# 151. *The Calculation of Atom Self-polarizabilities and Similar Quantities in the Molecular-orbital Theory.*

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Attention is drawn to a formula for $\pi$-electron densities which is often the most convenient to use for calculations. An analogous kind of formula is derived for atom self-polarizabilities. It is particularly useful for numerical work. For illustration, the atom self-polarizabilities of a benzene position and the 1-position of butadiene are evaluated by use of the new formula.

Molecular-orbital quantities used for discussing chemical reactivities and other molecular properties, for example $\pi$-electron densities and atom self-polarizabilities, are usually calculated from formulae which were originally systematically derived by Coulson and Longuet-Higgins.[1] Thus the $\pi$-electron densities for all the atoms of a conjugated system are mostly computed from the molecular-orbital coefficients, while if the charge at just one atom of a large conjugated system is required the contour-integral formula, involving numerical integration, is mostly employed. Similar alternative techniques are utilised for calculating polarizabilities. The purpose of this paper is to draw attention to an alternative procedure which may often be used with advantage for such computations. In the case of $\pi$-electron densities this involves a formula which has been given previously by Coulson and Longuet-Higgins.[1] An analogous formula is derived below for atom self-polarizabilities.

Coulson and Longuet-Higgins derived the contour-integral formula for $\pi$-electron densities from the formula

$$q_\mu = -\sum_j \nu_j \frac{\Delta_{\mu\mu}(e_j)}{\Delta'(e_j)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\Delta$ is the secular determinant for the molecule under consideration, $\Delta_{\mu\mu}$ the determinant derived from $\Delta$ by omitting row $\mu$ and column $\mu$, $e_j$ is the energy of the $j$th molecular orbital, and $\nu_j$ the number of electrons occupying that orbital. $\Delta'$ is used to represent $\partial\Delta/\partial e$.

It is usual to divide each row of $\Delta$ by $\beta$ and make the substitution $(\alpha - e)/\beta = x$. Thus, we obtain the determinant $D(x)$ where if $\Delta$ is of the $n$th order

$$\beta^n D(x) = \Delta(e)$$

and then

$$\Delta'(e) = -\beta^{n-1} D'(x)$$

where $D'$ represents $dD/dx$. If these relationships are inserted into (1), we obtain

$$q_\mu = \sum_j \nu_j \frac{D_{\mu\mu}(x_j)}{D'(x_j)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Practical trials reveal that it is about as convenient to use equation (2) as to use the contour-integral procedure in the calculation of $q_\mu$ once the determinal zeros $x_j$ are known. Equation (2) has the advantage that it avoids the slight uncertainty generally associated with numerical integration, and the problem of whether there are any occupied orbitals with positive values of $x_j$ or unoccupied orbitals with negative values of $x_j$ does not cause any complications such as arise when using the contour-integral formula. If one wishes to calculate the resonance energy of a molecule and the $\pi$-electron density and atom-localization energy at a particular position the most convenient practical procedure is to determine the zeros of $D(x)$ and of $D_{\mu\mu}(x)$ and then calculate $q_\mu$ from equation (2); [$D'(x_j)$ is obtained while finding $x_j$ if Newton's method is employed].

A similar kind of formula to equation (2) is particularly convenient for calculating atom self-polarizabilities, $\pi_{\mu\mu}$, especially when the values of $x_j$, $D'(x_j)$, and $D_{\mu\mu}(x)$ are already known. This is usually the case because resonance energies and atom-localization energies

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[1] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.

are generally calculated before $\pi_{\mu\mu}$ is studied. The formula may be derived from the contour-integral formula [1]

$$\pi_{\mu\mu} = \frac{1}{\pi i}\int_{\Gamma}\left\{\frac{\Delta_{\mu\mu}(e)}{\Delta(e)}\right\}^2 \mathrm{d}e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where the contour $\Gamma$ encloses just the zeros of $\Delta$ corresponding to doubly occupied orbitals. The substitution $(\alpha - e)/\beta = x$ transforms equation (3) into

$$\pi_{\mu\mu} = \frac{-1}{\pi i\beta}\int_{\gamma}\left\{\frac{D_{\mu\mu}(x)}{D(x)}\right\}^2 \mathrm{d}x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$= -\frac{1}{\beta}\sum_j \nu_j R_j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

where $R_j$ is the residue of the integrand in (4) at the pole $x_j$. The pole $x_j$ is of the second order and, on writing $D(x) = (x - x_j)\mathrm{F}_j(x)$, we have

$$R_j = \frac{\mathrm{d}}{\mathrm{d}x}\left[\left\{\frac{D_{\mu\mu}(x)}{\mathrm{F}_j(x)}\right\}^2\right]_{x=x_j} = \frac{2D_{\mu\mu}(x_j)}{[\mathrm{F}_j(x_j)]^3}\left\{\mathrm{F}_j(x_j)D'_{\mu\mu}(x_j) - \mathrm{F}'_j(x_j)D_{\mu\mu}(x_j)\right\} \quad . \qquad (6)$$

