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THE CALCULATION OF ATOMIC CHARGES IN MOLECULES BY AN ELECTRONEGATIVITY EQUALIZATION PROCEDURE: A DESCRIPTION OF PROGRAM CHELEQ

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THE CALCULATION OF ATOMIC CHARGES IN MOLECULES BY AN ELECTRONEGATIVITY EQUALIZATION PROCEDURE: A DESCRIPTION OF PROGRAM CHELEQ

by

Winfield B. Perry and

William L. Jolly

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THE CALCULATION OF ATOMIC CHARGES IN MOLECULES BY AN ELECTRONEGATIVITY EQUALIZATION PROCEDURE: A DESCRIPTION OF PROGRAM CHELEQ

Abstract

Program CHELEQ is a Fortran IV computer program which calculates atomic charges in molecules containing up to 60 atoms by an electronegativity equalization procedure. In addition, the calculated charges may be correlated with experimentally determined ESCA core binding energies using the electrostatic potential equation, $E_B = kQ + V + \ell$, or using a relaxation corrected potential equation, $E_B = kQ + V + \ell + E_R$. The program determines the parameters k and ℓ by linear least squares analysis.

Introduction

Program CHELEQ is a Fortran IV computer program which requires approximately 64,400 (octal) core memory to load and 55,000 (octal) core to execute using the RUN76 Fortran compiler for the CDC 7600 computer at the Lawrence Berkeley Laboratory.* The program, as dimensioned in this write-up, can calculate charges on molecules containing up to 60 atoms, and each atom may be bonded to up to 6 other atoms. A further restriction is that the total number of bonds (a multiple bond equals only one bond) may not exceed 60.

The electronegativity equalization procedure[1] used by program CHELEQ to calculate atomic charges in molecules is based upon a

*The amount of required core memory can be significantly reduced if the dimensions of certain arrays are reduced. This possibility is discussed in Appendix A.

definition of electronegativity by Iczkowski and Margrave.[2] To calculate the atomic charges in a molecule using this method, the molecule is first represented by a valence bond structure, which may be the average of several resonance structures. Charge-dependent, orbital eletronegativities are then defined for each of the hybrid bonding orbitals represented in the valence bond structure. Charge is then transferred through the bonds until the electronegativities of each pair of mutually bonded orbitals are equalized. More specifically, one must solve one equation of the following type for each bond in the molecule:

$$\frac{7.3(h_m + h_n)}{(N_{nm})^{0.7}} q_{mn} + h_m \sum_{i \neq n} q_{mi} - h_n \sum_{i \neq m} q_{ni} =$$

$$x(p)_n - x(p)_m + \frac{S_{nm}}{(1 + \Pi_{nm})^{0.7}} \left[x(s)_n - x(p)_n \right] \qquad (1)$$

$$- \frac{S_{nm}}{(1 + \Pi_{nm})^{0.7}} \left[x(s)_m - x(p)_m \right] + c_n h_n F_n - c_n h_n F_n$$

The q_{ij} are the unknown quantities, and one obtains n equations and n unknown q_{ij}'s for a molecule containing n bonds. The charge on an atom <u>i</u> is given by:

$$Q_i = F_i + \sum_j q_{ij} \qquad (2)$$

The rationale for these formulas and definitions of the quantities appearing in the formulae appear in references 1 and 3. In Ref. 1, results are presented for molecules containing primarily first row atoms whereas Ref. 3 includes molecules containing heavier atoms. The program described in this work includes the revisions presented in Ref. 3 together with value for x(s), x(p) and h for the elements from hydrogen through radon.

The interpretation of ESCA core binding energies by the electrostatic potential equation[4] provides a simple method of evaluating atomic charges. This equation has the form:

$$E_B(A) = kQ_A + V + \ell \qquad (3)$$

where E_B is a core binding energy, k and ℓ are parameters, Q_A is the charge on atom A, and V is the potential due to the other atoms in the molecule and is equal to

$$e^2 \sum_{B \neq A} Q_B/R_{AB} \ .$$

A better description of ESCA chemical shifts should be given by a modification of this equation which includes the effects of the electronic rearrangement, or <u>relaxation</u>, which takes place during photoemission. This equation[3] has the form:

$$E_B(A) = kQ_A + V + \ell + E_R \qquad (4)$$

E_B, k, and ℓ are defined as before. In order to calculate the relaxation energy, E_R, two charge calculations must be made: one for the neutral molecule, and one for the isoelectronic cation which is obtained by substituting the core of the next heavier atom on the periodic

table (Z+1) for the core of the ionized atom (Z). Using the charges from these two calculations, the relaxation energy is given by:

$$E_R = k(Q_{Z+1} - Q_Z - 1)/2 + (V_{Z+1} - V_Z)/2 \quad (5)$$

Program CHELEQ includes the option of using the calculated charges to correlate ESCA binding energies by means of either Eqs. 3 or 4. In the latter case, the calculation for the isoelectronic cation is automatically carried out by the program.

Program Description

The topology of the valence bond structure, that is, which atoms are bonded to which other atoms, bond orders and formal charges, are read into the program atom by atom together with the atomic numbers of the atoms. The program then determines the hybridization of each atom from the topological data and calculates the right-hand side of Eq. 1, which is the charge independent part of the equation, for each bond. Then, the system of Eq. 1 is written in matrix form:

