# A Method of Least-Squares for Refining Electron-Diffraction Internuclear Distances using Spectroscopical Shrinkage Effects

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The Bastiansen-Morino shrinkage effect[1] was first time introduced for linear chains of atoms[2]. As pointed out by Morino,[3] the shrinkage effect may be computed in the linear case from a harmonic-vibration analysis. Recently it has been found that the same situation is present in several cases of non-linear shrinkage effects for highly symmetrical molecules[1]. The Bastiansen-Morino shrinkage effects should be taken into account when electron-diffraction measurements are interpreted. A refinement of the electron-diffraction $r^g$-values (mean internuclear distances) in germanium tetrachloride has been performed by means of the calculated shrinkage effect from spectroscopic data[4]. This case is very simple as the molecule contains only one structural parameter and one shrinkage effect. The same procedure has been generalized for an arbitrary number of structural parameters and shall be outlined in the following.

Assume a molecule with $N$ types of observable internuclear distances, $r_1$, $r_2$, $\ldots$, $r_K$, $r_{K+1}$, $\ldots$, $r_N$, of which $K$ may be considered as independent structural parameters. The remaining $N-K$ distance types are associated with $N-K$ independent shrinkage effects, which may be expressed as

$$-\delta_n = r_n{}^g - \sum_{k=1}^{K} c_{nk} r_k{}^g, \quad n = K+1, \ldots, N \qquad (1)$$

where $c_{nk}$ are constants. This is an extension of the *practical* shrinkage effect for three-particle configurations[1]. Let the observed $r^g$-values from electron-diffraction be denoted by $(r_i{}^g)^\circ$, and put

$$r_i{}^g = (r_i{}^g)^\circ + \varepsilon_i, \quad i = 1, 2, \ldots, N$$

where $\varepsilon_i$ represents the correction terms. The corrected values are required to fit accurately the $N-K$ eqns. (1) with "theoretic" $\delta$-values (from spectroscopic calculations). Hence

$$\Big(\sum_k c_{nk}[(r_k{}^g)^\circ + \varepsilon_k]\Big) - (r_n{}^g)^\circ - \varepsilon_n = \delta_n \text{ (theor)}$$

or

$$\Big(\sum c_{nk}\, \varepsilon_k\Big) - \varepsilon_n = \delta_n \text{ (theor)} - \delta_n \text{ (expt)} \qquad (2)$$

This is a set of $N-K$ linear equations with $N$ unknowns ($\varepsilon_i$). Exactly the desired number of $K$ additional linear equations are obtained by minimizing the sum of squares,

$$P = \sum_{i=1}^{N} \varepsilon_i{}^2 \qquad (3)$$

This function may be expressed with the aid of eqns. (2) as a polynomial of second degree in $K$ independent variables, *e.g.*, $\varepsilon_k$ ($k = 1, 2, \ldots, K$). In consequence,

$$\frac{\partial}{\partial \varepsilon_k} P(\varepsilon_1, \ldots, \varepsilon_k) = 0 \qquad (4)$$

Now the complete set of linear eqns. (2), (4) may be solved for the $\varepsilon$'s. This method is adequate if all the observed internuclear distances may be treated indiscriminately, *i.e.*, they are assumed to be of the same accuracy. This condition is very often not fulfilled in practice. In such cases the present method may easily be modified by replacing the expression of (3) by

$$P' = \sum_{i=1}^{N} w_i \varepsilon_i{}^2 \qquad (5)$$

where $w_i$ represents some weight factors.

The method has been applied to benzene, on which a detailed report will be published later.

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