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An Extension of the "Uniformly Charged Sphere Approximation" to π -Electron Calculations for Twisted Conjugated Systems

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In 1952 Parr¹ introduced a simple formula for evaluating two-electron two-center Coulomb integrals for use in LCAO-MO calculations involving planar π -electron systems:

$$(pp|qq) = (14.395/r) \left(\frac{1}{2} + \frac{1}{2} [1 + (d/r)^2]^{-\frac{1}{2}} \right) \text{eV} \quad (1)$$

Here r is the distance between the atoms p and q , and d is the diameter of two uniformly charged tangent spheres defined for each type of atom. In cases where

atoms p and q are different, eqn. (1) becomes slightly more complicated.

As eqn. (1) shows, the integral values are expressed as the repulsion energy between pairs of point charges at the sphere centers. This method has been widely used because of its simplicity and good agreement with integral values obtained theoretically from Slater orbitals.

We will here report an extension of the method for applications to twisted molecules. Let us assume the molecule to have a general formula R_1-R_2 . R_1 and R_2 may be twisted an angle ϕ relative to each other. A coordinate system is introduced with the z axis along the R_1-R_2 bond, and the xz plane in the molecular plane when $\phi=0$.

Each integral is expressed as a sum of four inverse distances (between sphere centers), multiplied by a conversion factor, as in the planar case.¹ One of these distances will be given by the following expression when one atom from each of the groups R_1 and R_2 is involved:

$$r_1 = [(x_1 - x_2 \cos \phi \pm \frac{1}{2}d_2 \sin \phi)^2 + (\frac{1}{2}d_1 \pm x_2 \sin \phi \pm \frac{1}{2}d_2 \cos \phi)^2 + (z_1 - z_2)^2]^{\frac{1}{2}} \quad (2)$$

The atomic centers involved are labelled by the indices 1 and 2. Sphere diameters are denoted d_1 and d_2 . The x and z coordinates are atomic coordinates for the case $\phi=0$.

To obtain each separate r_1 value, the three symbols \pm in (2) have to be substituted in the same order from left to right by either

$$\begin{array}{l} (1) \quad + + + \\ \text{or } (2) \quad + - - \\ \text{or } (3) \quad - + - \\ \text{or } (4) \quad - - + \end{array}$$

Table 1. Comparison between theoretical and approximate values of some selected two-electron integrals. All values in eV.

Molecule	Integral	Method	Angle of rotation				
			0°	30°	60°	90°	120°
3,3'-Bithienyl	(2 2/6 6)	Theoretical Eqn. (3)	5.37	5.38	5.42	5.44	5.42
			5.37	5.38	5.41	5.43	5.41
2-Fluorobiphenyl	(13 13/8 8)	Theoretical Eqn. (3)	5.42	5.25	4.70	4.11	3.67
			5.42	5.24	4.74	4.15	3.69
	(13 13/7 7)	Theoretical Eqn. (3)	4.88	4.94	5.04	5.10	5.04
			4.88	4.96	5.12	5.20	5.12

The Coulomb integral (in eV) is finally obtained from these r_i values (in Å) by

$$(11|22) = 3.599 \sum_{i=1}^4 1/r_i \quad (3)$$

In the special case $\phi=0$, this is identical with Parr's formula.

The validity of eqn. (3) as a substitute for theoretical integrals, was tested in studies of 3,3'-bithienyl² and 2-fluorobiphenyl.³ The Coulomb integrals that are changed on rotation were calculated by both methods. The theoretical values were scaled by a distance-dependent factor given by the ratio between the approximate and the theoretical value of an integral over parallel p_π components.^{2,3}

For bithienyl the difference between the two methods was never larger than 0.01 eV. In Table 1 a few selected integral values are given as an illustration. The numbering of atoms is shown in Fig. 1.

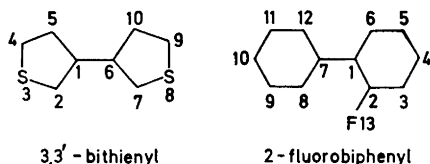


Fig. 1. Notation of atoms.

Integrals involving substituents in the *ortho* position to the R_1 - R_2 bond, are expected to show a larger difference between theoretical values and values obtained from eqn. (3). This is clearly demonstrated by the selected integral values for fluorobiphenyl, where the largest deviation is 0.1 eV.

Eqn. (3) will thus be a simple and satisfactory alternative to the laborious evaluation of theoretical integrals for use in semi-empirical MO calculations.

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The Valence Charge Distribution of Pyridine in the Iterative Extended Hückel Approach*

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Pyridine is a compound of fundamental interest in the series of six-membered, aromatic heterocyclics, and its electronic structure has, therefore, been the subject of numerous calculations in various approaches. Comparatively little attention has been paid to the electron density distribution of the molecule. In connection with the valence concept the valence charge distribution is of particular interest. Visualized in the form of contour diagrams, the valence charge distribution gives insight into several features which are associated with the first order density matrix. A comparison with the corresponding diagrams of the isoelectronic pyrylium ion¹ in the same approach is also of interest. The procedure for obtaining the level diagrams has been described earlier,² and here only some additional parameter values are given. The constants for nitrogen in the second order charge iterative process are in descending order of charge

-1.616 29.302 -131.703 for 2s orbitals
-1.038 24.522 -110.591 for 2p orbitals

For hydrogen the value 1.2 has been used for the exponent of the 1s Slater orbitals in the calculation of eigenvectors as well as the density itself.³ Atomic units has been used, and the contours represent the levels 0.01, 0.03, 0.06, ..., 0.30, 0.35, ..., 0.50, 0.70. The geometry of pyridine is taken from Bak *et al.*⁴

Comments. The σ charge distribution in the molecular plane (Fig. 1) indicates a distinct lone pair at the nitrogen atom. This nitrogen contributes with 1.63 electrons to the highest occupied orbital as compared to 1.12 for the oxygen atom in the pyrylium ion (the value 1.5

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