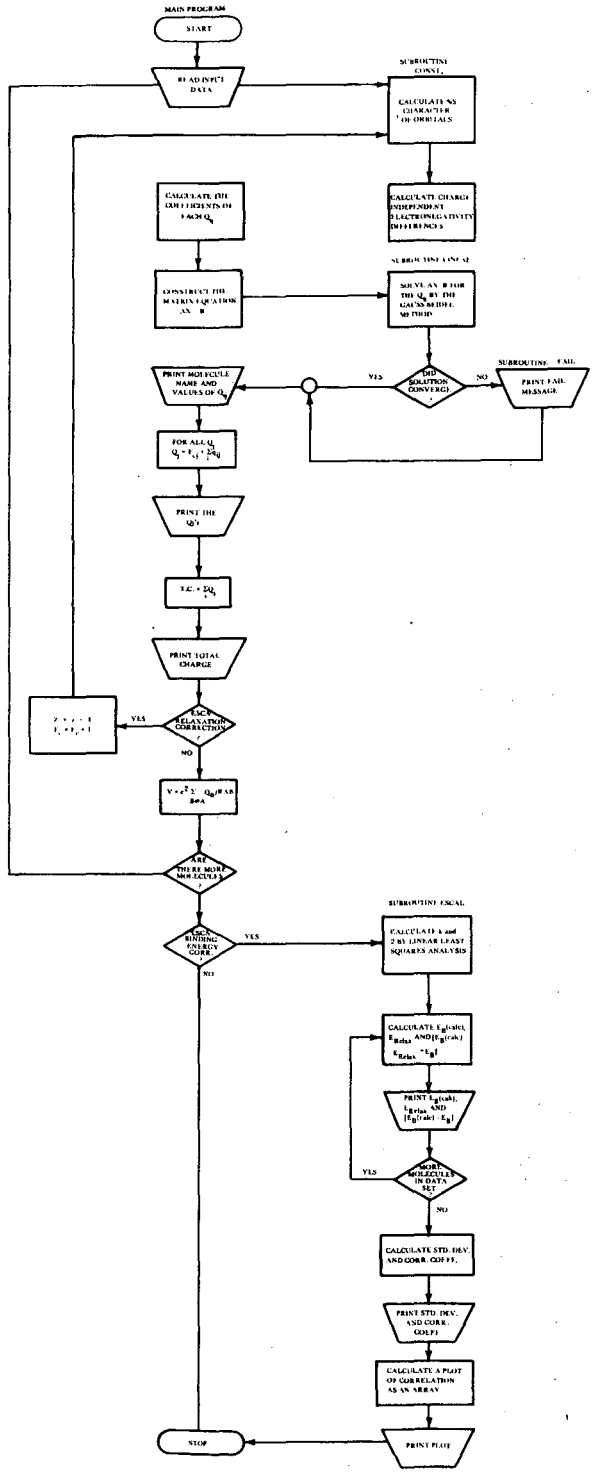
$$AX = B \quad (6)$$

where A is an n×n matrix of coefficients from the left-hand sides of Eq. 1, X is an n×1 matrix of the q_{ij} and B is an n×1 matrix of the right-hand sides of Eq. 1. The values of the q_i are determined by the Gauss-Seidel procedure for solving systems of linear equations. Atomic charges are then calculated by summing the appropriate q_{ij} for an atom and adding this sum to the formal charge of the atom.

If an ESCA core binding energy correlation including electronic relaxation effects is being made, the program increases the atomic number of the ionized atom, together with its formal charge, by one

unit, and the calculation is repeated for the isoelectronic cation. It is possible to specify a different topology for the isoelectronic cation than for the neutral molecule. The Q or Q^* and V or V^* terms are stored and/or calculated and then stored for each molecule in the data set which is being correlated. After all the charge calculations have been made, the program fits the data to the electrostatic potential equation by determining the parameters k and ℓ through least squares analysis. After printing the experimental and calculated binding energies, their difference, and the relaxation energy (if Eq. 4 was used for the correlation), the standard deviation and two correlation coefficients are calculated. Finally, a rough plot of the correlation is printed.

A simplified flow chart of the program is presented in Fig. 1.

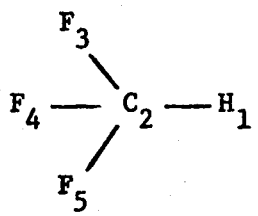


XBL 747-3703

Fig. 1

Data Input for Program

The first operation in supplying input data to the program is to numerically order the atoms in the molecules. For example:



These numbers will be used by the program as indices, and will specify which atoms are bonded to which other atoms.

Card 1: Data Set Card

columns 6-10 (right justified): The number of molecules in the data set (NC)

columns 16-20: punch NOFIT in these columns if just atomic charges are desired, i.e., no binding energy correlation. Leave these columns blank for a ground state correlation (equation 3). Punch RELAX into these columns for a correlation including relaxation effects (equation 4). (FIT).

columns 21-80: The title of the data set. Any combination of alphameric characters may be used (LABLE)

Restriction NC $\leq$ 75

Format (5X, I5, 5X, A5, 6A10)

Card 2: Title card for the (first) molecule

columns 1-80: Name, etc. of the first molecule. Any combination of alphameric characters may be used (CNAME)

FORMAT (10A8)

Card 3: General information about the molecule

columns 6-10 (right justified): the number of atoms in the molecule (NA)

columns 16-20 (right justified): the index of the (i.e. the number assigned to) the core ionized atom (MESCA). This may be left blank if no ESCA correlation is desired.

columns 26-35: the core binding energy of the ionized atom in electron volts (BEX). This also may be left blank if no ESCA correlation is desired.

Restriction NA $\leqslant$ 60

Format (5X, I5, 5X, I5, 5X, F10.0)

Cards 4 ···: Atom data cards. One card for each atom in the molecule. The order of these cards is important. The first card must contain the information about the atom which was assigned the index 1, the second card must be for the atom assigned index 2, etc.

columns 6-10 (right-justified): The atomic number of the atom represented by this card (NZ).

columns 16-20: The formal charge of the atom (C).

