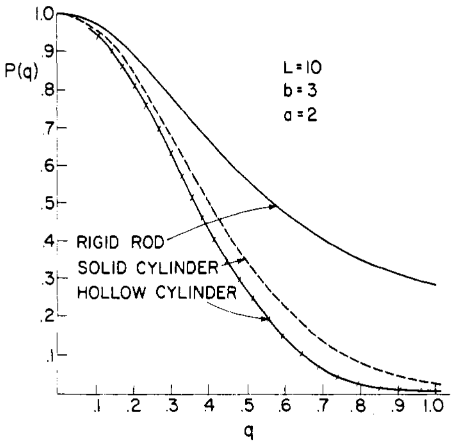

Figure 1. Intramolecular structure factor for cylindrical shapes. Numerical evaluation of eq 2 for $L = 10$: (——) rigid rods, $b = a = 0$; (- - -) $a = 0$, $b = 3$; crossed line, hollow cylinder, $a = 2$, $b = 3$.

may be found in ref 4, especially the case of a radially stratified cylinder. It is important to recognize that this expression has the proper limiting behavior.

(1) In the limit $b \rightarrow 0$, $a \rightarrow 0$, one obtains the *rigid rod* result[6]

$$P(\mathbf{q}) = u^{-1}\int_0^u \mathrm{d}x \left(\frac{\sin x}{x}\right)^2 \tag{3}$$

with $u = (qL/2)$. The limit $a \rightarrow 0$ corresponds to the case of a right circular cylinder of finite thickness.

(2) In the limit $L \rightarrow 0$, $a \rightarrow 0$, one obtains the *solid disk* result[7]

$$P(\mathbf{q}) = \int_0^{\pi} \mathrm{d}(\cos\theta)\, F(z\sin\theta) = \left(\frac{2}{z^2}\right)[1 - F(2z)] \tag{4}$$

where $F(x) = 2J_1(x)/x$ and $z = bq$. The equality in eq 4 was originally correctly stated by Kratky and Porod[7] and is frequently repeated without proof.[4,5] A direct proof requires some ingenuity.[8]

(3) In the limit of an *infinitesimal shell* $a \rightarrow b$, one obtains

$$P(\mathbf{q}) = \frac{1}{2}\int_0^{\pi} \mathrm{d}\theta \sin\theta \left[\frac{\sin(u\cos\theta)}{u\cos\theta}J_0(z\sin\theta)\right]^2 \tag{5}$$

which is consistent with the result for rings given by Oster and Riley.[9]

(4) In the limit $q \rightarrow 0$, one obtains the *low q* result:

$$P(\mathbf{q}) = 1 - \frac{q^2S^2}{3} + \mathcal{O}(q^4) \tag{6}$$

where S^2 is, by necessity,[10] the radius of gyration of the hollow cylinder

$$S^2 = \frac{b^2 + a^2}{2} + \frac{L^2}{12} \tag{7}$$

(5) Limiting expressions in the *large q* limit depend upon the relative magnitude of the parameters. For example, in the limit $qL \rightarrow \infty$, qa, qb finite one obtains

$$P(\mathbf{q}) = \frac{\pi}{2qL}\left\{\frac{1}{b^2 - a^2}[b^2F(bq) - a^2F(aq)]\right\}^2 \tag{8}$$

The quadrature in eq 2 cannot be evaluated analytically but, of course, can be numerically evaluated for pertinent values of the parameters q, L, b, and a. In addition, useful expansions may be constructed in various regions of interest. For example, in the limit of a hollow "needle", where $a/L \ll 1$, $b/L \ll 1$, and $u = qL/2 \sim 1$, one may easily show, to order $(a/L)^2$ and $(b/L)^2$

$$P(\mathbf{q}) = \left[1 - \left(\frac{b^2 + a^2}{L^2}\right)u^2\right]P_{\mathrm{rod}}(\mathbf{q}) + \left(\frac{b^2 + a^2}{2L^2}\right)\left[1 - \frac{\sin(2u)}{2u}\right] \tag{9}$$

where $P_{\mathrm{rod}}(\mathbf{q})$ is given by eq 3.