From the definition of $\mathrm{F}_j$ we have

$$D'(x_j) = \mathrm{F}_j(x_j)\,; \quad D''(x_j) = 2\,\mathrm{F}'_j(x_j)$$

hence equation (6) can be expressed in terms of $D$ and its derivatives and $D_{\mu\mu}$ and its derivative. The expression (5) for the polarizability thus becomes

$$\pi_{\mu\mu} = \frac{1}{\beta}\sum_j \nu_j \frac{D_{\mu\mu}(x_j)}{[D'(x_j)]^3}\left\{D_{\mu\mu}(x_j)D''(x_j) - 2D'(x_j)D'_{\mu\mu}(x_j)\right\} \quad . \quad . \quad . \qquad (7)$$

To illustrate the ease with which equation (7) can be employed the self-polarizability of the terminal atom of butadiene will be calculated.

From the secular determinants, we have

$$D(x) = x^4 - 3x^2 + 1 \text{ and } D_{11}(x) = x(x^2 - 2)$$

hence $\qquad D'(x) = 2x(2x^2 - 3)\,; \quad D'_{11}(x) = 3x^2 - 2$

and $\qquad D''(x) = 6(2x^2 - 1)$

The two most negative zeros of $D$, and the values of the above functions at these zeros are :

| $x_j$ | $D'$ | $D''$ | $D_{11}$ | $D'_{11}$ | $-\nu_j R_j$ |
|---|---|---|---|---|---|
| $-(\sqrt{5}+1)/2$ | $-(\sqrt{5}+5)$ | $6(\sqrt{5}+2)$ | $-1$ | $(3\sqrt{5}+5)/2$ | $7\sqrt{5}/50$ |
| $-(\sqrt{5}-1)/2$ | $-(\sqrt{5}-5)$ | $6(2-\sqrt{5})$ | $+1$ | $(5-3\sqrt{5})/2$ | $7\sqrt{5}/50$ |

and so $\qquad \pi_{11} = 28\sqrt{5}/100\beta = 0{\cdot}62609903/\beta.$

It is clear from equation (4) that we are concerned primarily with $D_{\mu\mu}/D$. If the molecule has sufficient symmetry or if accidentally $D$ has a repeated zero then a corresponding common factor in $D$ and $D_{\mu\mu}$ can be cancelled, thus reducing somewhat the labour of computation. The simplification occurs in the calculation of the self-polarizability of a benzene position. Thus we have

$$D = (x^2 - 1)^2(x^2 - 4) \text{ and } D_{\mu\mu} = x(x^2 - 1)(x^2 - 3)$$

and, after cancellation of the common factor,

$$D' = 2x(2x^2 - 5) \qquad\qquad D_{\mu\mu} = x(x^2 - 3)$$
$$D'' = 2(6x^2 - 5) \qquad\qquad D'_{\mu\mu} = 3(x^2 - 1)$$

These give the values

| $x_j$ | $D'$ | $D''$ | $D_{\mu\mu}$ | $D'_{\mu\mu}$ | $-\nu_j R_j$ |
|---|---|---|---|---|---|
| $-2$ | $-12$ | 38 | $-2$ | 9 | 35/108 |
| $-1$ | $-6$ | 2 | 2 | 0 | 2/27 |

The self polarizability of a benzene position therefore amounts to $43/108\beta$.

It is clear from equation (5) that $-R_j/\beta$ represents the contribution of an electron in the $j$th orbital to the atom self-polarizability. Formula (7) may therefore prove convenient for the analysis of the relative contributions from different occupied orbitals, *e.g.*, both occupied orbitals of butadiene contribute equally to the polarizability of the 1-position.

Expressions analogous to equation (7) can similarly be derived for the other polarizabilities introduced by Coulson and Longuet-Higgins (*loc. cit.*), but less use has been made of these than of the atom self-polarizabilities. It may be noted that formula (7) is readily applicable to heterocyclic systems and non-alternant systems. The problem of whether there are any occupied orbitals with positive values of $x_j$ or unoccupied orbitals of negative values of $x_j$ does not cause any complications such as arise when the contour-integral formula is used.

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