The next data on the card are for the bonds between the atom represented by this card and other atoms in the molecule. BNDSTO is the index previously assigned to an atom in the molecule, and N is a bond order.

columns 22, 23 (right justified): BNDSTO for the 1st bond, that is, the index of an atom which is bonded to the atom represented by this card. Any bond may be used for the "first" bond.

columns 25-28: N for the first bond

columns 30,31 (right justified): BNDSTO for the 2nd bond (if any).

columns 33-36: N for the second bond (if any).

columns 38,39 (right justified): BNDSTO ···

columns 41-44: N ···

columns 46,47 (right justified): BNDSTO ···

columns 49-52: N ···

columns 54,55 (right justified): BNDSTO ···

columns 57-60: N ···

columns 62,63: (right justified): BNDSTO ···

columns 65-68: N ···

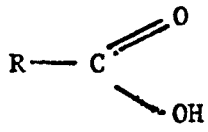
columns 70-80: The distance from the atom represented by this card to the ESCA ionized atom, in Angstroms. (If this card represents the ionized atom, R = 0.0). This datum may be omitted if no ESCA correlation is desired (R).

Restrictions NZ ≤ 86; an atom may be bonded to no more than 6 other atoms.

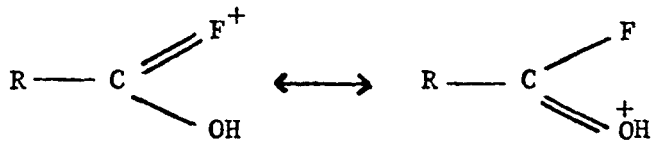
Default Value If, for any bond, the field for N is left blank, the program will assume N = 1 (a single bond).

Format (5X, I5, 5X, F5.0, 6(1X, I2, 1X, F4.0), 1X, F11.0)

Calculations made for the isoelectronic cations used in relaxation correlations sometimes have different bond orders than do the neutral molecules. For example, the ground state of a carboxylic acid can be represented by the structure:



The isoelectronic cation for a carbonyl core-ionized oxygen could, however, be represented as an intermediate between the two structures:

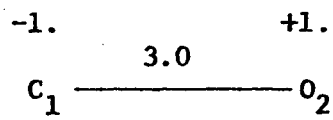


To use different bond orders and formal charges in the calculation for the isoelectronic cation than were used for the neutral molecule, the following procedure is followed. Punch a 1 in column 1 of each atom data card where there will be a change in the bond orders or the formal charge. Immediately following such an atom data card is another card with C, BNDSTO, and N information punched in columns 16-68 using the same format as the atom data card. When this procedure is used for the card representing the ionized atom, the formal charge on that atom, for the isoelectronic cation, is the charged punched onto the second card, not $F_c + 1$, as is the case for "normal" molecules. Cards which represent atoms with the same bond orders and formal charges in both the ion and the neutral molecule, for example the atoms in the R group of the carboxylic acid, need not be altered.

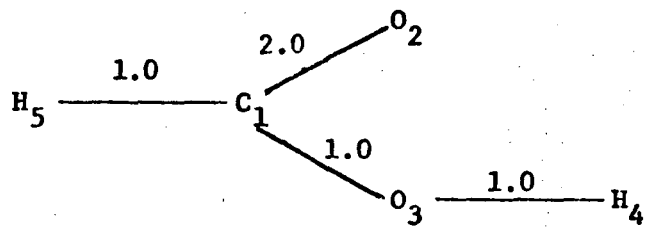
Format (15X, F5.0, 6(1X, I2, 1X, F4.0))

Card 5: The title card for the second molecule in the data set. The second and subsequent molecules are treated exactly the same as the first molecule.

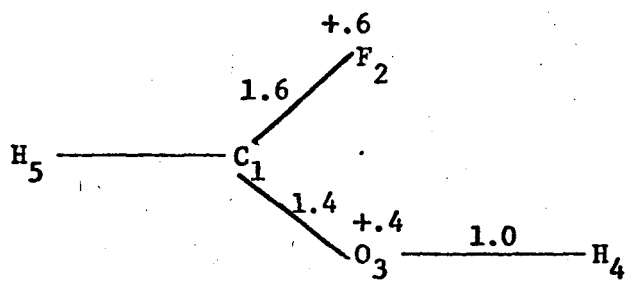
Sample input data for three molecules is given below. Carbon monoxide, a molecule which has multiple bonding and non-zero formal charges, is represented by the structure



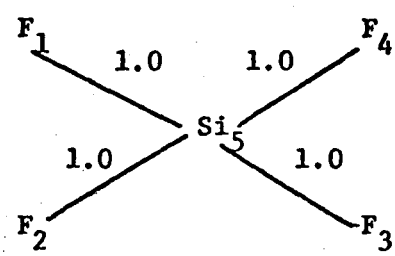
where the atom indices are written as subscripts, the bond order is written above the bond and the formal charges are written above the appropriate atoms. Formic acid has different structure representing the neutral molecule and the isoelectronic cation for the carbonyl oxygen. The structure for the neutral molecule is:



The structure for the carbonyl oxygen isoelectronic cation is:



Finally the structure for SiF_4 is simply:



SAMPLE DATA FOR PROGRAM CHELEQ

```
CARBON MONOXIDE     C 1S BINDING ENERGY
     2          1      296.02
     6      -1.0    2 3.0                                          0.0
     8      1.0     1 3.0                                          1.128


FORMIC ACID     O 1S, CARBONYL BINDING ENERGY
     5          2      538.79
1    6      0.0     2 2.0    3 1.0    5 1.0                        1.213
            0.0     2 1.6    3 1.4    5 1.0
1    8      0.0     1 2.0                                          0.0
            0.6     1 1.6
1    8      0.0     1 1.0    4 1.0                                 2.27
            0.4     1 1.4    4 1.0
     1      0.0     3 1.0                                          2.64
     1      0.0     1 1.0                                          1.98


SILICON TETRAFLUORIDE     SI 2P 3/2 BINDING ENERGY
     5          5      111.79
     9              5                                              1.54
     9              5                                              1.54
     9              5                                              1.54
     9              5                                              1.54
    14              1        2        3        4                   0.0
```

0 0 0 0 4 2 0 6 8 9 5

References

1. W. L. Jolly and W. B. Perry, J. Am. Chem. Soc. 95, 5442 (1973).
2. R. P. Iczkowski and J. L. Margrave, J. Am. Chem. Soc. 83, 3547 (1961).
3. W. L. Jolly and W. B. Perry, Inorg. Chem.
4. K. Siegbahn, et al., "ESCA Applied to Free Molecules", North Holland, Amsterdam, 1969.