Figure 1 presents results for $P(q)$ obtained from numerical evaluation of eq 2 for illustrative values of the parameters: $L = 10$, $b = 3$, and $a = 2$. The hollow cylinder results lie very close to the comparable solid cylinder result for $L = 10$, $b = 3$, and $a = 0$, although it is somewhat more sharply peaked in the forward direction. This suggests that intensity angular distribution measurements are not sensitive to the internal configuration of molecular multisubunit assemblies.

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CNDO/2 Charge Density Calculation for Large Molecules

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Molecular mechanics calculation is a popular technique for investigating intramolecular and intermolecular properties of macromolecules.[1] It requires the evaluation of atomic charge densities so as to calculate the electrostatic interaction energy. The use of the semiempirical CNDO/2 and ab initio MO methods has become popular for this purpose,[2,3] although bond moments, electronegativities of atoms, and Del Re charges are still used for a simple estimation of the charge distribution. However, these MO methods cannot easily be applied to large molecules because of limited computer core memory; the charge densities of large molecules are usually estimated from those of the smaller model compounds. This note describes the direct calculation of charge densities of large molecules at the level of the CNDO/2 approximation.[4]

In the SCF CNDO method, the orthogonal **C** matrix which satisfies

$$\tilde{\mathbf{C}}\mathbf{F}\mathbf{C} = \mathbf{E} \tag{1}$$

must be found, where **F** is the Fock matrix and **E** is the diagonal orbital-energy matrix. The charge densities are calculated from the diagonal elements of the density matrix, **R**, which is constructed by the occupied part of the **C** matrix:

$$\mathbf{R} = \mathbf{C}_{\mathrm{o}}\tilde{\mathbf{C}}_{\mathrm{o}} \tag{2}$$

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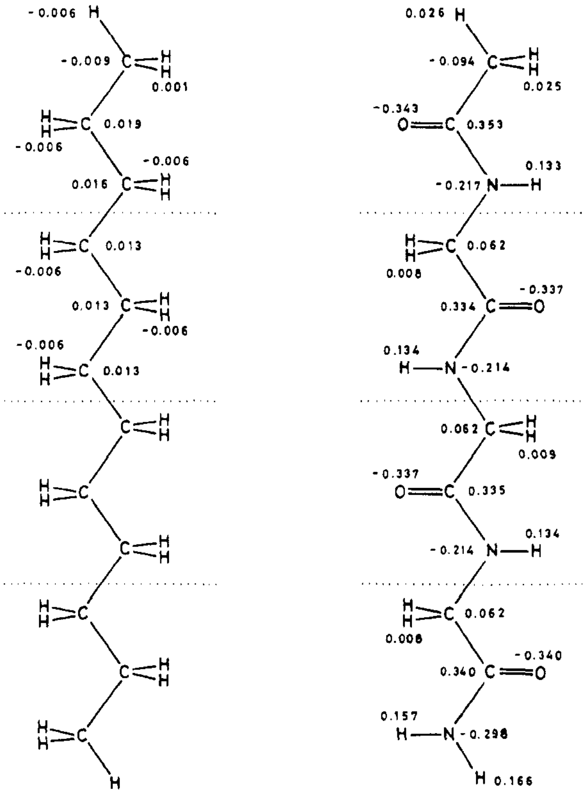


I

II

Figure 1. CNDO/2 charge distributions of model compounds. The dotted lines indicate the division of the molecules into fragmental groups. The two procedures described here give these exact SCF values.

For large molecules (with more than 300 valence atomic orbitals), the sizes of the **F** and **C** matrices are very large, and it may be impossible to keep all of the matrix elements in a computer's core storage. A method should be employed in which only small parts of the matrices are stored in the core storage at any given time. Here, the molecule is divided into N fragmental groups, and the **F** and **C** matrices are expressed as supermatrices which are composed by the matrices between the groups.

$$\mathbf{F} = \begin{bmatrix} \mathbf{F}_{11} & \mathbf{F}_{12} \cdots & \mathbf{F}_{1N} \\ \mathbf{F}_{21} & \mathbf{F}_{22} \cdots & \mathbf{F}_{2N} \\ \cdots & \cdots\cdots & \cdots \\ \mathbf{F}_{N1} & \mathbf{F}_{N2} \cdots & \mathbf{F}_{NN} \end{bmatrix}$$

All of the matrices between groups are stored in direct-access random files with their own record numbers. They are read into the core successively in order to carry out the calculation necessary for the determination of **R**. Two practical procedures, repeated diagonalization of the **F** matrix and iterative construction of the density matrix, were examined by using model compounds I and II; their division into fragmental groups is indicated by dotted lines in Figure 1. The computation times required for these two procedures were compared with those of the *standard* SCF method[5] in which all of the matrix elements are completely kept in the core storage. It is noted that the charge densities calculated by these two procedures (Figure 1) are identical with those obtained by the *standard* SCF method, since no further approximations are involved in these two procedures.

