8.807 (12.82)	0.97 (1.02)	6.326 (8.67)
Pyridazine	8.775 (13.32)	9.147 (12.73)	1.188 (1.76)	6.370 (9.27)
Pyrimidine	7.944 (11.86)	8.431 (12.16)	1.155 (1.58)	5.843 (8.53)
Pyrazine	8.138 (12.06)	7.460 (13.34)	1.239 (1.14)	5.612 (8.85)
s-Triazine	8.269	8.239	1.197	5.902
s-Tetrazine	8.344	9.588	1.568	6.500
Pyrrole	4.870	8.250	1.290	4.803
Furan	6.824	6.977	1.489	5.097
Fluoro-benzene	9.871	9.587	0.965	6.808
1,4-Difluorobenzene	10.077	9.461	0.866	6.801
1,3-Difluorobenzene	10.505	9.997	0.835	7.112
1,2-Difluorobenzene	9.965	10.599	0.642	7.069
p-Benzoquinone	3.107	19.404	0.844	7.785
Aniline	9.195	9.865	1.344	6.801

^a CNDO/S-CI values³ in parenthesis; ^b experimental values in square brackets; A D Buckingham and N J Bridge 1966 *Proc. R. Soc. (London)* **A295** 334.

states only by a maximum of 60 configurations (Marchese and Jaffe 1977), our CNDO/S-CHFT prescription introduces electron correlation into *both* the ground and excited states through 100 configurations. Besides, various semi-empirical calculations for planar molecules using all-valence AO basis sets indicate (Teixeira-Dias and Sarre 1975) that (i) the calculated out-of-plane polarizability component (α_{zz}) is always *much less* than the experimental value, and (ii) the $\{\alpha_{\mu\mu}\}$ are always *smaller* than the corresponding experimental values; however, the values improve gradually with the extension of the AO-basis set (Gupta and Bhattacharyya 1984a).

Table 1 shows that in the case of *benzene*, the molecule for which experimental data is available, the $\alpha_{\mu\mu}$ (CNDO/S-CHFT) $<$ $\alpha_{\mu\mu}$ (experimental) $<$ $\alpha_{\mu\mu}$ (CNDO/S-CI), $\mu = x$ or y , which corroborates the remark mentioned above. This, in turn, implies that CNDO/S-CHFT is probably more balanced than the CNDO/S-CI.

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