ACKNOWLEDGEMENTS

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APPENDIX A

Reducing the Core Memory Required by Program CHELEQ

As listed in this write-up, program CHELEQ can handle molecules containing up to 60 atoms. This limit may be larger than is necessary for many users. If this dimension is reduced, considerable savings of core memory will result. The following arrays, may be redimensioned from 60 to some other number, n.

CON (60,60) → CON(n,n)[a,b]

LAB (60,60) → LAB(n,n)[a]

S(60,60) → S(n,n)[a,b]

BNDSTO (60,12) → BNDSTO(n,12)[a,b]

N(60,12) → N(n,12)[a,b]

B(60) → B(n)[c]

C(60) → C(n)[a,b]

Cl(60) → Cl(n)[a]

NZ(60) → NZ(n)[a,b]

RAD(60) → RAD(n)[a]

SQ(60) → SQ(n)[a]

X(60) → X(n)[c]

COMMON/ARRAYS/V(60,61) → V(n,n+1)[a,b]

COMMON/ARRAYS/A(60,61) → A(n,n+1)[c,d]

The array PLOT(60,60) in subroutine ESCAL should not be redimensioned.

---

[a] appears in the main program

[b] appears in subroutine CONST

[c] appears in subroutine LINEQ

[d] appears in subroutine ESCAL

```
      PROGRAM CHELEQ (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C     PROGRAM CHELEQ CALCULATES NET ATOMIC CHARGES USING AN ORBITAL
C     ELECTRONEGATIVITY EQUALIZATION METHOD DEVELOPED BY W.L.JOLLY
C
C     PROGRAM IS PARAMETERIZED FOR THE ELEMENTS H THROUGH RN
C     MAXIMUM NUMBER OF ATOMS IS 60, MAXIMUM NUMBER OF (SIGMA) BONDS IS 60
C
C     THIS VERSION CONTAINS A LEAST SQUARES FIT OF THE CHARGE DISTRIBUTIONS
C     TO EXPERIMENTAL BINDING ENERGIES USING THE ESCA POTENTIAL MODEL
C     EB=K*Q+V+L
C     TO OBTAIN A FIT OF BINDING ENERGY AGAINST CHARGE (I.E. TO IGNORE
C     THE POTENTIAL TERM) OMIT THE BOND DISTANCES ON THE DATA CARDS
C     MAXIMUN NUMBER OF COMPOUNDS IN BINDING ENERGY CORRELATION IS 75
C       INPUT
C     CARD 1       NUMBER OF COMPOUNDS IN THE RUN
C                  FOR A RELAXATION CORRECTED FIT OF CHARGES TO BINDING
C                  ENERGIES, PUNCH RELAX IN COLUMNS 16-20.
C                  IF NO FIT OF CHARGES TO BINDING ENERGIES IS WANTED,
C                  PUNCH  NOFIT  IN COLUMNS 16-20. GENERAL ALPHAMERIC
C                  INFORMATION ABOUT THE DATA SET MAY BE PUNCHED IN
C                  COLUMNS 21-80.
C                  FORMAT (5X,I5,5X,A5,6A10)
C     CARD 2       NAME, ETC.  FORMAT (10A8)
C     CARD 3       NUMBER OF ATOMS IN COMPOUND,NUMBER OF THE IONIZED ATOM,
C                  EXPERIMENTAL BINDING ENERGY  FORMAT (5X,I5,5X,I5,5X,F10.0)
C                  IF NO FIT IS WANTED, BINDING ENERGIES AND IONIZED ATOM
C                  NUMBER MAY BE OMITTED
C     CARDS 4,...    (ONE PER ATOM)  ATOMIC NUMBER, FORMAL CHARGE, (NEXT
C                    INFO LISTED PAIRWISE FOR EACH BOND) NUMBER OF
C                    ATOM BONDED TO, BOND ORDER OF THAT BOND (UP TO SIX
C                    BONDS PER ATOM), DISTANCE TO IONIZED ATOM (ANGSTROMS)
C                   FORMAT(I1,4X,I5,5X,F5.0,6(1X,I2,1X,F4.0),1X,F11.0)
C         **NOTE**
C     TO USE DIFFERENT BONDORDERS IN THE ISOELECTRONIC CATION (IN
C     RELAXATION CORRECTED  EB FITS), SEE PROGRAM WRITEUP (LBL REPORT).
C
C     ADDITIONAL COMPOUNDS PUNCHED IN SAME MANNER
C
C     PROGRAMMED BY W.B.PERRY AT U.C.B.
C
      DIMENSION CNAME(10,75),NZ(60),BNDSTO(60,12),N(60,12),LAB(60,60)
      DIMENSION CON(60,60),C(60),S0(60),MOR(60),C1(60)
      DIMENSION LABLE(6), BEX(75),RAD(60),VA(75),QESCA(75)
      DIMENSION S(60,60)
      REAL N
      INTEGER BNDSTO
      COMMON/COEFFT/B(100),CK,A
      COMMON/ARRAYS/V(60,61)