Repeated Diagonalization of F. Diagonalization of the **F** matrix is achieved by the following procedure.

(i) The orthogonal **O** matrix is found which forces $\mathbf{F}_{ij}$ and $\mathbf{F}_{ji}$ to be zero matrices.

$$\mathrm{O} = \begin{bmatrix} \mathrm{O}_{ii} & \mathrm{O}_{ij} \\ \mathrm{O}_{ji} & \mathrm{O}_{jj} \end{bmatrix}$$

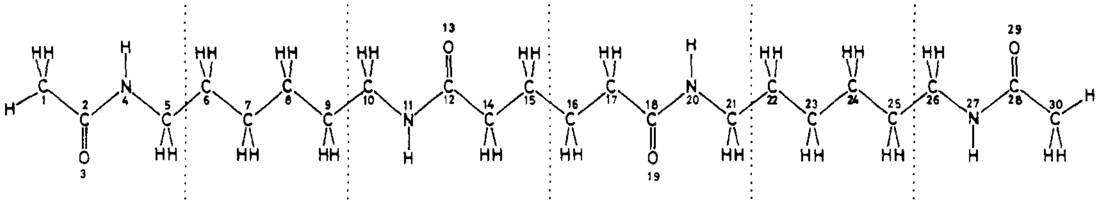
$$\tilde{\mathrm{O}} \begin{bmatrix} \mathrm{F}_{ii} & \mathrm{F}_{ij} \\ \mathrm{F}_{ji} & \mathrm{F}_{jj} \end{bmatrix} \mathrm{O} = \begin{bmatrix} \mathrm{F}_{ii}' & 0 \\ 0 & \mathrm{F}_{jj}' \end{bmatrix}$$

(ii) The new **F** matrix with $\mathbf{F}_{ij} = \mathbf{F}_{ji} = \mathbf{0}$ is calculated by

$$\tilde{\mathrm{C}}_1 \mathrm{F} \mathrm{C}_1 \qquad (3)$$

$$\mathrm{C}_1 = \begin{bmatrix} 1 & 0 & \cdots & & & & & \\ & \ddots & & & & & & \\ 0 & & 1 & & & & & \\ \vdots & & & \ddots & & & & \\ \vdots & & & & \mathrm{O}_{ii} \cdots \mathrm{O}_{ij} & & & \\ \vdots & & & & \vdots \quad \vdots & & & \\ \vdots & & & & \mathrm{O}_{ji} \cdots \mathrm{O}_{jj} & & & \\ \vdots & & & & & \ddots & & \\ \vdots & & & & & & & 1 \end{bmatrix}$$

(iii) The above two steps are continued until the **F** matrix is produced with all zero off-diagonal matrices.



III

Figure 2. Structure and numbering of the backbone of the polyamide-66 model. In the charge density calculation, the hybridization of each atom was assumed to be sp^2 or sp^3, and the all-trans structure was assumed; the bond lengths employed are the standard values given in Sutton's table.[8]

Table I
Calculated Atomic Charge Densities of Polyamide III

atom[a]	calc 1[b]	calc 2[c]	calc 3[d]
1C	−0.089	−0.089	−0.089
2C	0.356	0.356	0.358
3O	−0.368	−0.368	−0.365
4N	−0.206	−0.206	−0.194
4H	0.102	0.102	0.105
5C	0.119	0.120	0.097
6C	−0.003	−0.004	
7C	0.017	0.017	
8C	0.017	0.017	
9C	−0.003	−0.004	
10C	0.119	0.120	0.097
11N	−0.207	−0.207	−0.194
11H	0.102	0.102	0.105
12C	0.349	0.349	0.358
13O	−0.371	−0.371	−0.365
14C	−0.055	−0.055	−0.089
15C	0.025	0.025	

[a] The numbering of atoms is shown in Figure 2. [b] The values obtained by means of iterative construction of the density matrix in which the molecule is divided into six fragments; these are also obtained by the standard SCF CNDO/2 calculation. [c] The values obtained by using the approximation in which the Fock matrix elements between nonadjacent groups are neglected. [d] The values estimated from the CDNO/2 charge densities of the smaller model compound IV.