      COMMON/ERELAX/DQ(75),DV(75)
      DATA AFIT/5HNOFIT/
      DATA RELAX/5HRELAX/
      READ (5,5) NOCMPD, FIT, LABLE
      WRITE (6,6) LABLE
      DO 400 NC=1,NOCMPD
      DO 15 I=1,60
```

```
      DO 15 J=1,12
      BNDSTO(I,J)=0
15    N(I,J)=0.0
      READ (5,10) (CNAME(I,NC), I=1,10)
      READ (5,20) NA, MESCA, BEX(NC)
      DO 40 I=1,NA
      READ (5,30) MOR(I),NZ(I),C(I),((BNDSTO(I,J),N(I,J)),J=1,6),RAD(I)
      IF (MOR(I)+1 .EQ. 2) 31, 34
31    READ (5,32) C1(I), ((BNDSTO(I,J), N(I,J)),J=7,12)
34    CONTINUE
      DO 35 J=1,12
35    IF (N(I,J)+1.0 .EQ. 1.0) N(I,J)=1.0
40    CONTINUE
      DO 400 NT=1,2
      IF (NT .EQ. 2 .AND. FIT .NE. RELAX) GO TO 400
      IF (NT .EQ. 2) NZ(MESCA)=NZ(MESCA)+1
      IF (NT .EQ. 2) C(MESCA)=C(MESCA)+1.0
      IF (NT .EQ. 2) 42,48
42    DO 46 I=1,NA
      IF (MOR(I)+1 .EQ. 1) GO TO 46
      C(I)=C1(I)
      DO 44 J=1,6
      BNDSTO(I,J)=BNDSTO(I,J+6)
      N(I,J)=N(I,J+6)
44    CONTINUE
46    CONTINUE
48    CONTINUE
      CALL CONST(NA,BNDSTO,NZ,C,N,CON,S)
      NB=0
      DO 50 I=1,NA
      DO 50 J=1,6
      K = BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 50
      NB = NB+1
50    CONTINUE
      NB = NB/2
      NB1 = NB+1
      DO 55 I=1,60
      DO 55 J=1,61
55    V(I,J)=0.0
      L=0
      DO 60 I=1,NA
      DO 60 J=1,6
      K = BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 60
      IF (I .GT. K) GO TO 60
      L = L+1
      LAP(I,K) = L
      V(L,NB1) = CON(I,K)
60    CONTINUE
      L=0
      DO 200 I=1,NA
      NZI = NZ(I)
      DO 200 J=1,6
      K = BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 200
```

```
      IF (I .GT. K) GO TO 200
      NZK = NZ(K)
      L = L+1
      DO 110 JJ=1,6
      CA=1.0
      KK = BNDSTO(I,JJ)
      IF (KK+1 .EQ. 1) GO TO 110
      IF (I .GT. KK) 70, 90
 70   DO 80 LA=1,NB
      IF (KK .EQ. K) CA = CK/(N(I,J)**A)
      IF (LAB(KK,I) .EQ. LA) V(L,LA) = V(L,LA)+B(NZI)*CA
 80   CONTINUE
      GO TO 110
 90   DO 100 LA=1,NB
      IF (KK .EQ. K) CA = CK/(N(I,J)**A)
      IF (LAB(I,KK) .EQ. LA) V(L,LA) = V(L,LA)-B(NZI)*CA
100   CONTINUE
110   CONTINUE
      DO 160 JJ=1,6
      CA=1.0
      KK = BNDSTO(K,JJ)
      IF (KK+1 .EQ. 1) GO TO 160
      IF (K .GT. KK) 120, 140
120   DO 130 LA=1,NB
      IF (KK .EQ. I) CA = CK/(N(I,J)**A)
      IF (LAB(KK,K) .EQ. LA) V(L,LA) = V(L,LA)-B(NZK)*CA
130   CONTINUE
      GO TO 160
140   DO 150 LA=1,NB
      IF (KK .EQ. I) CA = CK/(N(I,J)**A)
      IF (LAB(K,KK) .EQ. LA) V(L,LA) = V(L,LA)+B(NZK)*CA
150   CONTINUE
160   CONTINUE
200   CONTINUE
      IF (NB .EQ. 1) 202, 204
202   NZI = NZ(1)
      NZK = NZ(2)
      V(1,NB1) = -CON(1,2)/((B(NZI)+B(NZK))*CK/(N(1,1)**A))
      GO TO 206
204   CALL LINEQ (NB)
206   CONTINUE
      DO 215 I=1,NA
215   SQ(I) = C(I)
      WRITE (6,250) (CNAME(I,NC), I=1,10)
      DO 240 L=1,NB
      DO 230 I=1,NA
      DO 230 J=1,6
      K = BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 230
      IF (I .GT. K) GO TO 230
      IF (LAB(I,K) .EQ. L) 210, 230
210   WRITE (6,220) I, K, V(L,NB1), I, K, S(I,K), K, I, S(K,I)
      SQ(I) = SQ(I)+V(L,NB1)
      SQ(K) = SQ(K)-V(L,NB1)
      GO TO 240
230   CONTINUE
```

```
  240  CONTINUE
       TOTCHG=0.0
       VA(NC)=0.0
       DO 270 I=1,NA
       TOTCHG = TOTCHG+SQ(I)
       IF (RAD(I)+1.0 .EQ. 1.0) 246, 243
  243  VA(NC) = VA(NC) + 14.4*SQ(I)/RAD(I)
  246  CONTINUE
       IF (I .EQ. MESCA) QESCA(NC) = SQ(I)
       WRITE (6,260) I, SQ(I), NZ(I), C(I), (BNDSTO(I,J),N(I,J),J=1,6),
     1 RAD(I)
  270  CONTINUE
       WRITE (6,280) TOTCHG
       IF (NT .EQ. 1) SAVE1=QESCA(NC)
       IF (NT .EQ. 1) SAVE2=VA(NC)
       IF (NT .EQ. 2) QESCA(NC)=0.5*(QESCA(NC)+SAVE1)-0.5
       DQ(NC)=0.0
       DV(NC)=0.0
       IF (NT .EQ. 2) DQ(NC)=QESCA(NC)-SAVE1
       IF (NT .EQ. 2) VA(NC)=0.5*(VA(NC)+SAVE2)
       IF (NT .EQ. 2) DV(NC)=VA(NC)-SAVE2
  400  CONTINUE
       IF (FIT .EQ. AFIT) GO TO 500
       CALL ESCAL(NOCMPD,BEX,CNAME,QESCA,VA)
C
C    FORMAT STATEMENTS
C
    1  FORMAT (1H1)
    5  FORMAT (5X,I5,5X,A5,6A10)
    6  FORMAT (// 20X,6A10 //)
   10  FORMAT (10A8)
   20  FORMAT (5X,I5,5X,I5,5X,F10.0,5X)
   30  FORMAT (I1,4X,I5,5X,F5.0,6(1X,I2,1X,F4.0),1X,F11.0)
   32  FORMAT (15X,F5.0,6(1X,I2,1X,F4.0))
  220  FORMAT (20X,2HQ(,I3,1H,,I3,4H) = ,F8.5,10X,2HS(,I3,1H,,I3,4H) = ,
     1 F8.5,5X,2HS(,I3,1H,,I3,4H) = ,F8.5)
  250  FORMAT (//// 10A8 ////)
  260  FORMAT (/ 10X,14HCHARGE ON ATOM,I3,3H = ,F10.5,10X,I5,5X,F7.4,
     1 6(1X,I2,1X,F5.3),5X,F7.4)
  280  FORMAT (// 25HTOTAL MOLECULAR CHARGE = ,F10.5 //)
  500  STOP
       END
```

```
      SUBROUTINE CONST(NA,BNDSTO,NZ,C,N,CON,S)
C
C     SUBROUTINE CONST CALCULATES THE CONSTANT TERMS IN THE ELECTRONEGATIVITY
C     EQUALIZATION EQUATIONS
C
      DIMENSION BNDSTO(60,12),NZ(60),S(60,60),XS(100),XP(100)
      DIMENSION C(60),N(60,12),CON(60,60)
      COMMON/COEFFT/B(100),CK,A
      REAL N, NIJ, NMIN
      INTEGER BNDSTO
      DATA (XS(I),I=1,100) / 2.21,0.0,2*0.0,3.25,4.84,6.70,8.98,10.31,
     1 11.44,0.74,1.77,2.69,3.88,4.62,5.12,6.26,7.35,0.77,1.36,1.20,
     2 1.32,1.45,1.56,1.60,1.64,1.70,1.75,1.75,1.66,3.18,4.06,3.84,
     3 4.97,5.94,6.00,0.50,1.26,1.11,1.22,1.23,1.30,1.36,1.42,1.45,1.35,
     4 1.42,1.46,2.88,3.80,4.22,4.81,5.06,5.00,2*0.0,1.08,14*0.0,1.23,
     5 1.33,1.40,1.46,1.52,1.55,1.44,1.42,1.44,2.44,2.35,2.58,3.06,3.9,
     6 4.7,14*0.0 /
      DATA XS(2), XS(3), XS(4) / 2.75, 0.84, 2.15 /
      DATA XS(55), XS(56) / 0.4, 1.15 /
      DATA (XS(I),I=58,71) / 1.06,1.07,1.07,1.07,1.07,1.01,1.11,1.10,
     1 1.10,1.10,1.11,1.11,1.06,1.14 /
      DATA (XP(I),I=1,100) / 4*0.0,1.26,1.75,2.65,3.49,3.90,4.40,0.32,
     1 0.56,1.11,1.82,2.23,2.63,2.95,3.50,0.38,0.42,1.20,1.32,1.45,
     2 1.56,1.60,1.64,1.70,1.75,1.75,1.66,1.22,2.09,2.40,2.56,2.62,
     3 3.00,0.54,0.34,1.11,1.22,1.23,1.30,1.36,1.42,1.45,1.35,1.42,
     3 1.46,0.92,2.08,2.36,2.77,2.52,2.60,2*0.0,1.08,14*0.0,1.23,1.33,
     5 1.40,1.46,1.52,1.55,1.44,1.42,1.44,0.94,1.28,1.44,1.76,1.96,
     6 2.4,14*0.0 /
      DATA XP(3), XP(4), XP(55), XP(56) / 0.47,0.82,0.4,0.25 /
      DATA (XP(I),I=58,71) / 1.06,1.07,1.07,1.07,1.07,1.01,1.11,1.10,
     1 1.10,1.10,1.11,1.11,1.06,1.14 /
      DATA (B(I),I=1,100) / 12.85,3*0.0,8.4,11.2,12.1,15.3,17.0,19.0,
     1 4.67,5.30,5.85,7.37,10.75,9.82,11.1,9.50,2.88,4.52,10*5.0,6.32,
     2 6.80,8.68,12.40,9.40,10.00,4.18,4.24,10*5.0,6.02,4.35,8.71,
     3 11.87,9.15,9.00,4.0,4.0,24*5.0,6.0,5.0,8.0,10.0,9.0,8.0,14*0.0 /
      DATA B(2),B(3),B(4) / 15.0,4.6,6.3 /
      DATA XS(55),XP(55),B(55) /9.6,4.7,20.0 /
      DATA A, CK, D1, HFAC / 0.70, 7.3, 2.7, 10.0 /
      D2=D1*1.6/2.7
      DO 50 I=1,NA
      IF (NZ(I) .GT. 2) GO TO 10
      DO 5 J=1,6
      K=BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 5
      S(I,K)=1.0
    5 CONTINUE
      GO TO 50
   10 CONTINUE
      IF (NZ(I) .GT. 10) GO TO 25
      SS=0.0
      SN=0.0
      DO 15 J=1,6
      K=BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 15
      IF (N(I,J) .LE. 1.0) GO TO 15