(iv) Diagonalization of the diagonal parts of **F**, $\mathbf{F}_{ii}$ (i = 1, 2, ..., N), is achieved.

(v) The **C** matrix which can diagonalize the **F** matrix in (1) is calculated by

$$\mathbf{C} = \mathbf{C}_1\mathbf{C}_2\mathbf{C}_3... \tag{4}$$

This diagonalization procedure is a simple extension of Jacobi's method, and the SCF solution of (1) is obtained by repetition of this procedure. The present method, however, requires a number of matrix multiplications appearing in eq 3 and 4. This wastes much computation time. Our model calculations of I and II, in which the structures are divided into four fragments, showed that the computation time is about 2.5 times that of the *standard* method in which the **F** and **C** matrices are completely kept in the core storage.

Iterative Construction of Density Matrix. In the charge density calculation, we need only the density matrix; it is not necessary to evaluate the **C** matrix itself. The steepest descent method proposed by McWeeny[6] is thus suitable for the present purpose. From McWeeny,[6] the SCF density matrix of the closed-shell system can be obtained by a successive construction of **R** by the following equations:

$$\mathbf{R}^{i+1} = \mathbf{R}^i + \delta\mathbf{R}^i$$

$$\delta\mathbf{R}^i = -\lambda(\mathbf{I} + \mathbf{IJ})$$

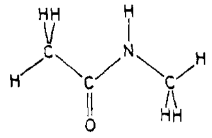
$$\lambda = -\frac{\mathrm{Tr}\ (\mathbf{IF}^i)}{2\ \mathrm{Tr}\ (\mathbf{IJF}^i)}$$

$$\mathbf{I} = (1 - \mathbf{R}^i)\mathbf{F}^i\mathbf{R}^i + \mathbf{R}^i\mathbf{F}^i(1 - \mathbf{R}^i)$$

$$\mathbf{J} = (1 - \mathbf{R}^i)\mathbf{F}^i\mathbf{R}^i - \mathbf{R}^i\mathbf{F}^i(1 - \mathbf{R}^i)$$

This iterative construction of the density matrix also uses direct-access files in order to store large-size matrices, and it requires the matrix multiplication between the groups. However, the total amount of multiplication is exactly same as that required in the *standard* method in which all of the matrices are kept in the core storage. Thus the computation time will be comparable with that of the *standard* method. This was confirmed by the model calculations of I and II. One-cycle computation time of the density matrix method was $^2/_3$ that of the standard diagonalization method.[5] The SCF convergence speed of the former method is slower than that of the latter. As a result, both methods require comparable computation time to give the SCF charge densities of I and II.

Polyamide. It has been shown here that the iterative construction of **R** by the steepest descent method is efficient for the charge density calculation of large molecules. This method was applied to polyamide-66, III, in which 162 valence atomic orbitals are involved. The charge densities are listed in the second column of Table I; the values are identical with those obtained by the *standard* SCF method. In most molecular mechanics calculations, the charge densities of macromolecules are estimated from smaller model compounds. It is thus interesting to compare the charge distribution of III with that estimated from the model compound IV. As may be seen from Table I, the charge densities estimated from the model compound are clearly different from those obtained by the SCF calculation for the whole molecular system.



IV

The present SCF procedure with the density matrix formalism has an advantage. For large molecular systems, some of the off-diagonal $\mathbf{F}_{ij}$ matrices in the **F** supermatrix can safely be neglected,[7] if the interaction between i and j fragmental groups is expected to be small. In this case, computation time required for the evaluation of the **I** and **J** matrices can be saved. For the case of polyamide III, neglect of the interactions between nonadjacent groups reduced the computation time by 20%. The charge densities calculated by this approximation agree with the exact SCF values within 0.0005, including all hydrogen atoms (Table I).

Our computer program is written in Fortran. It can be applied to a molecule with 20 fragmental groups, each of which can involve 50 valence atomic orbitals. The core memory size required for double-precision calculation is 120K words.

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