      SS=SS+1.0
```

```
      SN=SN+N(I,J)
15    CONTINUE
      DO 20 J=1,6
      K=BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 20
      SIK=4.0+SS-SN
      IF (SIK .GT. AINT(SIK+0.05)) SIK=AINT(SIK)
      S(I,K)=1.0/SIK
20    CONTINUE
      GO TO 50
25    CONTINUE
      TS=0.0
      SS=0.0
      SN=0.0
      PS=0.0
      PN=0.0
      NMIN=1.0
      DO 30 J=1,6
      K=BNDSTO(I,J)
      IF(K+1 .EQ. 1) GO TO 30
      NIJ=N(I,J)
      TS=TS+1.0
      IF (NIJ .GT. 1.0) SS=SS+1.0
      IF (NIJ .GT. 1.0) SN=SN+NIJ
      IF (NIJ .LT. 1.0) PS=PS+1.0
      IF (NIJ .LT. 1.0) PN=PN+NIJ
      IF (NIJ .LT. NMIN) NMIN=NIJ
30    CONTINUE
      DO 45 J=1,6
      K=BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 45
      NIJ=N(I,J)
      IF (PS .EQ. TS .AND. C(I) .GE. 0.5) GO TO 40
      SIK=4.0+SS-SN+PS-PN
      IF (SIK .GT. AINT(SIK+0.05)) SIK=AINT(SIK)
      S(I,K)=1.0/SIK
      GO TO 42
40    CONTINUE
      IF (NIJ .EQ. NMIN) S(I,K)=(NIJ-0.5)/NIJ
      IF (TS .EQ. 5 .AND. PN .LE. 3.95) GO TO 41
      IF (NIJ .NE. NMIN) S(I,K)=(NIJ-0.6667)/NIJ
      GO TO 42
41    CONTINUE
      IF (NIJ .NE. NMIN) S(I,K)=(NIJ-0.5)/NIJ
42    CONTINUE
      IF (S(I,K) .LT. 0.0) S(I,K)=0.0
45    CONTINUE
50    CONTINUE
      DO 70 I=1,NA
      NZI = NZ(I)
      CFI=D1
      IF (NZI .GT. 18) CFI=D2
      DO 60 J=1,6
      K = BNDSTO(I,J)
      IF (K+1 .EQ. 1) GO TO 60
      NZK = NZ(K)
```

```
      CFK=D1
      IF (NZK .GT. 18) CFK=D2
      NIJ = N(I,J)
      IF (NIJ .LT. 1.0) NIJ=1.0
      CON(I,K) = HFAC*(XP(NZI)-XP(NZK)+S(I,K)/NIJ**A*(XS(NZI)-
     1 XP(NZI))-S(K,I)/NIJ**A*(XS(NZK)-XP(NZK)))+(B(NZI)*C(I)*CFI-
     2 B(NZK)*C(K)*CFK)
   60 CONTINUE
   70 CONTINUE
      RETURN
      END


      SUBROUTINE  LINEQ (N)
C
C   SUBROUTINE LINEQ SOLVES N SIMULTANEOUS EQUATIONS IN N UNKNOWNS
C   BY THE METHOD OF GAUSS-SEIDEL
C
      DIMENSION B(60), X(60)
      COMMON/ARRAYS/A(60,61)
      DATA EPS / 0.0001 /
      DATA MAX /100/
      ITER=1
      N1=N+1
      DO 1 I=1,N
      B(I)=A(I,N1)
    1 X(I)=0.0
   10 BIG=0.0
      DO 70 I=1,N
   20 SUM=0.0
      IF (I .EQ. 1) GO TO 40
      LAST=I-1
      DO 30 J=1,LAST
   30 SUM=SUM+A(I,J)*X(J)
      IF (I .EQ. N) GO TO 60
   40 INITL=I+1
      DO 50 J=INITL,N
   50 SUM=SUM+A(I,J)*X(J)
   60 TEMP=(B(I)-SUM)/A(I,I)
      IF (ABS(TEMP-X(I)) .GT. BIG) BIG=ABS(TEMP-X(I))
   70 X(I)=TEMP
      IF (ITER .GE. MAX) GO TO 80
      ITER=ITER+1
      IF (BIG .GE. EPS) GO TO 10
      GO TO 90
   80 CALL FAIL
   90 DO 100 I=1,N
  100 A(I,N1)=X(I)
      RETURN
      END


      SUBROUTINE FAIL
      WRITE (6,1)
    1 FORMAT (// 10X,38HGAUSS-SEIDEL SOLUTION DID NOT CONVERGE //)
      RETURN
      END
```

```
      SUBROUTINE ESCAL (NC,BEX,CN,QE,V)
C
C   SUBROUTINE ESCAL DETERMINES THE POTENTIAL MODEL PARAMETERS K AND L
C   BY A LEAST SQUARES FIT TO THE DATA, AND PLOTS THE CORRELATION
C
      DIMENSION PLOT(60,60),CN(10,75),BE(75),BEX(75),QE(75),V(75)
      COMMON/ARRAYS/A(60,61)
      COMMON/ERELAX/DQ(75),DV(75)
      EQUIVALENCE (A(1),PLOT(1))
      DATA  DOT,O,X,Y,BLANK / 1H.,1HO,1HX,1HY,1H /
      SUMX = 0.0
      SUMY = 0.0
      XSQ = 0.0
      YSQ = 0.0
      XYPROD = 0.0
      DO 10 M=1,NC
      SUMX = SUMX + QE(M)
      SUMY = SUMY + (BEX(M)-V(M))
      XSQ = XSQ + (QE(M))**2
      YSQ = YSQ + (BEX(M)-V(M))**2
      XYPROD = XYPROD + QE(M)*(BEX(M)-V(M))
   10 CONTINUE
      SLOPE = (NC*XYPROD-SUMX*SUMY)/(NC*XSQ-SUMX**2)
      CEPT = (XSQ*SUMY-SUMX*XYPROD)/(NC*XSQ-SUMX**2)
      WRITE (6,1)
      WRITE (6,20)
      WRITE (6,30) SLOPE, CEPT
      WRITE (6,20)
      WRITE (6,40)
      DEVSQ = 0.0
      DO 50 M=1,NC
      WRITE (6,60) (CN(I,M),I=1,10)
      WRITE (6,70) QE(M), V(M)
      BE(M)=SLOPE*QE(M)+V(M)+CEPT
      ER=SLOPE*DQ(M)+DV(M)
      WRITE (6,80) BE(M), BEX(M), ER
      DEV=BE(M)-BEX(M)
      WRITE (6,90) DEV
      DEVSQ=DEVSQ+DEV**2
   50 CONTINUE
      STDDEV=SQRT(DEVSQ/(NC-1))
      CCOEFT = (NC*XYPROD-SUMX*SUMY)/SQRT((NC*XSQ-SUMX**2)*(NC*YSQ-
     1 SUMY**2))
      SUMX = 0.0
      SUMY = 0.0
      XSQ = 0.0
      YSQ = 0.0
      XYPROD = 0.0
      DO 55 M=1,NC
      SUMX = SUMX + BE(M)
      SUMY = SUMY + BEX(M)
      XSQ = XSQ + (BE(M))**2
      YSQ = YSQ + (BEX(M))**2
      XYPROD = XYPROD + BE(M)*BEX(M)
   55 CONTINUE
      CCOEFF = (NC*XYPROD-SUMX*SUMY)/SQRT((NC*XSQ-SUMX**2)*(NC*YSQ-
```

```
    1 SUMY**2))
      WRITE (6,100)
      WRITE (6,110) STDDEV
      WRITE (6,115) CCOEFT
      WRITE (6,116) CCOEFF
      WRITE (6,100)
      WRITE (6,40)
      DO 120 M=1,60
      DO 120 N=1,60
      PLOT(M,N) = BLANK
  120 CONTINUE
      DO 130 M=1,60
      MM = 61-M
      PLOT(MM,M) = O
      PLOT(1,M) = DOT
      PLOT(M,1) = DOT
      PLOT(60,M) = DOT
      PLOT(M,60) = DOT
  130 CONTINUE
      BEMIN = BE(1)
      BEMAX = BE(1)
      DO 140 M=1,NC
      IF (BE(M) .LE. BEMIN) BEMIN = BE(M)
      IF (BE(M) .GE. BEMAX) BEMAX = BE(M)
      IF (BEX(M) .LE. BEMIN) BEMIN = BEX(M)
      IF (BEX(M) .GE. BEMAX) BEMAX = BEX(M)
  140 CONTINUE
      FACTR = (56.0)/(BEMAX - BEMIN)
      DO 150 M=1,NC
      IX=IFIX(FACTR*(BE(M)-BEMIN))+3
      IY=58-IFIX(FACTR*(BEX(M)-BEMIN))
      SYM=X
      IF (PLOT(IX,IY) .EQ. X .OR. PLOT(IX,IY) .EQ. Y) SYM=Y
      PLOT(IX,IY)=SYM
  150 CONTINUE
      WRITE (6,1)
      WRITE (6,160)
      WRITE (6,170) PLOT
      WRITE (6,180)
      WRITE (6,190)
      WRITE (6,200)
      WRITE (6,210)
      BEMIN=BEMIN-2.0/FACTR
      BEMAX=BEMAX+2.0/FACTR
      WRITE (6,220) BEMIN, BEMIN
      WRITE (6,230) BEMAX, BEMAX
C
C   FORMAT STATEMENTS
C
    1 FORMAT (1H1)
   20 FORMAT (5X,58H.......................................................
     1....... /)
   30 FORMAT(5X,2H. , 18HBINDING ENERGY = (, F10.5, 11H)*Q + V + (,
     1 F10.5, 7H)  EV .)
   40 FORMAT (2H   ///)
   60 FORMAT (5X,10A8/)
```

```
 70  FORMAT (5X,4HQ = , F10.5, 15H   POTENTIAL = , F10.5, 3H EV/)
 80  FORMAT (5X,10HEB CALC = ,F10.5,3H EV,5X,9HEB EXP = ,F10.5,3H EV,
    1 5X,9HERELAX = ,F10.5,3H EV /)
 90  FORMAT (10X,12HDEVIATION = , F10.5, 3H EV//)
100  FORMAT (5X,38H..................................... /)
110  FORMAT (5X,23H. STANDARD DEVIATION = ,F10.5, 5H EV .)
115  FORMAT (5X,28H. CORRELATION COEFFICIENT = ,F8.5,2H .,5X,13HEB-V V
    1S. KQ+L)
116  FORMAT (5X,28H. CORRELATION COEFFICIENT = ,F8.5,2H .,5X,13HEB VS.
    1 KQ+V+L)
160  FORMAT (10X,62HLEAST SQUARES PLOT OF OBSERVED VS. CALCULATED BIND
    1ING ENERGIES )
170  FORMAT (60A2)
180  FORMAT (// 10X,6HLEGEND //)
190  FORMAT (5X, 39HX-AXIS IS THE CALCULATED BINDING ENERGY /)
200  FORMAT (5X, 37HY-AXIS IS THE OBSERVED BINDING ENERGY/)
210  FORMAT (5X, 105HAN X INDICATES ONE DATA POINT ASSIGNED THAT POSIT
    1ION. A Y INDICATES TWO (OR MORE) POINTS AT THE POSITION.//)
220  FORMAT (5X,15H ORIGIN IS AT (, F10.5, 1H,, F10.5, 4H) EV /)
230  FORMAT (5X,21H (XMAX, YMAX) IS AT (, F10.5, 1H,, F10.5, 4H) EV
    1 /////)
     RETURN
     END
```

0 0 0 0 4 2 0 0 9 0 1

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